Component development for all-vanadium redox flow batteries: Membrane design and cell characterization

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Component development for all-vanadium redox flow batteries: Membrane design and cell characterization

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

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Summary

All-vanadium redox flow batteries (VRBs) are a promising technology for efficient energy storage from renewable sources and grid stabilization. Polymeric separators and carbon electrodes are regarded as core components of VRBs. Polymeric separators have significant impact on their efficiency as well as cycle and calendar lifetime. Whereas an extensive cross-over of vanadium species through the separator results in reduced capacity and current efficiency of a VRB cell, its high ohmic resistance impairs the voltage efficiency of the cell. On the other hand, carbon electrodes provide the surface on which the respective electrochemical reactions occur within the redox flow cell. Activation, ohmic and concentration polarization losses, associated with the performance and stability of carbon electrodes, are also crucial for the VRB efficiency and must be minimized. For this, carbon electrodes must be selected which provide high and stable catalytic activity towards vanadium redox reactions, excellent electrical conductivity as well as good wettability and mass transport properties.

In this work, design strategies for preparation of highly selective ion exchange membranes with minimized vanadium cross-over and reduced ohmic resistance are presented. They are based on the radiation induced grafting technique and subsequent functionalization. Furthermore, insight into the performance and stability of selected commercially available carbon electrode materials (with and without thermal treatment) is provided.

The first chapter of this thesis provides an overview of existing redox flow battery chemistries with the focus on the most advanced all-vanadium redox flow technology. It also gives a brief introduction to the previous research made on different components of all-vanadium redox flow cells including flow fields, vanadium electrolyte, electrodes and membranes. It presents different design and modification strategies which were proposed for the various components of a VRB cell with the aim to optimize their performance.

In the subsequent chapter, the performance and stability of selected commercially available carbon electrode materials (pristine and thermally treated) are compared under VRB operating conditions to identify especially promising types. Moreover, in this chapter possible reasons for the observed differences in the cycling stability of studied carbon electrodes are discussed.
Chapter four of the thesis focuses on ion exchange membranes containing sulfonic acid and amidoxime groups, which are known in the literature for their ability to complex vanadium ions in seawater. The modification of membranes with amidoxime groups results in significant improvement of their vanadium barrier properties, whereas the presence of protogenic sulfonic acid groups allows the reduction of their ohmic resistance. As a consequence of improved selectivity, cells with these membranes show higher charge/discharge efficiency and a less pronounced capacity fading compared to the cells with the state-of-the-art material, Nafion® 117.

The next chapter of this thesis combines an experimental and in silico study of interactions between amidoxime groups and vanadium ions in different oxidation states and at different pH. It was found that although amidoxime groups can complex vanadium ions in neutral environment, under acidic conditions the complexation is strongly disfavored. Instead of acting as chelating agent, the protonated and, thus, positively charged amidoxime groups prevent vanadium ions from entering the membrane, providing an effective vanadium barrier under VRB conditions.

Finally, ion exchange membranes based on functionalized vinylpyridine are presented for the use in VRBs. The modification of membranes with positively charged vinylpyridinium units results in significant suppression of their vanadium permeability and the presence of sulfonic acid groups reduces their ohmic resistance. Cells with these membranes also show higher round trip efficiency and less pronounced capacity decay compared to the cells with Nafion® 117. Furthermore, vinylpyridine based membranes are compared to Nafion® 117 and membranes containing amidoxime and sulfonic acid groups. Vanadium uptake and permeance experiments reveal significant differences in the interaction of various membranes with vanadium ions in different oxidation states. Moreover, it was found that also net volumetric transfer of electrolyte across various membranes studied in this work differs significantly. Whereas in the cells with Nafion® 117 and amphoteric amidoximated membranes volumetric transfer towards the positive half-cell is observed, in the cell with VP based membranes water transport occurs in the opposite direction. However, in both cells with amphoteric membrane net volumetric transfer is significantly less pronounced compared to the cells with Nafion® 117, owing to reduced vanadium cross-over.
Amphoteric ion exchange membranes prepared by radiation induced grafting technique have been shown to reduce vanadium cross-over and associated capacity fading in the VRB cell. Their design principles as well as tuning possibilities are presented in this work. Moreover, performance and stability of selected commercially available carbon electrode materials (with and without thermal treatment) are discussed.
Zusammenfassung


Zusammenfassung

Im folgenden Kapitel werden die Leistung und Stabilität ausgewählter, handelsüblicher Kohlenstoffelektroden (vor und nach der thermischen Behandlung) verglichen, um besonders vielversprechende zu ermitteln. Darüber hinaus werden in diesem Kapitel mögliche Gründe für die beobachteten Unterschiede in der Zyklenstabilität der untersuchten Kohlenstoffelektroden diskutiert.


Weiterhin werden Vinylpyridin-basierte Membranen mit Nafion® 117 und Membranen, die Amidoxim- und Sulfonsäuregruppen enthalten, verglichen.
Zusammenfassung


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First of all, I want to express my gratitude to my supervisor Dr. Lorenz Gubler for his patient support, valuable advice and continuous encouragement during my PhD studies. I also want to thank Professor Thomas Schmidt for being always available and offering help and valuable advice.

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Table of content

Summary .......................................................................................................................... 3
Zusammenfassung .......................................................................................................... 6
Acknowledgments ......................................................................................................... 9
Table of content ............................................................................................................ 10
Declaration of Self-Citations ....................................................................................... 13
Chapter 1: Introduction ............................................................................................... 15
  1.1 Motivation ........................................................................................................... 15
  1.2 Redox flow batteries ......................................................................................... 17
    1.2.1 Construction of redox flow batteries and their features ......................... 17
    1.2.2 Different chemistries proposed for the use in redox flow batteries .......... 20
    1.2.2.1 Redox flow batteries based on aqueous solvents ......................... 21
    1.2.2.2 Redox flow batteries based on aprotic solvents ......................... 27
  1.3 All-vanadium redox flow batteries .................................................................... 29
    1.3.1 Operating conditions ............................................................................... 30
    1.3.2 Components of all-vanadium redox flow cells .................................. 31
    1.3.2.1 Flow field designs .......................................................................... 31
    1.3.2.2 Vanadium electrolytes and their modification methods ................. 32
    1.3.2.3 Electrode materials and their modification methods ..................... 34
    1.3.2.4 Design principles for polymeric separators .................................. 37
Chapter 2: Materials and methods .............................................................................. 52
  2.1 Materials and chemicals .................................................................................... 52
  2.2 Redox flow test station ...................................................................................... 53
  2.3 Pretreatment of Nafion® and synthesis of functionalized grafted membranes ...... 54
  2.4 Ex situ characterization of carbon electrodes .................................................... 58
    2.4.1 Electrode materials used in the cell and cell architecture .................... 58
    2.4.2 X-ray photoelectron spectroscopy ....................................................... 60
    2.4.3 Raman Spectroscopy ........................................................................... 60
  2.5 Ex situ characterization of membranes ............................................................... 61
    2.5.1 Infrared Spectroscopy .......................................................................... 61
    2.5.2 Scanning electron microscopy coupled with energy dispersive X-ray ...... 61
Table of content

2.5.3 Ion exchange capacity ........................................................................................................ 62
2.5.4 Vanadium permeance ......................................................................................................... 63
2.5.5 Uptake of vanadium ions into membranes ......................................................................... 67
2.5.6 Ex situ conductivity ............................................................................................................. 68

2.6 In situ characterization of electrodes .................................................................................... 71
2.6.1 Polarisation curves and reference electrode measurements ............................................. 71
2.6.2 Charge/discharge cycling ................................................................................................... 72

2.7 In situ characterization of membranes .................................................................................. 73
2.7.1 OCV measurements ............................................................................................................ 73
2.7.2 Measurements of area resistance ....................................................................................... 73
2.7.3 Redox flow cell experiments .............................................................................................. 74

Chapter 3: Performance and stability of different carbon electrode materials .......................... 76
3.1 Abstract ...................................................................................................................................... 77
3.2 Introduction ............................................................................................................................. 77
3.3 Experimental ........................................................................................................................... 80
3.4 Results and Discussion ........................................................................................................... 83
3.5 Conclusions ........................................................................................................................... 95
3.6 Supporting Information .......................................................................................................... 96

Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups ...... 102
4.1 Abstract ...................................................................................................................................... 103
4.2 Introduction ............................................................................................................................. 103
4.3 Experimental ........................................................................................................................... 105
4.4 Results and Discussion ........................................................................................................... 109
4.5 Conclusions ........................................................................................................................... 121
4.6 Supporting Information .......................................................................................................... 122

Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH .... 130
5.1 Abstract ...................................................................................................................................... 131
5.2 Introduction ............................................................................................................................. 131
5.3 Experimental ........................................................................................................................... 135
5.4 Results and discussion ........................................................................................................... 139
5.5 Conclusions ........................................................................................................................... 152
5.6 Supporting Information .......................................................................................................... 153
Table of content

Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes ........................................ 173

6.1 Abstract ..................................................................................................................................... 174
6.2 Introduction ............................................................................................................................ 174
6.3 Experimental .......................................................................................................................... 177
6.4 Results and Discussion ........................................................................................................... 181
6.5 Conclusions ........................................................................................................................... 197
6.6 Supporting Information ........................................................................................................... 198

Chapter 7: Conclusions and Outlook .......................................................................................... 207

List of Abbreviations .................................................................................................................... 228
Publication List ............................................................................................................................. 231
Declaration of Self-Citations

This manuscript is a cumulative doctoral thesis which combines four peer-reviewed articles. Chapter 3, 4, 5 and 6 are based on reproduced publications. Each of these chapters starts with a short summary which gives an overview of the performed studies. In addition, the thesis contains newly written chapters (Chapter 1, 2 and 7).

The published manuscripts used in this thesis are listed in the following table:

<table>
<thead>
<tr>
<th>ID</th>
<th>Publication</th>
</tr>
</thead>
</table>
Declaration of Self-Citations

O. Nibel designed and carried out experiments, analyzed and visualized data (P1-P4) and wrote the manuscripts (P1-P4).

Susan M. Taylor participated in the experiments, analysis and data visualization for MS1 and co-wrote this manuscript. Susan M. Taylor carried out Raman measurements.

Emiliana Fabbri performed XPS experiments for MS1 and discussed results.

Alexandra Pătru discussed results and edited MS1.

L. Gubler and T.J. Schmidt supervised the performed investigations, discussed results from experimental work and edited manuscripts MS1-MS4.

Marta Bon carried out in silico investigations for MS3 and co-wrote MS3.

Teodoro Laino and Michael L. Agiorgousis supervised the work of Marta Bon and edited MS3.

Tomasz Rojek performed ion chromatography (IC) and constructed the calibration curve (alkylation degree in % from IC versus peak area ratios at 1640/820 cm\(^{-1}\)) for MS4.

Chapters 1, 2 and 7 in this manuscript contain excerpts and/or ideas from peer-reviewed published articles MS1-MS4. Chapters 3-6 represent the reproduction of four peer-reviewed published articles MS1-MS4. The published manuscripts used in the corresponding chapters of this thesis are listed below:

<table>
<thead>
<tr>
<th>Publication</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS1-MS4</td>
<td>1, 2 and 7</td>
</tr>
<tr>
<td>MS1</td>
<td>3</td>
</tr>
<tr>
<td>MS2</td>
<td>4</td>
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<td>MS3</td>
<td>5</td>
</tr>
<tr>
<td>MS4</td>
<td>6</td>
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</tbody>
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Chapter 1: Introduction

The first chapter of this thesis gives a brief introduction to the existing types of flow batteries with the focus on the most advanced all-vanadium redox flow battery (VRB). Moreover, it provides an overview about previous research made on different components of all-vanadium redox flow cells including flow fields, vanadium electrolyte, electrodes and membranes. It presents different design and modification strategies proposed for the various components of an all-vanadium redox flow cell.

1.1 Motivation

The growing trend of world population and energy consumption are among the highly challenging problems of our time. Nowadays, fossil fuels, including natural gas, oil and coal, belong to the most important primary energy sources and are used for heating, electricity generation, industrial processes as well as transportation. The total concentration of carbon dioxide and other greenhouse gases released by burning fossil fuels have continuously increased over the past decades resulting in rising global mean surface temperature. Thus, to meet the continuous growing global need for more energy and at the same time reduce the output of carbon dioxide causing global warming, the implementation of alternative, cleaner energy sources is required. Alternatively to fossil fuels, nuclear power plants can be used for power generation. However, the use of nuclear energy is associated with serious drawbacks, e.g. nuclear waste management. Moreover, renewable energy sources, including hydropower, biomass, geothermal, marine as well as solar and wind energy, show significant promise in helping to reduce the use of fossil fuels.\textsuperscript{1-4}

Especially for electricity generation, the use of renewable energy sources, such as wind and sunlight, is predicted to grow worldwide by more than 25 % by 2030.\textsuperscript{5} In contrast to conventional power plants, many of the renewable energy sources, including wind, solar and marine energy, are intermittent,\textsuperscript{4} and grids are expected to become unstable if their contribution to the electricity mix will exceed more than 20 %.\textsuperscript{6}
The introduction of intermittent renewable energy sources such as wind and sunlight into the grid requires, therefore, development of adequate energy storage scenarios. It is essential to store the energy from intermittent renewable sources if excess is produced and release it in times of demand.\textsuperscript{6,7}

Redox flow batteries (RFB) exhibit great potential for energy storage from renewable sources and grid stabilization.\textsuperscript{6} Among all existing RFBs, the all-vanadium redox flow battery, which uses vanadium ions in different oxidation states on the negative and the positive electrode, is the most advanced technology.\textsuperscript{8} The key components of all-vanadium redox flow cells comprise polymeric separators and carbon electrodes, which largely determine their performance and cycle lifetime.

Electrodes provide the surface on which the respective electrochemical reactions occur. Thus, their catalytic activity, wettability and mass transport properties significantly affect the VRB performance and must be optimized. Furthermore, electrode materials should be stable under VRB operating conditions to ensure long-term operation of the battery.

Uncharged microporous separators or charge-carrying ion exchange membranes (IEMs), which separate the porous electrodes in the VRB cell, prevent cross-mixing of negative and positive electrolyte while allowing the transport of supporting electrolyte ions, such as protons.\textsuperscript{9} An extensive cross-over of vanadium species through separators results in capacity and efficiency losses and limits the use of VRBs as energy storage devices.\textsuperscript{10} On the other hand, high ohmic resistance of separators leads to significant ohmic losses in VRB cells diminishing their efficiency as well. Thus, many research projects around the world are focusing on the design of membranes characterized by low vanadium permeability, low resistance, good chemical stability and low cost.\textsuperscript{10}

Nowadays, perfluoroalkylsulfonic acid (PFSA) membranes, such as Nafion\textsuperscript{8}, are still considered to be the state-of-the-art separators in the VRB field. They provide good stability in vanadium electrolyte and high conductivity. However, they also have significant drawbacks, such as high vanadium permeability and high cost. For this reason, the development of alternative membranes, which will fulfill requirements for VRB applications mentioned above, is essential. One of the attractive and scalable methods to prepare membranes for VRB applications is based on the technique of radiation induced grafting.
Chapter 1: Introduction

Radiation grafting of pre-existing chemically and mechanically stable polymeric materials can be used to introduce proton conducting functionalities and vanadium barrier motifs to reduce the ohmic losses and vanadium cross-over in the VRB cell. In addition, the properties of final radiation grafted membranes can be readily tuned and adjusted by varying their graft level and/or the ratio of introduced functional groups.

1.2 Redox flow batteries

1.2.1 Construction of redox flow batteries and their features

There are various types of energy storage technologies including mechanical (compressed air, flywheels or hydropower), electrical (supercapacitors), thermal or electrochemical energy storage.\(^{11}\) In Figure 1.1 discharge time and power rating of different energy storage technologies are compared.

![Figure 1.1. Discharge time and power rating for various energy storage technologies.\(^{12}\)](image)

As shown in Figure 1.1, electrochemical energy storage technologies involving batteries such as sodium sulfur, lithium ion and redox flow batteries can cover a wide range of applications ranging from kW to GW power scale.
Moreover, batteries offer significant benefits for energy storage. For example, in contrast to compressed air and hydropower energy storage, which have specific geographical or geological requirements, they have no specific location related requirements and can be sited anywhere.\textsuperscript{4, 5, 13} Compared to flywheel and thermal energy storage, batteries have significantly better response time.\textsuperscript{13} Moreover, batteries such as sodium sulfur, lithium ion and redox flow batteries exhibit high round trip efficiencies ranging from 70 to 95\%, which are comparable to the round trip efficiency of hydropower energy storage (70-85\%) and considerably higher compared to the round trip efficiency of power-to-gas energy storage (25-58\%).\textsuperscript{5, 11, 13, 14} The power-to-gas process, which can convert renewable electric energy via water electrolysis into storable gaseous energy carriers, such as hydrogen or methane, can also play an important role in a future energy system.\textsuperscript{15}

Conventional rechargeable batteries provide an efficient and simple way to store electricity. However, their development up to now largely focused on portable and, especially more recently, on transportation applications. While for these applications the weight and the size of the battery play a crucial role, they are less important for grid-scale energy storage. In contrast, grid-scale energy storage requires batteries with good scalability, charge/discharge cycling durability, high round-trip efficiency and of course reasonable capital costs (typical system capital cost target of around 150 \$ kWh\textsuperscript{-1}).\textsuperscript{16, 17} Among the electrochemical storage technologies, redox flow batteries (RFBs) are expected to meet many of mentioned above requirements.\textsuperscript{9} Some of the promising applications of redox flow batteries include integration of intermittent renewable sources (wind/solar power) into the grid, load management of large-scale electricity supply to the grid (e.g., peak shaving) as well as remote area power supply.\textsuperscript{18, 19} Redox flow batteries typically use two soluble redox couples as electroactive materials to store the energy via oxidation and reduction reactions. Their operation principle consists of charging and discharging and their performance is mainly characterized by coulombic (CE), voltage (VE) and energy (EE) efficiency, which can be described with the following equations:

\[ \text{CE} = \frac{\int I_{d} dt}{\int I_{c} dt} \cdot 100\% \]  
\[ \text{VE} = \frac{\text{mean discharge voltage}}{\text{mean charge voltage}} \cdot 100\% \]  
\[ \text{EE} = \text{CE} \times \text{VE} \]  

18
where d and c represent the charge and discharge process and \( I \) and \( t \) correspond to current and time, respectively.

Furthermore, other parameters including electrolyte utilization, capacity fading as well as power and energy density also belong to important characteristics of redox flow batteries.\(^{19}\)

Redox flow batteries consist of cells where redox reactions occur, two tanks filled with electrolytes containing redox-active species, a pumping system for electrolyte circulation, and a power conditioning system to connect the battery to the grid. A schematic representation of a redox flow battery containing only a single redox flow cell is shown in Figure 1.2. To realize high voltage for practical uses, several single redox flow cells can be assembled to a cell stack.\(^{13,18}\)

![Figure 1.2](image.png)

**Figure 1.2.** A schematic representation of a redox flow battery consisting of a single redox flow cell.\(^{8}\)

Due to their flexible design demonstrated in Figure 1.2, flow batteries can be used in applications ranging from kW to GW power scale with typical discharge times ranging from 4 to 10 hours.\(^{5,6,16,20}\)

Although redox flow batteries have low energy (10-50 Wh kg\(^{-1}\)) and power density, which renders their use for portable applications unsuitable, for grid-scale energy storage they can offer a number of significant advantages.\(^{21}\)

The key advantage of redox flow batteries over conventional rechargeable grid-scale batteries, such as sodium sulfur, is their independent scalability of energy and power.\(^{13,19,22}\)
While the power of a RFB is determined by number of cells in the stack and their geometric area, its energy capacity is governed by the concentration of redox-active species in the RFB electrolyte and its volume.\textsuperscript{8,9,21}

Moreover, as shown in Figure 1.2, in RFBs the electrolyte solutions are stored separately in two different tanks reducing the self-discharge of batteries during stoppage and stand-by modus.\textsuperscript{22} In contrast to conventional batteries, such as lead-acid batteries, redox flow batteries have also deep discharge capability.\textsuperscript{13,18,19}

A further significant benefit is that in comparison to secondary batteries, redox flow technology uses fully soluble redox couples and inert electrodes. As a consequence, undesirable electrode processes such as structural changes of the electrodes during repeated charge/discharge cycling can be prevented resulting in higher cycling lifetime.\textsuperscript{8,13,18} Moreover, redox flow batteries are reported to provide high round trip efficiencies ranging from 65 to 85\%, which are comparable to those of other grid-scale batteries, such as sodium sulfur.\textsuperscript{12-14}

### 1.2.2 Different chemistries proposed for the use in redox flow batteries

During operation of a single redox flow cell, on one side of the membrane redox-active species are oxidized while those on the opposite side undergo reduction. The selection of redox couples for both sides of the redox flow cell largely determines its performance, stability as well as energy and power density.

Thus, by the choice of redox couples for positive and negative electrode reactions following criteria must be considered:

- Redox couples yielding a high cell voltage need to be selected, but at the same time side reactions are to be prevented.
- The selected redox couples should provide rapid and reversible electrode reactions.
- The redox couples of choice should have good stability and solubility in the used solvents.
- The redox species must be of low cost, accessible and environmentally friendly.
Chapter 1: Introduction

Various redox couples based on metals, non-metals or their combination were proposed for the use in RFBs. As shown in Figure 1.3, besides one-phase all-liquid batteries, also multiphase systems, such as Zn/Br₂, H₂/Br₂ and Li based batteries, have gained increasing attention in the RFB field.

![Redox-flow batteries classified according to electrolyte system and aggregate state.](image)

Figure 1.3. Redox-flow batteries classified according to electrolyte system and aggregate state.

However, compared to all-liquid batteries, the operation of multiphase batteries presents more challenges. For instance, in multiphase redox flow batteries it is important to provide uniform metal deposition, continuous gas feed/storage and continuous circulation of the suspensions.

1.2.2.1 Redox flow batteries based on aqueous solvents

A variety of metal-based redox flow batteries containing protic solvents have been considered for the use in VRBs.

Figure 1.4 provides an overview of selected combinations of redox pairs based on aqueous solutions (protic solvents).
Figure 1.4. Selected examples of inorganic redox couples for applications in redox flow batteries. A = half-cell study, B = prototype tested, C = technology has been commercialized. Most of batteries are based on aqueous solutions. The colors in the table correspond to the pH value of the electrolytes (red => acidic, blue => basic, orange => neutral).  

Compared to aprotic solvents, aqueous electrolytes have significant benefits in terms of cost and ionic conductivity. The ionic conductivity of the electrolyte as well as of the separator is higher in aqueous than in non-aqueous medium. On the other hand, aqueous electrolytes have a restricted operating potential window.

As can be seen from Figure 1.4, most of the batteries based on aqueous solutions have an acidic electrolyte. Thus, their pH-dependent stability needs to be taken into account (Figure 1.5). To ensure that the operating voltage of the redox flow cell is as large as possible and at the same time hydrogen and oxygen evolution are prevented, each of the equilibrium potential of the redox couples should be chosen close to the opposite extreme ends of the electrochemical stability window of aqueous electrolyte. Moreover, also the stability of each redox-active species (Pourbaix diagram) and other components of the electrolyte must be considered.
Chapter 1: Introduction

![Figure 1.5](image.png)

**Figure 1.5.** Standard potential (E versus NHE) versus the pH value for hydrogen and oxygen evolution reactions (dashed lines) including overpotentials at carbon-based electrodes (solid lines) in aqueous media.\(^{23}\)

Some of the metal-based technologies presented in Figure 1.4, including Zn/Br, V/V and Cr/Fe, have reached the state of commercialization.

For instance, the Fe\(^{3+}\)/Fe\(^{2+}\) and Cr\(^{3+}\)/Cr\(^{2+}\) redox couples can be employed in the cathodic and anodic electrolytes of RFBs, respectively, resulting in an equilibrium cell voltage of 1.19 V (discharging (→) and charging (←) of an RFB).

Positive electrode: \[ \text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \quad E^0 = 0.77 \text{ V} \] (1.4)

Negative electrode: \[ \text{Cr}^{2+} \rightleftharpoons \text{Cr}^{3+} + e^- \quad E^0 = -0.42 \text{ V} \] (1.5)

Cell reaction: \[ \text{Fe}^{3+} + \text{Cr}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{Cr}^{3+} \quad E^0 = 1.19 \text{ V} \] (1.6)

The iron-chromium redox flow battery belongs to the one-phase (all liquid) technology. Whereas the Fe\(^{3+}\)/Fe\(^{2+}\) redox couple has good reversibility and fast kinetics, the Cr\(^{3+}\)/Cr\(^{2+}\) redox couple shows only slow kinetics (with graphite felt as electrodes and 1 M HCl as solvent).\(^{24}\) Moreover, the low redox potential of the Cr\(^{3+}\)/Cr\(^{2+}\) couple may cause H\(_2\) evolution, which competes with Cr\(^{2+}\)/Cr\(^{3+}\) reaction during the charging process and impairs the performance of the redox flow cell.\(^{25}\)

Furthermore, this technology suffers from irreversible cross-contamination of electrolyte as consequence of the chromium and iron cross-over through an ion exchange membrane.\(^{24}\)
Chapter 1: Introduction

The Zn-Br battery is classified as a hybrid flow battery. In this type of the battery, the reaction on the positive electrode involves the reduction of Br\(_2\) and oxidation of Br\(^-\), while the negative side is based on Zn, which is plated during charge as metallic zinc onto the anode electrode surface and stripped off the electrode during discharge (discharging \(\rightarrow\) and charging \(\leftarrow\) of a VRB).

Positive electrode: \(\text{Br}_2 + e^- \rightleftharpoons 2 \text{Br}^-\) \(E^o = 1.06 \text{ V}\) (1.7)

Negative electrode: \(\text{Zn} \rightleftharpoons \text{Zn}^{2+} + e^-\) \(E^o = -0.76 \text{ V}\) (1.8)

Cell reaction: \(\text{Br}_2 + \text{Zn} \rightleftharpoons 2 \text{Br}^- + \text{Zn}^{2+}\) \(E^o = 1.82 \text{ V}\) (1.9)

The capacity of the Zn-Br battery is often limited by the amount of zinc deposited.\(^{23}\) Furthermore, the plating of zinc onto a carbon plate negative electrode can lead to dendrite growth and penetration of separators resulting in reduced efficiency or complete cell failure.\(^{26}\) ZnBr\(_2\) has high solubility over 2.0 M, but in the charged state Br\(_2\) is less miscible in aqueous medium limiting the achievable energy density of the Zn-Br battery. To address this problem and to conserve Br\(_2\) in aqueous medium, halides (such as bromide and chloride ions) and complexing agents (such as quaternary ammonium bromides) can be added.\(^{23}\) Moreover, the corrosiveness and toxicity of Br\(_2\) limits the use of the Zn-Br battery.\(^{25}\)

Nowadays, the most advanced RFB is the all-vanadium redox flow battery (VRB), which uses vanadium ions in different oxidation states (V\(^{2+}\), V\(^{3+}\), VO\(^{2+}\) and VO\(^{2+}\)) dissolved in diluted sulfuric acid (concentration range from 2 to 5 M) on both sides of the membrane. The following half-cell reactions take place during discharging \(\rightarrow\) and charging \(\leftarrow\) of a VRB, leading to a standard equilibrium cell voltage of 1.25 V:

Positive electrode: \(\text{VO}_2^+ + 2 \text{H}^+ + e^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}\) \(E^o = 1.00 \text{ V}\) (1.10)

Negative electrode: \(\text{V}^{2+} \rightleftharpoons \text{V}^{3+} + e^-\) \(E^o = -0.25 \text{ V}\) (1.11)

Cell reaction: \(\text{VO}_2^+ + \text{V}^{2+} + 2 \text{H}^+ \rightleftharpoons \text{VO}^{2+} + \text{V}^{3+} + \text{H}_2\text{O}\) \(E^o = 1.25 \text{ V}\) (1.12)

By employing the same element in both half-cells the irreversible cross-contamination of the electrolytes can be prevented in VRBs, reducing their maintenance costs.\(^{27}\)
Electrolytes based on metal complexes in combination with protic solvents were also studied. For instance, Wen et al. studied various Fe(III)/Fe(II)-complexes as anolyte-active and Br₂/Br⁻ as catholyte-active species using aqueous sodium acetate as supporting electrolyte. It was shown that complexation of Fe with EDTA, citrate and oxalate leads to a remarkable negative shift in the potential of the redox couple. The formal potentials of −0.104, −0.190, and −0.213 V (vs. SCE) were reported for the complexes with EDTA, oxalate, and citrate, respectively. Whereas the highest solubility (0.8 M) was achieved by combining Fe with citrate, the highest charge/discharge performance was observed at a current density of 10 mA cm⁻² for the cell with Fe(III)/Fe(II)-EDTA complexes (energy efficiency of 80 % at 10 mA cm⁻²). An open circuit voltage of around 1.1 V was observed for the cell based on a combination of Fe(III)/Fe(II)-EDTA complexes with the Br₂/Br⁻ redox pair.²⁸

Furthermore, several aqueous redox flow batteries based on metal-free quinone derivatives were demonstrated.²⁹, ³⁰ For instance, Lin et al. presented quinone-based flow batteries using alkaline solutions as electrolyte (1 M KOH), where hydroxylated anthraquinones are highly soluble and bromine on the anode side can be replaced with the non-toxic ferricyanide. Functionalization of 9,10-anthraquinone (AQ) with electron-donating groups such as OH has been reported to lower the reduction potential and expand the battery voltage (Figure 1.6).

![Figure 1.6](image_url)

**Figure 1.6.** Quinone based redox flow battery using functionalized 9,10-anthraquinone (AQ) in the negative and ferricyanide in the positive side.³⁰
Combination of anthraquinone derivatives, such as 2,3,6,7-tetrahydroxyantraquinone, on the negative side with ferricyanide on the positive side resulted in an even higher cell voltage of 1.3 V. The cell containing anthraquinone derivatives and ferricyanide was cycled at a low constant current density of ± 0.1 A cm$^{-2}$ for 100 cycles and a stable coulombic efficiency of around 99% with a stable round-trip energy efficiency of 84% was observed. Capacity decline of only 0.1% was reported for this battery during cycling and was explained with the electrolyte leakage from the cell. An energy density of 18.8 Wh L$^{-1}$ was predicted for the optimized battery based on anthraquinones and ferricyanide.$^{30}$

Furthermore, Janoschka et al. proposed non-corrosive, low-cost polymeric materials in aqueous NaCl solution as redox-active species for RFB applications (Figure 1.7a).

**Figure 1.7.** Working principle of polymer based redox flow batteries.$^{31}$

TEMPO radical units in the P1 polymer used on the positive side were oxidized during the charging process, while the divalent viologen (Viol) cations in the P2 polymer underwent reduction (Figure 1.7b) leading to an OCV of around 1.1 V. An energy density of around 10 Wh L$^{-1}$ was observed for the polymer based battery.
This battery in a static, unpumped mode has been reported to exhibit stable performance and retention of 80% of the initial capacity after extended long-term tests over 10,000 cycles. However, in a pumped cell, a faster capacity decline was observed. Authors related this phenomenon to a possible side-reaction caused by oxygen, which can enter the electrolyte as a result of mechanical abrasion of the tubes in the peristaltic pump resulting in the oxidation of Viol in the P2 polymer.  

1.2.2.2 Redox flow batteries based on aprotic solvents

In contrast to aqueous systems, non-aqueous electrolytes allow a wider window of electrochemical stability and the operation of redox flow batteries at higher voltages (> 2 V). However, compared to protic solvents non-aqueous electrolytes have very significant limitations including high cost (use of expensive solvents and fluorinated salts), low conductivities and other disadvantages such as toxicity and flammability. Compared to aqueous electrolytes (6 × 10^{-8} S cm^{-1} for pure water) they have conductivities around 10^{-8} – 10^{-10} S cm^{-1} in the absence of conductive salt. The conductivities of non-aqueous electrolytes can be improved by adding suitable salts up to 10^{-2} S cm^{-1}. However, the addition of higher concentrations of supporting salts can also result in lower solubility of redox-active species.

Various electrolytes based on metal complexes in combination with aprotic solvents were proposed for the use in RFBs. Compared to the transition metal ions, metal complexes have larger size allowing reduction of the cross-over of redox-active species through the separators. Although many of batteries based on metal complexes in combination with aprotic solvents have been shown to exhibit high cell potentials (> 2 V), their utilization is still limited due to the poor solubility of redox-active species in aprotic solvents and resulting low efficiencies. For instance, V(acac)_3 in combination with aprotic solvents has attracted considerable interest because of the cell voltage of around 2.2 V (discharging (→) and charging (←) of a VRB).

Positive electrode: \([\text{V(acac)}_3]^+ + e^- \rightleftharpoons [\text{V(acac)}_3]\] \(E^o = 0.45\) V \(\text{(1.13)}\)

Negative electrode: \([\text{V(acac)}_3]^- \rightleftharpoons [\text{V(acac)}_3] + e^-\] \(E^o = -1.76\) V \(\text{(1.14)}\)

Cell reaction: \([\text{V(acac)}_3]^+ + [\text{V(acac)}_3]^- \rightleftharpoons 2 [\text{V(acac)}]\] \(E^o = 2.21\) V \(\text{(1.15)}\)
Herr et al. demonstrated only low solubility of V(acac)$_3$ in 1,3-dioxolane, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and acetylacetone which correspond to 0.80 M, 0.40 M, 0.25 M and 0.30 M, respectively. In their report Maurya et al. used 40 mL of 0.01 M V(acac)$_3$ in combination with 0.1 M tetraethyl ammonium tetrafluoroborate (TEABF$_4$) in acetonitrile (CH$_3$CN) as anolyte and catholyte solution in a redox flow cell and achieved an energy efficiency of 85.9 % at a very low current density of 0.1 mA cm$^{-2}$ and flow rate of 10 mL min$^{-1}$ (Neosepta AHA anion exchange membrane was used).

Moreover, metal free organic compounds dissolved in aprotic solvents were investigated for the use in RFBs. For instance, Li et al. used TEMPO (Figure 1.8 a) for the cathode and N-methylphtalimide (Figure 1.8 b) for the anode side. NaClO$_4$ was added as the conductive salt to acetonitrile in which both redox-active species were dissolved. The combination of TEMPO with N-methylphtalimide has been shown to yield a high equilibrium cell potential of around 2.0 V. However, electron transfer for most organic active species involves the formation of stable radicals which are reactive and short-lived. The high reactivity of the formed radicals limits the long-term cycling and storage stability of electrolytes based on organic compounds in aprotic solvents. Due to the stability issues the most of the batteries based on metal free organic compounds in aprotic solvents were operated at low current densities ranging from 0.1 to 35 mA cm$^{-2}$ so far, and even at these low current densities the maximal energy efficiency of only around 70 % was observed.

![Figure 1.8. Redox reactions occurring in the redox flow cell based on TEMPO for the cathode and N-methylphtalimide for the anode side.](image-url)
Furthermore, two-phase flow batteries based on aprotic solvents have been considered for VRB applications. Among different two-phase batteries, for instance those based on Li ions have attracted considerable attention. Lithium provides a lower potential than most redox species (-3.04 V vs. SHE) and is therefore beneficial to obtain a high cell voltage. Semi-solid lithium flow batteries have been presented in the literature to increase the energy density by keeping the main advantage of RFBs: decoupled energy and power. For instance, Duduta et al. demonstrated a semi-solid flow battery with LiCoO$_2$ (3.9 V versus Li/Li$^+$) suspension (20 vol %, 10.2 M and 1.5 % Ketjen black) as the cathode and Li$_4$Ti$_5$O$_{12}$ (1.55 V versus Li/Li$^+$) suspension (10 vol %, 2.3 M and 2 % Ketjen black) as the anode material (both Li compounds in 1 M LiPF$_6$ in dimethyl carbonate). In this report, an energy density of around 130-250 Wh kg$^{-1}$ was predicted in the optimized system, being much higher compared to the energy densities (10-50 Wh kg$^{-1}$) reported for various existing redox flow batteries in the literature so far.

Despite of the perspective to increase the power and energy density, the operation of semi-solid lithium flow batteries presents however a number of difficulties including the pumping of suspensions.

1.3 All-vanadium redox flow batteries

The all vanadium redox flow battery is the most developed so far and will be the focus of this thesis. A single all-vanadium redox flow cell uses an ion exchange membrane as polymer electrolyte and separator of the two half-cells, which contain porous carbon electrodes and current collector plates (Figure 1.9). It can be distinguished between redox flow cells with flow-through and flow-by configuration. In cells with flow-by configuration electrolyte distributors (flow fields) are additionally used.

The overall performance of the single all-vanadium redox flow cell strongly depends on the properties of the used membrane, electrolyte, electrodes as well as flow fields, and can be improved by selecting the most advanced materials or by modifying them. Operating conditions, including flow rate, temperature and current density, have also significant effect on the performance of redox flow cells.
In the following section, the impact of different operating conditions on the overall performance of an all-vanadium redox flow cell will be discussed in more detail. Furthermore, the remaining part of the introduction will provide an overview of previous research made on components of all-vanadium redox flow cells including flow fields, vanadium electrolyte, electrodes and membranes. Their design as well as modification methods will be presented.

### 1.3.1 Operating conditions

Operating conditions have been shown to have significant influence on the performance of VRBs. For instance, the performance of a single VRB cell in the temperature range from -20 to 50°C was studied by Xi et al. It was shown that CE decreases with increasing temperature while the VE presents the opposite tendency. The EE was shown to go up with temperature and exhibit a maximum at 30°C in the current density range from 40 to 200 mA cm$^{-2}$, with further temperature increase EE dropped again. Moreover, while the charge/discharge capacity increased at higher temperatures, the capacity fading was more and more pronounced as a result of higher vanadium ion cross-over through the Nafion® 117 membrane.\(^{37}\)

Furthermore, the electrolyte flow rate has been shown to have significant impact on the performance of a VRB. Tang et al. predicted an increase of CE, VE, EE and charge/discharge capacity at higher flow rates. While increasing the flow rate can yield higher cell and stack efficiency, the use of higher flow rates increases pumping energy consumption, which in turn offsets the cell/stack efficiency again and lowers system efficiency.\(^{21,38}\)
In our laboratory the influence of the flow rate on the performance of the redox flow cell was also investigated by charging and discharging the redox flow battery at a current density of 40 mA cm\(^{-2}\) at three different flow rates, namely 15 mL min\(^{-1}\), 30 mL min\(^{-1}\) and 60 mL min\(^{-1}\) (a cell with an active area of 25 cm\(^2\) was used). The change of the operating flow rate from 15 to 60 mL min\(^{-1}\) resulted in a significant increase of CE, VE, EE and discharging capacity being in good agreement with the literature.\(^{39}\)

Furthermore, the current density has been shown to have notable effect on the performance of a redox flow cell. CE increased with increasing current density. However, VE, EE and charge/discharge capacity dropped.\(^{40}\) Whereas at higher current density the capacity fading per cycle was reduced because of the shorter cycles and shorter time available for the vanadium ions to diffuse across the membrane, capacity decay per unit time increased.\(^{41}\)

1.3.2 Components of all-vanadium redox flow cells

1.3.2.1 Flow field designs

The choice of flow field design has a significant impact on the mass transport losses, which limit the VRB performance. Improved convective mass transport from the flow fields into porous electrodes has been shown to improve the performance and vanadium electrolyte utilization of VRBs.\(^{42-44}\) Different flow fields were proposed for the use in VRBs including spiral, parallel, serpentine and interdigitated designs (Figure 1.10).

![Different flow field designs proposed for the use in VRBs.\(^{45}\)](image-url)
Chapter 1: Introduction

For instance, pristine SGL 10 AA carbon papers (3 layers in each half-cell) were combined with different flow field designs, namely spiral, parallel, serpentine and interdigitated flow field plates. Among the tested flow fields, cell configurations based on the serpentine flow field plates paired with carbon papers appeared to deliver the best performance, the highest peak power and limiting current density.\(^{45}\)

Houser et al. also combined SGL 10 AA carbon papers (410 µm nominal thickness) with interdigitated and serpentine flow field plates showing strong dependence of the used flow field design on the thickness of used electrodes, operating current density and flow rate. For instance, if one layer of carbon paper was used in each half-cell, configurations based on interdigitated flow fields showed superior performance compared to the cells containing serpentine flow fields over a wide range of current densities (from 40 to 500 mA cm\(^{-2}\)) and at a given flow rate of 20 mL min\(^{-1}\). In contrast, cell assembled with five layers of SGL 10 AA carbon papers on each side exhibited superior performance with serpentine flow fields at the same flow rate and over a range of current densities from 40 to 200 mA cm\(^{-2}\). However, at higher current densities the use of interdigitated flow field design instead of serpentine one appeared again more beneficial.\(^{43}\)

Kumar et al. paired SIGRACELL\textsuperscript{®} GFA6 EA carbon felt electrodes (6 mm thickness), which are widely used in VRBs, with interdigitated and serpentine flow field plates and demonstrated that the cell assembled with the serpentine flow field design allowed better cycling performance.\(^{46}\)

1.3.2.2 Vanadium electrolytes and their modification methods

The vanadium electrolyte solutions are one of the key components of a VRB system. The current VRBs still exhibit very low energy density of < 25 Wh kg\(^{-1}\), which is mainly limited by poor solubility and stability of vanadium electrolytes. As shown in Figure 1.11, V\(^{2+}\), V\(^{3+}\) and VO\(^{2+}\) show poor stability at relatively low temperatures, whereas VO\(_2^+\) can undergo precipitation at higher vanadium concentrations and temperatures to form V\(_2\)O\(_5\).\(^{47}\)

The effect of the sulfuric acid concentration on the stability of dissolved vanadium ions has been studied. Whereas a higher concentration of sulfuric acid would result in precipitation of V\(^{3+}\) and VO\(^{2+}\), lower H\(_2\)SO\(_4\) concentration favors VO\(_2^+\) precipitation.\(^{48}\) Jing et al. investigated charge/discharge
behavior of VRB with different concentrations of $\text{H}_2\text{SO}_4$ and $\text{VOSO}_4$ and reported the best performance in case of redox flow cells operated with 1.6 m $\text{VOSO}_4$ and 2.8 m $\text{H}_2\text{SO}_4$.\textsuperscript{49}

![Stability of different vanadium electrolytes](image)

**Figure 1.11.** Stability of different vanadium electrolytes in the temperature window from -40°C to 50°C.\textsuperscript{47}

Various approaches were proposed to overcome the performance limitations caused by solubility and stability of vanadium based electrolytes.\textsuperscript{50} The use of mixed sulfate/chloride background electrolyte has been shown to allow an increase of energy capacity of more than 70% compared to a pure sulfate system and to broaden the operational temperature range up to 50°C.\textsuperscript{51}

Several organic additives have been screened for the use as potential additives to inhibit the precipitation of vanadium ions at higher concentrations and temperatures. Some of the additive combinations, e.g., 1 % glycerol + 2 % ammonium oxalate, have been demonstrated to be effective in stabilizing the negative and positive half-cell electrolyte. However, both components reacted with $\text{VO}_2^+$ ions generating $\text{CO}_2$ gas and giving rise to an imbalance between the two half-cell electrolytes.\textsuperscript{52}

The use of cyclic organic additives with tertiary $-\text{OH}$ groups, such as inositol, which would not be oxidized to $\text{CO}_2$, resulted in enhanced thermal stability of $\text{VO}_2^+$ electrolyte and in better and more stable charge/discharge characteristics.\textsuperscript{53}

A significant improvement in energy density has also been achieved in the presence of inorganic precipitation inhibitors, such as $\text{H}_3\text{PO}_4$ + ammonium sulfate additives mixture, which are not susceptible to oxidation of $\text{VO}_2^+$.\textsuperscript{52}
1.3.2.3 Electrode materials and their modification methods

Redox reactions of vanadium ions occur on the surface of electrodes making them a key component of a VRB cell. The voltage losses in a VRB cell, which arise from activation, ohmic and concentration polarization, must be minimized. For this, optimal electrodes for VRBs should be found which provide high and stable catalytic activity towards vanadium redox reactions, excellent electrical conductivity as well as good wettability and mass transport properties. Figure 1.12 demonstrates different materials which have been proposed as electrodes for VRB applications.

To these materials belong non-carbon based IrO$_2$ coated dimensionally stable anode electrodes or carbon based electrodes including graphite felt, carbon felt, graphene, graphene oxide, carbon paper or carbon nanofibers.$^{54}$

Cost-effective carbon based electrodes have been identified as the best materials for the use in both negative and positive half-cells of a VRB cell. It is notable that the precursor materials used for the synthesis of carbon electrodes can have a profound effect on their performance. For instance, rayon based and polyacrylonitrile (PAN) based carbon felt electrodes have been shown to differ in their electrical conductivity, specific surface area and the way they interact with oxygen. These differences have to be considered when selecting suitable carbon based electrodes for the use in VRBs.$^{55}$

Numerous modification techniques have been developed to improve the activity of carbon based electrodes towards both vanadium redox reactions. These modification methods include various surface treatment methods, such as thermal,$^{56-58}$ chemical,$^{59,60}$ electrochemical,$^{61}$ plasma$^{62}$ or a combination of corona discharge and hydrogen peroxide treatment.$^{63}$

Recently, Zhou et al. reported a new surface activation method of carbon papers and carbon cloth electrodes by their thermal treatment and subsequent etching with KOH.$^{64,65}$

Incorporation of various metals or metal oxides, such as iridium,$^{66}$ zirconium dioxide$^{67}$ or cerium dioxide$^{68}$, in carbon based electrodes have been shown to enhance their electrochemical activity as well.
Figure 1.12. Historical flow chart for research on electrodes for applications in all-vanadium redox flow batteries.\textsuperscript{54}
Moreover, Santamaria et al. reported that modification of graphite felt with bismuth (Bi) nanoparticles can effectively suppress hydrogen evolution in the negative half-cell of a VRB and, thus, enhance the reversibility of the $V^{2+}/V^{3+}$ redox reaction.\(^{69}\)

Also, Hsueh et al. demonstrated the potential use of TiO$_2$/C integrated carbon felt electrode materials for improvement of the $V^{2+}/V^{3+}$ redox process, in particular by hindering hydrogen evolution. Furthermore, carbon based electrodes were decorated with nanomaterials such as graphene-nanowalls\(^{70}\) or graphite carbon nanotubes resulting in improvement of their performance.\(^{71}\)

Most of the pre-treating approaches found in the literature introduce oxygen functionalities onto the carbon electrode surface. The increasing wettability and activity towards vanadium redox reactions in the case of modified carbon electrodes are, therefore, often attributed to the increased concentration of surface oxygen functional groups. Among various surface treatments introducing oxygen functionalities on the surface of carbon electrodes, thermal treatment is still regarded as the most common and easy.\(^{54}\)

Using this technique the role of oxygen functional groups on the catalytic activity of carbon electrodes towards VO$^{2+}$/VO$_2^+$ and V$^{3+}$/V$^{2+}$ redox reactions was examined by several research groups.\(^{72, 73, 74}\) For instance, Fink et al. studied pristine as well as heat-treated rayon (a regenerated cellulose fiber) based GFA carbon felt and polyacrylonitrile (PAN) based GFD carbon felt. According to his study, whereas the normalized rate constant for the $V^{3+}/V^{2+}$ redox reaction increased with increasing number of oxygen functionalities, the rate constant for the VO$^{2+}$/VO$_2^+$ redox process was reduced for both types of felt electrodes.\(^{72}\) Also Bourke et al. reported that electrochemical oxidation treatment of various carbon electrodes, such as glassy carbon, carbon paper, carbon fiber and carbon xerogel, enhances reaction kinetics of $V^{3+}/V^{2+}$ whereas electrochemical reduction treatments of the same carbon materials improves the reaction kinetics of VO$^{2+}$/VO$_2^+$.\(^{74}\)

Whereas the effect of oxygen functionalized surfaces on both $V^{3+}/V^{2+}$ and VO$^{2+}$/VO$_2^+$ reactions has been carefully studied, it has been shown that the overpotential associated with the negative half-cell dominates the voltage losses of the VRB and limits its performance.\(^{75-77}\)
Chapter 1: Introduction

1.3.2.4 Design principles for polymeric separators

Separators are regarded as essential components of all-vanadium redox flow batteries since they largely avoid cross-mixing of the negative and positive vanadium electrolytes and at the same time allow the transport of charge balancing species (e.g. protons, (bi)sulfate ions) across the membrane to complete the electric circuit during the passage of current. They are often identified as the stumbling block towards commercialization of all-vanadium redox flow batteries since they can account for about half of the stack cost.\(^\text{20}\)

Separators largely determine the performance of VRBs. Their vanadium barrier properties govern coulombic efficiency (CE) of a VRB whereas the ohmic losses associated with their ohmic resistance directly affect its voltage efficiency (VE). Membranes with high cell resistance reduce the VE of the cell and those with poor vanadium barrier properties impair its CE, diminishing the energy efficiency (EE) and increasing the imbalance of electrolyte.\(^\text{78}\) Moreover, high rates of cross-over of vanadium ions through the separators leads to continuous capacity decay and self-discharge limiting the use of a VRB as energy storage device.\(^\text{79}\) The cross-over flux of vanadium ions across the separators has been reported to occur due to diffusion, convection (osmotic and electro-osmotic) and migration. During charge/discharge cycling not only the total vanadium ion concentration but also the negative and the positive electrolyte volumes undergo changes as result of water transfer across the separator used. Preferential water transfer in the redox flow cell can lead to precipitation of vanadium salts due to the increasing ion concentration in one half-cell electrolyte and dilution of the other one.\(^\text{80}\)

Thus, separators designed for VRB applications must fulfill several requirements. An ideal membrane must possess low cross-over of water and redox-active species to minimize associated self-discharge and to allow high coulombic efficiency. Moreover, separators must be characterized by a high conductivity (low ohmic resistance) in the supporting electrolyte, low manufacturing cost as well as high chemical and mechanical stability in the VRB environment.\(^\text{10, 81, 82}\)

Using different design principles, various separators were proposed for the use in VRBs. Classification of various membranes developed for VRB application can be found in Figure 1.13. Generally, membranes developed for VRB applications can be classified into uncharged and charge-carrying separators (ion exchange membranes).
In the VRB field, ion exchange membranes (IEMs) have received more attention than porous uncharged separators and will be, therefore, discussed in the following sections of the introduction in more detail. It can be distinguished between perfluorinated, partially fluorinated and non-fluorinated ion exchange membranes. IEMs with perfluorinated backbone offer excellent mechanical and chemical stability in the VRB environment. They are however of high cost. Alternatively, partially fluorinated membranes were proposed for the use in VRBs. The use of partially fluorinated CEMs is advantageous because they have reduced cost compared to perfluorinated compounds along with excellent stability.

Figure 1.13. Classification of separators proposed for VRB applications due to the absence/presence of ion exchange groups, nature of their polymeric backbone and nature of ionic groups they carry. CEMs = cation exchange membranes; AEMs = anion exchange membranes; AIEMs = amphoteric ion exchange membranes.

Also low-cost non-fluorinated IEMs have been widely investigated in the VRB field. Unfortunately, many of these membranes showed poor stability under VRB conditions and require further modifications.

Additionally, depending on the nature of the fixed ionic groups, ion exchange membranes can be subdivided into cation, anion and amphoteric ion exchange membranes. Cation exchange membranes (CEMs) that contain negatively charged functional groups, such as -SO_3^-, -COO^- or -PO_3H^-, allow the transport of cations, while anion exchange membranes (AEMs) with positively charged groups, such as -NH_3^+, -NR_3^+ or -SR_2^+, allow for the passage of anions. Amphoteric membranes (AIEMs) contain both cation and anion exchange functionalities.
Porous membranes without ion exchange groups

Porous membranes which contain no ion exchange groups have been studied for the use in VRBs. Their use was based on the idea of using pore size exclusion to achieve high selectivity of ion transport (V/H selectivity). Different porous membranes were prepared via a phase inversion method including membranes based on poly (vinylidene fluoride) (PVDF), poly (acrylonitrile) (PAN) or poly (ether sulfone) (PES). To control their pore size distribution different parameters were used including polymer concentration in the casting solution, the choice of casting solvent or addition of co-solvents, solvent evaporation time and thickness of the cast layer. Several approaches were proposed to further optimize the selectivity of ion transport in case of uncharged separators. For instance, the morphology and the performance of PES membranes were tuned by introducing additives such as hydrophilic poly (vinyl pyrrolidone) (PVP) in PES casting solutions. Also introduction of silica into the pores of uncharged membranes such as PAN or poly (vinylchloride) (PVC) has been shown to enhance their ion selectivity. Lu et al. reported the preparation of PES based porous membranes with tunable morphology (their morphology was tuned by PVP introduction in PES casting solutions) and their significantly improved performance using a solvent treatment method.

Recently, porous polybenzimidazole (PBI) membranes have received increasing attention due to their excellent vanadium barrier properties. It is noteworthy that PBI membranes differ significantly from already discussed uncharged separators because they can be protonated in dilute sulfuric acid (background electrolyte in the VRB) and positively charged. It is known that PBI membranes, which have poor conductivity in their pristine state, can be doped with polyprotic acids such as phosphoric or sulfuric acid. Doping of PBI membranes with highly concentrated H\(_2\)SO\(_4\) is expected to increase their conductivity significantly.

Indeed, Luo et al. showed remarkable increase in conductivity of PBI membranes after being equilibrated in 10 M H\(_2\)SO\(_4\). However, this effect was not stable and conductivity decreased rapidly after being in contact with 2.5 M sulfuric acid, which is often considered as typical concentration of sulfuric acid background electrolyte in VRBs. Thus, the use of PBI membranes with high H\(_2\)SO\(_4\) doping level is not reasonable for VRB applications. The synthesis of porous PBI membranes with various thicknesses was presented by Yuan et al. for the use in VRBs. Redox flow cells with mPBI membranes
having thickness of ≤ 68 µm showed superior cycling performance compared to the cell containing Nafion® 115 at a given current density of 80 mA cm⁻². The porosity of PBI membranes has also been shown to be tunable by introducing polyethylene glycol (PEG) into the casting solution used for their preparation. After casting PEG was removed from the membrane matrix by washing. The amount of added PEG determined the porosity and ion selectivity of PBI membranes.

Perfluorinated ion exchange membranes

Cation exchange perfluoroalkylsulfonic acid (PFSA) membranes, such as Nafion®, have found widespread application in the VRB field and are regarded as the state-of-the-art material. These perfluorinated membranes exhibit high proton conductivity together with excellent chemical stability. However, they also have serious drawbacks, such as high manufacturing cost and poor vanadium barrier properties, leading to serious capacity fading and self-discharge of a VRB (Figure 1.14).

There are various commercially available Nafion® membranes, including NR211 and NR212 (dispersion-cast membranes) or N115 and N117 (extruded membranes). In particular Nafion® 117 is often considered as state-of-the-art benchmark IEM for VRBs.

![Figure 1.14](image)

**Figure 1.14.** Capacity decline observed in a redox flow cell containing Nafion® 117 as separator (chemical structure of perfluorosulfonic acids materials such as Nafion® is shown in blue box).
High cross-over in case of Nafion® membranes can be attributed to their specific morphology with large size of hydrophilic water channels (with ~2.5 nm diameter) originating from nanophase separation of the hydrophobic PTFE backbone and sulfonic acid groups (water channel model).  

Several studies showing the effect of Nafion® membrane thickness on VRB performance have been reported. Jiang et al. compared the performance of redox flow cells containing Nafion® 212 (50 µm), Nafion® 1135 (88 µm), Nafion® 115 (125 µm) and Nafion® 117 membranes (175 µm) in a broad current density range from 40 to 320 mA cm\(^{-2}\) and a flow rate of 60 mL min\(^{-1}\) (a cell with an active area of 25 cm\(^2\) was used). According to this study, cells operated with Nafion® 115 presented the highest energy efficiency and electrolyte utilization at a current density from 120 to 240 mA cm\(^{-2}\). Up to 120 mA cm\(^{-2}\) the use of thicker Nafion® 117 appeared to be beneficial. At the highest current density of 320 mA cm\(^{-2}\) the cell with the thinnest Nafion® 212 membrane seemed to have the highest energy efficiency, yet also very poor electrolyte utilization and capacity retention along with significant volume changes in the negative and positive half-cells.

Different approaches have been proposed to enhance vanadium barrier properties of Nafion® membranes. Various Nafion® 117/inorganic nanocomposite membranes were prepared including Nafion®/SiO\(_2\), Nafion®/graphene oxide or colloidal zeolite (aluminosilicate crystals) Nafion® composite membranes. Whereas Nafion®/SiO\(_2\) hybrid membranes were prepared according to the \textit{in situ} sol–gel method, Nafion®/graphene oxide and colloidal zeolite Nafion® composite membranes were obtained using the casting technique. All Nafion® 117/inorganic nanocomposite membranes have been shown to improve CE and EE of all-vanadium redox flow cells compared to the cells with unmodified Nafion® 117.

Alternatively, Nafion®/organic hybrid materials were synthesized. For instance, various Nafion®/organic composite membranes have been demonstrated. Luo et al. provided a Nafion® 117 membrane with a polyethylenimine barrier layer by means of interfacial polymerization using isophthaloyl dichloride. Alternatively, the surface of Nafion® 117 was modified with poly(diallyldimethylammonium chloride) (PDDA)/ poly(sodium styrene sulfonate) (PSS) multilayer using a layer-by-layer assembly technique (Figure 1.15).
Moreover, Nafion®/organic blend membranes were proposed for the use in VRBs. Modification of Nafion® 117 with fluorocarbon surfactants (potassium nonafluoro-1-butanesulfonat) using the casting technique has been for instance reported to result in significant improvement of its ion selectivity.\textsuperscript{102} Nafion®/polyvinylidene fluoride (PVDF) blends with defined PVDF content were also prepared by the casting method and have been shown to have encouraging performance with respect to pristine Nafion® material.\textsuperscript{104}

Although various modifications of perfluorinated Nafion® membranes have been demonstrated to be helpful in enhancing their vanadium barrier properties, none of them alleviate the high cost of the membranes still limiting their use in commercial applications.

**Partially fluorinated ion exchange membranes**

As mentioned above, the use of partially fluorinated CEMs in VRB environment is advantageous because they have reduced cost compared to perfluorinated compounds along with their excellent chemical and mechanical stability. Partially fluorinated membranes can be prepared using radiation induced grafting technique.
Chapter 1: Introduction

**Cation exchange membranes**

For instance, partially fluorinated cation exchange membranes were prepared by radiation induced grafting of styrene and maleic anhydride onto PVDF membrane followed by sulfonation. These radiation grafted membranes showed better vanadium barrier properties compared to Nafion\textsuperscript{®} 117 in *ex situ* experiments. The cycling data were not provided.\textsuperscript{105} Luo et al. reported preparation of low-cost poly (vinylidene fluoride)-graft-poly(styrene sulfonic acid) (PVDF-g-PSSA) cation exchange membrane using radiation induced grafting. The redox flow cell with PVDF-g-PSSA membranes (graft level = 22%, thickness of around 115 µm) exhibited a higher and more stable performance than that with Nafion\textsuperscript{®} 117 under the same operating conditions.\textsuperscript{106}

**Anion exchange membranes**

Also, partially fluorinated anion exchange membranes were proposed for the use in VRBs. While cation exchange membranes often show poor vanadium barrier properties they guarantee high proton conductivity. In contrast anion exchange membrane may significantly reduce the cross-over of vanadium ions due to the Donnan exclusion effect.\textsuperscript{107} However, despite the reduced vanadium permeability AEMs suffer from lower conductivities compared to CEMs.\textsuperscript{10} It must be also considered that in the presence of concentrated electrolytes, such as the solutions of \(\sim 5 \text{ M} \) (or greater) acid and 1.5 M (or greater) vanadium, the Donnan exclusion of anions from the membrane breaks down.\textsuperscript{108}

Qiu et al. reported, for instance, the synthesis of ETFE-g-PMAOEDMAC anion exchange membranes (ETFE = ethylene–tetrafluoroethylene, PMAOEDMAC = ethlenpoly(methacryloxyethyl dimethyl ammonium chloride) using radiation induced grafting. Grafted membranes showed superior vanadium barrier properties compared to Nafion\textsuperscript{®} 117 in *ex situ* experiments. Cycling data and stability of redox flow cells containing these membranes were not provided.\textsuperscript{109}

**Amphoteric exchange membranes**

Furthermore, the synthesis of partially fluorinated amphoteric ion exchange membranes has been reported. Poly(vinylidene difluoride) (PVDF) films were for instance grafted with styrene (St) and dimethylaminoethylmethacrylate (DMAEMA).\textsuperscript{110}
Alternatively, α-methyl styrene (AMS) and dimethylaminoethyl methacrylate (DMAEMA) were grafted into poly(vinylidenedifluoride) (PVDF) films, followed by sulfonation and protonation processes. Amphoteric membranes with AMS instead of St have been reported to exhibit better chemical stability in ex situ experiments. In both cases no cycling experiments were carried out. Amphoteric exchange membranes containing styrene (St) and dimethylaminoethyl methacrylate (DMAEMA) units were alternatively obtained by a combination of radiation grafting and solution phase inversion. First, both monomers were grafted into PVDF powder and the grafted powder was made into a film by casting followed by sulfonation and protonation. Also in case of these membranes cycling performance of redox flow cells with prepared membranes was not investigated.

Non-fluorinated membranes

Various low-cost membranes based on non-fluorinated aromatic polymers have been developed for the use in VRBs. These membranes are usually prepared by casting. Due to the less pronounced hydrophilic/hydrophobic phase separation (as result of a less hydrophobic backbone and less acidic sulfonic acid groups), the proton transport channels in these membranes are narrower and their vanadium barrier properties are better compared to Nafion® membranes.

Cation exchange membranes

Synthesis of different non-fluorinated cation exchange membranes has been reported. Chemical structures of selected non-fluorinated aromatic cation exchange membranes are shown in Figure 1.16. Sulfonated poly(sulfone) membranes, also known as S-Radel, exhibited for instance lower permeability of vanadium ions with slightly higher ohmic resistance compared to Nafion®. However, physical and chemical stability of S-Radel under VRB operating conditions was very poor resulting in rapidly decrease of CE in case of the cells with these membranes already after 40 cycles at a current density of 50 mA cm⁻².

Sulfonated poly(ether ether ketone) (SPEEK) based membranes were considered to be one of the attractive options to replace Nafion® membranes because of their low cost and high proton to vanadium ion selectivity. But they also showed insufficient stability.
Various approaches have been used to improve the stability of SPEEK membranes. Different SPEEK/organic hybrid membranes were synthesized including composite as well as blend compounds. Poly(ether ether ketone) (SPEEK)/polypropylene (PP)/perfluorosulfonic acid (PFSA) layered composite membranes with improved stability were prepared. The cells with these membranes were compared to those containing thinner Nafion® 212 and showed higher CE but lower VE. The energy efficiency of both cells did not differ significantly.115 Luo et al. reported preparation of Nafion®/sulfonated poly(ether ether ketone) (SPEEK) layered composite membrane prepared by casting. The cross-linking between SPEEK and Nafion® was achieved using 1,1 carbonylimidazole and 1,6 hexanediamine. The resulting membranes showed worse cycling performance compared to Nafion® 117 (overall energy efficiency of a VRB single cell with these membranes was lower).117

Sulfonated poly(ether sulfone) (SPES) (Figure 1.16) and sulfonated poly(ether ether ketone) (SPEEK) (SPES/SPEEK) blend membranes were presented by Ling et al. and exhibited superior cycling performance and capacity retention compared to Nafion® 212 along with encouraging cycling stability (stable CE and EE).118
Chapter 1: Introduction

Recently, Yu et al. proposed an interesting design concept to overcome the poor cycling stability of SPEEK membranes by sandwiching them between two porous PTFE (polytetrafluoroethylene) films. In addition to improved stability, the redox flow cells operated with these membranes have been shown to exhibit better cycling performance and capacity retention compared to the cells with Nafion® 115 (161 μm).\textsuperscript{125}

Anion exchange membranes

Various non-fluorinated anion exchange membranes were proposed for the use in VRBs.\textsuperscript{107, 126-128} The chemical structure of selected non-fluorinated anion exchange membranes are shown in Figure 1.17.

![Figure 1.17](image)

**Figure 1.17.** Chemical structure of functionalized anion exchange membranes based on PPEK and polysulfone.

Non-fluorinated anion exchange membranes based on poly (phthalazinone ether ketone/sulfone) (PPEK) membranes were for example prepared by chloromethylation and subsequent quaternization using chloromethyl methyl ether and triethylamine. Long-term cycling stability of non-fluorinated AEMs under real operating condition of a VRB was not investigated.\textsuperscript{128}
Zhang et al. reported the preparation of non-fluorinated AEMs based on polysulfone. To introduce anion exchange properties into polysulfone films, they were chloromethylated and quaternized using pyridine.\textsuperscript{126} Alternatively, anion exchange membranes containing positively charged pyridine moieties were prepared by pore-filling porous polyethylene (PE) substrates with poly(4-vinylbenzyl chloride) followed by amination with pyridyl functional groups.\textsuperscript{107}

**Amphoteric ion exchange membranes (AIEMs)**

Various non-fluorinated amphoteric ion exchange membranes, which carry cation as well as anion exchange groups, have been developed for VRB applications. Their synthesis occurred for instance via polymerization of functionalized monomers,\textsuperscript{129} polymerization of defined monomers with subsequent functionalization\textsuperscript{130, 131, 132} or blending technique.\textsuperscript{133, 134}

Using casting technique non-fluorinated membranes based on sulfonated poly (fluorenyl ether ketone) with quaternary ammonium groups (SPFEKA) were prepared (Figure 1.18).

![Chemical structure of amphoteric ion exchange membranes based on SPFEKA.](image)

**Figure 1.18.** Chemical structure of amphoteric ion exchange membranes based on SPFEKA.
Chapter 1: Introduction

These membranes were shown to have better performance compared to Nafion® 115 in VRB single cell test. However, capacity fading and cycling stability in case of redox flow cells with these membranes was not studied.\textsuperscript{129}

Liu et al. demonstrated the synthesis of acid-base blend membranes composed of sulfonated poly (ether ether ketone) (SPEEK) and polyetherimide (PEI) using the casting technique (Figure 1.19). It has been shown that redox flow cells containing blend membranes with defined composition have superior cycling performance compared to the cells with Nafion® 117.\textsuperscript{133}

![Chemical structure of acid-base membranes based on SPEEK and PEI.](image)

\textbf{Figure 1.19}. Chemical structure of acid-base membranes based on SPEEK and PEI.\textsuperscript{133}

\begin{center}
\textbf{Preparation of membranes using radiation-induced grafting technique}
\end{center}

For the use in VRBs, this thesis presents two different types of amphoteric ion exchange membranes based on partially fluorinated backbone. Both types of membranes were prepared by radiation induced grafting technique.

Radiation induced grafting is a powerful, scalable and industrially applicable method which allows the modification of physical and chemical properties of pre-existing cost-effective polymeric materials by imparting them with defined functionalities. The radiation induced grafting technique enables the combination of very different types of polymeric materials (hydrophobic backbone and hydrophilic side chains) without the need of film casting or other difficulties associated with the film formation. Using this technique, various base films, monomers or monomer combinations and their modification methods such as functionalization can be selected to tailor the properties of the final membranes and to adjust them to desired applications.\textsuperscript{135-138} A schematic representation of the grafting process with subsequent functionalization is shown in Figure 1.20.
Various methods are known for the radiation-induced grafting process, including simultaneous irradiation and pre-irradiation method. The later one was used in the framework of this thesis. In the so-called simultaneous irradiation method, the polymeric backbone is irradiated in the presence of monomers. Irradiation can be carried in various environments (for instance in air, in inert atmosphere or under vacuum) resulting in the formation of active sites on the polymeric backbone and monomer units. The pre-irradiation method includes two steps. In the first step the polymeric backbone is irradiated to introduce active sites. Subsequently, the irradiated polymer backbone is allowed to react with monomers. If pre-irradiation is carried out under vacuum or in an inert atmosphere, the generated radicals remain trapped in the polymeric materials and initiate the grafting reaction in the presence of monomers. In contrast, when irradiated in air, the created radicals react with oxygen to form hydroperoxides and peroxides. In the presence of monomers the irradiated polymeric backbone can initiate grafting by thermal decomposition of (hydro)peroxides.

Although the simultaneous irradiation method consists of only one step it has serious limitations, such as a high level of homopolymer formation. Moreover, compared to the simultaneous grafting the pre-irradiation grafting method allows the grafting reaction to be spatially and temporally separated from the irradiation procedure.\textsuperscript{136, 137, 139}

The graft penetration into polymeric films during the grafting reaction has been shown to follow the so-called ‘front mechanism’. At low graft levels grafting takes place only at the surface of the polymeric material. Subsequently, the grafted layers swell in the reaction medium and allow the monomers to diffuse through the swollen grafted layers into the bulk of the polymer until the grafting front reaches the center of the film.\textsuperscript{137}
Properties of the final radiation grafted membranes strongly depend on the choice of radiation type and dose, base polymer as well as experimental conditions including the selection of solvent, monomer concentration/composition, reaction temperature and time. For instance, a strong effect of radiation dose and reaction temperature on the distribution of grafts in the cross-section of polymeric films was observed.\textsuperscript{140}

\textit{The choice of base film for preparation of ion exchange membranes}

In the framework of this thesis commercially available partially fluorinated ETFE polymeric material was used as base film. For the radiation induced grafting technique, base films must be selected which have the ability to yield a sufficient density of stable active sites after irradiation. For example, polymeric materials with aromatic units, such as poly (ether ketones) or polysulfones, have been shown to be highly resistant to radiation induced chemical changes and exhibit only a low radical yield upon irradiation, which makes them not suitable for radiation grafting. In contrast, polyolefines, such as polyethylene or polypropylene, and fluoropolymers such as ETFE or PVDF have been widely applied as base materials for radiation induced grafting.\textsuperscript{138, 139, 141} In particular, fluoropolymers have received broad attention due to their excellent chemical and thermal resistance.

Fluoropolymers can be in generally classified into scission and crosslinking type. Irradiation of materials and resulting cleavage of bonds can lead not only to the formation of active centers but also to numerous other processes, such as formation of crosslinks, scission of the main chain, creation of double bonds, cyclization and release of volatile products, e.g. H\textsubscript{2}. Fluoropolymers which belong to crosslinking type are desired for radiation induced grafting due to its high resistance towards radiation induced degradation. The trend for polymer degradation upon irradiation has been reported to increase with increasing fluorine content in the polymer backbone:

\[
\text{PTFE} > \text{PFA} \sim \text{FEP} > \text{ETFE} > \text{PVDF}
\]

Among all fluoropolymers mentioned above, ETFE is especially of high interest. The polymer degradation upon irradiation in case of ETFE is less pronounced compared to the perfluorinated materials (PTFE, PFA and FEP).
Moreover, Mitov et al. measured the radical yield by means of electron resonance spectroscopy (ESR) for the selected base films including ETFE, PVDF and FEP and reported the highest radical yield for ETFE and the lowest for FEP.\textsuperscript{142}

*Selection of irradiation type and dose for preparation of ion exchange membranes*

In the first step of the grafting process, active sites such as radicals are created in the pre-existing polymeric material by means of irradiation. The choice of irradiation type and dose has a significant impact on the amount and distribution of active centers formed in the polymer and strongly influences the subsequent grafting process. Amphoteric ion exchange membranes which will be discussed in this thesis were prepared starting from ETFE base films irradiated with a high energy MeV class e-beam. The irradiation dose ranged from 5 to 15 kGy. The absorbed radiation dose is defined as the amount of energy exposed to matter and has the unit of Gray (Gy).\textsuperscript{137, 143}

In generally, the formation of active sites in pre-existing polymers can be carried out using various methods, such as ultraviolet (UV) light irradiation, plasma treatment or high energy irradiation.\textsuperscript{139} For irradiation of fluoropolymers such as ETFE a photon energy of \(> 0.1\) MeV is, however, desired.\textsuperscript{137} In contrast to plasma-induced and UV-induced graft copolymerization, which produces only surface modification in polymers, high energy irradiation allows the bulk modification of polymeric materials.\textsuperscript{139} Furthermore, depending on the used radiation source, the homogeneity of introduced activation within the given material can significantly differ. The linear energy transfer (LET) describes the energy transfer to the materials per unit length for a defined type of radiation. The average LET of a 1 MeV electron or a 60Co \(\gamma\)-ray in water is around 0.3 keV \(\mu\)m\(^{-1}\) and leads to homogeneous distribution of energy in the irradiated matter. In contrast, irradiation with heavy elements having LET of around 100 keV \(\mu\)m\(^{-1}\) results in highly localized damage areas (latent tracks).\textsuperscript{136, 144}
Chapter 2: Materials and methods

This chapter gives an overview about experimental techniques used in the framework of this thesis. Moreover, this chapter provides a deeper insight into details of conducted experimental work.

2.1 Materials and chemicals

The base polymer ETFE was obtained from DuPont (Tefzel® 100LZ, Circleville, USA, 25 μm film). Nafion® 117 and 212 from DuPont were used as benchmark materials. For all experiments ultra-pure water (18.2 MΩ × cm) was used.

Styrene (>99 %), acrylonitrile (>99 %) and 4-vinylpyridine (95 %) monomers were received from Sigma Aldrich. All monomers were used as received without removal of inhibitors. For the sulfonation reaction chlorosulfonic acid (Fluka, 98 %) and dichloromethane (VWR, 99 %) were used. Hydroxylamine hydrochlorid (96 %), sodium hydroxide (97 %) and 1-methyl-2-pyrrolidone (99.5 %) were obtained from Sigma Aldrich. Acetamide oxime (>97 %) were purchased from TCI (item number A2646) and sodium sulfate (99 %) from Merck. 3-aminobenzenesulfonic acid (97 %) and 1,10-dibromodecane (97 %) were obtained from Sigma Aldrich. Sulfuric acid (96 %), 2-propanol (technical) and acetone (technical) were purchased from VWR. Potassium chloride (>99 %) was obtained from VWR and potassium hydroxide solution for 1000 mL, c(KOH) = 0.1 mol L⁻¹ (Titrisol), from Merck. The potassium hydroxide solution was diluted prior to use to a concentration of 0.05 mol L⁻¹.

Vanadium(IV) sulfate oxide hydrate (VOSO₄·nH₂O, 99.9 %) was obtained from Alfa Aesar and n was determined to be 3 by means of thermogravimetric analysis.¹⁴⁵ Vanadium(III) chloride (97 %) and vanadium(V) oxide (98 %) were purchased from Sigma Aldrich.

Carbon electrodes such as SGL 10 AA and SGL 39 AA (DIN A4 sheets) were received from SGL group. Carbon felt GFD 4.6 (DIN A4 sheets) was obtained from Scribner Associates Inc (manufacturer SGL group).
Chapter 2: Materials and methods

2.2 Redox flow test station

A redox flow test station (Model 857 from Scribner Associates Inc) was used to prepare vanadium electrolytes for \textit{ex situ} characterization of ion exchange membranes (measurements of vanadium uptake and permeance). Moreover, the redox flow station was required for testing of different carbon electrode materials and membranes under real VRB operating conditions. The components of the redox flow test station are shown in Figure 2.1.

![Figure 2.1. Components of redox flow test station.](image)

To avoid oxidation of $V^{2+}$ species, the test station was purged with argon during all measurements. Tubes (Tube Tygon E-LFL LS Taille 14) used for electrolyte pumping were exchanged after extended use (1-2 months) due to their abrasion.
Chapter 2: Materials and methods

2.2.1 Preparation of vanadium electrolytes in redox flow test station

Vanadium electrolyte solutions, containing VO$^{2+}$, VO$^{2+}$, V$^{2+}$ and V$^{3+}$ ions were prepared in the redox flow test station using the following protocol. VOSO$_4$ solutions with desired concentration were prepared by dissolving VOSO$_4$ salt in 2 M H$_2$SO$_4$ and filled into both tanks of the redox flow system. The double amount of VOSO$_4$ solution was used on the positive side. The solutions were charged at 1.6 V and were considered fully charged at a current density of 2 mA cm$^{-2}$. After the charging process was completed, the excessive amount of VO$^{2+}$ electrolyte was removed from the positive side. The vanadium electrolyte solutions from both sides in charged/uncharged state are shown in Figure 2.2.

![Vanadium electrolyte solutions](image)

**Figure 2.2.** Vanadium electrolyte solutions from both sides in charged/uncharged state.

2.3 Pretreatment of Nafion® and synthesis of functionalized grafted membranes

2.3.1 Pretreatment of Nafion® membranes

The as-received Nafion® 117 was pretreated at 80°C in 32 % nitric acid for 1 h, followed by rinsing with pure water and boiling for 1 h in water. The boiling in water was repeated three times. Subsequently, the membranes were stored in pure water. Nafion® 212 was used as received.
Chapter 2: Materials and methods

2.3.2 Preparation of ETFE films for grafting reaction

14 cm × 16 cm samples were cut from the ETFE (DuPont Tefzel® 100LZ, 25 µm thickness) base film roll, washed with ethanol, dried under reduced pressure in the oven overnight and placed into zip-lock PE bags. The ETFE films were irradiated with a MeV class e-beam in an air atmosphere at LEONI Studer AG in Däniken (Switzerland) and were subsequently stored at -80°C until further use.

2.3.3 General procedure for synthesis of grafted films

The grafting reaction was carried out in glass reactors shown in Figure 2.3 under nitrogen atmosphere. For the grafting reaction, pre-irradiated films with the size of 7 cm × 7 cm were quickly cut and introduced into the solution containing monomers of choice.

Figure 2.3. Reactor used for grafting reaction and subsequent functionalization of grafted films.
Chapter 2: Materials and methods

Oxygen was removed from the grafting solution by bubbling with nitrogen for one hour. Subsequently, reactors containing monomer solutions and ETFE films were placed in a thermostatic water bath, pre-heated to a desired temperature.

The graft level was determined as follows:

\[ \text{GL} = \frac{m_g - m_o}{m_o} \cdot 100\% \]  

(2.1)

where \( m_o \) and \( m_g \) represent the weight of the sample before and after grafting, respectively.

2.3.4 Synthesis of ETFE-g-poly(S-co-AN)

A grafting solution with the following composition was used: 20 % (v/v) monomer solution + 70 % (v/v) iso-propanol + 10 % (v/v) ultra-pure water. Monomer solutions with different molar fractions of styrene and acrylonitrile were prepared. The molar fractions of both monomers in the final grafted films were estimated using a calibration curve determined previously in our group.\textsuperscript{146} Irradiated films (irradiation dose corresponding to 5 kGy) with the size of 7 cm × 7 cm were introduced into the grafting solution and oxygen was removed by nitrogen purging. Subsequently, reactors containing the grafting solutions and irradiated films were placed in a thermostatic water bath at the 60°C. After a defined reaction time, grafted films were removed, immersed in acetone overnight and then dried under vacuum at 80°C.

2.3.5 Functionalization of ETFE-g-poly(S-co-AN)

Amidoximation of nitrile groups was performed in a small glass reactor using 2 M solution of hydroxylamine hydrochloride in N-methylpyrrolidone (NMP). The pH value of the solution was adjusted to 7 by adding aqueous NaOH. NaCl, which was formed after addition of NaOH, underwent precipitation and was removed from the solution using a Büchner funnel. Subsequently, grafted films were introduced into the reactors with prepared solution and the reactors were placed in a thermostatic water bath at 70°C for 2 days.
Chapter 2: Materials and methods

Amidoximated membranes were removed from the solution and rinsed with ultra-pure water. Amidoximation was also carried out in other solvents and solvent mixtures including pure H$_2$O, H$_2$O/EtOH, H$_2$O/iso-propanol and H$_2$O/THF. However, the use of these solvents for the amidoximation reaction resulted in a significantly prolonged reaction time of around 5 days.

Sulfonation of styrene was performed in a 2 L glass reactor using a 3 % (v/v) solution of chlorosulfonic acid in dichloromethane. Grafted films were introduced into the solution and reacted for 6 h at room temperature under stirring. Afterwards, the sulfonated films were removed from the reaction mixture, washed with ultra-pure water and hydrolyzed at 80°C in pure water for 16 h.

The films were first amidoximated and then sulfonated. Films that were first sulfonated and then amidoximated contained, as evidenced by the signature of carbonyl stretch vibration at around 1'700 cm$^{-1}$ in FTIR spectra, not only sulfonic acid and amidoxime groups but also carboxyl groups. The presence of carboxyl groups is attributed to the partial hydrolysis of nitrile groups during sulfonation.

2.3.6 Synthesis of ETFE-g-poly(VP)

A grafting solution with the following composition was prepared: 50 % (v/v) vinylpyridine + 50 % (v/v) iso-propanol. Irradiated films (irradiation dose corresponded to 5 and 15 kGy) with the size of 7 cm $\times$ 7 cm were introduced into the grafting solution and oxygen was removed by nitrogen purging. Subsequently, reactors containing irradiated ETFE films and monomer solutions were placed in a thermostatic water bath at 60°C. After the reaction, grafted films were immersed in iso-propanol for 18 h and dried under vacuum at 80°C.

2.3.7 Functionalization of ETFE-g-poly(VP)

The first step of functionalization (alkylation) was performed in a 60 ml glass reactor using a 0.25 M solution of 1,10-dibromodecane in NMP. Prior to use, the flask containing 1,10-dibromodecane was held for 20 minutes in a beaker filled with warm water to liquify the hard, solid chemical. Vinylpyridine grafted films were introduced into the reactors with prepared solution and placed in a thermostatic water
bath at 45°C for a given amount of time. Subsequently, the films were removed from the reaction mixture and rinsed with iso-propanol.

The second step of functionalization (nucleophilic substitution of alkyl bromide by 3-aminobenzenesulfonic acid) was performed in a 60 ml glass reactor using a 0.05 M solution of 3-aminobenzenesulfonic acid in NMP. Grafted films were introduced into the small reactor containing the prepared solution and placed in a thermostatic water bath at 45°C for a defined period of time. Subsequently, functionalized films were immersed in 2 M H$_2$SO$_4$ overnight.

2.4 Ex situ characterization of carbon electrodes

2.4.1 Electrode materials used in the cell and cell architecture

The redox flow cell used for all experiments performed in this work contained following components:

- PAN based carbon electrodes and flow frames required to adjust the compression of the used carbon materials
- triple serpentine flow fields
- ice cube sealing with the thickness of 0.5 and 0.8 mm to avoid the leakage of vanadium electrolyte from the cell
- gold plated copper current collector plates
- aluminum end plates with reactant input/output ports

Four commercially available PAN based carbon materials were used in this work: SGL 39 AA carbon papers (thickness: ~280 µm), SGL 10 AA carbon papers (thickness: ~360 µm), Toray carbon papers TGP-H-120 (thickness: ~370 µm) and SGL SIGRACELL® GFD4.6 EA carbon felt electrodes (thickness: ~4300 µm) (Figure 2.4). A thickness gauge, Heidenhain ND287, was used to determine the thickness of carbon electrode materials.
Chapter 2: Materials and methods

**Figure 2.4.** Different carbon electrodes tested in an operating redox flow cell in the framework of this thesis.

To adjust the compression of carbon electrodes in the redox flow cell different frames were used. In the cell with carbon felt, PTFE (Teflon) flow frames allowed a compression of around 30% (Figure 2.5a). The compression in the cells containing various carbon papers was adjusted with aluminium frames (0.5 and 0.8 mm) and transparent PEN frames (50 µm) (Figure 2.5b).

**Figure 2.5.** Different frames used for compression adjustments in the cells with carbon electrodes.
Heat treatment (HT) of carbon materials: Carbon electrode pieces with a size of 5 cm × 5 cm were cut from DIN A4 sheets using a cutting tool. The carbon electrodes were placed in a tube furnace at 400°C under a steady flow of synthetic air (30 mL min⁻¹) for 30 hours.

2.4.2 X-ray photoelectron spectroscopy (XPS)

XPS was used to determine the total oxygen content (O/C ratio) and identify the different oxygen groups on the surface of the carbon materials. Samples of pristine and freshly heat treated GFD4.6 EA and SGL 39 AA were analysed as well as HT-GFD4.6 EA and HT-SGL 39 AA after extended cycling. As a comparison of the cycled materials, HT-GFD4.6 EA and HT-SGL 39 AA electrodes were each soaked in 2 M H₂SO₄ solution for a week (duration of a typical cycling experiment) to evaluate the influence of sulfuric acid alone on the oxygen content of the electrodes. Electrodes were rinsed thoroughly using deionised water and dried before being analysed by XPS. A VG ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al Kα monochromatic source and a magnetic lens system was used. High resolution spectra of the C1s and O1s peaks were used to determine the surface oxygen to carbon ratio (O/C ratio) for all electrode samples. All curves were fitted according to a Gaussian-Lorentzian function. Background subtraction was performed according to the Shirley method, and the atomic sensitivity factors (ASF) of Scofield were applied to estimate the atomic composition. Deconvolution of the C1s core level spectra was carried out fitting the following peaks: 284.1 eV, 284.9 eV, 285.96 eV, 288.2 eV, 290.4 eV and 291.61 eV (±0.8eV) arising from C-C, C-H, C-OR (including C-OH and O-C=O), C=O, COOH and shakeup satellite contributions, respectively.¹⁴⁷, ¹⁴⁸

2.4.3 Raman Spectroscopy

A Raman microscope (Labram HR800 Horiba-Jobin Yvon, Japan) with a He-Ne laser (632.8 nm) and a 50x objective (ULWDMS Plan 50, NA = 0.55, Olympus, Japan) was used to investigate the near-to-surface region of both untreated and heat treated SGL 39 AA carbon papers and GFD4.6 EA carbon felt electrodes and HT-SGL 39 AA and HT-GFD4.6 EA electrodes after cycling. The measurements were
performed with a grating of 600 lines mm$^{-1}$ and a laser power of 20 mW. First order Raman spectra were recorded in the range 1000 to 2000 cm$^{-1}$.

2.5  *Ex situ* characterization of membranes

2.5.1 Infrared Spectroscopy

Compositional changes of polymer films after the grafting reaction with selected monomers and in various stages of functionalization were analyzed using Fourier transform infrared spectrometry (Bruker Vertex 70 spectrometer). IR spectroscopy was also used to check for signatures of aging in the membranes after extended cycling experiments. All membranes were analyzed in dry state. FTIR spectra were recorded in absorbance mode at a resolution of 4 cm$^{-1}$ in a spectral range from 4000 to 400 cm$^{-1}$.

Furthermore, IR spectroscopy was used to determine the alkylation degree of vinylpyridine units after the first functionalization step. For this, the ratio of peak areas at 1’640 cm$^{-1}$ (quaternized pyridine ring C=N stretch) and 820 cm$^{-1}$ (C-H ring mode) was determined using Bruker OPUS spectroscopy software.

2.5.2 Scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX)

Sample holders used for analysis of membranes and various carbon materials are shown in the Figure 2.6. SEM images were taken using a FESEM Ultra 55 from Carl Zeiss and energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK).

SEM/EDX was used to analyze the elemental distribution in the cross-section of membranes. For this, membranes were stored in water for 1 h, frozen in liquid nitrogen and broken to obtain a sharp cross-section. A Leica EM SCD500 high vacuum sputter coater with Cr target was used to prepare samples for the measurements. An acceleration voltage of 10 keV was used.
The surface morphology of carbon materials was analyzed by scanning electron microscopy (SEM). An acceleration voltage of 2 keV was used. Carbon papers and carbon felt electrodes were introduced into the chamber of the SEM separately from each other due to the significant differences in their thickness.

![Sample holders used for surface and cross-section analysis of various carbon materials and membranes in the SEM.](image)

**Figure 2.6.** Sample holders used for surface and cross-section analysis of various carbon materials and membranes in the SEM.

### 2.5.3 Ion exchange capacity (IEC)

The cation exchange capacity (CEC) and anion exchange capacity (AEC) of membranes were obtained by the titration method using Titrino 702 SM and 877 from Metrohm.

For CEC measurements, two pieces of a membrane (two discs with a diameter of 2 cm in swollen state) were stored in a beaker filled with 40 mL of 0.5 M KCl solution overnight. Subsequently, the number of released protons was determined by titration to pH 7 using 0.05 M KOH. The cation exchange capacity was calculated with the following equation:

\[
CEC = \frac{n(H^+)}{m_{dry}} \quad (2.2)
\]
Chapter 2: Materials and methods

where \( n(\text{H}^+) \) corresponds to the number of moles of protons and \( m_{\text{dry}} \) to the weight of dry membrane in \( \text{H}^+ \) form.

The CEC was determined for three sets of two membrane samples. The acidity of the amidoxime groups was taken into consideration (Figure 2.7), and prior to titration with 0.05 M KOH, membranes containing protonated amidoxime groups were removed from the storage solution and rinsed with ultra pure water.

![Figure 2.7. Acidity of amidoxime groups](image)

To determine the AEC, discs of membranes (protonated in 1 M HCl) were exposed to 0.5 M KCl solution to exchange protons attached to sulfonic acid groups against \( \text{K}^+ \) ions. Subsequently, membranes were stored in 0.005 M KOH. The amount of the consumed KOH was determined by titration using 0.05 M HCl. Prior to titration membranes were removed from the solution and rinsed with ultra pure water. The AEC was determined for three sets of two membrane samples.

2.5.4 Vanadium permeance

Transport of vanadium ions (\( \text{VO}^{2+} \), \( \text{VO}_2^+ \) and \( \text{V}^{3+} \)) across different membranes was studied using homemade diffusion cells consisting of two round bottom flasks separated by the membrane of interest. Figure 2.8 shows a schematic representation of the home-made diffusion cell filled with \( \text{VOSO}_4 \) electrolyte on the left side and illustrates the changes of vanadium ion concentration over time in the right compartment of the cell assembled with Nafion® 117 membrane as separator.
Chapter 2: Materials and methods

The left compartment of the diffusion cell was filled with 150 mL of 1 M vanadium electrolyte based on 2 M H₂SO₄ while the right one was filled with 150 mL 1 M solution of MgSO₄ in 2 M H₂SO₄. The exposed membrane area (A) was 4.52 cm². The concentration of permeated vanadium ions in the Mg²⁺ solution was determined as function of time using UV-Vis spectroscopy. High precision quartz Suprasil cuvettes with a light path of 1 cm from Hellma Analytics were used for measurements.

Figure 2.8. Schematic representation of home-made diffusion cell filled with VOSO₄ electrolyte on the left side and an example representing typical concentration increase of vanadium ions in the right compartment of the diffusion cell assembled with Nafion® 117 as separator. The changes of vanadium ions concentration on the right side of the cell over time were measured with UV-Vis spectroscopy.

The concentration of permeated VO²⁺ was determined as a function of time via UV-Vis spectroscopy based on the absorption band at 766 nm using an extinction coefficient of 14.0 ± 2.0 L mol⁻¹ cm⁻¹ (an extinction coefficient of 13.40 L mol⁻¹ cm⁻¹ was reported in the literature¹⁵⁰). To determine the extinction coefficient of VO²⁺ ions at 766 nm, three VOSO₄ solutions with known concentration were prepared and their absorbance was measured with UV-Vis spectroscopy. The resulting calibration curve (Figure 2.9)
was used for determination of the extinction coefficient using the Beer-Lambert law, which states a proportionality relationship between the absorbance and concentration of a substance:

\[ A = \varepsilon \cdot c \cdot d \]  

(2.3)

where \( A \) represents absorbance, \( \varepsilon \) the extinction coefficient, \( c \) the concentration and \( d \) the path length through the cell, respectively.

![Figure 2.9. Beer’s law plot for VO\textsuperscript{2+} ions. The absorbance of VO\textsuperscript{2+} containing solutions with known concentration was determined at 766 nm.](image)

Next, the concentration of permeated VO\textsuperscript{2+} ions was plotted versus time. An example representing the concentration of permeated VO\textsuperscript{2+} ions through Nafion\textsuperscript{®} 117 membrane versus time is shown below in Figure 2.10.

The rate of VO\textsuperscript{2+} cross-over, the permeance, was then calculated from the slope \( m \) of the regression line. The permeance values reported in the study are given as a current density equivalent \( j_{V(IV)} \) according to

\[ j_{V(IV)} = m \cdot F \cdot \frac{V}{A} \]  

(2.4)

where \( F \) is the Faraday constant (26.8 Ah mol\textsuperscript{-1}). In the example above for Nafion\textsuperscript{®} 117, a permeance of \( j_{V(IV)} = 0.64 \pm 0.03 \) mA cm\textsuperscript{-2} is obtained.
To determine the concentration of permeated V$^{3+}$ and VO$_2^+$ ions through membranes of interest, both solutions were first prepared in the redox flow cell starting from 1 M VOSO$_4$ electrolyte on both sides. The concentration of permeated V$^{3+}$ and VO$_2^+$ ions through membranes was then determined in home-made diffusion cells shown in Figure 2.8 as a function of time via UV-Vis spectroscopy based on the absorption bands at 605 and 210 nm, respectively. Extinction coefficients of $7.79 \pm 0.39$ (an extinction coefficient of $5.85 \text{ L mol}^{-1} \text{ cm}^{-1}$ was reported in the literature) and $6245 \pm 30 \text{ L mol}^{-1} \text{ cm}^{-1}$ were determined for V$^{3+}$ and VO$_2^+$ ions at the absorption bands at 605 and 210 nm, respectively.

For determination of extinction coefficients, VCl$_3$ and V$_2$O$_5$ were used to obtain the calibration curves based on the VCl$_3$ and V$_2$O$_5$ solutions with the known content of both vanadium species. In contrast, in the literature vanadium solutions were prepared in a redox flow cell starting from VO$_2^+$ electrolyte to determine the extinction coefficient for V$^{3+}$ ions. This may explain the difference between the reported in the literature extinction coefficient for V$^{3+}$ ions and those determined in our laboratory.
Chapter 2: Materials and methods

2.5.5 Uptake of vanadium ions into membranes

2.5.5.1 Uptake of vanadium ions into membranes at low pH

To determine the VO\(^{2+}\) uptake of the membranes, they were immersed in 20 mL of 1 M VO\(^{2+}\) electrolyte based on 2 M H\(_2\)SO\(_4\) for 14 days. Subsequently, the membranes were rinsed with water and immersed in 2 M sulfuric acid overnight to enable the release of absorbed VO\(^{2+}\) ions back into solution. The amount of released VO\(^{2+}\) was determined using UV-Vis spectroscopy (Cary 4000, Varian). The complete release of VO\(^{2+}\) ions into solution was verified by direct investigation of the membranes using UV-Vis spectroscopy. Sample holders used for solid UV-Vis spectroscopy are shown in Figure 2.11.

**Figure 2.11.** Sample holders used for solid UV-Vis spectroscopy.

Prior to the storage in 2 M sulfuric acid, the absorption of VO\(^{2+}\) ions present in the membrane could be observed. However, no absorption by VO\(^{2+}\) ions could be detected after regeneration of the membranes in acid. The uptake of VO\(_2^+\) and V\(^{3+}\) ions was determined using the same procedure. As already described above, VO\(_2^+\) and V\(^{3+}\) electrolytes were prepared starting from 1 M VOSO\(_4\) solution based on 2 M H\(_2\)SO\(_4\) in the redox flow test system (Model 857, Scribner) after charging, and their pH was determined to be around 0.
Chapter 2: Materials and methods

2.5.5.2 Influence of pH and the presence of Na\(^+\) ions on the uptake of vanadium ions by membranes

To increase the pH of the vanadium electrolyte, a 1 M solution of VOSO\(_4\) in H\(_2\)O instead of 2 M sulfuric acid was prepared. For the vanadium uptake experiment in the presence of Na\(^+\) ions, an aqueous solution containing VOSO\(_4\) (1 M) and Na\(_2\)SO\(_4\) (0.5 M) was prepared. To have the same amount of VO\(^{2+}\) and Na\(^+\) ions in the solution, the concentrations of the corresponding salts were chosen to be 1 and 0.5 M. Using an autotitrator (Titrino 702 SM, Metrohm), the pH of the two aqueous solutions with and without Na\(^+\) ions was determined to be approximately 2. Again, the membranes were stored in aqueous vanadium solutions with and without Na\(^+\) ions for 14 days, and their vanadium uptake was determined using the same procedure as for the vanadium uptake experiments explained above.

2.5.5.3 Experimental study of VO\(^{2+}\)/acetamide oximes interactions in solutions with different pH

A 0.01 M solution of blue VOSO\(_4\) salt in water was prepared. Colorless acetamide oximes were introduced into the solution so that the ratio of VOSO\(_4\) and acetamide oximes was 1:1. The pH of the solution containing acetamide oximes and VO\(^{2+}\) ions was measured to be 3.5 (Titrino 702 SM, Metrohm). Subsequently, 2 M H\(_2\)SO\(_4\) was added to this solution to adjust the pH to 2. UV-Vis spectroscopy (Cary 4000, Varian) was used to monitor the changes in the solution containing VO\(^{2+}\) species after the addition of acetamide oximes and 2 M sulfuric acid.

2.5.6 Ex situ conductivity

The conductivity of membranes equilibrated in 20 mL H\(_2\)O and in a solution of 1.0 M VOSO\(_4\) in 2.0 M H\(_2\)SO\(_4\) (vanadium electrolyte) was measured at a frequency of 20 Hz using a Keysight LCR meter (model E4980AL) and a four-point probe cell (Bekkttech BT-112) in in-plane configuration (Figure 2.12). For this, rectangular samples (3.0 cm × 1.2 cm) of hydrated membranes were cut and inserted into the cell. To ensure the hydration of membranes during the measurements, the four-point probe cell was placed into a container filled with ultra-pure water. Conductivity measurements were performed with samples equilibrated in water and in vanadium electrolyte after 3, 6 and 7 days. The conductivity did not change significantly for an equilibration time of 7 days. Therefore, the experiment was discontinued. The in-plane conductivity was calculated with the following equation:
Chapter 2: Materials and methods

\[ \sigma = \frac{d}{R_w t} \]  

(2.5)

where \( \sigma \) represents the proton conductivity in \( \text{S cm}^{-1} \), \( R \) the measured resistance in \( \text{k}\Omega \), \( t \) thickness of the membrane (\( \mu \text{m} \)), \( w \) the width of the sample in cm (1.2 cm in the present case), and \( d \) the distance between the two voltage sense probes (4.2 mm). A thickness gauge, Heidenhain ND287, was used to determine the thickness of membranes.

![Four-point probe cell](image)

**Figure 2.12.** Four-point probe cell for measurements of in-plane conductivity of membranes. To ensure humidification of membrane the four-point probe cell was placed in ultra-pure water during the measurements.

### 2.5.7 Calculation of selectivity parameters

The area specific ohmic resistance (measured inside the redox flow cell) and \( \text{VO}^{2+} \) cross-over values (determined in home-made diffusion cells) of selected membranes were used to calculate the (dimensionless) selectivity parameter \( \alpha \) with the following equation:  

\[ \alpha = \frac{RT}{F} \cdot \frac{1}{R_{\Omega} \cdot i_x} \]  

(2.6)

where \( T \) is taken as 298 K.
Chapter 2: Materials and methods

2.5.8 Determining the degree of alkylation in 4VP based membranes

The degree of alkylation (%) of pyridine functionalities was determined by means of ion chromatography (Metrohm 882 Compact IC Plus) with an anion exchange column (Metrosepp A Supp 5 150) and conductivity detection with a suppression system.

For this, the functionalized sample in bromide form was placed in 0.1 M HCl for 8 h in a well stirred vessel and the concentration of bromide anions exchanged against chloride anions was measured in the leachate using IC.

In the next step, a correlation between the measured alkylation degree of selected membranes and their peak area ratios at 1’640 and 820 cm\(^{-1}\) in IR spectra was established. The IR spectra were obtained using a Bruker Vertex 70 spectrometer. Ratio of peak areas at 1’640 cm\(^{-1}\) (quaternized pyridine ring C=N stretch) and 820 cm\(^{-1}\) (C-H ring mode) was determined using Bruker OPUS spectroscopy software. The obtained calibration curve (alkylation degree in % from IC versus peak area ratios at 1640/820 cm\(^{-1}\)) allowed determination of the degree of quaternization in further membranes of interest by analyzing their IR spectra only (Figure 2.13):

![Figure 2.13](image)

**Figure 2.13.** Degree of alkylation of vinylpyridine units in selected VP based membranes determined from ion chromatography (IC) versus the ratio of the peaks at 1’640 and 820 cm\(^{-1}\) obtained from IR spectra of the same membranes. The slope of the linear fit represented in the graph was 37.2 ± 1.6.
Chapter 2: Materials and methods

2.6  *In situ* characterization of electrodes

**2.6.1 Polarisation curves and reference electrode measurements**

Discharge polarization curves were recorded galvanostatically with freshly charged electrolytes (100 \% SoC) at an electrolyte flow rate of 30 mL min\(^{-1}\). A single-pass method was used to measure polarization curves, whereby no recirculation of the electrolyte into the storage tanks occurred and the discharged electrolyte was collected externally. This ensured a 100 \% SoC electrolyte entered the cell throughout the experiment. Data points were measured at current densities of 0, 20, 40, 60, 100, 140, 180, 220, 260 mA cm\(^{-2}\) holding for 20 seconds at each point. The current limit of this system was 280 mA cm\(^{-2}\).

A Hg/Hg\(_2\)SO\(_4\) reference electrode (C3 Prozess- und Analysentechnik GmbH) was connected to the cell in an ‘edge-type’ configuration in which an extension of the Nafion\textsuperscript{®} 117 membrane was placed in contact with the reference electrode used in the cell (Figure 2.14).\textsuperscript{151-153} The junction region was kept hydrated with a 2 M H\(_2\)SO\(_4\) solution.

![Figure 2.14](image.jpg)

*Figure 2.14.* Representation of the redox flow cell connected with a reference electrode via an extension of the Nafion\textsuperscript{®} 117 membrane. The Nafion\textsuperscript{®} 117 membrane was maintained in contact with the reference electrode using a glass tube filled with 2 M H\(_2\)SO\(_4\).
Chapter 2: Materials and methods

2.6.2 Charge/discharge cycling

To compare the performance of the cells containing different carbon materials, charge/discharge cycling was carried out at a flow rate of 30 mL min$^{-1}$ and a current density of 40 mA cm$^{-2}$ using 70 mL of 1 M vanadium electrolyte on each side of the cell (poor performance of pristine carbon felt required a reduced current density of 20 mA cm$^{-2}$). The upper and lower cell potential cut-off limits were set to 1.7 V and 0.8 V, respectively. The key characteristics of operating redox flow battery are coulombic (CE), voltage (VE) and energy (EE) efficiency. CE, VE and EE were determined from the 2$^{nd}$ cycle following a procedure described in the literature.$^{81}$ Following equations were used for their calculations:

$$CE = \left( \frac{\text{discharge capacity}}{\text{charge capacity}} \right) \cdot 100\% = \frac{\int I_d dt}{\int I_c dt} \cdot 100\%$$  \hspace{1cm} (2.7)

$$VE = \left( \frac{\text{mean discharge voltage}}{\text{mean charge voltage}} \right) \cdot 100\%$$  \hspace{1cm} (2.8)

$$EE = CE \cdot VE$$  \hspace{1cm} (2.9)

where d and c represent charge and discharge process and $I$ and $t$ are current and time, respectively.

Charge/discharge capacity as well as mean charge/discharge voltage were extracted from charge/discharge curves obtained in cycling experiments. To calculate voltage efficiency the whole potential area between cut-off limits (1.7 V and 0.8 V) was considered. An example for charge/discharge curves obtained by cycling with Nafion® 117 is shown in Figure 2.15:

![Charge/discharge curves obtained from the second cycle with Nafion® 117 as separator.](image)

**Figure 2.15.** Charge/discharge curves obtained from the second cycle with Nafion® 117 as separator.
Chapter 2: Materials and methods

In order to probe the stability of selected carbon materials (heat treated SGL 39 AA carbon papers and GFD6.4 EA carbon felt) under operating VRB conditions, extended cycling experiments were carried out over 35 charge/discharge cycles at 100 mA cm$^{-2}$ and an additional 38 cycles at 120 mA cm$^{-2}$ (with 100 mL of 1 M vanadium electrolyte at each side of the cell and a flow rate of 30 mL min$^{-1}$).

2.7 **In situ** characterization of membranes

2.7.1 OCV measurements

The cell was potentiostatically charged at 1.6 V until an open circuit voltage of 1.47 V was achieved and then the open circuit voltage was measured as a function of time at a flow rate of 5 mL min$^{-1}$. 100 mL of 0.75 M vanadium solutions in 2 M H$_2$SO$_4$ were used as negative and positive electrolyte, respectively.

2.7.2 Measurements of area resistance

The area resistance of single redox flow cells was measured at fully charged state by means of electrochemical impedance spectroscopy. An AC amplitude of 10 mV and frequency range from 100’000 to 0.1 Hz was used.

It is noteworthy that cell components other than the membrane, such as the liquid electrolytes, also contribute to the measured area resistance in this configuration. By measuring the in-plane conductivity of selected membranes in a four-point probe cell in in-plane configuration (after equilibration in vanadium electrolyte), the contribution of all the cell components excluding the membrane and including thermally treated carbon felt (one sheet on each side) and carbon papers (3 layers on each side) was estimated to be around 0.57 and 0.37 Ohm cm$^2$, respectively.

The area resistance of single redox flow cells with all cell components was determined in the Nyquist plot from the intercept of the spectrum with the real axis (Figure 2.16, red circle), fitted for the equivalent circuit shown in Figure 2.16.
Area resistance of cells containing membranes with amidoxime and sulfonic acid groups was measured with 3 layers of SGL 10 AA carbon papers on each side (10 % compression). Further investigations of different carbon materials revealed superior performance and stability of GFD 4.6 carbon felt compared to SGL carbon papers. Thus, area resistance of cells containing functionalized vinylpyridine based membranes was determined using one sheet of GFD 4.6 carbon felt on each side (30 % compression). For comparative purposes, area resistance of the cell containing one layer of GFD 4.6 carbon felt on each side and the best performing amidoximated and sulfonated membrane was also measured.

2.7.3 Redox flow cell experiments

A redox flow test system was used. 3 sheets of pristine SGL 10 AA carbon papers (each 350 µm thick) with an active area of 25 cm$^2$ were used in each half-cell (10 % compression) for cycling experiments at a current density of 40 mA cm$^{-2}$.

For cycling at a current density of 120 mA cm$^{-2}$, one layer of heat treated SGL SIGRACEIL$^\circledR$ GFD4.6 EA carbon felt electrode (thickness: 4300 µm) was used in each half-cell (30 % compression). All experiments were carried out at room temperature.
Charge/discharge cycling of the redox flow cells was performed at a constant current density of 40 mA cm\(^{-2}\) and 120 mA cm\(^{-2}\) using 1.7 V as upper and 0.8 V as lower voltage limit. The flow rate was 30 mL min\(^{-1}\). 60 mL of 0.75 M and 100 mL of 1 M VOSO\(_4\) solution in 2 M H\(_2\)SO\(_4\) were used as electrolytes for cycling at 40 mA cm\(^{-2}\) and 120 mA cm\(^{-2}\), respectively.

### 2.7.4 Imbalance of electrolyte

To characterize the net volumetric transfer qualitatively the electrolyte volumes on both sides were measured after a number of charge/discharge cycles and electrolyte imbalance was calculated with the following equation:

\[
\text{Imbalance} = \frac{\Delta V}{V} = \frac{V_+ - V_-}{V_+ + V_-} \frac{1}{2(V_+ + V_-)}
\]  
(2.10)

where \(V_+\) and \(V_-\) are the volumes of the positive and negative electrolyte, respectively. At the beginning of all cycling experiments both the positive and the negative tank were filled with 100 mL of vanadium electrolyte. Overall losses of electrolyte volume were attributed to trapping of liquid in the cell, tubes and connections, and evaporation, since the tanks are continuously purged with argon.
Electrodes provide the surface on which electrochemical reactions occur in the VRB cell. Their catalytic activity, wettability and mass transport properties significantly affect the VRB performance and must be optimized. Furthermore, electrode materials should be stable under VRB operating conditions to ensure long-term operation of the battery. In this chapter, the performance and stability of selected commercially available carbon electrode materials (pristine and thermally treated) are compared under VRB operating conditions with the aim to identify especially promising ones. Moreover, possible reasons for the observed differences in the cycling stability of studied carbon electrodes are discussed.

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Chapter 3: Performance and stability of different carbon electrode materials

3.1 Abstract

This work focuses on the performance and stability of selected commercial carbon electrode materials before and after heat treatment in an operating all-vanadium redox flow battery (VRB). Heat treatment results in improved cell performance for all tested materials, with SGL 39 AA carbon papers and SIGRACELL® GFD4.6 EA carbon felt showing the best performance. Further investigation of these two materials by in situ reference electrode measurements reveal that improvements after heat treatment originate mainly from the negative electrode or V\(^{2+}/V^{3+}\) side of the cell. Upon extended cycling, carbon felt is found to be stable. Carbon papers, however, show significant performance losses originating from the negative electrode side. The potential limit during charging and the exposure to very negative potentials appears to be a critical issue at the negative electrode in the VRB. Analysis of both materials after cycling by scanning electron microscopy, Raman spectroscopy and x-ray photoelectron spectroscopy reveal significant differences in their surface chemistry, structure and morphology. These differences give valuable insights into the behaviour and degradation of different carbon materials used in VRBs.

3.2 Introduction

Redox flow batteries (RFBs) are a promising technology for efficient energy storage and grid stabilization.\(^6\),\(^9\) The all-vanadium redox flow battery (VRB), which uses vanadium ions in different oxidation states at the positive and negative electrodes, is the most advanced RFB to date.\(^8\) The electrodes are a crucial component of the VRB, as they provide the surface on which the respective electrochemical reactions occur. Thus, catalytic activity, wettability and mass transport properties of the electrodes strongly affect VRB performance. Ideal electrodes for the VRB should provide both: long-term durability and stable catalytic activity. Various materials have been considered as electrodes for the use in VRBs including non-carbon based dimensionally stable anode electrodes and carbon based electrodes such as carbon felt, carbon paper, carbon nanotubes, carbon nanofibers or graphene oxides.\(^5,4\)
Chapter 3: Performance and stability of different carbon electrode materials

To enhance electrochemical activity and wettability of carbon based materials in VRBs, different surface modification methods have been used. Carbon electrodes have been coated with metals such as iridium,\textsuperscript{66} doped with nitrogen\textsuperscript{154} or decorated with nanomaterials such as graphene-nanowalls\textsuperscript{70} or graphite carbon nanotubes.\textsuperscript{71} Recently, Zhou et al. reported activation of carbon papers and carbon cloth by heat treatment and subsequent etching with KOH.\textsuperscript{64, 65} The performance of carbon materials have also been shown to be improved by means of thermal,\textsuperscript{56-58} chemical,\textsuperscript{59, 60} electrochemical,\textsuperscript{61} plasma\textsuperscript{62} or a combination of corona discharge and hydrogen peroxide treatment.\textsuperscript{63}

Most of these surface treatment approaches introduce functional groups, commonly oxygen onto the carbon electrode surface. This leads to increased wettability and redox activity, which is generally attributed to the increased concentration of surface-active oxygen functional groups.\textsuperscript{56} Among the various surface modifications, heat treatment is still regarded as the most common and facile approach to incorporate oxygen groups onto the surface of carbon materials.\textsuperscript{54}

In an effort to better understand the role of oxygen functional groups on electrode performance, Fink et al. studied pristine and heat-treated Rayon (a regenerated cellulose fiber) based GFA carbon felt and a polyacrylonitrile (PAN) based GFD carbon felt. According to this study, the normalized rate constant for the $\text{V}^{3+}/\text{V}^{2+}$ redox reaction increased with increasing number of oxygen functional groups, the rate constant for the $\text{VO}^{2+}/\text{VO}^{2+}$ redox reaction decreased for both types of carbon felt electrodes.\textsuperscript{72} Miller et al. demonstrated that the introduction of oxygen containing functionalities enhances the kinetics of $\text{V}^{3+}/\text{V}^{2+}$ and inhibits the kinetics of $\text{VO}^{2+}/\text{VO}^{2+}$.\textsuperscript{73} Similar observations were made in a study by our group, where oxygen groups alone were not found to play a crucial role in the activity of glassy carbon electrodes for vanadium (V) reduction. However, surface modification leading to increased roughness and number of defects appeared to play a positive role for this reaction.\textsuperscript{145} Many recent studies focusing on both vanadium redox reactions involved in the VRB have shown that the overpotential associated with the negative half-cell dominates the voltage losses of the VRB and limits performance.\textsuperscript{75-77, 155}

Many efforts have been successfully undertaken to improve the electrochemical activity of various carbon materials, which result in better VRB performance. However, despite these improvements, some
of the modified carbon materials are not suitable for use in the VRB because of their poor operational lifespan.

The use of heat treated carbon materials such as Rayon based carbon felt GFA6 or PAN based carbon papers SGL 10 AA resulted in an initial performance increase in the VRB. However, the cycling stability of both modified carbon electrodes was found to be very poor, with electrodes losing their initial activity after a number of charge/discharge cycles.\textsuperscript{76, 156}

In this study, the performance of a set of commercial carbon materials before and after heat treatment is investigated in a commercial VRB test system. The two best performing materials were selected and studied in more detail. Reference electrode measurements were used to decouple the positive and negative reaction contributions to the overall performance. Cycling stability of the two selected materials was investigated over an extended period. The materials were characterized by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron microscopy (SEM) before and after cycling. Valuable insights into the limiting reaction of this system and the different stabilities of two carbon based materials are discussed.
Chapter 3: Performance and stability of different carbon electrode materials

3.3 Experimental

3.3.1 Electrode materials and preparation

Four commercial PAN based carbon electrode materials were used in this work: SGL 39 AA carbon papers (thickness: ~280 µm), SGL 10 AA carbon papers (thickness: ~360 µm), Toray carbon papers TGP-H-120 (thickness: ~370 µm) and SGL SIGRACELL® GFD4.6 EA carbon felt electrodes (thickness: ~4300 µm). The heat treatment (HT) was carried out according to the procedure described in the literature.\textsuperscript{58}

The carbon electrodes were placed in a tube furnace at 400°C under a steady flow of synthetic air (30 mL min\(^{-1}\)) for 30 hours. HT has been used to denote heat treated materials throughout the text.

3.3.2 Cell architecture and electrolyte preparation

A commercial redox flow test system (Model 857, Scribner) with an active area of 25 cm\(^2\), serpentine flow fields and a Nafion\textsuperscript{®} 117 membrane was used. Nafion\textsuperscript{®} 117 was pretreated at 80°C in 32 % nitric acid for 1 h, followed by rinsing and boiling for 1 h in water.\textsuperscript{157} 1 M vanadium solution was prepared by dissolving VOSO\(_4\)\(_n\)H\(_2\)O (Alfa Aesar, 99.9 % purity, where \(n\) was determined to be 3 by thermogravimetric analysis) in 2 M H\(_2\)SO\(_4\). The solutions were charged following a typical protocol and considered fully charged (100 % state of charge, SoC) at a current density of 2 mA cm\(^{-2}\).\textsuperscript{158} Three layers of SGL 10 AA carbon papers were identified previously as the optimum number for best performance in a VRB and this number was used here.\textsuperscript{57} To maintain the same thickness of layered carbon papers in the cell, three toray TGP-H-120 and four SGL 39 AA papers were used on either side of the cell. One piece of carbon felt (GFD4.6 EA) was used on either side of the cell.

3.3.3 Polarisation curves and reference electrode measurements

Discharge polarisation curves were recorded galvanostatically with freshly charged electrolytes (100 % SoC) at an electrolyte flow rate of 30 mL min\(^{-1}\).
A single-pass method was used to measure polarisation curves, whereby no recirculation of the electrolyte into the storage tanks occurred and the discharged electrolyte was collected externally. This ensured a 100 % SoC electrolyte entered the cell throughout the experiment. Data points were measured at current densities of 0, 20, 40, 60, 100, 140, 180, 220, 260 mA cm$^{-2}$ holding for 20 seconds at each point. The current limit of this system was 280 mA cm$^{-2}$.

A Hg/Hg$_2$SO$_4$ reference electrode (C3 Prozess - und Analysentechnik GmbH) was connected to the cell in an ‘edge-type’ configuration in which an extension of the Nafion$^\text{®}$117 membrane was placed in contact with the reference electrode used in the cell.$^{151-153}$ The junction region was kept hydrated with a 2 M H$_2$SO$_4$ solution.

### 3.3.4 Charge/discharge cycling

Charge/discharge cycling was carried out at 30$^\text{o}$C, with a flow rate of 30 mL min$^{-1}$ at current density of 40 mA cm$^{-2}$ using 70 mL of 1 M vanadium electrolyte at each side of the cell (poor performance of pristine carbon felt required a reduced current density of 20 mA cm$^{-2}$). The upper and lower cell potential cut-off limits were set to 1.7 V and 0.8 V respectively. Coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) were calculated from the 2$^\text{nd}$ cycle following a procedure in the literature.$^{81}$

Extended cycling stability of selected heat treated materials (HT-SGL 39 AA and HT-GFD4.6 EA) was carried out with 100 mL of 1 M vanadium electrolyte at each side of the cell, 35 charge/discharge cycles at 100 mA cm$^{-2}$ and an additional 38 cycles at 120 mA cm$^{-2}$ were measured under the same conditions described previously.

### 3.3.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to determine the total oxygen content (O/C ratio) and identify the different oxygen groups on the surface of the carbon materials. Samples of pristine and freshly heat treated GFD4.6 EA and SGL 39 AA were analysed as well as HT-GFD4.6 EA and HT-
SGL 39 AA after extended cycling. As a comparison for the cycled materials, HT-GFD4.6 EA and HT-SGL 39 AA electrodes were each soaked in 2 M H₂SO₄ solution for a week (duration of a typical cycling experiment) to evaluate the influence of sulfuric acid alone on the oxygen content of the electrodes. Electrodes were rinsed thoroughly using deionised water and dried before being analysed by XPS. A VG ESCALAB 220iXL spectrometer (Thermo Fischer Scientific) equipped with an Al Kα monochromatic source and a magnetic lens system was used. High resolution spectra of the C1s and O1s peaks were used to determine the surface oxygen to carbon ratio (O/C ratio) for all electrode samples.

All curves were fitted according to a Gaussian-Lorentzian function. Background subtraction was performed according to the Shirley method, and the atomic sensitivity factors (ASF) of Scofield were applied to estimate the atomic composition. Deconvolution of the C1s core level spectra was carried out fitting the following peaks: 284.1 eV, 284.9 eV, 285.96 eV, 288.2 eV, 290.4 eV and 291.61 eV (±0.8 eV) arising from C-C, C-H, C-OR (including C-OH and O-C-O), C=O, COOH and shakeup satellite contributions, respectively.¹⁴⁷,¹⁴⁸

### 3.3.6 Raman Spectroscopy

A Raman microscope (Labram HR800 Horiba-Jobin Yvon, Japan) with a He-Ne laser (632.8 nm) and a 50x objective (ULWDMS Plan 50, NA = 0.55, Olympus, Japan) was used to investigate the near-to-surface region of both untreated and heat treated SGL 39 AA carbon papers and GFD4.6 EA carbon felt electrodes and HT-SGL 39 AA and HT-GFD4.6 EA electrodes after cycling. The measurements were performed with a grating of 600 line mm⁻¹ and a laser power of 20 mW. First order Raman spectra were recorded in the range 1000 to 2000 cm⁻¹.

### 3.3.7 Scanning Electron Microscopy (SEM)

The surface morphology of carbon materials was analyzed by scanning electron microscopy (SEM). SEM images were taken using a FESEM Ultra 55 from Carl Zeiss with an acceleration voltage of 2 keV.
Chapter 3: Performance and stability of different carbon electrode materials

3.4 Results and Discussion

3.4.1 Performance of carbon materials before/after heat treatment

The performance of four pristine, commercially available carbon electrode materials was studied in an operating VRB cell. The effect of heat treatment on these materials was investigated. Carbon felt electrodes (GFD4.6 EA) that are widely used in VRBs were compared to various carbon papers including SGL 10 AA, SGL 39 AA and Toray TGP-H-120. Figure 3.1 shows the polarisation curves measured for the untreated and heat treated materials and the key performance indicators for these materials are summarised in Table 3.1.

![Figure 3.1](image)

Figure 3.1. Discharge polarization curves measured in an operating VRB (SoC: 100 %) with a) untreated and b) heat treated commercial carbon electrode materials.

Among the untreated materials, the SGL 39 AA carbon papers showed the best performance (Figure 3.1a). After heat treatment, all electrode materials showed an improvement in overall cell performance. The HT-GFD4.6 EA carbon felt and HT-SGL 39 AA carbon papers showed the best performance of all heat treated materials tested in this study (Figure 3.1b).

Untreated SGL 39 AA showed the highest energy efficiency (68 %) and discharge capacity (59 %) for the pristine materials. Carbon felt showed the worst performance, even at a reduced current density (20 mA cm\(^{-2}\)) a very low energy efficiency (48 %) and discharge capacity (34 %) were observed.
Table 3.1. Key performance indicators for untreated and heat treated carbon materials. Coulombic efficiency (CE), voltage efficiency (VE), energy efficiency (EE) and discharge capacity ($C_{dis}$) determined from the 2nd cycle at 40 mA cm$^{-2}$ (20 mA cm$^{-2}$ in case of untreated carbon felt*). Discharge capacity ($C_{dis}$) calculated as $C_{dis, measured}/C_{dis, theoretical}$ expressed in %. Flow rate: 30 mL min$^{-1}$, upper and lower cutoff potentials of 1.7 V and 0.8 V respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>untreated carbon materials</th>
<th>heat treated carbon materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CE</td>
<td>VE</td>
</tr>
<tr>
<td>[-]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>Toray TGP-H-120</td>
<td>42</td>
<td>59</td>
</tr>
<tr>
<td>SIGRACET® SGL 39 AA</td>
<td>91</td>
<td>75</td>
</tr>
<tr>
<td>SIGRACET® SGL 10 AA</td>
<td>87</td>
<td>73</td>
</tr>
<tr>
<td>SIGRACELL® GFD4.6 EA</td>
<td>88*</td>
<td>54*</td>
</tr>
</tbody>
</table>

After heat treatment the HT-SGL 39 AA carbon papers and HT-GFD4.6 EA carbon felt showed the highest energy efficiencies of 79 % and 81 % respectively of all the heat treated materials. See the Supplementary Information for further details related to cycling history with various untreated and heat treated carbon electrodes (Figure S3.1). These materials were selected for further investigation and will be the focus of the remainder of this work.

3.4.2 Polarisation curves with reference electrode

A reference electrode included in the operating system allowed the decoupling of the contributions of the positive and negative electrode reactions to the overall performance. Figure 3.2a and b show the polarisation curves for both carbon paper and carbon felt before and after heat treatment and illustrate the overpotential contributions from both the positive and negative electrode reactions.
Chapter 3: Performance and stability of different carbon electrode materials

Figure 3.2. Discharge polarization curves (SoC: 100%) for untreated and heat treated a) SGL 39 AA carbon papers and b) GFD4.6 EA carbon felt showing contributions from the positive and negative reactions to the overall full cell voltage.

The observed improvements after heat treatment originate from the negative electrode side for both materials. The $V^{2+}/V^{3+}$ redox reaction appears to benefit significantly after heat treatment of the electrode materials. This observation is in line with several previous studies.\textsuperscript{55, 73, 75-77} The positive half-cell does not show any significant changes in overpotential before and after heat treatment of the electrode materials.

3.4.3 Cycling stability

Cycling stability of HT-GFD4.6 EA carbon felt and HT-SGL 39 AA carbon papers was investigated under VRB operating conditions. At the high current densities (100 and 120 mA cm\textsuperscript{-2}), HT-GFD4.6 EA carbon felt showed superior cycling performance, including higher VE and charge/discharge capacity. However both systems experienced slight VE decreases and significant capacity fading during the cycling experiments, this effect was more pronounced for HT-SGL 39 AA carbon papers (Figure 3.3a and b).

In general, capacity fading and decrease in VE during cycling experiments can be explained by two reasons: (1) as a result of high vanadium cross-over through the Nafion\textsuperscript{®} 117 membrane and/or (2) as a result of electrode degradation under VRB operating conditions.
Chapter 3: Performance and stability of different carbon electrode materials

Figure 3.3. Cycling history for a) HT-SGL 39 AA carbon papers b) HT-GFD4.6 EA carbon felt; Cycling performance of the cell in the 2nd cycle of long-term experiment and in the 2nd cycle after replacement of
imbalanced electrolyte for c) HT-SGL 39 AA carbon papers d) HT-GFD4.6 EA carbon felt; Polarization curves measured before and after 73 cycles (with freshly prepared electrolyte) as well as corresponding changes on the positive and negative side for (e) HT-SGL 39 AA carbon papers (f) HT-GFD4.6 EA carbon felt.

To separate the effect of electrolyte cross-over and possible electrode degradation, the vanadium electrolyte was replaced after cycling with a fresh electrolyte and the cell was charged and discharged again. If capacity / VE decline was solely a consequence of electrolyte imbalance caused by cross-over through the membrane, replacement of the imbalanced electrolyte should allow the restoration of the original cycling performance observed before the cycling experiments. If however electrolyte imbalance was accompanied by electrode degradation, it would not be possible to restore the original cycling performance by replacing the electrolyte with a fresh one.

In the case of HT-GFD4.6 EA carbon felt, the use of fresh electrolyte allowed the full recovery of the original cycling performance (Figure 3.3d). Only a very small decrease in discharge capacity (2 %) and VE (2 %) was observed. In this case the losses observed during cycling were associated only with electrolyte imbalance and not with carbon felt degradation. In contrast to this, the original cell performance could not be restored for HT-SGL 39 AA carbon papers upon replacement of the electrolyte (Figure 3.3c). Discharge capacity decreased by 22 % and VE by 4 %. This is an indication that the performance decline is not only associated with electrolyte imbalance but also with electrode degradation.

Polarisation curves measured after extended cycling support these observations. The HT-GFD4.6 EA carbon felt showed almost no change in overall performance before and after cycling (Figure 3.3f). However, a significant performance loss was observed for HT-SGL 39 AA carbon papers after cycling (Figure 3.3e). The performance loss originated mainly from the negative electrode side.

Although both carbon materials were activated using the same heat treatment method, HT-GFD4.6 EA carbon felt showed superior cycling stability compared to HT-SGL 39 AA carbon papers under VRB operating conditions. Other studies in the literature have reported poor stabilities of heat treated SGL 10 AA carbon papers and GFA6 carbon felt. Following these observations, the surface properties of the electrode materials before and after extended cycling experiments were investigated by XPS, Raman spectroscopy and SEM.
3.4.4 Electrode characterisation before and after cycling

3.4.4.1 Investigations of surface oxygen functionalities by XPS

XPS was used to investigate changes in surface oxygen content on the carbon materials before/after heat treatment and after extended cycling and soaking experiments. Figure 3.4 shows the changes in total oxygen content (O/C) and the distribution of different oxygen groups on the carbon materials under investigation.

After heat treatment, the oxygen content (O/C ratio) increased slightly for HT-SGL 39 AA carbon papers from 0.02 to 0.03 (Figure 3.4a). A slight decrease in O/C ratio was observed from 0.075 to 0.05 for HT-GFD4.6 EA carbon felt (Figure 3.4b).

![Figure 3.4](image)

**Figure 3.4.** XPS analysis of pristine, heat treated, acid soaked and cycled electrodes showing O/C ratios for a) SGL 39 AA carbon papers (CP) and b) GFD4.6 EA carbon felt (CF) and comparison of different oxygen functional groups for c) SGL 39 AA carbon papers and d) GFD4.6 EA carbon felt.
This decrease was also observed by Zhong et al. and explained by the removal of volatile C-O contaminants during heat treatment.\textsuperscript{55} The different behaviour upon heat treatment is an indication that the two materials interact differently with oxygen, this could be related to the different structures of the two pristine materials. The O/C ratio after acid soaking increased significantly for both materials, in line with findings by previous authors.\textsuperscript{156}

After long-term cycling the oxygen content of both cycled materials were compared to the acid-soaked samples as a baseline. A decrease in O/C ratio of approximately 33% was observed for both carbon materials from the negative half-cell. The O/C ratio for HT-GFD4.6 EA carbon felt from the positive half-cell showed a slight decrease in O/C ratio compared to the acid soaked samples. However, HT-SGL 39 AA carbon papers showed an increase in the O/C ratio after cycling at the positive half-cell.

In both cases the negative electrode showed lower oxygen content after cycling compared to the positive side. It is known that highly oxidising potentials experienced by the positive electrodes are well in the limit of known electrochemical oxidation of carbon.\textsuperscript{159} Additionally the vanadium ions themselves have also been suggested to induce changes in the oxygen content of carbon electrodes.\textsuperscript{156}

The type of oxygen groups is shown in Figure 3.4c and 3.4d. C-OR, C=O and COOH groups were present on the surface of heat treated and acid soaked carbon paper and carbon felt with C-OR groups being the most abundant (see Supplementary Information, Figures S3.2, S3.3 and S3.4). After long-term cycling experiments, C-OR groups were still the dominant groups on the surface of both materials. The surface of pristine carbon papers showed a larger amount of higher oxide groups (such as C=O and COOH) compared to carbon felt. After thermal treatment, the amount of higher oxide groups decreased for carbon papers and increased for carbon felt. Interestingly, in the case of both carbon electrodes, the most oxygen functionalities were introduced onto the surface not as a consequence of thermal treatment but after soaking in 2 M H\textsubscript{2}SO\textsubscript{4} (see Figure 3.4a and 3.4b). In this case, the bonding nature of the groups introduced was not the same for the two materials. For carbon papers, the amount of higher oxides was reduced after soaking in acid, with C=O/C-OH ratio decreasing from 0.38 to 0.28 and COOH/C-OH ratio from 0.28 to 0.20. For carbon felt, a reduction in the concentration of the higher oxide groups (C=O and COOH) was also observed, but was more pronounced in this case. The C=O/C-OH ratio changed from 0.46 to 0.23 and the COOH/C-OH ratio decreased even more from 0.23 to 0.08. It
appears that the presence of COOH groups relative to C-OH groups is much less favoured on the surface of carbon felt than on the surface of carbon papers in 2 M H₂SO₄ (see Supplementary Information, Table S3.1).

After extended cycling experiments, COOH groups disappear completely from the surface of carbon felt on both the positive and negative electrodes. The C=O/C-OH ratio increases from 0.23 to 0.50 and 0.45 for the negative and positive sides respectively. In contrast to this, the amount of COOH and C=O groups relative to COH groups remains very similar after cycling for carbon papers.

Changes in the amount of oxygen functionalities on the surface of carbon materials and in their bonding nature may occur for a number of different reasons. We have shown here the effect of 2 M sulphuric acid on the amount of surface oxygen functionalities and their bonding nature for two different carbon materials.

Vanadium ions have also been shown to influence the amount of oxygen containing functional groups on the surface of carbon electrodes. For instance V⁵⁺ and V³⁺ ions have been reported to reduce the oxygen content on the carbon surface, while VO₂⁺ ions have been shown to increase the oxygen content.156 Thus the very similar decrease (around 33 %) in oxygen content observed at the negative electrode for both materials after cycling could be related to the presence of V⁵⁺ and V³⁺ ions. Changes in O/C ratio on the surface of electrodes from the positive half-cell (decrease for GFD4.6 EA carbon felt and increase for SGL 39AA carbon papers) may be caused by interactions of both carbon electrodes with VO₂⁺ ions. Moreover, exposure to highly positive potentials as well as very negative potentials during cycling can also influence the oxygen content of the surface.

3.4.4.2 Investigation of carbon materials by Raman spectroscopy and SEM

The extent of graphitisation and amount of defects present in the carbon materials was investigated by Raman spectroscopy. The peaks at ~1350 (D), 1590 (G) and 1620 cm⁻¹ (D') in the Raman spectrum of carbon can be assigned to the disordered graphitic lattice (edges), the ideal graphitic lattice and disordered graphitic lattice (surface layer) respectively.77, 160 The Raman spectra of the carbon papers and carbon felt after heat treatment and extended cycling experiments are shown in Figure 3.5.
Chapter 3: Performance and stability of different carbon electrode materials

Figure 3.5. Raman spectra showing SGL 39 AA carbon papers and GFD4.6 EA carbon felt before/after heat treatment and after cycling the heat treated electrodes at the positive and negative side of the VRB.

Heat treatment of carbon papers resulted in an increase in the $I_D/I_G$ ratio from 0.48 to 0.72, indicating an increase in the defects at the surface of the carbon fibres. XPS revealed the introduction of oxygen functionalities onto the surface of the carbon fibres, which is in line with the increase in defect density observed by Raman spectroscopy.\textsuperscript{161}

In contrast to this, heat treatment of carbon felt resulted in a decrease in the $I_D/I_G$ ratio from 1.97 to 1.34. This decrease in the $I_D/I_G$ ratio indicates an increase in the size of graphitic domains in the material after heat treatment.\textsuperscript{162} XPS in this case showed a decrease in surface oxygen functionalities after heat treatment, which is in line with the increased degree of graphitisation observed by Raman spectroscopy.

The effect of extended cycling on both the positive and negative electrodes was examined. It appears that both positive and negative electrodes undergo similar structural changes after cycling. In the case of the HT-SGL 39 AA carbon papers, a further increase in the $I_D/I_G$ ratio is observed for both heat treated electrodes after cycling. The corresponding $I_D/I_G$ ratios can be found in the Supplementary Information (Figure S3.5). Again, this can be interpreted as a further increase in disorder and defects (edge sites) at the surface of this material in line with the increase in oxygen functionalities observed by XPS.
Chapter 3: Performance and stability of different carbon electrode materials

The HT-GFD4.6 EA carbon felt however sees a further decrease in the $I_D/I_G$ ratio after cycling. The appearance of the peak at 1620 cm$^{-1}$ is notable and is attributed to defects in the graphite lattice at the surface layer and could be linked to the increased oxygen observed after cycling.

Furthermore, the surface morphology was examined by SEM, see Figure 3.6. Based on the SEM results, the pristine carbon felt and carbon papers differ in the surface appearance of the fibres. The carbon felt has an uneven surface morphology with sharp edge-structures and apparent grooves in the fibres. Carbon papers exhibit a smoother fibre surface with small flakes scattered on the surface. Heat treatment did not cause any visible changes in the morphology of the fibres for both carbon materials. However, after long-term cycling HT-GFD4.6 EA carbon felt appears to have a rougher surface morphology compared to the pristine material.

![SEM images showing morphological changes of SGL 39 AA carbon papers and GFD4.6 EA carbon felt before/after heat treatment and after cycling the heat treated electrodes at the positive and negative side of the VRB.](image)

**Figure 3.6.** SEM images showing morphological changes of SGL 39 AA carbon papers and GFD4.6 EA carbon felt before/after heat treatment and after cycling the heat treated electrodes at the positive and negative side of the VRB.
3.4.5 Comparison and overview of different carbon materials

In order to investigate the influence, if any, of the starting precursor used to synthesise the carbon materials and their performance, the results from this work on two heat treated PAN based carbon materials (HT-SGL 39 AA and HT-GFD4.6 EA) were compared with a heat treated Rayon based carbon felt (GFA6) used in a previous study by Derr. et al.\textsuperscript{76}

Table 3.2 summarises the key findings. No correlation between the precursor materials used to synthesise the carbon electrodes and their operational lifespan can be seen. A notable difference between the three carbon materials shown in Table 3.2 is their residence times at cell voltages between 1.6 – 1.7 V during charging. HT-SGL 39 AA carbon papers and Rayon based carbon felt (GFA6) from Derr et al. were exposed to cell potentials above 1.6 V for a significantly longer period of time during charging compared to the stable HT-GFD4.6 EA carbon felt from this study. It follows that the polarisation at either or both positive and negative electrodes is greater for these materials, resulting in the higher cell potentials observed during charging.

<table>
<thead>
<tr>
<th>PAN based carbon papers SGL 39 AA</th>
<th>PAN based carbon felt GFD4.6 EA</th>
<th>RAYON based carbon felt GFA6\textsuperscript{†}</th>
</tr>
</thead>
<tbody>
<tr>
<td>cycling stability in 0.8-1.7 V potential window</td>
<td>unstable</td>
<td>stable</td>
</tr>
<tr>
<td>period of time in 1.6-1.7 V potential window</td>
<td>long</td>
<td>short</td>
</tr>
<tr>
<td>oxygen groups present in stressed electrodes after cycling</td>
<td>C-OR*; C=O; COOR</td>
<td>C-OR*; C=O</td>
</tr>
<tr>
<td>(\frac{I_D}{I_G}) ratio of pristine materials</td>
<td>0.48</td>
<td>1.97</td>
</tr>
</tbody>
</table>

\textsuperscript{†}reference\textsuperscript{76}

*major functional groups detected on the carbon surface
During charging at a fixed current density, the negative half-cell potential is seen to become more negative with time (see Supplementary Information Figure S3.6). Since the degradation of the carbon papers is observed mainly at the negative electrode side, it can be deduced that more negative potentials at the negative electrode have a detrimental effect on electrode stability. This was confirmed by measurements in which the cut-off cell voltage during charging was reduced from 1.7 V to 1.6 V. In this case, less performance losses were observed at the negative electrode for HT-SGL 39 AA carbon papers after extended cycling measurements (see Supplementary Information, Figure S3.7). Thus it appears that the electrode degradation is strongly related to the potential at the negative electrode, particularly during the charging stage.

It has been shown previously that the range of negative potentials experienced by the negative electrode in the VRB fall into a region in which the electrode can be deactivated by reduction. Oxygen surface groups have been shown to have a positive influence on \( V^{2+/3+} \) redox reaction kinetics. However, the stability of oxidised carbon surfaces has also been found to be affected by very negative electrode potentials. In this study, XPS analysis revealed that after cycling, the oxygen content at the negative electrode decreased for both carbon materials relative to the acid soaked samples. This decrease in oxygen content could result from exposure to very negative electrode potentials and ultimately contribute to the loss in activity observed at the negative electrode. However, this observation alone does not fully explain the loss in activity observed for the carbon papers and not for carbon felt.

Previous studies have suggested that activity losses at the negative electrode could be due to a combination of factors including hydrogen evolution, passivation effects and losses in surface active groups such as oxygen. The two materials in this study differ significantly in their structures, observed by Raman spectroscopy and surface morphology seen by SEM. The structural properties and morphology of the carbon materials could also play a key role in the different stabilities of the carbon materials studied here. It appears that stability and degradation of carbon materials in VRBs is a complex issue. It is likely that a combination of different effects is responsible, including material properties and surface chemistry as is seen in this work. However, other issues such as hydrogen evolution and mass transport also need to be considered in order to gain a full overview of factors contributing to electrode stability and degradation in VRBs.
3.5 Conclusions

A preliminary investigation into performance and electrode stability of selected commercial materials under VRB operating conditions was carried out in this study. Heat treatment was found to be beneficial for cell performance with all materials, HT-SGL 39 AA carbon papers and HT-GFD4.6 EA carbon felt showed the best overall performance.

Reference electrode measurements with these two materials revealed that most of the improvements after heat treatment came from the negative electrode or the V$^{2+}$/V$^{3+}$ side. Upon extended cycling, HT-GFD4.6 EA carbon felt was found to be stable and no significant performance losses could be observed. HT-SGL 39 AA carbon papers however showed significant losses in performance which originated primarily from the negative electrode. The degradation at the negative electrode appears to be related to the negative electrode potential itself. XPS revealed losses in oxygen at the negative electrode after cycling for both materials. Losses in surface oxygen could contribute to the losses in activity observed for HT-SGL 39 AA carbon papers, however it does not appear to be the only factor responsible. Raman spectroscopy and SEM revealed significant structural and morphological differences between the two materials. These properties may also play a key role in the stabilities of the two materials studied here.

This study gives an initial insight into the stability and degradation of carbon electrodes used in VRBs. Further investigations into other possible contributing effects such as mass transport and material structural properties including porosity and morphology are ongoing in our group. Nonetheless, the negative electrode requires significant attention regarding improvements in activity and stability specifically at negative potentials as is highlighted in this work. These insights will help in the understanding and optimisation of a more stable negative electrode material for the VRB system.

Acknowledgements

The authors thank The Swiss National Science Foundation (SNF) for their financial support within the REPCOOL project (Grant No. 147 661).
3.6 Supporting Information

Figure S3.1. Charge/discharge curves for cells with various carbon electrodes before/after thermal treatment. Cycling was carried out at a current density of 40 mA cm$^{-2}$ (20 mA cm$^{-2}$ in case of untreated carbon felt). 70 mL of vanadium electrolyte on each side (composition: 1.0 M vanadium in 2 M H$_2$SO$_4$) and a Nafion®117 membrane were used. Flow rate: 30 mL min$^{-1}$. 1.7 V was used as upper and 0.8 V as lower voltage limit.
Figure S3.2. XPS C1s spectra for SGL 39 AA carbon papers before/after thermal treatment and after cycling at the positive and negative side.
Figure S3.3. XPS C1s spectra for SIGRACELL® GFD4.6 EA carbon felt before/after thermal treatment and after cycling at the positive and negative side.
Figure S3.4. XPS C1s spectra for SGL 39 AA carbon papers (left) and SIGRACELL® GFD4.6 EA carbon felt (right) after being stored in 2 M H$_2$SO$_4$ for one week.

Table S3.1. Comparison of different oxygen functional groups on the surface of SGL 39 AA carbon papers and GFD4.6 EA carbon felt.

<table>
<thead>
<tr>
<th></th>
<th>pristine</th>
<th>thermally treated</th>
<th>acid soaked</th>
<th>after cycling (-) side</th>
<th>after cycling (+) side</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SGL 39 AA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O/COH</td>
<td>0.45</td>
<td>0.38</td>
<td>0.28</td>
<td>0.31</td>
<td>0.27</td>
</tr>
<tr>
<td>COOH/COH</td>
<td>0.42</td>
<td>0.28</td>
<td>0.20</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td><strong>GFD4.6 EA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O/COH</td>
<td>0.32</td>
<td>0.46</td>
<td>0.23</td>
<td>0.50</td>
<td>0.45</td>
</tr>
<tr>
<td>COOH/COH</td>
<td>0.15</td>
<td>0.23</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure S3.5. Raman spectra showing carbon papers SGL 39 AA and carbon felt SIGRACELL® GFD4.6 EA before/after thermal treatment and after cycling at the positive and negative side. Changes in $I_D/I_G$ ratios for both carbon materials after thermal treatment and after extended cycling experiments.

Figure S3.6. a) Charge and b) discharge curves measured for thermally activated SIGRACELL® GFD4.6 EA carbon felt at a current density of 40 mA cm$^{-2}$. Insight into contributions of the positive and negative electrode reactions to the overall performance determined with reference electrode for both charging and discharging process.
Figure S3.7. Polarization curves measured for thermally activated SGL 39 AA carbon papers before and after 73 cycles (with freshly prepared electrolyte) as well as corresponding changes on the positive and negative side. Cycling experiments were performed with different operating potential window.
Polymeric separators are regarded as core components of all-vanadium redox flow cells and have significant impact on their efficiency and cycle lifetime. Whereas an extensive cross-over of vanadium species through separators results in reduced capacity and current efficiency of the VRB cell, their high ohmic resistance impairs their voltage efficiency. This chapter presents amphoteric ion exchange membranes containing sulfonic acid and amidoxime groups for VRB applications. Amidoxime groups are known in the literature for their ability to complex vanadium ions in sea water. The modification of membranes with amidoxime groups results in significant improvement of their vanadium barrier properties, whereas the presence of protogenic sulfonic acid groups allows the reduction of their ohmic resistance. As a consequence of improved selectivity, cells with these membranes show higher charge/discharge efficiency and a less pronounced capacity fading compared to the cells with the state-of-the-art material, Nafion® 117.

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Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

4.1 Abstract

The need for electrochemical energy storage increases along with the growing share of fluctuating renewables for power generation. The all-vanadium redox flow battery (VRB) has experienced increasing attention in this context. Its electrolyte membrane is a key component, yet currently perfluorinated materials (e.g., Nafion®) are mainly used in VRBs, which have neither been designed for this particular application, nor are they cost-effective. The cross-over of redox-active vanadium species impairs cell efficiency, in particular in case of thin Nafion® membranes with low ohmic resistance. Here, we present a potentially generic concept of a bifunctional ion-conducting membrane prepared by radiation grafting with sulfonic acid proton exchange sites and amidoxime moieties. The cross-over of vanadium ions is reduced four-fold in the presence of amidoxime groups without markedly impairing the conductivity of the membrane. A VRB cell containing such membrane shows increased energy efficiency and negligible capacity fading over 122 charge / discharge cycles compared to cells with Nafion® membrane, which showed a loss of discharge capacity of around 35 % after 35 cycles and considerable electrolyte imbalance.

4.2 Introduction

The growing need for energy and urge to reduce CO₂ emissions require clean and renewable energy sources, such as wind and solar power.², ³, ¹⁶⁶ Since these primary energies are inherently intermittent,⁴ the development of adequate energy storage scenarios is essential.⁶, ⁷ Among the various energy storage concepts, batteries have been shown to be especially promising.¹², ¹³ Batteries for grid-scale energy storage require good cycling stability, rapid response to changes, high round-trip efficiency and reasonable lifecycle costs. Redox flow batteries (RFBs) can fulfill these requirements⁹ to target applications in the MW to GW power scale with typical charge/discharge times of 4 to 6 h.¹⁶ Key
advantages over conventional rechargeable grid-scale batteries, such as Na-S batteries, are the independent scalability of energy and power, inherent safety, deep discharge capability and low self-discharge. A redox flow battery consists of two external tanks filled with liquid electrolyte and a stack of cells that contain porous electrodes separated by an ion exchange membrane (IEM). The IEM avoids cross-mixing of redox-active species and allows the transport of background electrolyte ions. The all-vanadium redox flow battery (VRB) is the most advanced type. VRBs use the same redox-active element on the negative and positive electrode, preventing irreversible cross-contamination of the electrolytes.

The membrane is a key cost driver in a VRB system and can account for the major share of the stack cost. An ideal membrane for an RFB should have low cross-over of redox-active species and water, low cost, high conductivity, and high chemical stability in the respective electrolyte solution. Depending on the nature of the exchange groups, IEMs are generally classified into cation and anion exchange membranes (CEMs, AEMs). Various IEM types have been considered for VRBs. There is a preference for CEMs such as Nafion®, as the high mobility of protons of the supporting acid electrolyte can be exploited, whereas AEMs suffer from lower conductivities. Nafion® and other perfluoroalkylsulfonic acid (PFSA) membranes are widely used in VRBs, but high vanadium cross-over and high cost are a downside. To overcome the cross-over problem, Nafion® has been modified using various approaches. However, in addition to the remaining cost issue, the area resistance of Nafion® often increased as a result of these modifications. Alternatively, non-fluorinated membranes are being developed with a view to reducing cost and improving vanadium barrier properties. Again, various approaches are used to design non-fluorinated membranes for the specific requirements of the VRB. Yet, chemical stability is often a critical factor for these materials. The use of amphoteric membranes is an interesting approach to combine advantages of AEMs and CEMs. A versatile and potentially low-cost method to prepare membranes with desired functional groups is radiation grafting.

Herein we present a potentially generic design concept of a bifunctional membrane for VRB applications containing protogenic styrene sulfonic acid and amidoxime groups. Amidoximes are vanadium complexing groups, yet are shown here to provide effective vanadium barrier properties in the membrane under low pH conditions.
4.3 Experimental

4.3.1 Pretreatment of Nafion® membranes

The as-received Nafion® 117 was pretreated at 80°C in 32% nitric acid for 1 h, followed by rinsing with pure water and boiling for 1 h in water. The boiling in water was repeated three times. Subsequently, the membranes were stored in pure water. Nafion® 212 was used as received.

4.3.2 Synthesis of radiation grafted membranes

ETFE films (DuPont Tefzel® 100LZ, 25 µm thickness) were irradiated with a MeV class e-beam to a dose of 5 kGy and stored at -80°C. Details of the synthesis procedure can be found elsewhere. The grafting reaction was carried out in glass reactors under nitrogen atmosphere. For that, a grafting solution with the following composition was prepared: 20% (v/v) monomer solution + 70% (v/v) isopropanol + 10% (v/v) ultra-pure water. Irradiated films with the size of 7 × 7 cm were introduced into the grafting solution. Subsequently, the grafting solution containing the irradiated film was degassed for 1 h by bubbling with N₂ and placed in a thermostatic water bath at the 60°C. After a defined reaction time, grafted films were removed, immersed in acetone overnight and then dried under vacuum at 80°C. The graft level was determined as follows:

\[
GL = \frac{m_g - m_o}{m_o} \cdot 100\%
\]

where \(m_o\) and \(m_g\) represent the weight of the sample before and after grafting, respectively.

Amidoximation of nitrile groups was performed in a small glass reactor using 2 M solution of hydroxylamine hydrochloride (Alfa Aesar) in N-methylpyrrolidone (Sigma Aldrich).

The pH value of the solution was adjusted to 7 by adding aqueous NaOH (Sigma Aldrich). Subsequently, grafted films were introduced into the prepared solution and the reactor was placed in a thermostatic water bath at 70°C for 2 days. Amidoximated membranes were removed from the solution and rinsed with ultra-pure water.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

Sulfonation of styrene was performed in a 2 L glass reactor using a 3 % (v/v) solution of chlorosulfonic acid (Fluka) in dichloromethane (VWR). Grafted films were introduced into the solution and reacted for 6 h at room temperature under stirring. Afterwards, the sulfonated films were removed from the reaction mixture, washed with ultra-pure water and hydrolyzed at 80°C in pure water for 16 h. The films were first amidoximated and then sulfonated. Films that were first sulfonated and then amidoximated contained, as evidenced by the signature of carbonyl stretch vibration around 1700 cm\(^{-1}\) in FTIR spectra, not only sulfonic acid and amidoxime groups but also carboxyl groups, which is attributed to the partial hydrolysis of nitrile groups during sulfonation.

### 4.3.3 Composition analysis

Compositional changes of polymer films after grafting and subsequent functionalization were studied using Fourier transform infrared spectrometry (Perkin-Elmer System 2000).

### 4.3.4 Elemental mapping

The elemental distribution in the cross-section of membranes was analyzed by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX). For this, membranes were stored in water for 1 h, frozen in liquid nitrogen and broken to obtain a sharp cross-section. SEM images were taken using a FESEM Ultra 55 from Carl Zeiss and energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK).

### 4.3.5 Ion exchange capacity (IEC)

The cation exchange capacity (CEC) and anion exchange capacity (AEC) of membranes were obtained by the titration method using Titrino 702 SM and 877 from Metrohm. The acidity of the amidoxime groups was taken into consideration. For CEC measurements membranes were stored in 0.5 M KCl solution overnight and the number of released protons was determined by titration using 0.05 M KOH. To determine AEC, membranes protonated in 1 M HCl were exposed to 0.5 M KCl solution and
subsequently stored in 0.005 M KOH. The amount of the consumed KOH was determined by titration using 0.05 M HCl.

4.3.6 Vanadium ion permeance

Vanadium ion cross-over through membranes was determined using home-made diffusion cells consisting of two round bottom flasks separated by the membrane. The left compartment was filled with a 1 M solution of VOSO$_4$ (Alfa Aesar) in 2 M H$_2$SO$_4$ (VWR) while the right one was filled with a 1 M solution of MgSO$_4$ (Alfa Aesar) in 2 M H$_2$SO$_4$. Solutions in both compartments were stirred and the concentration of diffused VO$_2^+$ ions was determined via UV-Vis (Cary 4000, Varian). The VO$_2^+$ permeance is given as a current density equivalent (cf. Supplementary Information, Figure S4.2, and associated text, for details).

4.3.7 Ex situ conductivity

The conductivity of membranes equilibrated in 20 mL H$_2$O and in a solution of 1.0 M VOSO$_4$ in 2 M H$_2$SO$_4$ (vanadium electrolyte) was measured at a frequency of 20 Hz using a Keysight LCR meter (model E4980AL) and a four-point probe cell (Bekktech BT-112) with in-plane configuration. Conductivity measurements were performed with samples equilibrated in water and in vanadium electrolyte after 3, 6 and 7 days. Conductivity did not change significantly over 7 days, after which the experiment was discontinued.

4.3.8 VO$_2^+$ uptake of the membranes after storage in the VRB electrolyte

The VO$_2^+$ uptake of the membranes after storage in the VRB electrolyte for 14 days was determined using UV-Vis spectroscopy. For this purpose, membranes were rinsed with water and immersed in 2 M sulfuric acid to allow the release of VO$_2^+$ ions back into solution. The complete release of VO$_2^+$ ions into solution was proved by direct investigation of membranes with UV-Vis spectroscopy. Before storage in 2 M sulfuric acid, absorption of VO$_2^+$ ions present in the membrane could be observed.
However, no absorption by VO$^{2+}$ ions could be detected after regeneration of membranes in acid (cf. Supplementary Information, Figure S4.5).

### 4.3.9 Redox flow cell experiments

A redox flow test system (Model 857, Scribner) was used. 3 sheets of SGL 10 AA carbon paper (each 350 $\mu$m thick) with an active area of 25 cm$^2$ were used in each half-cell (10 % compression) for all in situ experiments excluding cycling at a current density of 120 mA cm$^{-2}$. For the latter, one layer of heat treated SGL SIGRACELL® GFD4.6 EA carbon felt electrode (thickness: 4300 $\mu$m) was used in each half-cell (30 % compression). The heat treatment was carried out according to the procedure described in the literature.$^{58}$ Vanadium electrolytes were prepared using a protocol reported in the literature.$^{158}$ All experiments were carried out at room temperature.

The area resistance of single redox flow cells was measured at fully charged state by means of electrochemical impedance spectroscopy. An AC amplitude of 10 mV and frequency range from 100'000 to 0.1 Hz was used.

The battery was potentiostatically charged to 1.47 V and then the open circuit voltage was measured as a function of time at a flow rate of 5 mL min$^{-1}$. 100 mL of 0.75 M vanadium solutions in 2 M H$_2$SO$_4$ were used as negative and positive electrolyte, respectively. Charge/discharge cycling of the redox flow cells was performed at a constant current density of 40 mA cm$^{-2}$ and 120 mA cm$^{-2}$ using 1.7 V as upper and 0.8 V as lower voltage limit. The flow rate was 30 mL min$^{-1}$. 60 mL of 0.75 M and 100 mL of 1 M VOSO$_4$ solution in 2 M H$_2$SO$_4$ were used as electrolytes for cycling at 40 mA cm$^{-2}$ and 120 mA cm$^{-2}$, respectively.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

4.4 Results and Discussion

4.4.1 Synthesis and Characterization of Proton Exchange Membranes with Vanadium-Barrier Groups

The synthesis of membranes with desired functional groups starts with the preparation of ETFE-g-poly(S-co-AN) grafted films (Figure 4.1a). These films were obtained using radiation induced graft copolymerization of styrene (St) and acrylonitrile (AN) onto ethylene tetrafluoroethylene (ETFE) films of 25 µm thickness. Subsequently, grafted films were functionalized to yield proton-conducting sulfonic acid and amidoxime groups.¹⁷⁰

Figure 4.1. Synthesis procedure of membrane and elemental mapping of its cross-section. a) Schematic of the process of membrane preparation. Bifunctionalized ETFE-g-poly(S-co-AN) membranes are obtained via activation by electron-beam irradiation, grafting of styrene (S) and acrylonitrile (AN), followed by amidoximation and sulfonation. b-d) Cross-sectional analysis of grafted membrane. SEM image (b) of an ETFE-g-poly(S-co-AN) grafted membrane (amidoximated & sulfonated) with a graft level of 40 %, and EDX elemental mappings of sulfur (c, associated with sulfonic acid) and nitrogen (d, associated with amidoxime).

A cost estimate performed for a similar membrane for application in fuel cells showed that production costs for a grafted ion-conducting membrane could be severalfold lower compared to Nafion® membranes.¹⁷¹ The success of the grafting reaction as well as the subsequent functionalization of ETFE-
g-poly(S-co-AN) films was probed using FT-IR spectroscopy. After the grafting reaction, peaks representative of acrylonitrile and styrene units could be observed in the FT-IR spectrum (Figure 4.2).

**Figure 4.2.** FT-IR analysis of films and membranes in various stages of functionalization. Important vibrational bands are highlighted. In the spectrum of the S/AN co-grafted film, the characteristic absorption peak of nitriles was identified around 2’230 cm\(^{-1}\). After amidoximation this peak disappears and a new peak at around 1’655 cm\(^{-1}\) (C=N stretching vibration in amidoxime) appears, indicating the conversion of nitrile to amidoxime. After sulfonation of ETFE-g-poly(S-co-AN) films absorption bands at 763 cm\(^{-1}\) and 702 cm\(^{-1}\) disappear, indicating sulfonation of the benzene ring. In addition, new peaks appear, i.e., the peaks at 1’007 cm\(^{-1}\) and 832 cm\(^{-1}\), associated with the presence of the SO\(_3\)\(^{-}\) group, and the peak at 1’414 cm\(^{-1}\), corresponding to the aromatic C=C \textit{para}-disubstituted stretching vibration. The asterisk (*) indicates a shoulder probably originating from protonated amidoxime units, which disappears upon immersion of the membrane in aqueous KCl or KOH (cf. Supplementary Information, Figure S4.1). The region between 1’030 and 1’330 cm\(^{-1}\) is hidden due to excessive absorption by the ETFE backbone polymer.

Based on the results obtained by FT-IR spectroscopy it was also found that films that were first sulfonated and then amidoximated contained not only sulfonic acid and amidoxime groups but also carboxyl groups, because of the partial hydrolysis of nitrile groups during sulfonation. In contrast, films that were first amidoximated and then sulfonated contained no carboxyl groups. Therefore, the yield of
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

amidoximation was higher in the latter case. Membranes with partially hydrolyzed nitrile groups showed inferior properties compared to membranes with nitrile units completely converted to amidoxime and therefore will not be further discussed in this article.

To obtain further structural information, elemental distribution in the cross-section of prepared membranes was analyzed by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) (Figure 4.1b-d). Sulfur as well as nitrogen elemental mappings obtained on functionalized membranes indicate the presence of sulfonic acid and amidoxime groups in the membranes. These results were in good agreement with IR analysis. Moreover, EDX analysis shows that with the chosen reaction conditions homogeneous distribution of grafts across the thickness was obtained.

The impact of the presence of amidoxime groups on the ion transport properties of grafted membranes was investigated. For this purpose, VO$^{2+}$ cross-over and ohmic resistance were studied \textit{ex situ} and in the single cell, respectively, using membranes with and without amidoximation. Nafion® 212 and Nafion® 117 were used as benchmark. VO$^{2+}$ ions were chosen for cross-over experiments because they readily dissolve in 2 M H$_2$SO$_4$ and the resulting electrolyte solution has excellent stability. VO$^{2+}$ transport across membranes was determined using home-made diffusion cells. As a device-relevant property, the area resistance of a redox flow test cell comprising the respective membrane was measured in the fully charged state by means of electrochemical impedance spectroscopy. It is noteworthy that cell constituents other than the membrane, such as the liquid electrolytes, also contribute to the measured ohmic resistance in this configuration.

The comparison of membranes with a graft level of 40 % and a grafts composition of around 40 % styrene and 60 % acrylonitrile units shows that the introduction of the amidoxime leads to a lowering of the VO$^{2+}$ permeance from 1.6 mA cm$^{-2}$ to 0.4 mA cm$^{-2}$ (Figure 4.3a), which represents a decrease by a factor of ~4, whereas the ohmic resistance is not significantly affected (Figure 4.3d). In comparison to the Nafion® membranes, the V(IV) cross-over is notably lower in case of the amidoximated grafted membrane. Nafion® 117 is the most widely used membrane in VRB applications. With the development of high power density VRB technology in the last decade, however, the need for low-ohmic-resistance membranes, such as Nafion® 212, has increased.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

Figure 4.3. Key device-relevant membrane properties. a-c) Vanadium-ion permeance measured \textit{ex situ} in a diffusion cell, expressed as current density equivalent. d-f) Ohmic resistance determined in the device (charged state). g-i) Selectivity parameter $\alpha$ calculated from the ohmic resistance $R_G$ and the permeance $i_x$ according to $\alpha = \frac{RT}{F} \cdot \frac{1}{R_G \cdot i_x}$, where $R$ and $F$ have their usual meaning, and $T$ is taken as 298 K. Various grafted membranes are compared to Nafion\textsuperscript{®} 117 (N117) and Nafion\textsuperscript{®} 212 (NR212) membranes. Panels a, d and g show the influence of the presence of amidoxime groups, b, e and h the influence of the graft level (GL) at a fixed styrene molar fraction in the grafts of $X_S=0.4$ ($X_{AN}=1-X_S$), c, f and i the effect of the composition of the grafts at a fixed graft level of 40%. Errors bars in case of VO\textsuperscript{2+} permeance are derived from the standard deviation of the slope of the regression line obtained from diffusion cell measurements (concentration of VO\textsuperscript{2+} vs. time, cf. example in Supplementary Information, Figure S4.2). For the ohmic resistance, the error bars indicate the standard deviation.
of 3 measurements. The error bars on the selectivity data are obtained via the law of error propagation. For numerical values cf. Supplementary Information, Table S4.1.

Considering these requirements, amidoximated radiation grafted membranes present an attractive combination of properties for the use in the VRB, since they exhibit not only lower vanadium permeance compared to Nafion® 117 (200 μm thickness in the swollen state) but also area resistance comparable to that of Nafion® 212 (60 μm). This is reflected in the improved selectivity parameter compared to that of Nafion® (Figure 4.3g).

The key design parameters of the grafted membranes used in this study are the graft level and ratio of S and AN monomer units in the grafts. Hence, the influence of these two properties was studied independently. The graft level is adjusted by the reaction time whereas the composition of the grafts is tuned by varying the monomer ratio in the grafting solution. A decrease in the graft level from 40 to 36 and 33 % leads to an increase in the ohmic resistance of the cell (Figure 4.3e), as expected, which is a result of the lower concentration of sulfonic acid groups in the membrane. At the same time, the vanadium barrier properties improve (Figure 4.3b).

The maximum in the selectivity is observed at a graft level of 36 % (Figure 4.3h). The change of the monomer ratio in the grafts has a strong influence on the membrane properties: an increase of the styrene content $X_S$ from 0.4 to 0.5 (decrease of AN content from 0.6 to 0.5) leads to a strong increase in vanadium cross-over (Figure 4.3c), whereas a decrease of the styrene content to 0.3 leads to a dramatic increase in cell ohmic resistance (Figure 4.3f). An optimum balance with a maximum in selectivity is obtained at a styrene content of 0.4 (Figure 4.3i). On the whole, membranes with a graft level of around 36 % and styrene content of 0.4 showed especially promising properties for VRB application, demonstrating not only very low cross-over of vanadium species but also area resistance comparable to that of Nafion® 212.

The co-existence of sulfonic acid and amidoxime groups imparts the membrane with cation exchange as well as anion exchange groups. Amidoximes are known to have acid-base character. Therefore, our amidoximated and sulfonated membranes are expected to exhibit an amphoteric character. Cation exchange capacity (CEC) and anion exchange capacity (AEC) of radiation grafted membranes were determined via acid-base titration. Experimental CEC and AEC values of membranes containing only
sulfonic acid or only amidoxime groups are in good agreement with theoretical values, indicating a high yield of functionalization (Table 4.1).

Table 4.1. Comparison of measured and theoretical ion exchange capacities. Cation exchange capacity (CEC) and anion exchange capacity (AEC) are obtained by titration from S/AN co-grafted membranes with S/AN molar content in the grafts of 0.4/0.6 with selected functionalization of comonomer units. Calculation of theoretical ion exchange capacity: cf. Supplementary Information.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graft level</th>
<th>Measured CEC [mmol g⁻¹]</th>
<th>Theoretical CEC [mmol g⁻¹]</th>
<th>Measured AEC [mmol g⁻¹]</th>
<th>Theoretical AEC [mmol g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amidoximated &amp; sulfonated</td>
<td>38</td>
<td>0.82 ± 0.04</td>
<td>1.25</td>
<td>1.56 ± 0.38</td>
<td>1.88</td>
</tr>
<tr>
<td>Only sulfonated</td>
<td>38</td>
<td>1.36 ± 0.04</td>
<td>1.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amidoximated &amp; sulfonated</td>
<td>35</td>
<td>0.70 ± 0.12</td>
<td>1.19</td>
<td>1.29 ± 0.51</td>
<td>1.79</td>
</tr>
<tr>
<td>Only amidoximated</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>2.03 ± 0.76</td>
<td>1.98</td>
</tr>
</tbody>
</table>

In contrast, membranes containing sulfonic acid as well as amidoxime groups show generally lower CEC and AEC values than expected. This suggests some degree of interaction between the sulfonic acid and amidoxime groups, e.g., polyion condensation or formation of ionic crosslinks, resulting in lower measured CEC and AEC values. A similar phenomenon has been observed by Liu et al.¹³³ and Liao et al.¹³¹ Therefore, the measured ion exchange capacity (IEC) values in case of bifunctional membranes are not a true reflection of the content of the respective exchange group, but have to be considered as an ‘effective’ or ‘apparent’ IEC.

The fundamental materials property governing the ohmic resistance of the membrane is its ionic conductivity. Nafion® exhibits a conductivity of around 0.1 S cm⁻¹ in water at room temperature in its protonated form, yet the value drops significantly in the VRB electrolyte due to the partial exchange of protons by vanadium ions.¹⁶⁷,¹⁷⁴ The conductivity of various grafted membranes and Nafion® 117 was therefore measured in protonated form in water and after equilibration in VRB electrolyte (1 M VOSO₄ in 2 M H₂SO₄) in a four-point probe conductivity cell.
In addition, the VO\(^{2+}\) uptake of the membranes after storage in the VRB electrolyte for 14 days was determined using UV-Vis spectroscopy. In case of the membrane equilibrated in water, the measured conductivity is the proton conductivity, as protons are the only mobile ions in this case. For the membrane equilibrated in the vanadium electrolyte, all the ions absorbed in the membrane (VO\(^{2+}\), H\(^+\), HSO\(_4^-\)) contribute to the overall conductivity, yet the major fraction is expected to be carried by the proton, owing to its high mobility. Nafion\(^\circledast\) 117 experienced a drop in conductivity from 81 to 27 mS cm\(^{-1}\) upon exposure to the VRB electrolyte, which is in good agreement with values reported in the literature.\(^{167}\) For the grafted membrane without amidoxime functionalization (only sulfonated), a similar drop in conductivity from 74 to 21 mS cm\(^{-1}\) was observed, whereas only a slight decrease in conductivity from 26 to 21 mS cm\(^{-1}\) could be seen in case of the amidoximated membrane (Table 4.2).

To the best of our knowledge, this is the first report on the comparison of the conductivity of an amphoteric membrane between water-swollen and VRB electrolyte equilibrated condition. In most of the studies using amphoteric membranes, the conductivity values reported refer to the water-swollen state.\(^{111, 112}\)

### Table 4.2. *Ex situ* membrane properties. Cation exchange capacity (measured and theoretical), conductivity \(\sigma\) and VO\(^{2+}\) uptake of membranes equilibrated in water and vanadium electrolyte (1 M VOSO\(_4\)/2 M H\(_2\)SO\(_4\)), respectively. S molar fraction of 0.4 in grafts of S/AN co-grafted membranes. (amd = amidoximated, sulf = sulfonated).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graft level</th>
<th>Measured CEC [\text{mmol g}^{-1}]</th>
<th>Theoretical CEC [\text{mmol g}^{-1}]</th>
<th>(\sigma) in water [\text{mS cm}^{-1}]</th>
<th>(\alpha) in V-electrolyte [\text{mS cm}^{-1}]</th>
<th>VO(^{2+}) uptake [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grafted S/AN, amd + sulf</td>
<td>36</td>
<td>0.70 ± 0.12</td>
<td>1.21</td>
<td>26</td>
<td>21 ± 0.7</td>
<td>7 ± 1(^a)</td>
</tr>
<tr>
<td>Grafted S/AN, sulf</td>
<td>36</td>
<td>1.36 ± 0.04</td>
<td>1.29</td>
<td>74</td>
<td>21 ± 0.9</td>
<td>64 ± 6(^a)</td>
</tr>
<tr>
<td>Nafion(^\circledast) 117</td>
<td>-</td>
<td>1.03 ± 0.01</td>
<td>0.91</td>
<td>81</td>
<td>27 ± 0.1</td>
<td>36 ± 13(^b)</td>
</tr>
</tbody>
</table>

\(^a\) based on calculated CEC; \(^b\) based on measured CEC

The results shown here highlight the importance of measuring the conductivity in the respective environment. Furthermore, the difference to the conductivity in the water-swollen state can provide
some insight into the way the vanadium species interact with the polymer. A correlation between VO$_{2}^{+}$ uptake of membranes and the difference in their conductivity in water and vanadium electrolyte is observed (Table 4.2). Nafion® 117 and the membrane containing sulfonated styrene and non-amidoximated AN exhibit a VO$_{2}^{+}$ uptake higher than 30% and their conductivity decreases significantly after equilibration in vanadium electrolyte. The unique feature of the amidoximated membrane is the fact that it shows very little VO$_{2}^{+}$ uptake (7%) and experiences only a slight drop in conductivity upon equilibration in VO$_{2}^{+}$ containing electrolyte.

The amidoxime groups were originally incorporated into the graft copolymer with the intention to complex vanadium species and thereby prevent more vanadium to enter and pass through the membrane, thus providing barrier functionality. The VO$_{2}^{+}$ uptake results combined with the conductivity data, however, suggest the opposite: the VO$_{2}^{+}$ uptake in the amidoximated membrane is much lower than in non-amidoximated membranes. VO$_{2}^{+}$ seems to be prevented from entering the membrane. This can be explained by the fact that amidoximes are protonated at low pH. The pK$_{a1}$ of aliphatic amidoximes was recently estimated to be around 5.8. Therefore, the group is protonated when the membrane is in contact with the VRB electrolyte. The protonated amidoxime, through coulombic repulsion, thus prevents the passage of VO$_{2}^{+}$ species, while the conductivity of the membrane is largely maintained by rapid exchange of the protons within the water and acid-swollen domains of the grafted polymer domains.

4.4.2 Device-Level Characterization

The cross-over of vanadium species through the membrane in the VRB impairs the efficiency of the cell. The effective cross-over can be determined via a self-discharge experiment, whereby the open circuit voltage (OCV) of the cell is measured as a function of time (Figure 4.4). The decrease in OCV is the result of gradual loss of state of charge due to cross-over of vanadium species, and a sudden drop indicates that the capacity is depleted. The OCV of cells with grafted membrane (graft levels of 36 and 32%) can be maintained for a longer period of time compared to cells with Nafion® membrane. These results are in good agreement with the ex situ measurements in diffusion cells (Figures 4.3a-c) and highlight that the cross-over of vanadium ions can be reduced significantly using grafted membranes.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

with adequate graft level and grafts composition. Moreover, it shows that the measurement of VO\(^{2+}\) cross-over is an adequate approach to mimic effective vanadium cross-over in the cell.

![Graph](image)

**Figure 4.4.** Open circuit voltage (OCV) hold test of redox flow cells with various membranes. Electrodes: 3 x SGL 10 AA carbon paper (compression: 10 %) in each half-cell. 100 mL of 0.75 M vanadium in 2 M H\(_2\)SO\(_4\) were used as negative and positive electrolyte, respectively. Flow rate: 5 mL min\(^{-1}\).

Cycling performance of redox flow cells containing the membranes of interest was assessed by measuring charge/discharge curves. Initially, cycling experiments were carried out at a current density of 40 mA cm\(^{-2}\) (see Supplementary Information, Figure S4.3), since this had been considered a typical operating point for VRBs up to about 10 years ago.\(^{19}\)

Recent developments have shown that with proper cell engineering much higher power densities can be achieved.\(^{158}\) Therefore, charge / discharge cycling was performed at a current density of 120 mA cm\(^{-2}\). This required the use of modified carbon materials for higher cell performance. The heat treatment of carbon paper electrodes was demonstrated as a powerful method to improve the performance of a VRB and to allow cycling at higher current densities.\(^{58}\)

However, since heat treated carbon paper electrodes showed poor stability during operation of the redox flow cell,\(^{156}\) heat treated carbon felt electrodes were chosen in this study for cycling experiments at 120 mA cm\(^{-2}\). Figure 4.5 shows charge/discharge cycles at the beginning of test and after 35 cycles for the cells with grafted membrane (graft level: 36 %), Nafion\(^{®}\) 117 and Nafion\(^{®}\) 212. The theoretical capacity at the beginning of test was 2.68 Ah (100 ml of 1 M vanadium solution on either side). The
redox flow cells with Nafion® 117 and Nafion® 212 experienced significant decline of the discharge capacity from 1.69 to 1.07 Ah and from 1.38 to 0.88 Ah, respectively, after 35 cycles.

In case of the cell with the grafted membrane, the initial discharge capacity was 1.58 Ah. The value increased after 35 cycles to 1.64 Ah and dropped to 1.54 Ah at the end of test after 122 cycles. Hence, capacity fading was very small.

The charge/discharge history of the cycling experiments is shown in Figure 4.6. Coulombic and voltage efficiencies were calculated according to the procedure described in the literature. Figure 4.6a shows the decrease in discharge capacity for the cells with Nafion® membrane over 35 cycles, whereas the cell with the grafted membrane largely maintained its capacity over the testing period of 122 cycles. The coulombic as well as the voltage efficiency (Figure 4.6b) during charge/discharge cycling was higher in case of the grafted membrane. In addition, the voltage efficiency of the cells with Nafion® membrane decreased over time in conjunction with the decline in capacity (Figure 4.6a). In Figure 4.6c, the efficiency values averaged over 35 cycles are shown. The efficiencies averaged over 122 cycles in case of the cell with the grafted membrane differed only insignificantly from the values after 35 cycles.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

Figure 4.6. Charge/discharge cycling of single cells. The radiation grafted membrane with a graft level of 36% and a styrene molar fraction in the grafts of $X_S=0.4$ exhibits a selectivity parameter $\alpha$ (cf. Figure 4.3) of 480, compared to that of Nafion® of 60. Current density: 120 mA cm$^{-2}$. 100 mL of 1.0 M vanadium in 2 M H$_2$SO$_4$ were used as negative and positive electrolyte, respectively. Flow rate: 30 mL min$^{-1}$. a) Discharge capacity. b) Coulombic and voltage efficiency. c) Cycling efficiencies averaged over 35 cycles (the energy efficiency is the product of coulombic and voltage efficiencies). The complete charge/discharge cycling history over 122 cycles of the cell with grafted membrane can be found in the Supplementary Information, Figure S4.4. d) Capacity loss with respect to the capacity measured in the first discharge and imbalance of electrolyte volumes at the end of test (cells with Nafion® membrane: 35 cycles; cell with grafted membrane: 122 cycles). For details cf. Supplementary Information, Table S4.2.

The overall energy efficiency, i.e., the product of coulombic and voltage efficiency, was 71.4 ± 0.8 % under the given conditions of cycling for the cell with the grafted membrane, compared to 66.4 ± 1.2 % and 63.1 ± 1.2 % in case of the cell with Nafion® 117 and Nafion® 212, respectively. This indicates the superior performance and cycling stability of the used grafted membrane. The fading of the capacity in case of cells with Nafion® membrane is well-known and a result of electrolyte imbalance building up.\textsuperscript{79}
A straightforward way to characterize this imbalance qualitatively is to measure the electrolyte volume after a number of charge/discharge cycles. A considerable imbalance of electrolyte volumes of 30-40 % was found in case of the Nafion® cells after 35 cycles, which agrees well with the loss of capacity (Figure 4.6d). For the cell with the grafted membrane the electrolyte imbalance was only around 10 % after 122 cycles. The superior capacity retention of the cell with grafted membrane and the higher energy efficiency highlights the prospects for the application of this class of membrane materials in VRB, also considering the potentially much lower membrane manufacturing cost.

4.4.3 Post-test analysis of membrane

After 122 cycles the grafted membrane was retrieved from the cell, stored in 0.5 m KOH for 18 hours and analyzed using IR spectroscopy to check for signatures of aging. Two peaks at 1’660 cm⁻¹ and 1’562 cm⁻¹ were present in the IR spectrum of the tested membrane. The peak at around 1’660 cm⁻¹ can be assigned to the C=N stretch vibration of the amidoxime group and could be also found at the same position in the IR spectrum of the amidoximated membranes before sulfonation (Figure 4.2). The peak at 1’562 cm⁻¹ may be assigned to the N-H stretch vibration of the amidoxime group (cf. Supplementary Information, Figure S4.1). We also took into consideration that the peak at 1’562 cm⁻¹ may arise from the C=O stretch vibration of deprotonated carboxyl groups that could be formed by hydrolysis of amidoximes. As discussed above and shown in Table 4.2, the VO²⁺ uptake of membranes containing sulfonic acid and amidoxime groups (7 ± 1 %) is much lower than that of non-amidoximated membranes containing carboxyl groups (partially hydrolyzed AN) with a GL of around 36 % (64 ± 6 %). Consequently, if amidoxime groups in the membrane are hydrolyzed to carboxyl groups the VO²⁺ uptake of the membrane is expected to increase. The VO²⁺ uptake by the membrane used in the extended cycling experiment (36.2 % GL), measured after equilibration in fresh VO²⁺ electrolyte for 7 days, was 12 %. Thus, the uptake of VO²⁺ increased from 7 to 12 % after the cycling experiment, yet the value is still much lower than that of a non-amidoximated membrane that contains sulfonated styrene and partially hydrolyzed AN. Moreover, no changes in coulombic efficiency and discharging capacity could be observed in case of cells with the amidoximated grafted membrane over 122 cycles, indicating encouraging stability of these membranes in the VRB environment. However, the
development of reliable stability studies is still required to judge long-term stability of amidoximated
grafted membranes under operating conditions of the VRB.

4.5 Conclusions

We present a membrane design concept for the all-vanadium redox flow battery (VRB). The
combination of sulfonic acid and amidoxime groups in the electrolyte membrane boosts the selectivity
of ion transport by significantly reducing the cross-over of redox-active species while largely
maintaining the ionic conductivity of the material. Amidoximes are known as vanadium complexing
agents, yet here, amidoximes are used as vanadium barrier motifs, as they are protonated when exposed
to the sulfuric acid based vanadium electrolyte, which leads to a significant reduction of vanadium
uptake and, thus, to a decrease of vanadium cross-over. On the device-level, the charge/discharge
efficiency is improved compared to state-of-the-art perfluorinated membrane materials, such as
Nafion®, and capacity fading is minimized. Cells with Nafion® membranes showed a notable loss of
discharge capacity of around 35 % over 35 cycles, which could be correlated to a build-up of electrolyte
imbalance, whereas the cell with the grafted membrane showed a loss of discharge capacity of only 3 %
over 122 cycles with an electrolyte imbalance of 11 % at the end of test. The design principle for a
bifunctional ion exchange membrane with amphoteric character may be applicable to other classes of
ionomer membranes and redox flow battery types.

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Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

4.6 Supporting Information

Calculation of theoretical ion exchange capacity

The calculation of the theoretical cation and anion exchange capacities is based on the assumption of a 100% yield of functionalization of the respective monomer units. In case of styrene only grafted membranes the theoretical cation exchange capacity (CEC) is obtained from the following expression:

$$
CEC = \frac{GL}{M_S + GL \cdot M_{SSA}} \tag{S4.1}
$$

where $GL$ is the (mass based) graft level (cf. Equation 4.1 in the main text), $M_S$ and $M_{SSA}$ are the molar masses of styrene (104 g mol$^{-1}$) and styrene sulfonic acid (184 g mol$^{-1}$). In case of styrene (S) and acrylonitrile (AN) co-grafted membranes, the CEC of sulfonated and amidoximated samples is calculated according to

$$
CEC = \frac{GL}{(M_S + \frac{M_{AN}}{F})(1 + GL) + GL \cdot M_{SO_3} + \frac{GL}{F}(M_{AN-AMD} - M_{AN})} \tag{S4.2}
$$

where $F$ is the molar ratio of styrene to acrylonitrile units in the poly(S-co-AN) grafts, $M_{SO_3}$, $M_{AN}$ and $M_{AN-AMD}$ are the molar masses of SO$_3$ (80.1 g mol$^{-1}$), acrylonitrile (53.1 g mol$^{-1}$) and amidoximated acrylonitrile (86.1 g mol$^{-1}$), respectively. The molar fraction $F$ of monomer units can be expressed using the molar fractions of styrene, $X_S$, and acrylonitrile, $X_{AN}$, in the grafts as follows:

$$
F = \frac{X_S}{X_{AN}} = \frac{X_S}{1-X_S} \tag{S4.3}
$$

because $X_S + X_{AN} = 1$. In the standard case $X_S$ is 0.4. In case of only sulfonated membranes, the third term in the denominator of S4.2, $GL/F(M_{AN-AMD} - M_{AN})$, is omitted, because the AN units are not amidoximated. Strictly speaking, the AN units undergo partial hydrolysis during sulfonation (~30 %),$^{146}$ which is not taken into account. The deviation associated with this simplification is around 0.01 mmol g$^{-1}$ in case of the membranes used here.
The theoretical anion exchange capacity (AEC) of sulfonated and amidoximated membranes, assuming single-site protonation of the amidoxime units, is calculated as follows:

\[
AEC = \frac{GL}{(F \cdot M_S + M_{AN})(1 + GL) + F \cdot GL \cdot M_{SO_3} + GL \cdot (M_{AN - AMD} - M_{AN})}
\]  

(S4.4)

Obviously, the relationship \(CEC/AEC = F\) holds. For membranes that are only amidoximated and not sulfonated, the second term in the denominator of S4.4, \(F \cdot GL \cdot M_{SO_3}\), is omitted.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

**Table S4.1.** Ohmic resistance, vanadium cross-over and selectivity. Ohmic resistance and VO$^{2+}$ cross-over values for selected membranes are extracted from Figure 4.3. $X_S$ is the molar fraction of styrene in the grafts ($X_{AN} = 1 - X_S$). The selectivity parameter $\alpha$ is calculated as a membrane figure of merit. Grafted membranes were both amidoximated and sulfonated, except sample #2, which was only sulfonated. Samples #1-4: effect of amidoximation and comparison with Nafion® membranes; samples #5-7: effect of the variation of the graft level at constant composition of grafts; samples #8-10: effect of the composition of grafts at constant graft level.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Membrane</th>
<th>Graft Level</th>
<th>Grafts composition</th>
<th>Ohmic resistance $R_\Omega$ [Ω cm$^2$]</th>
<th>Permeance $i_x$ [mA cm$^{-2}$]</th>
<th>Selectivity $\alpha^a$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Grafted S/AN</td>
<td>40</td>
<td>0.4</td>
<td>0.45 ± 0.06</td>
<td>0.37 ± 0.02</td>
<td>154 ± 23</td>
</tr>
<tr>
<td>2</td>
<td>Grafted S/AN, only sulf.</td>
<td>40</td>
<td>0.4</td>
<td>0.43 ± 0.02</td>
<td>1.64 ± 0.09</td>
<td>36 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>Nafion® 117</td>
<td>-</td>
<td>-</td>
<td>0.64 ± 0.15</td>
<td>0.65 ± 0.03</td>
<td>62 ± 15</td>
</tr>
<tr>
<td>4</td>
<td>Nafion® 212</td>
<td>-</td>
<td>-</td>
<td>0.41 ± 0.01</td>
<td>1.01 ± 0.05</td>
<td>62 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>Grafted S/AN</td>
<td>32</td>
<td>0.4</td>
<td>0.60 ± 0.11</td>
<td>0.12 ± 0.01</td>
<td>358 ± 67</td>
</tr>
<tr>
<td>6$^b$</td>
<td>Grafted S/AN</td>
<td>36</td>
<td>0.4</td>
<td>0.47 ± 0.05</td>
<td>0.11 ± 0.01</td>
<td>479 ± 60</td>
</tr>
<tr>
<td>7</td>
<td>Grafted S/AN</td>
<td>40</td>
<td>0.4</td>
<td>0.43 ± 0.06</td>
<td>0.37 ± 0.02</td>
<td>161 ± 25</td>
</tr>
<tr>
<td>8</td>
<td>Grafted S/AN</td>
<td>40</td>
<td>0.3</td>
<td>1.15 ± 0.18</td>
<td>0.21 ± 0.003</td>
<td>108 ± 17</td>
</tr>
<tr>
<td>9</td>
<td>Grafted S/AN</td>
<td>40</td>
<td>0.4</td>
<td>0.43 ± 0.06</td>
<td>0.37 ± 0.02</td>
<td>161 ± 25</td>
</tr>
<tr>
<td>10</td>
<td>Grafted S/AN</td>
<td>40</td>
<td>0.5</td>
<td>0.37 ± 0.13</td>
<td>1.25 ± 0.02</td>
<td>55 ± 19</td>
</tr>
</tbody>
</table>

$^a$ calculated according to reference$^9$: $\alpha = \frac{RT}{F} \cdot \frac{1}{R_\Omega i_x}$, where $T$ is taken as 298 K.

$^b$ membrane chosen for cycling test in redox flow cell.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

**Table S4.2.** Battery data at the end of test. Loss of discharge capacity after charge/discharge cycling at a current density of 120 mA cm\(^{-2}\) of Naﬁon® membranes and the grafted membrane, and corresponding electrolyte volumes and associated imbalance. The volume of the positive and negative electrolyte at the beginning of test was 100 mL each. Overall loss of electrolyte volume is due to trapping of liquid in the cell, tubes and connections, and evaporation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>no. of cycle</th>
<th>Discharge capacity</th>
<th>Electrolyte vol.</th>
<th>Imbalance$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cycle</td>
<td>cycle #2</td>
<td>last cycle</td>
<td>loss</td>
</tr>
<tr>
<td></td>
<td>[Ah]</td>
<td>[Ah]</td>
<td>[Ah]</td>
<td>[mL]</td>
</tr>
<tr>
<td>Grafted (36 %)</td>
<td>122</td>
<td>1.58</td>
<td>1.54</td>
<td>0.04 (3 %)</td>
</tr>
<tr>
<td>Nafion® 117</td>
<td>35</td>
<td>1.69</td>
<td>1.07</td>
<td>0.63 (37 %)</td>
</tr>
<tr>
<td>Nafion® 212</td>
<td>35</td>
<td>1.38</td>
<td>0.88</td>
<td>0.50 (36 %)</td>
</tr>
</tbody>
</table>

$^a$ Imbalance $= \frac{\Delta \nu}{\nu} = \frac{\nu_+ - \nu_-}{\frac{1}{2}(\nu_+ + \nu_-)}$
Figure S4.1. Origin of IR signature around 1’715 cm\(^{-1}\). The peak at 1’715 cm\(^{-1}\) appears in case of the protonated amidoxime groups, which corresponds to the pristine membrane after amidoximation and sulfonation. The peak at around 1’670 cm\(^{-1}\) can be assigned to the C=N stretch vibration of the amidoxime. Upon immersion of the membrane in aqueous KCl solution, the signature around 1’715 cm\(^{-1}\) gradually disappears owing to ion exchange. After storage of the membrane in 1 M KOH the signature around 1’715 cm\(^{-1}\) disappears completely and a new peak appears at around 1’570 cm\(^{-1}\), which can be assigned to N-H stretching in amidoxime groups. It is noteworthy that the phenomenon described above is reversible. Upon immersion of the membrane in 2 M sulfuric acid, the peak at around 1’570 cm\(^{-1}\) disappears whereas the signature at around 1’715 cm\(^{-1}\) can be observed again. Therefore, the signature at 1’715 cm\(^{-1}\) does not indicate the presence of carboxyl groups in the membranes, which could be formed by hydrolysis of amidoxime groups in acidic environment. The presence of the peak at 1’715 cm\(^{-1}\) in amidoximated and sulfonated membranes may be explained by the interaction between sulfonic acid and amidoxime groups, which leads to different chemical environments for the chemical bonds in both groups. These interactions, which were also indicated by the measured IEC values (cf. Table 4.1), may be disturbed by the presence of KCl or KOH, leading to the observed changes in the IR spectrum.
Figure S4.2. Diffusion cell experiment. A two-compartment cell consisting of two round bottom flasks separated by the membrane to be evaluated was used as diffusion cell setup. The exposed membrane area was $A = 4.52 \text{ cm}^2$. Each flask contained $V = 150 \text{ cm}^3$ of solution, one being $1 \text{ M}$ of VOSO$_4$ in $2 \text{ M}$ H$_2$SO$_4$, the other $1 \text{ M}$ of MgSO$_4$ in $2 \text{ M}$ H$_2$SO$_4$. This configuration, with variations in the concentration of the species, has been widely reported in the research on membranes for the VRB, e.g.$^{110, 131, 178}$ The concentration of permeated VO$^{2+}$ in the solution with Mg$^{2+}$ is determined as a function of time via UV-Vis spectroscopy based on the absorption band at 766 nm, using a calibration curve with known content of VO$^{2+}$, yielding an extinction coefficient of $13.96 \text{ L mol}^{-1} \text{ cm}^{-1}$. The rate of VO$^{2+}$ cross-over, the permeance, is then calculated from the slope $m$ of the regression line. The permeance values reported in the study are given as a current density equivalent $j_{V(IV)}$ according to

$$j_{V(IV)} = m \cdot F \cdot \frac{V}{A} \quad (S4.5)$$

where $F$ is the Faraday constant ($26.8 \text{ Ah mol}^{-1}$). In the example above for Nafion® 117, a permeance of $j_{V(IV)} = 0.64 \pm 0.03 \text{ mA cm}^{-2}$ is obtained.
Figure S4.3. Charge/discharge cycling at a current density of 40 mA cm$^{-2}$. Electrodes: 3 × SGL 10 AA carbon paper (compression: 10 %) in each half-cell. 60 mL of 0.75 M vanadium in 2 M H$_2$SO$_4$ were used as negative and positive electrolyte, respectively. Flow rate: 30 mL min$^{-1}$. a) Discharge capacity. b) Coulombic efficiency. c) Voltage efficiency. d) Cycling efficiencies averaged over 40 cycles in case of Nafion$^\circledR$ membranes and the 36 % grafted membrane, and 80 cycles in case of the 34 % grafted membrane.
Chapter 4: Amphoteric ion exchange membranes with sulfonic acid and amidoxime groups

Figure S4.4. Extended charge/discharge cycling of a single cell with grafted membrane (36 % graft level). Current density: 120 mA cm\(^{-2}\), flow rate: 30 mL min\(^{-1}\). a) Discharge capacity. b) Corresponding coulombic and voltage efficiency.

Figure S4.5. Evidence of VO\(^{2+}\) uptake and release. UV-Vis of Nafion\textsuperscript{®} immersed in V(IV) electrolyte, followed by rinsing and drying, shows the typical signature of VO\(^{2+}\), cf. spectrum of electrolyte solution with 3 mM VO\(^{2+}\). A similar spectrum is recorded in the case of an amidoximated and grafted membrane (graft level 36 %), yet with much lower intensity, indicating a reduced uptake of VO\(^{2+}\) species. After the regeneration of the membrane in 2 M sulfuric acid, the signature of VO\(^{2+}\) has disappeared, indicating effective exchange of the VO\(^{2+}\).
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Ion exchange membranes (IEMs) with amidoxime groups, known for their ability to complex various metal ions including vanadium, were identified as promising electrolyte membranes for VRB applications. The cross-over of vanadium ions was reduced four-fold in the presence of amidoxime groups without markedly impairing the conductivity of the membrane. Experimental and in silico studies of interactions between amidoxime groups and vanadium ions in different oxidation states and at different pH were carried out to shed light on the working principle of membranes containing amidoximes. Whereas the vanadium uptake of various membranes with and without amidoxime groups was determined experimentally only, investigations of a model system based on acetamide oximes were performed both experimentally and in silico. It was found that although amidoxime groups can complex vanadium ions in neutral environment, under acidic conditions the complexation is strongly disfavored. Instead of acting as chelating agent, the protonated and, thus, positively charged amidoxime groups prevent vanadium ions from entering the membrane, providing an effective vanadium barrier under VRB conditions.

This chapter consists of a reproduction of the following publication:


5.1 Abstract

The all-vanadium redox flow battery (VRB) has attracted increasing attention because of the growing share of fluctuating renewables for power generation. However, the high cross-over rate of vanadium ions through the electrode separator is the major cause of capacity fading and efficiency loss in the VRB, limiting its use as an energy storage device. Ion exchange membranes (IEMs) with amidoxime groups, known for their ability to complex various metal ions, including vanadium, were prepared to address vanadium cross-over and were identified as promising electrolyte membranes. In this article, we provide an experimental and theoretical basis to explain how amidoximated membranes act as an effective vanadium barrier in the VRB. A very low vanadium uptake was observed for amidoximated membranes at low pH around 0, suggesting that vanadium ions, instead of being complexed, are prevented from entering amidoximated membranes. By increasing the pH from 0 to 2, a significantly higher vanadium uptake resulted for membranes containing amidoximes. Experimental and in silico investigations using acetamide oximes as a model compound provided the most probable coordination motifs of acetamide oximes and vanadium ions at different pH conditions. They also revealed that for vanadium ions in all oxidation states the complexation by acetamide oximes is strongly discouraged in strong acidic conditions, whereas favored in neutral environment.

5.2 Introduction

Nowadays, reliable energy storage systems attract increasing attention because of the increasing share of fluctuating renewables for power generation. In this field, redox flow batteries (RFB) exhibit great potential for energy storage and grid stabilization. The most advanced RFB is the vanadium redox flow battery (VRB), which uses vanadium ions in different oxidation states on the negative and the positive electrode. Inside the VRB cell, the porous electrodes are divided by microporous uncharged separators or charge-carrying ion exchange membranes (IEMs) to avoid convective cross-mixing of redox-active species while allowing the passage of supporting electrolyte ions, such as protons.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

A high cross-over of vanadium ions in VRBs through separators results in capacity and efficiency losses, which limits their use as energy storage devices.\textsuperscript{10} For this reason, research is focusing on membranes with low vanadium permeability, but being also characterized by high supporting electrolyte conductivity (low resistance), chemical stability, and low cost.\textsuperscript{10}

Various membranes have been proposed for use in VRBs.\textsuperscript{81} For instance, cation exchange perfluoroalkylsulfonic acid (PFSA) membranes (CEMs), such as Nafion\textsuperscript{®}, have found wide-spread application as they exhibit higher conductivities than anion exchange membranes (AEMs)\textsuperscript{10} and good chemical stability under VRB operating conditions. However, they also have serious drawbacks, such as high vanadium permeability and cost. Various approaches have been used to reduce the cross-over when using Nafion\textsuperscript{®} membranes. For instance, Nafion\textsuperscript{®} membranes were modified by incorporation of SiO\textsubscript{2} nanoparticles,\textsuperscript{99} blended with a barrier polymer,\textsuperscript{104} or coated with polyelectrolyte layers.\textsuperscript{103} However, in addition to the remaining issue of cost, these modifications were often accompanied by reduced proton conductivity of the membranes leading to their higher area resistance.\textsuperscript{104,168}

As an alternative, low-cost non-fluorinated membranes are being developed. To tailor their vanadium barrier properties and conductivity, again diverse design concepts are used, including synthesis of membranes with an embedded silica-rich layer,\textsuperscript{113} preparation of acid-base blends,\textsuperscript{133} or sandwich-type composite materials containing several layers of different types of membranes.\textsuperscript{40} However, chemical stability is often a critical factor for these materials.\textsuperscript{82} Amphoteric membranes containing not only cation, but also anion exchange functionalities were also prepared, and show promise for use in VRBs.\textsuperscript{111,130}

To the best of our knowledge, tuning vanadium barrier properties of IEMs by incorporation of functionalities such as amidoximes, known for their ability to complex VO\textsuperscript{2+} and VO\textsubscript{2}\textsuperscript{+} ions in sea water,\textsuperscript{179,180} was reported for the first time in our previous work.\textsuperscript{157} The ability of VO\textsuperscript{2+} and VO\textsubscript{2}\textsuperscript{+} ions to bind strongly to amidoxime groups is regarded as the greatest shortcoming when amidoxime absorbents are used for uranium recovery from sea water.\textsuperscript{181} Thus, the incorporation of amidoxime groups is an interesting approach to adjust the vanadium barrier properties of IEMs in VRBs. To decrease the resistivity while retaining the low permeability to vanadium ions induced by amidoximes groups, our IEMs were also provided with protogenic sulfonic acid groups. Membranes with desired
functionalities were obtained using radiation-induced graft copolymerization of styrene (S) and acrylonitrile (AN) onto ethylene tetrafluoroethylene (ETFE) films of 25 µm thickness and subsequent functionalization. The presence of amidoximes in the grafted membranes resulted in a significant reduction of their VO$^{2+}$ permeability compared with membranes without amidoximes, whereas their area resistance in the vanadium electrolyte was largely maintained. As a result of the suppressed crossover of vanadium species, redox flow cells assembled with amidoximated membranes exhibited a higher efficiency and less pronounced capacity loss than the cells with Nafion® membranes. Moreover, at a current density of 120 mA cm$^{-2}$ stable cycling performance (no changes in coulombic and voltage efficiency) was observed for the cell with amidoximated membrane over 122 cycles, indicating encouraging stability of this membrane in the VRB environment. However, the working principle of amidoximated membranes remained unclear and poorly understood.

Here, an experimental and theoretical basis is provided to explain how membranes with amidoxime groups can exhibit effective vanadium barrier properties under VRB operating conditions. Currently, only few studies related to the interactions of vanadium ions with amidoxime groups can be found. In addition, these studies focus only on interactions of VO$_2^+$ and VO$^{2+}$ ions with amidoximes under conditions typical for seawater (pH of 7.5-8.5). We are, however, interested in the ability of amidoxime groups to complex VO$^{2+}$, VO$_2^+$, V$^{3+}$ and V$^{2+}$ ions, which represent the main constituent of the aqueous, sulfuric acid based vanadium electrolyte typical for VRBs.

First, the uptake of VO$^{2+}$, VO$_2^+$, V$^{3+}$ ions in case of different membranes with and without amidoxime groups was determined under acidic conditions. V$^{2+}$ ions were excluded from uptake experiments because they easily oxidize to V$^{3+}$. Then, in order to better understand the working principle of amidoximated membranes, this study was extended to higher pH values (from 0 to 2), analyzing only the behavior of the VO$^{2+}$ species as prototypical system. VO$^{2+}$ ions were chosen for the experiments at higher pH because they readily dissolve not only in 2 M H$_2$SO$_4$, but also in H$_2$O. In addition, whereas pH values ≤ 3 are required to maintain a thermodynamically stable state of VO$_2^+$, V$^{3+}$ or V$^{2+}$ species, VO$^{2+}$ ions are thermodynamically stable at pH values up to 4.97.

Understanding the basic mechanism within the membrane framework is a very challenging task. In fact, by its nature, the membrane is a highly disordered system and, because of its amorphous character, any
molecular dynamics simulation will have to cope with the limitation of rendering a realistic system at the atomistic scale. Therefore, to gain further insight into the interactions and binding motifs of simple amidoxime groups with vanadium ions, experimental and *in silico* investigations of a model system based on acetamide oximes in solution were carried out. For the *in silico* investigations, single vanadium ions in different oxidation states were placed into boxes containing 3 acetamide oxime molecules. Subsequently, the interactions of the vanadium ions with acetamide oximes were studied in acidic and neutral conditions. Because the primary interest of this work is the study of such interaction, counter ions were not explicitly included. Our results from the experimental and *in silico* investigations showed that acetamide oximes and IEMs bearing amidoxime groups can complex vanadium ions in neutral environment, but that at acidic conditions the complexation is strongly disfavored.
5.3 Experimental

Vanadium(IV) sulfate oxide hydrate (VOSO$_4$·nH$_2$O, 99.9 %) was obtained from Alfa Aesar, and $n$ was determined to be 3 by means of thermogravimetric analysis.$^{145}$ Styrene (>99 %) and acrylonitrile monomers (>99 %) were received from Sigma Alrich. Acetamide oxime (>97 %) were purchased from TCI (item number A2646) and natrium sulfate (99 %) from Merck. Sulfuric acid (96 %) and 2-propanol (technical) were received from VWR. Details about the chemicals used for the functionalization of grafted membranes and pretreatment of Nafion® membranes can be found elsewhere.$^{157}$

5.3.1 Synthesis of radiation-grafted membranes

ETFE films (DuPont Tefzel® 100LZ, 25 µm thickness) were irradiated with a MeV class e-beam to a dose of 5 kGy and stored at -80°C. Details of the synthesis procedure can be found elsewhere.$^{146}$ The grafting reaction was carried out in glass reactors under nitrogen atmosphere. For that, a grafting solution with the following composition was prepared: 20 % (v/v) monomer solution + 70 % (v/v) iso-propanol + 10 % (v/v) ultra-pure water. Irradiated films with a size of 7 cm × 7 cm were introduced into the grafting solution. Subsequently, the grafting solution containing the irradiated film was degassed for 1 h by bubbling with N$_2$, and then placed in a thermostatic water bath at 60°C. After a defined reaction time, the grafted films were removed, immersed in acetone overnight, and dried under vacuum at 80°C. The graft level was determined as follows:

$$GL = \frac{m_g - m_o}{m_o} \cdot 100\%$$  \hspace{1cm} (5.1)

where $m_o$ and $m_g$ represent the weight of the sample before and after grafting, respectively. Subsequently, the grafted films were functionalized. To obtain membranes bearing amidoxime and sulfonic acid groups (SS/AO), amidoximation of AN was carried out, followed by sulfonation of the styrene units. Membranes without amidoximes (SS/AN/CA) were synthesized by sulfonation of grafted films, whereas membranes containing only amidoxime groups (S/AO) were obtained by amidoximation of AN without subsequent sulfonation of the styrene units. Details of the amidoximation of AN and the
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

sulfonation of styrene units can be found elsewhere.\textsuperscript{157,146} The success of grafting reaction and subsequent functionalization was confirmed using FT-IR spectroscopy and energy-dispersive x-ray spectroscopy coupled with scanning electron microscopy (EDX-SEM).\textsuperscript{157}

5.3.2 Ex situ conductivity

The conductivity of membranes equilibrated in 20 mL H\textsubscript{2}O and in a solution of 1.0 M VOSO\textsubscript{4} in 2.0 M H\textsubscript{2}SO\textsubscript{4} (vanadium electrolyte) was measured at a frequency of 20 Hz using a Keysight LCR meter (model E4980AL) and a four-point probe cell (Bekktech BT-112) in in-plane configuration. Conductivity measurements were performed with samples equilibrated in water and in vanadium electrolyte after 3, 6 and 7 days. The conductivity did not change significantly for an equilibration time of 7 days. Therefore, the experiment was discontinued.

5.3.3 Uptake of vanadium ions into membranes at low pH

To determine the VO\textsuperscript{2+} uptake of the membranes, they were immersed in 20 mL of 1 M VO\textsuperscript{2+} electrolyte based on 2 M H\textsubscript{2}SO\textsubscript{4} for 14 days. Subsequently, the membranes were rinsed with water and immersed in 2 M sulfuric acid to enable the release of absorbed VO\textsuperscript{2+} ions back into solution. The amount of released VO\textsuperscript{2+} was determined using UV-Vis spectroscopy (Cary 4000, Varian). The complete release of VO\textsuperscript{2+} ions into solution was verified by direct investigation of the membranes using UV-Vis spectroscopy. Prior to the storage in 2 M sulfuric acid, the absorption of VO\textsuperscript{2+} ions present in the membrane could be observed. However, no absorption by VO\textsuperscript{2+} ions could be detected after regeneration of the membranes in acid (see Supplementary Information, Figure S5.1). The uptake of VO\textsubscript{2+} and V\textsuperscript{3+} ions was determined using the same procedure. VO\textsubscript{2+} and V\textsuperscript{3+} electrolytes were prepared starting from 1 M VOSO\textsubscript{4} solution based on 2 M H\textsubscript{2}SO\textsubscript{4} in the redox flow test system (Model 857, Scribner) after charging, and their pH was determined to be around 0.

5.3.4 Influence of pH and the presence of Na\textsuperscript{+} ions on the uptake of vanadium ions by membranes

To increase the pH of vanadium electrolyte, 1 M solution of VOSO\textsubscript{4} in H\textsubscript{2}O instead of 2 M sulfuric acid was prepared. For the vanadium uptake experiment in the presence of Na\textsuperscript{+} ions, an aqueous solution
containing VOSO$_4$ (1 M) and Na$_2$SO$_4$ (0.5 M) was prepared. To have the same amount of VO$^{2+}$ and Na$^+$ ions in the solution, the concentrations of the corresponding salts were chosen to be 1 and 0.5 M. Using an autotitrator (Titrino 702 SM, Metrohm), the pH of the two aqueous solutions with and without Na$^+$ ions was determined to be approx. 2. Again, the membranes were stored in aqueous vanadium solutions with and without Na$^+$ ions for 14 days, and their vanadium uptake was determined using the same procedure as for the vanadium uptake experiments explained above.

### 5.3.5 Experimental study of VO$^{2+}$/acetamide oximes interactions in solutions with different pH

A 0.01 M solution of blue VOSO$_4$ salt in water was prepared. Colorless acetamide oximes were introduced into the solution so that the ratio of VOSO$_4$ and acetamide oximes was 1:1. The pH of the solution containing acetamide oximes and VO$^{2+}$ ions was measured to be 3.5 (Titrino 702 SM, Metrohm). Subsequently, 2 M H$_2$SO$_4$ was added to this solution to adjust the pH to 2. UV-Vis spectroscopy (Cary 4000, Varian) was used to document the changes in the solution containing VO$^{2+}$ species after the addition of acetamide oximes and 2 M sulfuric acid.

### 5.3.6 Computational study of vanadium/acetamide oximes interactions at different pH conditions

The interactions between single vanadium ions used in all-vanadium redox flow batteries (oxoions in the case of V(IV) and V(V)) and amidoxime groups were studied at neutral and acidic conditions. For this purpose, each of the vanadium ions (V(IV), V(V), V(III) and V(II)) in an aqueous medium containing forty water molecules and three acetamide oxime molecules (eight systems in total) was simulated. Acidic conditions were reached by introducing hydronium ions (H$_3$O$^+$) into the aqueous medium and protonating (H7) of the oxime N atom (N1) in the amidoxime group (Figure 5.1), according to previous studies. All simulations were performed with periodic boundary conditions using a cubic cell with a side length of about 12 Å. The $ab$ initio MD simulations were conducted using Quickstep, which is a module of the CP2K package. Born–Oppenheimer forces were used to propagate the nuclei dynamics and a convergence criterion of $5 \times 10^{-6}$ a.u. for optimization of the wave function.
Valence electrons were treated explicitly using the DZVP basis set, whereas interactions with frozen atom cores were described with GTH pseudopotentials. The charge-density plane-wave cutoff was set to 400 Ry and the PBE exchange-correlation density functional in a spin-unrestricted formalism was adopted for the V(II), V(III), and V(IV) species. V(II) and V(III) cations were considered to be of high spin state in the open-shell calculations, whereas for V(IV) the spin multiplicity was set to two. Equations of motion were integrated with a time step of 0.5 fs. The temperature was controlled using the stochastic velocity-rescaling thermostat. After NPT relaxation of the box using classical force-field methods, each system was equilibrated for about 30 ps using \textit{ab initio} gradients and subsequently the metadynamics simulations were carried out in the NVT ensemble at 300 K. Metadynamics is an enhanced sampling technique that facilitates the exploration of the configurational space thanks to the addition of a time-dependent repulsive bias potential. This potential acts on slow degrees of freedom, called collective variables (CVs), and discourages the system from revisiting already sampled configurations. These boosted simulations were used to find several possible mechanisms of the complexation of vanadium ions by acetamide oxime molecules. As CVs, the coordination number between vanadium and oxygen atoms of the H$_2$O molecules (coord[O]) and the coordination number between vanadium and the center of mass of the acetamide oximes molecules (coord[AO]) were used. Calculations were parallelized taking advantage of the Multiple Walkers algorithm. Following a computational protocol similar to our previous work, the Gaussian hill height was set to 8 kJ mol$^{-1}$, the deposition rate was chosen equal to 50 fs and the bias potential was updated every 100 fs. The different complexation geometries found were then ranked according to the basis of the energy of the system, evaluated in 5 ps of NVT MD simulations (see Supporting Information).
5.4 Results and discussion

5.4.1 Uptake of vanadium ions into membranes with and without amidoximes at various pH conditions

5.4.1.1 Uptake at low pH

To gain insight into interactions of membranes containing amidoximes with vanadium ions, their vanadium uptake was determined at various pH and compared with that of membranes without amidoxime groups. Various membranes were used for this study, including membranes containing sulfonated styrene (SS) and amidoximes (AO) (Figure 5.2a), membranes with non-sulfonated styrene (S) and amidoximes (Figure 5.2b), and membranes carrying sulfonated styrene and non-amidoximated acrylonitrile (AN) that was partially hydrolyzed to carboxyl groups (CA) during sulfonation (Figure 5.2c). All grafted membranes used for this study had a styrene molar fraction \( x \) of 0.4 in the grafts and a graft level of approx. 36 %. The extent of hydrolysis in the case of SS/AN/CA membranes was estimated to be around 27 %.\(^{146}\) In addition, Nafion® 117 was used for comparison.

![Figure 5.2.](image-url) Structures of the grafted and functionalized membranes used for vanadium uptake experiments: a) membranes with sulfonated styrene and amidoximes (styrene molar fraction \( x = 0.4 \)); b) membranes with non-sulfonated styrene and amidoximes (styrene molar fraction \( x = 0.4 \)); c) membranes with sulfonated styrene, non-
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

amidoximated AN and carboxyl groups (styrene molar fraction \(x = 0.4\) and molar fraction of unhydrolyzed AN \(y = 0.4\)).

As can be seen in Table 5.1, at low pH (around 0), the highest VO\(^{2+}\) uptake of approx. 0.86 \(\pm\) 0.11 mmol g\(^{-1}\) could be observed for membranes containing sulfonic acid, carboxyl groups and unhydrolyzed AN. The VO\(^{2+}\) uptake of Nafion\(^{®}\) 117 was calculated to be 0.37 \(\pm\) 0.17 mmol g\(^{-1}\), whereas membranes containing sulfonic acid and amidoxime groups exhibited a much lower vanadium uptake of 0.08 \(\pm\) 0.02 mmol g\(^{-1}\). Membranes containing only amidoximes and non-sulfonated styrene units had an even lower uptake of VO\(^{2+}\) species.

**Table 5.1.** Conductivity \(\sigma\) and VO\(^{2+}\) uptake of membranes equilibrated in water and vanadium electrolyte (1 M VOSO\(_4\)/ 2 M H\(_2\)SO\(_4\)), respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GL [%]</th>
<th>(\sigma) in water [mS cm(^{-1})]</th>
<th>(\sigma) in V-electrolyte [mS cm(^{-1})]</th>
<th>VO(^{2+}) uptake [mmol g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS/AO</td>
<td>36</td>
<td>26</td>
<td>21.0 (\pm) 0.7</td>
<td>0.08 (\pm) 0.02</td>
</tr>
<tr>
<td>SS/AN/CA</td>
<td>36</td>
<td>74</td>
<td>20.9 (\pm) 0.9</td>
<td>0.9 (\pm) 0.1</td>
</tr>
<tr>
<td>S/AO</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>0.020 (\pm) 0.002</td>
</tr>
<tr>
<td>Nafion(^{®}) 117</td>
<td>-</td>
<td>81</td>
<td>27.3 (\pm) 0.1</td>
<td>0.4 (\pm) 0.2</td>
</tr>
</tbody>
</table>

The high vanadium uptake of cation exchange membranes without amidoximes can be explained by the exchange of protons of the sulfonic acid groups against VO\(^{2+}\) ions. SS/AN/CA membranes show a higher uptake of VO\(^{2+}\) species compared to Nafion\(^{®}\) 117, presumably as result of their higher cation exchange capacity (CEC). Via acid-base titration, CEC values of SS/AN/CA (36 % GL) and Nafion\(^{®}\) 117 membranes were determined to be 1.36 \(\pm\) 0.04 mmol g\(^{-1}\) and 1.03 \(\pm\) 0.01 mmol g\(^{-1}\), respectively.\(^{157}\) Thus, SS/AN/CA membranes have higher number of sulfonic acid groups per unit mass, whose protons can be exchanged against vanadium ions.

Moreover, the presence of carboxyl groups (CA groups) in SS/AN/CA membranes can lead to an additional uptake of vanadium ions. For instance, it has been shown that the introduction of CA groups
in amidoximated chelate-type resins increases their absorption rate of uranium ions. The presence of amidoximes in membranes with sulfonic acid groups leads to much lower vanadium uptake, suggesting a prevention of the proton exchange against VO\(^{2+}\) species in this type of membrane.

It is already known that Nafion® 117, which exhibits a conductivity of approx. 0.1 S cm\(^{-1}\) at room temperature in protonated form in water, suffers from a significant conductivity drop after exposure to VRB electrolyte because of the partial exchange of protons by vanadium ions. Taking this into consideration, the conductivity of Nafion® 117 in protonated form in water and after equilibration in VRB electrolyte was compared with the conductivity of grafted membranes with and without amidoximes.

A correlation between the VO\(^{2+}\) uptake and the conductivity of all membranes investigated was observed. Nafion® 117 and the membrane containing sulfonated styrene and non-amidoximated AN take up 0.37 ± 0.17 mmol g\(^{-1}\) and 0.86 ± 0.11 mmol g\(^{-1}\), respectively, and their conductivity decreases significantly upon exposure to vanadium electrolyte. For instance, Nafion® 117 experiences a conductivity drop from 81 to 27 mS cm\(^{-1}\) (Table 5.1), which is in good agreement with values reported in the literature. The unique feature of the amidoximated membrane is the fact that it has very little VO\(^{2+}\) uptake (0.08 ± 0.02 mmol g\(^{-1}\)) and exhibits only a slight decline in conductivity from 26 to 21 mS cm\(^{-1}\) after having been in contact with VO\(^{2+}\) species.

In addition, the VO\(_2\)\(^+\) and V\(^{3+}\) uptake of membranes at low pH around 0 was also determined (Figure 5.3). All membranes investigated showed a higher affinity to VO\(^{2+}\) than to V\(^{3+}\) ions. This could be explained by ion pairing between vanadyl and sulfate ions giving rise to the neutral VOSO\(_4\) ion pair, which may be more easily absorbed by ion exchange membranes compared to vanadium ions such as V\(^{3+}\). Of the membranes investigated, those containing sulfonic acid, carboxyl groups and unhydrolyzed AN had the highest absorbance of V\(^{3+}\) ions, followed by Nafion® 117.

Amidoximated membranes exhibited a very low uptake of V\(^{3+}\) cations, leading to the assumption that at low pH also V\(^{3+}\) species are prevented from entering membranes with amidoximes, instead of being complexed. In the case of VO\(_2\)\(^+\) ions, only little uptake was detected for all membranes. Nafion® 117 especially exhibited an extremely low affinity towards VO\(_2\)\(^+\), which is in good agreement with results from the literature.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

At first, vanadium ions were assumed to enter the membrane and be complexed by amidoxime groups. However, the vanadium uptake results combined with the conductivity data suggest the opposite. At low pH, amidoximated membranes have a much lower vanadium uptake than non-amidoximated membranes. Thus, under strong acidic VRB conditions, vanadium species, instead of being complexed, seem to be prevented from entering the membrane containing amidoximes.

A possible reason can be the protonation of amidoxime groups and the associated loss of their ability to complex metal ions. The pK\textsubscript{a1} values of aliphatic amidoximes and acyclic amidoximes in poly(acrylamidoxime) fibers were determined to be 5.8 and 6.1, respectively. Consequently, amidoximes should be protonated in strongly acidic VRB electrolyte. The presence of protonated amidoximes in the membrane may cause the repulsion of positively charged vanadium ions leading to a lower uptake of these cations.

5.4.1.2 Influence of pH and the presence of Na\textsuperscript{+} ions on the uptake of vanadium ions into membranes with and without amidoxime groups

Next, the influence of the pH and the presence of Na\textsuperscript{+} ions on the VO\textsuperscript{2+} uptake of various membranes were studied. For the membranes containing amidoximes and sulfonic acid groups, a change in vanadium uptake from 0.08 ± 0.02 to 0.41 ± 0.13 mmol g\textsuperscript{-1} was observed after adjusting the pH to 2 instead of 0 (Figure 5.4).
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Figure 5.4. Influence of the pH and of the presence of additives (Na⁺ ions) on the VO²⁺ uptake of various membranes. The pH of 1 M vanadium electrolyte in 2 M H₂SO₄ is around 0. The pH of VO²⁺ electrolytes prepared by dissolving vanadium salt in H₂O with/without sodium salt is approximately 2.

In contrast, the VO²⁺ uptake of Nafion® 117 and grafted membranes with sulfonic acid and carboxyl groups seemed to experience no significant change. Various reasons may lead to the remarkable changes in VO²⁺ uptake for amidoximated and sulfonated membranes after the pH increase. At higher pH (around 2), VO²⁺ ions can enter the membrane and be exchanged against protons attached to -SO₃⁻ groups. Alternatively, the complexation ability of amidoxime groups is expected to increase with pH, which will result in a higher uptake of metal ions.

In analogy, for instance, Hu et al. studied interactions between Eu(III) ions and amidoximated fibers and observed no uptake of Eu(III) ions by fibers at a pH of 1, whereas at a pH of 2 the uptake of ions strongly increased, which suggests the formation of amidoxime/europium(III) complexes.

The uptake of membranes with non-sulfonated styrene and amidoxime groups also underwent a remarkable increase from 0.020 ± 0.002 to 0.22 ± 0.08 mmol g⁻¹. Moreover, the color of the amidoximated membrane changed from transparent to light yellow after storage in VOSO₄ electrolyte with pH of 2, indicating the formation of complexes between vanadium ions and amidoximes.

Hu et al. also observed that white amidoximated fibers undergo a color change from white to yellow-green after having been in contact with europium(III) ions at a pH of 2 as result of complex formation.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

In a further series of experiments at pH 2, Na₂SO₄ was used as a background electrolyte to compensate partially the loss of ionic strength associated with the absence of sulfuric acid. The influence of Na⁺ ions on the VO²⁺ uptake of various membranes (with and without amidoximes) was investigated. Interestingly, in the additional presence of Na⁺ ions compared to the case when VO²⁺ is the only cation present, VO²⁺ uptake decreased from 0.40 ± 0.02 to 0.22 ± 0.01 mmol g⁻¹ for Nafion® 117 (Figure 5.4). A decrease in VO²⁺ uptake is also observed in case of the grafted membrane without amidoximes (SS/AN/CA), yet the values are associated with higher uncertainty due to the larger error bars. However, the VO²⁺ uptake of amidoximated membranes did not significantly change (from 0.41 ± 0.13 to 0.37 ± 0.09 mmol g⁻¹). This suggests that at pH 2 VO²⁺ is complexed by amidoxime groups and therefore not easily replaced by Na⁺ ions.

5.4.2 Model system based on acetamide oximes for a deeper understanding of vanadium/amidoximes interactions and binding motifs at different pH

5.4.2.1 Interactions of V(IV)-VO²⁺/acetamide oximes in solution

Acetamide oximes were selected as model system to mimic the interactions between amidoxime groups and vanadium ions in membranes at different pH. For the experimental part, VO²⁺ ions were again chosen because of their good stability at different pH conditions, whereas in the computational study the extension of the investigation to all four possible vanadium oxidation states was possible.

First, 0.01 M colorless acetamide oximes were mixed with an equal amount of VOSO₄ salt in aqueous medium. The pH of this solution was 3.5. The color of the 0.01 M VOSO₄ solution changed from blue to yellow after addition of acetamide oximes, suggesting the formation of VO²⁺/AO complexes. The yellow coloration was also seen in the case of membranes containing non-sulfonated styrene and amidoximes after storage in aqueous VO²⁺ electrolyte. These results indicate that VO²⁺/AO complex formation also occurs in only amidoximated membranes (styrene units not sulfonated).

After the addition of sulfuric acid to the acetamide oxime/VOSO₄ solution to obtain a pH of 2, the color changed back from yellow to blue, indicating complex dissociation and release of VO²⁺ ions back into
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

solution. UV-Vis spectroscopy was used to follow the changes in the solution containing VO\textsuperscript{2+} species after addition of acetamide oximes and sulfuric acid.

As can be seen in Figure 5.5, an absorption peak at approx. 847 nm was observed after mixing the VO\textsuperscript{2+} solution with acetamide oximes. After addition of sulfuric acid, the peak at 847 nm shifted to 763 nm, which is a typical wavenumber for absorption of free VO\textsuperscript{2+} ions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure55.png}
\caption{UV-Vis spectra of H\textsubscript{2}O-based solutions containing VOSO\textsubscript{4} (0.01 M) and acetamide oximes (0.01 M) in 1:1 ratio before and after the addition of sulfuric acid, and their coloration before and after having been in contact with sulfuric acid.}
\end{figure}

\textit{Ab initio} metadynamics molecular dynamics (Meta-MD) simulations were carried out on a model system consisting of one vanadium ion and three acetamide oxime molecules. Handling the small experimental pH variations is a very daunting task for \textit{ab initio} simulations when working with systems of reasonable length-scales (with characteristic lengths on the order of tens of Å). For this reason, we simulated the system in two extreme cases: acidic (pH = 0) and neutral conditions (pH = 7).

The stable structures were classified based on the number of acetamide oxime molecules complexing the vanadium ion (coord[AO]), which can have values between 0 and 3.

The Meta-MD study showed that the complexation of vanadium by acetamide oximes is more favorable in neutral conditions than in acidic environment (see for example Figure 5.6).
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

**Figure 5.6.** Free energy surfaces (FESs) describing VO\(^{2+}\)/AO interactions at acidic (left) and neutral (right) conditions. These maps are obtained after 300 ps of *ab initio* Metadynamics (MD). The free energy differences and the configurations corresponding to the important free energy minima highlighted here are reported in the Supporting Information (Figure S5.9 and Table S5.3). Complexation of VO\(^{2+}\) by acetamide oximes is more favorable in neutral environment than at the acidic condition: this leads to a FES exhibiting less and shallower metastable free energy minima in acidic conditions than in neutral environment.

See the Supporting Information for further details (Figures S5.3-S5.6 and Tables S5.1-S5.4). In agreement with the literature,\(^\text{201}\) four patterns for the coordination of vanadium ions by acetamide oximes were distinguished (Figure 5.7).

**Figure 5.7.** Possible patterns\(^\text{201}\) for vanadium ion complexation by acetamide oxime molecules. Complexation is represented with dashed lines, covalent bonds with solid lines. The protonation state of N1 and O1 depends on the pH of the solution,\(^\text{149}\) therefore H is represented in parentheses.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

The first three involve only the oxime functionality, in which either N1 (type I) or O1 (type II) coordinates the metal. The third is characterized by a simultaneous complexation of N1 and O1 (type III). The fourth coordination pattern (type IV) involves the amidato moiety in addition. The computational study showed that under acidic conditions the most favorable structure for V(IV) is the one in which no acetamide oxime molecules take part in the first solvation sphere of vanadium (coord[AO]=0 in Figure 5.8).

Figure 5.8. The most stable first solvation shell configurations for V(IV) at different values of coord[AO] in acidic (red boxed) and neutral (blue boxed) conditions. In the plot, we report the difference in terms of potential energy (kJ mol$^{-1}$), assuming the pristine molecule (coord[AO]=0) as reference structure. Red marks correspond to acidic, blue marks to neutral conditions. A detailed table reporting the structure descriptions of the different configurations is given in the Supplementary Information.

In this configuration, the coordination complex exhibits an octahedral geometry, in agreement with previous studies.$^{190, 202}$ In contrast, in neutral environment, the most stable structure (about 84 kJ mol$^{-1}$ less than the configuration corresponding to coord[AO]=0) is the one in which an acetamide oxime is complexing the vanadium ion following path I. This structure exhibits a square pyramidal coordination.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

geometry, with the oxygen bound to the vanadium forming the apex of the pyramid, in agreement with previous studies.\(^{201}\)

Complexation by two acetamide oximes (coord[AO]=2) is also close in energy to the pristine molecule (less than 4 kJ mol\(^{-1}\) difference). In this structure, both acetamide molecules complex the vanadium ion following path IV. The geometry adopted is squared-pyramidal, similar to the structure corresponding to coord[AO]=1.

Complexation by three acetamide oximes is discouraged even in neutral conditions (more than 418 kJ mol\(^{-1}\) higher than the structure corresponding to coord[AO]=0). That structure also presents a square pyramidal geometry, but the complexation by acetamide oximes in these cases occurs only via coordination of N2 to V(IV) without chelation. See the Supplementary Information for further details (Figures S5.9 and Tables S5.9-S5.10).

Our experimental investigations and the computational study of the interactions between acetamide oximes and VO\(^{2+}\) ions again lead to the conclusion that amidoxime groups can complex vanadium ions at a higher pH, whereas this ability disappears after the pH has been lowered. These results are in good agreement with those obtained by direct investigation of membranes bearing amidoxime groups. Interestingly, several stable structures of protonated acetamide oximes found in acidic medium revealed that the proton, initially bound to N1, is highly mobile. This could contribute to the conductivity of membranes containing protonated amidoximes.

5.4.2.2 Interactions of V(II)-V\(^{2+}\)/acetamide oximes in solution

In agreement with previous studies,\(^{190, 202, 203}\) we found that V\(^{2+}\) retains its single ion identity in time scales on the order of hundreds of picoseconds, and, when not complexed by any acetamide oximes (coord[AO]=0 in Figure 5.9), exhibits a six-fold complexation geometry described by an octahedron in both acidic and neutral conditions. In acidic environment, this structure is favored over the one in which the first vanadium solvation shell contains one or more acetamide oximes (coord[AO]>1 in Figure 5.9).

In contrast, at neutral conditions, the structure in which V\(^{2+}\) is complexed by one acetamide oxime is favored in energy (about 42 kJ mol\(^{-1}\) less than the configuration corresponding to coord[AO]=0). In this configuration (coord [AO]=2), type I complexation is more likely than type IV. Simultaneous
complexation by two or three acetamide oximes is unlikely to occur even in neutral environment. See the Supporting Information for further details (Figures S5.7 and Tables S5.5-S5.6).

Figure 5.9. The most stable first solvation shell configurations for V(II) at different values of coord[AO]. We have used the same key as in Figure 5.8.

5.4.2.3 Interactions of V(III)-V\(^{3+}\)/acetamide oximes in solution

Analogously to V\(^{2+}\) and consistent with previous studies,\(^{190,202-204}\) the \([\text{V(H}_2\text{O)}_6]^{3+}\) pristine coordination complex (coord[AO]=0 in Figure 5.10) shows a hexacoordinated solvation structure. In acidic conditions, this is the most probable structure and complexation by acetamide oximes is unlikely (Figure 5.10).

In neutral conditions, V\(^{3+}\) can be complexed by acetamide oxime molecules. Interestingly, it was found that the structures with coord[amid]=1, 2 and 3 are close in energy, which means that at neutral conditions even the simultaneous complexation of V\(^{3+}\) by two or three acetamide oximes is possible. For coord[AO]=1 and 2, the complexation follows path IV.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

In contrast, for coord[AO]=3, one acetamide oxime molecule participates with N2 in the first solvation shell of V$^{3+}$ (path IV), whereas two remaining molecules coordinate V$^{3+}$ following path II. For this last complexation motif, a transfer of the proton from O1 to N1 is required. See the Supporting Information for further details (Figures S5.8 and Tables S5.7-S5.8).

Figure 5.10. The most stable first solvation shell configurations for V(III) at different values of coord[AO]. We have used the same key as in Figure 5.8.

5.4.2.4 Interactions of V(V)-VO$_2^+$/acetamide oximes in solution

V(V) in solution is an oxo-complex bound to two oxygens. Consistently with a previous study, we found that the pristine molecule (coord[AO]=0) can adopt a tetrahedral geometry. This structure is the most stable at acidic conditions, whereas in neutral environment it is higher in energy (by more than 159 kJ mol$^{-1}$) than the configuration in which V(V) is complexed by an acetamide oxime (coord[AO]=1 in Figure 5.11). In this case, complexation follows path I and the first solvation shell of V(V) is again tetrahedral. This structure is very similar to one of the most probable V(V) complexation structures formed by formamidoximate molecules. At neutral conditions, even the simultaneous
complexation by two acetamide oximes (coord[AO]=2) is favored over the pristine molecule, being 15 kJ mol\(^{-1}\) less than the structure at coord[AO]=0.

In this configuration, one acetamide oxide (a) complexes V(V) as described by path I; the other (b) follows path IV, giving the rise to a five-fold coordination geometry, in which the two oxygens bound to vanadium and a hydroxide ion occupy the equatorial plane, whereas the nitrogen atoms of the two amidoxime molecules form the two vertices of the trigonal bipyramid. In contrast to other oxidation states, no metastable configuration for V(V) were found that corresponds to coord[AO]>1 at acidic and to coord[AO]=3 at neutral conditions. See the Supporting Information for further details (Figures S5.10 and Tables S5.11-S5.12).

Figure 5.11. The most stable first solvation shell configurations of V(V) at different values of coord[AO]. We have used the same key as in Figure 5.8.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

5.5 Conclusions

Ion exchange membranes containing amidoxime groups, which are known for their ability to complex vanadium ions in sea water, were prepared to address the cross-over problem of vanadium ions in VRBs and were identified as very promising separators. Here, an experimental and theoretical basis is provided to explain their mechanism of actions. Investigations of a model system based on acetamide oximes were carried out both experimentally and in silico, while the vanadium uptake of various membranes with and without amidoxime groups was determined experimentally only.

At a pH around 0, which is characteristic for VRB, the presence of amidoximes in the membranes drastically reduced the VO$_2^+$ and V$_3^+$ uptake, indicating that at low pH these ions, instead of being complexed, are prevented from entering membranes containing amidoximes. The uptake of VO$_2^+$ ions at low pH was discouraged in all membranes investigated, irrespective of the presence of amidoximes.

To gain a deeper understanding of the interactions between amidoximes and vanadium ions at different pH values, experimental and in silico studies of a model system based on acetamide oximes were carried out. From both investigations, we could conclude that for vanadium ions in all oxidation states the complexation by acetamide oximes is strongly discouraged in acidic conditions, whereas it is possible in neutral environment. Computational studies also provided insight into the most probable coordination motifs of acetamide oximes to vanadium ions in different oxidation states at neutral conditions. In general, these coordination motifs were found to depend on the oxidation states of the vanadium ions.

Our investigation showed that complexation of all vanadium ions by amidoxime groups is strongly disfavored in the acidic VRB environment. Instead of being complexed, vanadium ions cannot enter and pass through the membrane bearing amidoximes at low pH. As a consequence of this, the cross-over of vanadium ions in the cells containing those membranes is significantly reduced, resulting in higher efficiency and less pronounced capacity fading. Thus, to improve the performance of VRBs, the use of membranes with very low vanadium uptake, which was shown to be tunable in a targeted manner by introducing additional functionalities such as amidoximes, is recommended.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

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5.6 Supporting Information

Evidence of VO$^{2+}$ V(IV) Uptake and Release

**Figure S5.1**: UV-Vis spectrum of Nafion® 117 stored in VO$^{2+}$ electrolyte, followed by rinsing and drying, shows the signature characteristic for VO$^{2+}$ ions. The same signature is observed in spectrum of electrolyte solution with 3 mM VO$^{2+}$. A similar spectrum is recorded in the case of a functionalized grafted membrane. The typical signature of VO$^{2+}$ ions has, however, much lower intensity, suggesting a reduced uptake of these species. After the regeneration of the membrane in 2 M sulfuric acid, the signature of VO$^{2+}$ has disappeared, indicating complete release of VO$^{2+}$ ions from the functionalized grafted membrane.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Model System: Study with Acetamide Oximes in Solution

We report, for each vanadium oxidation state, the results of the Metadynamics Molecular Dynamics (MD) simulations. As collective variables (CVs), we have chosen the coordination number of vanadium ions with the oxygens of the H$_2$O molecules (coord[O]), and the coordination number of vanadium ions with the center of mass (COM) of the acetamide oximes (AO) molecules (coord[AO]).

For V(IV) and V(V) systems we have counted the oxygens bound to the vanadium ion (one for V(IV) and two for V(V)) as oxygens of water molecules. In this way, we have left these molecules naturally free to complex the vanadium ions following different paths$^{201}$ (as described in Figure 5.7 of the manuscript).

We have studied the systems at acidic and neutral conditions, obtaining two different Free Energy Surfaces (FESs) for each vanadium oxidation state (eight maps reported in Figures S5.3, S5.4, S5.5, and S5.6). From the Free Energy differences (indicated with ΔG in Tables S5.1, S5.2, S5.3, and S5.4), we observed that for all vanadium oxidation states, at neutral conditions the values for ΔG of the configurations corresponding to coord[AO] ≥ 0 decreases if compared with the ones obtained at acidic conditions. This means that the complexation is more favorable at neutral conditions than in the acidic environment.

For some minima of the FES (Figures S5.3, S5.4, S5.5, and S5.6) we have found different structures, characterized by highly similar distances between vanadium ion and COM of the acetamide oxime(s), but differing from complexation pattern. In order to have an insight on the most probable mechanism of complexation for each Free Energy basin, we have run 5 ps of unbiased equilibrated ab initio MD simulations, starting from all the different configurations. Stable structures have been ranked according to their potential energy.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Metadynamics MD Simulations

The CV Coordination Number

The CV coordination number between two groups of atoms $G_1$, $G_2$ is implemented in CP2K as

$$s = \sum_{i \in G_1} \sum_{j \in G_2} s_{ij}$$

(S5.1)

where this sum is extended to all pairs of atoms with $i \in G_1$ (in our specific case $G_1$ is made by the vanadium ion) and $j \in G_2$. The individual contributions $s_{ij}$ are defined using a switching function, which, in the present case, is given by:

$$s_{ij} = \begin{cases} 1, & \text{if } r_{ij} \leq 0 \\ \frac{1 - \left( \frac{r_{ij}}{r_0} \right)^n}{1 - \left( \frac{r_{ij}}{r_0} \right)^m}, & \text{otherwise} \end{cases}$$

where $r_{ij} = |r_i - r_j|$, with $n$ and $m$ arbitrary parameters.

Error Assessment and Quality Control of Convergence

As previously said, each Metadynamics MD simulation gives rise to a FES, function of the two CVs biased. In each FES we have found several minima, corresponding to metastable configurations. Each minimum is associated to a Free Energy value, that depends on the simulation time (since the exploration of the Free Energy landscape depends itself on the simulation time). The thermodynamic quantity we have monitored is the Free Energy difference between the several minima and the basin corresponding to the most stable pristine molecule (coord[AO]=0), considered the reference structure. After an initial transient, this quantity oscillates around a mean value, to which we have assigned an error.$^{205}$

We report in Figure S5.2, as an example, the exploration of FES of the system VO$^{2+}$- V(IV) in acidic conditions, and the behavior in time of the Free Energy difference between the basin of the reference structure (minimum A) and the others.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

**Figure S5.2.** VO$^{2+}$ - V(IV)/AO interactions at acidic conditions. FES estimation obtained after 10 ps, 60 ps, 120 ps, 180 ps, 240 ps, and 300 ps., as a function of coord[AO] and coord[O]. We report the Free Energy difference between basin. A) and B) (a) basin. A) and C) (b), basin. A) and D) (c), and basin. A) and E (d); the mean value for the Free Energy difference is sketched in red. FES displayed in d is also reported in Figure S5.5, with a different scale (here from 0 to 1560 kJ mol$^{-1}$, in Figure S5.5 from 0 to 480 kJ mol$^{-1}$).
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

**V^{2+}-V(II):** Figure S5.3: FESs describing V^{2+}/AO interactions at acidic (left) and neutral (right) conditions. These maps are obtained after 300 ps of Metadynamics MD, and the corresponding Free Energy differences are reported in Table S5.1. To the right of each label, we report in brackets the number of different structures found for each minimum. The corresponding configurations are shown in Figure S5.7.

Table S5.1: Free Energy differences (ΔG) describing V^{2+}/AO interactions at acidic (left) and neutral (right) conditions. These values are obtained after 300 ps of Metadynamics MD, and come from the Free Energy Surfaces displayed in S5.3. Configurations belonging to the different Free Energy minima are shown in Figure S5.7.

<table>
<thead>
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<th>Neutral conditions</th>
</tr>
</thead>
<tbody>
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<td>ΔG (10^2 kJ mol⁻¹)</td>
<td>coord[AO]</td>
</tr>
<tr>
<td>A (1)</td>
<td>Reference</td>
<td>0</td>
</tr>
<tr>
<td>B (1)</td>
<td>3.5 ± 0.6</td>
<td>0</td>
</tr>
<tr>
<td>C (1)</td>
<td>5.3 ± 0.4</td>
<td>1</td>
</tr>
<tr>
<td>D (1)</td>
<td>5.6 ± 0.5</td>
<td>1</td>
</tr>
<tr>
<td>E (2)</td>
<td>6.6 ± 0.9</td>
<td>2</td>
</tr>
<tr>
<td>F (1)</td>
<td>6.7 ± 0.8</td>
<td>3</td>
</tr>
</tbody>
</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

\( \text{V}^{3+} \text{-V(III)} \): Figure S5.4: FESs describing \( \text{V}^{3+}/\text{AO} \) interactions at acidic (left) and neutral (right) conditions. These maps are obtained after 300 ps of Metadynamics MD, and the corresponding Free Energy differences are reported in Table S5.2. The legend is the same of Figure S5.3. The configurations belonging to the different Free Energy minima are shown in Figure S5.8.

Table S5.2: Free Energy differences (\( \Delta G \)) describing \( \text{V}^{3+}/\text{AO} \) interactions at acidic (left) and neutral (right) conditions. These values are obtained after 300 ps of Metadynamics MD, and come from the Free Energy Surfaces displayed in S5.4. Configurations belonging to the different Free Energy minima are shown in Figure S5.8. At acidic conditions, we have not found any stable (in 5 ps - \textit{ab initio} MD) structure for minima D, and F.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Acidic conditions</th>
<th>Structure</th>
<th>Neutral conditions</th>
</tr>
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<tr>
<td></td>
<td>( \Delta G ) (10^2 \text{kJ mol}^{-1})</td>
<td>coord[AO]</td>
<td>( \Delta G ) (10^2 \text{kJ mol}^{-1})</td>
</tr>
<tr>
<td>A (1)</td>
<td>Reference</td>
<td>0</td>
<td>A (1)</td>
</tr>
<tr>
<td>B (1)</td>
<td>1.0 ± 0.5</td>
<td>0</td>
<td>B (1)</td>
</tr>
<tr>
<td>C (1)</td>
<td>1.4 ± 0.3</td>
<td>1</td>
<td>C (2)</td>
</tr>
<tr>
<td>D (0)</td>
<td>1.5 ± 0.5</td>
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<td>D (3)</td>
</tr>
<tr>
<td>E (1)</td>
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<td>E (2)</td>
</tr>
<tr>
<td>F (0)</td>
<td>2.5 ± 0.9</td>
<td>3</td>
<td>F (2)</td>
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<tr>
<td>F (0)</td>
<td>3.4 ± 0.6</td>
<td>3</td>
<td>F (1)</td>
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</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

$\text{VO}^{2+}$-$\text{V(IV)}$: Figure S5.5: FESs describing $\text{VO}^{2+}$/AO interactions at acidic (left) and neutral (right) conditions. These maps are obtained after 300 ps of Metadynamics MD, and the corresponding Free Energy differences are reported in Table S5.3. The legend adopted is the same of Figure S5.3. The configurations belonging to the different Free Energy minima are shown in Figure S5.9.

![Figure S5.5: FESs describing $\text{VO}^{2+}$/AO interactions at acidic (left) and neutral (right) conditions.](image)

Table S5.3: Free Energy differences ($\Delta G$) describing $\text{VO}^{2+}$/AO interactions at acidic (left) and neutral (right) conditions. These values are obtained after 300 ps of Metadynamics MD, and come from the Free Energy Surfaces displayed in S5.5. We have not found any stable structure corresponding to minimum B at acidic conditions and to minimum C at neutral conditions. Configurations belonging to the different Free Energy minima are shown in Figure S5.9.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Acidic conditions</th>
<th>Neutral conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (1)</td>
<td>Reference</td>
<td>Reference</td>
</tr>
<tr>
<td>B (0)</td>
<td>$1.2 \pm 0.5$</td>
<td>$0.1 \pm 0.4$</td>
</tr>
<tr>
<td>C (1)</td>
<td>$2.4 \pm 0.3$</td>
<td>$0.4 \pm 0.5$</td>
</tr>
<tr>
<td>D (1)</td>
<td>$2.0 \pm 0.4$</td>
<td>$0.7 \pm 0.6$</td>
</tr>
<tr>
<td>E (3)</td>
<td>$4.0 \pm 0.2$</td>
<td>$1.0 \pm 2.0$</td>
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<tr>
<td>F (3)</td>
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</tr>
<tr>
<td>coord[AO]</td>
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<td>coord[AO]</td>
</tr>
</tbody>
</table>

159
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

$\text{VO}_2^+\text{-V(V): Figure S5.6: FESs describing VO}_2^+/\text{AO interactions at acidic (left) and neutral (right) conditions.}$

These maps are obtained after 300 ps of Metadynamics MD, and the corresponding Free Energy differences are reported in Table S5.4. The legend adopted is the same of Figure S5.3. The configurations belonging to the different Free Energy minima are shown in Figure S5.10.

![Diagram showing FESs for VO$_2^+$/AO interactions at acidic and neutral conditions](image)

**Table S5.4:** Free Energy differences ($\Delta G$) describing VO$_2^+$/AO interactions at acidic (left) and neutral (right) conditions. These values are obtained after 300 ps of Metadynamics MD, and come from the Free Energy Surfaces displayed in S5.6. Configurations belonging to the different Free Energy minima are shown in Figure S5.10.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Acidic conditions</th>
<th>Neutral conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G$ (10$^2$ kJ mol$^{-1}$)</td>
<td>coord[AO]</td>
</tr>
<tr>
<td>A (1)</td>
<td>Reference</td>
<td>0</td>
</tr>
<tr>
<td>B (1)</td>
<td>0.8 ± 0.5</td>
<td>0</td>
</tr>
<tr>
<td>C (0)</td>
<td>0.8 ± 0.7</td>
<td>1</td>
</tr>
<tr>
<td>D (1)</td>
<td>1.3 ± 0.7</td>
<td>1</td>
</tr>
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<td>E (0)</td>
<td>2.7 ± 0.6</td>
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</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

*Ab initio* MD Simulations

We show all the structures found, with the corresponding potential energy difference from the pristine molecule. The lower potential energy structures are reported in the manuscript (Figures 5.8, 5.9, 5.10, and 5.11), and described in Tables S5.5 – S5.12. For each configuration, we have specified the geometry of the vanadium first solvation shell, if the atoms N1 and O1 are protonated (+) or not (-) and the complexation pattern (as defined by Figure 5.7 of the manuscript).
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

\( V^{2+} - V(II) \)

**Figure S5.7:** \( V^{2+}/AO \) interactions: energy difference corresponding to the several configurations found for FES in Figure S5.3. The values obtained correspond to 5 ps of unbiased equilibrated trajectories. In the plot we linked the configurations with the lower potential energy, with dashed arrows (red for the acidic conditions, blue for neutral conditions). These structures are reported in the manuscript. Acidic conditions: E.a and E.b belong to the same Free Energy minimum (E in Figure S5.3). Neutral conditions: C.a, C.b, and C.c belong to the same Free Energy minimum (C in Figure S5.3); D.a, D.b, and D.c belong to the basin D in Figure S5.3. Complexation is indicated with colored-lines, while bonds are indicated in black.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Table S5.5: \( V^{2+} \) at acidic conditions. This table refers to Figures 5.9 (manuscript), and S5.7. We have reported the characteristics of the most stable structures for different values of coord[AO]. \( V(II) \) first solvation shell can be described by an octahedron (Oct.) or trigonal bipyramid (Tr. Bip). N1 and O1 can deprotonate during the MD, hence we report the protonation state of both atoms. Complexation types are then reported, following the description of reference\(^{201}\) (Figure 5.7 of the manuscript).

<table>
<thead>
<tr>
<th>configuration</th>
<th>geometry</th>
<th>prot.</th>
<th>complex. pattern</th>
<th>prot.</th>
<th>complex. pattern</th>
<th>prot.</th>
<th>complex. pattern</th>
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</thead>
<tbody>
<tr>
<td>coord[AO]=0 (A)</td>
<td>Oct.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coord[AO]=1 (C)</td>
<td>Oct.</td>
<td>N1 (+)</td>
<td>IV</td>
<td>O1 (+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coord[AO]=2 (E.a)</td>
<td>Oct.</td>
<td>N1 (+)</td>
<td>II</td>
<td>N1 (+)</td>
<td>IV chel.</td>
<td>O1 (+)</td>
<td>O1 (-)</td>
</tr>
<tr>
<td>coord[AO]=3 (F)</td>
<td>Tr. Bip.</td>
<td>N1 (+)</td>
<td>IV</td>
<td>N1 (+)</td>
<td>IV</td>
<td>N1 (+)</td>
<td>IV chel.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1 (+)</td>
<td>O1 (+)</td>
<td>O1 (-)</td>
<td></td>
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<td></td>
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</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

**Table S5.6:** $\text{V}^{2+}$ at neutral conditions. This table refers to Figures 5.9 (manuscript) and S5.7. V(II) first solvation shell can be described by an octahedron (Oct.) or trigonal bipyramid (Tr. Bip). We have used the same key of Table S5.5.

<table>
<thead>
<tr>
<th>configuration</th>
<th>geometry</th>
<th>AO a)</th>
<th>AO b)</th>
<th>AO c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coord[AO]=0 (A)</td>
<td>Oct.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coord[AO]=1 (C.a)</td>
<td>Oct.</td>
<td>N1 (-)</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1 (+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coord[AO]=2 (D.a)</td>
<td>Tr. Bip.</td>
<td>N1 (-)</td>
<td>III</td>
<td>N1 (+)</td>
</tr>
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<td></td>
<td></td>
<td>O1 (+)</td>
<td></td>
<td>O1 (+)</td>
</tr>
<tr>
<td>coord[AO]=3 (E)</td>
<td>Tr. Bip.</td>
<td>N1 (-)</td>
<td>IV</td>
<td>N1 (+)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1 (+)</td>
<td></td>
<td>O1 (+)</td>
</tr>
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</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

V$^{3+}$-V(III)

Figure S5.8: V$^{3+}$/AO interactions: energy difference corresponding to the several configurations found for FES in Figure S5.4. The values obtained correspond to 5 ps of unbiased equilibrated trajectories. Acidic conditions: no stable configurations have been found for coord[AO]=3. Neutral conditions: C.a, and C.b are associated to the Free Energy minimum C; D.a, D.b, and D.c to basin D; E.a and E.b to minimum E and F.a and F.b to F (cfr. Figure S5.4). Complexation is indicated with colored-lines, while bonds are indicated in black. In the plot we linked the configurations with the lower potential energy, with dashed arrows (red for the acidic conditions, blue for neutral conditions). These structures are reported in the manuscript.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Table S5.7: V\textsuperscript{3+} at acidic conditions. This table refers to Figures 5.10 (manuscript) and S5.8. For V(III) we have not found any metastable configuration corresponding to coord[AO]=3. V(III) first solvation shell can be described by an octahedron (Oct.) or tetrahedron (Tetr.). We have used the same key of Table S5.5.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>coord[AO]=0 (A)</td>
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<td></td>
</tr>
<tr>
<td>coord[AO]=1 (C)</td>
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<td></td>
<td></td>
<td>O1 (-)</td>
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</tr>
<tr>
<td>coord[AO]=2 (E)</td>
<td>Tetr.</td>
<td>N1 (+)</td>
<td>II</td>
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<tr>
<td></td>
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<td>O1 (+)</td>
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</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

**Table S5.8**: $V^{3+}$ at neutral conditions. This table refers to Figures 5.10 (manuscript) and S5.8. V(III) first solvation shell can assume an octahedral (Oct.), tetrahedral (Tetr.) or squared-pyramidal (Sq. Pyr.) geometry. We have used the same key of Table S5.5.

<table>
<thead>
<tr>
<th>configuration</th>
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<th>AO a)</th>
<th>AO b)</th>
<th>AO c)</th>
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<td></td>
<td></td>
</tr>
<tr>
<td>coord[AO]=1 (D.a)</td>
<td>Tetr.</td>
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<td>IV</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>O1 (-)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Sc. Pyr.</td>
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</tr>
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<td>O1 (-)</td>
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<td>O1 (-)</td>
<td>O1 (+)</td>
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$V^{3+}$ - V(III) at Acidic Conditions
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

\( \text{VO}^{2+} - \text{V(IV)} \)

**Figure S5.9:** \( \text{VO}^{2+}/\text{AO} \) interactions: energy difference corresponding to the several configurations found for FES in Figure S5.5. The values obtained correspond to 5 ps of unbiased equilibrated trajectories. Acidic conditions: structures E.a, and E.b belong to minimum E in Figure S5.5. Neutral conditions: configurations E.a, E.b, and E.c belong to the same Free Energy (E); F.a, F.b, and F.c are part of the same basin (F in Figure S5.5). In the plot we linked the configurations with the lower potential energy, with dashed arrows (red for the acidic conditions, blue for neutral conditions). These structures are reported in the manuscript.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Table S5.9: VO$^{2+}$ at acidic conditions. This table refers to Figures 5.8 (manuscript) and S5.9. V(IV) first solvation shell can assume an octahedral (Oct.), tetrahedral (Tetr.) or squared-pyramidal (Sq. Pyr.) geometry. We have reported the characteristics of the most stable structures for different values of coord[AO].

<table>
<thead>
<tr>
<th>coord[AO]</th>
<th>geometry</th>
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<th>AO a) prot. complex. pattern</th>
<th>AO b) prot. complex. pattern</th>
<th>AO c) prot. complex. pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (A)</td>
<td>Oct.</td>
<td>coord[AO]=0</td>
<td>N1 (+)</td>
<td></td>
<td>I</td>
</tr>
<tr>
<td>1 (D)</td>
<td>Tetr.</td>
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<td>O1 (-)</td>
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</tr>
<tr>
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<td>O1 (-)</td>
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</tr>
<tr>
<td>3 (E.b)</td>
<td>Sc. Pyr.</td>
<td>coord[AO]=3</td>
<td>N1 (-)</td>
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</table>
Table S5.10: VO\(^{2+}\) at acidic conditions. This table refers to Figures 5.8 (manuscript) and S5.9. V(IV) first solvation shell can assume an octahedral (Oct.), or squared-pyramidal (Sq. Pyr.) geometry. We have reported the characteristics of the most stable structures for different values of coord[AO].

<table>
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<th>Prot. complex. pattern</th>
<th>AO b)</th>
<th>Prot. complex. pattern</th>
<th>AO c)</th>
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</tr>
<tr>
<td>coord[AO]=1 (E.a)</td>
<td>Tetr.</td>
<td>N1 (-)</td>
<td>I</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>coord[AO]=2 (F.a)</td>
<td>Sc. Pyr.</td>
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<td>IV</td>
<td>N1 (-)</td>
<td>IV</td>
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<tr>
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<tr>
<td>coord[AO]=3 (F.c)</td>
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<td>IV</td>
<td>N1 (-)</td>
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<td>O1 (+)</td>
<td>O1 (+)</td>
<td></td>
<td>O1 (+)</td>
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</table>
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

VO$_2^+$-V(V)

**Figure S5.10**: VO$_2^+$/AO interactions: energy difference corresponding to the several configurations found for FES in Figure S5.6. The values obtained correspond to 5 ps of unbiased equilibrated trajectories. Acidic conditions: no stable structures have been found for coord[AO]=2, and 3. Neutral conditions: structures D.a, and E.b belong to the same Free Energy minimum (D in Figure S5.6). No stable structures have been found for coord[AO]=3. In the plot we linked the configurations with the lower potential energy, with dashed arrows (red for the acidic conditions, blue for neutral conditions). These structures are reported in the manuscript.
Chapter 5: Interaction mechanism between amidoxime groups and vanadium ions at various pH

Table S5.11: VO₂⁺ at acidic conditions. This table refers to Figures 5.11 (manuscript) and S5.10. For V(V) we have not found any metastable configuration corresponding to coord[AO]=2, and 3. In the structures found, V(V) first solvation assumes a tetrahedral (Tetr.) geometry. We have used the same key of Table S5.5.

<table>
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<th>configuration</th>
<th>geometry</th>
<th>prot.</th>
<th>complex. pattern</th>
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<td>Tetr.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>coord[AO]=1 (D)</td>
<td>Tetr.</td>
<td>N1 (+)</td>
<td>IV</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>O1 (-)</td>
<td></td>
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</tr>
</tbody>
</table>

Table S5.12: VO₂⁺ at neutral conditions. This table refers to Figures 5.11 (manuscript) and S5.10. For V(V) we have not found any metastable configuration corresponding to coord[AO]=3. In the structures found, V(V) first solvation can assume either a tetrahedral (Tetr.) or a trigonal bipyramidal (Tr. Bip.) geometry. We have used the same key of Table S5.5.

<table>
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<th>AO a)</th>
<th>AO b)</th>
<th>configuration</th>
<th>geometry</th>
<th>prot.</th>
<th>complex. pattern</th>
<th>prot.</th>
<th>complex. pattern</th>
</tr>
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<tbody>
<tr>
<td>coord[AO]=0 (A)</td>
<td></td>
<td>Tetr.</td>
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<tr>
<td>coord[AO]=1 (D.a)</td>
<td></td>
<td>Tetr.</td>
<td>N1 (-)</td>
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<td>O1 (+)</td>
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<tr>
<td>coord[AO]=2 (E)</td>
<td></td>
<td>Tr. Bip.</td>
<td>N1 (-)</td>
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<td>N1 (+)</td>
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A new design concept for amphoteric ion exchange membranes for VRB application is presented, based on radiation-induced grafting of vinylpyridine into an ethylene-tetrafluoroethylene base film and a two-step functionalization to introduce cationic and anionic exchange sites, respectively. The modification of membranes with positively charged vinylpyridinium units results in significant suppression of their vanadium permeability and the presence of sulfonic acid groups reduces their ohmic resistance. Cells with these membranes show higher round trip efficiency and less pronounced capacity decay compared to the cells with Nafion® 117. Vinylpyridine based membranes were compared to Nafion® 117 and membranes containing amidoxime and sulfonic acid groups. Vanadium uptake and permeance experiments reveal significant differences in the interaction of various membranes with vanadium ions in different oxidation states. Also net volumetric transfer of electrolyte across various membranes studied in this work differed significantly.

This chapter consists of a reproduction of the following publication:


Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

6.1 Abstract

All-vanadium redox flow batteries (VRBs) have attracted considerable interest as promising energy storage devices which can allow the efficient utilization of renewable energy sources. The membrane, which separates the porous electrodes in a redox flow cell, is one of the key components in VRBs. High rates of cross-over of vanadium ions and water through the membrane impair the efficiency and capacity of a VRB. Thus, membranes with low permeation rate of vanadium species and water are required, also characterized by low resistance and stability in the VRB environment. Here, we present a new design concept for amphoteric ion exchange membranes, based on radiation-induced grafting of vinylpyridine into an ethylene-tetrafluoroethylene base film and a two-step functionalization to introduce cationic and anionic exchange sites, respectively. During long-term cycling, redox flow cells containing these membranes showed higher efficiency, less pronounced electrolyte imbalance and significantly reduced capacity decay compared to the cells with the benchmark material Nafion® 117 and 212.

6.2 Introduction

All-vanadium redox flow batteries (VRBs) are a promising energy storage technology, which can enable the efficient utilization of renewable energy sources such as wind and sunlight.\textsuperscript{6, 18, 206} VRBs use the same element, i.e. vanadium, in both half cells, which prevents irreversible cross-contamination of electrolytes and thus reduces the maintenance cost.\textsuperscript{18, 27, 81} Within the VRB cell, the electrodes are typically separated by an ion exchange membrane (IEM) to prevent cross-mixing of redox-active species and associated self-discharge while allowing the transport of background electrolyte ions, such as protons, to maintain charge balance.\textsuperscript{19} The membrane can account for about half of the stack cost.\textsuperscript{20} High rates of cross-over of vanadium ions through the separator leads to continuous capacity decay and lower efficiency and limits the use of a VRB as energy
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

storage device. During charge/discharge cycling not only the total vanadium ion concentration but also the electrolyte volumes undergo changes in both redox flow half-cells as result of water transfer across the separator used. Preferential water transfer in the redox flow cell can lead to precipitation of vanadium salts due to the increasing ion concentration in one half-cell electrolyte and dilution of the other. Consequently, high and constant output performance of a VRB over a long period of time can be ensured only by prevention of vanadium ion cross-over and water transfer through the separator. The ideal membrane for VRBs should, therefore, exhibit a low permeation rate of redox-active vanadium species and water. Furthermore, they must be also characterized by a high conductivity (low resistance) in the supporting electrolyte, high chemical stability and low manufacturing cost to reduce the overall cost of the battery.

Various types of separators have been considered for VRB applications. Porous films which contain no ion exchange groups were, for instance, tested in VRBs. To optimize the selectivity of ion transport of uncharged separators, additives such as silica were introduced into their pores or their pore size was tuned.

Ion exchange membranes (IEMs) have received more attention in the VRB field. Depending on the nature of the exchange groups, IEMs are generally classified into cation and anion exchange membranes (CEMs, AEMs). Currently, perfluorinated cation exchange perfluoroalkylsulfonic acid (PFSA) membranes, such as Nafion®, have become the benchmark materials in VRBs. They provide high proton conductivity together with excellent chemical stability, yet they are of high cost and have poor vanadium barrier properties, which causes self-discharge and capacity fading. Various approaches have been used to reduce the cross-over of PFSA membranes. However, the cost issue remains.

Alternatively, various non-fluorinated low-cost CEMs with encouraging VRB performance were proposed. Yet, hydrocarbon-based membranes are still not widely used in VRBs because of their poor chemical stability mainly due to the susceptibility of the polymer backbone attack by H2SO4 and VO2+ species. Instead of CEMs also different fluorinated or non-fluorinated AEMs were proposed for VRB applications since they can be advantageous in reducing vanadium cross-over due to the Donnan exclusion effect.
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

It must be considered, however, that in the presence of concentrated electrolytes, such as the solutions of \( \sim 5 \text{ M} \) (or greater) acid and \( 1.5 \text{ M} \) (or greater) vanadium ions, the Donnan exclusion of anions from the membrane is overcome.\(^{108}\) In addition, despite of reduced vanadium permeability AEMs suffer from lower conductivities compared to CEMs.\(^{10}\) Furthermore, amphoteric ion exchange membranes (AIEMs), which combine advantages of AEMs and CEMs, have been shown to be promising for VRB applications.\(^{110-112, 129-131, 157, 211}\)

Interestingly, not only the cross-over of vanadium ions but also the direction of volumetric transfer has been shown to depend strongly on the nature of the used separator. Whereas for a cell containing a CEM net volumetric transfer toward the positive half-cell was observed, for cells with AEM and non-ionic separators net water transport was in the opposite direction.\(^{212}\) To the best of our knowledge, the volumetric transfer in cells with AIEMs was reported for the first time in our previous work using amphoteric membranes with amidoxime and sulfonic acid groups.\(^{157}\)

Herein, a new design concept for amphoteric IEMs for VRB applications is presented. This concept is based on radiation-induced grafting of 4-vinylpyridine into ethylene-tetrafluoroethylene base film followed by a subsequent two-step functionalization. Improved vanadium barrier properties of the new AIEMs are targeted by introduction of positively charged alkylated vinylpyridinium units and a small degree of crosslinking, whereas the presence of protogenic sulfonic acid groups is expected to reduce their ohmic resistance. The performance, capacity decay and electrolyte transfer phenomena in cells with amphoteric IEMs are investigated and compared with results obtained from cells containing Nafion\(^\text{®} 117\) CEMs and AIEMs carrying amidoxime and sulfonic acid from our previous study.\(^{157}\)
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

6.3 Experimental

6.3.1 Materials

4-vinylpyridine (VP, 95 %), 3-aminobenzenesulfonic acid (97 %), 1-methyl-2-pyrrolidinone (99.5 %) and 1,10-dibromodecane (97 %) were obtained from Sigma Aldrich. Sulfuric acid (96 %) and 2-propanol (technical) were purchased from VWR. Vanadium(IV) sulfate oxide hydrate (VOSO$_4$·$n$H$_2$O, 99.9 %) was obtained from Alfa Aesar and $n$ was determined to be 3 by means of thermogravimetric analysis.\textsuperscript{145} Nafion\textsuperscript{®} 117 from DuPont was used as benchmark. Details about chemicals used for pretreatment of Nafion\textsuperscript{®} 117 membranes can be found elsewhere.\textsuperscript{157}

6.3.2 Synthesis of radiation grafted membranes

The ETFE base films (DuPont, 25 µm thickness) were irradiated using an MeV class electron beam in air and stored at –80°C. The irradiation dose was 5 kGy and was measured using a radiation dosimeter. The grafting reaction was carried out in glass reactors under nitrogen atmosphere. For that, a grafting solution with the following composition was prepared: 50 % (v/v) vinylpyridine + 50 % (v/v) iso-propanol. The grafting solution containing irradiated films was bubbled with N$_2$ for 1 h. Subsequently, the reactor was placed in a thermostatic water bath at 60°C. After the reaction, grafted films were immersed in iso-propanol for 18 h and dried under vacuum at 80°C. The graft level was determined as follows:

\[
GL = \frac{m_g - m_o}{m_o} \cdot 100\%
\]  

(6.1)

where $m_o$ and $m_g$ represent the weight of the sample before and after grafting, respectively.

The first step of functionalization (alkylation) was performed in a 60 ml glass reactor using 0.25 M solution of 1,10-dibromodecane in $N$-methyl-2-pyrrolidone (NMP). Vinylpyridine grafted films were introduced into the prepared solution and placed in a thermostatic water bath at 45°C for a given amount of time. Subsequently, the films were removed from the reaction mixture and rinsed with iso-propanol.
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

The second step of functionalization (nucleophilic substitution of alkyl bromide by 3-aminobenzenesulfonic acid) was performed in a 60 ml glass reactor using a 0.05 M solution of 3-aminobenzenesulfonic acid in NMP. Grafted films were introduced into the small reactor containing the prepared solution and placed in a thermostatic water bath at 45°C for a defined period of time. Subsequently, functionalized films were immersed in 2 M H₂SO₄ overnight.

6.3.3 Composition analysis

Compositional changes of polymer films after grafting with vinylpyridine and in various stages of functionalization were analyzed using Fourier transform infrared spectrometry (Bruker Vertex 70 spectrometer). IR spectroscopy was also used to check for signatures of aging in the membranes after extended cycling experiments. Furthermore, IR spectroscopy was used to determine the alkylation degree of vinylpyridine units after the first functionalization step. For this, the ratio of peak areas at 1’640 cm⁻¹ (quaternized pyridine ring C=N stretch) and 820 cm⁻¹ (C-H ring mode) were determined using Bruker OPUS spectroscopy software.

6.3.4 Elemental mapping

The presence of aminobenzesulfonic acid units in the membranes was examined by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX). The same methodology was used to analyze the elemental distribution in the cross-section of membranes. For this, membranes were stored in water for 1 h, frozen in liquid nitrogen and broken to obtain a sharp cross-section. SEM images were taken using an FESEM Ultra 55 from Carl Zeiss and energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK).

6.3.5 Vanadium ion permeance

Transport of vanadium ions (VO²⁺, VO₂⁺ and V³⁺) across different membranes was studied using home-made diffusion cells consisting of two round bottom flasks separated by the membrane of interest. The
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

left compartment was filled with 150 mL (V) of 1 M vanadium electrolyte based on 2 M H₂SO₄ while the right one was filled with 150 mL 1 M solution of MgSO₄ in 2 M H₂SO₄. The exposed membrane area (A) was 4.52 cm². Solutions in both compartments were stirred and the concentration of diffused vanadium ions was determined using UV-ViS (Cary 4000, Varian). The rate of vanadium cross-over, i.e., the permeance, was calculated as a current density equivalent using following equation:

\[ i_x(V) = m \cdot F \frac{V}{A} \]  

(6.2)

where the slope \( m \) was obtained by fitting the graphs of concentration of diffused vanadium ions across different membranes (in mol L⁻¹) versus time (in hours). \( F \) is the Faraday constant (26.8 Ah mol⁻¹). More details can be found elsewhere.¹⁵⁷

6.3.6 Uptake of vanadium ions into membranes at low pH

To determine \( V^{3+} \), \( VO^{2+} \) and \( VO_2^{+} \) uptake of the membranes they were immersed in 20 mL of 1 M vanadium electrolyte based on 2 M H₂SO₄ for 14 days. Subsequently, membranes were rinsed with water and immersed in 2 M sulfuric acid to allow the release of absorbed vanadium ions back into solution. The amount of released vanadium ions was determined using UV-Vis spectroscopy (Cary 4000, Varian). Direct investigation of membranes with UV-Vis spectroscopy was carried out to verify the complete release of vanadium ions into solution. More details can be found elsewhere.¹⁵⁷ \( VO_2^{+} \) and \( V^{3+} \) electrolytes were prepared starting from 1 M VOSO₄ solution based on 2 M H₂SO₄ in the redox flow test system (Model 857, Scribner) using a procedure described in the literature.¹⁵⁸

6.3.7 Redox flow cell experiments

A redox flow test system (Model 857, Scribner) including a cell with an active area of 25 cm² was used. The cell contained serpentine flow fields for electrolyte distribution and one layer of thermally activated SGL SIGRACELL® GFD4.6 EA carbon felt electrodes (thickness: 4’300 µm) in each half-cell. The thermal treatment was carried out according to the procedure described in the literature.⁵⁸ The
compression in the redox flow cell was adjusted to around 30 %. 1 M vanadium solution was prepared by dissolving VOSO$_4$$\cdot$$n$H$_2$O (Alfa Aesar, 99.9 % purity, where $n$ was determined to be 3 by thermogravimetric analysis) in 2 M H$_2$SO$_4$. Starting from VOSO$_4$ solution, vanadium electrolytes were prepared using a protocol reported in the literature. The solutions were considered to be fully charged when the current density dropped to a value of 4 mA cm$^{-2}$ at 1.7 V. At fully charged state, the open circuit voltage of the cells containing functionalized radiation grafted membranes and Nafion® 117 membranes was around 1.63-1.65V.

The area resistance of single redox flow cells containing membranes of interest was measured at fully charged state by means of electrochemical impedance spectroscopy. The cell contained one layer of heat treated SGL SIGRACELL® GFD4.6 EA carbon felt electrodes in each half-cell. An AC amplitude of 10 mV and frequency range from 100’000 to 0.1 Hz was used.

Charge/discharge cycling of the redox flow cells was performed at a constant current density of 120 mA cm$^{-2}$ using 1.7 V as upper and 0.8 V as lower voltage limit. 100 mL of 1 M vanadium electrolyte solutions were used on each side. The flow rate was 30 mL min$^{-1}$. 

180
6.4 Results and Discussion

6.4.1 Synthesis and characterization of functionalized vinylpyridine based ion exchange membranes

The synthesis of amphoteric IEMs started with the preparation of ETFE-g-poly(4-vinylpyridine) films by radiation induced graft polymerization of 4-vinylpyridine (VP) into ethylene-tetrafluoroethylene (ETFE) films of 25 µm thickness. Subsequently, VP grafted films were modified to introduce desired functionalities according to the Scheme 6.1.

In contrast to our previously reported amidoximated and sulfonated membranes,\textsuperscript{157} which showed amphoteric character only after being exposed to an acidic environment, which leads to protonation of the amidoxime groups (induced amphotericity),\textsuperscript{213} the functionalized VP based membranes reported here exhibit an intrinsic amphoteric nature due to the presence of alkylated and, thus, positively charged vinylpyridinium units.

It is notable that in contrast to grafted membranes containing amidoxime and sulfonic acid groups, in case of the VP based membranes in this study the synthetic route was significantly simplified. Whereas both functionalization steps for the preparation of amidoximated and sulfonated membranes required 70 hours, mainly at higher reaction temperatures of around ≥ 70°C, the completely functionalized ETFE-g-poly(4-vinylpyridine) membranes with significantly improved vanadium barrier properties could be obtained after 30 hours with reduced reaction temperatures of around 45°C.

Additionally, dangerous and environmentally unfriendly chemicals, such as hydroxylamine hydrochloride and chlorosulfonic acid, used for preparation of amidoximated and sulfonated membranes, were replaced in the synthetic route of functionalized VP based membranes by much less harmful substances, namely 3-aminobenzenesulfonic acid and 1,10-dibromodecane (see Scheme 6.1).

After complete functionalization of VP grafted membranes Br\textsuperscript{−} anions, released from 1,10-dibromodecane in the process of alkylation, are exchanged to HSO\textsubscript{4}\textsuperscript{−} after immersion of the membrane in 2 M H\textsubscript{2}SO\textsubscript{4}, which is the background electrolyte in the VRB cell.
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

Scheme 6.1. Schematic representation of the synthesis of functionalized ETFE-g-poly(VP) membranes.

The success of the grafting reaction and subsequent functionalization of ETFE-g-poly(VP) films was confirmed using FT-IR spectroscopy and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX). In the FTIR spectrum of the VP grafted film, the characteristic absorption peak of the pyridine ring was identified at around 1’600 cm\(^{-1}\) (Figure 6.1). After the alkylation step with 1,10-dibromodecane the intensity of this peak decreases whereas a new peak characteristic for pyridinium appears at around 1’640 cm\(^{-1}\). After the nucleophilic substitution of alkyl bromide and subsequent rinsing in 2 M H\(_2\)SO\(_4\), the peak at 1’600 cm\(^{-1}\) disappears completely, suggesting that pyridine units that were not converted to quaternized pyridinium in the alkylation step were protonated in 2 M H\(_2\)SO\(_4\) and thus positively charged.
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

Figure 6.1. FT-IR analysis of ETFE-g-poly(VP) membranes in various stages of functionalization. Important vibrational bands are highlighted. FT-IR analysis was performed using membranes with around 43 ± 2 % graft level. Reaction conditions for functionalization were: 1st step => 24h, 45°C and 2nd step => 6h, 45°C. The area labeled with a red asterisk shows the influence of the reaction time and temperature of the 1st functionalization step on the conversion of vinylpyridine to vinylpyridinium units.

Moreover, after the nucleophilic substitution of alkyl bromide two new peaks appear at 1'500 cm⁻¹ and 830 cm⁻¹. The signature at around 1'500 cm⁻¹ can be assigned to the N-H deformation vibration of the attached aminobenzenesulfonic acid unit and the peak at 830 cm⁻¹ is associated with the presence of the SO₃⁻ group. The presence of desired functionalities in the membranes was also examined by SEM/EDX. Sulfur mapping is indicative of the presence of –SO₃⁻ units in the membrane, confirming the success of second functionalization step (Figure 6.2). These results are in good agreement with IR analysis. Moreover, the distribution of grafts in the cross-section of membranes was analyzed by EDX. If films irradiated with 15 kGy were selected for the grafting reaction, membranes with a homogenous distribution of grafts across the thickness could be obtained only in case of higher graft levels
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

(GL > 60 %). In case of membranes with lower graft levels the grafting time was too short to achieve homogenous distribution of grafts in the thickness direction of the membranes (see Supplementary Information, Figure S6.1). In contrast, films irradiated with 5 kGy resulted in longer reaction time and allowed the synthesis of membranes with lower graft levels (GL < 50 %) and homogenous distribution of grafts in the cross-section (Figure 6.2).

![Cross-sectional analysis of ETFE-g-poly(VP) membrane (~43 % GL) that was prepared using ETFE film irradiated with 5 kGy. Reaction conditions for functionalization were: 1\textsuperscript{st} step => 24h, 45°C and 2\textsuperscript{nd} step => 6h, 45°C. EDX elemental mappings of sulfur (associated with sulfonic acid) and nitrogen (associated with vinylpyridinium and aminobenzenesulfonic acid units).](image)

Figure 6.2. Cross-sectional analysis of ETFE-g-poly(VP) membrane (~43 % GL) that was prepared using ETFE film irradiated with 5 kGy. Reaction conditions for functionalization were: 1\textsuperscript{st} step => 24h, 45°C and 2\textsuperscript{nd} step => 6h, 45°C. EDX elemental mappings of sulfur (associated with sulfonic acid) and nitrogen (associated with vinylpyridinium and aminobenzenesulfonic acid units).

A part of the IR spectrum labeled with the red asterisk (Figure 6.1) shows the influence of the reaction time and temperature in the alkylation step on the degree of vinylpyridine quaternization. Non-functionalized membranes contain only non-alkylated vinylpyridine units (y = 100 % in Scheme 6.1), which are protonated in 2 M H\textsubscript{2}SO\textsubscript{4}. The reaction time and temperature of the alkylation step determines the ratio between the unreacted vinylpyridine (labeled with y in Scheme 6.1) and alkylated vinylpyridinium (labeled with x and 1-x-y in Scheme 6.1). After the 1\textsuperscript{st} functionalization step, alkylated vinylpyridine units have Br end groups, which can react with aminobenzenesulfonic acid in the 2\textsuperscript{nd} functionalization step and/or with unreacted vinylpyridine in the 1\textsuperscript{st} and 2\textsuperscript{nd} functionalization step, leading to cross-linked chains. If the alkylation of vinylpyridine is complete in the first functionalization step, the final fully functionalized membrane will contain no unreacted vinylpyridine (y = 0 % in Scheme 6.1).
To estimate the ratio between alkylated (x and 1-x-y units) and non-alkylated vinylpyridine (y units) in VP based membranes with a defined synthetic route, ion chromatography (IC) was used. For this, the functionalized samples in bromide form were placed in 0.1 M HCl for 8 hours in a well stirred vessel and the concentration of bromide anions exchanged against chloride anions was measured in the leachate using IC (see Supplementary Information, Figure S6.2 for further details). In the next step, a correlation between the measured alkylation degree of selected membranes and their peak area ratios at 1’640 and 820 cm\(^{-1}\) in IR spectra was established (Supplementary Information, Figure S6.2). The obtained calibration curve (alkylation degree in % from IC versus peak area ratios at 1640/820 cm\(^{-1}\)) allowed determination of the degree of quaternization in further membranes of interest by analyzing their IR spectra only. Using IR spectroscopy, the degree of vinylpyridine quaternization (magnitude of x and 1-x-y in Scheme 6.1) was estimated to be 25 ± 1 % and 38 ± 2 % if the alkylation step was carried out at 45°C for 24 and 48 hours, respectively. If the alkylation was performed for 24 hours at a higher reaction temperature of 60°C, an even higher degree of quaternization was achieved (65 ± 3 %). An increase of reaction time from 24 to 48 hours at 60°C resulted in complete conversion of vinylpyridine to vinylpyridinium salt. In contrast, a short reaction time of 8 hours at 45°C led to a low degree of quaternization of 8 ± 2 %. For further details see Supplementary Information (Table S6.1).

In general, alkylated vinylpyridine units have Br end groups, which for their part can react with other non-reacted vinylpyridine in the 1\(^{st}\) and 2\(^{nd}\) functionalization step leading to cross-linking of the polymer. To determine to which extent the cross-linked vinylpyridine (1-x-y units) and alkylated vinylpyridine (x units) contribute to the peak at 1’640 cm\(^{-1}\) in the IR spectrum after the alkylation step is not straightforward. To get an insight into the ability of vinylpyridine moieties to react with Br end groups of other alkylated vinylpyridine and, thus to estimate the amount of 1-x-y units in the final membranes, following experiment was carried out. A VP based membrane with a GL of around 36 % was allowed to react with 1,10-dibromodecane in 1-methyl-2-pyrrolidone (NMP) at 45°C for 24 hours. Subsequently, the membrane was placed in NMP at 45°C for an additional 30 hours. The changes in the area ratio of peaks at 1’640 and 820 cm\(^{-1}\) in the subsequent step (without addition of dibromodecane) could be caused only by reaction of vinylpyridine moieties with Br end groups of other alkylated vinylpyridine moieties. The degree of alkylation was found to be very similar (16.6 ± 0.2 and 17.1 ± 0.2 %) for membranes without and with additional treatment in NMP at 45°C (Supplementary
Information Table S6.1). These results strongly indicate that single vinylpyridine units in the membranes have a very low ability to react with each other. Thus, the degree of cross-linking between single vinylpyridine units (amount of 1-x-y units) in VP based membranes seems to be very low. However, a very small degree of cross-linking cannot be completely excluded.

The effect of functionalization on the key device-relevant properties of VP based membranes, such as area resistance and vanadium permeance, was investigated and is shown in Figure 6.3. Nafion® 117 was used as benchmark.

![Figure 6.3](image_url)

**Figure 6.3.** Key device-relevant membrane properties. a and c) Vanadium-ion permeance measured *ex situ* in a diffusion cell, expressed as current density equivalent (cross-over rates of vanadium ions in cm² h⁻¹ were also calculated and can be found in the Supplementary Information, Table S6.5), b and d) Area resistance determined in the device (charged state). Panels a and b show the effect of the functionalization and reaction time (in hours) for the alkylation step; c and d show the influence of graft level and reaction time (in hours) for the sulfonation step. The (1 / 2 / 3 / 4) code in case of different membranes has the following meaning: 1 = reaction time for the
alkylation step, 2 = reaction time for sulfonation step, 3 = graft level (GL), 4 = without [-] & with [+ \text{ protonation} between the 1\text{st} and 2\text{nd} functionalization step.

First, permeance of VO$^{2+}$ ions through different membranes was measured \textit{ex situ} in a diffusion cell and expressed as current density equivalent. VO$^{2+}$ ions were used since they readily dissolve in 2 M H$_2$SO$_4$ and the resulting electrolyte solution has good stability.$^{172}$ The area resistance of a redox flow test cell comprising the membrane of interest was determined in the fully charged state by means of electrochemical impedance spectroscopy. It is noteworthy that cell components other than the membrane, such as the liquid electrolytes, also contribute to the measured area resistance in this configuration. By measuring the in-plane conductivity of selected membranes in a four-point probe cell in in-plane configuration (after equilibration in vanadium electrolyte), the contribution of all the cell components excluding the membrane and including thermally treated carbon felt as electrodes was estimated to be around 0.57 Ohm cm$^2$.

Already unmodified ETFE-g-poly(4-vinylpyridine) membranes with GL of 43 ± 2 \% show better VO$^{2+}$ barrier properties compared to Nafion$^\circledR$ 117, presumably because of the vinylpyridine units that are positively charged after protonation in 2 M H$_2$SO$_4$. A mitigating effect of positively charged moieties in membranes on their vanadium permeability has been previously shown and was attributed to the Donnan exclusion effect between cations in the membrane and vanadium ions.$^{111}$ Interestingly, unmodified ETFE-g-poly(4-vinylpyridine) membranes exhibit also area resistance comparable to that of Nafion$^\circledR$ 117. Good proton conductivity of vinylpyridine containing membranes has been already shown in the literature.$^{107, 126}$ Seo et al. prepared anion exchange membranes containing pyridine moieties and compared their transport characteristics of H$^+$ and SO$_4^{2-}$ ions with those of commercially available AEMs (AMX, Tokuyama, Japan). Interestingly, protons were found to have a larger transport number in vinylpyridine containing AEMs than SO$_4^{2-}$. In contrast to AEMs with vinylpyridine functionalities, the commercially available AMX AEMs exhibited the typical characteristic of anion exchange membranes showing a low transport number of H$^+$ and high transport number of SO$_4^{2-}$ anions.$^{107}$ After the alkylation step, permeance of membranes for VO$^{2+}$ significantly decreases and their area resistance increases (Figure 6.3a and b). This may be explained by the presence of additional carbon chains in the membrane, as a consequence of partial alkylation of vinylpyridine units using dibromodecane.
These carbon chains can lead to a denser and more hydrophobic polymer structure resulting in decreased VO$^{2+}$ permeance and higher area resistance. Also a small extent of cross-linking between single vinylpyridine units in the membrane, which cannot be excluded completely, may increase the structural density of the polymer and hinder proton and vanadium ion transport.\textsuperscript{131} After the second functionalization step, membranes are imparted with protogenic sulfonic acid groups. As a result, lower area resistance is observed accompanied with a slightly higher VO$^{2+}$ permeance. In general, functionalization of VP grafted membranes (43 ± 2 % GL) allows considerable improvement of their properties including significantly improved vanadium barrier properties along with maintained area resistance. After functionalization, membranes with very low VO$^{2+}$ permeability and area resistance comparable to that of Nafion® \textsuperscript{117} are obtained.

Increasing the reaction time of the alkylation step from 8 to 24 hours also allows further substantial reduction of VO$^{2+}$ permeance whereas the area resistance of membranes experiences a slight increase (Figure 6.3a and b). Further reduction of VO$^{2+}$ permeance can be a consequence of an even denser polymer structure. This can be explained by further filling of membranes pores with additional functional moieties, such as carbon chains and aminobenzene sulfonic acid units,\textsuperscript{104} an additional small extent of cross-linking of single vinylpyridine units,\textsuperscript{131} and/or cross-linking associated with the interactions between positively and negatively charged groups within the membrane.\textsuperscript{133} Further increase of reaction time leads to further suppression of VO$^{2+}$ permeability. However, in addition to the associated increase of area resistance also the mechanical stability of membranes suffers. Completely functionalized membranes (containing no unfunctionalized vinylpyridine units) are very brittle.

If the reaction time of the second functionalization step is increased from 6 to 30 hours more protogenic sulfonic acid groups are expected to be introduced into membranes, resulting in a lower area resistance. However, against expectations an increased reaction time during the second functionalization step yields higher area resistance and lower permeance of VO$^{2+}$ ions (Figure 6.3c and d). In general, two parallel reactions can take place during the second functionalization step: (1) introduction of aminobenzenesulfonic acid units, which yield a decrease of the area resistance of the membrane and (2) an additional small extent of cross-linking between vinylpyridine units, which lead to the opposite effect. Thus, if a prolonged second functionalization step is desired to lower the membrane’s resistance the additional cross-linking must be prevented. This can be done, for instance, by protonation in 2 M
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

H$_2$SO$_4$ of vinylpyridine units that remained unreacted after the alkylation step. Figures 6.3c and d show that if the membranes are stored in 2 M H$_2$SO$_4$ before the reaction with aminobenzensulfonic acid the increase of reaction time resulted in a slightly reduced area resistance.

Using the measured area resistance ($R_\Omega$) and VO$^{2+}$ permeance ($i_x$) values, the selectivity parameter $\alpha$ (Figure 6.4a) of membranes was calculated using following equation: $94$

$$\alpha = \frac{RT}{F} \cdot \frac{1}{R_\Omega i_x}$$  \hspace{1cm} (6.3)

The corresponding calculations can be found in the Supplementary Information (Table S6.2).

### 6.4.2 Device-Level Characterization

The membranes with the dashed frames from Figure 6.3 were chosen for cycling experiments. Cycling performance of redox flow cells containing selected membranes and thermally treated carbon felt electrodes was assessed by measuring charge/discharge curves at a constant current density of 120 mA cm$^{-2}$.

A correlation between calculated selectivity parameters for membranes and their performance in an operating redox flow cell was observed. For instance, the redox flow cell containing the membrane with the highest selectivity parameter (770 ± 40) showed the lowest capacity fading during extended charge/discharge cycling (Figure 6.4b) of 7 ± 1.1 mAh h$^{-1}$ or 9 ± 0.8 mAh cycle$^{-1}$ compared to a capacity fading of 18 ± 3.3 mAh h$^{-1}$ or 16 ± 1.0 mAh cycle$^{-1}$ for the cell containing Nafion® 117, which has a selectivity parameter of 47 ± 2 (Figure 6.4b). More details to the procedure used for determination of capacity fading in case of cells with various membranes can be found in the Supplementary Information (Table S6.3). Figure 6.4d shows the decrease in discharge capacity for the cells with Nafion® and the VP grafted membrane with the highest selectivity over 40 cycles.

Among the investigated VP based membranes, non-functionalized materials showed the lowest selectivity parameter (150) and the most pronounced capacity losses (12 mAh h$^{-1}$).
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

Figure 6.4. The *ex situ* properties and *in situ* performance (cycling experiments were performed out at 120 mA cm\(^{-2}\) using 1.7 V as upper and 0.8 V as lower voltage limit at a flow rate of 30 mL min\(^{-1}\)) of various VP grafted membranes compared to Nafion® 117 (N117). a) Selectivity parameter calculated from the area resistance \(R_\Omega\) and the permeance \(i_x\) according to \(\alpha = RT/F - 1/(R_\Omega i_x)\) (Ref.\(^{94}\)), where \(R\) and \(F\) have their usual meaning, and \(T\) is taken as 298 K. b) Capacity losses in Ah h\(^{-1}\) for cells containing different membranes, determined from 40 cycles for all membranes except the non-functionalized VP grafted membrane (for this membranes only 30 cycles were carried out). c) Coulombic and energy efficiency for cells with Nafion® 117 and VP grafted membrane with the highest selectivity parameter (the energy efficiency is the product of coulombic and voltage efficiencies). d) Discharge capacity for the cells with Nafion® and VP grafted membrane with the highest selectivity parameter over 40 cycles (theoretical capacity for both cells was 2.7 Ah). The (1 / 2 / 3) code in case of different membranes has the following meaning: 1 & 2 = reaction time for 1\(^{st}\) and 2\(^{nd}\) functionalization step, 3 = graft level (GL).

Only a small difference in selectivity was observed for membranes with the same reaction time for the alkylation and various reaction times for the nucleophilic substitution step (6 and 30 hours without
protonation of the membrane in between). The selectivity parameters for these two membranes were 395 ± 3 and 368 ± 5. The capacity fading in case of redox flow cells operated with these membranes was also very similar (~ 9 mAh h⁻¹ for both membranes). These results indicate that if considerable reduction in the capacity losses in the redox flow cell is targeted, the selectivity parameter of the used membranes needs to be increased significantly. Small changes in membrane selectivity parameters seem to have almost no effect on the performance of redox flow cell.

Additionally, Figure 6.4c represents cycling performance of the redox flow cell containing the membrane with the highest selectivity in this study and its comparison to the cell with Nafion® 117. Coulombic and voltage efficiencies were calculated according to the procedure described in the literature. The cell with functionalized VP based membrane showed higher coulombic and energy efficiency compared to the cell with Nafion® 117 (Figure 6.4c). The coulombic efficiency averaged over 40 cycles in case of the cell with VP grafted membrane was 98.3 ± 0.7 % compared to 93.4 ± 1.3 % in case of the cell with Nafion® 117. Under the given conditions of cycling, also the overall energy efficiency, i.e., the product of coulombic and voltage efficiency, was higher for the cell with VP based membrane (71.4 ± 0.7 %) than for the cell containing Nafion® 117 (68.4 ± 1.2 %).

6.4.3 Net volumetric transfer across various membranes

Considerable fading of the capacity in case of cells with Nafion® membranes observed here is well-known and a result of electrolyte imbalance caused by high cross-over of vanadium ions through these membranes. It has been previously shown that during charge/discharge cycling with Nafion® membranes not only the total vanadium ion concentration but also the electrolyte volume changes in the two redox flow half-cells. The changes in electrolyte volume can be explained with the water transfer across the membrane, which is driven by the osmotic pressure difference between the two half-cells and caused by transfer of vanadium ions and/or charge balancing species and the water molecules in their hydration spheres. Preferential water transfer in the redox flow cell can lead to precipitation of vanadium salts due to the increase of concentration in one half-cell electrolyte and dilution of the other.
In addition to vanadium cross-over, water transport behavior across different ion selective membranes has therefore been investigated. Mohammadi et al. has previously shown that the direction of the volumetric transfer is dependent on the type of separator used in the redox flow cell. For a cell containing an anion exchange membrane or an uncharged separator net volumetric transfer towards the negative half-cell was observed. In contrast, in a cell with cation exchange membrane water was transported towards the positive half-cell during charge/discharge cycling.\textsuperscript{212}

After long-term cycling, we, therefore, investigated not only capacity losses but also volume transfer behavior in cells with different membranes including AIEMs. To characterize the net volumetric transfer qualitatively the electrolyte volumes on both sides were measured after a number of charge/discharge cycles and electrolyte imbalance was calculated. Volume changes of positive and negative electrolyte after cycling experiments with different membranes are summarized in Supplementary Information (Table S6.4). At the beginning of all cycling experiments both the positive and the negative tank were filled with 100 mL of vanadium electrolyte. Overall losses of electrolyte volume were attributed to trapping of liquid in the cell, tubes and connections, and evaporation, since the tanks are continuously purged with N\textsubscript{2}. Whereas cells with Nafion\textsuperscript{®} membranes were operated for 35 cycles, in case of the cells with functionalized radiation grafted membranes extended cycling experiments over 120 cycles were carried out. Thus, a higher overall loss of electrolyte volume was observed in cells with functionalized grafted membranes.

A significant imbalance of electrolyte volumes of 30-40% was found in case of the Nafion\textsuperscript{®} cells after 35 cycles. The total volume increased in the positive and decreased in the negative half-cell being in good agreement with the literature.\textsuperscript{79, 168, 214} After 35 cycles with Nafion\textsuperscript{®} 117 the positive and the negative electrolyte volumes were determined to be 112 and 81 mL, respectively. For Nafion\textsuperscript{®} 212 even more imbalance was observed. The positive side contained 115 mL of vanadium electrolyte after cycling and the negative one only 77 mL.

The volumetric imbalance in the cell containing amphoteric grafted membranes with vanadium-blocking amidoxime and sulfonic acid groups was studied in our previous work.\textsuperscript{157} As a result of significantly suppressed vanadium cross-over in the cells with amidoximated membranes much less pronounced capacity fading and volumetric imbalance of around 11% was determined. After 122 cycles the positive electrolyte volume was 85 mL and the negative one 76 mL.
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

It is notable that although the amount of the transferred volume significantly differed for cells with amidoximated membranes and Nafion® membranes, in both cases the electrolyte transport occurred in the same direction, i.e., from the negative to the positive side.

Interestingly, for the cell containing amphoteric VP based membrane also only very low imbalance of electrolyte volume around 12% was observed, presumably again as a result of reduced vanadium cross-over in this cell. However, the direction of volumetric transfer changed from the positive towards the negative side. The volume decreased from 100 to 88 mL for the positive and from 100 to 78 mL for the negative side in the cell operated with VP based AIEM.

Summing up, whereas the net volume transfer from the negative to the positive side occurred in the cells with cation exchange Nafion® and amphoteric membranes containing amidoximes and sulfonic acid groups, in case of cells with amphoteric membranes carrying positively charged vinylpyridinium and sulfonic acid functionalities the direction of volumetric transfer changed from the positive to the negative half-cells. Thus, amidoximated and sulfonated membranes seem to have more cation exchange and functionalized VP based membranes more anion exchange character.

6.4.4 Vanadium uptake and permeance of various membranes

Following these observations, VO^{2+}, V^{3+} and VO_2^{+} uptake of different membranes was investigated at a pH of around 0, which is characteristic for VRB (Figure 6.5).

Moreover, to shed the light on the working principle of various membranes their permeance was measured not only towards VO^{2+} but also towards V^{3+} and VO_2^{+} species in a diffusion cell. V^{2+} ions were excluded from both experiments because they show poor stability and readily oxidize to V^{3+}.

Considerable differences were observed in the vanadium uptake behaviour of different membranes (see Figure 6.5a). For Nafion® 117 the highest uptake was measured in case of VO^{2+} ions followed by V^{3+} and VO_2^{+}. Sulfonated and amidoximated membranes (SS/AO) showed only small and very similar uptake of all vanadium ions, indicating that all vanadium ions are hindered from entering these membranes in a VRB environment. Interestingly, functionalized VP based membranes also exhibited only very low uptake of VO^{2+} and V^{3+} species but their VO_2^{+} uptake was very high. These results
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

suggest that whereas VO\(^{2+}\) and V\(^{3+}\) species are hindered from entering functionalized VP based membranes, VO\(_2^+\) uptake readily takes place.

Figure 6.5. Vanadium uptake and permeance determined at low pH of around 0. Nafion\(^\circledR\) 117 (N117), sulfonated and amidoximated membranes (SS/AO) from our previous study\(^{157}\) and functionalized vinylpyride based membranes (VP) were used for these experiments. a) VO\(^{2+}\), V\(^{3+}\) and VO\(_2^+\) uptake of various membranes after being stored in corresponding 1 M vanadium electrolyte in 2 M H\(_2\)SO\(_4\). b) Vanadium-ion permeance measured ex situ in a diffusion cell containing corresponding vanadium electrolyte, expressed as current density equivalent.

A good correlation between vanadium uptake of membranes and their vanadium permeance in a diffusion cell was established at a low pH of around 0 (Figure 6.5b). It was found that the higher was the uptake of single vanadium ions for a membrane the more permeable this membrane was towards this species, except for functionalized VP grafted membranes. Whereas VO\(_2^+\) uptake of these membranes was very high at a pH of around 0, in a diffusion cell only very low permeance of these
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

ions was measured. Furthermore, the colour of the VP based membrane remained the same after storage in VO$^{2+}$ and V$^{3+}$ electrolyte, but changed from colourless to dark brown after storage in VO$_2^+$ solution. These results strongly indicated the complexation of VO$_2^+$ species by functionalized VP membranes.

Most research groups developing membranes for VRB applications have tended to limit their permeation measurements to the VO$^{2+}$ species. Our results from uptake and permeance experiments revealed significant differences in the interaction of various membranes with vanadium ions in different oxidation states. Whereas Nafion® 117 showed the highest affinity for VO$^{2+}$ ions followed by V$^{3+}$ and VO$_2^+$, in case of functionalized VP based membranes a higher affinity towards VO$_2^+$ species was observed followed by VO$^{2+}$ and V$^{3+}$. Thus, to understand the working principle of membranes in the cell the measurement of cross-over rates of all vanadium ions is recommended.

6.4.5 Complexation of VO$_2^+$ ions by functionalized VP membranes

Next, we tried to understand the complexation behaviour of single charged VO$_2^+$ ions in functionalized VP membranes. In general, VO$_2^+$ ions can be coordinated by two functionalities in the membrane: (1) by aminobenzene sulfonic acid units or/and (2) by alkylated or, in 2 M H$_2$SO$_4$ protonated vinylpyridinium units. To find out by which groups VO$_2^+$ ions are coordinated in the membrane, two VP grafted membranes with the same graft level were synthesized and only one of them was functionalized. Thus, one membrane contained only protonated vinylpyridinium units and the other one sulfonic acid groups along with alkylated and protonated vinylpyridinium. VO$_2^+$ uptake of these two membranes was measured at low pH of around 0 and was found to be very similar (see Figure S6.3). Also the color of both membranes changed from nearly colorless to brown.

Consequently, the coordination of VO$_2^+$ ions seems to be related to the presence of unreacted vinylpyridinium units in the membranes, which are expected to be protonated in 2 M H$_2$SO$_4$. Polymeric ligands based on partly or fully quaternized poly(vinylpyridine) (PVP) have been previously described in the literature and were used for removal of heavy metals such as various Cr(VI) salts, gold and uranium from aqueous solutions. For instance, PVP-chlorochromate and PVP-dichromate reagents
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

were easily prepared by reaction of PVP with chromium trioxide-HCl for the former and with chromium trioxide water for the latter.\textsuperscript{217}

\subsection{6.4.6 Post-test analysis of membrane}

To probe the stability of functionalized VP based membranes under VRB operating conditions an extended cycling experiment was carried out at a current density of 120 mA cm\textsuperscript{-2}. Stable coulombic, voltage and energy efficiency was observed over 120 cycles without any significant changes. Furthermore, after 120 cycles the tested membrane was removed from the cell and analyzed with IR spectroscopy to check for signatures of aging. No significant differences were observed in the IR spectra of the membrane before and after long-term cycling (Figure S6.4) indicating encouraging stability of this membrane in the VRB environment.
6.5 Conclusions

A new design concept for amphoteric IEMs for application in VRB was presented. These AIEMs were obtained by radiation-induced grafting of vinylpyridine monomers on ETFE films followed by their subsequent two-step functionalization. Improved vanadium barrier properties of new AIEMs were achieved by introduction of alkylated vinylpyridinium units into these polymeric materials, whereas the presence of protogenic sulfonic acid groups resulted in reduced area resistance. By means of functionalization AIEMs were obtained with significantly improved vanadium barrier properties and area resistance comparable to that of Nafion® 117. Compared to the cells operated with Nafion® 117, cells with functionalized VP based membranes showed not only higher energy efficiency but also reduced capacity fading and less pronounced changes in electrolyte volumes in the half-cells during extended charge/discharge cycling. Furthermore, properties of functionalized VP based membranes could be easily tuned by varying their graft level and/or reaction time for each of the functionalization steps.

To shed the light on working principle of amphoteric VP based membranes, their vanadium uptake and permeance towards $\text{VO}_2^+$, $\text{VO}_2^+$ and $\text{V}_3^+$ ions was measured at low pH, characteristic for VRBs. The permeance of membranes towards all vanadium ions was very low. Furthermore, it was found that whereas $\text{VO}_2^+$ and $\text{V}_3^+$ species are hindered from entering VP based membranes at a pH of around 0, uptake of single charged $\text{VO}_2^+$ species takes place readily, presumably owing to their coordination by non-alkylated vinylpyridine units within the membrane. These results suggest that both approaches, the minimization of vanadium ion uptake as well as their complexation by adequate membrane functionalities, are effective in reducing vanadium permeability of membranes.

Net volumetric transfer of electrolyte across amphoteric IEMs was studied. Whereas in the cells with Nafion® 117 and amphoteric amidoximated membranes (from our previous work) net volumetric transfer towards the positive half-cell was observed, in the cell with VP based membranes water transport occurred in the opposite direction. In both cells with amphoteric membrane net volumetric transfer was significantly less pronounced compared to the cells with Nafion® 117, owing to reduced vanadium cross-over.
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

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6.6 Supporting Information

Figure S6.1. Mass based graft level of vinylpyridine (VP) grafted films as a function of reaction time. 5 and 15 kGy pre-irradiated ETFE films with a thickness 25 µm were used as base polymer. Grafting reaction was carried out at 60°C using a grafting solution with 50 % (v/v) vinylpyridine + 50 % (v/v) iso-propanol.
Figure S6.2. Degree of alkylation of vinylpyridine units in selected VP based membranes determined from ion chromatography (IC) versus the ratio of the peaks at 1’640 and 820 cm\(^{-1}\) obtained from IR spectra of the same membranes. The slope of the linear fit represented in the graph was 37.2 \(\pm\) 1.6. The alkylation level (\%) of pyridine functionalities was determined by means of ion chromatography (Metrohm 882 Compact IC Plus) with anion exchange column (Metrosepp A Supp 5 150) and conductivity detection with a suppression system. For this, the functionalized sample in bromide form was placed in 0.1 M HCl for 8 h in a well stirred vessel and the concentration of bromide anions exchanged against chloride anions was measured in the leachate using IC. The IR spectra were obtained using a Bruker Vertex 70 spectrometer. Ratio of peak areas at 1’640 cm\(^{-1}\) (quaternized pyridine ring C=N stretch) and 820 cm\(^{-1}\) (C-H ring mode) was determined using Bruker OPUS spectroscopy software.
### Table S6.1. Alkylation degree (%) in selected membranes determined from the ratio of peak areas (at 1’640 and 820 cm⁻¹) in their IR spectra. These membranes were prepared using different reaction temperature and time in the 1st functionalization step.

<table>
<thead>
<tr>
<th># of investigated membranes*</th>
<th>Graft level [wt-%]</th>
<th>Reaction temperature of alkylation step [°C]</th>
<th>Reaction time of alkylation step [hours]</th>
<th>Peak area ratio [1’640/820 cm⁻¹]</th>
<th>Alkylation degree [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42 ± 2</td>
<td>45</td>
<td>8</td>
<td>0.19</td>
<td>7.1 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>42 ± 2</td>
<td>45</td>
<td>8</td>
<td>0.20</td>
<td>7.4 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>43 ± 2</td>
<td>45</td>
<td>8</td>
<td>0.27</td>
<td>10.0 ± 0.4</td>
</tr>
<tr>
<td>4</td>
<td>43 ± 2</td>
<td>45</td>
<td>24</td>
<td>0.62</td>
<td>23.1 ± 1.0</td>
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<tr>
<td>5</td>
<td>36 ± 2</td>
<td>45</td>
<td>24</td>
<td>0.67</td>
<td>24.9 ± 1.1</td>
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<tr>
<td></td>
<td>43 ± 2</td>
<td>45</td>
<td>48</td>
<td>1.03</td>
<td>38.3 ± 1.6</td>
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<tr>
<td></td>
<td>43 ± 2</td>
<td>60</td>
<td>24</td>
<td>1.74</td>
<td>64.7 ± 2.8</td>
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<tr>
<td></td>
<td>43 ± 2</td>
<td>60</td>
<td>48</td>
<td>2.69</td>
<td>100.1 ± 4.3</td>
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<td></td>
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<td></td>
<td></td>
<td>0.457b</td>
<td>17.0 ± 0.7</td>
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<td></td>
<td>0.442b</td>
<td>16.4 ± 0.7</td>
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<td></td>
<td></td>
<td>0.458b</td>
<td>17.0 ± 0.7</td>
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<td></td>
<td></td>
<td>0.460b</td>
<td>17.1 ± 0.7</td>
</tr>
</tbody>
</table>

*a # of different membranes used for determination of peak area ratios showing deviation in determined peak area ratios of various membranes with the same synthetic route

*b three random positions were chosen on the membranes of interest and used for IR analysis to show the deviations of peak area ratios determined within the same membrane at different positions

*c this membrane was placed in 1-methyl-2-pyrrolidinone at 45°C for additional 30 hours (without the presence of 1,10-dibromodecane) after the alkylation step to get an insight into the ability of vinylpyridine moieties to react with Br end groups of other alkylated vinylpyridine units within the given membrane.
Table S6.2. Ohmic resistance, vanadium cross-over and selectivity: Ohmic resistance and VO$^{2+}$ cross-over values for selected membranes are extracted from Figure 6.3. The selectivity parameter $\alpha$ is calculated as a membrane figure of merit. Samples #2-4: effect of functionalization on properties of VP grafted films; samples #5-6: effect of the graft level on properties of functionalized membranes; samples #7-8: effect of the reaction time for the alkylation step; samples #9-10: effect of the reaction time for the sulfonation step.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Membrane</th>
<th>Graft level</th>
<th>Reaction time of 1st/2nd functionalization step</th>
<th>Ohmic resistance $R_{\Omega}$ [Ω cm$^2$]</th>
<th>Permeance $i_x$ [mA cm$^{-2}$]</th>
<th>Selectivity $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nafion® 117</td>
<td>-</td>
<td>-</td>
<td>0.84 ± 0.012</td>
<td>0.65 ± 0.03</td>
<td>47 ± 2</td>
</tr>
<tr>
<td>2$^b$</td>
<td>Grafted VP unmodified</td>
<td>43 ± 2</td>
<td>-</td>
<td>0.91</td>
<td>0.19 ± 0.003</td>
<td>147</td>
</tr>
<tr>
<td>3</td>
<td>Grafted VP functionalized</td>
<td>43 ± 2</td>
<td>8/-</td>
<td>1.24</td>
<td>0.09 ± 0.001</td>
<td>231</td>
</tr>
<tr>
<td>4</td>
<td>Grafted VP functionalized</td>
<td>43 ± 2</td>
<td>8/6</td>
<td>0.82</td>
<td>0.12 ± 0.002</td>
<td>282</td>
</tr>
<tr>
<td>5</td>
<td>Grafted VP functionalized</td>
<td>43 ± 2</td>
<td>8/6</td>
<td>0.82</td>
<td>0.12 ± 0.002</td>
<td>282</td>
</tr>
<tr>
<td>6$^b$</td>
<td>Grafted VP functionalized</td>
<td>36 ± 2</td>
<td>8/6</td>
<td>0.90 ± 0.004</td>
<td>0.07 ± 0.001</td>
<td>395 ± 3</td>
</tr>
<tr>
<td>7</td>
<td>Grafted VP functionalized</td>
<td>43 ± 2</td>
<td>8/6</td>
<td>0.82</td>
<td>0.12 ± 0.002</td>
<td>282</td>
</tr>
<tr>
<td>8$^b$</td>
<td>Grafted VP functionalized</td>
<td>43 ± 2</td>
<td>24/6</td>
<td>0.87 ± 0.003</td>
<td>0.04 ± 0.002</td>
<td>771 ± 41</td>
</tr>
<tr>
<td>9$^b$</td>
<td>Grafted VP functionalized</td>
<td>36 ± 2</td>
<td>8/6</td>
<td>0.90 ± 0.004</td>
<td>0.07 ± 0.001</td>
<td>395 ± 3</td>
</tr>
<tr>
<td>10$^b$</td>
<td>Grafted VP functionalized</td>
<td>36 ± 2</td>
<td>8/30</td>
<td>1.01 ± 0.010</td>
<td>0.07 ± 0.001</td>
<td>368 ± 5</td>
</tr>
<tr>
<td>11$^c$</td>
<td>Grafted S/AN functionalized</td>
<td>36 ± 2</td>
<td>-</td>
<td>0.7 ± 0.114</td>
<td>0.11 ± 0.010</td>
<td>329 ± 58</td>
</tr>
</tbody>
</table>

$^a$ calculated according to Ref.94: $\alpha = \frac{R T}{P} \cdot \frac{1}{R_0 \cdot \delta x}$, where $T$ is taken as 298 K.

$^b$ membrane chosen for cycling test in redox flow cell

$^c$ grafted membrane carrying amidoxime and sulfonic acid groups, more details about this type of membranes are provided in Ref. 157
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

**Table S6.3.** Capacity fading determined after a given number of cycles in the cells with various membranes. To calculate capacity losses all cycling experiments were repeated 3 times with 3 different freshly prepared membranes of each class. Only in case of Nafion® 212 charge/discharge cycling was carried out one time. It is notable that in case of cells containing various membranes the duration of charge/discharge cycles is different and depends on the used separator. Taking this into account, we expressed the capacity fading after a given number of cycles not only in mAh cycle⁻¹ but also in mAh h⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graft level</th>
<th># of cycles</th>
<th>Capacity fading [%]</th>
<th>[mAh cycle⁻¹]&lt;sup&gt;a&lt;/sup&gt;</th>
<th>[mAh h⁻¹]&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion® 117</td>
<td>-</td>
<td>35</td>
<td>16.3 ± 1.0</td>
<td>18.4 ± 3.3</td>
<td></td>
</tr>
<tr>
<td>Nafion® 212</td>
<td>-</td>
<td>35</td>
<td>14.7 ± 0.4</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>functionalized ETFE-g-poly(S-co-AN)</td>
<td>~36</td>
<td>40</td>
<td>8.8 ± 1.0</td>
<td>7.6 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>functionalized ETFE-g-poly(VP)</td>
<td>~40</td>
<td>40</td>
<td>8.9 ± 0.8</td>
<td>6.8 ± 1.1</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> capacity loss after a given number of cycles was calculated and divided by the number of cycles

<sup>b</sup> capacity loss after a given number of cycles was calculated and divided by the time (hours) required for the corresponding cycling experiment
Chapter 6: Amphoteric 4-vinylpyridine based ion exchange membranes

**Table S6.4.** Electrolyte imbalance determined from the changes in the negative and positive electrolyte volume after extended cycling experiments with various membranes. Charge/discharge cycling was performed at a current density of 120 mA cm\(^{-2}\). Nafion\textsuperscript{®} 117, Nafion\textsuperscript{®} 212, membranes with amidoxime groups and functionalized VP based membranes were used for these experiments as separators. The volume of the positive and negative electrolyte at the beginning of test was 100 mL each. Overall loss of electrolyte volume is due to trapping of liquid in the cell, tubes and connections, and evaporation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graft level</th>
<th># of cycles</th>
<th>Electrolyte vol.</th>
<th>Imbalance(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(V_–)</td>
<td>(V_+)</td>
</tr>
<tr>
<td>Nafion\textsuperscript{®} 117</td>
<td>-</td>
<td>35</td>
<td>81</td>
<td>112</td>
</tr>
<tr>
<td>Nafion\textsuperscript{®} 212</td>
<td>-</td>
<td>35</td>
<td>77</td>
<td>115</td>
</tr>
<tr>
<td>functionalized ETFE-g-poly(S-co-AN)</td>
<td>~36</td>
<td>122</td>
<td>76</td>
<td>85</td>
</tr>
<tr>
<td>functionalized ETFE-g-poly(VP)</td>
<td>~40</td>
<td>120</td>
<td>88</td>
<td>78</td>
</tr>
</tbody>
</table>

\(\text{Imbalance}^a = \frac{\Delta V}{V} = \frac{V_+ - V_–}{\frac{1}{2}(V_+ + V_–)}\)
Figure S6.3. $\text{VO}_2^+$ uptake of VP based membranes after being stored in corresponding 1 M vanadium electrolyte in 2 M $\text{H}_2\text{SO}_4$ for 14 days. Membrane 1 was completely functionalized and thus contained vinylpyridinium units along with aminobenzenesulfonic acid groups; membrane 2 was not functionalized and carried therefore only positively charged vinylpyridinium functionalities.
Table S6.5. Vanadium permeability of selected membranes measured in home-made diffusion cells. The (1 / 2 / 3 / 4) code in case of different membranes has the following meaning: 1 = reaction time for the alkylation step, 2 = reaction time for sulfonation step, 3 = graft level (GL), 4 = without [-] & with [+] protonation between the 1st and 2nd functionalization step.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>VO$_2^{+}$ permeability</th>
<th>V$^{3+}$ permeability</th>
<th>VO$_2^{+}$ permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(× 10$^{-5}$ cm$^2$ h$^{-1}$)</td>
<td>(× 10$^{-5}$ cm$^2$ h$^{-1}$)</td>
<td>(× 10$^{-5}$ cm$^2$ h$^{-1}$)</td>
</tr>
<tr>
<td>Nafion® 117</td>
<td>32.1</td>
<td>20.4</td>
<td>11.2</td>
</tr>
<tr>
<td>(-/-43 ± 2%)</td>
<td>2.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8/-43 ± 2%)</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8/6/43 ± 2%/[-])</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(24/6/43 ± 2%/[-])</td>
<td>0.56</td>
<td>0.10</td>
<td>2.90</td>
</tr>
<tr>
<td>(8/6/36 ± 2%/[-])</td>
<td>1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8/30/36 ± 2%/[-])</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8/30/36 ± 2%/[+])</td>
<td>1.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS/AO (36% GL)</td>
<td>1.53</td>
<td>2.73</td>
<td>2.91</td>
</tr>
</tbody>
</table>
Figure S6.4. Stability study of functionalized VP grafted membranes in an operating VRB. Charge/discharge cycling of the redox flow cells was performed at a constant current density of 120 mA cm\(^{-2}\) using 1.7 V as upper and 0.8 V as lower voltage limit. 100 mL of 1 M vanadium electrolyte solutions were used on each side. The flow rate was 30 mL min\(^{-1}\). A functionalized VP grafted membranes with around 43% GL (reaction time for 1\(^{st}\) and 2\(^{nd}\) functionalization step are 24 and 6 hours respectively) was selected for this experiment. IR spectroscopy was used to check for signatures of aging in the membranes after extended cycling experiments. a) Decrease in discharge capacity for the cells with Nafion® 117 and functionalized VP grafted membrane over 40 cycles; b) over 120 cycles; c and d) IR spectra of the VP based membrane before (black line) and after (red line) extended cycling experiment.
Chapter 7: Conclusions and Outlook

Conclusions

The need for electrochemical energy storage increases along with the growing share of fluctuating renewables for power generation. The all-vanadium redox flow battery (VRB) has gained increasing attention in this context. To the core components of all-vanadium redox flow cells belong separators and carbon electrodes. Separators with high cell resistance reduce the voltage efficiency (VE) of the redox flow cells and those with poor vanadium barrier properties impair their coulombic efficiency (CE). Moreover, high rates of cross-over of vanadium ions through the separators leads to continuous capacity decay and self-discharge limiting the use of a VRB as energy storage device. On the other hand, activation, ohmic and mass transport losses associated with the insufficient performance of carbon electrodes must be minimized to allow high performance of a VRB cell. Carbon electrodes should exhibit not only high but also durable catalytic activity, electrical conductivity as well as mass transport properties to ensure the long-term operation of a VRB.

For VRB applications, this thesis presents design strategies for amphoteric ion exchange membranes, based on radiation induced grafting of selected monomers into pre-existing polymeric films followed by subsequent functionalization. Furthermore, in this thesis performance and stability of selected commercially available carbon electrodes (before and after thermal treatment) are evaluated. Performance and stability of commercially available carbon paper electrodes, such as SGL 39 AA, SGL 10 AA, Toray TGP-H-120 as well as GFD4.6 EA carbon felt electrodes, were studied in the framework of this thesis. After heat treatment (HT) the performance of cells with all carbon materials was enhanced. Reference electrode measurements revealed that most of the improvements came from the \( \text{V}^{2+}/\text{V}^{3+} \) side. The cells containing HT-SGL 39 AA carbon papers and HT-GFD4.6 EA carbon felt showed the best overall performance and their durability was probed under VRB operating conditions. Upon extended cycling, the performance of the cell with carbon felt was found to be stable. Redox flow cells containing carbon papers showed however significant losses in performance which originated primarily from the negative electrode. It was found that the unstable carbon papers were
Chapter 7: Conclusions and Outlook

exposed to cell potentials above 1.6 V for a significantly longer period of time during charging compared to the stable carbon felt. This means that carbon papers experienced more negative potentials during charging process in the negative half-cell. XPS results revealed a decrease in O/C ratio of approximately 33 % for both stressed carbon materials from the negative half-cell. Thus, losses in oxygen containing functionalities could contribute but do not fully explain the loss in activity observed for the carbon papers and not for carbon felt. Raman spectroscopy and SEM showed significant structural and morphological differences between the two materials. It appears that stability of carbon materials in VRBs depends on a combination of different aspects such as their structure, morphology and surface chemistry.

For the use in VRBs, this thesis presents amphoteric ion exchange membranes containing sulfonic acid and amidoxime groups, which are known in the literature for their ability to complex vanadium ions in sea water at a pH of around 7. These membranes were obtained by radiation induced grafting of styrene and acrylonitrile monomers into pre-existing ETFE films followed by subsequent functionalization. The decoration of membranes with amidoxime groups resulted in significant suppression of their vanadium permeability. Moreover, the presence of protogenic sulfonic acid groups in the membranes allowed the reduction of their ohmic resistance. As a consequence of improved selectivity, cells with membranes bearing amidoxime and sulfonic acid groups showed higher charge-discharge efficiency and a less pronounced capacity fading compared to the cells with the state-of-the-art material, Nafion® 117.

To shed the light on the working principle of amidoximated membranes under VRB operating conditions, the interactions between amidoxime groups and vanadium ions in different oxidations states and at different pH were investigated experimentally and in silico. The vanadium uptake of various membranes with and without amidoxime groups was determined experimentally only. In contrast, the use of a model system based on acetamide oximes allowed to study the interactions between amidoxime groups and vanadium ions experimentally as well as in silico. It was found that although amidoxime groups can complex vanadium ions in neutral environment, under acidic conditions the complexation is strongly disfavored. Instead of complexing, the protonated and, thus, positively charged amidoxime groups prevent vanadium ions from entering the membrane, providing an effective vanadium barrier in the VRB environment.
Finally, amphoteric ion exchange membranes containing positively charged vinylpyridinium units and sulfonic acid groups were proposed for VRB applications. These membranes were obtained by radiation induced grafting of vinylpyridine monomers into pre-existing ETFE films followed by subsequent functionalization. The decoration of membranes with positively charged vinylpyridinium units resulted in significant improvement of their vanadium barrier properties whereas the presence of sulfonic acid groups lowered their ohmic resistance. Cells containing functionalized vinylpyridine based membranes exhibited higher energy efficiency and better capacity retention compared to the cells operated with the state-of-the-art material Nafion® 117.

The interactions of various membranes, including Nafion® 117, membranes with amidoxime groups and functionalized vinylpyridine based membranes, with vanadium ions in different oxidation states (VO$^{2+}$, VO$_2^+$ and V$^{3+}$) were compared. For this, their vanadium uptake and permeance were determined at pH 0. Vanadium uptake and permeance experiments revealed significant differences in the interaction of various membranes with vanadium ions in different oxidation states. Nafion® 117 showed high uptake and permeance for VO$^{2+}$ ions followed by V$^{3+}$ and VO$_2^+$. In contrast, in case of membranes with amidoxime groups only very low vanadium uptake and permeance was observed for all vanadium species used in the study. Additionally, it was found that whereas VO$^{2+}$ and V$^{3+}$ ions are also hindered from entering vinylpyridine based membranes at low pH of around 0, uptake of single charged VO$_2^+$ species takes place readily. Although high VO$_2^+$ uptake was observed in case of vinylpyridine based membranes, their permeance towards these ions was very low.

As a consequence of suppressed vanadium cross-over, in both cells with amphoteric ion exchange membrane net volumetric transfer of electrolyte was significantly less pronounced compared to the cells with Nafion® 117. However, significant differences in net volumetric transfer of electrolyte across various amphoteric membranes were observed. In the cells containing amphoteric amidoximated membranes volumetric transfer towards the positive half-cell occurred. The transport of electrolyte volume towards the positive side was observed also in the cells with cation exchange membranes such as Nafion® 117. In contrast in the cells with VP based membranes water transport in the opposite direction occurred, from the positive to the negative half-cell.
Chapter 7: Conclusions and Outlook

Outlook

Ion exchange membranes and carbon electrodes belong to the core components of all-vanadium redox flow cells and largely determine their performance.

Two different types of amphoteric ion exchange membranes were proposed in this thesis for the use in VRBs. To probe the stability of synthesized membranes under VRB operating conditions, extended cycling experiments including 120 cycles were carried out at a current density of 120 mA cm\(^{-2}\). Stable coulombic, voltage and energy efficiency were observed over 120 cycles for both types of membranes. However, to judge the long-term stability of those membranes in the VRB environment the development of reliable accelerated stress tests is still required.

Moreover, the synthetic route of membranes can be further optimized by selecting a more appropriate solvent for functionalization process and/or another ways to introduce cation and anion exchange moieties into membranes. For instance, for functionalization of vinylpyridine based membranes sodium 2-bromoethanesulfonate can be used instead of 3-aminobenzenesulfonic acid and 1,10-dibromodecane. The use of cost-effective harmless sodium 2-bromoethanesulfonate can enable one-step functionalization of vinylpyridine grafted films.

The same ETFE base film was used in this thesis for the synthesis of all membranes. However, the utilization of other base films can also be of interest. For instance, non-fluorinated polyethylene or polypropylene films can be considered instead of partially fluorinated ETFE base films, allowing further reduction of membranes cost.

Furthermore, in this work the optimization of membranes targeted two different current densities: 40 and 120 mA cm\(^{-2}\). At these current densities vanadium permeance of membranes as well as their area resistance determine the performance of redox flow cells and must be minimized. Amphoteric membranes which were identified as especially promising at 40 and 120 mA cm\(^{-2}\) may, however, be unsuitable for operation at higher current densities (≥ 120 mA cm\(^{-2}\)) because under these conditions the area resistance of membranes will dominate the performance of the redox flow cell. Thus, the operation of redox flow cells at higher current densities will require further optimization of polymeric
separators presented in this work or even development of new materials. Modified porous separators, functionalized and/or multi-layer composites, can be interesting in this context.

In this thesis, vanadium uptake and permeance of various ion exchange membranes were determined \textit{ex situ} and revealed significant differences in the interaction of studied separators with vanadium ions in different oxidation states. Next it will be interesting to explore the transport of vanadium ions through various membranes directly in the operating redox flow cell. Additionally, highly selective amphoteric membranes synthesized in the framework of this thesis have been shown to reduce electrolyte imbalance in the redox flow cell, which occurred due to the asymmetric diffusion of vanadium ions through polymeric separators. However, vanadium ions are transported through various membranes not only because of diffusion but also because of convection (osmosis/electro-osmosis) and migration. Whereas migration has been reported to have only small impact on the transport of vanadium ions across the membrane in the literature, convection contributed significantly to electrolyte imbalance. Therefore, in the next step vanadium transfer associated with the convection can be addressed for further reduction of capacity decline and electrolyte imbalance in a redox flow cell. This can be for instance done by varying operating condition of redox flow cells.

Performance and stability of thermally treated SGL 39 AA carbon papers and GFD4.6 EA carbon felt were studied under VRB operating conditions in the framework of this thesis. Whereas stable performance of the cell with carbon felt was observed at a current density of 120 mA cm\(^{-2}\), redox flow cells containing carbon papers experienced significant performance decline which originated from the negative electrode. XPS revealed a decrease in O/C ratio of approximately 33\% for both stressed carbon materials from the negative half-cell. Raman spectroscopy and SEM showed significant structural and morphological differences between the two PAN based carbon materials. In order to gain a full overview of factors contributing to electrode stability in VRBs, it is necessary to investigate other issues, such as hydrogen evolution, for both carbon electrodes. Bismuth (Bi) nanoparticles have been shown in the literature to suppress hydrogen evolution in the negative half-cell of a VRB and, thus, enhance the reversibility of the V\(^{2+}/V^{3+}\) redox reaction. It might be interesting to add bismuth nanoparticles to the unstable carbon papers on the negative side and to study their degradation behaviour. If the hydrogen evolution results in degradation of carbon papers, the addition of bismuth nanoparticles may improve their cycling stability.
Moreover, to further improve the performance of operating all-vanadium redox flow cells also optimization of other cell components, such as the vanadium electrolyte, will be required. Commercially available electrolyte from Oskem (with H$_3$PO$_4$ additive) was for example found in our laboratory to improve charge/discharge capacity significantly. Also other additives can be taken into consideration to stabilize vanadium electrolyte.
Chapter 8: References


Chapter 8: References


Chapter 8: References


161. P. Han, H. Wang, Z. Liu, X. Chen, W. Ma, J. Yao, Y. Zhu, G. Cui, Graphene oxide nanoplatelets as excellent electrochemical active materials for VO$^{2+}$/VO$^{3+}$ and V$^{2+}$/V$^{3+}$ redox couples for a vanadium redox flow battery. *Carbon* **49** (2011) 693-700.


<table>
<thead>
<tr>
<th>Abbr.</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEC</td>
<td>Anion exchange capacity</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion exchange membrane</td>
</tr>
<tr>
<td>AIEM</td>
<td>Amphoteric ion exchange membrane</td>
</tr>
<tr>
<td>AN</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>AO</td>
<td>Amidoximes</td>
</tr>
<tr>
<td>CA</td>
<td>Carboxyl groups</td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
</tr>
<tr>
<td>CEM</td>
<td>Cation exchange membranes</td>
</tr>
<tr>
<td>CF</td>
<td>Carbon felt</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>CP</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>EE</td>
<td>Energy efficiency</td>
</tr>
<tr>
<td>ETFE</td>
<td>Poly (ethylene tetrafluoroethylene)</td>
</tr>
<tr>
<td>FEP</td>
<td>Poly(tetrafluoroethylene-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GL</td>
<td>Graft level</td>
</tr>
<tr>
<td>HT</td>
<td>Heat treated</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>IEC</td>
<td>Ion exchange capacity</td>
</tr>
<tr>
<td>IEM</td>
<td>Ion exchange membrane</td>
</tr>
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List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>kGy</td>
<td>Kilogray</td>
</tr>
<tr>
<td>MD</td>
<td>Metadynamics</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidone</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PBI</td>
<td>Polybenzimidazole</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly (ethylene glycol)</td>
</tr>
<tr>
<td>PFA</td>
<td>Poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether)</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorosulfonic acid</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly (tetrafluoroethylene)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly (vinylidene fluoride)</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly (vinylpyrrolidone)</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox flow batteries</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SoC</td>
<td>State of charge</td>
</tr>
<tr>
<td>St</td>
<td>Styrene</td>
</tr>
<tr>
<td>SS</td>
<td>Sulfonated styrene</td>
</tr>
<tr>
<td>SPES</td>
<td>Sulfonated poly (ether sulfone)</td>
</tr>
<tr>
<td>SPEEK</td>
<td>Sulfonated poly (ether ether ketone)</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethylpiperidinyloxyl</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UT</td>
<td>Untreated</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>VE</td>
<td>Voltage efficiency</td>
</tr>
<tr>
<td>VP</td>
<td>Vinilpyridine</td>
</tr>
</tbody>
</table>
List of Abbreviations

| VRB          | All-vanadium redox flow battery |
Publication List

Peer review publications:


Patent application:


Contributed Talks and Posters:


Olga Nibel, Thomas J. Schmidt, Lorenz Gubler, Highly selective ion exchange membranes for the all-vanadium redox flow battery, E-MRS Spring Meeting, Strasbourg, France, June 22-26, 2017 (Oral Presentation).