Investigations of Current Density Inhomogeneities in Polymer Electrolyte Fuel Cells

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Summary

The present work is concerned with locally resolved investigations of inhomogeneities in the current density distribution in polymer electrolyte fuel cells (PEFCs). For the studies, an optimized cell, previously used in the power train of a fuel cell powered car has been used. The results are therefore relevant on a technical scale.

The central themes in the thesis are the spatial non-uniformities of operating conditions, which evolve due to the operating principle of fuel cells as flow-through reactors. The terms “local” and “integral” cell performance act as guidelines throughout the thesis.

As the gaseous reactants are fed in channels, covering the active area of the fuel cell, during the electrochemical conversion of the educts, hydrogen and oxygen, into water and heat, major gradients evolve along the reactants’ stream path. Of particular interest are gradients of oxygen partial pressure at the cathode, the water partial pressure in general due to its high impact on the electrolyte conductivity, and the influence of impurities at the anode.

A major part of the thesis is therefore devoted to investigations on the implications of a non-uniform distribution of these parameters on local cell performance and correlating the findings with changes in integral cell performance. The effects of these parameters on local and integral cell performance were investigated individually.

The implications of oxygen partial pressure gradients, which evolve when using air as the oxidant were analyzed. Emphasis was put on investigating the effects of varying air stoichiometries on local current generation. At low air stoichiometries, a strong decrease in oxygen partial pressure along the channel evolves. As a result, the current generation becomes highly inhomogeneous, implying a non-uniform thermal load distribution over the active area. This can have a negative influence on the lifetime of the cell. Therefore, in order to minimize these effects, an alternative approach to high air stoichiometries to homogenize the current density distribution was investigated. In order to counteract local
oxygen partial pressure differences, redistribution of the cathode catalyst is the chosen strategy. It was shown that a homogenization of the current density in PEFCs being operated at air stoichiometries below 2.0 can be achieved by a catalyst redistribution concept. While current homogenization could be achieved, no increase in cell performance was observed because a redistribution of the catalyst implies the same or slightly higher average overvoltages than for the case of a homogeneous loading. This is because of the non-linear relation between current density and activation and mass transport overvoltages.

The effects of membrane thickness and reactants humidification on local current generation were further investigated. Comparison of cell performance with dry reactant streams showed that humidification of the process air has a much stronger influence than humidification of the hydrogen. Under operation with dry air, the local current generation is determined by the volume flow, i.e. stoichiometry, and thickness of the membrane while the influence of oxygen losses due to permeation through the electrolyte, with the corresponding increase in cathodic mass transport resistance, were found to be of only minor influence.

Bearing in mind that humidification of the reactants is a heavy burden for the fuel cell system, and considering the results obtained in the investigations on the influence of reactants humidification on cell performance, a concept for the internal humidification of the process air was presented. The concept comprises the direct utilization of the product water for humidification of the process air in each cell. The concept was tested and characterized first in the laboratory and then in the field with a 1.3 kW stack, which was integrated in a portable 1 kW net power system. With this concept, the power obtained at nominal load was less than 4 percent lower as compared to the power obtained with external humidification of the process air.

Transient and steady state effects of carbon monoxide in the fuel on poisoning of the anode catalyst were investigated for different CO concentrations. Effects of an internal air bleeding due to oxygen permeation from the cathode to the anode were analyzed with
varying membrane thickness. Through locally resolved current density measurements and mass spectrometric monitoring of the anode exhaust gas, information on the local transient of CO poisoning of the anode catalyst was obtained. The results showed that CO poisoning does not proceed uniformly along the channel. CO poisons the catalyst preferentially in the upstream regions of the fuel channel. Therefore, the onset for CO electrooxidation occurs first in the regions close to the fuel inlet, diminishing the CO concentration in the fuel along the channel. An additional CO concentration diminishment occurs due to an internal air bleeding by permeated oxygen from the cathode. The time dependent mass balance of CO/CO$_2$ in the exhaust fuel stream was analyzed, confirming the internal air bleeding mechanism. Consequently, transient and steady state local CO poisoning of the catalyst depend upon location along the fuel channel, initial CO concentration in the fuel, and membrane thickness. CO tolerance in cells operated with 10 and 50 ppm CO increased with decreasing membrane thickness. For the case of 100 ppm CO, the membrane thickness did not influence CO tolerance significantly, since differences in the rates of oxygen permeation did not reduce CO concentration in the fuel significantly anymore.

The use of a technical cell allowed further inclusion of local current density measurements in individual cells at stack level to investigate the coupling behaviour of cells in a stack. Differences in the individual operating conditions of cells in a stack and their implications for adjacent and non-adjacent cells were investigated in 2- and 3-cell stacks. The stacks were therefore modified by implementing a second, independent reactant and coolant supply, separating the cells in two groups, each cell-group having an independent media supply. This allowed the selective introduction of anomalies in the operating conditions of a single cell in the stack. Two anomalies, as encountered in “real” stacks, were investigated: i) air starvation at single cell level and ii) thermal anomaly, as encountered at peripheral cells in a stack. The results showed that anomalies inducing significant variations in local current density, such as air starvation, influence the performance of cells located also in non-immediate adjacent positions to the anomalous cell. Through locally resolved current density measurements the nature of the coupling phenomena was identified. The coupling has an electronic character and takes place via
the common bipolar plate. Consequently, anomalies which do not induce considerable changes in local current density are confined to the anomalous cell.
Zusammenfassung


Sich räumlich ändernde Betriebsbedingungen, die sich für die Brennstoffzelle aus dem Prinzip des Durchflussreaktors ergeben, stellen die zentralen Punkte dieser Dissertation dar. Dies führt zur Unterscheidung der Begriffe „lokale-“ und „integrale Zellleistung“, deren Verknüpfung der Leitfaden dieser Studie ist.


Zuerst werden die Auswirkungen von Gradienten im Sauerstoffpartialdruck untersucht, die aus der Verwendung von Luft als Oxidationsmittel entstehen. Besonderes Augenmerk liegt dabei auf dem Einfluss der Luftstöchiometrie auf die lokale Stromgeneration. Ist der stöchiometrische Faktor gering, wird ein starker Abfall des Sauerstoffanteils entlang des Kanals beobachtet. Daraus ergibt sich eine stark inhomogene Stromverteilung, die sich unter anderem auf die Verteilung der thermischen Last über die Zelle auswirkt und deren


peripheren Zellen in einem Stapel beobachtet wird. Die Resultate zeigen, dass Anomalien, die eine starke Inhomogenität in der lokalen Stromdichte induzieren (wie z.B. teilweise Blockierung der Reaktanden), auch den Betrieb von Zellen beeinflussen, die sich nicht in unmittelbarer Nachbarschaft der gestörten Zelle befinden. Durch die ortsaufgelösten Stromdichtemessungen konnte der Mechanismus des Kupplungsphänomens identifiziert werden, es handelt sich dabei um elektrische Ausgleichsströme über die Bipolarplatte, die die benachbarten Zellen verbindet. Das bedeutet andererseits, dass Anomalien, die keine bedeutenden Änderungen in der lokalen Stromdichte hervorrufen, auf die gestörte Zelle beschränkt bleiben.