Doctoral Thesis

Chemical and electrochemical reactions of the 2-dimensional materials boron nitride and reduced graphene oxide

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CHEMICAL AND ELECTROCHEMICAL REACTIONS
OF THE 2-DIMENSIONAL MATERIALS BORON
NITRIDE AND REDUCED GRAPHENE OXIDE

A thesis submitted to attain the degree of
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(Dr. sc. ETH Zurich)

presented by
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Abstract

In the first part of this work the reactivity of hexagonal boron nitride (h-BN) towards a few selected compounds is tested. It has been found that preliminary tests carried out with Fe$_2$O$_3$, TiO$_2$ and Prussian blue nanoparticles show slight differences in mutual assembly of h-BN platelets and the tested nanoparticles. Reaction between BN and molten 1,12-diaminododecane revealed a kind of exfoliation and delamination of the layered phase resulting in a rubber-like Product. In another tested reaction between boron nitride and LiNH$_2$, the formation of an alkali-metal dinitridoborate with the composition Li$_3$BN$_2$ was observed. The same experiments carried out with NaNH$_2$ yields the corresponding sodium dinitridoborate. This shows the relatively stable boron nitride can be employed as a precursor for formation of nitride compounds by reaction with alkali metal nitrides.

A series of experiments with tetramethoxysilane was carried out over the period of days to a week showing that under such conditions a selective functionalization of the rims of h-BN platelets appears forming rings of SiO$_2$. The mechanism of this process has been explained through theoretical calculations carried out by Dr. Riccarda Caputo and demonstrates, supporting the experimental data, that for a successful functionalization two prerequisites are necessary: 1) the presence of water for the hydrolyzation of boron nitride platelets at the edges in order to introduce functional groups and 2) the heterogeneous nucleation of silica nanoparticles at selected positions on the h-BN platelets.

The second part of this work is focused on the reactivity of differently oxidized graphene, i.e. graphite oxide (GO) or partially reduced graphite oxide (GOpr). It has been demonstrated that GOpr-based electrodes in supercapacitors, once they are anodically activated in mixtures of selected organic carbonates with EMIM BF$_4$, behave in a similar way to known acetonitrile/EMIM BF$_4$ systems. This is manifested in a permanent increase of the capacitance of the material and the formation of intercalation products, which lead to different layer separations compared to the starting material GOpr. To a certain extent this characteristic behavior has been observed dependent on the kind of carbonate. For
dimethyl- and propylene carbonate a change of the layer distances was directly observed while for vinlylene carbonate no characteristic Bragg reflections appears meaning that no gross ordering takes place. In all cases electrocatalytic reactions proceed between GOpr and the electrolyte involving fluorine groups. In the case of vinlylene carbonate the observed irreversible current is about three times as large as for the other electrolytes indicating to a multistep electroactivation eventually leading to a polymeric structure. While the cathodically induced intercalation phenomena appear to be stable during further redox cycles the post mortem washing of the electrodes with acetonitrile yields new specific layer distances of the GOpr base material intermediate to both, the initial values and the ones in activated state.

GOpr, furthermore, showed to be a good stabilizer of Sb-based anodic materials for Li-ion batteries. In fact it has been found that it can improve the cycling stability of the anode and provide capacities which are comparable, and in some cases superior, to the same anodic materials in absence of GOpr.

For both GO and GOpr, a similar tendency like for h-BN demonstrated namely a functionalization by silica mainly at the rims. The fact that less functionalized platelets, if compared with BN, have been observed, may be traced back to differences in specific functionalizations of the two layered materials. The functionalization of Cu-doped GOpr platelets proceeds through a concerted reaction in which SiO$_2$ is selectively deposited and coated by copper oxide through a migration process of the latter. This is due to the presence of some Cu impurities of unknown origin in starting GO and GOpr.
Riassunto

Nella prima parte di questo lavoro è stata investigata la reattività del nitruro di boro esagonale (h-BN) nei confronti di diversi composti selezionati. E’ stato visto che i test preliminari condotti con nanoparticelle di Fe₂O₃, TiO₂ e Blu di Prussia mostrano leggere differenze nell’interazione mutuale tra esse e le piastrine di h-BN.

La reazione fra h-BN e l’1,12-diamminododecano fuso ha rivelato una sorta di esfoliazione e delaminazione della fase a strati che ha poi portato ad un prodotto simile alla gomma. In un’altra reazione condotta tra nitruro di boro e LiNH₂ è stata osservata la formazione di un dinitruroborato alcalino di composizione Li₃BN₂. Gli stessi esperimenti condotti con NaNH₂ portano alla formazione del corrispondente dinitruroborato di sodio. Questo dimostra che il relativamente stabile nitruro di boro può essere usato come precursore per la formazione di nitruri tramite la reazione con nitruri alcalini.

Una serie di esperimenti con tetrametossisilano è stata condotta in un lasso di tempo che varia dai giorni alle settimane e ha mostrato che in queste condizioni si manifesta una funzionalizzazione selettiva dei bordi delle piastrine di h-BN, formando anelli di SiO₂. Il meccanismo di questo processo è stato spiegato attraverso calcoli teorici condotti dalla Dott.ssa Riccarda Caputo e dimostra, supportando i dati sperimentali, che per una funzionalizzazione di successo sono necessari due prerequisiti: 1) la presenza d’acqua per l’idrolisi delle piastrine di nitruro di boro ai bordi, al fine di introdurre i gruppi funzionali e 2) la nucleazione eterogenea delle nanoparticelle di silice in posizioni definite sulle piastrine di h-BN.

La seconda parte di questo lavoro si è focalizzata sulla reattività del grafene con diversi gradi di ossidazione, come ossido di grafite (GO) o ossido di grafite parzialmente ridotto (GOpr). E’ stato dimostrato che nei supercondensatori gli elettrodi a base di GOpr, una volta attivati in soluzioni di ben definiti carbonati organici in EMIM BF₄, si comportano in modo simile ai già noti sistemi a base di acetonitrile/EMIM BF₄. Ciò si è manifestato in un aumento permanente della capacità del materiale e la formazione di prodotti di intercalazione che hanno portato a
ben diverse separazioni fra gli strati, se paragonate al GOpr di partenza. Questo in parte è stato visto essere dipendente dal tipo di carbonato utilizzato. Per il dimetilcarbonato e il propilencarbonato il cambio nelle distanze fra gli strati è stato osservato in modo diretto, mentre per il vinilencarbonato non compare nessuna riflessione di Bragg caratteristica, il che significa che non ha luogo nessun riordinamento generale. In tutti i casi hanno luogo delle reazioni elettro-catalitiche fra GOpr e l'elettrolita che coinvolgono i gruppi contenenti fluoro. Nel caso del vinilencarbonato la carica irreversibile osservata è circa tre volte quella degli altri elettroliti, il che indica un'elettro-attivazione a passaggi multipli che alla fine porta ad una struttura polimerica. Mentre i fenomeni di intercalazione catodicamente indotti sembrano essere stabili durante ulteriori cicli redox, il lavaggio post-mortem degli elettrodi con acetonitrile porta a nuove distanze specifiche fra gli strati di GOpr, di dimensioni intermedie fra quelle iniziali e quelle allo stato attivato.

GOpr, inoltre, si è dimostrato essere un buon stabilizzatore di materiali anodici a base di Sb per le batterie agli ioni-Li. Infatti, è stato visto che può migliorare la stabilità ciclica dell’anodo e fornire capacità paragonabili, e in alcuni casi addirittura superiori, agli stessi materiali anodici in assenza di GOpr.

Sia per il GO sia per il GOpr è stata dimostrata una tendenza simile a quella osservata per il h-BN, a formare una funzionalizzazione, da parte della silice, principalmente sui bordi. Il fatto che, in confronto al h-BN, siano state osservate meno piastrine funzionalizzate, può essere riconducibile a differenze nelle specifiche funzionalizzazioni dei due materiali a strati.

La funzionalizzazione delle piastrine di GOpr drogata con Cu procede tramite una reazione concertata in cui SiO$_2$ viene depositato selettivamente e ricoperto da ossido di rame tramite un processo di migrazione di quest’ultimo. Ciò è dovuto alla presenza di alcune impurezze di Cu di origine sconosciuta nei GO e GOpr di partenza.
Abbreviations

XRD X-Ray Diffraction
HOMO Highest Occupied Molecular Orbital
LUMO Lowest Unoccupied Molecular Orbital
LIB Li-ion Batteries
NIB Na-ion Batteries
EDLC Electrical Double Layer Capacitor
GO Graphite Oxide
GOpr Partially Reduced Graphite Oxide
WE Working Electrode
RE Reference Electrode
CE Counter Electrode
EC Ethylene Carbonate
DMC Dimethyl carbonate
EPDM Ethylene-Propylene-Diene-Monomer
EMIM BF₄ 1-Ethyl-3-Methylimidazolium Tetrafluoroborate
PEEK Polyether Ether Ketone
SEM Scanning Electron Microscopy
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>EDXS</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid Electrolyte Interface</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethylcellulose</td>
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<tr>
<td>FEC</td>
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1. Introduction – Two dimensional materials

The knowledge on two dimensional materials dates back quite far in human culture. Layered field spars - clays, slate and mica have always been around in nature and probably been used already in stone age. The same is true for graphitic materials which had early uses, surely as a paint. Mica denotes a class of layered oxides, phyllosilicates, all of which contain hydroxy and/or fluoride groups which induce the layering. In the 19th century micas came into application by a number of reasons and it still is as dielectric. “Their sheets are chemically inert, dielectric, elastic, flexible, hydrophilic, insulating, lightweight, platy, reflective, refractive, resilient, and range in opacity from transparent to opaque. Mica is stable when exposed to electricity, light, moisture, and extreme temperature” [1]. The largest documented single crystal of mica (phlogopite) was found in Lacey Mine, Ontario, Canada; it measured 10 × 4.3 × 4.3 m and weighed about 330 tonnes [2]. Similar to carbon for which graphene and nanotube modifications are known, so-called serpentine silicates which derive from scrolled up layers, were mentioned already by Plinius the older with the recommendation that it should help against snake bites [3]. Probably the oldest proven uses date back to 4500 BC and belong to asbestos pottery in Finland [4, 5]. The real snake in there was realized only in the 20th century after vast applications of asbestos which was proven to induce lung cancer over long periods. Asbestos is still being mined by 2 million tons per year [6]. The use of clays belongs to the oldest achievement of mankind, not long after usage of stones and of fire. They are the basis for ceramics manufacturing and oldest traces of that were found in Japan and date back to 14000 BC [7]. Today, pillared clays have widespread applications mostly in different kinds of catalysis especially due to their large surface area of 200-500 m²/g and their chemical inertness [8]. More recently, layered sulfides of transition metals have come into use, especially MoS₂ which is being applied as a dry lubricant beating graphite’s properties. However, a real boom with respect to research and applications did only start right after the discovery of carbon nanotubes and is still going on. The corresponding mineral molybdenide is found together with other sulfide ores [9]. Today, its
semiconducting properties and its great thermal stability and resistance against sulfur make it a valuable catalyst [10]. In 2014 its ability in water splitting which was published 30 years ago was rediscovered [11].

Graphite occurs naturally and was used already in the 4th millennium B.C. in southeastern Europe as a ceramic paint for decorating pottery [12]. Unnoticeably, over the millennia people will have produced individual sheets which are called by now graphene. The modern usage of graphite is legion and spans many scientific and industrial areas [13]. After two decades of nanofiber and nanotube focus there is renewed interest in two dimensional (2D) nanostructures and so-called 2D crystals [14-17] triggered by the fascinating properties of graphene [18].

1.1 Graphene

Graphene which dates back to th 1960th was moulded by H.-P- Boehm [19] is a single layer from graphite built as a planar six ring net (chicken wire). The IUPAC definition says: "previously, descriptions such as graphite layers, carbon layers, or carbon sheets have been used for the term graphene... it is incorrect to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure. The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed."[20]. Systematically such layers have only been fabricated and isolated in the 21st century by Novoselov and Geim who received the Nobel Prize in Physics for their groundbreaking work [21].

The flat graphene sheet contains regular C₆ rings with a C-C bond length of 1.42 Å [22].
1. Introduction – Two dimensional materials

![Graphene Structure]

*Figure 1: shows one of the limit resonance structures of graphene.*

Carbon atoms in graphene are $sp^2$ hybridized, which means that they have three $\sigma$-bonds oriented along the plane forming three 120° angles (Fig. 1). The fourth valence electron occupies the orthogonal $p_z$-orbital perpendicular to the plane and forming a $\pi$-bond, that is responsible for the high electrical conductivity of graphene [23].

Theoretically graphene may be considered the precursor of other carbon modifications such as graphite, single and multi wall carbon nanotubes. The first is a tridimensional stacking of graphene sheets while the second one can be seen as a graphene sheets rolled up to form cylinders seamed in such ways that all six-rings remain intact. Fullerenes, are also a relative recent allotropic form of carbon which has 12 of its $C_6$ rings substituted by $C_5$ rings (Fig.2).
It has been found that the surface area of graphene is equal to 2630 m$^2$/g for a single sheet [24] which is larger than that of carbon black (with a value less than 900 m$^2$/g [25]) and of carbon nanotubes (usually between 100 and 1000 m$^2$/g [24]) and comparable only to that determined for activated carbon [26]. Furthermore it presents outstanding physical properties such as huge mechanical strength about 200 times larger than steel [27], high thermal and electronic conductivity the latter of which is of ballistic nature like in metallic carbon nanotubes and optical transparency for visible light [28].

Graphene can be functionalized but only through highly oxidizing media which mainly attack the $\pi$ system [29]. However, its preparation is not easily scalable and industrial applications may remain for a while in the range of the available graphite patch sizes [30]. Graphene will be an outstanding candidate for many future applications in microelectronics, electro-optics and in new energy storage devices (batteries, supercapacitors, etc.) [31, 32]. The application as hydrogen storage system has to be judged with scepticism, yet [15, 33] but absorption
and transport of other gases have become of interest, too. This is directly linked to explorations on thin film gas-sensing devices. Supercapacitor applications are at hand, straight away, and blue prints for novel micro-electronics are becoming legion - not only for graphene but also for other 2D materials and their possible combinations [15]. Especially, combinations of chemical and physical effects through graphene seem to open a fascinating field of future research [34]. A broader account on reactions which modified graphene, the so-called reduced graphene oxide, is being presented in chapter 5.1.

1.2 Graphite

As mentioned above graphite is made of graphene single layer stacks forming a 3-D layered structure that may follow many the stacking rules, but with the lowest energy in (AB)_n form. That means that half of the carbon atom of each layer are centering the C_6 rings of the sheets immediately above and below. This stacking is the one of the most frequent modification, the hexagonal one (also known as α-graphite) which is sketched in Figure 3.

Figure 3: AB stacking of α-graphite after [35].
1. Introduction – Two dimensional materials

Sheets are held together by van der Waals forces with a binding energy of only 0.07 eV while the one for C-C bonds inside the sheet is equal to 4.3 eV. This more than 60 times weaker interaction between the layers explain the layer distance of 3.35 Å and the facility to exfoliate graphite to prepare stable suspensions or its excellent lubricant properties [36]. The delocalized π-electrons form a two-dimensional metallic system providing its ballistic electrical conductivity along the plane. The conductivity along the stacking direction is by about four order of magnitude smaller. Its excellent thermal conductivity makes it a good candidate in for different uses like cooling devices, brake linings, foundry facings. Combining chemical and electric properties make it a valuable electrode material in many different applications. Its capability to get intercalated was exploited more than 100 years ago but in the last 30 years it became especially known by use for anodes in Li-ion batteries. It was long denied that any modified or pure graphite could become superconducting. Only recently a few of its intercalation compounds exhibit superconducting behaviour, like CaC$_6$ for example (Fig. 4), with a superconducting transition temperature of $T_c = 11.5$ K at standard pressure [37].

![Figure 4: CaC$_6$ rombohedral structure seen from two different views after [38].](image)

It has been noted that AB$_n$ stacking is not the only one found in modifications of graphite, there is a rhombohedral modification (β-graphite) with an (ABC)$_n$ stacking as shown in Figure 5.
1. Introduction – Two dimensional materials

1.3 Graphene- and graphite oxide

Graphene oxide and graphite oxide can be considered as the oxidation product of graphene and graphite, respectively, being different only with respect to the precursors but hardly concerning the reaction products. If conditions are not too harsh which results in complete transformation into CO and CO₂, then they result in the layered graphene oxide (GO) as shown in Figure 6. In graphene oxide or layers of graphite oxide of the σ-bonding systems of the C₆ rings are practically intact and about only 25% of all carbons remain in planar π-bonded situation. 75% of all carbon centers are functionalized and reveal sp³ configuration. The most frequent functional groups are hydroxy- and epoxy- groups. Around these sp³ centers the layers corrugate while the other 25% remain flat. On the rims, may they be due to crystal or holes there also carboxylate groups are being found [40] but these are in smaller frequency than other functional groups.

Figure 5: ABC stacking of 6-graphite after [39].

Figure 6: Model of a GO sheet after [41].
GO appears as a brownish solid which is semiconducting different from graphite, because of the destruction of the $\pi$-bands due to the presence of O-containing functional groups. Its large thermal lability shows that the driving force back to graphene is very strong. GO can be reduced already at 100 °C in vacuum [41]. Its properties can be tuned by changing the amount of functional groups and this can be done by applying a controlled thermal reduction process on GO precursor material, which leads to a black powder which is called partially reduced graphite oxide (GOpr) or reduced graphite oxide (RGO), which denote similar products with different amounts of functional groups dependent on the chosen reduction process parameters. Thanks to the large number of O-containing groups, GO is quite easily dispersed and forms stable suspensions, not only in water [42, 43], that can be used to produce graphitic membranes or films for many different practical applications [44, 45]. More investigation on applications of GO are coming up not only to delaminate graphite and fabricate individual graphene sheets through chemical preparation, i.e. of graphene nanoribbons field-effect transistors [46] or of antennas able to modulate the mid-infrared light [47], but also by utilizing the functional groups in specific ways for catalysis, photocatalytic systems [48, 49] and for membrane formation [50], just to mention a few.

1.4 Hexagonal boron nitride

Boron nitride can be considered as the isostructural and isoelectronic analogue to graphite consisting of alternating B and N atoms in analogy to the old Grimm-Sommerfeld rule for semiconductors. The polar B-N interactions are responsible for the AA’ stacking as shown in Figure 7. Due to its unique physical and chemical properties, described in more detail in chapter 2.1, it makes a good candidate for many potential applications such as electrical insulators, lubricants, optoelectronics, membrane technologies etc.
It has been found that h-BN can constitute a valuable support for graphene sheets alternative to traditional SiO₂ supports and it is interesting to note that graphene exhibits enhanced carrier mobility if epitaxially fitted to boron nitride; one should also see that the 2D character is much better defined than for SiO₂ supports [51]. Syntheses and characterizations of various boron nitride nanostructures are reported by help of chemical vapor deposition or high temperature physical processes like arc melting and thermal annealing and their properties were studied [52]. These nanostructured materials, far different from the common hexagonal boron nitride, are legion, some of which appear as nanocage clusters, nanotubes, nanohorns and nanoparticles [52] with their many different functionalizations and inclusions of other nanostructures (Fig. 8-11).
1. Introduction – Two dimensional materials

**Figure 8:** Boron nitride nanocage $\text{B}_{36}\text{N}_{36}$ empty (a) and containing an Y atom (b) from $\text{YB}_6$ used as precursor with their relative HREM images (c and d) after [52].

**Figure 9:** (a) Low magnification micrography of boron nitride nanotube and (b) HREM image of a nanotube containing a $\text{B}_{36}\text{N}_{36}$ nanocluster after [52].
Figure 10: HREM showing hollow nanohorns (a-e) and a nanohorn containing an amorphous phase (f) marked with a green star. Structural modes for triple-wall nanohorns with different tip angles: 20° (g), 40° (h), 60° (i), 84° (j), 112° (k) after [52].
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![Figure 11: (a) SEM micrography showing BN nanoparticles with their typical fivefold axes. Thanks to this axis some nanoparticles appear star-shaped (b). In (c) atomic structure models of $B_{164}N_{156}$, $B_{328}N_{312}$ and $B_{656}N_{624}$ are presented after [52].](image)

It can be noticed that multilayered nanohorns and nanoparticles as shown in Figure 10 and 11 present a layered structure similar to the one of hexagonal boron nitride but bent or folded. Another example of layered deformed boron nitride nanostructure are the nanoribbons, that can be obtained by splitting BN nanotubes by intercalating them with K (Fig. 12) [53].
1. Introduction – Two dimensional materials

![Scheme representing the opening of BN nanotubes due the chemical pressure of intercalating K atoms after [53].](image)

Figure 12: Scheme representing the opening of BN nanotubes due the chemical pressure of intercalating K atoms after [53].

In this case, layers exhibit various bending and in some case there are still some small nanotubes left. These BN nanostructures, together with other like nanocorns, metallofullerens and nanocorns can find interesting practical applications such as optoelectronic and high-performances electronic devices, gas storage materials, semiconductros, nanomaterials and nanowires with particular magnetic properties and so on [54, 55].

Cubic boron nitride (c-BN), which was assumed to be the second hardest material after diamond [56], has been synthesised in form of nanoparticles with dimension of ≈3.5 nm [57] through a laser-induced photochemical reaction.

1.5 Other layered materials

Related layered compounds are diboride dicarbides with stoichiometries M’BC and MB₂C₂, respectively MB₂C₂ compounds with M = Ca, Y, Ln, Ce, Pr, Nd, Sm, ... are all isostructural (except M = Sc).

CaB₂C₂ and Mg B₂C₂ show semiconducting properties [58] and crystallize with a structures that resembles an intercalated hetero graphite. In this case the intercalating agents are the Ca²⁺ ions (Fig. 13).
1. Introduction – Two dimensional materials

**Figure 13:** Section of the structure of layered CaB$_2$C$_2$ along [100] (Ca, light gray; B, black; C, white) after [58].

For CaB$_2$C$_2$ the B-C bond lengths are 1.55 and 1.59 Å, respectively. This is considerably larger than the C-C distance in graphite with 1.42 Å pointing to a reduced bond strength due to a weaker heteropolar bond and an additional weakening by the effective negative charge on the anionic layers according to Ca$^{2+}$[B$_2$C$_2$]$^2^-$. Comparable B-C lengths have been observed in the four- and eight-membered rings of SmB$_2$C$_2$ (1.61 Å and 1.52 Å) [59].

MgB$_2$C$_2$ is another example of layered borocarbide with hetero graphite that shows enhanced ionic conductivity and quick conversion to LiBC by contact to a molten lithium salt, due to the fact that only 50% of the possible cation sites are occupied by Mg$^{2+}$[60]. Its orthorhombic crystal structure is shown in Figure 14. With B-C distances of 1.58 and 1.59 Å for LiBC (see below) there is hardly a matrix effect to be found, i.e. the cation size has only little influence on the B-C separations. This tells that the marked difference between unipolar C-C bonds and comparably bound B-C layers are quite marked. Higher charge then should lead to even more enlargement of the separation and this is proven by the B-B distance in MgB$_2$ (1.78 Å) which may be represented as Mg$^{2+}$[B$_2$]$^2^-$. 


Figure 14: Structure of MgB$_2$C$_2$ along a) [001] and b) [100] where the puckering of the layered structure is more evident. Mg$^{2+}$ = large white and shaded circles; B = black circles; C = small white circles after [60].

Rogl et al. investigated electronic properties of borocarbides and reported quite a number of them with rare metals. Among them, LaB$_2$C$_2$, LaB$_2$C$_4$, ScB$_2$C$_2$, ThB$_2$C and UB$_2$C, for example, belong to the same structural type that have a 2D-network with a net layered structure [61]. Figure 15 shows two the examples of LaB$_2$C and α-UB$_2$C and show different planar BC networks adapted to the different cation sizes. To be evidenced is the presence of structural elements similar to channels in correspondence of the cations and bond lengths comparable for both structures.
1. Introduction – Two dimensional materials

**Figure 15:** Crystal structure of a) LaB$_2$C$_2$ and b) $\alpha$-UB$_2$C; M atoms = large circles; B = medium circles; C = small circles after [60].

LiBC, is another layered heterographite example with a hexagonal structure similar to MgB$_2$C$_2$ but fully intercalated, i.e. every hexagonal prism is occupied by Li$^+$ (Figure 16). The AA stacking makes it a filled up pseudo-BN type. This because of the presence of B atoms that substitute C atoms and to the fact that towards oxidation it behaves like graphite [62]. The difference of band gaps between graphite/graphene on the one hand and BN/MBC arises from a symmetry breaking due to the BC alternation. The band difference between BN and anionic BC compounds is traced back to the charge on the polymeric anion and the lower electronegativity difference between boron and carbon compared to boron and nitrogen. Deintercalation of Li$^+$ ions is possible but irreversible [63]. A huge superconducting transition temperature of close to $T_c$=90K was calculated for the oxidized form Li$_{0.5}$BC [64] which however cannot be prepared experimentally due to severe distortions of the BC layers by loss of negative charge, i.e. oxidation of the valence band electrons [63]. If existent, it would have been a challenge for BCS theory, though.

**Figure 16:** Crystal structure of LiBC showing a clear layered structure with trigonal prismatic coordination of B,C by Li. B = black; C = white; Li = corners of the prism after [62].
1. Introduction – Two dimensional materials

It has been demonstrated that this compound is a semiconductor [65] and has an smaller ionic conductivity than the abovementioned isoelectronic MgB$_2$C$_2$ [60] but a recent theoretical studies carried out by Ma et al. show that this compound may show superconducting properties if conveniently doped, by substituting a C by B atoms [66].

A classical kind of BCS superconducting behavior was found for borographite MgB$_2$. With $T_c$ of 39 K it at the edge of BCS theory in terms of coupling strength indicating quite high phonon frequencies of the tightly bound BC layers [67].

We believe that much chemistry and physics is still hidden concerning very well defined quasi atomically thin 2D phases and their individual layers. This work is meant to shed some light selected modifications of GOpr, BN as well as their microscopic structures.
2. Rim-Functionalization of h-BN with SiO$_2$: Synthesis, Characterization and Theoretical Modelling

2.1 Introduction

Boron nitride belongs to the quite rare two dimensional atomic systems meaning that their third dimension is only of atomic size, i.e. in the range of a few Ångströms. This is different from composite 2D-systems like for example MoS$_2$ where interlayer separations start not before 1nm. Due to huge attention for graphene and its derivatives, there has been a renewed interest in the hexagonal boron nitride (h-BN) for its unique physical and chemical properties such as high melting point, thermal conductivity, thermal stability, chemical inertness and oxidation resistance, together with low density and small dielectric constant [68, 69]. The hexagonal boron nitride is isostructural to graphite and consists of two-dimensional planar six-ring nets, too. Different from graphite the BN layers are kept together by strong Coulombic interactions arising from the difference in electronegativity of B and N whereas interlayer interactions in graphite are only of weak Van der Waals type. This leads to an AA’ stacking mode for h-BN, with a considerable band gap of 5.6 eV. Different from graphite, modifications of BN are electronic insulators. The particular interlayer interaction in h-BN together with its large band gap makes intercalation or functionalization attempts of delaminated BN-layers much more difficult compared to graphite [70]. One recent interest in h-BN has been focused on searching for new chemical and physical routes towards its functionalization and on making it exploitable for different technological applications, like ion conducting membranes for example. Straightforward ways of activation of BN would be intercalation with appropriate molecules or ions, as it happens for instance during the oxidation process of graphite to graphite oxide [71], or exfoliation. However, both ways turned out to be difficult to achieve and only a few more or less successful reports exists, some of which claim intercalation of BN like the reductive intercalation with Li metal at high temperatures and the oxidative intercalation with S$_2$O$_2$F$_6$ thanks to the oxidizing SO$_3$F$^-$ radical
by Shen et al. [72, 73]. It remains though unclear to what extent irreversible decomposition reactions have taken place. Kovtyukhova et al showed that h-BN can be reversibly intercalated with Brønsted acids by exploiting the interaction between those and both basic N atoms and acidic B atoms of h-BN [74]. The method described by Coleman et al. to exfoliate graphite [75], can also be exploited to MoS$_2$ [76] and many other layered materials, h-BN among them, in order to prepare and characterize suspensions in selected solvents at different concentrations [77]. Lin and coworkers focused their attention on the functionalization of micrometer-sized h-BN and coated the surfaces with octadecylamine (ODA) and amine terminated poly-ethylene glycol (PEG) in order to increase the solubility of the so modified layered material in THF and water, respectively [78]. The same authors also reported enhanced functionalization with ODA aided by ball milling which induces defects in the h-BN crystallites [79]. Remarkable is the successful attempt to create new ceramic composites by hot pressing a mixture of the pristine h-BN powder with SiO$_2$ which may be an indication of good physicochemical compatibility between the two compounds [80]. In another investigation, the MOCVD process of a SiO$_2$ thin film on h-BN particles through alternating exposures with SiCl$_4$ and H$_2$O [81].

In this chapter, it was explored the possibility to create new functional materials by combining h-BN and SiO$_2$, similarly to the work reported by as Zhai et al. [80], but without the need of working at high temperatures or through gas phase deposition. The synthesis of SiO$_2$ nanoparticles via the Stöber process [82], which was carried out in-situ in a dispersion of solvent and h-BN. Parallel to the experiments the reactivity of the {100} plane to SiO$_2$, H$_2$O, CH$_3$OH and CH$_3$CH$_2$OH via Density Functional Theory (DFT) was studied, in order to get an insight into possible mechanisms for the functionalization reaction.
2. Experimental part and Computational Methodology

2.2.1 Synthesis

The hexagonal boron nitride (h-BN, 99%) and tetra methyl orthosilicate (TMOS, ≥99%) were purchased from Fluka and stored in air, ethanol (EtOH, ≥98.5%) from Scharlau and NH₃(aq) (25%) from Merck. All chemicals were used without any further purification.

700 mg of commercial h-BN were added to a solution of 3.2 ml H₂O and 10.3 ml NH₃(aq) in 16.3 ml EtOH. The so prepared mixture was afterwards ultra-sonicated for 15 minutes at 20 °C. For the in-situ synthesis of SiO₂ nanoparticles, 0.13 ml TMOS were added to the mixture at room temperature under vigorous stirring to prevent undesired aggregation of silica. The resultant mixture was kept under magnetic stirring for 12 hours and then allowed to age without stirring for 4 different times (3, 6, 9, 14 days) in order to explore the reactivity window. The products were then filtered on a glass frit (ROBU GLASFILTER porosity class = 4, pores dimension = 10-16 μm), washed 5 times with EtOH to remove all the unbound SiO₂ nanoparticles and dried at 100 °C for 48 hours.

To prove the importance of water in the functionalization process, 300 mg of commercially available h-BN were dried at 500 °C for 36 hours in air while 50 mg SiO₂ nanoparticles were dried at 250 °C under the same conditions. Both dried h-BN and SiO₂ particles were then put in a glass flask together with 30 ml EtOH dry under vigorous stirring for 12 hours. The mixture was aged without stirring for 21 days. The products were then filtered on a glass frit (ROBU GLASFILTER porosity class = 4, pores dimension = 10-16 μm), washed 5 times with EtOH to remove most isolated SiO₂ nanoparticles and dried at 100 °C for 48 hours. The whole procedure was carried out in glove box in order to keep the system as water-free as possible. The very first stirring process was carried out outside the glove box in the sealed flask under argon.
Another sample was prepared with exactly the same conditions as the previous one but it was ultrasonicated for 4 hours. In this case, both first stirring and ultrasonication processes were carried out in a sealed glass flask under Ar.

In order to prove the importance of the order of addition of chemicals, a suspension of SiO\textsubscript{2} nanoparticles was prepared by adding 0.13 ml TMOS in a solution of 3.2 ml H\textsubscript{2}O and 10.3 ml NH\textsubscript{3}(aq) in 16.3 ml EtOH. The suspension was stirred for 1 hour and afterwards 700 mg of commercially available h-BN was added. The system was ultrasonicated for 15 minutes, kept under stirring for 12 hours and then let age without stirring for 12 days.

2.2.2 Computational methodology

In cooperation with Dr. Riccarda Caputo a study based on the Density Functional Theory (DFT) was carried out in order to calculate the total energy of the optimized intermediate structures in order to evaluate possible molecular reaction mechanisms. In particular the CASTEP code was used, as implemented in Materials Studio 6.0 employing norm-conserving pseudopotentials in reciprocal space representation for all atoms. The Brillouin zone was sampled by using a fine mesh commensurate to the specific lattice dimensions, with the actual spacing below 0.025 Å. The energy threshold, the maximum atomic displacement, the maximum atomic force and the lattice stress were set to 0.001 meV/atom, 0.0005 Å, 0.001 eV/ Å and 0.002 GPa, respectively. Local Density (LDA) and the generalized gradient form (GGA) of the exchange-correlation functional and in particular the Perdew-Burke-Ernzerhof96 (PBE) one were used. The dispersion term, one of the important long range contributions to the total energy, non-covalent forces and in particular van der Waals interactions, was introduced by using damped atom pairwise dispersion corrections of the form C\textsubscript{6}R\textsuperscript{-6}, proposed by Grimme [83] as implemented in CASTEP. The molecular dynamics of the canonical ensemble (NVT) at T = 27°C of supercells of different sizes of the (0 1 0) edge was performed by using CASTEP. The h-BN bulk contains two formula units and the surface
was modelled cleaving the (0 1 0) plane of a 3x3x2 supercell, which accordingly contains 36 formula units, surrounded by a vacuum region of 15 Å width. A double of that supercell was employed in the molecular dynamics. The time step was set to 2 fs and the total simulation time to 10 ps.

2.3 Results and Discussion

2.3.1 Electron microscopy

The educt h-BN sample consists of thin plate-like crystals with a broad size distribution: the diameters of the plates ranged from some 100 nm up to ca. 10 µm (Fig. 17a). The crystals are formed by extended ab-planes that are stacked in direction of the crystallographic c-axis. The {hk0} planes are terraced and the edges of the h-BN crystals smoothly rounded. After the functionalization, the basic morphology of the educt h-BN crystals is preserved during the reaction as revealed by SEM investigation (Fig. 17). It is eye-catching that the edges of most crystals of the reaction product are modified: a bulging rim appears with bright contrast in the SEM images indicating the presence of a SiO$_2$ (Fig. 17 b-d) independent of the actual patch sizes of the h-BN plates (diameter ca. 200 nm, Fig. 17 c). Although there are few bead-like SiO$_2$ nanoparticles around, they appear only scarcely on the planes but more frequently at the rims with a tendency to fuse into continuous protruding rings (Fig. 17 d). It is a remarkably slow reaction, as the functionalization process requires at least an aging time of 6 days before the bulges at the rims become clearly observable by SEM.
Figure 17: SEM images of h-BN crystals a) pristine BN  b-d) after the reaction with TMOS (reaction time = 12 days)

The structure and composition of the SiO$_2$ rims was further probed by HAADF-STEM and EDXS analysis. HAADF-STEM images show an intensity distribution that strongly increases with the scattering potential leading to atomic number (Z) contrast ($I \sim Z^3$). Therefore in our samples, the presence of SiO$_2$ is indicated by a bright contrast against the BN cores ($Z_{Si} = 14 > Z_{N} = 7; Z_{B} = 5$; cf. Fig. 18) in agreement with the SEM images (Fig. 17 b-d). The thicknesses of the SiO$_2$ rims are in the range of 20-50 nm. Consequently, EDX spectra of selected areas indicate that SiO$_2$ indeed is present at the bright sites in the HAADF-STEM images whereas the gray areas in the center of the plates are SiO$_2$-free and consist of pure BN (Fig. 18). These findings confirm that the functionalization of h-BN with SiO$_2$ preferentially happens at the
crystal edges. Yet, some SiO$_2$ beads can be found both on the h-BN surface, in form of isolated nanoparticles (area 2 in Fig. 18), while some are incorporated into the rims of the ceramic crystallite (cf. Fig. 17b-c) indicating to preferred nucleation conditions at some spots.

Figure 18: HAADF-STEM image of the functionalized h-BN. EDXS analyses focusing on 3 different areas confirm the presence of a SiO$_2$ rim and of SiO$_2$ beads on some planes.

Further investigations were carried out in order to try to understand the very first steps of such a functionalization. In principle one can focus on the role that H$_2$O plays in the whole process, not only in the SiO$_2$ formation. The role of water during the ring-formation was probed by further experiments carried out under water-free conditions. In the absence of water there is no evident formation of SiO$_2$ rings at the edges of the crystallites (cf. Fig. 19b). In both cases, randomly distributed SiO$_2$ nanoparticles were formed only. From these results
it seems quite likely that the presence of H$_2$O is fundamental for the consecutive condensation of SiO$_2$ to the edges of h-BN, due to a hydrolysis process (Fig. 19a). Furthermore, the slow Stöber-type reaction is also a crucial factor for the functionalization mechanism, because no SiO$_2$-rings are observed if the sample was prepared by adding h-BN after the formation of SiO$_2$ nano particles albeit in the presence of H$_2$O (Fig. 19c).

**Figure 19:** SEM images of h-BN crystals a) after the interaction with TMOS (reaction time = 21 days), b) after the interaction with TMOS under dry conditions (reaction time = 21 days) and c) after the interaction with the previously prepared SiO$_2$ nano bead suspension (reaction time = 12 days).
2.3.2 XRD analysis

The XRD patterns of the products after four different reaction times reveal the same patterns corresponding to pure h-BN as the starting material, suggesting that neither intercalations nor bulk structural modifications of the layered BN took place during the functionalization process with TMOS. The resulting SiO$_2$ is obviously amorphous/glassy (Figure 20).

![X-ray powder diffractograms of h-BN compared to those of h-BN-SiO$_2$ composites at four different reaction times.](image)

*Figure 20: X-ray powder diffractograms of h-BN compared to those of h-BN-SiO$_2$ composites at four different reaction times.*
2.3.3 AFM analysis

The morphological features of the composite has been further investigated through atomic force microscopy (AFM) in taping mode. The image demonstrates that the growth of SiO$_2$ on the rims is rather homogenous and height profile reveals a crater-like cross-section with a higher thickness at the crystal edges (Fig. 21). The height of the functionalizing material at two different points selected on the rims of the same crystallite are quite similar to each other and reaching the value of 16 nm for point A and 13 nm for point B above the level of the central h-BN plate. Between point A and point B, the platelet surface of the BN is apparently not functionalized and differs from the one at the edges for its rather constant flatness.
2. Rim-Functionalization of h-BN with SiO2: Synthesis, Characterization and Theoretical Modelling

![Diagram of tapping mode AFM image of h-BN particles and corresponding height profile measurement.](image)

**Figure 21.** Tapping mode AFM image of h-BN particles (top) and the corresponding height profile measurement along the marked line (bottom).

### 2.3.4 Computational Results

As the experimental part clearly reveals the importance of water in the functionalization process first the reactivity of h-BN to water was studied computationally at DFT level of theory. The hexagonal structure of the bulk was first optimized at GGA and LDA level with and without accounting in the dispersion contributions in order to evaluate the lattice parameters and the bonding description dependences on the exchange-correlation functionals. The results are reported in Table 1.
2. Rim-Functionalization of h-BN with SiO2: Synthesis, Characterization and Theoretical Modelling

Table 1: Lattice parameters of h-BN optimized by using the GGA and LDA approximations with different functionals of the exchange-correlation. In both cases the \(c\)-parameter is underestimated compared to the experimentally reported one, indicating that the dispersion contribution along the stacking direction of the BN layers is overestimated.

<table>
<thead>
<tr>
<th>Functional</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA-PBE-D</td>
<td>2.50(7)</td>
<td>6.18(1)</td>
<td>Gradient-corrected functional plus dispersion contribution (D)</td>
</tr>
<tr>
<td>GGA-PW91-D</td>
<td>2.50(1)</td>
<td>6.53(3)</td>
<td></td>
</tr>
<tr>
<td>LDA-CA-PZ</td>
<td>2.48(5)</td>
<td>6.51(1)</td>
<td>Local functional without/ with the dispersion contribution</td>
</tr>
<tr>
<td>LDA-CA-PZ-D</td>
<td>2.47(7)</td>
<td>6.02(6)</td>
<td></td>
</tr>
<tr>
<td>experimental</td>
<td>2.50(4)</td>
<td>6.65(9)</td>
<td>[84]</td>
</tr>
</tbody>
</table>

The dispersion correction contribution is essential in order to reproduce the lattice parameters closest to the experimental ones, in particular the \(c\) parameter and hence the right description of the interlayer interactions. The GGA with PW91 functional plus the dispersion contribution provided the best approximation of the experimental lattice parameters, and accordingly that was chosen for the following surface calculations. The \((0\ 0\ 1)\) surface of h-BN is well known for its poor reactivity, unless supported on metal surfaces or
2. Rim-Functionalization of h-BN with SiO2: Synthesis, Characterization and Theoretical Modelling

depicted in graphite [85, 86]. As the SEM images suggested the active surface is indeed at the edge of
the platelets formed by stacking layers of the (0 0 1) planes. the (0 1 0) edge was modelled
by cutting the h-BN bulk and forming the surface (0 1 0). The impurity-free surface reaches
minimum energy by bending and forming new B-N interlayers bonds, as shown in Figure 22.
The length of the inner B-N bonds on the layers remained almost unchanged: 1.44(4) Å in
the bulk and 1.45(0) Å in the optimized (0 1 0) edge. The new B-N bonds formed at the edge
are 1.46(3) Å and are commensurate to the interlayer distance, this is why the inner atomic
distances are not affected by the bending of the uppermost atoms on the border and
consequently the XRD pattern did not catch any difference compared to pristine h-BN. As
expected, the reactivity of the B and N atoms on the edges is enhanced in comparison to
that of atoms on the (0 0 1) surface. In fact, even when the layers of the edge has linked two
by two, the electron acceptor feature of the boron atoms in particular is enhanced with
respect to bulk atoms. However, neither the geometry optimization nor the molecular
dynamics at room temperature showed any indication to cleave the new B-N bonds by
reaction with H_2O molecules close to the edge. Though the water molecules were polarized
and temporarily interacted with the acceptor side of boron atoms, the inter-layer B-N bonds
once formed remain kinetically stable. Therefore, in the absence of any possible reactive
species i.e. in vacuo, the calculations suggest that the layers of the edge are closed two by
two by the new B-N bonds. Quite different are the results when exposing h-BN rim atoms
with dangling bonds to water molecules. The water molecules split by forming B-OH and N-
H bonds, as shown in Figure 22. An excess of water molecules will saturate all the available
and active B atoms on the edge, while a deficiency of water molecules will make possible a
mixture of interlayer B-N bonding and functional group formation. Our calculations do
explain what Lin and coworkers did already prove experimentally [87]: when h-BN is ultra-
sonicated in water it tends to break and become reduced in lateral size and forms terminal
hydroxyl groups at boron atoms on the edges. In parallel, N-H bonds appear through
electrophilic attack of H\(^+\) at terminal nitrogen atoms. This functionalization increases the
ability of h-BN to be dispersed in H_2O because of improved hydrophilicity of the platelets.
thanks to the new B-OH and N-H bonds. In order to get an insight into the mechanism of the Stöber reaction on the edges, namely the condensation of the SiO₂, the reaction h-BN with Si(OH)₄ molecules in the presence and absence of water molecules was studied. In particular, the role of the water molecules for the rim functionalization was investigated. Border atoms that have not yet saturated by formation of new B-N interlayers bonds (see Fig. 22) are functionalized in the presence of water molecules, and thereafter serve as centers for the reaction with Si(OH)₄ molecules via proton exchange. The oxygen atoms of water are polarized towards the boron atoms, and eventually bind. The first step of the mechanism is accordingly driven by the B-O interaction followed by the proton exchange with water molecules and the formation of N-H bonds. The oxygen atoms, from which protons move, interact with the nearest OH groups initiating the SiO₂ condensation sustained by the B-O interaction on the rims. The consequent growth of silica on the edge was then promoted by proton exchange between near OH groups and by the lone pairs of nitrogen atom on the edge. The snapshot in Figure 22 shows the trajectory at 300K, in the lateral and top views, of the h-BN edge with the incipient SiO₂ condensation mediated by the H-OH bond cleavage of the water molecules and the interaction of boron atoms with the OH groups of Si(OH)₄ molecules.
Figure 22: (a) A 3D-view of the h-BN bulk with the AA’ stacking along the c-direction. (b) Cutting through the plane (0 1 0) the edge of the surface (0 1 0) is created, which border atoms bend to form new B-N interlayer bonds. (c) A view of the (0 1 0) edge optimized in defect of H$_2$O molecules, which split in H-OH forming new N-H and B-OH bonds. The interlayer B-N bonds are 1.466 Å, the B-O bonds are 1.378 Å and the N-H bonds are 1.018 Å. (d) A lateral view and (e) a top view of a trajectory at 27°C of the (0 1 0) edge. In (d) the black circles indicate the H-transfer from the OH group to N atom and the split of H$_2$O with the formation of B-O and N-H bonds and the H-bridge. Representing colours: B, pink; N, blue; O, red; H, green; Si, yellow.
2.4 Conclusions and outlook

Despite the electronic and structural similarities between h-BN and graphite, BN is much more difficult to intercalate or functionalize most probably due to stronger interactions along the stacking direction of layers (i.e. the c-axis). Exploiting the h-BN capability to get hydrolyzed on the edges and the Stöber process for the synthesis of SiO₂ nanoparticles it has been demonstrated that it is possible to functionalize and stabilize chemically the edges of the micron-sized h-BN crystallites directly by SiO₂ local precipitation. The process proceeds without any intercalation reaction, as no shifts of the (0 0 2) reflections in the XRD pattern of the h-BN-SiO₂ composite were observed compared to the bulk and untreated h-BN. SEM and STEM micrographs of the composites showed the morphology of the functionalized edge and their behavior in the presence of SiO₂ nanoparticles. The STEM/EDXS analysis confirmed the modification of the edges. AFM tapping mode characterization provided quantitative information about the height profile of a functionalized h-BN platelet, suggesting a rather homogeneous growth of SiO₂ on the edges. Combining the experimental evidences and the computational results a possible mechanism of the edge functionalization with silica, as SEM images suggested, can be proposed. Under the conditions used in the present work, TMOS quantitatively hydrolyzes and forms [SiO₂](OH)ₓ nano precipitates at B-O bonds at the water-functionalized edges perpendicular to the [001] zone. The subsequent SiO₂ growth is then driven by the Stöber type reaction, mediated by the water molecules present in the reaction. In fact, both the failure of synthesis experiments in completely dried conditions and the molecular dynamics suggest the primary role of water molecules as B-O bond forming and H-bonding agents in the condensation process of the silica precursor. Finally, the failed functionalization in the presence of water but with already existent SiO₂ nanoparticles suggests the importance of the in-situ reaction of water and TMOS with the h-BN crystallites. Future work will be focused on the optimization of the described functionalization of h-BN with modified SiO₂ that could allow the interaction of h-BN patches for the preparation of complexes functional structures, such as membranes or porous materials.
3. General explorative reactions with h-BN.

3.1 Introduction

This chapter deals with general aspects of reactions with h-BN as substrate and has some explorative character. Besides learning more about boron nitride’s chemical reactivity there was the idea to first delaminate and then link BN sheets together again to an ion-conducting membrane of high strength. It may be stated already here that this was not achieved but the closest approach to this goal was probably reached in chapter 2 through combinations of BN and SiO$_2$. The very first part of these chemical explorations on h-BN was carried out with selected nanoparticles of great interest in modern technological fields. Hematite is a mineral which is known since ancient times and whose nanoparticles as well as its bulk form are still arising interest in the most recent energy storage research fields like photocatalysis and photovoltaics [88], Li-ion batteries [89-93] as well as sodium ion batteries [94, 95]. It has also recently found out their possible applications, together with Pt or by doping with carbon in photoelectrochemical water splitting processes [96, 97].

The main goal of our experiments was the delamination of boron nitride and a consecutive functionalization of its single layers.

In a similar way experiments with Fe$_4$[Fe(CN)$_6$]$_3$ nanomaterial (Prussian blue) which were also strongly motivated by the results obtained through the reaction of boron nitride and SiO$_2$ (see chapter 2 of this dissertation). The goal was to functionalize or decorate in the same way the h-BN crystallites or, still better, to exfoliate and functionalize the single layers. The combination of Prussian blue with h-BN may become a hot topic in the energy-storage field since its nanoparticles have already found many applications in Li/Na-ion batteries [98-101], not only as a pigment [102]. Electrodeposited prussian blue on graphene nanosheets in the presence of Pt and can also work as a high-efficiency catalyst for methanol oxidation processes [103], which increases interest in trying to create composites between this pigment and 2D-materials like h-BN.
3. General explorative reactions with h-BN.

It is also known that several organic compounds like octadecylamine (ODA) and \(O,O'-\text{bis}(3\text{-amino propyl})\text{polyethylene glycol (PEG)}\) \([104-109]\) or peptide nucleic acid (PNA) \([110]\) may functionalize carbon nanotubes and furthermore PEG can be considered one of the first organic compounds used to functionalize BN nanotubes thanks to the interaction between its basic amino groups and acidic boron atoms of boron nitride \([111]\). An experiment with h-BN and a long aliphatic-chain diamine such 1,12-diaminododecane was carried out in order to see if this diamine may not only have a kind of interaction with h-BN surface but also if it is able to get attached to BN single layers and cause an intercalation thanks to both terminal amino groups that may give a 2-points functionalization.

3.2 Experimental part

3.2.1 h-BN + α-Fe\(_2\)O\(_3\)

300 mg h-BN (99%, Fluka) have been ultrasonicated in 20 mL benzyl alcohol (≥99%, Acros) for 15 minutes in a glass tube. Afterwards 200 mg Fe(acac)\(_3\) (97%, Aldrich) was added to the system and let dissolve in the alcohol, which gave an intense red color to the solution. The system was afterwards stirred for 30 minutes and then the glass inlet was put in a Teflon inlet which was then closed in a metal autoclave. The autoclave was heated in a hoven at 150 °C for 48 hours and then let react without stirring at room temperature for 12 days. After that time the reddish product has been washed with EtOH (≥98.5, Scharlau) and kept at 100 °C for 3 days.

3.2.2 Prussian blue – Fe\(_4[\text{Fe(CN)}_6]_3\)

400 mg \(K_4\text{Fe(CN)}_6\) trihydrate (≥99.5%, Fluka) were dissolved in 100 mL distilled \(H_2O\) and to this 180 mg anhydrous \(\text{FeCl}_3\) (98%, ABCR) was added until a deep blue stable suspension was obtained.
3. General explorative reactions with h-BN.

3.2.3 h-BN + Fe₄[Fe(CN)₆]₃

700 mg h-BN were put in ≈ 16 mL EtOH together with 3.2 mL of the suspension of Prussian blue and stirred for 12 hours. The system was let react for 11 days until the Fe₄[Fe(CN)₆]₃ nanoparticles precipitated together with h-BN platelets and let on the top a colourless liquid phase which has been removed through centrifugation. The remaining blue powder-like solid was afterwards dried under vacuum at room temperature for 48 hours.

3.2.4 h-BN + 1,12 diaminododecane

50 mg h-BN was reacted together with 500 mg 1,12-diaminododecane (≥97%, Fluka) in a closed round flask under N₂ atmosphere for four days in a oil bath at a temperature of 140 °C under magnetic stirring and then is let cool down at room temperature. In the present case after a first sublimation of the diamine the rest of it started to melt assuming a yellow-orange coloration at the end of the heating process. After cooling down the product seems a kind of rubber flexible polymeric membrane.

3.3 Results and discussion

SEM pictures in show the presence of few-nm sized hematite nanoparticles attached randomly on the surface of h-BN platelets without showing any preference nor tendency to assemble on any specific part of the crystallites (Fig. 23a and 23b) but with the tendency to form aggregates

![Figure 23: SEM micrographies of h-BN after the interaction with Fe₂O₃ nanoparticles.](image-url)
3. General explorative reactions with h-BN.

From the pictures it appears that the crystallites are not subjected to exfoliation nor intercalation as it is after all demonstrated by the powder pattern (Fig. 24). That gives, in fact, evidences of the presence of both h-BN and Fe$_2$O$_3$ phases without any further common products but the fact that the platelets are somehow decorated with the nanoparticles shows that there is a certain affinity between the two phases. This view may be supported by the results from chapters 2 and 5.4 and the micrographs therein. However, it is not clear of which character the attractive forces between specific nanoparticle faces and active sites on BN may be.

![Figure 24: Powder patterns of the product showing a heterogeneous mixture of h-BN stacks and Fe$_2$O$_3$.](image)

Figure 24: Powder patterns of the product showing a heterogeneous mixture of h-BN stacks and Fe$_2$O$_3$. 

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3. General explorative reactions with h-BN.

This interaction seems to be quite different, i.e. practically not existent in the case of the system with h-BN and prussian blue since, as it is shown in Figure 25, nanoparticles are scarcely arranged on any surface portion of h-BN crystallites and seem to be all deposited on the sample holder.

![Figure 25: SEM micrographies of h-BN platelets and Fe₄[Fe(CN)₆]₃ nanoparticles showing no peculiar interaction tendency.](image)

XRD powder pattern shown in Figure 26, furthermore, shows only the presence of crystalline h-BN without any evidence of reflections of prussian blue. The presence of the latter is undeniable because the sample characterized presented a clear light-blue coloration and SEM micrographies clearly shows the presence of few-nm sized spheres-shaped particles together with boron nitride crystallites. Consequently, under these experimental conditions only the formation of amorphous prussian blue nanoparticles appears and no crystal ordering yet. It may be interesting to verify if the same phenomenon can be observed also in the case of a in-situ nanoparticles heterogeneous nucleation together with h-BN. The theoretical pattern shows, overall at high 2 theta values, intensities that don’t fully correspond to those experimentally observed because of technical problems due to the
3. General explorative reactions with h-BN.

exported reference pattern from both Match and XPOW software. During the simple visualization of both patterns, in fact, the intensities of reflections are coincident.

**Figure 26:** Powder pattern of h-BN after the interaction with Prussian blue nanoparticles showing the only presence of h-BN reflections. The unidentified reflection is marked with a star.
3. General explorative reactions with h-BN.

The explorative reaction of h-BN with the 1-12 diamine carried out under the above mentioned conditions in order to get exfoliation and functionalization of h-BN for the sake of the preparation of a membrane brought about an orange rubber-like material easily scratchable from the walls of the reaction flask (Fig. 27).

![Product obtained after letting h-BN react with 1-12 diaminododecane](image)

**Figure 27:** Product obtained after letting h-BN react with 1-12 diaminododecane

The orange colour may be explained by a partial oxidation of the long chain amine, due to some oxygen presence inside the flask. Through the thermal treatment, it seems that the crystallites of h-BN are embedded in a matrix of 1-12 diaminododecane reaction products as shown in SEM micrograph in Figure 28. The figure shows also a portion of the sample where a layer of solidified amine teared off from boron nitride and may show some tendency of to a partial exfoliation of the layered material together with a deformation of the crystallite which gets bent.
3. General explorative reactions with h-BN.

![Figure 28: SEM micrograph of a portion of the obtained product after the interaction between h-BN and 1,12-diaminedodecane which shows a partial exfoliation of boron nitride.](image)

Furthermore, thin layers are visible stuck to the solidified material in the micrograph that can be attributed to exfoliated few-layered sheets of h-BN. This effect may be seen similar to the scotch tape method [112]. As there is a strong inter-layer interaction in bulk BN this may indicate a pretty strong interaction of the molten phase with the surface of boron nitride, too. Elastical properties of the resolidified amine may explain the mechanical stress that could have caused the bending of the layers constituent the crystallite boron nitride.

### 3.4 Conclusions and outlook

In this chapter, some preliminar explorative experiments with h-BN were carried out. Reactions with hematite showed some selectivity towards BN platelets or special sites of them. Prussian Blue exhibited a net inferior tendency to interact with BN.
3. General explorative reactions with h-BN.

Experiments with organic species such as 1,12-diaminododecane exhibited covering of h-BN and embedding into the organic matrix after the cooling process with partial exfoliation of the layered structure. Tuning the length of the organic chain of the amine may not only cover the crystallite but also favour the exfoliation process as well as the functionalization of single sheets.
4. Dinitridoborates

4.1 Introduction

Since the 1960\textsuperscript{th}, the family of dinitridoborates has been, first by Goubeau et al. \cite{113} and then largely investigated by other solid state chemists mainly for pure academic interest. They contain the linear BN\textsubscript{2}\textsuperscript{3−} unit which is isoelectronic to the neutral CO\textsubscript{2} parent molecule and related the anionic species NO\textsubscript{2}\textsuperscript{+}, N\textsubscript{2}O, CNO\textsuperscript{−}, N\textsubscript{3}\textsuperscript{−}, CN\textsubscript{2}\textsuperscript{2−}, CBN\textsuperscript{4−}, CCC\textsuperscript{4−}, and CBC\textsuperscript{5−} \cite{114-127}, all of which are doubly bonded 16 electron systems with different counter cations. There are also borate anions BX\textsubscript{2}\textsuperscript{3−} with X = P, As \cite{127} and with heavier central atoms where the existence of double bonds though are questionable like in TlTlTl\textsuperscript{7−} \cite{128}, SiAgSi\textsuperscript{7−} \cite{129}, SiCuSi\textsuperscript{7−} \cite{130}. Like for other semipolar species there is a principle ambiguity whether to use extreme charge separation or a semipolar notation like for those for which double bonding is clearly present:

\[
\left[ \begin{array}{c} \text{N} & \equiv & \text{B} & \equiv & \text{N} \\ \end{array} \right]^{2−} \leftrightarrow \left[ \begin{array}{c} \text{N} & \equiv & \text{B} & \equiv & \text{N} \\ \end{array} \right]^{2−} \leftrightarrow \left[ \begin{array}{c} \text{N} & \equiv & \text{B} & \equiv & \text{N} \\ \end{array} \right]^{2−}
\]

\textit{Scheme 1: Limiting resonance structures of the BN}\textsubscript{2}\textsuperscript{3−} unit.

The MO diagram of carbon dioxide is given in Figure 29. It is clear that electronegativity differences of the constituent atoms must lead to relative shifts of levels in energy.
Figure 29: MO diagram of carbon dioxide according to [131].

The heavier homologues may be represented in different ways due to their less pronounced tendency for double bonding like, for example, [Si]$^4^-$ - [Ag]$^+$ - [Si]$^4^+$ or [Si – Ag – Si]$^7^-$, while [Si=Ag=Si]$^7^-$ has to be ruled out due to the full shell 4d$^{10}$ configuration and no indication of 5p contributions to bonding according to quantum mechanical investigations [129]. The projection of band structure states on atomic coefficients indicates to an occupation of 16 electrons for the three atomic unit according to [Si - Ag - Si]$^7^-$. 
According to Evers, B-N bond distances are $d_{\text{B-N}} \approx 1.34$ Å for the two known Li$_3$BN$_2$ and Na$_3$BN$_2$ in accordance with the resonance structures of Scheme 1.
4. Dinitridoborates

Solid boron nitride BN and the [BN₂]³⁻ anion are two limiting species between the infinite ensemble and the smallest molecular representative. The latter can be thought of as molecular precursor for a polymerization via different oligomeric intermediates finally into BN. Such species would be very interesting nanoscopic objects and could have potential for accessing new forms of extended BN structures. However, there is no report on related preparations, hitherto.

Several synthetic ways have been described for the preparation of boron nitrides. Earlier studies already did show that alkali and alkaline earth dinitridoborates can be utilized as catalyst-solvents for the preparation of cubic boron nitride (c-BN), starting from hexagonal BN by employing high pressure reactions [132]. Kulinich et al. gave an overview of different possibilities of catalysts for the synthesis of c-BN and described three novel nitridoborates with formulas Ca₆BN₅, Mg₆BN₅ and Li₃Mg₃B₂N₅ [133]. The synthetic routes adopted by this group for Ca₆BN₅ is based on the reaction between Ca₃N₂ and h-BN mixed in a molar ratio Ca₃N₂:h-BN = 2:1 and heated between 950 °C and 980 °C for at least 3 h [134]. Older work by Goubeau and Anselment reports that mixing the same educts and the same reaction conditions in a different molar ratio (Ca₃N₂ : h-BN = 1:1) does yield a different product mixture containing Ca₃(BN)₂ plus either Ca₃N₂ or Ca₆BN₅ [113].

Semenenko’s group showed that treating twice the mixture Mg₃N₂:h-BN = 2:1 at a pressure of 2.0 GPa and a temperature of 1600 °C lead to the formation of a magnesium boronitride with formula Mg₆BN₅, stable up to 900 °C [135]. It was furthermore demonstrated that lower pressures than 2.0 GPa gave a different boronitride which is low pressure modification of Mg₃BN₃ while under higher pressures a mixture of Mg₆BN₅ and Mg₃BN₃ in its high pressure form can be obtained [135]. As far as the above mentioned novel Li₃Mg₃B₂N₅ is concerned Kulinich et al. carried out their synthesis by heating a mixture of Li₃N, Mg₃N₂ and h-BN in the molar ratio Li₃N: Mg₃N₂: h-BN = 1:1:2 at a temperature between 950 °C – 1000 °C for 4 hours [132].
On the other hand, Somer et al. showed that heating a stoichiometrical mixture of Li$_3$N, Mg$_3$N$_2$ and h-BN at about 1300 °C allows to synthetize a different Li-Mg dinitridoborate with of the composition LiMg[BN$_2$] [136].

Another method for the preparation of lithium dinitridoborates, is based on thermal dehydrogenation of quaternary hydride Li$_3$BN$_2$H$_8$ synthetized through reaction between LiBH$_4$ and LiNH$_2$. More precisely it has been shown that by ball milling LiBH$_4$ with two equivalents of LiNH$_2$, or by heating this mixture at 95 °C yields Li$_3$BN$_2$H$_8$ which loses hydrogen at 250 °C and results in Li$_3$BN$_2$ in different phases [137, 138]. Furthermore, it has been demonstrated that dehydrogenation of products like Li$_3$BN$_2$H$_8$ [139] and Li$_2$BNH$_6$ [140] from ball-milling of LiBH$_4$/LiNH$_2$ mixtures takes place at considerably lower temperatures in the presence of CoCl$_2$ as catalyst.

Using a mild thermal dehydrogenation process Somer et al. [141] reproduced the already known synthetic route for the synthesis of Na$_3$BN$_2$ from a mixture of NaNH$_2$:NaBH$_4$ in molar ratio 2:1 by heating it at = 600 °C and of Na$_2$KBN$_2$ by employing NaBH$_4$ and KBH$_4$ and heating at = 410 °C.

There is one example of direct synthesis of nitridoborates from h-BN and a metal amide, which is Ba$_3$B$_2$N$_4$ that can be prepared by heating a mixture of barium amide and h-BN (1:1) at least 700 °C for 3 hours [113].

In this work it is demonstrated that it is possible to synthesize a series of dinitridoborates of alkaline metals very easily from boron nitride.

4.2 Experimental part

Synthesis of Li$_3$BN$_2$ und Na$_3$BN$_2$

For the preparation of Li$_3$BN$_2$ two basic synthesis were carried out with 2 different experimental conditions listed below.
4. Dinitridoborates

Procedure (A). 3.790 g (0.165 mol) of LiNH₂ (Aldrich, 95%) and 0.145 g of h-BN (99%) \((5.84\cdot10^{-3} \text{ mol})\) were weighted and ground together in a fine mixture. Thereafter, the powder was transferred into an Mo crucible which was inserted in a quartz tube filled with dry argon. This procedure, included the sealing of the external tube was entirely carried out in a glovebox filled with Ar \((O_2 < 0.1 \text{ ppm}, H_2O < 0.1 \text{ ppm})\). The system was heated at 410 °C under constant \(N_2\) flux for 48 hours and a heating rate of 200 °C/h. The system was afterwards brought to room temperature.

Procedure (B). A mixture of 1.04 g (0.045 mol) of LiNH₂ and 0.145 g of h-BN \((5.8\cdot10^{-3} \text{ mol})\) was prepared in the same way as in (1). The powder was then put in a Nb crucible and put under inert atmosphere as described above. The sample was heated under constant \(N_2\) flux with the following gradient and then cooled down at room temperature:

1. Reaction temperature \((T_1) = 400 °C\); heating rate = 200 °C/h; reaction time =48 hours.
2. Reaction temperature \((T_2) = 480 °C\); heating rate = 50 °C/h; reaction time =24 hours.
3. Reaction temperature \((T_3) = 570 °C\); heating rate = 50 °C/h; reaction time =24 hours.
4. Reaction temperature \((T_4) = 480 °C\); heating rate = 50 °C/h; reaction time =24 hours.

In both cases, grey crystalline products in form of powder were collected in the glove box and kept under argon.

In a similar way, the synthesis of \(Na_3BN_2\) was carried out. As starting material a finely ground mixture of 2.2g (0.056 mol) of NaNH₂ (Aldrich, 95%) and 0.175 g (0.007 mol) of h-BN was prepared in a glovebox under Ar atmosphere \((O_2 < 0.1 \text{ ppm}, H_2O < 0.1 \text{ ppm})\) and transferred into a Nb crucible which was placed inside a quartz tube under the conditions explained above for the preparations of \(Li_3BN_2\). The mixture was heated under continuous \(N_2\) flux at a temperature of 400 °C for six days with a heating rate of 200 °C/h.
The obtained grey crystalline powder was collected and kept under Ar, as well. An attempt to purify the so obtained Na$_3$BN$_2$ with an extra heating step was carried out in order to remove eventual traces of unreacted NaNH$_2$, as explained below.

### 4.3 Results and discussion

The product of procedure (A) was characterized by XRD. The pattern show the presence of the trilithium dinitridoborate together with some unreacted LiNH$_2$, Li$_2$O (whose theoretical pattern is not shown) and another unidentified phase whose very weak reflection can be seen in Fig. 31.

The product obtained procedure (B) shows reflections of Li$_3$BN$_2$ as well but more intense than procedure (A) (Fig. 31).

It can be seen that the second pattern presents much more intense reflections of Li$_3$BN$_2$ while those of LiNH$_2$ are weaker. This means that in the second experiment LiNH$_2$ and h-BN reacts with higher yields of dinitridoborate. A probable reason in the higher yield in Procedure (B) may be due not properly on the use of a different ratio LiNH$_2$/BN but to the adoption of a more complex heating gradient which take into account probable formation of lithium imide through thermal decomposition of lithium amide as it is shown in Equation (1).

\[
2 \text{LiNH}_2 \rightarrow \text{Li}_2\text{NH} + \text{NH}_3 \quad (1)
\]

Step 1 of the gradient is designed to let h-BN interact with molten LiNH$_2$ since the white crystalline amide melts at 373 °C [142] while increasing the temperature in steps number 2, 3 and 4 would mean a probable formation of lithium imide. It has been in fact demonstrated by Opp et al. that lithium imide can obtained by heating under vacuum LiNH$_2$ at 360 °C for three-four hours and at 450 °C for two hours [143].
Figure 31: Powder diffractograms of the product of procedure (A) and (B) compared to theoretical powder patterns of $\text{Li}_3\text{BN}_2$ and of $\text{LiNH}_2$. Reflections belonging to $\text{Li}_2\text{O}$ are marked with orange stars, while unidentified reflections are marked with black stars.
Similarly, Pinkerton in his work claimed that formation of Li$_2$NH is possible by heating LiNH$_2$ under Ar at about 300 °C and showed a shift of the decomposition point along a large temperature range in dependence of different experimental conditions, such as ball-milling degree of the starting material and heating rates [144]. The presence of Li$_2$NH may have played an important role in the formation of Li$_3$BN$_2$ overall at the temperature reached in step 3 (570 °C).

As far as the preparation of Na$_3$BN$_2$ is concerned, the diffractogram of the system shows an almost quantitative preparation of the wished compound (Fig 32). Other reflections can be seen which testifies the presence, as in the case of Li$_3$BN$_2$ preparation, of unreacted starting material like NaNH$_2$. Other weak reflections are evidence of the presence of unidentified borates. These compounds may be explained by presence of O$_2$, probably because the system was not enough tight, like in the case with Li$_3$BN$_2$.

In this case the heating process may have initiated the decomposition of NaNH$_2$ to its elemental constituents, as it is shown in Equation (2).

$$2\text{NaNH}_2 \rightarrow 2\text{Na} + \text{N}_2 + 2\text{H}_2$$  \hspace{1cm} (2)

This phenomenon was observed by Titherley et al. who carried out the decomposition of NaNH$_2$ under vacuum but as far as they report they did not observe any significant gas evolution arising from the amide before reaching the range 500-600 °C [145]. The decomposition could have favoured the formation of Li$_3$BN$_2$ in combination with the relatively long reaction times. Na seemed to be furthermore absent in the product, probably due to its sublimation aided by the N$_2$ stream. The two diffractograms, before and after the final heating treatment at 530 °C for six days, result in almost the same product, indicating the inefficiency of this approach to yield a pure dinitridoborate (Fig. 32 and 33).
Figure 32: Experimental powder diffractogram of Na$_3$BN$_2$ before the heating treatment, compared with the theoretical one.
Figure 33: Experimental powder diffractogram of Na$_3$BN$_2$ after the heating treatment, compared with the theoretical one.
4. Dinitridoborates

As the XRD investigations reveal proof of concept but incomplete reactions, the products are phase mixtures. IR- and Raman investigations which are a proper tool for tracing the linear [BN$_2$]$^3^-$ anion were employed.

The Na$_3$BN$_2$ containing product shows signals fully comparable to those analyzed before by Somer et al. [141].

Fig. 34 shows clearly the presence of the symmetric stretching $\nu_1$, visible only in the Raman spectrum as a single signal at 1012 cm$^{-1}$, in full accordance with results obtained by Koz where $\nu_1 = 1015$ cm$^{-1}$. On the other hand, the IR spectrum exhibits the presence of two different modes, the asymmetric stretching $\nu_2$ and the bending mode $\nu_3$, both splitted due to the $^{10}$B / $^{11}$B natural isotopic distribution. While for $\nu_3$ the values are in excellent accordance with those found by Somer et al., including the further splitting of both $^{10}$B and $^{11}$B signals due to the site symmetry reduction (C$_1$), for $\nu_2$ there is a slight discordance but the ratio ($\nu_2^{10}$B) / ($\nu_2^{11}$B) satisfies the relationship $\nu_2^{(10)}B / \nu_2^{(11)}B = \sqrt{(11/10)} \approx 1.049$. 


Figure 34: Vibrational spectra of Na₃BN₂ present in the product (IR on the upper part, Raman on the bottom one). Inset: zoomed area of the portion of graph between 600 and 850 cm⁻¹.

A further synthesis was carried out in order to prepare a dinitridoborate of composition MₓM'ᵧ[BN₂] with x+y=3 and M₁ = Li, M₂ = Na. To carry out this reaction a mixture of 1.1 g of NaNH₂ (0.028 mol) and 0.645 g LiNH₂ (0.028 mol) were put and ground together with 0.175 g h-BN (0.007 mol) in order to have an homogeneous mixture. That was afterwards put in a Nb crucible and closed in a quartz tube with protective quartz inlet under Ar in the same way it has been done for the previous synthesis. Then the sample was heated at 400 °C for 6 days with a ramping temperature of 200 °C under constant stream of dry N₂. The product was
4. Dinitridoborates

afterwards collected and kept under inert atmosphere as previously done for other synthesis.

The XRD characterization (Fig. 35) shows that no compounds with lithium nitridoborate was formed but some Li₂O. The only dinitridoborate present in the product is that of sodium. The additional evidence that no Na₂O was observed, seems to testify the competitiveness of Na⁺ in the formation of dinitridoborates in the presence of Li⁺ and the corresponding higher tendency of the latter ion to form oxides in the competing presence of O₂.
Figure 35: Experimental powder diffractogram of the Na$_3$BN$_2$-containing product from the heating treatment of the mixture LiNH$_2$:NaNH$_2$:h-BN. Below the theoretical patterns of both Na$_3$BN$_2$ and Li$_2$O.
4. Dinitridoborates

4.4 Conclusions and outlook

In this chapter a new successful approach for the preparation of alkali metal dinitridoborates has been investigated. The approach is characterized by the direct interaction of boron nitride in its hexagonal form with molten alkali metal amides. This synthetic route has the advantage to work at standard pressures and at temperatures comparable with those of other methods, in many cases much lower but it presents the disadvantage of longer reaction times. While it has been seen that this strategy works pretty well with the preparation of Li$_3$BN$_2$ and Na$_3$BN$_2$, it is at the same time ineffective for the synthesis of dinitridoborates containing both Li$^+$ and Na$^+$. 

Future works on these systems could be focused on the optimization of the general experimental conditions. Furthermore, longer Nb crucibles may be used in order to allow reacting mixtures to remain inside without attacking the surrounding quartz vessels. Slower temperature ramps could be also taken into account, not only to avoid the sudden gas development but also to obtain higher quality crystals.

Once optimized, the method could be of a certain interest to exploit it for the systematic preparation and investigation of dinitridoborates containing 1 or more metallic ions, chosen among the whole series of alkaline and earth alkaline metals.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

5.1 Introduction

The following investigations on the capacitive behaviour of partially reduced graphite oxide (GOpr) go along with voltage-induced reactions of electrolyte molecules with functional groups of GOpr. As the detailed steps of such reactions have not yet been unravelled, a number of possible reaction schemes which are likely to happen have been assembled in the appendix as a means of comparison for the disposed reader [146-158].

Carbon based materials have been widely studied for their promising technological applications and excellent physical properties. Many investigations, to be more precise, focused their attention on two important relatively new modifications of carbon, named carbon nanotubes (CNT) and graphene (G). Recently, they found great interest in many research fields, applied and academical, because both of them carry a number of extraordinary properties like, for example, high mechanical strength and electronic conductivity [159, 160]. The huge amount of studies related to graphite and its intercalation processes is legion and testifies the importance of this modification in terms of mechanical and physical properties, besides its specific electronic conductivity, which is larger than that of copper [161].
Graphite oxide (GO) is a non-stoichiometric material obtained by treating graphite with drastic oxidizers according to the method of Brodie [163, 164]. It derives from the layered structure of graphene and also can stack like graphite but at a larger spacing between sheets (5.74 Å, as reported by Hantel et al. [165]) compared to the 3.3 Å of graphite [166]. The layers are partially puckered due to loss of the π-interactions by presence of epoxy-, hydroxyl- and carboxyl-groups on both sides of the sheets, such that 75% of its framework carbon atoms are sp³ hybridized. Dependent on how integration is being done GO may be assigned to a higher surface area than to graphene. So, GO may become a very important material for a number of future applications, including hydrogen storage devices, fuel cell or desalination membranes, solid electrolytes, sensing or photo-catalytical devices just to mention a few [156, 167-170].

In Figure 37 some structural models of GO are represented.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

**Figure 37:** Structural representations of GO reported by a) Hofmann, b) Ruess, c) Scholz-Boehm, d) Nakajima-Matsuo taken from [171] and adapted by Ruoff et al. [156].

Due to the enormous stability of graphene, the yellow-greenish GO can quite easily be reduced to a black material which has lost most of the hydroxyl groups but still carries a considerable amount of epoxy groups and thus may have layer separations around 4.4 Å, i.e. significantly smaller than those for the different GOs and clearly larger than for graphite [146]. GOpr is insofar an extremely interesting material because it contains a reasonable number of functional groups, which are docking sites for reactants and still has large excellently well electronically conducting patches. It is anticipated that this evolves from a self ordering of the epoxy groups into strands and islands on the layers (Figure 38).

**Figure 38:** TEM micrographs of a) graphene, b) GO and c) GOpr adapted from [172].

*Graphitic regions are colored in green, holes in blue and regions with oxygen functionalities in red.*
Recent research projects did also focus on the study of GO and GOpr for the development of new generation electrochemical double layer capacitors (EDLC) starting from the works on graphene by Rao et al. [173].

It has been shown that using GO combined with with tetraethylammonium tetrafluoroborate (TEABF₄) and acetonitrile (AN), an ELDC can be constructed with a capacity of 220 F/g [146, 174]. This result is obtained through an electrochemical activation of the above-mentioned layered material by applying voltage sweeps up to 1.8V. A GOpr electrode undergoes, as a consequence of this activation, an irreversible increase in the interlayer spacing to up to 12 Å. Further investigations with partially reduced graphite oxide (GOpr) showed an increase of capacitance of up to 200 F/g if it interacts with a solution of AN in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF₄) as electrolyte. These recent successfully developments show that GOpr can be a good candidate for supercapacitors electrodes, providing up to 300 F/g if Li-based electrolytes are used [147].

The activation of GOpr in the first anodic half cycle is a surprising fact and hints at some concerted electrocatalysis by GOpr and the solvent chosen for the oxidation of the anion BF₄⁻. As the huge activation capacity is irreversible it must be consumed by quantitative oxidation of electrolyte species and thus cannot be just an initialization of a polymerization. As it furthermore shows up only in the first oxidative half cycle which leads to the large expansion of the interlayer distance of GOpr it is practically unavoidable that it involve functional groups of GOpr which after being reacted are not anymore available for similar reactions. From those experiments it was conjectured that BF₄⁻ as the only anionic entity in the system is very likely to be oxidized first from a certain threshold potential on. This potential is about 2V against H/H⁺ for the pure EMIM BF₄ electrolyte and lowers dependent on an admixed active species like for example acetonitrile (AN) which is a firm hint to electrocatalysis.

The electrocatalysis should also depend on the nature of the active sites at the catalyst and on the kind of substrate, i.e. solvent as well as anions to be discharged. Consequently, it was found that an activation occurring in the first oxidative half cycle only consumes an
irreversible current which matches the amount of remaining epoxy groups (after partial reduction) on GOpr if a one electron reaction per epoxy group is assumed \[146, 147\]. The most likely position for an oxidation on GOpr is on carbon atoms being in the direct neighborhood of an epoxy group as those carbons must be lacking $\pi$ bond possibilities. So even if electrons are formally assumed to be extracted from the conduction band of GOpr the positive charge will most probably be located at those carbon atoms and will induce nucleophilic reactions, there. Considering the lowering of activation potential by presence of AN \[147\], AN must play a role in the electrocatalysis of the irreversible activation reaction.

The present work aims at investigations of further ELDC systems in the presence of different electrolyte combination in order to shed more light on the roles of the admixed liquids by recording the terms of the changing irreversible currents, specific capacitances and electrochemical activation potentials. The results are being compared with those already obtained using EMIM BF$_4$/AN as electrolyte in order to examine activation processes different from that of the acetonitrile-based system.

The results have been assembled mainly through cyclic voltammetry (cyclovoltammogram) and post-mortem XRD analysis of the GOpr samples in order to prove not only an increase in the capacity of the electrode but also an irreversible intercalation of the same. This kind of intercalation is mediated, according to the mechanism proposed by M. Hantel et al., by covalent interactions between the electrolyte molecules and the layers of GOpr.

Goal of this work is the preparation of different electrolyte solutions to be investigated for anodical activation reactions in a supercapacitor setup. Solvents have been chosen from a set of carbonate compounds which typically are used in Li-ion batteries together EMIM BF$_4$ as ionic liquid. The reason for this was first to eventually contribute to the understanding of decomposition reactions into SEI formation in battery electrodes which contain graphite and GOpr and second to remain in a regime of organic reactions, i.e. carbonyl reactions which are relatively well known.
5.2 Experimental part

5.2.1 Preparation of graphite oxide (GO)

GO was synthesized by using a modified Brodie’s method [175]. 30.2 g of graphite (TIMREX SFG 6 Graphite, TIMCAL) and 20 g of sodium chlorate were ground together with a mortar. 0.5 ml fuming nitric acid (100% GR for analysis, Merck) was added to the mixture every ten minutes until 20 ml were added. Since the reaction is highly exothermal, the mixture was cooled down to -20 °C with a cryostat. The product of this process was a dark green slurry which was kept overnight at room temperature. Afterwards the product was slowly heated up to 60°C and kept overnight at 60°C. The product in the end was washed several times with deionized water until the pH-value was close to 7. The last two washing steps were carried out with Milli-Q high purity water to remove trace of salts between the GO layers. The obtained product was dried at 100°C overnight.

5.2.2 Preparation of partially reduced graphite oxide (GOpr)

The reaction consists on a thermal reduction of GO powder in a quartz crucible, using a tube furnace under argon atmosphere. The temperature gradient in this preparation is crucial and small variations in the final maximum temperature lead to different degrees of reduction indicated by different interlayer distances.

For the preparation of GOpr with an interlayer distance of 4.3 Å (GOpr43), the following temperature program was used:

1. 10 K/h up to 170 °C.
2. 5 K/h up to 190 °C.
3. 1 K/h up to 250 °C.
4. 20 K/h up to 1000 °C.
At the end of the treatment the furnace was switched off. The small heating rates between 170°C and 250°C are necessary to prevent any uncontrolled gas evolution in the graphitic structure with consequent deflagration risks of the product.

5.2.3 Preparation of the electrode

Free standing films for the preparation of working electrodes (WE) were prepared by mixing 80% wt. GOpr flakes with 10% wt. conductive additive (Super P, TIMCAL, Switzerland) and 10% wt. polytetrafluoroethylene (PTFE, Alfa Aesar, USA) in ethanolic suspension. PTFE suspension was added to the GOpr/Super P mixture and, after that, 500 mL ethanol were added under vigorous stirring. The mixture was then ultrasonicated at full power for 4 hours and the solvent was let evaporate completely at 50 °C, under stirring, in a large becher glass. Once dried the electrode material was kneaded and flattened many times with the help of small additions of EtOH until the film was achieved. WEs were afterwards obtained by cutting the sheet in pieces with thickness between 180 and 200 μm.

As far as the material for counter electrodes (CE) is concerned, in this work it was provided by PSI and it was prepared with 80 wt.% active carbon (YP17, Kuraray Chemical, Japan) and 20 wt.% PTFE without the use of any conductive additive. The sheet was used to prepare CEs by cutting circular pieces of 0.8 mm diameter and 1.25 mm thickness.

5.2.4 Preparation of the electrolytes

For the preparation of electrolytes, ionic liquids are used as solvents while the role of the solute is played by different additives whose capability to increase the capacitance of the working electrode is investigated in this work. Previous investigations showed that EMIM BF₄ (Fig. 39) is a good ionic liquid for the supercapacitor applications in question thanks to its
Reactivity of GO/GOpr - Supercapacitors with GOpr

stability in a wide potential window [176]. Electrolytes were prepared using a ratio EMIM BF$_4$ : additive = 0.01 : 0.004 (mol/mol)

![Figure 39: Structure of EMIM BF$_4$.](image)

The additives which have been chosen and dissolved in EMIM BF$_4$ are listed in Table 2.

**Table 2:** Structural formuli of the additives used for the electrolytes of supercaps experiments.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Structural Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>H$_3$C=≡N</td>
</tr>
<tr>
<td>Dimethyl carbonate</td>
<td>O</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>O</td>
</tr>
<tr>
<td>Vinylene carbonate</td>
<td>O</td>
</tr>
</tbody>
</table>
5.2.5 Electrochemical investigations

In order to investigate electrochemical behavior of systems with different additives and to trace the occurring reactions, cyclovoltammogram measurements were carried out which show how much current flows in the material as a function of the applied potential. The integral of the curve of the monitored intensities, over a defined potential window, gives informations related to the current consumptions of the electrodes at different oxidative or reductive potentials. This offers a tool for the evaluation of the detailed capacitance profiles of every system investigated and their comparison with the already well-studied systems such as those with pure EMIM BF$_4$ and EMIM BF$_4$/Acetonitrile. In these measurements the potential was changed linearly with a constant sweep rate of 0.3 mV/s.

To carry out cyclovoltammogram experiments a setup with 3 electrodes was used in order to keep separated reference electrode (RE) and CE. The internal part of the device is shown in Fig. 40.
Figure 40: Internal structure of the three-electrode cell with related details of the slot of electrodes, separator and electrolyte. The drawing is taken from [146] and adapted from [177]. PEEK = polyether ether ketone; RE = reference electrode; WE = working electrode; CE = counter electrode.

Additional technical data

Piston diameter: 13 mm

Material of the body: polyether-ether ketone

Separator between WE and CE: glass fiber

Separator between WE and RE: glass fiber

Pressure over the electrode sandwich: 50 Ncm$^{-2}$ [177]
5. Reactivity of GO/GOPr - Supercapacitors with GOPr

RE was placed in one of the lateral entrance of the PEEK cylinder and fixed with the titanium screw, while the electrolyte was injected through the other lateral entrance using a glass syringe and a PEEK injection tube. The whole cell was sealed using ethylene-propylene-diene-monomer (EPDM) O-rings. The whole preparation procedure was carried out in an Ar filled glovebox (≤ 0.1 ppm H2O and O2). After every usage, the cell was disassembled and washed with H2O and soap and then ultrasonicated for 30 minutes with acetone. A similar ultrasonication cleaning procedure was repeated in distilled H2O. The cell was afterwards dried overnight in a vacuum oven at 70-80 °C.

5.2.6 SEM

Scanning electron microscopy (SEM) analysis was performed on a Zeiss Gemini 1530 operated at 1 kV SEM pictures provide useful informations over the morphology of the material before and after the intercalation.

5.2.7 XRD analysis

X-ray powder diffraction (XRD) patterns of the samples were recorded with a STOE Stadi P diffractometer equipped with a germanium monochromator and CuKa1 radiation (operated at 35 mA, 35 kV). As in-situ experiments were not possible during this work, the XRD characterizations of the electrodes were carried out before and after the electrochemical activation for comparing possible shifts in the (0 0 1) reflections which are an important hint to intercalation.

5.3 Results and discussion

Cyclovoltammogram experiments were carried out varying the potential from 0 to 0.5 V for three cycles before and after the activation in order to compare them and quantify the
charge accumulated by the supercaps after the pillaring reactions. The electrochemical insertions were driven by varying the potentials from 0 V to 2V at a sweep rate of 0.3 mV/s.

Philipp Reibisch and Moritz Hantel had already shown that the system with EMIM BF$_4$ / AN increases the specific capacitance of the electrode and decreases in parallel the activation potential of the intercalation process. This is clearly seen in Fig. 41 where a maximum of the current flow is observed at about 4830 seconds corresponding to a potential of +1.45 V. This indicates a different process than the one of the pure EMIM BF$_4$ system where the activation takes place at a potential of 1.90 V. This means that AN catalyzes the activation process which is accompanied by some kind of pillaring process. This is not the only process whose rate is affected, since another process is starting at 1.60 V. This is proved by the increase of the increasing current flow at that potential which is probably due to the decomposition of EMIM BF$_4$ or to not yet investigated side-reactions. This process happens in case of pure of EMIM BF$_4$ as well but not before 2.05 V. Goal of this project is to explore whether other additives may influence the activation energy of the mentioned intercalation processes increasing the specific capacitance of the material like the system EMIM BF$_4$/AN did.

Most of the additives tested with EMIM BF$_4$ (such as, for example, methanol, acetone and chlorobutane) do not show real improvement in the specific capacitance if the electrochemical activation is carried out under the same conditions previously used for pure EMIM BF$_4$ and AN. This indicates to a more general function of the additive which though important for the activation remains unspecific during the reversible electrochemical processes.

On the contrary, the carbonates which have been tested in this work show a behavior compatible to the one observed with AN. For all the carbonates soluble in EMIM BF$_4$ and tested, a shift in the activation peak current can be observed, which is a clear evidence of the different activities of the carbonates. Furthermore, an increase of the specific capacitances of 5 orders of magnitude becomes evident thanks to the 3 cycles set, carried out after the activation reaction. The scansions showed the rectangular shape typical of the supercaps’ cyclovoltammograms curves, which appear much different from the previous 3
before the activation. Nevertheless Fig. 41 shows that none of the carbonates tested catalyzes the pillaring process as nice as acetonitrile does and every system manifests substantial differences from each other, as far as shapes of curves and positions of peaks are concerned.

Figure 41: Comparison of time dependent current flows cyclovoltammogram for pure EMIM BF$_4$, EMIM BF$_4$ and acetonitrile and EMIM BF$_4$ combined with different liquid carbonates.

In terms of potentials Fig. 42 shows that for the system with pure EMIM BF$_4$ there is a first activation potential peak with maximum current at 1.9 V while the decomposition of the solvent does not appear before the 2V.
The slight shift of the activation peaks in the blue and red curves may be due to the fact that two different potentiometers in two different labs (ETH, EMPA) were used, but they may also arise from small differences in terms of preparation. That gives an insight to the approximate reproducibility of these measurements meaning that differences in peak position and in slope of this amount may always be present. However, the reproducibility of the main characteristics of the CV curves seems to be sufficiently good for the interpretations drawn in this work.

**Figure 42**: Potential (Ewe) vs. current plots of the system for pure EMIM BF₄ electrolytes. Differences of activation potentials are clearly seen. The inset shows a zoomed portion of the plot in correspondence of the activation of 0.5 V.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

Going back to the systems with carbonates, the similarities, in terms of activation voltages, between the system with EMIM BF₄/ AN (Fig. 43) and the one with EMIM BF₄/ vinylene carbonate (Fig. 44) are eye catching. They seem to have the nearest specific current peak but the one of the electrolyte with carbonate has a much weaker current intensity. This state of low current is fully compensated afterwards, starting from about 5500 seconds (≈ 1.7 V), where the process gives rise to a very intense current peak. This may find explanation in the decomposition of EMIM BF₄, decomposition that takes place much earlier than that in the system without any additive where it seems not to happen before 2V (Fig. 42).

Figure 43: Cyclovoltammograms of the system EMIM BF₄/acetonitrile for different activation potentials. The inset shows a zoomed portion of the plot in correspondence of the activation of 0.5 V.
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Figure 44: Cyclovoltammograms of the system EMIM BF$_4$/vinylene carbonate for different activation potentials. The inset shows a zoomed portion of the plot in correspondence of the activation of 0.5 V.

A behavior similar to the one found in the system EMIM BF$_4$/vinylene carbonate is observed for the activations carried out with the solution of propylene carbonate (Fig. 45). It is evident here that the current flow during the anodic activations is larger than the one for the system with the unsaturated carbonate.
The profile of the activation curve is furthermore rather indented and irregular. This may be traced back to gas evolution and/or contact losses in the electrode which can change the contact between a large surface of WE and the titanium piston. This phenomenon seems to be smaller for the other systems examined. The activation process carried out with a solution EMIM BF₄/dimethyl carbonate as electrolyte seems to undergo a more complex behavior because instead of only one activation peaks it exhibits two: the first one has its maximum intensity at 1.54 V and the second one at 1.75 V. This double maximum hints at a
two-stage reaction with two different Gibbs free energies, clearly seen before the third large peak sets in, which is being related to the unsupported decomposition of the BF₄⁻ (Fig. 46). One clear difference compared to the other carbonates is that DMC is not cyclic. So one may suppose that fluoromethane might be split off during the concerted oxidation of the BF₄⁻. Furthermore, it could be that the two of the methyl groups undergo that reaction consecutively at slightly different potentials according to

\[
\text{CH}_3\text{O-CO-OCH}_3 + \text{BF}_4^- - 1 \text{e}^- \rightarrow \text{CH}_3\text{F} + [\text{CH}_3\text{O-CO-O}] \text{BF}_3 \quad (3)
\]

\[
[\text{CH}_3\text{O-CO-O}] \text{BF}_3 + \text{BF}_4^- - 1 \text{e}^- \rightarrow \text{CH}_3\text{F} + \text{F}_3\text{BO}=\text{C}=\text{O} \text{BF}_3 + \frac{1}{2} \text{O}_2 \quad (4)
\]

\[
\text{CH}_3\text{O-CO-OCH}_3 + 2\text{BF}_4^- - 2\text{e}^- \rightarrow \text{F}_3\text{BO}=\text{C}=\text{O} \text{BF}_3 + 2\text{CH}_3\text{F} + \frac{1}{2} \text{O}_2 \quad (5)
\]

As mentioned in the beginning, BF₄⁻ is the only charged entity in the system and it is a very likely assumption that it will be oxidized from a certain threshold potential on. There are different possibilities how the strong Lewis acid BF₃ may behave and were it would dock to, however it seems quite clear that it has to. Most probable positions are electron rich hard sites, i.e. oxygen groups on GOpr (epoxy) or of the admixed solvent. In this respect the formulations in eq. (3)-(5) may only be considered as intermediates out of a number of other aggregation possibilities. The aggregation reaction of BF₃ with amines is well known, also the one with ethers (commercial product BF₃ OEt₂), alcohols and carboxylic acids according to

\[
4 \text{BF}_3 + 3 \text{HOR} \rightarrow 3 \text{HBF}_4 + \text{B(OR)}_3 \quad (6)
\]

Furthermore, being a strong Lewis acid, BF₃ catalises Friedel-Crafts type reactions with carbocations as intermediates.
Figure 46: Cyclovoltammograms of the system EMIM BF₄ / dimethyl carbonate for different activation potentials. The inset shows a zoomed portion of the plot in correspondence of the activation of 0.5 V.

As shown in Fig. 47 (a) the first irreversible charge consumption appears at 1.54 V. It is evidence of a first electrochemical activation since the three subsequent small cycles show an increase of the capacitance of the electrode in comparison with that of the very first three cycles before the activation.

The amount of specific charge accumulated in the first cycle (≈17 C/g), however, is more than three times lower than the amount obtainable by the system after activation in a wider potential window. This is clearly visible by carrying out the activation cycle up to the potential of 1.86 V. After the activation, the three reversible sweeps assume a more defined
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

squared shape with larger area and consequently higher capacities than those after the activation at 1.54 V (Fig. 47 (b)). The capacities are no further increased by activating the system in the potential window 0 V - 2.00 V because the following reversible sweeps maintain essentially the same shape and integrated capacity of those of the system activated only up to 1.86 V (Fig. 47 (c)). The activation up to only 1.66 V however leaves the system at poor reproducibility, as the comparison of the areas of the peaks in Fig. 47 (a), Fig. 47 (b) and Fig. 47 (c).

**Figure 47:** Cyclovoltammograms of the activation cycle for the System EMIM BF$_4$/dimethyl carbonate at a)1.66 V, b)1.86V and c)2.00 V with the relative subsequent cycles between 0 - 0.5 V.
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It is eye catching that, after the electrochemical activation, all systems exhibit an increase of the specific current, which is directly connected to the total specific charge accumulated by the WE and to the specific capacitance. As expected, Fig. 48. shows that less current flows through the system with pure EMIM BF₄, while it increases for cycles with acetonitrile and carbonates admixtures. During the discharge process the system EMIM BF₄/dimethyl carbonate yields a relatively low specific current, compared to other tested systems with EMIM BF₄ admixtures.

That curve presents also a less squared shape which moves away from the standard behavior of electrochemical double layer capacitors. For more details, the total specific charges connected with the current values of every single system are listed in Table 4. These values show that Coulombic efficiency is always larger than 100%, which has no physical meaning. This behavior can be explained by artifacts caused by some side decomposition reactions of the solvent during the discharge process and differs as such from the results of the previous experiments carried out by Philipp Reibisch where the only overestimated value of Coulombic efficiency was obtained using pure EMIM TFSI as solvent. Such a difference of behavior is not yet well explained.
Figure 48: Specific currents of GOpr electrodes activated with different electrolytes as given in the inset.

Table 3 shows the activation potentials of the systems with the respective specific charges flowing during both oxidation and reduction for the different tested additives. Due to the sometimes insufficient reproducibility of these experiments more than one maximum in the activation peaks were observed. For the system with EMIM BF₄/dimethyl carbonate, both the first and the second activation peaks are reported.
Table 3: Specific charges for both oxidation and reduction flowing through the systems during the activation processes. Irreversible specific charges are also reported.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Oxidation (charge flown) [C/g]</th>
<th>Reduction (charge flown) [C/g]</th>
<th>Irreversible (charge flown) [C/g]</th>
<th>Activation potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIM BF₄/AN</td>
<td>912</td>
<td>436</td>
<td>476</td>
<td>1.44, 1.45, 1.52,</td>
</tr>
<tr>
<td>EMIM BF₄/ dimethyl carbonate</td>
<td>790</td>
<td>414</td>
<td>376</td>
<td>1) 1.46, 1.54, 1.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2) 1.76, 1.77</td>
</tr>
<tr>
<td>EMIM BF₄/ propylene carbonate</td>
<td>810</td>
<td>495</td>
<td>315</td>
<td>1.62, 1.64</td>
</tr>
<tr>
<td>EMIM BF₄/ vinylene carbonate</td>
<td>1457</td>
<td>354</td>
<td>1103</td>
<td>1.48, 1.52</td>
</tr>
<tr>
<td>EMIM BF₄ pure</td>
<td>540</td>
<td>286</td>
<td>254</td>
<td>1.90, 1.96</td>
</tr>
</tbody>
</table>
Table 4: Specific charge flow in the systems after the electrochemical activation with the relative Coulombic efficiencies.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$Q_{in}$ [C/g]</th>
<th>$Q_{out}$ [C/g]</th>
<th>$Q_{out}/Q_{in}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIM BF$_4$/AN</td>
<td>75.1</td>
<td>77.3</td>
<td>103</td>
</tr>
<tr>
<td>EMIM BF$_4$/dimethyl carbonate</td>
<td>61.8</td>
<td>64.9</td>
<td>105</td>
</tr>
<tr>
<td>EMIM BF$_4$/propylene carbonate</td>
<td>70.6</td>
<td>73.3</td>
<td>104</td>
</tr>
<tr>
<td>EMIM BF$_4$/vinylene carbonate</td>
<td>64.4</td>
<td>67.8</td>
<td>105</td>
</tr>
<tr>
<td>EMIM BF$_4$ pure</td>
<td>48.3</td>
<td>51.6</td>
<td>107</td>
</tr>
</tbody>
</table>

5.3.1 XRD characterization

Detailed XRD investigations of GOpr supercap electrodes have been published by Hantel et al. recently [147]. Inspection of the (001) reflection before and after activation shows that the layer distance of pristine GOpr of 4.4 Å has increased to about 12 Å. The 12 Å are a lower
bound and electrodes activated with EMIM BF$_4$ / AN cycle between 12 Å and 16 Å constantly. This cycling behavior has been investigated by in-situ synchrotron experiments, too. They prove that the anodic activation of this system yields a pillaring between the GOp layers which remains during cycling allowing for a flattening at positive charged and a corrugation for discharged states, respectively. This has been recorded through correlated appearance and diminishing of the (001) reflection during cycling [147]. Post mortem washing with AN lead to loss of the pillars providing the 12 Å separations but resulted in a GOp sample with 5.6 Å layer distance which is clearly distinct from the pristine GOp by expansion of about 1.2 Å [178]. The nature of this process has not yet been unraveled and this was part of the motivation for the present work.

In our first experiments with EMIM BF$_4$/dimethyl carbonate and EMIM BF$_4$/propylene carbonate, after washing the WE in acetonitrile and drying them under vacuum at 80 °C for 48 hours, we found the following post mortem characteristics: 1. the diffraction peak of the (001) planes of the pristine GOp has vanished; 2. nor the same shifted, for both the additives tested, was observed, let arise the doubt that acetonitrile may redissolve the pillared species in the layered structure.

For this reason the above mentioned two systems were characterized again by XRD without any after-treatment with acetonitrile. The diffractogram in this way shows a clearly visible shift of the (001) reflection towards smaller 2θ values, while the one at 2θ = 20.4° diminished. Fig. 49 shows, for example, the pattern of the EMIM BF$_4$ / dimethyl carbonate system in comparison with the one of pristine GOp and with that of the electrode activated with pure EMIM BF$_4$. Post mortem washing was done with a solution of EMIM BF$_4$ / dimethyl carbonate. A shift of the (001) reflection of Δ2θ = 9.2° which corresponds to a change of the interplanar distance of 3.6 Å, in other words, this corresponds, to a shift from 4.3 Å to a 7.9 Å separation. The behavior of the system treated with pure EMIM BF$_4$ finds a contradiction with the behavior observed by Reibisch in his experiments. In previous experiments, in fact, a probable partial activation of the WE was observed. This could be proved by the fact that after the activation of the system by cyclovoltammogram, XRD characterizations show a
splitting of the pristine (001) reflection into two different: one towards 6.4 Å and the other one, broader, towards 3.7 Å, this latter close to the interlayer distance in graphite. This behavior hasn’t found any explanation yet. The fact that the diffractogram of pure EMIM BF₄ in these experiments (Fig. 49) shows only a broad reflection centered at 2θ = 7.5° (d = 11.7 Å) indicates that the system behaves essentially like that with dimethyl carbonate and the activation, under these conditions, seems to be complete.

Figure 49: XRD patterns of pristine GOpr, GOpr+EMIM BF₄ and GOpr+EMIM BF₄/DMC.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

The new peak at 22.5° corresponds from separations around 3.9 Å and indicates to a reshuffling of the epoxy groups such that they diminish on some parts of the graphitic layers seemingly for the sake of the 7.9 Å separation.

Furthermore, it can be observed that there is another (001) shift for EMIM BF₄ activated system after washing with acetonitrile (Fig. 50a). It is clearly visible that the broad reflection centered at 7.5 Å disappears and there is an increase of intensity at lower angles.

A similar behavior is observable for the system EMIM BF₄/acetonitrile (Fig. 50b) where the diffractogram of the not washed sample has a sharp shifted reflection which disappears after the washing with acetonitrile. The same variations of both XRD patterns before and after the treatment with acetonitrile are observed for anodic activations with dimethyl carbonate and propylene carbonate as additives; to evaluate the shift of the (001) reflection of GOpr, therefore, WEs were not washed.

Figure 50: Post mortem XRD patterns of GOpr after cyclovoltammogram measurements for a) pure EMIM BF₄ and b) a EMIM BF₄ / acetonitrile activated sample before and after the washing with acetonitrile.
Until now no carbonates among those tested seemed to increase the interlayer spacing of GOpr as far as acetonitrile does (Fig. 51); even pure EMIM BF$_4$ seems to give a larger increase in the interlayer distance but, as already mentioned, the (001) reflection appears much broader than for acetonitrile or carbonate activations. Fig. 51 shows that propylene carbonate / EMIM BF$_4$, leads to a very similar result compared to the acetonitrile activation with a corresponding interlayer distance of 10.1 Å. This separation is about 2.2 Å larger than the one for EMIM BF$_4$ / dimethyl carbonate activation.

Vinylene carbonate behaves in a different to the other electrolyte systems: after the activation, the (001) reflection of pristine GOpr has disappeared but no new shifted (001) reflections are found. This means in this case the degree of order of the stacking is practically gone. Remarkable in this context is the enormous irreversible capacity of the vinylene carbonate electrolyte which is a clear indication of an activation process very different from the other electrolyte systems tested here. It is quite likely that here this irreversible current is not only used for activation of the carbonyl and nitrile groups of the electrolyte but also for the activation of the C=C double bond. Compared to the other carbonyl-based electrolytes the vinylene carbonyl consumes at least twice and up to 3.5 times as much irreversible charge. This is a clear indication to a very different kind of oxidation process, eventually with a fluorination of the double bond system. A simple transfer of the epoxy group of GOpr to the vinylidene would not be a charge consuming process but only to be catalyzed.

The reversible capacities of 64.4 C/g for charge and 67.8 C/g for discharge are not really different to those of the other electrolytes where a stable pillaring has been established. This can be understood by the classical flow of BF$_4^-$ ions in between and out of the interlayer spaces of the GOpr sheets as expected for an ELDC system. Since no in situ-XRD measurements are available it is not possible to verify whether (001) reflections remain during charging or discharging or not.
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*Figure 51*: XRD patterns of GOpr activated with different additives dissolved in EMIM BF$_4$. 
5. Reactivity of GO/GOPr - Supercapacitors with GOPr

Table 5: Positions of the (001) reflections of GOPr after the electrochemical activations for different electrolytes and corresponding interlayer distances.

<table>
<thead>
<tr>
<th></th>
<th>$2\theta_{(001)}$ [deg]</th>
<th>Layer distance [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine GOPr</td>
<td>20.4</td>
<td>4.3</td>
</tr>
<tr>
<td>GOPr + EMIM BF$_4$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GOPr + EMIM BF$_4$/acetonitrile</td>
<td>7.3</td>
<td>12.0</td>
</tr>
<tr>
<td>GOPr + EMIM BF$_4$/dimethyl carbonate</td>
<td>11.2</td>
<td>7.9</td>
</tr>
<tr>
<td>GOPr + EMIM BF$_4$/propylene carbonate</td>
<td>8.8</td>
<td>10.1</td>
</tr>
<tr>
<td>GOPr + EMIM BF$_4$/vinylene carbonate</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Furthermore, the XRDs hint to a tendency of GOPr to get intercalated during the charging process and to form ordered islands with more defined interlayer distances, which tends to remain, except for the case of vinylene carbonate, also after the discharging process. This would mean a woven intercalated graphitic-like structure like the one shown by M. Hantel [147] and would explain the presence of a sharp (001) reflection at angles lower than those.
found for pristine GOpr. These sharp reflections are at the center of a broader signal, which testifies the presence of many other interlayer distances and which does not disappear after post mortem washing with acetonitrile. The broad distributions of interlayer distances is also observed at higher 2θ angles (between $12 < 2\theta < 27$) but these fade when washing with AN.

The general understanding of these composites is that, after anodic activation, a high degree of disorder with ordered islands, the latter being stabilized by local intercalation phenomena of the reaction species. These persist as long as the system is not washed. After the treatment with acetonitrile these intercalations vanish as indicated by the disappearance of the broad signals between $2\theta = 12^\circ$ and $2\theta = 27^\circ$.

5.3.2 SEM

Scanning electron microscopy characterizations give evidence of the fact, that the GOpr composites do not get exfoliated after the pillaring process. The tubular structures present on the samples are residuals from the glass fiber separator (Fig. 52-56).

Figure 52: SEM pictures showing pristine GOpr.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

**Figure 53:** Post-mortem SEM pictures showing GOpr activated in the presence of EMIMBF$_4$/dimenthyl carbonate.

**Figure 54:** Post-mortem SEM pictures showing GOpr activated in the presence of EMIMBF$_4$/propylene carbonate.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

**Figure 55:** Post-mortem SEM pictures showing GOpr activated in the presence of EMIMBF$_4$/acetonitrile

**Figure 56:** Post-mortem SEM pictures showing GOpr activated in the presence of EMIMBF$_4$/acetonitrile.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

5.4 Conclusions and Outlook

In this work some carbonates have been investigated in order to test their ability of additives in EMIM BF₄ based electrolytes during electrochemical oxidative processes of partially reduced graphite oxide.

The higher capacities and specific charges reached by the material after activations (up to 73 C/g for EMIM BF₄/propylene carbonate system), compared to the systems with pure EMIM BF₄, indicate that this class of compounds behaves similarly to the already tested acetonitrile: they increase the capacitance of the material and make the electroactivation of BF₄⁺ easier, which testifies good catalytic properties of the additives plus composite systems. While all other carbonates tested show one activation peak, dimethyl carbonates shows two signals together the standard signal at high potentials due, probably, to decomposition two-step fluorination through EMIM BF₄. In all cases there is a significant increase in the disorder of the graphitic structure of WE together with partial intercalation phenomena, which are not observed for vinylene carbonates. This layers could be bent and kept together by pillaring structures, such as coordinating BF₄⁺ ions or reacted additives molecule which can be easily removed washing the electrode with acetonitrile. The treatment with acetonitrile, as it is shown by XRD patterns, does not only remove the “intercalation islands” but also decrease the interlayer distances in the activated material. At very low angles the increase in the intensity of very broad XRD scattering hints to a larger disorder of the layered composite. In all cases through all electrochemical activations a certain aggregation of GOpr remains, as it is testified by SEM.

Future characterizations such as in situ XRD, solid state NMR, elementary analysis and galvanonstatic measurements may help to better understand how the electro-activation happens and figure out possible reactions mechanisms. Elucidation of possible activation mechanisms together with the identification of intercalated species would furthermore help to correlate to the observed interlayer distances and to finally set up reasonable models for these fascinating reaction, inter- and deintercalation processes. It would also be very helpful to search for additives with specific intercalation properties in order to modify the GOpr.
5. Reactivity of GO/GOpr - Supercapacitors with GOpr

There would still be a possibility of producing some kind of cationic species during oxidation, however this seems to be quite unlikely because carbocations would be transient and thus their appearance would probably not be quantitative.
6. Application of GO/GOpr in Lithium-ion batteries

6.1 Introduction

The redox couple Li\(^+\)/Li has the most negative potential in aqueous solution throughout the periodic table (-3.04 V vs standard hydrogen potential) and per weight units lithium can hardly be beaten except by hydrogen. This is why lithium metal has found that much attention among researchers who have been working on better solutions in the field of the electrochemical storage devices. The very first Li-batteries were investigated in the 70’s but did not reach market because of safety issues due to severe problems of their metallic Li anode. The first generation of the so-called rocking chair batteries are still present in some portable devices like watches but the need to deal with more complex and thus more energy consuming portable electronic devices lead researchers to design new rechargeable systems with different chemical processes behind. Besides increasing numbers of portables devices and hand-held tools one of the greatest future battery markets lies in car and electric grid applications which have become a top priority due to the increasing air pollution in megacities and oil-related prospects in terms of conflict, supply and pricing.

The real revolution in the technological field of rechargeable batteries came with the introduction of already lithiated layered materials like Olivine-type materials with structure LiMPO\(_4\) (M = Fe, Co, Ni, Mn) [179-182], as well as dioxides whose forefather can be considered Li\(_x\)CoO\(_2\) [183]. Many further investigations on that material as well on Li\(_x\)MnO\(_2\) and Li\(_x\)NiO\(_2\) and their mixtures followed afterwards [184-188]. That allowed to study Li-batteries on their discharged state without the use of metallic Li which was seen to cause formation of dendritic structures during the charge-discharge processes with the consequent risk of shortcut or explosions. To avoid this problem anodic part was also redesigned in favour of insertion materials [189] that allow Li-ions to be intercalated instead of redepoting on the anode surface. The research of this topic leads to the commercialization of the C/LiCoO\(_2\) rocking chair batteries starting from the one by SONY Corp. in 1991. After
graphite, great effort was put on the research of alternatives materials like Si, Ge, Sn that show 2-10 times higher capacities than the former [190] but at the same time the tendency to undergo drastic volume changes for full lithiated compounds like Ge which shows a volume change of about 390 % at the first lithiation similarly to Si and Sn [191]. For this reason this research field pointed towards the development of films or nanostructures like nanocrystals and nanowires [192-198] that may buffer the volume change during the lithiation-delithiation processes and enhance both the kinetics and the tendencies towards the formation of alloys.

Fig. 57 shows a schematic sketch of a Li-ion battery and how it works.

Figure 57: Working mechanism of a Li-ion battery. In a) formation of dendrites on the surface of Li is shown; b) shows how this safety problem is resolved thanks to the use of insertion materials in the anodic part [199].
In both cathode and anode Li\(^+\) ions are inserted and deinserted during the charge-discharge cycling of the battery. During the charging process, more precisely, positive electrode material will be oxidized while the negative electrode will be lithiated. During the discharge the opposite process takes place and the Li-ions will be extracted from the negative material and go back to the positive host. Between cathode and anode a solution of lithium salts (usually LiPF\(_6\)) in a mixture of organic solvents like ethylene carbonate (EC) and dimethyl carbonate (DMC) works as electrolytes. These organic solvents are fairly stable during the electrochemical processes that take place during cycling. The processes are described as follows:

**Cathode:**

\[
\text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + x\text{e}^- \rightleftharpoons \text{LiMO}_2 \quad (7)
\]

**Anode:**

\[
\text{Li}_x\text{C}_6 \rightleftharpoons 6\text{C} + x\text{Li}^+ + x\text{e}^- \quad (8)
\]

**Overall equation:**

\[
\text{Li}_{1-x}\text{MO}_2 + \text{Li}_x\text{C}_6 \rightleftharpoons \text{LiMO}_2 + 6\text{C} \quad (9)
\]

In recent years investigations on Sb-based anodic material and its capability to form alloys with Li were carried out [191, 200] while studies carried out by Kovalenko et al. demonstrated that nanoparticles with dimension of 10 and 20 nm show better performances in terms of cycling stability, specific capacities and rate capability than bulky Sb [201].

In this work GOpr was used as additive for the Sb-based anodic material in order to investigate any improvements in the the anodical electrochemical performances in terms of capacitance and cycling stability. The idea behind is to use a layered material, that can physically support the active nanoparticles in order to prevent disgregation processes that may infere the electrochemical performances of the anodic material. This goal was similarly achieved by Kovalenko et al. in a work where Sb-based composites were supported by Cu nanowires in order to prevent the pulverization of the anodic material during cyclization [202].
6. Application of GO/GOpr in Lithium-ion batteries

6.2 Experimental part

6.2.1 Preparation of Sb nanocrystals

Sb nanocrystals were prepared by M. Walter following the procedure by reducing SbCl$_3$ with NaBH$_4$ at 60 °C. These particles have an average diameter of about 20 nm [202].

6.2.2 Preparation of electrolyte

As electrolyte a 1 M solution LiPF$_6$ (Novolite) in ethylene carbonate/dimethyl carbonate is used and to this 3% Vol. fluoroethylenecarbonate (FEC) is added in order to stabilize the solid electrolyte interface (SEI).

6.2.3 Preparation of current collectors and batteries

The working electrode is prepared by mixing Sb nanocrystals (53.7 wt%) together with carbon black (CB, Super C65, Timcal) as conductive additive (21.3 wt%), carboxymethylcellulose (CMC, Sigma-Aldrich) as polymeric binder (14.9 wt%) and partially reduced graphite oxide (GOpr) as stabilizer (10.1 wt%). Since CMC is soluble in water the mixture was ball-milled in deionized water for one hour at 500 rpm with a zirconia ball mill in order to obtain homogeneous slurry. Once the slurry is ready, this is pasted with a paintbrush on the surface of a Cu current collector. The current collector is afterwards let dry at room temperature for five hours and then overnight under vacuum. Before to build the batteries, the current collectors are kept under vacuum at room temperature for one hour.

In order to test the anodic materials produced in that way, current collectors are mounted on both Ti cells and steel coin cells in a glove box under inert atmosphere (0.1 ppm O$_2$ and 0.1 ppm H$_2$O). Li discs are used as cathodic materials and volume of electrolyte used depends on the system used: 600 μL for titanium cells and 300 μL for coin cells.
6.3 Results and discussion

Galvanostatic measurements were carried out on half cells containing Sb nanoparticles (10% wt.) as active material with current densities of 1320 mA/g (2C) showed a high cycling stability by reaching almost 1000 cycles at a specific capacity of about 720 mAh/g which is remarkable 80% of the initial 900 mAh/g. Right in the initial half cycle high currents are observed due to the formation of the SEI (Fig. 58). It is interesting to note the faster capacity during the first 300 cycles compared to the slower decay in consecutive cycles indicating to a kind of stabilization of the system. The steps in Figure 58 before 200 cycles are reached due to lower C rates (in this case 50 mA/g) during a rate-capability test. It is evident that for lower C rates the retention of the capacity increases going further with the charge-discharge process since the variation in the specific capacity is higher in correspondence of the 50th cycle than of the 100th. The Coulombic efficiency is at 99.7 % for the whole range of the measurement.
6. Application of GO/GOpr in Lithium-ion batteries

**Figure 58**: Galvanostatic measurement of anodic material with Sb and GOpr (10% wt.) carried out at 2C (1320 mA/g). In the inset a zoomed portion of the diagram in correspondence with the rate capability test is showed. Mass of the active material: 0.19 mg.

Fig. 59 shows another example of a system made of 10% wt. Sb but this time at 1 C current (660 mA/g). In this specific case after a pretty constant trend of the first 200 cycles at about 725 mAh/g, a sudden decrease in the capacity was observed. Unexpectedly, after the 600th cycle the capacity stops to decrease and until the 1000th cycle. After the measurement protocol stopped, a constant specific capacity value of 570 mAh/g was determined. This capacity is unexpectedly lower than the one observed for the measurements carried out at 2C. This is probably due to an initial deterioration of the active material maybe ascribable to the building process of the half cell, because the first 200 cycles at 1 C show also higher
6. Application of GO/GOpr in Lithium-ion batteries

capacities (between 800 and 900 mAh/g) than those at 2 C (between 700 and 740 mAh/g) in spite of the higher initial stability of the latter. This loss of capacity cannot be, for this reason, ascribable to the change of C rates during the rate capability test. As far as this latter is concerned in the experiment carried out at 1 C, by changing the C rate during the rate capability test from 660 mA/g to 50 mA/g denotes a much higher retention rate which is in accordance with the higher stability shown by the system tested at 1C-rate.

**Figure 59:** Galvanostatic measurement of anodic material with Sb and GOpr (10% wt.) carried out at 1C (660 mA/g). In the inset a zoomed portion of the diagram in correspondence with the rate capability test is showed. Mass of the active material: 0.10 mg.
Galvanostatic measurements present in Fig. 60 show the difference in terms of capacity for both the systems prepared in the same way and running at 1C-rate with and without GOpr until 700 cycles.

The system with GOpr shows a higher capacity until the end of the measurements: during the first 200 cycles and the last 150 cycles the two cells show a difference of about 50 mAh/g in terms of capacity, between 200 and 550 cycles the difference between them decreases due to the mentioned loss of stability of the system with GOpr. At around 700 cycles the curve of the capacity of the latter seems to reach a plateau, while that of other system continues to decrease. In terms of rate capability, on the other hand, the two systems behave quite similar because they show decreasing capacities at every current variation towards current values of 50 mA/g.

**Figure 60:** Effect of the presence of GOpr (10%) in the anode on the electrochemical performances of two cells with C-rate = 2 (1320 mA/g). Active material mass for anode with GOpr = 0.10 mg; Activ material mass for anode without GOpr = 0.50 mg.
It is important to note that experiments carried out at 1C and at 2C, respectively C had relatively low loadings of active material of 0.10 mg and of 0.19 mg of the nanoparticles. Although other measurements with higher loadings have never shown such a high stabilities, the low masses of these two experiments may give rise to larger errors in the measurements of the capacities. These are estimated to up to 10%. Since 0.55 mg of Sb were used for the experiment without GOpr, the capacity measured in this experiment may have been influenced accordingly. The difference between both the capacity curves of the systems with and without GOpr may therefore not be that reliable but the evidence of a higher stability of the system in the presence of GOpr still persists. GOpr therefore may give a decisive contribution to a further stabilisation in the systems with low mass loadings.

In these systems, in fact, to the low concentration of Sb on the surface of the current collector allows changes in the nanoparticles volumes during lithiation and delithiations without important stresses or degradation of the anodic material. This stress is much more frequent for anodes where more Sb volume work shows up. Variation of the weight percentage of GOpr, did not show any improvement in the electrochemical performances compared to the electrode with 10% GOpr.

CV analysis of the anodic Sb-based material (Fig. 61) with 0.19 mg of GOpr shows in the first discharge cycle two peaks, one broad at about 1.6 V and one sharper at about 1.3 V that may be explained by the formation of SEI. After these peaks the lithiation signal is present at about 0.7 V. This process corresponds to the formation of two compounds of Li and Sb with the stoichiometries LiSb_2 and Li_3Sb, respectively. During the charging process and Li-removal from the nanoparticles, only a single signal at about 1.1 V is found which appears during both, the second and the third charging cycles. Furthermore, the second and the third discharging cycles show a shift of the lithiation peak towards lower potentials (here about 0.85 V) as it was observed with the Sb-based LIB tested by Kovalenko et al. without the use of GOpr. Furthermore, the fact that both the lithiation and the delithiation signal of second and third cycle are overlapping reveals a good cyclability and stability of the system in the presence of GOpr.
6. Application of GO/GOpr in Lithium-ion batteries

**Figure 61:** CV measurement of a Li-ion half-cell in the presence of Gopr (10 \%wt.) as additive in the Sb-based anode. Sweep rate: 0.1 mV/s.

XRD in Fig. 62 corresponds to the antimony samples right after ball milling and after 1 full charge-discharge cycle and shows the presence of broadened reflections of Sb. These reflections slowly disappear over the cycles as it is shown in Fig. 63. This may be explained by the amorphization of the active material after several lithiation/delithiation cycles by consecutive destruction of its crystalline structure. As the crystallinity is lost before the 100\textsuperscript{th} cycle, the amorphous state is responsible for most of the of anode working life. It would be interesting to find out whether X-ray reflections are already diminished after about 20 cycles when the capacity losses reduce markedly and whether reflections may reappear on weak current cycling.
Reflections marked with a star could not be identified. As their intensities and shapes remain practically unchanged independent of the cycle number they may not be related to an antimony compound. They may be caused by any kind of side reaction.

**Figure 62:** Powder pattern of the anodic material after 1 cycle of charge and discharge and directly after ball milling without any electrochemical test, showing the presence of Sb reflections together with some unidentified reflections. Green stars mark unidentified reflections from pattern obtained by the sample directly after ball milling, while blue stars those observed from both patterns.
Figure 63: Powder patterns of the anodic material after 1, 4, 99 and 999 charge/discharge cycles, showing the presence of Sb reflections that fade before the 100th cycle. Marked unidentified reflections don’t decrease in intensity nor broaden during cycling.

6.4 Conclusions and outlook

In this work experiments with Sb-based anodes in presence of GOpr showed capacities comparable, and in some case superior, to the already investigated analogues anodes without GO-based additives. Furthermore, the anodes with GOpr show an improvement of their cycling stabilities persisting to 1000 cycles, at least. This means that GOpr is a additive for the preparation of long-lived and high capacity anodes. Future work may be focused on the investigation of other graphitic materials as stabilizers and the study of further high...
6. Application of GO/GOpr in Lithium-ion batteries

performance active materials under different conditions like, for example, higher mass loading, higher C-rates and larger wt.% of active materials. Fundamental will be also investigations of the mechanism that rules the improvement in the cycling stability in order to clarify if the degree of oxidation of GOpr does influence the electrochemical performances.

Similar investigations may also be performed for other kinds of electrochemical devices like those based on Na$^+$- and Mg$^{2+}$-ions as transport species.
7. Investigations on the silicon oxide decoration of GOpr

7.1 Introduction

Due to the experiences outlined in the preceding chapter TEM / EDX and elemental mapping investigations have been performed in order to better understand the complexity of the composite formed from GOpr in a Stöber kind of reaction. The deposition of SiO$_2$ at GOpr may be a model case for attachment of other oxides at GOpr, in future.

7.2 Experimental part

According to the conclusions drawn from chapter 2 a shorter reaction time and variations of TMOS contents have been employed:

30 mg of GOpr or GO are added to a solution of 2 ml H$_2$O and 10.3 ml NH$_3$(aq) in m ml EtOH. Then, n ml TMOS are added to the mixture at room temperature under ultrasonication. The resultant mixtures are kept under ultrasonication for 24 hours and then centrifugated at 12100 rpm for 30 minutes in order to separate the supernatant from the precipitate, which thereafter was dried at room temperature.

The following table contains the reaction data m and n.
7. Investigations on the silicon oxide decoration of GOpr

**Table 6: reaction data of silicon oxide deposition on GOpr**

<table>
<thead>
<tr>
<th>Denotation of experiment</th>
<th>m (ml EtOH)</th>
<th>n (ml TMOS)</th>
<th>mg GOpr</th>
<th>Sonication time</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF 483*</td>
<td>16</td>
<td>0.13</td>
<td>15</td>
<td>3d</td>
</tr>
<tr>
<td>MF 484</td>
<td>16</td>
<td>0.13</td>
<td>30</td>
<td>1d</td>
</tr>
<tr>
<td>MF 485</td>
<td>6</td>
<td>0.043</td>
<td>30</td>
<td>1d</td>
</tr>
<tr>
<td>MF 486</td>
<td>13</td>
<td>0.013</td>
<td>30</td>
<td>1d</td>
</tr>
<tr>
<td>MF 487</td>
<td>6</td>
<td>0.043</td>
<td>30</td>
<td>1d</td>
</tr>
<tr>
<td>MF 488</td>
<td>13</td>
<td>0.013</td>
<td>30</td>
<td>1d</td>
</tr>
<tr>
<td>MF 489</td>
<td>16</td>
<td>0.13</td>
<td>30</td>
<td>1d</td>
</tr>
</tbody>
</table>

*results already discussed in chapter 2

We first analyze the results for MF 484 which are not much different in terms of experimental conditions from MF 483 of chapter 2 except doubling of the GOpr part and reduction of reaction time to 24h which was then kept for all further experiments. MF 484, MF 485 and MF 486 are a series with increasingly lowered TMOS concentration. The other, MF 487, MF488 and MF 489 were repeat experiments in order to consolidate the results.
7. Investigations on the silicon oxide decoration of GOpr

7.3 Results and discussions

The supernatant extract of experiment MF 484 exhibits lighter rims of particles corresponding to electron-rich elements. In Figure 64 two slightly fused particles appear which might be more or less spherical but could also be flat. The carbon map (b) shows that there is carbon everywhere where contrast is found, most prominently of course at support positions.

Figure 64: Experiment MF 484 supernatant extract; (a) Z-contrast micrograph showing two slightly fused particles; (b) carbon map showing the support carbon but also some carbon in the patches; (c) Cu map indicating to concentrations at rims and also some but lower Cu content over the full areas; (d) Cu (red) + O (blue) map; (e) oxygen map; (f) Si(green) +Cu (red) map; (g ) silicon map; (h) EDX spectrum with assigned elements.
7. Investigations on the silicon oxide decoration of GOpr

This would speak for thin carbon patches covered with SiO$_2$ and copper oxide, most likely CuO or Cu$_2$O$_3$ as oxygen is found wherever silicon and/or copper appear. Clearly, Cu is most concentrated at rims where oxygen is found, too over the whole rim areas (cf. Figs. 64 (c), (d) and (f)). The somewhat lower but constant Cu content over the flat areas can be understood as coating of the more voluminous SiO$_2$, here (cf. Figs. 64 (d), (e) and (g)). Consequently, the EDX spectrum proves all these elements in considerable concentrations (Fig. 64 (h)).

The solid part of the centrifuged MF 485 product contains somewhat finer structures which allow better to follow SiO$_2$ precipitation. For example, carbon patches are not fully covered anymore in comparison to MF 484 (cf. Fig. 65). In detail, there is a nearly free-hanging GOpr patch with only some contact to the support grid on the left. EDX and Z-contrast show some heavier element nucleation at some rim parts which can be assigned to mostly silicon (Fig. 65 (b)). Carbon and oxygen maps nicely demonstrate a large scale oxygen coverage on the carbon patch but with local structuring. This is what is believed to happen for GOpr, namely those islands of mostly epoxy groups assemble through a bond switching mechanism. This becomes especially clear by comparing Fig. 65 (e) and (f) which allows to separate SiO$_2$ domains from epoxy areas. It is difficult however, to determine certain other regularities in the epoxy distribution beyond the general clustering behavior. This may be due to a still too low resolution of these maps and a overlapping of top and underlayer information because numerous EM pictures reveal that single layer GOpr patches are not very likely to spot.

The SiO$_2$ distribution which we can infer from Figs. 65 (f) – (h) appears to be nucleation of individual particles which form aggregates at some rim parts and also around one point on the patch. One may conjecture that this may be around whole in the GOpr but that is only likely and cannot be proven by the existing data.

In Figure 66 there is obviously a stack of GOpr patches extending into the grid opening. The upper layer(s) of this stack are reduced to a finger-like form such that the rim becomes very well visible, especially in the Z-contrast micrograph (b). The carbon map does not tell what the rim decoration is, only that the stack is clearly a carbon-based one (Fig. 66 (c)). However,
7. Investigations on the silicon oxide decoration of GOpr

O and Si maps clearly reveal a continuous decoration of this rim by SiO$_2$ (d)-(f). The combined Z-contrast and Si map in Fig. 66 (h) proves that a SiO$_2$ rimming similar the one demonstrated on boron nitride patches appears besides the abovementioned island-like precipitations of silicon dioxide.

**Figure 65:** Experiment MF 485 precipitation part. (a)TEM micrograph showing a carbon patch in between the grid frame; (b) Z-contrast micrograph and EDX analysis; (c) carbon map showing the support only on the left but mostly an isolated GOpr patch; (d) oxygen map nicely showing a scattered but pretty dense distribution on the GOpr patch; (e) C + O map making the oxygen distribution a bit more pronounced; (f) silicon map; (g) O + Si map with clearly located Si assemblies at some parts of the GOpr rim; (h) C + Si map.
Investigations on the silicon oxide decoration of GOpr

**Figure 66:** Experiment MF 485 precipitation part. (a) TEM micrograph showing a carbon patch in between the grid frame; (b) Z-contrast micrograph and EDX analysis; (c) carbon map showing the support only on the left but mostly an isolated GOpr patch; (d) oxygen map nicely showing a scattered but pretty dense distribution on the GOpr patch; (e) silicon map; (f) O + Si map with clearly located Si assemblies at some parts of the GOpr rim; (g) C + Si map (e) Z-contrast and Si map.
Figure 67. Experiment MF 485 precipitation part. (a) Z-contrast micrograph; (b) carbon map the isolated GOpr stack; (c) oxygen map nicely showing again a scattered but pretty dense distribution on the GOpr patch; (d) C + O map making the oxygen distribution again more pronounced; (e) silicon map; (f) O + Si map with clearly located Si assemblies at some parts of the GOpr rim; (g) C + Si map; (h) Z-contrast and Si map.
7. Investigations on the silicon oxide decoration of GOpr

From Figure 66 it becomes evident that island-like clustering and rim-nucleation show up simultaneously. Rims are seen quite prominently in Z-contrast as well as in oxygen maps (cf. Fig. 67 (c) and (d)) while the Si map does only reveal a few of these assemblies (Fig. 67 (e) and (f)). This has to be attributed to copper oxide(s) which also assemble both on carbon rims and on silicon oxide islands. This is nicely seen from the next set of micrographs and EDX analyses which have been taken for experiment MF 486 and MF 487. In Figures 68 and 69 the copper content shows clearly up but is much higher for the supernatant extract than for the particles on the GOpr.

![Micrograph of GOpr with marked content of copper oxide(s) on SiO₂ particles aggregates.]

**Figure 68:** Experiment MF 486 precipitation part. There is a marked content of copper oxide(s) on the SiO₂ particles aggregates.
Figure 69: Experiment MF 486 supernatant part. There is a much higher content of copper oxide(s) on the SiO$_2$ particles from the dried solution part.
7. Investigations on the silicon oxide decoration of GOpr

If this conjecture is right then one should also find some probes where reiterative core-shell entities show up. Indeed this is the case for some parts of the sample as can be seen in Figure 70. It seems as if the SiO$_2$ nanoparticles would “fish away” the copper oxide(s) from the GOpr.

**Figure 70:** Experiment MF 486 supernatant part. (a) and (d) two Z-contrast micrographs of small ensembles of intergrown nanoparticles; comparing elemental maps (b), (c) and (e), (f) one can infer that intermediate steps of nucleation have been captured.
Figure 71. Experiment MF 487 supernatant part. (a) and (c) two Z-contrast micrographs of small ensembles of intergrown nanoparticles; comparing elemental maps (b) as well as (d) and (e), respectively, one can infer that intermediate steps of nucleation have been captured. For (c), (d) and (e) the reformation process is practically finished and nearly all copper oxide is already located on the surface of the triply nucleated core-shell particle.
7. Investigations on the silicon oxide decoration of GOpr

This is even more surprising as the copper seems to be quite fixed to GOpr if no silicon oxide is present. According to the present stage of research it is most likely that the production of core-shell particles \( \text{CuO}_x@\text{SiO}_2 \) happens during the nucleation process during the Stöber reaction and is likely being catalyzed by GOpr because prior to the Stöber reaction the copper oxide is found exclusively attached on GO and GOpr.

In Figure 70 already Z-contrast images indicate to copper oxide islands inside of larger silicon oxides precipitates. This appears to be different nucleation stages where \( \text{SiO}_2 \) nucleates on preexisting \( \text{CuO}_x \) particles and, consecutively, copper ions move to the outside of the composite particles to form the surface of the combined core-shell particles, in the end. Such intermediate stages are found in all experiments presented here which were run over only 24h.

Figure 71 presents another set of Z-contrast micrographs of small ensembles of intergrown nanoparticles; comparing elemental maps (b) as well as (d) and (e), respectively, it appears that intermediate steps of nucleation have been captured. Similarly for Figure 71 (c), (d) and (e), the reformation process is practically finished and nearly all copper oxide has already been transferred to the surface of the triply nucleated core-shell particle.

One would like to infer that some surface tension effect is responsible for the redistribution process which transports the copper oxide to the surfaces, as it is well-known that such small \( \text{SiO}_2 \) nanoparticles are of glassy structure. If so it should also be noted that obviously the geometric form in which particles come together is being preserved, as one can nicely see from Figure 71 (c).

The large number of micrographs as well as of elemental maps which have been taken from different experiments (cf. Table 6), from their precipitates and their dried solutions, reveal a common picture of a beautiful multistage nucleation process in which predeposited copper oxide must play an important part. In review of the investigations of this chapter it is most likely like this because the copper oxide exists on the GOpr prior to the Stöber reaction. In
7. Investigations on the silicon oxide decoration of GOpr

the end, however, copper oxide tends practically exclusively to be on the surfaces of silicon oxide nanoparticles and, although much, less at edges of GOpr.

Out of the large stock of data taken, selected representative ones have been displayed here in order not to overload this work. This notion, though, is important because singular TEM micrographs have practically no information about chance and probability. The high frequency of consistent data allows to infer a common growth mechanism, here.

7.4 Conclusions and outlook

In this work, a series of experiments with GO and GOpr have been carried out, in order to functionalize their epoxy- and hydroxyl groups by SiO₂ using a Stöber reaction. The brave hope to make functional groups visible through a posteriori electron microscopy techniques was not realized, though. SEM characterizations show the presence of a functionalization mainly on the rims but also on some portions of the planes. The presence of unexpected CuOₓ in the functionalizing SiO₂ is due to the accidental presence of some impurities in the starting GO and luckily led to the formation of an additional functionalization of the silica nanoparticles, only. A fascinating result, here, is that the primary locations of the copper oxide on GOpr change during the short Stöber process such that CuOₓ migrates to the surfaces of the silica nanoparticles. For the future, it may be interesting to perform similar experiments with other metal compounds of interest, for example with catalytically active metals like Rh, Pd, Pt and Au.
8. Future prospects of the research field

The 2D systems investigated in this work are of very timely interest due to an upcoming “graphene period”. Both boron nitride and reduced graphite oxide (GOpr) are related to graphene but different in specific properties like electronic and ionic conductivities, functionalization possibilities and chemical stabilities. In common to all of them is mechanically and geometrically very stable backbone, belonging to the most stable ones thinkable in terms of specific stability, which means stability per weight unit. In this respect, graphene, GO, GOpr and BN establish a toolbox with outstanding possibilities for research and applications.

Reduced graphite oxide turns out more and more to become a very interesting starting material for further functionalizations with respect to consecutive applications in the domain of two dimensional nanodevices, photochemistry and catalysis as well as membrane formation. Not least this is due, on the one hand, to the special character of GOpr being an extended electronic system with outstanding long range electronic and thermal conductivities and on the other to quite defined functionalization sites of functional C-O groups. Another aspect of GOpr is its large thermal, mechanical and chemical stabilities which make it applicable for a broad range of different conditions.

In this work GOpr was investigated in terms of selected electrochemical and chemical reactions in order to introduce site specific reactions or composite formations. The electrochemical activations reveal a set of similar pillaring reactions which introduce local columns indicated by characteristic changes of the GOpr stacking distances. In all cases these studs, may they be of single molecules or assemblies of molecules – due to the known ordering of functional groups on GOpr – remain during electrochemical cycling if they have been introduced by electrophilic or oxidation reactions, in other words by cathodic initialization. Results of previous and of this work indicate that cyclic puckering and stretching of GOpr layers does not change the characteristic extensions of the layer.
separation. However, there must be more than just fixation of individual molecules on functional sites because after a posteriori washing with the electrolyte solvent a reduced layer separation is found, which though is markedly larger than the a priori separation of about 4.4 Å. The enlargements found here ranges between 1 Å and 3.5 Å and depend on the nature of the solvent molecules which play a pivotal role in the catalytic discharge of the electrolyte anions BF$_4^-$.

After this work, one may guess that there are attractive perspectives for electrocatalysis reactions on GOpr–based electrodes including elegant fluorination reactions. This is a quite timely aspect, as fluorinated molecules have gotten much attention in homogeneous catalysis over the last decade. Similarly interesting are electro catalytic reactions which selectively modify functional sites at GOpr which may become a trigger for future applications of this remarkable material.

In a different approach, Cu-impregnated GOpr modified into a composite of SiO$_2$@CuO$_x$ nanoparticles attached seemingly to specific sites on GOpr, may be directed by local functionalization islands on the planes of graphite oxide, but that will have to be confirmed in future. Having very small core-shell nanoparticles of catalyst on glassy cores attached to an electronically conducting support, may be seen as a blueprint for a new kind of catalytic systems. It should be noted at this point, that the extended electronic system of GOpr may provide a very useful electron reservoir for catalysis, in general. Future will show whether this expectation will hold or not.

Considering the yet known modification reactions on GOpr, may they be through chemical or by electrochemical procedures, one may not be too brave in expecting a new era combining molecular, supramolecular and catalytical chemistry together with electrocatalysis and nanoelectronics. In addition detailed investigation on such model systems in a capacitor setup may give further clues to the mechanisms of the formations of solid electrolyte interfaces, both on the anode and the cathodes of battery systems.
8. Future prospects of the research field

Some of the arguments stated above may also hold for future BN-based systems, some of course not, because BN is an electronic insulator. As such boron nitride provides a set of characteristics which is complementary to graphene and GOpr, i.e. pure ionic conductivity and oxidation stability. However, its stability against dissolution reactions is not as large as expected, which led to some failures in our experiments, especially under delamination conditions when BN sheets become more exposed to the reactands. Due to that, functionalization of BN is possible but more difficult to control than for graphene. The novel rimming of BN provides a stabilization which may turn out to be very helpful for second order functionalizations, i.e. membrane formation by use of BN. It is likely to assume that thinner functionalized boron nitride platelets may be easier to assemble together towards the formation of complex architectures like membranes. Future work must therefore focus attention on delaminated boron nitride, followed by controlled functionalization of the thin sheets by selected reactions, with compounds such as modified silica or, in general, molecules that promote the self-assembly of the platelets.

It seems that present research and application attempts on 2D materials are just in their infancies, today, and much new science and new devices can be expected from them, in future.
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Appendix


Appendix

Experimental methodologies

Electron microscopy

- Scanning electron microscopy (SEM) analysis was performed with a Zeiss Gemini 1530 operated at 1 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out on a Tecnai F30 microscope (FEI; FEG cathode) operated at 300 kV and equipped with an energy dispersive X-ray spectrometer (EDXS; Gemini system of EDAX).

X-ray powder diffraction (XRD)

- STOE Stadi P diffractometer equipped with a germanium monochromator and CuKa1 radiation (operated at 35 mA, 35 kV).

Atomic force microscopy (AFM)

- Asylum AFM instrument (MFP 3D) in tapping mode with cantilever AC 160TS from Olympus, operating with a resonant frequency of 300 KHz and k ~26 N/m.

IR measurements

- Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beamsplitter (range 600 – 3500 cm\(^{-1}\)) in ATR mode.
Appendix

Raman measurements

- Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with Nd:YAG laser, plasma filter and a Ultra-InGaAs detector. Measurements were taken in a range between 10 and 3500 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\).

Electrochemical measurements

- Galvanostatic and cyclic voltammetry measurementst carried out using ASTROL software.

Ball milling

- Fritsch Planetary Mono Mill PULVERISETTE 6 classic line.

Furnaces

- Herascus Ro 4/50 resistivity tube furnace \((T_{\text{max}} = 1100 \, ^\circ\text{C})\).
- Nebertherm L 9/11/SM/P330 muffle furnace \((T_{\text{max}} = 1100 \, ^\circ\text{C})\).
- Electric arc furnace under Ar atmosphere.

Survey of possible activation reactions at GOpr

From synthetical and mechanistic points of view, the electrochemistry at GOpr electrodes is insofar very interesting as it allows to explore potential induced reactions as well as electrocatalysis. At the same time, many of these reaction types do apply for GO, too, and
may become valid for graphene, either. The big difference of GO on the one hand and GOpr as well as graphene on the other, is that the latter allow for electronic charging and thus for electrocatalysis while GO could only be activated by ionic loading due to its electronically insulating property.

Both electrophilic and nucleophilic attack can be induced by the charge loading of the GOpr sheets. Here we concentrate on nucleophilic reactions which are triggered by positive or oxidative potentials at the electrodes because in most cases these gave rise to irreversible current flows and irreversible changes of the GOpr layers. Different from that, negative potential or reductive stimulation appeared mainly reversible for electrode systems investigated so far according to [146] and this work.

In general, a positive potential on GOpr corresponds to electronegatively acting layers beyond H₂/H⁺ and at +2V reaches practically fluorine electronegativity. This though is a crude comparison, because loading of fluorine atoms reduces electron affinity dependent on the actual partial charge due to its compactness thus highly correlated electron system. This is not the case for the GOpr layers as they provide large electron systems which in principle have an unlimited electron affinity due to the external electronic charge flow. In this respect, comparisons which are taken here with known chemical reaction types may be handicapped. On the other hand, nucleophilic reactions must occur when the loading of the GOpr sheets goes beyond certain threshold potentials and a corresponding survey seems to be justified, especially as such an analysis provides means for planning more targeted experiments, in future.

There will be two main scenarios to be considered: 1. The nucleophilic attack leads to a binding of activated reaction species to the GOpr layers and 2. the GOpr layers just play a catalyst role by generating and stabilizing reaction intermediates which desorb again after reaction and/or after discharging of the layers. Both of this seems to be the case as 1. irreversible activation reactions leave GOpr in most cases with modified interlayer separations, but 2. pillaring distances of about 12 Å appearing during charge / discharge cycles reduce after post mortem washing of the electrodes by some 6 Å (cf. Table 5). The
latter hints to only a transient coupling of some of the reaction products to the GOpr layers - though stable under the electrochemical cycles, they not sustain the washing procedures.

Figure 72 displays a schematically the situation around an epoxy center during positive charging of the layer.

![Figure 72: a) Part of a GOpr layer with an epoxy group and four neighboring reactive carbon centers; b) attack of an F radical to one of the carbenium centers.](image)

The four C atoms adjacent to the epoxy group are subject to a weakened bonding because they are lacking proper participation in the delocalized π system. Here, the primary carbocationic center will be become active. These are also centers which may become fluorinated during the irreversible discharge of BF$_4^-$ anions. This is the most general irreversible reaction process for all electrode systems we investigated. It is interesting to note that (CF)$_{1.12}$, which is the π-perfluorinated graphene with some terminal F-centers according to (CF)(CF$_{term}$)$_{0.12}$, exhibits layer separations between 5.6 and 6.3 Å. This is in the range of layer distances one obtains after post mortem washing of the activated GOpr electrodes. It is interesting to note, that Hantel et al. had found that the irreversible current in the first oxidative half cycle for an GOpr / EMIM BF$_4$ / AN electrode correlates to the amount of epoxy groups on GOpr [146].
The activation peaks listed in Table 3 for GOpr / EMIM BF₄ / Carbonate electrodes occur at potentials clearly lower than the one for GOpr / EMIM BF₄ hinting at a combined catalytic action of GOpr, the carbonates and EMIM BF₄. This means that the carbonates as well AN must become involved in the activation processes.

For the GOpr / EMIM BF₄ / AN electrode a Ritter type reaction has been proposed recently [147] in which a carbenium ion reacts with a nitrile to a nitronium intermediate (Scheme 2):

![Scheme 2: Representation of a type of Ritter reaction after [147].](image)

The latter can stay attached to the GOpr layer or go on reacting in different ways, i.e. attacking another nitrile molecule or giving a fluorination through the discharge of an BF₄⁻ anion (Scheme 3):

![Scheme 3: Attack mechanism of a second nitrile group with possible fluorination after [147].](image)
Appendix

According to the abovementioned correlation of activated GOprs and (CF)$_{1.12}$ it appears fairly sure that some of the fluorination takes part on GOpr. However, also the molecular species may become fluorinated, too. Also amide formation has been reported as a special kind of Ritter reaction [148].

This seems to be the case for DMC having irreversible activation peaks may undergo a two step fluorination and consecutive decomposition of the molecule as proposed in Equation 10:

\[
\text{CH}_3\text{O-CO-OCH}_3 + 2\text{BF}_4^- - 2e^- \rightarrow \text{F}_3\text{B} \text{O}=\text{O} \text{BF}_3 + 2\text{CH}_3\text{F} + \frac{1}{2} \text{O}_2
\]  

(10)

According to the next scheme [149], instead of hydroxyl groups GOpr-F centers could react with DMC forming fluoromethane instead of methanole:

\[\text{Scheme 4: Formation of carbonates with evolution of methanol.}\]

If methylation also takes place, which is a common behavior for DMC as a classical methylation agent, then CO$_2$ might be formed in addition to CH$_3$F, both of which are gaseous at room temperature. This may explain the special instability of the GOpr / EMIM BF$_4$ / DMC electrode (cf. Fig. 47) which was traced back to gas formation during activation. In addition, methylation of special active carbon centers on GOpr may be found, too (Equation 11). As
this might be an irreversible bond formation, with GOpr larger post mortem layer separations than those, typically found by C-F formation, should evolve.

\[
\text{ArCH}_2\text{X} + (\text{CH}_3\text{O})_2\text{CO} \rightarrow \text{ArCH(CH}_3\text{)X} + \text{CO}_2 + \text{CH}_3\text{OH} \tag{11}
\]

The GOpr / EMIM BF\(_4\) / VC electrode reveals about three times as much irreversible capacity as the others. As this means that considerable irreversible currents have flown it must have some quantitative meaning. We assume here that in addition to the activation reaction of the other carbonyl additives the vinylene undergoes addition of two fluorine atoms to the double bond resulting in formation of difluoro ethylene carbonate according to part of the classical Diels-Alder reaction [150] (Scheme 5):

\[
\text{C}_2\text{H}_2\text{OCO}_2 + 2 \text{F}^- \rightarrow \text{C}_2\text{H}_2\text{F}_2\text{OCO}_2
\]

\textbf{Scheme 5: Diels-Alder reaction and followed by fluorination of the vinylene molecule to fluorinated ethylene carbonate (FEC).}
Whether there is only an interim or a permanent fluorination of active GOpr carbon sites, in any case Friedel-Crafts-type reactions have to be expected (a) because of the evolution of carbenium ion centers during positive charging of the layers and (b) because of the oxidation of BF$_4^-$ to BF$_3$ which as a strong Lewis acid, is a Friedel-Crafts catalyst. Together with a prior fluorination of active carbon sites all prerequisites for Friedel-Crafts reactions are given. The acylation reaction displayed in Scheme 6 below suggests that carbonyle groups of nearly all kinds, i.e. from aldehydes, ketones, carboxylic acids and acid anhydrides or carbonates can undergo this kind of reaction.
Scheme 6: Mechanism of the Friedel-Crafts acylation [150].
It has to be inferred that this is the common activation reaction for all carbonate additives investigated here. A special kind of Friedel-Crafts, the so-called Haworth reaction represents a typical blueprint for what may be the essence of the GOpr attack on the carbonates with an intramolecular acylation [151] (Scheme 7).

![Scheme 7: Haworth reaction of carboxylic anhydrides or carbonates, adapted from [152].](image)

The reductive part of the Haworth reaction may become active only after discharging to V=0 or to negative voltages. Whether this is necessary, it will depend strongly on the repair driving force of the graphene sheets, though. This means, that whether the primary coupling to GOpr survives is an open question as the driving force for reinstalling intact graphene sheets is large. Thus, the acylation may be an intermediate stage which switches over to a molecular coupling reaction or, in other words, to an oligomerisation. This would explain why the in situ layer separations during the activation and redox cycles remain at about 12 Å but reduce to about 6-8 Å after post mortem washing.

The formation of oligo and polycarbonates has also been reported repeatedly as essential step in building up cathodic solid electrolyte interfaces in Li-ion batteries. During anodic sweeps these oligo- and polymeric precipitates are being converted into anionic species which, in Li-batteries, are being lithiated [153].

It can also not be excluded that in the course of both positive and/or negative activation epoxy groups may become hydroxyl functions which consecutively undergo ether formation.

Attachment of Si-O functions belongs to this class of reactions and has been successfully demonstrated only recently [154] (Scheme 8):
Other reactions with hydroxyl and/or carboxyl groups have been reported such as carbamate and amide functionalizations [155] (Scheme 9):

**Scheme 8:** Representation of the preparation of POSS-modified GOpr taken from [154].

**Scheme 9:** Taken from [155] showing a) the functionalization process of GO with carbamate and amide functionalities and b) FT-IR spectra of GO and of the functionalized GO.
Another route utilizes the epoxy groups through amination forming amine links and hydroxyl groups which has been used to functionalize GO into GO-silicon oxide composites [156, 157] (Scheme 10):

**Scheme 10:** Covalent functionalization of epoxy groups of graphene oxide sheets by silane groups taken from [156].

Both, hydroxyl and epoxy groups are being reduced and refunctonalized by a reductive treatment with hydrazine and concerted coupling to diazonium cations [156, 158] (Scheme 11):
Scheme 11: Covalent functionalization of reduced graphene oxide with sodium dodecylbenzenesulfonate taken from [156].

These different reaction scenarios demonstrate convincingly the huge potential of GO and GOpr as well as of graphene for a large variety of catalytically and/or electrocatalytically driven reactions on these two dimensional substrates.
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