



In-situ XRD and dilatometry investigation of the formation of pillared graphene via electrochemical activation of partially reduced graphite oxide



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ABSTRACT

The electrochemical activation reaction observed for oxygen rich graphitized carbons is known to irreversibly modify the properties of the material. After activation such carbons show for example an enhanced ion storage capability. In case of partially reduced graphite oxide (GOpr) this resulted in a specific capacitance of up to 220 Fg⁻¹ and 300 Fg⁻¹ using an aprotic and a lithium electrolyte in acetonitrile, respectively. In the present study this activation mechanism is investigated by means of in-situ XRD and in-situ dilatometry in more detail. The combined information of the two in-situ techniques reveals the electrochemical activation to modify the interlayer distance of GOpr irreversibly. The resulting interlayer spacing of anodically activated GOpr was measured to be up to 14.7 Å in the discharged state, which equals slit-like micropores of up to 12.3 Å. This observed pillaring of the graphene layers to a distinct distance was traced down to a consolidation reaction within the first polarization of the electrode material. Combining the results from the in-situ characterizations with previous results from literature a reaction mechanism for the electrochemical activation reaction is proposed. These findings explain the achieved specific capacitance of GOpr and reveal a viable synthesis route to pillared graphene which can be useful for various applications.

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1. Introduction

Pillaring of layered materials has been a prominent target of functionalization of 2D-objects, for decades. Pillared clays have gained widespread industrial usage and are being produced on large scale, these days [1,2]. Layered double hydroxides, perovskites and hydrotalcites have been targeted for staging modifications by different research groups in order to design new nano structures as well as hierarchical materials and to apply them, for example, for catalysis or for sensing [3–5].

Recently graphene [6] – the 2D building block of graphite – and graphene based structures have drawn much attention [7]. Its theoretical specific surface area (SSA) of 2630 m²g⁻¹ [8,9] makes it an ideal candidate for surface demanding applications like hydrogen storage [10], electrochemical double layer capacitors (EDLCs)

[11] or lithium batteries [12], amongst others. However, in order to utilize the full theoretical SSA a stage design of graphene based materials is either advantageous or even necessary.

First approaches to synthesize porous graphene structures were based on the intercalation of graphite and are legion, today. They date back to the 19th century utilizing metals, cations or smaller anionic groups like sulfate and perchlorate accompanied by redox reactions. A patent from 2002 by W. Goddard et al. [13] describes the intercalation of alkali metals into graphite in order to irreversibly increase the interlayer distance up to 12 Å to yield pillared graphite suitable for hydrogen storage.

Following this approach, computational studies revealed that a most favorable pillared graphene structure may be achieved by carbon nanotube based pillars between the graphene layers [14–16]. Such structure would not only benefit from tunable pore sizes [16] but would also provide improved electrical [17] and thermal [18] conductivity as well as enhanced mechanical stability [19]. However, the synthesis of such pillared graphene structures is challenging and first experimental results were not very promising [20], even though a recent patent [21] claims an optimized synthesis route based on intercalation of fullerenes.

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Another way of synthesizing pillared graphene is to start from graphite oxide and use chemical linkers to set a fixed separation of the graphene oxide layers. Examples of such pillared carbons are silylated graphite oxide 12–13 Å [22], graphene oxide linked with benzene-1,4-diboronic acid 8–11 Å [23], graphene oxide linked with boronic acids 11 Å [24], reduced graphene oxide with nanodiamond spacers [25] and cross linked thermally exfoliated graphene [26]. Even though these synthesis routes resulted in pillared graphene structures with interlayer distances of up to 13 Å, due to the use of graphene oxide these materials are non-conductive and, hence, only suitable for gas storage but not for EDLC application.

In contrast to these new chemical pillared carbons the typically pillared graphene used as EDLC electrode is based on graphene composites with hetero structures like metal nanoparticles [27], carbon black [28] or carbon nanotubes [29]. Even though such composites were reported to reach specific capacitances of up to 200 Fg⁻¹ in the organic electrolyte tetraethylammonium tetrafluoroborate in propylene carbonate (TEABF₄/PC) [29], there was no proof of a layered structure with distinct interlayer distance.

Recently our group demonstrated that the electrochemical activation of partially reduced graphite oxide (GOpr) leads to an irreversible increase in interlayer distance [30]. Such electrochemical activation reaction was first introduced by Takeuchi et al. [31,32] for KOH activated calcined petroleum cokes and pitches. By employing these materials as EDLC electrodes they observed the first polarization to be some kind of formation step, yielding an increase in specific capacitance. This formation/activation cycle was described as an electric field induced intercalation of cations and anions, respectively, with solvent. The starting voltage of intercalation measured in a full cell setup was found to depend on the employed solvent and the interlayer distance of the graphitized carbon, which ranged from 3.6 to 3.8 Å [32]. Further characterizations revealed the electrochemically activated electrodes to have a slightly increased interlayer distance [31]. In case of GOpr a sample with an initial interlayer spacing of 4.4 Å (GOpr44) was chosen, as GOpr44 has both in-plane epoxide and hydroxide functionalities and it exhibits the smallest activation potential [33]. Due to the electrochemical activation the initial interlayer distance of 4.4 Å was increased to 13.0 Å using the organic electrolyte tetraethylammonium tetrafluoroborate in acetonitrile (TEABF₄/AN) [30]. This irreversible change in interlayer spacing was verified by in-situ X-ray diffraction measurements. Previous characterizations of GOpr already indicated the activation reaction to promote an ion insertion process in-between the graphene-like layers for organic electrolytes [33–35], diluted ionic liquids [36] and lithium electrolytes [37].

The present study does focus on a complementary in-situ XRD and in-situ dilatometry investigation of the electrochemical activation reaction of GOpr. In-situ XRD allows tracing the electrochemically triggered changes in interlayer spacing, like the insertion of organic ions into graphite [38]. In addition in-situ dilatometry maps the electrochemical induced increase in electrode height which facilitates the study of charge induced morphology changes with high accuracy [39,40]. Combining the information of both in-situ techniques, an elaborated model of the electrochemical activation reaction will be developed to explain the formation of electrochemically pillared graphene.

2. Experimental

2.1. Material synthesis

Partially reduced graphite oxide (GOpr) with an interlayer distance of $d_{001} = 4.43 \text{ \AA}$ (GOpr44) was synthesized from the synthetic flaked graphite (SFG6, TIMCAL Ltd., Bodio, Switzerland)

by chemical oxidation using a modified Brodie method [41,42] followed by thermal reduction at 240 °C under argon. A detailed description of the synthesis is given in ref. [33,43]. The chemical composition of GOpr44 was determined by elemental analysis to be approximately C₈O_{1.13}(OH)_{0.33} [33]. GOpr44 was processed to polytetrafluoroethylene (PTFE) bound composite electrodes consisting of 80 wt.% GOpr44, 10 wt.% carbon black (SuperP, TIMCAL Ltd., Bodio, Switzerland) and 10 wt.% PTFE with a thickness of 200 and 500 μm for the dilatometry and XRD measurement, respectively.

2.2. In-situ XRD

The in-house designed and custom made two-electrode electrochemical cell described in Ref. [44] was employed for the in-situ XRD measurements. It is based on a two-electrode setup with an approximately 30 times oversized counter electrode (CE) resulting in a potential drift of less than 200 mV. 25 μm thick aluminum windows were used for the beam inlet and outlet and additionally sealing the cell from atmospheric moisture. Prior to the in-situ XRD measurement the fully assembled cell was dried for 12 h at 120 °C at 10³ Pa and filled with the organic electrolyte 1 M TEABF₄/AN in an argon containing glove box with less than 1 ppm H₂O and O₂. The in-situ XRD characterization was performed at the Materials Science beamline (MS-X04SA) of the Swiss Light Source (SLS) of the Paul Scherrer Institute (PSI) [45], utilizing an X-ray wavelength of 0.07085 nm. An automatic sample changer [46] connected to a galvanostat (BatSMALL, Astrol Electronic AG, Switzerland) was employed for the measurements, allowing to continuously perform the electrochemical characterization while the WEs of the test cells were alternately investigated by XRD. The electrochemical activation of GOpr44 was initialized by cyclic voltammetry employing 1 M TEABF₄/AN with different vertex potentials and a sweep rate of 0.06 mVs⁻¹.

2.3. In-situ dilatometry

For the dilatometric characterization an in-house developed three electrode cell was employed which is described in full detail in ref. [47]. PTFE bound activated carbon (YP17 Kuraray Chemical Co., Japan) was employed as counter and quasi-reference electrode (QRE). The potential of the QRE was determined to be 3.0 ± 0.05 V vs. Li/Li⁺ in the 1 M TEABF₄/AN electrolyte [48]. In order to have a fixed reference level for the electrode dilatation a glass frit (porosity P2: 40–100 μm) combined with a cellulose-based paper separator (Maxwell Technologies, Switzerland) was used as the separator. The GOpr44 electrodes were compressed between the glass frit and a movable Ti plunger with an additional weight load of 10 N. Prior to the experiments the assembled dilatometry cell was dried at 120 °C under vacuum of 10³ Pa for 12 hours. 1 M TEABF₄/AN was introduced into the electrodes in an argon filled glovebox containing less than 1 ppm H₂O and O₂. Cyclic voltammetry was carried out using an IME6e potentiostat (Zahner-Elektrik GmbH & Co. KG, Germany). The sweep rate was kept constant for all measurements at 1 mV/s. Any expansion during the electrochemical experiments was recorded by a DP1S displacement transducer (Solartron Metrology, UK), with an accuracy of 60 nm. During the measurements the dilatometer cell was kept at a constant temperature of 20 °C using a temperature chamber (Binder, Germany).

2.4. Post mortem analysis of the electrodes

After the electrochemical characterization the electrodes were disassembled from the electrochemical cells and cleaned from residual electrolyte using a soxhlet reactor with acetonitrile as the extraction solvent for at least 6 h [49]. The electrodes were then further investigated by means of SEM (FE-SEM Ultra55 microscope

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