



Ion intercalation into HOPG in supercapacitor electrolyte – An X-ray photoelectron spectroscopy study

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ABSTRACT

Highly oriented pyrolytic graphite electrodes were electrochemically treated in electrochemical double layer capacitor electrolyte and studied by X-ray photoelectron spectroscopy (XPS). The used electrolyte was 1 M tetra-ethyl-ammonium tetra-fluoroborate (Et_4NBF_4) dissolved in propylene carbonate. Intercalation of the ions into the graphitic host structure results in core level shifts of the XP-spectra. The spectra of the host and the intercalating species shift towards higher values of binding energy for the negatively and towards lower values for the positively polarized electrodes, which is ascribed to the Fermi level shifts of the intercalation compound. The reversibility of ion insertion is quantified by deconvolution of the XP signals and is shown to be less for the Et_4N^+ cation than for the BF_4^- anion.

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1. Introduction

Electrochemical double layer capacitors (EDLCs) utilize activated carbon (AC) electrodes providing a high surface area of $>1000\text{ m}^2/\text{g}$ for charge storage in the electrochemical double layer. The electrolyte consists of quaternary ammonium salts like tetra-ethyl-ammonium tetra-fluoroborate (Et_4NBF_4) dissolved in organic solvents, such as propylene carbonate (PC) or acetonitrile (AN). Ideally, charge storage occurs entirely via electrostatic forces at the electrode/electrolyte interface [1–4]. However, a number of studies concerned with the aging of the devices have shown that insertion of ions as well as electron transfer reactions can also occur, especially at elevated cell voltages [5–7].

Electron transfer reactions can result in the formation of gaseous, solid or soluble degradation products from electrolyte decomposition. X-ray photoelectron spectroscopy (XPS) was shown to be a powerful tool to determine changes in the chemical composition of aged electrodes proving that blockage of porosity by solid degradation products is one important issue for aging of EDLCs [5–7]. Recently, Ruch et al. applied XPS to investigate a possible dependence of cell voltage and polarity on the composition of solid degradation products formed in $\text{Et}_4\text{NBF}_4/\text{AN}$ electrolyte showing

that decomposition of the used poly(tetra-fluoro-ethylene) (PTFE) binder on the negative electrodes and blockage of porosity caused by oxidation of AN in combination with the formation of fluorinated carbon species on the positive electrodes occur at elevated cell voltages [8].

Besides decomposition of the electrolyte, electrochemical ion insertion into carbon electrodes is suggested to affect the aging of EDLCs [9,10], however, it has also been reported that this process could enhance the charge storage capability [11]. The electrochemical intercalation of R_4N^+ and BF_4^- ions into graphite has been studied by cyclic voltammetry (CV) [12], thermogravimetry [13], *ex situ* X-ray diffraction (XRD) [13,14] *in situ* atomic force microscopy (AFM) [15], *in situ* Raman spectroscopy [16] and *in situ* XRD [10].

To date, however, no XPS study about these intercalation processes is available, although, this method is expected to be very sensitive regarding the detection and quantification of electrochemically intercalated species in the topmost layers of the electrodes. For instance, XPS has been used to study the sodium and lithium intercalation into V_2O_5 films [17,18] as well as barium [19] or lithium ion [20] intercalation into graphite. Besides reduction of the V^{5+} ions in V_2O_5 caused by charge transfer from the alkali metal to the host structure, Fermi and core level shifts due to charge transfer were observed. XPS was also used to study the doping of single-wall carbon nanotubes (SWCNTs) by strong Brønsted acids [21]. The authors observed p-type doping of the SWCNTs leading to a general broadening and a shift of the C 1s spectra towards lower binding energies. Stability and amount of change of Fermi level position was dependent on the chosen acid. Preparation of the intercalation compounds (ICs) mentioned above was

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Table 1
Elemental composition of the HOPG surfaces after electrochemical preparation determined from the high resolution XP-spectra of each element.

Name	Reference	$E = -2.3$ V charged	$E = -2.3$ V discharged	$E = 2.0$ V charged	$E = 2.0$ V discharged
B (at.%)	0.3	–	0.3	2.3	1.4
C (at.%)	96.7	89.3	89.0	81.0	85.4
F (at.%)	1.4	3.4	2.1	8.1	5.9
N (at.%)	0.2	1.1	1.3	1.0	1.3
O (at.%)	1.4	6.2	7.3	7.6	6.0

either performed *in situ* in the ultra high vacuum system or under protecting atmosphere by evaporation or liquid phase reaction with the intercalant.

Electrochemical ion intercalation is described in few XPS studies. Momose et al. observed Fermi and core level shifts towards higher energies caused by Li^+ intercalation into silver-graphite electrodes [22]. Światowska-Mrowiecka et al. reproduced the reduction of V^{5+} to V^{4+} caused by charge transfer from the 2s level of intercalated Li to the empty V 3d level [23]. To our knowledge only one XPS study of electrochemical anion intercalation has been published so far [24]. The authors intercalated perchlorate ions from aqueous solution into highly oriented pyrolytic graphite (HOPG) and observed species at lowered binding energies in all XP signals corresponding to the formed IC (Cl 2p, O 1s, C 1s). This observation was also explained by an energy shift of the Fermi level.

The aim of the present study is to investigate intercalation in HOPG following electrochemical treatment in non-aqueous EDLC electrolyte ($\text{Et}_4\text{NBF}_4/\text{PC}$) using XPS. HOPG was chosen as a model electrode for sp^2 hybridized carbons utilized in EDLCs. Particularly high electrochemical potentials were applied for preparation of the electrodes in order to infer the stability of the electrolyte. Intercalation of the ions results in shifts of binding energy explainable by Fermi level shifts. The observations are of importance for XPS data interpretation, especially when conclusions have to be drawn regarding the composition of intercalation compounds and electrochemical film formation on graphite in which intercalation of ions is also expected to occur.

2. Experimental

HOPG was used as a working electrode in an electrochemical cell in which the counter and reference electrodes consisted of PTFE-bound activated carbon. The potential of the used carbon reference electrode (CRE) has been determined to be +3 V vs. Li/Li^+ reference electrode [25]. The electrolyte was 1 M Et_4NBF_4 salt dissolved in PC. All materials were dried at 120 °C under a vacuum better than 10^3 Pa for at least 24 h. Assembling of the cell and electrochemical preparation was performed in an argon filled glove box with <1 ppm O_2 and H_2O . The HOPG was cleaved with adhesive tape prior to each electrochemical experiment. For comparison of the charged (intercalated) and discharged (de-intercalated) states the electrodes were either removed from the electrolyte at the corresponding preparation potential or after scanning back to $E = 0.0$ V ($dE/dt = 10$ mV/s). Polarization time was set to 30 min. After electrochemical preparation, the HOPG electrode was removed from the electrochemical cell under potential control, rinsed with PC, blown dry with N_2 gas, and, subsequently, investigated by XPS. XPS measurements were performed using a VG ESCALAB 220iXL spectrometer using Mg $K\alpha$ radiation for excitation (constant analyzer energy (CAE) mode, 20 eV pass energy, power 200 W). Quantitative analysis was performed using Scofield's excitation cross-sections [26].

For evaluation of the efficiency of the rinsing procedure one HOPG sample was exposed to the electrolyte in the electrochemical cell without polarization, rinsed with PC, blown dry, and subsequently, investigated with XPS (Table 1, reference). The carbon

content on the reference sample was determined to be 96.7 at.%. Another set of reference data has been taken from the Et_4NBF_4 salt prepared on a copper foil by evaporation of the solvent.

3. Results and discussion

3.1. Electrochemistry

The recorded current density potential curves (CV) of HOPG in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte are depicted in Fig. 1. Starting from $E = 0.0$ V for the negative potential sweep the reduction current starts to significantly increase at potentials below $E = -2.0$ V (Fig. 1a) showing a maximum of -0.025 mA/cm² at $E = -2.2$ V (C1). This behavior is in good agreement with our previous findings on HOPG and graphite powder electrodes [10,15]. From these investigations it is known that the corresponding process is mainly insertion of Et_4N^+ cations together with solvent molecules between the graphene sheets. At $E = -2.4$ V (C2) a second maximum of current density of -0.025 mA/cm² occurs which can be attributed to further intercalation. In parallel to intercalation

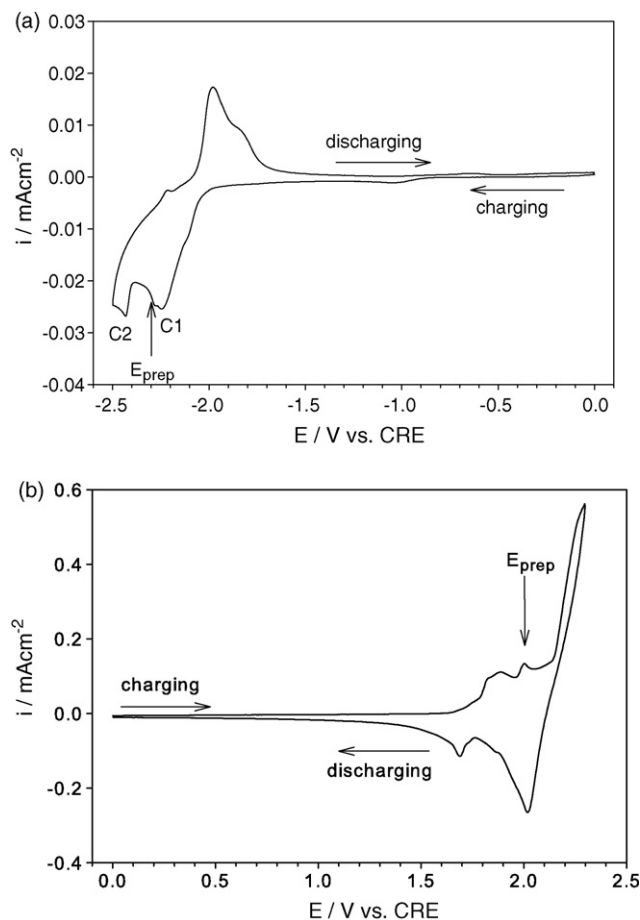


Fig. 1. CVs of HOPG in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$; $dE/dt = 10$ mV/s, (a) cathodic scan; (b) anodic scan; scan directions and preparation potentials as indicated.

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