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In situ atomic force microscopy study of dimensional changes during Li^+ ion intercalation/de-intercalation in highly oriented pyrolytic graphite

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Abstract

The knowledge of dimensional changes during the electrochemical intercalation of Li^+ ions in a secondary Li^+ ion battery is of fundamental importance for a comprehensive understanding of the degradation mechanism of the negative electrode. In this work in situ electrochemical atomic force microscopy was used to measure the step height change during the intercalation/de-intercalation of Li^+ into the graphene layers of highly oriented pyrolytic graphite (HOPG). During the first intercalation/de-intercalation cycle an irreversible increase of graphene layer spacing of about 24 ± 7% was evidenced. During consecutive repetitive scanning between 3 and 0.005 V vs. Li/Li^+, a reversible change of the step height of the HOPG of about ±17% could be observed in 1 M $LiClO_4$ in ethylene carbonate and dimethyl carbonate in a 1:1 (w/w) ratio. The statistical procedure to determine the height changes introduced in the present study is superior to the evaluation of single line scans.

Keywords: In situ atomic force microscopy; Highly oriented pyrolytic graphite; Graphite; Lithium intercalation; Organic electrolyte; Solid electrolyte interphase

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1. Introduction

The demand for lithium ion secondary batteries is continuously growing and the research and development work for future applications is still ongoing. For lithium ion secondary batteries, carbonaceous materials are the most adequate hosts for Li^+ at the negative electrode. During the first charge half-cycle, a passivation film is formed by decomposition of the electrolyte solution [1], which covers the surface of the carbon. This film (solid electrolyte interphase, SEI) prohibits further electrolyte decomposition but its formation consumes charge. The SEI is permeable for Li^+ ions, so that intercalation/de-intercalation into e.g. the highly oriented pyrolytic graphite (HOPG) planes/defects can occur during the charge/discharge process.

Several research groups have investigated the morphology of the SEI by in situ electrochemical atomic force microscopy (EC-AFM) in various electrolyte salts and solvents, both at room temperature [2–4] and at elevated temperature [5]. Koltypin et al. [6] observed topographic and morphological changes on synthetic graphite powder during SEI formation and for the different insertion stages of Li^+. However, the expansion of the graphene planes during the intercalation of Li^+ was never quantified by in situ EC-AFM.

Song et al. [7] performed quantum mechanical calculations and determined a change of interlayer distance

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from an ABAB… HOPG-structure (layer distance of 3.355 Å) to a fully intercalated LiC_6 structure A···Li···A···Li···A (layer distance of 3.706 Å) of 10.46%. For this process, Dahn et al. [8] showed by in situ X-ray diffraction on synthetic graphite powder an expansion of ∼10.2%. Besenhard et al. [9] observed by in situ dilatometry a swelling on a HOPG sample of 150% in 1 M $LiClO_4$ in ethylene carbonate (EC)/1,2-dimethoxyethane (DME) (1:1 by volume). In this setup, the edge planes of the HOPG sample were in contact with the electrolyte. Ohzuku et al. [10] showed with the same type of measurement on a natural graphite powder a swelling of about 100% in 1 M $LiClO_4$ in propylene carbonate (PC)/DME (1:1 by volume). Winter et al. [11] observed by dilatometry on synthetic graphite a swelling of about 10% in 1 M $LiN(SO_2CF_3)_2$ in EC/dimethyl carbonate (DMC) (1:1 by volume) and a swelling of >700% in 1 M $LiN(SO_2CF_3)_2$ in PC.

The possibility to determine dimensional changes of HOPG by atomic force microscopy also on a local scale was demonstrated previously by Alliata et al. [12] during anion intercalation processes in aqueous electrolyte. However, in contrast to the above approach [12], the formation of the SEI in organic electrolyte before and during Li^+ intercalation significantly obscures the topography of the substrate and renders the direct measurement of dimension changes almost impossible. According to earlier in situ AFM measurements [13] the thickness of the SEI is in the order of 25 nm, which is significantly larger than the expected step height changes introduced by Li^+ intercalation.

The statistical procedure introduced in the present communication to determine the height change on rough surfaces is superior to the evaluation of single line scans.

In the present investigation, in situ EC-AFM has been used to study the intercalation/de-intercalation process of Li^+ on HOPG in EC and DMC in a 1:1 (w/w) ratio with 1 M $LiClO_4$ electrolyte. This method allows observation and analysis of local changes of the graphene interlayer distance of HOPG occurring during the intercalation/de-intercalation process.

2. Experimental

In situ EC-AFM measurements were performed on a Molecular Imaging (MI) (AZ, USA) PicoLE Scanning Probe Microscope (SPM). The calibration of the scanner was performed with a height calibration grating TGZ01 −25.5 nm (NT-MDT, Moscow, Russia). The SPM measurements were performed in contact mode at low constant force with a 100 μm scanner and a scan rate of 1 Hz. The cantilever used in the present study was a contact Si_3N_4 type FM (Nanosensors™), with a force constant of 0.6 N/m. The scratching behavior from the tip of the SEI morphology was accepted and did not affect the measurement. Hirasawa et al. [14] pointed out this behavior of the contact mode and suggested to use tapping mode. The tapping mode (also known as intermittent- or acoustic mode) showed in our study more instability during scanning, and the same effect of scratching was observed.

The in situ EC-AFM measurements were performed in a "flow through" type glove box (MI) purged with argon (Ar). A Michell Instruments dew point sensor was used to monitor H_2O concentration in the glove box. During the measurement the dew point was constantly below −35 °C.

Electrochemical experiments were performed with a PicoStat (MI) potentiostat and were carried out in a home-made electrochemical cell (see Fig. 1). The cell consists of two parts of poly(ether ether ketone) polymer (PEEK™). An open area on the upper part provides space for two pieces of lithium foil (Alfa Aesar, purity 99.9%), which are contacted by two Ti wires and used as counter and reference electrode. All potentials are quoted with respect to the Li/Li^+ reference electrode. The separation of the two cell parts is provided by an ethylene propylene diene monomer (EPDM) O-ring (d = 15.6 mm). This O-ring is placed on the substrate and confines the active surface of 1.91 cm^2.

A HOPG crystal (Advanced Ceramics Corporation, Lakewood, OH, USA) type ZHA was used as working electrode. Before use the HOPG crystals were always heated at 80 °C for 2 days under vacuum, then stored under Ar and cleaved with adhesive tape. The electrode had a thickness of 1.2 mm and a length of 2 cm.

The height of a HOPG step was obtained from the AFM image by calculating the difference between the mean values of the heights measured by an average of five areas on different locations on the steps for different images at different potential.

Cyclic voltammograms were performed in the potential window from 3 to 0.005 V vs. Li/Li^+ with a scan rate

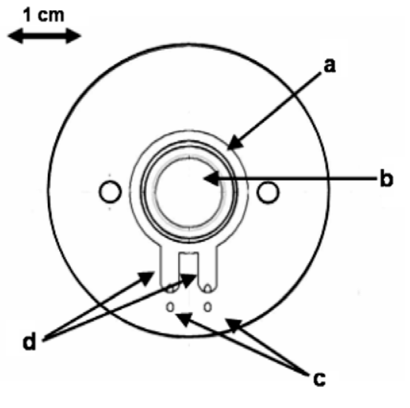

Fig. 1. Sketch of the used in situ AFM cell. (a) EPDM O-ring, (b) HOPG (working electrode), (c) lead through for Ti wire to contact the Li-foil, (d) space for the Li-foil (reference and counter electrode).