

Degradation Mechanism of Graphite Negative-electrodes in LiPF₆-based Electrolyte at Higher Potential Region

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Introduction

Graphite and LiPF₆ are widely used as negative-electrode and Li salt in lithium-ion batteries, respectively. Consequently, it is very important to investigate the degradation mechanism of graphite in LiPF₆-based electrolyte. While changes in the surface morphology of the highly oriented pyrolytic graphite (HOPG) basal plane at higher potential region in LiPF₆-based electrolyte were previously reported using scanning probe microscope, consistent results were not obtained; one reported the graphite exfoliation and the other reported surface film formation.^{1,2} In this study, we used the HOPG basal plane as a model electrode, and observed changes in the surface morphology of it using electrochemical atomic force microscope (AFM). We also investigated the surface crystallinity using *in situ* Raman spectroscopy. X-ray photoelectron spectroscopy (XPS) and Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) were used to characterize the composition of a solid electrolyte interphase (SEI). Based on these investigations, we discuss the degradation mechanism of graphite negative-electrodes in LiPF₆-based electrolyte at higher potential region.

Experimental

Immediately prior to each experiment, the HOPG basal plane (Momentive, ZYH, mosaic spread: $3.5 \pm 1.5^\circ$) was freshly cleaved with an adhesive tape, and served as a working electrode. The electrolyte solution was 1 M LiPF₆ dissolved in a 1:1 (by volume) mixture of ethylene carbonate and diethyl carbonate (Kishida Chemical). The counter and reference electrodes were Li foil. All potentials in the text reflect V versus Li⁺/Li.

Electrochemical AFM observations were performed in a conventional contact mode with a three-electrode electrochemical cell. All AFM observations were carried out at a room temperature of ca. 25 °C in an Ar-filled glove box with a dew point of lower than -80 °C.

The electrochemical Raman cell with airtight structure and optically flat Pyrex[®] glass was used.³ The HOPG basal plane was irradiated with a He-Ne laser beam (632.81 nm line, 50 mW) through the optical window.

The HOPG electrodes after the electrochemical experiments were washed with dimethyl carbonate in an Ar-filled glove box, and were sealed in a vessel to be transferred into XPS sample chamber without being exposed to air. After the XPS measurements, they were set in an ATR accessory with a hermetically-sealed structure under Ar atmosphere to obtain FTIR-ATR spectra without exposure to air.

Results and Discussion

No noticeable change in surface morphology of the HOPG basal plane electrode was observed at 3.0 V within 12 h. AFM observations under potential control showed

that a number of pits and fine particles formed on the terrace of the HOPG basal plane at around 1.75 and 1.5 V, respectively. We first elucidate changes in the surface morphology of the graphite in LiPF₆-based electrolyte at higher potential region, where the electrochemical intercalation of Li⁺ does not take place; pit formation (graphite exfoliation) and surface film formation successively occur with decrease in the electrode potential.

In Raman spectra, G band peak was observed at around 1580 cm⁻¹ at a potential range from an open circuit potential of about 3 V to 1.75 V regardless of storage time. After storage at 1.5 V for 24 h, two peaks newly appeared at around 1330 and 1620 cm⁻¹, which assigned to D and D' band, respectively, while these peaks were not observed immediately after potential-step to 1.5 V. These two peaks appear in the case of imperfections in carbonaceous materials. Therefore, the surface crystallinity of the HOPG basal plane should lower with storage at 1.5 V. After the electrode potential was back to 3.0 V, the ratio of D band to G band and full width at half maximum of G band were decreased, which indicates that the surface crystallinity of the HOPG basal plane should recover at 3.0 V in LiPF₆-based electrolyte. Therefore, change in the surface crystallinity between 3.0 and 1.5 V is quasi-reversible.

The results of XPS and ATR-FTIR reflect that LiF and phosphates lie on the surface of the SEI formed at around 1.5 V on graphite negative-electrode in LiPF₆-based electrolyte and that carbonates and phosphates are contained in the interior of the SEI.

The pit formation leads to the missing of active materials in real batteries. The particle formation and subsequent growth of the SEI cause a decrease in the discharge capacity, and an increase in internal resistance, respectively. In addition, quasi-reversibility of the surface crystallinity indicates that the degradation of graphite is hard to occur beneath the surface. Therefore, the degradation of graphite negative-electrode at higher potential region in LiPF₆-based electrolyte would occur at the surface of graphite.

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