

In Situ Investigation of Electrochemical Lithium Intercalation into Highly Oriented Pyrolytic Graphite (HOPG)

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Introduction

Two mechanisms for the SEI film formation on graphite are commonly adopted to explain the experiment results. One is that the solvent can co-intercalate into the graphite to form a ternary graphite intercalation compound $[\text{Li}(\text{solv})_y\text{C}_n]$ and the decomposition of intercalated solvent forms a SEI film. Another scenario is that the SEI film is formed directly by the decomposition solvent. Two mechanisms can be distinguished by the information of SEI formation on the base section and the edge section because only edge section allow the electrolyte to co-intercalate. Graphite power electrode is not suitable for this kind study because the contributions of both basal and edge planes could not be separated. Highly oriented pyrolytic graphite (HOPG) has a highly anisotropic structure with well-defined basal and edge plane, which can be used for the mechanism of SEI film formation.

To directly probe whether the interface formation processes via a ternary GIC, the thickness and the surface topography of HOPG were monitored by diatometry and electrochemical scanning tunneling microscopy (STM), respectively. However, these unambiguous results could not resolve the detailed reaction mechanism. The solvent intercalation into graphite can be monitored by the intrinsic resistance across the based section and the edge section of HOPG because the solvent intercalation from edge side of HOPG will change the electric resistance. The in situ intrinsic resistance measurement and electrochemical impedance spectroscopy (EIS), which are powerful techniques to investigate the SEI formation [1-5], is used to monitor the SEI formation on the basal and edge plane of HOPG in different electrolytes and temperature, as well as their cycling stability.

Experimental

Electrochemical measurements were carried out using conventional three-electrode cells. A block of HOPG (Advanced Ceramics Cooperation, Lakewood, OH, USA) was cut into small rectangular piece (6 mg). The in-situ intrinsic resistances of HOPG across the basal section and the edge section were measured by DC current or special EIS protocol. The in-situ intrinsic resistance of HOPG in two direction was measured by the two voltage induced from two flowing DC current (1.0 mA) when the HOPG anode is charged/discharged through Cu wire. Two lithium foils were used as both counter and reference electrodes. Two electrolytes (1.0 M LiPF_6 dissolved in 1:1:3 PC:EC:DMC and 4:1:3:2 EC:PC:DMC:EMC respectively) are used to study the influence of solvent co-intercalation on SEI film formation. Charge (lithium intercalation) and discharge

(lithium extraction) characteristics were measured using an Arbin (College Station, TX) automatic battery cycler. The special EIS protocols [2, 3] were used to investigate the degree of solvent intercalation into HOPG. EIS was measured over the frequency range 65 kHz to 1.0 mHz at a potentiostatic signal amplitude of 5 mV, using a frequency response analyzer (Solartron, PRA 1250) and an electrochemical interface (Solartron, model 1286).

Results and Discussion

Figure 1 shows the potential and intrinsic resistances of HOPG across the basal and edge plane during first Li insertion-extraction in EC-PC-DMC-EMC electrolyte. The potential profile of HOPG is quit different from the graphite powder electrode, and more like a coke. The less prominent potential plateau at around 0.7 V is due to the small surface area comparing to graphite powder. The long Li diffusion length due to large HOPG bulk retard the Li_xC_6 stage transformation, result in a smooth decrease in potential profile below 0.2 V and small Li extraction capacity. The intrinsic resistance of basal plane decreases with Li insertion and shows a plateau at potential around 0.7 V. SEI film formation on the basal plane is responsible to this potential plateau. Unlike the intrinsic resistance across basal plane, the intrinsic resistance across the edge section shows an increase at around 0.7 V with some fluctuations, which suggested that electrolyte co-intercalation into HOPG through edge plane. This intrinsic resistance increase of edge section becomes more prominent in EC-PC-DMC (1:1:3) electrolyte due to lower EC content. A semicircle in intrinsic impedance of both basal and edge section appeared at 0.7 V due to the SEI film formation between current collector and HOPG. The performance of HOPG at -30 and $+60$ °C have also been investigated by special EIS and intrinsic resistance measurement.

References

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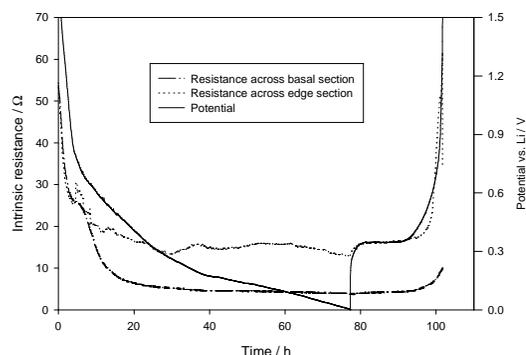


Figure 1. Potential and intrinsic resistance of HOPG electrode during the first lithium insertion-extraction cycle in 1 M LiPF_6 in EC-PC-DMC-EMC (4:1:3:2). Charge-discharge current: 6 mA/g. Current for measuring intrinsic resistance: 1 mA

