



Investigating continuous co-intercalation of solvated lithium ions and graphite exfoliation in propylene carbonate-based electrolyte solutions

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HIGHLIGHTS

- Graphite exfoliation is a problem in propylene carbonate (PC)-based electrolytes.
- Interfacial reactions affecting SEI formation were studied by in-situ AFM and CV.
- No changes were observed over 10 cycles in ethylene carbonate-based electrolytes.
- Overlapping blisters caused graphite exfoliation in PC-based electrolytes.
- PC-solvated Li ions can pass through the blister structures freely.

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ABSTRACT

Forming an effective solid electrolyte interphase (SEI) is a significant issue in lithium ion batteries that utilize graphite as a negative electrode material, because the SEI determines the reversibility of the intercalation and de-intercalation of lithium ions into graphite for secondary batteries. In propylene carbonate (PC)-based electrolyte solutions, ceaseless co-intercalation of solvated lithium ions takes place because no effective SEI is formed. It is indisputable that this continuous co-intercalation leads to graphite exfoliation; however, the reason for this is currently not well understood. In this study, we investigate interfacial reactions that contribute to SEI formation on highly oriented pyrolytic graphite (HOPG) in ethylene carbonate (EC) and PC-based electrolyte solutions by in situ atomic force microscopy. The blisters formed on HOPG after the decomposition of solvated lithium ions within the graphite layers do not change over the course of ten electrochemical cycles in an EC-based electrolyte solution. In contrast, when cycling in PC-based electrolytes, the blisters continually change, and the height at the vicinity of the graphite edge plane increases. These morphological changes are attributed to the continuous co-intercalation of solvated lithium ions in PC-based electrolyte solutions.

1. Introduction

In electrochemical systems, electrolyte solutions generally act as paths that allow ions to flow between the positive and negative electrodes during oxidation and reduction reactions. However, they also play another significant role in lithium ion batteries (LIBs). Commercial secondary LIBs have a high operating voltage because graphite is used as the negative electrode, where the intercalation and de-intercalation of lithium ions take place at extremely low potentials (0.25–0.0 V vs. Li^+/Li) during charge and discharge processes [1–6]. For this reason, even organic electrolyte solutions with wider potential windows than aqueous electrolyte solutions will reductively decompose before the intercalation of lithium ions into graphite negative electrodes can take place [7–9]. In addition, it is easier to intercalate solvated lithium ions

into graphite because of lower activation energy than that of lithium ion intercalation [10–12]. If these reactions occur continually, graphite negative electrodes never allow the intercalation of lithium ions during the charge process. Therefore, it is important to suppress further decomposition of the electrolyte solution and co-intercalation of solvated lithium ions to ensure reversible intercalation and de-intercalation of lithium ions at graphite negative electrodes in LIBs.

Surface films commonly form within/on graphite negative electrodes during the reductive decomposition of organic electrolyte solutions [5–9]. These surface films determine the reversibility of the graphite negative electrodes as they are able to suppress further decomposition of the electrolyte solution and co-intercalation of solvated lithium ions by forming an effective surface film called a solid electrolyte interphase (SEI) [13,14]. An effective SEI will only conduct

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lithium ions, not electrons. Hence, the formation of an effective SEI is considered to be a significant issue at graphite negative electrodes. Thus, electrolyte solutions must not only act as ion conduction pathways, but also as SEI-forming reagents in order to ensure reversible intercalation and de-intercalation of lithium ions at the graphite negative electrodes in LIBs.

It is well known that the properties of the SEI are greatly dependent on the type of organic solvent used [15,16]. Ethylene carbonate (EC)-based solutions have been most widely used as electrolytes in LIBs owing to its outstanding SEI-forming abilities [7–9,17–19]. On the other hand, continuous co-intercalation and decomposition reactions of solvated lithium ions take place without the formation of effective SEI in propylene carbonate (PC)-based electrolyte solutions [15,16,19]. Consequently, graphite negative electrodes show good reversibility (lithium intercalation and de-intercalation) in EC-based electrolyte solutions but irreversibility (graphite exfoliation) in PC-based electrolyte solutions. However, EC is also co-intercalated with lithium ions into graphite negative electrodes at about 1 V vs. Li^+/Li before the intercalation of unsolvated lithium ions, in the same manner as the co-intercalation of PC-solvated lithium ions. After this, reductive decomposition products are formed within the graphite layers, but there are significant differences between the subsequent reactions in EC- and PC-based electrolyte solutions, as mentioned above. This indicates that the decomposition products within the graphite layers play a significant role in suppressing further co-intercalation of solvated lithium ions. Indeed, surface decomposition reaction that form surface film on graphite take place after the suppression of the co-intercalation reaction [18,20]. Therefore, the co-intercalation of solvated lithium ions must be suppressed first in order to allow completion of SEI formation [21–23].

SEI at graphite negative electrodes have been investigated by various in situ techniques, including in situ atomic force microscopy (AFM), and in situ Fourier transform infrared spectroscopy (FTIR), which are powerful tools for investigating the SEI formation process and decomposition products [16–18,24,25]. Additionally, the reason for graphite exfoliation in PC-based electrolyte solutions has been explained using steric hindrance and gas evolution models [16,19,26–29]. There is no doubt that continuous co-intercalation reactions cause graphite exfoliation. However, the reason for continuous co-intercalation reactions at graphite negative electrodes in PC-based electrolyte solutions is not clearly understood. In this study, we used fast cyclic voltammetry (CV) scan rates of 5 and 10 mV s^{-1} and investigated the SEI formation process via in situ AFM to understand interfacial reactions between graphite and PC-based electrolyte solutions. In addition, intercalation and de-intercalation reactions into/from graphite layers were investigated using in situ Raman spectroscopy of graphite during oxidation and reduction in a PC-based electrolyte solution.

2. Experimental

Electrochemical properties were investigated by CV in either a 1:1 (by volume) mixture of EC and diethyl carbonate (DEC) (EC + DEC) or PC, with both solutions containing 1 mol dm^{-3} LiClO_4 . CV was carried out to investigate the effect of scan rate at 0.5 and 10 mV s^{-1} , respectively, with a laboratory-made three-electrode cell [30]. Highly oriented pyrolytic graphite (HOPG) was used as a working electrode. Lithium foil was used for reference and counter electrodes.

A specially fabricated three-electrode cell was used for in situ AFM [31]. HOPG was used as a model electrode that allowed nanoscale changes to be observed due to its flat surface. Morphological changes on the HOPG basal plane were observed during CV at fast scan rates (5 and 10 mV s^{-1}). Lithium foil was used for reference and counter electrodes. EC + DEC or PC containing 1 mol dm^{-3} LiClO_4 were selected as electrolyte solutions to allow a comparison of their different SEI formation processes. AFM observations were carried out in contact mode using a microscope (Molecular Imaging, PicoSPM) equipped with a potentiostat (Molecular Imaging, PicoStat). All in situ AFM

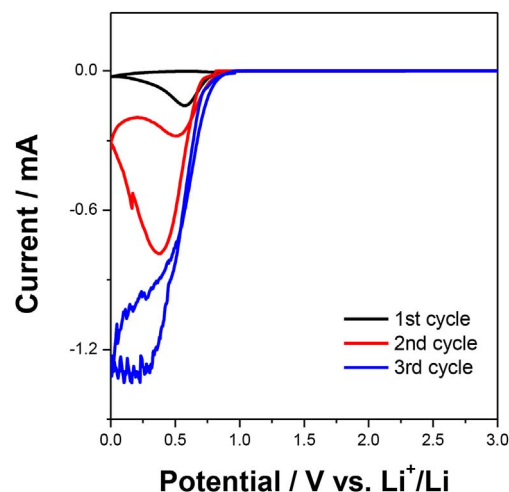


Fig. 1. Cyclic voltammograms of HOPG in 1 mol dm^{-3} LiClO_4/PC . Scan rate = 0.5 mV s^{-1} .

observations were performed in an Ar-filled glove box.

In situ Raman spectroscopy was performed to investigate the intercalation and de-intercalation of solvated lithium ions at the graphite negative electrode in 1 mol dm^{-3} LiClO_4/PC . A three-electrode cell was assembled using a quartz cell in an Ar-filled glove box [4]. HOPG and lithium foil were used as the working electrode and the reference/counter electrodes, respectively. The electrochemical cell was sealed to avoid exposure to air during the in situ Raman measurements. An argon ion laser (514.5 nm line) was scattered on HOPG during CV measurement at 5 mV s^{-1} . Raman spectra were obtained using a triple monochromator (Jobin-Yvon, T64000) equipped with a charge-coupled device detector.

3. Results and discussion

3.1. Effect of CV scan rate on electrochemical properties

Fig. 1 shows cyclic voltammograms of HOPG in 1 mol dm^{-3} LiClO_4/PC at a low scan rate (0.5 mV s^{-1}). A cathodic current was confirmed below 1 V, which corresponds to the co-intercalation of solvated lithium ions into graphite layers. All the solvated lithium ions within the graphite were reductively decomposed during the reduction process, as no anodic peak can be seen. Furthermore, the cathodic current increased with increasing cycle number, which can be attributed to graphite exfoliation increasing the surface area. However, both reduction and oxidation peaks could be seen in 1 mol dm^{-3} LiClO_4/PC at a fast scan rate (10 mV s^{-1}), as shown in Fig. 2a. Although reduction peaks were still observed between 1 and 0.5 V during each of the five cycles, the cathodic current decreased after the first cycle, contrary to the result at the low scan rate. Moreover, a small anodic current was observed that increased in intensity after the first cycle. The results indicated that at the fast scan rate in PC-based electrolyte solutions, reversible reduction and oxidation reactions took place above the lithium ion intercalation/de-intercalation potential. However, on returning to the lower scan rate of 0.5 mV s^{-1} after the five cycles at the fast scan rate, only the cathodic current indicating an irreversible reaction was observed, with the oxidation peak having disappeared (Fig. 2b). It was founded that electrochemical properties are affected by the CV scan rate, and that graphite exfoliation in PC-based electrolyte solutions can be suppressed for five cycles at a fast scan rate without forming an effective SEI. Fig. 2c shows cyclic voltammograms of HOPG in 1 mol dm^{-3} $\text{LiClO}_4/\text{EC} + \text{DEC}$. During the first cycle, three reduction peaks were observed below 1 V, with an additional peak at about 0 V that was attributed to the intercalation of lithium ions. These reduction peaks disappeared after the first cycle. Based on the literature, the

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