

A simple method of electrochemical lithium intercalation within graphite from a propylene carbonate-based solution

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Lithium ions can be intercalated into and de-intercalated from graphite electrochemically. The electrochemical reactions engendering the intercalation and de-intercalation are highly reversible in ethylene carbonate (EC)-based solutions containing lithium salts such as LiClO₄, LiPF₆, and LiBF₄. The discovery of EC-based electrolyte systems is a seminal breakthrough that has enabled the electrochemical preparation of lithium-graphite intercalation compounds (Li-GICs), allowing the use of graphite as a negative electrode in commercially available lithium-ion secondary batteries. Propylene carbonate (PC)-based solutions used in commercially available primary lithium batteries are attractive electrolyte systems owing to their superior ionic conductivities when compared to EC-based solutions at low temperatures. However, Li-GICs are not formed with PC-based systems because these systems fail to yield a solid electrolyte interface (SEI) on graphite in the absence of SEI-forming agents or without the use of concentrated solutions. In this work, we suggest a new method of electrochemical preparation of Li-GICs in PC-based solutions. We could form an effective SEI on graphite by lowering the reaction temperature.

Natural graphite powder (The Kansai Coke and Chemicals Co., NG-7) was used for the charge/discharge tests. The test electrode was prepared by coating a mixture of the graphite powder (90 wt%) and a polymeric binder (10 wt%) on copper foil, as described elsewhere [7]. Four kinds of non-aqueous solutions, containing 1 mol dm⁻³ of LiClO₄, each dissolved in PC, EC, and PC containing 3 wt% of vinylene carbonate (VC), and a solution 3.27 mol kg⁻¹ of LiClO₄ dissolved in PC, were used as the electrolytes. All these reagents (purchased from Panax E-Tec) were used as received. Electrochemical measurements were carried out using a three electrode cell in a glove box (Three-Shine, SK-G1200) filled with Argon with dew point below -70 °C. Lithium foil was used as the counter and reference electrodes. The test electrode was charged and discharged at a constant current of 37.2 mA g⁻¹ between 0.0 and 3.0 V at 25 and -15 °C. All potentials were referred to as volts versus Li⁺/Li. Raman spectra of the electrolyte solutions were recorded at 25 and -15°C by using a laser Raman spectroscopy system (DeltaNu, Inspector Raman).

Lithium ions were intercalated into and de-intercalated from graphite reversibly at -15 °C despite the use of pure PC as the solvent. However, ceaseless solvent decomposition and intense exfoliation of graphene layers occurred at 25 °C. The results of the Raman spectroscopic analysis indicated that the interaction between PC molecules and lithium ions became weaker at -15 °C by chemical exchange effects, which suggested that the thermodynamic stability of the solvated lithium ions was an important factor that determined the formation of a solid electrolyte interface (SEI) in PC-based solutions. Charge-discharge analysis revealed that the nature of the SEI formed at -15 °C in 1 mol dm⁻³ of LiClO₄ in PC was significantly different from that formed at 25 °C in 1 mol dm⁻³ of LiClO₄ in PC containing vinylene carbonate, 3.27 mol kg⁻¹ of LiClO₄ in PC, and 1 mol dm⁻³ of LiClO₄ in ethylene carbonate.

Reference

- 1) S.-K. Jeong et al., *Electrochemistry Communications*, **31**, 24 (2013).