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Quantitative and qualitative study on the solid electrolyte interface formed by 2-(5H) furanone: A novel additive for propylene carbonate-based lithium-ion battery electrolytes

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ABSTRACT

To improve the poor solid electrolyte interface (SEI) formed with propylene carbonate (PC)-based electrolyte on a graphite electrode, 2(5H)-furanone was assessed as a novel electrolyte additive together with fluoroethylene carbonate (FEC). The mass change during the formation of the SEI was monitored with different 2(5H)-furanone to FEC ratio using an electrochemical quartz crystal microbalance. The single addition of FEC was insufficient to prevent the decomposition of the electrolyte and damage of graphite electrode, due to FEC's more negative reduction potential compared to PC, leading to serious irreversible charge loss during the 1st charge-discharge process. On the other hand, 2(5H)-Furanone suppressed the graphite damage effectively, which resulted in relatively higher discharge capacity. However, for the electrolyte containing only 2(5H)-furanone, minor charge loss due to electrolyte reduction continued even after the SEI formation. This led to SEI with excessive amount and resistance, which resulted in a severe capacity drop at rapid discharge rates. The mixed additive of 2(5H)-furanone and FEC suppressed both the damage of the graphite electrode and residual reduction currents. The LIBs with this co-additive system exhibited much lower film resistance associated with the SEI and showed superior electrochemical performances.

1. Introduction

Li-ion secondary battery (LIB) is one of the most popular energy storage devices on the current market and is used in a wide range of technologies from mobile devices to electric vehicles, due to relatively high energy density and good reversibility [1,2]. The performances of LIBs have been improved by various types of electrolyte additives. One of the main purposes of those additives is the formation of stable solid electrolyte interface (SEI) [3,4]. SEI is an electron-insulating and ion-conducting layer that forms mainly on the anode surfaces (typically graphite or metallic electrode), which prevents the decompositions of the electrolyte components and plays a fundamental role in the cycle life and safety of LIBs [5]. The popular usage of ethylene carbonate (EC) as one of the main electrolyte component is mainly due to its ability to form a relatively stable SEI on graphite electrode [6,7]. Nevertheless, the quest for a better electrolyte with superior electrochemical performance is still ongoing, particularly for specialized types of batteries, which includes those requiring extremely fast charge-discharge rates [8,9] or operable at extreme temperatures [10,11]. Additives for such electrolytes have been studied extensively because there are few electrolytes that form a stable SEI and maintain good performances under a severe operating condition or on the newly-developed active materials [12–14].

Since propylene carbonate (PC) has relatively high dielectric constant (64), high boiling point (242 °C), and low melting point (−49 °C), the PC-based electrolyte has a good potential to realize LIBs with superior performances [15,16]. However, the PC-based electrolyte cannot form a stable SEI in the absence of additives because the intercalation of PC to the graphite electrode causes severe degradation of the electrode due to the exfoliation of the layered structure of graphite [17–19]. Electrolyte additives, such as fluoroethylene carbonate (FEC) [20–23] and vinylene carbonate (VC) [3,23] have been studied as SEI forming additives in the PC-based electrolytes and showed acceptable electrochemical performance under limited experimental conditions.

In the present study, 2(5H)-furanone (herein referred to as “furanone”) was newly proposed as SEI forming additive for the PC-

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based electrolyte. The co-additive effect with FEC was also discussed to determine the mechanism of the SEI formation by furanone and to achieve the better electrochemical performance of LIBs. Cyclic voltammetry (CV) performed in an electrochemical quartz crystal microbalance (EQCM) provided insight into the reduction phenomenon of each additive of interest and co-additive systems. Electrochemical data, such as the coulombic efficiency and dQ/dV on the first formation cycle were analyzed for the understanding of the SEI formation phenomenon. Electrical impedance spectroscopy (EIS) was also performed to assess the resistance of the resulting SEI. The results are expected to contribute to a better understanding of the formation of SEI within PC-based electrolytes.

2. Experimental

Battery-grade electrolyte components, propylene carbonate (PC), diethylene carbonate (DEC), and $LiPF_6$, were obtained from Solbrain Co. (Seongnam, Korea). Fluoroethylene carbonate (FEC) and 2(5H)-furanone ("furanone") were purchased from Sigma-Aldrich Korea (Yongin, Korea). All electrolytes were treated with a molecular sieve to maintain their water contents under 15 ppm, which was further verified with Karl Fischer Coulometer C20 (Mettler Toledo Co., Columbus, USA). The graphite and $LiCoO_2$ (LCO) mass-production grade electrodes were supplied by Enerland Co. (Icheon, Korea). Celgard 2320 (Celgard, Charlotte, USA) was used as a separator.

3-Electrode beaker cells (Working (W) electrode, graphite or LCO; Counter (C) electrode, Li metal; and Reference (R) electrode, Li metal) were fabricated and used in LSV experiment with the Model 920D SECM device (CH Instruments, Inc., Texas, USA). LSV was performed over the potential range of 3.0–0.0 V for graphite and 3.7–4.2 V for LCO electrode (vs Li/Li^+) with a scan rate of 0.2 mV/s. For the measurement of the EQCM cells (W: Pt, C: Li metal, R: Li metal) by CV technique, a QCM922 (Princeton Applied Research Co., Oak Ridge, USA) EQCM device was used with a QA-A9M-PT quartz electrode (0.2 cm^2 Pt on 9.0 MHz AT-cut quartz). CV technique was performed over the potential range of 3.2–0.5 V (vs Li/Li^+), and with a scan rate of 5.0 mV/s.

The graphite-LCO pouch cells were assembled within a glove box filled with pure argon gas (99.999%). The electrochemical performances of these cells were evaluated using a WBCS 3000 battery cycler (WonATech Co., Ltd., Seoul, Korea). EIS was conducted using an electrochemical workstation IM6 (ZAHNER-Elektrik GmbH & Co. KG, Kronach, Germany; Cell potential, 4.2 V; frequency range, 10 mHz–200 kHz; and amplitude, 10 mV).

3. Results and discussion

3.1. Reduction behaviors of electrolyte additives in PC-based solvent

In this study, two types of voltammetry were conducted to analyze the electrochemical reactions of the electrolyte additives and the formation of SEI: LSV performed with 3-electrode beaker cells (W: graphite or LCO, C: Li metal, R: Li metal) and CV performed with 3-electrode EQCM cells (W: Pt, C: Li metal, R: Li metal).

Fig. 1 shows the LSV results of the 3-electrode beaker cells containing the reference electrolyte (1.0 M $LiPF_6$ in PC/DEC, 1:1 by volume) or electrolytes containing additives (furanone and FEC in the reference electrolyte, 1.5 wt% for each). Fig. 1a represents the anode part of the typical Li-ion battery, which was performed with graphite as a working electrode. For the reference electrolyte, a major PC reduction/intercalation peak from 1.0 V to 0.0 V was observed. With the addition of 1.5 wt% FEC, PC intercalation peak was considerably decreased without additional observable reduction peak of FEC prior to the PC intercalation. Jeong et al. reported the formation of the SEI with PC containing FEC and observed the reduction of FEC prior to PC reduction on highly oriented pyrolytic graphite with *in-situ* electrochemical atomic force microscopy (AFM) [23]. However, the addition of FEC to the reference electrolyte used in this research produced no additional reduction current prior to the PC intercalation starting at 1.0 V (Fig. 1), probably due to the different components used: PC/DEC with $LiPF_6$ instead of PC with $LiClO_4$ [23]. It seems that for our electrolyte system, the formation of a stable SEI by FEC occurred after the potential where the intercalation of PC had already begun (1.0 V) and the reduction peak was obscured by the massive PC intercalation currents.

The energy of the lowest unoccupied molecular orbital (LUMO) of the additives and electrolytes are shown in Supplementary Materials, Table S1. According to the molecular orbital theory, lower LUMO energy value can be viewed as more feasible electron acceptance, and the molecule should be more easily reduced [24]. As can be seen in Table S1, FEC and furanone both showed more negative LUMO values compared to PC and DEC, which mean they would more easily receive electron and turn into a reduced form. This is somewhat contradictory to our results in Fig. 1, where no reduction peak of FEC was found prior to PC reduction/intercalation. There are many reasons for disparities between theoretical and experimental values of the reaction potential (overpotential),

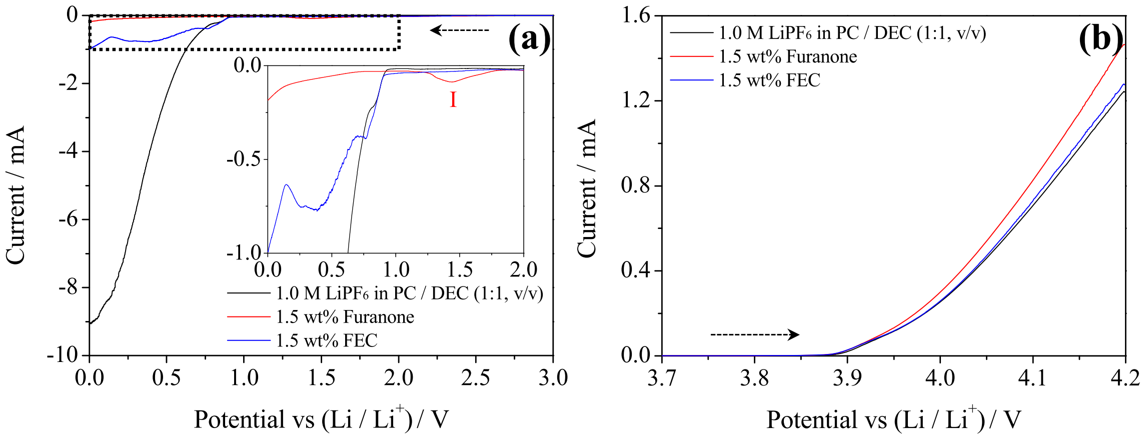

Fig. 1. LSV results of the 3-electrode beaker cells which used Li metal as a counter and a reference electrode. The cells contained reference electrolyte (1.0 M $LiPF_6$ in PC/DEC, 1:1 by volume) or the electrolyte containing additives (1.5 wt% furanone or FEC in the reference electrolyte). (a) Graphite as a working electrode. The inset shows the magnification of the marked area. (b) LCO as a working electrode. The scan rate for both was 0.2 mV/s.