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Comparative Study on the Solid Electrolyte Interface Formation by the Reduction of Alkyl Carbonates in Lithium ion Battery

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ABSTRACT

Mixed alkyl carbonates are widely used as solvent for a various lithium-ion battery applications. Understanding the behavior of each solvent in the mixed system is crucial for controlling the electrolyte composition. In this paper, we report a systematic electrochemical and spectroscopic comparison of the reduction of propylene carbonate (PC), ethylene carbonate (EC), and diethyl carbonate (DEC) when used as single (PC), binary (EC/PC, EC/DEC), and ternary (EC/PC/DEC) solvent systems. The reduction products are identified based on Fourier transform infrared spectroscopy (FTIR) after employing linear sweep voltammetry to certain potential regions and their possible formation mechanisms are discussed. FTIR analyses revealed that the reduction of EC and PC was not considerably influenced by the presence of other alkyl carbonates. However, DEC exhibited a different reduction product when used in EC/DEC and EC/PC/DEC solvent systems. The reduction of EC occurred before that of PC and DEC and produced a passivating surface film that prevented carbon exfoliation caused by PC. Battery performance test, cyclic voltammetry, electrochemical impedance spectroscopy, and scanning electron microscope is employed to study the surface films formed. The binary EC/DEC solvent system demonstrated more favorable performance, smaller impedance, and higher Li+ ion diffusivity than did the other solvent systems used in this study.

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1. Introduction

In recent years, lithium-ion batteries have become the predominant rechargeable power source for portable electronic devices. Lithium-ion batteries consist of a low potential lithium (Li) insertion anode along with a high potential Li insertion cathode and a nonaqueous electrolyte. The electrolytes used in secondary lithium-ion batteries are primarily mixtures of aprotic organic solvents and conductive salts for achieving wide electrochemical windows [1,2], however polymer [3] and ionic liquid-based electrolytes [4,5] are also being investigated. Electrolytes are a major concern related to lithium-ion batteries because their properties, such as viscosity, ionic conductivity, thermal stability, and wettability, can determine the performance of a battery. Both the salt and the type and composition of solvents affect the performance,

cycle ability, and safety of lithium-ion batteries [2,6–9]. Smart et al. [10] explained how electrolyte composition may influence Li plating and Li intercalation kinetics at an anode. Aurbach et al. [9] reported that conductivity, electrochemical stability, operating temperature range, and safety concerns should be considered when selecting electrolytes and their compositions. Satisfying all of these demands by using a single solvent is nearly impossible. Therefore, solvents exhibiting different physicochemical properties are frequently mixed for use in a variety of lithium-ion battery applications.

The performance of a lithium-ion battery can be related to the solid electrolyte interface (SEI) layer formed on an electrode surface, and this SEI film formation primarily depends on electrolyte composition. Therefore, understanding the formation mechanism and the properties of an SEI comprising various electrolyte components is vital to electrolyte selection. Numerous studies have examined SEI formation by the reduction of electrolytes. However, the composition of SEI layers and their formation mechanism remain unclear, particularly when a solvent mixture is used.

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Understanding why solvent cointercalation occurs in neat propylene carbonate (PC), but not in the presence of ethylene carbonate (EC), ethylene carbonate/diethyl carbonate (EC/DEC), or ethylene carbonate/dimethyl carbonate (EC/DMC) is one of the debated topics. Fong et al. [11] proposed that EC reduction can form a stable SEI film, thereby preventing PC intercalation; however, the SEI film composition and its formation were not clearly reported. Several studies have attempted to investigate the distinct electrochemical behaviors of EC and PC by considering their comparable properties [12,13]. Zhuang et al. [13] reported that EC and PC exhibited different reduction pathways on graphite electrodes based on Fourier transform infrared (FTIR) analyses. Several studies [12,14,15] have attempted to elucidate the various interfacial phenomena associated with EC- and PC-based electrolytes. However, a cosolvent, such as ethyl methyl carbonate (EMC), DMC, and DEC, is frequently used with EC, which causes the direct comparison of EC with neat PC to be considerably difficult. Whether cosolvents interact with each other and how such interactions influence an SEI remain unanswered.

This paper reports a direct comparison of the reduction of alkyl carbonates in single, binary, and ternary solvent systems by using PC, EC/PC, EC/DEC, and EC/PC/DEC solvents for a LiPF$_6$ electrolyte. The surface species formed in the single and mixed solvent systems were determined by combining FTIR, cyclic voltammetry (CV), and calculated reduction potentials. Electrochemical tests and scanning electron microscopy (SEM) analysis were used to compare the chemistry and properties of the surface species formed on the anode in various solvent systems. The reduction mechanism of various alkyl carbonates in mixed solvent systems was comprehensively analyzed and compared with each other. According to our research, this is the first systematic comparison of SEI formation that was performed using PC, EC, and DEC as single, binary, and ternary solvent systems.

2. Experimental

All electrolyte preparation, purification, CV, linear sweep voltammetry (LSV), attenuated total reflectance FTIR (ATR-FTIR) measurements, and cell assembling and disassembling were performed inside an argon-filled glove box (H$_2$O and O$_2$ < 1 ppm) at room temperature. PC (Aldrich, 99.7%), EC (Acros Organics, 99 + %), DEC (Acros Organics, 99%), and LiPF$_6$ (Novolyte Technologies) were used to prepare electrolyte solutions, namely 1 M LiPF$_6$ in PC, 1 M LiPF$_6$ in EC/PC (3:2 v/v), 1 M LiPF$_6$ in EC/DEC (1:1 v/v), and 1 M LiPF$_6$ in EC/PC/DEC (3:2:5 v/v). Before preparing the electrolytes, we dried all of the solvents to obtain a moisture content of less than 20 ppm by using a 4A molecular sieve. The compositions of EC/PC and EC/PC/DEC were based on those used in previous studies [16–19] and the composition of EC/DEC was based on that of commercial electrolytes. The electrolytes were dried using a 4A molecular sieve for 24 h and degassed by purging with argon gas (99.99%) for 15 min to remove trace impurities such as oxygen [20]. CV and LSV were performed using a three-electrode Teflon cell comprising either a mesocarbon microbead (MCMB) working electrode and Li foil, both as counter and reference electrodes, or type 304 stainless steel working and counter electrodes (Yang Cheng Packing Co.; area, 1 cm^2) and a Li reference electrode. A VMP3 multichannel potentiostat (Bio-Logic Science Instruments) was used at a scan rate of 0.1 mVs^{-1} for conducting the CV and LSV measurements. Before each measurement, the stainless steel electrodes were polished with 0.05 μm of colloidal silica, washed with ethanol and deionized water, and stored in a vacuum overnight. The stainless steel electrode and MCMB electrode in the two aforementioned cell configurations demonstrated markedly similar electrochemical and spectroscopic performance in the reduction of the solvents [21].

Regarding FTIR measurement, ex situ ATR analysis, performed inside of the glove box, and in situ diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFTS) were used to record surface spectroscopy. Both techniques yielded considerably similar spectra [21]. A Bruker Optics spectrometer equipped with a single-reflection ATR sampling accessory and a Nicolet 6700 FTIR spectrometer equipped with a DRIFTS sampling accessory and a mercury-cadmium-telluride (MCT/A) detector were used. The same procedure used in our previous paper [20] was followed for performing ex situ ATR analysis. For the in situ DRIFTS analysis, a house-designed Teflon cell equipped with a ZnSe window was used, and the background was collected from the bare electrode (MCMB in this experiment). The design of the spectroelectrochemical cell and the detailed procedure used for conducting the in situ DRIFTS analysis have previously been described [21].

For performing the charge–discharge tests, 2032-type coin cells were assembled using an electrode composed of 93 wt% mesocarbon microbeads (MCMB-2528, Osaka Gas), 3 wt% TIMREX® KS4 graphite as a conductive additive, and 4 wt% polyvinylidene difluoride as a binder. Li foil was used as the counter electrode and the two electrodes were separated using a Celgard 2320 separator. The same group of cells was used for the charge–discharge test and electrochemical impedance spectroscopy (EIS) analyses. In all the experiments, the MCMB electrode was lithiated at a constant rate of 0.1 C from 3 V to 10 mV, followed by a constant voltage until the current decreased to one-twentieth of its initial value, and then delithiated back to 3 V at a rate of 0.1 C. An EIS measurement was performed on the same cells after the first and tenth cycles when they were in a completely delithated state (0% state of charge, SOC) by using a VMP3 multichannel potentiostat with ac oscillation that was 5 mV in amplitude at frequencies ranging from 1 MHz to 10 mHz. For SEM measurements, the same batch of commercial MCMB electrodes were used to assemble Li/MCMB cells and the cells were subjected to one formation cycle. The results were similar with the previous group of cells used for EIS and cycling measurements. Prior to SEM measurement, the MCMB electrodes after the first charge/discharge cycles were disassembled inside a glove box, washed with DMC, dried, and then transferred to an SEM chamber without air exposure by using an argon-filled sample box. The SEM images were captured using a Hitachi S-4700 microscope using an accelerating voltage of 15 kV.

Theoretical calculations of geometry optimizations and the lowest unoccupied molecular orbital (LUMO) energy levels were performed using the Gaussian 09 package [22] at the B3LYP computational level [23–26], with a 6-311 + +G(d,p) basis set. The implicit solvent effect was addressed by using the implicit solvation model with density method (SMD) [27] as implemented in Gaussian 09, for which the dielectric constants of 64.92, 79.84, and 41.32 were selected when considering PC, EC/PC (3:2), and EC/PC/DEC (3:2:5), respectively.

3. Results

3.1. Electrochemical cycling

Fig. 1a shows a comparison of the first charge–discharge profiles of the Li/MCMB cells with 1 M LiPF$_6$ in the PC, EC/PC (EP), EC/DEC (ED), and EC/PC/DEC (EPD) solvent systems. During lithiation, the cell containing an LiPF$_6$/PC electrolyte exhibited a plateau of constant electrode potential near 0.75 V, which did not approach the potential of unsolvated Li intercalation (< 0.2 V vs. Li/Li$^+$). This is because Li intercalation could not occur in the MCMB electrode, which is attributable to MCMB exfoliation caused by the cointercalation of PC [28]. Adding EC and DEC to the PC-based electrolyte remarkably changed the cycling behavior of the MCMB electrode,