



Effect of temperature on the dissolution of solid electrolyte interface on mesocarbon microbeads electrodes in propylene carbonate-based electrolytes



Yan-Syun Wang^a, Chien-Mei Huang^a, Han-Wei Hsieh^b,
Yu-Fang Lin^b, Chi-Yen Lin^b, Jyh-Tsung Lee^{a,c,*}

^a Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

^b Advanced Lithium Electrochemistry Co., Ltd., Taoyuan City 33068, Taiwan

^c Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

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ABSTRACT

The effects of temperature on the dissolution of solid electrolyte interface (SEI) films in the propylene carbonate (PC)-based electrolyte are investigated. The SEI films on the mesocarbon microbeads (MCMB) electrode of the Li|1.0M LiPF₆-PC/DEC (= 7/3, v/v)|MCMB cell are characterized by cyclic voltammetry, scanning electron microscopy (SEM), AC impedance, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The SEM and electrochemical results show that the MCMB electrode cannot undergo the lithiation and delithiation process at 30 °C due to the co-intercalation of PC and the exfoliation of MCMB. By contrast, the Li|MCMB cell can be successfully discharged and charged at 0 °C because a PC-based SEI film forms on MCMB. The energy capacity of the MCMB electrode is 281.3 mAh g⁻¹ at 0.2 C. However, the SEI film dissolves in the PC-based electrolyte as the temperature is increased to 30 °C. The results of Raman spectroscopy and XPS also confirm that the composition of the PC-based SEI formed at 0 °C consists of LiF, Li_xPF_y, Li_xPO_yF_z, RO₂Li, and ROCO₂Li.

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1. Introduction

Carbonate-based electrolytes are the most popular electrolytes for commercial lithium-ion batteries. The electrolyte solvents are categorized into cyclic and linear carbonates, of high and low polarity, respectively [1]. Typically, for commercial electrolytes the two types of solvents are mixed in different percentages. For the cyclic carbonates, there are mainly ethylene carbonate (EC) and propylene carbonate (PC). They have a similar cyclic carbonate structure, so the reduction potential of lithium ions is also similar [2,3]. However, the electrochemical performances of cells with graphite anodes in EC- or PC-based electrolytes are significantly different [1,4,5]. Several papers have reported on the possible mechanisms from various aspects [6–14]. For the EC-based electrolytes, the melting point of EC is 36 °C. Therefore, EC-based electrolytes exhibit poor low-temperature performance. However, EC can form good quality solid-electrolyte interface (SEI) films that enhance electrochemical performances of batteries. A large number of papers has

also studied on the chemical composition of EC-based SEI films [1,9–13]. In contrast, PC-based electrolytes have exceptional low-temperature performance attributed to the low melting point of PC (−49 °C) as a result of its asymmetric structure [1]. However, PC is co-intercalated with lithium ions into graphite and electrochemically decomposed to inflate the structure of graphite-active materials [14–17]. To improve the electrochemical performance, electrolyte additives are used, such as vinylene carbonate, allyl ethyl carbonate, vinyl acetate, vinyl ethylene carbonate, ethylene sulfite, propylene sulfite, and so on [18]. The additives are electrochemically reduced prior to the decomposition of electrolytes to form an effective SEI on electrodes so as to inhibit the reductive decomposition of electrolytes. Therefore, the SEI is mainly contributed by additives, instead of PC.

There are a only few studies on the composition of PC-based SEI films on graphite electrodes since it is difficult to obtain the PC-based SEI [1,14–17]. Jeong *et al.* [19] first reported that PC-based electrolytes with high LiPF₆ concentrations can form a good SEI film to suppress the co-intercalation of PC. Lucht *et al.* [20] have reported that PC-based SEI can be formed at high concentrations of LiPF₆ salt and found that the PC-based SEI is mainly composed of LiF, allowing lithiation/delithiation. At low concentrations of LiPF₆ salt,

* Corresponding author. Tel.: +886 7 5253951; fax: +886 7 5253951.
E-mail address: jtleee@faculty.nsysu.edu.tw (J.-T. Lee).

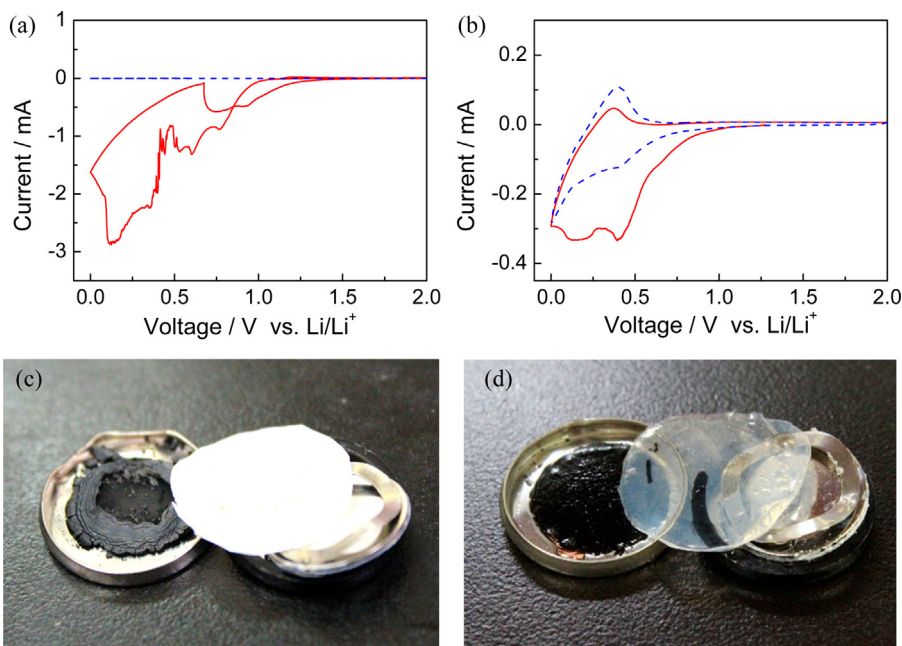


Fig. 1. The first (red solid line) and second (blue dash line) cycles of CVs for MCMB electrodes in a 1.0 M LiPF₆-PC/DEC (= 7/3, v/v) electrolyte at (a) 30 °C and (b) 0 °C. Corresponding photographs for disassembled cells after 5 CV-cycles at (c) 30 °C and (d) 0 °C.

the composition of SEI is lithium propylene dicarbonate (LPDC) that is not an effective SEI for suppressing decomposition of electrolytes [21]. Furthermore, Jeong *et al.* reported that PC-based cells could be charged/discharged at a low temperature (−15 °C) [22]. Therefore, there are two approaches to cycling the cell with graphite anodes in PC-based electrolytes without additives. The mechanism and properties of the PC-based SEIs are still not fully understood. We believe that one of the crucial differences between EC and PC-based SEIs is their solubility in electrolytes. The PC-based SEI is expected to be more dissolvable in electrolytes, which results in an inefficient SEI. However, no experimental work has been conducted to confirm this hypothesis.

In this paper, we report that the PC-based SEI film can be formed at 0 °C due to its low solubility at low temperatures. Therefore, the MCMB electrode can undergo the lithiation and delithiation process. As the temperature is increased to 30 °C, the PC-based SEI film readily dissolves into the electrolyte due to its high solubility. Furthermore, the surface morphology of SEI films are observed using scanning electron microscopy (SEM). The chemical structure of SEI films are characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of the electrodes are investigated using cyclic voltammetry (CV) and charge-discharge performance measurements.

2. Experimental

The mesocarbon microbeads (MCMB, China Steel Chemical Corp., Taiwan) electrode is composed of MCMB (90 wt.%), polyvinylidene difluoride (PVDF, 7 wt.%) and Super P (3 wt.%) on copper foil. For the electrochemical measurements, a coin cell (CR 2032) was utilized. The MCMB electrode was used as a working electrode; lithium was used as both the counter and reference electrode. The electrolyte was composed of 1.0 M LiPF₆ in PC/DEC (diethyl carbonate) or EC/DEC (= 7/3 in volume) and Celgard 2500 was used as the separator. The cell was assembled in an Ar-filled glove box. The electrochemical measurements were conducted at either 0 or 30 °C. For CV measurements, the scanning window was set between 2.0 and 0.0 V vs. Li/Li⁺, at a scanning rate of 0.05 mV/s. After five CV cycles, the coin cell were disassembled. The MCMB

electrodes were subsequently washed with the PC/DEC (= 7/3, in volume) solvent and then with DEC. Note that the temperature of the washing solvents was either 0 or 30 °C. Finally, the MCMB electrodes were dried in a vacuum oven. For the charge-discharge experiment, the cells were charged and discharged between 2.0 and 0.0 V at a constant current of 0.2 C. For AC impedance measurement, the scanning frequencies ranged from 100 kHz to 0.05 Hz with an AC amplitude of 10 mV. The electrochemical properties were measured by a CHI model 6081 C electrochemical analytical instrument. The MCMB electrodes were observed by a field emission scanning electron microscope (FESEM, Zeiss Supra 55 VP) with an accelerating voltage of 10 kV and a current of 10 μA, equipped with an energy dispersive X-ray (EDX) spectrometer. The MCMB electrodes were measured by a Micro-Raman (Confocal Raman Microscope Alpha300 R, WITec) with a 632.8 nm laser. An X-ray photoelectron spectroscope (XPS, ULVAC-PHI, PHI Quantera SXM) with a focused monochromatic Al K α radiation (1486.6 eV) was employed to measure the chemical states of carbon, fluorine, oxygen, and phosphorus on the MCMB electrodes. A mixture of Gaussian and Lorentzian functions was used for XPS peak fitting.

3. Results and discussion

3.1. Electrochemical measurements

Figs. 1a and 1b show CVs for Li||MCMB cells with a 1.0 M LiPF₆-PC/DEC (= 7/3, v/v) electrolyte cycled at 30 °C and 0 °C, respectively. As the literature report [20,22,23], the CV (Fig. 1a) at 30 °C only shows reduction peaks, but there is no oxidation peak in the first cycle, indicating the decomposition of the electrolyte and the co-intercalation of PC into MCMB. In the second cycle, the CV curve does not show any redox peaks. The result indicates that the MCMB electrode is unable to undergo the lithium intercalation and de-intercalation process since the PC-based electrolyte could not form an effective SEI film on MCMB at 30 °C. However, Fig. 1b shows that the MCMB electrode can undergo the lithium intercalation and de-intercalation process at 0 °C. In this case, the reductive decomposition of the PC-based electrolyte was suppressed by decreasing temperatures, indicating that a stable SEI is formed on MCMB at

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