Effects of Lithium Salt on Electrochemical Reactions at a SiC Electrode in Propylene Carbonate-based Solutions

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Abstract. The effect of electrolyte salts, such as $LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, and $LiBF_4$, on the redox reactions of lithium ions at a SiC electrode was investigated, focusing on the interfacial reaction between the SiC electrode and the electrolyte solution. Lithium salts were found to exert a large influence on the magnitude of resistance of the solid-electrolyte interphase (SEI), and its reversible and irreversible capacities. There was negligible effect on the potential at which the SEI was generated, but the amount of charge required for generation was greatly affected by the type of lithium salt used.

1. Introduction

Secondary batteries convert electrical energy into chemical energy for internal storage, and when electricity is needed, they convert the stored chemical energy back into electrical energy for release. This energy storage and release is accomplished by electrochemical redox reactions at the positive and negative electrodes of the battery. Lithium secondary batteries are widely employed in electronic devices and use redox reactions of lithium ions, which are monovalent cations, as the electrode reactions. This means that any material capable of a redox reaction with lithium ions can be used as an electrode material. However, the amount of energy stored or released by a cell depends on the type of electrode material.

Silicon-based materials have been actively studied as negatively charged electrode materials capable of storing and releasing a large amount of energy. Energy is stored when lithium ions are electrochemically reduced at the silicon-based electrodes and released when the ions are electrochemically oxidized. These electrochemical reactions are known to be highly dependent on electrolyte composition. A film is formed on the surface of the electrode due to electrolyte decomposition accompanied by the redox reaction of lithium ions, mainly during the first charge/discharge cycle [1−5]. This film is called a solid electrolyte interphase (SEI) [6, 7], and its physicochemical properties greatly influence the performance of the battery, affecting reversible capacity, rate capability, and safety. In order for the battery to exhibit excellent performance, an SEI with excellent properties must be formed on the electrode surface, and this is closely related to the electrolyte composition.

SEI formation on SiC electrodes is expected to contribute to their capacity during the first cycle and capacity fading in subsequent cycles. Reversible cycling and long-term stability are closely related to the effectiveness of surface passivation, which depends on the physicochemical properties of the SEI [8]. Therefore, SEI formation is a very important step in the electrochemical reaction in lithium secondary batteries that employ SiC as a negatively charged electrode. In graphite electrodes used in commercial lithium secondary batteries, lithium salt—one of the constituent components of the electrolyte solution—strongly affects the properties of the SEI [9, 10]. Various lithium salts have been

developed and studied to form high-quality SEIs on the surface of graphite electrodes. Similarly, in this study, the effects of lithium salts on the physicochemical properties of the SEI generated on a SiC electrode were investigated. Four lithium salts ($LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, and $LiBF_4$) were used as electrolyte salts for the SiC electrode. This paper reports the effects of lithium salts based on the results of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses of a SiC electrode, including its charge/discharge capacity.

2. Experimental

SiC powder (Aldrich, 99%) was used for charge/discharge tests. The test electrode was prepared by coating a mixture of SiC powder (80 wt.%), carbon black (20 wt.%), and poly(vinylidene difluoride) binder (10 wt.%) on copper foil. The base electrolyte solvent was a 1:1 (by volume) mixture of propylene carbonate (PC) and dimethyl carbonate (DMC) (PC + DMC, Panax E-Tec. battery grade). Four types of lithium salts ($LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, and $LiBF_4$) were separately dissolved (1 mol dm^{-3} [M] each) in the base solvent. All the reagents were purchased from Panax E-Tec. and used as received. The water content in each solution was <30 ppm, as confirmed by Karl-Fischer titrations (MKC-210, Kyoto Electronics Manufacturing Co., Ltd.).

CV and EIS were performed using a laboratory-made three-electrode cell, as shown in Fig. 1. The working electrode was mounted on the bottom of the cell and brought into contact with the electrolyte solution using an O-ring. The geometrical surface area was 0.8 cm^2. Lithium foil was used as both the counter and reference electrodes. CV was conducted between 3.0 and 0.0 V at a sweep rate of 0.5 mV s^{-1}. The electrochemical impedance was obtained after the electrode was polarized at a constant potential for a sufficient amount of time (i.e., until the current became negligible [typically <1 μA]). The impedance was measured with a potentiostat (PGZ 402, VoltaLab) over the frequency range 0.1 Hz to 100 kHz. The alternating amplitude was 5 mV. Charge/discharge measurements were performed using a coin-type cell (CR 2032) between 1.5 and 0.0 V at a C-rate of 0.1.

CV and EIS measurements and coin cell assembly were performed in an argon-filled glovebox (Three-Shine, SK-G1200) with a dew point below −60 °C. All potentials are presented as volts vs. Li^+/Li.
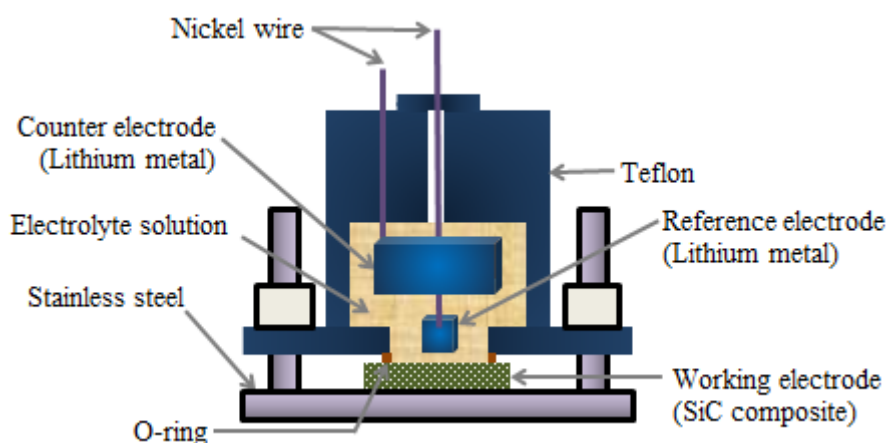

Figure 1. Schematic illustration of the three-electrode cell used for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements.

3. Results and Discussion

CV was performed to gain a basic understanding of the electrochemical reactions between SiC electrodes and PC-based electrolyte solutions containing different types of lithium salts. The electrochemical behavior of a battery system can be understood by recording the amount of current flowing through the electrode while changing the potential applied to the electrode at a constant rate (Fig. 2). This figure shows the cyclic voltammograms of the SiC electrode in four PC-based solutions. CV is a very useful technique for obtaining information about fairly complicated electrode reactions. During the first cycle, a minor reductive current begins to flow at ~2.4, ~2.3, ~2.5, and 2.2 V in

solutions containing $LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, and $LiBF_4$, respectively. This difference is presumably due to the influence of anions present in the electrolyte solution. Three major reductive peaks centered at ~1.9, ~1.1, and ~0.3 V appear for all the solutions. These reductive peaks, including the minor current, are absent from the second cycle, indicating that their presence and subsequent disappearance are the result of irreversible electrolyte decomposition, which might be closely related to the formation of the SEI.

Although scientific correlations between irreversible electrolyte decomposition and SEI formation are unclear in the present work, there is no doubt that SEIs are generated on the SiC electrodes, irrespective of the type of lithium salt, because the stable charge and discharge reactions shown in Fig. 2 do not occur without an SEI [11]. In addition to the irreversible reductive peaks, two reversible reductive peaks are observed at potentials of ~0.7 and ~0 V. The oxidative peaks corresponding to these peaks are observed at potentials of ~0.9 and ~0.2 V. These two reductive and oxidative peaks can be assigned to lithium insertion and extraction events, respectively. However, the reductive peaks are believed to represent a large proportion of the irreversible lithium insertion because the charge consumed in this process is greater than that consumed for oxidation. This is confirmed by the charge/discharge results shown in Fig. 2. Additionally, each lithium insertion and extraction peak varies slightly in shape and size.
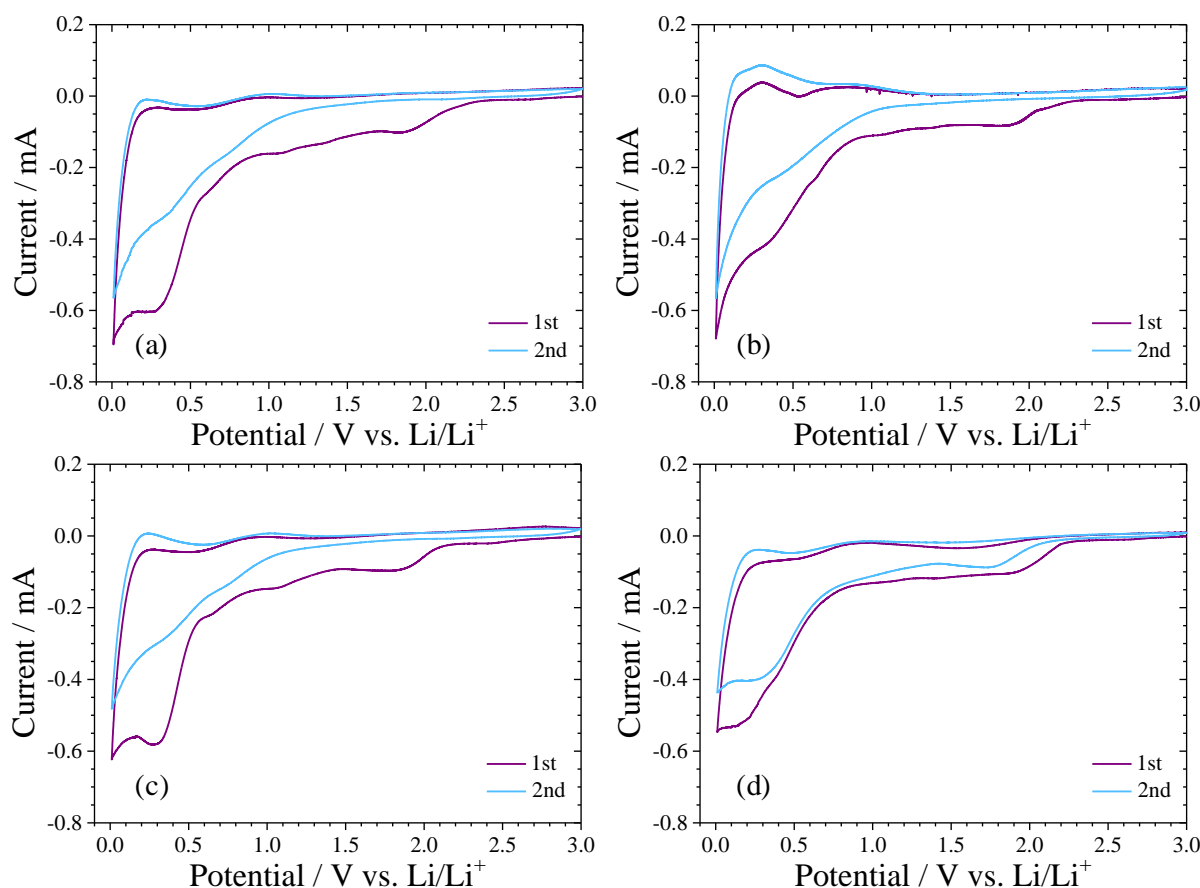

Figure 2. First and second cyclic voltammograms of SiC powder at 0.5 mV s^{-1} in propylene carbonate and dimethyl carbonate (PC + DMC) containing 1 M of (a) $LiPF_6$, (b) $LiClO_4$, (c) $LiCF_3SO_3$, and (d) $LiBF_4$.

The potential profiles of the SiC electrode during initial charging (lithium insertion) and discharging (lithium extraction) in four PC-based solutions are shown in Fig. 3. In the $LiPF_6$ solution, the charge and discharge capacities during the first cycle are ~175 and ~50 mAh g^{-1}, respectively, indicating rather low coulombic efficiency (Fig. 3(a)). Behavior similar to that shown in Fig. 3(a) is observed in

the $LiBF_4$ solution (Fig. 3(d)) during the first cycle. In contrast, in the $LiClO_4$ and $LiCF_3SO_3$ solutions, the SiC electrode exhibits large discharge capacities and low coulombic efficiencies (Figs. 3(b and c)). The irreversible capacities observed in all electrolyte solutions are likely consumed during the decomposition of the electrolyte solution to form an SEI on the SiC electrode [8]. The relatively large irreversible capacities in solutions containing $LiClO_4$ and $LiCF_3SO_3$ are observed between 0.75 and 0.25 V, which means that these solutions take a long time to produce a stable SEI. However, SEIs produced in this manner are effective for the redox reaction of lithium ions in terms of reversible capacity.
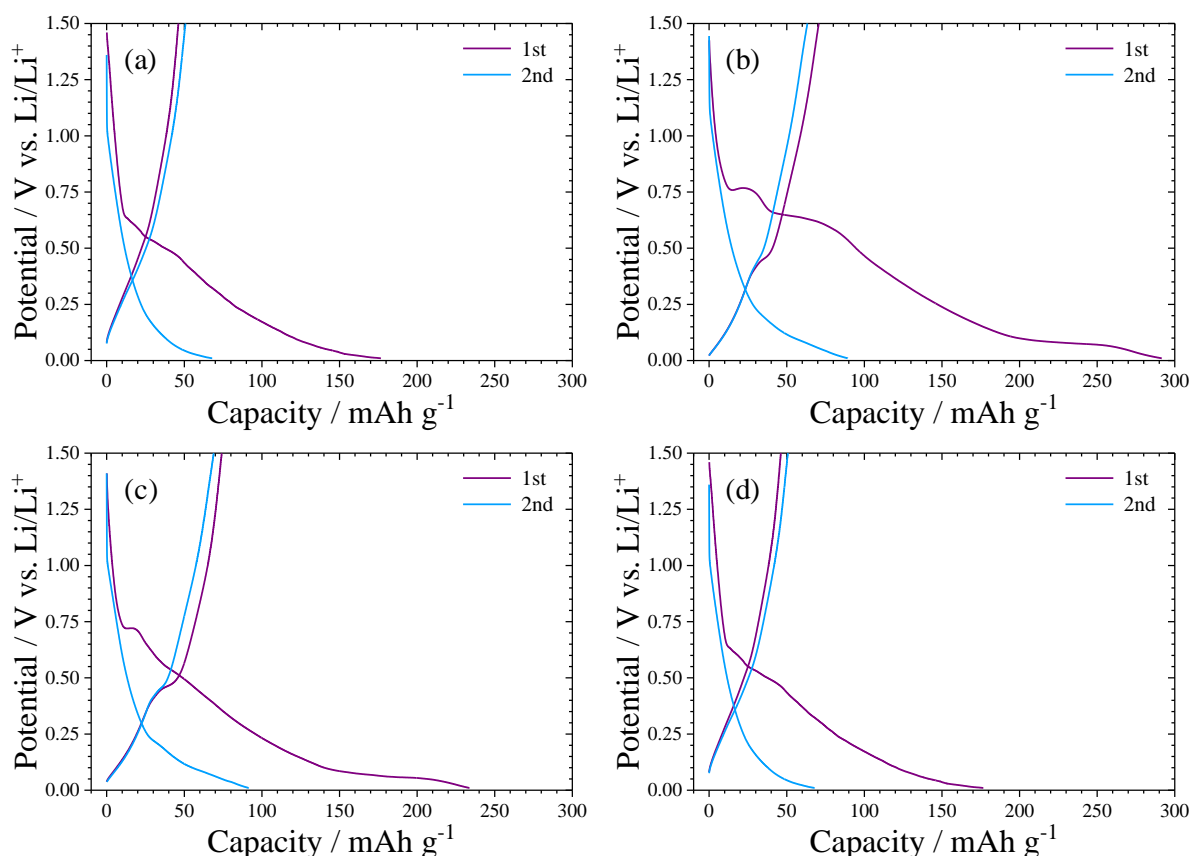

Figure 3. Charge and discharge curves in the first and second cycles of SiC powder in propylene carbonate and dimethyl carbonate (PC + DMC) containing 1 M of (a) $LiPF_6$, (b) $LiClO_4$, (c) $LiCF_3SO_3$, and (d) $LiBF_4$.

The charge and discharge results described above indicate that the nature of the interfacial reactions between the SiC electrode and the electrolyte solutions during cycling vary depending on the type of lithium salt used. Impedance spectra of the SiC electrodes were collected at 1.2 V to understand the interfacial reactions. The spectra obtained in each solution are in the form of a depressed arc (Fig. 4). It is widely accepted that there are two impedance components in the electrode where the redox reaction of lithium ions proceeds. One is impedance due to lithium ion migration through the SEI, and the other is impedance due to charge-transfer reactions [12−14]. The arcs shown in Fig. 4 denote impedance due to the former reaction. The latter reaction hardly proceeds at 1.2 V, where the impedance is obtained. The impedance decreases in the order $LiPF_6 > LiBF_4 > LiClO_4 > LiCF_3SO_3$ corresponding to the SEIs produced in these solutions. The SEI generated in the $LiPF_6$ solution exhibits the largest impedance. In contrast, a larger decrease in magnitude is found in the $LiCF_3SO_3$ solution. This decrease might be closely related to the large reversible capacity shown in Fig. 3(c), indicating that the SEI can have a positive effect on the insertion and extraction of lithium ions into/from the SiC electrode. Structural or compositional differences in the SEI generated in the four

PC-based solutions may lead to differences in the magnitude of impedance; however, direct correlations between the physicochemical properties of the SEI and the magnitude of impedance are unclear. A detailed interpretation of these correlations is beyond the scope of the present work and will not be discussed further here.
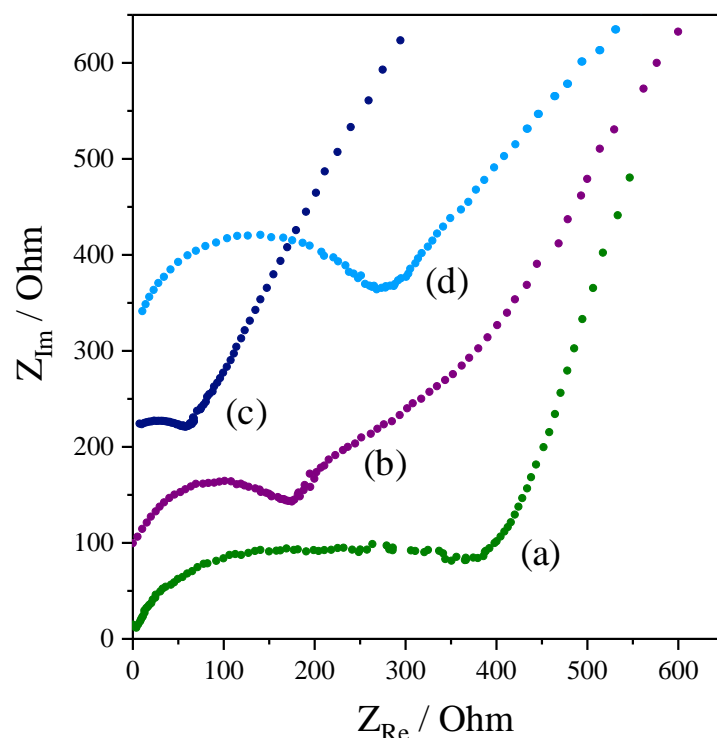

Figure 4. Nyquist plots of the SiC electrode in propylene carbonate and dimethyl carbonate (PC + DMC) containing 1 M (a) $LiPF_6$, (b) $LiClO_4$, (c) $LiCF_3SO_3$, and (d) $LiBF_4$.

4. Conclusions

Formation of a stable and effective SEI on the electrode surface is very important in order to utilize the redox reactions of lithium ions as the electrode reactions. Based on our studies, I suggest that $LiCF_3SO_3$ is a good SEI-forming salt for SiC electrodes employing PC-based solutions as an electrolyte solvent. $LiCF_3SO_3$ plays an important role in reducing the impedance of the SEI and results in improved charge/discharge performance. $LiPF_6$ is known to generate an excellent SEI when graphite is used as an electrode. Therefore, the results obtained in the present work suggest that good performance of an electrolyte in terms of SEI generation depends on the electrode. On the other hand, the specifics of the SEI produced in solutions containing $LiCF_3SO_3$ are still unclear. In the future, we plan to investigate the chemical composition and physical structure of this SEI.

5. References

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