

# Investigation of the electrochemical properties of a propylene carbonate-derived SEI in an ethylene carbonate-based solution

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**Abstract.** Herein, we aim to explore and analyze the influence of electrolytes on the creation of a solid electrolyte interface (SEI) within ethylene carbonate (EC) and propylene carbonate (PC)-based electrolyte solutions. Our investigation reveals that despite variations in the charge consumption during SEI formation, a comparable SEI is generated in a high-concentration PC-based electrolyte as observed in an EC-based electrolyte. However, it is noteworthy that the SEI originating from the PC-based electrolyte exhibits a significantly higher resistance to lithium ion transport when compared to the SEI formed from the EC-based electrolyte. Moreover, an increase in the charge transfer resistance at the graphite/electrolyte interface is observed in the PC-based electrolyte. These significant findings strongly imply that the choice of electrolyte solvent is a critical factor that must be taken into consideration in order to achieve the formation of an effective SEI.

## 1 Introduction

Lithium-ion batteries (LIBs) are electrochemical energy storage devices that employ redox reactions of lithium ions as electrode reactions to store and release energy. During the charging process, the positive electrode (typically a transition metal oxide, such as  $\text{LiCoO}_2$ ) undergoes oxidation, while the lithium ions are extracted and reduced at the negative electrode (usually a carbon material, such as graphite). This leads to the storage of electrical energy in the form of chemical energy. Conversely, during the discharge process, the negative electrode undergoes oxidation, while the lithium ions are released and inserted into the positive electrode through reduction. This results in the conversion of chemical energy to electrical energy. One notable feature of LIBs is their high energy density, which stems primarily from the negative electrode reaction. This is because the energy density of a battery is the product of its capacity and voltage. To increase the energy density of a battery, it is necessary for the negative electrode reaction to occur at a low potential and for the positive electrode reaction to occur at a high potential. Compared to other batteries, LIBs generally exhibit a relatively high battery voltage due to the low potential of the negative

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electrode reaction (typically 0.0-1.0 V vs. Li/Li<sup>+</sup>, except for a few high-potential negative electrode materials, such as Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>).

Although graphite, the negative electrode material used in LIBs, does not have a high energy density, it is widely employed due to its high reversibility and excellent cycle characteristics in the redox reactions of lithium ions. The insertion (reduction) and extraction (oxidation) reactions of lithium ions on the surface of graphite occur in a low potential range (0.0-0.25 V vs. Li/Li<sup>+</sup>) [1-4], which causes electrolyte decomposition as a result of the electrode reactions, leading to the formation of a film on the surface of graphite [5]. This film is known as the solid electrolyte interface (SEI) [6], which forms through the irreversible decomposition of the electrolyte before the insertion of lithium ions into the graphite. The SEI film permits the passage of lithium ions while blocking the movement of electrons, thus suppressing additional electrolyte decomposition caused by electron movement between the electrode and electrolyte. Consequently, after the SEI film is formed, only the selective insertion and extraction of lithium ions can take place, and it becomes a critical component of LIBs responsible for both the irreversible capacity and the protection of the electrolyte from continuous decomposition.

The formation of an SEI film on the surface of graphite electrodes in LIBs is heavily influenced by the type of electrolyte employed. Since the discovery that ethylene carbonate (EC) decomposition leads to an excellent SEI film, EC-based electrolyte solutions have become widely used in commercial LIBs. The SEI film comprises a mixture of organic and inorganic compounds containing polymers [7-15]. It acts as a resistance component to the insertion and extraction of lithium ions in the graphite electrode. However, the SEI film formed on graphite during the initial charging cycle is not stable until the end of battery life. It is destructed by the repeated contraction and expansion of the electrode during the cycling process, ultimately leading to battery degradation. Currently, there is ongoing research into the potential of propylene carbonate (PC) as a substitute electrolyte solvent for EC, due to its superior ionic conductivity at lower temperatures and lower cost compared to EC. Although PC is frequently employed as a solvent for the electrolyte in commercial lithium primary batteries that feature lithium metal as the negative electrode, its use is restricted in LIBs that employ graphite as the negative electrode. This is primarily because the formation of an SEI film on the graphite surface is hampered when utilizing PC, except in certain cases, leading to electrode deterioration during the initial charging process. One such exception is the physicochemical phenomenon of forming a stable SEI film on the graphite surface by increasing the concentration of the electrolyte dissolved in PC to a certain level or higher. Although this phenomenon is of great interest, a clear scientific interpretation of it has not yet been obtained. In this study, we investigate the electrochemical stability of the SEI film formed from a high-concentration PC-based electrolyte solution.

## 2 Experimental

### 2.1 Electrode preparation

Natural graphite (The Kansai Coke and Chemicals Co., NG-7) was utilized as the working electrode, while a mixture of natural graphite powder and poly(vinylidene fluoride) (PVdF, average MW 534000, Sigma-Aldrich) binder in a ratio of 9:1 (wt%) was combined in 1-Methyl-2-pyrrolidinone to form a slurry. Subsequently, this slurry was coated onto Cu foil and subjected to drying in a vacuum oven at a temperature of 120 °C for a duration of 12 hours. To prepare the electrolyte solutions, LiClO<sub>4</sub> was dissolved either in PC or in a 1:1 mixture (by volume) of EC and dimethyl carbonate (DMC) (EC + DMC). All of these

aforementioned reagents were procured from Kishida Chemical Co. and utilized as received, without any modifications. The moisture content in each solution was determined to be below 30 ppm through the utilization of a Karl–Fischer moisture titrator (Kyoto Electronics Manufacturing Co., MKC-210).

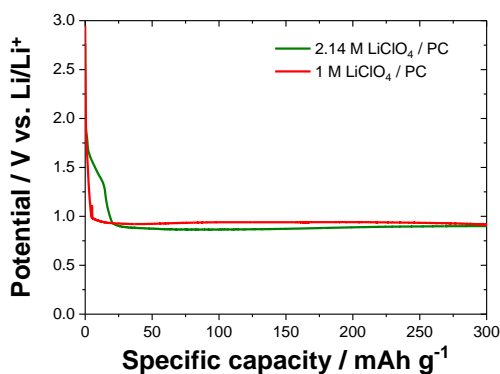
## 2.2 Electrochemical measurements

For conducting charge-discharge tests and electrochemical impedance spectroscopy (EIS), a three-electrode cell, consisting of a lithium foil employed as the counter and reference electrodes, was utilized. The charge-discharge tests were carried out by applying a constant current of 0.1 C (where 1 C equals  $372 \text{ mA g}^{-1}$ ) within a potential range spanning from 3.0 to 0.0 V. To obtain EIS spectra, the electrode was polarized at a constant potential until the current reached a negligible level (typically less than  $1 \mu\text{A}$ ) using a potentiostat (PGZ 402, VoltaLab) across a frequency range extending from 0.1 Hz to 100 kHz, while the alternating amplitude was set at 5 mV. All electrochemical measurements were performed within an argon-filled glovebox (Three-Shine, SK-G1200) that maintained a dew point below  $-60 \text{ }^\circ\text{C}$ .

## 3 Results and discussion

### 3.1 Reduction of graphite electrode in PC

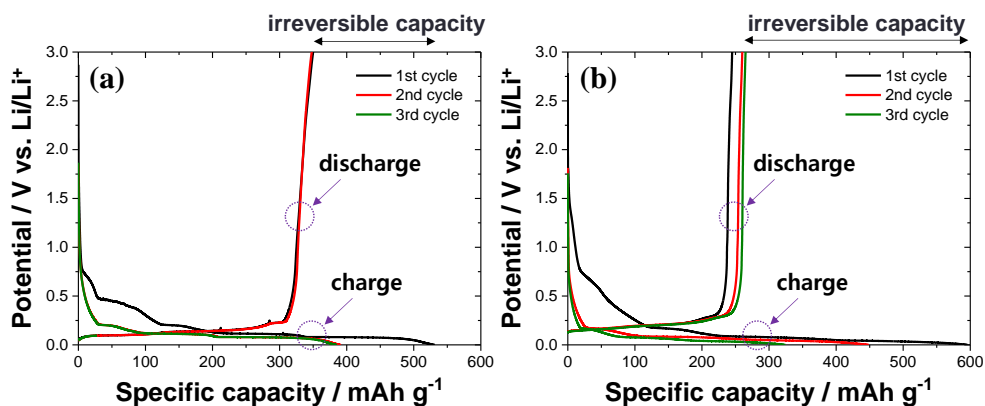
Figure 1 shows the charging behavior of graphite electrodes in two different electrolyte solutions, both of which contain relatively low concentrations of  $\text{LiClO}_4$  (1 and 2.14 mol  $\text{dm}^{-3}$  (M)) dissolved in PC. During the initial charging, the potential of the graphite electrode decreased abruptly to roughly 0.9 V. This is a typical phenomenon that has been observed in previous studies when PC is used as the electrolyte solvent. The potential then stabilized as the solvated lithium ions were inserted into the graphite layers. However, this process resulted in electrode destruction and continuous electrolyte decomposition because the solid electrolyte interface (SEI) was not formed on the graphite electrode surface. As mentioned in the introduction, this is why PC cannot be used as an electrolyte solvent for an extended period of time.



**Fig. 1.** Charge curves for the first cycle of natural graphite powder (NG-7) in PC.

### 3.2 Reduction of graphite electrode in PC

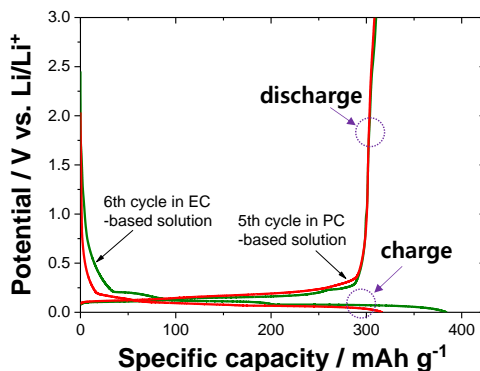
In contrast to the results shown in Figure 1, increasing the concentration of  $\text{LiClO}_4$  dissolved in PC produced an effective SEI. This SEI prevented the destruction of the graphite electrode and the continuous decomposition of the electrolyte, which allowed lithium ions to insert into the graphite layers, as illustrated in Figure 2. This lithium ion insertion behavior is comparable to the typical charge-discharge behavior observed in EC-based electrolytes, as shown in Figure 2(b). The first cycle of PC- and EC-based electrolytes revealed large irreversible capacities (values obtained by subtracting the charge capacity from the discharge capacity) of approximately 180 and 350  $\text{mAh g}^{-1}$ , respectively. These results indicate that PC-based electrolytes are beneficial for generating an effective SEI.



**Fig. 2.** Charge and discharge curves for first cycle of natural graphite powder (NG-7) in (a) 3.27 M  $\text{LiClO}_4/\text{PC}$  and (b) 1 M  $\text{LiClO}_4/\text{EC} + \text{DMC}$ .

### 3.3 Electrochemical stability of PC-derived SEI

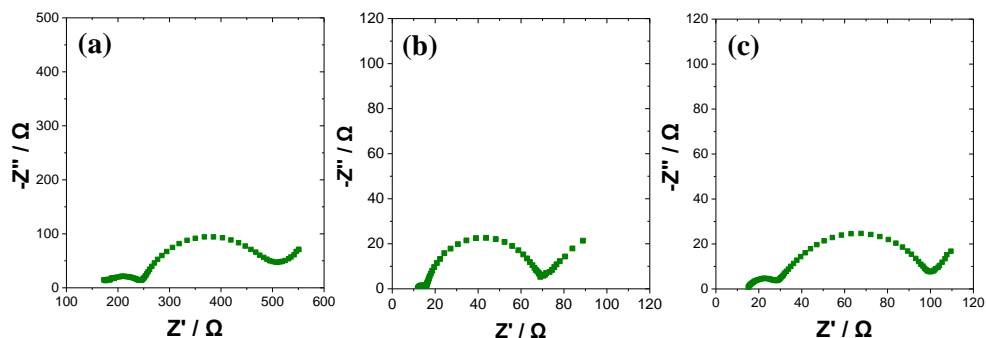
The formation of the SEI differs between PC- and EC-based electrolytes in terms of the amount of charge consumed and the potential at which SEI formation begins. In PC-based electrolytes, SEI formation begins at below 0.8 V, while it starts from 1.4 V in EC-based electrolytes. These differences in charge consumption and formation potential may affect the properties of the SEI formed in each electrolyte solution. To investigate this, an SEI-formed graphite electrode in PC-based electrolyte was transferred to EC-based electrolyte for charge-discharge behavior evaluation. As shown in Figure 3, the electrolyte modification caused a change in the charge capacity, but the discharge capacity remained almost unchanged. This indicates a slight increase in irreversible capacity. However, after cycling the graphite electrode for 5 cycles in PC-based electrolyte, it exhibited stable charge-discharge behavior in EC-based electrolyte. This suggests that the SEI formed in PC-based electrolyte is not entirely protective against electrolyte decomposition, but it still functions effectively.



**Fig. 3.** Charge and discharge curves in the fifth and sixth cycles of natural graphite powder (NG-7). The initial five cycles were conducted in 3.27 M LiClO<sub>4</sub>/PC, followed by the sixth cycle was carried out in 1 M LiClO<sub>4</sub>/EC + DMC.

### 3.4 Electrochemical interfacial resistances

The electrochemical impedance of the graphite electrode was measured at 0.7 V to obtain detailed information on the SEI formed in PC- and EC-based electrolytes. The Nyquist plots, illustrated in Fig. 4, exhibit depressed arcs in the high- and mid-frequency regions, which can be attributed to the impedance of lithium ion migration through the SEI layer ( $R_{SEI}$ ) and charge transfer reactions ( $R_{CT}$ ), respectively [16,17]. These plots present the real part ( $Z'$ ) and the imaginary part ( $Z''$ ) of a frequency response function on the complex plane, with frequency being an implicit variable. Comparing the PC-based electrolyte to the EC-based electrolyte (Figure 4(a)), it was observed that the  $R_{SEI}$  value was higher in the former, indicating the presence of a thicker SEI layer or a different SEI composition. In the EC-based electrolyte, there were no significant differences in  $R_{SEI}$  between SEIs derived from EC (Figure 4(b)) and PC (Figure 4(c)). It is plausible that structural or compositional variations in the SEI layer resulting from PC and EC electrolytes could explain the disparities in  $R_{SEI}$  magnitude, although the direct correlations between the physicochemical properties of the SEI layer and the magnitude of  $R_{CT}$  remain unclear. However, this study does not delve into a detailed interpretation of these correlations, as it falls beyond the scope of the current work.



**Fig. 4.** Nyquist plots of the graphite electrode in (a) 3.27 M LiClO<sub>4</sub>/PC, (b) 1 M LiClO<sub>4</sub>/EC + DMC, and (c) 1 M LiClO<sub>4</sub>/EC + DMC after initial five cycles in 3.27 M LiClO<sub>4</sub>/PC.

## 4 Conclusions

In this study, we conducted a comprehensive investigation of the electrochemical properties of an SEI that originated from PC. It was observed that, in the presence of a 3.27 M LiClO<sub>4</sub>/PC solution, reversible lithium intercalation and de-intercalation reactions took place at the graphite negative electrode, primarily due to the formation of an exceptionally effective SEI. A comparison between this electrolyte solution and a 1 M LiClO<sub>4</sub>/EC + DMC solution revealed a significantly superior electrochemical performance in terms of reversible capacity within the 3.27 M LiClO<sub>4</sub>/PC solution. However, it should be noted that the electrochemical properties of the SEI displayed noteworthy variations between these two electrolyte solutions. Notably, the PC-based solution required a lesser amount of charge to generate the SEI, but the resulting SEI exhibited high resistivity, ultimately leading to a substantial charge transfer resistance. As of now, further research is actively underway to gain a comprehensive understanding of the composition and structure of the SEI derived from PC.

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