Lithium-ion Transfer Kinetics through Solid Electrolyte Interphase on Graphite Electrodes

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ABSTRACT

For the development of lithium-ion batteries (LIBs) for electric vehicles, the reduction in the internal resistance of LIBs is strongly required. On the graphite negative electrodes, solid electrolyte interphase (SEI) is inevitably formed and causes partly the internal resistances. In addition, SEI covers the surface of graphite negative electrodes and affects the active sites for lithium-ion intercalation/deintercalation reactions. In this study, we investigated the influence of SEIs derived from vinylene carbonate (VC), fluoroethylene carbonate (FEC), and ethylene carbonate (EC) on the active sites for lithium-ion intercalation/deintercalation at highly oriented pyrolytic graphite (HOPG). We clarified the relation between the standard rate constant ($k_0$) of [Ru(NH₃)_6]³⁺/²⁺ that is a parameter for the edge site of graphite and the interfacial lithium-ion transfer resistance ($R_{ct}$) in various electrolyte solutions that deliver different SEIs. In the plots of $k_0$ vs. $R_{ct}$, there is a positive linear correlation between these two parameters, and the slopes increased in the order VC < EC < FEC. Additionally, the activation energy for the interfacial lithium-ion transfer remained unchanged despite the variation in SEIs. Based on these results, we conclude that SEIs affected the frequency factor of Arrhenius equation for the interfacial lithium-ion transfer on graphite.

1. Introduction

Lithium-ion batteries (LIBs) are recently used as a power source of electric vehicles (EVs). LIBs for EVs should meet some special requirements such as high safety, long-term durability, and high rate capability, etc. Among these requirements, the rate capability is the most important factor, because the current LIBs for EVs need longer time to be charged and discharged, as compared with short refueling time of gasoline vehicle. Therefore, the short charging time is an essential requirement for LIBs. As for the graphite electrodes, it is well known that lithium-ion intercalation reaction occurs at the edge sites of graphite, and it could be expected that there is a simple linear relationship between the number of edge sites and the number of lithium-ion intercalation sites. Actually, however, it is not so simple. Accompanied with lithium-ion intercalation, a thin film (solid electrolyte interphase, SEI) is simultaneously formed on graphite as a result of the decomposition of solvents and salts. This thin film covers the edge sites of graphite and finally increases the interfacial resistance for lithium-ion intercalation. Therefore, the influence of SEI should be considered to investigate lithium-ion transfer kinetics on graphite. Domi et al. investigated the morphology of SEI formed on highly oriented pyrolytic graphite (HOPG) in 1 mol dm⁻³ LiClO₄ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v%) containing VC and FEC. They elucidated that VC- and FEC-derived SEIs were more rigid than that derived from EC, and that VC produced the thinnest and densest SEI. In our previous study, we used an outer-sphere electron-transfer reaction [Ru(NH₃)₆]³⁺/²⁺ as a probe to evaluate the fraction of edge sites of HOPG. We calculated the standard rate constant ($k_0$) of [Ru(NH₃)₆]³⁺/²⁺ redox reactions and clearly related $k_0$ with lithium-ion transfer resistances. However, only a mixture of EC and dimethyl carbonate (DMC) was used as an organic electrolyte. As mentioned above, the properties of SEI strongly depend on the electrolyte solutions, and different electrolytes produce different SEIs. However, there has been no report on the quantitative analysis of active sites of graphite for lithium-ion intercalation, which is covered with various SEIs. To evaluate the influence of SEI on lithium-ion transfer kinetics on graphite, in this study, we investigated lithium-ion transfer resistances of HOPG covered with various types of SEIs, and shed light on the relation the resistances with $k_0$ of redox reaction of [Ru(NH₃)₆]³⁺/²⁺.

2. Experimental

The basal plane of HOPG (Momentive Performance Materials Quartz, Inc. The grade was ZYH) was used as a working electrode. All HOPGs were cleaved with Scotch tape and some of them were...
scratched by knife to increase the surface area. The $k^b$'s were examined by cyclic voltammetry. A three-electrode cell with a pristine or a scratched HOPG as, Pt-mesh as a counter electrode, and Ag/AgCl in saturated KCl aqueous solution as a reference electrode were used. As an electrolyte solution, 1 mol dm$^{-3}$ KCl (Nacalai Tesque, Inc.) aqueous solution containing 1 mmol dm$^{-3}$ [Ru(NH$_3$)$_6$]Cl$_3$ (Aldrich) was prepared. CV was conducted in the potential range of $-0.4$ to $-0.2$ V (vs. Ag/AgCl) with scan rate of 100 mV s$^{-1}$. The $k^b$ values were obtained by fitting of cyclic voltammograms using digital simulation. In addition to $k^b$, double layer capacitance ($C_{dl}$) was also evaluated by CV (0.05 to 0.25 V vs. Ag/AgCl, 100 mV s$^{-1}$) as edge site related parameter since McDermott et al. reported that as the amount of anthraquinone-2,6-disulfonate (AQDS) adsorption (the amount of edge sites) increases, observed $C_{dl}$ increases. Lithium-ion transfer resistance ($R_{ct}$) was measured in various electrolyte solutions by AC impedance spectroscopy under an Ar atmosphere. After measuring $k^b$ and $C_{dl}$, the used cells were washing with the deionized water and drying under vacuum without disassembling. For the AC impedance spectroscopy, lithium metals were used as a counter electrode and a Ag reference electrode against the used cells. Electrolyte solutions were 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC (1:1, v/v%, Tomiyama Pure Chemical Industries) with or without 3 wt% additives. VC (Kishida Chemical) and FEC (Tomiyama Pure Chemical Industries) were chose as additives. Before AC impedance spectroscopy, SEI was formed by cyclic voltammetry with scan rate 0.1 mV s$^{-1}$ in the potential range of 0 to 0.3 V (vs. Li/Li$^+$). The cycle number was two cycles. After that, the electrode potential was lowered by linear sweep voltammetry from 3.0 V to 0.2 V with scan rate 0.1 mV s$^{-1}$ and potential was held at 0.2 V (vs. Li/Li$^+$) for 18 h. AC impedance spectroscopy was conducted in the frequency range of 100 kHz to 10 mHz with an applied ac voltage amplitude of 5 mV. The electrode potential was 0.2 V (vs. Li/Li$^+$).

3. Result and Discussion

Figure 1 shows cyclic voltammograms of (a) a cleaved HOPG and (b) a scratched HOPG in 1 mol dm$^{-3}$ KCl aqueous solution containing 1 mmol dm$^{-3}$ [Ru(NH$_3$)$_6$]Cl$_3$. Currents were normalized by the peak value of oxidation curves. Solid lines are experimental curves and broken lines are fitted curves.

![Figure 1. Cyclic voltammograms of (a) a cleaved HOPG and (b) a scratched HOPG in 1 mol dm$^{-3}$ KCl aqueous solution containing 1 mmol dm$^{-3}$ [Ru(NH$_3$)$_6$]Cl$_3$. Currents were normalized by the peak value of oxidation curves. Solid lines are experimental curves and broken lines are fitted curves.](image1)

Figure 2. Cyclic voltammograms of HOPGs in 1 mol dm$^{-3}$ KCl aqueous solution containing 1 mmol dm$^{-3}$ [Ru(NH$_3$)$_6$]Cl$_3$. Sweep range was 0.05$-$0.25 V (vs. Ag/AgCl).

![Figure 2. Cyclic voltammograms of HOPGs in 1 mol dm$^{-3}$ KCl aqueous solution containing 1 mmol dm$^{-3}$ [Ru(NH$_3$)$_6$]Cl$_3$. Sweep range was 0.05$-$0.25 V (vs. Ag/AgCl).](image2)

decomposition of electrolyte on the surface of graphite below 0.65 V (vs. Li/Li$^+$). Therefore, this irreversible peak is attributed to the electrolyte decomposition reaction and it shows the following the SEI formation reaction occurred. In Figs. 3b and 3c, the irreversible reduction reaction at around 1.1 and 1.0 V (vs. Li/Li$^+$) were observed at the 1st cycle, respectively. These peaks were assigned to the reductive decomposition reactions of additives. Since the reductive decomposition reaction potentials were different, the SEIs are thought to be formed from different sources. In Fig. 3c, the peak...
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Figure 3. Cyclic voltammograms of HOPGs in 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC (1:1, v/v%) containing no additive (a), VC (b), and FEC (c).

Figure 4. (a) Nyquist plots of HOPGs in 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC (1:1, v/v%) at 0.2 V (vs. Li/Li$^+$). (b) Enlarged figure of (a) in high frequency region.

appeared from 2.5 to 1.2 V (vs. Li/Li$^+$) is reductive reaction of moisture. In all electrolyte solutions, the reduction/oxidation peaks attributed to the lithium-ion intercalation/deintercalation reaction were observed.

After forming SEI from each electrolyte solutions, $R_\text{ct}$ was evaluated by AC impedance spectroscopy at 0.2 V (vs. Li/Li$^+$). Figure 4 shows the Nyquist plots of the cleaved HOPG and the scratched HOPG in 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC containing no additives. In Fig. 4, two semi-circles appeared in the high and low frequency regions. The small semi-circle in the high frequency range (Fig. 4b) is attributed to the impedance of SEI. The large semi-circle in the low frequency range (Fig. 4a) is attributed to the impedance of the interfacial lithium-ion transfer ($R_\text{ct}$). The $R_\text{ct}$ of the scratched HOPG was smaller than that of the cleaved HOPG. It is considered that $R_\text{ct}$ becomes smaller due to the increase of the number of lithium-ion intercalation sites by scratching. Therefore, scratching of HOPGs enlarged both edge sites and lithium-ion intercalation sites in this study. Similarly, the same tendencies were observed in 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC containing VC and FEC (Fig. S1 of the Supporting Information). As a result, the relation between the $R_\text{ct}$ and $k_0$ would give the influence of SEI to the lithium-ion intercalation/deintercalation reaction. In order to obtain the relation between $k_0$ and $R_\text{ct}$, $R_\text{ct}^{-1}$ was plotted against $k_0$. In this case, $R_\text{ct}^{-1}$ is proportional to the reaction rate of the lithium-ion intercalation/deintercalation. Figure 5 shows the relation between $k_0$ and $R_\text{ct}^{-1}$, which was obtained in each electrolyte solution. In the case of 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC containing no additive, the positive correlation was observed and it can be assumed that the active site for lithium-ion intercalation and the active site for redox reaction of [Ru(NH$_3$)$_6$]$_3^{3+/2+}$ are proportional, that is, the edge site is the active site. This result is consistent with that of Yamada. There were also positive correlation between $k_0$ and $R^{-1}$ obtained in 1 mol dm$^{-3}$ LiClO$_4$/EC+DEC containing VC and FEC. However, the slopes seemed to be different. Linear approximation to each $k_0$-R$^{-1}$ plot was performed. The values of the slopes of the straight lines of with no additive, VC, and FEC were 0.04, 0.02, and 0.05 s$^{-1}$ cm$^{-1}$, respectively. The slope of the straight line varied with electrolyte solutions, and that with of VC was smaller compared to others. In addition, as shown in Fig. 6, the same tendency was observed in $C_\text{dl}$-R$^{-1}$ plot. The smaller slope of VC containing electrolyte solution means that VC-derived SEI impaired the reaction rate for the lithium-ion intercalation/deintercalation.

The reason of the impaired reaction rate should be (1) increasing in the activation energy by SEI or (2) decreasing in the frequency factor by SEI based on the Eq. (1).

(a)

(b)

(c)
energy was 55 kJ mol⁻¹. The coefficients of determination are 0.88, 0.63 and 0.91 for no additive, VC and FEC, respectively.

A is the frequency factor, $E_a$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. In the former case, we would obtain the different activation energies experimentally. Therefore, $E_a$ in each electrolyte was measured. The result of temperature dependence of $R_{ct}$ between 10 to 30°C obtained for each electrolyte is shown in Fig. 7. The electrode potential was set to 0.2 V. In the case of LiClO₄/EC+DEC with no additive, activation energy was 55 kJ mol⁻¹. We reported that the activation energy of lithium-ion transfer resistance at the graphite/electrolyte interface in EC-based electrolytes is 50–60 kJ mol⁻¹. This is attributed to the desolvation process of EC from lithium-ion. The activation energies with VC- and FEC-derived SEIs were 52 kJ mol⁻¹ and 53 kJ mol⁻¹, respectively, which were almost the same as that with no additive. This means $E_a$ did not depend on the nature of the SEI, and it is considered that the difference in the reaction rate for the lithium-ion intercalation/deintercalation is due to the change in the frequency factor.

As mentioned above, it was reported that VC-derived SEI was quite dense and mainly composed of inorganic compounds that have no lithium-ion conductivity. Thus, VC-derived SEI covers the edge sites on HOPG with lithium-ion insulating compounds and partly blocks the reactive sites. In contrast, FEC-derived SEI is also dense and contains LiF, and such LiF is important to enhance the electrochemical properties of graphite negative electrodes. Based on the above results of $k^0$ plots, it can be concluded that the advantage of FEC as a SEI-forming additive stems from the fact that the frequency factor for interfacial lithium-ion transfer was larger.

4. Conclusion

The influence of SEIs on HOPG for the lithium-ion intercalation/deintercalation reactions was investigated by estimating the standard rate constant ($k^0$) of redox reaction of $[\text{Ru(NH}_3)_6]^{3+}^{2+}$ and the interfacial lithium-ion transfer resistance ($R_{ct}$). The values of $k^0$ were dependent on the scratching condition of HOPGs, $k^0$ can be used as a parameter of the number of edge sites. These two parameters ($k^0$ and $R_{ct}$) showed positive correlation, and the slope of the straight lines varied with the electrolyte solutions used for SEI formation. The slope for the electrolyte containing VC was the smallest value, that is, the reaction rate for lithium-ion intercalation/deintercalation was smallest in the case of the VC-derived SEI. In contrast, FEC-derived SEI led to a higher reaction rate. Since the activation energy for interfacial lithium-ion transfer was almost the same, irrespective of the electrolyte solutions used in this study, it can be concluded that SEIs changed the frequency factor of Arrhenius equation for the interfacial lithium-ion transfer on graphite.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00077.

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