Lithium-ion transfer between Li$_x$CoO$_2$ and polymer gel electrolytes

Izumi Yamada, Yasutoshi Iriyama, Takeshi Abe, Zempachi Ogumi*

Graduate School of Engineering, Kyoto University, Kyoto daigaku-katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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Abstract

Lithium-ion transfer at the interface between Li$_x$CoO$_2$ electrodes and polyvinylidene fluoride (PVdF)-based polymer gel electrolytes was studied by AC impedance spectroscopy. In addition to a conventional LiCoO$_2$ composite electrode, LiCoO$_2$ thin films were prepared by pulsed laser deposition. For both the composite and thin film electrodes, the impedance ascribed to lithium-ion transfer through the interface, i.e., charge transfer resistance, was observed in the mid-to-lower-frequency regions in Nyquist plots. The charge transfer resistance decreased in the initial stage of charging up to about 3.9 V vs. Li/Li$^+$ and then increased from about 4 V. The charge transfer resistances for LiCoO$_2$ thin film electrodes were much greater than those for LiCoO$_2$ composite electrodes due to their small reaction area. Based on these results, the design of thin film lithium-ion batteries using polymer gel electrolytes is discussed.

Keywords: Lithium-ion batteries; LiCoO$_2$; Polymer gel electrolyte; Lithium-ion transfer

1. Introduction

Lithium-ion batteries have been widely used in the field of portable electronic devices. Recently, due to limitations regarding the use of Cd, the application of lithium-ion batteries has been expanded to electric power tools, and Ni–Cd batteries are gradually being replaced by lithium-ion batteries. Two major driving forces underlie recent R&D on Li-ion batteries. One is the need to improve small-scale Li-ion batteries for use in electronic devices and the other is the need to enhance the performance of large-scale lithium-ion batteries for use in hybrid electric vehicles (HEV).

Several factors must be considered for the practical use of lithium-ion batteries in HEV. Among them, the enhancement of rate performance and the improvement of safety are critical issues. We have focused on lithium-ion transfer at the electrode/electrolyte interface and found that there are large activation barriers for the transfer of lithium ion at the interface [1–10]. Based on our results thus far, we have proposed a design for lithium-ion batteries with high rate-performance. Although enhancement of the rate performance of lithium-ion batteries needs to be investigated further, in this study we focused on the serious issue of safety.

Solid polymer electrolytes have been extensively studied since Wright et al. [11] reported an acceptable ionic-conductive complex of alkali metal salts and poly(ethylene oxide). Solid polymer electrolytes have received considerable attention as promising materials for lithium-ion batteries due to advantages in safety, high-energy density, and ease of manufacture. However, some problems, such as low ionic conductivity and poor contact with active materials, still remain to be solved for the practical use of solid polymer electrolytes in lithium batteries. Poor contact between a polymer electrolyte and the active electrode material is a very serious problem, and hence polymer gel electrolytes, which consist of polymer matrices, plasticizers, and lithium salt, have recently attracted attention probably because plasticizers in the polymer matrix enhance the compatibility between the electrolyte and the active electrode material. Polymer gel electrolytes enhance the safety of lithium-ion batteries compared with conventional liquid electrolytes.

Much work has been done on the optimization of the components of polymer gel electrolytes. However, little attention has been paid to interfacial reactions between...
electrodes and polymer gel electrolytes, despite the fact that the battery reaction rate depends on the rate of interfacial reactions and the diffusion rate through active matrices.

We report here lithium-ion transfer at the interface between Li$_x$CoO$_2$ and polyvinylidene fluoride (PVdF)-based polymer gel electrolytes using AC impedance spectroscopy.

2. Experimental

2.1. Preparation of polymer gel electrolytes

Polymer gel electrolytes were prepared from PVdF, polyethylene glycol dimethyl ether (PEGDME) and lithium salts such as LiCF$_3$SO$_3$, LiN(CF$_3$SO$_2$)(C$_4$F$_9$SO$_2$), and others. PEGDMEs with molecular weights of 250, 500 and 1000 were used. The weight ratio of PVdF to PEGDME was set at 3:7. LiCF$_3$SO$_3$ was added at a ratio of ethylene oxide unit in PEGDME/Li = 25. A mixture of PVdF, PEGDME, and LiCF$_3$SO$_3$ was melted at 407 K, and the solution was then cooled in a Teflon template to form transparent gel electrolytes 300-μm thick. The ionic conductivities of the polymer gel electrolytes were determined by AC impedance spectroscopy with a Sorlatron 1255.

2.2. Preparation of LiCoO$_2$ composite electrode

A LiCoO$_2$ composite electrode was prepared from LiCoO$_2$, acetylene black, and polymer gel electrolytes, with weight ratios of 20, 7, and 73 wt%, respectively. These weight ratios gave sufficient electric and ionic conductivities for the resulting electrode.

2.3. Preparation of LiCoO$_2$ thin film electrode

LiCoO$_2$ thin films were prepared by pulsed laser ablation using a KrF excimer laser with a wavelength of 248 nm (Japan Storage Battery, EXL-210). The substrate was a polished Pt plate. The detailed conditions for preparation were reported previously [12]. The resulting LiCoO$_2$ thin films were characterized by X-ray diffraction to be highly oriented along the c-axis.

2.4. AC impedance measurement

Lithium-ion transfer at the interface between Li$_x$CoO$_2$ and polymer gel electrolytes was studied by AC impedance spectroscopy using a Sorlatron 1255 in the frequency range of 100 kHz–1 mHz. A three-electrode cell was used regardless of the electrodes. Li metal was used for the counter and reference electrodes. Measurement took place from 3.40 to 4.15 V. Each potential was held for 5 h to reach a steady state.

3. Results and discussion

Fig. 1 shows the ionic conductivities of PVdF-based polymer gel electrolytes with various plasticizers plotted against reciprocal temperatures. With an increase in the molecular weight of the plasticizers, the temperature-dependence of ionic conductivity became VTF-type. Polymer gel electrolytes using PEGDME250 gave ionic conductivities higher than 10$^{3.5}$ S cm$^{-1}$ at room temperature, while other polymer gel electrolytes gave somewhat lower conductivities due to the high viscosities of the plasticizers. For polymer gel electrolytes with PEGDME1000, a rapid increase in conductivity can be seen at around 303 K. At these temperatures, PEGDME1000 melts, resulting in an increase in conductivity.

Fig. 2 shows Nyquist plots for a Li/polymer gel electrolyte/LiCoO$_2$ composite electrode cell at various electrode potentials. Open squares, circles, triangles, and solid circles denote the potentials 3.464, 3.840, 3.920, and 4.000 V, respectively. The inset figure shows a Nyquist plot for an electrode containing only PVdF and acetylene black in 1 mol dm$^{-3}$ LiClO$_4$/ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 by volume). The plasticizer is PEGDME250 and the lithium salt is LiCF$_3$SO$_3$. At a potential of 3.464 V, only one semi-circle was observed in the high-frequency region, and in the middle-to-lower-frequency region, the electrode exhibited typical blocking-electrode-type behavior. In contrast, two semi-circles were observed at potentials above 3.84 V, as shown in Fig. 2.
In the high-frequency region, resistance was independent of the potential, while in the middle-to-lower-frequency region resistance depended on the potential. The characteristic frequencies of the latter semi-circles were around 1 Hz. To characterize these Nyquist plots, we first fabricated a composite electrode without LiCoO₂. The Nyquist plot is shown in the inset in Fig. 2. In the absence of LiCoO₂ as an active material, a similar semi-circle was observed in the higher-frequency region. Therefore, the semi-circle at the higher-frequency region in Fig. 2 may not be due to the relaxation process related to LiCoO₂, but rather to the electric contact resistance of the electrode. Hence, it is very reasonable that the semi-circle at the lower-frequency region remains unchanged.

We next used liquid electrolytes containing various concentrations of LiClO₄, and studied reactions at the electrode/electrolyte interface. In this case, the composite LiCoO₂ electrode consists of LiCoO₂, PVdF, and acetylene black, at weight ratios of 85, 10, and 5 wt%, respectively. Figs. 3(a)–(c) show Nyquist plots for the interfacial reactions between a LiCoO₂ electrode and propylene carbonate (PC) solutions containing 0.125, 0.250, and 0.500 mol dm⁻³ LiClO₄, respectively. The potential was kept constant at 3.90 V. The onset values of Z' are superimposed to make it easier to compare the low-frequency region. The first semi-circle observed in the higher-frequency region is almost unchanged, which indicates that these relaxation processes are independent of the cation or anion. This result is in good agreement with the above suggestion. In contrast, the dependency of the second semi-circles observed in the lower-frequency region on the electrolyte concentration reveals that lithium-ion transfer at the interface between LiCoO₂ and the electrolyte is responsible for the observed semi-circle in AC impedance spectroscopy in Fig. 3.

Based on the above results, the semi-circle in the higher-frequency region in Fig. 2 should be ascribed to contact resistance in the electrode, and that in the lower-frequency region can be identified as charge (lithium-ion) transfer resistance.

When a thin film electrode of LiCoO₂ was used, the Nyquist plot became very simple. Nyquist plots for the liquid electrolyte/LiCoO₂ thin film interface are shown in Fig. 4. The electrolyte was 1 mol dm⁻³ LiCF₃SO₃/PC. As is clearly shown in Fig. 4, only one semi-circle was observed at potentials higher than 3.92 V. At lower potentials, blocking-electrode-type behavior was again observed. Thus, the semi-circle in Fig. 4 was ascribed to charge transfer resistance.

Based on the above results and discussion, it is clear that the semi-circle observed in the lower-frequency region in Fig. 2 is due to lithium-ion transfer across the interface. Fig. 5 shows the variation in charge transfer resistance with the electrode potential. Two different salts of LiCF₃SO₃ and Li(CF₃SO₂)(C₄F₉SO₂), corresponding to solid squares and open circles, respectively, were used. Regardless of the salt used, the charge transfer resistance decreased in the initial stage of charging up to about 3.9 V vs. Li/Li⁺ and then increased from about 4.0 V. After charging up to above 4.1 V, charge transfer resistance did not decrease.
with a decrease in potential, indicating that a surface film may be formed by decomposition of the electrolyte. The minimum resistance of ca. 10 $\Omega$ can be seen at around 3.9–4.0 V.

Fig. 6 shows the variation in charge transfer resistance with the electrode potential in the case of a LiCoO$_2$ thin film electrode. The charge transfer resistance decreased with an increase in electrode potential up to around 4.1 V, and then gradually increased up to 4.3 V. In this case, the rapid increase in charge transfer resistance seen in Fig. 5 is not observed. The contact area between a LiCoO$_2$ thin film electrode and liquid electrolyte was regulated by an o-ring to be 0.785 cm$^2$. Therefore, decomposition of the electrolyte is kinetically suppressed by the small reactive site. A minimum resistance of ca. 30 $\Omega$ was also seen at around 4.0 V. In Fig. 6, we used LiCoO$_2$ thin film electrodes, while...
in Fig. 5 we used powder LiCoO$_2$. Nevertheless, the charge transfer resistances are almost identical in order. The powder LiCoO$_2$ should give a lower charge transfer resistance due to the large reaction sites for the insertion and extraction of lithium ion. When we consider the roughness factors, the minimum charge transfer resistance in Fig. 5 should be much smaller than those observed for a LiCoO$_2$ thin film electrode.

The large charge transfer resistance is principally due to the low wettability between LiCoO$_2$ and the polymer gel electrolyte. The large charge transfer resistances are more explicit for LiCoO$_2$ thin film electrode/polymer gel electrolyte interface as shown in Fig. 7. By comparing the results in Figs. 6 and 7, the minimum values of the charge transfer resistances differ by 5 times. Since lithium ion cannot jump as an electron does, atomic contact between LiCoO$_2$ and the polymer gel electrolyte is essential for the insertion and extraction of lithium ion at the electrode. The low wettability decreases the reactive sites and increases the charge transfer resistance. Before polymer gel electrolytes are used in lithium-ion batteries for high-rate use, wettability must be further improved.

The temperature dependence of charge transfer resistance was studied to elucidate the activation energies. Fig. 8 shows the variation in the temperature dependence of charge transfer resistance for a Li$_x$CoO$_2$/gel electrolyte cell at 3.8 V. The Li salt was LiCF$_3$SO$_3$ and the plasticizers were PEGDME250, -500, and -1000. Based on the slopes, the values of the activation energy were calculated to be 56.4, 60.6, and 71.4 kJ mol$^{-1}$ for PEGDME250, -500, and -1000, respectively. The activation energy increases with an increase in the molecular weight of the plasticizer. An increase in molecular weight has been reported to stabilize lithium ion \[13\], leading to higher activation energies. Therefore, the plasticizer also plays an important role on lithium-ion kinetics at electrode. Higher molecular weight of plasticizer will give higher safety of lithium-ion batteries, but the lithium-ion kinetics will become slower.

4. Conclusion

Lithium-ion transfer at LiCoO$_2$ and polymer gel electrolyte interface was studied by AC impedance spectroscopy. The charge (lithium ion) transfer resistances were found to be very large even for LiCoO$_2$ composite electrode due to the wettability between LiCoO$_2$ and polymer gel electrolyte. In addition, the plasticizer plays an important role on lithium-ion kinetics at LiCoO$_2$ electrode.

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