Behavior of lithium/electrolyte interface in organic solutions

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Abstract

The charge/discharge behavior of a lithium negative electrode is intensively affected by the structure of the lithium electrode/organic electrolyte interface and the composition of the electrolyte solution. Addition of some metal ions such as Mg^{2+}, Zn^{2+}, In^{3+}, Ga^{3+}, etc., to electrolyte solutions improves the coulombic efficiencies of the electrode during the charge/discharge cycles. Some organic additives, e.g., 2-methylthiophene, 2-methylfuran, benzene, etc., also improve the coulombic efficiencies for lithium cycling. The mechanisms of these additives are discussed in connection with the structure of the electrode/electrolyte interface.

Introduction

The electrochemistry of lithium (Li) electrode/organic electrolyte interface is one of the important issues to develop practical rechargeable Li batteries. The charge/discharge behavior of a Li electrode is intensively affected by the structure of the Li electrode/organic electrolyte interface and the composition of the electrolyte solution [1–3]. Therefore, a large number of combinations between organic solvents and electrolytic salts have been presented [4, 5]. Some papers [6–11] have demonstrated that addition of small amounts of inorganic or organic compounds to the electrolyte solutions improves the cycling performances of the Li electrode and the rechargeability of the battery.

The structure of Li electrode/electrolyte interface has been investigated. Peled [12, 13] represented the existence of the solid-electrolyte interface (SEI) through which electrons are not allowed to pass. At the same time, impedance of the Li electrode/electrolyte or the film formation on Li electrode was studied [12–16]. In these studies, various kinds of films on Li electrode were investigated, and the impedance was analyzed. Thevenin and Muller [15] presented the compact-stratified layer (CSL) model whose equivalent circuit consists of the circuit of a SEI layer in series with the circuit of a SEI or a polymer electrolyte interface (PEI) layer. On the other hand, in connection with surface layers on Li, ellipsometric studies were reported [17], and Fourier-transform infrared spectroscopy (FT–IR) has been used to analyze the products of reaction between Li and the electrolyte solutions [18–21].

In the present paper, the mechanisms of organic and inorganic additives are discussed in connection with each structure of the Li electrode/organic electrolyte interface.

Lithium/organic electrolyte interface

Most solvents used generally in Li batteries decompose at the surface of the Li negative electrode as cited above [18–21]. Sometimes, a Li^+-ion permeable film is formed at the Li surface as a solid electrolyte [12–15]. Common electrolytic salts for Li batteries are $LiClO_4$, $LiBF_4$, $LiPF_6$ and $LiAsF_6$, whose anions might be reduced at the Li electrode surface during the charge/discharge cycling. Further serious problems would be caused by the formation of a Li dendrite and/or electrically-isolated Li parts during the charge/discharge cycling. The adoption of stable solvents and Li salts is essential to realizing practical rechargeable Li batteries.

The electrical double-layer structure between a Li electrode and an organic electrolyte should be an important issue for the basic studies on rechargeable Li batteries. In mixed solvent systems, a solvent having higher donicity tends to coordinate preferentially with Li^+ ion (specific or selective solvation), and it would have more chance to contact and react with Li metal or Li^+ ion at the Li-electrode/organic electrolyte interface [4, 22].

Inorganic additives

One of the effective techniques to obtain a prominent Li electrode/organic electrolyte interface is addition of a small amount of inorganic ions such as Mg^{2+}, Zn^{2+}, In^{3+}, Ga^{3+}, etc. [7]. The experimental details have been mentioned in a previous paper [7]. The addition of these metal ions improves the coulombic efficiencies of the Li electrode during the charge/discharge cycles.

Figures 1 and 2 show typical results for these inorganic additives. Here, the coulombic efficiencies for charge/discharge cycling of Li were measured in propylene carbonate (PC)/$LiClO_4$(1 M) solutions containing Mg^{2+} or Zn^{2+} under a constant current of 1.0 mA cm^{-2}. The addition of Mg^{2+} and Zn^{2+} to the PC-based solutions
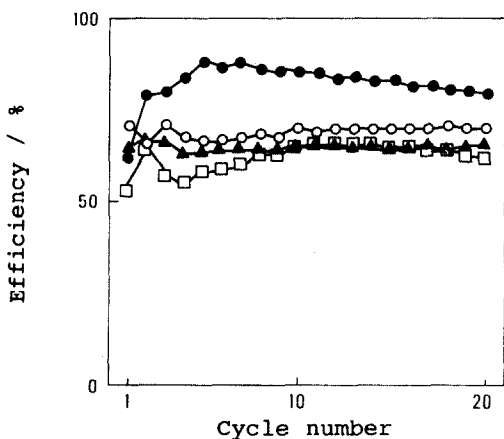

Fig. 1. Addition effect of Mg^{2+} on charge/discharge coulombic efficiency of Li(PC/LiClO$_4$); current density: 1.0 mA cm^{-2}, charged electricity: 0.1 C cm^{-2}, surface area of the test electrode: 0.95 cm^2. (○) 0 ppm, (●) 10 ppm, (▲) 100 ppm, and (□) 1000 ppm.
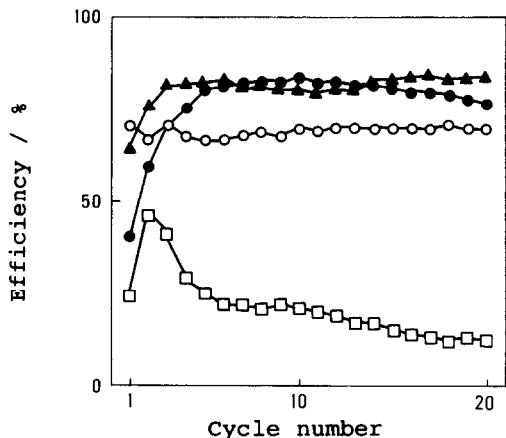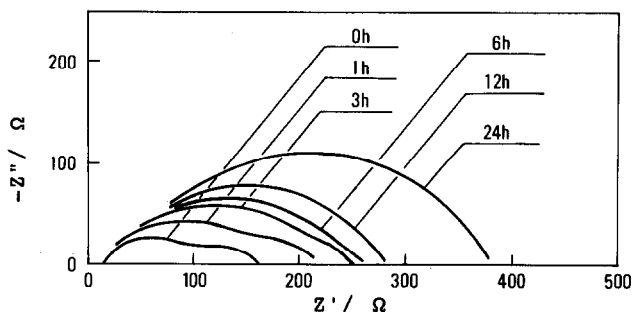
Fig. 2. Addition effect of Zn^{2+} on charge/discharge coulombic efficiency of Li(PC/LiClO$_4$); current density: 1.0 mA cm^{-2}, charged electricity: 0.1 C cm^{-2}, surface area of the test electrode: 0.95 cm^2. (○) 0 ppm, (●) 10 ppm, (▲) 100 ppm, and (□) 1000 ppm.

Fig. 3. Cole–Cole plots of the impedance at Li electrode in 1.0 M LiClO$_4$/PC with 100 ppm Mg^{2+}; surface area of the test electrode: 0.95 cm^2.

improved the coulombic efficiency. There were optimum concentration ranges for these metallic ions to obtain excellent addition effects.

The effects of the additives have been investigated by cyclic voltammetry, scanning electron microscopy (SEM) observation and a.c. impedance measurements. A typical result for the impedance measurements is shown in Fig. 3, where the variation of the a.c. impedance at the Li electrode in PC/LiClO$_4$ containing Mg^{2+} is plotted (Cole–Cole plot). The size of the semicircle in the plot, which is equivalent to the resistance at the interface, increased with time duration, i.e. the immersion time of Li in the electrolyte. Time constant ($R\,C_d$) of the impedance was calculated, and its time duration is shown in Fig. 4. The result suggests that the composition of the electrode surface changed with time duration. The composition change at the interface was assumed to be caused by the formation of a thin film of a Li alloy though it has not been ascertained experimentally. For an example, Li–Al alloy is lower conductive than Li and Li can diffuse in the alloy. Such phenomena would be consistent with the results of voltammetric measurements [7].
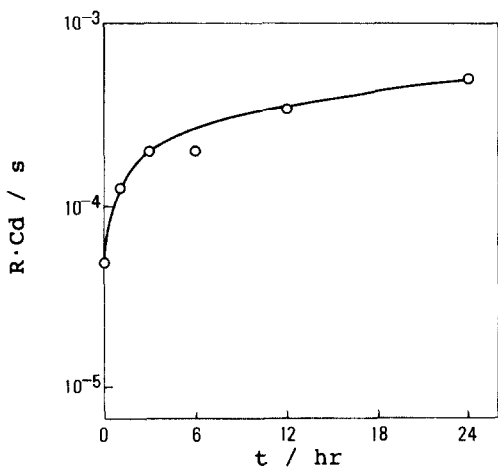
Fig. 4. Variation of $R\,C_d$ with time; (O) Mg 100 ppm.

Similar addition effects have been observed in the electrolyte solutions containing Sn^{4+}, Al^{3+}, In^{3+}, Ga^{3+} and Bi^{3+}. These inorganic ions would form thin layers of Li alloys at the electrode surface during cathodic deposition of Li, and the resulting thin films suppress the dendritic deposition of Li that causes the lowering of the coulombic efficiencies in the charge/discharge cycles.

Organic additives

Some organic additives in organic electrolyte solutions also improve the coulombic efficiencies of Li during the charge/discharge cycles [8–11]. Among the additives, cyclic compounds containing hetero-atoms and conjugated double bonds, such as 2-methyl-thiophene (2MeTp) and 2-methylfuran (2MeF), are excellent. Also, some aromatic compounds such as benzene is one of the effective additives in the electrolyte solutions of rechargeable Li batteries. The experimental details have been described in a previous paper [11].

Figure 5 shows a comparison of the coulombic efficiencies during the charge/discharge cycles in PC/LiClO$_4$ containing 2MeTp (0.5 vol.%) and benzene (5.0 vol.%) measured under a constant current of 1.0 mA cm^{-2}. The addition of these compounds improved the coulombic efficiency of Li. Under these experimental conditions, the optimum concentration of benzene was 5.0 vol.%, though that of 2MeTp was very low [10, 11, 23–25].

The results of the impedance measurements are presented in Fig. 6. In general, the impedance at the interface of Li electrode/organic electrolyte solution increased with time duration. However, the magnitude of the resistance increase was suppressed by addition of these additives.

The time constants calculated from the Cole–Cole plots are shown in Fig. 7. The time constants in PC/LiClO$_4$ with or without benzene were almost constant with the immersion time, but those in PC/LiClO$_4$ with 2MeTp or 2MeF increased with time duration. These results suggest that, in PC/LiClO$_4$ with or without benzene, the chemical composition of the surface film does not change during the immersion of Li but the
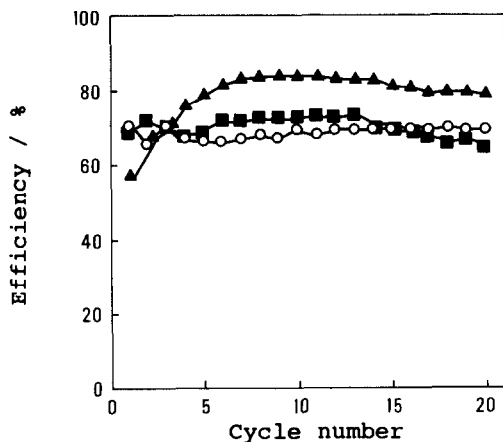
Fig. 5. Addition effect of organic additives on charge/discharge coulombic efficiency of Li; current density: 1.0 mA cm^{-2}, charged electricity: 0.1 C cm^{-2}, surface area of the test electrode: 0.95 cm^2. (○) PC/LiClO$_4$(1 M), (■) PC/LiClO$_4$ + 2MeTp(0.5 vol.%), and (▲) PC/LiClO$_4$ + benzene 5 vol.%).
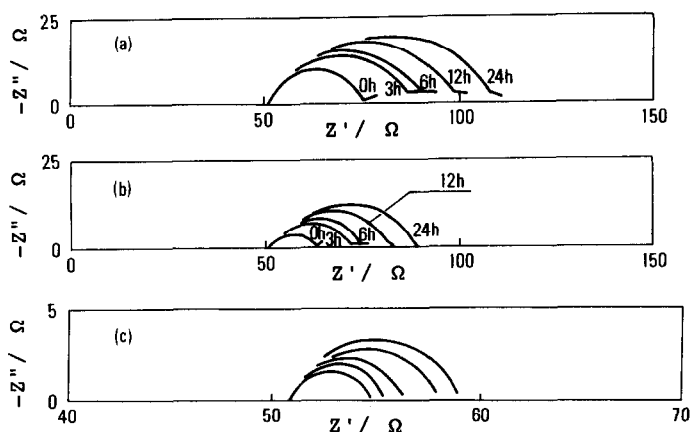

Fig. 6. Cole–Cole plots of the impedance at Li electrode in: (a) 1.0 M LiClO$_4$/PC, (b) 1.0 M LiClO$_4$/PC with 2MeTp(0.5 vol.%), and (c) 1.0 M LiClO$_4$/PC with benzene(5 vol.%). Surface area of the test electrode: 0.95 cm^2.

film thickness increases with time. That is, benzene would adsorb weakly on the Li electrode surface and suppress the dendrite formation. However, in the latter case, 2MeTp reacts with Li and a stable thin Li$^+$-ion conducting film would be formed on the Li electrode surface. This is suggested by the fact that the time constant gradually changed with the immersion time.

As mentioned above, the mechanisms of the addition effects of benzene and 2MeTp or 2MeF are different. Therefore, the reaction between Li and the cyclic compounds containing hetero-atoms and conjugated double bonds, 2MeTp and 2MeF, would form SEI, but benzene adsorbs weakly on Li electrode in the electrolyte solution and Li electrode reaction would proceed on bare Li surface with smaller area. Therefore,
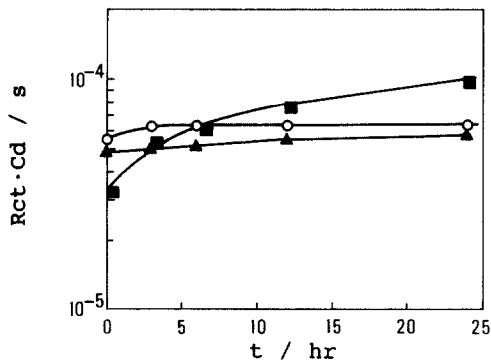
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Fig. 7. Variation of $R_{ct} C_d$ with time; current density: 1.0 mA cm^{-2}, charge electricity: 0.1 C cm^{-2}. (O) PC/LiClO$_4$(1 M), (■) PC/LiClO$_4$+2MeTp(0.5 vol.%) and (▲) PC/LiClO$_4$+benzene (5 vol.%).

the addition effect of benzene cannot explain the SEI. These differences of the mechanisms between two groups of the organic additives are very interesting.

Future directions

Addition of inorganic and organic compounds to the organic electrolyte solutions of rechargeable Li batteries provided high coulombic efficiencies for the Li cycling. The mechanism of the additives should be clarified in the near future. In the present, much interest is focused on rechargeability of rocking chair type electrodes. However, the use of a Li metal electrode would realize rechargeable Li batteries with high energy densities. The adoption of effective additives for the electrolyte solutions should be one of the beneficial ways to the development of practical rechargeable Li batteries.

Acknowledgements

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