

Control of lithium metal anode cycleability by electrolyte temperature

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Abstract

Precycling of lithium (Li) metal on a nickel substrate at low temperatures (0 and -20°C) in propylene carbonate (PC) mixed with dimethyl carbonate (DMC) and Li hexafluorophosphate (LiPF_6) ($\text{LiPF}_6\text{-PC/DMC}$) was found to enhance Li cycleability in the subsequent cycles at a room temperature (25°C). In contrast when the precycling at the low temperatures was performed in PC mixed with 2-methyltetrahydrofuran (2MeTHF) and LiPF_6 ($\text{LiPF}_6\text{-PC/2MeTHF}$), no improvement in the Li cycling efficiency was observed in the subsequent cycles at 25°C . These results suggest that the low-temperature precycling effect on the Li cycleability depends on a co-solvent used in the PC-based electrolytes. Ac impedance analysis revealed that the precycling in the low-temperature $\text{LiPF}_6\text{-PC/DMC}$ electrolyte provided a compact Li interface with a low resistance. In marked contrast to this, a Li anode interface formed by the precycling in the $\text{LiPF}_6\text{-PC/2MeTHF}$ system was irregular and resistive to Li-ion diffusion. The origins of the low-temperature precycling effect dependent on the co-solvents were discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Rechargeable lithium battery; Lithium metal anode; Electrolyte temperature; Coulombic efficiency; Precycling; Ac impedance

1. Introduction

It is widely known that the characteristics of an interface between a lithium (Li) metal anode and an organic electrolyte are much correlated with the charge–discharge performance of a Li metal anode. To date the poor charge–discharge cycling efficiency of the Li metal anode has limited practical use of secondary batteries with the Li metal anode. Many attempts to improve the Li cycling efficiency have so far been reported. Among them, inorganic [1–3], organic [1,2,4], and gaseous [5,6] additives to electrolytes for the rechargeable Li-metal batteries have been proposed. The chemical properties of a Li interface are known to affect the Li cycling efficiency. Thus the chemical modification of the Li interface with the additives would be a promising approach. In contrast little is known about the utilization of physical factors for improving Li interface properties and the cycling efficiency. Although a pressure effect on the Li cycling performance was reported [7], the effect of other physical parameters on the Li interface and the cycling performance remains to be elucidated. Recently we reported the utilization of an alternative physical parameter, electrolyte temperature, for the Li-interface modification favorable to the Li cycling

[8,9]; our findings were that the charge–discharge ‘precycling’ of the Li anode in low-temperature ethylene carbonate/dimethyl carbonate (DMC) binary electrolytes improved the Li cycling efficiency in the subsequent cycles at a room temperature [8]. We found, furthermore, that lithium hexafluorophosphate (LiPF_6) was effective as an electrolytic salt in the enhancement of the Li cycling efficiency with the low-temperature precycling [9]. This study focuses on a co-solvent effect on the low-temperature precycling in propylene carbonate (PC)-based electrolytes containing LiPF_6 .

2. Experimental

The solvents, PC, DMC, and 2-methyltetrahydrofuran (2MeTHF) (Mitsubishi Chemical, Battery Grade) were used as received. The electrolytes used were 1.0 mol dm^{-3} solutions of LiPF_6 (Tomiyama Chemicals) dissolved in a 1:1 mixture by volume of PC with DMC or with 2MeTHF: these binary electrolytes are expressed as $\text{LiPF}_6\text{-PC/DMC}$ and $\text{LiPF}_6\text{-PC/2MeTHF}$, respectively.

A conventional beaker-type glass cell with three electrodes was used for charge–discharge cycling tests and ac impedance analysis. The test electrode was a nickel (Ni) disk, whose surface area exposed to the electrolyte solutions was 0.50 cm^2 . The reference and the counter elec-

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trodes were a Li chip (Li/Li⁺) and a Li sheet, respectively. The charge–discharge cycling efficiency of Li was determined by a galvanostatic deposition (charge)–dissolution (discharge) technique using the Ni disk test electrode in the cell. Both the charge and discharge currents were 0.5 mA cm⁻² (of the test electrode), the charged electricity was 0.1 C cm⁻², and the cutoff potential for the discharge was 1.5 V vs. Li/Li⁺. The rest time after the discharge in each cycle was 50 s. The charge–discharge cycling was carried out for 30 cycles under constant-temperature conditions (at 25, 0, and -20°C) and under varied temperature conditions (initially at 0 or -20°C, then at 25°C). When 10 cycles at 0 or -20°C were followed by 20 cycles at 25°C, the interval rest time for an increase in temperature after the initial 10 cycles was 30 min.

The ac impedance at the Li-deposited electrode–electrolyte interface was measured by a frequency analyzer (Solartron, SI 1260) and a potentiostat (Solartron, SI 1287) after 20th and 30th charging in the cell. The charge–discharge conditions for the ac impedance measurements were identical to those for the coulombic efficiency tests. The ac potential of 10 mV_{p-p} was applied to the Li-deposited electrode under open-circuit conditions. The frequency was scanned from 65 kHz to 10 mHz. All the electrochemical measurements were carried out under an argon atmosphere.

3. Results and discussion

Fig. 1 displays the charge–discharge cycling efficiencies of Li on the Ni substrate in LiPF₆-PC/DMC under various temperature conditions. The LiPF₆-PC/DMC system showed ‘the low-temperature precycling effect’ [8] as follows. The efficiencies observed in LiPF₆-PC/DMC at 0 and -20°C were much higher than that at 20°C. When 10

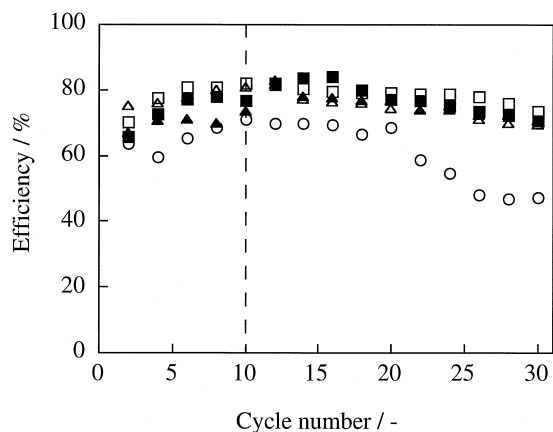


Fig. 1. Variation in Li cycling efficiency with cycle number in LiPF₆-PC/DMC; ○: at 25°C, △: at 0°C, ◻: at -20°C, ▲: the initial 10 cycles at 0°C and the subsequent cycles at 25°C, ■: the initial 10 cycles at -20°C and the subsequent cycles at 25°C.

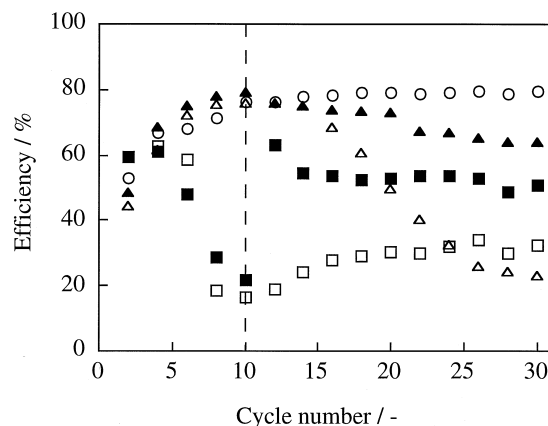


Fig. 2. Variation in Li cycling efficiency with cycle number in LiPF₆-PC/2MeTHF; ○: at 25°C, △: at 0°C, ◻: at -20°C, ▲: the initial 10 cycles at 0°C and the subsequent cycles at 25°C, ■: the initial 10 cycles at -20°C and the subsequent cycles at 25°C.

cycles at 0 and -20°C were followed by 20 cycles at 25°C, the charge–discharge at 25°C resulted in improved cycleability; the efficiencies after an increase in temperature to 25°C were comparable to that observed after the 10th cycle at the constant temperatures of 0 and -20°C as shown in Fig. 1. This result demonstrates that precycling in the low-temperature LiPF₆-PC/DMC electrolyte improved the charge–discharge cycling efficiency after rising the temperature. The effect of the low-temperature precycling on the cycling efficiency in the PC/DMC electrolyte is notable because it may provide a novel treatment process for Li metal anodes [8]. LiPF₆ and its decomposition products such as HF may play an important role in the precycling effect [8]. It is widely known that a Li surface film is derived from solvents and anions in Li battery electrolytes, and the chemical and physical properties of this film govern the Li anode performance. In the LiPF₆-PC/DMC system, one may presume that the Li interface formed with the initial cycling at the low temperatures should remain even at 25°C and affect the performance of the subsequent cycling at 25°C.

On the other hand, when Li on the Ni substrate was cycled in LiPF₆-PC/2MeTHF at the low temperatures, 0 and -20°C, observed coulombic efficiencies faded during the cycling as indicated in Fig. 2. After ca. 20th cycle in LiPF₆-PC/2MeTHF the efficiencies at the low temperatures were much lower than that at 25°C. Furthermore, when 10 cycles at 0 and -20°C were followed by the cycling at 25°C, although once the cycleability at 25°C was improved in few cycles, the efficiency faded in the subsequent cycles as shown in Fig. 2. Judging from the results obtained in the LiPF₆-PC/DMC and LiPF₆-PC/2MeTHF systems, a co-solvent (DMC or 2MeTHF) included in PC binary systems should be a crucial factor to the Li anode performance with the low-temperature precycling as well as under constant temperature conditions.

To characterize the Li anode interface with and without the precycling at the low temperature in the above electrolyte systems, ac impedance analysis of the respective Li-deposited electrodes was performed at 25°C after 20 and 30 cycles. In the LiPF₆-PC/DMC system with the precycling at –20°C a relatively low-impedance interface was observed after the 20 and 30 cycles in comparison with an interface after the 20 and 30 cycles at the constant temperature of 25°C as shown in Fig. 3. This result suggests that the precycling in LiPF₆-PC/DMC at the low temperature provided a stable, low-resistance interface which remained even after the rise in temperature to 25°C. In the alternative electrolyte system, LiPF₆-PC/2MeTHF, overall impedance under all the temperature conditions was higher than that observed in the LiPF₆-PC/DMC system as indicated in Fig. 4. The low-temperature precycling in LiPF₆-PC/2MeTHF at –20°C did not reduce the overall impedance at the Li anode interface. It is notable that each impedance profile observed in LiPF₆-PC/DMC was composed of semicircles, whereas each profile obtained in LiPF₆-PC/2MeTHF contained a semicircle in the high-frequency region and a straight line implying a diffusion-control process in the low-frequency region or suggesting high roughness at the Li interface. One may presume, therefore, that interface films formed in LiPF₆-PC/DMC should be well-ordered, and each film would be uniform. In contrast surface films formed in LiPF₆-PC/2MeTHF should be irregular and impede the diffusion of a Li ion. It was reported that a Li interface formed during cycling in carbonate-type electrolytes containing LiPF₆ is composed of a compact LiF outer layer producing good Li cycling efficiency [10]. In the present LiPF₆-PC/DMC system a thin, compact, and low-resistance LiF layer formed with the initial low-temperature cycling may remain even at 25°C and maintain the high efficiency in the subsequent cycling at 25°C. On the other hand, the interface films derived from the cycling in LiPF₆-PC/2MeTHF would be irregular regardless of the electrolyte temperature. A THF-type co-solvent is known to penetrate inorganic surface layers such as LiF and Li₂O and decompose at an inner Li-metal surface [11]. This

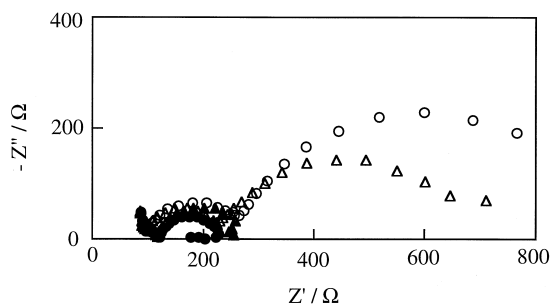


Fig. 3. Cole–Cole plots of the ac impedance for Li deposited on the Ni substrate during cycling in LiPF₆-PC/DMC; ○: after 20 cycles at 25°C, △: after 30 cycles at 25°C, ●: after the initial 10 cycles at –20°C and the subsequent 10 cycles at 25°C (total 20 cycles), ▲: after the initial 10 cycles at –20°C and the subsequent 20 cycles at 25°C (total 30 cycles).

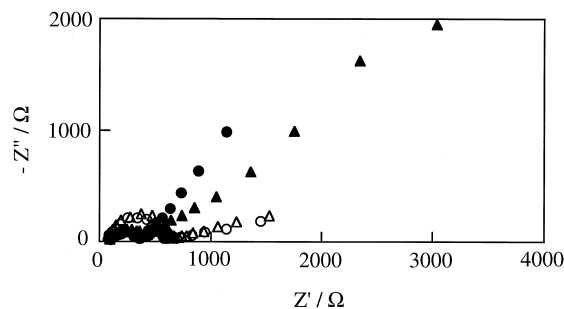


Fig. 4. Cole–Cole plots of the ac impedance for Li deposited on the Ni substrate during cycling in LiPF₆-PC/2MeTHF; ○: after 20 cycles at 25°C, △: after 30 cycles at 25°C, ●: after the initial 10 cycles at –20°C and the subsequent 10 cycles at 25°C (total 20 cycles), ▲: after the initial 10 cycles at –20°C and the subsequent 20 cycles at 25°C (total 30 cycles).

behavior of the THF-type co-solvent should damage an uniform, compact interface and impede high-rate Li-ion diffusion due to the resulting solvent decomposition products even if once a compact LiF layer is formed in the initial process at the low temperature in LiPF₆-PC/2MeTHF. This should be a reason why no desirable precycling effect was observed in the LiPF₆-PC/2MeTHF system.

4. Conclusions

Low-temperature (0 and –20°C) precycling of Li on the Ni substrate in LiPF₆-PC/DMC was found to improve Li cycleability in the subsequent cycles at 25°C. In contrast when the low-temperature precycling was performed in LiPF₆-PC/2MeTHF, no increase in the Li cycling efficiency was observed in the subsequent cycles at 25°C. These results suggest that the low-temperature precycling effect on the Li cycleability depends on a co-solvent used in the PC-based electrolytes. Ac impedance analysis revealed that the precycling in the low-temperature LiPF₆-PC/DMC electrolyte provided a compact Li interface such as a thin LiF layer with a low resistance. On the other hand, the Li anode interface formed by the precycling in the LiPF₆-PC/2MeTHF system was irregular and resistive to Li-ion diffusion. THF-type solvents are known to be more penetrative to inorganic layers such as a LiF film than carbonate-type solvents. This property of the THF-type co-solvents should damage the compact interface and impede high-rate Li-ion diffusion due to the resulting solvent decomposition products even if once a compact LiF layer is formed in the initial process. This should be a reason why no desirable precycling effect was observed in the LiPF₆-PC/2MeTHF system.

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