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Journal of Power Sources 97–98 (2001) 262–264

JOURNAL OF
**POWER
SOURCES**

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Optimization of physicochemical characteristics of a lithium anode interface for high-efficiency cycling: an effect of electrolyte temperature

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Received 16 June 2000; accepted 31 December 2000

Abstract

Precycling of lithium (Li) metal on a nickel substrate at a low-temperature (-20°C) in propylene carbonate (PC) mixed with dimethyl carbonate (DMC) and Li hexafluorophosphate (LiPF_6) ($\text{LiPF}_6\text{-PC/DMC}$) enhanced Li cycleability in the subsequent cycles at a room temperature (25°C). In $\text{LiPF}_6\text{-PC/DMC}$, not only the low-temperature precycling in the initial 10 cycles was effective in the improvement of Li cycle life but also the first low-temperature Li deposition followed by room temperature cycling enhanced the Li cycle life. Such a precycling effect was observed with various current densities at the initial Li deposition and the subsequent cycling. When the current density of the cycling was high, improved cycling efficiency was observed and the efficiency of the Li electrode undergoing the precycling was close to that at a constant temperature of -20°C . © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rechargeable lithium battery; Lithium metal anode; Electrolyte temperature; Coulombic efficiency; Cycle life; Precycling

1. Introduction

Low charge–discharge cycling efficiency of Li metal has limited, practical use of rechargeable batteries with a Li metal anode. To date many attempts to improve Li (charge–discharge) cycling efficiency have been reported. Among them, inorganic [1–5], organic [1,2,6], and gaseous [7,8] additives to electrolytes for rechargeable Li-metal batteries have been proposed. These approaches are categorized into chemical modification of a Li interface; the characteristics of an interface between Li metal and an organic electrolyte relate much to charge–discharge performance of a Li metal anode. Especially, chemical properties of the Li interface are known to affect the Li cycling efficiency. In contrast, relatively little is known about utilization of physical factors for improving Li interface properties and the cycling efficiency. A factor known widely as a physical aspect is a pressure effect on the Li cycling performance [9]. Recently, we have reported the utilization of an alternative physical parameter, electrolyte temperature, for the Li-interface modification favorable to the Li cycling [10–12]. Our findings were that the charge–discharge “precycling” of the Li anode

in low-temperature binary carbonate electrolytes (e.g. ethylene carbonate (EC) or propylene carbonate (PC) mixed with dimethyl carbonate (DMC)) improves the Li cycling efficiency in the subsequent cycles at a room temperature [10,12]. We found, furthermore, that lithium hexafluorophosphate (LiPF_6) is effective as an electrolytic salt in the enhancement of the Li cycling efficiency with the low-temperature precycling [11,12]. This study focuses on effects of cycling current density and temperature-elevation timing upon cycling behavior of the Li electrode undergoing the low-temperature precycling in PC-based electrolytes containing LiPF_6 .

2. Experimental

The electrolyte used was a 1 M ($\text{M} = \text{mol dm}^{-3}$) solution of LiPF_6 (Tomiya Chemical) dissolved in a 1:1 mixture by volume of PC and DMC (Mitsubishi Chemical, Battery Grade). The test electrode (area: 0.283 cm^2) was a Ni disk; the counter and the reference electrodes were a Li sheet and a Li chip (Li/Li^+), respectively. Cycle life tests of the Li electrode were performed using a test cell with these electrodes. Metallic Li was plated on the Ni test electrode with a charge of 2.4 C cm^{-2} at the initial deposition followed by

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the Li discharge–charge cycles with a constant stripping/plating charge of 0.24 C cm^{-2} . This means that the depth of discharge (DOD) was 10%. The current density applied to the initial Li plating was varied: 1.0 or 2.0 mA cm^{-2} . The current density for the subsequent cycling after the initial plating was also changed between 0.5 and 2.0 mA cm^{-2} . The cycle life and the mean efficiency of the test electrode were evaluated from the number of possible cycles until the cycle termination which means that the active Li metal no longer remains on the Ni substrate [13]. The charge–discharge cycling was carried out under constant temperature conditions (at 25 and -20°C) and under two types of varied temperature condition: (i) initial deposition at -20°C , then the subsequent cycles at 25°C ; (ii) initial deposition and the following 10 cycles at -20°C , then at 25°C . The interval rest time for an increase in temperature was 30 min. All the electrochemical measurements were carried out under an Ar atmosphere.

3. Results and discussion

Fig. 1 displays the mean potential (versus Li/Li^+) of the Li electrode during Li charging (below 0 V) and discharging (over 0 V) at each cycle in the $\text{LiPF}_6\text{-PC/DMC}$ electrolyte under various temperature conditions. The current density both for the initial Li plating and the Li cycling was 2.0 mA cm^{-2} . The longest cycle life (81 cycles) was obtained at a constant temperature of -20°C while a constant temperature of 25°C resulted in the shortest cycle life (20 cycles). When the initial Li plating and then 10 cycles at -20°C were followed by cycling at 25°C , the cycle life was enhanced (50 cycles) in comparison with that at a constant temperature of 25°C (20 cycles). This effect is so-called “low-temperature precycling effect” that we have previously reported [10–12]. In our previous work, ac impedance analysis

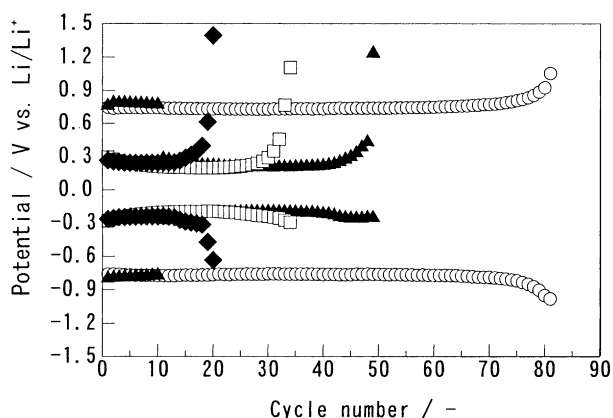


Fig. 1. Mean potential of the Li electrode during Li charge (below 0 V) and discharge (over 0 V) at each cycle in $\text{LiPF}_6\text{-PC/DMC}$, initial plating current = cycling current = 2.0 mA cm^{-2} , (O) -20°C ; (▲) -20°C (initial deposition, +10 cycles) followed by 25°C ; (□) -20°C (initial deposition) followed by 25°C ; (◆) 25°C .

of the Li-deposited electrodes suggested that the precycling in $\text{LiPF}_6\text{-PC/DMC}$ at the low-temperature provided a stable, low-resistance interface which remained even after the rise in temperature to 25°C [11,12]. Our previous study also suggested that interface films formed in $\text{LiPF}_6\text{-PC/DMC}$ should be well ordered, and each film would be uniform [11,12]. It was known that a Li interface formed during cycling in carbonate-type electrolytes containing LiPF_6 is composed of a compact LiF outer layer producing good Li cycling efficiency [14]. In the present $\text{LiPF}_6\text{-PC/DMC}$ 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 .

An alternative temperature-elevating procedure, a rise in temperature after the initial Li deposition, also gave a similar precycling effect; the cycle life was enhanced up to 35 cycles (also shown in Fig. 1). The latter was shorter than the cycle life with the low-temperature precycling in the initial and then 10 cycles but longer than that without the precycling. This suggests that the initial Li deposition process would dominate the subsequent cycling behavior; the interfacial films formed at the initial low-temperature Li plating should fairly remain during the subsequent cycling.

Fig. 2 shows relationship between the current density at the initial plating and the mean efficiency calculated from each possible cycle number under various temperature conditions. The current density for the Li cycling except the initial Li plating was 1.0 mA cm^{-2} . The initial plating current density slightly affected the efficiency; an increase in the current, a little decreased the mean efficiency. This result implies, however, that the initial interface-film properties as well as the initial Li morphology would be almost independent of the current density applied here. At both current

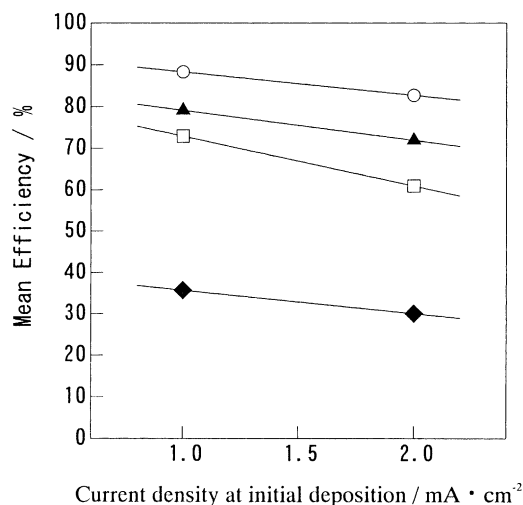


Fig. 2. Variation in mean efficiency of the Li electrode with current density at the initial deposition in $\text{LiPF}_6\text{-PC/DMC}$, cycling current = 1.0 mA cm^{-2} , (O) -20°C ; (▲) -20°C (initial deposition, +10 cycles) followed by 25°C ; (□) -20°C (initial deposition) followed by 25°C ; (◆) 25°C .

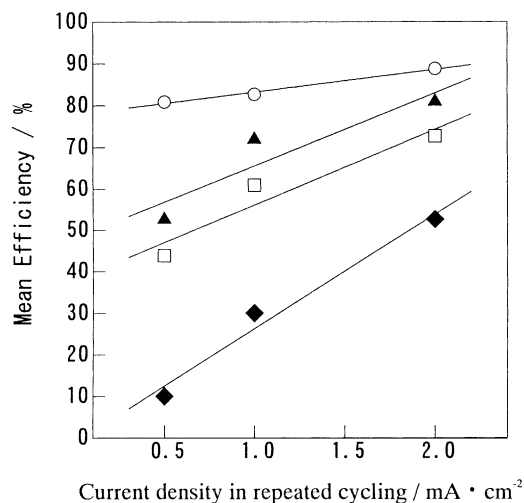


Fig. 3. Variation in mean efficiency of the Li electrode with current density in repeated cycling in $\text{LiPF}_6\text{-PC/DMC}$, initial plating current = 2.0 mA cm^{-2} , (○) -20°C ; (▲) -20°C (initial deposition, +10 cycles) followed by 25°C ; (□) -20°C (initial deposition) followed by 25°C ; (◆) 25°C .

densities, the low-temperature processes increased the efficiency.

Fig. 3 indicates the effect of the cycling current density on the mean efficiency under various temperature conditions, when the current density at the initial deposition was 2.0 mA cm^{-2} . The mean efficiency increased with an increase in the cycling current. Under every temperature condition, the efficiency at a constant temperature of -20°C was best while the efficiency at a constant temperature of 25°C was lowest. It is notable that the low-temperature precycling effect was observed at every cycling current (between 0.5 and 2.0 mA cm^{-2}). This means that the precycling effect would have a general aspect at least in the present electrolyte system. Especially at relatively high-current density, the mean efficiency undergoing the precycling at the initial and 10 cycles was close to that at a constant temperature of -20°C .

The cycling charge applied in the tests was constant of 0.24 C cm^{-2} , with various current densities. This means that an increase in the current shortened the cycling period at each cycle. It is supposed that the shorter cycling period would prevent undesirable side reactions such as corrosion of Li from occurring at the interface to enhance the cycling efficiency. Judging from our results, the shorter cycling period is advantageous to the high-efficiency cycling, and at least up to 2.0 mA cm^{-2} an increase in current density does not induce degradation of interfacial properties such as Li morphology.

In conclusion, in $\text{LiPF}_6\text{-PC/DMC}$, not only the low-temperature precycling in the initial 10 cycles was effective in the improvement of Li cycle life but also the first low-temperature Li deposition followed by room temperature cycling enhanced the Li cycle life. Such a precycling effect was observed with various current densities at the initial Li deposition and the subsequent cycling. These results mean that the precycling effect would have a general aspect at least in the present electrolyte system.

Acknowledgements

This work was supported by Grant-in-Aids (nos. 131250 and 11118253) for Scientific Research on Priority Area of "Electrochemistry of Ordered Interfaces" and a Grant-in-Aid (no. 12650813) from Ministry of Education, Science, Sports and Culture, Japan. This study was partially supported as a partial study of "Dispersed type Battery Energy Storage Technology Research and Development" under the contact with New Energy and Industrial Technology Development Organization (NEDO) for the "New Sunshine Program" by Agency of Industrial Science and Technology, Ministry of International Trade and Industry, Japan.

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