

Pretreatment of Li metal anode with electrolyte additive for enhancing Li cycleability

Masashi Ishikawa^{a,b,*}, Hiromi Kawasaki^c, Nobuko Yoshimoto^c, Masayuki Morita^c

^a Department of Applied Chemistry, Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

^b Research and Development Organization of Industry-University Cooperation, Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

^c Department of Applied Chemistry & Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan

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Abstract

A Li sheet electrode was galvanostatically cycled only once as a pretreatment process in a binary electrolyte, propylene carbonate (PC) with dimethyl carbonate (DMC), containing Li bis(perfluoroethylsulfonyl)imide [$\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$] in the presence of an additive, aluminum iodide (AlI_3). The Li electrode pretreated in this manner showed a high cycleability in the subsequent cycles even after it was transferred to an electrolyte without any additives; its cycleability was higher than that of a Li electrode without the pretreatment. This means that the primary Li cycle in the presence of the additive can provide an enhanced Li cycleability no longer with the need for additives during the subsequent cycles. The enhancement effect was significant under various charge–discharge conditions, i.e., depth of discharge (DoD) and current density, when an appropriate amount of AlI_3 was applied to the pretreatment process. Aluminum derived from the pretreatment was found to remain at the Li electrode still in charge–discharge cycles. Such residual Al in Li, inevitably composing Li alloy, contributes to stabilize the properties of Li electrode interface, e.g., an interfacial resistance, thereby enhancing the charge–discharge cycling efficiency of Li. Thus, the pretreatment of Li metal anode with a single cycle in $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}/\text{PC}/\text{DMC}$ electrolyte containing an appropriate amount of AlI_3 can provide a durable Li interface with better Li cycleability even in an electrolyte without AlI_3 under various charge–discharge conditions.

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1. Introduction

Much effort has so far been devoted to controlling the physicochemical properties of Li metal surface to obtain desirable Li anode performance [1–5]. Among various investigations related to Li surface modification, the use of an additive to an electrolyte has been one of common strategies [2,6–13]. We previously reported that the effect of inorganic additives for electrolytes on the charge–discharge cycling efficiency of Li metal anode; some metal iodides such as aluminum iodide (AlI_3) as an electrolyte additive can enhance Li cycling efficiency [2,9–12]. Such a type of additive can make a Li-alloy layer at a Li anode interface, and the alloying layer

can limit the growth of Li dendrites or fine brittle Li, resulting in the enhancement of Li cycleability [2,9–12]. Although the metal iodide additives are effective in increasing Li cycling efficiency and the amount of the additives is reasonably small: their effective concentration is around 100–600 ppm, still preferable would be a “clean” electrolyte simply containing an electrolytic salt and base solvents without extra components like the additives. The reason for this is that generally such a redox active species in an electrolyte might induce undesirable phenomena, i.e., internal self-discharge and/or a side reaction at a cathode, even if its concentration is quite low.

In an attempt to cope with both effective additives and “clean” electrolyte system, we thought up a novel approach that the additives are utilized as a premodification reagent for a Li metal anode. That is, if the additives can provide a

* Corresponding author. Tel.: +81 6 6368 0952; fax: +81 6 6339 4026.

E-mail address: masaishi@ipcku.kansai-u.ac.jp (M. Ishikawa).

preferably modified Li surface only at the initial cycle, and besides, the modified interface is durable, we could still get a fine cycling efficiency even after transferring the “treated” Li electrode into an electrolyte without any additives. On the basis of this concept, we recently reported some preliminary results shortly; we found the premodification of Li metal interface with the metal iodides is effective in increasing Li cycleability [14]. In some cases, this approach can provide better Li cycleability than that all along with the additives due to the optimal interface properties of premodified Li such as a stable low resistance. We would like to report herein such a pretreatment effect on a Li metal anode under various conditions, i.e., various depths of discharge (DoD) and current densities, to confirm the availability of the pretreatment process.

2. Experimental

The electrolytes used was a 1 M ($M = \text{mol dm}^{-3}$) solution of $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ (3M Co) 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 Li sheet; the counter and reference electrodes were a Li sheet and Li chip (Li/Li^+), respectively. The additive for the electrolyte was anhydrous AlI_3 , which was used as a pretreatment reagent for the Li anode as follows. Metallic Li was galvanostatically (dc) discharged, and then charged (2.0 and -2.0 mA cm^{-2} of the Li anode at depth of discharge (DoD) of 2%) on the Li sheet in the electrolyte containing AlI_3 , followed by the transfer of the resulting “dc-pretreated” Li electrode to the corresponding additive-free electrolyte. After that this electrode was repeatedly cycled in 20 or 50 cycles with a constant DoD and current density. The mean efficiency of the Li electrode was evaluated from the quantity of electricity required for completely discharging Li, which remained still after the cycles. These tests as well as the following impedance measurements of a Li anode were performed using a glass cell equipped with the above electrodes.

The ac impedance at a Li electrode–electrolyte interface was measured by a frequency analyzer (Solartron, SI 1260) and a potentiostat (Solartron, SI 1287); an ac potential of $10 \text{ mV}_{\text{p-p}}$ was applied to the Li electrode under open-circuit potential conditions.

The scanning frequencies were 65 kHz to 10 mHz. All the electrochemical measurements were carried out under an Ar atmosphere.

3. Results and discussion

Fig. 1 shows the mean coulombic efficiencies of Li electrode in cycles with and without the dc pretreatment in the presence of AlI_3 at various DoD. The pretreatment of Li electrode in the presence of 400 ppm Al^{3+} increased the coulombic

efficiency when compared to the efficiency without the pretreatment (Fig. 1a). This effect declined, however, with an increase in DoD; especially at the DoD of 2%, the efficiency with the pretreatment was almost same as that without the pretreatment. When the higher AlI_3 concentration (Al^{3+} : 600 ppm) was applied, the enhancement effect of the pretreatment became to be notable; although the efficiency with the pretreatment decreased still with an increase in DoD, a considerable enhancement of the efficiency was observed even at the DoD of 2% (Fig. 1b). On the basis of ac impedance analysis as shown in Fig. 2, the Li electrode interface pretreated with 600 ppm Al^{3+} provided lower interfacial resistance than that pretreated with 400 ppm Al^{3+} even after 50 cycles at the DoD of 2%. This lower interfacial resistance in cycles (Fig. 2b) is likely to correlate with the higher mean efficiency observed with the pretreatment at 400 ppm Al^{3+} (Fig. 1b).

To evaluate how much Al was deposited on a Li electrode by the pretreatment in the presence of AlI_3 as well as how much the co-deposited Al remained in the Li electrode still after the subsequent cycles, atomic absorption analysis was applied to the respective Li electrodes. The obtained data are summarized in Table 1. The presence of 600 ppm Al^{3+} in the pretreatment process contributed obviously to the higher content of Al in Li electrodes than the condition of 400 ppm Al^{3+} . In this regard, such a high Al content was observed not only before as well as after the pretreatment but also even after the subsequent cycles. A high Al content observed in a Li electrode would mean the formation of an Al–Li alloy layer effective to enhance Li cycling efficiency [2,9–12]. A Li interface modified with Al^{3+} at the first cycle fairly remained during the following cycles without Al^{3+} . That is, a Li-alloy layer derived from the premodification can persist even during the subsequent cycles when an appropriate concentration of AlI_3 is applied to the pretreatment.

Because the Al^{3+} concentration of 600 ppm was, based on the above results, found to be favorable for the effective pretreatment enhancing the coulombic efficiency even under relatively high DoD condition, we comprehended if the effect derived from the pretreatment on the coulombic efficiency is still significant with various charge as well as discharge current densities. Fig. 3 shows the coulombic efficiencies as a function of charge–discharge current density with and without the pretreatment in the presence of 600 ppm

Table 1
Al content in Li anode with the pretreatment in the presence of Al^{3+} ion^a

Criterion for evaluation	Al^{3+} concentration (ppm)					
	400			600		
	A ^b	B ^b	C ^b	A ^b	B ^b	C ^b
Al content ($\times 10^{-7}$ mol)	1.5	2.1	1.5	2.9	7.1	4.7
Al/Li anode (wt.%)	0.11	0.15	0.11	0.20	0.49	0.34

^a DoD: 2%, discharge/charge current density: $2.0/-2.0 \text{ mA cm}^{-2}$.

^b A, before dc treatment (30 min from cell assembly); B, after dc treatment; C, after 50 cycles.

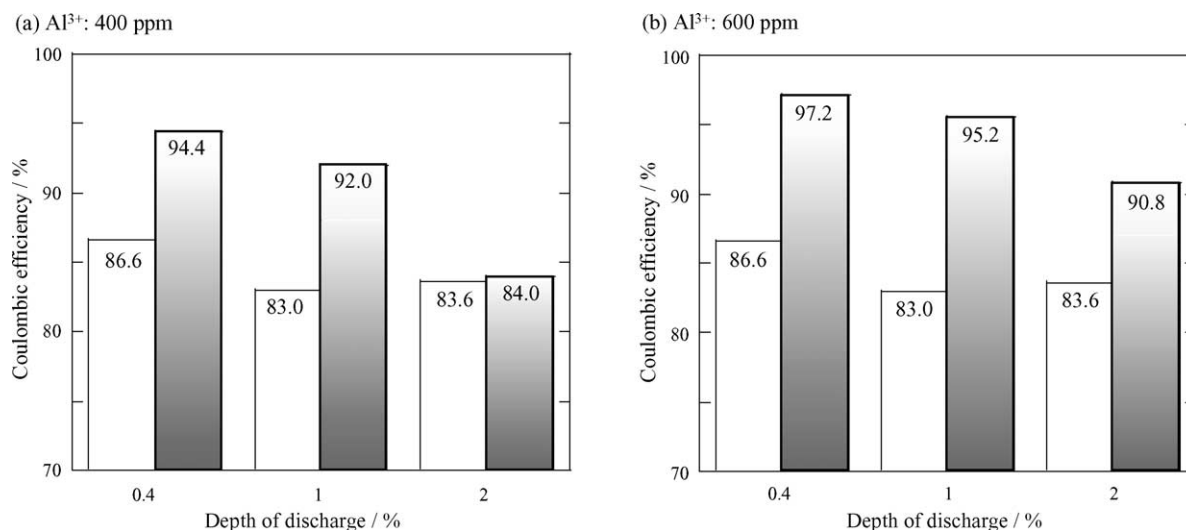


Fig. 1. Mean coulombic efficiencies of Li sheet electrode in 1.0 M Li(C₂F₅SO₂)₂N/PC-DMC in cycles with and without the dc pretreatment in the presence of AlI₃ (Al³⁺: (a) 400 ppm and (b) 600 ppm) at various DoD. Unpainted bars indicate the efficiencies without the pretreatment (without AlI₃). Discharge/charge current density: 2.0/−2.0 mA cm^{−2}.

Al³⁺. A ballpark tendency observed here was that a higher discharge current as well as lower charge current provided a higher coulombic efficiency, and besides, the pretreatment with AlI₃ was always effective to increase the Li cycling efficiency. Especially, when the discharge and charge current densities were 4.0 and −1.0 mA cm^{−2}, respectively, the Li

electrode undergoing the pretreatment showed an outstanding coulombic efficiency of 99.5%. These data indicates that the pretreatment can be regarded as one of methods favorably controlling the Li interface properties, being available under various conditions. All tested electrodes undergoing the pretreatment were found to contain a considerable amount of Al still after the 50th cycle as listed in Table 2. Moreover, ac impedance analysis revealed that the pretreated Li electrode interface, which led to higher efficiency provided relatively lower resistance at various current densities as shown in Fig. 4.

In conclusion, the pretreatment of Li metal interface with an appropriate amount of AlI₃ was found to be effective in increasing Li cycleability under various charge–discharge conditions, i.e., DoD and current density. Aluminum derived

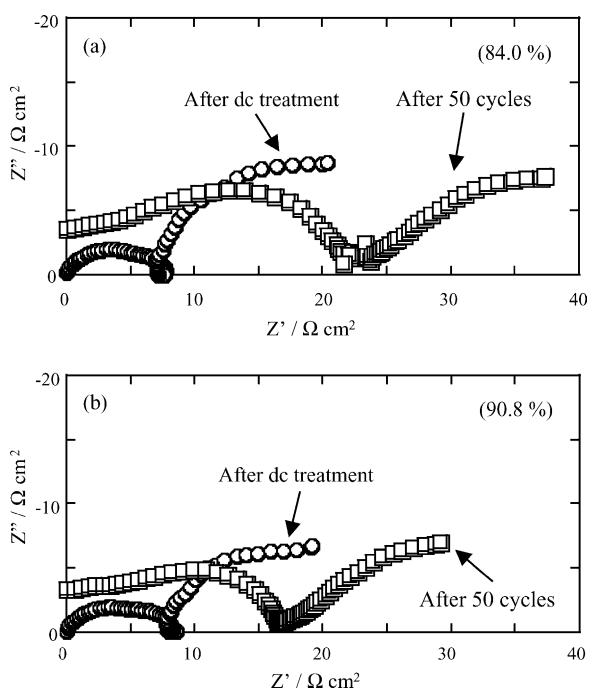


Fig. 2. Nyquist plots of ac impedance at Li electrode in 1.0 M Li(C₂F₅SO₂)₂N/PC-DMC with the dc pretreatment in the presence of AlI₃ (Al³⁺: (a) 400 and (b) 600 ppm) at DoD of 2%. Discharge/charge current density: 2.0/−2.0 mA cm^{−2}. Percentage in parentheses inside figures (a) and (b) indicates the mean coulombic efficiency under each condition (see Fig. 1).

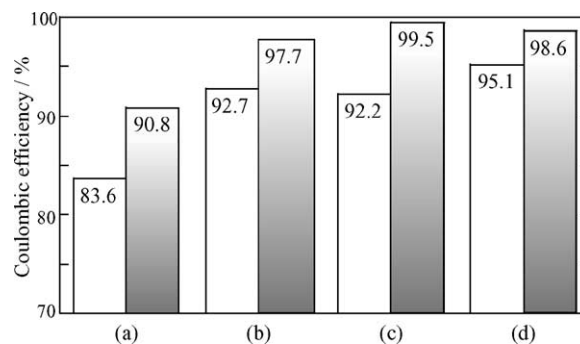


Fig. 3. Mean coulombic efficiencies of Li sheet electrode in 1.0 M Li(C₂F₅SO₂)₂N/PC-DMC in cycles with and without the dc pretreatment in the presence of AlI₃ (Al³⁺: 600 ppm) at DoD of 2% at various discharge/charge current densities. Unpainted bars indicate the efficiencies without the pretreatment (without AlI₃). Discharge/charge current density: (a) 2.0/−2.0 mA cm^{−2}, (b) 2.0/−1.0 mA cm^{−2}, (c) 4.0/−1.0 mA cm^{−2} and (d) 7.3/−1.0 mA cm^{−2}.

Table 2
Al content in Li anode after 50 cycles at various current densities^a

Criterion for evaluation	Discharge/charge current density (mA cm ⁻²)			
	2.0/-2.0	2.0/-1.0	4.0/-1.0	7.3/-1.0
Al content ($\times 10^{-7}$ mol)	4.7	5.8	5.6	5.4
Al/Li anode (wt.%)	0.34	0.41	0.39	0.38

^a Al³⁺: 600 ppm for the pretreatment, DoD: 2%.

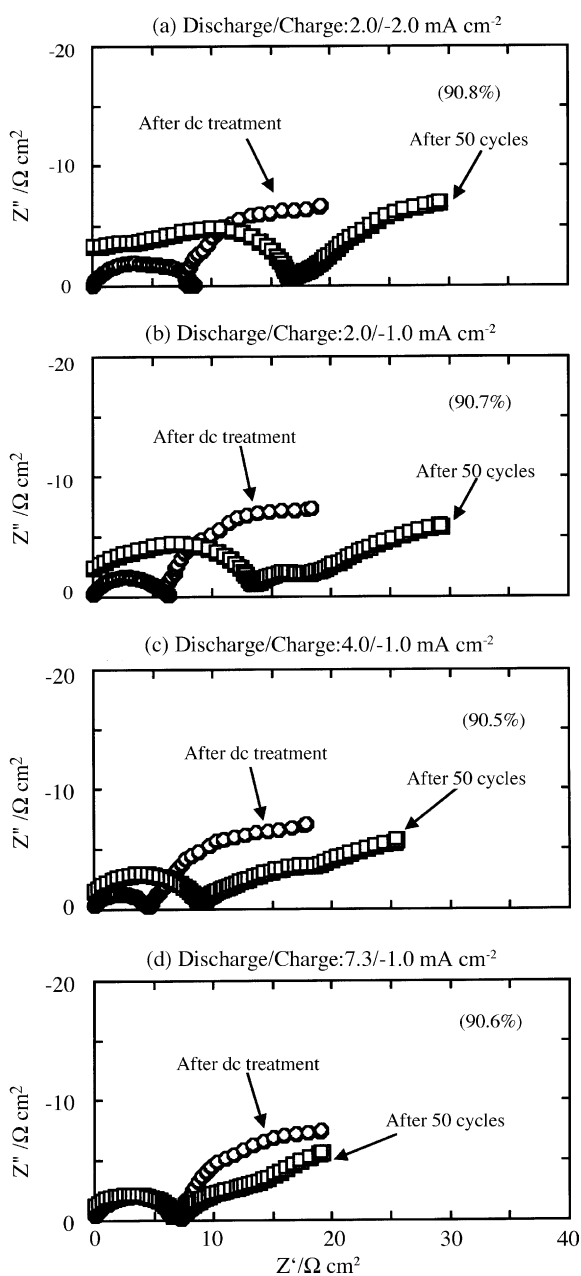


Fig. 4. Nyquist plots of ac impedance at Li electrode in 1.0 M Li(C₂F₅SO₂)₂N/PC-DMC with the dc pretreatment in the presence of AlI₃ (Al³⁺: 600 ppm) at DoD of 2%. Discharge/charge current density: (a) 2.0/-2.0 mA cm⁻², (b) 2.0/-1.0 mA cm⁻², (c) 4.0/-1.0 mA cm⁻² and (d) 7.3/-1.0 mA cm⁻². Percentage in parentheses inside figures indicates the mean coulombic efficiency under each condition (see Fig. 3).

from the pretreatment remains at the Li electrode still in charge–discharge cycles. Such residual Al in Li, inevitably composing Li alloy, contributes to stabilize the properties of Li electrode interface, e.g., an interfacial resistance, thereby enhancing the charge–discharge cycling efficiency of Li. Thus, the pretreatment of Li metal anode with a single cycle in 1.0 M Li(C₂F₅SO₂)₂N/PC-DMC electrolyte containing an appropriate amount of AlI₃ provides a durable Li interface with better Li cycleability even in an electrolyte without AlI₃.

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References

- [1] L.A. Dominey, Lithium batteries, in: G. Pistoia (Ed.), Industrial Chemistry Library, vol. 5, Elsevier, Amsterdam, 1994, Chapter 4.
- [2] M. Ishikawa, M. Morita, in: G.-A. Nazri, G. Pistoia (Eds.), Lithium Batteries Science and Technology, Kluwer Academic Publishers, New York, 2004, p. 297.
- [3] M. Ishikawa, Y. Takaki, M. Morita, Y. Matsuda, J. Electrochem. Soc. 144 (1997) 90.
- [4] K. Naoi, M. Mori, Y. Naruoka, W.M. Lamanna, R. Atanasoski, J. Electrochem. Soc. 146 (1999) 462.
- [5] T. Hirai, I. Yoshimatsu, J. Yamaki, J. Electrochem. Soc. 141 (1994) 611.
- [6] D. Aurbach, Y. Gofer, M. Ben-Zion, P. Aped, J. Electroanal. Chem. 339 (1992) 451.
- [7] K. Kanamura, H. Tamura, S. Shiraishi, Z. Takehara, J. Electrochem. Soc. 142 (1995) 340.
- [8] T. Osaka, T. Momma, T. Tajima, Y. Matsumoto, J. Electrochem. Soc. 142 (1995) 1057.
- [9] M. Ishikawa, S. Yoshitake, M. Morita, Y. Matsuda, J. Electrochem. Soc. 141 (1994) 159.
- [10] M. Ishikawa, M. Morita, Y. Matsuda, J. Power Sources 68 (1997) 501.

- [11] M. Ishikawa, S. Machino, M. Morita, J. Electroanal. Chem. 473 (1999) 279.
- [12] M. Ishikawa, S. Machino, M. Morita, Electrochemistry 67 (1999) 1200.
- [13] R. Mogi, M. Inaba, S. Jeong, Y. Iriyama, T. Abe, Z. Ogumi, J. Electrochem. Soc. 149 (2002) A1578.
- [14] M. Ishikawa, K. Inoue, N. Yoshimoto, M. Morita, Electrochemistry 71 (2003) 1046.