ELSEVIER

Effect of organic additives in electrolyte solutions on lithium electrode behavior

Yoshiharu Matsuda *, Masaaki Sekiya

Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Yamate-cho 3-3-35, Suita, Osaka 564-0073, Japan

Abstract

Charge–discharge behavior of Li and Li–Al anodes has been investigated by measurement of AC impedance and polarization resistance. The anodes showed lower interfacial resistance in ethylene carbonate (EC)–dimethyl carbonate (DMC)/1 M $LiPF_6$ than that in EC–diethyl carbonate (DEC)/1 M $LiPF_6$. The interfacial resistance between Li–Al electrode and electrolyte solution decreased with content of Al in the alloy. Further, addition of 2-methylfuran (2MeF), 2-methyltetrahydrofuran (2MeTHF), 2-methylthiophene (2MeTp) and polyethylene oxide (PEO) in the electrolyte solutions decreased the polarization resistance. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organic additives; Lithium–aluminium alloy; Lithium/electrolyte interface; Interfacial resistance

1. Introduction

In the course of development of lithium metal rechargeable batteries, one of major problems is the formation of a suitable interphase between Li electrode and the electrolyte solution. Many papers have reported the effect of organic additives such as 2-methylfuran (2MeF) [1–4], 2-methyltetrahydrofuran (2MeTHF) [1,5], 2-methylthiophene (2MeTp) [4], benzene [4,6], fluorinated surfactants [7,8], etc., on Li electrode performance. These additives absorb on Li electrodes, or chemically and electrochemically react with Li electrode and suppress the formation of dendrite. Furthermore, they would connect to the formation of solid electrolyte interface on Li electrode [9]. Behavior of Li electrode is affected by the film formation on Li electrode surface and the film composition has been analyzed by FTIR, XPS and other methods [10–12]. In the present work, organic additives, 2MeF, 2MeTp, 2MeTHF and PEO, were added to 1 M $LiPF_6$ solutions of ethylene carbonate (EC)–dimethyl carbonate (DMC), EC–diethyl

carbonate (DEC) and EC–PC and their effect on Li and Li–Al electrode behavior was investigated.

2. Experimental

Lithium and lithium–aluminum (0.1, 0.5 and 1.0 wt.%) were 0.2 mm thick sheet from Mitsui Mining and Smelting. Electrolyte solutions, EC–DMC (1:1 vol.)/1 M $LiPF_6$ and EC–DEC (1:1 vol.)/1 M $LiPF_6$, and solvents, EC, PC and 2MeTHF, were supplied by Mitsubishi Chemical. $LiPF_6$ was supplied by Morita. 2MeF and 2MeTp were special grade by Wako and MW of polyethylene oxide was around 70,000. The solutions containing the additives were prepared by dissolving the additive and diluting to a fixed volume with an electrolyte solution or a solvent. Beaker type electrolyte cells with lithium test, counter and reference electrodes were used. The apparent surface area of the test electrode was 1.13 or 1.0 cm^2. Solartron Electrochemical Measurement SI 1280Z and Charge–Discharge Unit Hokuto HJ-101SM6 were used for measurement of impedance and polarization resistance. 1 C cm^{-2} (1.0 mA cm^{-2}, 1000 s) was passed galvanostatically during charge–discharge. Polarization resistance was measured galvanostatically with a electrometer Hokuto HE-104. Fre-
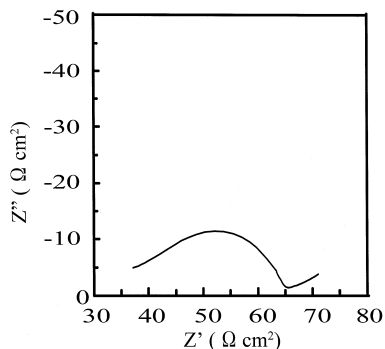
Fig. 1. Typical complex plane impedance plot of lithium electrode. ac Frequency range: 20 kHz–0.1 Hz. Working electrode: Li 100%. Electrolyte solution: EC–DMC (1:1 by vol)/1 M LiPF$_6$.

quency range applied in impedance measurement was between 20 kHz and 0.1 Hz. Measurement was carried out under dry argon atmosphere.

3. Results and discussion

A typical impedance plot in the present work is shown in Fig. 1. Frequency range applied was between 20 kHz and 0.1 Hz. In Fig. 1, one semi-circle which would correspond to interfacial impedance and the trace of another one which would connect to charge transfer at higher frequency region are observed.
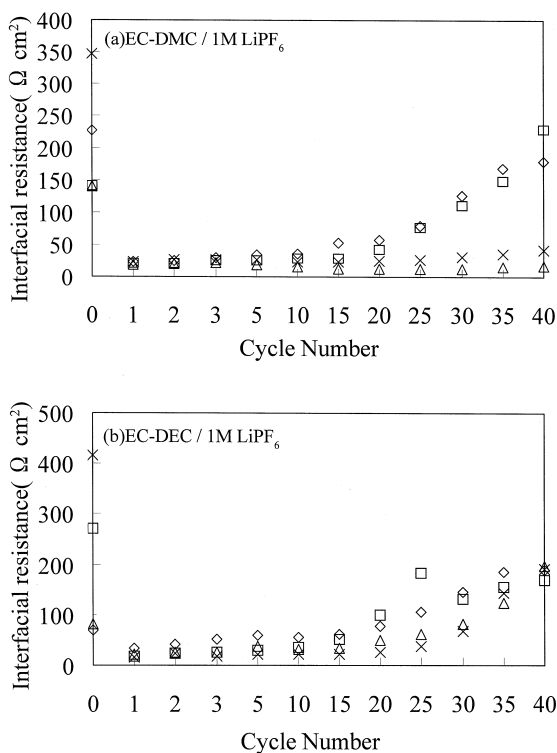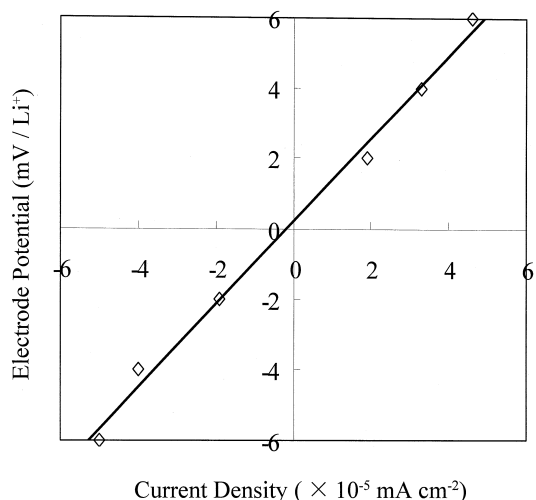

Fig. 3. Current density as a function of electrode potential. Electrode: Li–1.0 wt.% Al. Electrolyte: EC-PC-2MeTHF (35:35:30)/1 M LiPF$_6$.

Fig. 2 shows interfacial resistance on lithium and lithium–aluminum alloy electrodes in EC–DMC (1:1 vol.)/1 M LiPF$_6$ and EC–DEC (1:1 vol.)/1 M LiPF$_6$ as a function of cycle number. High interfacial resistance before discharge would be due to oxide film on lithium electrode surface and the oxide film was probably removed during first charge–discharge cycle. The interfacial resis-
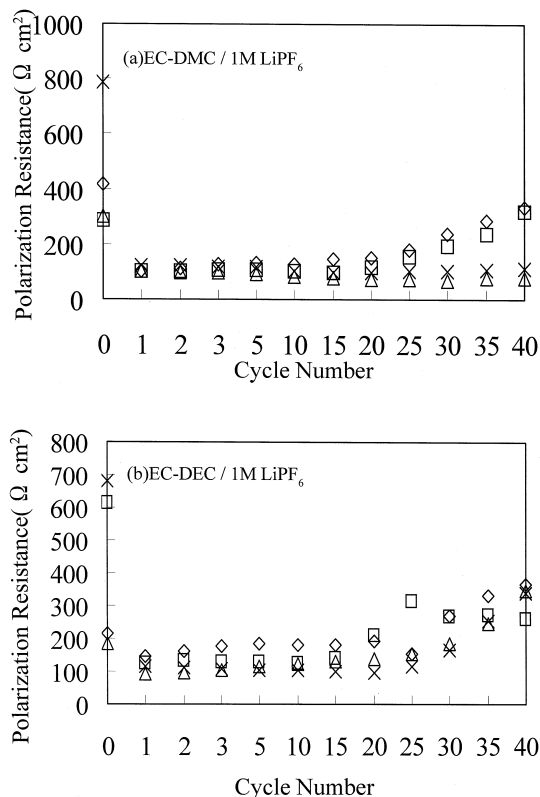

Fig. 2. Interfacial resistance on negative electrodes at low frequency range as a function of cycle number. ◇: Li 100%, □: Li–0.1 wt.% Al, △: Li–0.5 wt.% Al, ✕: Li–1.0 wt.% Al.

Fig. 4. Polarization resistance on negative electrodes as a function of cycle number. ◇: Li 100%, □: Li–0.1 wt.% Al, △: Li–0.5 wt.% Al, ✕: Li–1.0 wt.% Al.
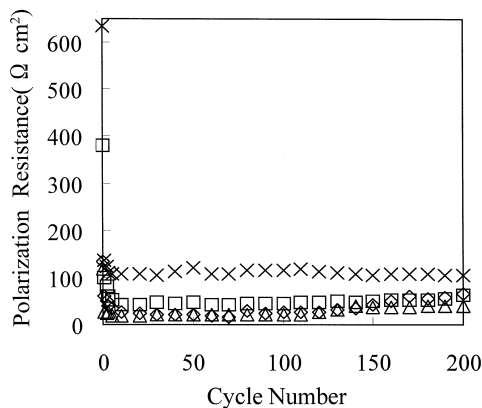
Fig. 5. Polarization resistance on negative electrodes (Li) as a function of cycle number. EC–DMC/1 M LiPF$_6$. Additives: ×: Blank, ◇: 2 MeF, □: 2MeTp, Δ: Poly(ethylene oxide).

tance decreased after 20 cycles. However, on Li–0.5 wt.% Al and Li–1.0 wt.% Al in EC–DMC (1:1 vol.)/1 M LiPF$_6$, the interfacial resistance was small (under 50 Ω cm) and almost constant during cycling. These phenomena is probably due to the formation of a lithium ion permeable thin, stable film which would prevent the dendrite formation on the electrode surface.

Fig. 3 represents a typical current-potential diagram for determining polarization resistance. Form slopes in similar figures, the polarization resistance was calculated by Eq. (1).

$$\eta = \frac{RT}{nFi_0} i \qquad (1)$$

where i is current density, η is overpotential, i_0 is exchange current density, R is the gas constant, F is the Faraday constant, and n is a unit.

Polarization resistance on the electrodes previously cited is shown in Fig. 4. The polarization resistance did not agree with the interfacial resistance in Fig. 2, because the polarization resistance would correspond to the charge transfer process and the interfacial resistance of the interface. However, similar tendency was obtained in the data of polarization resistance measurement in comparison with that of the interfacial resistance.

The affect of the addition of 2MeF (1 vol.%), 2MeTp (5 vol.%) and PEO (1.0 g in 50 ml) is shown in Fig. 5. Polarization resistance decreased in a presence of addi-

tives. 2MeF and 2MeTp in PC/LiClO$_4$ were reported as effective additives in a previous paper [4]. PEO showed more suppressive effect than that of 2MeF and 2MeTp for the polarization resistance of the lithium electrode. These results suggest that PEO is the excellent additive for electrolyte solutions of rechargeable lithium batteries.

Synergetic effect of blended 2MeTHF and lithium–aluminum alloying is shown in Fig. 3. Li–1.0 wt.% Al electrode in EC–PC–2MeTHF (0.35:0.35:0.30) showed low polarization resistance and stable cycling.

4. Conclusion

The additives, 2MeF, 2MeTp, PEO and 2MeTHF, in the electrolyte solutions form a thin, lithium ion permeable interface and decrease the interfacial resistance between negative electrodes, lithium and lithium–aluminum electrodes, and the electrolyte solutions. Lithium–aluminum alloy electrodes contribute to form stable interface between the electrode and the electrolyte solution during charge–discharge cycling. Among organic additives investigated, PEO is excellent for electrolytes of rechargeable lithium batteries.

References

[1] K.M. Abraham, J.S. Foos, J.L. Goldman, J. Electrochem. Soc. 131 (1994) 2197.
[2] K.M. Abraham, J. Power Sources 14 (1985) 179.
[3] S. Tobishima, T. Okada, Denki Kagaku 53 (1985) 742.
[4] M. Morita, S. Aoki, Y. Matsuda, Electrochimica Acta 37 (1992) 119.
[5] Y. Matsuda, J. Power Sources 20 (1987) 19.
[6] M. Yoshio, H. Nakamura, K. Isono, S. Ito, Holtstleither, Prog. Batteries Solar Cells 7 (1988) 271.
[7] A.T. Ribes, P. Beaunier, P. Wollmann, D. Lemordant, J. Power Sources 58 (1996) 189.
[8] M. Mori, Y. Naruoka, Y. Kakuta, D. Fauuteux, K. Naoi, 64th Meeting Electrochem. Soc. Abst. (1997), p. 22.
[9] E. Peled, J. Electrochem. Soc. 126 (1979) 2047.
[10] D. Aurbach, B. Markovsky, A. Shechter, Y. Ein-Eli, J. Electrochem. Soc. 143 (1996) 3809.
[11] K. Kanamura, H. Tamura, S. Shiraishi, Z. Takehara, J. Electroanal. Chem. 394 (1995) 49.
[12] K. Kanamura, S. Shiraishi, Z. Takehara, J. Electrochem. Soc. 143 (1996) 2187.