



ELSEVIER

Journal of Power Sources 97–98 (2001) 589–591

JOURNAL OF
**POWER
SOURCES**

www.elsevier.com/locate/jpowsour

Effect of organic additives in electrolyte solutions on behavior of lithium metal anode

Yoshiharu Matsuda*, Takatorno Takemitsu, Takashi Tanigawa, Tsuyoshi Fukushima

*Department of Applied chemistry, Faculty of Engineering and High-Technology Research Center,
Kansai University Yamatecho 3-3-35 Suita, Osaka 564-8680, Japan*

Received 20 June 2000; accepted 7 January 2001

Abstract

Addition effect of polymer materials, polyvinylpyrrolidone (PVP), polyacrylonitrile (PAN) and polyethylene oxide (PEO) in the electrolyte solutions, ethylene carbonate (EC)–propylene carbonate (PC) (1:1 vol.)/ 0.25 mol/l LiBF₄ or Li (CF₃SO₂)₂N, was investigated. In the electrolyte solutions containing PVP the charge–discharge current efficiency of lithium on Ni electrode was the highest and the interface resistance between a lithium metal electrode and the electrolyte solution was small during charge–discharge cycle. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyvinylpyrrolidone; Lithium metal batteries; Dendrite

1. Introduction

For the development of practical rechargeable lithium metal batteries, the most serious problem is the formation of dendrite on a lithium metal electrode. For the purpose of the prevention of these phenomena, some additives have been added in the organic electrolyte solutions. These additives were organic compounds such as 2-methylfuran and 2-methylthiophene, sugar esters, etc. [1–7], and inorganic ions such as Al³⁺, Mg²⁺ and I[−] [7,8], and CO₂ [9]. These additives would adsorb on the active sites on lithium electrode surface and suppress the formation of the dendrite.

One of the authors reported the addition effect of polyethylene oxide (PEO) previously [5], but the effect of other polymers have not been represented. In this work, some polymer materials have been investigated as the additives in the electrolyte solutions of rechargeable lithium batteries. Among these polymers, polyvinylpyrrolidone (PVP) showed excellent addition effect.

2. Experimental

Lithium was a 0.2 mm thick sheet, and solvents were EC and PC (Ube Ind.). Electrolyte salts were LiBF₄ (Morita

and Li(CF₃SO₂)₂N (Ube Ind.). Polymer materials were PVP (MW: 40,000), PEO (MW: 400,000) (Daiwa Kasei) and polyacrylonitrile (PAN, MW: 150,000) (Aldrich). A beaker type cell with two electrodes, a Ni working electrode and a large lithium counter electrode, and another beaker type cell with a lithium test, a lithium counter and a lithium reference electrodes were used. The electrolyte solutions were mainly 0.25 M LiBF₄ and 0.25 M Li(CF₃SO₂)₂N/ethylene carbonate (EC)–propylene carbonate (PC) (1:1 vol.). Usually 0.2 g of the additive was dissolved in 50 ml of the electrolyte solution.

For the measurement of charge–discharge current efficiency, the cell with two electrodes was used. The apparent surface area of the Ni working electrode was 1 cm² and that of the counter electrode was large. The charge–discharge current was 1.0 mA/cm² and charged electricity was 0.20 C/cm². The cut-off potential at charging was 1.5 V versus Li⁺/Li. Charge–discharge current efficiency of lithium deposition and dissolution on the Ni electrode was calculated from the ratio of discharge-time/charge-time. A charge–discharge equipment (Hokuto HJ-101 SM6) was used for the cycling of the working electrode. In the measurement of the interface resistance and capacitance using the cell with three electrodes a Solartron SI 12280B was used. The charge–discharge electricity was 1.0 Ccm^{−2} (1.0 mA cm^{−2}, 1000 s). All measurement was carried out under dry Ar atmosphere at ambient temperature.

* Corresponding author. Tel.: +816-368-1121; fax: +81-6-339-4026.

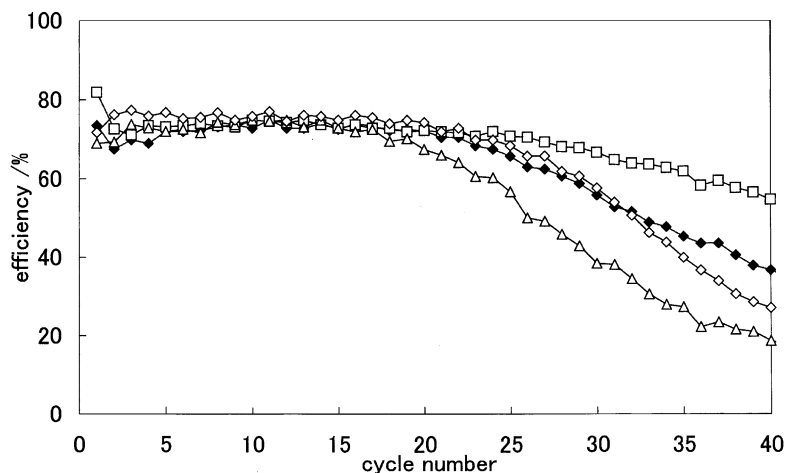


Fig. 1. Cycling current efficiency of lithium on nickel substrate in EC-PC (1:1 vol.)/0.25 mol/l LiBF_4 50 ml without additive (◆), with PVP (□), PAN (△), and PEO (◇) 0.02 g.

3. Results and discussion

Fig. 1 shows the addition effect of the polymer materials in EC-PC (1:1 vol.)/0.25 mol/l LiBF_4 . The charge–discharge current efficiency of lithium on Ni electrode improved by addition of PVP; but the addition of PAN and PEO did not show the effect on the current efficiency. The effective influence on the cycling current efficiency of PVP would be caused by pyrrolidone group. Further the effect of difference of molecular weight might appear on the results in Fig. 1. Similar results obtained on lithium cycling in EC-PC (1:1 vol.)/0.25 mol/l $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$.

The addition effect of PVP in EC-PC (1:1 vol.)/0.25 mol/l $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ on the interface resistance between the lithium electrode and electrolyte solutions with the additives are plotted in Fig. 2. The interface resistance on lithium electrodes was estimated from the diameter of semicircle in low frequency region on impedance plane plots. In EC-PC

(1:1 vol.)/0.25 mol/l $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ the addition of PVP suppressed the growth of interface resistance during cycling and stable charge–discharge was achieved. Low interface resistance corresponds to the formation of thin film in which Li^+ transfers fast and to the prevention of side reactions between the electrode and electrolyte solution. The addition effect of PEO and PAN was smaller than that of PVP. Similar tendency was observed in EC-PC (1:1 vol.)/0.25 mol/l LiBF_4 . The polarization resistance was measured in the same systems. At the early stage of cycling the polarization resistance was rather high but after ca. 100 cycles it was smaller and stable. Fig. 3 shows the effect of the amount of added PVP on the interface resistance. The additional amount of 0.1 and 0.2 g/50 ml showed low interfacial resistance for long duration. In the electrolyte solutions containing 1.0 and 2.0 g PVP, the interface resistance increased in early stage of cycling. This result shows the addition of large amount of PVP in the electrolyte solution

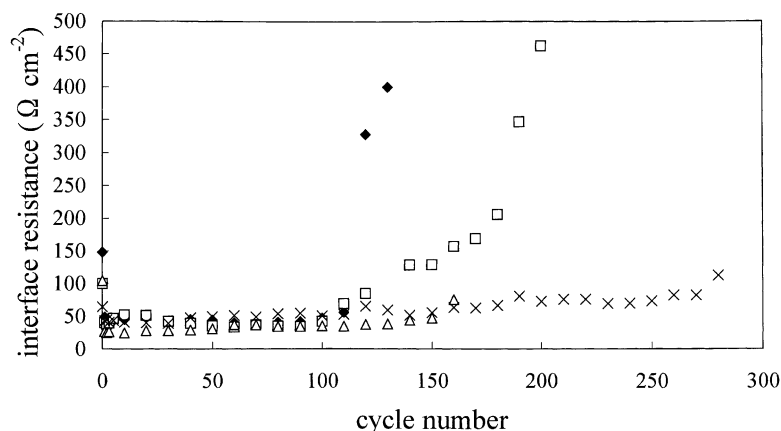


Fig. 2. Interface resistance on negative electrodes at low frequency range as a function of cycle number. EC-PC (1:1 vol.)/0.25 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ 50ml/ additive 0.2 g. (◆) Blank, (□) PAN, (◇) PEO, (×) PVP.

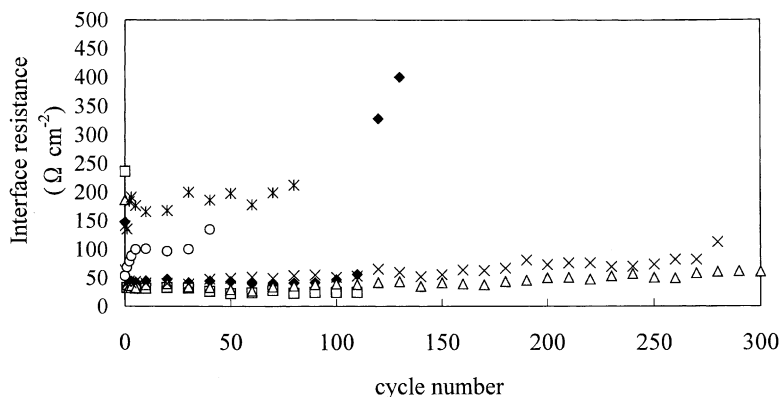


Fig. 3. Interface resistance on negative electrodes at low frequency range as a function of cycle number. EC-PC (1:1 vol.)/0.25 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ 50 ml/PVP. (◆) Blank, (□) 0.02 g, (△) 0.1 g, (×) 0.2 g, (*) 1 g, (○) 2 g.

gave wrong effect on the film formation on lithium electrode.

4. Conclusions

Addition effect of polymer materials, PVP, PAN, and PEO on lithium electrode performance was investigated in EC-PC solutions containing 0.25 mol/l LiBF_4 and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ respectively. Among these polymers PVP showed excellent addition effect on the lithium electrode performance by means of the measurement of charge–discharge current efficiency and the interfacial resistance between the lithium electrode and electrolyte solution.

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, *Electrochim. Acta* 37 (1992) 119.
- [5] Y. Matsuda, M. Sekiya, *J. Power Sources* 81/82 (1999) 759.
- [6] Y. Matsuda, M. Sekiya, in: *Proceedings of the 49th Meeting ISE, Ext. Abstract*, 1998, p.643.
- [7] M. Ishikawa, S. Yoshitake, M. Morita, Y. Matsuda, *J. Electrochem. Soc.* L159 (1994) 141.
- [8] Y. Matsuda, M. Ishikawa, S. Yoshitake, M. Morita, *J. Power Sources* 54 (1995) 301.
- [9] T. Osaka, T. Momma, T. Tajima, Y. Matsumoto, *J. Electrochem. Soc.* 142 (1995) 1057.