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Improved morphology of plated lithium in poly(vinylidene fluoride) based electrolyte

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Abstract

The morphology of electrodeposited lithium was observed in the gel electrolyte consisting of the poly(vinylidene fluoride)-hexafluoropropylene (PVdF-HFP) copolymer as a host polymer, $LiClO_4$, and the propylene carbonate (PC)/ethylene carbonate (EC) organic solvents. The dendritic deposition was effectively suppressed in the PVdF-HFP gel electrolyte compared to the $LiClO_4$-PC/EC liquid electrolyte or the polyethylene oxide (PEO) based gel electrolyte. Charge–discharge efficiency of the lithium metal anode was higher in the PVdF-HFP gel electrolyte than that in the liquid or the PEO gel electrolyte, and it was enhanced by CO_2 addition as well as observed in the $LiClO_4$-PC/EC liquid electrolyte. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium secondary battery using lithium metal as an anode is the most attractive candidate for higher energy power sources for portable electronic devices, electric vehicles, and load leveling systems. Lithium metal demonstrates a remarkably low electrochemical equivalent and the most negative redox potential among all metallic elements, however, it has some disadvantages as a metal anode in comparing to the carbon anode. The charge–discharge cycle ability of the lithium metal anode is degraded by the formation of dendritic deposits. And it causes the isolation of active lithium metal and also leads to short circuit with the cathode. Another reason for the poor cycle life of the lithium anode might be the formation of an interfacial layer between lithium metal and electrolyte with a low ionic or electronic conductivity as already discussed by some researchers [1,2]. One of the effective methods to improve the lithium anode properties for rechargeable

battery is to add the effective additive, e.g., CO_2 [3–7] or HF [8,9], to the liquid electrolyte system.

The gel electrolyte, which consists of polymer matrix, organic solvent and supporting electrolyte, was introduced as a novel material in the field of rechargeable battery applications as early as 1975 [10–12]. The advantages of the gel electrolyte applied to batteries include the fact that the electrolyte solution does not leak out from the cell, and that the electrolyte can be prepared as a thin film, which enables to construct a solid state and high energy density battery. In particular, the gel electrolyte demonstrates a high ionic conductivity of about 10^{-3} S cm^{-1} at room temperature and has a sufficient mechanical strength. Examples of the host polymer of the gel electrolyte are poly(acrylonitrile [13,14], poly(methylmethacrylate) [12,13], a new copolymer of vinylidene fluoride with hexafluoropropylene (PVdF-HFP) [1,15–17]. The first reliable and practical rechargeable Li-ion plastic battery, which contained the carbon material as the anode, was developed in 1996 by using the PVdF-HFP copolymer type gel electrolyte [2].

Since we recently confirmed that poly(ethylene oxide) (PEO)-based gel electrolyte effectively suppressed the dendritic deposition of lithium [18]. We study in the present

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paper the charge–discharge performance of lithium metal anode using the PVdF-HFP gel electrolyte system. Furthermore, the effect of CO_2 addition to the PVdF-HFP gel electrolyte was additionally investigated.

2. Experimental details

The PVdF-HFP and the PEO gel electrolytes were prepared in Ar atmosphere as follows. As for the PVdF-HFP gel electrolyte, 2 g of PVdF-HFP (Elf Atochem, Kynar 2801, ca. 10 wt.% as hexafluoropropylene units) and 4.2 cm^3 of 1 mol dm^{-3} $LiClO_4$ solution with a mixture of EC and PC (EC:PC = 1:1 in volume ratio) were dissolved in 30 cm^3 of tetrahydrofuran (THF). The THF solution was placed in a petri dish (30 mm in diameter) and dried under vacuum for more than 12 h. The PVdF-HFP membrane, thus obtained, was soaked for 15 min in 1 mol dm^{-3} $LiClO_4$-EC/PC at the low pressure of 210 Torr or at 760 Torr with the addition of CO_2 [3–5]. The PVdF-HFP gel electrolyte film had a transparent and elastic appearance with a thickness of about 300 μm. The ionic conductivity of the PVdF-HFP gel electrolyte was ca. 2.1×10^{-3} S cm^{-1}. The experiment with poly(tetrafluoroethylene) (PTFE) contacting with the lithium metal was performed to check the interfacial reaction layer for the purpose of comparison with the PVdF-HFP–lithium metal system.

The PEO gel electrolyte consisted of PEO (M.W. 4,000,000; Aldrich), $LiClO_4$, and PC solution. PEO (0.6 g) and $LiClO_4$ (0.3623 g) were dissolved in 50 cm^3 acetonitrile (AN). The membrane was formed by casting 1 cm^3 of the AN solution directly onto the Ni electrode (10 mm in diameter) and drying in vacuum for more than 12 h. The film was subjected to swelling by dropping 30 μl of 1 mol dm^{-3} $LiClO_4$-PC with or without the addition of CO_2. The ionic conductivity of the PEO gel electrolyte was ca. 5.0×10^{-4} S cm^{-1}. All chemicals used were of reagent or battery grade.

Lithium metal was charged (deposited) on a nickel electrode with 1.0 C cm^{-2} and discharged (dissolved) until the voltage reached 1.0 V, and the charge–discharge cycle was repeated at 0.5 mA cm^{-2}. After each charge during cycles, the rest period of 3 min was operated. The charge–discharge cycling efficiency at each cycle was calculated according to Eq. (1):

$$\text{Efficiency} (\%) = Q_{\text{discharge}} / Q_{\text{charge}} \times 100 \qquad (1)$$

$Q_{\text{discharge}}$ and Q_{charge} correspond to the quantities of charge for discharging and charging, respectively. The morphology of the deposited lithium was examined with an optical microscope after each charge.

The details of the electrochemical cell used for observing the lithium morphology in situ and for performing charge–discharge cycle tests were described previously [19]. All electrochemical measurements were carried out at room temperature. A.c. impedance spectroscopy was mea-

sured at the open-circuit potential with the frequency range from 20 kHz to 100 mHz after each charge.

3. Results and discussion

Fig. 1 shows the morphology of the lithium deposited in the gel electrolytes at 0.5 mA cm^{-2} after the first and the fifth charges. When the charge–discharge cycling was performed at a lower depth-of-discharge and a lower current density, a higher efficiency and a longer lifetime were obtained. However, in this study, we used a higher charge/discharge current density, i.e., 0.5 mA cm^{-2}. In this direct observation cell, the current distribution was more critical than the normal coin type cell [18,19] because the cell structure was designed for the direct observation, not for the cycling [18].

As described previously [18,19], the dendritic deposition was suppressed in the PEO gel electrolytes owing to the mobility of the electrolyte molecules. When comparing the morphologies in the PEO gel and the PVdF-HFP gel electrolytes in Fig. 1, they are clearly different from each other. In the case of the PEO gel electrolyte, the roughness in morphology increases with increasing number of cycles. After the fifth cycle, we could not focus the microscope on the entire lithium surface because of its high roughness. In contrast, the surface of the lithium operated in the PVdF-HFP gel is more uniform than that in the PEO gel. This difference is attributed to the differences in chemical behavior and immobility of the electrolyte molecules. Actually, the PVdF-HFP gel film has a higher mechanical strength and two times higher conductivity than the PEO gel film. The addition of CO_2 to the PVdF-HFP gel makes the surface slightly smooth as seen in Fig. 1b and c.

The results of a.c. impedance measurements at first and fifth cycles in various gel electrolyte systems are shown in Figs. 2–4. In the case of the PEO gel electrolyte, the interface resistance was about 17 Ω cm^2 at the first cycle and it increased after the fifth cycles. In contrast, in the case of the PVdF-HFP gel electrolyte, the interface resistance was obviously smaller than the PEO gel electrolyte at both the first and the fifth cycles. It is likely that the interface between the gel electrolyte and the lithium metal plays the most important role in determining cycling characteristics. The white color of PTFE, which contains fluorine as does the copolymer of PVdF-HFP, turns black to produce the appearance of carbon in contact with lithium metal. Actually, in the case of PTFE, it might be carbonized by a reaction with alkali metal, which propagates throughout the polymer. From this consideration, it is likely that the decrease of the interface resistance obtained with the PVdF-HFP is due to the formation of some protective layers, such as LiF, on the lithium as a result of the reductive reaction of the $-CF_3$ units in the HFP by lithium metal. And it also seems to due to the high stability
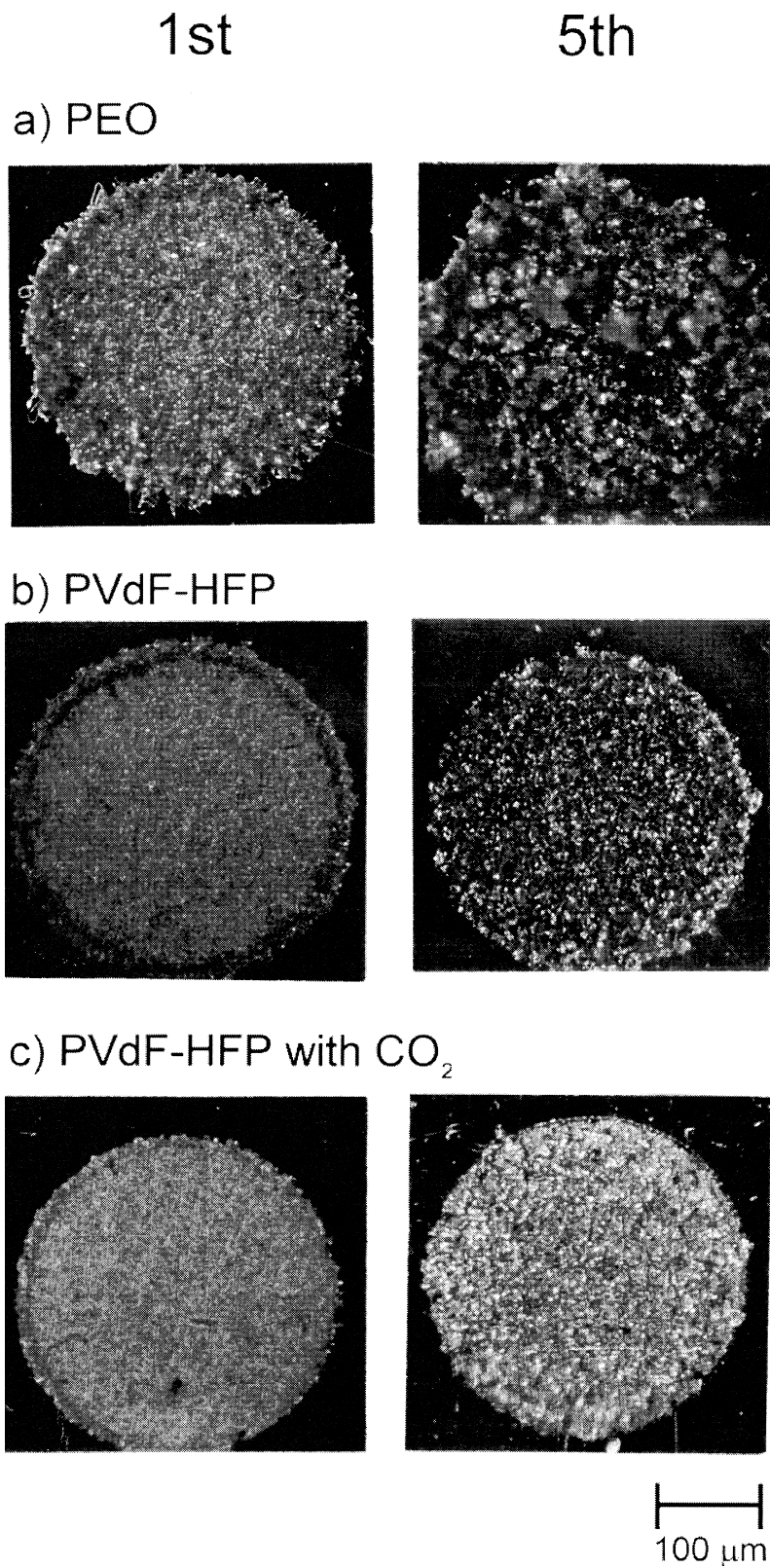
1st   5th

a) PEO

b) PVdF-HFP

c) PVdF-HFP with CO$_2$

|— —|
100 μm

Fig. 1. Micrographs of lithium metal anode at the first and fifth cycles in (a) PEO gel without CO_2, (b) PVdF-HFP gel without CO_2, and (c) PVdF-HFP gel with CO_2.

of PVdF, which results from the fact that the $-CH_2$-units are not affected by the lithium metal.

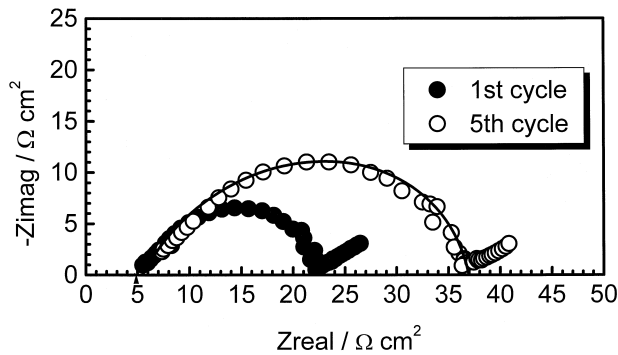The addition of CO_2 to the PVdF-HFP gel electrolyte decreases the interface resistance from 9 Ω cm^2 to 7 Ω

Fig. 2. Cole–Cole plots of lithium electrodeposited at the first and fifth cycles in PEO gel electrolyte.

Fig. 4. Cole–Cole plots of lithium electrodeposited at the first and fifth cycles in PVdF-HFP gel electrolytes with CO_2.

cm^2. This CO_2 efficiency on the lithium metal anode was similar to that found in the PC liquid system [13,14].

Fig. 5 shows the variation of charge–discharge cycling efficiency of the lithium anode with the number of cycles in various electrolyte systems. As shown in Fig. 5a, the lithium operated in the EC/PC liquid displayed a relatively high efficiency only in the first cycle, and the steady state efficiency in the liquid electrolyte obtained after the second cycle was ca. 75%. This efficiency was similar to that obtained with the PEO gel electrolyte, and the lithium anode in the PVdF-HFP gel electrolyte showed an about 10% higher efficiency than the liquid or the PEO gel electrolyte. It is believed that the efficiency obtained with the gel electrolytes depends on the kind of polymer matrix. There are some apparent differences between the PEO and the PVdF-HFP gel electrolyte, i.e., in the chemical behavior of polymer matrix and in the mobility of the electrolyte molecules. Fig. 5b compares coulombic efficiencies of the PVdF-HFP gel electrolyte system with and without CO_2 addition. The efficiency was increased by the CO_2 addition to 90–97%. Although a similar tendency was obtained by using the PEO gel electrolyte, the efficiency for the CO_2-containing PVdF-HFP is higher than that for the CO_2-containing PEO, i.e., ca. 84%. These results confirm that CO_2 addition is effective not only for the liquid electrolyte but also for the gel electrolyte. The combination of the PVdF-HFP electrolyte with CO_2 addition did enhance the efficiency of lithium anode more effectively.
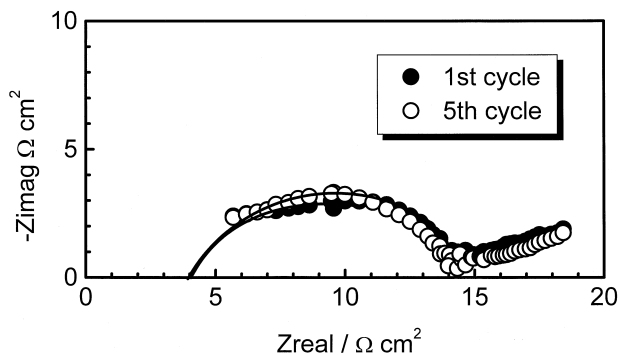
From these results, it is concluded that there is a possibility of enhancing the properties of the lithium anode by properly selecting and designing the combination of host polymer, supporting electrolyte, solvent and additives.

Fig. 5. Charge–discharge cycling efficiency of lithium metal anode at 0.5 mA cm^{-2} (a) in EC/PC liquid, PEO gel and PVdF-HFP gel electrolyte systems without CO_2, and (b) in PVdF-HFP gel electrolyte system with and without CO_2 addition.

Fig. 3. Cole–Cole plots of lithium electrodeposited at the first and fifth cycles in PVdF-HFP gel electrolytes without CO_2.

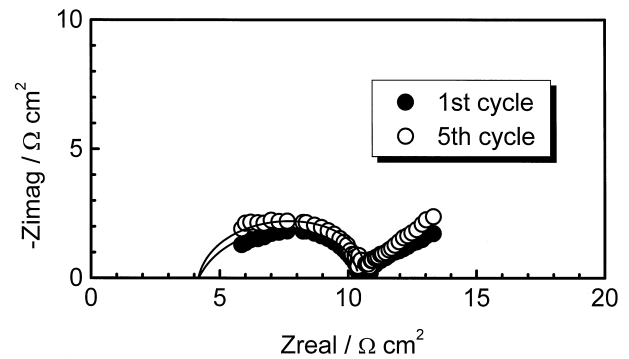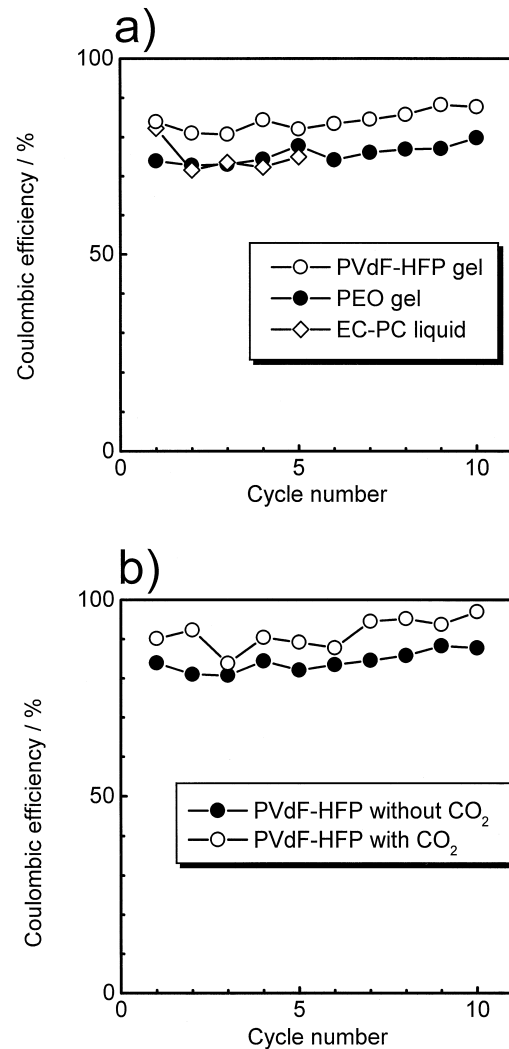The combination of PVdF-HFP gel system with CO_2 saturation is one of the candidates for making the lithium metal anode usable in rechargeable batteries.

4. Conclusions

The performance of the lithium metal anode was studied in the PVdF-HFP gel electrolyte. By using the PVdF-HFP gel electrolyte, we obtained a more uniform morphology, smaller interface resistance, and a higher coulombic efficiency (ca. 85%) of the lithium metal anode than those obtained with the PC/EC liquid or the PEO gel electrolyte. It is likely that it was because the PVdF-HFP gel electrolyte was most stable to the lithium metal anode compared to the PC/EC liquid or the PEO gel electrolyte. Additionally, the performance of the lithium metal anode was investigated in the PVdF-HFP gel electrolyte by adding CO_2. The interface resistance was decreased and the coulombic efficiency was improved further to ca. 95% by CO_2 addition. Therefore, the combination of PVdF-HFP gel electrolyte with CO_2 addition is one of the most attractive candidate for the lithium secondary battery systems.

Acknowledgements

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