Improvement on cycling efficiency of lithium by PEO-based surfactants in cross-linked gel polymer electrolyte

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Abstract

The effect of poly(ethylene oxide) (PEO)-based surfactant in the gel polymer electrolyte on the cycling efficiency of lithium was investigated by means chronopotentiometry. The gel polymer electrolyte was prepared by thermal curing using bisphenol A ethoxylate diacrylate as a cross-linker. While an improvement in cycling efficiency of lithium was found for the electrolytes containing both of perfluorinated and star-shaped PEO-based surfactants, the better cycling efficiency was observed for the star-shaped surfactants than that for the perfluorinated surfactant. More than 90% of cycling efficiency of lithium was achieved for the polymer electrolyte using star-shaped PEO surfactants. The cycling efficiency of lithium in the gel polymer electrolyte containing star-shaped surfactant increased as increasing of the molecular weight of side chain. By using star-shaped PEO surfactant, the interface resistance was almost constant during the repeated cycles. The star-shaped PEO-based surfactants seem to be very effective to form stable SEI layer.
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Keywords: Gel polymer electrolyte; PEO-based surfactant; Cycling efficiency of lithium; Interface resistance

1. Introduction

In recent years, there has been a growing demand for the high energy density and high power rechargeable batteries for portable electronic devices, hybrid electric vehicles and load leveling systems. The lithium metal is considered to be one of the promising anode materials with high energy density per volume and weight [1,2]. Lithium metal anode has high theoretical specific capacity ($3800\,Ah\,kg^{-1}$) and low negative potential ($-3.05\,V$ vs. NHE^{-1}). However, main disadvantages of lithium metal as an anode material are low cycling efficiency of lithium and poor safety due to the formation of dendrite on the lithium anode. These disadvantages are mainly due to the high reactivity of lithium metal with the electrolyte components such organic solvents, lithium salts and impurities [3,4]. Therefore, finding electrolytes with low reactivity with lithium is an important issue to realize the commercial application of lithium metal rechargeable batteries.

Recently, it has been reported that some inorganic [5–8], organic [6–12] and gaseous [13–15] additives to the electrolytes can improve the cycling efficiency of lithium electrode. Metallic ions in electrolyte such as Al^{3+} and Sn^{2+} showed better cycling efficiency of lithium by the formation of alloys on the surface when lithium was deposited [8]. The cycling efficiency of lithium was improved by the addition of organic solvents such as benzene, methylfuran and 2-methylthiophene in liquid electrolyte [16]. Vinylene carbonate (VC) as an additive to the electrolyte was also introduced in order to improve the cycling efficiency of the lithium battery [17]. It was reported that the CO_2 dissolved in the electrolyte enhanced the cycling performance of lithium batteries by forming a surface film of Li_2CO_3 on the lithium metal anode [13]. These additives would absorb on the active sites on the surface of lithium electrode and suppressed the formation of dendrite.

Many researches have been studied on the gel polymer electrolyte (GPE) containing polar organic solvents such as ethylene carbonate (EC) and propylene carbonate (PC) for the replacement of the liquid electrolyte. Polymer matrix such as

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polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) [18,19], poly(ethylene oxide) (PEO) [20,21], poly(methyl methacrylate) (PMMA) [22] and poly(acrylonitrile) (PAN) [23,24] were used for the gel polymer electrolyte. Advantages of the gel polymer electrolyte are: (i) high conductivity ($\sim 10^{-3}$ S cm^{-1}) because gel polymer electrolytes are prepared by immobilization of the liquid electrolyte as a ion carrier and a plasticizer into polymer matrix; (ii) ease in the battery manufacturing process owing to their self-supporting properties; and (iii) good safety due to the free of leakage compared with that of liquid electrolytes. The GPE has been used for the suppression of dendrite formation on lithium even though the mechanism has not been clearly elucidated. It was reported that the gel electrolyte using PAN could suppress the formation of dendrite when the polymer concentration was larger than 5 wt.% [25].

In this paper, we characterized effects of the perfluorinated and the star-shaped poly(ethylene oxide) based surfactants as additives for GPE on the cycling efficiency of lithium. The nonionic PEO surfactant such as poly(ethyleneglycol) dimethyl ether was used as an additive to stabilize the lithium surface by the formation of the uniform path of lithium ion [26]. Thus, it seems worthwhile to investigate the effect of the chemical structure of the PEO-based surfactant systematically. We synthesized perfluorinated and start-shaped PEO-based surfactants which had different end group and molecular weight of PEO, and examined the effect of additives on the cycling efficiency of lithium. The gel polymer electrolyte was prepared by using bisphenol A ethoxylate diacrylate as a cross-linker for the studying lithium electroch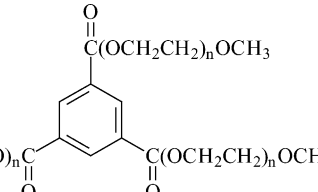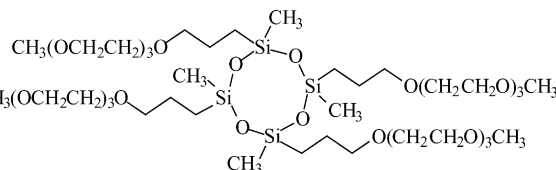emical plating/stripping behavior. Interface between the lithium electrode and the gel polymer electrolyte was investigated by means of the impedance analysis.

2. Experimentation

Bisphenol A ethoxylate diacrylate (EO/phenol = 4) (BPAEDA) was purchased from Aldrich and purified by using silica–gel column chromatography (ethyl acetate: hexane = 1:1, v/v). A 1:1 mixture of ethylene carbonate and propylene carbonate was purchased from Merck and LiAsF$_6$ and LiPF$_6$ were from Aldrich as battery grade materials and used as received. Perfluoropolyether (PFPE, MW = 4500) was purchased from Aldrich and other PEO-based surfactants such as Tri–OH, Tri, BTC and D4-TEG were synthesized in our laboratory. Chemical structures of surfactants used in this study are listed in the Table 1. All surfactants were dried in the vacuum oven at 80 °C for 24 h before use.

The gel polymer electrolyte was prepared by the cross-linking reaction of a homogenous solution composed of BPAEDA, liquid electrolyte (EC/PC = 1:1, v/v), 1 M lithium salts, surfactants and radical initiator. Benzoyl peroxide (BPO) was used as a radical initiator. The amount of radical initiator was 1 wt.% of the used cross-linker. After a microporous polyolefin separator was immersed in the homogeneously mixed precursor solution for an hour, the wetted separator was sandwiched between nickel plate and Li metal for the test cell of cycling efficiency of lithium. The test cell was sealed in an aluminum coated plastic pouch to perform electrochemical measurements. All procedures for preparing the test cell were carried out in a dry-box filled with argon gas in which water content was less than 1 ppm. The

Table 1
The chemical structures and molecular weights of PEO-based surfactants

Structure	Abbreviation	Molecular weight
$CF_3-(CF_2CF_2O)_n-CF_2CF_3$	PFPE	4500
$HO-(CH_2CH_2O)_3-\overset{\overset{O}{\parallel}}{C}(-CF_2)_6-CF_3$	Tri–OH	114
$F_3C-(CF_2)_6-\overset{\overset{O}{\parallel}}{C}O-(CH_2CH_2O)_3-\overset{\overset{O}{\parallel}}{C}(-CF_2)_6-CF_3$	Tri	210
	BTC164 ($n=3$) BTC750 ($n=16.2$) BTC350 ($n=7.2$)	651 2409 1209
	D4-TEG	1057

assembled test cell was cured in convection oven at 100 °C for 20 min.

The cycling efficiency of lithium at each cycle was calculated by using the equation [16]:

$$\text{Efficiency}\,(\%) = \frac{Q_s}{Q_p} \times 100$$

where Q_p and Q_s correspond to the electrical charge of plating and stripping, respectively.

The plating/stripping cycling efficiency of lithium was measured by means of chronopotentiometry using a Toyo battery test system (TOSCAT-3100). The lithium was plated on a nickel electrode with $0.1\,\text{C}\,\text{cm}^{-2}$ of plating electricity and stripped until the voltage reached 1.0 V, and the plating/stripping cycle was repeated with current density of $0.1\,\text{mA}\,\text{cm}^{-2}$.

Interfacial resistance (R) was measured with complex impedance analyzer (Zahner Elektrik, 1 M6e) at the open-circuit potential with the frequency range from 100 KHz to 10 mHz after the lithium plating cycle. All the electrochemical measurements were carried out at 30 °C in constant temperature oven.

3. Results and discussion

3.1. Cycling efficiency of lithium

The cycling efficiencies of lithium were determined by a chronopotentiometry using the nickel as a working electrode. Fig. 1 shows the results of the cycling efficiencies of lithium on the nickel substrate using different lithium salts and EC/PC contents. The higher content of EC/PC in the GPE had the better cycling efficiency of lithium for both of $LiAsF_6$ and $LiPF_6$. It was noticed that the cycling efficiency of lithium in the electrolyte using $LiAsF_6$ was higher than that using $LiPF_6$. This result was consistent with the report that the cycling efficiency of lithium in polar aprotic solvents with $LiAsF_6$ was much higher than that with $LiPF_6$ [27]. This

enhancement of cycling efficiency of lithium was attributed to the electronic properties of the solid electrolyte interface (SEI) layer formed on the lithium electrode which contained the AsF_6^- reduction products, mostly LiF [8]. Stable SEI layer formed on the lithium/electrolyte interface may reduce the lithium reactivity and enhances the uniformity of Li deposition processes.

To improve cycling efficiency we added various PEO-based surfactants in gel polymer electrolytes. The effect of various surfactants in GPE using $LiAsF_6$ is shown in Fig. 2. The cycling efficiencies of lithium on nickel electrode were improved by both of the perfluorinated and star-shaped surfactants. As shown in Fig. 2(a), the cycling efficiency of PFPE is higher than that of perfluorinated esters such as Tri–OH and Tri. Fig. 2(b) shows that the star-shaped PEO-based surfactants such as BTC750 and D4-TEG effectively improve the cycling efficiency. Among the surfactants used in this study, star-shaped PEO surfactants such as D4-TEG and BTC seemed to be the most effective additives for enhancing the cycling efficiency of lithium.

The effect of the concentration of D4-TEG as an electrolyte additive on the cycling efficiency of lithium is shown in Fig. 3. The suitable concentration was found to be in
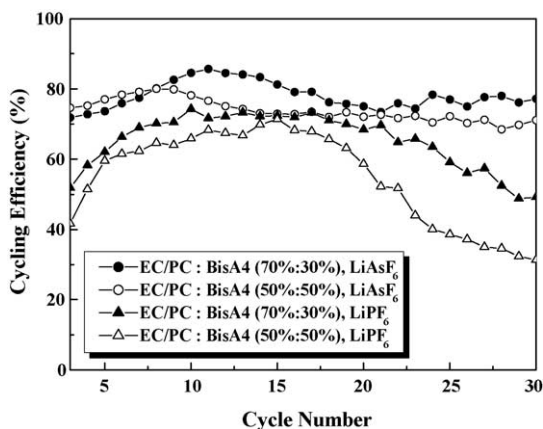

Fig. 1. Plating/stripping efficiency of lithium on nickel substrate vs. cycle number for GPE with different lithium salts and liquid electrolyte contents.
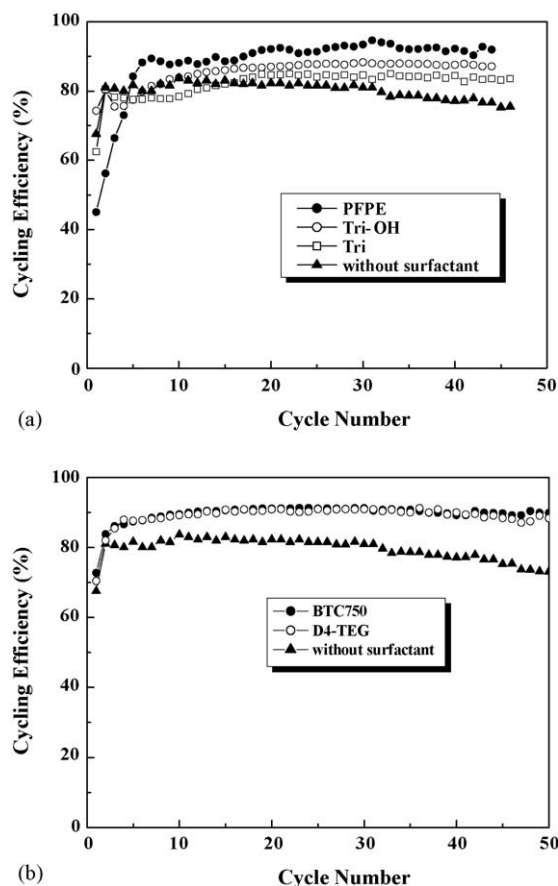

Fig. 2. Plating/stripping efficiency of lithium vs. cycle number for GPE with various surfactants: (a) perfluorinated surfactants and (b) star-shaped surfactants. Concentration of surfactant was 500 ppm; lithium salts was $LiAsF_6$.
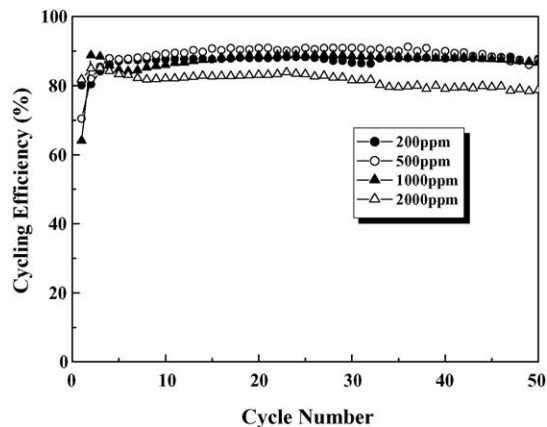
Fig. 3. Effect of concentration of D4-TEG on cycling efficiency of lithium. Lithium salts was LiAsF$_6$.

Fig. 5. Variations of the interfacial resistance with cycle number using different surfactants. Concentration of surfactant was 500 ppm; lithium salts was LiAsF$_6$.

the range from 200 to 1000 ppm of D4-TEG. The effect of molecular weight of the star-shaped BTC on cycling efficiency is shown in Fig. 4. The cycling efficiency of lithium in the electrolyte with star-shaped BTC increased as increasing the molecular weight of PEO side chain. Specially, the cycling efficiency of lithium using BTC750 was measured to be more than 90% and changed little with the cycle number.

3.2. Lithium/GPE interface properties

Fig. 5 shows the interface resistance change as a function of the cycle number in the GPE containing various surfactants. The interface resistance of Li|GPE without surfactant increased with the repeated cycles. On the other hand the interface resistance of Li|GPE with the PEO-based surfactants such as BTC750, Tri and Tri–OH, which were effective to enhance the cycling efficiency of lithium, remained almost constant during the repeated cycles. Furthermore, the interface resistance with BTC750 was around 400 Ω and was smaller than that of other surfactants used in this study. The
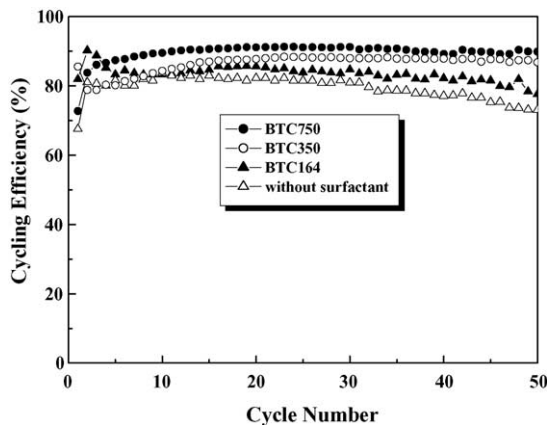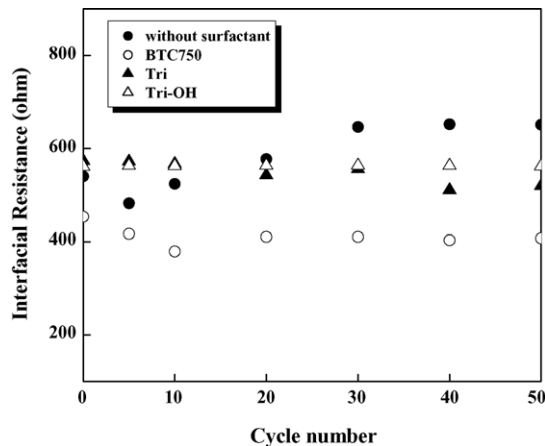
increased cycling efficiency of lithium with the additives may be explained by the formation of a Li ion permeable thin and stable SEI layer, which would prevent the dendrite formation on the electrode surface [28]. Interface resistance may decrease by forming the ionic conducting solid electrolyte interface (SEI) layer. The star-shaped PEO-based surfactant seemed to be very effective to form the stable SEI layer.

4. Conclusion

The cycling efficiency of lithium in GPE with various PEO-based surfactants as additives was studied using Li|GPE|Ni test cells. We found that the cycling efficiency of lithium was improved by GPE containing of perfluorinated surfactants and star-shaped PEO surfactants. GPE with the star-shaped surfactant showed improved cycling efficiency of lithium than that with perfluorinated surfactants. More than 90% cycling efficiency of lithium was achieved for the gel polymer electrolyte using star-shaped PEO surfactants. Optimum concentration of D4 was found to be in the range of 200–1000 ppm. The electrolyte with BTC increased the cycling efficiency of lithium as increasing of the molecular weight of PEO side chain. In the polymer electrolyte using the star-shaped PEO surfactant, the interface resistance remained almost constant during the repeated cycles. It seems that the star-shaped PEO-based surfactant is very effective to form the stable SEI layer on the surface of lithium.

Fig. 4. Effect of molecular weight of BTC on cycling efficiency of lithium. Concentration of surfactant was 500 ppm; lithium salts was LiAsF$_6$.

Acknowledgement

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