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Cycling performances and interfacial properties of a Li/PEO-Li(CF₃SO₂)₂N-ceramic filler/LiNi_{0.8}Co_{0.2}O₂ cell

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Abstract

The cycling performances of the cell with poly(ethylene oxide) (PEO)-based composite polymer electrolyte using BaTiO₃, TiO₂, and Al₂O₃ as filler, lithium metal anode, and LiNi_{0.8}Co_{0.2}O₂ cathode at 80°C have been examined. The cycling performance depended on the filler in PEO-Li(CF₃SO₂)₂N electrolyte. The best result was obtained in the electrolyte with the BaTiO₃ filler. The good cycling performance in the cell of Li/PEO₁₉Li(CF₃SO₂)₂N-BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ was explained by the improved interfacial stability between the electrolyte and the electrode. The cycling performance of PEO-based polymer electrolyte cell was influenced by the charge and discharge cut-off voltage. The electrochemical window of PEO₁₉Li(CF₃SO₂)₂N-BaTiO₃ composite electrolyte was estimated to be <4.0 V. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Lithium cell; Composite polymer electrolyte; Cell performance

1. Introduction

Lithium polymer batteries are expected to result in the improvement of energy density and applying for versatility in the battery design with a plastic configuration under relatively low costs [1]. Now two types of lithium polymer batteries have been developed, namely, the gel polymer electrolyte type and dry polymer electrolyte type. The dry type polymer batteries have the advantages of better chemical stability and high energy density. The most important technology in this field is to achieve a good cyclability, which is related to the anode/electrolyte and cathode/electrolyte interfaces as well as electrode materials. The reaction of electrolyte with electrode materials can lead to a high resistance passivation film, such as LiF and Li₂O [2]. Electrolyte decomposition usually occurs in the range of high cell voltage, which is the possible reason for the capacity fade.

It has been reported that the poly(ethylene oxide) (PEO)-based polymer electrolyte was improved in the mechanical strength [3], interface properties between the electrolyte and

lithium metal electrode [4], and the electrical conductivity [5] by addition of the ceramic fillers like TiO₂, γ-LiAlO₂, and Al₂O₃. In the previous papers [6,7], we have reported that the ionic conductivity and the interfacial properties of PEO-based electrolyte can be improved by addition of BaTiO₃ as a filler [8,7]. In this study, the interfacial resistance between the PEO-Li(CF₃SO₂)₂N-ceramic filler and the electrodes, and the cyclic performance of the cell, Li/PEO₁₉-Li(CF₃SO₂)₂N-BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ have been examined.

2. Experimental

High molecule weight (MW = 6 × 10⁵) PEO (Aldrich) and lithium salts (LiClO₄ (Aldrich Chemical), LiBF₄ (Aldrich Chemical), LiPF₆ (Aldrich Chemical), and Li(CF₃SO₂)₂N (Fluka Chemical)) were used as-received. BaTiO₃ (Aldrich Chemical (0.6–1.2 μm) and Osaka National Research Institute (1.8, 0.5, 0.1 μm)), rutile TiO₂ (Aldrich Chemical, 0.1 μm), and γ-Al₂O₃ (Daidou, 0.1 μm) were dried under vacuum at 100–150°C. PEO was dissolved in acetonitrile (Nacalai 99.5% purity) with lithium salts by stirring at ambient temperature for 24 h in an Ar-filled dry box. The ceramic fillers were added into the solution with continuous stirring. The homogeneous slurry was then cast on a clean Teflon plate. The solvent was allowed to

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evaporate slowly at 25°C for 24 h and then the composite polymer electrolyte film was dried at 100°C under vacuum condition for 6 h.

Appropriate ratios of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (Prepared by heating a mixture of Li_2O , NiO and CoO at 720°C for 24 h) and acetylene black (Denkikagaku, Japan) were added into the $\text{PEO}_{19}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ solution dissolved in acetonitrile, and the paste was strongly stirred in a dry box for 12 h. The obtained homogeneous slurry was coated onto a stainless steel mesh (250 mesh). After the cathode composite was dried under vacuum at 100°C, it was pressed to form thin electrode pellet with 200 μm in thick. The typical weight ratio of active material, polymer electrolyte, and acetylene black in the cathode mixture was 65, 20 and 15%, respectively. The polymer composite electrolyte film (about 200 μm in thick) was sandwiched between the lithium metal foil anode (active area of 1.13 cm^2) and the cathode composite pellet (active area of 0.5 cm^2).

Cycling experiments of the cells were performed under galvanic condition at 80°C. Impedance spectroscopy was recorded from 1 MHz to 0.05 Hz by using a Solatron 1260 frequency analyzer.

3. Results and discussion

In the previous paper [7], we have reported that the interfacial resistance between the PEO-LiX electrolyte and the lithium metal electrode was stabilized by addition of the ceramic filler of BaTiO_3 . The interface resistance was <100 Ωcm^2 after stored at 80°C for 700 h. Fig. 1 shows the interfacial resistance of the cathode mixture ($\text{LiNi}_{0.8}\text{Co}_{0.8}\text{O}_2$, acetylene black, and polymer electrolyte)/ $\text{PEO}_{19}\text{-LiX-10 wt.}\%$ (w/o) BaTiO_3 /the cathode mixture. The interface resistance is <100 Ωcm^2 when stored at

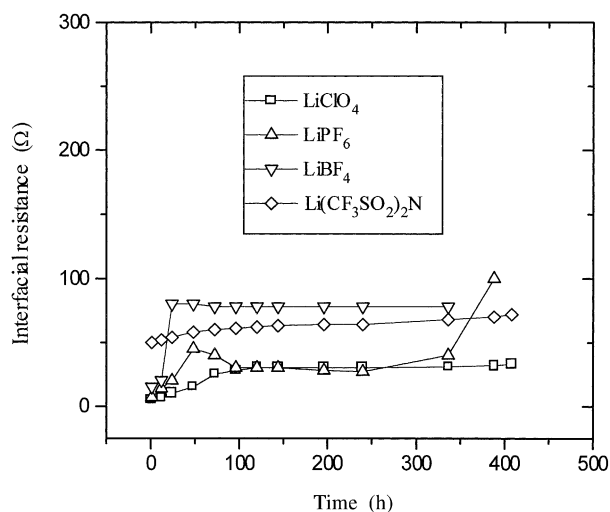


Fig. 1. Time dependence of the interfacial resistance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2/\text{PEO}_{19}\text{LiX-10 w/o BaTiO}_3/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ at 80°C. Electrode area: 0.5 cm^2 .

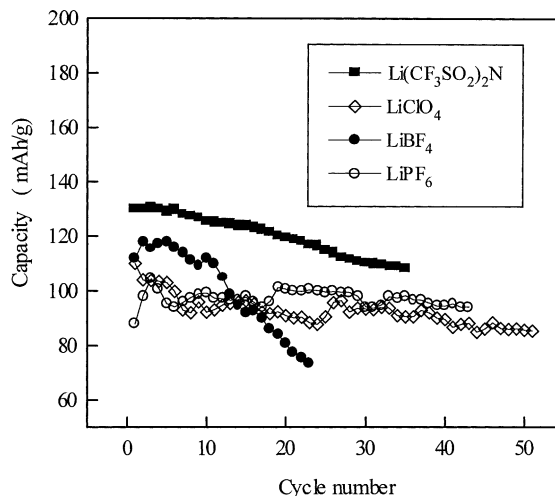


Fig. 2. Discharge capacity of $\text{Li/P(EO)}_{19}\text{LiX-10 w/o BaTiO}_3/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ at 80°C and at 0.2 mA/cm^2 (cathode). Voltage limit: 2.5 V for discharge and 3.9 V for charge. Anode area: 0.5 cm^2 and cathode area: 1.1 cm^2 .

80°C for 400 h, which is almost similar to that of $\text{Li/PEO}_{19}\text{LiX-BaTiO}_3/\text{Li}$. The similar interfacial behavior was found on the interface of the cathode mixture and $\text{PEO}_{19}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ with different fillers of $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 . The cathode and electrolyte interfacial resistance is comparable to the lithium ion resistance of the 30 μm thick of $\text{PEO}_{19}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N-10 w/o BaTiO}_3$, which was estimated to be about 25 Ω from the conductivity and lithium ion transport number [8].

Fig. 2 shows the cycling performance for the cell $\text{Li/PEO}_{19}\text{LiX-10 w/o BaTiO}_3/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ at 80°C. The particle size of the filler of BaTiO_3 was about 0.1 μm . The cut-off voltages of charging and discharging were selected as 3.9 and 2.5 V, respectively, because of the large capacity fading at high charge cut-off voltage as shown in the later part of the paper. The cycling performance of these cells depends on the salt in the polymer electrolyte. The fast fade of discharge capacity on cycling was observed in the cell with the electrolyte using LiBF_4 as the salt. The significant capacity fade could be explained by the high interfacial resistance in $\text{Li/PEO}_{19}\text{LiBF}_4\text{-10 w/o BaTiO}_3/\text{Li}$ as shown in the previous paper [8]. The highest discharge capacity and good cycling performance were observed in the electrolyte with $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ as the salt and BaTiO_3 as the filler. The charge and discharge cycling efficiency was close to 100%. The first discharge capacity, which was calculated from the amount of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in the cathode mixture, was almost the same as that of the cell with liquid electrolyte. In the previous paper [8], we have reported that the addition of small amount of ferroelectric BaTiO_3 into the $\text{PEO-Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ electrolyte enhanced the interface stability with lithium anode and the electrical conductivity. We have examined the cycling performance of the cell $\text{Li/PEO}_{19}\text{-Li}(\text{CF}_3\text{SO}_2)_2\text{N-1.5 w/o BaTiO}_3/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The addition of a small amount of the ferroelectric BaTiO_3 into

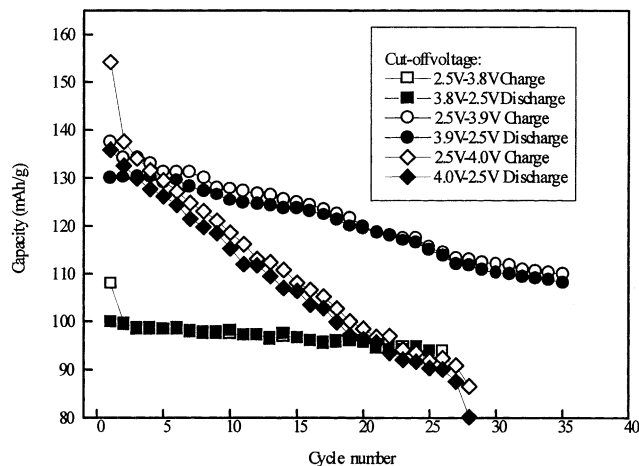


Fig. 3. Cut-off voltage dependence for cycling performance of Li/PEO₁₉Li(CF₃SO₂)₂N-10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ at 80°C and at 0.2 mA/cm², Electrode area: 1.1 cm².

PEO-Li(CF₂SO₂)₂N electrolyte was also effective to obtain high cyclic performance polymer electrolyte cells.

An important parameter in characterization of a given polymer electrolyte is electrochemical stability window. This parameter has been measured by linear sweep voltammetry. The stability windows in PEO₈LiClO₄-10 w/o γ-LiAlO₂ [9] and PEO₈LiClO₄-10 w/o BaTiO₃ [6] was estimated to be at least 4 V at 90 and 70°C, respectively. Appetecchi et al. [4] also measured the electrochemical stability window for PEO₂₀LiBF₄-20 w/o γ-LiAlO₂ electrolyte, which was around 3.7 V. We examined linear sweep voltammetry in a Li/PEO₁₉LiX-10 w/o BaTiO₃/stainless steel cell. It is difficult to estimate the accurate decomposition voltage in these electrolytes from these sweep voltammetry. It is not sure that the small current (<2 μA/cm²) in a voltage range of higher than 3.5 V was due to the decomposition of electrolyte or not. We have examined the dependence of the cut-off voltage on the cycling performance in Li/PEO₁₉Li(CF₃SO₂)₂N-10 w/o BaTiO₃(0.1 μm)/LiNi_{0.8}Co_{0.2}O₂. Fig. 3 illustrates the cut-off voltage dependence on the capacity versus cycling time curves at 80°C and at 0.2 mA/cm², where the capacity was calculated from the

amount of LiNi_{0.8}Co_{0.2}O₂ in the cathode mixture. The cell capacity is decreased rapidly with cycling by charging up to 4.0 V and discharging to 2.5 V. On the other hand, no significant capacity fade is observed by charging to 3.9 V or less. We can conform from these results that the decomposition voltage of the electrolyte examined may be around 3.9 V.

4. Conclusion

The results reported in this work demonstrate that the interfacial resistance between PEO-LiX and LiNi_{0.8}Co_{0.2}O₂ is stable and the cycling performance is improved by addition of BaTiO₃. The Li/PEO₁₉(CF₃SO₂)₂N-BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ cell shows a good cyclic performance in the cut-off voltage of 2.5 and 3.9 V at 80°C.

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