

Four volts class solid lithium polymer batteries with a composite polymer electrolyte

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Abstract

Polyethylene oxide (PEO)-based polymer electrolytes with BaTiO₃ as a filler have been examined as electrolytes in 4 V class lithium polymer secondary batteries. A mixture of 90 wt.% LiN(CF₃SO₂)₂–10 wt.% LiPF₆ was found to be the best candidate as the salt in PEO, and showed high electrical conductivity, good corrosion resistance to the aluminum current collector and low interfacial resistance between the lithium metal anode and the polymer electrolyte. The cyclic performance of the cell, Li/[PEO₁₀–(LiN(CF₃SO₂)₂–10 wt.% LiPF₆)]–10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂/Al, showed good charge–discharge cycling performance. The observed capacity fading on charging up to 4.2 V at 80 °C in the cell was about 0.28% per cycle in the first 30 cycles, compared to that of 0.5% for the polymer electrolyte without LiPF₆ in the lithium salt. © 2002 Published by Elsevier Science B.V.

Keywords: All solid polymer electrolyte aluminum corrosion; Thermal safety; Four volts class; Capacity fade

1. Introduction

Solid lithium polymer batteries have been focused upon for the development of high power–high energy density secondary lithium batteries as a result of the necessity for performance, safety, and reliability. One of the main purposes for developing solid polymer batteries is for vehicle applications [1]. The most important requirements for this application are safety and high energy density. During the last decade two types of lithium batteries for electric vehicles have been developed; one of them is the so-called lithium ion battery and the other the lithium polymer battery [2]. Lithium ion batteries were commercialized as early as the 1990s for mobile applications with smaller size cells. The safety of small capacity lithium ion batteries (around several Wh) has been established over the last 10 years. However, an appreciable amount of flammable gas will appear in large batteries, in particular those with a large amount of liquid electrolyte, when the electrolyte decomposes due to the destruction of the protective layer at carbon surface [3]. Lithium batteries using a solid polymer are quite attractive from safety aspect, because they have no flammable electrolyte.

The possibility of practical solid rechargeable lithium battery using polymer electrolytes was proposed by Armand et al. [4] in 1978. A major effort to develop advanced electric vehicle batteries began in the early 1990s by 3M and Hydro-Québec [5]. The polymer batteries contain a lithium metal anode, a polymer electrolyte based on polyethylene oxide (PEO), and a vanadium oxide (VO_x) cathode. The reversibility of lithium intercalation and deintercalation in VO_x is quite good, but the average discharge voltage of cells with the VO_x cathode is lower than those with LiCoO₂ in lithium ion batteries. Recently, alternative cathode materials, Li_xMnO₂ [6] and Cu_{0.1}V₂O₅ [7] have been proposed for lithium polymer batteries. These cathode materials showed a good charge and discharge cycle performance in the voltage range 3.5–2.0 V. High cell voltage cathode materials such as LiCoO₂, LiNiO₂, and LiMn₂O₄, which have been extensively used in liquid electrolyte cells, have a much lower reversible lithium intercalation capacity in solid polymer electrolyte cells [8–10]. However, no details for high voltage cathode materials in polymer electrolytes have been reported in these papers. The poor rechargeability was assumed to result from the low decomposition potential compared that of conventional liquid electrolytes. Xia et al. [6] estimated that the decomposition potential of PEO to be 3.8 V versus Li/Li⁺. Also, Appetecchi et al. have reported that the decomposition process was observed at

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roughly 3.7 V in $\text{PEO}_{20}\text{LiBF}_4 + 20 \text{ wt.}\% \gamma\text{-LiAlO}_2$ by sweep voltammetry [11]. On the other hand, the decomposition potential of $\text{PEO-LiClO}_4\text{-1.4 wt.}\% \text{BaTiO}_3$ [12] and $\text{PEO-LiCF}_3\text{SO}_3\text{-10 wt.}\% \gamma\text{-LiAlO}_2$ [11] was estimated to be more than 4.0 V versus Li/Li^+ . A low decomposition potential of the electrolyte provides a low cathode capacity with LiCoO_2 and LiMn_2O_4 . The decomposition potential of PEO-based polymer electrolytes also depends on the lithium salt in the electrolyte. In a previous paper [13], the cyclic performance of the cell, $\text{Li/PEO}_{19}\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{-10 wt.}\% \text{BaTiO}_3/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, at 80 °C was reported. The cell did not show significant capacity fade at a cut-off voltage 2.5–3.9 V, or significant capacity loss at a cut-off voltage 2.5–4.0 V.

In this paper, the charge–discharge performance of all solid lithium polymer cells with the high cell voltage cathode, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, has been examined. The addition of LiPF_6 to $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is quite effective to obtain high cathode capacity.

2. Experimental

The PEO-based composite electrolytes were obtained by a solvent casting technique using acetonitrile (AN) as a carrier solvent [14]. High molecular weight PEO (Aldrich, 6×10^5 average molecular weight), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Fluka Chemical), $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ (3 M) and LiPF_6 (Aldrich) were used as received. Barium titanate (Sakai Chemicals, 0.5 μm average particle size) was dried under vacuum at 100–150 °C for 24 h. Preparation of the composite electrolytes involved the dispersion of the BaTiO_3 powder and lithium salt (LiX) in AN followed by the addition of PEO. The slurry was completely homogenized and then cast onto a flat polytetrafluoroethylene vessel. The solvent in the slurry was allowed to evaporate slowly under flow of nitrogen gas for 24 h at room temperature. Finally the composite polymer electrolyte films were dried at 60–95 °C under vacuum for 48 h. This procedure yield homogenous and mechanically stable membranes with an average thickness of about 300 μm .

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was prepared from the mixture of Li_2O_2 (Aldrich) and $(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}$ precursor which was obtained from the decomposition of the hydroxide at 300 °C for 1 h. The mixture was heated at 700 °C for 24 h under O_2 gas flow. The SEM observation showed that the active material thus obtained consisted of particles of around 10 μm in average.

The composite cathode was prepared as follows: proper amounts of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and acetylene black (AB) (Denki Kagaku Co., Japan) were added to the PEO-LiX-BaTiO_3 slurry in AN and the mixture was strongly stirred for 24 h before casting on the aluminum substrate. After the cathode composite material was dried, it was pressed into a thin film of about 40 μm in thickness. The amount of active material was around 3–5 mg and the ratio of active material, AB, and polymer electrolyte was 65:20:15 in weight ratio.

The aluminum dissolution potential was estimated with the help of cyclic voltammograms in the cell $\text{Li/PEO-LiX-10 wt.}\% \text{BaTiO}_3/\text{Al}$ at 80 °C, where a Solartron 1287 potentiostat was run at a scan rate of 10 mV/s and the dissolution potential was determined at a corrosion current of 5 $\mu\text{A}/\text{cm}^2$. By a similar method, the quasi decomposition potential was measured with the cell, $\text{Li/PEO-LiX-10 wt.}\% \text{BaTiO}_3/\text{Ni}$ at 80 °C. Thermal studies were performed using a Rigaku DSC 8230 Thermo Plus. Samples were sealed into aluminum pans in the dry box. The heating and cooling rate was selected at 10 °C/min.

The electrical conductivity of the polymer electrolyte films and the interfacial resistance between the electrolyte and the electrodes (the Li metal anode and the composite cathode) were measured by an ac impedance method using a Solartron 1260 frequency analyzer. Stainless steel blocking electrode cells were used for conductivity measurements, and symmetrical nonblocking lithium electrodes (or the composite cathode) cells were used to investigate the interfacial phenomena. A 10 mV ac amplitude was applied, and the data were collected by recording 10 points per decade over a frequency range from 1 MHz to 1 Hz in conductivity measurements, and from 10 MHz to 0.05 Hz in interfacial resistance measurements.

Mechanical properties of electrolyte films were measured by use of a TP-101 tension tester (Sekegu, Japan) at 10 cm/min stretching speed at different temperatures. These measurements were carried out in a dry box.

The test cells were assembled by sandwiching the polymer electrolyte disk between a lithium foil and the composite cathode. The conductivity measurement cells and the batteries were sealed in an Ar-filled dry box. The cells were kept under a constant mechanical pressure (by spring-loaded terminal) and at a constant temperature (by housing them in a constant temperature chamber). The charge–discharge performance tests of the cells were performed galvanostatically at a constant current of 0.2 mA/cm^2 and at a regulated cut-off voltage. The current density was calculated from the active cathode area (about 0.5 cm^2). The active area of the lithium anode was around 1.0 cm^2 and the anode capacity was several times higher than that of the cathode.

3. Results and discussion

3.1. Aluminum corrosion with polymer electrolyte at higher temperatures and electrochemical stability window of new composite polymer electrolytes

High lithium ion conductivity and low interfacial resistance between the electrolyte and the electrode as well as a high polymer electrolyte decomposition voltage are required to obtain high performance polymer lithium batteries. In previous studies [12,14,15], we examined the electrical conductivity and interfacial resistance at the Li/polymer electrolyte interface in the PEO-LiX-filler system and found

that the best candidate of the examined systems for use as a polymer electrolyte in lithium secondary batteries was PEO–LiN(CF₃SO₂)₂–BaTiO₃. The stability of the interface between the lithium and polymer electrolyte was enhanced by addition of the ferroelectric oxide, BaTiO₃. The electrical conductivity and the lithium ion transport number of PEO–LiN(CF₃SO₂)₂ were also enhanced by the addition of 10 wt.% of BaTiO₃. The electrical conductivity of [PEO₁₂–LiN(CF₃SO₂)₂]-10 wt.% BaTiO₃ was 1.2×10^{-3} S/cm at 80 °C and 6.5×10^{-6} S/cm at 25 °C. The Li/electrolyte interface resistance was only 66 Ω cm² at 80 °C after annealing at 80 °C for 30 days. The high electrical conductivity and the low interfacial resistance of this system provide high performance secondary lithium polymer batteries. However, the electrochemical window of the electrolyte was slightly narrow compared to conventional liquid electrolytes. The cathode capacity of the cell, Li/[PEO₁₉LiN(CF₃SO₂)₂]-10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ was decreased drastically by cycling at a cut-off voltage 2.5–4.0 V at 80 °C [13]. The capacity fade could be explained by the electrolyte decomposition and the corrosion behavior of the aluminum current collector in contact with the cathode composite LiNi_{0.8}Co_{0.2}O₂-AB-PEO–LiN(CF₃SO₂)₂-BaTiO₃. The aluminum current collector undergoes serious corrosion in carbonate-based electrolyte solutions containing LiN(CF₃SO₂)₂. Recently, Yang et al. [16] reported that a protective film formed on the aluminum surface when LiPF₆ and LiBF₄ was used as the salt in propylencarbonate (PC) and could also inhibit corrosion in LiN(CF₃SO₂)₂/PC. We have examined the effect of LiX in LiN(CF₃SO₂)₂ for aluminum corrosion at a higher temperature. Table 1 shows the aluminum dissolution voltage and the Al/PEO–LiX interfacial resistance at 80 °C. The aluminum dissolution voltage of PEO–LiN(CF₃SO₂)₂ was estimated to be 3.8 V, which was enhanced up to 4.5 and 4.3 V by addition of 10 wt.% LiPF₆ and LiBF₄, respectively, as suggested by Yang et al. [16]. Recently an alternative lithium salt with high corrosion resistance for aluminum, bisperfluoroethyl-sulfonimide [LiN(C₂F₅SO₂)₂], has been proposed [17]. This lithium salt exhibits a higher dissolution voltage compared to LiN(CF₃SO₂)₂ in polymer electrolytes. The addition of 10 wt.% LiPF₆ and LiBF₄ in LiN(CF₃SO₂)₂ and LiN(C₂F₅SO₂)₂ enhances the Al dissolution potential. The

addition of LiClO₄ shows no effect on the Al dissolution voltage. The contact resistance between aluminum and the electrolyte was determined in the symmetrical cell Al/PEO–LiX–10 wt.% BaTiO₃/Al by an ac impedance method. The contact resistance reached 80 Ω cm² in the electrolyte with LiN(CF₃SO₂)₂ after annealing at 80 °C for 550 h. This resistance may be due to formation of an interface layer on aluminum with a high resistance. The addition of LiPF₆ and LiBF₄ in LiN(CF₃SO₂)₂ depressed the interfacial resistance as observed in liquid electrolytes [16].

Another important parameter in the characterization of a given polymer electrolyte is the electrochemical stability window. The drastic decrease of the cathode capacity upon cycling when charged to 4.0 V versus Li/Li⁺ could be caused by the decomposition of the polymer electrolyte. The electrochemical stability window was evaluated by linear sweep voltammetry using a two-electrode cell with a stainless steel working electrode and lithium film counter electrode. Fig. 1 shows typical voltammetry results for the PEO–LiX–BaTiO₃ system at 80 °C. We notice that the sweep may be extended to over 4 V versus Li/Li⁺ in the anodic region before observing appreciable current, when the sweep rate was 0.1 mV/s. It is a little difficult to estimate the exact decomposition potential if the scan rate cannot be kept sufficiently low. However, we can say that the addition of LiPF₆ to LiN(CF₃SO₂)₂ in the polymer electrolyte improves the electrochemical stability. The high decomposition voltage in the polymer with mixed LiN(CF₃SO₂)₂ and LiPF₆ salts may be ascribed to the formation of a protective layer on the lithium metal.

3.2. Electrical conductivity and the compatibility with electrode materials of PEO–LiN(CF₃SO₂)₂-LiPF₆-BaTiO₃

By the addition of LiPF₆ into PEO–LiN(CF₃SO₂)₂-BaTiO₃, the aluminum dissolution potential was enhanced and the electrochemical stability window was also improved. The PEO–LiN(CF₃SO₂)₂-LiPF₆-BaTiO₃ systems are quite attractive for use as the electrolyte in lithium polymer rechargeable batteries, if they have a high electrical conductivity and show good compatibility with electrode materials.

Fig. 2 shows the Arrhenius plots of some selected examples of the PEO–LiN(CF₃SO₂)₂-LiPF₆-10 wt.% BaTiO₃

Table 1
Aluminum dissolution potential in PEO–LiX and the contact resistance between aluminum and PEO–LiX

LiX	Al dissolution potential vs. Li/Li ⁺ (V)	Contact resistance (Ω cm ²)		
		Pt	Al (99.99%)	Al foil
LiX free			2	2
LiN(CF ₃ SO ₂) ₂	3.8	2	50	80
LiN(C ₂ F ₅ SO ₂) ₂	4.1	2	20	55
LiN(CF ₃ SO ₂) ₂ -10 wt.% LiPF ₆	4.5		17	38
LiN(C ₂ F ₅ SO ₂) ₂ -10 wt.% LiPF ₆	4.4		18	39
LiN(CF ₃ SO ₂) ₂ -10 wt.% LiBF ₄	4.3			50
LiN(CF ₃ SO ₂) ₂ -10 wt.% LiClO ₄	3.8			94

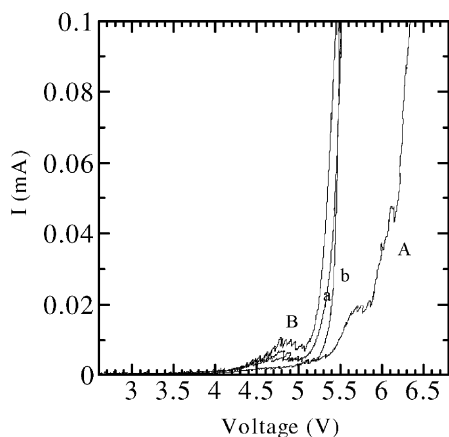


Fig. 1. Cyclic voltammety curves for PEO-LiX-10 wt.% BaTiO₃ at 80 °C with a stainless steel working electrode and the Li metal counter electrode. a, LiN(CF₃SO₂)₂; A, LiN(CF₃SO₂)₂-10 wt.% LiPF₆; b, LiN(C₂F₅SO₂)₂; B, LiN(C₂F₅SO₂)₂-10 wt.% LiPF₆. Scan rate, 0.1 mV/s; electrode area, 1.13 cm².

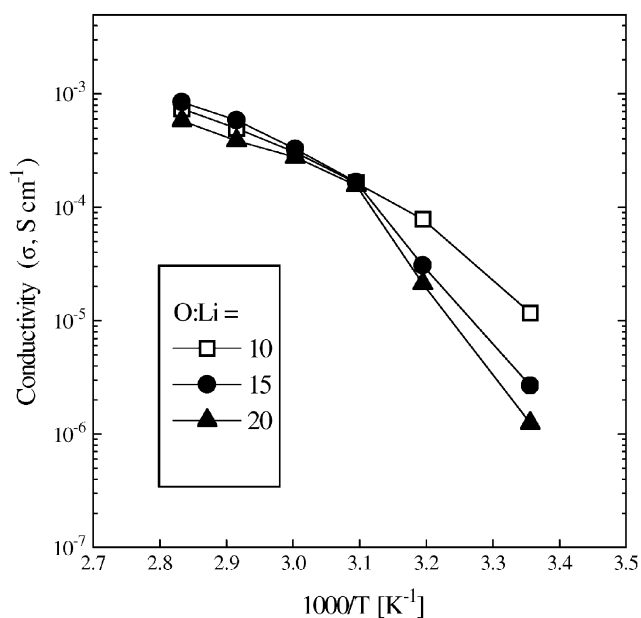


Fig. 2. Arrhenius plots for the composite polymers [PEO-LiN(CF₃SO₂)₂-10% LiPF₆]-10% BaTiO₃ (0.5 μm) as a function of O/Li.

system, and the conductivity values at 80 at 25 °C are summarized in Table 2. The conductivity decreases with increasing LiPF₆ content as indicated by the low conductivity of PEO-LiPF₆ [15]. A conductivity maximum at 80 °C is found at the intermediate concentration of salts of O/Li = 15. On the other hand, at a high salt content of O/Li = 10, maximum conductivity at room temperature was obtained. This behavior is often explained in terms of the trade-off between increasing number of charge carries and ion migration and increased viscosity due to ionic cross-linking. The conductivity values of 7×10^{-4} S/cm at 80 °C and 1.2×10^{-5} S/cm at 25 °C for PEO₁₀[LiN(CF₃SO₂)₂-10 wt.% LiPF₆]-10 wt.% BaTiO₃ are useful for electrolytes in polymer lithium batteries. The high conductivity at lower temperature of the polymer electrolyte is quite attractive for practical battery applications. The high conductivity at a low temperature may be due to amorphous phase of the polymer at lower temperatures (see Fig. 3). Generally, the fraction of current transported by cations in polymer electrolytes is lower than that of anions [18]. The lithium ion transport number for PEO-LiN(CF₃SO₂)₂-LiPF₆-BaTiO₃ measured by combination of ac impedance and dc polarization measurements [19] was found to be around 0.1, which is comparable to that of PEO₁₀LiN(CF₃SO₂)₂-10 wt.% BaTiO₃ [15].

The mechanical property of the polymer film was measured with the help of a conventional tension tester at different temperatures. Typical results are shown in Table 2. The room temperature mechanical strength of the polymer electrolyte is comparable to that of cross-linked PEO-based polymer electrolytes [10].

The interfacial resistance between the electrode and the electrolyte are shown in Table 3, where the resistance was measured for the cell, Li(or cathode mixture)/PEO-LiX-10 wt.% BaTiO₃/Li (or cathode mixture), annealed at 80 °C for about 360 h. The cathode mixture consisted of LiNi_{0.8}Co_{0.2}O₂-polymer electrolyte-AB (70:15:15 weight ratio). The lithium interfacial resistance increased slightly upon addition of LiPF₆ to LiN(CF₃SO₂)₂ and LiN(C₂F₅SO₂)₂. Borghini et al. [20] have reported that the interfacial resistance between lithium and PEO-LiN(CF₃SO₂)₂-γ-LiAlO₂ was about 30 Ω cm² at 70 °C when stored at room temperature

Table 2
Electrical conductivity in [PEO_x-(LiN(CF₃SO₂)₂-yLiPF₆)]-10 wt.% BaTiO₃

LiPF ₆ (wt.%)	Temperature (°C)	Conductivity, O/Li ratio in PEO-LiX (S/cm)			Mechanical properties	
		10	15	20	100% elongation (MPa O/Li = 10)	Broken point (MPa O/Li = 10)
0	80			1.7×10^{-3}		
	25			7.9×10^{-6}		
5	80			6.7×10^{-4}		
	25			1.7×10^{-6}		
10	80	7.4×10^{-4}	8.5×10^{-4}	5.8×10^{-4}	0.11	0.21
	25	1.2×10^{-5}	2.7×10^{-6}	1.3×10^{-6}	3.5	3.9

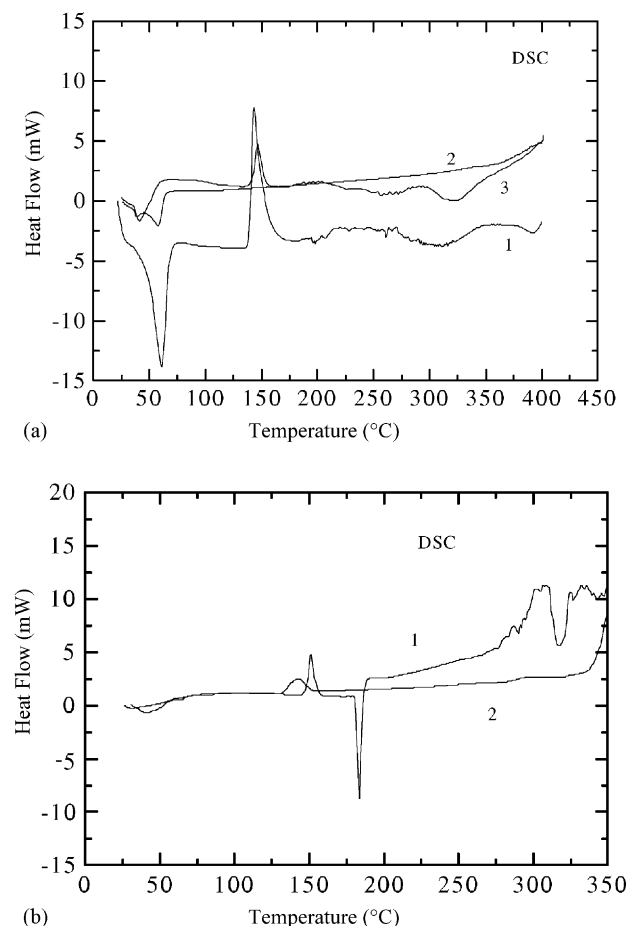


Fig. 3. DSC curves for the composite polymer electrolyte (a) and the mixture of composite polymer electrolyte and the electrode materials (b). (a) 1, PEO-LiPF₆-10% BaTiO₃; 2, PEO-LiN(CF₃SO₂)₂-10 wt.% BaTiO₃; 3, PEO-(LiN(CF₃SO₂)₂-10 wt.% LiPF₆)-10 wt.% BaTiO₃. (b) 1, mixture of Li metal and PEO-LiN(CF₃SO₂)₂; 2, mixture of LiNi_{0.8}Co_{0.2}O₂ and PEO-LiN(CF₃SO₂)₂.

for 2000 h. In addition, Appetecchi et al. [11] observed the lithium interfacial resistance of PEO₁₂LiCF₃SO₃-10 wt.% γ -LiAlO₂ to be 200 Ω cm² at 85 °C stored for 20 days at 85 °C. Our interfacial resistance results are comparable to previous results and acceptable for battery use.

LiPF₆ is a popular lithium salt in lithium-ion batteries. Although LiPF₆ containing carbonate-based electrolyte have good ionic conductivity and good electrochemical stability, the use of LiPF₆ in polymer electrolytes has a

distinct problem; LiPF₆ decomposes at temperatures as low as 100 °C, compared to 350 °C for LiN(CF₃SO₂)₂. Fig. 3 shows the DSC curves for PEO₁₂[LiN(CF₃SO₂)₂-10 wt.% LiPF₆]-BaTiO₃, a mixture of electrolyte and Li metal, and a mixture of electrolyte and LiNi_{0.8}Co_{0.2}O₂. The polymer electrolyte without LiPF₆ shows an endothermic peak around 60 °C, which corresponds to the melting point of PEO. An exothermic peak appears in the region of 150 °C in the sample with LiPF₆. We can assign the peak at 150 °C to the decomposition of LiPF₆. The reaction of polymer electrolyte and the electrode materials has also been examined also. The mixture of lithium metal and polymer electrolyte shows an endothermic peak at 180 °C and an exothermic peak in the range of 280 °C. The former peak corresponds to the melting of lithium metal and the latter the reaction of lithium metal and the polymer electrolyte. The high decomposition temperature at 150 °C of the lithium salt in the polymer electrolyte could be acceptable in electrolytes for the lithium polymer batteries. The decomposition product of LiPF₆ does not give rise to serious problem by further reaction with lithium metal and polymer electrolyte.

3.3. Charge-discharge characteristics of the Li/[PEO₁₀(LiN(CF₃SO₂)₂-10 wt.% LiPF₆)]-10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ cell

The layered phase LiNi_{1-x}Co_xO₂ is an attractive cathode material for rechargeable lithium batteries, because of the high specific capacity and low cost compared LiCoO₂ [21]. For this reason, it has been examined for the next generation of lithium-ion secondary batteries. LiNi_{0.8}Co_{0.2}O₂ as this level of doping of Co is thought to provide the best electrochemical properties [22]. The cyclic performance of the cell with a lithium metal anode and LiNi_{0.8}Co_{0.2}O₂ cathode in EC-DMC with LiPF₆ electrolyte at room temperature is shown in Fig. 4. The LiNi_{0.8}Co_{0.2}O₂ cathode shows a high initial capacity of 180 mAh/g and a capacity decrease with cycling to 160 mAh/g after 40 cycles at a cut-off voltage of 3.0–4.2 V. These results are comparable to those reported previously by Aragane et al. [22]. The capacity depends on the cut-off voltage. At a cut-off voltage of 2.5–3.9 V the initial capacity of 130 mAh/g decreases to 110 mAh/g after 55 cycles. We have examined the cathode materials in all solid polymer electrolyte cells. Lithium metal was used as the anode and the cathode consisted of

Table 3
Interfacial resistances of PEO-LiX-10 wt.% BaTiO₃ polymer electrolytes with lithium metal and the cathode composite at 80 °C

LiX	Li/electrolyte		Cathode/electrolyte	
	Period day	Resistance (Ω)	Period day	Resistance (Ω)
LiN(CF ₃ SO ₂) ₂	10	70	17	35
LiN(CF ₃ SO ₂) ₂ -10 wt.% LiPF ₆	11	50	15	70
LiN(C ₂ F ₅ SO ₂) ₂	17	65	17	30
LiN(C ₂ F ₅ SO ₂) ₂ -10 wt.% LiPF ₆	17	70	15	60

Cathode composite:LiNi_{0.8}Co_{0.2}O₂;electrolyte:acetylene black (65:20:15).

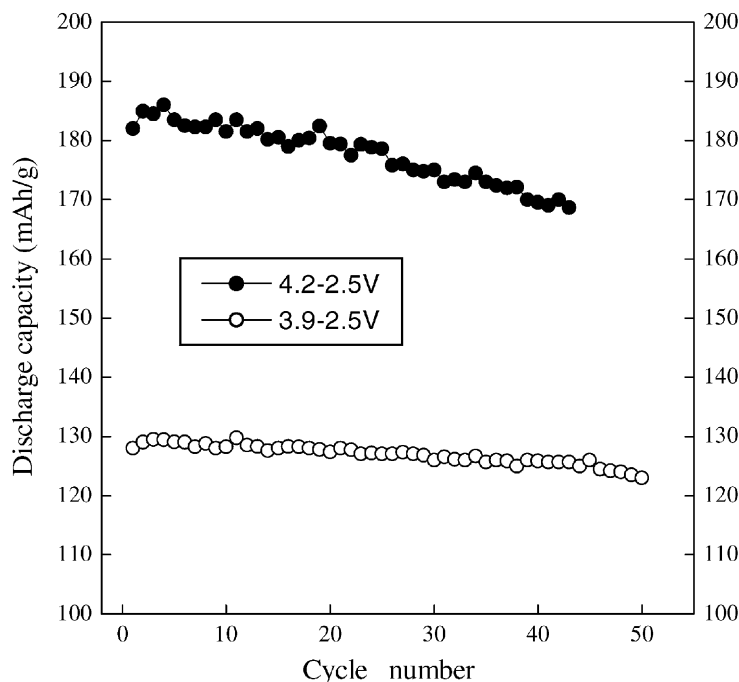


Fig. 4. The discharge capacity of Li/EC-DMC-1 M LiPF₆/LiNi_{0.8}Co_{0.2}O₂ at room temperature.

a mixture of LiNi_{0.8}Co_{0.2}O₂, polymer electrolyte, and AB (65:20:15 weight ratio). Fig. 5 shows a typical charge–discharge profile at a cut-off voltage of 2.5–4.2 V and at current density of 0.2 mA/cm² at 80 °C. The capacity corresponds to that of LiNi_{0.8}Co_{0.2}O₂, because the anode capacity was several times large than that of the cathode. The charge–discharge profiles shown in Fig. 6 are similar to those of the liquid electrolyte [23]. The capacity of the first several cycles at a cut-off voltage of 4.2–2.5 is around

150 mAh/g. These values are a little lower than those in liquid electrolyte systems. Some polymer electrolytes give rise to a significant interfacial resistance between the lithium metal anode and solid polymer electrolyte [11]. The polymer electrolyte proposed in this study exhibited a low interfacial resistance of 55 Ω cm² after annealing at 80 °C for 400 h as shown in Table 2. Therefore, the low capacity may be due to high electrode polarization at the polymer electrolyte and electrode. One important matter for the practical application

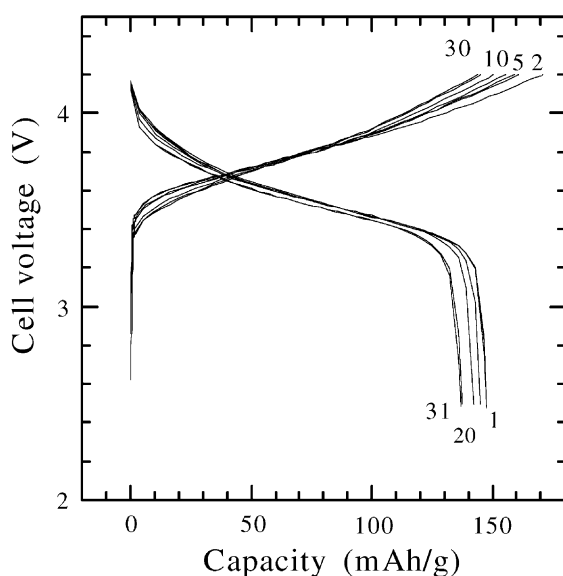


Fig. 5. Charge–discharge profiles for Li/[(PEO₁₀-(LiN(CF₃SO₂)₂-10 wt.% LiPF₆)]-10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ at 80 °C. Cut-off voltage, 4.2–2.5 V.

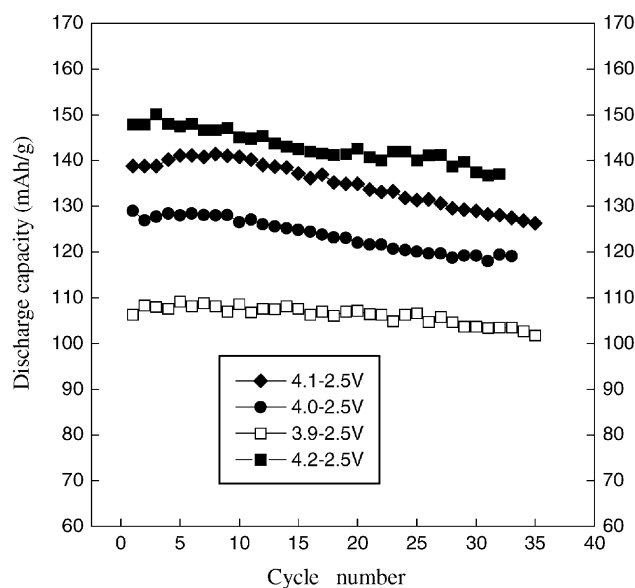


Fig. 6. The cut-off voltage dependence of cycle performance for Li/[PEO₁₀-(LiN(CF₃SO₂)₂-10 wt.% LiPF₆)]-10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ at 80 °C.

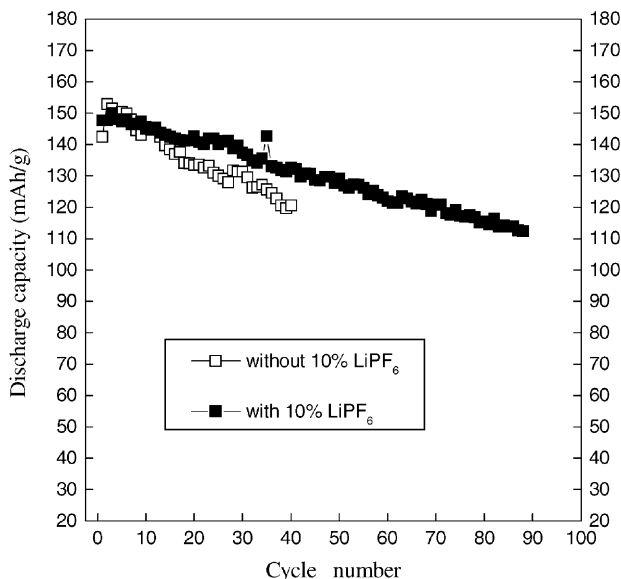


Fig. 7. The cycle performance of Li/[PEO₁₀–(LiN(CF₃SO₂)₂–*x* wt.% LiPF₆)]–10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ at 80 °C. Cut-off voltage, 4.2–2.5 V.

of all solid polymer lithium batteries is good durability upon charge–discharge cycling at operation temperatures. Very few papers have reported the cyclic performance for all solid polymer electrolyte cells. All these cells showed capacity fading upon cycling [6,13,24]. The capacity fading can be ascribed to irreversible structural change of the cathode, deformation and contact losses in composite electrodes, as well as to polymer decomposition [6,25]. In Fig. 6, the cathode capacity changes upon cycling are plotted as a function of the cut-off voltage, where the polymer electrolyte contains the mixed lithium salt of 90 wt.% LiN(CF₃SO₂)₂–10 wt.% LiPF₆. To compare the effect of the addition of LiPF₆, similar cyclic performances of cells with polymer electrolytes without LiPF₆ are shown in Fig. 7. In Table 4, the fading rate of the cathode capacity upon cycling at 80 °C are summarized for the different types of polymer electrolytes. The fading rate depends on the polymer electrolyte. The addition of LiPF₆ improves cycling performance. The lowest fading rate is observed at 10 wt.% LiPF₆. In addition, low O/Li ratio (high content of LiX in PEO) shows good cycling performance. Similar cyclic performance between the cells with the polymer electrolyte

Table 4

Average cathode capacity fade over the first 30 cycles for Li/[PEO–LiN(CF₃SO₂)₂–LiPF₆]]–10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ at 80 °C

O/Li in PEO–LiX	LiPF ₆ wt.% in LiN(CF ₃ SO ₂) ₂ (%)				
	0	5	10	15	22
20	0.44	0.56	0.59	0.60	0.60
15			0.30		
10		0.30	0.20	0.37	

Cut-off voltage, 3.9–2.5 V.

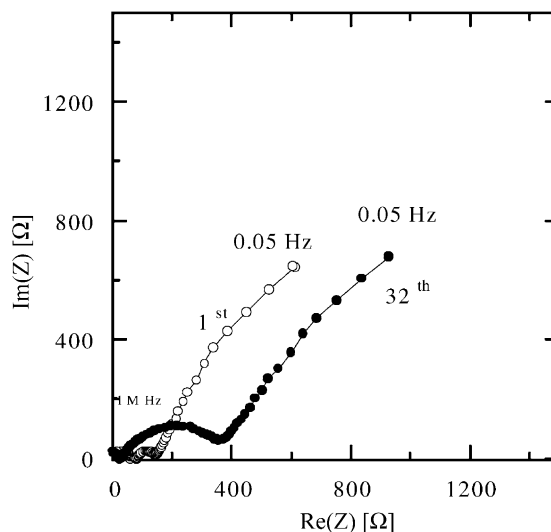


Fig. 8. Cole–Cole plots for Li/[PEO₁₀–(LiN(CF₃SO₂)₂–10 wt.% LiPF₆)]–10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ at 3.34 V vs. Li/Li⁺ before cycling and after cycling at 80 °C.

and the liquid electrolyte (see Figs. 4 and 6) shows that the capacity fading mechanism may be explained by irreversible structural change of LiNi_{0.8}Co_{0.2}O₂, but not by polymer decomposition. For low content of lithium salt, where viscosity is lower than that at high salt content, the contact loss in the composite cathode upon cycling may induce the capacity loss. In Fig. 8, the impedance response of the Li/PEO₁₀[LiN(CF₃SO₂)₂–10 wt.% LiPF₆]]–10 wt.% BaTiO₃/LiNi_{0.8}Co_{0.2}O₂ cell is shown before cycling and after 32 cycles, for the case where the cell was charged to 4.2 V and discharged to 2.5 V. It was found that the interfacial resistance increases upon cycling. The increase in interfacial resistance upon cycling may be due to the mixed effect of the contact loss in the cathode mixture and increasing of interfacial resistance between the electrolyte and the electrode as well as between the cathode and aluminum current collector. It should be emphasized that the capacity fade upon cycling for the cell with a solid polymer electrolyte is comparable to that with liquid electrolytes. No significant capacity fade is observed upon cycling when charged up to 4.2 V versus Li/Li⁺ at 80 °C.

4. Conclusion

The 4 V class lithium polymer secondary batteries with a relatively low capacity fade by cycling have been developed using the composite polymer electrolyte [PEO–LiN(CF₃SO₂)₂–LiPF₆]]–10 wt.% BaTiO₃ and the LiNi_{0.8}Co_{0.2}O₂. The addition of about 10 wt.% LiPF₆ to LiN(CF₃SO₂)₂ as the salt in PEO is effective to enhance the corrosion potential of aluminum and improves cycling performance. No significant capacity fade upon cycling is observed upon charging up to 4.2 V at 80 °C. It can be concluded that

[PEO–LiN(CF₃SO₂)₂–LiPF₆]-10 wt.% BaTiO₃ is one of the best candidates as a polymer electrolyte in 4 V class lithium polymer batteries.

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