



New gel-type polyolefin electrolyte film for rechargeable lithium batteries

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ABSTRACT

A random poly(ethylene-co-acrylic acid) (PE-A) with an acrylic acid (AA) content of 5.0–20 mol% was functionalized by esterifying acrylic acid group with poly(ethylene glycol) monomethyl ether. Polyethylene oxide functional groups such as a pendant were introduced into the polyethylene backbone chain. The resulting polymer (PEGM-g-EAA) can be easily formed to a thin sheet and possesses the adhesion property such as gluing. Its thin film could absorb and hold a large quantity of the electrolyte solutions employed for the lithium batteries. The ionic conductivity of the PEGM-g-EAA gel electrolyte obtained with the starting PE-A with acrylic acid content of 9.0 mol% was a value of around $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C. The ionic conductivity results obtained for the network type gel, which was entangled with the present PE-A-based polymer, were $1.1 \times 10^{-3} \text{ S cm}^{-1}$ and $5.5 \times 10^{-3} \text{ S cm}^{-1}$ at 0 °C and 80 °C, respectively. The characteristics of good thermostability, transparency and good adhesion to the electrodes have also been demonstrated. As an example, the test cell consisted of the proposed polyolefin gel electrolyte, a LiCoO₂ cathode and a lithium anode showed excellent charge/discharge characteristics.

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1. Introduction

Polymer electrolytes have been actively studied in an attempt to develop safer and thinner rechargeable lithium batteries. Solid polymer electrolytes (SPEs) proposed by Wright [1] have been extensively studied by Armand and Duclot [2]. Although much research effort has been devoted to the development of SPEs, conductivity of SPE such as a poly(ethylene oxide) (PEO) [1] remains too low for practical batteries operating at room temperature. In order to overcome the disadvantage for practical usage, in the last two decades, so-called polymer gel electrolytes (PGEs) that are capable of holding stably a considerable amount of electrolyte solution within polymer matrices have attracted both basic research and industry attentions, as more promising materials for the practi-

cal use. The various PGEs based on polyethylene oxide (PEO) [2], polyacrylonitrile (PAN) [3–7], poly(methacrylate) (PMA) [8–10] and polyvinylidene fluoride (PVdF) [11] with ionic conductivities of $10^{-3} \text{ S cm}^{-1}$ at room temperature have been initially prepared and applied for lithium batteries. However, their thermostabilities of traditional PGEs were not sufficient for the practical usage in a wide temperature range. Frequently, it was found that poor interaction of a polymer matrix and solvent cannot prevent completely the solvent leakage. One of the procedures to advance their properties and functions is an introduction of suitable functional groups to side chains on a backbone polymer.

A new challenge in the development of polymers used for PGEs is the preparation of sticky film such as post-it®. Such polymer adheres easily to the electrode, separator and package, so that the physical adhesion at the interface between the polymer electrolyte and electrode expect to be improved.

In this work, we introduce a sticky self-standing film of an ethyleneoxide side chain modified polyethylene-based PGE applied for lithium battery. As well known, polyolefin material is used as a chief component of a separator in lithium batteries, but it is not so far regarded as a PGE material, because a polyolefin does not absorb and hold organic solvents used for lithium batteries. Even if polyethylene contains a functional group of acrylic acid (AA), this polymer does not possess the property of gelation. Therefore, by using the functional group of acrylic acid on a poly(ethylene-co-acrylic acid) (PE-A), we try to alter the PE-A to a polyolefin-based

Abbreviations: AA, acrylic acid; PE-A, poly(ethylene-co-acrylic acid); PEGM, poly(ethyleneglycol)monomethyl ethers; PEGM-g-EAA, graft copolymer of PE-A esterified with PEGM; PPG-MEHE, poly(propyleneglycol)mono-2-ethylhexyl ether; PEG-b-PPG-MEHE, poly(ethyleneglycol)-b-(polypropyleneglycol)mono-2-ethylhexyl ether; PMA, polymethacrylate; PEO, poly(ethyleneoxide); PVdF, polyvinylidene fluoride; PVdF-HFP, poly(vinylidene fluoride)-polyhexafluoropropylene copolymer; PC, propylenecarbonate; EC, ethylenecarbonate; DMC, dimethylcarbonate; PGE, polymer gel electrolyte; SPE, solid polymer electrolyte; SEI, solid electrolyte interface.

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PGE in this study. The acrylic acid group on the PE-A is esterified with a poly(ethyleneglycol)monomethyl ether (PEGM) and thus oligo(ethyleneoxide) side chains of the $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ type is introduced on the polyethylene, being like pendants dangling from the polyethylene backbone. The synthesis method for such a grafted copolymer has been reported by Hallden and Wesslen in order to improve the adhesion properties such as painting, printing and gluing [12]. We are interested in whether the resulting graft copolymers (PEGM-g-EAA) can be expected to form a self-standing film which absorbs a large quantity of electrolyte solutions, since an ethylene oxide functional group grafted on a polyethylene backbone takes a behavior of the polar one. The PE-A with acrylic acid group of the content of around 10 mol% will be selected as the best reactant base polymer for the synthesis at the present research. Here, we report that new non-halogen polyolefin films make it possible to provide as a PGE for a Li secondary cell.

Furthermore, to improve the mechanical and thermal properties of the present PGE we introduce a polymer network having probably a three-dimensional structure that includes the PE-A within the crosslinked polymer network matrix. The resulting PGE possesses not only a high thermostability at 80 °C but also a high flexibility, adhesion and transparency properties. Therefore, the present polyolefine-based material is very promising one to be used as a PGE in battery, electrochemical capacitor, dye-sensitized solar cell and electrochromic device.

2. Synthesis

2.1. Materials

PE-A was a random polyethylene-poly(acrylic acid) copolymer with an acrylic acid content of 9.0 mol%, produced by Du Pont–Mitsui Polychemicals Co., Ltd. Its number-average molecular weight (M_n) was estimated to be 10,500, unless otherwise stated, using GPC with *o*-dichlorobenzene at 135 °C according to a standard procedure with use of polystyrene. (However, the PE-A having an acrylic acid content of 10.0 mol% and the weight-average molecular weight (M_w) of 50,000 was used in Tables 3 and 4.) PEGM with average molecular weight 550 and 750 were used for esterifying the acrylic acid group on polyethylene backbone. *p*-Toluene sulfonic acid monohydrate, toluene and methanol were the reagents of Kanto Chemical Co. Poly(vinylidene fluoride)-polyhexafluoropropylene copolymer (PVDF-HFP) used in the plastic Li cells was purchased from Aldrich Co.

Propylenecarbonate (PC), ethylenecarbonate (EC) and dimethylcarbonate (DMC) were all the lithium-battery-grade and obtained from Tomiyama Pure Chemical Inc., Japan. Lithium-battery-grade LiBF_4 and LiPF_6 were obtained from Hashimoto Kasei Inc., Japan. Lithium metal foils of 300 μm thickness were obtained from Kyokuto Kinzoku Inc., Japan. All materials used for electrochemical measurements were stored in a vacuum dry box filled with argon (99.99%) in which the dew point was ca. -60 °C and the oxygen concentration was <5 ppm. All the reagents were used without further purification.

2.2. Preparation of PE-A esterified with PEGM (PEGM-g-EAA)

The preparation of PEGM-g-EAA copolymer is depicted in Fig. 1. Esterification of PE-A with PEGM was performed according to the method by Hallden and Wesslen [12]. The basic operation of the esterification reaction is described below. First, an acid catalyst of *p*-toluenesulfonic acid is added to the PEGM of a polyalkylene oxide having a hydroxyl group at one terminal thereof under the heated and stirred conditions, followed by the addition of PE-A to conduct

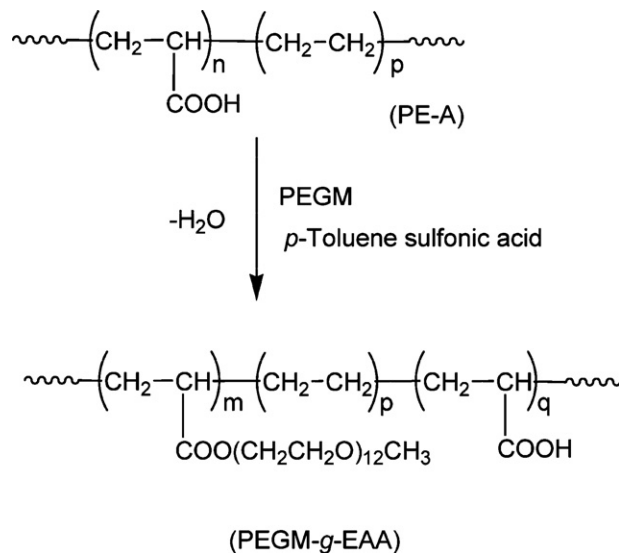


Fig. 1. Chemical structures of the reactants and that of the resulting polymer (PEGM-g-EAA).

the reaction for several tens of hours. After conducting the reaction, the reaction product is washed with water and by being immersed in methanol or ethanol to remove unreacted polyalkylene oxide and catalyst, and is dried in vacuum. In the present experimental the compounds PE-A and PEGM are mixed with from 0.8 to 2.0 at a molar ratio (PEGM/PE-A) formula,

$$\frac{\text{PEGM}_{\text{HYD}}}{\text{PE-A}_{\text{CAR}}}$$

wherein PEGM_{HYD} is a molar quantity of hydroxyl groups of the PEGM and PE-A_{CAR} is a molar quantity of carboxylic (or acrylic) acid groups of the PE-A (here, the carboxylic acid group includes not only a carboxyl group but also a carboxylic ester group and a carboxylic anhydride group being calculated as two carboxyl groups).

As an example, the polymer no. 1 in Table 1 is synthesized as follows: PE-A (100 g, acrylic acid content, 0.28 mol) was slowly added to a stirring solution of PEGM (M_n 550, 183 g) in toluene (100 g) containing *p*-toluene sulfonic acid monohydrate (1.50 g) as a catalyst and the solution was refluxed for 24 h at 140 °C. In order to purify the resulting PEGM-g-EAA, the reaction mixture was slowly poured into distilled water (1500 g) to coagulate PEGM-g-EAA that was subsequently separated from the mixture by centrifugation. The separated polymer was dispersed in distilled water at room temperature under stirring for 2 h and separated by centrifugation. The polymer was further put into methanol, stirred for 30 min and separated. This procedure of washing with methanol was repeated three times. The obtained PEGM-g-EAA was spread over a stainless tray and dried in vacuum at 50 °C for 20 h. The product was 172 g (68% yield to the theoretical amount based on PE-A).

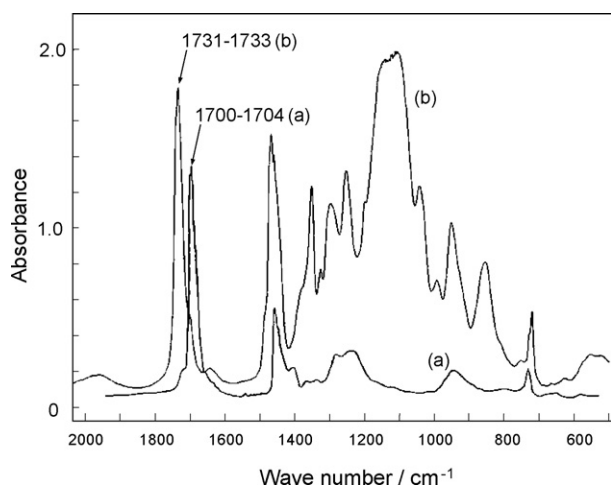
Successful introduction of PEO groups to the PE-A was confirmed by FT-IR spectroscopy. FT-IR instrument of a PerkinElmer Spectrum 2000 was used for characterization of the synthesized polymers. For IR analysis a film sample with thickness of ca. 50 μm was prepared by hot-press molding 0.5 g polymer sample sandwiched between two Teflon sheets. The obtained PEGM-g-EAA only slightly showed an absorption peak of CO in the unesterified carboxylic acids at 1700–1704 cm^{-1} , while the peak of CO in the carboxylic esters were observed at 1731–1733 cm^{-1} as shown in Fig. 2. Unesterified acrylic acid content in PEGM-g-EAA was estimated to be 0.00–0.023 mol% of the initial acrylic acid content by potentiometric titration analysis.

Table 1

Components for the polymer materials synthesized with the different molar ratio of poly(ethyleneglycol) or poly(propyleneglycol) derivative vs. PE-A

Polymer no.	Ethylene (<i>P</i>)	Non-reacted acrylic acid (<i>q</i>)	PEGM- <i>g</i> -EAA		PEG- <i>b</i> -PPG-MEHE		PEGM _{HYD} ^c /PE-A _{CAR}	Reaction time (h)
			(m)	(Mn ^a)	(m)	(Mn ^b)		
1	31.5	0	68.5	550	–	–	1.18	24
2	32.5	0.4	67.1	550	–	–	1	16
3	36.8	2.2	61	550	–	–	0.8	16
4	32.3	0	67.7	750	–	–	1.18	24
5 ^d	23.9	0	–	–	76.1	840	1.18	30

Reaction temperature used for synthesis of the polymers nos. 1–5 is kept at 140 °C.

^a Average molecular weight of PEGM is 550 or 750.^b Average molecular weight of PPG-MEHE is 840.^c Expressed with the molar ratio. PEGM_{HYD}: a molar quantity of hydroxyl groups of the PEGM, PE-A_{CAR}: a molar quantity of acrylic acid groups of the PE-A.^d Grafted with poly(ethyleneglycol) (PEG)-block-poly(propyleneglycol) (PPG) mono-2-ethylhexyl ether (MEHE).**Fig. 2.** IR Spectrum of the compounds on (a) a random poly(ethylene-co-acrylic acid) (PE-A) with the acrylic acid content of 9.0 mol% and (b) the resulting polyethylene copolymer (PEGM-*g*-EAA) esterified acrylic acid group of polymer EAA with poly(ethylene glycol) monomethyl ether (MPEG) (Mn = 550).

Differential scanning calorimetry (DSC) analysis was carried out under nitrogen gas using a DSC2910TA instrument at a 10 °C min⁻¹ increasing temperature rate. Average molecular weight analysis of PE-A esterified with PEGM was run using a GPC-224 (WATERS) in tetrahydrofuran at 23 °C. DSC analysis as shown in Fig. 3 demonstrated that PEGM-*g*-EAA does not melt at 76 °C, being a characteristic to polyethylene crystalline. The PEGM-*g*-EAA polymer of which structure is shown in Fig. 1 becomes, itself, the transparent, homogeneous and self-standing film containing an electrolyte. The number of *q* in

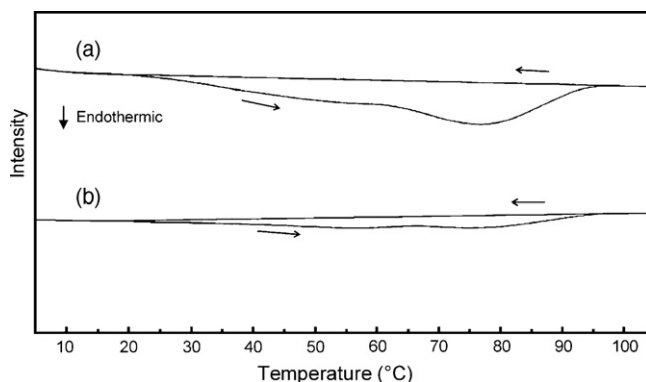
**Fig. 3.** DSC Thermograms for the polymers of (a) PE-A and (b) PEGM-*g*-EAA (no. 3 in Table 1).

Fig. 1 expresses a molar content of the unesterified acrylic acid groups.

2.3. PEGM-*g*-EAA polymer gel electrolytes

PEGM-*g*-EAA gel electrolytes were prepared as follows: PEGM-*g*-EAA polymer was melted alone or with a nonvolatile organic solvent, and was molded into a self-standing film or sheet by casting method or T-die method. The polymer electrolyte containing a Li salt was prepared by impregnating the self-standing film with organic solvent containing 1.0 M (mol dm⁻³) of Li salt. The impregnation was performed by immersing the present synthesized polymer film in an organic solvent containing the Li salt during suitable time at 20 °C, unless otherwise mentioned in the test. Solvent content was in a range of 30–90% by weight unless stated otherwise. Li salts such as LiBF₄, LiPF₆, or LiClO₄ were used. The composition of the gel electrolyte will be given in the following text as PEGM-*g*-EAA/(organic solvent-Li salt) (*x*/*y*), where *x*/*y* in the parentheses being the weight ratio of the copolymer to the electrolyte solution. Li salt concentration was kept constant at 1.0 M throughout the experiments.

Mechanical strength of PEGM-*g*-EAA gel electrolyte film was measured by using a Perkin-Elmer DMA 7. A gel sample (ca. 5 mm × 5 mm × 4 mm (height)) was placed on a plate (diameter: 18.5 mm) [6] and a static force of 50 mN was applied vertically to the gel with a probe (diameter: 10 mm) by changing the temperature in the range between –50 °C and 120 °C at a rate of 10 °C min⁻¹.

2.4. Preparation of polymer network

The improved PGE having a high ionic conductivity and a high heat stability is prepared by constructing a gel structure which is so-called as semi-IPN (semi-Interpenetrating Polymer Network) by interlacing the present described PEGM-*g*-EAA polymer with a network having a three-dimensional structure polymerized with crosslinkable monomers, as described below.

At first we prepare the reactant solution which is a reaction mixture comprising a non-aqueous solvent containing a Li electrolyte, in which are dissolved the PEGM-*g*-EAA, a polymerization initiator and a crosslink monomer. The reaction mixture was poured into a silicone rubber frame as a spacer having a thickness of 300 μm, which is placed on a TEFLON sheet having a thickness of about 3 mm. An excess quantity of the solution was eliminated by using a hand coater (a manual coating device). Then, an ultraviolet ray having a peak at 360 nm was irradiated from above onto the reaction mixture having a thickness of 300 μm coated on the TEFLON sheet for 15 min, thereby performing the polymerization of the crosslinkable monomers. During this period, the UV ray intensity was measured with a UV ray illuminometer (Model UV-MO2-35 of Oak Seisakusho, Japan) to find that it was 10 mW cm⁻². In this

manner, the polymer network of semi-IPN for the film-shaped PGE was prepared.

2.5. Visual evaluation for liquefaction and flexibility of gel film

The liquefaction temperature of the gel electrolyte was measured as follows. A gel film having a square shape of about $2.5\text{ cm} \times 2.5\text{ cm}$ and a thickness of $300\text{ }\mu\text{m}$ was put in a glass vessel filled with dry argon and a lid was placed thereon. Then, it was heated in a hot-air circulation type thermostatic chamber whose temperature was set to $80\text{ }^\circ\text{C}$. After one hour, the gel film was taken out, and the change in the shape was observed. The level of the thermostability was evaluated by the following three stages:

GOOD: No change in the shape of gel film is observed before and after heating. (Note that slight shrinkage of the film due to the heating is not counted in the evaluation.)

FAIR: Part of the gel film is liquefied or slight phase separation into gel and solution due to the heating.

NO GOOD: About a half or more of the gel film is liquefied or significant phase separation into gel and solution due to the heating.

The flexibility of the gel electrolyte was measured as follows. A gel film having a thickness of $300\text{ }\mu\text{m}$ was placed on an aluminum foil having a thickness of $30\text{ }\mu\text{m}$, bent together with the aluminum foil to an angle of 90° , and then straightened back. The property was evaluated by the following three stages:

GOOD: No crack is produced and the crease is not substantially arisen.

FAIR: No crack is produced but the crease is clearly marked.

NO GOOD: A crack is produced.

3. Electrochemical measurement

3.1. Ionic conductivity

A TEFLON spacer having a square shape of $3.5\text{ cm} \times 3.5\text{ cm}$ with a thickness of $300\text{ }\mu\text{m}$ (and having a hole of $2\text{ cm} \times 2\text{ cm}$ made at its center) was placed on a lithium metal foil having a square shape of $3\text{ cm} \times 3\text{ cm}$ with a thickness of $100\text{ }\mu\text{m}$. Then, the gel film having a described thickness of $80\text{ }\mu\text{m}$, $100\text{ }\mu\text{m}$ or $300\text{ }\mu\text{m}$ was set in the center hole, and another metallic lithium foil similar to the above was laid upon it. On both sides, stainless (SUS304) foils having a thickness of $100\text{ }\mu\text{m}$ were, respectively attached as current collectors. On both sides of such the configuration cell, glass plates having a thickness of 2 mm were attached and they were fixed together with clips. Thus, a cell for the gel evaluation was assembled, and lead lines were connected thereto to measure its electrochemical properties. The assembly of the cell for the gel properties was carried out in a glove box having an argon atmosphere.

Ionic conductivity of PEGM-g-EAA gel electrolytes was measured by an ac method in a temperature range between $-20\text{ }^\circ\text{C}$ and $85\text{ }^\circ\text{C}$. Ionic transport number of Li^+ ion was evaluated by ITIC (isothermal transient ionic current) methods [13].

Electrochemical measurements were carried out with the test cells using a potentiostat/galvanostat (Model 273, Princeton Applied Research). The test cells with a PEGM-g-EAA containing LiBF_4 or LiPF_6 were subjected to potential cycling over 50 cycles in a potential range between $+0.50\text{ V}$ and -0.50 V vs. Li/Li^+ at a scan rate of 10 mV s^{-1} at a selected temperature. Ac impedance measurements were conducted on the cells at ac 5 mV , with frequency from 65 kHz to 0.1 Hz by using a Solartron 1250 frequency response analyzer before and after the CV-polarization. All these electro-

chemical experiments were conducted in the vacuum dry box at $25\text{ }^\circ\text{C}$, if otherwise described.

3.2. Effect on the dendrite formation

Polymer gel films having the same composition as the polymers of sample no. 6 in Table 2 and no. 8 in Table 4 were prepared to see the effect on the formation of dendrite. The polymer gel film was sandwiched between two lithium metal foils each having a thickness of $100\text{ }\mu\text{m}$ and a square shape of $3\text{ cm} \times 3\text{ cm}$. Glass plates having a thickness of 2 mm were placed on both surfaces of the sandwiched film, and fixed with clips, fabricating a cell for evaluation. Configuration of the test cell is similar to that of Kahanda and Tomkiewicz [14]. The geometrical area of the lithium electrode was 5 mm^2 ($1\text{ mm} \times 5\text{ mm}$). The thickness of the electrolyte (the distance between the two lithium electrodes) was 3 mm . All procedures were performed in the vacuum dry box.

On the cell, a constant current electrolysis was carried out at 1 or 3 mA cm^{-2} for an hour with a Solartron SI1287. All these electrochemical experiments were conducted in the vacuum dry box at $25\text{ }^\circ\text{C}$. After the electrolysis, the lithium foil/electrolyte interface at which lithium had been deposited was observed by using an optical microscope with a CCD camera in order to examine whether a prominent dendrite in the lithium foil interface is generated or not.

3.3. Charge/discharge cycle performance

A test cell was fabricated, using the same polymer gel composition and the preparation method as previously [6], with lithium cobaltate (LiCoO_2) coated on an aluminum current collector used for cathode electrode and with lithium metal used for an anode electrode. The polymer gel film of $100\text{ }\mu\text{m}$ was interposed between the cathode electrode and anode electrode. Nickel foils at the back-sides of the aluminum current collector for the cathode and of lithium metal anode were used to make electrical connection to a charge/discharge property measuring apparatus of BS2500 of Keisoku Giken.

The cell with a construction of $\text{Li}/\text{PGE}/\text{LiCoO}_2$ was preliminary charged and discharged in a range of $4.05\text{--}2.5\text{ V}$ at $20\text{ }^\circ\text{C}$.

4. Results and discussion

4.1. Synthesis and characterization of PEGM-g-EAA

A novel polyolefin-type gel electrolyte synthesized in the present paper was based on a graft copolymer PEGM-g-EAA with a polyethylene backbone grafted with polyethylene oxide. By changing the reactants, the amount of reagents and the synthesized conditions such as temperature and reaction time, polymer materials with various compositions and a variety of properties were obtained. However, PEGM-g-EAA synthesized from PE-A with an acrylic acid content of less than $5.0\text{ mol}\%$ and more than $20\text{ mol}\%$ did not give PGE's at room temperature. Therefore, the PE-A copolymer with an acrylic acid content of around $9.0\text{ mol}\%$ was selected as the best starting material for PGE because of the reasons described below. When the content of an acrylic acid is less than $5\text{ mol}\%$ in the PE-A, the melting temperature of the PE-A resin raises and furthermore the viscosity of the resulting liquid increases. Therefore, for this polymer the temperature of the esterification reaction with the PEGM must be elevated, so that difficulty in the reproducibility of the product rises. When the content of an acrylic acid more than $20\text{ mol}\%$ of PE-A is used for the esterification reaction with the PEGM, the resulting product is liquefied at $25\text{ }^\circ\text{C}$ and did not become a self-standing film. This is because the molar ratio of PEGM on PE-A increases.

Table 2

Ionic conductivities (at 20 °C) for the polymer gel electrolyte (PGE) of the samples numbered in Table 1

Sample no.	Electrolyte solution	Ionic conductivity ($S\text{ cm}^{-1}$)	Polymer no. (shown in Table 1)
1	1.0 M LiBF_4 , PC/EC (1:1)	1.7×10^{-3}	1
2	1.0 M UBF_4 , PC/EC (1:1)	1.5×10^{-3}	2
3	1.0 M LiBF_4 , PC/EC (1:1)	1.4×10^{-3}	3
4	1.0 M LiBF_4 , PC/EC (1:1)	1.5×10^{-3}	4
5	1.0 M LiBF_4 , PC/EC (1:1)	7.8×10^{-4}	5
6	1.0 M LiBF_4 , EC/DMC (1:2)	1.4×10^{-3}	1
7	1.0 M LiPF_6 , PC/EC (1:1)	1.5×10^{-3}	1
8	1.0 M LiBF_4 , PC/EC (1:1)	1.5×10^{-3}	PVdF-HFP ^a

All PGEs with 80 μm thickness obtained after being immersed in the solution given in each numbered column during 5 h, respectively.

^a Poly(vinylidene fluoride)-polyhexafluoro-propylene copolymer.

Table 1 shows that the contents of unreacted acrylic acid of PEGM-g-EAA ($M_n = 10,500$) gel electrolytes depends upon the ratio of $\text{PEGM}_{\text{HYD}}/\text{PEA-A}_{\text{CAR}}$. The esterification goes essentially to completion at the molar ratio above 1.18. The PGE's prepared from the polymers containing more than 3.0 wt% unreacted acrylic acid changed their viscosity from low to very high, finally solid-like during one week or one month, even if the gel-electrolyte was stocked in a dry argon atmosphere at a dew point below -60°C . This increase in the viscosity is probably induced by in the slow side-reactions of non-reacted acrylic acid with impurities left in the resulting polymer.

The copolymers in Table 1 become transparent and rubber-like viscous gel electrolyte. The changes of molecular weight of PEGM from 550 to 750 for PEGM-g-EAA and another pendant material of PEG-b-PPG-MEHE from PEGM to PPG-MEHE were also performed. However, the polymers of nos. 4 and 5 summarized in Table 1 showed the elasticity and the adhesion property to glass substrates.

4.2. Absorption of electrolyte solution

In order to examine the absorption ability of the PGE, the present synthesized polymers were reformed in a state of the thin film as described below. The polymer materials shown in Table 1 were compression-molded to film in a heated hydraulic press between Teflon sheets. A 2.0 g of polymer was pressed with stepwise-addition of suitable pressure (2.6 MPa) for 5 min at the temperature of 80°C . The thickness of the film is $80 \pm 10\ \mu\text{m}$. The film was immersed in a test electrolyte solution of 1.0 M LiBF_4 salt at the temperature of 25°C or 80°C for 24 h. The weight of the polymer gel consisted of polymer matrices and absorbed electrolyte solution was measured before and after immersion. Organic solvents having the property of low viscosity or high dielectric constant which is suitable for an electrolyte solution were selected as the absorption test for the film. In the case of the electrolyte solution of diethylcarbonate (DEC) and *N*-methylpyrrolidone, the weight ratio of the electrolyte solution for the film material is almost 1 to 1. However, the ratio was two to one in the case of DMC and γ -butyrolactone. Highest ratio of three to one was observed in the case of the mixtures of 1:1 weight ratios of PC and EC and of EC and DMC. Tendencies similar to for sample no. 1 were observed for the adsorption behavior of organic solvents into the copolymers of sample nos. 2–5 in Table 1. It was found that organic solvents having the low viscosity were favorable for the absorption into the present film. As shown in Fig. 4, the immersion time-dependences of weight gain for the 80 μm polymer film no. 1 in Table 1 in the electrolytes of PC/EC (1:1 weight ratio) and EC/DMC (1:2 weight ratio) containing 1.0 M LiBF_4 were examined by changing the immersed solution temperature at 20°C and 80°C . Absorption of the PGE of sample no. 1 in Table 1 was attained to almost saturation after 5 h at 20°C and the contents of the electrolytes for overall weight of the PGE in PC/EC and EC/DMC are 61.3% and 72.4% by weight, respectively.

When the immersed solution of 80°C was used for the evaluation of absorption, gain of the electrolyte into the film was attained to saturation after around 3 h. The contents of electrolytes in the PC/EC and EC/DMC solutions were 83.5% and 88.6% by weight, respectively. It was found that five to ten times weight of an electrolyte solution per the polymer, which is used for the commercial available Li ion battery, can be incorporated and hold into the polymer materials described here. In this case, the 80 μm thickness film acquired the thickness of 160 μm , after being impregnated with the electrolyte, which was an increase of 2 times. The solution inserted within the film at a high temperature of 80°C was held without leakage, even when the temperature changes back from 80°C to 20°C . The degree of absorption property of the resulting film is similar to that of PVdF-HFP.

4.3. Ionic conductivity

The 80 μm thickness films described in Table 1 were immersed in a mixture solution of PC/EC (1:1 weight ratio) containing 1.0 M of LiBF_4 for 5 h. By using the resulting film of PGE, the cell measuring the ionic conductivity and the lithium ion transport number (t_{Li^+}) of the PGE was constructed. The PGE was inserted between the two pieces of lithium metal foils. As shown in Table 2, these PGEs except for the sample no. 5 exhibited ionic conductivities around $1 \times 10^{-3}\text{ S cm}^{-1}$. The lithium ion transport number was around 0.2 for all of the polymers in Table 1, which have been generally reported for other polymer electrolytes. For the PGE obtained by impregnating a PVdF-HFP manufactured by Aldrich Co. with

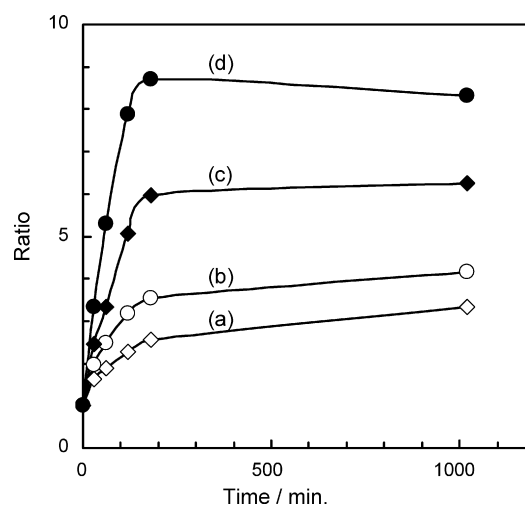


Fig. 4. Absorption properties of the polymer film (for the sample no. 1 in Table 1) in the 1.0 M LiBF_4 solutions of (a) PC/EC (1/1) and (b) EC/DMC (1/2) at 20°C , (c) PC/EC (1/1) and (d) EC/DMC (1/2) at 80°C . Ratio: weight ratio of electrolyte (solvent and salt)/polymer.

a mixture solution of PC/EC, the ionic conductivity and lithium ion transport number at room temperature were also measured, compared with the present PGEs. As seen from the results summarized in Table 2, it was demonstrated that the polymer materials introduced here possessed the properties comparable to those of the PVdF-HFP electrolyte. All of these PGEs except for polymer no. 5 described in Table 1 exhibited ionic conductivities ca. $1 \times 10^{-3} \text{ S cm}^{-1}$ at temperatures above 10°C . Therefore these PGEs demonstrated that favorable ionic conductivities were obtained even at low temperatures.

Fig. 5 shows the temperature dependency of conductivities for the PGEs of polymer sample nos. 1–3 in Table 2. The Arrhenius plots were performed in the temperature range of 253–353 K. All of them, except for the points of 253 and 263 K, showed the linear variation of $\log \sigma$ vs. $1/T$ plots, meaning that ionic conduction in polymer is the Arrhenius-type thermally activated process and there is no phase transition in the polymer matrix or domain. Their activation energies obtained with the PGEs of polymer sample nos. 1–3 are $17.1 \pm 0.1 \text{ kJ mol}^{-1}$, which are similar to one obtained in the solution of the same electrolyte [15]. Here, the same amount of electrolyte (73 wt%) was impregnated in three polymer samples.

When the points of 253 K and 263 K are added to the plots in Fig. 5, the curvature in the Arrhenius plots is observed in the range of the low temperature. The temperature dependence will be described by the Vogel–Tamman–Fulcher (VTF) equation [16], in which one of the fitting parameters is related to the glass transition temperature. However, a more detailed study needs to fit the conductivity data to a VTF equation and determine the activation energy and critical temperatures from the fit.

One can notice that the values of the ionic conductivity of all PGEs were $\sim 10^{-3} \text{ S cm}^{-1}$ range at the room temperature and about one order smaller than that of the solution. The difference seems to stem mainly from that the value of diffusion coefficient for the gel having the high viscosity reveals in general lower than one for in the solution. For the PGE of PEGM-g-EAA synthesized at the present paper, it was found that the conductivity strongly depends on the content of the adsorbed liquid electrolyte and thus approaches the

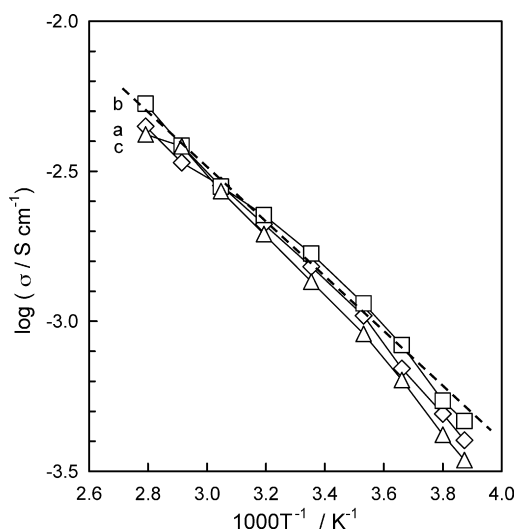


Fig. 5. Conductivity vs. reciprocal temperature of the samples: (a) no. 1, (b) no. 2 and (c) no. 3 in Table 2. All PGEs with $80 \mu\text{m}$ were obtained after being immersed in the solution of PC/EC (1:1) containing 1.0 M LiBF_4 during 5 h at 20°C , by which the same amount of electrolyte (73 wt%) was impregnated in each sample. Dotted line shows the straight line calculated by the least-squares method for the points of the sample no. 2, except for the points at 253 K and 263 K.

conductivity of liquid solution as increasing the content. To elucidate the fundamental mechanisms whether the polymer chain aids or hinders Li ion transport in these membranes, the values of the conductivity and activation energies should be examined as a function of electrolyte content impregnated in the gel polymer. However, the related research is beyond the scope of the present work.

In order to see the effect for suppressing the formation of dendrite, the electrolysis was conducted at a constant current of 3 mA cm^{-2} for 1 h and, then, the interface between lithium and the polymer electrolyte was observed by using a CCD camera, as reported previously [6]. The surface of the lithium metal electrode was smooth, and it was found that the PGE of the samples described in Tables 2 and 4 suppressed dendrite formation to a conspicuous degree on the interface of the lithium electrode, as demonstrated in Fig. 6. The mechanism of the inhibition effect of the gel electrolyte on the dendrite formation has not yet been elucidated. One of the possibilities is that the viscoelastic gel mechanically suppresses the formation. As another reason, we can consider that physical adhesion at the interface between the polymer electrolyte and Li electrode suppresses the dendrite formation.

The mechanical properties of the PGEs were observed with the measurement method described in experimental. For the PGE of polymer no. 4 shown in Table 2, the original height observed at 25°C was kept constant in the range of temperature between -50°C and 40°C . The measured height started to decrease at 50°C and 20% decreasing from the original height was observed at 70°C . It was found that the film was melt partially above the temperature more than 70°C . However, it was found that the softness of the PGE maintains constant above 70°C by a crosslinking procedure of polymer materials.

4.4. Properties of network type gel

4.4.1. Preparation

To increase stabilization of the gelation properties of the present PGE in wide-temperature range (-20°C to 85°C), we interlace the PEGM-g-EAA with a network having three-dimensional structure. 7.5 g of the dried non-crosslinked polymer PE-A ($M_n = 50,000$) was added to 92.5 g of an electrolyte solution prepared by dissolving LiBF_4 as a supporting electrolyte at 1 M in a mixture solvent of EC and PC at a ratio of 1:1, and then the mixture was stirred at 70°C for an hour while heating to dissolve the polymer. Thus, the polymer solution (SA) was prepared.

The SA, a diacrylate of polyethylene glycol having a polymerization degree (n) of 9 (to be called crosslinkable monomer MA hereinafter) as a crosslinkable monomer, and benzyldimethylketal (BDK) were mixed together in amounts specified in Table 3, and thus 6 types of reaction mixtures were prepared (polymers sample nos. 1–6 in Table 3). By using the crosslinking polymerization method with the UV ray described in experiment, 6 types of film-shaped PGEs were prepared.

It should be noted that the preparations of the gel films of sample nos. 1–6 in Table 3 were all carried out in a dry room where the dew point was below -50°C . These gel films were evaluated by the above-described evaluation methods in terms of the electrochemical properties (ionic conductivity), thermostability and flexibility. The results were also shown in Table 3. As is clear from the results shown in Table 3, the gel films of sample nos. 2–4 in Table 3 of the present paper were transparent gel films that did not exhibit any melting or phase separation even when heated to 80°C , and showed an excellent thermostability and a high ionic conductivity. On the other hand, since the gel prepared in sample no. 6 in Table 3 was a physical gel that had not crosslinked structure, it was

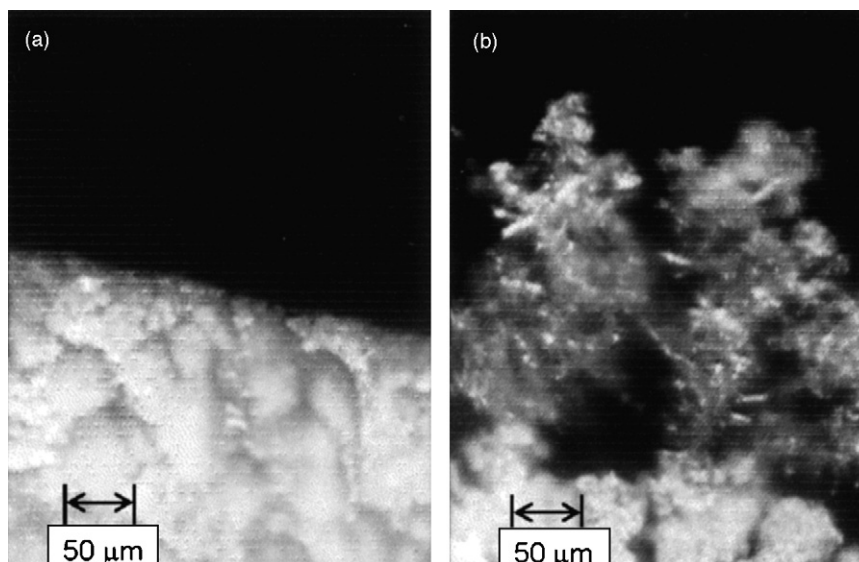


Fig. 6. Optical micrographs of lithium foil surfaces contacted on (a) the PEGM-g-EAA gel electrolyte of sample no. 6 in Table 2 and (b) the EC/DMC (1:2) solution electrolyte containing 1.0 M LiBF₄, after performing an electrochemical deposition with 3 mA cm⁻² for 1 h.

Table 3

Typical properties of network type gel

Sample no.	Non-crosslinked polymer solution SA ^a (g)	Crosslinkable monomer MA ^b (g)	BDK ^c (g)	Ion conductivity at 20 °C (S cm ⁻¹)	Thermostability	Flexibility
1	10	0.25	0.01	3.5×10^{-3}	Fair	Good
2	10	0.50	0.02	3.2×10^{-3}	Good	Good
3	10	0.75	0.03	3.1×10^{-3}	Good	Good
4	10	1.00	0.04	2.8×10^{-3}	Good	Good
5	10	1.50	0.06	2.3×10^{-3}	Good	Fair
6	10	None	None	1.7×10^{-3}	No good	Fair

Reaction temperature used for synthesis of the nos. 1–5 is kept at 140 °C.

^a SA: the solution of the PE-A (7.5 wt%) dissolved in an EC/PC solution containing 1.0 M LiBF₄, where PE-A denotes the non-crosslinked polymer that is the ethylene/acrylic acid (molar ratio 90/10, Mw = 50,000) copolymer esterified with a one-terminal methylated polyethylene glycol (polymerization degree $n=9$).

^b MA: the crosslinkable monomer of the diacrylate of polyethylene glycol (polymerization degree $n=9$).

^c Benzylidimethylketal.

melted when heated to 80 °C, and showed a very poor thermostability.

A dried non-crosslinked polymer PE-A (Mn = 50,000) was dissolved into an electrolyte solution (EA) to prepare a polymer solution having a non-crosslinked polymer PE-A concentration of 3–33% (non-crosslinked polymer PE-A/EA = 3/97 to 33/67 in weight ratio). As shown in Table 4, the polymer solution, crosslinkable monomer MA and BDK were mixed in various amounts to prepare a total of 14 types of reaction mixtures as sample nos. 1–14 in Table 4. With each reaction mixture, a gel film was prepared as in sample no. 1 in Table 3, and the ionic conductivity, thermostability and flexibility were evaluated similarly. The results are shown in Table 4.

As is clear from the results shown in Table 4, the samples of nos. 1 and 2 were in a state of solution even after the irradiation of UV ray, and therefore a test cell for evaluation could not be prepared in Table 4. On the other hand, the gel films of sample nos. 11–14 in Table 4 were in a hard gel state, which had some thermostability, but were brittle and poorly flexible. In particular, the gel film of sample no. 14 in Table 4 was brittle and hard to handle, and therefore it difficult to assemble a cell for evaluating its electrochemical properties.

As compared to these examples, samples of nos. 4–10 in Table 4 of the present research had an appropriate flexibility and were easy to handle, and they also exhibited excellent ionic conductivity, thermostability and transparency (as shown in Fig. 7).

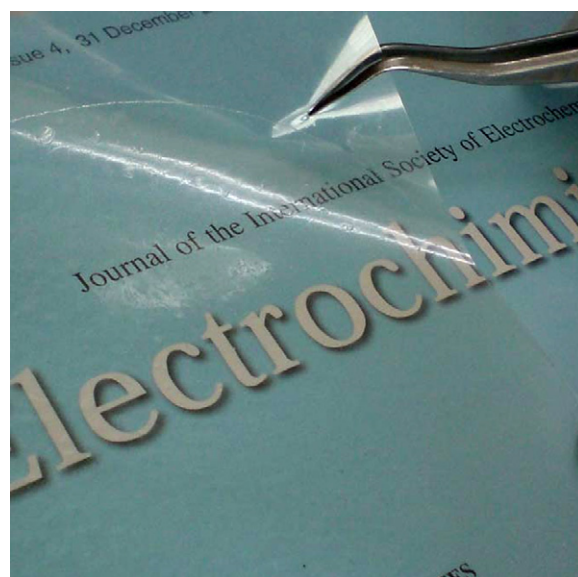


Fig. 7. Photograph for the network type gel of PEGM-g-EAA film (0.2 mm in thickness). The polymer gel of sample no. 8 in Table 4 contains 1.0 M LiBF₄ EC/PC (1:1) solution.

Table 4
Property changes of polymer gel electrolytes synthesized by changing the composition and the concentration of reactants

Sample no.	Non-crosslinked polymer PE-A ^a (g)	Electrolyte solution ^b (g)	Crosslinkable monomer MA (g)	Non-crosslinked polymer/crosslinkable monomer (weight ratio)	BDK (g)	Ion conductivity at 20 °C (S cm ⁻¹)	Thermostability	Flexibility
1	3	97	0.2	1/0.07	0.01	Immeasurable	No good	Solution state
2	5	95	0.2	1/0.04	0.01	Immeasurable	No good	Solution state
3	5	95	0.5	1/0.10	0.02	3.2×10^{-3}	Fair	Good
4	5	95	5	1/1.0	0.1	3.0×10^{-3}	Good	Good
5	5	95	10	1/2.0	0.2	2.8×10^{-3}	Good	Good
6	7	93	3.5	1/0.5	0.1	3.1×10^{-3}	Good	Good
7	7	93	7	1/1.0	0.2	2.9×10^{-3}	Good	Good
8	10	90	2.5	1/0.4	0.1	3.2×10^{-3}	Good	Good
9	10	90	5	1/0.5	0.2	2.7×10^{-3}	Good	Good
10	15	85	5	1/0.33	0.2	2.5×10^{-3}	Good	Good
11	20	80	2.5	1/0.125	0.12	1.8×10^{-3}	Good	Fair
12	25	75	2.5	1/0.10	0.12	1.2×10^{-3}	Good	Fair
13	30	70	5	1/0.17	0.2	5.0×10^{-4}	Good	No good
14	30	70	10	1/0.33	0.4	Immeasurable	Good	No good

Other abbreviations are the same as ones in Table 3. Reaction temperature used for synthesis of the samples nos. 1–14 is kept at 140 °C.

^a PE-A denotes the none-crosslinked polymer of the ethylene/acrylic acid (molar ratio 90/10, Mw = 50,000).

^b EC/PC solution containing 1.0 M LiBF₄.

From these results, it is found that an appropriate ratio between the non-crosslinked polymer and crosslinkable monomer of the present paper is about 1/0.1 to 1/2, and the amount of the non-aqueous solvent should be at least three times of the weight of the non-crosslinked polymer of the PE-A.

4.4.2. Ionic conductivity

The gel film prepared in sample no. 8 in Table 4 exhibited an ionic conductivity of 3.2×10^{-3} S cm⁻¹ at 20 °C. The transport number with respect to Li⁺ ion was 0.23 ± 0.01 . In addition, we found that the gel film of sample no. 8 in Table 4 exhibited a value of 1.1×10^{-3} S cm⁻¹ even at 0 °C, and thus has excellent ionic conductivity even at a low temperature. Therefore, it can be expected that when this gel electrolyte is used for a lithium secondary battery, the battery exhibits excellent properties.

4.4.3. Cyclic voltammogram and charge–discharge curve

Two kinds of the test cells were used for the evaluation of the PGE: one consisted of Li foil/PGE/carbon sheet (cell-A) and the other consisted of Li foil/PGE/LiCoO₂ sheet (cell-B). Fig. 8 shows the cyclic voltammograms (CVs) of the second potential cycle for the cell-A

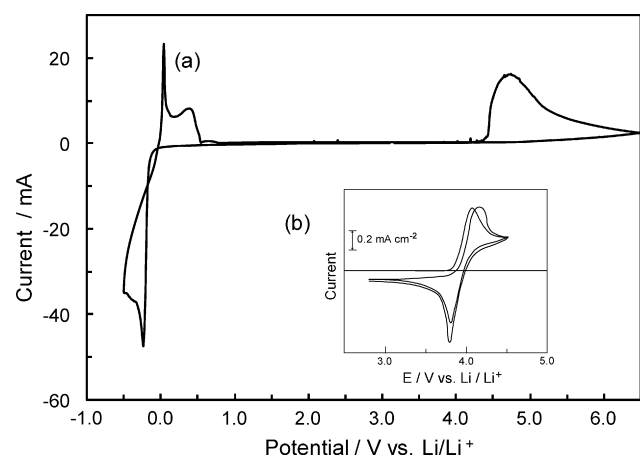


Fig. 8. Typical cyclic voltammograms obtained at the second potential cycle for cell-A and cell-B, in which the PGE of the polymer no. 8 in Table 4 was employed. (a) At the scan rate 1.0 mV s^{-1} with cell-A consisted of carbon sheet/PGE/Li foil (working electrode) and (b) at the scan rate of 0.1 mV s^{-1} with cell-B consisted of Li foil/PGE/LiCoO₂ sheet (working electrode).

and the cell-B, in which the PGE of polymer sample no. 8 described in Table 4 was used. From the CV obtained with the cell-A, we can evaluate the electrochemical potential window on the PGE of the PEGM-g-EAA material. At potential 4.5 V vs. Li metal, the oxidation current, seemingly due to the oxidation of the polymer itself or the solvents, was observed. It was found obviously that the limit of positive potential window is around 4.5 V. At the negative potential more than 0.0 V vs. Li metal, the reduction current due to the reduction of Li ion was observed. However, small reduction current at ca. +1.0 V by first potential sweep was rarely observed. The origin of such a reduction current at +1.0 V is not clear but probably results in a reaction of the impurities left in the PEGM-g-EAA material or that of reaction subproducts produced by contact between Li anode and the PEGM-g-EAA. We can imagine that the pre-reduction wave at +1.0 V is resembled to the behavior observed with graphite anode during the intercalation Li ion into graphite at the first potential sweep. It is well known that the reduction observed during the initial potential sweep with a carbon anode induces the formation (referred to the so-called solid electrolyte interface; SEI) of a passivating film on the surface of the carbon electrode due to the decomposition of electrolyte [17,18].

The CV obtained with the cell-B was also shown in Fig. 8. The potentials of the LiCoO₂ working electrode were scanned between 2.8 V and 4.5 V at a scan-rate of 0.1 mV s^{-1} . The stable CV was observed, even if the potential cycling is repeated over 50 times. The behavior indicates that the in-and-out behavior of Li ion at the interfacial between the gel electrolyte and the cathode is consistent. An outstanding performance of the polymer electrolyte could be expected when it is applied to Li secondary battery as its electrolyte.

Therefore, by using lithium cobaltate (LiCoO₂) coating (thickness of 88 μm) formed on an aluminum current collector (thickness of 25 μm) as a positive electrode and lithium metal (thickness of 200 μm) as a negative electrode, and a gel film of sample no. 8 in Table 4, a test cell was fabricated to examine the present PGE properties for the lithium battery performance. The test cell was subjected to a charge/discharge test at 20 °C, with a voltage set at 2.5 V and at 4.05 V, as shown in Fig. 9. The charge/discharge mode employed here was a constant current mode of 0.25 mA cm^{-2} . The charge/discharge rate was 0.4 C and the rest time was 30 min. The results of the charge/discharge cycle test indicated that the test cell maintained 92% of the discharge capacity of the initial one even after 100th charge/discharge cycle. Thus, it was verified that the gel electrolyte was stable with respect to a voltage change from 2.5 V to 4.05 V.

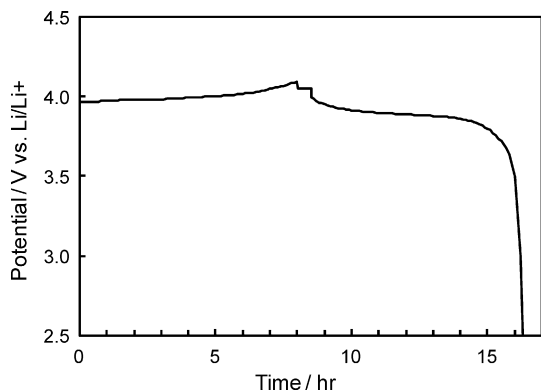


Fig. 9. Charge–discharge curves of LiCoO₂/PGE/Li foil cells, where PGE is prepared by the polymer no. 8 in Table 4. Rates of charging and discharging are 0.2 C, respectively.

As described above, the PGE composition of the present invention has, not only a high thermostability of 80 °C and an excellent ionic conductivity of $1.1 \times 10^{-3} \text{ S cm}^{-1}$ or higher at 0 °C, but also a high flexibility and adhesion. Therefore, when manufacturing a battery, the electrolyte composition can be wound in combination with the positive electrode or negative electrode. Further, it is easy to integrate the gel composition with the positive electrode or negative electrode by gelling it after applied on the surface of the respective electrode. A good adherence between the gel electrolyte and electrode material can be achieved, and the interface resistance with regard to the electrode material becomes stable. Therefore, it is possible with the present paper to easily manufacture electrochemical devices such as a high-performance lithium polymer battery [19,20], an electric double layer capacitor, and an electrochromic display device.

5. Conclusion

New PGE composed of polyolefin derivatives and organic electrolyte solution was prepared and applied as electrolyte materials for lithium secondary cells. The introduction of about 9.0% by

ethylene mol unit of oligo(oxyethylene) group grafted into the polyethylene induced to exhibit the properties absorbing and holding a large amount of the organic electrolyte solution. The ionic conductivity of the resulting PGE was a high value of $1.1 \times 10^{-3} \text{ S cm}^{-1}$, even when at 0 °C. The PEGM-g-EAA synthesized at the present paper possessed the characteristics of good adhesion and transparency. The test cell of Li rechargeable battery consisted of the present PGE, LiCoO₂ cathode and Li foil anode showed a good performance on the charge–discharge responses.

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