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# Electrochemical characterization of gel polymer electrolytes prepared with porous membranes

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## Abstract

A highly porous polymer membrane with high affinity for electrolyte solution is prepared and characterized. In preparing this membrane, a blend of P(VdF-co-HFP) and PAN is used as a matrix polymer in order to attain high ionic conductivity and good mechanical strength. Gel polymer electrolytes are prepared by soaking the porous membranes in an electrolyte solution, and their electrochemical characteristics are investigated. A lithium-ion polymer cell is assembled with the gel polymer electrolyte prepared in the porous membrane and the charge–discharge cycling performance is evaluated. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Electrochemical characteristics; Gel polymer electrolyte; Lithium-ion polymer battery; Porous membrane

## 1. Introduction

Gel polymer electrolytes which comprise a matrix polymer plasticized with a solution of lithium salt in organic solvents are of practical interest for the rechargeable lithium batteries because they usually exhibit ionic conductivities in excess of $10^{-3}$ S/cm. A variety of polymers, ranging from poly(ethyleneoxide) (PEO), polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA) to poly(vinylidene fluoride) (PVdF), has been used to prepare such gel polymer electrolytes [1–9]. Films of gel polymer electrolyte are usually prepared by casting a mixture of the electrolyte solution and a matrix polymer in a low boiling point solvent. This process requires, however, a moisture-free environment because of the higher water sensitivity of the lithium salt. Besides their mechanical properties are often very poor, and the films have to be hardened by either chemical or physical curing. Bellcore's group successfully overcame these difficulties and developed a liquid extraction and activation method to prepare the polymeric electrolyte materials for plastic lithium-ion batteries [9,10]. The Bellcore's processes are the plasticization of a copolymer of vinylidene fluoride and hexafluoropropylene (P(VdF-co-HFP)), subsequent removal of the plasticizer, and final swelling in an electrolyte solution. This procedure requires critical moisture control during only the last activation step. The ability to absorb and retain the electrolyte solution is critical to applications in lithium batteries.

To enhance the uptake of electrolyte and the ionic conductivity of polymer film, we attempt in this study to prepare a highly porous polymer membrane which has high affinity for electrolyte solution. The porous membrane is prepared by a phase-inversion method, which has been shown to be effective for producing a porous structure [11,12]. To attain high ionic conductivity and good mechanical strength of the gel polymer electrolytes, we use a blend of P(VdF-co-HFP) and PAN as a matrix polymer. It is considered that PAN can give mechanical integrity and structural rigidity to a porous membrane without inorganic fillers. With these porous P(VdF-co-HFP)/PAN membranes, gel polymer electrolytes are prepared by soaking in electrolyte solution. The advantage of this method is that the conductivity and mechanical property can be controlled independently by designing the structure of the porous polymer membrane and by selecting a suitable electrolyte solution. We investigate the electrochemical characteristics of gel polymer electrolytes prepared with P(VdF-co-HFP)/PAN membranes, and discuss the possibility of using them as electrolyte material for lithium-ion polymer batteries.

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## 2. Experimental

### 2.1. Preparation of membrane and electrodes

P(VdF-co-HFP) with 12 mol% HFP (Kynar Flex 2801, Elf Atochem) was dissolved in *N*-methyl pyrrollidone (NMP). PAN (Aldrich Chemicals) was dissolved in dimethyl sulfoxide (DMSO). After complete dissolution, the two solutions were mixed. To prepare a porous membrane with structural rigidity and higher uptake of electrolyte solution, the weight ratio of P(VdF-co-HFP) and PAN was optimized at 80:20. When complete homogenization of the mixture was achieved, the resulting viscous solution was cast with a doctor blade on to a glass plate. The resulting film was then immersed in a pool of excess de-ionized water for 5 h to induce phase inversion. After exchange of organic solvents (NMP and DMSO) and water, the resulting film contains substantial amounts of water. The resulting membrane was then vacuum dried at 40°C for 24 h. Differential scanning calorimetry (DSC) thermal analysis was performed to measure the thermal properties of polymers, with a heating rate of 10°C/min from 25 to 250°C. The morphology of the porous membrane was examined using a scanning electron microscope (JEOL, JSM-6300). The carbon negative electrode (anode) was prepared by coating a slurry of mesophase carbon fiber, MCF (Petoca, Ltd.), poly(vinylidene fluoride) (PVdF) and super-P carbon on a copper foil. The positive electrode (cathode) contained the same binder (PVdF) and super-P carbon along with $LiCoO_2$ (Japan Chemical), and was cast on aluminum foil. The thickness of the electrodes ranged from 100 to 120 μm, and their active mass loading corresponded to capacity of about 3.5 mAh/cm$^2$.

### 2.2. Electrical measurements

The dried membrane was transferred to a glove box and soaked in either 1 M $LiPF_6$ or 1 M $LiBF_4$ ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) for 10 min. Because the membrane is highly porous, this time is sufficient to absorb the electrolyte solution. After activation, the membrane was removed from the electrolyte solution and excess electrolyte solution on the surface was wiped with filter paper. The wetted membrane was cut into 4 cm$^2$ squares and sandwiched between two stainless-steel (SS) electrodes for conductivity measurements. The cell was enclosed in an aluminum plastic pouch and sealed in order to permit testing outside of a glove box. The ac impedance measurements were performed by means of a Zahner Elektrik IM6 impedance analyzer over the frequency range 10 Hz to 100 kHz. Linear sweep voltammetry was performed on a SS working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1.0 mV/s. A lithium-ion polymer cell with an electrode area of 15 cm$^2$ was assembled by sandwiching the gel polymer electrolyte between a MCF anode and a $LiCoO_2$ cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. All cell assemblies were carried out in a dry box filled with argon gas. Charge and discharge cycling tests of lithium-ion polymer cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000U).

## 3. Results and discussion

A typical scanning electron micrograph of a porous membrane prepared with P(VdF-co-HFP) and PAN by the phase-inversion method is presented in Fig. 1. The image of the vacuum-dried film shows that pores of 1–10 μm are formed. Most of the membranes are found to have large voids and cavities of various sizes. Large pores formed in the membrane reflect a high exchange rate between the organic solvents and water during immersion precipitation. A decrease in the polymer concentration in the casting solution gives rise to an increase in both the number and size of the cavities. If the pore size is greater than about 10 μm, however, it becomes difficult for the membrane to retain the electrolyte solution and its mechanical strength is poor. The pore volume was measured to be 76%. The thickness of the membrane was between 40 and 50 μm.

For compatible polymer blends, the glass transition temperature ($T_g$) is expected to be intermediate between that of the two polymer components. In the case of the P(VdF-co-HFP)/PAN blended membrane, $T_g$ for the polymeric component is not observable, since the P(VdF-co-HFP) copolymer is semicrystalline, as shown in Fig. 2. The P(VdF-co-HFP) copolymer shows a endothermic peak at 141°C; this is attributable to melting of the polymer. On the other hand, the P(VdF-co-HFP)/PAN membrane displays a broad endothermic peak at a lower temperature (139°C) and a lower heat of melting by about 8 J/g, which reflects a lower degree of crystallinity. The depression of the melting point and the reduction of the heat of fusion indicate that PAN is somewhat compatible with P(VdF-co-HFP). Therefore, an addition of small amounts of highly amorphous PAN can prevent the crystallization of P(VdF-co-HFP) copolymer, and result in the preservation

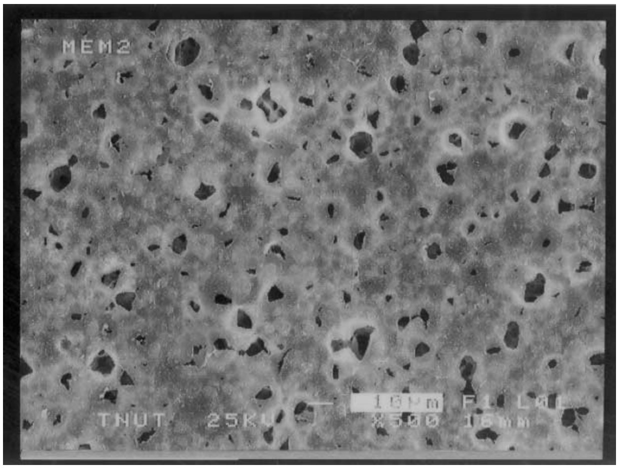

Fig. 1. Scanning electron micrograph of porous P(VdF-co-HFP)/PAN membrane.

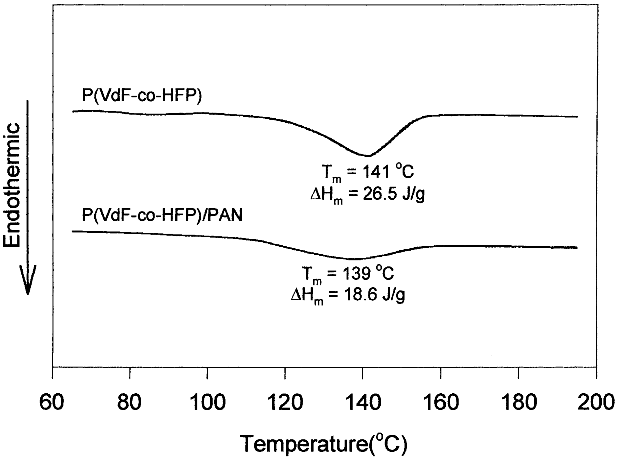

Fig. 2. DSC thermograms of P(VdF-co-HFP) and P(VdF-co-HFP)/PAN membrane.

of amorphous domains, which are responsible for the high affinity to an electrolyte solution.

The uptake of an electrolyte solution in the porous membranes and the room-temperature conductivity after soaking of the membranes in the electrolyte solution are given in Table 1. The uptake of electrolyte solution was determined as follows:

$$\text{uptake}(\%) = \left(\frac{W - W_0}{W}\right) \times 100 \qquad (1)$$

where $W$ and $W_0$ are the weights of the wet and dried membrane, respectively. For comparison, the microporous polyethylene (PE) separator(Asahi Kasei, thickness 25 μm, porosity 40%) used in a commercial lithium-ion battery was soaked in the same electrolyte solution; the experimental data are also given in Table 1. For the P(VdF-co-HFP)/PAN membranes, the amount of electrolyte solution absorbed is greater than that absorbed by the PE membrane. This result is due to the fact that the PE membrane has poor affinity for electrolyte solution and lower porosity compared with P(VdF-co-HFP)/PAN membrane. For both membranes, the type of salt ($LiPF_6$ or $LiBF_4$) dissolved in EC/DMC did not affect the uptake of electrolyte solution. The membranes soaked in $LiPF_6$-based electrolyte solution, however, exhibit a higher ionic conductivity. The difference in conductivity arises from the difference in the ionic conductivity of the electrolyte solution. When comparing the ionic conductivities of the two electrolyte solutions added to the porous polymer membrane, $LiPF_6$–EC/DMC ($1.1 \times 10^{-2}$ S/cm) exhibits higher ionic conductivity than $LiBF_4$–EC/DMC ($5.2 \times 10^{-3}$ S/cm). From Table 1, it can be concluded that gel polymer electrolytes prepared with the P(VdF-co-HFP)/PAN membrane exhibit high ionic conductivities, i.e. $>10^{-3}$ S/cm, at room temperature.

In order to investigate the encapsulating property for an electrolyte solution of the porous membrane, electrolyte resistance was measured as a function of storage time in sealed cells. The time-dependence of ionic conductivity for electrolytes prepared with PE and P(VdF-co-HFP)/PAN membrane is given in Fig. 3. Clearly, the ion conduction behavior with time is different for each parent membrane. This difference is due to the change in the quantity of electrolyte solution encapsulated in the porous membrane. Since the PE separator has poor affinity for the electrolyte solution, liquid electrolyte encapsulated in the micropores moves out, and ionic conductivity is continuously decreased. By contrast, the ionic conductivity of gel polymer electrolyte prepared with a P(VdF-co-HFP)/PAN membrane remains constant over the same period of time, which suggests the complete gelation of the P(VdF-co-HFP)/PAN membrane with an electrolyte solution. From these results, it is concluded that the electrolyte solution is well encapsulated in the matrix polymer by physical gelation, which gives no leakage problem in this system.

The electrochemical stability of the gel polymer electrolyte was evaluated by linear sweep voltammetric measurements. Voltammograms for cells prepared with a porous membrane which contains an electrolyte solution of $LiPF_6$–EC/DMC or $LiBF_4$–EC/DMC are presented in Fig. 4. The decomposition voltage limit can be defined as the potential at which a rapid rise in current is observed and continues to increase as the potential is scanned, since the onset of the current flow may be associated with the decomposition of the given electrolyte. The decomposition voltage of each gel polymer electrolyte is found to be high; no electrochemical oxidation occurs until a potential of 4.6 V. These results suggest that a P(VdF-co-HFP)/PAN membrane soaked with electrolyte solution is acceptable for high-voltage cathode materials, such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. The low residual current with the absence of any peaks at a lower voltage than 4.6 V indicates that the porous polymer membrane has high purity. The decomposition voltage appears not be substantially influenced by the type of lithium salt dissolved in a mixture of EC and DMC, as shown in Fig. 4.

Table 1
Uptake of electrolyte solution and room temperature ionic conductivity

| Characteristics | Electrolyte | | | |
|---|---|---|---|---|
| | P(VdF-co-HFP)/PAN membrane | | PE separator | |
| | $LiPF_6$, EC/DMC | $LiBF_4$, EC/DMC | $LiPF_6$, EC/DMC | $LiBF_4$, EC/DMC |
| Uptake (%) | 82 | 80 | 52 | 51 |
| Ionic conductivity (S/cm) | $1.9 \times 10^{-3}$ | $1.2 \times 10^{-3}$ | $3.7 \times 10^{-4}$ | $1.7 \times 10^{-4}$ |

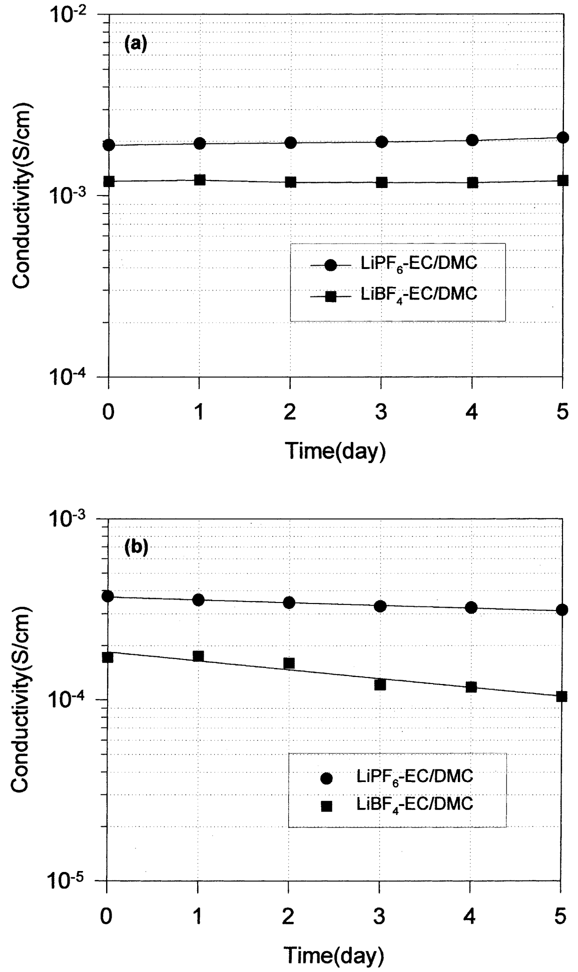

Fig. 3. Ionic conductivities of P(VdF-co-HFP)/PAN and PE membranes containing different electrolyte solutions as function of storage time at 25°C: (a) P(VdF-co-HFP)/PAN membrane; (b) PE membrane.

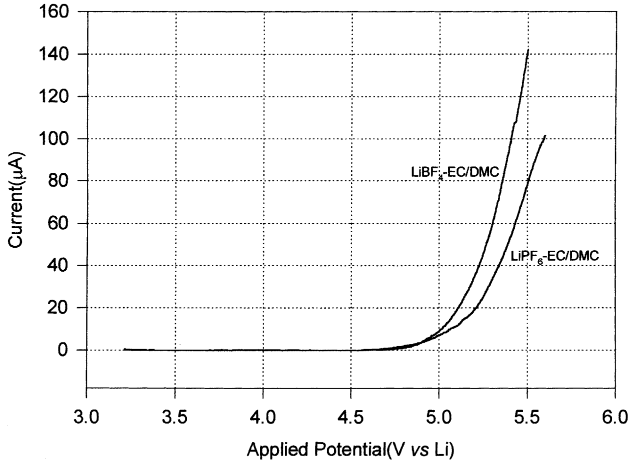

Fig. 4. Linear sweep of the cells prepared with a porous membrane containing an electrolyte solution of $LiPF_6$–EC/DMC or $LiBF_4$–EC/DMC (scan rate: 1 mV/s).

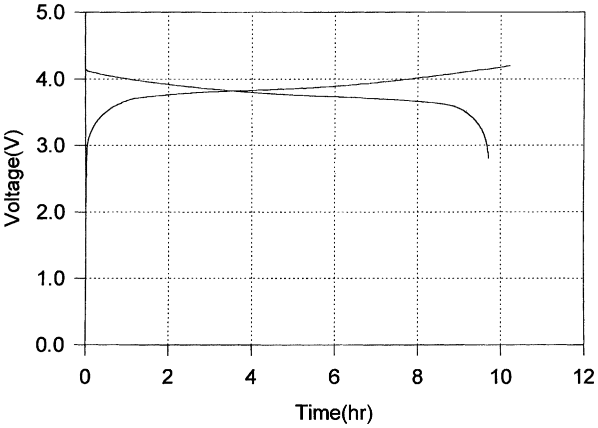

Fig. 5. First preconditioning cycle of lithium-ion polymer cell with porous membrane containing $LiPF_6$–EC/DMC (C/10 rate).

In order to evaluate the electrochemical performance of a lithium-ion cell using the gel polymer electrolyte (GPE) prepared with the porous P(VdF-co-HFP)/PAN membrane, we fabricated a MCF/GPE/$LiCoO_2$ cell. The assembled cell

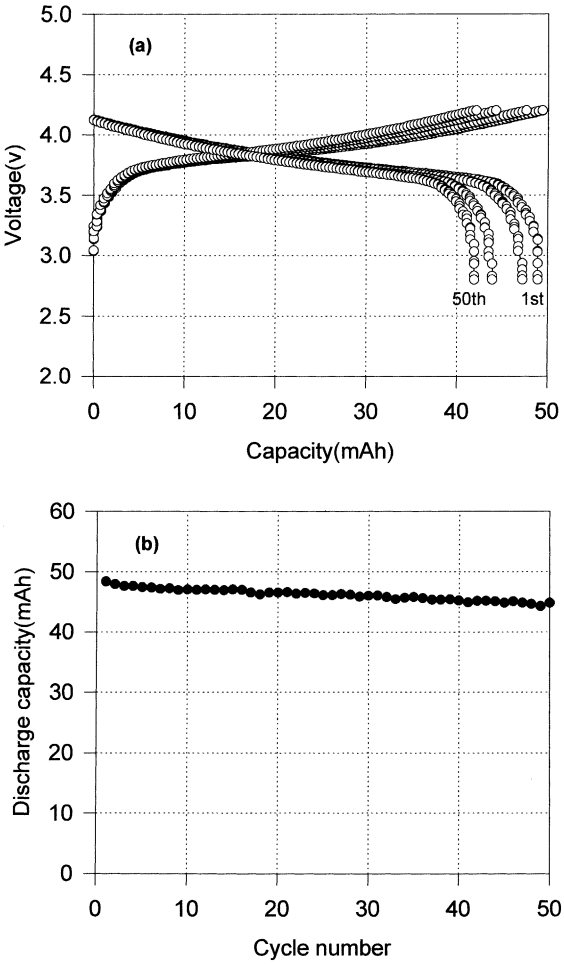

Fig. 6. (a) Charge and discharge curves of lithium-ion polymer cell with repeated cycles at C/5 rate; (b) discharge capacity of lithium-ion polymer cell as function of cycle number at C/5 rate.

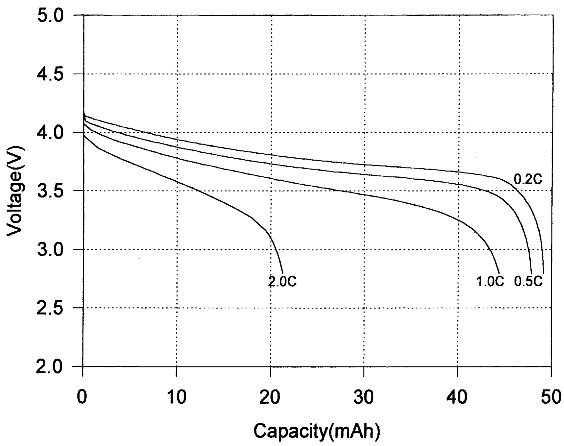

Fig. 7. Discharge profiles of lithium-ion polymer cell. Charge rate of 0.2*C* with 4.2 V cut-off.

was subjected to cycle tests in the following order: preconditioning with cut-off voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at the *C*/10 rate (5.2 mA) for the first preconditioning cycle and subsequent cycling at the *C*/5 rate (10.4 mA). The preconditioning charge–discharge cycle of a lithium-ion polymer cell with a gel polymer electrolyte prepared from the porous P(VdF-co-HFP)/PAN membrane and $LiPF_6$–EC/DMC is shown in Fig. 5. This cell delivered a discharge capacity of 50.5 mAh during the first preconditioning cycle. This value is equivalent to capacity of 131 mAh/g for active $LiCoO_2$ material in the cathode. The coulombic efficiency, which is defined as the ratio of the discharge capacity to charge capacity, is 95% for the first preconditioning cycle. For further constant-current cycles at the *C*/5 rate, a plot of the voltage profiles after 1, 10, 20, 50 cycles at 25°C is shown in Fig. 6(a). The discharge capacity versus cycle number for a cell subjected to 50 cycles is shown in Fig. 6(b). The initial capacity is 48.4 mAh and decreases slightly with cycling. This decline in capacity is primarily due to the loss of interfacial contact between the electrodes and the gel polymer electrolyte upon cycling, which gradually increases the internal resistance of the cell. The discharge capacity is 44.8 mAh at 50th cycle, i.e. 93% of the initial capacity.

An attempt was made to determine the rate capability of the lithium-ion polymer cell. The discharge curves of the cell at different current rates are given in Fig. 7. In this cell, the gel polymer electrolyte is a P(VdF-co-HFP)/PAN membrane soaked in $LiPF_6$–EC/DMC. The voltage drop in passing from charge to discharge increases with the current rate, which reflects a large polarization that reduces the discharge capacity. A promising capacity of 45 mAh is obtained at the 1.0*C* rate, which is 91% of the discharge capacity at the 0.2*C* rate. The discharge capacity falls, however, at 2.0*C* rate, i.e. the cell retains only 43% of the discharge capacity at the 0.2*C* rate. This is not sufficient to give high-rate performance in a lithium-ion polymer cell, and has to be improved. Further research is being conducted in the authors' laboratories to improve the high-rate performance of the lithium-ion polymer cell. Strategies to achieve this include: soaking of the porous membrane with highly conductive electrolyte solution; optimization of porosity in the porous membranes; improvement in the assembling method for better interfacial contact between the electrodes and the gel polymer electrolyte.

## 4. Conclusions

Highly conductive, gel polymer electrolytes have been prepared by soaking porous P(VdF-co-HFP)/PAN membranes in electrolyte solutions. The observed high ionic conductivity of the gel polymer electrolyte is attributed to the high volume of pores formed in the porous membrane and a high affinity of the membrane for electrolyte solution. These porous membranes are found to encapsulate high amounts of electrolyte solution, without solvent leakage, while maintaining good mechanical properties. Lithium-ion polymer cell employing these gel polymer electrolytes have been assembled, and their charge–discharge cycling performance evaluated. Cycle-life and high-rate performance are considered to be insufficient for portable electronics applications. Given more efforts to improve the cell performance, gel polymer electrolytes prepared by soaking porous membranes in electrolyte solutions are thought to be promising candidate electrolyte materials for rechargeable lithium-ion polymer batteries.

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