PEGDA/PVdF/F127 gel type polymer electrolyte membranes for lithium secondary batteries

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Abstract

A novel porous gel polymer electrolyte (GPE) membrane based on poly(ethylene glycol) diacrylate (PEGDA), poly(vinylidene fluoride) (PVdF), and polyethylene oxide-co-polypropylene oxide-co-polyethylene oxide (PEO-PPO-PEO, F127) was fabricated by a phase inversion technique. The PEGDA cross-linking oligomer could be randomly mixed with unraveled PVdF polymer chains to form the interpenetrating polymer network (IPN) structure. Several experimental techniques including infrared (IR) spectra, differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and potentiostat/galvanostat were employed to investigate the characteristics of the polymer membranes. PEGDA and F127 influenced the porous size and structure. The mechanical strength and flexibility of the membrane were controlled by its composition. The membrane with the composition of PEGDA/PVdF/F127 (0/4/4) showed the highest electrolyte uptake of 152.6% and the maximum ionic conductivity of $2.0 \times 10^{-3} \, \mathrm{S \, cm^{-1}}$ at room temperature. All GPEs prepared in this study were electrochemically stable up to 4.5 V.
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Keywords: Gel polymer electrolyte; Membrane; Phase inversion; Interpenetrating polymer network; Ionic conductivity

1. Introduction

In the past few years, the lithium-ion battery using polymer electrolytes has been known as a preferred power source for various applications because of its high energy density, long life cycle, and the absence of a "memory" effect. Numerous works have been dedicated to explore the promising polymer electrolytes with high ionic conductivity, high chemical, thermal and electrochemical stabilities, and high mechanical strength [1–4]. Among many polymer electrolyte systems, poly(ethylene-oxide) (PEO)-based solid polymer electrolytes have been most widely studied [5–7]. A significant drawback of this conventional electrolyte system is low conductivity at room temperature. Since various approaches involving the addition of ceramic fillers/additives and polar plasticizers in literatures [7–14], the fabrication of gel type polymer electrolyte (GPE) system becomes a promising approach to create high ionic conductivity with other desirable properties. Some poly-mers such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), poly(vinylidene fluoride) (PVdF), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) have been employed in the fabrication of GPEs. PVdF has been a favorable choice as a polymer matrix because of its appealing properties of high dielectric constant ($\varepsilon \approx 8.4$) associated with strong electro-withdrawing groups (−C−F) [15–18].

Although GPEs exhibit high ionic conductivity in excess of $10^{-3} \, \mathrm{S \, cm^{-1}}$, there is still a problem that the addition of polar solvents usually deteriorates the mechanical strength [19]. In view of this standpoint, poly(ethylene glycol) diacrylate (PEGDA) was added in this study to produce chemical cross-links for enhancement of mechanical strength. The cross-linked network structure can maintain better thermal and dimensional stability with lower exudation of electrolyte solution.

As the PEO-PPO-PEO copolymers [20,21] have a good affinity for the electrolyte solution, addition of this kind surfactant, in our case F127, is expected to increase and tune the pore structure and size of polymer membranes and thus improve the conducting performance of the GPE membranes.

The typical phase inversion method was used to fabricate the ternary polymer membranes composed of PEGDA/PVdF/F127

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where the interpenetrating polymer network (IPN) structures were formed via physical and chemical cross-link. Several techniques including infrared (IR) spectra, differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), and potentiostat/galvanostat were used to characterize the polymer membranes. Electrolyte uptake, ionic conductivity and electrochemical stability were also studied.

2. Experimental

2.1. Raw materials

PEGDA with a molecular weight of 258 was purchased from Aldrich (Milwaukee, WI) to be used as a precursor. 2,2′-Azobisisobutyronitrile (AIBN), an initiator and the battery-grade lithium perchlorate (LiClO$_4$), a salt, to be dried at 120 °C under vacuum for 24 h, were purchased from Aldrich. PVdF ($M_w = 275,000$ g mol^{-1}), F127 (mole ratio of EO/PO/EO = 106/70/106, $M_w = 12600$ g mol^{-1}), ethylene carbonate (EC), and propylene carbonate (PC) were supplied from Aldrich and used without further purification. Dimethylformamide (DMF) and acetone (reagent grade) were used as the solvent.

2.2. Membrane synthesis

The polymer membranes with a thickness of 150–300 μm were prepared by a phase inversion technique [22–25]. PVdF was dissolved in a mixture of acetone and DMF (1:3, v/v) and stirred at 60 °C to form a homogeneous solution. PEGDA and F127 were then added. After the PEGDA/PVdF/F127 solution was formed, an initiator, 2,2′-azobisisobutyronitrile (AIBN), was added to the solution under vigorous stirring for 12 h at 60 °C to cross-link PEGDA. The resulting viscous solution was spread on a glass substrate and was put into an air stream for 5–10 min to remove solvent. When the surface of membrane was dry, it was immersed in water at room temperature for an hour to induce phase inversion. The product was placed in a vacuum oven at 80 °C for at least 24 h for further cross-linking of PEGDA and evaporation of solvent. Further drying was carried out in a dry box under nitrogen environment to remove any trace of solvents. In this film preparation, the weight ratios of PEGDA/PVdF/F127 mixtures were 0/4/4, 1/4/3, 2/4/2, 3/4/1, 4/4/0, 4/4/1, 4/4/2, 4/4/3, and 4/4/4, respectively. The gel electrolyte was obtained when the polymer membrane was soaked in a 1.0 M LiClO$_4$-EC/PC (1:1) solution at room temperature for 24 h.

2.3. Membrane characterization

The IR absorption spectra were taken using an attenuated total reflection Fourier transform infrared spectrometer (ATR–FT-IR, FT-IR-660, Jasco, Japan) over the range from 600 to 1700 cm^{-1}. The thermal transition behavior was investigated using a differential scanning calorimetry (DSC, DSC7, Perkin-Elmer Cetus Instruments, Norwalk, CT). Each sample was sealed in an alu-

minum alloy pan and heated from 30 to 200 °C at a heating rate of 10 °C min^{-1}. After thermal stabilization, the chosen sample was cooled to 30 °C at the same rate using liquid nitrogen, and then re-heated to 200 °C at 10 °C min^{-1}. Thermal stability data were obtained under nitrogen atmosphere using a thermogravimetric analyzer (TGA 2950, DuPont) at a heating rate of 20 °C min^{-1}. A scanning electron microscope (SEM, JSM 5410LV, JEOL, Japan) was used to analyze the membrane morphologies.

The porosity of membranes was measured by immersing the membranes into n-butanol for 1 h. The porosity was calculated using the following equation [20,23,26]:

$$\text{Porosity} (\%) = \frac{M_b/\rho_b}{(M_p/\rho_p) + (M_b/\rho_b)} \tag{1}$$

Here, M_p is the weight of membrane, M_b the weight of absorbed n-butanol, ρ_p the density of the membrane and ρ_b is the density of n-butanol, respectively.

The electrolyte uptake was calculated by:

$$\text{Uptake} (\%) = 100 \times \frac{W_i - W_0}{W_0} \tag{2}$$

Here, W_i and W_0 are the weights of the wet and dry membrane, respectively.

The stress and strain mechanical properties of the blend membranes were measured using a universal tensile machine (Instron model 5565, Lloyd, UK) with a constant cross-head speed of 20 mm min^{-1}.

The ionic conductivity of the polymer electrolyte was determined using an electrochemical impedance spectroscopy (EIS) in the temperature range from 25 to 80 °C. The samples were sandwiched between two stainless steel blocking electrodes. The impedance measurements were carried out by a frequency response analyzer (FRA Solartron model 1260, Solartron, UK) with a Solartron model 1287 electrochemical interface in the frequency range from 0.1 Hz to 1 MHz. The electrochemical stability window of the polymer electrolyte was examined with a potentiostat/galvanostat (Parstat 2263, Par, USA) at the potential scanning rate of 100 mV s^{-1}. For this measurement, polymer electrolytes were placed between two pure lithium electrodes with a working area of 0.785 cm^2. The measured electrochemical cell was assembled in a glove box with nitrogen environment.

3. Results and discussion

3.1. IR spectra

The FTIR spectra of PEGDA, F127, PVdF homo and PEGDA/PVdF/F127 blend membranes with various compositions are depicted in Fig. 1. In Fig. 1(A), the characteristic peak at 1105 cm^{-1} mostly corresponds to the IR absorption in the C–O bond of F127. While a strong peak was clearly observed in the pure F127 spectrum, it was scarcely observed in the spectra of PEGDA/PVdF/F127 blend systems regardless of the concentration of F127. Even if the content of F127 was fixed in PEGDA/PVdF/F127 membranes as shown in Fig. 1(B), the same behavior was observed as one in Fig. 1(A). The characteristic peaks of PVdF at 835, 877, 1074, 1172, 1232 and 1406 cm^{-1}
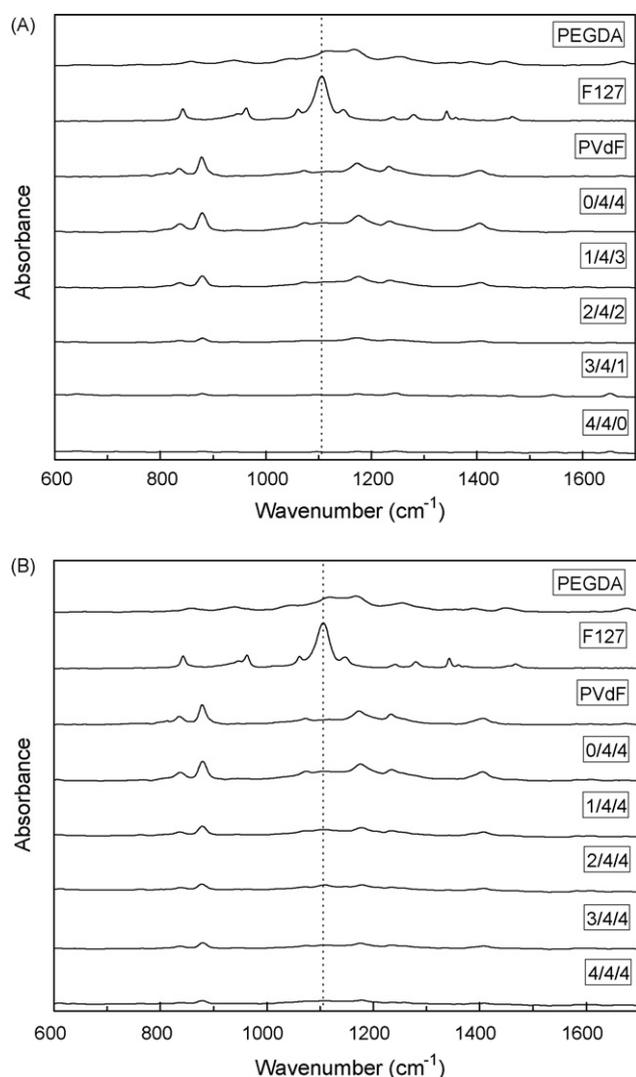
Fig. 1. (A and B) IR spectra of PEGDA, F127, PVdF and PEGDA/PVdF/F127 systems.

Fig. 2. (A and B) DSC patterns of PEGDA, F127, PVdF and the PEGDA/PVdF/F127 membranes with various weight ratios.

decreased in intensity little by little with the increasing content of PEGDA in Fig. 1(A and B). Those observations in FTIR spectra can be interpreted in terms of the specific interaction between fluorine in PVdF and the carbon connected to oxygen of PEGDA. As the electron donating of fluorine to carbon weakens the C–O band, it can be inferred that PVdF has a stronger interaction with PEGDA than that of F127.

No peaks observed at 1600 cm^{-1} indicates that the >C=C< bond in uncross-linked PEGDA disappeared via cross-linking when the membrane was prepared. It means that most of F127 molecules were extracted by water during the phase inversion process, while PEGDA molecules were participated in crosslinking reaction to form IPN structure with PVdF.

3.2. Thermal behavior

The thermal behaviors of the PEGDA/PVdF/F127 membranes were investigated using a DSC. Fig. 2 displays the DSC thermograms of PEGDA, F127, PVdF homo and PEGDA/PVdF/F127 blend membranes. By assuming the pure
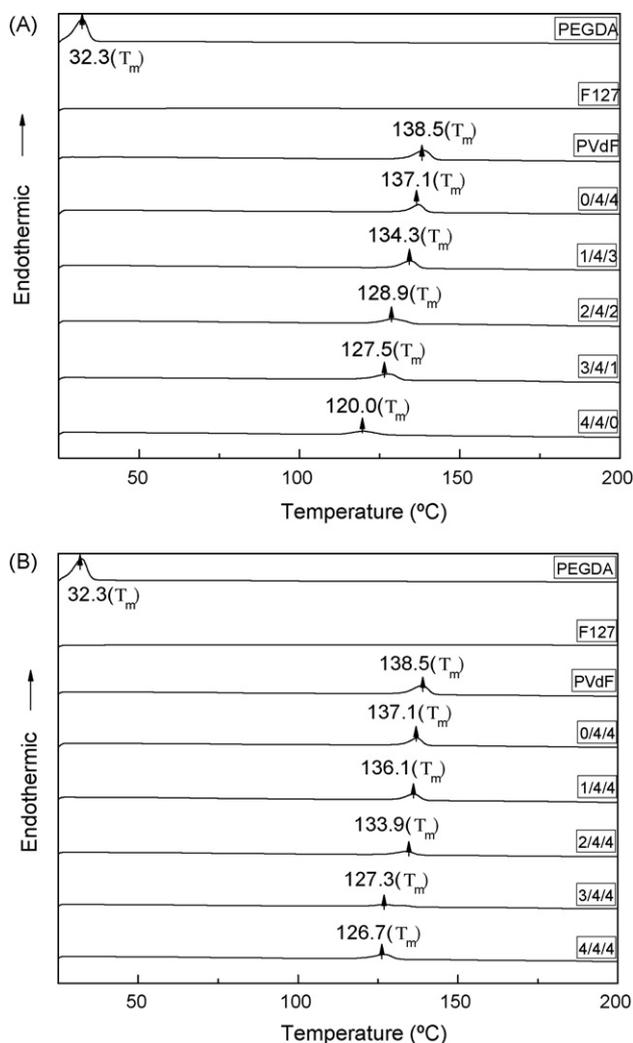
PVdF being 100% crystalline, the relative crystallinity (X_c) of the polymer membrane could be calculated from the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \tag{3}$$

where ΔH_m^0 is the crystalline melting heat of pure PVdF, 105 J g^{-1} [27] and ΔH_m is the heat of fusion for the PEGDA/PVdF/F127 membranes. The data of X_c, ΔH_m and the crystalline melting temperature (T_m) for all polymer membranes are shown in Table 1. In fact, all DSC curves of the PEGDA/PVdF/F127 membranes in Fig. 2 exhibited an endothermic peak. In this ternary system, PVdF is a semi-crystalline but F127 is an amorphous polymer. While F127 was extracted during the phase inversion process, PEGDA, a cross-linkable oligomer which is responsible for the formation of IPN structure takes a role in decreasing crystallinity. Therefore, the degree of crystallinity and T_m of the PEGDA/PVdF/F127 membranes were depressed after the addition of PEGDA. All blend membranes had the crystallinity less than 41.29%. The depression of T_m indicates that PVdF is compatible with PEGDA [20].

Table 1
Thermal data for the PEGDA/PVdF/F127 membranes

Sample name	T_m (°C)	ΔH_m (mJ mg^{-1})	Crystallinity (%)
PVdF	138.5	48.760	100
4/4/0	120.0	43.352	41.29
3/4/1	127.5	39.278	37.41
2/4/2	128.9	37.338	35.56
1/4/3	134.3	36.904	35.15
0/4/4	137.1	34.380	32.74
1/4/4	136.1	30.198	28.76
2/4/4	133.9	27.355	26.05
3/4/4	127.3	23.482	22.36
4/4/4	126.7	23.247	22.14

The TGA plots of PEGDA/PVdF/F127 membranes are presented in Fig. 3. The thermal decomposition temperature can be determined from the differential curve. The absence of weight losses after T_m indicates that the impurities such as solvent and water were not present any more, and confirms that the drying under vacuum and nitrogen gas was efficient in preparation of the membrane sample. All blend membranes were thermally stable up to 200 °C, which is high enough to be applied in lithium batteries.

3.3. Morphology

Fig. 4 shows typical SEM images of the PEGDA/PVdF/F127 blend membranes. As can be seen from the SEM micrographs, more and bigger pores were distributed on the surface of membrane with increasing content of F127 when the composition of PEGDA was fixed. This resulted from the extraction of more amount of F127 during the phase inversion/washing process. In addition, the comparison of two cross-sectional views of 4/4/4 and 3/4/4 samples suggests that the increasing content of PEGDA resulted in more compact network structure and thereby smaller pores. Therefore, PEGDA and F127 have important roles on the formation of pore in the polymer membrane although the
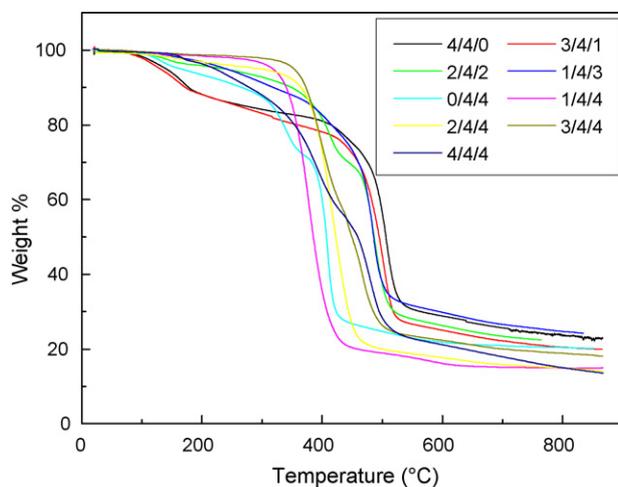

Fig. 3. TGA plots of the PEGDA/PVdF/F127 membranes with the various weight ratios.

pore formation in membrane is also known to be dependent on the preparation condition such as the type of solvent, evaporating temperature and casting method.

3.4. Porosity and electrolyte uptake

According to Saito et al. [28], the porosity, one of the important parameters of porous polymer membranes in lithium batteries [26,29], can dominate the conduction properties of the carriers. Here, n-butanol absorption technique was used to measure the porosity of the blend membranes. In Fig. 5, it is observed that the porosity, when the ratio of F127 is fixed, decreases with increasing content of PEGDA due to the increasing cross-linking density. At the PEGDA ratio of 0, the maximum porosity of 56.6% was measured. When the content of F127 increased (while the content of PEGDA decreasing), the porosity increased much more quickly. The membrane with higher weight ratio of F127 possessed higher porosity from the comparison of membranes containing the same amount of PEGDA. (Compare the porosities of two samples, 1/4/3 and 1/4/4, for example.)

As shown in SEM pictures, the pore formation is dependent on F127 rather than PEGDA in the phase inversion process. F127 and PEGDA are more soluble in DMF compared to PVdF because both are water-soluble polymers. As DMF was extracted by water, more and more pores were produced in polymer membrane. At the same time, most of polymer chains of F127 could be extracted by water during the phase inversion process while PEGDA intended to form the IPN structure in blend system. The amorphous structure of F127 resulted in the reduction of shrinkage of the polymer wall when DMF was extracted with water. F127 could form micelles in water because of its surfactant effect on polymer [30]. The F127 micelles possibly formed in DMF/acetone mixed solvents were thought to be extracted with steam during the phase inversion process so that pores with the size similar to that of micelles were formed in the polymer membranes. Thereby, all these factors contributed to the production of pore structure and the porosity.

GPEs are expected to possess high liquid electrolyte uptake and ionic conductivity. In contrast to the electrolyte uptake of 152.6% in the membranes without cross-linking structure in Fig. 5, lower electrolyte absorption was observed for membranes containing cross-linking structure. More cross-links resulted in denser network structure, and thus hindered the swelling of the polymer chain by liquid electrolyte. Higher electrolyte uptake was observed for the polymer membrane with higher concentration of F127, by comparison of the membranes with same concentration of PEGDA in Fig. 5. Actually, the tendency of the electrolyte uptake is similar to that of porosity. According to Saito and co-workers [31,32], there are two distinct steps for liquid electrolyte uptake in PVdF-based porous gel polymer membranes. Firstly, the liquid electrolyte occupied some pore spaces of the membrane. Then, those electrolytes in pores penetrated and swelled the polymer chains to form the gel. The electrolyte uptake was found to depend on the porosity of the polymer membranes in this work.

3.5. Mechanical properties

In view of the practical applications in lithium batteries, it is important for polymer electrolyte membranes to hold good mechanical strength and flexibility [15]. Figs. 6 and 7 exhibit the mechanical properties as a function of composition for PEGDA/PVdF/F127 polymer membranes. It is demonstrated from all data that the mechanical strength can be enhanced from 55.856 to 120.22 MPa with increasing content of PEGDA. Meanwhile, the strain at break decreased with the addition of PEGDA in blend membranes, suggesting that the flexibility reduced due to the high brittleness of cross-linked IPN structure.

The mechanical strength and flexibility is strongly dependent on the IPN structure formed by curing of the PEGDA oligomers rather than the porous structure. The PEGDA concentration was thus more important in controlling the mechanical strength of membranes.

3.6. Conductivity

Ionic conductivity is one of the most important properties of electrolyte membranes in their practical application. Fig. 8 illustrates the ionic conductivity of the PEGDA/PVdF/F127 polymer membranes containing 1.0 M LiClO$_4$/EC-PC electrolyte solu-
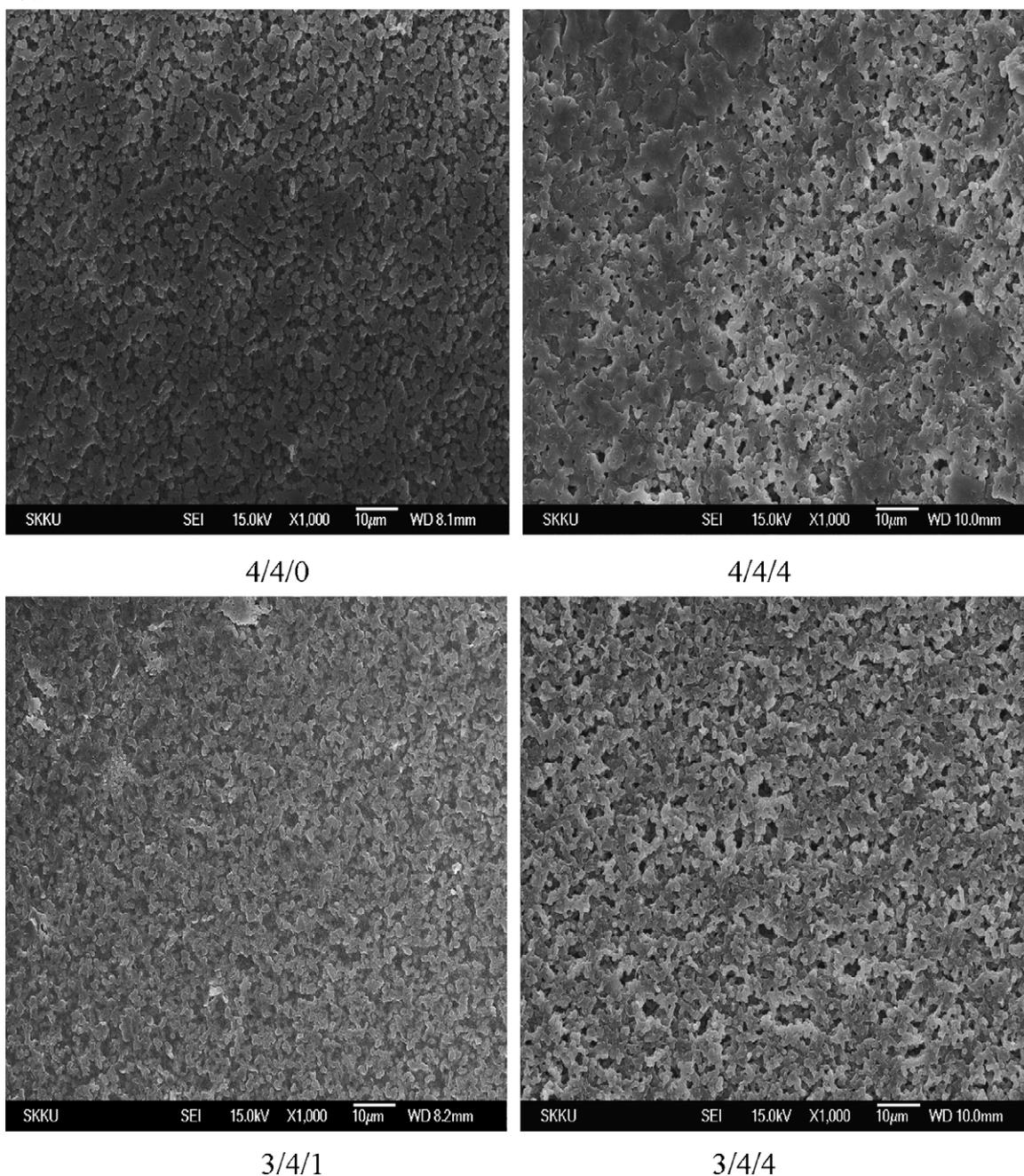
Fig. 4. Typical SEM micrographs of PEGDA/PVdF/F127 membranes: (a) surface (×1000) and (b) cross-section view (×5000).
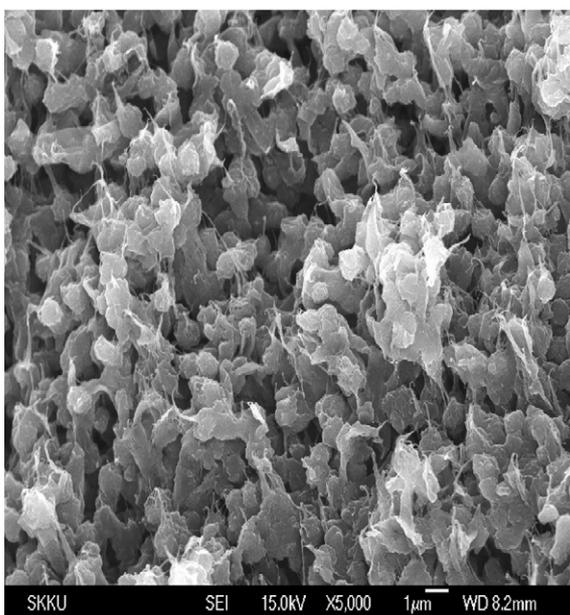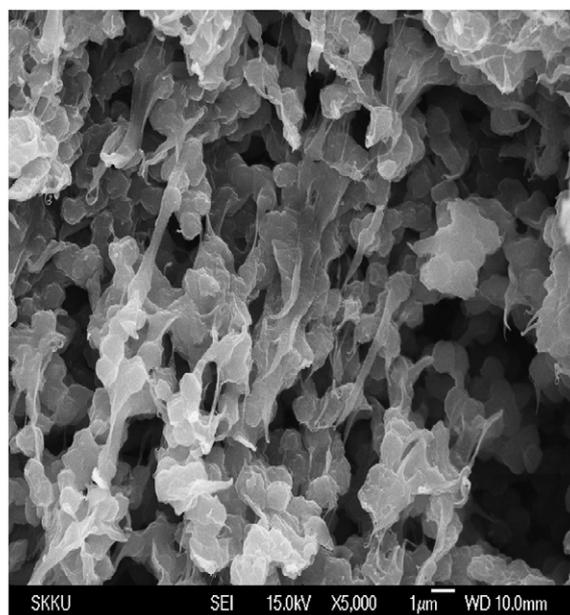
(b) Cross-section view:
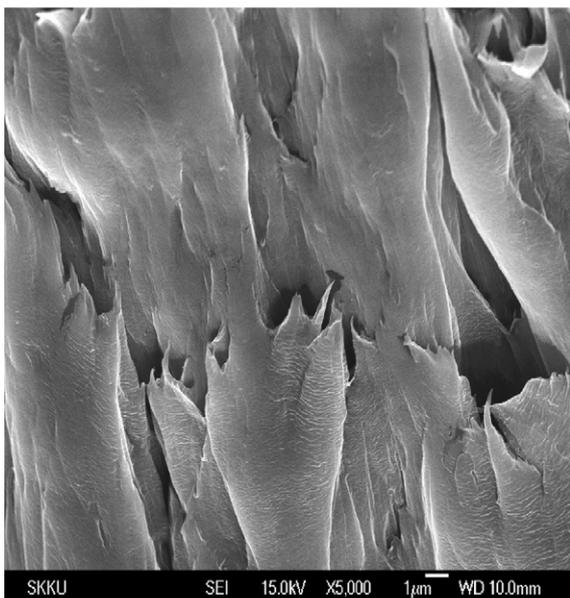
4/4/0
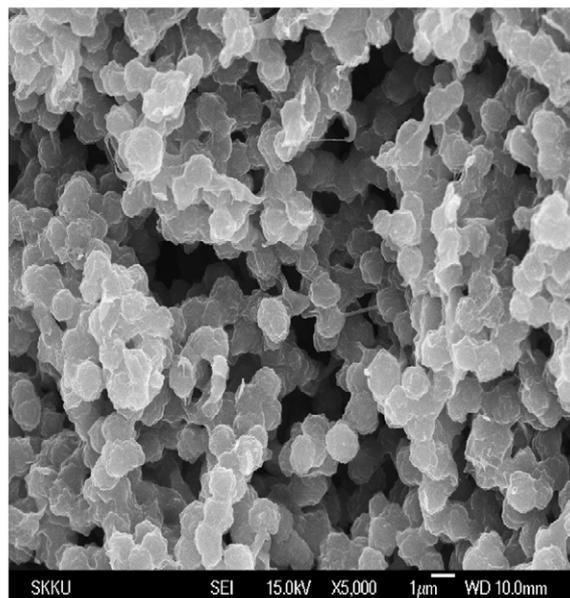
4/4/4

3/4/1

3/4/4

Fig. 4. (*Continued*).

tion. It is observed that the conductivity of all samples increases when temperature increases. The ionic conductivity of the GPE sample without cross-linked IPN structure is the highest among all compositions. In PEGDA/PVdF/F127 GPE systems, the ionic conductivity decreased with increasing content of PEGDA, as the chemically cross-linked structure retarded the conducting ionic mobility in the gel state [33]. Actually, the ionic conductivity was closely relative to porosity and electrolyte uptake. Higher porosity leads to higher electrolyte uptake and ionic conductivity of the membrane [34]. The room temperature conductivity of the PEGDA/PVdF/F127 GPEs is shown in Fig. 9. It is evident

that the PEGDA/PVdF/F127 electrolytes with the weight ratio of F127 above 2 have conductivity higher than 10^{-3} S cm^{-1}, which is high enough for practical applications in lithium batteries.

3.7. Electrochemical stability

The current–voltage responses of the PEGDA/PVdF/F127 polymer electrolytes containing 1.0 M LiClO$_4$/EC-PC at room temperature are shown in Fig. 10. Here, all PEGDA/PVdF/F127 GPE samples were prepared by immersing the dry polymer membranes into a 1.0 M LiClO$_4$-EC/PC (1:1) solution at room
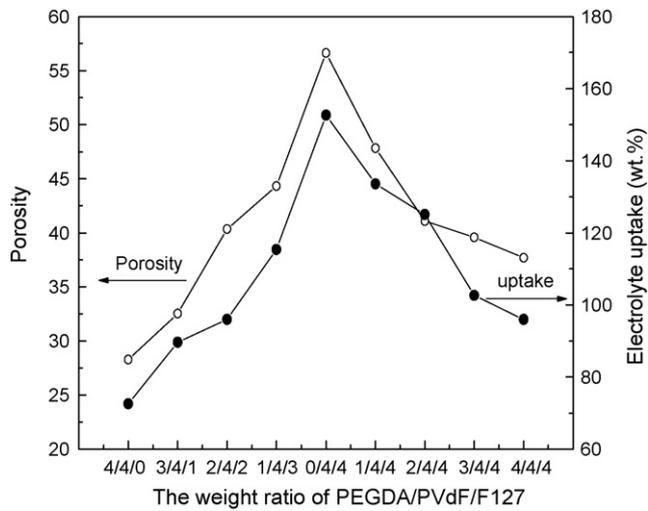
Fig. 5. Porosity and electrolyte uptake for the PEGDA/PVdF/F127 membranes with various weight ratios.
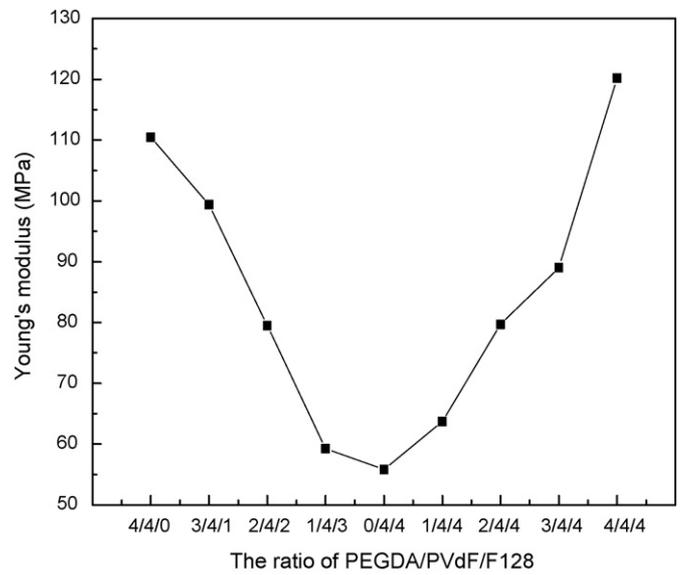

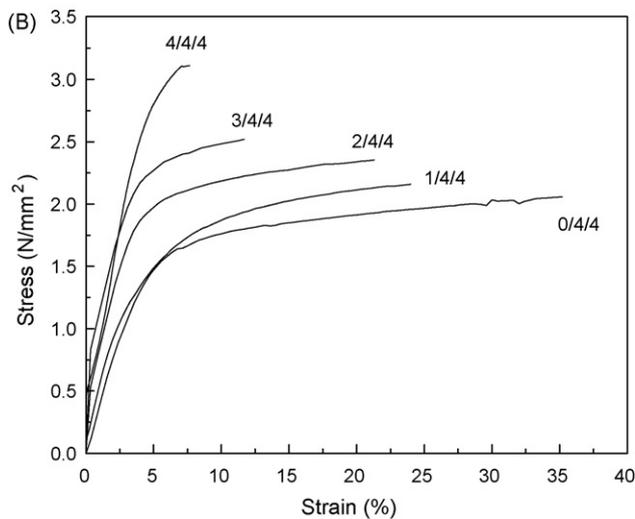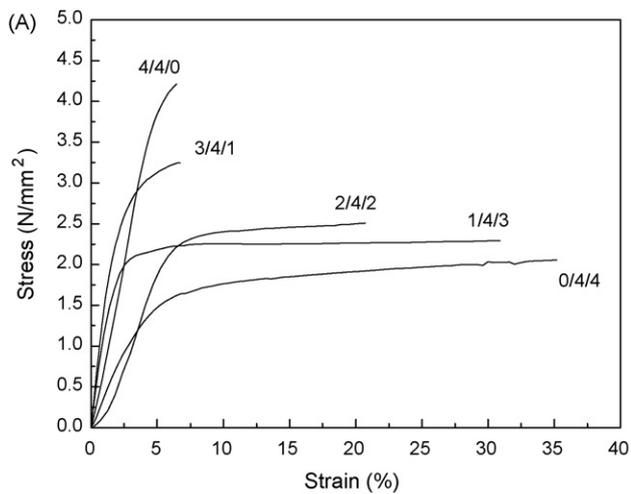Fig. 7. Variation of Young's modulus for the PEGDA/PVdF/F127 membranes.

Fig. 6. (A and B) Stress vs. strain curves for the PEGDA/PVdF/F127 membranes.
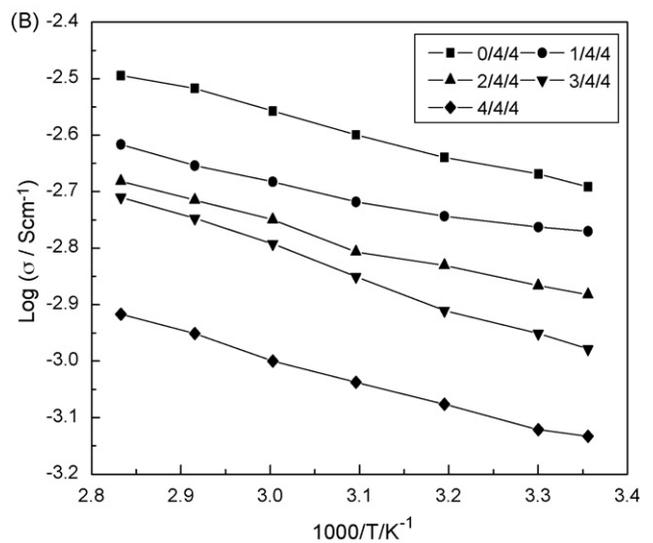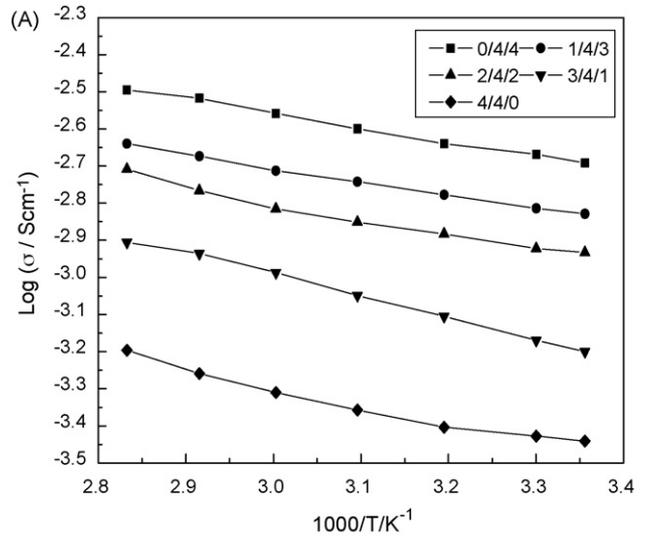

Fig. 8. (A and B) Variable temperature conductivities as a function of weight ratios for the PEGDA/PVdF/F127 polymer electrolytes.
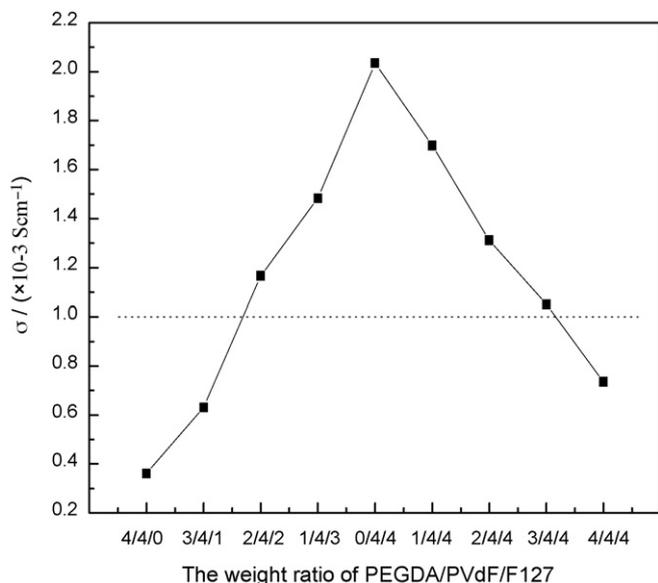
Fig. 9. Room temperature conductivity as a function of weight ratios for the PEGDA/PVdF/F127 membranes.

temperature for 24 h. The amount of electrolyte solution in each membrane can be found in Fig. 5. It is well known that the linear sweep voltammetry for a given electrolyte can be used to evaluate the electrochemical stability windows of the polymer electrolyte [35]. For all PEGDA/PVdF/F127 GPEs in this study, the current responses are negligible below ~4.5 V, indicating no decomposition of any components in this potential region. Above 4.5 V, the currents rise up rapidly. As the lithium rechargeable batteries generally operate between 3.0 and 4.5 V, the PEGDA/PVdF/F127 polymer electrolytes have suitable electrochemical stability for the practical application.
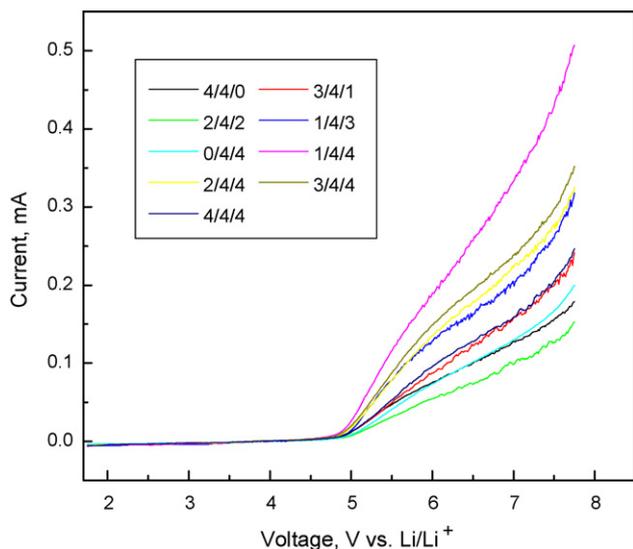

Fig. 10. Electrochemical stability windows of the PEGDA/PVdF/F127 polymer electrolyte membranes containing 1.0 M LiClO$_4$/EC-PC.

4. Conclusions

The cross-linked porous GPE systems comprised of PEGDA, PVdF, F127, EC, PC and LiClO$_4$ were developed. The porous structure in polymer matrix was achieved by a phase inversion method. The IR absorption spectra revealed that PEGDA was involved in the formation of IPN structure with PVdF since F127 was extracted by water during the fabrication of membranes. The unique endothermic peak in DSC trace and the corresponding crystallinity depression revealed that PVdF was compatible with PEGDA. The thermal stability of the blend membranes in TGA measurement was high enough to be applied in lithium batteries. SEM and porosity measurement indicated that the production of pores was established mostly by extraction of F127, but their size was by both F127 and PEGDA. The higher electrolyte uptake was observed in the membranes prepared at higher F127 concentration, as higher porosity was produced at higher concentration of F127. The analysis of mechanical properties proved that the higher strength and better flexibility of the blend membrane could be established by combination of PEGDA network, PVdF and F127. The ionic conductivity of the PEGDA/PVdF/F127 GPEs was strongly related to F127 content because of the porosity difference. At the weight ratios of F127 above 2, the room temperature conductivity was higher than 10^{-3} S cm^{-1}. The present GPEs assured electrochemical stability up to 4.5 V.

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