Thermal, mechanical, swelling, and electrochemical properties of poly(vinylidene fluoride)-co-hexafluoropropylene/poly(ethylene glycol) hybrid-type polymer electrolytes

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Abstract

Porous poly(vinylidene fluoride)-co-hexafluoropropylene/poly(ethylene glycol) (PVDF-HFP/PEG) hybrid-type polymer electrolytes are prepared by partially extracting the PEG molecules during the film-casting process. Thermal, mechanical, swelling, and electrochemical properties of the prepared polymer electrolytes are significantly affected by PEG content, as it changes the structure and size of the pores produced. The ion conductivity is dependent on the amount of electrolyte salt and liquid incorporated. The temperature dependence of ion conductivity is well described by Williams–Lewis–Ferry (WLF) equation. The polymer electrolyte systems are electrochemically stable up to about 5 V.
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1. Introduction

With the rapid growth of the electrical and electronic industries, the development of long-term, usable and lightweight batteries with high specific power and specific energy is essential [1–3]. The secondary lithium battery can possibly meet these requirements [1–3].

Secondary lithium batteries are divided into two types by the physical state of electrolyte. While the liquid electrolyte system uses an organic solvent as the electrolyte, the solid system employs a polymer [4,5]. The liquid electrolyte system raises the problem of electrochemical instability due to the repeated oxidation/restoration reaction at the interface between the electrode and electrolyte.

Solid polymer electrolyte system can be categorized into three types, namely pure polymer gel-type polymer, and hybrid-type polymer electrolyte. The pure polymer electrolyte system is generally prepared by mixing high molecular weight branched polyethers (e.g. polyether, polysiloxane, polyphosphazene) and plasticizing salts.

The gel-type polymer electrolyte is composed of a polymer host material and a liquid platicizer or solvent. This electrolyte system is mechanically stabilized by the host polymer, but the ion conduction is given by the ion-activity of the liquid electrolyte. To improve mechanical properties, cross-linked or thermoset materials are often incorporated into the polymer matrix. Gel-type polymer electrolytes generally have higher ion conductivity, but weaker mechanical strength, than pure polymer electrolytes at room temperature [6–8].

Hybrid-type polymer electrolytes are generally prepared by injecting organic liquid electrolytes into the small pores of the polymer matrices. These pores usually have below sub-micron diameters. Liquid electrolytes are prepared by blending organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), with salts [9]. The ion conductivity can be as high as 10^{-3} S cm^{-1} [2]. Organic solvent acts as a medium for real ion conduction through the polymer matrix. After long-time usage, the organic solvent can leak form polymer matrix, and it may cause a decrease in ion conductivity with deterioration of the lithium electrode and other components.

In the commercial preparation process of hybrid polymer electrolytes, the permeation rate of electrolyte solution into the polymer pores is of real importance, as it strongly affects the final production rate. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is one of the widely used polymer matrixes for hybrid-type polymer

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electrolytes as it has excellent mechanical and chemical stability [10]. Poly(ethylene glycol) (PEG) is a well known hydrophilic polymer and has been studied for long time for application as a solid or gel-type polymer electrolyte. In this research, PVDF-HFP/PEG, hybrid-type polymer electrolytes are prepared by blending PEG and PVDF-HFP. The thermal, mechanical, swelling and electrochemical properties of the polymer electrolytes are investigated.

2. Experimental

2.1. Preparation of PVDF/PEG composite membranes

Oligomeric PEG ($\bar{M}_n = 200\,\mathrm{g\,gmol^{-1}}$, Aldrich, Milwaukee, WI) and PVDF-HFP ($\bar{M}_n = 130,000\,\mathrm{g\,gmol^{-1}}$, Aldrich) were mixed with the surfactant polyoxyethylene sorbitan monooleate (Tween 80, Aldrich) in N,N-dimethylacetamide solvent (DMAC, Aldrich). The polymer solution was poured and coated on glass slide. The thickness was controlled with a doctor blade. Thin, solid, polymer films were produced by immersing the coated polymer solution in water at 70 °C. The coated film was dried in a vacuum oven at 70 °C for at least 24 h. As the PEG component in the polymer blend was slowly dissolved in water, pores were generated during the film-casting process [11–13]. Polymer composition, film-casting time, and temperature were the major parameters that affected pore size and porosity. Ethylene carbonate (Aldrich)and propylene carbonate (Aldrich) were used as plasticizers, and lithium tetrafluoroborate (LiBF$_4$, Aldrich) as electrolyte salt.

2.2. Chemical structure and porosity

The presence of PEG molecules before and after the film-casting process was investigated using Fourier transform infrared (FT-IR) spectroscopy (FT-IR660plus, Jasco, Japan). A scanning electron microscope (SEM, JSM 5410LV JEOL, Japan) was used to analyze the pore structure and size. The porosity, P, was determined by weighing samples with and without 1-butanol and using the following relationship [1].

$$P = \frac{m_a/\rho_a}{m_a/\rho_a + m_p/\rho_p} \tag{1}$$

where m_a is film weight after impregnation with 1-butanol, m_p the dried film weight, and ρ_a and ρ_p the densities of 1-butanol and dried film, respectively.

2.3. Thermal property

Thermogravimetric analyzer (TGA, TGA7, Perkin-Elmer, USA) was used to investigate the thermal stability of polymer electrolytes. Polymer samples (10 mg) were heated from 25 to 700 °C at a scanning rate of 10 °C min^{-1} in the presence of nitrogen gas.

2.4. Swelling experiment

The dynamic and equilibrium swelling properties of polymer films were measured by a gravimetric method. Polymer films with different porosities were swollen in solution composed of EC and PC (1:1 by weight). Samples were periodically weighed until no weight change was observed. The swelling ratio was defined by the weight ratio of the net liquid uptake to the dried polymer sample. The samples were rectangular with dimensions of 15 mm × 15 mm × 0.2 mm.

2.5. Mechanical strength

Tensile strength was measured at room temperature by means of a universal tensile machine (Instron model 5565, Lloyd) at a full-out velocity of 50 mm min^{-1}. The sample thickness was 100 μm. Measurements were performed five times for each sample, and the average value was calculated [14].

2.6. Cell fabrication and electrochemical properties

The ac impedance spectroscopy was used to measure the ion conductivity of the prepared polymer electrolytes. The apparatus was composed of a Solartron 1260 frequency response analyzer and a 287 electrochemical interface which were controlled by electrochemical impedance system software. The membrane electrode assembly (MEA) was fabricated as follow. The dried polymer membrane was immersed in EC/PC (1:1 by weight) solution with different amounts of LiBF$_4$. After at least 5 h, the wet membrane was removed from the electrolyte solution, and the excess electrolyte solution on the surface was wiped off with soft tissues. The polymer electrolyte composite was sandwiched between two stainless-steel electrodes for ionic conductivity measurements. All samples were prepared in a glove-box filled with argon gas. The test frequency ranged from 0.1 to 5 MHz. Each conductivity value was obtained from the intercept on the real axis of a typical Nyquist plot. The thickness of the sample was measured with a micrometer. Ion conductivity measurements were conducted from room temperature to 75 °C.

In order to examine the cyclic voltammetric behavior of polymer electrolytes, the electrolytes were sandwiched between stainless-steel working and lithium counter and reference electrodes. The area of the working electrode was 0.785 cm^2. A PAR 263A potentiostat/galvanostat with a PAR 263A universal program was used for these measurements a potential scanning rate of 100 mV s^{-1}.

3. Results and discussion

3.1. Chemical and physical structure of polymer films

The FT-IR spectra of homo PEG and the polymer electrolyte films prepared before and after the casting process
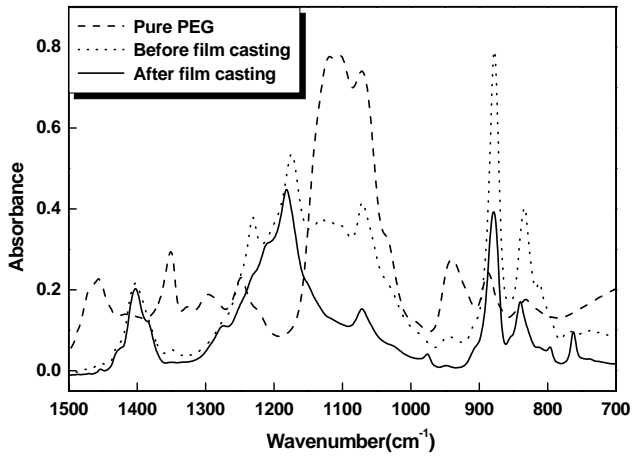
Fig. 1. FT-IR spectra of pure PBG and polymer electrolyte films prepared before and after casting process.
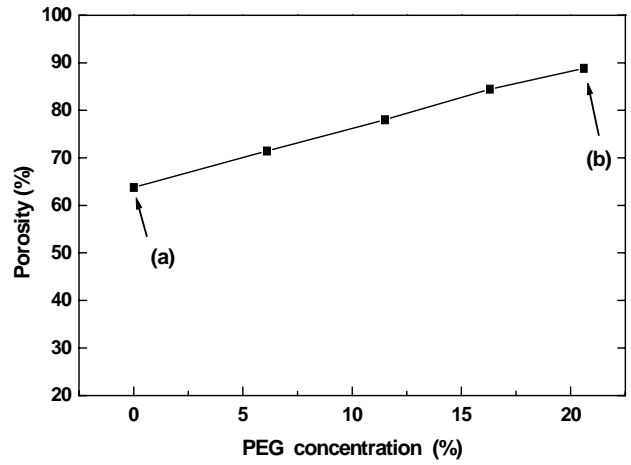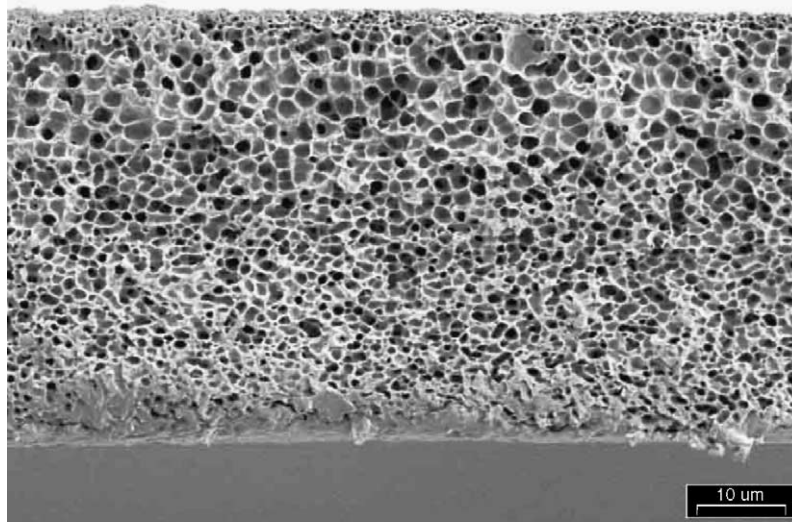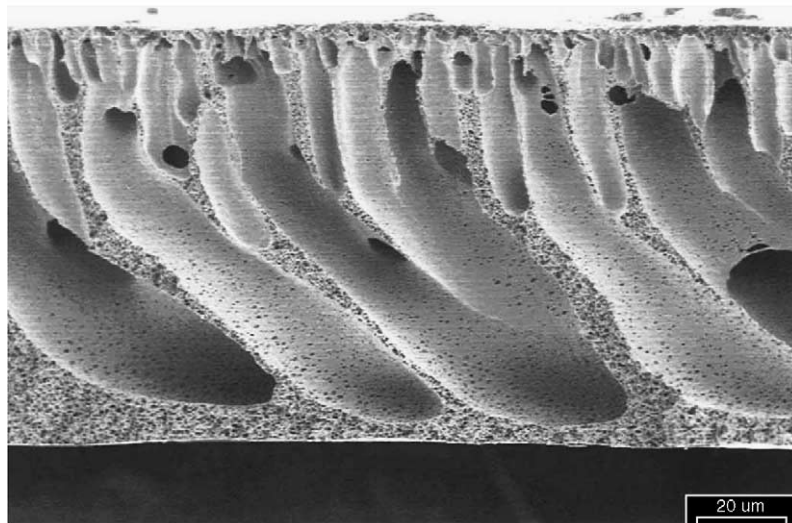

Fig. 2. Influence of PEG concentration on porosity of PVDF-HFP/PEG membranes prepared after immersion in water for 10 h.

(a)

(b)

Fig. 3. Scanning electron micrographs of porous PVDF-HFP/PEG membrane when incorporated PEG concentration is (a) 0 wt.% and (b) 20 wt.%.

are shown in Fig. 1. The peak around $1100\,cm^{-1}$ originates from the presence of PEG molecules. Its disappearance after film-casting indicates that the PEG molecules were extracted from PVDF-HFP polymer films and dissolved in water during the film-casting process.

The effect of PEG concentration on the porosity of polymer electrolytes was determined using Eq. (1) (Fig. 2). When the film-casting time was 10 h, the porosity linearly increased from 63 to 90% with increasing PEG concentration 0–20 wt.%. Scanning electron micrographs of the PVDF-HFP polymer matrix without and with (20 wt.%) PEG are shown in Fig. 3a and b, respectively. It is found that much larger pores are produced when PEG is incorporated in the polymer matrix. The structure and size of pores are not uniform due to the skin effect established during the film-casting process; relatively more pores are produced in the water-contacting surface than in the substrate (glass)-contacting surface.

The porosity increases with increasing casting time up to 7 h when the PEG concentration is fixed at 15 wt.% (see Fig. 4). After 7 h, no more porosity change is observed because all the PEG molecules have been extracted from the PVDF-HFP matrix.

3.2. Dynamic and equilibrium swelling behaviour

In order to increase the ion conductivity and production rate, more and faster impregnation of liquid electrolyte is required, and the polymer films must remain mechanically and chemically stable. The dynamic swelling behaviour of PVDF-HFP/PEG polymer electrolyte systems in EC/PC (1:1 by weight) solution at room temperature is shown in Fig. 5. The equilibrium swelling ratio Q increases from 2.1 to 5.7 with increasing PEG concentration from 0 to 16.3% as more and larger pores are produced. The swelling rate also increases with increasing PEG content for the same reason.

Fig. 5. Dynamic swelling behaviour of PVDF-HFP/PBG polymer electrolytes in EC/PC solution (1:1 by weight) at room temperature.

3.3. Thermal properties

Polymer electrolyte films must be thermally stable, as heat is generated when one uses battery. Fig. 6a and b shows TGA results for the polymer electrolyte systems with
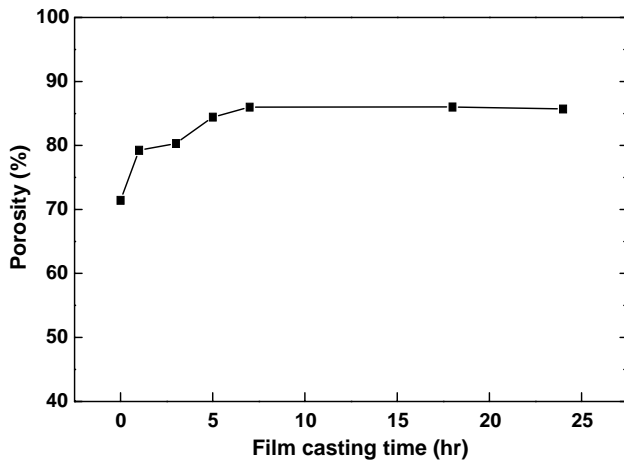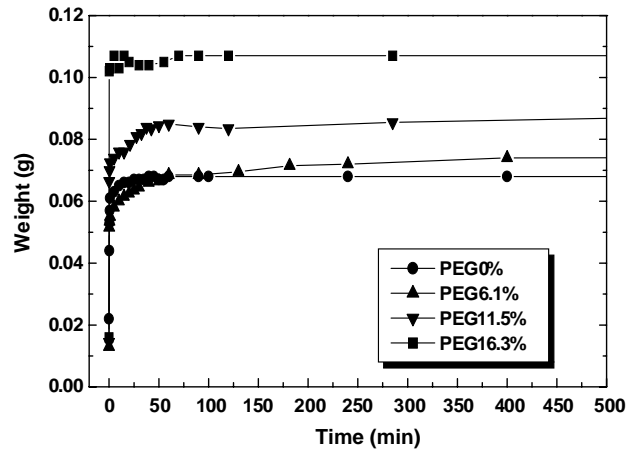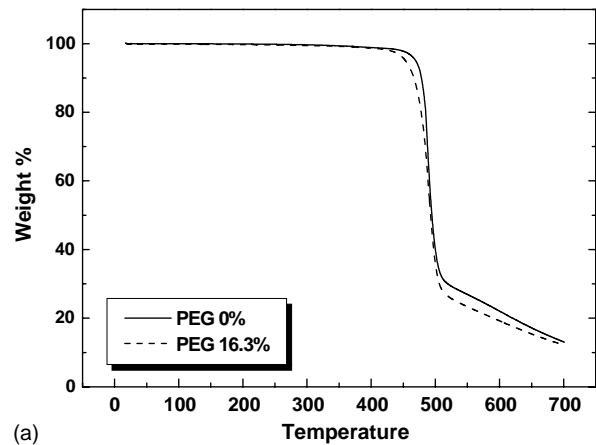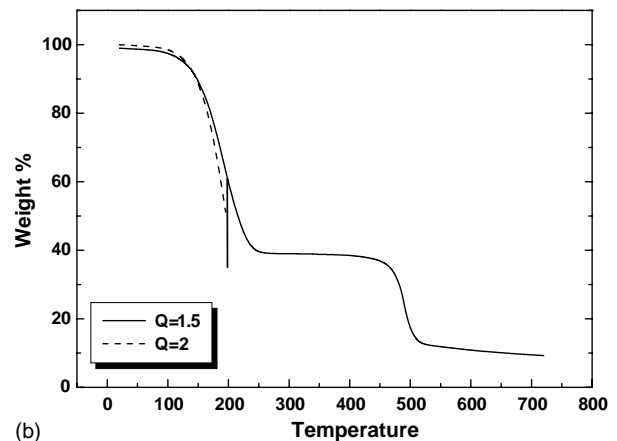

Fig. 4. Dependence of porosity of PVDF-HFP/PEG membrane on film-casting time when PEG concentration is 15 wt.%.

Fig. 6. TGA thermograms of PVDF-HFP/PEG films: (a) dried films with 0 and 16.3 wt.% PEG; (b) wet films with swelling ratio (Q) of 1.5 and 2.

and without electrolyte liquid, respectively. No significant difference was observed between the thermal behaviors of polymer electrolytes, as all PEG molecules were extracted during the sample preparation. Both systems were stable up to 450 °C. In Fig. 6b, the liquid electrolyte incorporated polymer films are shown to be stable up to 120 °C, above which the solvent evaporated.

3.4. Mechanical properties

The tensile properties of dried and solvent-incorporated polymer electrolyte samples with different PEG concentrations are presented in Fig. 7a and b, polymer electrolyte samples with different PEG concentrations are presented in Fig. 7a and b, respectively. The blending of more amount of PEG molecules resulted in lower ultimate tensile strength and modulus, as more and larger voids are produced in samples. The effect of PEG concentration on the mechanical strength of plasticized polymer films is similar to that of dried ones. Even though the modulus and tensile strength are lower than those of dried ones, the polymers are me-

chanically so stable that they can be used without breakage when stretched to 1.5 times their original length. Polymer electrolyte systems without PEG molecules can be stretched to even 3.5 times their initial length without failure.

3.5. Ion conductivity

The effect of salt concentration on the room temperature ion conductivity of the PVDF-HFP electrolyte system when the blended PEG content is 0–20 wt.% is shown in Fig. 8. An increasing swelling ratio (PEG concentration) increases the ion conductivity due to increasing molecular mobility. The room temperature conductivities of all the present polymer electrolyte systems are higher than 10^{-3} S cm^{-1} which is the typical ion conductivity of commercially available electrolyte. Incorporation of more electrolyte salts to a certain concentration, in this case 1 M, results in higher ionic conductivities. Beyond this concentration the ionic conduction decreases as the molecular motion is too restricted to attain high ion transport.

The temperature dependence of the ion conductivity of PVDF-HFP electrolyte system when the swelling ratios of the samples are 2.4, 3.6 and 4.5 is presented in Fig. 9. The salt concentration is fixed at 1 m, as the maximum ion conduction is achieved at this concentration (Fig. 8). Ion conductivity increases with increasing amounts of liquid electrolytes absorbed.

The temperature dependence of the ion conductivity of the polymer electrolyte systems at a fixed swelling ratio ($Q = 2.4$) when the Li salt concentration is 0.3, 0.66 and 1.0 M is given in Fig. 10. Higher ion conductivity is obtained at a higher salt concentration at all temperature. The ion conductivity linearly increases with temperature on a logarithmic scale (see Figs. 9 and 10).

The Williams–Lewis–Ferry (WLF) equation can be used to fit the temperature dependence of ion conductivity,
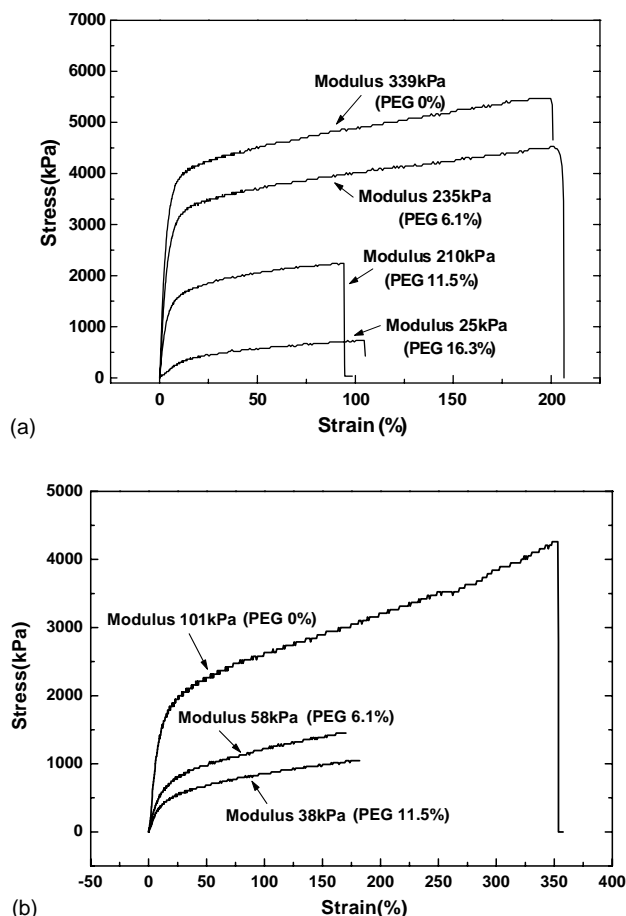

(a)

(b)

Fig. 7. Tensile behaviour of PVDF-HFP/PEG films: (a) dried film with 0, 6.1, 11.5 and 16.3 wt.% PEG; (b) wet films absorbing 1 M LiBF$_4$ electrolyte solution of EC and PC (1:1 by weight) to equilibrium. PEG concentration is 0, 6.1 and 11.5 wt.%.
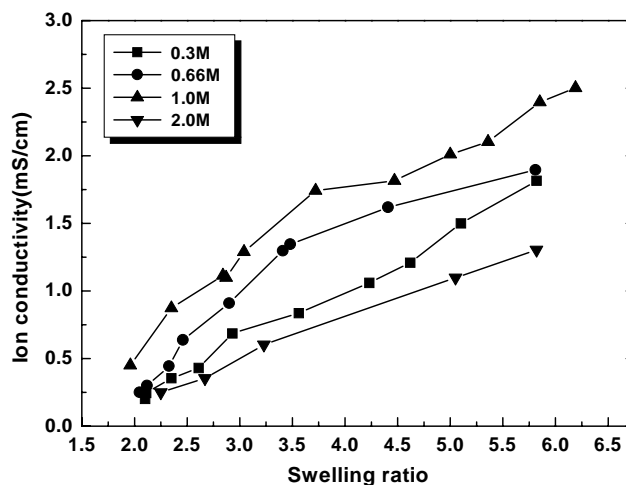

Fig. 8. Effect of ratio on ion conductivity of PVDF-HFP/PEG polymer electrolyte at room temperature when LiBF$_4$ concentration is 0.3, 0.66, 1.0 and 2.0 M.
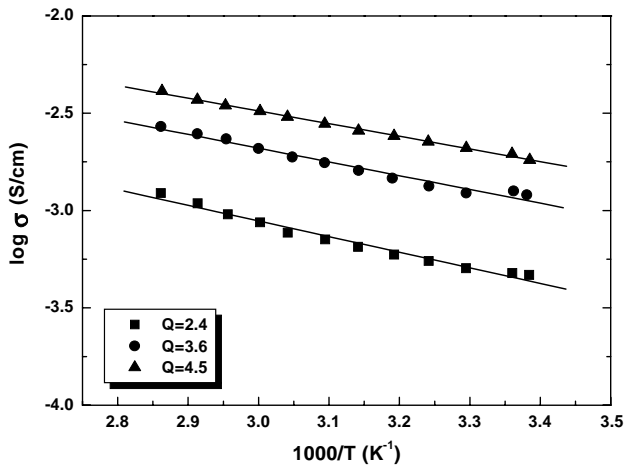
Fig. 9. Effect of temperature on ion conductivity of PVDF-HFP/PEG polymer electrolytes incorporation 1 M LiBF$_4$ solution composed of EC and PC (1:1 by weight). Swelling ratio (Q) is 2.4, 3.6, 4.5.
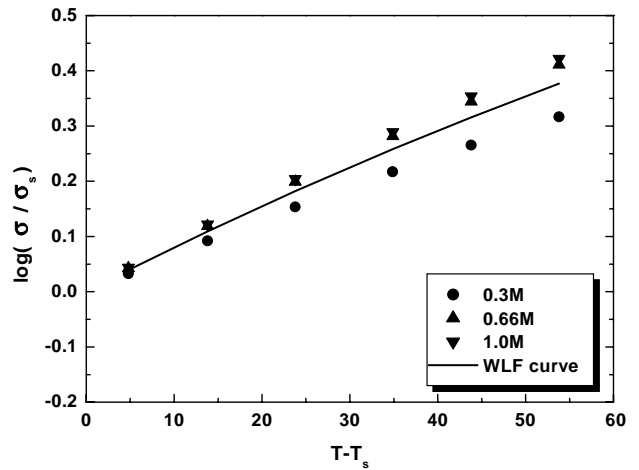

Fig. 12. Effect of temperature on ion conductivity of PVDF-HFP/PEG polymer electrolytes when experimental data referred to T_s. Solid symbols represent experimental data (solid curves) the WLF description.
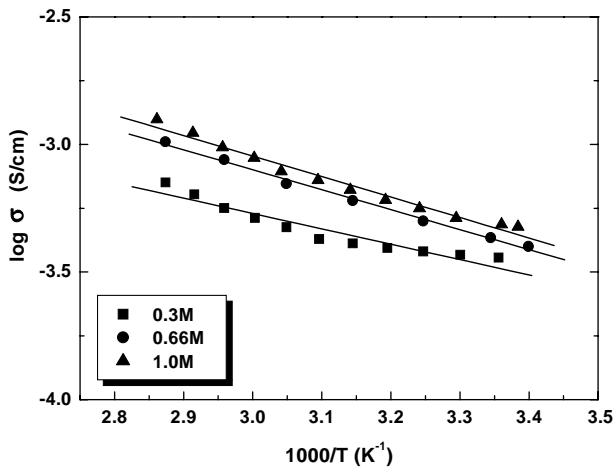

Fig. 10. Effect of temperature on ion conductivity of PVDF-HFP/PEG polymer electrolytes with swelling ratio of 2.4 LiBF$_4$ concentration is 0.3, 0.66, and 1.0 M.
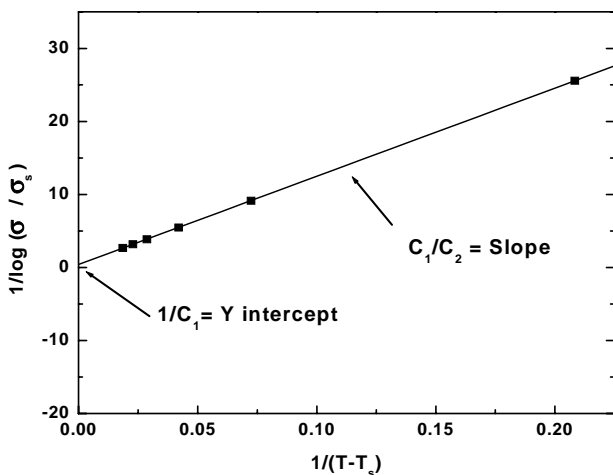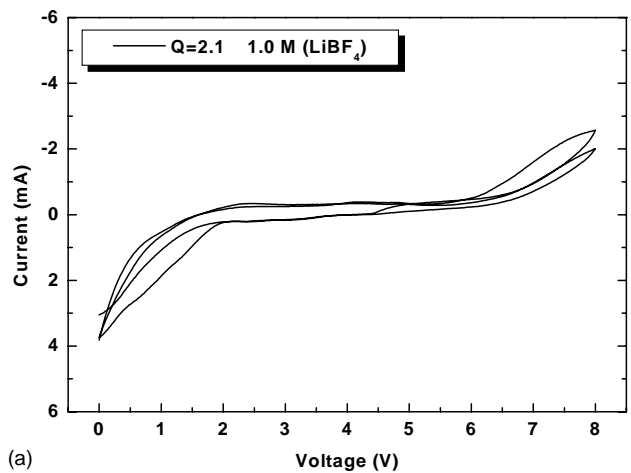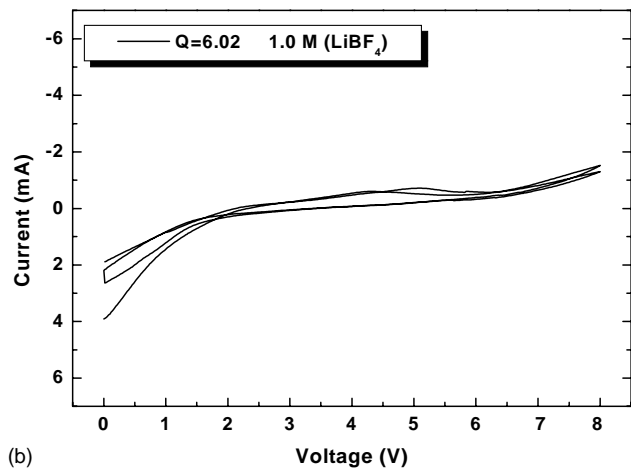

Fig. 11. Linear fit of experimental data relating $1/(\log(\sigma/\sigma_s))$ and $1/(T-T_s)$.

Fig. 13. Cyclic voltammograms for PVDF-HFP/PEG electrolyte systems absorbing 1 M LiBF$_4$ electrolyte solution composed of EC/PC (1:1 by weight) when swelling ratio (Q) is (a) 2.1 and (b) 6.0.

provided it is assumed that ions are transported by random motion of polymer segments and the ions can diffuse into free volume, i.e.

$$\log \frac{\sigma}{\sigma_s} = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)} \qquad (2)$$

T_s is the reference temperature, i.e. about 50 K above T_g.

The free volume constants C_1 and C_2 determined form the best fit of the experimental data by relating $l/(\log(\sigma/\sigma_s))$ and $l/(T - T_s)$ as shown in Fig. 11. In this relationship, the *y*-intercept is $1/C_1$ and slope is C_2/C_1. The values of C_1 and C_2 are found to be 2.43, and 294.3, respectively. The resulting temperature dependence of the ion conductivity after the data are shifted to the reference temperature is shown in Fig. 12. As all data points are aligned around a single curve, the temperature dependence of the observed ion conductivity is found to be well described by the WLF equation.

3.6. Electrochemical stability

The cyclic voltammograms for the polymer electrolytes are shown in Fig. 13. The electrochemical stability of the 1 M electrolyte composite for $Q = 2.1$ and 6.0 is shown in Fig. 13a and b, respectively. All polymer electrolyte systems were electrochemically stable up to about 5 V. A current rise is observed above 5 V, where oxidation of the polymer electrolyte systems takes place.

4. Conclusions

Porous PVDF-HFP polymer films are prepared by a film-casting process. The porosity is controlled by the film-casing time and PEG concentration. The polymer films have high thermal and mechanical stabilities, even when a large amount of liquid electrolyte is impregnated. The dynamic and equilibrium swelling behavior is controlled by the size and the amount of pores. The conductivities of PVDF-HFP electrolyte films increase with increasing PEG concentration, as more liquid electrolyte is possibly incorporated. When the amount of absorbed solvent is fixed, the maximum ion conductivity is obtained when the added Li salt concentration is 1 M. Addition of more Li salt restricts the molecular motion required to attain high ion transport. The dependence of the ion conductivity on temperature is linear an a logarithmic scale. When the experimental data are shifted to the reference temperature, they are well fitted by the WLF equation. The prepared PVDF-HFP polymer electrolyte composites are stable up to about 5 V.

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