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Poly(vinylidenefluoride)-hexafluoropropylene gel electrolytes based on N-(2-hydroxyethyl)-N-methyl morpholinium ionic liquids

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Abstract−Poly(vinylidenefluoride)-hexafluoropropylene (PVdF(HFP))-ionic liquid gel electrolytes were prepared by using ionic liquids based on N-(2-hydroxyethyl)-N-methyl morpholinium tetrafluoroborate and N-(2-hydroxyethyl)-N-methyl morpholinium hexafluorophosphate. TGA and FT-IR analyses confirmed that the solvent, N,N-dimethylacetamide (DMAC), used for mixing the PVdF(HFP) polymer with the ionic liquid, was almost totally removed during the gelling and drying processes. SEM photographs were taken of the surface structure of the PVdF(HFP)-ionic liquid in order to evaluate the morphology of the film's surface according to the mixing ratio, as well as the nature of the ionic liquid. The thermal behaviors of PVdF(HFP)-ionic liquid gels were observed to be similar to those of neat ionic liquids through a DSC analysis, and the compatibility between the polymer and the ionic liquid was investigated by an XRD analysis. The ionic conductivities of all the gels were 10^{-4}-10^{-8} S·cm^{-1} in a temperature range of 20 °C to 70 °C.

Key words: Ionic Liquid, Morpholinium Cation, Gel Polymer, PVdF(HFP), Ionic Conductivity

INTRODUCTION

Many types of polymer gel electrolytes have been investigated for use in diverse applications such as secondary batteries, electrochromic displays, sensors, and a variety of ionic devices [Yoshizawa et al., 2001], because of their potential for use as solid-state electrolytes. Generally, polymer electrolytes can be simply prepared from a plasticizing solvent consisting of a polar organic solvent and electrolyte salts in a polymer matrix. In particular, many polymer gel electrolytes based on ionic liquids (ILs) have been investigated to promote the safety and performance of systems using solid-state electrolyte. ILs used as electrolytes have recently been of great interest in research concerning electrochemical devices owing to the advantages of their use, such as very low melting points, non-volatility, thermal stability, non-flammability, and an extremely high ionic conductivity [Southall et al., 1996; Ohno et al., 2003; Kim et al., 2004a; Yeon et al., 2005a].

In an early inquiry into polymer gel electrolytes based on ILs, Carlin et al. attempted a reductive and oxidative intercalation of ions into graphite using an imidazolium cation and $AlCl_4^-$, BF_4^-, and PF_6^- anions in a two-electrode battery configuration. Additionally, Fuller et al. [Tiyapiboonchaiya et al., 2002; Capiglia et al., 2000] have developed ionic liquid-polymer gel electrolytes based on hydrophilic and hydrophobic imidazolium salts and poly(vinylidene fluoride)-hexafluoropropylene (PVdF(HFP)), and thereby realized a new gel electrolyte based on IL. However, in the imidazolium cation used, a problem in terms of the chemical and electrochemical stability caused by a possible reaction with C(2) carbon was reported [Fuller et al., 1998].

As one measure for solving the aforementioned problem, novel ILs based on the 1-(2-hydroxyethyl)-3-methyl-imidazolium cation and the N-(2-hydroxyethyl)-N-methyl-morpholinium cation were developed in a previous study [Yeon et al., 2005a; Cha et al., 2005]. Past investigations have revealed that RTILs based on a 1-(2-hydroxyethyl)-3-methyl-imidazolium cation with three different anions ($[BF_4]^-$, $[TFSI]^-$, and $[PF_6]^-$) possess the desired physical and electrochemical properties for electrolyte applications. In addition, a successful application of an IL-polymer gel electrolyte using an IL based on a 1-(2-hydroxyethyl)-3-methyl-imidazolium cation has been achieved [Yeon et al., 2005b].

However, room-temperature ionic liquids (RTILs) based on an N-(2-hydroxyethyl)-N-methyl-morpholinium cation with three different anions ($[BF_4]^-$, $[TFSI]^-$, and $[PF_6]^-$) show lower properties in their electrolyte characteristics compared to ILs based on an hydroxyethyl imidazolium cation [Yeon et al., 2005a]. Moreover, there are several limitations concerning its use as an electrolyte in various battery systems, as N-(2-hydroxyethyl)-N-methyl-morpholinium hexafluorophosphate is a solid state at room temperature owing to its high melting temperature. Nevertheless morpholinium cation-based ILs remain as potential electrolytes as a result of their uncomplicated synthesis and purification processes, improved ionic conductivity of the oxygen group in the cation, and their economical efficiency as a source of cations.

In this study, the structural surface morphologies, thermal properties, and ionic conductivities of PVdF(HFP)-IL gels based on prepared N-(2-hydroxyethyl)-N-methyl-morpholinium tetrafluoroborate ($[HEMMor][BF_4]$) and N-(2-hydroxyethyl)-N-methyl-morpholinium hexafluorophosphate ($[HEMMor][PF_6]$) are examined in order to evaluate their characteristics as polymer-IL gel electrolytes.

EXPERIMENTAL

1. Materials

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The chemicals (source, grade, and purification) used in the synthesis of ionic liquids were as follows: 4-methyl-morpholine (Aldrich, 99%; used without purification), 2-bromoethanol (Aldrich, 99.5%; used without purification), sodium tetrafluoroborate (Aldrich, 98%; used without purification), and potassium hexafluorophosphate (Aldrich, 98%; used without purification). Solvents used were deionized water from a Millipore purification unit, dichloromethane (Merck, 99.9%), acetone (Merck, 99.9%), and acetonitrile (Merck, 99.9%).

Poly(vinylidenefluoride)-hexafluoropropylene copolymer (PVdF (HFP), Atofina, Kynar flex 2801-00, Mw=477,000) was used as received. N,N-dimethylacetamide (Aldrich; 99.9% HPLC grade, used without purification) was used as the solvent for mixing the PVdF(HFP) polymer and the prepared ionic liquids.

2. Preparation of Ionic Liquids

The two ionic liquids used in this study were synthesized along with their corresponding chloride or bromide precursors. Fig. 1 shows the synthesis scheme of the two prepared ionic liquids.

2-1. N-(2-hydroxyethyl)-N-methyl-morpholinium Bromide [HEMMor] [Br]

1-Methyl-Morpholine (0.3 mol) was reacted with an excess of hydroxyethyl bromide (2-bromoethanol, 0.35 mol) in a round-bottom flask in a nitrogen atmosphere (80-90 °C, 48 hr), using 200 mL of acetonirile as a solvent, to produce N-(2-hydroxyethyl)-N-methyl morpholinium halide ([HEMMor][Br]). This molten salt of white crystalline solids was obtained by recrystallization at room temperature (52 g, yield 77%) with acetone.

2-2. N-(2-hydroxyethyl)-N-methyl-morpholinium Tetrafluoroborate [HEMMor][BF_4]

The N-(2-hydroxyethyl)-N-methyl-morpholinium bromide was reacted with an equimolar amount of sodium tetrafluoroborate in acetone (25 °C, for 24 hr), which resulted in the formation of the ionic liquid [HEMMor][BF_4]. The residual of sodium bromide in this ionic liquid was removed by low temperature filtration using celite [Yeon et al., 2005a]. The organic liquid obtained from the filtration was tested for residual bromide salt with a concentrated $AgNO_3$ solution, and a slight precipitation of AgCl was confirmed visually.

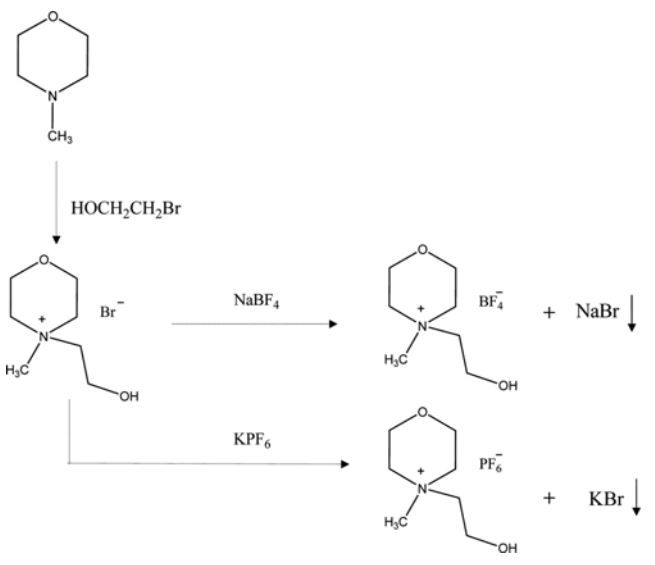


Fig. 1. Synthesis of ionic liquids, [HEMMor][BF_4] and [HEMMor] [PF_6].

2-3. N-(2-hydroxyethyl)-N-methyl-morpholinium Hexafluorophosphate [HEMMor][PF_6]

This ionic liquid was synthesized in the same manner as was [HEMMor][BF_4]; [HEMMor][Br] and potassium hexafluorophosphate were used to form the N-(2-hydroxyethyl)-N-methyl-morpholinium hexafluorophosphate, Acetone was used as a solvent. The residual of sodium bromide in this ionic liquid was removed by low temperature filtration using celite. The $AgNO_3$ test was conducted in the same manner as the [HEMMor][BF_4].

3. Preparation of PVdF(HFP) - Ionic Liquid (ILs) Gel

The polymer-ionic liquid gel films were prepared according to procedures outlined in previously published literature [Kim et al., 2004b]. Following this example, 0.528 g PVdF(HFP), 0.587 g ionic liquid, and 2.5 mL DMAC (N,N-dimethylacetamide) were mixed under ambient conditions to produce a transparent solution of a 47.4 wt% of PVdF(HFP) polymer, in which two kinds of ionic liquids, [HEMMor][BF_4] and [HEMMor][PF_6], were used. The final gel samples of the two prepared ILs were made by various polymer concentrations. To facilitate the miscibility of the polymer on the ionic liquids, a DMAC with polar properties was chosen in spite of the high boiling temperature of nearly 165 °C. The transparent solution gelled in 5 min when deposited onto glass Petri dishes that were placed on a hot plate and preheated to approximately 80 °C. To remove any residual solvent (i.e., DMAC) in the gels, the films were placed in ambient air for 24 hr. Table 1 shows the film thickness and appearance according to the various mixing ratios of the PVDF(HFP) and ILs at room temperature.

4. Thermal Measurement (DSC and TGA)

The differential scanning (DSC Q1000 V7.0 Build 244) data were obtained in a sealed aluminum pan with a cooling and heating rate of 10 °C/min under a He purge, at 50 $cm^3 \cdot min^{-1}$. Thermogravimetric analysis (TGA Q500 V5.0 Build 164) data were taken in air and at a heating rate of $10 \cdot min^{-1}$ under a N_2 purge, at 100 $cm^3 \cdot min^{-1}$.

5. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra were recorded under a nitrogen atmosphere on a JASCO 470 PLUS spectrometer, covering a range of 400 to 4,000 cm^{-1}.

6. Scanning Electron Micrographs (SEM)

Scanning electron microscopy (SEM) was performed on an XL-

Table 1. Mixing ratio and film thickness of PVdF(HFP)-ionic liquid gels

Ionic liquid	PVdF(HFP) mass ratio (wt%)	Film thickness (mm)	Appearance
[HEMMor][BF_4]	0	-	viscous liquid
	33.3	0.27	white rubbery film
	47.4	0.125	white rubbery film
	66.7	0.11	opaque film
[HEMMor][PF_6]	0	-	white solid
	33.3	0.12	white film
	47.4	0.145	white rubbery film
	66.7	0.07	opaque rubbery film

30S FEG (Philips Co.) device. The samples were sputter-coated with approximately 10 nm of gold before analysis.

7. X-Ray Diffraction (XRD)

XRD patterns were obtained from wide-angle X-ray diffractometry (model D/MAX IIIB; Rigaku), with a scintillation counter detector using CuKα - radiation as a source at a generator voltage of 40 kV and a generator current of 40 mA. The scanning speed and the step were 2°/min and 0.02°, respectively. Angles (2θ) ranged from 2° to 60°.

8. Ionic Conductivity

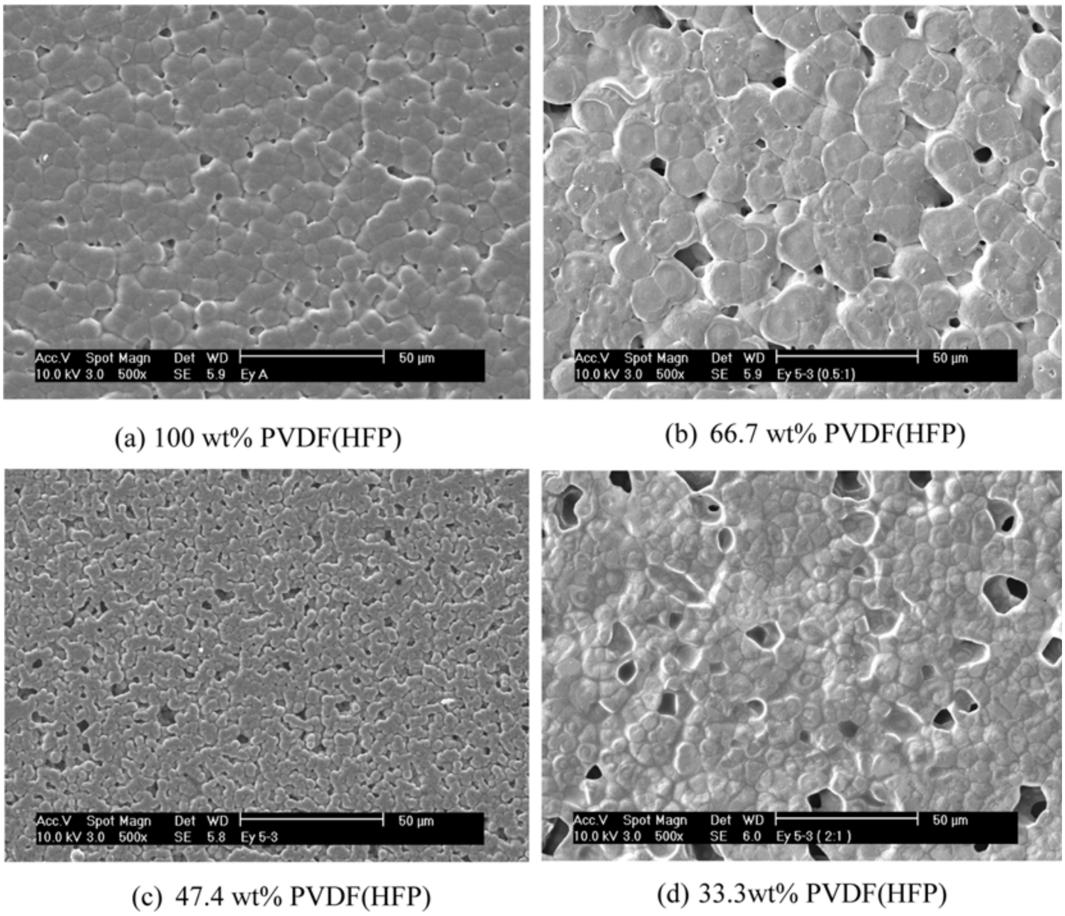
The specific ionic conductivity was measured with a Solartron 1260A frequency response analyzer (FRA). This apparatus was connected to a sealed cell containing a pair of SUS plate electrodes. To take the temperature dependency into account, this cell was placed in an oven well with a controlled temperature.

RESULTS AND DISCUSSION

1. Morphologies of the PVdF(HFP)-Ionic Liquid Gel Films

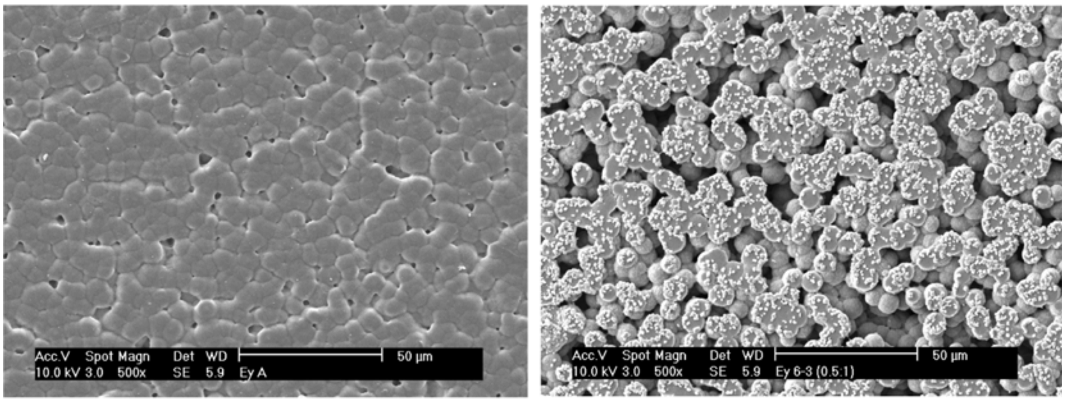
The morphology of the prepared PVdF(HFP)-ionic liquid gels was investigated by scanning electron micrographs (Fig. 2 and 3). The percent weight (wt%) ratios of polymer to ionic liquid were (a) 0 : 100, (b) 66.7 : 33.3, (c) 47.4 : 52.6, and (d) 33.3 : 66.7, respectively. The 100 wt% PVdF(HFP) gel made solely from the PVdF (HFP) polymer was a freestanding, translucent film and showed a morphology composed of many spherical grains. In the case of the PVdF(HFP)-[HEMMor][BF$_4$] gel (Fig. 2), the 66.7 wt% PVdF(HFP) film in [HEMMor][PF$_6$] appeared to have a larger grain size (~15.625 μm) than both that observed in the 100 wt% PVdF(HFP) film (~9.375 μm), and in the 47.4 wt% PVdF(HFP) film. In the 47.4 wt% PVdF (HFP) film, the weight ratio of polymer to ionic liquid was 1 : 1.1, and showed a porous morphology having a smaller grain size (3.125 μm) than either (a) or (b) without the phase separation phenomenon. The 33.3 wt% PVdF(HFP) film, which had a greater amount of [HEMMor][BF$_4$] than the PVdF(HFP) polymer, displayed a surface morphology consisting of multi-sized grains in a boundary, with large cavities.

In the case of the PVdF(HFP)-[HEMMor][PF$_6$] gels, the film with 66.7 wt% PVdF(HFP), unlike the 66.7 wt% PVdF(HFP)-[HEMMor] [BF$_4$] film, exhibited a small grain size (9.375 μm). However, in film (c), which had nearly an equivalent PVdF(HFP) to [HEMMor] [PF$_6$] ratio, there was a sharp decrease in grain size (0.3125 μm), and some grains were aggregated sparsely. In the two films, (b) and (c), in terms of mechanical strength, it was found that film (b) was weaker and more fragile than the film (c), which had a small grain size and a packed structure. However, in the 33.3 wt% PVdF(HFP) film of the [HEMIm][PF$_6$] system, the grain disappeared, and the surface became more porous. This surface abundance in cavities may have been caused by the low compatibility between the [HEMMor] [PF$_6$] and the PVdF(HFP) polymer owing to the large amount of

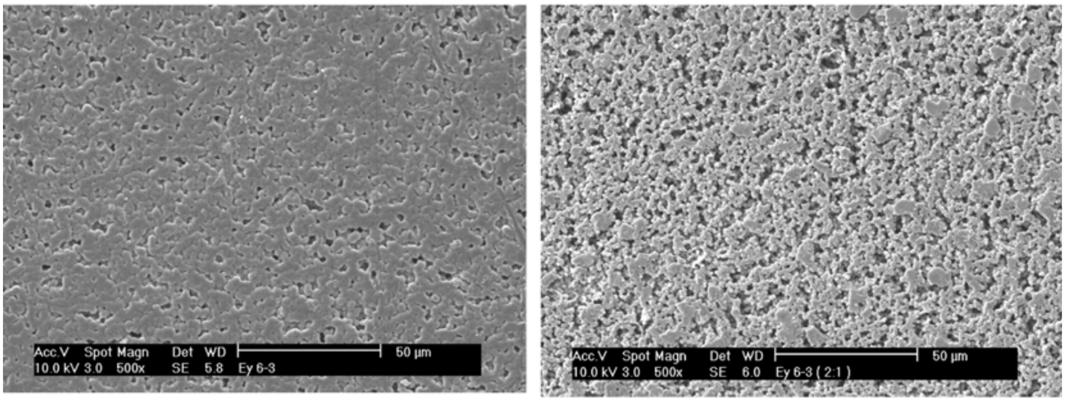


(a) 100 wt% PVDF(HFP)
(b) 66.7 wt% PVDF(HFP)
(c) 47.4 wt% PVDF(HFP)
(d) 33.3wt% PVDF(HFP)

Fig. 2. Scanning electron micrographs ((a), (b), (c), and (d): ×500) of PVdF(HFP) gels in [HEMMor][BF$_4$] system.



(a) 100 wt% PVDF(HFP) (b) 66.7 wt% PVDF(HFP)



(c) 47.4 wt% PVDF(HFP) (d) 33.3 wt% PVDF(HFP)

Fig. 3. Scanning electron micrographs ((a), (b), (c), and (d): ×500) of PVdF(HFP) gels in [HEMMor][PF_6] system.

solid [HEMMor][PF_6]. The resulting structure of the PVdF(HFP) gels (including [HEMMor][PF_6]) indicates that, unlike [HEMMor][BF_4]-PVdF(HFP) films made by [HEMMor][BF_4] of a liquid state at room temperature, as the amount of [HEMMor][PF_6] of solid state at room temperature is increased it becomes difficult to form a stable and rubbery film because of the low miscibility with solid [HEMMor][PF_6].

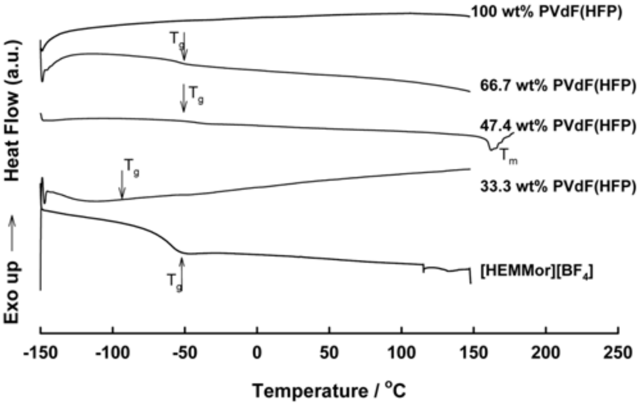


Fig. 4. Differential scanning calorimeter thermograms of PVdF (HFP) powder and PVdF(HFP)-[HEMMor][BF_4] gels on warming at 10 °C·min^{-1} (all data: second run state).

2. Thermal Properties of PVdF(HFP)-Ionic Liquid Gels

In order to study the thermal behaviors and stabilities of PVdF (HFP)-ionic liquid gels, the DSC and TGA were investigated. Figs. 4 and 5 show the DSC data for the variance of the PVdF(HFP) composition in the PVdF(HFP)-[HEMMor][BF_4] and PVdF(HFP)-[HEMMor] [PF_6] gels, respectively. The neat [HEMMor][BF_4] showed a liquid state at room temperature, a glass transition temperature (T_g) of −59 °C, and did not melt at temperature ranging from −150 °C to 150 °C [Yeon et al., 2005a]. The thermal behaviors of 33.3 wt%, 47.4 wt%, and 66.7 wt% PVdF(HFP) in the [HEMMor][BF_4] system were similar with those of the neat [HEMMor][BF_4]. While the T_g of pure [HEMMor][BF_4] was −59 °C, the T_g of the 33.3 wt% PVdF(HFP) film decreased to −74.13 °C. However, as in 47.4 wt% PVdF(HFP) film, the T_g again increased to −42.08 °C. The changes in the T_g were not consistent with a variance in the PVdF(HFP) amount. On the other hand, when the amount of [HEMMor][BF_4] was decreased, the magnitude of the endothermic peak on T_g tended to decrease: consequently, it disappeared completely in the 100 wt% PVdF(HFP) film. In order to reconfirm the thermal behavior of the 100 wt% PVdF(HFP) film, the DSC data of the neat PVdF(HFP) powder is shown in Fig. 4 in a temperature range from −150 °C to 200 °C. The final melting point of the PVdF(HFP) polymer powder was observed to be 160.4 °C.

In the case of the PVdF(HFP)-[HEMMor][PF_6] system in Fig. 5, the neat [HEMMor][PF_6] exhibits multiple thermal transitions, pos-

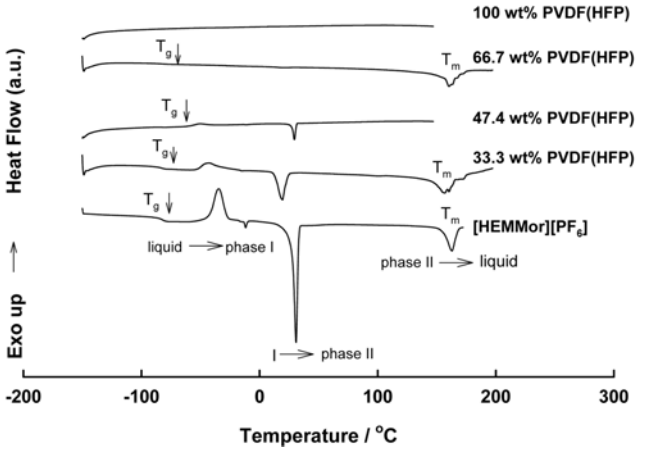


Fig. 5. Differential scanning calorimeter thermograms of PVdF (HFP)-[HEMMor][PF$_6$] gels on warming at 10 °C·min^{-1} (all data: second run state).

sessing a richer crystalline behavior than the neat [HEMMor][BF$_4$] described here. In detail, the glass transition temperature was observed to be approximately −74 °C, and one exothermic peak appears at approximately −30 °C that represents the crystallization behavior from a supercooled liquid to a low-temperature stable solid phase (phase I). Phase I then transformed into a higher temperature solid phase (phase II) at 30 °C, exhibiting a final melting point of 160.4 °C [Yeon et al., 2005a]. However, more pertinent research may be needed in order to identify the small endothermic peak at −10 °C, whether it represents the essential thermal quality or the existence of contaminants.

As indicated in Fig. 4, the thermal behaviors of the small PVdF (HFP) component films (33.3 wt% and 47.4 wt% PVdF(HFP) films were similar to those of the neat [HEMMor][PF$_6$]. In the 66.7 wt% PVdF(HFP) film, the exotherm and endotherm peaks, except for the melting point and T$_g$, nearly disappeared. In the 100 wt% PVdF (HFP) film, however, all of the thermal peaks disappeared. In all of the prepared films except the 100 wt% PVdF(HFP) film, T$_g$ was measured in the vicinity of −80 °C, according to the variation of the PVdF(HFP) component.

The TGA data of Fig. 6 show the thermal stabilities representative of two films, the 47.4 wt% PVdF(HFP)-[HEMMor][BF$_4$] and 47.4 wt% PVdF(HFP)-[HEMMor][PF$_6$] films. In a past investigation [Yeon et al., 2005a] by the authors, it was reported from a TGA experiment that the neat [HEMMor][BF$_4$] and [HEMMor][PF$_6$] were stable around 300 °C. At the same time, the two films, PVdF(HFP)-[HEMIm][BF$_4$] and PVdF(HFP)-[HEMIm][PF$_6$], started to decompose at the original temperature of the neat ionic liquid. Unlike pure ionic liquids such as [HEMMor][BF$_4$] and [HEMMor][PF$_6$], the gel mixtures of 47.4 wt% PVDF(HPF)+[HEMMor][BF$_4$] and 47.4 wt% PVDF(HPF)+[HEMMor][PF$_6$] showed weight loss of 70% at 400 K and 450 K, respectively, due to the mixed compounds of polymer and pure ionic liquid. A TGA analysis was conducted on all of the prepared films in various concentrations, and the same results were observed in all samples. Therefore, it can be asserted that the prepared films are composed of only a polymer and an ionic liquid with little residual solvent.

3. FTIR Study

Infrared spectroscopy measurements were conducted in order to identify the residual solvent of DMAC in the prepared gels by observing the spectra showing a band originating from vibrations of the amide group (O=C-N) in the DMAC. Fig. 7 shows the FTIR data of the 47.4 wt% PVDF(HFP) films, including both [HEMMor][BF$_4$] and [HEMMor][PF$_6$]. Typically, the relevant band of the amide functional group appears from 1,690 cm^{-1} to 1,650 cm^{-1} [Ege, S., third edition]. Because the FTIR data showed that the band of the amide functional group was not observed in their vibrational frequency bands, it was inferred that the residual solvents were almost totally removed from both films. In all samples ranging from 1,690 cm^{-1} to 1,650 cm^{-1}, the bands of the amide functional group were not detected.

4. XRD Study

Fig. 8(a) shows the XRD pattern of the 100 wt% PVdF(HFP) film. There were four peaks that appear at 2θ=8.753°, 18.368°, 19.980°, and 39.041°. With the addition of [HEMMor][BF$_4$] into PVdF(HFP), these peaks shifted slightly toward the high 2θ. At the same time, it was found that as the area of 2θ=19.980° is increased according to an increase in the amount of [HEMMor][BF$_4$], the crystal mor-

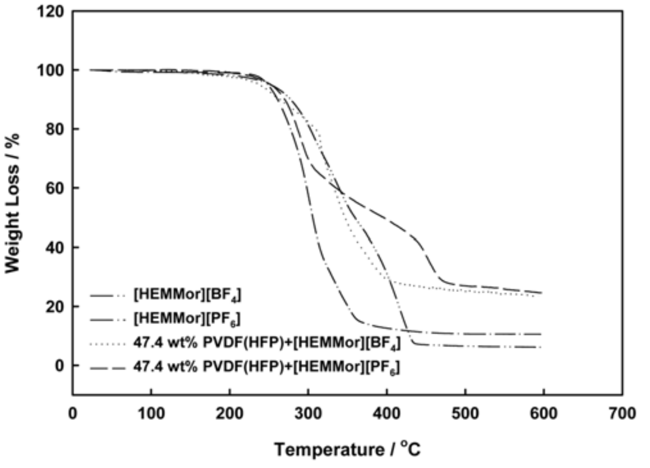


Fig. 6. TGA data of neat ionic liquids and of 47.4 wt% PVdF(HFP)-ionic liquid gels based on [HEMMor][BF$_4$] and [HEMMor][PF$_6$].

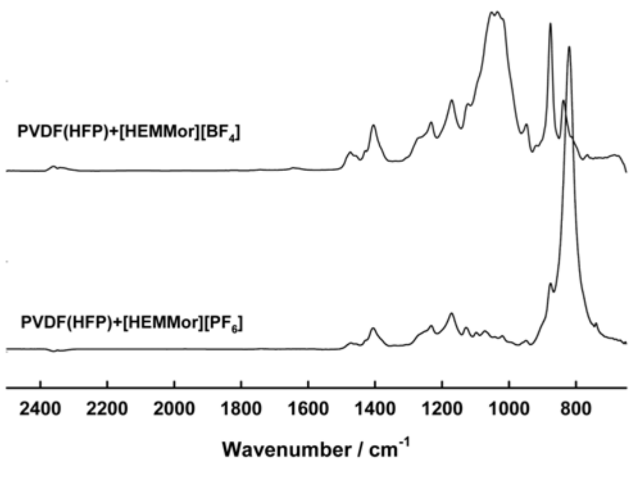


Fig. 7. FTIR of 47.4 wt%PVdF(HFP)-ionic liquid gels based on [HEMMor][BF$_4$] and [HEMMor][PF$_6$].

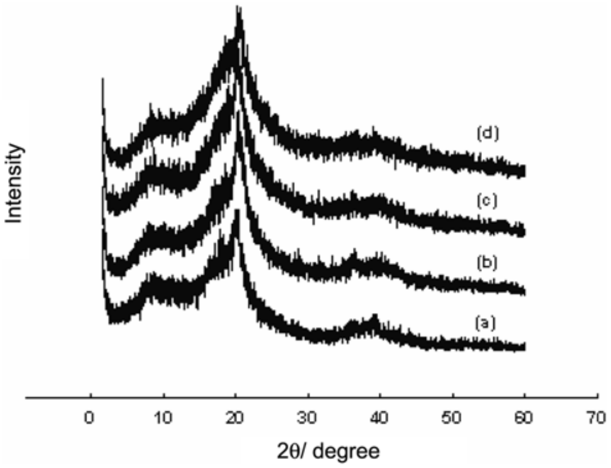


Fig. 8. XRD patterns of PVdV(HFP)-[HEMMor][BF_4] gels: (a) 100 wt% PVdF(HFP), (b) 66.7 wt% PVdF(HFP), (c) 47.4 wt% PVdF-(HFP), and (d) 33.3 wt% PVdF(HFP).

phology around the peak tends to be amorphous, indicating that the d-spacing around $2\theta=20^\circ$ of the 66.7 wt% PVdF(HFP)-[HEMMor][BF_4] gel, and the 47.4 wt% PVdF(HFP)-[HEMMor][BF_4] gel increased from 4.3754 Å to 4.3882 Å, respectively. Additionally, it was shown that the crystal peak around $2\theta=18.368^\circ$ of the 100 wt% PVdF(HFP) gel gradually disappeared with a greater addition of [HEMIm][BF_4] after this peak was shifted to $2\theta=17.663^\circ$ in the 66.7 wt% PVdF(HFP) film. From these results, it is noted that PVdF (HFP) and [HEMIm][BF_4] possess good reciprocal miscibility to facilitate the forming of a stable film. In addition, a similar trend can be predicted from the result in which the d-spacing around $2\theta=8^\circ$ of the 100 wt% PVdF(HFP) film and the 33.3 wt% PVdF(HFP)-[HEMIm][BF_4] film is increased from 10.0946 Å to 11.1802 Å, respectively.

Fig. 9 shows the XRD pattern of the PVdF(HFP)-[HEMMor][PF_6] gels. In this figure, the XRD pattern of the neat [HEMMor][PF_6] (b), which has a solid state at room temperature, was compared with that of the 44.7 wt% PVdF(HFP) film (c). In the neat [HEMMor][PF_6], a strong crystalline peak was shown at $2\theta=18.659^\circ$. Conversely, in 47.4 wt% PVdF(HFP) film, this peak shifted to $2\theta=18.682^\circ$ with a sharp decrease in the peak area. Therefore, it is expected that the reduction of crystallization is considerably achieved during the gelling process between the polymer PVdF(HFP) and the solid [HEMMor][PF_6].

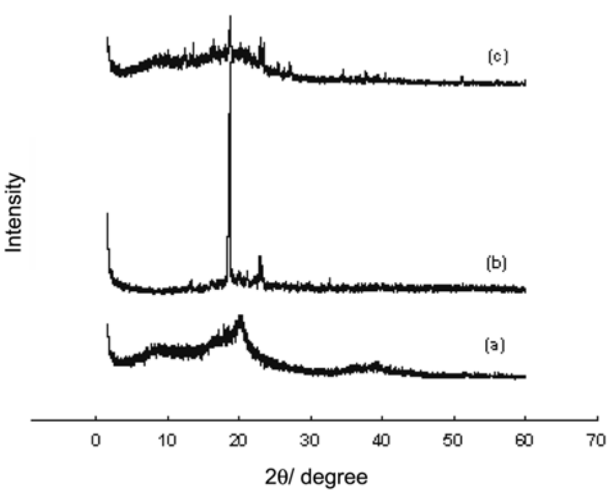


Fig. 9. XRD patterns of (a) 100 wt% PVdF(HFP) film, (b) [HEMMor][PF_6] powder, and (c) 40.0 wt% PVdF(HFP)+60.0 wt% [HEMMor][PF_6] gel film.

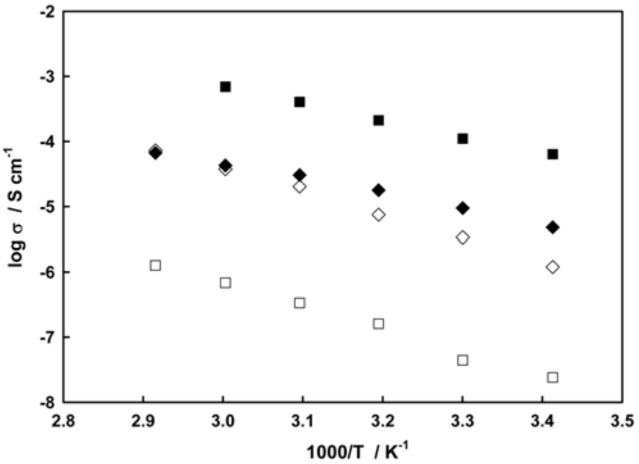


Fig. 10. Ionic conductivity of the PVdF(HFP) gel in [HEMMor][BF_4] system as a function of temperature: 0 wt% PVdF (HFP) (■), 33.3 wt% PVDF(HFP) (◆), 47.4 wt% PVdF (HFP) (◇), 66.7 wt % PVdF(HFP) (□).

5. Ionic Conductivity of PVDF(HFP)-Ionic Liquid Gels

The prepared N-(2-hydroxyethyl)-N-methyl morpholinium derivatives were incorporated with various amounts of the PVdF(HFP) copolymer. Figs. 10 and 11 depict the temperature dependences of the ionic conductivities according to the PVDF(HFP) composition (0-66.7 wt%) in the [HEMMor][BF_4] and [HEMMor][PF_6] systems, respectively.

While the neat [HEMMor][BF_4], which is in a liquid state in a wide temperature range (−150 °C to 150 °C), showed a relatively high ionic conductivity of 10^{-3}-10^{-4} S·cm^{-1} at 20 °C to 70 °C, the neat [HEMMor][PF_6], being in a solid state at room temperature (T_m=

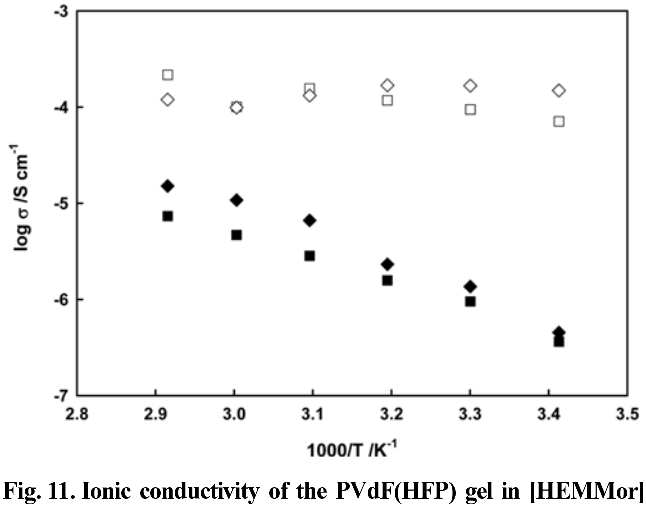


Fig. 11. Ionic conductivity of the PVdF(HFP) gel in [HEMMor][PF_6] system as a function of temperature: 0 wt% PVdF (HFP) (■), 33.3 wt% PVDF(HFP) (◆), 47.4 wt% PVdF (HFP) (◇), 66.7 wt% PVdF(HFP) (□).

160.04 °C), indicated a low ionic conductivity of 10^{-5}-10^{-7} S·cm^{-1} at 20 °C to 70 °C. Although the ionic conductivity might be influenced by its polarity, ion size, solubility with the mixture, and so on, it is expected that anions, PF_6^- and BF_4^-, of [HEMMor][PF$_6$] and [HEMMor][BF$_4$], might not play an important role in the property of polarity because of the symmetric structure of F in the center of P and B. Therefore, PVdF-[HEMMor][BF$_4$] having more miscibility with polymer and IL might show higher ionic conductivity than PVdF-[HEMMor][PF$_6$].

Generally, the ionic conductivity of a polymer-ionic liquid gel is lower than that of a neat ionic liquid, because the ionic motion of the polymer gel is connected with the local segmental motions of the polymer chain matrix and improvements in carrier-ion density or mobility are difficult to accomplish [Tiyapiboonchaiya et al., 2002]. In the case of the PVdF(HFP)-[HEMIm][BF$_4$] system, when the PVdF(HFP) content is higher, the ionic conductivities of the gels are lower. Specifically, in the 66.7 wt% PVdF(HFP) film, the poor ionic conductivity of 10^{-6}-10^{-7} S·cm^{-1} was measured by adding a small amount of [HEMMor][BF$_4$].

However, a dissimilar trend was also observed in the PVdF(HFP)-[HEMMor][PF$_6$] system of Fig. 11. In the neat [HEMMor][PF$_6$] and the 33.3 wt% PVdF(HFP) film, the ionic conductivities were decreased with an decrease in temperature, indicating a low ionic conductivity of 10^{-5}-10^{-7} S·cm^{-1} from 70 °C to 20 °C. In the 47.4 wt% and 66.7 wt% PVdF(HFP) films, a more improved ionic conductivity (~10^{-4} S·cm^{-1}) than that of the neat [HEMMor][PF$_6$] and the 33.3 wt% PVdF(HFP) film was shown. This might account for the distinct differences in compatibility between the [HEMMor][PF$_6$] and the PVdF(HFP) polymer. In Fig. 3, while the 66.7 wt% and 47.4 wt% PVdF(HFP) films formed various grains with different grain sizes, these grains were not observed in the 33.3 wt% PVdF (HFP) film. These phenomena might have resulted from the very low compatibility caused by an improper ratio in the concentration between the [HEMMor][PF$_6$] and the PVdF(HFP) polymer.

Table 2. Thermal data of PVdF(HFP)-ionic liquid gels

Ionic liquid	PVdF(HFP) mass ratio (wt%)	T_g (°C)	T_m (°C)	Measured temperature range (°C)
[HEMMor][BF$_4$]	0	−59	-	−150150
	33.3	−74.13	-	−150150
	47.4	−42.08	162.28	−150200
	66.7	−53.77	-	−150150
	100	-	160.4	−150200
[HEMMor][PF$_6$]	0	−85	160.04	−150200
	28.6	−82.75	160.08	−150200
	33.3	−82.13	157.15	−150200
	47.4	−80.33	160.04	−150200
	66.7	−83.36	160.33	−150200

Table 3. Ionic conductivities of PVdF(HFP)-ionic liquid gels

Ionic liquid	PVDF(HFP) mass ratio (wt%)	σ(S·cm^{-1}) 25 °C
[HEMMor][BF$_4$]	0	8.7×10^{-5}
	33.3	2.28×10^{-6}
	47.4	8.7×10^{-5}
	66.7	3.41×10^{-8}
[HEMMor][PF$_6$]	0	$6.56*10^{-7}$
	33.3	$9.05*10^{-7}$
	47.4	$1.5*10^{-4}$
	66.7	$8.4*10^{-5}$

In addition, unlike the samples of the neat [HEMMor][PF$_6$] and the 33.3 wt% PVdF(HFP) film, it was observed that the ionic conductivities of the 47.4 wt% and 66.7 wt% PVdF(HFP) films did not depended much on a variance in temperature. The room temperature ionic conductivities at approximately 25 °C are listed in Table 3.

Compared with data taken at room temperature for a PVdF(HFP)-[BMIm][PF$_6$] (1-butyl-3-methyl-imidazolium hexafluorophosphate) system that used methyl-2-pentanone as a solvent, the ionic conductivity of prepared 47.4 wt% PVdF(HFP)-[HEMMor][PF$_6$] is five times higher than that of 47.4 wt% PVdF(HFP)-[BMIm][PF$_6$]. However, the ionic conductivity of the prepared 33.3 wt% PVdF (HFP)-[HEMMor][PF$_6$] is far lower than that of 33.3 wt% PVdF (HFP)-[BMIm][PF$_6$].

Although this enhanced value, 10^{-3}-10^{-4} S·cm^{-1}, of ionic conductivity can usually be obtained by using an ionic liquid-polymer gel prepared from the ionic liquid having a liquid state at room temperature, the improved ionic conductivity of the PVdF(HFP)-[HEMMor][PF$_6$] gel prepared from a solid [HEMMor][PF$_6$] at room temperature will present a greater possibility for application as a solid electrolyte.

CONCLUSION

PVdF(HFP)-ionic liquid gels based on the ionic liquids (N-(2-hydroxyethyl)-N-methyl morpholinium tetrafluoroborate and N-(2-hydroxyethyl)-N-methyl morpholinium hexafluorophosphate were prepared with various mixing ratios. The gels, which included prepared ionic liquids, were freestanding, rubbery films. They were prepared with increasing amounts of ionic liquid, and their surface morphology consisted of numerous spherical grains with small pores distributed throughout the gel. The thermal behaviors of the gels, including the glass transition temperature, the crystallization temperature, and the melting temperature, were similar to those shown by neat ionic liquids. However, the heat flow magnitude of the thermal peak decreased with increasing amounts of PVdF(HFP); additionally, in the 100 wt% PVdF(HFP) film, it was difficult to see any of the thermal peaks in the temperatures ranging from −150 °C to 150 °C.

The XRD pattern of PVdF(HFP)-[HEMMor][BF$_4$] gels generally followed that of the neat PVdF(HFP) film. It can be expected from the XRD patterns that the PVdF(HFP)-[HEMMor][BF$_4$] gels showed an amorphous morphology caused by the high compatibility between the two materials with the addition of [HEMMor][BF$_4$] into the PVdF(HFP). However, in the case of the PVdF(HFP)-[HEMMor][PF$_6$] gels, as the strong crystalline peak at $2\theta=18.659^\circ$ shown in the neat [HEMMor][PF$_6$] was sharply decreased in the 47.4 wt% PVdF(HFP) film, it is expected that a reduction of crystallization was significantly achieved in the gelling process between the polymer PVdF(HFP) and the solid [HEMMor][PF$_6$].

The ionic conductivity of the gels based on [HEMMor][BF$_4$] and [HEMMor][PF$_6$] was measured as 10^{-4}-10^{-7} S·cm^{-1} in a temperature range of 20 °C to 70 °C, while the ionic conductivity of the neat [HEMMor][BF_4] and the neat [HEMMor][PF_6] showed 10^{-3}-10^{-4} $S\cdot cm^{-1}$ and 10^{-5}-10^{-7} $S\cdot cm^{-1}$, respectively, in all temperature ranges [Yeon et al., 2005a]. Particularly, the neat [HEMMor][PF_6], which had a high melting point of 160.4 °C, showed a very low ionic conductivity because of it being in a solid state in all temperature ranges. In the gels based on [HEMMor][BF_4], the ionic conductivity generally had a tendency to decrease with an increasing polymer amount. However, it is estimated that the slight difference on the ionic conductivities between the 33.3 wt% and the 47.4 wt% PVdF(HFP) films resulted from the decrease of ionic conductivity in the 33.3 wt% PVdF(HFP) film due to the large pores produced during the preparation process of the film. In addition, for the gels based on [HEMMor][PF_6], although the ionic conductivity of the neat [HEMMor][PF_6] is very low for application as a solid electrolyte, it can be expected that the polymer gels based on [HEMMor][PF_6] present the possibility for viable use as a solid electrolyte, having a value of 10^{-4}-10^{-5} $S\cdot cm^{-1}$.

1. Purity of Ionic Liquids

The evaluation of the purity of the prepared ILs was conducted by ^{1}H NMR, FAB mass, ionic chromatography, and measurement of water contents. The ^{1}H NMR and FAB mass spectra were recorded on a Bruker DMX 300 MHz NMR spectrometer and FAB mass JMS-HX110A, respectively. The possible presence of residual Cl^- was examined by a precipitation test of $AgNO_3$ and ionic chromatography (Bio-LC DX-300 (Dionex, Sunny-vale, CA, USA), Detector: Suppressed Conductivity (PED2), Column: ICSep AN 300 with ICSep ANSC guard). All of the ionic liquids were rigorously dried at 50 °C under 0.03 torr for 5 days. The water contents of all prepared ILs were measured by a Karl-Fischer titration (756 KF Coulometer, Metrohm, Switzerland) in a dry atmosphere.

1-1. [HEMMor][Br]

The 1H-NMR(DMSO, δ/ppm, relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.47(t, 2H), 3.53(t, 2H), 3.6(t, 2H), 3.89(s, 2H), 3.95(s, 4H), 5.32(t, 1H). FAB mass showed m/z=146 [HEMMor]$^+$.

1-2. [HEMMor][BF_4]

The 1H-NMR(DMSO, δ/ppm, relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.47(t, 2H), 3.53(t, 2H), 3.6(t, 2H), 3.89(s, 2H), 3.95(s, 4H), 5.32(t, 1H). FAB mass showed m/z=146.03 [HEMMor]$^+$. The content of bromide anion was 130 ppm. The water content was 192.4 ppm.

1-3. [HEMMor][PF_6]

The 1H-NMR(DMSO, δ/ppm, relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.47(t, 2H), 3.53(t, 2H), 3.6(t, 2H), 3.89(s, 2H), 3.95(s, 4H), 5.32(t, 1H). FAB mass showed m/z=146.1 [HEMMor]$^+$. The content of bromide anion was 158 ppm. The water content was 78 ppm.

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REFERENCES

Capiglia, C., Saito, Y., Kataoka, H., Kodama, T., Quartarone, E. and Mustarelli, P., "Structure and transport properties of polymer gel electrolytes based on PVdF-HFP and $LiN(C_2F_5SO_2)_2$," *Solid State Ionics*, **131**, 291 (2000).

Cha, J.-H., Kim, K.-S., Choi, S., Yeon, S.-H., Lee, H., Kim, H. S. and Kim, H., "Thermal and electrochemical properties of morpholinium salts with bromide anion," *Korean J. Chem. Eng.*, **22**, 945 (2005).

Ege, S., *Organic chemistry structure and reactivity*, third edition, D. C. Heath and Company.

Fuller, J., Breda, A. C. and Carlin, R. T., "Ionic liquid-polymer gel electrolytes from hydrophilic and hydrophobic ionic liquids," *J. Electoanal. Hem.*, **459**, 29 (1998).

Kim, K.-S., Choi, S., Demberelnyamba, D., Lee, H., Oh, J., Lee, B. B. and Min, S. J., "Ionic liquis based on N-alkyl-N-methylmorpholinium salts as potential electrolytes," *Chem. Commun.*, 828 (2004a).

Ohno, H., Yoshizawa, M. and Ogihara, W., "A new type of polymer gel electrolyte: zwitterionic liquid/polar polymer mixture," *Electrochimica Acta*, **48**, 2079 (2003).

Southall, J., Hubbard, P. H. V. St. A., Johnston, S. F., Rogers, V., Davies, G. R., McIntyre, J. E. and Ward, I. M., "Ionic conductivity and viscosity correlations in liquid electrolytes for incorporation into PVDF gel electrolytes," *Solid State Ionics*, **85**, 51 (1996).

Tiyapiboonchaiya, C., Macfarlane, D. R., Sun, J. and Forsyth, M., "Polymer-in-ionic-liquid electrolytes," *Macromol. Chem. Phys.*, **203**, 1906 (2002).

Yeon, S. H., Kim, K. S., Choi, S., Cha, J. H. and Lee, H., "Characterization of PVdF(HFP) gel electrolytes based on 1-(2-hydroxylethyl)-3-methyl imidazolium ionic liquids," *J. Phys. Chem. B*, **109**(38), 17928 (2005b).

Yeon, S. H., Kim, K. S., Choi, S., Lee, H., Kim, H. S. and Kim, H., "Physical and electrochemical properties of 1-(2-hydroxylethyl)-3-methy limidazolium and N-(2-hydroxyethyl)-N-methyl morpholinium ionic liquids," *Electrochimica Acta*, **50**, 5399 (2005a).

Yoshizawa, M., Hirao, M., Ito-Akita, K. and Ohno, H., "Ion conduction in zwitterionic-type molten salts and their polymers," *J. Mater. Chem.*, **11**, 1057 (2001).