

N-Butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide–PVdF(HFP) gel electrolytes

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Abstract

Ionic liquid–polymer gels were prepared by incorporating *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide (Mor_{1,4}TFSI) and poly(vinylidene fluoride)–hexafluoropropylene copolymer (PVdF(HFP)) using three different methods in order to observe the variation of ionic conductivities according to the presence of propylene carbonate (PC) and various weight ratios between Mor_{1,4}TFSI and gel polymer electrolyte (GPE). Ionic conductivities for each gel polymer electrolyte were measured with increasing temperature. Ionic conductivities of the GPEs increased with increasing temperature and weight ratio of Mor_{1,4}TFSI. In addition, the addition of PC into GPE led to the improvement of ionic conductivities. Thermogravimetric analysis (TGA) showed the suggested gel polymer electrolytes composed of only ionic liquid and polymer were stable up to approximately 400 °C. TGA and infrared spectroscopy data indicated that residual PC remains after evaporating PC in a vacuum oven, which did not affect the ionic conductivities. The GPEs containing PC displayed high conductivity (ca. 10⁻² S cm⁻¹) at 60 °C.

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1. Introduction

Recently, polymer electrolyte systems have been actively researched owing to their many advantages over their liquid counterparts, which have some practical problems associated with the leakage of harmful liquids or gassing [1]. From a practical viewpoint, the facility of producing miniaturized structures, long-term safety, and the wide operating temperature range of the polymer electrolyte are particularly attractive characteristics [2–4]. More specifically, gel polymer electrolytes (GPEs) are currently of great interest commercially as they are seen as an attractive alternative to solvent-free systems with regard to achieving higher and more practical ionic conductivities. Generally, GPEs are formed by dissolving a salt in a polar liquid and adding them into a polymer network to lend the material mechanical stability. GPEs have

several beneficial properties: (1) high ionic conductivities; (2) wide electrochemical windows; (3) negligible volatility; (4) non-flammability; (5) high thermal stability [2–6]. However, the vapor pressure of the polar additives such as ethylene carbonate (EC), propylene carbonate (PC), and *N*-methyl pyrrolidone (NMP), which have high dielectric constants, cannot be negligible.

Watanabe et al. have directed their attention toward the attribute that certain kinds of onium salts, such as pyridinium and imidazolium salts, forming room temperature molten salts exhibiting high ionic conductivity [7]. They speculated that if the room temperature molten salts were used as electrolyte salts for a compatible polymer, they would function as plasticizing electrolytes toward the polymers. This would result in the decoupling of the segmental motion from the ionic transport and in consistent increases in both of the carrier density and its mobility with increasing molten salt concentration. Based on this hypothesis, Watanabe et al. developed new polymer electrolytes based on 1-butylpyridium

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bromide/aluminium chloride room temperature molten salts in which poly(1-butyl-4-vinyl pyridinium bromide) was dissolved. They found that these polymer complexes exhibited a high ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ at room temperature. However, ionic liquid (IL) with halide anion, generally, has revealed some problems such as hygroscopicity, low decomposition temperature, and high viscosity. Hence, GPEs containing other anions have been investigated. Meanwhile, Angell et al. proposed a completely new concept, which they termed “polymer-in-salt” electrolytes, in an effort to obtain highly conducting polymer electrolytes [2,8,9]. The materials were described as ionic rubbers, where the polymer-in-salt mixture achieves good rubbery state maintaining high conductivity.

In this context, we suggested novel ionic liquid–polymer gel electrolytes composed of morpholinium salt and poly(vinylidene fluoride)–hexafluoropropylene copolymer (PVdF(HFP)). In our recent publication, the preparation and properties of *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide ($\text{Mor}_{1,4}\text{TFSI}$) as a novel ionic liquid were reported [10]. Morpholinium salt was chosen as a component for forming a GPE after some preliminary considerations: (1) simple synthesis and purification and short reaction time; (2) economical cost; (3) wide electrochemical window; (4) non-detectable vapor pressure; and (5) high thermal stability up to near 400°C . In this investigation, $\text{Mor}_{1,4}\text{TFSI}$ was synthesized according to our previous report [10]. $\text{Mor}_{1,4}\text{TFSI}$ –PVdF(HFP) GPEs were prepared using three different methods to examine ionic conductivities depending on the contents of PC and IL in GPE. Thermal analysis and infrared spectroscopy were conducted to investigate thermal stability and check for the presence or absence of PC after vaporization of PC for the given systems. The thermal and electrochemical data must be first investigated and carefully checked to determine whether the suggested GPE is suitable as an electrolyte for electrochemical devices.

2. Experimental

2.1. Synthesis of ionic liquids

Scheme 1 shows the synthesis mechanism of $\text{Mor}_{1,4}\text{TFSI}$. The ^1H NMR and FAB mass spectra were recorded on a Bruker DMX 600 MHz NMR spectrometer and FAB mass

JMS-HX110A, respectively. The possible presence of residual Br^- was examined by a precipitation test of AgNO_3 and ionic chromatography (System: Bio-LC DX-300 (Dionex, Sunnyvale, CA, USA), Detector: Suppressed Conductivity (PED2), Column: ICsep AN300 with ICsep ANSC guard).

2.1.1. *N*-Butyl-*N*-methylmorpholinium bromide ($\text{Mor}_{1,4}\text{Br}$)

Under vigorous stirring, 137 g (1 mol) of 1-bromobutane was added to a solution of 101 g (1 mol) of 4-methylmorpholine in 200 mL of acetonitrile under N_2 . The mixture was stirred at 60°C for 6 h. The molten salt was placed in a freezer at -20°C . The acetonitrile was decanted from the solids and the mixture was recrystallized from acetone to yield white crystalline solids, which were dried in vacuum at 40°C to give a 95% yield of the $\text{Mor}_{1,4}\text{Br}$.

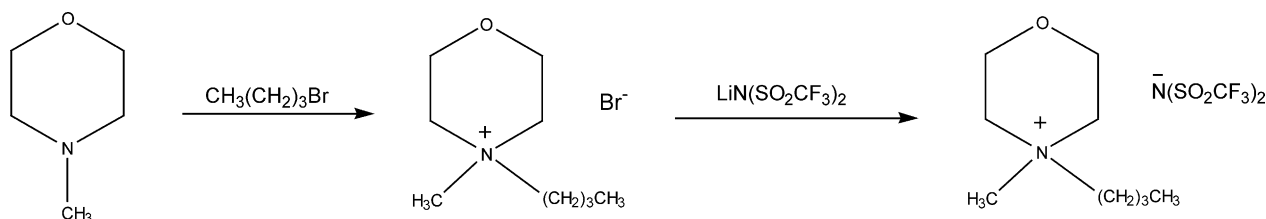
2.1.2. *N*-Butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide ($\text{Mor}_{1,4}\text{TFSI}$)

Twenty-nine grams (0.1 mol) of LiTFSI was added to 24 g (0.1 mol) of $\text{Mor}_{1,4}\text{Br}$ in dichloromethane. The mixture was stirred for 1 day, and the LiBr filtered from the reaction mixture. The resulting ionic liquid was stirred with activated charcoal for 12 h, and the IL was, then, passed through a neutral aluminum oxide and silica gel columns to give a colorless IL, which was dried under vacuum at 40°C for more than 72 h, 29 g of the product was obtained (85% yield): ^1H NMR (DMSO, δ/ppm relative to TMS): 4.08 (s, 4H), 3.56–3.47 (m, 6H), 3.21 (s, 3H), 1.82–1.80 (m, 2H), 1.46–1.42 (m, 2H), 1.01–0.98 (t, 3H). FAB MS: $m/z=158$ [$\text{Mor}_{1,4}$] $^+$. Br^- contents: no precipitation of AgBr and not detected by ion chromatography.

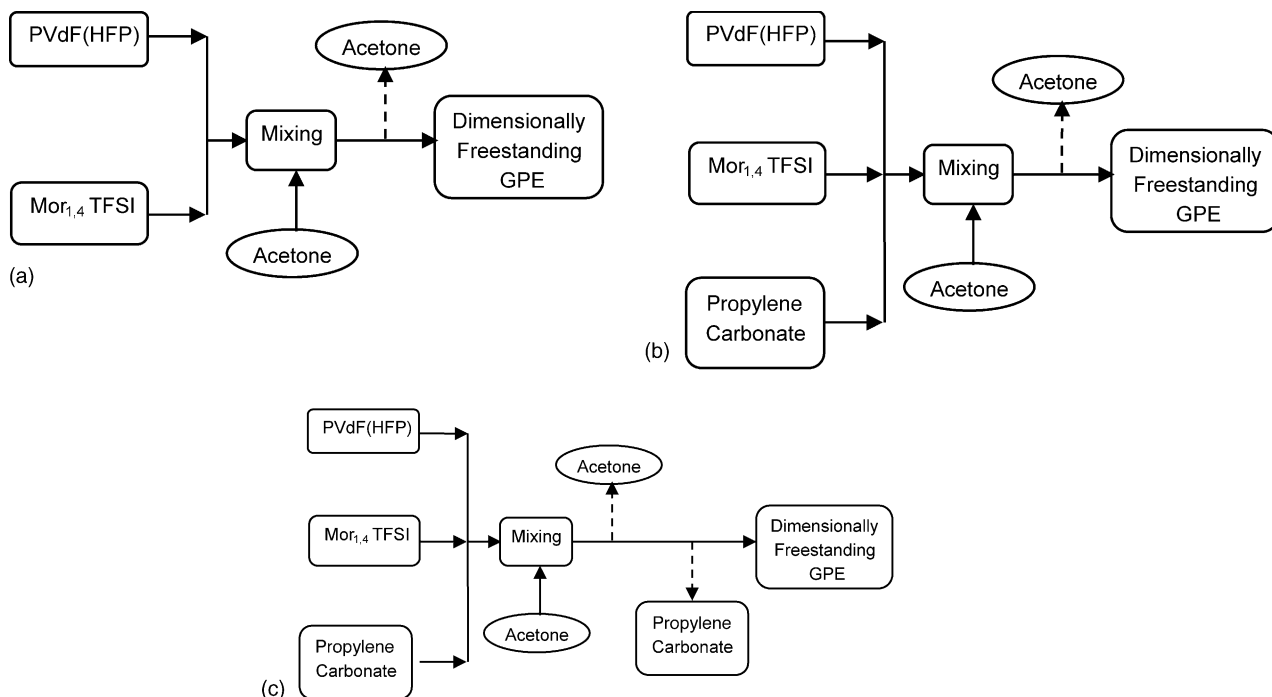
2.2. Preparation of ionic liquid–polymer gel electrolyte

2.2.1. Preparation of $\text{Mor}_{1,4}\text{TFSI}$ –PVdF(HFP) gel polymer electrolyte (Scheme 2a)

PVdF(HFP) (Atofina) was kynar flex 2801-00. $\text{Mor}_{1,4}\text{TFSI}$ and PVdF(HFP) copolymer were mixed with acetone for 24 h. This mixture was poured on a flat Petri-dish and a doctor-blade was used to form a thin and uniform film. The acetone in the mixture on the Petri-dish was then evaporated for 24 h at the ambient temperature. GPE1, GPE2, and GPE3 presented in Table 1 were prepared according to the Scheme 2a procedure.



Scheme 1. Synthesis of $\text{Mor}_{1,4}\text{TFSI}$.



Scheme 2. Three different preparations of $\text{Mor}_{1,4}\text{TFSI}$ -PVdF(HFP) gel polymer electrolyte.

2.2.2. Preparation of $\text{Mor}_{1,4}\text{TFSI}$ -PVdF(HFP)-PC gel polymer electrolyte (Scheme 2b)

PVdF(HFP) copolymer, $\text{Mor}_{1,4}\text{TFSI}$ and propylene carbonate (PC) were mixed with acetone completely for 24 h. This mixture was poured on a flat Petri-dish. The acetone in the mixture on the Petri-dish was then evaporated for 24 h at the ambient temperature. GPE1–40 and GPE2–48 presented in Table 1 were prepared according to the Scheme 2b procedure. The numbers, 40 and 48 of GPE1–40 and GPE2–48, indicate the weight percent of PC, respectively.

2.2.3. Vaporization of PC from $\text{Mor}_{1,4}\text{TFSI}$ -PVdF(HFP)-PC gel polymer electrolyte (Scheme 2c)

PC was evaporated under vacuum for 6 h at 60 °C from the gel polymer electrolytes prepared by the Scheme 2b process. GPE1–40-woPC and GPE2–48-woPC presented in Table 1

were prepared according to the Scheme 2C procedure. The mark, “woPC”, indicate vaporization of PC.

2.3. Apparatus and procedure

2.3.1. Ionic conductivity

Solid films were sandwiched between two stainless steel (SS) electrodes. The ionic conductivities of the electrolyte films were measured by a complex impedance analysis using a Solartron 1260 impedance/gain-phase analyzer and a 1287 electrochemical interface coupled to an IBM computer over a frequency range of 100 Hz–1.8 MHz. An ac perturbation of 10 mV was applied to the cell. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity could be calculated from the bulk resistance (R_b) found in the complex impedance diagram. Also, the specific

Table 1
Weight ratio of each component forming GPE

	Weight ratio of PVdF(HFP) vs. $\text{Mor}_{1,4}\text{TFSI}$		
	PVdF(HFP) (g)	$\text{Mor}_{1,4}\text{TFSI}$	Weight ratio
GPE1	0.5030	0.5114	1:1
GPE2	0.5173	1.0072	1:2
GPE3	0.5083	1.5061	1:3
Weight ratio of (PVdF(HFP) + $\text{Mor}_{1,4}\text{TFSI}$) vs. PC			
	Components	Weight ratio between PVdF(HFP) and $\text{Mor}_{1,4}\text{TFSI}$ (wt.% of PC)	
GPE1–40	GPE1 + PC	1:1 (40)	
GPE2–48	GPE2 + PC	1:2 (48)	
GPE1–40-woPC	Vaporization of PC from GPE1–40		
GPE2–48-woPC	Vaporization of PC from GPE2–48		

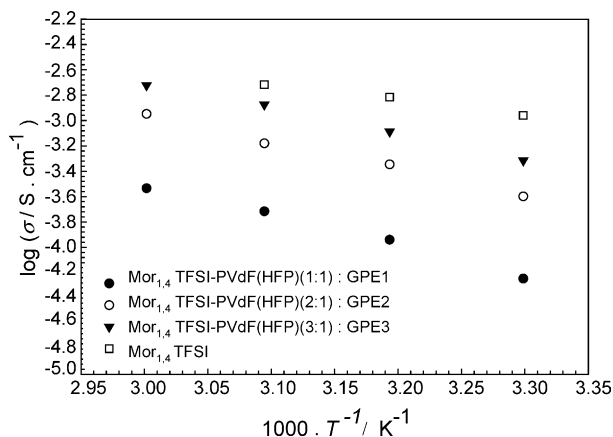


Fig. 1. Ionic conductivities of GPE1, 2, 3, and $\text{Mor}_{1,4}\text{TFSI}$.

ionic conductivity of $\text{Mor}_{1,4}\text{TFSI}$ was measured by Solartron 1260A frequency response analyzer (FRA). This apparatus was connected with a sealed cell containing a pair of SUS plate electrodes 9 mm apart and measured by our laboratory. The cell constant is 1.29 cm^{-1} .

2.3.2. Thermal analysis—thermogravimetric analyzer (TGA)

Thermal analysis and decomposition temperature of the gel polymer electrolytes were detected using a TA instrument thermogravimetric analyzer (TGA) Q500 coupled with an IBM computer. Samples of the gel polymer electrolyte were loaded in flat platinum pans and measurements were taken in a temperature range from 30 to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

2.3.3. Infrared spectroscopy (FT-IR)

The FT-IR spectra were recorded in the absorption mode on a Bomem-MB 100 FT-IR spectrometer covering a range from 400 to 4000 cm^{-1} .

3. Results and discussion

The gel polymer electrolytes were prepared via three different methods as shown in Scheme 2 to observe the variation of ionic conductivities according to the presence of propylene carbonate and various weight ratios between $\text{Mor}_{1,4}\text{TFSI}$ and GPE. Table 1 shows the weight ratios of components forming GPEs. In the cases of GPE1, 2, and 3, free-standing and dimensionally stable gel films were easily prepared using only acetone as a solvent. However, the electrolyte film was not prepared at the more content of IL than that of IL in GPE3. In preparing GPE the use of only acetone simplifies the overall process in that acetone is easily and completely evaporated. Ionic conductivities of all GPEs were determined using a Solartron 1260A frequency response analyzer (FRA) in a temperature range from 30 to 60°C . The ionic conductivities of neat $\text{Mor}_{1,4}\text{TFSI}$ were also measured

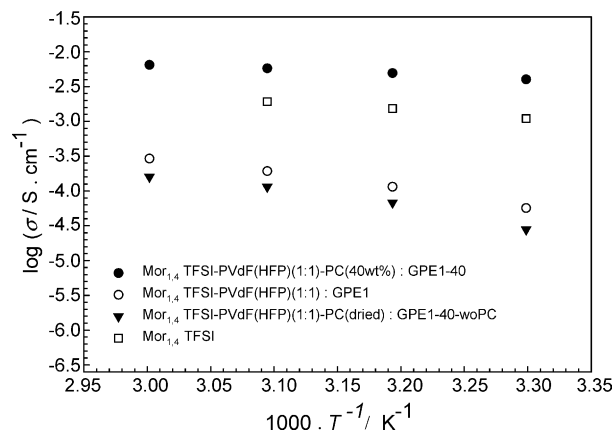


Fig. 2. Ionic conductivities of GPE1, 1–40, 1–40-woPC, and $\text{Mor}_{1,4}\text{TFSI}$.

over the temperature range from 30 to 50°C in order to compare the conductivities of GPEs with those of IL. Figs. 1–3 show the temperature dependence of the ionic conductivity of the prepared GPEs. The neat $\text{Mor}_{1,4}\text{TFSI}$ showed the relatively high ionic conductivities of $10^{-3} \text{ S cm}^{-1}$. Ionic conductivities of the GPEs increased with increasing tempera-

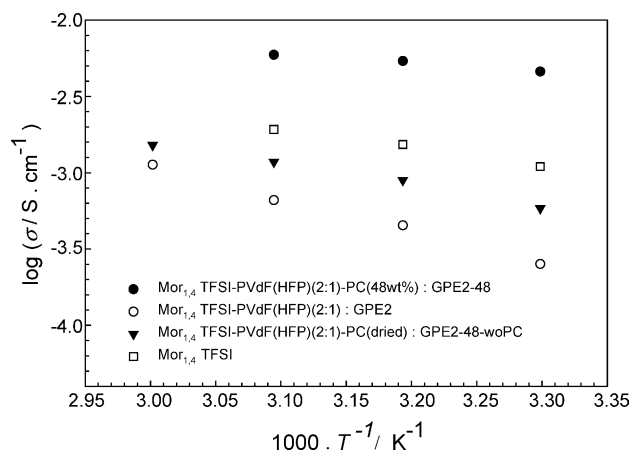


Fig. 3. Ionic conductivities of GPE2, 2–48, 2–48-woPC, and $\text{Mor}_{1,4}\text{TFSI}$.

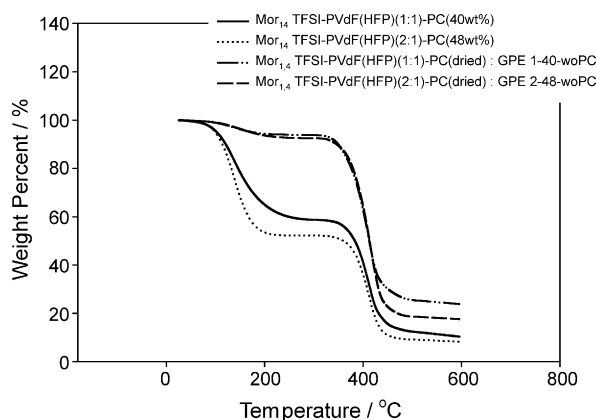


Fig. 4. TGA diagram of GPE1–40, 2–48, 1–40-woPC, and 2–48-woPC.

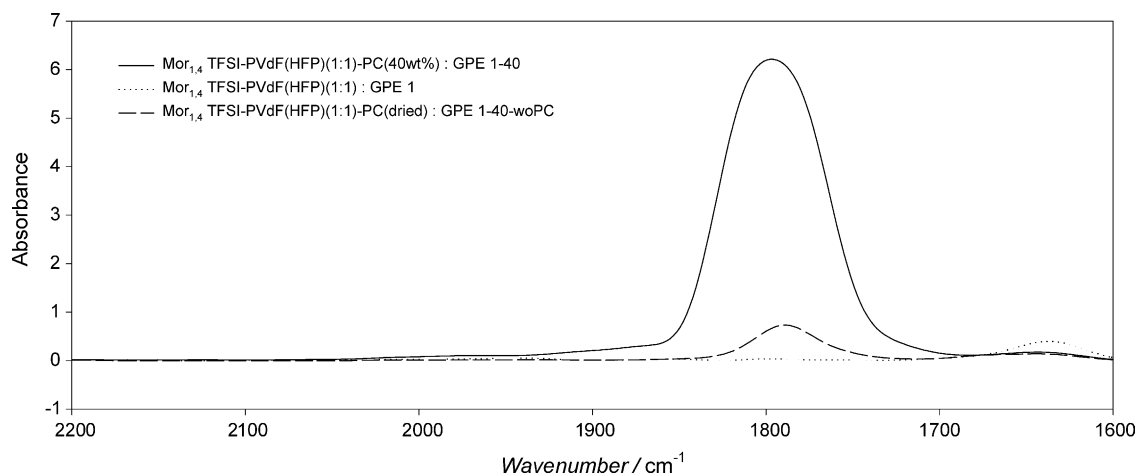


Fig. 5. IR spectra of GPE1, 1-40, and 1-40-woPC.

ture and weight ratio of IL, as shown in Fig. 1. While the ionic conduction of GPE2 and GPE3 reached approximately $2.0 \times 10^{-3} \text{ S cm}^{-1}$ at 60°C , GPE1 displayed low ionic conductivity of $6.0 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C . The resulting phenomena of ionic conduction are attributed to increases in carrier ion density and its mobility as the concentration of IL and temperature increase. Acetone could not affect the ionic conductivities of the GPEs as it was totally removed. On the other hand, an outstanding increase in ionic conductivities was observed when PC was added into GPE1 and GPE2 as shown in Figs. 2 and 3. The ionic conductivities of GPE1-40 and GPE2-48 rose to $8 \times 10^{-3} \text{ S cm}^{-1}$ at 60°C and $6 \times 10^{-3} \text{ S cm}^{-1}$ at 50°C , respectively. The ionic conductivities of GPEs in which PC was eliminated from the polymer matrix after the addition of PC (GPE1-40-woPC and GPE2-48-woPC) were similar to those of GPEs composed of only two, IL and polymer (GPE1 and GPE2). Also, the ionic conductivities of GPEs containing PC (GPE1-40 and GPE2-48) were much higher than those of GPEs without PC. The GPE1-40 displayed the highest ionic conductivity (ca. $10^{-2} \text{ S cm}^{-1}$ at 60°C). It is also of interest to indicate the overall comparisons of conductivities between neat IL and GPEs. The ionic conductivities of $\text{Mor}_{1,4}\text{TFSI}$ were higher than those of GPEs without PC because the ion mobility in the given GPE systems was interfered by polymer chain. In contrast, the conductivities of neat IL were lower than those of GPEs containing PC. In GPE systems, the degree to which the ions are complexed to polymer chain affects conductivities. Therefore, low molecular weight organic solvents of high dielectric constants reduce the potential barrier to ionic motion in polymer matrix. Plasticizers with high dielectric constants dissociate IL and thereby enhance the number of charge carriers and consequently ionic conductivities. The experimental data indicate the PC could plasticized $\text{Mor}_{1,4}\text{TFSI}$ in the polymer matrix, thus leading to high ionic conductivities. PC is a well known cyclic carbonate and is the one of the best solvents for making the nonaqueous electrolytes. A PC with a high dielectric constant can effectively dissolve

salts and separate ions, whereas a low viscosity is beneficial for conducting the ions. Consequently, PC satisfies some requirements for producing an electrolyte of a high electrolytic conductivity. However, the vapor pressure and narrow potential window of a polar solvent such as PC tend to result in the low performance and increased hazardousness [11].

The scanning of the thermogravimetric analysis (TGA) was conducted. The temperature range of the trace was $30\text{--}600^\circ\text{C}$ with a $10^\circ\text{C min}^{-1}$ heating rate under N_2 ambient. The degradation temperatures of GPE1, 2, and 3 were consistent with the degradation curve of $\text{Mor}_{1,4}\text{TFSI}$ [1]. Fig. 4 presents the curves of PC and $\text{Mor}_{1,4}\text{TFSI}$ for GPE1-40 and GPE2-48, respectively. Vaporization curves of PC below 100°C were observed despite its high boiling point. This indicates that the vapor pressure of PC could lead hazardous conditions in electrochemical devices. In spite of the elimination of PC in a vacuum oven from the GPEs, decomposition of PC occurred, as shown in Fig. 4. Fig. 5 shows the infrared absorbance of GPEs over a wavenumber range from 2200 to 1600 cm^{-1} . The characteristic C=O stretching bands of PC for GPE1-40 and GPE1-40-woPC were detected at 1800 cm^{-1} . The weak absorbance peak of GPE1-40-woPC indicates incomplete elimination of PC by evaporation, which is consistent with the TGA results, as shown in Fig. 4. The results from TGA and IR spectra indicated a small amount of PC remained in the polymer matrix after drying PC in a vacuum oven. However, the little residual PC did not affect the ionic conductivities. In contrast, the GPE without added PC did not show any absorbance at 1800 cm^{-1} , indicating that there was no acetone in GPE1.

4. Conclusion

New GPEs have been proposed based upon an investigation of $\text{Mor}_{1,4}\text{TFSI}$ and PVdF(HFP) copolymer. Three kinds of GPEs were prepared to observe the variation of ionic conductivities according to the presence of PC and var-

ious weight ratios between $\text{Mor}_{1,4}\text{TFSI}$ and GPE. The ionic conductivity, TGA, and IR spectroscopy were measured for each GPE. Ionic conductivities of the GPEs increased with increasing temperature and weight ratio of $\text{Mor}_{1,4}\text{TFSI}$. In addition, the addition of PC into GPE led to an improvement of ionic conductivities. IR spectroscopy and TGA results demonstrate that residual PC remained after evaporating PC from the GPE in a vacuum oven, which did not lead to meaningful improvement of ionic conductivity. Although the GPE containing PC displayed the ionic conductivity of about $10^{-2} \text{ S cm}^{-1}$ at 60°C , the vapor pressure of the solvents such as PC could lead to hazardous conditions. The key advantage of the GPEs composed of only IL and polymer is their non-volatility. GPE systems based on ILs would be more desirable for safe battery design and construction.

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