

Proton-Conducting Gel Polyelectrolytes Based on Lewis Acid

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ABSTRACT: A novel proton-gel-conducting polymer electrolyte was prepared by blending boron trifluoride diethyl etherate with poly(ethylene oxide) (PEO), glycerol, and propylene carbonate (PC) at certain molar ratios. The electrolytes exhibited ambient conductivity from 10^{-5} to 10^{-3} S/cm. DSC results indicated that the electrolytes were amorphous. The $^1\text{H-NMR}$ and Raman spectra showed strong

interactions between the Lewis acid and the hydroxyl groups both of glycerol and of PEO. This resulted in the formation of protons for ionic conduction. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1267–1272, 2003

Key words: polyelectrolytes; composites; gels

INTRODUCTION

Solid polymer electrolytes (SPE) have been intensively investigated in recent years. Many studies have been carried out, and considerable efforts have been made to achieve high ionic conductivity at room temperature. Proton-conducting polymer electrolytes, as important member of the SPE family, also have attracted a great deal of attention because of their promising application in fuel cells.

Usually, proton-conducting polymer electrolytes can be obtained by doping polymers with strong acid or ammonium salts.^{1,2} Polyethers such as poly(ethylene oxide) (PEO) often serve as the polymer matrix because of their excellent ability to solvate ionic compounds. It also has been reported that polybenzimidazole (PBI) can be used as the matrix because it is a completely amorphous polymer with a high glass-transition temperature (T_g), 420°C.³ On the other hand, H_2SO_4 and H_3PO_4 are the most frequently used strong acids because they enable high ionic conductivity and good electrical properties to be obtained. Moreover, different kinds of low-molecular-weight plasticizers with a high dielectric constant are also used to improve the conductivity of polyelectrolytes by decreasing the glass-transition temperature.

Proton-conducting polymer electrolytes can be divided into two categories. Hydrous proton-conduct-

ing polymer electrolytes form one category; they can use, as a typical example, the perfluorosulfonic ionomer Nafion® (acid form). It is known that hydration of the hydrophilic polymer phase is an essential step for obtaining high proton conductivity.⁴ Moreover, research of other hydrous systems, such as poly(vinyl alcohol) (PVAI)–hypophosphorous acid (H_3PO_2)–water (H_2O), has also been reported.⁵ However, the disadvantage of water-based electrolytes lies in their comparatively low operating temperature, which must be kept below the boiling point of water.⁶ The other category of proton-conducting polymers is anhydrous electrolytes. Many articles concerning this kind of electrolyte have been reported.^{3,7} They show some superiority to the hydrous electrolytes in that they partly overcome instability and hygroscopicity.

In this article we report a novel anhydrous gel proton electrolyte prepared by using a strong Lewis acid—boron trifluoride diethyl etherate (BFEE)—glycerol, PEO matrix, and propylene carbonate (PC), which are all insulative or low-conductive materials. The conductivity of the electrolyte can achieve 1×10^{-4} S/cm at room temperature. The materials of the proton electrolyte are cheap, and the preparation process is easy. The obtained electrolyte is transparent and colorless. Although it may not be suitable for fuel cells, it has potential applications in a variety of devices for energy conversion, such as electrochromic displays and electrochemical hydrogen sensors.

EXPERIMENTAL

Materials

Boron trifluoride diethyl etherate (BFEE) with a BF_3 concentration of 48.24% and a water content of 0.245%

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TABLE I
Composition at Various Molar Ratios and Conductivity Values at Room Temperature of the Composite Polymer Electrolyte under Study

Sample No.	PEO:Glycerol:BFEE:PC (molar ratio)	Conductivity at room temperature (S/cm)
I	9:4:3:0.3	3.4×10^{-5}
II	9:3:3:0.3	1.2×10^{-5}
III	9:2:3:0.3	1.3×10^{-5}
IV	9:1:3:0.3	6.4×10^{-5}
V	9:1:4:0.3	2.0×10^{-4}
VI	9:1:5:0.3	4.9×10^{-4}

(by volume) was purchased from Beijing Changyang Chemical Plant (Beijing, China) and used after distillation. Poly(ethylene oxide) (PEO) with a molar mass of 10,000 g was purchased from Beijing Donghuan Joint Chemical Engineering Company (Beijing, China) and was dried under vacuum at 70°C for 48 h. Glycerol of analytical reagent grade was a product of Tianjin Bodi Chemical Engineering Company, Limited (Tianjing, China). Commercial chemical pure-grade propylene carbonate (PC) was purchased from the First Reagent Plant of Shanghai (Shanghai, China).

All materials except BFEE were used without further purification.

Preparation of composite polymer electrolyte

Proper stoichiometric amounts of PEO and glycerol (O: glycerol) were mixed in a small glass reactor; then a blend of BFEE and PC of the desired quantity was added to the reactor. The mixture was stirred magnetically below 80°C until homogenous. The electrolyte was poured into a cuboid cell that had two stainless-steel sheets (2 cm × 2 cm) as the electrodes and then was cooled to room temperature. The electrodes were cleaned in an ultrasonic bath and rinsed with deionized water and ethanol before use and placed 0.5 cm apart. The cell was put in a sealed desiccator (dried with anhydrous P₂O₅). The compositions of the polymer electrolytes are listed in Table I.

Measurements

Impedance measurements were carried out on a Model 1025 frequency response detector coupled with a Model 283 potentiostat–galvanostat (EG&G Princeton Applied Research). The typical frequency range was 5×10^6 – 4×10^{-3} Hz, which sometimes changed to 1×10^6 – 1×10^{-3} Hz. A typical Nyquist impedance plot of the composite conducting polymer electrolyte is shown in Figure 1(a). The spectrum shows a compressed semicircle in the high-frequency region and an inclined straight line in the low-frequency region.

The high-frequency semicircle, as reported, represents the bulk relaxation of the polymer electrolyte, whereas the straight line after the semicircle is a result of ionic migration⁸ and the surface inhomogeneity of the electrodes.⁹ In Figure 1(a) the low-frequency end of the semicircle and the high-frequency end of the straight line coincide with the bulk resistance of the conducting polymer electrolyte.¹⁰ Then, the ionic conducting of the samples can be calculated by the following equation:

$$\sigma = \frac{1}{R} \cdot \frac{d}{s} = \frac{K_{cell}}{R}$$

where σ is ionic conductivity, d is cuboid cell thickness, s is the area of stainless-steel electrodes in contact with the polymer electrolyte, R is bulk resistance, and K_{cell} is the cell constant. However, when the bulk resistance of the conducting polymer electrolyte became fairly small, the intercept part of the inclined straight line on the real part of the axis became too small to determine. In that situation bulk resistance could be obtained from the Bode plot shown in Figure 1(b). The frequency–impedance horizontal line gives

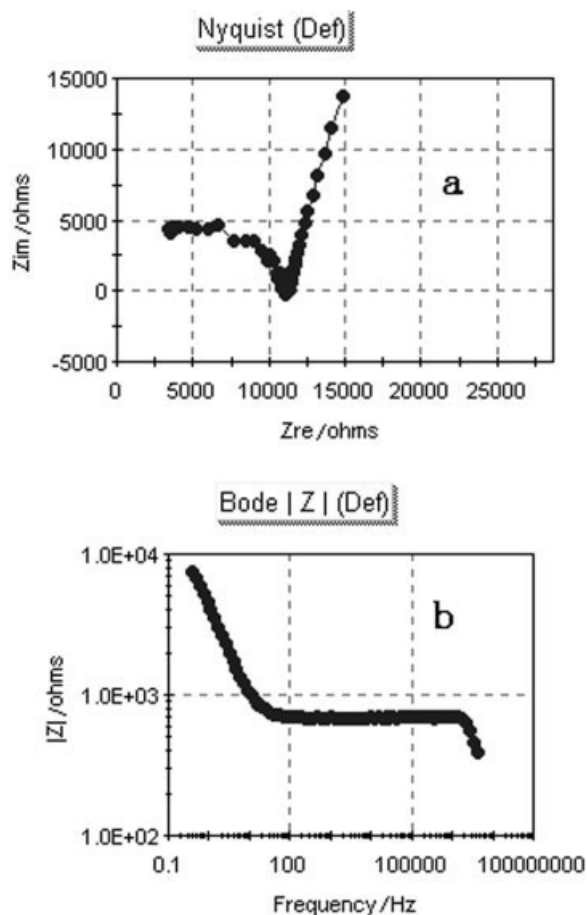


Figure 1 A typical Nyquist impedance plot and a typical Bode plot of sample III at (a) 27°C and (b) 59°C.

TABLE II
Conductivity of the Electrolyte at Various Molar Ratios of Glycerol to BFEE

Glycerol:BFEE (molar ratio)	Conductivity (S/cm)
1:2	6.0×10^{-4}
1:3	1.5×10^{-3}
1:4	2.3×10^{-3}
1:5	2.5×10^{-3}

the bulk resistance. The impedance measurements were carried out in the temperature range of 273–380 K.

Electrolysis was carried out on a Model 283 potentiostat–galvanostat (EG&G Princeton Applied Research) using Pt wire, Pt wire, and Ag/AgCl as the working, counter, and reference electrodes, respectively.

Calorimetric investigations were performed on a Netzsch DSC 204 scanning calorimeter between -50°C and 80°C . The heating rate was $10^{\circ}\text{C}/\text{min}$.

The $^1\text{H-NMR}$ spectra were recorded using an AC-P2000Q NMR spectrometer (Bruker), with CDCl_3 as the solvent.

Raman spectra were recorded on a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, UK) employing a 514-nm laser beam and a charge-coupled detector (CCD) with a 4 cm^{-1} resolution. The spectra were recorded by using a $10\times$ objective, and laser power was always kept very low to avoid destruction of the samples. The liquid sample was sealed in a clean capillary tube.

RESULTS AND DISCUSSION

System selection

It is known that BFEE exists in diethyl ether as a polar molecule $[(\text{C}_2\text{H}_5)_3\text{O}^+]\text{BF}_4^-$,¹¹ and the existence of a small amount of water complexes BF_3 into $\text{H}^+(\text{BF}_3\text{OH})^-$, which furnishes a conductivity medium.¹² However, the conductivity of pure BFEE at room temperature is fairly low, measured as between 2×10^{-4} and $4 \times 10^{-4}\text{ S/cm}$. The addition of a small amount of glycerol into BFEE can greatly increase the conductivity of the medium, as listed in Table II, possibly because the reaction between the hydroxyl groups of glycerol and BF_3 resulted in the formation of protons.

Poly(ethylene oxide) has two hydroxyl terminal groups. Therefore, a new kind of solid polymer electrolyte can be made by mixing BFEE and PEO. Indeed, polymer electrolytes composed of $(\text{PEO})_{8-12}$ and $(\text{BFEE})_1$ (molar ratio of the PEO repeat unit to BFEE) showed ambient conductivity values of 10^{-7} – 10^{-5} S/cm (Table III). SPE conductivity can be improved by the addition of a certain amount of glycerol. Moreover, a small amount of PC was added into the system

TABLE III
Conductivity of the Polyelectrolyte at Various Molar Ratios of PEO to BFEE

PEO:BFEE (O:BFEE) (molar ratio)	Conductivity (S/cm)
8:1	1.8×10^{-5}
10:1	3.4×10^{-6}
12:1	1.3×10^{-7}

to improve the homogeneity of the electrolyte. Hence, electrolytes with the compositions listed in Table I had conductivities of 10^{-5} – 10^{-3} S/cm at room temperature.

Properties of proton polymer electrolyte

Figure 2 shows how ionic conductivity in the PEO–glycerol–BFEE–PC composite polyelectrolyte is dependent on temperature. As can be seen in Figure 2, if the molar ratios of the other three components of the electrolytes remained constant, the conductivity of the electrolyte increased with an increase in BFEE content (curves IV–VI). However, with an increase in glycerol concentration, the conductivity of the electrolyte showed a different changing tendency, even though the molar ratio of the other three components remained constant (curves I–III).

Three factors affected the conductivity of the electrolyte: charge carrier number, ionic mobility, and electrolyte viscosity. An increase in charge carrier number and ionic mobility led to improvement in electrolyte conductivity, whereas an increase in electrolyte viscosity resulted in a decrease in electrolyte conductivity. Because the carrier ion—proton—was produced by the interaction between the hydroxyl groups and BFEE, higher conductivity could be achieved by increasing either the glycerol or the BFEE content. Moreover, an increase in BFEE content caused

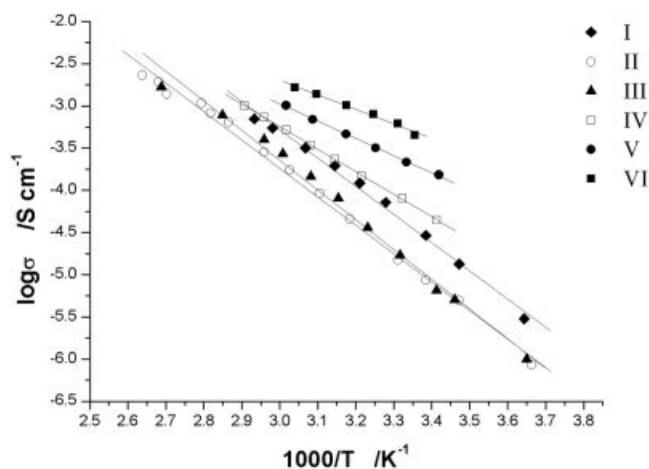


Figure 2 Plots of conductivity versus reciprocal temperature for samples I–VI.

TABLE IV
Arrhenius Activation Energy Values of the Composite Polymer Electrolytes

Sample No.	E_a (kJ/mol)
I	27.80
II	29.71
III	31.87
IV	22.18
V	17.00
VI	14.31

a decrease in electrolyte viscosity; so conductivity of the electrolyte invariably improved with an increase in BFEE content. However, the effect of glycerol on electrolyte conductivity lies in two opposite aspects. On the one hand, increasing glycerol concentration can increase the carrier number and the ionic mobility, leading to improvement in conductivity. On the other hand, a higher concentration of glycerol will result in increasing system viscosity, consequently leading to a decrease in conductivity. So the variation in conductivity with increasing glycerol concentration is complex.

The linear variation in the $(\sigma - 10^3/T)$ plots suggests an Arrhenius-type thermally activated process. This can be expressed as $\sigma(T) = \sigma_0 \exp(-E_a/RT)$, where σ_0 is a preexponential factor, E_a is the activation energy, and R is the ideal gas constant. The calculated E_a values of the electrolytes are given in Table IV. As can be seen from the values in Table IV, if the molar ratio of other components remained constant, the activation energy almost was invariable with a change in glycerol content. However, with increasing BFEE content, and the molar ratios of the other components remaining constant, the activation energy of the electrolyte gradually decreased. This indicates that the BFEE had a greater effect than the glycerol on decreasing the activation energy of the electrolytes.

DSC results

Figure 3 shows the DSC curves for the PEO-glycerol-BFEE-PC system at various molar ratios and a heterogeneous sample with a molar ratio of 9:3:3 (PEO:glycerol:BFEE). The heterogeneous sample had a melting peak at about 58°C, which corresponds to the melting of PEO. When PC was added to the system, the melting peak of PEO disappeared, confirming that PC could improve the system's homogeneity. As shown in Figure 3, the glass-transition temperature of all the homogeneous composite polymer electrolytes are close to 273 K. Another distinct feature of the DSC curves that differed from other systems was the lack of a molting peak, indicating that the electrolytes were amorphous in the measured temperature scales. However, it also can be seen that the polymer electrolytes

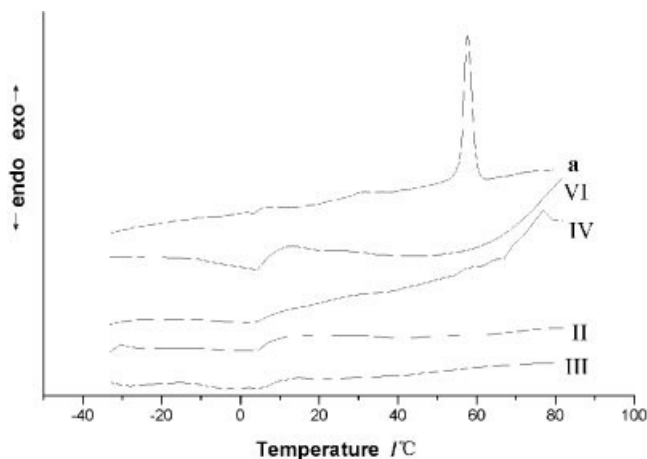


Figure 3 DSC curves of samples II–IV and VI and (a) a heterogeneous sample (PEO:glycerol:BFEE) with molar ratio of 9:3:3.

with a high BFEE concentration always had poor thermal stability (samples IV and VI), whereas with increasing glycerol concentration, the stability of the system could be improved. If the mole ratio of glycerol to BFEE was greater than 2:3, the systems had relatively good thermal stability (samples II and III), not decomposing until the temperature reached about 135°C.

Stability of the polymer electrolytes

The composite polymer electrolytes were put into vessels that were placed in a sealed desiccator containing anhydrous P_2O_5 , and then their impedance was measured intermittently at 15°C. The variation of conductivity with time is shown in Figure 4. As can be seen from Figure 4, the conductivity of the polymer elec-

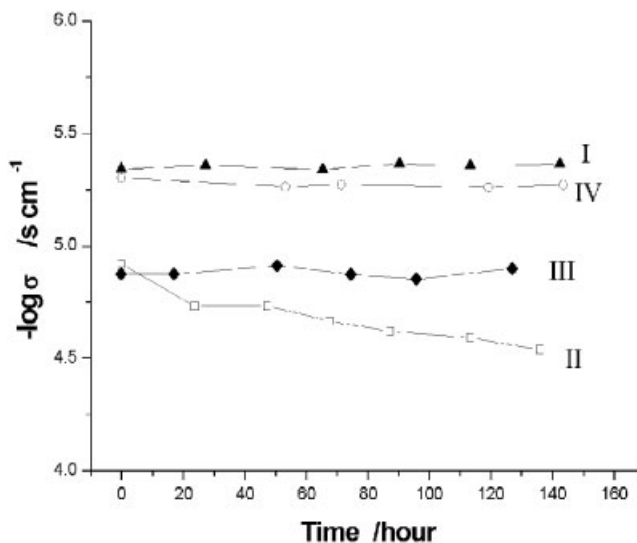


Figure 4 Conductivity variation with time for samples I–IV at 15°C.

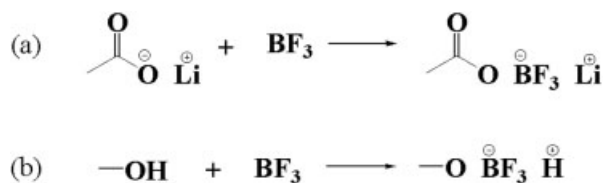


Figure 5 Mode of (a) electrolyte–plasticizer interaction and (b) BF_3 –hydroxyl interaction.

trolyte that had a high BFEE concentration (sample IV) showed an upward trend with an increase in the sample store time, possibly because of the high-BFEE-content electrolyte having free BFEE, part of which may have hydrolyzed. As a consequence, electrolyte conductivity increased. However, if the molar ratio of glycerol to BFEE was greater than 2:3, the electrolyte showed relatively good stability.

Nature of the polymer electrolytes

It has been reported that when BF_3 was added into the polymer–salt system as a plasticizer, it could be sandwiched between the cation and the anion and weakened the interaction between the ion and the polymer.^{13,14} This resulted in increased polyelectrolyte conductivity. Instead of carboxyl groups by hydroxyl groups, it is reasonable to deduce that BF_3 could also be sandwiched between the oxygen and hydrogen of the hydroxyl, with protons released as transporting ions (Fig. 5).

To prove this assumption and find the conductive mechanism of the electrolyte, several types of measurement were used. All results supported the assumption that the hydroxyl groups interacted with BFEE and the hydrogen ion was the transporting ion.

Figure 6 shows the $^1\text{H-NMR}$ spectra of pure glycerol and glycerol–BFEE systems. The one sharp peak at 5.2 ppm in Figure 6(a) was assigned to the hydrogen of the hydroxyl groups in glycerol. The double strong peaks at 3.5 and 3.9 ppm were attributed to the hy-

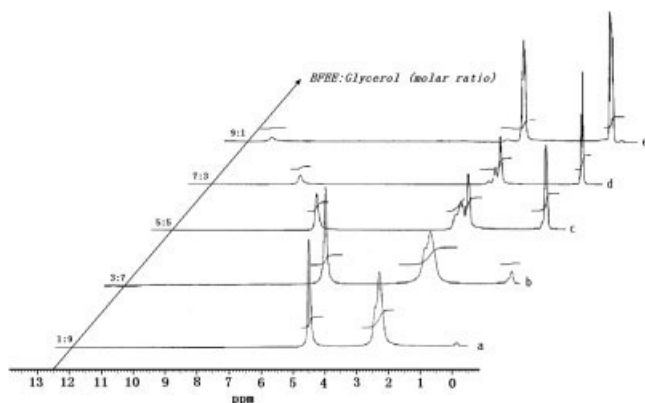


Figure 6 $^1\text{H-NMR}$ spectra of (a) pure glycerol and (b) glycerol–BFEE system with a molar ratio of 1:6.

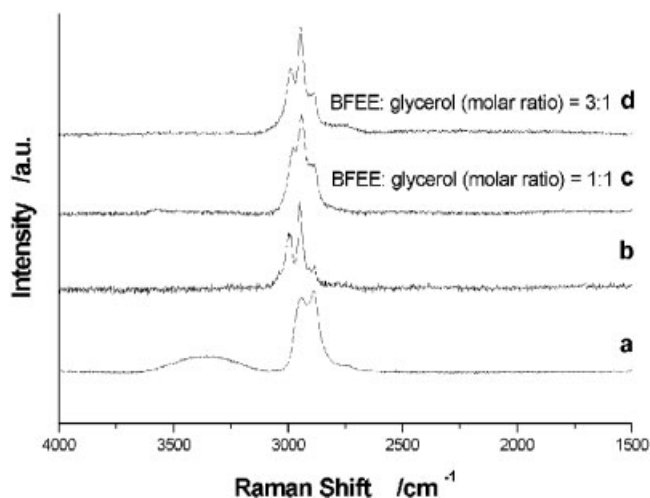


Figure 7 Raman spectra of (a) pure glycerol, (b) BFEE, and (c) glycerol–BFEE system with a molar ratio of 1:1, and (d) glycerol–BFEE system with a molar ratio of 1:3.

drogen of the carbon chain in glycerol. As can be seen in Figure 6(b), when BFEE was added to glycerol, a new peak at 11.4 ppm could be observed. This clearly confirmed the formation of protons and thus is strong evidence that the hydroxyl groups of glycerol interacted with BFEE and released protons as transporting ions.

The Raman spectra of pure glycerol and the BFEE and glycerol–BFEE systems are shown in Figure 7. The fairly weak and broad peak in the Raman shift in the region of 3300–3400 cm^{-1} was assigned to the hydroxyl groups of glycerol. When mixed with BFEE, the Raman signal in this region disappeared, indicating a certain interaction concerned with the hydroxyl groups of glycerol, a finding that coincides with the results of $^1\text{H-NMR}$.

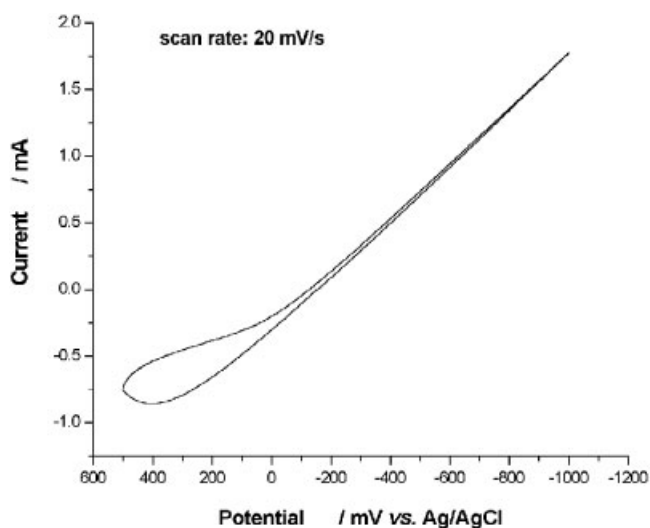


Figure 8 Cyclic voltammogram of glycerol–BFEE system with molar ratio of 1:1.

Furthermore, a electrolysis experiment was carried out potentiostatically at -0.4 V (vs. Ag/AgCl) (Fig. 8). Little bubbles were produced distinctively on the surface of a working electrode after electrolysis had occurred for several seconds. It must be hydrogen that was produced by the proton reaction.

CONCLUSIONS

A novel anhydrous proton electrolyte was made up of insulative or low-conductive materials: a strong Lewis acid—boron trifluoride diethyl etherate (BFEE)—alcohol, a polymer matrix, and a plasticizer. Based on the $^1\text{H-NMR}$ and Raman spectra, it can be concluded that BFEE interacted with the hydroxyl groups and was sandwiched between the oxygen and hydrogen of the hydroxyl group, while protons were released as the transporting ions. Electrolyte conductivity of 1×10^{-4} S/cm at room temperature was achieved. A gel-like polyelectrolyte without a crystalline phase could be obtained by adjusting the components of the electrolyte. However, a high BFEE concentration led to poor thermal and time stability. The polyelectrolytes with a molar ratio of glycerol to BFEE higher than 2:3 had good stability.

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