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Electrical and structural studies of ionic liquid-based poly(vinyl alcohol) proton conductors

Chiam-Wen Liew [a], K.H. Arifin [a], J. Kawamura [b], Y. Iwai [b], S. Ramesh [a],*, A.K. Arof [a]

[a] Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia
[b] Institute of Multidisciplinary Research for Advance Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

Ionic liquid-based proton conducting polymer electrolytes containing poly(vinyl alcohol) (PVA), ammonium acetate (CH_3COONH_4) and 1-butyl-3-methylimidazolium bromide (BmImBr) are prepared and investigated in this present work. The ionic conductivity of polymer electrolytes increases with temperature as shown in temperature dependent-ionic conductivity study. All the polymer electrolytes follow Vogel–Tamman–Fulcher (VTF) relationship. This principle infers the coupling effect of ionic hopping mechanism and free volume theory. The pseudo-activation energy of all the polymer electrolytes is also determined by fitting the plots with VTF empirical equation. The complexation between PVA, CH_3COONH_4 and BmImBr is verified in Attenuated Total Reflectance–Fourier Transform Infrared (ATR–FTIR) study. Addition of ionic liquid reduces the crystallinity of polymer electrolytes as proven in x-ray diffraction (XRD) by calculating the degree of crystallinity of polymer electrolytes. The crystallite sizes of polymer electrolytes are also determined using XRD. Proton nuclear magnetic resonance (H-NMR) spectrum reveals the rapid conduction mechanism in the polymer electrolyte by determining the ion diffusion coefficient.

1. Introduction

The leakage of liquid electrolytes makes the solid state polymer electrolytes become attractive materials in replacing the conventional electrolytes. These solid polymer electrolytes (SPEs) possess several advantages over liquid electrolytes, such as light in weight, easy handling and shaping due to high flexibility of polymer, excellent thermal stability, wider electrochemical potential window and low volatility as well as better chemical stability [1]. Polymer electrolytes are generally classified into few groups, namely solid polymer electrolytes, gel polymer electrolytes, composite polymer electrolytes [2]. Since the ionic conductivity of SPEs is very low and the ionic conductivity of composite polymer electrolytes is restricted, gel polymer electrolytes (GPEs) were developed with enhanced ionic conductivity. GPEs are known as gelionic solid polymer electrolytes or plasticized-polymer electrolytes. However, the plasticizer-added gel polymer electrolytes possess some shortcomings such as low mechanical strength, slow evaporation of the organic solvent, low flash point, poor dimensional stability and reduction in thermal, electrical and electrochemical stabilities. Ionic liquid is a good candidate to replace plasticizer because of its attractive properties. These beneficial properties are wide electrochemical potential window (up to 6 V), wide decomposition temperature range, negligible vapor pressure, non-toxic, non-volatile and non-flammable [2].

The poly(vinyl alcohol) (PVA)–ammonium acetate (CH_3COONH_4) polymer systems had been widely prepared by G. Hirankumar and coworkers in literature [3,4], however, the ionic conductivity of these polymer electrolytes is extremely low that is around 10^{-5} S cm^{-1}. So, we employ the alternative way which is the addition of ionic liquid to improve the ionic conductivity of polymer electrolytes. The effect of adding ionic liquid onto PVA–CH_3COONH_4 will be investigated throughout this present work. There is no similar polymer electrolyte system as in this manuscript that has been prepared, except our published work [5,6]. However, different counter anion of ionic liquid will be used in this work. We will focus on the electrical and structural properties of these polymer electrolytes in this work. Structural characterizations, for example FTIR, XRD and proton-NMR will be discussed in details. Deconvolution methods have been implemented in FTIR and XRD studies for the curve fitting process.

2. Materials and methods

2.1. Materials

Polymer electrolytes containing PVA, CH_3COONH_4 and BmImBr were prepared in this work. PVA (Sigma-Aldrich, USA, 99% hydrolyzed with molecular weight of 130,000 gmol^{-1}), CH_3COONH_4 (Sigma,

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* Corresponding author.
E-mail addresses: liewchiamwen85@gmail.com (C.-W. Liew), helmy29@siswa.um.edu.my (K.H. Arifin), kawajun@tagen.tohoku.ac.jp (J. Kawamura), iy@mail.tagen.tohoku.ac.jp (Y. Iwai), rameshtsubra@gmail.com (S. Ramesh), akarof@um.edu.my (A.K. Arof).

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Japan) and BmImBr (Merck, Germany) were used as polymer, salt and ionic liquid, respectively. All the materials were used as received.

2.2. Preparation of ionic liquid added poly(vinyl alcohol)-based polymer electrolytes

PVA/CH_3COONH_4-based polymer electrolytes were prepared by means of solution casting. PVA and CH_3COONH_4 served as polymer and salt (proton donor), respectively. PVA was initially dissolved in distilled water. Appropriate amount of CH_3COONH_4 was subsequently mixed in PVA solution. The weight ratio of PVA:CH_3COONH_4 was kept at 70:30 as the polymer electrolyte having this ratio had achieved the maximum ionic conductivity in the preliminary step. Different mass fraction of BmImBr was then doped into the PVA–CH_3COONH_4 aqueous solution to prepare ionic liquid-added polymer electrolytes. The resulting solution was stirred thoroughly and heated at 70 °C for few hours. The solution was eventually cast in a glass Petri dish and dried in an oven at 60 °C to obtain a free-standing polymer electrolyte film. The polymer electrolyte without addition of ionic liquid is designated as BR 0, whereas the polymer electrolyte with addition of 20 wt.%, 40 wt.% and 60 wt.% are assigned to BR 2, BR 4 and BR 6, respectively.

2.3. Characterization of ionic liquid added poly(vinyl alcohol)-based polymer electrolytes

2.3.1. Temperature dependent-ionic conductivity studies

Freshly prepared samples were subjected to ac-impedance spectroscopy for ionic conductivity determination. A digital micrometer screw gauge was used to measure the thickness of the samples. The thickness of BR 2, BR 4 and BR 6 is 0.01988 cm, 0.01888 cm and 0.02438 cm, respectively. The impedance of the polymer electrolytes was measured using the HIOKI 3532-50 LCR HiTESTER impedance analyzer over the frequency range between 50 Hz and 5 MHz from ambient temperature to 120 °C. The measurement was taken by sandwiching the polymer electrolyte between two stainless steel (SS) blocking electrodes at a voltage bias of 10 mV.

2.3.2. Attenuated Total Reflectance-Fourier Transform Infrared (ATR–FTIR)

Themoscientific Nicolet iS10 FTIR Spectrometer (from USA) was employed to perform ATR–FTIR study which is equipped with an ATR internal reflection system. The FTIR spectra were recorded with a resolution of 4 cm^{-1} in transmittance mode over the wavenumber range from 4000 cm^{-1} and 650 cm^{-1} at room temperature. The FTIR spectra and peak deconvolution were scrutinized using OMNIC 8 software which is provided by Thermo Fischer Scientific Inc. The transmittance mode of FTIR spectra was initially converted into absorbance mode for peak deconvolution process. In order to deconvolute the FTIR spectra, baseline correction and curve fitting must be implemented. The FTIR curve was fitted with Gaussian–Lorentzian mixed mode.

Table 1
The ionic conductivity of polymer electrolytes at different temperatures.

Temperature (°C)	Ionic conductivity of the polymer electrolytes (Scm^{-1})			
	BR 0	BR 2	BR 4	BR 6
Ambient temperature	1.94×10^{-5}	2.31×10^{-4}	1.43×10^{-3}	9.29×10^{-3}
30	3.22×10^{-5}	2.53×10^{-4}	1.54×10^{-3}	1.07×10^{-2}
40	5.49×10^{-5}	2.95×10^{-4}	1.74×10^{-3}	1.18×10^{-2}
50	8.69×10^{-5}	3.31×10^{-4}	1.96×10^{-3}	1.39×10^{-2}
60	1.11×10^{-4}	3.44×10^{-4}	2.13×10^{-3}	1.44×10^{-2}
70	1.30×10^{-4}	3.72×10^{-4}	2.26×10^{-3}	1.47×10^{-2}
80	1.37×10^{-4}	4.12×10^{-4}	2.44×10^{-3}	1.53×10^{-2}
90	1.52×10^{-4}	4.18×10^{-4}	2.57×10^{-3}	1.57×10^{-2}
100	1.64×10^{-4}	4.45×10^{-4}	2.73×10^{-3}	1.60×10^{-2}
110	1.94×10^{-4}	4.81×10^{-4}	2.81×10^{-3}	1.66×10^{-2}
120	2.31×10^{-4}	5.27×10^{-4}	2.91×10^{-3}	1.69×10^{-2}

2.3.3. X-ray diffraction (XRD)

The x-ray patterns were recorded using BTX benchtop x-ray diffractor with Cu-K_α radiation ($\lambda = 1.54060$ Å), over the range of $2\theta = 5–50°$ at ambient temperature. The characteristic peaks were analyzed and deconvoluted using origin software. The XRD patterns were fitted with Gaussian fitting mode. The degree of crystallinity (χ) of pure PVA and polymer electrolytes was determined using the following equation:

$$\chi_C = \frac{I_C}{I_T} \times 100\% \tag{1}$$

where I_c and I_t are area under the crystalline peak and area under all the peaks, respectively. Debye–Scherrer equation was used to determine

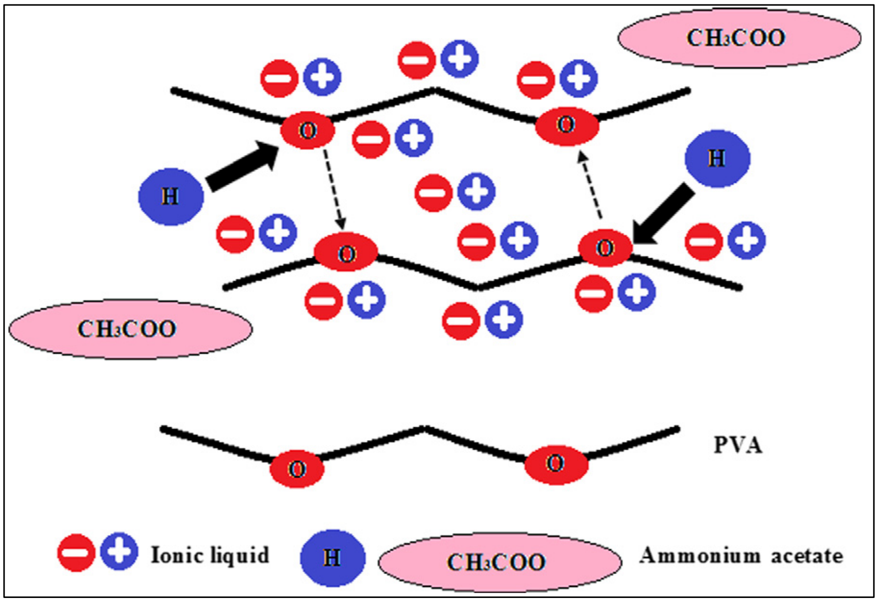

Fig. 1. The schematic diagram on the proton conduction in the ionic liquid-incorporated polymer electrolytes.