Effect of halide anions in ionic liquid added poly(vinyl alcohol)-based ion conductors for electrical double layer capacitors

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ABSTRACT

Poly(vinyl alcohol) (PVA)-based polymer electrolytes have been prepared using solution casting technique. Three different types of ionic liquids are added into PVA/ammonium acetate (CH_3COONH_4)-based polymer electrolytes, namely 1-butyl-3-methylimidazolium chloride (BmImCl), 1-butyl-3-methylimidazolium bromide (BmImBr) and 1-butyl-3-methylimidazolium iodide (BmImI). The ionic conductivity of ion conductors is increased by two orders of magnitude upon addition of ionic liquids, from $(1.94 \pm 0.01) \times 10^{-5}$ S cm^{-1} to (5.74 ± 0.01) mS cm^{-1} (BmImCl), (9.29 ± 0.01) mS cm^{-1} (BmImBr) and (9.63 ± 0.01) mS cm^{-1} (BmImI). Iodide system-based polymer electrolytes achieve the highest conductivity due to the lowest percentage of crystallinity as proven in X-ray diffractogram and the highest ion diffusion coefficient which can be proven in nuclear magnetic resonance spectroscopy (H NMR). Electrical double layer capacitors (EDLCs) are fabricated using the highest conducting polymer electrolyte from each system. The electrochemical properties of assembled EDLCs are further investigated through cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge (GCD). Among all the ionic liquids, BmImI-added polymer electrolyte is the most promising candidate as conducting medium in electrochemical device because of its highest ionic conductivity and capacitance value along with maximum power and energy densities.

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1. Introduction

Energy storage device such as supercapacitor, fuel cell and battery is one of the important components in power sources. Supercapacitors have emerged as new type of electrochemical devices to replace lithium ion batteries and conventional electrolytic capacitors. Supercapacitors deliver higher power density than lithium ion secondary batteries and exhibit higher energy density than conventional dielectric capacitors [1]. Supercapacitors are subdivided into three main types, viz. pseudocapacitors, EDLCs and hybrid capacitors. EDLC is a great choice as an electrochemical device because of its long charge–discharge cycle lifetime (over 10^6 cycles), low cost, high power density (up to 10 kW kg^{-1}), high dynamic of charge propagation (short term pulse), fast energy storage, higher ability to be charged and discharged continuously without degrading, maintenance-free long life operation and short charging time [2–6]. EDLCs do not involve any electrochemical Faradic reaction over the potential range of operation. The basic principle of charge storage in these non-Faradaic capacitors is related to the formation of Helmholtz layer (or well-known as double layer). The double layer formation is due to the electrostatic charge accumulation between the electrode and electrolyte without any chemical reaction.

An EDLC consists of two carbon-based electrodes and an organic electrolyte. Solid polymer electrolytes (SPEs) are emerging as versatile materials to replace liquid electrolytes because of poor safety performance of liquid electrolytes. However, the salt-doped polymer complexes exhibited low ionic conductivity due to high crystallinity. There are several approaches to improve the ionic conductivity of polymer electrolytes. Addition of ionic liquid is an alternative way to increase the ionic conductivity of polymer electrolytes. Ionic liquids have a number of beneficial properties, for example, wide electrochemical potential window (up to 6 V), wide decomposition temperature range, negligible vapor pressure, non-toxic, non-volatile and non-flammable with environmental friendly features [7–9]. The properties of RTILs such as excellent chemical, thermal and electrochemical stabilities, high ionic conductivity due to high ion concentration, good oxidative stability and superior ion mobility as well as high cohesive energy density make them promising candidates for use in polymer electrolytes (PEs) [10].

PVA-ammonium acetate (CH_3COONH_4) polymeric conductors have been widely prepared and investigated [11–13]. However, the ionic conductivity of the polymer electrolytes is relatively low that

is $\sim 10^{-5}$ S cm^{-1}. These polymer electrolytes are not applicable in any electrochemical devices due to low conductivity. Up to date, there is no report on the ionic liquid-added polymer electrolytes based on PVA and CH$_3$COONH$_4$, except our previous published works. Although some results of ionic liquid-added PVA-CH$_3$COONH$_4$ polymer electrolytes have been published in our work [14–15], three different ionic liquid counteranions (chloride, bromide and iodide) are compared in this work to study the effect of the counteranions on ion diffusion in the polymer electrolytes. The aim of this work is to evaluate the behavior of chloride, bromide and iodide-based polymer electrolytes and the electrochemical performances of fabricated EDLCs. Up to date, there is no report on which halide ion (chloride, bromide and iodide) possesses superior performances in the polymer electrolytes and EDLCs. Therefore, we investigate and report all the findings in this present work. In addition, we never report the XRD and H NMR in our previous published works. So, the XRD and H NMR results are discussed in detail in this present work. Deconvolution on XRD and NMR results are also enlightened in this work. As we know, there are many parameters to govern the ionic conductivity of polymer electrolytes such as degree of crystallinity, activation energy and ion diffusion coefficient. We can prove the relationship between these parameters and ionic conductivity in this present work which is an interesting study and novel work in the polymer electrolyte preparation.

2. Experimental

2.1. Materials

Polymer electrolytes containing PVA, CH$_3$COONH$_4$ and BmImCl, BmImBr, BmImI were prepared in this work. PVA (Sigma-Aldrich, USA, 99% hydrolyzed with molecular weight of 130,000 gmol^{-1}) and CH$_3$COONH$_4$ (Sigma, Japan) were used as polymer and salt, respectively. Ionic liquids BmImCl was obtained from Acros Organic, USA, while BmImBr and BmImI were obtained from Merck, Germany. All the materials were used as received.

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

Ionic liquid added PVA-based polymer electrolytes were prepared by solution casting technique. PVA was initially dissolved in distilled water. An appropriate amount of CH$_3$COONH$_4$ was subsequently mixed in PVA solution. The weight ratio of PVA:CH$_3$COONH$_4$ was kept at 70:30. Different mass fraction of ionic liquids was then doped into the PVA-CH$_3$COONH$_4$ aqueous solution to prepare ionic liquid-added polymer electrolytes. The resulting solution was stirred thoroughly and heated at 70 °C for a 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. Three types of polymer systems were prepared in this work, namely chloride system, bromide system and iodide system. The most conducting polymer electrolyte in each system is evaluated and compared in this present work. We found that the highest ionic conductivity of polymer electrolytes is achieved upon addition of 50 wt.% of BmImCl in the chloride system, 60 wt.% of BmImBr in the bromide system and 70 wt.% of BmImI in the iodide system, as reported in published works [14–15].

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

2.3.1. 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 the polymer electrolyte is 0.01–0.02 cm. 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 at room temperature. The measurement was taken from ambient temperature (25 °C) to 120 °C for temperature-dependent ionic conductivity studies. The ionic conductivity of polymer electrolytes was measured by sandwiching the electrolyte film between two stainless steel (SS) blocking electrodes at a signal level of 10 mV.

2.3.2. X-ray diffraction (XRD)

XRD was mainly used to determine the structural properties of polymer electrolytes especially the crystalline and amorphous region in the polymer. The X-ray patterns were recorded using BTX benchtop X-ray diffractor with CuK$_\alpha$ 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_c) 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.

2.3.3. Proton-nuclear magnetic resonance spectroscopy (H NMR)

All the polymer electrolytes were subjected to solid-state Bruker Avance 400 NMR Spectroscopy which is equipped with Topspin 2.1 software under an oscillating magnetic field of 9.4 T with a 5 mm broadband probe at a Larmor frequency of 400 MHz. The analysis was carried out under static probe condition with reference to the compound tetramethylsilane (TMS). For the spectrum measurement, the samples were analyzed with 90° ($\pi/2$) pulse width of 8 μs, intensity of -5 dB and spectral width of 250 ppm, ranging from -142 ppm to 108 ppm for 16 scans at ambient temperature. The sample is initially equilibrated at ambient temperature for 5 s prior to the measurement. The peak obtained from the NMR spectra is fitted by Gaussian mode using origin software to obtain the location, area under the peaks and height of the peaks. On the other hand, the proton self-diffusion measurement was carried out using the Hahn spin–echo of 90°–180° pulse ranging in length from 8 μs to 16 μs for 8 scans at room temperature. The diffusion measurement was performed within the diffusion time of 20 ms with effective gradient pulse duration of 1 ms and the maximum gradient strength of 1800 G cm^{-1}. The proton self-diffusion coefficient (D$^+$) in the ionic liquid added polymer electrolytes was determined by fitting the resultant data into the equation below [16]:

$$I = I_0 \exp\left[-\gamma^2 g^2 \delta^2 (<z^2>/2)\right] \tag{2}$$

where I stands for the intensity of the signal attenuation, I$_0$ defines as the intensity of the unattenuated signal, γ is the gyromagnetic ratio for the nucleus of interest, g represents the amplitude of the applied gradient pulses with duration of δ where δ is the correction factor for finite gradient and $<z^2>$ is the mean square displacement along the field gradient direction. For free isotropic diffusion, $<z^2>$ is written as [16]:

$$<z^2> = 2D\Delta \tag{3}$$

where D is the self-diffusion coefficient (in m^2 s^{-1}) and Δ represents diffusion time.

The attenuation for ordinary isotropic diffusion is expressed as follows by accounting for the finite length of the gradient pulse [17].

$$I = I_0 \exp\left[-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)\right] \tag{4}$$

$$I = I_0 \exp\left[-D(2\pi \, \gamma \, g \, \delta)^2 (\Delta - \delta/3) \times 10^{-4}\right] \tag{5}$$