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Investigation of ionic liquid-doped ion conducting polymer electrolytes for carbon-based electric double layer capacitors (EDLCs)

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ABSTRACT

Ionic liquid-based poly(vinyl alcohol) (PVA)/ammonium acetate (CH_3COONH_4) ion conducting polymer electrolytes are prepared by solution casting technique. Ionic liquid, 1-butyl-3-methylimidazoliumtrifluoromethanesulfonate (BmImTf) is then added to increase the ionic conductivity of polymer electrolytes by reducing the glass transition temperature (T_g).It is found that ionic conductivity of polymer electrolytes increases with temperature. The polymer electrolytes are found to obey the Vogel–Tamman–Fucher (VTF) rule in the conduction mechanism which is related to free volume model. Subsequently, two symmetrical electrodes containing activated carbon, carbon black and carbon nanotubes (CNT) are prepared through the dip coating method. Electric double layer capacitors (EDLCs) are then assembled using these electrodes and polymer electrolytes. Excellent electrochemical properties such as higher specific capacitance were obtained for EDLC comprising ionic liquid–doped polymer electrolytes. Power density of 18.37 kW kg^{-1} was obtained for the EDLC containing the most conducting ionic liquid–added polymer electrolyte.

1. Introduction

Supercapacitors are categorized as energy storage–based power devices. These supercapacitors are divided into three main categories, viz.: pseudocapacitors, electric double layer capacitors (EDLCs) and hybrid capacitors [1]. Pseudocapacitors are well-known as redox capacitors that involve redox reactions during the charge storage and charge transportation processes using electroactive materials. Although these electroactive materials can improve the capacity behavior of supercapacitors, they exhibit some limitations such as shorter cycle life, limited electrochemical stability and relatively more expensive than carbon-based electrodes [2]. On the other hand, the capacitance of an EDLC arises from the formation of electrical double layer that is related to the charge accumulation at the electrode–electrolyte boundary. Hybrid capacitors are new generation capacitors that combine pseudocapacitors and EDLCs.

Extensive research has been done to increase the specific capacitance of EDLCs by increasing the surface area, porosity and conductivity of carbon. Enhancement of these parameters can reduce the resistance and distance of ion transport and thus improve the charge storage between electrode and electrolyte interface [3]. Several types of carbon have been used in electrochemical device preparation such as activated carbon, carbon black, carbon nanotubes, carbon nanofibers, carbon foams and grapheme [3]. Activated carbon (also known as charcoals, AC) is a carbonaceous material mostly used in EDLC application. Activated carbon is chosen as electrode material due to its large microporosity (pore size <2 nm), high specific surface area (1000–2500 $m^2\ g^{-1}$) and cost effectiveness [4–5]. These features give rise to EDLCs with large capacitance, high power density and long cycle life [6]. However, activated carbon possesses several shortcomings such as low mesoporosity and poor accessibility of solvated ions in the electrolyte compared to the microporous structures of AC [7]. Therefore, carbon nanotubes (CNTs) are added to overcome these drawbacks as they have high electrolyte accessibility as reported in Lu and Dai [8]. These properties include superior chemical stability, reduced mass density, low resistivity, narrow distribution of mesopores (or high mesoporosity) and good charging/discharging rate capability [9–10]. CNTs have been recognized as potential materials owing to their excellent electrical conductivity, large specific surface area (100–1315 $m^2\ g^{-1}$), superior capability of charge transportation and unique mesopore structures as well as good adsorption characteristics [11–12]. We reported the electrochemical properties of EDLC using ionic liquid based-ion conducting polymer electrolytes in this present paper. Poly(vinyl alcohol)-based ion conductors are employed and characterized in this present work. PVA is a biodegradable, hydrophilic and nontoxic polymer with excellent mechanical strength [13]. PVA is chosen because of its superior characteristics, such as inexpensive, good optical properties, high temperature resistance, excellent biocompatibility, high dielectric constant, good charge storage capacity and high chain flexibility due to its greater extent of hydroxyl group [13–16]. CH_3COONH_4 is well-known as good proton donor with hydrophilic properties. Strong plasticizing effect and high solubility in water

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are the reasons of choosing CH_3COONH_4 as dopant [16]. Up to date, ionic liquids (ILs) are the best additive to enhance the ionic conductivity of polymer electrolytes significantly. ILs have emerged as promising candidates because of their unique physicochemical properties, for example, wide electrochemical potential window (up to 6 V), wide decomposition temperature range, negligible vapor pressure, non-toxic, non-volatile, non-flammable, good oxidative stability and superior ion mobility with environmental friendly feature [17–19]. Same polymer–salt system has been prepared and investigated in our published work but we used 1-butyl-3-methylimidazolium iodide (BmImI) as ionic liquid in our previous published work [20]. However, a different ionic liquid is employed in this research which is BmImTf. BmImTf is selected because of its appealing cations and high delocalization of triflate anions. The charge delocalization in triflate anions helps in ion dissociation [21–22]. Therefore, more charge carriers might be produced in the ion dissociation which reflects rapid ion conduction in the electrolyte. Apart from that, BmImTf was used as ionic liquid in our previous published work [23]. However, we applied this ionic liquid in the lithium ion conducting polymer electrolytes which are comprised of corn starch and lithium hexafluorophosphate ($LiPF_6$) in our published paper [23]. We would like to employ this ionic liquid into different types of conducting polymer electrolytes which is proton conducting polymer electrolytes in this present work. The purpose of this current work is to explore the effect of ionic liquid, BmImTf, in the PVA–CH_3COONH_4 based polymer electrolytes and EDLC application.

2. Experimental

2.1. Materials

PVA (Sigma-Aldrich, USA, 99% hydrolyzed with molecular weight of 130,000 g mol^{-1}), CH_3COONH_4 (Sigma, Japan) and BmImTf (Aldrich, USA) were used as host polymer, salt and ionic liquid, respectively. All the materials were used as received.

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

Ionic liquid added-polymer electrolytes were prepared by solution casting method. PVA was initially dissolved in distilled water. Appropriate amount of CH_3COONH_4 was subsequently mixed in PVA solution. The ratio of PVA:CH_3COONH_4 was initially optimized as a preliminary step in this research. Based on the preliminary result obtained from this work, the weight ratio of PVA:CH_3COONH_4 was kept at 70:30. Different weight ratios of BmImTf were added into the PVA–CH_3COONH_4 aqueous. The resulting solution was stirred thoroughly and heated at 70 °C for few hours. The solution was then cast on a glass Petri dish and eventually dried overnight in an oven at 60 °C to remove traces of water in the polymer electrolytes. The samples labeled TF 2, TF 4, TF 6 and TF 7 are polymer electrolytes with addition of 20 wt.%, 40 wt.%, 60 wt.% and 70 wt.% of BmImTf, respectively. Conversely, the ionic liquid-free polymer electrolyte is designated as TF 0.

2.3. Characterization of ionic liquid based-PVA polymer electrolytes

2.3.1. Differential scanning calorimetry (DSC)

DSC analysis was carried out using the TA Instrument Universal Analyzer 200 which comprises a DSC Standard Cell FC as main unit and Universal V4.7A software. The whole analysis was performed in a nitrogen atmosphere with a flow rate of 60 ml min^{-1}. Samples weighing 3–5 mg were hermetically sealed in the aluminum Tzero pan. An empty aluminum pan was hermetically sealed as reference cell. In order to remove any trace amount of water and moisture, the samples were heated from 25 °C to 105 °C at a heating rate of 10 °C min^{-1}. Heating was maintained at 105 °C for 5 min to ensure complete water evaporation. Beyond this step, an equilibrium stage was achieved at 25 °C. After that, the samples were heated from 25 °C to 150 °C followed by a rapid cooling to −50 °C at the pre-set heating rate. The samples were eventually reheated to 150 °C at the same heating rate. Glass transition temperature (T_g) was evaluated using the final heating scan with the provided software.

2.4. Temperature dependence-ionic conductivity studies

AC-impedance spectroscopy was used to determine the ionic conductivity of the samples. The thickness of the sample was first determined using a digital micrometer screw gauge. The ionic conductivity measurement was carried out by HIOKI 3532-50 LCR HiTESTER impedance analyzer over a frequency range between 50 Hz and 5 MHz with the configuration of stainless steel (SS) blocking electrode/polymer electrolyte/SS electrode. The measurement was recorded from ambient temperature to 120 °C at a signal level of 10 mV.

2.5. Linear sweep voltammetry (LSV)

The LSV responses of TF 0 and TF 7 were executed using CHI600D electrochemical analyzer. The cells were analyzed at a scan rate of 10 mV s^{-1} by sandwiching the polymer electrolyte between two stainless steel (SS) electrodes in the potential range of ±3 V with sample interval of 0.001 V. The sample was allowed to rest for 2 s prior to the analysis.

2.6. Electrodes preparation

The activated carbon-based EDLC electrodes were prepared by dip coating technique. The carbon slurry was prepared by mixing 80 wt.% of activated carbon (Kuraray Chemical Co Ltd., Japan, particle size is 5–20 μm, surface area is 1800–2000 m^2 g^{-1}), 5 wt.% of carbon black (Super P), 5 wt.% of multi-walled carbon nanotubes (CNTs) (Aldrich, USA) and 10 wt.% of poly(vinylidene fluoride) (PVdF) binder(molecular weight of 534,000 g mol^{-1} from Aldrich) in 1-methyl-2-pyrrolidone (Purity ≥99.5%from Merck, Germany). Activated carbon was treated chemically with sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) before the preparation of carbon slurry to increase the porosity of carbon. This slurry was stirred thoroughly for several hours at ambient temperature until homogenous slurry with smooth surface is obtained. The aluminum mesh electrode and the slurry were then subjected to a dip coater for dip coating process. The coated electrodes were finally heated in an oven at 110 °C for drying purpose.

2.7. EDLC fabrication

EDLC cell was fabricated by assembling the polymer electrolyte between two symmetrical activated carbon-based electrodes. The EDLC cell configuration was eventually placed in a cell kit for further electrochemical analyses.

2.8. EDLC characterization

The EDLC cell was subsequently subjected to cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) equipment for electrochemical characterization. The EDLC cell using the polymer electrolyte without doping of ionic liquid (denoted as TF 0) is designated as type I EDLC, whereas the cell using the most conducting ionic liquid–based polymer electrolyte is assigned as type II EDLC.

2.9. Cyclic voltammetry (CV)

CHI600D electrochemical analyzer was also used to examine CV electrochemical performance of EDLCs. Before taking the measurement, the capacitor cell was initially rested for 2 s. The EDLC cell was then evaluated at 10 mV s^{-1} scan rate within the potential range of 0–1 V where