



Enhanced capacitance of EDLCs (electrical double layer capacitors) based on ionic liquid-added polymer electrolytes



Chiam-Wen Liew^{a, 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 School of Foundation Studies, Xiamen University Malaysia Campus, Jalan Suria Serenia 1, Bandar Serenia, 43900 Sepang, Selangor Darul Ehsan, Malaysia

ARTICLE INFO

Article history:

Received 8 April 2015

Received in revised form

4 May 2016

Accepted 5 May 2016

Keywords:

Poly(vinyl alcohol)

Ionic liquid

Ion conductors

EDLCs

Capacitance

ABSTRACT

Ionic liquid added PVA (poly (vinyl alcohol))-based ion conductors are investigated for EDLCs (Electric Double Layer Capacitors) using electrochemical measurements. Polymer electrolytes incorporated with ammonium acetate ($\text{CH}_3\text{COONH}_4$) as salt and 1-butyl-3-methylimidazolium iodide (BmImI) as the ionic liquid exhibit VTF (Vogel–Tamman–Fulcher) relationship, which is associated with free volume theory. ATR–FTIR (Attenuated Total Reflectance–Fourier transform infrared) confirms the occurrence of complexation between PVA, $\text{CH}_3\text{COONH}_4$ and BmImI. Thermal stability of the polymer electrolytes is studied using TGA (thermogravimetry analysis). The electrochemical potential window of ionic liquid-added polymer electrolyte is extended from 3.3 V to 3.8 V. CV (Cyclic voltammetry) proves the improvement in specific capacitance of the EDLC containing ionic liquid-added polymer electrolyte. The specific capacitance is found to decrease as the scan rate increases. The specific capacitance of EDLCs obtained in CV is in good agreement with low frequency–EIS (electrochemical impedance spectroscopy) and GCD (galvanostatic charge–discharge) curve. This system is suitable for EDLC owing to its high energy and power densities.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Supercapacitor is one type of power source. Supercapacitors consist of one pair of electrodes and electrolyte. The electrode can be derived from many materials, such as carbon, metal oxide, conducting polymers and so on. Supercapacitors or ultracapacitors are divided into three main classes, i.e. pseudocapacitors, EDLCs (electric double layer capacitors) and hybrid capacitors. In pseudocapacitors fast Faradaic process occurs at the surface of the electrodes on application of a potential [1]. These Faradaic processes can be intercalation, under-potential deposition and redox reaction using electroactive conducting polymers or/and metal oxide-based electrodes. On the other hand, EDLCs do not involve any Faradaic reaction. The energy storage of EDLCs arises from the ion accumulation at the electrode–electrolyte interface of active materials through rapid and reversible adsorption of charges carriers [2,3]. Carbonaceous materials are well-known electrode materials for EDLCs. In contrast, hybrid capacitors are the new type of supercapacitors. These capacitors are the combinations of

pseudocapacitors and EDLCs. Asymmetrical electrodes will be used in these hybrid capacitors. EDLC fabrication will be our main concern in this present work. CNTs (Carbon nanotubes) are also added in the electrode preparation in this work because of high microporosity of activated carbon [4,5]. The bigger ions can hardly be diffused and adsorbed onto the smaller micropores of activated carbon. The mesoporous nature of CNTs can enhance the ion adsorption through its unique and well-defined hollow core shape [6]. Other features are superior mechanical stability, excellent electrical properties, high dimensional ratios, low mass density, high charge–discharge capability and better chemical stability [7–9].

On the other hand, the electrolyte can be liquid electrolyte, solid polymer electrolyte, gel polymer electrolyte or composite polymer electrolyte but it must be conductive with high ionic mobility. The ion accessibility from electrolyte to the electrode is an important parameter to govern the capacitance of supercapacitors. PVA- $\text{CH}_3\text{COONH}_4$ polymer system has been widely investigated by Hirankumar and co-workers [10,11]. However, the ionic conductivity of conventional polymer electrolytes containing polymer and salt are relatively low that is $\sim 10^{-5} \text{ S cm}^{-1}$. Therefore, several attempts have been done to improve the conductivity. Ionic liquid is

* Corresponding author. Tel.: +60 3 7967 4391; fax: +60 3 7967 4146.

E-mail address: rameshtsubra@gmail.com (S. Ramesh).

one of the new approaches to increase the ionic conductivity of polymer electrolytes because of its environmentally friendly feature. The effect of adding ionic liquid onto polymer electrolytes had been widely studied and investigated by many researchers recently. Sirisoponaporn et al. had prepared freestanding, transparent and flexible gel polymer electrolytes by trapping N-n-butyl-N-ethylpyrrolidinium N,N-bis(trifluoromethane)sulfonimide-lithium N,N-bis(trifluoromethane)sulfonamide (Py₂₄TFSI-LiTFSI) ionic liquid solutions in poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) copolymer matrices. The resulting membranes exhibited high ionic conductivity at room temperature, from 0.34 to 0.94 mS cm⁻¹. These polymer electrolytes can be operated up to 110 °C without any degradation and any IL leakage within 4 months storage time [12]. A new proton conducting PVdF-co-HFP copolymer membrane composing 2,3-dimethyl-1-octylimidazolium trifluoromethanesulfonylimide (DMOImTFSI) had been prepared. A maximum ionic conductivity of 2.74 mS cm⁻¹ was achieved at 130 °C, along with good mechanical stability [13].

Ionic liquid was also added onto the biodegradable polymers to form biopolymer electrolytes. Biopolymer electrolytes containing corn starch, LiPF₆ and ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BmImPF₆) or 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmImTf) were prepared using solution casting technique as reported in my published works [14–16]. Upon addition of ionic liquids in both systems, the ionic conductivity increased by three orders of magnitude. The highest room temperature ionic conductivity of 1.47×10^{-4} S cm⁻¹ is achieved with addition of 50 wt.% of BmImTf [14]. Higher ionic conductivity was observed for Tf-based system where its maximum ionic conductivity is 3.21×10^{-4} S cm⁻¹ [15]. Ning and co-workers synthesized ionic liquid plasticized-corn starch films. The maximum conductance of $10^{-1.6}$ S cm⁻¹ was achieved by introducing 30 wt.% of 1-allyl-3-methylimidazolium chloride (AmImCl) [17].

Solid state EDLCs has been widely fabricated in recent years. Singh and his coworkers prepare plastic crystal SN (succinonitrile) based gel polymer electrolytes in which its ionic conductivity is 2 mS cm⁻¹ at 20 °C [18]. They also constructed a new and symmetrical EDLC by using this conducting polymer electrolyte and GNPs (graphene nano-platelets) as electrodes. The fabricated EDLC showed the energy density of 8.2 Wh kg⁻¹ and power density of >4 kW kg⁻¹ [18]. Graphene based solid state supercapacitors with ionic liquid incorporated PAN (polyacrylonitrile) electrolyte were prepared by Tamilarasan and Ramaprabhu [19]. This ionic liquid added PAN electrolyte illustrated high ionic conductivity of 2.42 mS cm⁻¹ at 28 °C with excellent thermal stability. The graphene-based supercapacitors depicted excellent specific capacitance, energy storage properties and power density [19]. PVA (Poly(vinyl alcohol)) has a potential to be applied in electrochemical energy conversion devices, such as batteries, alkaline fuel cells and electrolyzers [20]. PVA-ionic liquid based electrolytes are prepared and investigated in this present work. Up to date, there is no report on the ionic liquid-added PVA-based polymer electrolytes, except our previous published work [21]. In addition, to our knowledge the PVA-CH₃COONH₄ polymer electrolytes have not been applied in any electrochemical device yet. EDLC comprising this ionic liquid-added polymer electrolyte is thus assembled in this work using two carbon-based electrodes. The effect of ionic liquid onto the electrochemical properties of EDLC is also further investigated.

2. Experimental

2.1. Materials

Polymer electrolytes containing PVA, CH₃COONH₄ and BmImI

were prepared in this work. PVA (Sigma–Aldrich, USA, 99% hydrolyzed with molecular weight of 130,000 g mol⁻¹), CH₃COONH₄ (Sigma, Japan) and BmImI (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

Poly(vinyl alcohol) polymer electrolytes were prepared by means of solution casting. PVA was initially dissolved in distilled water. An appropriate amount of CH₃COONH₄ was subsequently mixed in PVA solution. The weight ratio of PVA:CH₃COONH₄ was kept at 70:30. Different mass fractions of BmImI were then doped into the PVA-CH₃COONH₄ 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. The polymer electrolyte without addition of ionic liquid is designated as I 0, whereas the polymer electrolyte with addition of 30 wt.%, 40 wt.% and 70 wt.% are assigned as I 3, I 4 and I 7, 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 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 SS (stainless steel) blocking electrodes at a signal level of 10 mV. The ionic liquid-free and the highest conducting ionic liquid-added polymer electrolytes were subjected to LSV (linear sweep voltammetry) study and EDLC fabrication.

2.3.2. ATR–FTIR (Attenuated total reflectance–Fourier transform infrared)

Themoscientific Nicolet iS10 FTIR Spectrometer (from USA) was employed to perform ATR–FTIR study. This spectrometer is equipped with an ATR internal reflection system. The FTIR spectra were recorded with a resolution of 1 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 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.

2.3.3. TGA (Thermogravimetric analysis)

TGA was carried out using a thermogravimetric analyzer, TA Instrument Universal Analyzer 2000 with Universal V4.7A software. Samples weighing 2–3 mg were placed into a 150 μL silica crucible. The samples were then heated from 25 °C to 600 °C at a heating rate of 50 °C min⁻¹ in nitrogen atmosphere with a flow rate of 60 ml min⁻¹.

2.3.4. LSV (Linear sweep voltammetry)

CHI600D electrochemical analyzer was used to evaluate LSV

Download English Version:

<https://daneshyari.com/en/article/8073543>

Download Persian Version:

<https://daneshyari.com/article/8073543>

[Daneshyari.com](https://daneshyari.com)