Electrochimica Acta 129 (2014) 177–186

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Scaling of AC conductivity, electrochemical and thermal properties of ionic liquid based polymer nanocomposite electrolytes

A.K. Nath, A. Kumar*

Materials Research Laboratory, Department of Physics, Tezpur University, Assam 784028, India

ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 3 February 2014
Accepted 17 February 2014
Available online 3 March 2014

Keywords:
Polymer nanocomposite electrolytes
Ionic liquids
Ionic conductivity
Thermal properties

ABSTRACT

In the present study, polyaniline nanofibers have been grown inside the interlayer galleries of montmorillonite clay to form effective hybrid nanofillers. The effect of nanofillers on the properties of ionic liquid based polymer electrolytes has been investigated by varying the nanofiller concentration systematically. The dispersion of the hybrid nanofillers effectively enhances the ionic conductivity, electrochemical stability and the thermal stability. Scaling of AC conductivity shows that ion concentration and ion diffusion length change with changing nanofiller concentration. The dispersion of nanofillers increases free volume of the electrolyte to facilitate the ion hopping that result in increased ionic conductivity. Highest room temperature ionic conductivity of 7.7×10^{-3} S cm^{-1} is achieved at 7.5 wt. % of the nanofiller content. Electrochemical stability increases with increase in nanofiller concentration attaining a maximum value of 5.8 V at 7.5 wt. % of nanofillers concentration. The thermal stability is enhanced on the addition of nanofillers as they act as heat and mass transport barrier for volatile species.

1. Introduction

Polymer electrolytes have been studied extensively for applications in various electrochemical devices particularly in rechargeable batteries because of their shape versatility and the ability for miniaturization [1]. Most commonly studied polymer electrolytes are complexes of lithium salt with polyethylene oxide (PEO) due to their many attractive features such as chemical and mechanical stabilities and the ease in synthesis in thin film form [2]. However, their applications in electrochemical devices are restricted to lower values of room temperature ionic conductivity, electrochemical stability and thermal stability [3]. Several techniques such as addition of nanofillers and liquid plasticizers e.g. propylene carbonate, ethylene carbonate etc. have been explored to enhance the properties of the polymer electrolytes [4,5]. These efforts have been successful in increasing the ionic conductivity but have also led to compromises in mechanical properties. Recently researchers have reported that addition of nanofillers e.g. SiO_2, Al_2O_3, and TiO_2 [6,7], clays [8,9] and carbon nanotubes [10,11] into polymer electrolytes not only improve the ionic conductivity but also enhance the mechanical properties. Lately, incorporation of non-volatile, non-flammable ionic liquids (ILs) into polymer electrolytes has emerged as a promising approach to improve the ionic conductivity and interfacial property as it can act both as plasticizer and ion supplying material [12,13]. Ionic liquids are organic salts that exist in liquid state at temperature lower than 100 °C [14]. They have engrossed much attention of late due to their unique properties such as non-volatility, non-flammability, negligible vapor pressure at room temperature, wide electrochemical stability window ($\sim$ 4.5 V), high ionic conductivity ($\sim 10^{-2}$ S cm^{-1}), excellent thermal and chemical stability etc. [15–17]. Recently Raghavan et al. [18] studied the effect of dispersion of Al_2O_3, SiO_2 and $BaTiO_3$ nanoparticles on the properties of IL based polymer electrolytes.

In this study, we have successfully grown polyaniline (PAni) nanofibers within two-dimensional montmorillonite clay platelets to create hybrid 3D nanofillers and dispersed it in ionic liquid based polymer electrolytes with a view to utilizing favorable properties of both IL and nanofillers. The ionic conductivity, thermal stability and electrochemical stability of the nanocomposite polymer electrolytes have been investigated. Scaling of AC conductivity has been done considering change in ion concentration and ion diffusion length with changing nanofiller concentration.

2. Experimental

2.1. Preparation MMT-PAni nanocomposites

Polyaniline (PAni) nanofibers inside montmorillonite (MMT) layers were synthesized by intercalation of aniline monomers into the interlayer spacing of the MMT followed by oxidative

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* Corresponding author.
E-mail address: ask@tezu.ernet.in (A. Kumar).

http://dx.doi.org/10.1016/j.electacta.2014.02.101
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polymerization of aniline with ammonium persulfate (APS, $(NH_4)_2S_2O_8$). 5 g of MMT (Sigma-Aldrich) was added into 250 ml deionized water and stirred for 2 h at 50 °C followed by addition of 1 ml aniline (Sigma-Aldrich). After stirring for 6 h the mixture was ultrasonicated for 30 min to intercalate aniline monomers in the MMT interlayer galleries. Subsequently the mixture was washed with deionized water several times to remove excess unintercalated aniline. After that oxidant APS (Sigma-Aldrich) was added and stirred for 10 h for formation of PAni nanofibers within the MMT interlayer galleries. The MMT-PAni nanocomposite thus obtained was filtered and washed with deionized water and dried.

2.2. IL based polymer electrolyte dispersed with MMT-PAni nanocomposites

Ionic liquid based polymer electrolytes with MMT-PAni nanocomposite as hybrid nanofiller were prepared by solution casting technique. At first pre-determined amounts of Poly(vinylidene fluoride-co-hexafluoropropylene), PVdF-HFP (M_w = 400000, Sigma-Aldrich) were dissolved in acetone and stirred for 10 h at 50 °C. The ionic liquid 1-butyl-3-methylimidazolium bromide, BMIMBr (Sigma-Aldrich) was then added in the resulting solution in ratio of 1:1 (by weight). After stirring for 10 h, MMT-PAni nanocomposite was added and stirred for 15 h at 50 °C. The viscous slurry thus obtained was cast on petri dishes and dried for 2-4 days to get flexible and free standing thin films. Different electrolytes with 1.5, 2.5, 5, 7.5 and 10 wt. % of MMT-PAni nanocomposite were prepared to investigate the concentration dependant properties of the nanocomposite electrolyte films.

2.3. Analysis and characterization techniques

The formation of MMT-PAni nanocomposite was confirmed with HRTEM microscope (Jeol model JEM 2100). FTIR spectra were obtained using Nicolet Impact 410 spectrometer. X-ray diffraction patterns of the prepared films were obtained with a Rigaku miniflex diffractometer. Surface morphology of the electrolyte films was observed by scanning electron microscope (SEM, Jeol 6390 LV). The ionic conductivity of the electrolyte films was determined by AC impedance measurements in oxygen and moisture free inert nitrogen atmosphere using a Hioki 3532-50 LCR HiTester. The electrochemical stability was evaluated by linear sweep voltammetry using electrochemical workstation CHI600 C. The experiment was performed at room temperature using Pt as working and counter electrode and Ag/AgCl as reference electrode, at a sweep rate of 0.1 V s^{-1}. Thermal stability was studied using thermogravimetric analyzer (TGA, Perkin Elmer STA 6000). TGA measurements were performed in nitrogen atmosphere keeping the nitrogen flow rate of 20 ml min^{-1} using four different heating rates of 5, 10, 15 and 20 °C min^{-1}. The AC conductivity and dielectric properties were evaluated by measuring the impedance, capacitance and dielectric loss of the electrolytes using Hioki 3532-50 LCR HiTester in the frequency range from 42 Hz to 5 MHz. The interfacial stability of nanocomposites polymer electrolytes was studied by fabricating stainless steel/polymer electrolyte/stainless steel cells at room temperature and measuring ionic conductivity for 20 days.

3. Results and Discussion

3.1. High resolution transmission electron microscopy studies

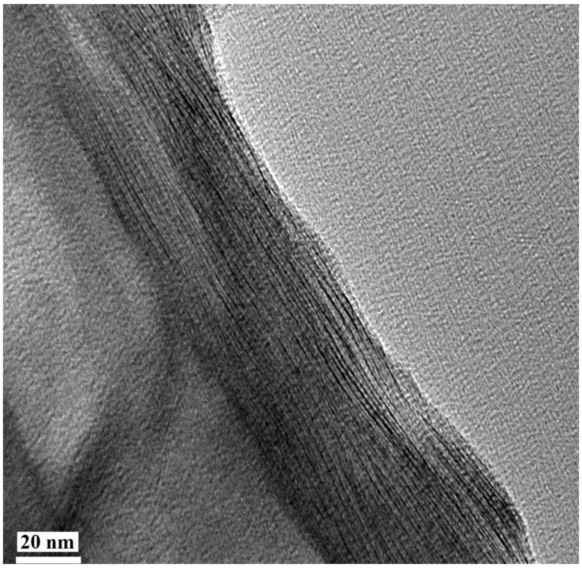

Fig. 1. HRTEM micrograph of MMT-PAni nanocomposite.

Fig. 1 shows the high resolution transmission electron microscope (HRTEM) image of MMT-PAni nanocomposite revealing spatial correlations of the layered silicates. The periodically alternating dark and light bands represent the formation of PAni nanofibers inside silicate layers. HRTEM image shows the presence of small thin bundles of silicate platelets with PAni nanofibers filling the space between the platelets. As observed from Fig. 1, it is evident the MMT-PAni nanocomposite has ordered stacked-layer structure consisting of lamellar stacks of diameter ~ 3 nm which is due to in-situ formation of PAni nanofibers inside the MMT interlayer galleries.

3.2. FTIR studies

The FTIR spectra of pure MMT, pure PAni and MMT-PAni nanocomposite is shown in Fig. 2. In the FTIR spectra of MMT, the band at 3260 cm^{-1} is due to the–OH stretching mode of interlayer water. The peak in the region of 1624 cm^{-1} is attributed to the–OH bending mode of absorbed water. The Si–O and Al–O bonds are, respectively, observed at 1050 and 918 cm^{-1} and the Mg–O is assigned to the band at 524 cm^{-1}. The characteristic peaks of PAni are observed at 1290 cm^{-1} and 1441 cm^{-1}. The ammonium ion of PAni nanofiber displays broad absorption in the frequency region 3350-3050 cm^{-1} because of N-H stretching vibration. The N-H bending vibration of secondary aromatic amine of PAni nanofiber occurs at 1507 cm^{-1}. The band at frequency 1572 cm^{-1} of PAni

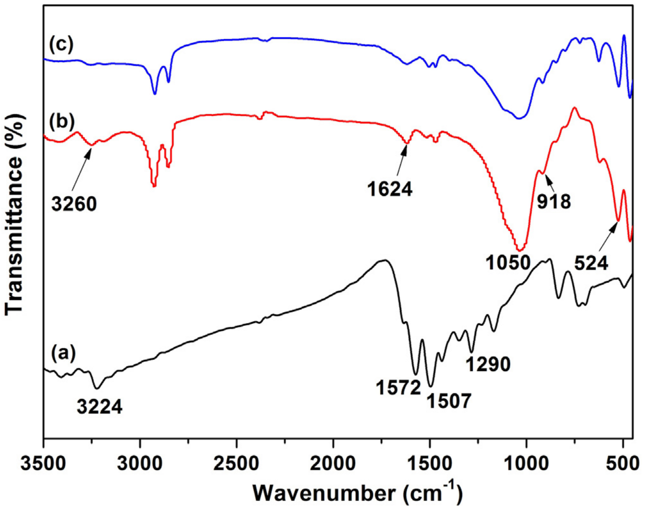

Fig. 2. FTIR spectra of (a) PAni, (b) MMT, (c) MMT-PAni nanocomposite.