



Ionic liquid incorporated nanocomposite polymer electrolytes for rechargeable lithium ion battery: A way to achieve improved electrochemical and interfacial properties



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ARTICLE INFO

Article history:

Received 6 March 2016

Received in revised form 20 June 2016

Accepted 27 June 2016

Available online 2 July 2016

Keywords:

Ionic liquid
Cyclic voltammetry
Ionic conductivity
Solution cast method

ABSTRACT

An ionic liquid incorporated nanocomposite electrolytes are prepared using solution cast technique by immobilizing a solution of lithium N,N-bis(trifluoromethanesulfonyl)imide (LiTFSI) in N-ethyl-N-methylimidazolium - bis(trifluoromethanesulfonyl) imide (EMImTFSI) ionic liquid (IL) with added mixtures of organic solvent and nanofiller such as acetonitrile and nanochitosan (32 nm) into a poly(ethylene oxide) (PEO) matrix. The achieved extreme ionic conductivity of ionic liquid based electrolyte is in the range of $10^{-2} \text{ S cm}^{-1}$ which is one order higher than that of (PEO)₈LiTFSI-10 wt% NC system. Cyclic voltammetry and linear sweep voltammetry (LSV) analyses indicates that the prepared electrolytes possesses an excellent electrochemical stability of 3.9 V. These unique properties allow the effective use of these membranes as active separators for the development of advanced lithium ion batteries.

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Introduction

The latest hasty development in the size diminution of electronic devices and the growth of multimedia industries has been increasing demand for compact electronic devices. In this perspective, the market size and demand has motivated a huge push worldwide into the development of lithium battery materials particularly designed for these applications [1–4]. The most promising options involve lithium ion technology employing polymer electrolytes as the separator of rechargeable batteries [5–7]. Last three decades, composite solid polymer electrolytes (CSPE) gaining great attention due to their wide range of potential application as electrolytes in different electrochemical devices,

batteries, fuel cells, hybrid electric vehicles and dye sensitized solar cells (DSSC) [8–12]. Among different polymer hosts, PEO is one of the most promising candidates because of its unique electrical, optical, electrochemical properties, as well as its ease of preparation and excellent environmental stability [13–15].

Moreover, PEO is able to dissolve all lithium salts due to its high dielectric constant in amorphous phase ($\epsilon = 8$). Even if, PEO film possesses good dimensional and mechanical stability, its room temperature ionic conductivity is quite low (10^{-6} to $10^{-7} \text{ S cm}^{-1}$) because of its high crystalline nature of PEO. Hence, many efforts arise to resolve the barrier. One of the efforts includes a type of ionic salt is embedded into the polymer matrix [16–20]. In the present work, LiTFSI is chosen as conducting salt because it gains interest owing to its large electro negativity, low lattice energy and delocalization of charge [21–25]. These properties promote high degree of dissociation of LiTFSI in the polymer matrix and allow the free ions to remain in its ionic state to incessantly participate in ion conduction. In the present work, nanochitosan (NC) is utilized as reinforcing agent. The biopolymer chitosan (poly-(1-4)-2-amino-2-deoxy- β -D-glucan) is a linear natural amino polysaccharide

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consists of polar groups (OH and NH₂), which can act as electron donors and interacts well with polymer host to form dative bond (co-ordinate) and made lithium ions free in the polymer host matrix. We previously reported the synthesis of NC [26,27] and its physicochemical and electrochemical effect on (PEO)₈ LiTFSI based electrolytes [28]. In this present report, the inclusion of ionic liquid in nanocomposite system and its combination effect with NC on the electrochemical and interfacial properties of ionic liquid based nanocomposite electrolytes are analyzed deeply. This in turn paves a way to utilization of the prepared ionic liquid based nanocomposite electrolytes in lithium ion battery. Because lithium ion coordination takes place predominantly in the amorphous domain, natural fillers are crystalline therefore NC alone cannot be a suitable medium for the production of highly conductive polymer electrolytes. Previously, Stefano Passerini [29–32] and his co-workers reported the incorporation of ionic liquid in polymer electrolyte system tremendously enhances the electrochemical, thermal and interfacial properties of polymer electrolytes. Recently our group reported the physicochemical and electrochemical properties of imiazolium based ionic liquid electrolytes and effect of nanoparticles along with it for battery applications [33]. Hence, we planned to investigate the effect of plasticizing agent ionic liquid EMImTFSI in (PEO)₈ LiTFSI-10 wt% NC matrix to suppress the crystalline nature of electrolytes further thereby increasing both electrochemical and interfacial properties. Nonetheless, reports on such electrolyte systems for lithium-ion batteries remain very scarce up to today and few examples of this class of materials for application in lithium batteries have been reported earlier [34]. To the best of our knowledge and for the first time, the effect of EMImTFSI on the electrical, electrochemical and interfacial properties of (PEO)₈LiTFSI-10% NC electrolytes have analyzed and the significant results are presented herein.

Experimental

Synthesis of nanochitosan (NC)

Nanochitosan was synthesized from chitosan according to the procedure as described earlier [26]. Explain in brief, chitosan was first boiled well with 40% NaOH and then dried to remove the residual protein. The obtained chitosan sample was treated with alkaline KMnO₄ for decolorization purpose. Initially, 3 g of purified chitosan samples was dissolved in 100 ml of 0.1 M HCl and stirred for an hour. To this, 5% H₂O₂ was added. The resulting mixture was heated and stirred for 4 h at 50 °C and then vacuum filtered.

The upper residue was neutralized with distilled water, baked and weighed. Ethanol was added to the filtrate, which was allowed to stand for 1 day to precipitate, after which it was filtered, dried and weighed. The precipitate thus obtained was dissolved in 1 L acetic acid and stirred for 1 h. Then 60 ml of micelle forming agent sodium tripolyphosphate (STPP) was added to the solution, stirred for 2 h at ambient temperature and then centrifuged at 2000 rpm/s. The isolated nanochitosan was rinsed with distilled water, freeze dried and weighed. The schematic diagram of synthetic process is shown in Scheme S1 (See supplementary file). The resulting nanochitosan was kept in a refrigerator with sodium azoture as a protectant against microorganisms. The FE-SEM image and XRD patterns of synthesized nanoparticle are provided as Figures S1 and S2 in supplementary section.

Materials and methods

All the precursor materials were dried under vacuum for 48 h at 50 °C before use. Polymer electrolytes consisted of polymer PEO with molecular weight (Mw) of 2×10^5 (Sigma Aldrich), LiTFSI (Alfa-Easer) as salt, EMImTFSI as plasticizing agent and

synthesized NC as an inert filler were prepared by solution casting method [35]. In brief, stoichiometric amounts of dry powders of LiTFSI and PEO, required for Li–O ratio of 8:1, were dissolved in acetonitrile and the solution was stirred well for 8 h. The weight content of polymer and lithium salt was maintained at 8:1 which indicated that there was sufficient number of available sites (O-atom in PEO) for lithium ion to hop from one site to another site. About 10 wt% of the synthesized NC was then added to the complex solution and stirred for 10 h. Followed by adding different wt% [$x = 5, 10, 15, 20\%$] of EMImTFSI in above solution and continuously stirred for about 16 h. The obtained coagulated pasty mass solution was transferred on to the glass plate and allowed to dry. The obtained membranes were dried under vacuum at 50 °C for 48 h for further removal of solvent present in membrane. The whole experiments were performed under inert and moisture free atmosphere. The resulting membranes were usually examined for its dryness and free standing nature.

Instrumentation

The prepared electrolytes were subjected to various physicochemical characterizations. X-ray diffractograms were recorded using BRUKER AXSD8 advanced X-ray diffractometer with CuK α radiation ($\alpha = 1.5412 \text{ \AA}$). The accelerating voltage was set at 40 kV with 30 mA flux at a scanning rate of 20°/m in the 2θ range between 0 and 50°. DSC analysis was carried out to determine the thermal behavior of polymer electrolytes in the temperature range 20–80 °C at a scan rate of 10 °C/min in nitrogen atmosphere using SDT. The FT-IR spectra were recorded using JASCO 4100 LE ATR-FTIR (Attenuated Total Reflection-Fourier Transform Infra Red) spectrophotometer in the region 400–4000 cm⁻¹. Mechanical stability of the electrolytes was obtained using the universal testing machine INSTRON equipped with test x-pert V8.1 program. Samples in the form of strips with thickness of 0.1 mm were cut out from the electrolytes with dimensions of 0.5 × 0.7 cm. Each strip for the tensile test was mounted in the metallic grips covered with rubber, which was designed for testing polymeric materials. The same grip span of 4 cm was used for each sample and they were all subjected to uniaxial tensile force at a constant crosshead speed of 10 mm/min. All the measurements were executed at ambient temperature. The electrical properties of prepared electrolytes were analyzed by electrochemical impedance spectroscopy (EIS) using electrochemical impedance analyzer (Zahner IM6, Germany) connected to a computer for data acquisition. The whole ionic conductivity studies were performed in the frequency range 100 mHz to 100 kHz with signal amplitude of 1 V from 303 to 343 K. The samples were thermally equilibrated at each temperature for at least half an hour prior to the measurements. The temperature measurements were carried out by placing the conductivity cells inside a thermal vacuum oven having a temperature precision of $\pm 1 \text{ }^\circ\text{C}$. The increase in ionic conductivity was due to increase in charge carriers were evidenced by dielectric analysis. Cyclic voltammetry and linear sweep voltammetry analyses performed for cells containing electrolytes were sandwiched between two Li electrodes at a scan rate 10 mV s⁻¹. The area and thickness of the Li electrodes were 0.8 cm² and 120 μm respectively. The lithium interfacial stability of the prepared electrolyte was analyzed by subjecting the Li/ILPE/Li symmetric cell into impedance analysis continuously for 240 h at 333 K.

Results and discussions

X-ray diffraction analysis

XRD studies are performed to investigate the observed change in crystalline phase of PEO after it has been added with EMImTFSI.

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