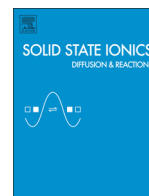




Contents lists available at ScienceDirect

Solid State Ionics

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

Electrochemical characterization of poly(vinylidene fluoride-co-hexafluoro propylene) based electrospun gel polymer electrolytes incorporating room temperature ionic liquids as green electrolytes for lithium batteries

Prasanth Raghavan^a, Xiaohui Zhao^a, Hyunji Choi^a, Du-Hyun Lim^b, Jae-Kwang Kim^{a,b}, Aleksandar Matic^b, Per Jacobsson^b, Changwoon Nah^c, Jou-Hyeon Ahn^{a,*}

^a Department of Chemical and Biological Engineering and Research Institute for Green Energy Convergence Technology, Gyeongsang National University, 900, Gajwa-dong, Jinju 660-701, Republic of Korea

^b Department of Applied Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

^c Department of Polymer-Nano Science and Technology, Chonbuk National University, 664-14 Duckjin-dong, Jeonju 561-756, Republic of Korea

ARTICLE INFO

Article history:

Received 14 May 2013

Received in revised form 17 October 2013

Accepted 21 October 2013

Available online xxxx

Keywords:

Electrospinning

Nanofibrous membrane

Gel polymer electrolyte

Room temperature ionic liquid

1-Alkyl-3-methylimidazolium

bis(trifluoromethylsulfonyl)imide

ABSTRACT

A series of gel polymer electrolytes (GPEs) based on electrospun membranes of poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-co-HFP)] incorporating room temperature ionic liquids (RTILs), 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide complexed with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) as electrolytes have been prepared and their fundamental electrochemical properties were investigated. The morphology of electrospun membranes was examined by a field emission scanning electron microscope (FE-SEM). The membranes show uniform morphology with an average fiber diameter of 780 nm, high porosity and high electrolyte uptake. GPEs were prepared by soaking the electrospun membranes in 1 M LiTFSI in RTILs for 1 h and exhibit a high ionic conductivity of 2.4×10^{-3} – 4.5×10^{-3} S cm⁻¹ at 25 °C. A Li/GPEs/LiFePO₄ cell using these RTILs delivers high discharge capacity (~140 mAh g⁻¹) when evaluated at 25 °C at 0.1 C-rate and exhibits a very stable discharge capacity under continuous cycling. Among the GPEs, EMITFSI shows the highest electrochemical properties although the solid electrolyte interface (SEI) layer was not formed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Room temperature ionic liquids (RTILs) are primarily molten salts composed of bulky and asymmetric organic anions and cations having low melting point and exist as liquids at or below room temperature [1,2], which have been considered as promising green electrolytes due to their excellent characteristics. Their physicochemical properties can be tuned by using different combinations of cations and anions. With a large number of possible anions, for example [BF₄]⁻, [PF₆]⁻, [N(CN)₂]⁻, [C₄F₉SO₃]⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻, [N(CF₃SO₂)₂]⁻, and [CF₃CONCF₃SO₂]⁻, the properties of a RTIL can be tailored through the selection of cation and anion [2–4]. Unlike molecular solvents RTILs can be potentially used as safe electrolytes due to their thermal stability, wide liquid phase range, hydrophobicity in some cases, non-flammability, very low or negligible vapor pressure, low toxicity [3,4], high ionic conductivity and wide electrochemical window [2]. Due to these distinctive properties of ionic liquids, they can be used for preparation of safer gel

polymer electrolytes (GPEs) with unique properties. Also, LiTFSI salt has good electrochemical oxidation stability, low dissociation energy between Li cation and TFSI anion and high thermal stability [5].

There has been much effort in trying to increase the ionic conductivity of gel polymer electrolytes at room temperature by immobilizing large amounts of liquid electrolyte in a polymer host [1,2]. The polymer hosts are membranes adapted specifically for the gel polymer electrolytes with pores of nanometer to micrometer in size that retain the liquid electrolyte. The membranes should have the capability to absorb the liquid electrolyte without leakage, and be chemically compatible with electrode materials.

The host polymer membrane properties such as pore size, porosity and pore distribution are strongly dependent on its processing method. Different methods such as electrospinning [6–9], solvent casting [10], plasticizer extraction [11], and phase inversion [12] have been adopted for preparing such porous membranes. Electrospinning is a versatile and easy method to prepare polymer membranes that are made up of thin fibers of micron and sub-micron diameters. Such membranes are particularly suitable as host matrices for GPEs since the interlaying of fibers generates large porosity with fully interconnected pore structure facilitating the easy transport of ions [9,13].

* Corresponding author. Tel.: +82 55 772 1784; fax: +82 55 772 1789.

E-mail address: jhahn@gnu.ac.kr (J.-H. Ahn).

We have earlier reported good electrochemical performance for a series of GPEs containing 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMImTFSI), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (PMImTFSI) and ceramic fillers (SiO_2 , Al_2O_3 and BaTiO_3) for use in lithium metal polymer batteries (LMPBs) [14,15]. P(VdF-co-HFP) membranes prepared by electrospinning are suitable as host polymers for preparing GPEs due to its high affinity to the electrolyte, good electrochemical stability and desirable adhesion with the electrode.

In the present study, we report the preparation and electrochemical properties of electrospun P(VdF-co-HFP) based GPEs incorporated with a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide based RTILs for the use in LMPBs. Due to the unique properties and high room temperature ionic conductivity, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (PMImTFSI), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMImTFSI) were chosen as the electrolyte components in this study, and the electrochemical properties of the GPEs incorporating them were compared.

2. Experimental

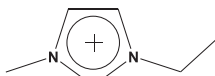
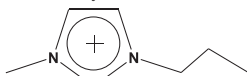
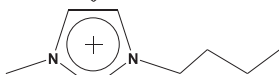
2.1. Materials

P(VdF-co-HFP) (Kynar Flex 2801, $M_w = 4.77 \times 10^5$, VdF/HFP ratio: 88/12, Elf Atochem) was vacuum dried at 60 °C for 24 h before use. Acetone, *N,N*-dimethylacetamide (DMAc) (Aldrich, HPLC grade), and lithium salt, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) were used as received. The RTILs, i.e., EMImTFSI, PMImTFSI and BMImTFSI, were from Aldrich and used after vacuum drying.

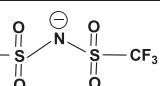
2.2. Preparation of GPEs

A microporous membrane of P(VdF-co-HFP) was prepared by electrospinning as per the procedure standardized in our laboratory [9]. A 16 wt.% solution of P(VdF-co-HFP) in a mixed solvent of acetone and *N,N*-dimethylacetamide (7/3, w/w) was electrospun by applying an electric voltage of 15 kV at room temperature. A fibrous membrane of 100 μm thickness was collected on aluminum foil. The membranes were dried on the collection drum at room temperature for 12 h and finally vacuum dried at 60 °C for 6 h. The structure of the ionic liquids used in this study is shown in Table 1. The GPEs were prepared by immersing the electrospun membrane in 1 M solution of LiTFSI in EMImTFSI, PMImTFSI, and BMImTFSI at 50 °C for 30 min, and then the solution was slowly cooled to room temperature.

Table 1
Ionic liquids used in this work.

Ionic liquid	Cation	Anion
EMITFSI		TFSI ⁻
PMITFSI		TFSI ⁻
BMITFSI		TFSI ⁻

TFSI⁻



2.3. Characterization and electrochemical evaluation of GPEs

The surface morphology of the membrane was observed with a field-emission scanning electron microscope (FE-SEM: Hitachi S-4800). The average fiber diameter (AFD) of the membrane was estimated from the micrograph taken at high magnification and about 250 fibers were investigated. Differential scanning calorimetry (DSC) experiments were performed using a Q1000 from TA Instruments at a heating rate of 10 °C min⁻¹. The samples were sealed in aluminum DSC pans in an argon-filled glove box ($\text{H}_2\text{O} < 5$ ppm). Typically the samples were first cooled at a rate of 20 °C min⁻¹ from 40 °C to -140 °C and then heated at 10 °C min⁻¹ to 180 °C.

The porosity of the membrane was determined by the *n*-butanol uptake method [17]. The electrolyte uptake was determined by soaking a circular piece of the membrane (diameter ~1.5 cm) in the electrolyte solution at 50 °C for 30 min. A higher temperature was employed to facilitate the easy penetration of the electrolytes into the pores of the membrane because the RTILs used are very viscous at room temperature. The wet membranes were slowly cooled to 25 °C and the excess electrolyte remaining on the surface of each membrane was removed by wiping with a tissue paper. The electrolyte uptake (χ) was calculated using the relation [8]:

$$\chi(\%) = (M - M_0) / M_0 \times 100$$

where M_0 is the mass of the dry membrane and M is the mass of the membrane after soaking in electrolyte.

The ionic conductivity of the GPEs was measured by sandwiching the GPE between two stainless-steel (SS) electrodes using complex impedance technique over the temperature range of -20 to 80 °C in a Swagelok® cell. The measurements were carried out using a computer interfaced Zahner IM6 frequency analyzer. The samples were thermally equilibrated at each temperature for 30 min in a temperature-controlled chamber prior to the measurement. The interfacial resistance (R_f) between the GPEs and the lithium metal electrode was measured by the impedance response of Li/GPE/Li cells. The ionic conductivity and the R_f measurements were carried out over the frequency range of 10 mHz to 2 MHz at an amplitude of 20 mV. Laboratory type two-electrode coin cells of 23 mm diameter were assembled by sandwiching GPEs between a lithium metal anode (300 μm thickness, Cyprus Foote Mineral Co.) and a carbon-coated lithium iron phosphate (LiFePO_4) cathode. LiFePO_4 was prepared in-house by mechanical activation followed by solid state reaction at high temperature [16] and the LiFePO_4 cathode (0.95 cm^2) was prepared as its blend with conductive carbon and PVdF binder in the ratio of 80:10:10 by weight. The GPE was prepared as 2.01 cm^2 size and electrochemical performance tests of Li/GPEs/ LiFePO_4 cells were carried out using an automatic galvanostatic charge–discharge unit, WBCS3000 battery cycler (WonA Tech. Co.) between 2.5 and 4.0 V at 25 °C at a current density of 0.1 C. The activation of porous membranes to prepare GPEs and the fabrication of test cells were carried out in an argon-filled glove box under the condition of <10 ppm moisture level.

3. Results and discussion

The surface morphology and fiber diameter distribution histogram of P(VdF-co-HFP) fibrous membrane prepared by electrospinning is presented in Fig. 1. The FE-SEM image (Fig. 1(a)) shows the membrane made up of nanofibers with smooth surfaces and well controlled average fiber diameter. The formation of well-architected membranes with bead free fibers during electrospinning is due to several combinational factors. High polarity of DMAc (dipole moment of 3.7 D and dielectric constant of 37.8 at 25 °C), high volatility of acetone (boiling point 56.2 °C), and polar nature of P(VdF-co-HFP) are the most probable reasons. It can be seen that the membrane has broad fiber diameter distribution (Fig. 1(b)) from micron to submicron. However, about 40% of fibers have fiber diameter of ~725 nm. The interlaying of the fibers

Download English Version:

<https://daneshyari.com/en/article/7745929>

Download Persian Version:

<https://daneshyari.com/article/7745929>

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