Solid State Ionics 317 (2018) 175–182

Contents lists available at ScienceDirect

Solid State Ionics

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

Ionic conductivity, SEM, TGA and rheological studies of Nano-dispersed silica based polymer gel electrolytes containing $LiBF_4$

Narinder Arora[a,*], Simranjit Singh[a], Rajiv Kumar[b], Rajesh Kumar[a], Anita Kumari[a]

[a] P.G. Department of Physics, D.A.V. College, Amritsar 143 001, Punjab, INDIA
[b] Department of Physics, G.G.D.S.D. College, Hoshiarpur 144 208, Punjab, INDIA

ARTICLE INFO

Keywords:
Polymer gel electrolyte
Nano-sized silica
Ionic conductivity
SEM
TGA
DMA

ABSTRACT

Polymethylmethacrylate (PMMA) based nano-dispersed polymer gel electrolytes containing lithium tetrafluoroborate ($LiBF_4$), non-volatile solvents: propylene carbonate (PC) as single solvent, binary solvent mixtures with *N,N*-dimethylformamide (PC:DMF) in different volume ratios and nano-sized silica have been prepared and characterized. Ionic conductivity of gel as well as liquid electrolytes depends mainly upon the donor number and viscosity of the solvents used. Maximum ionic conductivity of 9.4×10^{-3} S/cm at 25 °C has been obtained for nano-dispersed silica based polymer gel electrolyte having (PC:DMF = 1:1) volume ratio. Small content of PMMA in gel electrolyte improves the ionic conductivity, whereas small content of nano-sized silica not only enhances the ionic conductivity, but also improves the mechanical strength of the electrolyte. Two conductivity maxima observed at very low content of nano-sized silica in PMMA based gel electrolytes for binary solvent mixture having 2:1 and 1:1 volume ratios have been explained by double percolation threshold model. Moreover nano-dispersed silica based polymer gel electrolytes show good thermal properties, which have been confirmed by Differential Scanning Calorimetry (DSC) & Thermo Gravimetric Analysis (TGA) and mechanical properties have been studied by Dynamic Mechanical Analysis (DMA) studies. Also, the ionic conductivity of nano-dispersed silica based polymer gel electrolytes show typical curvature behavior as compared to polymer gel electrolyte over the temperature range of 10 °C–70 °C indicating their high amorphous nature. Also, the comparative results have been observed via activation energies for polymer gel electrolytes with and without silica, which have been calculated from logσ vs. 1000/T plot. The behavior of the plot does not show much change at all temperature regions (change is only by a factor), which compile acute in distinct electrochemical devices.

1. Introduction

In current research era, the advancement of ion-conducting polymer gel electrolytes (PGEs) due to their prospective applications in the field of solid state ionic devices viz. rechargeable portable power sources, electro-chromic devices, super capacitors, sensors, etc., which received worldwide attentiveness because of their distinct properties such as high ionic conductivity, flexibility, transparency, free from risk of leakage and fire hazards [1–7,40]. PGEs are usually preferred over liquid electrolytes, because it overcomes the restrictions associated with liquid electrolytes due to leakage of electrolyte, low energy density, bulky in size, short lifetime, pestiferous, corrosion, initiate fumes and fire hazards at ambient temperature. PGEs have numerous advancements such as high ionic conductivity, good mechanical properties, photochemical, structural & volumetric stability, low volatility, high energy density, easy handling, ease of preparation, lightweight, good electrode-electrolyte contact etc. which have tremendous potential in distinct electrochemical devices [8–11]. In the last few years, lithium ion conducting polymer gel electrolytes have gained lot of attention for their use as separators/electrolytes in electrochemical applications as they provide high ionic conductivity $\geq 10^{-4}$ S/cm with better electrochemical stability and safety when compared with the conventional liquid electrolytes [9].

PGEs comprise different polymers poly(ethylene oxide) (PEO), poly (acrylonitrile) (PAN), poly(vinylpyrrolidone) (PVP), polyvinyl alcohol (PVA), poly(methylmethacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(vinyl sulfone) (PVS), poly (ethyl methacrylate) (PEMA) in the solution of various salts [$LiPF_6$, $LiN(CF_3SO_2)_2$, $LiBF_4$, $LiClO_4$, NH_4SCN, NH_4ClO_4, $LiCF_3SO_3$] and organic solvents of low molecular weight like propylene carbonate (PC), -*N,N*-dimethylformamide (DMF), ethylene carbonate (EC), γ-butyrolactone (γ-BL), dimethyl carbonate (DMC), dimethylsulfoxide (DMSO) etc. and much more in mixture forms have been reported by various authors [6,8,10,11].

---

* Corresponding author.
E-mail address: n_arora2k@yahoo.com (N. Arora).

https://doi.org/10.1016/j.ssi.2018.01.023
Received 14 September 2017; Received in revised form 29 December 2017; Accepted 15 January 2018
0167-2738/

Role of the plasticizers (having higher dielectric constant/donor number and lower viscosity) in PGEs decrease the glass transition temperature of whole network and attenuate the backbone of the polymer, which generate and enhance segmental motion of ions. Role of polymer is also important in PGEs: PMMA is one of them, which is an amorphous in nature, colorless, transparent, preserves good mechanical properties and also less reactive towards the lithium electrode or it induces a more favorable passivation film on the electrode surface. So it is of great significance to realize the manipulation of transport properties of plasticized PMMA system. Nano-sized inorganic fillers [SiO_2, TiO_2, Al_2O_3, SnO_2, $BaTiO_3$, Antimony-Tin oxide, Sb_2O_5, γ-AlO(OH) etc.] increase the mechanical strength of the electrolyte [8,10,16,13,24,28]. The use of "classic" nano-oxide particle SiO_2 appears promising for the reinforcement of transparent polymers. In general, these are quasi-spherical nanoparticle that is used in transparent materials to prevent the diffusion phenomena.

In the present research work, we have synthesized the nano-dispersed PMMA based PGEs incorporating lithium tetrafluoroborate ($LiBF_4$) in PC and DMF in single and binary solvent mixtures with nano-sized silica filler. The prepared nano-dispersed PGEs have been investigated via their ionic conductivity behavior, morphology, thermal and rheological analysis. Impacts of the low and high content of PMMA and nano-sized SiO_2 in the PGEs have also been studied at room temperature. Effect of temperature on PGEs and nano-dispersed PGEs has also been studied in the range 10–70 °C. Morphological studies of PGEs in membrane form were characterized by Scanning Electron Microscope (SEM). Moreover, nano-dispersed PGEs show good thermal as well as better mechanical properties, which have been confirmed by simultaneous measurement of Differential Scanning Calorimetry (DSC) & Thermo Gravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA) respectively.

2. Experimental

2.1. Materials/reagents

The host polymer poly(methylmethacrylate) (PMMA) (Average $M_w = 1{,}20{,}000$ g/mol; $\rho = 1.18$ g/cm^3), doping salt, lithium tetrafluoroborate ($LiBF_4$) ($M_w = 93.746$ g/mol; $\rho = 0.852$ g/cm^3), the solvents; propylene carbonate (PC) ($M_w = 102.09$ g/mol; $\rho = 1.205$ g/cm^3), -*N,N*-dimethylformamide (DMF) ($M_w = 73.10$ g/mol; $\rho = 0.948$ g/cm^3) and nano-sized inorganic filler SiO_2 (Surface area = 175–225 m^2/g, $M_w = 60.08$ g/mol; $\rho = 2.65$ g/cm^3) were obtained from Sigma-Aldrich and used as starting materials for preparation of nano-dispersed polymer gel electrolytes as obtained.

2.2. Synthesis of polymeric gel membranes

Prior to the preparation of PGEs, the doping salt $LiBF_4$ and nano-sized SiO_2 were enclosed inside the desiccator and vacuum dried for 10–15 days. Then liquid electrolytes were prepared by dissolving the salt (in different molar concentrations) in single and binary solvent mixtures such as PC, DMF, PC:DMF (2:1), PC:DMF (1:1) respectively. After that polymer PMMA was added in liquid electrolytes along with continuous stirring for precise hours at 60 °C to obtain homogeneous gel matrix. The desired amount of SiO_2 was added to obtain nano-dispersed PGEs and to enhance the amorphous nature and mechanical strength of gel matrix, which were then used for various characterizations. These viscous gel electrolytes were poured in petri dish covering the top with aluminum foil enclosed inside the desiccator at room temperature for one week and the prepared membranes were finally dried at 70 °C for 24 h and then at 50 °C for 36 h to remove any traces of moisture present in the membrane. A typical photograph of the nano-dispersed SiO_2 based PGE membrane is shown in Fig. 1.

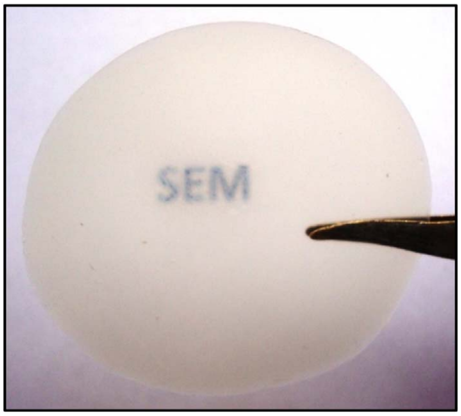

Fig. 1. A typical photograph of 0.05 wt% nano-sized SiO_2 based polymer gel electrolyte (in membrane form) containing 1 M $LiBF_4$ in PC:DMF (2:1).

2.3. Characterization

Ionic conductivity of PGEs was measured by dc conductivity meter (WTW 3210) with probe WTW TetraCon 325 which is based upon four probe method having inbuilt temperature sensors. Surface morphology of PGE membranes was scrutinized by using Scanning Electron Microscope (JEOL JSM-6100). The various SEM images were captured under a low vacuum after sputtering the membranes with gold by using Ion Sputter (JEOL JFC-1100). Thermal studies were carried out by Differential Scanning Calorimetry (DSC) and Thermo Gravimetric analysis (TGA) by using Perkin Elmer (STA 6000) analyzer. Prior the studies, samples were hold for 1 min at 40 °C, then heated from 40 to 200 °C at the heating rate of 5 °C/min. Further, the samples were again hold for 1 min at 200 °C. Dynamic mechanical analysis (DMA) was carried on a Rheometer (Anton Paar MCR 702) with heating element P-PTD 200 (Peltier temperature device) having Parallel plate 25 mm diameter geometry (PP25). Measurements of Storage and Loss Modulus of dried PGE samples were analyzed in compression mode at an angular frequency of 10 rad/s having constant temperature (25 °C) with an increase of Shear Strain.

2.4. Result and discussion

2.4.1. Morphological studies

Morphological studies were carried out by SEM to investigate the effect of nano-sized SiO_2 content on the surface morphology of the PMMA based PGEs and micrographs have been shown in Fig. 2. The image 2(a) shows a rough morphology with a great deal of micro-pores, a common occurrence for PMMA-based electrolytes prepared by the solvent casting method and similar results have already been reported [12–14] illustrating the presence of crystalline phase in PMMA. A dramatic improvement of surface morphology from roughness to smoothness is achieved {Fig. 2(b)} after the addition of small amount of SiO_2 nano-filler. The smooth surface morphology leads to the reduction of PMMA crystallinity via interaction between PMMA segments and SiO_2 nano-particles. Moreover, the pore-size has been observed to increase in this segment as compared to PMMA based PGEs (from ~9.143 μm to ~15.52 μm) suggesting the swelling of polymer with the influence of SiO_2 in membrane of PGE matrix.

The reduction of PMMA crystallinity with the lower content of nano-sized SiO_2 that introduces the topological disorder in the electrolyte making the electrolyte more flexible, and thus resulting an increase in segmental motion of the polymeric chains [15]. Moreover, the micrographs are dark in color as shown in Fig. 2(a) and (b), which represents a more amorphous region as already reported by *Monikowska* et al. [16]. As ions move more freely in the electrolyte with smoother surface morphology, causing an enhancement in the ionic conductivity