© 2018 IJSRST | Volume 4 | Issue 9 | Print ISSN : 2395-6011 | Online ISSN : 2395-602X
Themed Section: Science and Technology

Electrochemical Investigations on Poly (ethylene oxide)-Based Nanocomposites laden with $BaTiO_3$-Grafted-Graphene oxide

S.Padmaja[1], Suryasarathi Bose[2], R. Nimma Elizabeth[1*]
[1]Department of Physics, Lady Doak College, Madurai, Tamil Nadu, India
[2]Materials Engineering Department, Indian Institute of Science, Bangalore, Karnataka , India

ABSTRACT

Nanocomposite polymer electrolytes (NCPE) comprising poly(ethylene oxide)(PEO), lithium trifluro methane sulphonate (LiCF3SO3) and barium titanate-grafted-graphene oxide (BaTiO3-g-GO) were successfully prepared by a simple hot-press technique. The ionic conductivity was increased up to one order upon addition of BaTiO3-g-GO in the polymeric matrix. The membranes were subjected to themogravimetric, tensiles. Appreciable ionic conductivity, thermal stability and mechanical properties qualify these membranes as electrolytes for all-solid-state-lithium batteries.

Keywords: Electrochemistry; composites;ionic conductivity;tensile; thermogravimetric analysis (TGA)

I. INTRODUCTION

The increasing demand for energy due to fluctuation in oil prices and global warming has promoted researchers to find alternative energy resources across the world[1-2]. Electrochemical devices such as batteries, super capacitors, fuel cells are identified as strong contenders to fulfill the energy demands for the development of high performing materials have increased exponentially in past two decades[3]. Rechargeable lithium-ion batteries are considered as a potential system not only for consumer electronics but also for hybrid electric vehicles and stationary power grid applications[4-6].

The state-of-the-art lithium-ion batteries are composed of carbonaceous anode (LiC_6) and a lithium transition metal oxide cathode separated by a polyolefin membrane soaked in a non-aqueous electrolyte[7-8]. However, this system suffers from poor safety problems due to the presence of volatile and flammable organic solvents present in the electrolyte solution. The solid polymer electrolyte on the other hand has several advantages over its liquid counterpart such as no-leakage of electrolyte, flexible geometry, high energy density, and better safety[9,10]. In particular, the lithium polymer battery with lithium metal as anode is in focus of many researchers due to the unique properties of lithium metal such as low atomic weight(6.99 g mol^{-1}), high electro negativity (-3.05 V vs. SHE) and specific capacity(3.76 Ah g^{-1})[11].

The dry solid polymer electrolyte, for example poly(ethylene oxide) PEO based systems comprising a polymer host and a lithium salt (LiX) exhibit very low ionic conductivity(10^{-8} S cm^{-1}) at 25°C which excludes it from ambient temperature applications[12]. Although the appealing properties of gel polymer electrolyte such as high ionic conductivity (order of 10^{-3} Scm^{-1} at 30^0C) and transport numbers permit them to qualify as a potential candidate for room temperature applications, its poor mechanical integrity hampers it from commercialization[13-15]. Interestingly, in order to overcome these drawbacks nanoparticle ceramic fillers such as Al_2O_3, SiO_2, and TiO_2 were added in PEO-based electrolytes[16]. The addition of inert fillers

IJSRST184922 | Received : 08 July 2018 | Accepted : 22 July 2018 | July-August-2018 [4 (9) : 87-92]

not only increases the amorphous phase of the polymeric host but also promotes its electrochemical property and mechanical integrity[17-21]. The degree of enhancement, however, mainly depends on the nature of the ceramic filler and its surface states[22].

It has also been demonstrated that nanosized particles with Lewis-acidic surface properties received much attention in an attempt to increase the ionic conductivity and their large surface-to-volume ratio stabilizes the electrolyte/lithium interface[23]. Takeda et al[24] reported the electrochemical properties of mixed-phase electrolytes compromising $BaTiO_3$, $PbTiO_3$ and $LiNO_3$. The same group has reported the cycling behavior of Li/PEO+$BaTiO_3$+$LiCF_3SO_3$[25]. However, the cycling profile was found to be poor even at 70°C. The authors have also reported the interfacial properties of $BaTiO_3$-g-GO added PEO based electrolytes with different lithium salts[26].

In the present work, a unique hybrid nanoparticle consisting of $BaTiO_3$ which is chemically coupled to graphene oxide (GO) sheets was synthesized and employed as a filler[27,28]. This hybrid particle was suitably incorporated in a PEO matrix along with a lithium salt to design polymer electrolytes for all-solid-state lithium-batteries and its physical, thermal and electrochemical properties are studied.

II. METHODS AND MATERIAL

A. Preparation of NCPE

The nanocomposite polymer electrolyte (NCPE) samples were prepared by a simple hot press technique as reported earlier[29]. The electrolytes were prepared for the various compositions of PEO, $LiCF_3SO_3$, $BaTiO_3$-g-GO as displayed in Table 1. Briefly; all components, namely the selected $LiCF_3SO_3$, PEO and filler ($BaTiO_3$-g-GO) were dissolved in an anhydrous acetonitrile. The total weight of polymer, inert filler and lithium salt was set to be 100% by weight. The solution was continuously stirred in a magnetic stirrer for 6 hours at room temperature. The viscous solution was cast as a membrane. Upon evaporation of solvent the precursor was hot-pressed in order to get a uniform membrane. The thickness of the membrane was between 50-60μm. Subsequently, this membrane was stored in a vacuum oven for further characterization.

Table 1. Composition of PEO,$LiCF_3SO_3$,$BaTiO_3$-g-GO

Sample	**PEO wt(%)**	**$LiCF_3SO_3$ wt(%)**	**$BaTiO_3$-g-GO**
S1	98	2	0
S2	95	3	2
S3	90	5	5
S4	85	10	5
S5	80	12	8

B. Characterization of NCPE

In the present study sample S5 was used for both physical and electrochemical characterizations as this sample was found to be optimal in terms of ionic conductivity. The ionic conductivity of the samples was measured by sandwiching the samples between two stainless steel blocking electrodes. The measurements were performed using an electrochemical impedance analyzer (Bio-Logic InstrumentSP-31, France) between 100 kHz and 50 mHz for different temperatures between 30°C and 60 °C.

Thermogravimertic analysis (SIINT 6300, Japan) was performed between room temperature and 800°C at a heating rate of 10°C/min. The tensile strength of nanocomposite membrane was determined by a tensile machine (Tinus Olsen) with a constant cross-head speed of 10 mm min^{-1}. The sample was prepared according to ASTM standard D368.

III. RESULTS AND DISCUSSION

A. Ionic Conductivity

The conductivity of the polymer electrolyte can be calculated from the equation $\sigma = L/(AR)$, where A is the area of the electrode, L is the thickness of the film and R is the bulk resistance.

The ionic conductivity of NCPEs as a function of inverse temperature for various concentrations of PEO, $LiCF_3SO_3$ and $BaTiO_3$-g-GO are depicted in Figure 1.

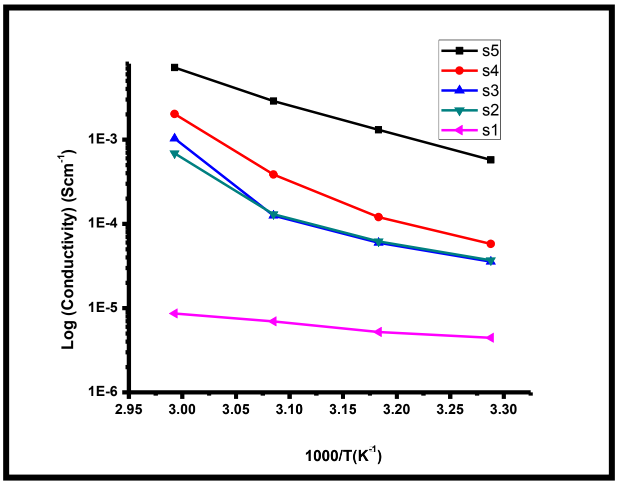

Figure 1. Variations of ionic conductivity as a function of inverse temperature of NCPE's

The ionic conductivity increases with the increase of temperature and also with the increase of $BaTiO_3$-g-GO content. The ionic conductivity varies from 10^{-5}Scm^{-1} to 10^{-3} Scm^{-1} for the sample S1(PEO+$LiCF_3SO_3$) to S5 (PEO+$LiCF_3SO_3$+ $BaTiO_3$-g-GO). Irrespective of the concentration of $BaTiO_3$-g-GO and $LiCF_3SO_3$ content all curves show a remarkable change in the slope at 50 °C beyond, which indicates the well-known transition of PEO from the crystalline to the amorphous phase. The incorporation of $BaTiO_3$-g-GO polymeric matrix has significantly increased the ionic conductivity of the NCPE. An increase of two order magnitude, in ionic conductivity is observed when the content of $BaTiO_3$-g-GO was 8 % (sample S5). Generally, for the NCPE materials the ionic conductivity is not a linear function of filler concentration. At lower concentration, diffusion effect takes place which tends to depress the ionic conductivity and is effectively opposed by specific interactions of Li^+ - ions and thus promoting fast ionic transport. At very higher filler content, the conductivity is reduced due to the predominant dilution effect. Thus the maximum ionic conductivity is achieved only in the concentration ranging between 2 and 8 wt.% however, it is mainly influenced by the nature of the filler.

Generally, Lewis acid groups of the added filler may compete with the Lewis acid lithium cations for the formation of complexes with the alkoxide of the PEO-chains, as well as with the anions of added $LiCF_3SO_3$. This results in structural modifications of filler surfaces due to the specific actions of the polar surface groups of the inorganic filler. The Lewis acid-base interaction centers on the electrolyte species, thus lowers the ionic coupling, and the salt dissolutions is promoted by the formation of "ion-filler complex" [27-30]. At higher filler content, the conductivity is reduced due to the predominant dilution effect.

In the present study, the observed increase in ionic conductivity is attributed to the interaction of Lewis acidic center of $BaTiO_3$-g-GO with anions of the $LiCF_3SO_3$ salt which reduces the crystallinity of the polymeric host[27-31]. This reduction in the value of crystallinity could be the reason for the increase in ionic conductivity. The activation energy was calculated for the various samples. When the salt concentration of $LiCF_3SO_3$ was increased, activation energy decreases which indicates that the Li^+ ions are able to migrate from one site to another site even at lower energy. The activation energy Ea has been calculated for the samples S1 and S5 as 0.6 keV and 0.2 keV respectively which further substantiates our conductivity data[32].

B. TG Analysis

The TG traces of nanocomposite polymer electrolyte samples S1 (PEO+LiCF$_3$SO$_3$) and S5 (PEO+LiCF$_3$SO$_3$+BaTiO$_3$-g-GO) are depicted in Figure 2. The TG curve shows a small endothermic peak below 50°C with a corresponding weight loss of 2% for S1 sample which is attributed to the removal of superficial moisture.

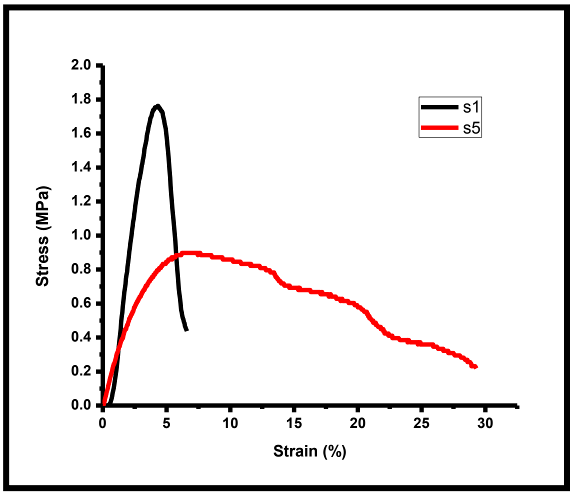

Figure 2. TG traces of Samples PEO,S1,S5

The weight loss occur at 70°C, is due to the melting of PEO and no significant peak was observed until 170°C. On the other hand, for the NCPE (sample S5) the irreversible decomposition starts at 310°C. This apparent increase in the thermal stability of NCPE is attributed to the shielding effect offered by added BaTiO$_3$-g-GO. A similar observation has been reported by Angulakhsmi et al. where the authors studied the thermal stability of MgAl$_2$O$_4$ composite polymer electrolytes[33,34.]

C. Tensile Study

The stress-strain behavior of sample S1 (PEO+LiCF$_3$SO$_3$)and S5 (PEO+LiCF$_3$SO$_3$+BaTiO$_3$-g-GO) are displayed in Figure 3. The tensile strength of sample S1 is 1.7MPa with an elongation-at-break value 6%. Upon addition of 8% BaTiO$_3$-g-GO the elongation-at-break is increased to 32% with a reduction in the mechanical strength (0.8 MPa). This reduction in mechanical strength was attributed from the plasticization of PEO matrix by BaTiO$_3$-g-GO[35].

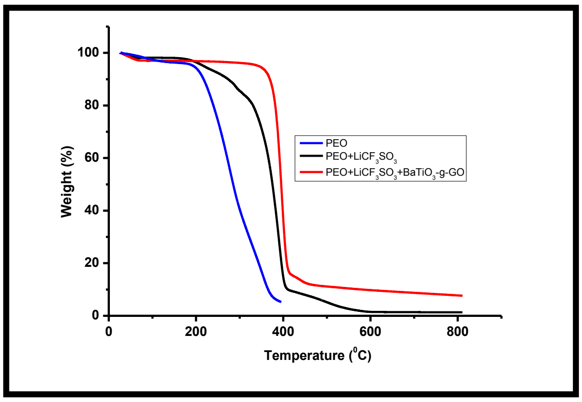

Figure 3. Stress vs. strain behavior of S1 and S5 at 25°C.

IV. CONCLUSION

The NCPE's composed of PEO+LiCF$_3$SO$_3$ + BaTiO$_3$-g-GO were prepared by a simple hot press technique and were subjected to physical and electrochemical characterizations. Both ionic conductivity and thermal stability of polymeric membrane were increased upon addition of BaTiO$_3$-g-GO in the polymeric matrix. Among the samples analyzed the polymeric membrane with the composition of PEO: LiCF$_3$SO$_3$: BaTiO$_3$-g-GO (80:12:8) was found to be optimal in terms of ionic conductivity.

V. REFERENCES

[1]. Tarascon, J.M.; Armand, M. (2008), Building better batteries,Nature, 451, 652-657.

[2]. Tarascon, J.M.; Armand, M.(2001),Issues and challenges facing rechargeable lithium batteries, Nature, 414, 359.

[3]. Bruce, P. G.;ScrosatiB.;Tarascon,J.M(2008),Nanomaterials for rechargeable lithium batteries.;Angew. Chem.Intl. Edn Engl. 47(16),2930-2946.

[4]. Tanaka, T.; Ohta, K.; Arai, N.; (2001), Year 2000 R&D status of large-scale lithium ion secondary

batteries in the national project of Japan ,J Power Sources, 97-98,2.

[5]. Dell, R. M.; Rand, D.A.J (2001),Energy storage-a key technology for global energy sustainability, J Power Sources,100,2

[6]. Tarascon, J.M.; Armand, M.(2001), Issues and challenges facing rechargeable lithium batteries. Nature, 414, 359.

[7]. Subramaniyan, V.; Luo, C.; Manuel Stephan, A.; Nahm, K. S.; Thomas, S. (2007),Supercapacitors from Activated Carbon Derived from Banana Fibers, J Phys Chem C, 111, 7527-7538.

[8]. Winter, M. R. J.; Bhod, (2004),What Are Batteries, Fuel Cells, and Supercapacitors ,Chem. Rev , 104,4245-4260.

[9]. Xue Z.; He D.; Xie X.(2015),Iron-catalyzed atom transfer radical polymerization, Polym. Chem.,6, 1660-1687.

[10]. Manuel Stephan,A. (2006), Review on gel polymer electrolytes for lithium batteries,Eur. Polym. J.,21, 21-42.

[11]. Bouchet, R.; Lascaud, S.; Rosso, M.; (2003), An EIS study of the anode Li/PEO-LiTFSI of a Li polymer battery, J Electrochem. Soc,150, A1385-A1389

[12]. Fenton,D.E.;Parker, J.M.;Wright, P.V.;1973, Solid polymeric electrolyte of poly(ethylene)oxide-50% epoxidized natural rubber-lithium triflate (PEO-ENR50-LiCF3SO3),Polymer ,14, 589.

[13]. Manuel Stephan,(2006), Review on gel polymer electrolytes for lithium batteries; Eur. Polym. J. 21,21-42.

[14]. Appetecchi G.B.;Croce F.; Scrosati, S.; 1990,Kinetics and stability of the lithium electrode in poly(methylmethacrylate,Electrochim Acta ,20,991-997.

[15]. Manuel Stephan, A.; Gopukumar, S.; Renganathan, N.G.; Nathan, M.A.K. (2005)A high-performance BaTiO3-grafted-GO-laden poly(ethylene oxide)-based membrane as an electrolyte for all-solid lithium-batteries; Eur.Poly . J,41,15-21.

[16]. Manuel Stephan, A.; Nahm, K.(2006),Review on composite polymer electrolytes for lithium batteries;Polymer,47, 5952-5964

[17]. Vincent, C.; Scrosati, B.; (2000) ,Polymer Electrolytes: The Key to Lithium Polymer Batteries,Matter.Res Soc 2000,25,28-30.

[18]. Weston, J.E.;Steele, B.C.H. (1982),Effects of inert fillers on the mechanical and electrochemical properties of lithium salt-poly(ethylene oxide) polymer electrolytes; Solid State Ionics,7,75-79

[19]. Scrosati,B. (2005)Power sources for portable electronics and hybrid cars: lithium batteries and fuel cells; Chem Rec,5,286-297.

[20]. Croce, F.; Appetecchi ,G.B.;Perci, L.; Scrosati, S.(1998),Nanocomposite polymer electrolytes for lithium batteries, Nature;394:456-458

[21]. Croce,F.; Curini ,R.; Martinelli, A.; Ronci, F.; Scrosati, B.; Caminiti, R.(1999), Physical and Chemical Properties of Nanocomposite Polymer Electrolytes, J Phys Chem;103,10632.-10638.

[22]. Croce, F.; Settimi, L.; Scrosati, B.;(2006), Nanocomposite, PEO-LiBOB polymer electrolytes for low temperature, lithium rechargeable batteries, Electrochem,8,364-368

[23]. Xi, J.; Qiu, X.; Cui, M.; Tang, X.; Zhu, W.; Chen, L.; (2006),High discharge capacity solid composite polymer electrolyte lithium battery,J Power Sources,156,581-588.

[24]. Sun, H. Y.; Takeda,Y.; Imanishi, N.; Yamamoto, O. (2000),Polymer Electrolytes for Lithium Polymer Batteries; Sohn H. J.; J Electrochem Soc,147, 2462-2467.

[25]. Li, Q.; Takeda,Y.; Imanishi,N.; Yang, J.; Sun, H. Y.; Yamamoto O. (2001),Ferroelectric Materials as a Ceramic Filler in Solid Composite Polyethylene Oxide-Based Electrolytes;J Power Sources,97-98,795-797

[26]. Li, Q.; Sun, H.Y.; Takeda, Y.; Imanishi, N.; Yang, J.; Sun,H. Y.; Yamamoto, O.;J Power Sources 2002,94,201-205

[27]. Shin, J.H.; Alessandrini, F.; Passerini, S. (2005), Electrochemical and mechanical properties of nanochitin-incorporated PVDF-HFP-based polymer electrolytes for lithium batteries; J Elecrochem. Soc,152,A283-A288.

[28]. Manuel Stephen, A.; Prem kumar, T.; Nathan, A.K.; Angulakshmi, N. (2009),Chitin-Incorporated Poly(ethylene oxide)-Based Nanocomposite Electrolytes for Lithium Batteries. J Phys Chem B,113,1963-1971.

[29]. Appetecchi G.B.;Hassoun, J.; Scrosati, S.; Croce F.;Cassel, F.; Salomon,M.; 2003, Hot-pressed, solvent-free, nanocomposite, PEO-based electrolyte membranes: II. All solid-state Li/LiFePO4 polymer batteries,Power Sources J29. ,124,246-253.

[30]. Croce, F.; Perci, L.; Scrosati, B.; Fiory, F. S.;Plichta, E.; Hendrickson, M. A,(2001),Composites polymer electrolytes for electrochemical devices,Electrochim Acta 2001,46,2457-2461.

[31]. Angulakshmi, N.;Nathan, M.A.K.;Kumar R.S.; Manuel Stephen, A.(2014) Composite Polymer Electrolytes Encompassing Metal Organic Frame Works: A New Strategy for All-Solid-State Lithium Batteries,J Phys.Chem 2014 C118, 240-247.

[32]. Gerbaldi,C.; Nair,J. R..; Nathan, M. A. K.; Kumar, R. S.; Ferrara, C.; Mustarelli, P.; Manuel Stephan, A. (2014),A high-performance BaTiO3-grafted-GO-laden poly(ethylene oxide)-based membrane as an electrolyte for all-solid lithium-batteries, J. Mater.Chem.,A 2, 9948- 9954.

[33]. Angulakshmi N.; Nahm,K.S.; Jijeesh, R. Nair; Gerbaldi, C; Bongiovanni,R; Penazzi, N; Manuel Stephan, (2013),Cycling profile of MgAl2O4-incorporated composite electrolytes composed of PEO and LiPF6 for lithium polymer batteries, Electrochimica Acta,90, 179–185

[34]. Shodai, T.; Owens,B. B.; Ostsuka,M.; Yamki,J. (1994),Electrochemical and mechanical properties of nanochitin-incorporated PVDF-HFP-based polymer electrolytes for lithium batteries, J Electrochem Soc,141, 2978-2981.

[35]. Fan, L. Z.; Maier,(2006), Composite effects in poly(ethylene oxide)–succinonitrile based all-solid electrolytes,J Electrochem Commun,8, 1753-1756.