IONIC CONDUCTIVITY, COMPATIBILITY AND CHARGE-DISCHARGE STUDIES OF PEO BASED NANOCOMPOSITE POLYMER ELECTROLYTE FOR LITHIUM SULFUR BATTERIES

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Abstract : Nanocomposite polymer electrolytes(NCPE) comprising poly ethylene oxide(PEO),$LiCF_3SO_3/LiClO_4/LiBF_4$ and filler $BaTiO_3$-g-GO for different composition were prepared by a simple hot press technique.The prepared membranes were subjected to ionic conducvitiy and compatbility studies. The addition of filler in the PEO+ $LiCF_3SO_3$ complexes has significantly enhanced the ionic conductivity and was attributed to Lewis acid-base interaction. Finally, a 2032-type Li-S was assembled and its cyclying profile was analysed at 60^0C.

Key words:ionic conductivity; comptability;cycling

I. INTRODUCTION :

Lithium–sulfur battery one of the most promising rechargeable batteries among various energy storage devices are boon to the battery technology owing to its ultrahigh theoretical capacity and low cost[1,2]. A major issue for its commercialization is the rapid capacity fading due to polysulfide dissolution and the formation of undesirable lithium dendrites. A tactic to improve the capacity and cyclability of Li-S batteries is the electrolyte optimization so as to reduce the loss of sulfur by dissolution in the liquid electrolyte [3-8]. Among the possible electrolyte alterations, replacement of the common liquid organic electrolytes with polymer electrolytes has been proved as promising and efficient. The advantages of these electrolytes include no-internal shorting, leakage of electrolytes and no non-flammable reaction products at the electrode surface [9–13]. The development of polymer electrolyte for lithium batteries focusses on enhancing ionic conductivity at ambient temperature, tensile strength, appreciable transference number thermal and electrochemical stabilities and better compatibility with electrodes [10-12,14]. 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[15]. Takeda et al[16] 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+$BaTiO_3$+$LiCF_3SO_3$[17]. However, the cycling profile was found to be poor even at 70°C. The authors have also reported the interfacial properties of $BaTiO_3$ added PEO based electrolytes with different lithium salts[18].

The filler was suitably incorporated in a PEO matrix along with a lithium salt to design polymer electrolytes for all-solid-state lithium-sulfur batteries and its electrochemical properties are studied.

II. EXPERIMENTAL DETAILS

Preparation of NCPE

The nanocomposite polymer electrolyte (NCPE) samples were prepared by a simple hot press technique as reported earlier[19,20]. In the present work, $BaTiO_3$-g-GO separately were prepared [21,22] as a filler. The electrolytes were prepared for the various compositions of PEO, LiX(X= $CF_3SO_3/ClO_4/BF_4$) and $BaTiO_3$-g-GO as filler displayed in Table 1. Briefly; all components, namely the selected LiX, PEO and filler 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, LiX, Filler

Sample	**PEO wt(%)**	**LiX ($X=CF_3SO_3/ClO_4/BF_4$) wt(%)**	**Filler ($BaTiO_3$-g-GO)**
S1	98	2	0
S2	95	3	2
S3	90	5	5
S4	85	10	5
S5	80	12	8

The ionic conductivity 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 30ºC and 60 °C.

The compatibility of NCPE with lithium metal anode was studied by assembling symmetric cell composed of Li/NCPE/Li and measuring its interfacial resistance R_i as a function of time under open circuit condition at 60°C.

Sulfur-Graphene(SG) binary composite cathodes for cycling studies were prepared by doctor blade-coating a slurry comprising 72 wt% of the SG, 12 wt% of Poly(vinylidene fluoride) and 16 wt% of Super P carbon dispersed in N-methyl-2-pyrrolidone on an aluminium foil, and was dried at 100 ◦C in an air oven. A 2032-type coin cell was assembled with SG electrode with areal sulfur loading of 0.5 mg/cm^2 and lithium metal foil (Foote Minerals) was used as anode. The NCPE was sandwitched between the two electrode. The Li-S cell was cycled between 1.6 and 3V.

III.RESULTS AND DISCUSSION

Ionic Conductivity

The ionic conductivity of the nano composite polymer electrolyte was calculated from the equation

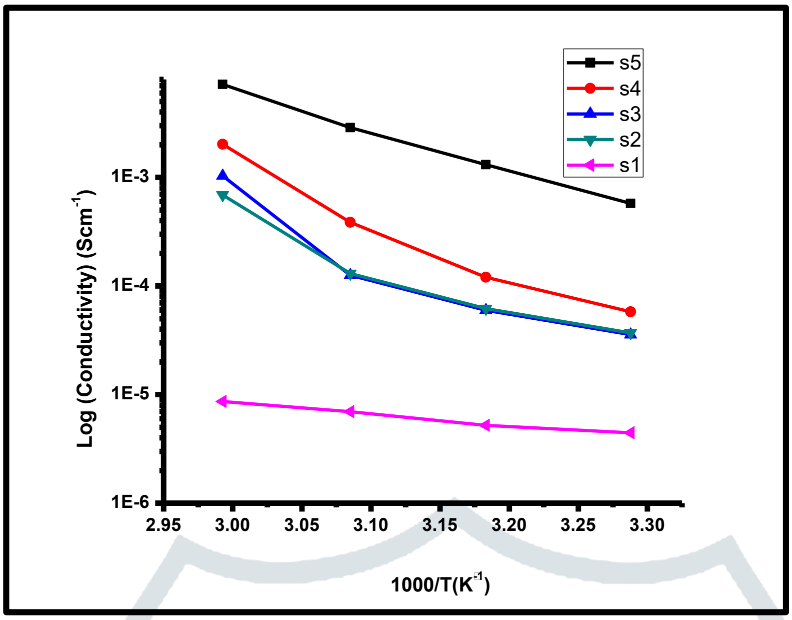

Fig. 1. Variation of ionic conductivity as a function of inverse temperature of NCPE for S1-S5 of salt $LiCF_3SO_3$ with filler $BaTiO_3$-g-GO

$\sigma = L/(AR)$

where A is the area of the electrode

L is the thickness of the film

R is the bulk resistance.

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).An increase of two orders magnitude, in ionic conductivity is observed when the content of $BaTiO_3$-g-GO was 8 % (sample S5).Irrespective of the content of $BaTiO_3$-g-GO and $LiCF_3SO_3$, all curves show a remarkable change in the slope beyond 50 °C, which indicates the well-known transition of PEO from the crystalline to the amorphous phase. The observed increase in ionic conductivity was 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[23-26].

At higher filler content, the conductivity is reduced due to the predominant dilution effect. Similarly, the ionic conductivity also increases with the increase of lithium salt concentration as evidenced in Fig 2.

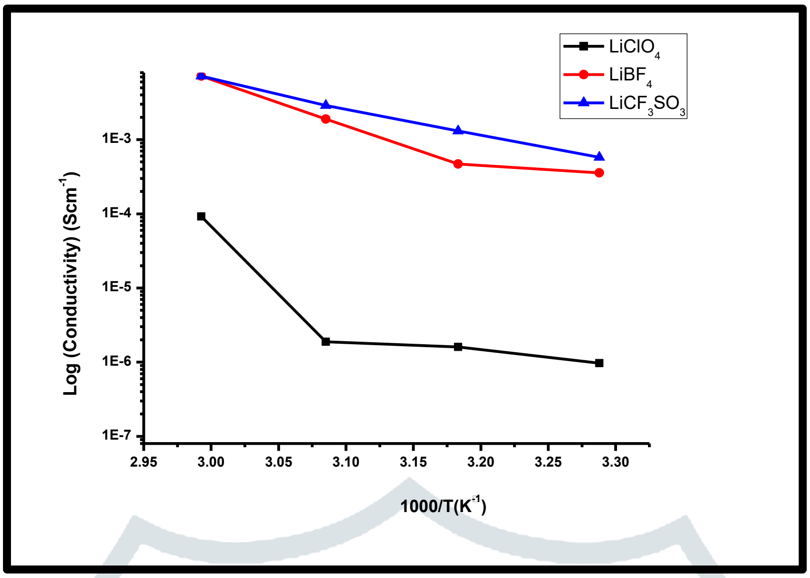

Fig 2 Variation of ionic conductivity as a function of inverse temperature of NCPE for S5 with different salts with $BaTiO_3$-g-GO as filler

Among the salts studied, the NCPEs with $LiCF_3SO_3$ as salt shows the maximum ionic conductivity and is attributed to the fact that there is a higher dissociation of bulky anion in the polymer host when compared with other salts. Also the fluorinated anions can be easily dissociated . In all the systems examined no discernable change was observed in the order of ionic conductivity values above 60^0C where the well know transition from crystalline to amorphous of PEO takes place.

Compatibility

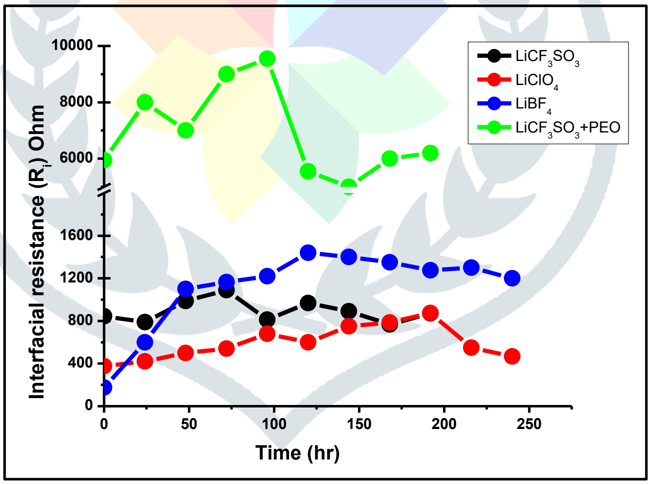

Fig 3: Variation of interfacial resistance as a function of time for the samples S1(PEO+$LiCF_3SO_3$) ,S5 (PEO+$LiCF_3SO_3$/$LiClO_4$/$LiBF_4$+$BaTiO_3$-g-GO)

The interfacial resistance plays a vital role in determining the properties that include shelf life, safety, lithium deposition, dissolution, efficiency and cycle life. The compatibility of NCPE with lithium metal anode was studied by assembling symmetric cell composed of Li/NCPE/Li and measuring its interfacial resistance R_i as a function of time under open circuit condition at 60°C.

In the present study, sample S5 was used for electrochemical characterizations as this sample was found to be optimal in terms of ionic conductivity.

Initially for the PEO+$LiCF_3SO_3$ complex the value of interfacial resistance, 'R_i' increases exponentially. The growth of the interfacial resistance does not follow a regular trend. The interfacial resistance of the NCPE has been significantly reduced upon the incorporation of $BaTiO_3$-g-GO and after 150 hours the 'R_i' values do not change much. This may be attributed to the morphological changes of the passivation films that varies with time to finally acquire a non-compact, possibly porous structure. This insulating layer will impede electrode reactions. This may very well have happened when excessive amount of the passive $BaTiO_3$ -g-GO phase were introduced into the polymer matrix.

It is quite apparent from the figure 3 that the values of interfacial resistance “R_i” for NCPE’s increases with increase of time and the value is found to be higher for the lithium salt which possesses fluorine compound. The salt which possesses no fluorine compound, for example, $LiClO_4$ exhibits minimum interfacial resistance “R_i”. However, the “R_i” values of the film with $LiCF_3SO_3$ are more or less similar to that of $LiClO_4$. The low compatibility of polymer electrolytes containing fluorinated lithium salts with lithium metal anode may be attributed to the following reasons. The amount of fluorine substances on the lithium surface increases according to the storage time. An important reason for the increase in “R_i” is due to the formation of fluorine compound LiF on the surface of lithium.

Charge-discharge

The Li-S cell with NCPE comprising PEO+$LiCF_3SO_3$+ $BaTiO_3$-g -GO was assembled as described in the experimental procedure. For cycling analysis the NCPE membrane PEO+$LiCF_3SO_3$+ $BaTiO_3$-g-GO was employed as this membrane exhibited high ionic conductivity and good electrochemical properties.

The polymer cells were characterized by galvanostatic cycling in the 1.4V-3.0V range at different current densities at 60°C. The performance of the cells was evaluated in terms of discharge capacity and cycle life. The cells were cycled at different current regimes from 0.1C to 5C-rates.

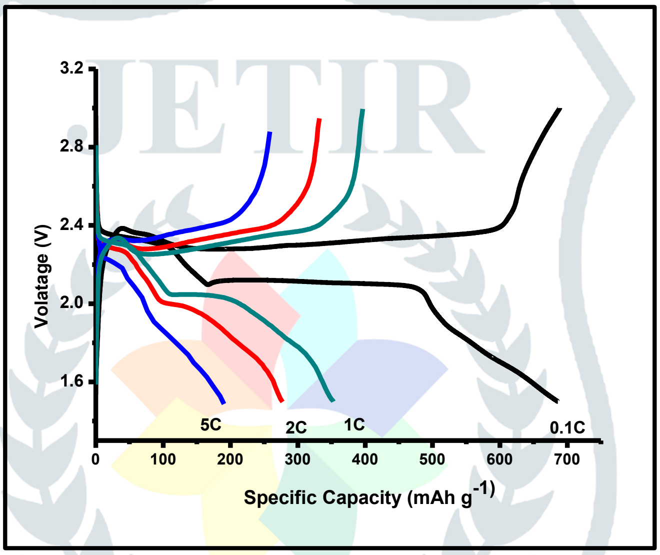

Fig 4: Cycling profile of Li-S cell PEO+$LiCF_3SO_3$+$BaTiO_3$-g-GO

The specific capacity of the material was calculated by the equation Specific capacity(mAh/g)= Time(h)x current(mA)/Material weight(g).

The cell shows a well defined stable plateau at 2.4V vs Li^+ on charge and 2.1V vs Li-on discharge at different C-rates. A small drop in voltage indicates a lower interfacial resistance and is attributed to the better adhesion of the NCPE on the electrode. It offers an initial discharge capacity of 698 mAh g^{-1} at 0.1C- rate and it decreases to 489 mAh g^{-1} at 1C- rate with the Coulombic efficiency 99% and at 2C- rate it drastically reduces to 280 mAh g^{-1} .The cell offers a discharge capacity of 198 mAh g^{-1} at 5C- rate without much in fade in capacity. Even this small fade in capacity with increase in C- rate is attributed to the following reasons. Composition of cathode material which has to be optimized.

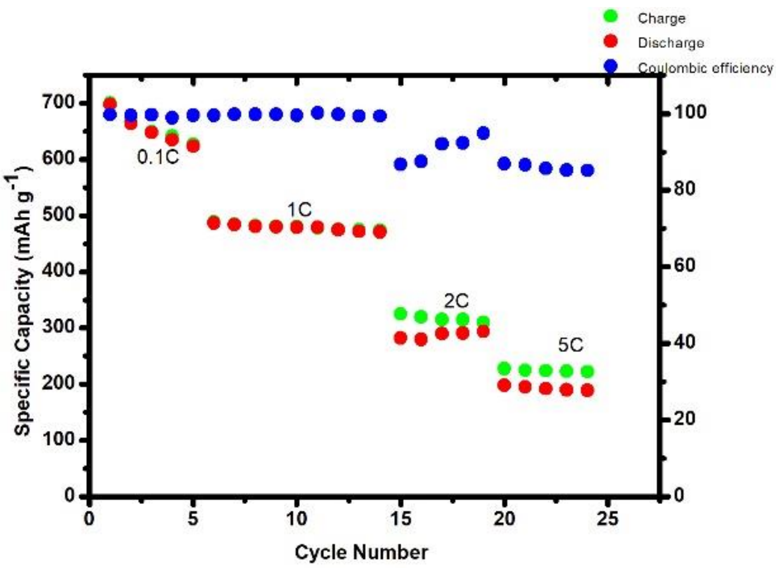

Fig 5: Discharge capacity as a function of cycle number- PEO+$LiCF_3SO_3$+$BaTiO_3$-g-GO

Typical characteristic of S is its low electronic conductivity and the limited diffusion of Li^+ ions into the structure, causing electrode polarization and the formation of a solid electrolyte interface. The declining discharge capacity at higher C- rates may also be due to the solid electrolyte interface(SEI) film formation with electrolyte decomposition.The better cyclability with appreciable Coulombic efficiency at low C- rates is attributed to the slower diffusion of polysulfides to the anode than the total electrochemical reaction time. Generally, measurement of Coulombic efficiency can be widely employed to quantify the shuttle process.

IV.CONCLUSIONS

The nanocomposite polymer electrolytes comprising PEO- $LiCF_3SO_3$-$BaTiO_3$-g-GO exhibited maximum ionic conductivity at 60ºC among the lithium salts analysed. The NCPE membranes with $LiBF_4$ and $LiClO_4$ also offered appreciable ionic conductivity above 45ºC. The higher ionic conductivity of the NCPE electrolytes with $LiCF_3SO_3$ as lithium salt is attributed to the easier dissociation of the bulky anion. It is attributed to the formation of an insulated layer of $BaTiO_3$-g-GO. The interfacial resistance “Ri” values have been reduced upon incorporation of fillers in the NCPEs and is The cycling profile of Li/NCPE/S cells at 60ºC showed that the cells composed of NCPEs (PEO+$LiCF_3SO_3$+ $BaTiO_3$-g-GO) are capable of delivering 689 mAh/g and can be considered for further improvement.

V.REFERENCES

1. Song, M.K., E.J. Cairns, Y. Zhang, 2013.Lithium/sulfur batteries with high specific energy: old challenges and new opportunities. Nanoscale, 5(6) : 2186-2204.
2. Bruce, P.G., Freunberger, S.A. Hardwick, L.J. Tarascon, J.-M. 2012. Li-O2 and Li-S batteries with high energy storage. Nat Mater, 11(2): 19-29.
3. Cheon, S.E.,Ko, K.S., Cho, J.H., Kim, S.W., Chin, E.Y., Kim, H.T. 2003.Rechargeable lithium sulfur battery. J. Electrochem. Soc. 150: A796–A799.
4. Liang, X.,Wen, Z., Liu, Y., Wu, M., Jin, J., Zhang, H., Wu, X.2011. Improved cycling performances of lithium sulfur batteries with LiNO3 − modified electrolyte. J. Power Sources , 196: 9839–9843

5. Choi, J.W.**,** Kim, J.K.**,** Cheruvally, G.**,** Ahn, J.H.**,** Ahn, H.J.**,** Kim, K.W.**2007.** Rechargeable lithium/sulfur battery with suitable mixed liquid electrolytes. Electrochimica. Acta, 52**(5):** 2075–2082.
6. Chang, D.R.,Lee, S.H.,Kim, S.W., Kim, H.T. 2002.Binary electrolyte based on tetra(ethylene glycol) dimethyl ether and 1,3-dioxolane for lithium-sulfur battery. J. Power Sources 112(2): 452–460. 34.
7. Kim, S., Jung, Y., Park, S.J. 2005.Effects of imidazolium salts on discharge performance of rechargeable lithium-sulfur cells containing organic solvent electrolytes. J. Power Sources 152: 272–277. 35.
8. Choi, J.W., Cheruvally, G., Kim, D.S.,Ahn, J.H., Kim, K.W., Ahn, H.J.2008. Rechargeable lithium/sulfur battery with liquid electrolytes containing toluene as additive. J. Power Sources, 183(1): 441–445.
9. Gray, F.M. 1991.Solid Polymer Electrolytes-Fundamentals and Technological Applications. VCH: New York, NY, USA.
10. Scrosati, B. 1993.Applications of Electroactive Polymers. Chapman Hall: London, UK.

11. Gray, F.M.1997. Polymer Electrolytes. The Royal Society of Chemistry: Canterbury, UK.
12. MacCallum, J.R.,Vincent, C.A.1987. Polymer Electrolytes Reviews-I. Elsevier: London, UK.

13. MacCallum, J.R., Vincent, C.A.1989. Polymer Electrolytes Reviews-II. Elsevier: London,UK.
14. Idris, N.H., Rahman, M.M.,Wang, J.Z., Liu, H.K.2012. Microporous gel polymer electrolytes for lithium rechargeable battery application. J. Power Sources 201: 294–300.
15. 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.
16. Sun, H. Y., Takeda,Y., Imanishi, N., Yamamoto, O.,Sohn H. J. 2000.Polymer Electrolytes for Lithium Polymer Batteries. J Electrochem Soc,147: 2462-2467.
17. 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
18. Li, Q., Sun, H.Y., Takeda, Y., Imanishi, N., Yang, J., Sun,H. Y., Yamamoto, O., 2002.Interface properties between a lithium metal electrode and a poly(ethylene oxide) based composite polymer electrolyte J Power Sources 94:201-205
19. 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.
20. 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.
21. Kar, G. P., Biswas, S. , Rohini, R. and Bose, S.J. 2015.,Tailoring the dispersion of multiwall carbon nanotubes in co-continuous PVDF/ABS blends to design materials with enhanced electromagnetic interference shielding , Mater. Chem. A, 7974–7985.
22. Sharma, M., Singh, M. P., Srivastava, C., Madras G. and Bose, S.2014. Poly(vinylidene fluoride)-based flexible and lightweight materials for attenuating microwave radiations ACS Appl. Mater. Interfaces 6:21151–21160.
23. Croce, F., Perci, L., Scrosati, B., Fiory, F. S.,Plichta, E.; Hendrickson, M. A.2001.Composites polymer electrolytes for electrochemical devices,Electrochim Acta,46:2457-2461.
24. Wieczorek, W., Florjancyk Z. ,and Stevens, J. R. 1995. Composite polyether based solid electrolytes. Electrochim.Acta, 40: 2251–2258.
25. Przluski, J. , Siekierski M.,and Wieczorek, W.1995 Effective Medium Theory in Studies of Conductivity of Composite Polimeric Electrolytes , Electrochim.Acta,40: 2101–2108.
26. Fauteux, D. 1988. Lithium Electrode/PEO-Based Polymer Electrolyte Interface Behavior Between 60° and 120°C. J. Electrochem. Soc.,135: 2231–2237