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Synthesis and characterisation of Solid Polymer Electrolyte(Supramolecular Polymer-$LiClO_4$) System for Battery Characterisation Studies

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Abstract: Ionic conducting polymer composites are important class of modern materials which have wide applications in high energy density solid-state batteries, supercapacitors, fuel cells, smart windows, sensors and electrochemical devices etc., Solid composite polymer electrolytes consisting of supramolecular polymer with lithium perchlorate ($LiClO_4$) as electrolyte salt and nanozinc ferrite (n-$ZnFe_3O_4$)/nanozinc oxide (n-ZnO) as fillers have been prepared by standard dispersion method. The interaction between supramolecular polymer and additives was characterised by Fourier Transform Infrared (FTIR) Spectroscopy to confirm the formation of complexation. The morphology and thermal stability data were obtained through X-ray Diffraction and Differential Scanning Calorimetry respectively. The SEM images showed that the filler was well distributed in the polymer matrix; the surface of electrolyte became rougher after the addition of nano-fillers. The ionic conductivity of the polymer composite electrolytes was studied by impedance spectroscopy. Using this polymer electrolyte system, a polymer battery with configuration Li/(Supramolecular polymer +$LiClO_4$+Filler)/C(graphite) was fabricated and its discharge characteristics are studied for a constant load. The open circuit voltage (OCV), short circuit current (SCC) and discharge time etc., were evaluated. All the results are correlated and discussed.

Keywords: solid-state battery, supramolecular polymer, nano fillers and discharge profile

Introduction

The development of novel solid polymer electrolytes (SPE) have increased in the recent research due to their potential applications in solid-state electrochemical devices and in particular in solid-state lithium batteries[1,2]. Solid polymer electrolytes for lithium batteries have many advantages over their counterpart liquid electrolytes, such as processing flexibility, but their conductivity at room temperature is usually too low to be applicable. An exemplary solid polymer electrolyte is a poly (ethylene oxide) (PEO) system containing lithium salts[3-6]. In the case of PEO:LiX electrolytes, the ions are transporated by the semi random motion of short polymer segments. To avoid these problems, ions can be transporated inside and through the host under the effect of an electric field by interactions with the host molecules[7-9]. Supramolecular solid polymer electrolytes are expected to contribute to the realization of lithium battery systems which have many advantages, namely high ionic conductivity, high specific energy, a solvent free condition, wide electrochemical stability windows, light and easy processability[10].

Most of the research efforts to improve the room temperature conductivity without the fall of thermal and potential stability have been directed towards the addition of nanoscale ceramic fillers such as SiO_2, Al_2O_3, ZnO, ZnF_2 and CeO_2 into supramolecular polymer based electrolytes[11-14]. According to this metal ferrite/oxide ceramic fillers dispersed in supramolecular polymer-LiX electrolyte forms complexes with the basic oxygen atoms in the supramolecular polymer chains and act as cross-linking centers for supramolecular polymer segments thereby reduce polymer chain reorganization and promotes Li^+ transport at the boundaries of the filler particles[16,17]. The particle size of the filler is also expected to have a wide influence on the ionic conductivity of the composite polymer electrolytes. The conductivity increases with decrese in particle size, i.e., increasing specific surface area of the ceramic fillers. This may be due to stronger lewis acid-base type interactions which enhance the dissociation of the supporting salt in the composite polymer electrolytes[18].

In this study, supramolecular polymer based solid polymer electrolytes prepared by the addition of zinc ferrite/zinc oxide nano-particles to supramolecular polymer-$LiClO_4$. The range of zinc ferrite /oxide concentration is kept narrow to find precise high conductivity concentration. Supramolecular solid polymer electrolytes were characterized by FTIR, XRD and DSC measurements. Ionic conductivity and morphology of the compositepolymer electrolytes were examined by Electronic Impedance Spectroscopy and SEM analysis. Our results show that the concentration of Zinc ferrite/Zinc Oxide nanoparticles in the supramolecular polymer-$LiClO_4$ matrix changes the thermal and the ionic conductivity of the composite polymer electrolytes, have been reported.

Experimental methods

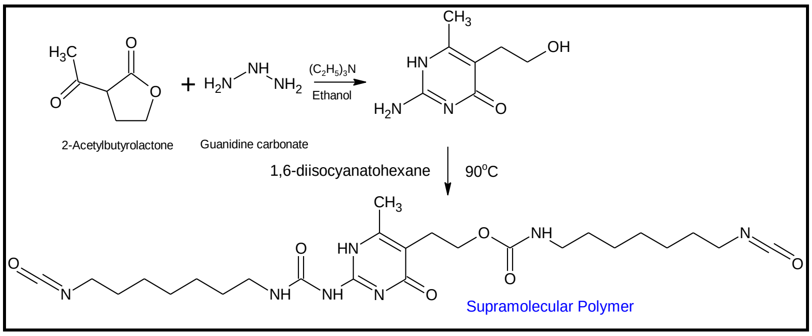
Materials

2-Acetylbutyrolactone, Guanidine carbonate, triethyl amine and 1,6-hexyl diisocyanate was purchased from Aldrich. All compounds without purification before used. The Lithium perchlorate ($LiClO_4.3H_2O$) salt, obtained from Aldrich, will be treated in 190^oC for 24 h. Pyridine and Ethanol obtained from SD Fine chemicals, were refluxed at room temperature before used. Iron chloride, Zinc acetate, Oxalic acid were purchased from SD Fine chemicals. Zinc chloride and sodium hydroxide purchased from Merck, were of purity 98-99%. The chemicals were used as such without further purification.

<u>Experimental procedure</u>

Synthesis of supramolecular polymer

2-Acetylbutyrolactone (2ml) and guanidine carbonate (3.3g) were put to reflux in ethanol (20ml) in the presence of triethylamine (5.2ml). The solution became yellow and turbid. After 6h heating at reflux, the solid was filtered, washed with ethanol and suspended in water. The pH was adjusted to a value of 6-7 by using HCL solution and the mixture was stirred for another 6 h finally the solid gave pure product. The solid product was suspended in 1,6-hexyldiisocyanate (12ml) and pyridine (1ml) was stirred at 90^oC. A clear solution developed and dropped into pentane giving a white precipitate as a product of supramolecular polymer.



Preparation of zinc ferrite nanofiller

Zinc ferrite nanoparticles were prepared by co-precipitation method[19], using starting materials of iron chloride hexahydrate, $FeCl_3.6H_2O$ and Zinc chloride. 25 ml of zinc chloride, $ZnCl_2$ solution were mixed with 25 ml of iron chloride solution in 250 ml beaker. The solution was constantly stirred with the help of magnetic stirrer. 25 ml of 1.5 M solution of NaOH was added drop wise to adjust the pH of solution 11-12, with constant stirring. The solution was then brought to reaction temperature of 80^{o}C. The solution was stirred for 60 minutes and subsequently cooled to room temperature. The solution was decanted and washed twice with distilled water and finally with ethanol to remove the impurities and excess surfactant. The synthesized nanoparticles were centrifuged for 15 minutes at 3500 rpm and dried overnight at 100^{o}C. The powder nanoparticles were used for further characteisation studies.

Preparation of ZnO nanofiller

300 ml of 0.15 M oxalic acid solution was slowly in drops to 300 ml of 0.1 M zinc acetate solution under stirring for 18 hrs. A white precipitate of zinc-oxalate was obtained, which was filtered and washed with acetone several times to remove impurities. The filtrate was then dried at 120^{o}C for 30 minutes and finally heated for 30 minutes at 450^{o}C to get nano ZnO.

Synthesis of nanoferrites/nano oxides doped supramolecular polymer electrolyte

The synthesis of zinc ferrite/oxide nanoparticles doped supramolecular polymer electrolyte system by wet chemical method, the supramolecular polymer blended with Lithium perchlorate salt by using acetonitrile as a solvent and the zinc ferrite/oxide nanoparticles were dispersed into the mixture and it was stirred at room temperature for 18 h. After reaction time, the solvent was evaporated. Finally the supramolecular polymer composite electrolyte material was recovered and used for further characterization studies.

Characterisation

The synthesized ferrite nanoparticles and nanocomposite based supramolecular electrolytes were characterized by various techniques. The formation of ferrite nanoparticles and the polymer elctrolyte were confirmed by Fourier transform infrared (FT-IR) spectroscopy wasmeasured in transmission mode with a Perkin Elmer model-4000. Structure and crystallinity of synthesized nanoparticles and polymer electrolyte were analysed by X-ray diffraction technique (XRD) using GEOL JDX-8P X-ray diffractometer having Cu Kα (0.154 nm) radiation to generate diffraction patterns from powder crystalline samples at ambient temperature in a 2θ range of 20^{o} to 90^{o}. The microstructure of the nanoparticles and its polymer electrolytes were determined from Scanning electron microscopy (SEM model LEICA S430) images. The crystallinity change during heating was analysed by Differential scanning calorimetry and thermogravimetric analysis (DSC/TGA, model STA 1640) in air at the heating rate of 20^{o}C/min.. The conductivity and dielectric properties was calculated by Electronic impedance spectroscopy.By using these electrolytes battery was performed and its parameters also calculated.

Result and discussion

FTIR Spectroscopy

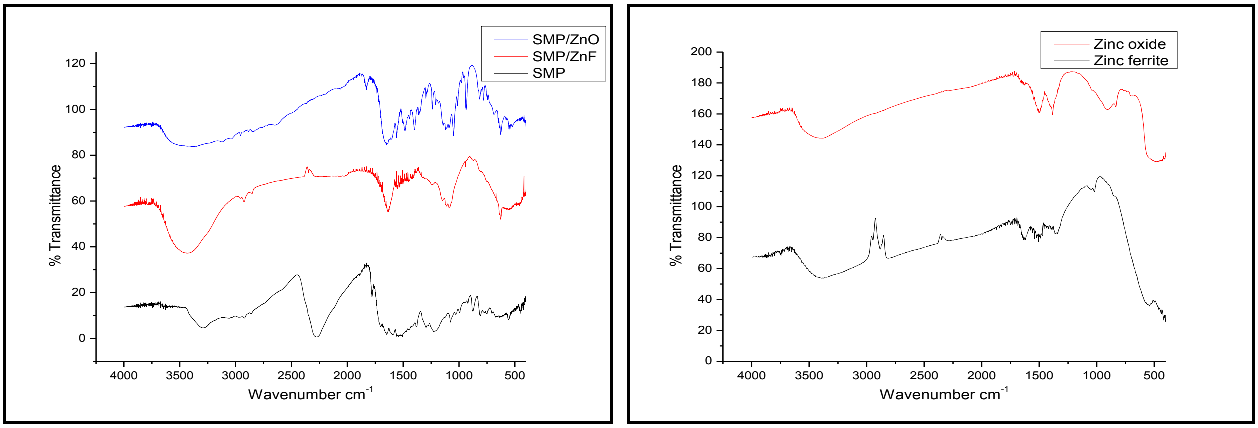


Fig 1. FTIR spectra of supramolecular polymer, ferrite/oxide nanopaticles and supramolecular polymer composites

The FTIR spectra of supramolecular polymer electrolyte, zinc ferrite/oxide nanoparticles and ferrite/oxide nanoparticles functionalized supramolecular polymer electrolyte are shown inFig. 1. The strong absorption band appearing at 2810 cm^{-1} indicates the CH_2 group in supramolecular polymer electrolyte. The hydroxyl group present at 3300 cm^{-1} in pure zinc-ferrite and oxide nanoparticles. The addition of nanoparticles into supramolecular polymer electrolyte exhibited the absence OH group in ferrite functionalized polymer electrolyte. The peak at 1630 cm^{-1} and 1640 cm^{-1} indicates the corresponding amine groups in zinc ferrite doped supramolecular polymer and zinc oxide doped polymer composites respectively.

XRD analysis

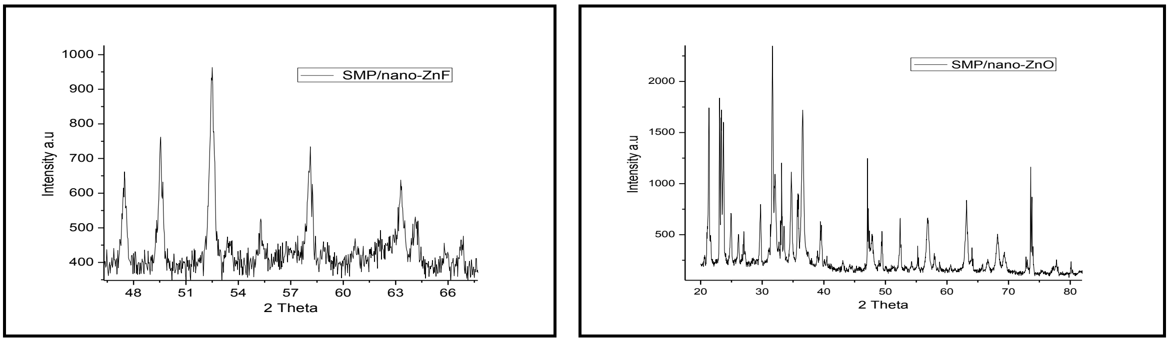


Fig 2. XRD patterens of zinc ferrite/oxide doped supramolecular polymer composites

Fig. 2 shows the complexation of zinc ferrite/oxide nanoparticles with the supramolecular polymer electrolyte analyzed by XRD studies. It shows the comparative profiles of the supramolecular electrolyte and the ferrite/oxide nanoparticle dopedpolymer electrolyte. The diffraction peaks observed for 2θ values at 28.2° and 37.3° were found to be less intence in zinc ferrite doped supramolecular polymer electrolyte compared to the zinc oxide doped supramolecular polymer electrolyte. This could be due to the dispurtion of the semi-crystalline structure of the supramolecular polymer electrolyte by ferrite/oxide nanoparticles. No peaks corresponding to ferrite naoparticles were observed in complexed polymer electrolyte, indicating the absence of ferrite/oxide nanoparticles in the ferrite/polymer electrolyte.

DSC analysis

Fig. 3 shows the DSC thermogram of zinc ferrite/oxide doped supramolecular polymer electrolyte. The temperature at 97.1°C of the ferrite nanoparticles functionalized polymer electrolyte, there is a change from the semi crystalline to amorphous phase transition. The endothermic peak of ferrite doped supramolecular polymer electrolyte consisting ferrite naoparticles in a polymer matrix appear at 280°C. This aspect indicates that an amorphous phase is being formed when adding the ferrite nanoparticles with the supramolecular polymer electrolyte. In the same way, the addition of zinc oxide nano fillers into supramolecular polymer melt at 76.4°C and the polymer matrix stable upto 337.6°C. The amorphous phase makes the electrolyte more flexible and facilitates segmental motion of the polymer.

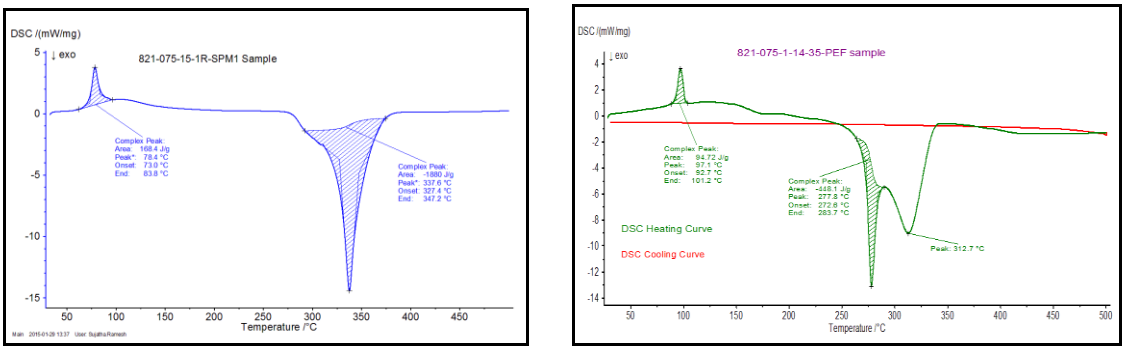


Fig 3. DSC thermogram ofzinc ferrite/oxide functionalized supramolecular polymer electrolyte

SEM analysis

SEM images of supramolecular polymer electrolyte, zinc ferrite/oxide nanoparticles and ferrite/oxide nanoparticles doped supramolecular polymer electrolyte are shown in Fig. 4. The supramolecular polymer electrolyte has crystalline structure and the addition of zinc ferrite/oxide nanoparticles to enhance the ionic conductivity of the supramolecular polymer composites.Scanning electron microscopy images show that addition of zinc ferrite (54nm) and zinc oxide (24nm) nanofillers disturbs the crystalline nature of original supramolecular polymer matrix.

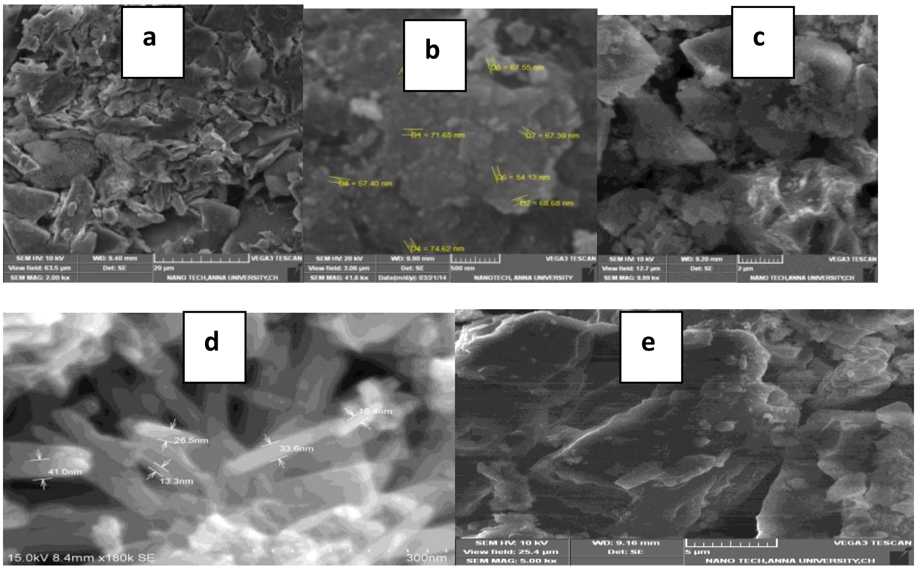


Fig 4. SEM images of a) supramolecular polymer, b) zinc ferrite nanopaticles c) zinc ferrite/solid polymer electrolyte d) nano zinc-oxide and e) zinc oxide/solid polymer electrolyte

DC conductivity

The ionic conductivity can be determined from the bulk resistance by using the following equation: $\sigma = t/R_bA$,where σ-ionic conductivity; t-thickness of the sample; A-surface area of the sample and R_b is the bulk resistance of the material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance. The data reveals that the conductivity of pure supramolecular polymer electrolyte is 5.8×10^{-9} S cm^{-1} about at room temperature. The addition of zinc ferrite/oxide nanoparticles into polymer electrolyte and its conductivity value is 4.02×10^{-6} S/cm and 2.70×10^{-6}S/cm respectively. The conductivity values changed due to the ferrite/oxide nanoparticles being relatively small in size (nm) compared with polymer molecules penetrate the polymer matrix and establish attractive forces with the chain segments. These forces between the polymer chains increase the segmental mobility, which enhance the conductivity and the discharge time. It is reported that the dissociation of salts thereby increasing the number $LiClO_4$ of charged carriers. In polymer electrolytes, change of conductivity with temperature is due to the segmental motion, which results in an increase in the free volume of the system. This increase in free volume would facilitate the motion of ionic charge.

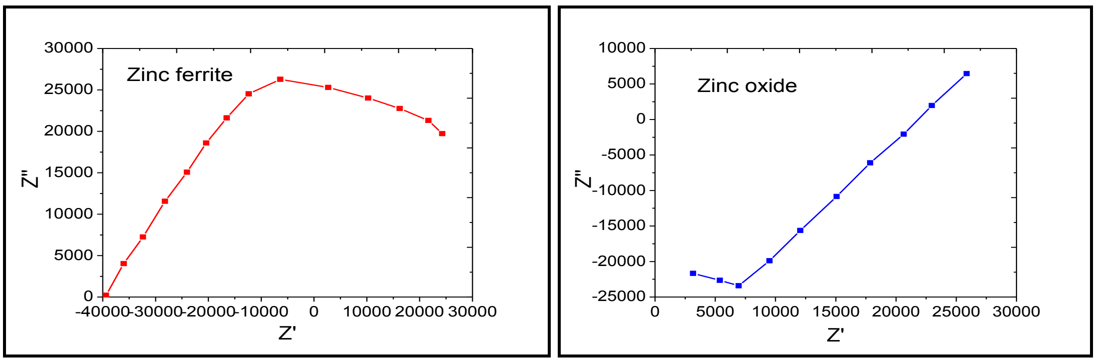


Fig. 5Nyquist plot region of zinc ferrite/oxide doped supramolecular polymer composites

Discharge profiles

Solid state electrochemical cells were fabricated with the configuration Li (anode)/zinc ferrite/oxide doped supramolecular polymer electrolyte/graphite (cathode) using ferrite/oxide functionalized supramolecular polymer electrolyte. Lithium based salts used as the negative electrode and graphite used as the positive electrode. The initial sharp decrease in voltage may be due to polarization of lithum salt at the electrode-electrolyte interface.

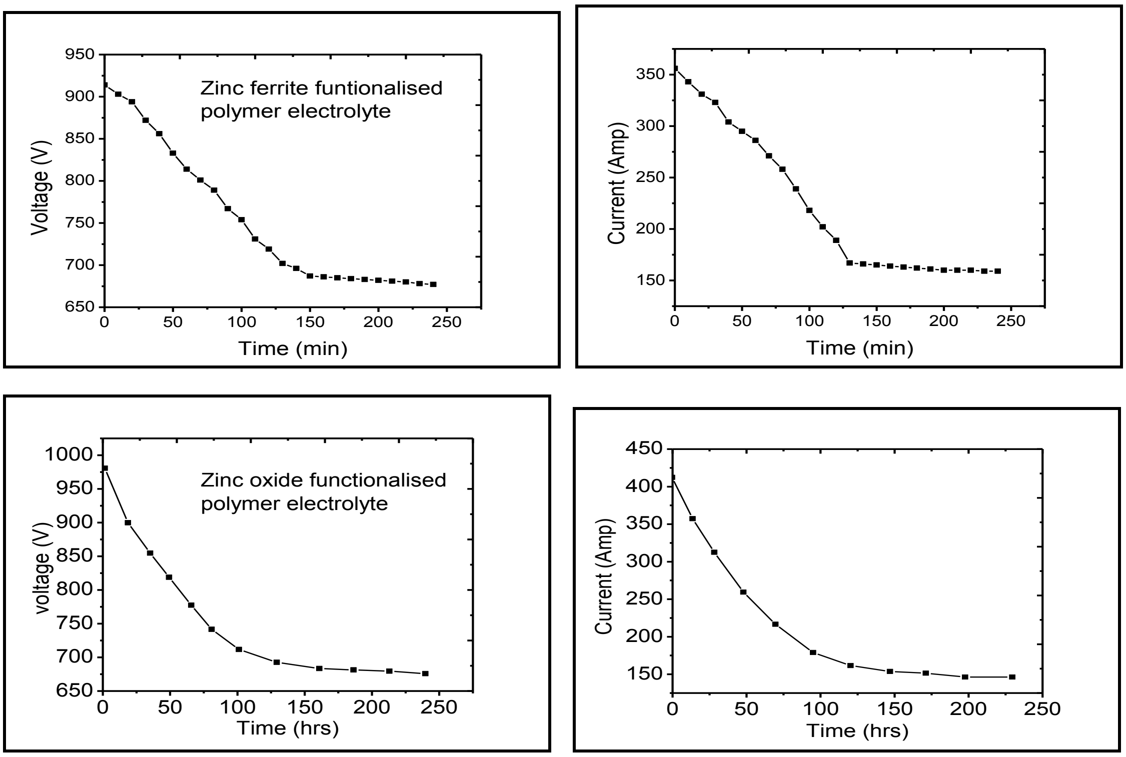


Fig. 6 Discharge characteristics of electrochemical cell.

The open circuit voltage (OCV) and the short circuit current (SCC) and other cell parameters for these cells are given in table 1. The data indicate that the cell parameters are better in the cell with the zinc ferrite/oxide nanoparticles. This suggests that ferrite/oxide nanoparticles functionalized supramolecular polymer electrolyte cells exhibit improved performance and better stability than pure polymer electrolyte. Nanoparticles based polymer electrolytes thus offer an interesting alternative system for fabricating solid state batteries at room temperature.

Table 1. various cell parameters for polymer electrolyte system

S.No	Cell parameters	Zinc ferrite functionalized supramolecular polymer	Zinc oxide functionalised supramolecular polymer
1.	Open Circuit Voltage (OCV)	0.93 V	0.98 V
2.	Short Circuit Current (SCC)	354 µA	412 µA
3.	Area of the cell	1.21 cm^2	1.32 cm^2
4.	Weight of the cell	1.12 g	1.08 g
5.	Thickness of the cell	128 µm	116 µm
6.	T.F.plateau region	68 h	72 h
7.	Power density	2.78 W/Kg	3.81 W/Kg
8.	Energy density	144.87Wh/Kg	274.66 Wh/Kg
9.	Current density	292.5 µA/cm^2	312.12 µA/cm^2

Conclusion

Nanoparticle based polymer electrolytes supports the practical application of solid-state batteries. This work describes the synthesis and characterization of zinc ferrite/oxide nanoparticles functionalized supramolecular polymer electrolyte which is used as solid separator in lithium ion based polymer batteries which operate at different temperatures. The electrolytes, prepared by wet chemical route from supramolecular polymer electrolyte and zinc ferrite/oxide nanoparticles. The experimental studies through FTIR, XRD, SEM, DSC and ionic conductivity shows that the zinc ferrite nanoparticles changes the physical and morphological behavior of nano-composite supramolecular polymer electrolyte. Using these electrolytes, electrochemical cells are fabricated and the parameters of the cells are reported.

References

1. Jaipal Reddy M, Sivakumar J, SuubbaRaoU.V and Peter P. Chu,structural, electrical and parametric studies of a peo based polymer electrolyte for battery applications. Solid State Ionics., 2006, 177; 253.
2. Croce F, Appetecchi GB, Persi L and Scrosati B,Nanocomposite polymer electrolytes for lithium batteries.Nature., 1998, 394; 456-458.
3. Sasikala U, Kumar P N, Rao V V R N and Sharma A K, Effect of nanoadditives on conductivity of solid polymer electrolytes.,Int J Engg Sci&Advd Tech., 2012, 2; 722.
4. Naresh Kumar K, Sreekanth T and Jaipal ReddyM.Study of transport and electrochemical cell characteristics of PVP:$NaClO_3$ polymer electrolyte system.Journal of Power Sources., 2001, 101; 130.
5. PankhurstQ.A, Connolly J and JonesS.K,Applications of magnetic nanoparticles in biomedicine. J Phys D: Appl Phys., 2003, 36; 167.
6. BerryC.C,Structural and magnetic characterizations of high moment synthetic antiferromagnetic nanoparticles fabricated using self-assembled stamps.J. Mater. Chem., 2005, 15; 543.
7. Sun X.G, LiuG and Xie J.B,New gel polyelectrolytes for rechargeable lithium batteries. Solid State Ionics., 2004, 175; 713.
8. Rajendran T V, Jaisankar V and Sivakumar EKT,AStudy on Conductivity Behaviour of Supramolecular Polymer Functionalized Magnetic Nanoparticles. Int J of Inno Res in Sci&Engi, ISSN 2014, 2347-3207.
9. Ketabi S and Lian K,Effect of SiO2 on Conductivity and Structural Properties of ... of PEO-EMIHSO4 Polymer ElectrolytesSolid State Ionics., 2012, 227; 86.
10. Yang X Q, Lee H S, Hanson L, Mc Breen J and Okamoto Y,Conductivity study of PEO–LiClO4 polymer electrolyte doped with ZnO nanocomposite ceramic filler J of Power Sources., 1995, 54; 198.
11. Rajendran S, Ramesh babuM and Usha rani M,Characterization of PVC/PEMA based polymer blend electrolytes. Int. J. Electrochem. Sci., 2008, 3; 282.
12. Rao S.S, ReddyM.J, NarasaihE.L and SubbaRao U.V,Optical, electrical and discharge profiles for (PVC + NaIO4) polymer electrolytes. Mater Sci Eng B., 1995, 33; 173.
13. P. Sivakumar, R. Ramesh and A. Ramanand,Synthesis and Characterization of NiFe2O4 Nanosheet via Polymer Assisted Co-Precipitation Method Mater Lett., 2011, 65; 483.
14. Ghosh G, Naskar M.K and Patra A,Synthesis and characterization of PVP-encapsulated ZnSnanoparticles.OptMateri., 2006, 28; 1047.
15. Elsayed A.H, MohyEldinM.S and Elsyed A.M,Synthesis and Properties of Polyaniline/ferrites Nanocomposites. Int J Electrochem Sci., 2011, 6; 206.
16. Wintersgill M.C and FontanellaJ.J,High pressure electrical conductivity studies of acid doped polybenzimidazole Electrochim. Acta., 1998, 43; 1533.
17. VincentC.A and ScrosatiB, Progress in lithium polymer battery R&D Bull. Mat. Soc., 2000, 25; 28.
18. OleksiakA.L and InerowiczH.D,Study on Poly (Ethylene-Oxide) Electrolytes with Ionophores for Lithium Batteries.J. Power Sources., 1999, 81; 813.

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