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CONDUCTING BEHAVIOR OF ZnO DOPED NANOCOMPOSITE POLYMER ELECTROLYTE

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ABSTRACT

Nanocomposite solid polymer electrolyte films comprising of PEO and $LiClO_4$ with 9 wt% concentration of ZnO nanoparticles was prepared using sol gel technique. Thermal stability of electrolyte film is confirmed by TG/DTA analysis in the temperature range, 300 K to 800 K. The Li^+ ionic transference number measurement showed ionic conduction in this nanocomposite polymer electrolyte. Conductivity measurement was carried out by ac impedance spectroscopy. The ionic conductivity of 1.2×10^{-5} S/cm^2 was found at room temperature of 309 K for nanocomposite film.

Keywords: Ionic conductivity, Impedance spectroscopy, Polymer electrolyte, Transference number, Ceramic fillers

I. INTRODUCTION

The solid polymer electrolytes are used as chemical sensors, electrochemical capacitors, analog memory devices and in high energy density rechargeable batteries. An exemplary solid polymer electrolyte is a poly (ethylene oxide) (PEO) system containing lithium salts. In the case of PEO:LiX electrolytes, the ions are transported by the semirandom motion of short polymer segments. The segmental motions promote ion mobility by making and breaking coordination bonds between cation and polymer. This provides free volume into which the ion can diffuse under the influence of an electric field. Cations moving between coordinating sites adopt transient state where cations are coordinated by both anions and polymer chain sites, before the segmental motion of polymer breaks one coordinating bond. However polymer in such a system tends to crystallize, resulting in a low room temperature ionic conductivity unsatisfied for practical application. Two approaches have been developed to solve this problem, that is, incorporation of plasticizers [1-4] and ceramic fillers.

The major issues in these modifications are focused on improving ionic conductivity, mechanical properties and interfacial stability with lithium electrode. Large surface area of the solid oxide filler prevents the local PEO chain reorganization, which leads to locking in high degree of disorder and favours high ion transport. According to Lewis acid base model interaction [5-7] ceramic surface group provides cross linking centres for the PEO segments and for the anions.

An extensive literature survey [8-9] shows that almost all polymer ceramic nanocomposites were prepared through mechanical blending of nanoscale ceramic particles, polymer and salt in a compatible solvent. Few studies have been published using sol-gel process, in which nanosize ceramic fillers are precipitated in the polymer matrix [10-11]. But in sol-gel process precursors may not be completely converted into nanosize ceramic fillers after hydrolysis and condensation reactions. In this study solid polymer electrolyte is prepared by the addition of 9 wt% ZnO nanoparticles to PEO-$LiClO_4$ polymer matrix. Ionic conductivity of the nanocomposite polymer electrolyte film was confirmed and examined by transference number measurement and AC impedance spectroscopy. Thermal stability of nanocomposite electrolyte was also confirmed by TG/DTA analysis.

II. EXPERIMENTAL

2.1 Preparation of nanocomposite polymer electrolyte film

Poly (ethylene oxide) (PEO) [MW: 300000] was obtained from Alfa Aesar, Ward Hill, MA 01835, USA. Zinc oxide (ZnO) nanopowder [Purity: 99%, APS: 20 nm] was purchased from Nanoshell, Wilmington, DE 19808, USA. Lithium perchlorate ($LiClO_4$) was analytically pure and dried at 353 K for one day before use. Acetonitrile was used as the solvent in the film casting process.

Poly (ethylene oxide) (PEO):$LiClO_4$ weight ratio was fixed to 90:10 and the mixture was blended with 9 wt% ZnO nanoparticles. To prepare composite samples first predetermined amount of $LiClO_4$ and 9 wt% ZnO nanoparticles was dissolved in acetonitrile. The solution was stirred for 1 hour and then calculated amount of PEO was added to the solution. The mixture was stirred vigorously for 5 to 6 hrs to obtain homogeneous mixture. Films were obtained by transferring the mixture on the plane Teflon plate. Films were first dried in the open atmosphere to allow the solvent to evaporate and then dried in vacuum for 24 hrs to completely remove the residual traces.

2.2 Characterization of sample

The thermal stability of the electrolyte was characterized by TG/DTA technique. Transference number measurement was carried out using Wagner polarization technique. The lithium ion transference number measurement was carried out using Wagner polarization technique. AC impedance of the composite electrolyte film was measured by using Wayne Kerr 4230 LCR meter (UK) between 100 Hz to 200 kHz with 0.5V amplitude by sandwiching the film between two copper electrodes in a sample holder.

III. RESULT AND DISCUSSION

3.1 Thermal analysis (TG/DTA)

In order to ascertain the thermal stability film was subjected to TG/DTA analysis in the range of 300 to 800 K at a heating rate of 10 K/min. Fig.1 shows that melting temperature (T_m) is at 337.92 K and glass transition temperature (T_g) of this film is low below 273 K. The TG curve shows first degradation at 351 K accompanied by a weight loss of 5%. This degradation is may be due to the evaporation of moisture absorbed by the sample during loading [12]. This first step of degradation is asserted by the DTA curve giving an endothermic peak at 337.92 K. The composite electrolyte film was found to be stable up to 471 K with a weight loss of 1%. Rapid weight loss observed in the TG curve after 471 K indicates the complete decomposition of composite electrolyte, which is evidenced by the exothermic peak observed in the DTA curve.

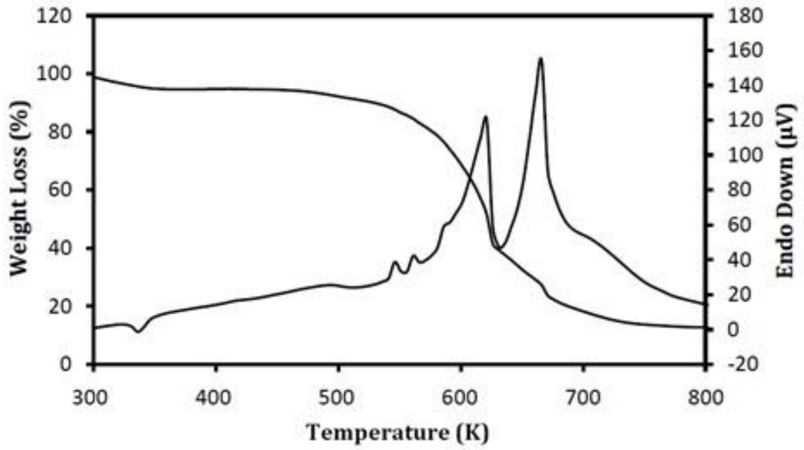

Figure1. TG/DTA plots for PEO - $LiClO_4$ - 9 wt% ZnO electrolyte

3.2 Lithium ion transference number

Since the electrochemical process of the electrodes consists of the intercalation and deintercalation of ions throughout the host compound lattice, electrolytes with transference number approaching unity are desirable for avoiding concentration gradient during the charge and discharge cycles. Therefore, the evaluation of this parameter is of great importance for the characterization of electrolyte materials designed for battery application. Various methods have been proposed for the determination of transference number in polymer electrolytes. In this work the lithium ion transference number measurement was carried out using Wagner polarization technique. In this technique, the d.c. current was monitored as a function of time on application of a fixed d.c. voltage across the Copper / Electrolyte / Lithium cell. Current verses time plot for the nanocomposite electrolyte is shown in Fig.2. Lithium ion transference number is calculated by using the equation, $t_{ion} = (I_0 - I_s) / I_o$. Where I_s and I_o are final steady state and initial current respectively. The value of t_{ion} for the nanocomposite electrolyte was found to be 0.89 which indicates that the charge conduction was predominantly ionic.

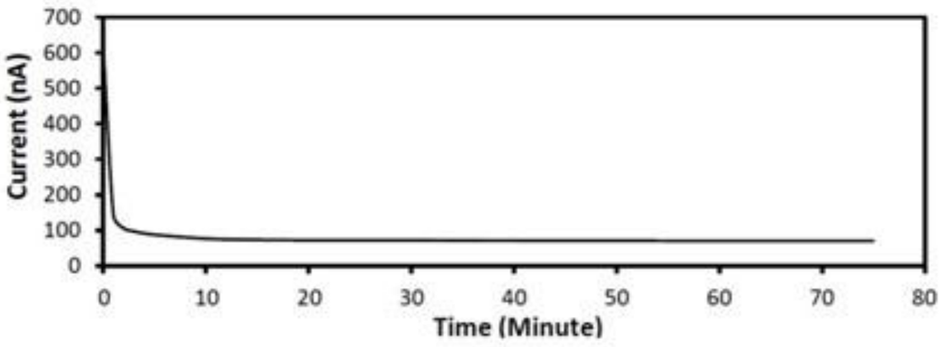

Figure2. Current - time plot for PEO - $LiClO_4$ – 9 wt% ZnO electrolyte

3.3 Conductivity studies

AC impedance spectra of PEO - $LiClO_4$ - 9 wt% ZnO nanocomposite polymer electrolyte film is shown in Fig.3. The continuous line shows the experimental data and the dots represent the extended data. The point of insertion between the arc in the high frequency range and the straight line in the low frequency range coincides with the bulk resistance of nanocomposite electrolyte film. At the low frequency end of the spectrum the non-vertical spike indicates roughness of the electrode/electrolyte interface [13]. In our experiment, the complete semicircle in the high frequency range was not observed, which may be concluded that the frequency is not high enough. The high frequency semicircle corresponds to the bulk response of the film while the spike corresponds to interfacial impedance of the electrolyte.

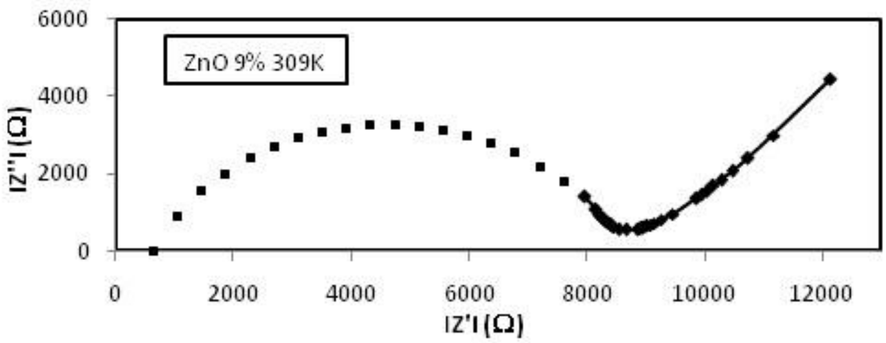

Figure3. AC impedance spectra of PEO-$LiClO_4$-9 wt% ZnO electrolyte

The curves at the low temperature suggest that the migration of ions occur through the volume of polymer matrix, which can be represented by a resistor. The immobile polymer chains, on the other hand, become polarized in the alternating field, and can therefore be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, and therefore, the portion of the semicircle can be observed at high frequencies [14]. The ionic conductivity of the polymer electrolyte measured by AC impedance spectroscopy at room temp 309 K is 1.2 x 10^{-5} S/cm^2.

IV. CONCLUSIONS

Nanocomposite solid polymer electrolyte films comprising of PEO and $LiClO_4$ with 9 wt% concentration of ZnO nanoparticles was prepared. Good thermal stability of polymer electrolyte system up to 471 K was confirmed by TG/DTA analysis. Ion conduction has found to be achieved by both the random diffusion within the amorphous PEO as well as by replacing the adjacent lithium vacancy on the doping surface. The transference number of the electrolyte was found to be 0.89 while its ionic conductivity was 1.2 x 10^{-5} S/cm^2. Since the polymer electrolyte exhibits good thermal stability and ionic conductivity values, this can be used as an electrolyte in lithium batteries and other electrochemical devices.

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