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Transport and optical studies of PEO/PVP/$LiClO_4$ based polymer blend electrolytes

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Abstract: Fixed ratio of poly (ethylene oxide)/poly (vinyl pyrrolidone) (PEO/PVP) and various concentrations of lithium perchlorate ($LiClO_4$) were prepared by solvent casting technique. The maximum ionic conductivity value was found to be 0.2307×10^{-5} Scm^{-1} for 8 wt% of $LiClO_4$ based system at ambient temperature. Three dimensional topographic image of the sample having a maximum ionic conductivity show small micropores which are responsible for the high ionic conductivity. The change in viscosity of the prepared samples were line with the ionic conductivity.

Key words – Blend electrolyte; Ionic conductivity; Micropores; Luminescence.

Introduction and Experimental techinique

Lithium ion batteries are energy storage devices appropriate to portable devices such as mobile phones etc.[1]. In comparison with other systems such as nickel-cadmium and nickel-metal batteries, they have advantages due to higher energy storage capacity and the higher number of charge-discharge cycles [2]. Membrane separators are a key element in battery systems and are responsible for its performance by controlling the number and mobility of ions between the cathode and anode [3]. Some characteristics such as porosity, ionic conductivity, mechanical properties and chemical stability are important issues in membrane separators. In this investigation, the host polymer is PEO because it is the most interesting base material and it has high chemical and thermal stability.

PVP is the second polymer, which deserves a special attention among the conjugated polymers because of its good environmental stability and easy processability. The local modification of the chemical structure induces drastic changes in electronic properties. The present paper explains the fixed ratio of PEO/PVP and various concentrations of $LiClO_4$ based solid polymer blend electrolytes by solvent casting technique. The change in local viscosity was studied by the photoluminescence studies.

The polymer PEO of average molecular weight 8000, PVP of average molecular weight 360,000 and salt $LiClO_4$ were procured from Sigma Aldrich chemicals limited, U.S.A. The electrolytes were prepared by solvent casting technique. The ionic conductivity of the prepared films was carried out stainless steel blocking electrodes using a computer controlled micro auto lab type III Potentiostat/Galvanostat in the frequency range of 100Hz-300KHz. The surface morphology and roughness factor of the sample were observed by atomic force microscope with the help of AFM (A100SGS). The photoluminescence studies were performed by Carry Eclipse Fluorescence Spectrometer.

Results and discussion

The behaviour of the electrochemical system can be studied by means of impedance plots over a wide range of frequencies at different temperatures by applying AC voltage or current. The ionic conductivity has been calculated using the equation $\sigma = l/R_bA$, where 'l' is the thickness of the film and 'A' is the surface area of the film. The highest room temperature ionic conductivity is found to be 0.2307×10^{-5} Scm^{-1} for 8wt % of $LiClO_4$ sample. Temperature dependence ionic conductivity values of the prepared samples are shown in Table 1. From Table 1, it is observed that as temperature increases, the ionic conductivity values also increase over the temperature range studied (303–353 K) and polymer could expand and observe a volumetric change in it. The resulting conductivity represented by the overall mobility of ion and polymer is determined by the free volume around the polymer chains. This leads to an increase in ion mobility and segmental mobility that assist ion transport and virtually compensate for the retarding effect of ion clouds [4].

The dependence of salt concentration on the ionic conductivity is shown in Fig. 1. The initial increase in conductivity is due to charge carriers in the matrix. For a higher $LiClO_4$ concentration the buildup of charge carriers is offset by the retarding effect of ion aggregates such as ions pairs and ion doublet formation which cause constrains in ionic and polymeric segmental mobility. Hence, the conductivity reaches the maximum value at 8wt% of $LiClO_4$ salt. At high salt concentrations the relative number of effective charge carriers diminishes at equivalent levels of segmental mobility [5].

Table 1. Temperature dependent ionic conductivity values of the prepared complexes.

Sample Code	**Wt% Compositions of PEO/PVP/$LiClO_4$**	**Ionic conductivity values (σ) x 10^{-5} Scm^{-1} at different temperatures**					
		303K	**313K**	**323K**	**333K**	**343K**	**353K**
B1	90:10:4	0.0994	0.2246	0.2898	0.4265	2.7439	3.9886
B2	90:10:6	0.1454	0.2299	0.2970	0.9621	3.2908	4.1435
B3	90:10:8	0.2307	0.3772	0.5353	1.2645	8.1513	10.2533
B4	90:10:10	0.1909	0.2571	0.3888	1.0549	5.0967	9.0096
B5	90:10:12	0.1727	0.2469	0.3235	1.0086	3.6281	4.2915

The topographic image clearly show the presence of pores which are responsible for the maximum ionic conductivity (Fig.2).The pores are helped to ensnare the large volume of the liquid in the pores accounting for the increased conductivity and the presences of pores in the microstructure is mainly due to solvent removal and by solvent retention ability of the electrolyte system.

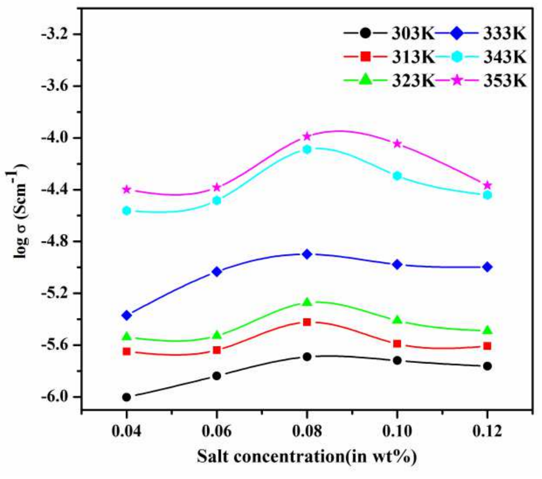

Fig. 1. Effect of salt concentration on PEO/PVP ((90/10) (wt %): $LiClO_4$ (X) (where X=4, 6,8,10 and 12 wt %) complexes at different temperatures.

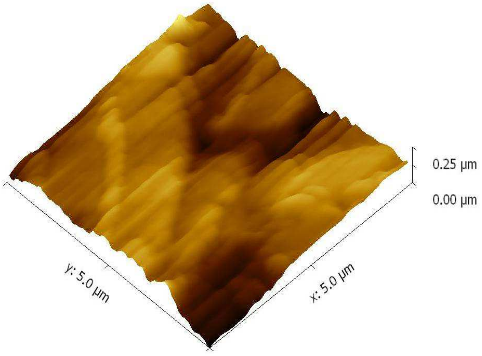

Fig.2. The topography 3D image of the sample B3 having a maximum ionic conductivity.

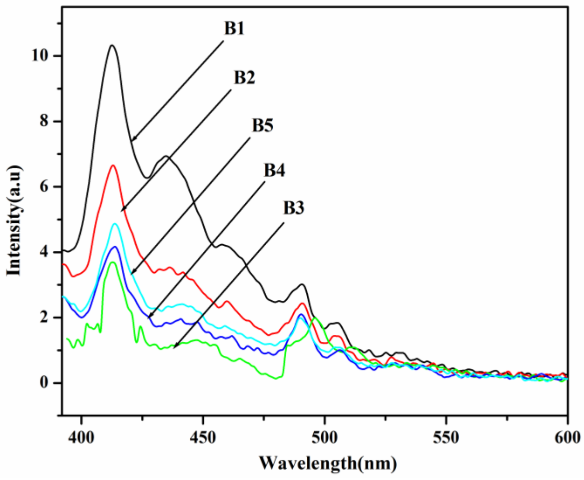

Fig. 3. Photoluminescence emission spectra of the prepared electrolyte samples.

In the present work, fluorescence emission spectra have been carried out for the prepared complexes at an excitation wavelength of 370 nm. It is found from Fig.3 that the sample B3 shows minimum intensity compared to other samples which may be attributed to the minimum local viscosity of the sample.

Conclusions

Solid polymer blend electrolytes were prepared by solvent casting technique. The maximum ionic conductivity of 0.2307×10^{-5} Scm^{-1} at 303K was observed for the sample B3. Three dimensional topographic image of the sample having a maximum ionic conductivity show a small number of micropores which is responsible for the high ionic conductivity. Photoluminescence intensities were in line with the ionic conductivity studies. Hence, the 8 wt% of $LiClO_4$ salt with 90 wt% of PEO and 10 wt% of PVP based polymer blend electrolyte is a potential candidate for lithium battery applications.

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