

# Preparation and characterization of novel solid polymer blend electrolytes based on poly (vinyl pyrrolidone) with various concentrations of lithium perchlorate



K. Kesavan<sup>a</sup>, Chithra M. Mathew<sup>a</sup>, S. Rajendran<sup>a,\*</sup>, M. Ulaganathan<sup>b</sup>

<sup>a</sup> School of Physics, Alagappa University, Karaikudi 630003, Tamilnadu, India

<sup>b</sup> Energy Research Institute @ NTU, Nanyang Technological University, Singapore 637 553, Republic of Singapore

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## ABSTRACT

A series of conducting novel solid polymer blend electrolytes (SPE) based on the fixed ratio of poly (ethylene oxide)/poly (vinyl pyrrolidone) (PEO/PVP) and various concentrations of salt lithium perchlorate (LiClO<sub>4</sub>) were prepared by solvent casting technique. Structural and complex formation of the prepared electrolytes was confirmed by X-ray diffraction and FTIR analyses. The maximum ionic conductivity value was found to be  $0.2307 \times 10^{-5} \text{ S cm}^{-1}$  for 8 wt% of LiClO<sub>4</sub> based system at ambient temperature. Thermal stability of the present system was studied by thermo gravimetric/differential thermal analysis (TG/DTA). Surface morphology of the sample having maximum ionic conductivity was studied by atomic force microscope (AFM). Optical properties like direct and indirect band gaps were investigated by UV–vis analysis. The change in viscosity of the polymer complexes were also identified using photoluminescence emission spectra. PEO(90)/PVP(10)/LiClO<sub>4</sub>(8) has the highest conductivity which is supported by the lowest optical band gap and lowest intensity in photoluminescence spectroscopy near 400–450 nm.

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## 1. Introduction

Solid polymer electrolytes (SPEs) are complexes formed between ionic salts and polymers with electron-donor atoms such as poly (ethylene oxide) (PEO) [1,2]. SPEs were recognized by Armand et al. [3] as potential substitutes for non-aqueous liquid electrolytes in rechargeable lithium batteries. Among the perceived advantages of these materials are good electrochemical properties, a reduction in both safety-related problems and environmental concerns, and virtual elimination of electrolyte leakage problems. These electrolytes may perform a multifunctional role in practical devices as separator, adhesive and cell sealant in electrochemical devices.

Li<sup>+</sup> based SPEs are considered to be attractive materials for application in various devices including galvanic cells, electrochromic displays and sensors [4]. The application of PEO based electrolytes in commercial solid state electrochemical devices has been unfortunately delayed by two main drawbacks: their poor processability and a marked tendency to crystallize. The latter aspect of SPE behavior is particularly limiting. PEO/salt complexes are

usually crystalline, but pristine or un-doped PEO is itself already semi-crystalline. To overcome these two disadvantages associated with conventional PEO based SPEs, three distinct strategies have been applied over the last two decades [1].

In general, salts with a polarizing cation and a large anion with well delocalized charge distribution and therefore also with low lattice energy, are the most useful for use in SPEs [5–8]. Most of the solid polymer electrolytes have been reported based on PEO, PPO, MEEP complexed with NaClO<sub>4</sub>, NaSCN, NaCF<sub>3</sub>SO<sub>3</sub> and NaPF<sub>6</sub> [9–13]. Some studies on Ag<sup>+</sup> ion conducting polymer electrolytes based on PEO are reported [14–16]. Recently, PEO and PVP based polymer electrolytes with sodium fluoride (NaF) based polymer electrolytes are reported by Kirankumar et al. [17]. To the best of authors' knowledge, no work has been reported on PEO/PVP/LiClO<sub>4</sub> based polymer blend electrolytes. Hence, we have chosen PEO and PVP with LiClO<sub>4</sub> salt in the present work to achieve higher ionic conductivity because lithium perchlorate remains a common choice of guest salt, in spite of the safety concerns raised by several authors and it has low lattice energy.

In this investigation, the host polymer is PEO because it is the most interesting base material and it has high chemical and thermal stability. PEO usually consists of a mixture of crystalline and amorphous phases which significantly influences the ion transport.

Poly (vinyl pyrrolidone) (PVP) is the second polymer, which deserves a special attention among the conjugated polymers

\* Corresponding author. Tel.: +91 4565 230251; fax: +91 4565 225202.

E-mail addresses: [kesavanphysics@gmail.com](mailto:kesavanphysics@gmail.com) (K. Kesavan), [sraj54@yahoo.com](mailto:sraj54@yahoo.com) (S. Rajendran).

because of its good environmental stability, easy processability, moderate electrical conductivity and rich physics in charge transport mechanism. The local modification of the chemical structure induces drastic changes in electronic properties [18].

The main goal of the present investigation is to optimize the concentration of  $\text{LiClO}_4$  in PEO/PVP based novel solid polymer blend electrolyte by solvent casting technique. The structural and ionic conductivity of the system were studied by XRD and impedance spectroscopy. The orders of local viscosity were identified with the help of photoluminescence studies.

## 2. Materials and methods

The polymer poly (ethylene oxide) (PEO) of average molecular weight 8000, poly (vinyl pyrrolidone) (PVP) of average molecular weight 3,60,000 and salt lithium perchlorate ( $\text{LiClO}_4$ ) were procured from Sigma–Aldrich chemicals limited, U.S.A. The obtained PEO, PVP and  $\text{LiClO}_4$  were dried at  $55^\circ\text{C}$  for 4 h to remove moisture. The fixed ratios of PEO and PVP with various concentrations of  $\text{LiClO}_4$  based electrolytes were prepared by solvent casting technique with methanol as a solvent. The polymers PEO and PVP were dissolved at  $50^\circ\text{C}$  and room temperature respectively. After that, the polymer-salt complex was stirred well for 24 h with the help of magnetic stirrer and degassed to remove air bubbles and poured on a well cleaned Petri dish. The solvent methanol was allowed to evaporate slowly at room temperature for 48 h. The free standing harvested films were stored in highly evacuated desiccator to avoid the moisture absorptions. Flexible thin films with thickness of about 0.1–0.5 mm were obtained. The prepared films were subjected to ac impedance analysis, in order to calculate the ionic conductivity. This was carried out with the help of stainless steel blocking electrodes using a computer controlled micro auto lab type III Potentiostat/Galvanostat in the frequency range of 100 Hz–300 KHz over the temperature range 303–353 K. The amorphousity of the polymer electrolytes has been investigated by XRD analysis with the help of X'pert PRO PANalytical X-ray diffractometer. The complex formation between the polymer and salt has been confirmed by FTIR spectra using SPECTRA RXI, PerkinElmer spectrophotometer in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Thermal stability of the polymer electrolytes was carried out by thermo gravimetric analysis (TG/DTA) using a PYRIS DIAMOND from room temperature to  $700^\circ\text{C}$  with the scan rate of  $10^\circ\text{C min}^{-1}$ . The surface morphology and roughness factor of the sample were observed by atomic force microscope with the help of AFM (A100SGS). The band gap energy was calculated by UV–vis analysis (Shimadzu UV-1601). The photoluminescence studies were performed by Carry Eclipse Fluorescence Spectrometer.

## 3. Results and discussion

### 3.1. X-ray diffraction studies

To obtain some information about the structural and crystalline nature of the prepared samples under investigation, X-ray diffraction studies were made. Fig. 1 represents the X-ray diffraction of pure  $\text{LiClO}_4$ , PEO, PVP and their complexes. Fig. 1(a) of  $\text{LiClO}_4$  shows high intense peaks at angles  $2\theta = 20.9, 22.92, 26.56, 32.75$  and  $35.4^\circ$  corresponding to the lattice planes (1 0 1), (1 1 0), (2 0 0), (2 0 1) and (2 1 0) which reveal the crystalline nature of the ionic salt. Two broad peaks are found at  $2\theta = 19.2$  and  $23.5^\circ$  corresponding to the reflection of (1 2 0) and (0 1 0) plane respectively which confirm the semi crystalline nature of PEO (Fig. 1(b)). A halo peak around  $22.7^\circ$  which is attributed to the amorphous nature of pure PVP has been shown in Fig. 1(c). However, on the addition of the salt to the

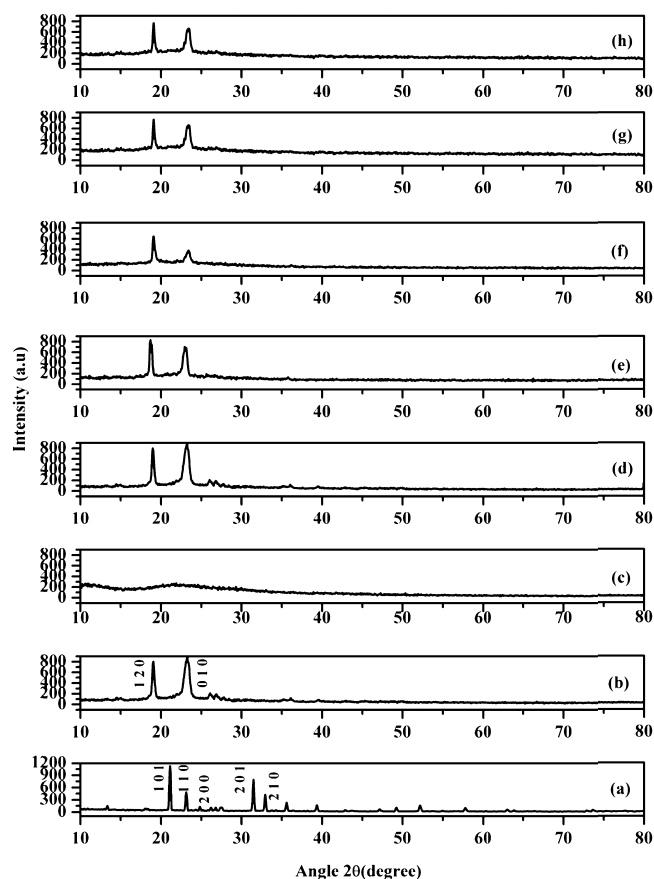


Fig. 1. XRD patterns of (a) pure  $\text{LiClO}_4$  (b) pure PEO (c) pure PVP (d) B1; (e) B2; (f) B3; (g) B4; (h) B5.

polymer blend, the intensity of these peaks decreases gradually and becomes relatively broader, suggesting a decrease in the degree of crystallinity of the complex. This could be due to the disruption of the crystalline structure of the film by  $\text{LiClO}_4$  salt. Hodge et al. [19] established a correlation between the intensity of the peak and the degree of crystallinity. They observed that the intensity of XRD pattern decreases as the amorphous nature increases with the addition of dopant. In the present XRD patterns, relatively broader peaks were found for higher concentrations (10 and 12 wt%) of  $\text{LiClO}_4$  salt in the complexes. This may be due to the formation of separate crystallization phase of excess salt in the complexes. The amorphous nature results in greater ionic diffusivity with high ionic conductivity, as amorphous polymers have flexible backbone [20]. Absence of peaks pertaining to lithium perchlorate salt in the complexes indicates the complete dissolution of salt in the polymer matrix.

### 3.2. FT-IR spectroscopic analysis

If the two polymers are completely incompatible, each individual polymer does not recognize, in infrared spectral terms, the existence of the other in the blend. On the other hand, if the polymers are compatible, there should be considerable differences between the infrared spectrum of the blend and the spectra of the pure components. These differences would be derived from chemical interactions resulting in band shifts and broadening.

Fig. 2. depicts the FT-IR transmission spectra in the range of  $4000\text{--}400\text{ cm}^{-1}$  of PEO/PVP with different  $\text{LiClO}_4$  concentrations. The vibrational bands observed at  $1343, 1282$  and  $1236\text{ cm}^{-1}$  are ascribed to  $\text{CH}_2$  bending, asymmetric twisting and symmetric twisting vibration of PEO respectively and these bands are shifted

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