

Morphology and Conductivity Studies of PVC Based Micro-Porous Polymer Electrolyte

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ABSTRACT

A micro-porous Polymer electrolyte based on Polyvinyl chloride (PVC) was obtained by a novel Polymer dissolution technique. Ionic conductivity of micro porous polymer electrolytes have been determined by impedance studies in the temperature of 303-343K by varying the PVA content in PVC matrix. It is observed that a 3M LiClO_4 solution of micro-porous polymer electrolyte has high ionic conductivity of 1.29×10^{-3} S/cm at ambient temperature. Complexation and the surface morphology of the micro-porous polymer electrolyte are studied by X-Ray Diffraction, FTIR, TGA/DTA & SEM analysis.

Keywords - Ionic conductivity, micro-porous polymer electrolyte, SEM, TGA/DTA, XRD.

I. Introduction

In the past decade, polymer electrolytes have been widely studied due to their advantages in the areas of solid state and electrochemical device application including batteries, fuel cells, super capacitors, electro chromic devices and chemical sensors [1]. Polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities play a major role in these applications [2].

The development of polymer electrolytes has passed mainly three stages, solid polymer electrolytes (SPEs) [3], gel polymer electrolytes (GPEs)[4] and micro-porous polymer electrolytes (MPEs) [5]. For industrial application MPEs have received considerable attention due to their high ionic conductivity and excellent mechanical properties [6,7]. Micro porous polymer electrolyte can be prepared by conventional phase inversion technique [8-10]. However, in this process, due to the use of large amounts of expensive, harmful and flammable solvents, contamination of the porous membrane may take place by the residual solvents. Moreover, preparation of MPEs by conventional phase inversion technology is costly and time consuming.

Hence in the present investigation we develop a simple, reliable, time saving and industrially feasible process for the fabrication of micro-porous polymer membrane, PVC based micro-porous membrane was prepared by extracting PVA from PVC-PVA blend film by using simple dissolution of PVA in DMSO. Moreover these membranes can be easily detached from the substrate and could be used for Li battery applications or many other applications depending upon the type of dopant to be used. The membrane morphology was investigated by XRD analysis.

II. Experimental descriptions

2.1. Materials and Methods:

PVC and PVA (Asldrich USA) were used without further purification for the preparation of micro-porous membranes. Reagent grade anhydrous lithium perchlorate was used after drying in vacuum at 110°C for 24 hours. The different composition of PVC-PVA was prepared by the solvent casting technique by dissolving appropriate amounts of the corresponding constituents in DMF and DMSO respectively. The films were dried at 80°C in vacuum oven for 3 hours to remove any further traces of DMF and DMSO. Finally the above prepared cast polymer films were immersed in DMSO for the preferential dissolution of PVA to get uniform micro-porous membranes of PVC which is then soaked in different molar concentration of lithium perchlorate with Propylene carbonate (PC) & Diethyl carbonate (DEC) in 1:1 ratio.

X-ray diffraction measurement was carried out using PHILLIPS Holland, XRD system PW 171 diffractometer employed with Cu-anode operated at 30kV/15mA. Ionic conductivity of polymer membrane electrolytes have been determined by impedance studies in the temperature of 303-343 K by varying the PVA content in PVC matrix. Scanning Electron Microscope (JEOL, JXA-840. Japan) was used for micro structural studies.

III. Result and discussion

3.1. X-ray diffraction analysis:

In order to investigate the influence of Lithium salt concentration on the micro-porous polymer membrane, XRD examinations were conducted by soaking the micro-porous polymer membrane in 1M LiClO_4 , 1.5M LiClO_4 , 3 M LiClO_4 and 3.5M LiClO_4 electrolyte solution. The XRD pattern of the PVC based micro porous polymer

membrane, & micro porous polymer membrane soaked in 1.5 M LiClO₄ and 3.5 M LiClO₄ electrolyte solution are given in fig. 1(a)-(c.) The following observations were made from the XRD pattern.

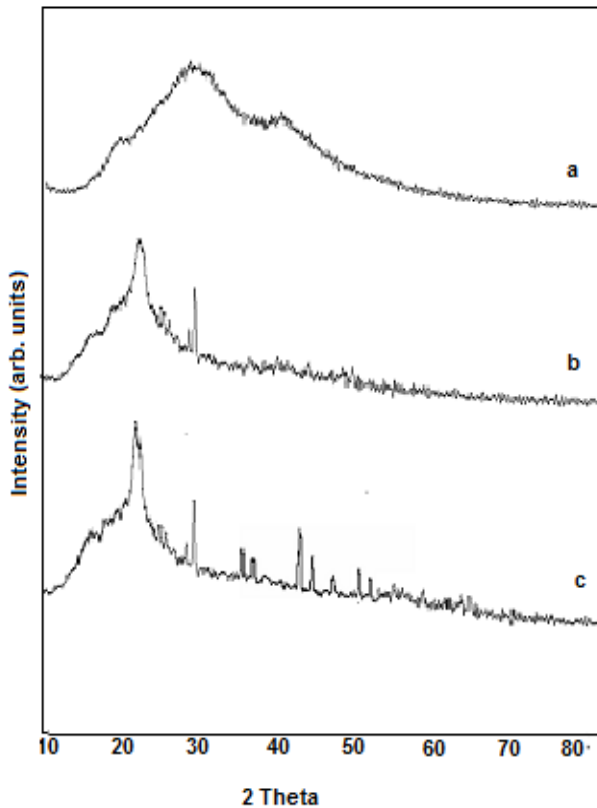


Figure. 2 XRD pattern for (a) micro-porous polymer membrane (b) micro-porous polymer membrane soaked in 1.5 M LiClO₄ and (c) micro-porous polymer membrane soaked in 3.5 M LiClO₄ electrolyte solution.

1. The intensity of the diffraction peaks of PVC based micro-porous polymer membrane increases with increase in salt concentration. This shows a increase in crystalline phase of the micro porous polymer electrolyte. It may be due to the incorporation of LiClO₄, which would have disturbed the amorphous phase and increased the crystallinity.
2. For PVC based micro-porous polymer membrane two amorphous peaks are formed and shown at $2\theta = 20.50^\circ$ and 29.10° , when the polymer membrane is soaked in Li-salt electrolyte solution(1.5M LiClO₄) these peaks are shifted to $2\theta = 22.56^\circ$ and 29.38° respectively. It conforms the complex formation between polymer membrane & Li- salt.
3. In addition, further increase in salt concentration (3.5M LiClO₄) increases the crystalline nature of the polymer electrolyte, which may be due to undissociation of LiClO₄ salt, which is evident from fig. 1(c).

3.2 FTIR analysis:

FTIR spectra of PVC based micro-porous polymer membrane and their micro-porous polymer electrolyte are depicted in fig 4. The characteristic bands of PVC can be classified into three regions. The first is called the C-Cl stretching region in the range from 600-700 cm⁻¹. The second region is called C-C stretching in the range from 900-1200 cm⁻¹. The third region is 1250-2970 cm⁻¹ in PVC (numerous CH modes). The frequency occurred at around 1750 cm⁻¹ is assigned to the carbonyl stretching vibration of PVA. In the region 2950-3000 cm⁻¹, namely at 2972, 2929 and 2910 cm⁻¹ are due to the C-H stretching vibration of the methylene, (C) CH₃ and ethylene (O) C₂H₅ groups which overlap [11]. The two bands at 1250 and 1265 cm⁻¹ are associated with different vibrations of the ester group. Frequency at 1479 cm⁻¹ is assigned to -CH₃ asymmetric bending of plasticizer such as propylene carbonate.

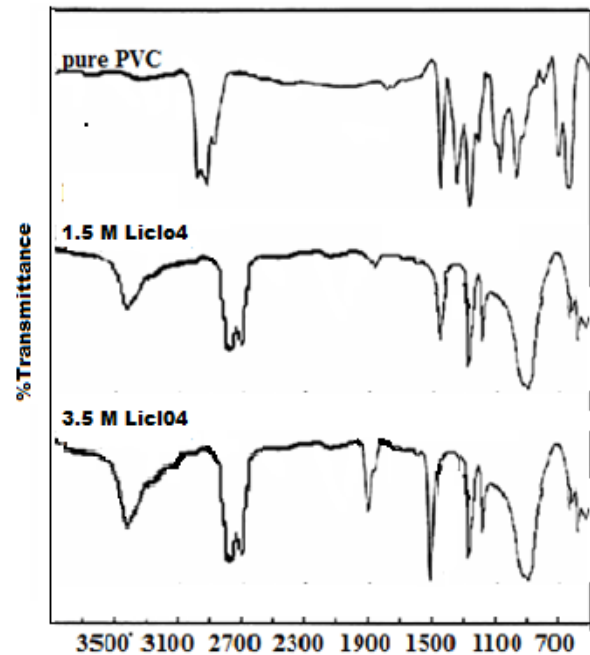


Figure 4. For (a) micro-porous polymer membrane (b) micro-porous polymer membrane soaked in 1.5 M LiClO₄ and (c) micro-porous polymer membrane soaked in 3.5 M LiClO₄ electrolyte solution

3.3 Thermal analysis:

Fig.3 shows TG and DTA curve of the PVC based micro-porous polymer electrolyte of high ionic conductivity system. It can be seen from the TG curve that a first decomposition of PVC occurs at 270.9 °C with a rapid weight loss of 32 % which is closely related with reported value [12]. It follows a complete decomposition of 98% upto 495.0 °C. This is due to low molecular weight of alkanes, alkenes, aldehydes, ketones & also acetic acid in case of pure PVC[13].

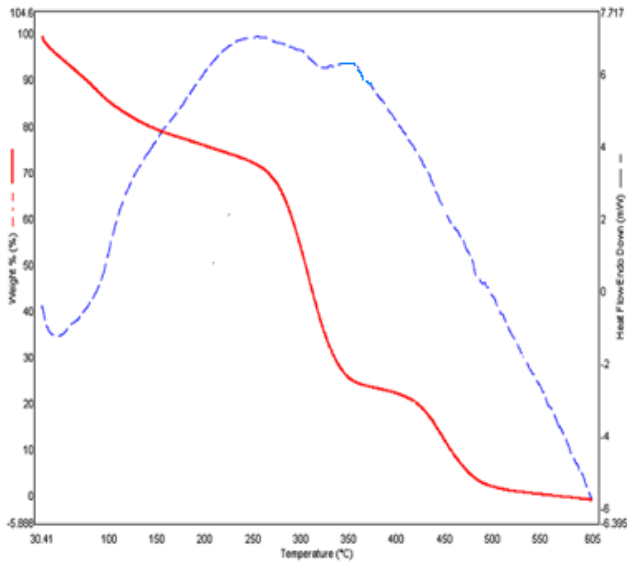
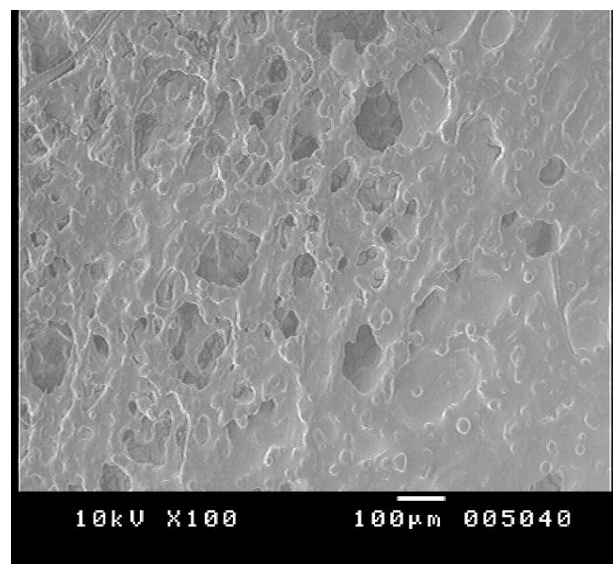
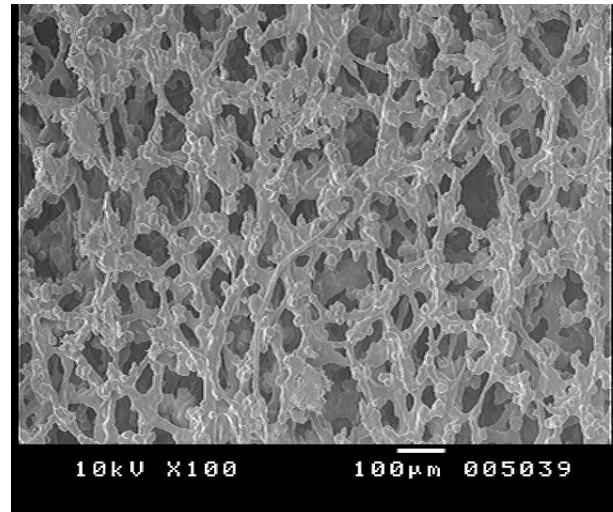


Fig. 3 TGA/ DTA curve for micro-porous polymer electrolyte

DTA trace shows an exothermic peak around 270 °C indicative of the maximum weight loss rate of the decomposition of PVC corresponds to the rapidest degradation temperature of the stage. From the above discussion, it is concluded that the thermal stability limit of the polymer blend electrolyte is about 270C.The surface morphology PVC based micro-porous membranes were studied by scanning electron microscopy (SEM) using Jeol model JSM 6390 LV.

3.4 SEM Analysis:

Fig. 4(a & b) shows the SEM photographs of the micro porous polymer membrane of high conductivity system before and after soaking in electrolyte solution. It can be seen from the photograph that the micro porous structure increases with increase in removal of PVA content. Hence the uptake of electrolyte solution by the micro porous polymer membrane is higher than that of conventional polymer film. After soaking in electrolyte solution, the micro porous membrane could not be observed with large Voids and cavities of different sizes due to the formation of complex process by the interaction of plasticizer and the polymer chain which is evident from Fig. 4(b).



(b)

Fig.4.SEM images for (a) PVC based micro porous polymer membrane & (b) PVC based micro porous polymer electrolyte

3.5. Conductivity measurements:

Ionic conductivity values of PVC based polymer electrolyte and micro porous polymer electrolyte are given in table 1. It can be seen from the Table that micro porous polymer electrolyte of composition 60:40 wt.% of PVC-PVA based polymer blend film has a higher ionic conductivity of 5.43×10^{-4} (S/cm)at room temperature than all other micro porous polymer electrolytes. Hence above blend ratio is chosen for optimized system. Finally the effect of different lithium salt concentration was carried out in the temperature range of 303-343k for the micro porous polymer electrolyte of high ionic conductivity System and are given in table 2.

Table 1.

Ionic conductivity values of micro-porous polymer membrane soaked in 1M concentration of LiClO₄ electrolyte Solution at room temperature

Sr.no.	PVC(%)	PVA(%)	Conductivity (Scm ⁻¹)	Film strength
1	100	0	0.129 x 10 ⁻⁴	excellent
2	90	10	0.334 x 10 ⁻⁴	excellent
3	80	20	0.876 x 10 ⁻⁴	good
4	70	30	2.638 x 10 ⁻⁴	good
5	60	40	5.431 x 10 ⁻⁴	good
6	50	50	5.412 x 10 ⁻⁴	poor

For all the concentration, conductivity increases with increase in temperature as expected [14]. It seems to obey the Arrhenius relation. The amorphous nature of the present polymer electrolyte facilitates the fast Li-ion motion in the polymer network and it further provides a higher free volume on increasing the temperature [15]. The micro-porous polymer electrolyte consists of 3M LiClO₄ electrolyte solution has high ionic conductivity of 1.29 x 10⁻³

S/cm at room temperature. Beyond this concentration (3M LiClO₄) ionic conductivity decreases. This is due the formation of ion pairs and the ion triplets, which causes constraints in the polymer segmental motion and also retards the ionic mobility due to the increase in crystalline nature of micro-porous polymer electrolyte.

Table. 2

Ionic conductivity values of micro-porous polymer membrane soaked in different concentration of LiClO₄ electrolyte solution at various temperature

concentration	Ionic conductivity(x 10 ⁻³) (S/cm)				
	303 K	313K	323K	333K	343K
1 M LiClO ₄	0.54	0.57	0.60	0.65	0.73
1.5 M LiClO ₄	0.62	1.01	1.98	2.78	3.29
3 M LiClO ₄	1.29	1.75	2.34	2.96	3.43
3.5 M LiClO ₄	1.03	1.67	2.26	2.59	3.27

Typical plot of log conductivity versus inverse temperature (1000/T) for micro-porous polymer electrolyte of high conductivity system in different salt concentration are shown in Fig.6. In general, on increase in temperature, the ionic conductivity increases due to internal activation, and decreasing *E_a* values which reduce the crystalline nature of the polymer-salt complexes. The plots suggest that the non linear ion transport in polymer electrolyte depends upon the segmental motion of the polymer electrolyte [16].

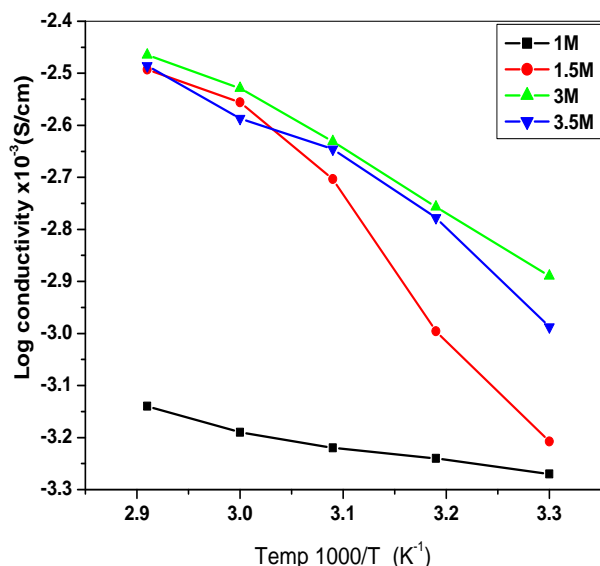


Fig.6 Arrhenius plot of micro-porous polymer electrolyte for different salt concentration.

IV. Conclusions

1. It is possible to prepare PVC based micro-porous polymer electrolyte by simple polymer dissolution technique by extracting one of the polymer from the polymer blend film.
2. The micro-porous polymer electrolyte has thermal stability up to 270 °C.
3. The maximum ionic conductivity of 1.29×10^{-3} S/cm is observed at room temperature when the micro-porous polymer membrane is soaked in 3M LiClO₄ electrolyte solution.
4. The dependence of the ionic conductivity on temperature is a nonlinear on logarithmic scale. It obeys the Arrhenius plot of conductivity.

V. Acknowledgements

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