
Highly Porous Polymer Electrolytes Based on PVdF-HFP / PEMA with Propylene Carbonate/Diethyl Carbonate for Lithium Battery Applications

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Abstract: The development of new materials is a vital to meet the challenges faced by battery technologies. Ionic conducting solid polymer electrolytes could reduce the risk of explosion with non-flammability and high thermal stability. The use of solid polymer electrolyte is the additional strength of the electrodes performances to increase the number of cycle for the rechargeable batteries. In the present study, preparation of PVdF-HFP/PEMA blend based solid polymer electrolytes enclosure of two different plasticizers such as propylene carbonate (PC) and diethyl carbonate (DEC) at different concentrations and the accumulation of lithium perchlorate as salt. To confirm the structural changes and complex formations, the prepared electrolytes were subjected into XRD and FTIR analyses, and the porous nature of the electrolytes was identified using scanning electron microscopy. AC impedance studies were performed at various temperatures from 303 K to 363K for the prepared samples. The results suggest that the PC/DEC (1:1) based electrolyte exhibited the higher ionic conductivity is 0.00477 S/cm at room temperature and 0.00843 S/cm at 363K. The temperature dependence of ionic conductivity also complies with the VTF relation.

Keywords: Solid Polymer Electrolyte, FTIR, XRD, SEM, Conductivity

1. Introduction

One of the most feasible challenges as a sustainable energy conversion and storage systems is the Rechargeable Lithium Ion Battery (LIB). The LIB is based on a cathode and an anode, which has the property of reversible insertion and extraction of lithium ions. Transfer of lithium ions is enabled by the addition of an organic liquid electrolyte and a mechanical separator between the anode (negative electrode) and the cathode (positive electrode). When the lithium ion is inserted and extracted in the cathode and the anode, electrical energy is generated by electrochemical oxidation and reduction process. The electrolyte between the anode and cathode has to be an ionic conductor, electronic insulator and is responsible for the transport of lithium ions. The optimal electrolyte should combine the conduction properties of liquid and the mechanical stability of solid with high chemical stability. Even though liquid electrolytes are commonly used, due to high ionic conductivity, application

of polymer and ionic liquid electrolytes also attract interest as they might improve the safety of lithium batteries [1]. A membrane (separator) is an important component of a battery, as it prevents short circuit by separating the anode from the cathode. In the LIB, the membrane is required to be capable of battery shutdown at a temperature below that at which thermal runaway occurs, and the shutdown should not result in loss of mechanical integrity. Otherwise, the electrodes could come into direct contact and the resulting chemical reactions cause thermal runaway. Shutdown is an important trait of a good membrane for the safety of lithium batteries. The promising membranes are those with high electrolyte permeability and mechanical strength, as well as good thermal, chemical, and electrochemical stability. In order to concentrate the above parameters, polymer electrolytes have been improved for better performance in the electrochemical characteristics devices with stretchy natures and concurrence with safety concern. Many kinds of P. Sivakumar et al: Highly Porous Polymer Electrolytes based on PVdF-HFP/PEMA with Propylene Carbonate/Diethyl Carbonate for Lithium Battery

Applications. polymers have been preferred as the matrix of poly (ethylene oxide) (PEO), poly (ethylene glycol) (PEG), poly (vinyl chloride) (PVC), poly (vinylidene fluoride) (PVdF), poly (acrylonitrile) (PAN), poly (vinyl acetate) (PVAc), poly (vinyl pyrrolidone) (PVP), poly (methyl methacrylate) (PMMA), etc. [2-9]. Among them, PVdF-HFP has good electrochemical stability, affinity to electrolyte solution, high dielectric constant ($\epsilon = 8.4$) and also it is chemical copolymer, which contains both amorphous (HFP) and crystalline (PVdF) phase, which provides plasticity and mechanical strength. PVdF-HFP based membranes tend to be opaque [10], while PEMA based membranes are transparent. Blend host matrices also help to increase the ionic conductivity [11]. In order to further increase the ionic conductivity, an attempt has been taken to incorporate the LiClO_4 as salt, PC and DEC as plasticizers with PVdF-HFP/PEMA based blend polymer. The prepared electrolytes are subjected into various studies, such as a.c. Impedance measurement, FTIR, XRD, SEM and their results are discussed.

2. Experimental

2.1. Materials

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, $M_w \sim 455,000$) in pellet form, Poly (ethyl methacrylate) (PEMA, average $M_w \sim 515,000$) in powder form, lithium perchlorate (LiClO_4 , $M_w = 106.39$, battery grade, purity 99.99 %,) are received from Sigma Aldrich and Propylene Carbonate (PC), Diethyl Carbonate (DEC), acetone are procured (Alfa Aesar) and used after laboratory purifications.

2.2. Preparation of PVdF - HFP / PEMA Based PEs

PVdF – HFP and PEMA blend based polymer electrolytes are prepared by solution casting technique. To enhance the ionic conductivity, PVdF-HFP/PEMA (as 18:12 (wt. %)), is dissolved in volatile solvent such as acetone separately. The LiClO_4 (8) was dissolved in the mixture of PC and DEC at various ratio (1:1, 1:2, 1:3 and 1:4) in an appropriate amount of acetone and then the polymer mixture was stirred continuously until obtained complete homogeneous solution. Further, polymer and salt were mixed together and the solution was stirred about 24 hours until to get the transparent resultant solution. The obtained homogeneous mixture was cast onto a cleaned glass plate and dehydrated at 45°C in an oven for 2-3 hours to evaporate the residual solvent. Upon cooling at room temperature, the mechanically stable and transparent membranes were carefully peeled from the glass plates and stored in the vacuum desiccators for further characterizations.

2.3. Characterization Techniques

To analyze the complexation behavior and structural modification of the electrolyte, FTIR spectrum was recorded using Perkin-Elmer-1600 in the range of $400 - 4000 \text{ cm}^{-1}$,

and X-Ray diffraction pattern was obtained using a computer controlled X'PERT PROPanalytical diffractometer with $\text{Cu-}\alpha$ radiation as the source at 40 kV with a scanning range between 10° to 80° . Impedance of the each sample was determined using electrochemical work station of Bio-Logic SAS instrument (SP-150 model). The measurement was carried out in the frequency range from 1 Hz to 1 MHz at various temperatures. The impedance studies were carried out by sandwich the polymer electrolyte membrane between two stainless steel (SS) electrodes under spring pressure. The thickness of each sample was measured by a Digital Caliper. The surface morphology of the films was examined using VEGA3 TESCAN Scanning Electron Microscope (SEM).

3. Result and Discussion

3.1. FTIR Analysis

“Figure 1.” shows the FTIR spectrum of pure PVdF-HFP, PEMA, LiClO_4 and (a) PVdF-HFP/PEMA (18/12) - LiClO_4 (8) – PC/DEC (1:1), (b) PVdF-HFP/PEMA (18/12) - LiClO_4 (8) - PC/DEC (1:2), (c) PVdF-HFP/PEMA (18/12) - LiClO_4 (8) - PC/DEC (1:3) and (d) PVdF-HFP/PEMA (18/12) - LiClO_4 (8) - PC/DEC (1:4) complexes. The vibrational peaks at $485, 487, 488 \text{ cm}^{-1}$ and $436, 437, 438 \text{ cm}^{-1}$ are assigned to the bending and wagging vibration of $-\text{CF}_2-$ in complexes. The crystalline phase of the PVdF – HFP polymer is identified at $969, 775 \text{ cm}^{-1}$ and $623, 624, 625 \text{ cm}^{-1}$ in the complexes. The peak at 1132 cm^{-1} is shifted from $1175, 1176 \text{ cm}^{-1}$ in film (a and c), $1389, 1394$ and 1398 cm^{-1} are assigned to the symmetrical stretching of $-\text{CF}_2-$ and $-\text{CH}_2$ groups, respectively [11]. The peak at 878 cm^{-1} in the complexes is assigned to the vinylidene group of the polymer. The PVdF-HFP skeletal vibration of $-\text{CF}_2-$ stretching vibration at 1054 cm^{-1} is shifted to $1030, 1032, 1033 \text{ cm}^{-1}$ in film (b, d and c). The vibrational peaks at $2965, 2977 \text{ cm}^{-1}$ and $2985, 2983 \text{ cm}^{-1}$ are attributed to the asymmetric C-H stretching vibration of the ethylene group of PEMA in the complexes. The functional groups corresponding to $-\text{CH}_2-$ scissoring and $-\text{CH}_2-$ rocking are observed at 1477 cm^{-1} and $752, 753 \text{ cm}^{-1}$ are shifted to 1469 cm^{-1} and 777 cm^{-1} in complexes. The C=O stretching band of PEMA are located at $1730, 1735$ and $1724, 1726 \text{ cm}^{-1}$ in complexes. The vibrational peaks at $713, 721, 768$ and 775 cm^{-1} belongs to the anion and cations are coordinated with the carbonyl carbon and carboxylic oxygen (C=O) presence in the polymer complexes. The skeletal vibration is identified at 1469 and 1478 cm^{-1} in the complexes which is assigned to $-\text{CH}_3-$ asymmetric bending of plasticizer such as propylene carbonate. The band position of C-O-C asymmetric stretching vibration and -C-O-C-O-skeletal vibration of diethyl carbonate (DEC) molecule located at 1213 and $1229, 1234 \text{ cm}^{-1}$ are observed in complexes. The frequencies at 835 cm^{-1} are assigned to C-Cl stretching vibrations of perchlorate. The vibrational peaks of LiClO_4 at 1149 cm^{-1} is shifted to 1133 cm^{-1} in complexes. Shifting of peaks and formation of new peaks imply the polymer – salt interaction in PVdF-HFP/PEMA blend based

polymer electrolytes systems.

3.2. X-ray Diffraction Analysis

“Figure 2.” shows the X-ray diffraction pattern of pure PVdF-HFP, PEMA, LiClO₄, (a) PVdF-HFP/PEMA (18/12) - LiClO₄ (8) – PC/DEC (1:1) and (b) PVdF-HFP/PEMA (18/12) - LiClO₄ (8) - PC/DEC (1:2) complexes.

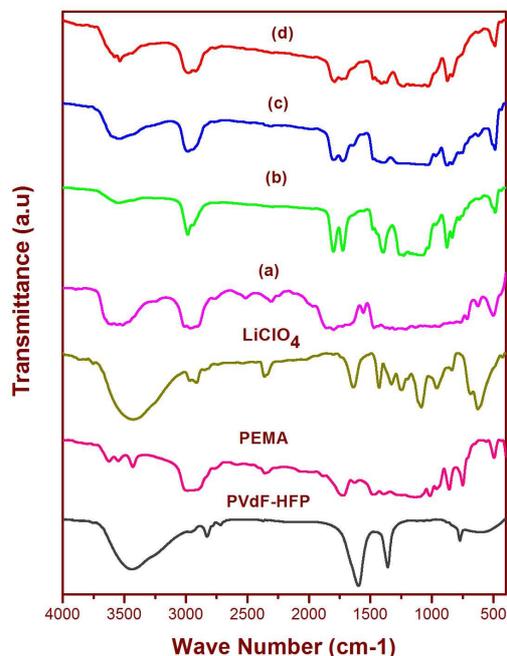


Fig. 1. FTIR spectrum of pure PVdF-HFP, PEMA, LiClO₄, (a) X - PC/DEC (1:1), (b) X - PC/DEC (1:2), (c) X - PC/DEC (1:3) and (d) X - PC/DEC (1:4). Where X = PVdF-HFP/PEMA (18/12) – LiClO₄ (8).

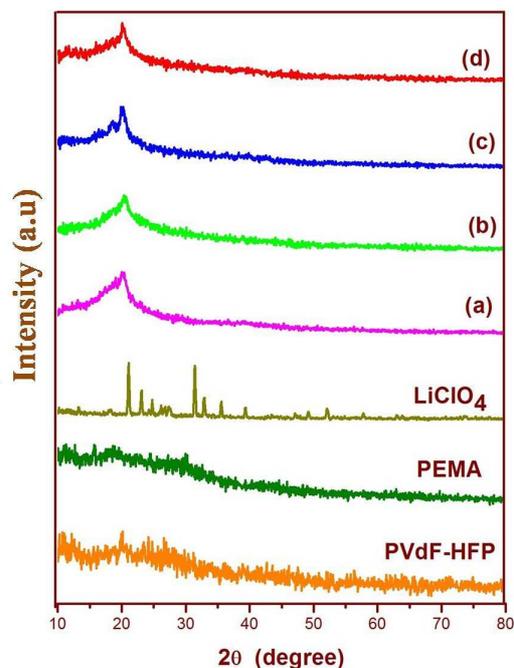


Fig. 2. XRD pattern of pure PVdF-HFP, PEMA, LiClO₄ and (a) X - PC/DEC (1:1), (b) X - PC/DEC (1:2), (c) X - PC/DEC (1:3) and (d) X - PC/DEC (1:4). Where X = PVdF-HFP / PEMA (18/12) – LiClO₄ (8).

The peaks found $2\theta = 18.05^\circ, 20.01^\circ, 20.19^\circ, 20.22^\circ, 20.45^\circ$ and 43° reveal the partial crystallization of PVdF units present in the complexes, giving an overall semi crystalline morphology of PVdF-HFP [12] and the presence of broad hump in the complexes confirms the amorphous nature of electrolytes. Furthermore, no peaks are found for LiClO₄ reveals the completely dissolution of salt in the polymer complex and therefore from these observations no diffraction peaks are identified at any separate phase of LiClO₄ in complexes, which confirm that the salt dissolution was completely dissolved and trace of plasticizer is also absent in the films.

3.3. Ionic Conductivity Studies

The ionic conductivity of the each sample was calculated using the equation $\sigma = t/R_b \cdot A$ (Scm⁻¹), where t is thickness of the electrolyte, R_b is the bulk resistance and A is the area of the electrolyte – electrode contact. The imaginary impedance (Z'') was plotted against the real impedance (Z') and the bulk resistance was obtained from the intercept with the real-axis [13]. “Fig. 3(a- d).” shows the complex impedance spectra of P(VdF-HFP)/PEMA – PC/DEC – LiClO₄ for the different concentrations of polymer blend based electrolyte system at different temperature with enlarged view of each complex impedance spectra.

According to the theoretical analysis given by Watanabe and Ogata [14], two semi circles should appear in an impedance spectrum for a symmetric cell. i.e., one at higher frequency related to bulk electrolyte impedance and other at lower frequencies related to the interfacial impedance. It is also reported [15] that high frequency semi-circle does not appear in our useful impedance plots for blend polymer membrane as shown in “FIG. 3(A) AND 3(B).” This phenomenon is quite reasonable since the too unproblematic mobility in this solid electrolyte system, when compared with liquid and gel polymer electrolytes.

“Fig. 4.” shows the polymer complexes obey the temperature dependant ionic conduction is good agreement with Vogel – Tamman – Fulchar (VTF) relations, which describes the transport in a viscous matrix [4]. It supports to initiative the ions movements through the plasticizer rich phase, which is the conducting medium and involved with lithium salt. The samples are having improved ionic conductivity to higher temperature from ambient temperature, which could be credited to the enhance the free volume of the polymer electrolyte membrane, hence the free volume in a solid polymer electrolyte increases as a result and the segmental motion also permits the ions to hop from one site to another site or given the pathway to ion migration.

TABLE.1 shows the a.c conductivity at different temperatures of different concentrations of plasticizer. Film (a) achieved the higher ionic conductivity as 4.77×10^{-3} Scm⁻¹ at room temperature and 8.43×10^{-3} Scm⁻¹ at 363 K. When the addition of plasticizer ratio as 1:1 helps to induce the amorphous region and exhibit maximum ionic conductivity at room temperature with flexible nature of

electrolyte membranes. When diethyl carbonate (DEC) increases with minimum of propylene carbonates in the complex (b), (c) and (d), its overall amorphous phase becomes reduced and hence low ionic conduction with poor mechanical strength.

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Table 1. Ionic conductivity ($10^{-3} S/cm$) at various temperatures.

Sample ID	303K	313K	323K	333K	343K	353K	363K
a	4.77	4.95	5.21	5.59	6.12	7.09	8.43
b	3.08	4.15	4.41	4.46	4.32	4.03	4.20
c	1.50	1.60	1.72	1.94	2.25	3.15	3.67
b	1.17	1.26	1.46	1.71	2.12	2.33	2.65

Where (a) = X - PC/DEC (1:1), (b) = X - PC/DEC (1:2). (c) X - PC/DEC (1:3) and (d) X - PC/DEC (1:4). Where X = PVdF-HFP/PEMA (18/12) - LiClO₄ (8)

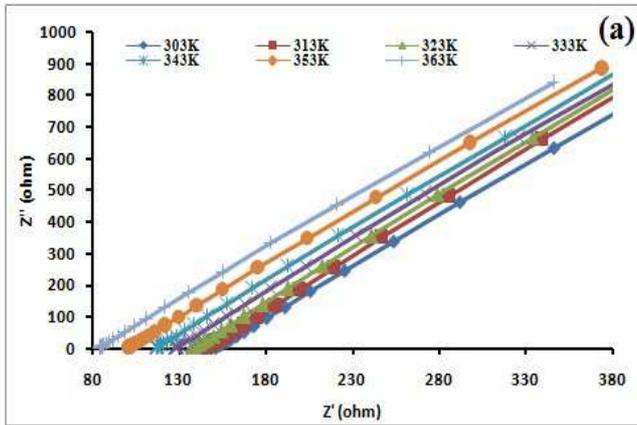


Fig. 3(a). Impedance spectra of PVdF-HFP/PEMA (18/12) - PC/DEC (1:1/62) - LiClO₄ (8).

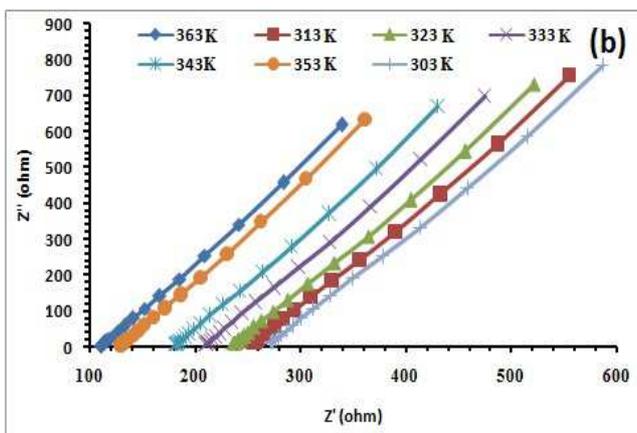


Fig. 3(b). Impedance spectra of PVdF-HFP/PEMA (18/12) - PC/DEC (1:2/62) - LiClO₄ (8).

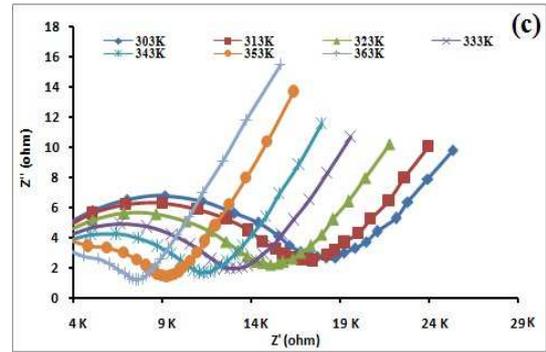


Fig. 3(c). Impedance spectra of PVdF-HFP/PEMA (18/12) - PC/DEC (1:3/62) - LiClO₄ (8).

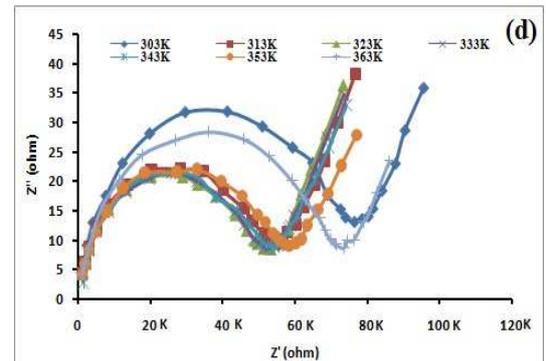


Fig. 3(d). Impedance spectra of PVdF-HFP/PEMA (18/12) - PC/DEC (1:4/62) - LiClO₄ (8).

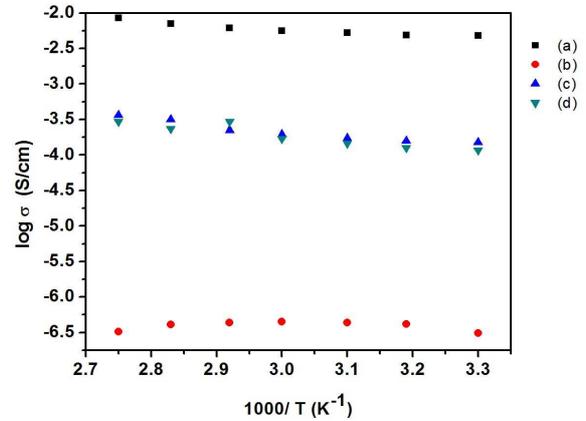


Fig. 4. Temperature Dependence of Ionic Conductivity.

3.4. SEM Analysis

SEM is one of the most quick-witted instruments for the examination and analysis of the microstructure characteristics of the substance. “Fig. 5 and 6.” are reveals the surface morphology of the polymer electrolytes which depend upon the mixture of PVdF-HFP and PEMA polymer blend at different concentrations of propylene carbonate and diethyl carbonate (1:1, and 1:4). It is transparent that the large porosity and small pore size are fundamental for a good separator and high conductivity. When propylene carbonate and diethyl carbonate are taken as 1:1 wt %, the surface shows enormous number of pores and hence higher ion

migration identified. The higher percentage of DEC shows lower conductivity which is due to fewer pores in the surface of the polymer electrolyte which is evident from SEM trace.

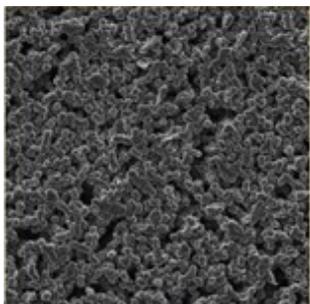


Figure 5. SEM image of PVdF-HFP/PEMA (18/12) -PC/DEC (1:1/62)-LiClO₄ (8).

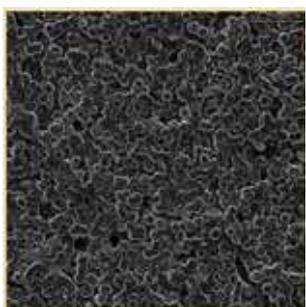


Figure 6. SEM image of PVdF-HFP/PEMA (18/12) -PC/DEC (1:4/62)-LiClO₄ (8).

4. Conclusions

PVdF-HFP/PEMA blend based polymer electrolytes are prepared by solvent casting technique. The structural and complex formations of PVdF-HFP/PEMA-PC-DEC-LiClO₄ systems have been confirmed by XRD and FTIR studies. These electrolytes show appreciable ionic conductivity even at room temperature. Maximum conductivity as 4.77×10^{-3} S/cm at room temperature with good mechanical stability has been observed in PVdF-HFP (18) – PEMA (12) – PC/DEC (62) – LiClO₄ (8) based system when plasticizer ratio as 1:1. Higher conductivity in this composition could be attributed due to higher amorphicity. SEM analysis reveals the presence of higher porosity in the polymer complex that is also an evidence for higher conductivity.

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