



**Complex Impedance Spectroscopic Studies of
PMMA_(80,70,60,50) : PC_(10,20,30,40) : PVP₍₁₀₎ : LiClO₄₍₅₎
Polymer Solid Electrolyte Systems**

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Abstract

Polymer solid electrolytes PMMA_(80,70,60,50) : PC_(10,20,30,40) : PVP₍₁₀₎ : LiClO₄₍₅₎ were synthesized according to stoichiometric ratios using solution cast method. FTIR study confirms the good complexation among the constituent materials in the polymers matrix. Complex impedance and electric modulus studies are carried out and explained. From cole-cole plots, maximum decrement of resistance is observed at a threshold ratio 70 Wt% PMMA: 20 Wt% PC: 10 Wt% PVP: 5 Wt% LiClO₄ and this could be due to the high mobility of the Li⁺ ion in the polymer network due to the plasticizer. The plasticizer plays an important role in decreasing the viscosity of the system, which in turn favors the mobility of segmental motion of polymer network and fast ion motion in the polymer. Real and Imaginary electric modulus spectra show the presence of relaxation peaks and confirm that the polymer solid electrolyte is an ionic conductor.



Article History

Received: 2 November 2020

Accepted: 23 December 2020

Keywords:

Segmental Motion,
Bulk Resistance,
Electric Modulus,
Ionic Conductor

Introduction

Recently a rapid increase in the application of electronic devices leading to the development of the

necessity of high energy stored secondary batteries¹. Mostly Li-ion-based batteries are available in a liquid state, but they possess leakage problems which

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Doi: <http://dx.doi.org/10.13005/msri/170310>

may cause fire and explosion, thereby raising safety issues^{2,3}. These problems have been minimized in polymer-based solid electrolytes and more research has been carried out and reported in solid polymer electrolyte membranes, namely PEO-PMMA-LiClO₄-Silica Aerogel⁴, PMMA-LiBF₄⁵, PEO-LiClO₄-ZnO⁶, Al₂O₃-EC-PEO-LiCF₃SO₃⁷, EC-PVC-LENR50⁸, PMMA-LiClO₄-Clay⁹, (PC+DEC)-LiClO₄-PMMA¹⁰, PMMA-LiClO₄-EC-PC-PEG-DMC¹¹, etc.. In the present work, we have studied and report the FTIR characterization, Cole-Cole plots and electric modulus of solid blend polymer electrolyte systems PMMA_(80,70,60,50): PC_(10,20,30,40): PVP₍₁₀₎: LiClO₄₍₅₎.

Experiment

PMMA (Mw ~1.2x10⁵), PVP(Mw ~3.6x10⁵), PC (Mw ~10⁵), DMF (N-N dimethylformamide), and

LiClO₄ chemicals were procured from Sigma Aldrich India. Solid polymer electrolytes were synthesized with varying PMMA (Polymethyl methacrylate) and PC (Polycarboxylic), keeping the remaining two chemicals PVP (Polyvinylpyrrolidone) LiClO₄ (Lithium perchlorate) kept constant using the solution casting method. Thereafter these were designated as PPSE1, PPSE2, PPSE3, and PPSE4, respectively, as shown in table-1. The above chemicals were dissolved in 30 ml of DMF and stirred for nearly 24 hours at ambient temperature until a homogeneous solution was formed; then the polymer mixture was poured into a petri dish and kept in a vacuum oven for about 70°C. A dried polymer film was formed after 48 hours.

Table 1: Designation of the polymer matrixes used in this work

Sl.No.	Polymer Matrix	Polymer Name
1	80Wt% PMMA : 10Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄	PPSE-1
2	70Wt% PMMA : 20Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄	PPSE-2
3	60Wt% PMMA : 30Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄	PPSE-3
4	50Wt% PMMA : 40Wt% PC : 10Wt% PVP : 5Wt% LiClO ₄	PPSE-4

Results And Discussion

Complex Impedance Plots

Complex impedance spectroscopy studies are carried out for different polymer solid electrolytes. Figure 1 shows the cole-cole plots at different temperatures for PPSE1, PPSE2, and PPSE3 solid polymer systems, respectively. The intercepts of the semicircle on the real axis give the bulk resistance (R_b) of the sample when a plot is drawn between Z' and Z'' at a given temperature. The conductivity of the sample is evaluated at a given temperature by using $\sigma = t / AR_b$

Where 't' is the thickness and 'A' is the area of the cross-section of the sample. From Cole-Cole plots, it has been observed that the magnitude of the bulk resistance (R_b) decreases with an increase in temperature in all these three polymer matrices^{6,9}. The maximum decrement of resistance is observed at a threshold ratio 70 Wt% PMMA: 20 Wt% PC: 10 Wt% PVP: 5 Wt% LiClO₄ (PPSE2) and this could be due to the high mobility of the Li⁺ ion in the polymer network.

Electric Modulus

The real (M') and imaginary (M'') electric modulus spectra as a function of temperature at different frequencies for PPSE2 have been shown in figures 2 and 3, respectively. Real electric modulus spectra show that there is dispersion at the high-frequency region and a long tail with '0' magnitude at low frequency, indicating the presence of large capacitance associated with the electrode. Imaginary modulus spectra in figure 3 show the peak at different temperatures. The left and right side of the peak gives information about the conduction process(long-range mobility of charge carriers) and the relaxation process of the conducting ions(short-range mobility of charge carriers)^{12,14}. There is a shift in the asymmetric peaks, which can be understood that there exists a correlation between the mobility of different charge carriers. The presence of relaxation peaks confirms that the polymer solid electrolyte is an ionic conductor^{13,14}.

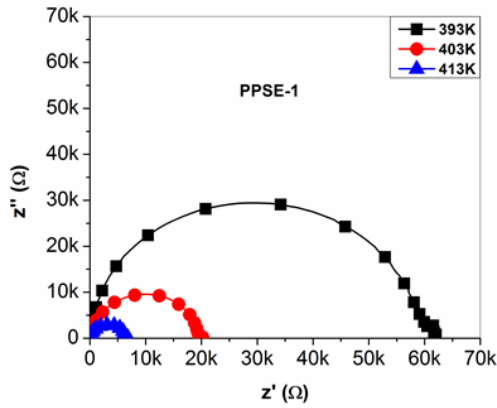


Figure 1(a)

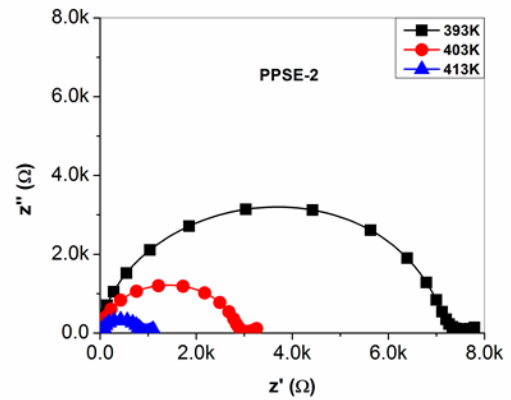


Figure 1(b)

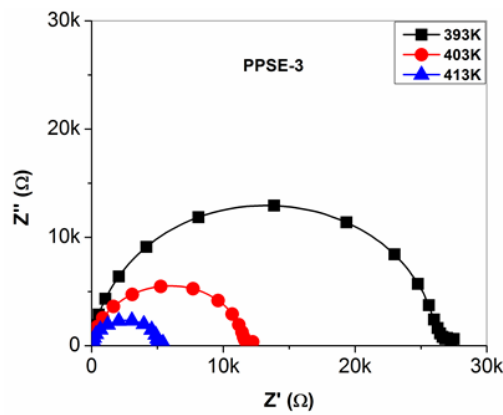


Figure 1(c)

Fig. 1(a), 1(b), and 1(c) Cole-Cole plots of the samples PPSE1, PPSE2, and PPSE3 at different temperatures

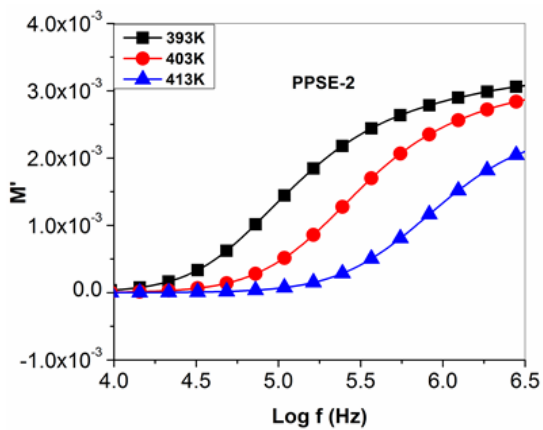


Fig. 2: Real Part Electric Modulus Spectra of PPSE-2 at various temperatures

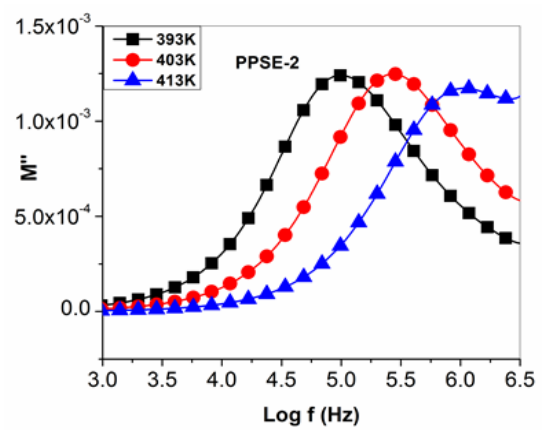


Fig. 3: Imaginary part Electric Modulus Spectra of PPSE-2 at various temperatures

FTIR

Figure 4 depicts the FTIR spectra of four polymer electrolyte systems; in pure LiClO_4 , a peak is located at 1630 cm^{-1} is related to vibration mode has been shifted to 1645 cm^{-1} , 1660 cm^{-1} , 1641 cm^{-1} , and

1643 cm^{-1} with peak broadening and decrease in the intensity in all the polymer matrices. This can be understood by the miscibility of the salt with the polymer matrix has properly taken place.

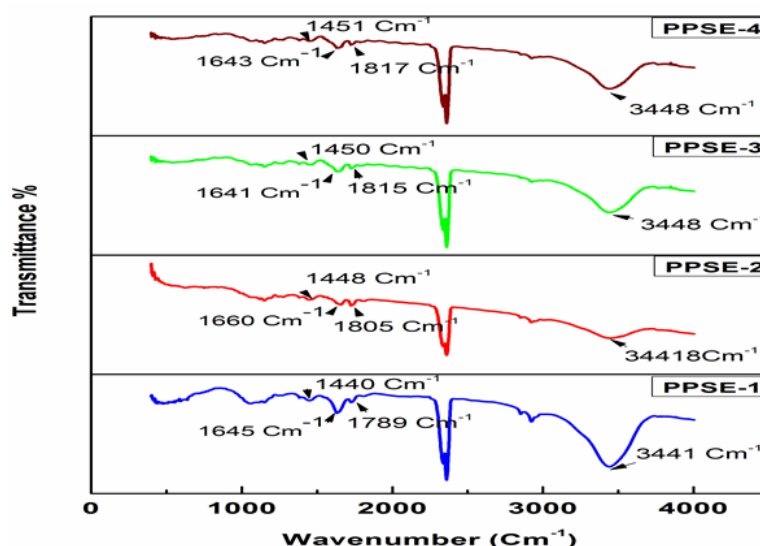


Fig. 4: FT-IR Spectra of $\text{PMMA}_{(80,70,60,50)}:\text{PC}_{(10,20,30,40)}:\text{PVP}_{(10)}:\text{LiClO}_{4(5)}$ polymer solid electrolyte system

A peak associated with PMMA corresponding to C=O stretching with wave no. 1737 cm^{-1} shifts from its original position in the PPSE1, PPSE2, PPSE3 and PPSE4 at 1734 cm^{-1} , 1726 cm^{-1} , 1732 cm^{-1} , 1730 cm^{-1} respectively. The C=O stretching at 1698 cm^{-1} is present in pure PC has been shifted to 1789 cm^{-1} in PPSE1, 1805 cm^{-1} in PPSE2, 1815 cm^{-1} in PPSE3 and 1817 cm^{-1} in PPSE4. The peak corresponding to 3441 in PPSE1 shifts to 3448 cm^{-1} with peak boarding. In pure PVP a peak at 1348 cm^{-1} related to C-H stretching shifts to 1440 cm^{-1} , 1448 cm^{-1} , 1450 cm^{-1} and 1451 cm^{-1} in respective polymer electrolytes. Overall results conclude that the good complexation has been taken place in the polymer matrix^{12,6}.

Conclusions

FTIR spectra of solid Polymer electrolytes of $\text{PMMA}_{(80,70,60,50)}:\text{PC}_{(10,20,30,40)}:\text{PVP}_{(10)}:\text{LiClO}_{4(5)}$ confirms the good miscibility of all the constituent chemicals with the shifting of position in each solid electrolyte. Cole-Cole plots show the decrease in the value of R_b with an increase in temperature could be due to the existence of more number of free

volumes present around the polymer chain and fast Li^+ ion mobility in the polymer network favored by PC. Electric modulus studies confirm the electrolyte is an ionic conductor. Frequency-dependent Electric Modulus spectra at different temperatures show the value of M' is '0' at lower frequencies and this could be due to the large value of capacitance associated with the electrode-electrolyte interface. The values of M' increases with respect to frequency this can be explained due to the short-range mobility of charge carriers and M'' (imaginary) spectra explains the conduction and relaxation of conducting ions.

Acknowledgements

Authors also thank the Head Dept. of Physics for providing experiment facility.

Funding Source

Authors acknowledge DST PURSE for the financial assistance in carrying out this work.

Conflict of the Statement

The authors do not have any conflict of interest.

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