

Vibrational, electrical, dielectric and optical properties of PVA-LiPF₆ solid polymer electrolytes

S. ABARNA, G. HIRANKUMAR*

Centre for Scientific and Applied Research, PSN College of Engineering and Technology, Melathediyoor,
Tirunelveli 627 152, Tamil Nadu, India

Solid polymer electrolytes based on polyvinyl alcohol (PVA) doped with LiPF₆ have been prepared using solution casting technique. Electrical properties of prepared electrolyte films were analyzed using AC impedance spectroscopy. The ionic conductivity was found to increase with increasing salt concentration. The maximum conductivity of $8.94 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ was obtained at ambient temperature for the film containing 20 mol% of LiPF₆. The conductivity enhancement was correlated to the enhancement of available charge carriers. The formation of a complex between the polymer and salt was confirmed by Fourier transform infrared spectroscopy (FT-IR). The optical nature of the polymer electrolyte films was analyzed through UV-Vis spectroscopy.

Keywords: *solid polymer electrolyte; conductivity; dielectric loss; optical property*

1. Introduction

Solid polymer electrolytes are promising materials in devices, such as batteries, supercapacitors, fuel cells and electrochromic applications [1]. Polymer electrolytes are normally prepared by complexing polar polymer with alkali salts [2]. Polyvinyl alcohol (PVA) is one of the polymers having desirable properties, such as good mechanical strength and thermal stability. It is biodegradable and transparent in nature. Hence, PVA based electrolytes have been extensively studied in the last two decades. Many research investigations have been dedicated to develop proton conducting [3–8] as well as Mg²⁺ [9], Cu²⁺ [10] Li⁺ [11–14] and Ag²⁺ ion conducting [15] electrolytes using PVA as a host polymer.

Electrical properties of polymers have been studied to understand the nature of charge transport through polymer chains while their optical properties have been analyzed to know the nature of optical band gap and transparency. The electrical and optical properties of polymers can be modified by the addition of suitable dopants.

Among all, lithium salt, LiPF₆ deserves a special attention because of its good ambient conductivity, forming stable SEI (solid electrolyte interface) film on the surface of electrode material and ability to passivate aluminum current collector [16]. Hence, it is the only salt used in practical lithium ion batteries up to now. Many researchers have been working on the development of LiPF₆ based solid polymer electrolytes [17–20]. Thus, it is of interest to prepare PVA-LiPF₆ electrolytes and study their electrical, dielectric and optical properties to find an electrolyte suitable for electrochemical/electrochromic devices. This paper presents the results of investigations on the vibrational, electrical, dielectric and optical properties of LiPF₆ doped PVA films.

2. Experimental

2.1. Materials and methods

PVA-LiPF₆ electrolytes were prepared using solution cast technique. PVA (S.D. Fine, Mw 85000 – 125,000 hydrolyzation – 88 %), LiPF₆ (Aldrich 98 %), dimethyl sulfoxide (DMSO) (Merck 99.5 %) were used as starting materials. DMSO was distilled prior to use.

*E-mail: drhirankumar@gmail.com

All the preparation processes were carried out inside a glove box with the moisture content less than 0.1 ppm.

2.2. Electrolyte preparation

Desired amount of LiPF_6 was dissolved in distilled DMSO using magnetic stirring for 30 minutes. Then, an appropriate amount of PVA was added into the solution which was stirred for about 3 hours. The resultant homogenous solution was casted in polypropylene dishes and allowed to evaporate. To increase the solvent evaporation rate, the solutions were transferred to a vacuum chamber where a pressure of ~ 1 kPa was maintained. The obtained polymer films were stored in desiccators.

2.3. Characterizations

FT-IR analysis was carried out by JASCO FT-IR-4100 spectrometer equipped with an ATR internal reflection system. The spectra of prepared polymer electrolytes were obtained with a resolution of 4 cm^{-1} in the wave number region between 4000 cm^{-1} and 550 cm^{-1} in transmittance mode. AC impedance measurement has been carried out in the frequency range of 1 Hz to 7 MHz with the amplitude voltage of 10 mV, using Biologic SP300 electrochemical workstation. Stainless steel was used as blocking electrodes on both sides of the polymer film. The thickness of the polymer films was measured using micro screw gauge. The optical absorption spectra were recorded in the wavelength region 200 nm to 1200 nm using Shimadzu UV-2600 spectrometer.

3. Results and discussion

3.1. Nyquist plot analysis

Fig. 1a shows the Nyquist plot of a salt-free PVA film. It can be seen that the plot contains two well defined regions such as (1) semicircle in higher frequency region (2) slanted line in low frequency region. The semicircle results from the bulk properties of electrolyte and slanted line is related to blocking electrodes. The point at which the semicircle ends or slanted region starts is known as bulk resistance of the material. The bulk resistance

is found to be $3940\ \Omega$. Fig. 1b shows the Nyquist plots of PVA films doped with different (5 mol%, 10 mol%, 15 mol% and 20 mol%) concentrations of LiPF_6 . From Fig. 1b, it can be seen that all the salt doped PVA films show slanted line region only. The absence of high frequency semicircle in Fig. 1b indicates that the conduction is mainly due to ions [18]. The point at which the slanted line region cuts the real z axis (z') is the mentioned bulk resistance. By fitting the experimental data with z -fit software, exact bulk resistance R_b values were extracted.

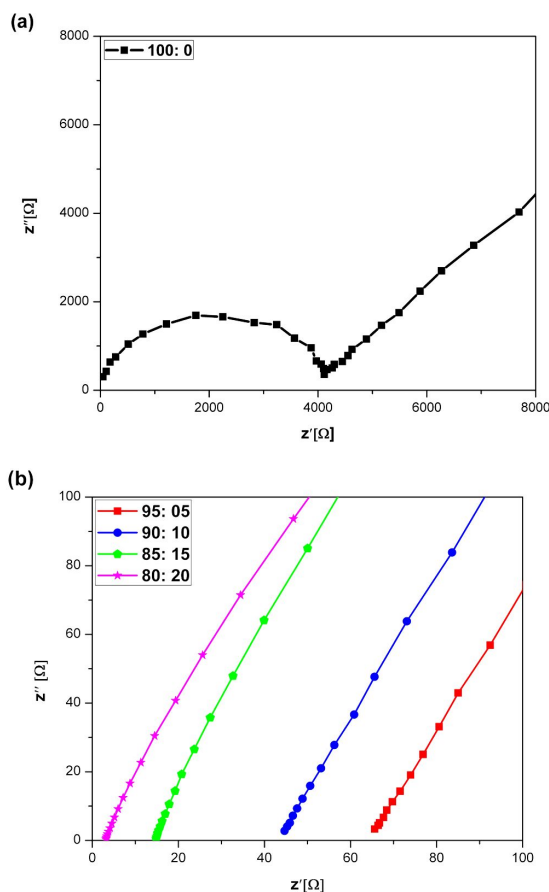


Fig. 1. Nyquist plots of (a) pure PVA, (b) LiPF_6 added PVA electrolytes.

The ionic conductivity was calculated using the equation

$$\sigma = t / (R_b \times A) \quad (1)$$

where t is the thickness of the polymer electrolyte film and A is the surface area of the film.

The calculated conductivity values are listed in Table 1. From Table 1 it is clear that the bulk resistance value decreases or the conductivity value increases due to addition of LiPF₆ into the PVA matrix. The conductivity of salt free PVA increases from $4.6 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ to $8.69 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ by the addition of 20 mol% of LiPF₆ into the PVA matrix. This is due to the enhancement of charge carrier concentration which happens due to the transformation from semi crystalline nature into amorphous. (Moreover, LiPF₆ incorporation into PVA enhances the mobility of charge carriers by the way of disturbing). This mobility enhancement will be discussed in dielectric loss analysis. Further, it was observed that the addition of 25 mol% of LiPF₆ with simultaneous decrease of PVA was not able to form a freestanding film.

3.2. Conductance spectra analysis

Fig. 2 shows the conductance spectra of LiPF₆ free PVA and LiPF₆ doped PVA films. The conductance spectrum of salt free PVA film shows three different regions such as low frequency dispersive region, mid frequency plateau region and higher frequency dispersive region. The low frequency and higher frequency dispersive regions are due to space charge polarization at the blocking electrodes. Mid frequency plateau region corresponds to DC conductivity of material [21].

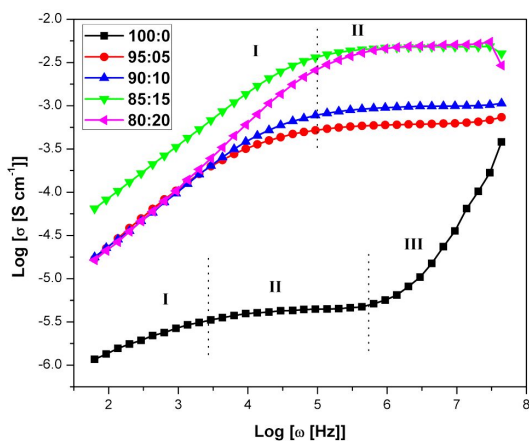


Fig. 2. Conductance spectra of PVA-LiPF₆ electrolytes.

On the addition of LiPF₆ into PVA matrix, high frequency dispersive region disappears, low

frequency dispersive region becomes more prominent and shifts to higher frequency on increasing the salt concentration. This is due to the enhancement of the available free charge carriers in the system. This result is well coincided with the result obtained from Nyquist plot analysis, where the semicircle region corresponding to high frequency dispersive region disappeared in LiPF₆ added PVA films. The extrapolation of plateau regions of salt free and salt added PVA films to zero frequency, gives the value of DC conductivity. The obtained DC conductivity values are listed in Table 1 and are well matched with the conductivity values which were obtained from Nyquist plot.

Rathod et al. [11], Rajeswari et al. [12] and Varishetty et al. [13] investigated PVA based lithium ion conducting polymer electrolytes and obtained highest conductivity in the range of $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ to $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at ambient temperature. Ibrahim et al. [18] studied PEO complexed with LiPF₆ and obtained conductivity of $6.75 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 303 K. Liew et al. [19] studied PEO complexed with LiPF₆ and obtained the maximum conductivity value of $6.0 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 383 K. In that research, conductivity of pure PVA was found to be $4.64 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 303 K and the value increased gradually to $8.94 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$, when 20 mol% LiPF₆ was added into the PVA. This value is higher than that reported for PVA based lithium ion conducting electrolytes and LiPF₆ based polymer electrolytes. Hence, it is suggested that the electrolyte PVA:LiPF₆ with the ratio of 80 mol%:20 mol% can deliver better performance while using electrolyte in electrochemical and electrochromic devices.

3.3. Dielectric loss and modulus analysis

Fig. 3. shows the dielectric loss spectra of salt free PVA films and PVA films doped with various amounts of LiPF₆. From Fig. 3, it is clear that the dielectric loss is higher in low frequency region and lower in high frequency region. In low frequency region, the dielectric loss values are found to increase with the increase in LiPF₆ concentration. The higher values of dielectric loss ϵ'' indicate the enhancement of free charge carrier motion

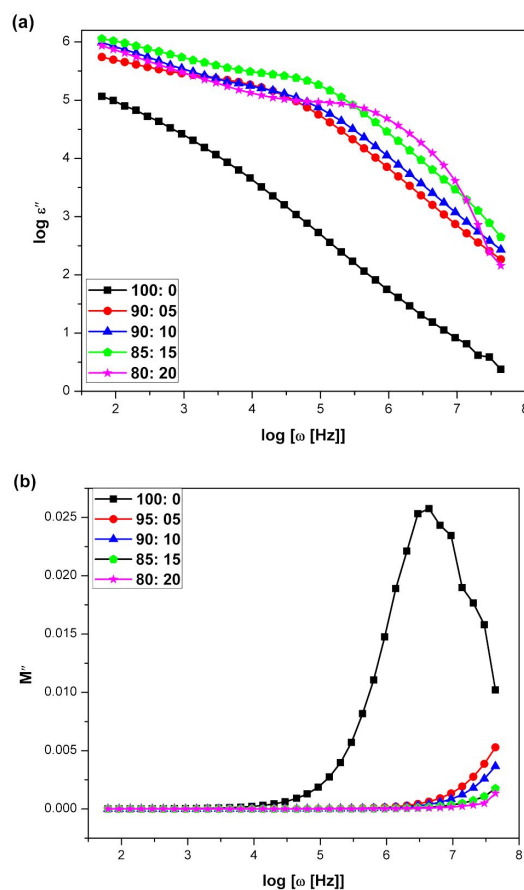
Table 1. Composition, bulk resistance and ionic conductivity values of PVA-LiPF₆ electrolytes.

S.No.	Composition [mol%]		Bulk resistance [Ω]	Ionic conductivity [$\text{S}\cdot\text{cm}^{-1}$] at 303 K	
	PVA	LiPF ₆		Nyquist plot	Conductance spectra
1.	100	0	3940	4.64×10^{-6}	4.27×10^{-6}
2.	95	05	65.97	6.06×10^{-4}	6.11×10^{-4}
3.	90	10	41.85	1.04×10^{-3}	1.04×10^{-3}
4.	85	15	14.2	6.57×10^{-3}	6.66×10^{-3}
5.	80	20	2.71	8.69×10^{-3}	8.94×10^{-3}
6.	75	25	———— No film forming ————		

within the material. Moreover, relaxation peaks are seen to appear for higher concentrations of LiPF₆, such as 15 mol% and 20 mol%. In case of low salt concentration (5 mol%, 10 mol%), polymer segmental motion governs the charge transport. But in the case of higher salt concentrations (15 mol%, 20 mol%), polymer side chains are already covered by ions and hence, new ions have less chance of getting attached to polymer chains. Hence, direct diffusion of ions (decoupled from motion of polymer segments) occurs. This type of ionic motion is faster than that of ion-segment coupled motion [22]. Thus, relaxation peaks are observed in the films containing higher concentration of LiPF₆.

3.4. Modulus study

Fig. 3b shows the imaginary part of modulus of PVA-LiPF₆ electrolytes as a function of frequency. Imaginary part of complex electric modulus is defined as, $M'' = \omega \cdot C_0 \cdot Z'$ where, C_0 is vacuum capacitance and is given by $\epsilon_0 \cdot A/t$, where A is area and t is thickness of the film, ω is angular frequency which is equal to $2\pi f$. From Fig. 3b it is noticed that LiPF₆ free polymer shows relaxation peak at high frequency whereas LiPF₆ added PVA films show a very long tail in low frequency and it increases in high frequency. The disappearance of M'' peak spectra in LiPF₆ added films is due to the experimental frequency limitation. The long tail with very low M'' value is due to large value of capacitance associated with electrode polarization effect, i.e. accumulation of charge carriers as the electrode/electrolyte interface is large. The high

Fig. 3. (a) dielectric loss spectra (b), modulus spectra of PVA-LiPF₆ electrolytes.

frequency rise is due to long range hopping of charge carriers. Hence, it may be concluded that in the case of LiPF₆ added PVA electrolytes, ion transportation occurs by long range hopping of charge carriers [23].

3.5. FT-IR study

Fig. 4 depicts the IR transmittance spectra of various compositions of PVA-LiClO₄ electrolytes in the region of 4000 cm⁻¹ to 550 cm⁻¹. Fig. 4a shows the FT-IR spectrum of LiPF₆ free PVA film. Characteristic peaks of PVA are well matched with the literature [6]. The broad peak appearing between 3700 cm⁻¹ to 3000 cm⁻¹ is attributed to -OH group vibration in PVA. On the addition of LiPF₆ into the PVA matrix, -OH group vibration peak is shifted towards higher wave number side. Moreover, new peaks are observed at 3641 cm⁻¹ in 10 mol%, 15 mol% and 20 mol% LiPF₆ added films (Fig. 4, graphs c to e). This observation confirms the interaction of LiPF₆ with -OH group of PVA.

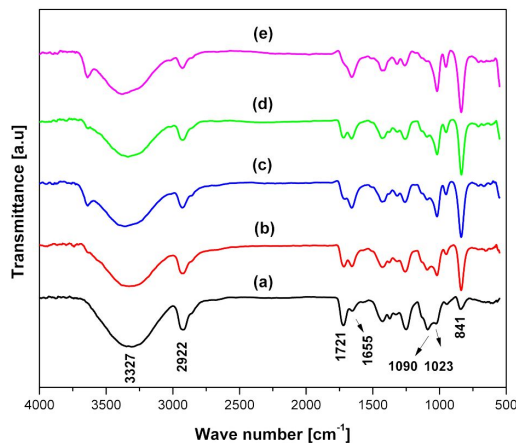


Fig. 4. FT-IR spectra of PVA-LiPF₆ electrolytes with various compositions (a) 100:0, (b) 95:05, (c) 90:10, (d) 85:15, (e) 80:20.

The band observed at 1721 cm⁻¹ (Fig. 4a) is attributed to C=O stretching vibration of pure PVA. It is found to be displaced towards lower wave number side with decreased relative intensity due to the addition of LiPF₆. Similarly, the band observed at 1655 cm⁻¹ in pure PVA is assigned to C-O stretching vibration and it is shifted to higher wave number side with increased relative intensity due to salt addition. This observation confirms the interaction of Li in salt with carbonyl oxygen of PVA. The bands present between 1100 cm⁻¹ and 1000 cm⁻¹ are attributed to C-OH stretching vibration of PVA. The band present at 1090 cm⁻¹

is displaced to higher wave number side with decreased relative intensity. The band appearing at 1023 cm⁻¹ in pure PVA is shifted to lower wave number side with increased intensity. This confirms the interaction of ionic salt with C-OH stretching vibration of PVA. In addition to the above functional group vibrations of PVA, other vibrations, such as CH wagging (1372 cm⁻¹), CH bending of CH₂ (1427 cm⁻¹) and C-O-C stretching vibrations (1249 cm⁻¹) are also affected while adding LiPF₆ into PVA matrix. Moreover, a vibrational peak observed at 841 cm⁻¹ corresponding to C-H rocking of pure PVA [18] is found to be shifted to lower wave number side with increasing intensity due to the addition of LiPF₆. These observations confirm the complex formation between PVA and LiPF₆.

3.6. UV-Vis spectra analysis

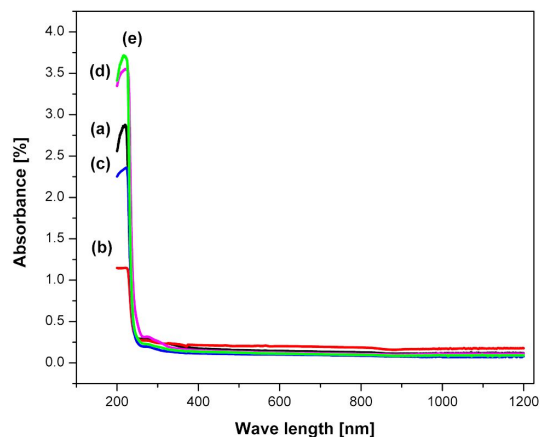


Fig. 5. UV absorption spectra of PVA-LiPF₆ films (a) 100:0, (b) 95:05, (c) 90:10, (d), 85:15 and (e) 80:20.

Fig. 5 shows the optical absorption spectra recorded for pure PVA and different LiPF₆ concentrations doped PVA matrix in the region of 200 nm to 1200 nm. In the UV region, the band at 215 nm is observed for PVA-LiPF₆ complexes. The absorption peak may be attributed to the $n \rightarrow \sigma^*$ transition [3]. In the visible region, (i.e. beyond 380 nm), no absorption peaks are observed. It reveals that all the samples are highly transparent in nature. Hence, it is suggested that the prepared films may be suitable for the fabrication of electrochromic

devices in which highly transparent electrolytes are needed [24]. The doped LiPF_6 does not introduce any new absorption peaks. It implies that no charge transfer complexes arise between the polymer host and LiPF_6 [3, 25].

To determine the value of optical band gap, $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ have been plotted as a function of photon energy ($h\nu$), where h is Planck constant, ν is the applied frequency and α is absorption coefficient. α is determined using the relation

$$\alpha = [\ln(1/T)]/d \quad (2)$$

where T is transmittance and d is the thickness of the sample. The direct and indirect optical band gap values have been extracted from Fig. 6a and Fig. 6b, respectively.

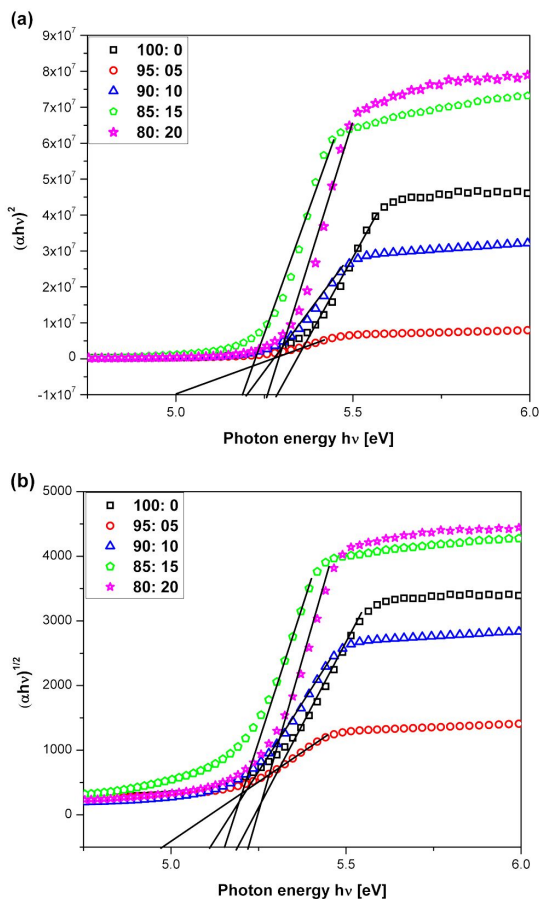


Fig. 6. (a) $(\alpha h\nu)^2$ vs. photon energy $h\nu$, (b) $(\alpha h\nu)^{1/2}$ vs. photon energy plots of PVA- LiPF_6 electrolytes.

The obtained band gap values are listed in Table 2. The direct band gap value of LiPF_6 free PVA

film was found to be 5.28 eV, whereas the band gap values are reduced slightly on the addition of LiPF_6 into the PVA matrix. Similarly, the indirect band gap value of pure PVA is 5.18 eV and for salt added films it slightly varies. This result once again confirms the absence of charge transfer complexes in the system.

Table 2. Direct and indirect band gap values of PVA- LiPF_6 films.

S. No.	Composition [mol%]		Band gap energy [eV]	
	PVA	LiPF_6	Direct	Indirect
1.	100	0	5.28	5.18
2.	95	05	5.00	4.99
3.	90	10	5.20	5.11
4.	85	15	5.18	5.15
5.	80	20	5.26	5.22

4. Conclusions

A series of PVA- LiPF_6 solid polymer electrolyte films have been prepared by varying LiPF_6 concentration. The film containing 80 mol% PVA and 20 mol% LiPF_6 shows the maximum conductivity of the order of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$. The obtained conductivity value is higher by two orders of magnitude than those reported in earlier works by researchers. Enhancement of charge carrier concentration in the PVA- LiPF_6 system is confirmed by Nyquist plot and conductance spectra analysis. The conductivity values which have been obtained from Nyquist plots, are well matched with the conductance spectra plot. Mobility of charge carriers within the polymer matrix has been analyzed through dielectric loss and imaginary part of electric modulus M'' studies. UV-Vis spectroscopy revealed that the prepared PVA- LiPF_6 complexes are highly transparent in nature and charge-transfer complexes are not formed between PVA and LiPF_6 . Based on all the results, it is concluded that the prepared PVA: LiPF_6 (80 mol%:20 mol%) film is a promising electrolyte for the fabrication of all solid state electrochemical (batteries, super capacitors) and electrochromic devices.

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