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Studies on AC Electrical Conductivity, Dielectric Properties and Ion Transport in PVA polymeric Electrolytes

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Abstract

In our studies, we prepared composite membranes from PVA, H_2SO_4, H_3PO_4, KOH, KCl and $K_3[Fe(CN)_6]$ by using a solution casting method. The prepared films are characterized by XRD and mechanical testing. XRD results display an amorphous character for all the prepared membranes. Highly flexible, bendable and conductive polyvinyl alcohol polymeric films were obtained. Electrical measurements show that polymer electrolyte films enclosing PVA - KOH - KCl - $K_3[Fe(CN)_6]$ with a weight ratio of 60: 23:23:4 exhibits the highest room temperature ionic conductivity of~10^{-2} S cm^{-1}. While pure PVA film gives the lowest ionic conductivity of 2.10×10^{-11} S/cm. Transport number data implies that the charge transportation in all electrolytes system is chiefly owed to cationic ions with transference number (t^+) are in the range of 0.97- 0.99. The dielectric constant value was found to decrease exponentially with increasing the applied frequency for pure PVA and doped PVA film composites.

Keywords: Polyvinyl alcohol; gel polymer electrolyte; PVA - KOH - KCl - $K_3[Fe(CN)_6]$ membrane; electrical conductivity.

1. Intruduction

Polymers are huge molecules that consist of thousands - even millions - of atoms that are attached in a copying design. Polymers already have a wide variety of applications that far surpasses that of any other style of substantial obtainable to man. Because various polymers are created of long, elastic chains, they become simply twisted. The disordered twisted of the polymer chains make what is known as an amorphous structure where ions can be easily diffuse in its matrix [1,2]. PVA is one of the greatest significant polymer matters, and it has several applications in manufacturing and business, it displays good film developing stuff and insulating electrical property [3]. The present work is concentrated on studying the electrical properties of PVA polymer electrolyte films prepared using different acid, base, and ionic salts.

2. Experimental

2.1. Materials

Resorcinol ($C_6H_6O_2$) was purchased from El-Goumhouria Co., formaldehyde solution (34.5-38%) and polyvinyle alcohol (PVA) from El-Nasr pharmaceutical Co. Potassium hydroxide (KOH), Potassium chloried (KCl) and Sodium carbonate (Na_2CO_3) provided from Adwic Co., Phosphoric acid (H_3PO_4), Sulphoric acid (H_2SO_4) and acetylene black (C_2H_2) were delivered by Sigma Aldrich.

2.2. Synthesis of Samples

2.2.1. Preparation of gel polymer electrolyte

A series of alkaline and acidic, basic PVA polymer electrolyte membranes were prepared. 0.02 mol of an individual or combined electrolytes of H_3PO_4, H_2SO_4, KOH, KCl was inserted into PVA (1g) in deionized water (10 ml) following by stirring and heating.

2.2.1.1. Preparation of alkaline gel polymer electrolyte

Alkaline PVA gel polymer electrolytes were fabricated according to the following method. 0.02 mol KOH was added to PVA (1g) in deionized water, as well as 0.01 mol KCl and 0.01 mol of KOH into PVA (1g) in deionized water (10 ml). These mixtures were stirred and heated at 90 °C until appearance homogeneous us viscous solution. The solutions were then transferred to glass petri dishes and leave over night at room temperature to evaporate the excess water and get thicks PVA–KOH and PVA-KOH-KCl gel polymers. Two ternary PVA–KOH–$K_3[Fe(CN)_6]$ gel polymers were also synthesized by dissolving 0.02 and 0.001mol of KOH and $K_3[Fe(CN)_6]$, respectively, in (1g) in deionized water(10 ml); and 0.02 as well as (0.0005) mol of KOH and $K_3[Fe(CN)_6]$, respectively, in (1g) in deionized water(10 ml) following by the same method mentioned above. Moreover, gel polymer electrolyte of PVA-KOH-KCl- $K_3[Fe(CN)_6]$ was prepared according to the previously mentioned procedure by dissolving 0.01 mol KOH, 0.01 mol KCl and 1x10^{-3} mol $K_3[Fe(CN)_6]$ in (1g) PVA in deionized water (10ml). A weight ratio of 1:0.46:0.46:0.4 was prepared according to the previously

mentioned procedure.

The gel polymers were denoted as PK, PKl, PKF2, PKF4, PKLF4 for the electrolytes PVA-KOH, PVA-KOH-KCl, PVA-KOH-(0.0005)mol $K_3[Fe(CN)_6]$, PVA-KOH-(0.001) mol $K_3[Fe(CN)_6]$, and PVA-KOH-KCl-(0.001) mol $K_3[Fe(CN)_6]$, respectively.

2.2.1.2 Preparation of acidic gel polymer electrolytes: (PVA- H_3PO_4) and polymer electrolyte

Polymer electrolyte of PVA- H_3PO_4 was fabricated by the solvent molding method, namely one gram of PVA was dispersed in 10 ml of bidistilled water with stirring to get a clear solution. After that, 0.02 mol of H_3PO_4 was inserted into the solution with continuous stirring at room temperature for 24 h. The obtained viscous solution was thrown onto Teflon frames and dried in an oven at 60 °C for 24 hours. The dried layers were stripped off from the casts and cut into 30 mm × 10 mm bands. This will be denoted as PP.

The PVA-H_2SO_4 polymer electrolyte was synthesized by the same method mentioned above but with replacing H_3PO_4. Initially, PVA (1g) was dispersed in 10 ml distilled water with continuous stirring at 90 °C for two hours to make a homogeneous solution. Next, 0.02 mol of H_2SO_4 was inserted to the homogeneous with stirring until the establishment of a gel-like solution was seen. The obtained viscous solution was dried as in the case of PP and the electrolyte obtained was denoted as PS.

2.3. Characterizations.

The crystal structure of the polymer electrolytes was distinguished by the XRD technique, using a D8 Advanced diffractometer, Bruker AXS (40 kV and 35 mA) with Cu Kα radiation (λ=1.5406 Å) in the range of 2θ=20-70°.

The mechanical properties of gel membrane were examined through stretching and bending. The polymer was cut into 30 mm×10 mm specimens, and the deformation was described under the action of appropriate forces.

The conductivity of the studied electrolyte systems was concluded from the impedance spectrum. The polymeric electrolyte was inset on a conductivity holder containing two cupper sheets as stopping electrode The ionic conductivity (σ_t) of the electrolyte was computed using the formula [4].

$$\sigma_t = d/ (R_b \times A)$$
(1)

where d is the space between the two cupper electrodes, R_b is the bulk resistance and A is the contact area of the electrolyte film with the cupper electrodes.

A fixed 1.5 dc- voltage is applied to the Wagner polarization cell Cu/ polymer electrolyte/Cu. The electric current spreading through the cell has been measured as a function of time.

3. Results and Discussion

3.1. Characterizations

Fig. 1 shows XRD analysis for pure and doped PVA membranes. The XRD pattern of pure PVA and their electrolyte with various compositions also shows a broad peak at ~ 20° matching to semicrystalline nature of pure PVA [5].The peak intensities of the PVA polymer electrolyte reduced with increasing in width of the diffraction peak when the electrolyte materials were added to PVA. This indicates that the PVA/electrolyte polymer films became much amorphous with adding the electrolytes. No new peaks matching with electrolyte materials were detected, which suggest a whole conclusion of electrolyte in the PVA polymer matrix.
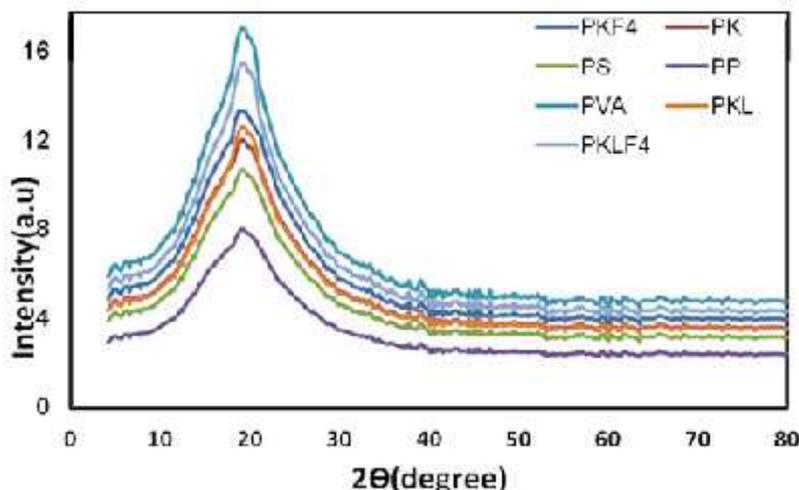

Fig. 1: XRD pattern for PVA and PVA electrolyte membranes.

3.2. Mechanical properties of the gel polymer.

The studied polymeric gels showed outstanding bending and stretching properties, Table 1. All the gel polymer bands are found to be easy bent into a circular arc and do not break even when they are bent over 180°.The gel polymer band can be elastically stretched to about (3.4 – 4.4) times length than its original according to the order PKLF4 > PKL > PKF4 > PKF2 > PP >PS >PK. The band rapidly recovered its original length after the external force was eliminated.

Table 1: Mechanical properties and surface textural data for all investigated gel polymeric electrolytes.

Sample	Length before stretching (cm)	Length after stretching (cm)	Bending angle (degree)
PK	0.5	0.8	No bent
PS	0.5	1.4	bent over 180
PP	0.5	1.5	bent over 180
PKF2	0.5	1.6	bent over 180
PKF4	0.5	1.8	bent over 180
PKL	0.5	2	bent over 180
PKLF4	0.5	2.4	bent over 180

3.3. Conductivity Studies

Electrolytes were examined using EIS at an open circuit potential and frequencies between 100 mHz and 100 kHz. The ionic conductivity of all the studied samples was fixed from the impedance spectra using a conductivity cell with Cu - blocking electrode. Cole-Cole plots for the polymeric electrolytes investigated are shown in Figs. (2-9). The impedance plots for all electrolytes membranes consist of two distinct regions. The circular arc in the high-frequency range yields information about the properties of the electrolyte namely the bulk resistance and bulk capacitance (Cb). The intercept of the circular arc on the real axis gives the bulk resistance value (Rb). The spike in the low-frequency range is due to the effect of the blocking electrodes and provides information about electrode / electrolyte interface [6]. For ideal electrodes and electrode / electrolyte interface, a vertical spike should have been obtained but the electrode spikes are non – vertical owing to the double layer capacitance at the blocking electrodes. These outcomes propose that the migration of charges (ions) may happen across the free volume of the matrix polymer, which can be exemplified by a resistor. On the other hand, non-migration charges (chains of polymer) polarized and can be therefore represented by a capacitor. The drop in resistance of the polymer electrolyte is attributed to the improvement of the ionic mobility and the number of carrier ions electrolyte concentration [7]. The ionic movement and bulk polarization are physically in parallel, and therefore, the semicircle at high frequency can be detected in all the samples. The ionic conductivity (σ_i) of the developed electrolytes is computed by using Eq. (1)

$$\sigma_i = \ell / (Rb \, S) \tag{1}$$

The results obtained are listed in Table 2. It can be seen that the conductivity values of electrolyte membranes are greater than that of pure PVA and increases according to the following order :

PKLF4 >PKL > PKF4 > PKF2 > PK >PS > PP > PVA

This is because the introducing of the electrolyte into polymeric matrix producing relatively more number of frees ions. This will increase the mobile charge carriers moving in the amorphous polymer matrix and consequently the conductivity increases. There is a relation between the amorphous nature of the polymer film and the conductivity, where the conductivity increases with decreasing the degree of crystallinity [8]. In our case, the conductivity was also found to increase with decreasing the ioconicity in our samples, as shown in XRD results.
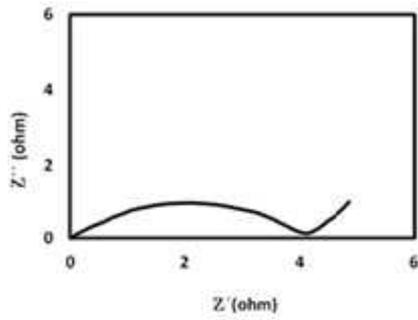
Fig. 2: Cole-Cole plots of PKF4-
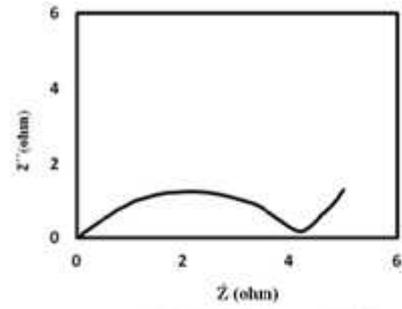electrolyte membrance

Fig. 3: Cole-Cole plots of PKF2-
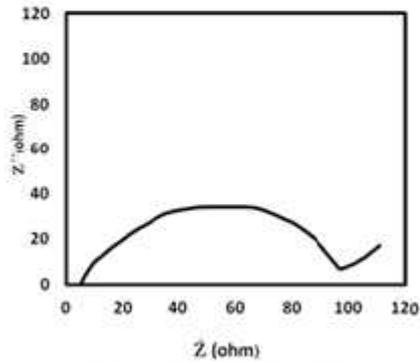electrolyte membrance

Fig. 4: Cole-Cole plots of PP -
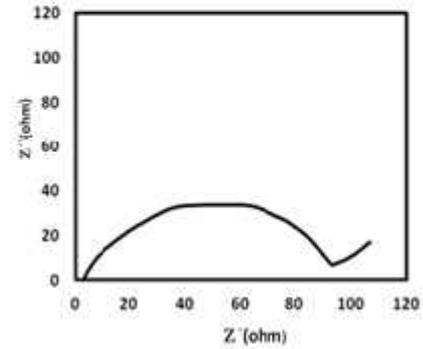electrolyte membrance

Fig. 5: Cole-Cole plots of PS -
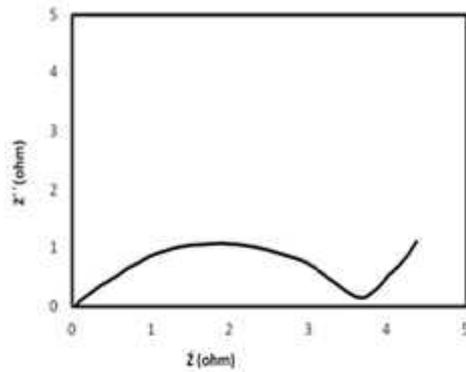electrolyte membrance

Fig. 6: Cole-Cole plots of PKLF4-
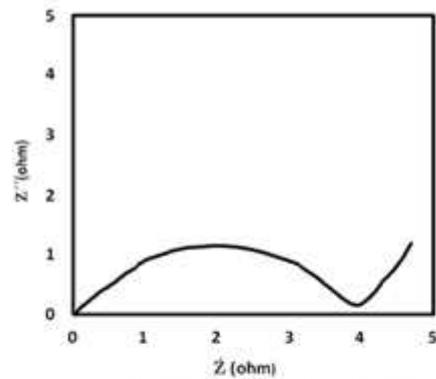electrolyte membranes

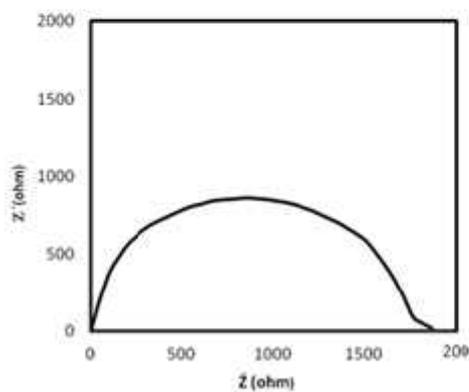Fig. 7: Cole-Cole plots of PKL-
electrolyte membranes

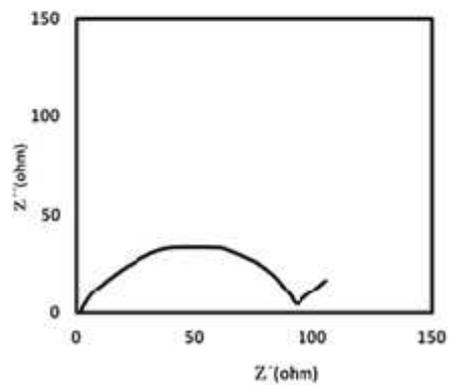Fig. 8: Cole-Cole plots of PVA-
electrolyte membranes

Fig. 9: Cole-Cole plots of PK-
electrolyte membranes

Table 2: Ionic conductivity and transference number of investigated polyelectrolyte membranes and the time constants of AC/gel electrolyte/AC supercapacitors.

Sample	Ionic Conductivity (S cm^{-1})	Transference number (t_{ion})	$_o$ (s)
PKLF4	7.1x 10^{-2}	0.990	10x 10^{-3}
PKL	4.3x10^{-2}	0.986	15x 10^{-3}
PKF4	2.1x 10^{-2}	0.980	21x 10^{-3}
PKF2	9.1x 10^{-3}	0.973	25x 10^{-3}
PK	7.5x 10^{-3}	0.972	51x 10^{-3}
PS	5.2x 10^{-3}	0.971	65x 10^{-3}
Pp	4.1x 10^{-3}	0.970	92x 10^{-3}
PVA	2.5x 10^{-10}	0.00	---

3.4. Dielectric Studies

Figure 10 shows the change in dielectric constant value (ε') with the measuring frequency for the investigated polymeric electrolyte samples at room temperature. The permittivity (ε') was evaluated by applying the following equation

$$^/ = C^/ l/ S _o \qquad (2)$$

Where l is the thickness of the sample, S *is* the surface area of the sample, $C^/$ is the capacitance of the specimen and $_o$ is the permittivity of free space. Fig. 10 shows that $\varepsilon'(\omega)$ reduces with the rise in frequency and reach a steady amount at higher frequencies analogous to that for polar substances [9]. The low-frequency area emerges because of the involvement of charge collection at the electrode-electrolyte interface. This is because at lower frequencies the dipoles have enough time to line up with the electric field before they convert their directions and subsequently, the dielectric constant is high. Whereas, the decrease of the dielectric constant with rising of applied frequency is due to the insufficient time present for dipoles to align before the field switches direction [10].The increase in conductivity goes in a parallel way with the increase in dielectric constant for all samples.
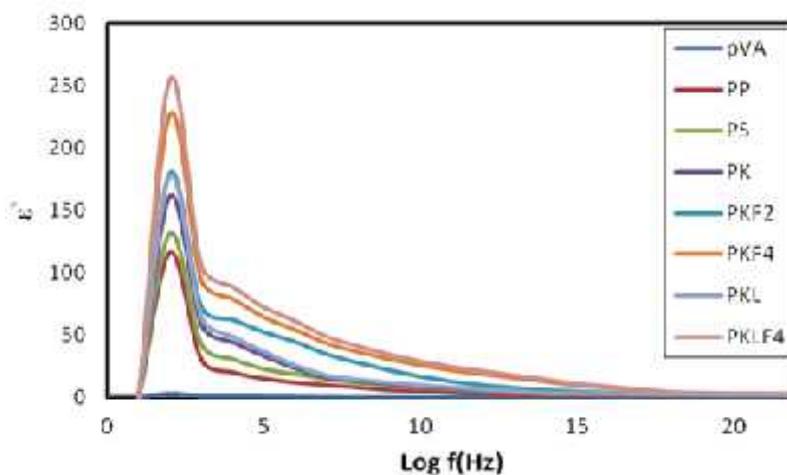

Fig. 10: Vs. F for all the investigated polymeric electrolyte samples at room temperature.

3.5. Transport analysis

The transference numbers equivalent to ionic (t_{ion}) and electronic (t_e) transport were computed for all studied samples using Wagner's DC. Polarization technique [11]. In this method, we applied a fixed dc voltage (1.5V) on the polymer electrolyte and measured the dc-current passage in the sample with copper blocking electrodes as a function of time.
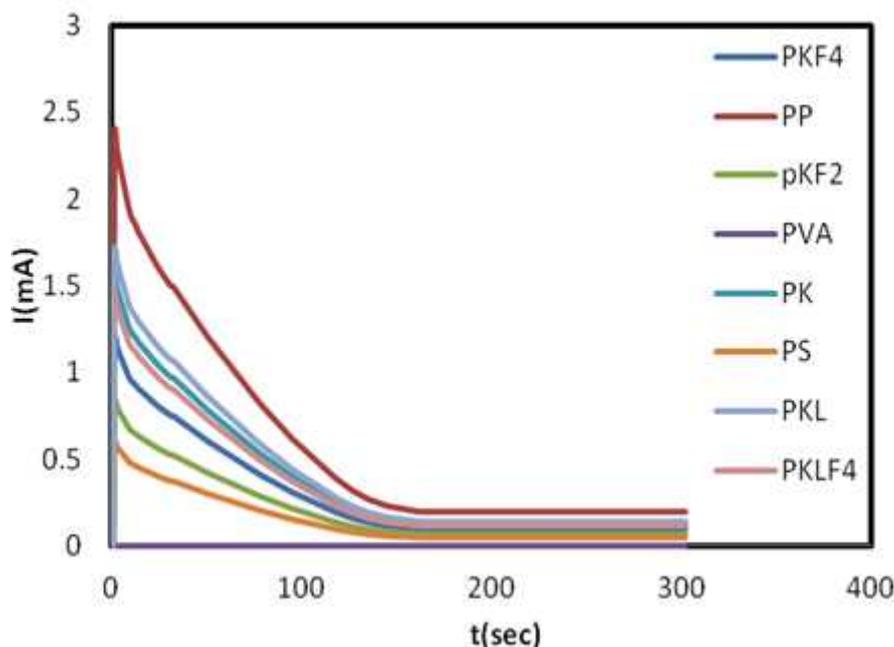

Fig. 11: Current (I) Vs. time (t) for all investigated samples.

Fig. 11 shows transference measurements outcomes for the investigated samples. It has been observed that the initial total current falls rapidly with time because of the reduction of the ionic species in the electrolyte/electrode interface and gets to be constant in the completely depleted state. Residual current is due to the electron passage through the electrolyte and interfaces.

The transference numbers were determined by applying the relations

$$t_{ion} = (I_i - I_f)/I_i \qquad (3)$$

$$t_{ele} = 1 - t_{ion}$$

Where I_i is the starting current at zero time and I_f is the final remaining current. The values of t_{ion} for all the studied electrolyte systems are listed in Table 2.The results obtained suggest that the charge transport in our samples is mainly due to ions, with insignificant involvement from the electrons.

4. Conclusion

In summary, we have prepared PVA-H_2SO_4, PVA-H_3PO_4, PVA-KOH, PVA–KOH–K_3 [Fe (CN) $_6$], PVA-KOH-KCl and PVA–KOH-KCl-K_3 [Fe(CN)$_6$] gel polymers electrolytes. XRD showed amorphous structure for all membranes. The amorphacity for the doped PVA is higher than that of pure one. The ionic conductivity (σ_t) of the developed electrolytes increases in the order: PKLF4 >PKL> PKF4> PKF2 > PK> PS > PP > PVA. The ionic transport number lies in the range of 97-99% for all electrolyte membranes. The dielectric constant of the electrolyte membranes reduces with the rise in frequency and reaches a steady quantity at superior frequencies analogous to that for polar substances. The increase in conductivity goes in a parallel way with the increase in dielectric constant for all samples.

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