Structural and Electrical Properties of Pure and NiCl$_2$ Doped PVA Polymer Electrolytes

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Abstract Polymer electrolytes of pure polyvinyl alcohol (PVA) and PVA complexed with nickel chloride of different concentrations were prepared by solution cast technique. Structural investigations were carried out by X-ray diffraction (XRD), Fourier transform infrared (FTIR) studies and differential scanning calorimetry (DSC) was used to determine the glass transition and melting temperatures. Electrical properties were studied; using complex impedance spectroscopy. Electrical conductivity was measured in the temperature range 303 K – 373 K and in the frequency range 1Hz - 1MHz, using Cole-Cole plots. The temperature dependence of electrical conductivity followed Arrhenius relation. The variation of total conductivity with frequency showed Jonscher's power law behavior. The charged species responsible for electric transport in this polymer electrolyte system was estimated from the transference number data using Wagner's polarization technique.

Keywords XRD, FTIR, DSC, Ionic Conductivity, Transference Number

1. Introduction

The principal motivation behind the study of solid polymer electrolytes is that these materials are found as promising materials for potential applications in advanced electrochromic display devices, super capacitors, fuel cells, gas sensors, solid state batteries etc, due to their excellent ionic conductivity, leak proof, good contact with electrodes and thermal stability when compared to liquid electrolytes. The efforts of research and development are mainly focused on the electrical conduction mechanism to understand the nature of charge transport prevalent in these materials and to improve electrical conductivity, ionic transport number and electrode–electrolyte interfacial reactions at ambient temperatures[1-5]. Polymer electrolytes formed by incorporating metal salts into a highly polar polymer matrix to make it ionically conductive are called polymer salt complexes. During the last few decades, the utilization of polymer salt complexes in various applications has led to intensive interest in these materials[6-8]. Polymer electrolytes complexed with monovalent metal ions were reported extensively. It is also possible to enhance the conductivity with bivalent metal ions such as zinc, cadmium, lead, cobalt, nickel, manganese and mercury. Polymeric systems based on bivalent metal salts are less reactive than the systems based on lithium salts, and hence they are more

advantageous for non-battery devices also[9].

In the present work polyvinyl alcohol (PVA) was selected as host polymer as it is relatively cheaper and is one of the most important polymeric materials which has many applications in industry due to its unique chemical and physical properties. The hydrogen bond between hydroxyl groups plays an important role in determining its properties like high water solubility, wide range of crystallinity and high crystal modulus[10]. Due to its high tensile strength and good abrasion resistance, PVA is used in double-layer capacitors and electrochemical windows etc[11]. The present work aimed to enhance electrical conductivity by doping NiCl$_2$ into PVA host matrix. NiCl$_2$ was taken as a dopant for a variety of reasons like its low cost, thermal stability and good electrical properties. In this paper an effort has been made to study the effect of addition of nickel chloride to PVA and study its structural and electrical properties. The results obtained from these measurements are analyzed and reported.

2. Experimental

2.1. Sample Preparation

Films (thickness ~150 µm) of pure PVA and various compositions of complexed films of PVA with NiCl$_2$ salt were prepared in the weight percent ratios (90:10), (80:20) and (70:30) by solution cast technique using double distilled water as a solvent. The solution was vigorously stirred for 10 to 12 h to get a homogeneous mixture and was cast onto poly propylene dishes and allowed to evaporate at room

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temperature to remove all traces of solvent. The dried polymer electrolyte films were carefully removed from the propylene dishes and stored inside a dry vacuum box.

2.2. Analytical Techniques

In the present study, X-ray diffraction spectra were recorded at room temperature in the range 10°-70° Bragg angle by a SEIFERT X-ray diffractometer. CuK_α radiation was used along with Zr filter for better monochromatic radiation. Infrared spectra of polymer electrolyte films were recorded using EO-SXB IR spectrometer with a resolution of 4 cm^{-1} in the range 400 - 4000 cm^{-1}. Differential scanning calorimetry (DSC) thermograms were recorded in the temperature range 303 K - 483 K using an SDT Q600 thermal analyzer at a heating rate of 10^oC per minute under nitrogen atmosphere. The impedance measurements were carried by a computer controlled phase sensitive multimeter (PSM 1700) in the frequency range 1Hz-1MHz and temperature range 303 K - 373 K. The temperature was measured by copper-constantan thermocouple. The transference numbers, both ionic (t_{ion}) and electronic (t_{ele}) for various complexed films were evaluated using Wagner's polarization technique.

3. Results and Discussion

3.1. XRD Analysis
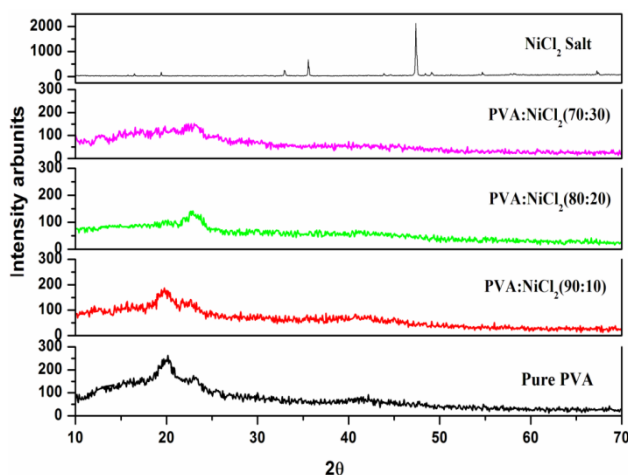
Figure 1. XRD patterns of pure PVA and NiCl$_2$ doped PVA polymer electrolytes

The XRD profiles of pure, doped PVA with different weight percentages of NiCl$_2$ and NiCl$_2$ salt are shown in Fig 1. XRD pattern of pure PVA shows a characteristic broad peak centered at around 20° (corresponds to crystalline orthorhombic lattice), superimposed on a broad hump between 10° - 30° (corresponds to amorphous content) indicating its semicrystalline nature[12]. With the addition of salt, the intensity of this peak decreases suggesting a decrease in the degree of crystallinity of the complex[13]. This could be due to the disruption of the PVA polycrystalline structure by NiCl$_2$ salt as suggested by Hodge

et al.[14]. They observed that the intensity of XRD pattern decreases as the amorphous nature increases with the addition of dopant. This amorphous nature results in greater ionic diffusivity with high ionic conductivity, which can be expected in amorphous polymers having flexible back bone[15]. The absence of peaks correspond to the NiCl$_2$ salt in XRD patterns of all polymer salt complexes indicates the complete dissolution of the salt in the polymer matrix.

3.2. FTIR

FTIR spectroscopy is one of the important investigation techniques of polymer structure that provides information about the structural components and interactions among various constituents of the polymeric films. Different types of bonds possess different natural frequencies. A molecule of particular type of bonding will interact with electromagnetic radiation if it has asymmetric charge distribution. Electromagnetic radiation of the correct (IR) frequency can produce a stretching of the bond between these atoms as the negative charged atom moves in a direction opposite to that of positively charged atom. This type of stretching results in a vibration of molecule and as a consequence, an oscillating electric field is established and this field is capable of interacting with the electric field associated with the radiation. If the frequency of the radiation matches with the natural vibrational frequency of the molecule, a net transfer of energy takes place, it undergoes a quantum jump in its vibrational (or rotational) energy and it results in a change in the amplitude of the molecular vibration. Consequently there will be absorption of radiation, giving rise to an absorption band (peak). Similarly, rotation or twisting or bending of asymmetric molecule around their centers of mass is possible. Hence the identification of an absorption peak at a particular frequency of the infrared region will reveal the nature of bonding[16]. FTIR spectra for pure PVA, NiCl$_2$ complexed PVA and NiCl$_2$ are shown in Fig 2. The absorption band in the region 3527-3063 cm^{-1} corresponds to O-H (inter molecular hydrogen bond) stretching of PVA shifted to 3649-3090 cm^{-1}, 3628-3055 cm^{-1} and 3625-3033 cm^{-1} in 10 wt%, 20 wt%, and 30 wt% NiCl$_2$ complexed PVA films respectively. The displacement of O-H band towards the lower wave numbers indicates that the positively charged nickel ions are coordinated through ionic bonds with the negatively charged hydroxyl groups belonging to different chains in PVA[17]. The broadening in the hydroxyl band in all the complexes confirms that the increase in the concentration of Ni reduces the intermolecular interaction between chains and expands the space between them[18].

In addition to this, C-H stretching of CH$_2$ showed an absorption band at 2992 cm^{-1} in pure PVA and is shifted to 2987 cm^{-1}, 2965 cm^{-1} and 2957 cm^{-1} as salt concentration increases. The C-H bending of CH$_2$ in pure PVA exhibited an absorption band at 1481 cm^{-1} and is shifted to 1472 cm^{-1}, 1470 cm^{-1}, and 1462 cm^{-1} in the complexed films for different wt% of NiCl$_2$ respectively. The shift in acetyle C–O stretching of PVA from 917 cm^{-1} to 935 cm^{-1}, 912 cm^{-1} and

902 cm^{-1} also supports the interaction of salt with the host matrix. C-C stretching occurring at 1173 cm^{-1} in pure PVA is shifted to 1171 cm^{-1}, 1148 cm^{-1} and 1146 cm^{-1} in 10 wt%, 20 wt%, and 30 wt% salt complexed polymer electrolyte films respectively. All these changes in the FTIR spectra are clear indications of the complexation of PVA with NiCl$_2$ salt.
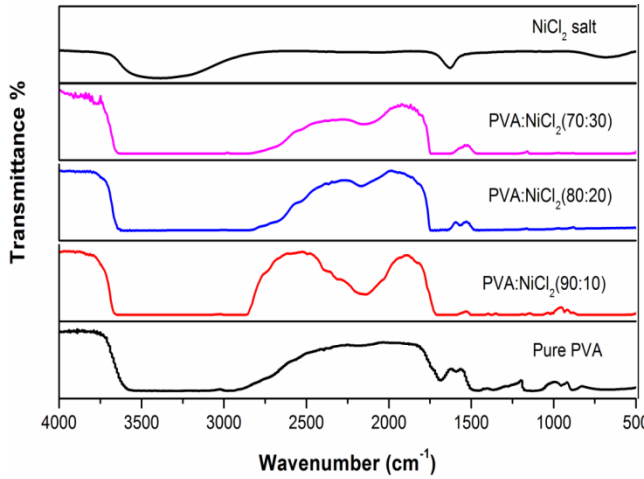
Figure 2. FTIR patterns of pure PVA and NiCl$_2$ doped PVA polymer electrolytes

3.3. DSC

Differential Scanning Calorimetry (DSC) is a technique to study the thermal transitions of a polymer. Using this technique the glass transition temperature (T_g), melting temperature (T$_m$) and the degree of crystallinity (χ_c) of the material can be identified. Fig.3 shows the DSC curves of pure PVA and PVA: NiCl$_2$ complexed films in the temperature range 300 - 550 K.
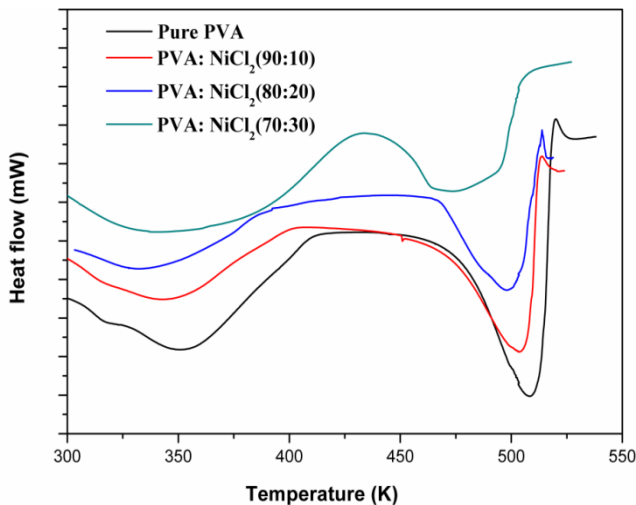
Figure 3. DSC spectra of pure and NiCl$_2$ doped PVA polymer electrolytes

DSC analysis was performed to correlate the glass transition temperature with the amorphosity and the ionic conductivity of the polymer electrolytes. From DSC thermo grams an endothermic peak was observed at around 320-350 K corresponding to the glass transition temperature (T_g) of

the polymer electrolytes. T_g decreases with increase in salt concentration. The observed shift in T_g values indicates the interaction between the polymer and the salt[21]. The low glass transition temperature leads the higher segmental motion of the polymer electrolyte[19]. Hence the ions move easily throughout the polymer chain. This enhances the ion transportation which leads higher ionic conductivity[20].

Another endothermic peak was observed around 498 K - 520 K corresponds to the melting point of the polymer electrolytes. Melting temperature is measured at apex of the endothermic peak and melting enthalpy is determined from the area of the peak. The relative percentage of crystallinity (%χ_c) was estimated using the equation[22].

$$\%\chi_c = \frac{\Delta H_m}{\Delta H_m^0}$$

where ΔH_m^0 is the melting enthalpy of pure PVA and ΔH_m is melting enthalpy of NiCl$_2$ complexed PVA. The measured values of glass transition temperature (T_g), melting temperature (T_m), and relative percentage of crystallinity (%χ_c) values are listed in Table 1.

Table 1. Glass transition temperature, melting temperature and relative percentage of crystallinity values of pure and different compositions of PVA: NiCl$_2$ polymer electrolytes

Sample	T_g K	T_m K	(%χ_c
Pure PVA	353	509	---
PVA: NiCl$_2$ (90:10)	345	504	77
PVA: NiCl$_2$ (80:20)	339	498	68
PVA: NiCl$_2$ (70:30)	333	490	42

From the table 1 it is clear that T_g values and relative crystallinity (χ_c) decrease with the increase of salt concentration. In addition, the melting endotherm is found to broaden with increase of salt concentration .The decrease in melting temperature and the broadening of the melting endotherm are clear indications of decrease in the degree of crystallinity and dominant presence of amorphous phase[23]. The glass transition temperature (T_g) and χ_c has been found to be low for 30wt% NiCl$_2$ doped polymer electrolyte system. The lower values of T_g and χ_c represents the high amorphous content of the complexed polymer electrolytes.

3.4. Impedance Analysis

Impedance spectroscopy was employed to establish the conduction mechanism. Sunandana et al[24] reported that the conductivity depends on the mobile ion concentration, the vibrational frequency of the mobile ions at equilibrium and the entropy of activation. Fig 4 shows the Cole-Cole plots of (PVA : NiCl$_2$) (70:30) wt% polymer film at different temperatures.

Complex impedance plots showed two well defined regions. A semi circle in the high frequency range related to the conduction process in the bulk of the complex and a linear region in low frequency range, which is attributed to the bulk effect of blocking electrodes. The bulk resistance for all samples was calculated from the interception of the semicircular arc on the real axis. Conductivities of the film at different temperatures were evaluated using the following formula

$$\sigma = \frac{L}{R_b \times A}$$

where L is the thickness of the polymer electrolytes (cm), A, the area of the blocking electrodes (cm^2) and R_b is the bulk resistance of the polymer electrolytes.

The bulk resistance R_b decreases with increase in salt concentration. This may be due to the increase in the mobile charge carriers by the addition of NiCl$_2$. The ionic conductivity increases with increasing NiCl$_2$ content from 10 wt% to 30 wt%. Hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer chains are the essential to assure high conductivity of the electrolyte[25, 26]. The conductivity values of the polymer electrolytes at room temperature are given in Table 2.

3.5. Temperature Dependent Conductivity

Electrical conductivity of pure and NiCl$_2$ doped polymer electrolytes was measured at different temperatures for doped samples. The variation of electrical conductivity as a function of inverse temperature for pure PVA: NiCl$_2$ (70:30) was inserted in Fig.4. The linear variation in $\log \sigma$ vs $1000/T$ plot suggests an Arrhenius type thermally activated process represented by the relation
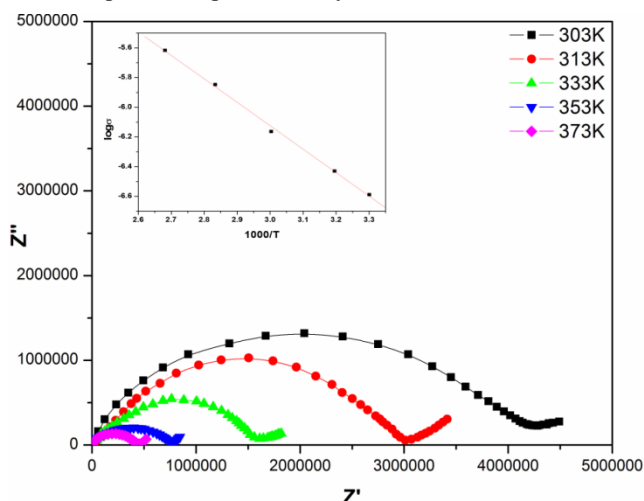
Figure 4. Cole-Cole plots of PVA: NiCl$_2$ (70:30) at different temperatures. Variation of conductivity with temperature is inserted inside the figure

$$\sigma_{dc} = \sigma_o \exp\left(-\frac{E_a}{KT}\right)$$

where σ_o is a pre exponential factor, E_a, the activation energy, K, the Boltzmann constant and T, the absolute temperature. ***The conductivity increases with increasing temperature for all complexes***. Druger et al[27] attributed the change in conductivity with temperature in solid polymer electrolytes to segmental motion, which results in an increase in free volume of the system. Thus, the segmental motion either permits the ions to hop from one site to another or provides a pathway for ions to move. In other words, the segmental movement of the polymer facilitates the translational ionic motion. From this, it is clear that the ionic motion is due to translation motion or hopping facilitated by the dynamic segmental motion of the polymer. As the amorphous region increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion to favor inter and intra chain ion hopping, thus increasing the conductivity.

The activation energy is a combination of the energy of defect formation and the energy of migration. The calculated values of activation energies for all polymer electrolyte films have been listed in Table 2. It was found that the highest conductivity was obtained for the polymer electrolyte with 30 wt% of NiCl$_2$ which also had the lowest activation energy. Polymer electrolytes having low activation energies are desirable[28] for electrochemical applications.

3.6. Total Conductivity

The variation of conductivity as a function of frequency at different temperatures for PVA: NiCl$_2$ (80:20) is shown in Fig 5.
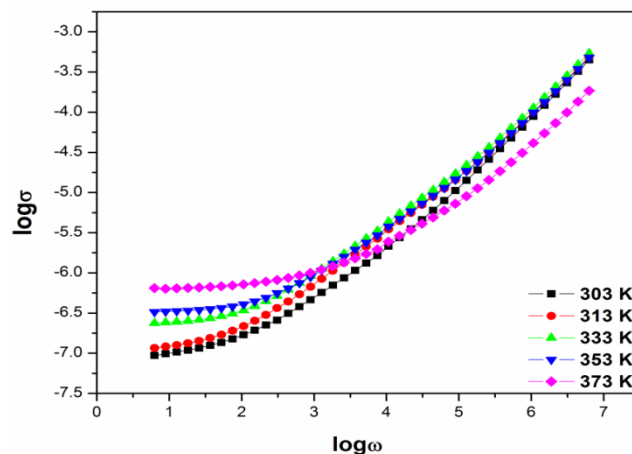
Figure 5. Conduction spectra of PVA: NiCl$_2$ (80:20) at different temperatures

The total conductivity of polymer electrolytes may be expressed using Jonsher's universal power law equation[29]. Jonscher's power law behavior is a universal property of materials that is related to the dynamics of hopping conduction, which has widely been observed in disordered materials like ionically conducting polymers and also doped crystalline solids and is generally believed to be reflected in the mechanism of charge transport behavior of charge carriers.

It is evident from figure 5, that two different trends appeared a frequency independent conductivity at low frequency range as plateau region and a frequency dependent conductivity at high frequency as dispersion region in each of these conductivity spectra. The frequency dependence of conductivity is a common response of amorphous polymers. This behavior is explained by Jonscher's universal power law equation $\sigma(\omega) = \sigma_{dc} + A\omega^{\alpha}$, which represents the fact that the total frequency dependent conductivity, is the sum of dc (σ_{dc}) and ac ($\sigma_{ac} = A\omega^{\alpha}$) components. The typical dc conductivity at low frequency arises from the activated hopping of ions, and at higher frequencies, the ionic conductivity increases with the increasing frequency which may be attributed to the couple of forward and backward ion displacements occurring simultaneously thus facilitating the frequency dependence of ionic motion in accordance with Jonscher's universal power law behavior. In Jonscher's model some of the localised charge may jump over several consecutive sites leading to a d.c. conduction current and some over a shorter distance; hopping to the adjacent site becomes a limiting case.

According to jump relaxation model reported by Funke[30], at very low frequencies, an ion can jump from one site to its neighboring vacant site successfully contributing to the dc conductivity. At higher frequencies, however the probability for the ion to go back again to its initial site increases due to the short time periods available. This high probability for the correlated forward-backward hopping at higher frequencies together with the relaxation of the dynamic cage potential are responsible for the high frequency conductivity dispersion. the power law exponent α relates the backhop rate to the site relaxation time as

$$\alpha = \frac{(\text{back hop rate})}{(\text{Site relaxation time})}$$

Table 2. Coductivity, activation energy, alfa and transference numbers values of pure PVA and NiCl₂ doped PVA polymer electrolytes

Polymer electrolytes	Conductivity at 303 K (S/Cm)	Activation energy (eV)	α at 303K	Transference numbers	
				t_{ion}	t_{ele}
Pure PVA	2.39×10^{-8}	0.45	0.86	-	-
PVA:NiCl₂ (90:10)	7.87×10^{-8}	0.36	0.82	0.953	0.047
PVA:NiCl₂ (80:20)	1.34×10^{-7}	0.34	0.73	0.958	0.042
PVA:NiCl₂ (70:30)	2.60×10^{-7}	0.32	0.69	0.962	0.038

If the ratio α is less than one, the backward hopping is slower than the site relaxation time, which results in translational motion of the Ni^{+2} ions. However, if the ratio exceeds one the backward hopping is faster than the site relaxation time. The values of α as a function of salt concentration for the present polymer electrolytes are listed in table 2. From the table 2, it is seen that α values were less than one and decreased with increase of salt

concentration. The low values of $\alpha(\alpha < 1)$ may be due to the formation of free sites for Ni^{+2} ion transport[31].

3.7. Transference Numbers
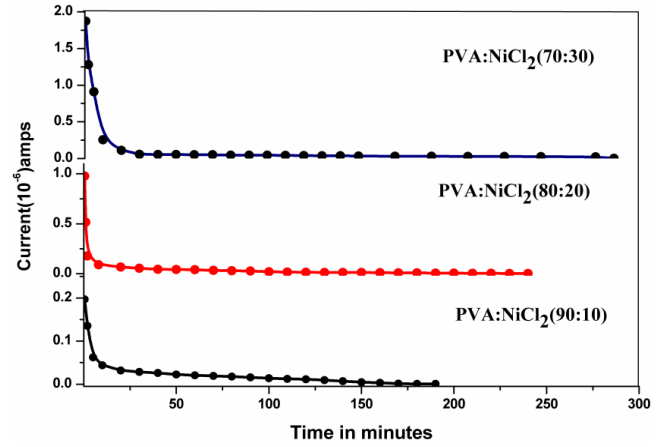
Figure 6. Transference plots of PVA: NiCl₂ polymer electrolyte films for different Compositions

Ionic transference number is one of the most important parameters for the characterization of polymer electrolyte materials. Transference numbers were evaluated using Wagner's polarizing technique[32]. To determine the ionic contribution to the total conductivity of the polymer samples, Ni/ (PVA+ NiCl₂) /C cell was polarized at 303 K by a constant dc potential of 1.5 V. The appearance of initial polarization current on application of the potential was proportional to the applied field but subsequently it starts decreasing with time. This happens when the migration of ions due to the applied electric field is balanced by diffusion due to the concentration gradient, and hence, the cell gets polarized. The polarization current is then exclusively carried by electrons or holes. The transference numbers (t_{ion}, t_{ele}) were calculated using the equations

$$t_{ele} = \frac{I_f}{I_i}$$

$$t_{ion} = 1 - \frac{I_f}{I_i}$$

where I_i is the initial current and I_f is the final current.

The polarization current versus time plots for different polymer electrolytes are shown in Fig 6. The resulting data is given in Table 2. From the table 2, the values of t_{ion} are in the range 0.953 - 0.962. This suggests that the charge transport in the investigated polymer electrolytes is predominately due to ions. The contribution of electrons to the current is negligible in all the samples. As suggested by the other workers[15, 33], the transference number (t_{ion}) of the present polymer electrolyte films is close to unity and hence these electrolytes are suitable for solid-state electrochemical cells applications.

4. Conclusions

The complexation of NiCl$_2$ salt with PVA was confirmed by XRD and FTIR studies. Thermal analysis indicates the glass transition temperature and crystallinity is low for PVA: NiCl$_2$ (70:30) polymer electrolyte. The conductivity was found to increase with increasing temperature in all polymer films. The activation energy values showed a decreasing trend with increasing dopant concentration. The lowest activation energy value (0.32 eV) was obtained for 30 wt% of NiCl$_2$. The ionic transport number data indicates that the conduction is predominantly due to ions rather than electrons.

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