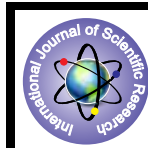


Ion Transport in Proton Conducting Pva Based Polymer Electrolyte



PHYSICS

KEYWORDS : AC impedance analysis, transport analysis

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ABSTRACT

Proton Conducting Solid Polymer electrolytes have been prepared by using Poly (vinyl alcohol) PVA doped with Ammonium Fluoride (NH₄F) in different molar ratios by Solution Casting Technique. The ionic conductivity of the polymer electrolyte has been determined by ac impedance spectroscopic techniques in the frequency range 42 Hz to 1 MHz. The highest ionic conductivity has been found to be $6.9 \times 10^{-6} \text{ Scm}^{-1}$ for 85 mol% PVA: 15 mol% NH₄F polymer electrolyte at an ambient temperature. Wagner's DC Polarisation technique confirms that the ionic conductivity is influenced by mobility and diffusion coefficient of cations (H⁺/NH₃) present in the salt NH₄F.

Introduction

Scientists and inventors have designed many different types and sizes of Fuel Cell like Solid Oxide Fuel Cell, Polymer Electrolyte Fuel Cell, Alkali Fuel Cell, Molten Carbonate Fuel Cell etc. in their research for greater efficiency. Many of the choices facing Fuel Cell developers are constrained by the choice of electrolyte since the electrolyte plays a vital role in the Fuel Cells. Polymer Electrolyte Fuel Cells use Nafion 117 polymer as an electrolyte. However relatively high price and limited operating conditions of Nafion 117 polymer limits the large scale commercialization of Fuel Cell. In the present study, efforts have been made to find a low cost PVA based polymer electrolyte to Proton Exchange membrane Fuel Cells (PEMFC).

PVA is low cost commercially available polymer [1]. Dopant dependent property, water solubility, good film formation, high mechanical strength of PVA has played a main role for the selection as host compared to other polymer matrices. From the Literature study, we know that Ammonium salts are very good proton donors to the polymer matrix. In the present work, the proton conducting polymer electrolytes have been prepared using PVA, inorganic salt NH₄F with Dimethyl Sulphoxide as solvent. The polymer electrolytes have been characterized by complex impedance spectroscopic analysis and Wagner's DC polarization technique.

Experimental Technique

PVA with molecular weight 125,000 (AR grade Sd fine chem. make), ammonium fluoride (NH₄F) (AR grade Merck) and dimethyl sulphoxide (DMSO) as solvent are used as starting material to prepare polymer electrolytes. Different molar ratios of PVA: NH₄F as (95:05), (90:10), (85:15) and (80:20) have been prepared by solution casting technique. In this technique, appropriate weight of PVA and NH₄F have been dissolved individually in DMSO and these solutions have been mixed together and stirred well by using magnetic stirrer to obtain a homogeneous mixture. To avoid absorption of water the powdery polymer PVA and the salt NH₄F are vacuum dried (80°C for 5 days) before usage. The obtained mixture is casted in glass Petri dish and is subjected for drying in a vacuum oven. Mechanically strong and flexible films have been obtained.

Characterisation

The prepared polymer electrolytes have been subjected to different studies.

Conductivity measurements

AC conductivity measurements have been carried out on PVA - NH₄F systems of uniform thickness having an area of 1 cm². Polymer electrolytes have been sandwiched between two stainless steel (SS) electrodes applying a potential of 1V from 42 Hz

to 1 MHz using HIOKI make LCZ meter (model 3532) interfaced to a computer. The conductivity has been calculated from complex impedance plots of measured impedance (Z) and phase angle (θ). The temperature of the cell has been controlled using a thermostat and electrical measurements of the polymer electrolytes have been carried out in the room temperature.

Wagner's DC Polarization technique:

A fixed DC voltage is applied to the Wagner polarization cell SS/polymer electrolyte/SS (SS-Stainless Steel). The polarization current passing through the cells has been monitored as a function of time

Results & Discussion

Impedance analysis

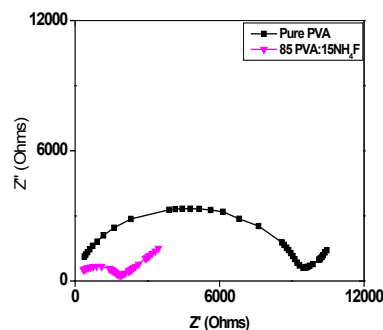


Figure 1 Impedance plot of PVA and 85PVA:15NH₄F polymer electrolyte at 303K

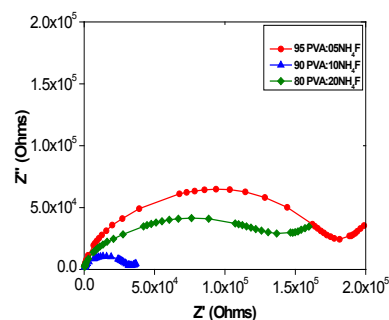


Figure 2 Impedance plot of 95PVA:05NH₄F 90PVA:15NH₄F, 80PVA:20NH₄F polymer Electrolytes at 303K

It is a tool to obtain the magnitudes of all the fundamental properties of the cell. In particular the effective DC resistance R_b can be easily obtained from Cole – Cole plot. Figure 1&2 show the impedance plots for PVA and PVA doped with different molar concentrations of NH_4F respectively. The plot contains two well defined regions.

The circular arc in the high frequency range yields information about the properties of the electrolyte namely the bulk resistance (R_b) and bulk capacitance (C_b)

The spike in the low frequency range yields information about electrode / electrolyte interface [2].

For ideal electrodes and electrode / electrolyte interface, a vertical spike should have been obtained. But the electrode spikes are non – vertical due to the double layer capacitance at the blocking electrodes. At high frequency, there is a circular arc. The same trend is observed for all plots. The intercept of the circular arc on the real axis gives the bulk resistance R_b . Then the ionic conductivity of the developed electrolytes is calculated by using the formula

$$\sigma = d / R_b A$$

Where A – area of the stainless steel electrode contacting with the polymer Electrolyte.

d – Thickness of polymer electrolyte.

R_b – Bulk resistance of the electrolyte.

The polymer electrolyte (85 mol% PVA: 15 mol% NH_4F) has the highest ionic conductivity $6.9 \times 10^{-6} \text{ Scm}^{-1}$ at ambient temperature. It indicates that the ionic conductivity of Pure PVA has been enhanced from the reported value $10^{-10} \text{ Scm}^{-1}$ to 10^{-6} Scm^{-1} by the addition of the dopant (NH_4F).

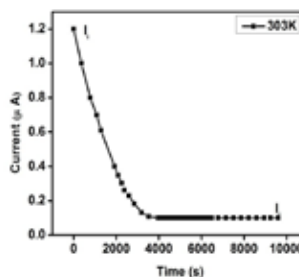
In the table 1, the ionic conductivity of polymer complexes increases from 5 mol% to 15 mol% of NH_4F doped polymer electrolytes. The enhanced ionic conductivity is attributed to the changes in both the mobility and carrier concentration. It is also observed that the ionic conductivity decreases when salt concentration is increased from 15 mol% to 25 mol%. As the salt concentration increases, the carrier concentration also increases in the complex. As a result, there is a formation of ion aggregates which will restrict the segmental motions of the charge carrier thereby reduces the ionic conductivity.

From the impedance plots, it has been observed that the centre of the experimental arc lies below the real axis. The reason might be due to the presence of poly dispersive relaxation time in the polymer complexes. It obeys the expression for impedance

$$Z^* = R_\infty + \frac{(R_o - R_\infty)}{1 + (i\omega)^{1-\alpha}}$$

Where R_o, R_∞ are the values of resistance at low and high frequencies respectively α is a measure of the distribution of relaxation time [3]. The value α can be calculated from the angle subtended by the radius of the circle with the Z' axis passing through the origin of the Z'' axis. From the table 1, it is found that the value of α ranges from 0.196 to 0.318. Since the value of α lies between 0 and 1, the system has broad distribution of relaxation times.

Transport analysis



Total ionic transference number of Polymer Electrolyte has been measured using Wagner’s DC. Polarization technique [4]. This technique has been used to analyse the mobile species in the electrolyte is either ions or electrons. A fixed d.c voltage is applied to the Wagner’s polarization cell SS / (85PVA:15 NH_4F) /SS (SS-Stainless Steel). The polarization current passing through the cells has been monitored as a function of time. Figure 3 shows transference measurements results for the sample 85PVA:15 NH_4F . Similar measurements have also been done for other samples 95PVA:05 NH_4F , 90PVA:10 NH_4F , 85PVA:15 NH_4F and 80PVA:20 NH_4F . It has been observed that the initial total current falls rapidly with time due to the depletion of the ionic species in the electrolyte and becomes constant in the fully depleted situation. Residual current is due to the electron migration across the electrolyte and interfaces.

The transference numbers are calculated using the relation

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

$$t_{ele} = I_f / I_i$$

where I_i is the initial current and I_f is the final residual current. The ionic transference number (t_{ion}) for all compositions of the PVA: NH_4F : electrolyte systems are found to be in the range 0.89-0.92. The transference number of F^- is so low because mass of the F^- ion is heavy compared to loosely bound proton. So the contribution of F^- ion to the conductivity is very low. This suggests that the charge transport in these polymer electrolyte systems is predominantly ionic accompanied by mass transport and electronic contribution to the total current is negligible.

The diffusion coefficients of cations (NH_4^+) and anions F^- of each polymer electrolytes have been calculated from the measured values of conductivity and ion transference number, using the following equations [5].

$$D = D_+ + D_- = kT\sigma / ne^2$$

$$t_{ion} = D_+ / (D_+ + D_-)$$

The ionic mobility of cations and anions of all the samples have been calculated using the following equations.

$$\mu = \mu_+ + \mu_- = \sigma / ne$$

$$t_{ion} = \mu_+ / (\mu_+ + \mu_-)$$

where e is the charge of the electron, k Boltzmann constant, T absolute Temperature, n is the number of charge carriers stoichiometrically related to the salt composition, μ_+ , μ_- is the ionic mobility of cation and anion respectively and D_+ , D_- is the diffusion coefficient of cation and anion respectively.

Table 2 shows the calculated value of transference number, ionic mobility and diffusion coefficient of cations (H^+NH_3) and anions (F^-) of all polymer electrolytes. The diffusion coefficient and ionic mobility of the high ionic conductivity electrolytes has maximum value compared with other electrolytes. From the calculation, cation mobility μ_+ has the greater value than anion mobility μ_- . The same behavior can be detected for D_+ . The study of Transference Number Measurements suggests that the conductivity has been influenced by μ_+ and D_+ [6].

Conclusion:

A polymer electrolyte has been prepared by incorporating salt NH_4F to the polymer PVA. The maximum ionic conductivity of 6.9×10^{-6} S/cm at room temperature is attained for 85PVA:15 NH_4F polymer electrolyte. The ionic conductivity of the samples has been influenced by mobility and diffusion coefficients of the cation and anion. Polarisation technique concrete that the prepared polymer electrolytes are proton conductors.

Composition PVA: NH_4F (mol %)	ALPHA	Ionic conductivity (S/cm)
95PVA:05 NH_4F	0.256308	8.3×10^{-8}
90PVA:10 NH_4F	0.318151	6.8×10^{-7}
85PVA:15 NH_4F	0.195806	6.9×10^{-6}
80PVA:20 NH_4F	0.242579	1.0×10^{-7}

Table-1 Alpha & ionic conductivity values for different compositions of PVA: NH_4F at 303K

Table-2 Concentration, Ionic mobility and diffusion coefficient of cations and anions of all PVA – NH_4F electrolytes

Composition (mol %)	n (cm^{-3}) 10^{21}	t_+	D_+ ($cm^2 s^{-1}$) 10^{-10}	D_- ($cm^2 s^{-1}$) 10^{-11}	μ_+ ($cm^2 V^{-1} s^{-1}$) 10^{-08}	μ_- ($cm^2 V^{-1} s^{-1}$) 10^{-09}
95PVA:05 NH_4F	0.82	0.89	0.15	0.18	0.06	0.07
90PVA:10 NH_4F	1.64	0.91	0.61	0.61	0.24	0.23
85PVA:15 NH_4F	2.46	0.92	4.20	3.65	1.61	1.40
80PVA:20 NH_4F	3.28	0.90	0.04	0.05	0.02	0.02

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