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A STUDY ON THE EFFECT OF STA/APTEOS IN THE PVA MATRIX BASED ORGANIC/INORGANIC COMPOSITE MEMBRANES

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ABSTRACT-The development of an organic-inorganic based membranes emerges because of its good film forming capabilities and enhanced electrochemical properties. Poly (vinyl alcohol) (PVA)/ -aminopropyl triethoxysilane (APTEOS) with the heteropoly acid Silicotungstic acid (STA) hybrid membranes were prepared by solvent casting technique. Incorporation of STA and APTEOS in the PVA matrix and its structural analyzation was carried out by X-ray diffraction (XRD) analysis. The uniform distribution of STA and APTEOS were indicated by the broadening of peaks in the complexes. The dielectric behavior such as dielectric loss, dielectric constant and tangent loss were studied for the prepared proton exchange membranes using electrochemical impedance technique.

Keywords- [PVA, Heteropoly acid, XRD, Dielectric studies]

1. INTRODUCTION

Polymer electrolytes have attracted much attention due to their potential applications in electrochemical devices such as rechargeable batteries, fuel cells,etc. Since conductivity is an important property of polymer electrolyte, researchers have tried various means to enhance conductivity [1]. Developing organic–inorganic hybrid membranes may provide a solution that will satisfy the requirements of an unchanged imprinted cavity and good film-forming properties [2]. PVA has been studied as a membrane because of its low cost, good film-forming properties, high hydrophilicity and good mechanical and chemical-resistant properties [3].

2. EXPERIMENTAL PROCEDURE

Chemicals Used

The host polymer Poly (vinylalcohol) (PVA), glutaraldehyde (Gl) and the - aminopropyl triethoxysilane (APTEOS) was purchased from Sigma Aldrich. Silicotungstic acid (STA) was purchased from SRL. Distilled water was used as a solvent.

Preparation of the Composite Membranes

The PVA was dissolved in distilled water at 80 °C with constant stirring. Then, 2 wt% of STA and the appropriate amount of glutaraldehyde were added to the PVA solution respectively. The predefined corresponding quantities of APTEOS was

added and stirred continuously for 24 hrs. Then the resultant viscous slurry was casted in a petri dish. The films were further dried in vacuum oven at 60ºC for 6h for the evaporation of solvents. After drying, the membranes were peeled off and stored it in a dessicator. The details of all the hybrid composite membranes are given in Table 1.

Characterization Technique

The prepared electrolytes have been characterized by FTIR analysis using Perkin Elmer IR spectrophotometer to analyze the complexation of the polymer and subjected to an ac impedance analysis to determine the highest ionic conductivity with the help of stainless steel blocking electrodes using a computer controlled µ-autolab type III Potentiostat/Galvanostat in the frequency range of 1 Hz to 1 MHz.

3. RESULTS AND DISCUSSION

X-ray diffraction measurements were performed for various hybrid composite membranes in order to determine the composite formation as shown in Fig. 1. The dispersion of APTEOS in the PVA matrix with heteropolyacid prevented the formation of semi-crystalline regions in the hybrid membranes and confirmed that the 2 of the peak was about 20° for all the composites. No phase changes were found to occur, even when changing the concentration of APTEOS.
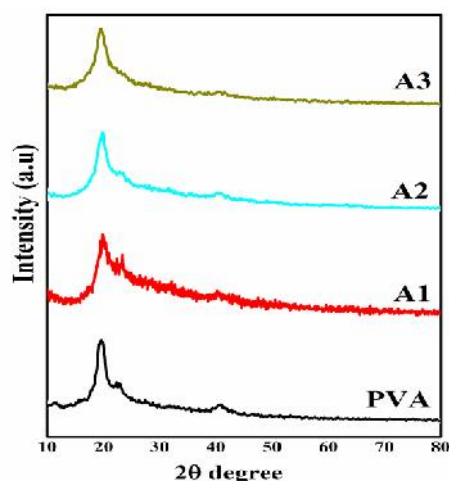

Figure 1- X-ray diffraction patterns of the pure PVA and complexes.

The complex permittivity of a system is defined by

$$\varepsilon^* = \varepsilon' + i\varepsilon''$$

Where ε' is dielectric constant (the real parts of complex permittivity) and ε'' is dielectric loss (the imaginary part of complex permittivity).

Using the impedance values, the dielectric constant and dielectric loss can be calculated from the equations,

$$\varepsilon' = \frac{Z''}{\check{S} C_0 \left(Z''^2 + Z'^2 \right)} \quad \text{and}$$

$$\varepsilon'' = \frac{Z'}{\check{S} C_0 \left(Z''^2 + Z'^2 \right)}$$

Here, Z' and Z'' are the real and imaginary parts of the complex permittivity. Where, $C_O = \varepsilon_0 A/t$, ε_0 is the permittivity of free space and $\omega = 2\pi f$, f is the frequency. A sharp peak increase of ε' and ε'' in the low frequency side is due to the presence of electrode polarization effects. Thus the polarization due

to charge accumulation decreases which leads to a decrease in values of ε′and ε″ [3]. From the fig. 2, the value of dielectric constant ε′

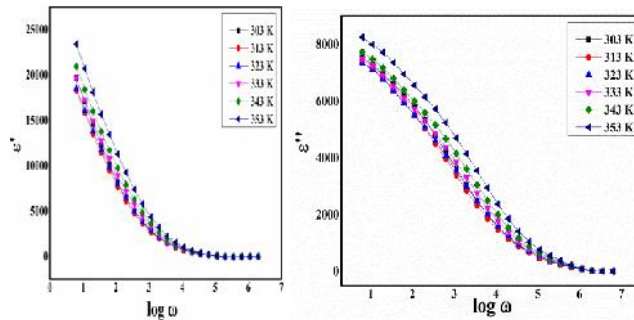for the sample A3 was found to be ~ -4.2284 for the frequency 1 MHz at 303K.

Figure 2- Frequency dependence of dielectric constant ν¼and dielectric loss ν″ of the prepared electrolyte PVA(80) - STA(2) - Gl(15)-APTEOS(3)[wt%].

Sample	PVA(80) - STA(2) - Gl(X)-APTEOS(Y) [wt%]	at RT x 10^{-4} (Scm^{-1})	ν¼(at 1 MHz)	‡ (s) Î 10^{-6}
A1	X=3; Y=15	4.149	-3.293	2.832
A2	X=10; Y=10	0.7821	-0.481	0.5035
A3	X=15; Y=3	6.858	-4.228	2.832

TABLE 1- Temperature dependent ionic conductivity of the prepared samples.

The dielectric behavior of the sample can also be studied using electric modulus. Electric modulus M* is defined in terms of the reciprocal of the complex relative permittivity ε*.

$$M* = \frac{1}{\nu *} = M'+M''$$

The frequency dependence of real (M′) and imaginary part (M″) of the dielectric modulus of the sample A3 is shown in fig. 3.
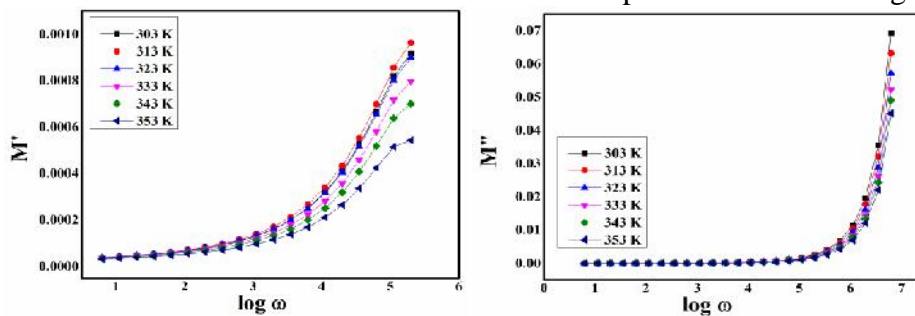

Figure 3- Frequency dependent electric modulus [a] Real part and [b] Imaginary part of PVA(80) - STA(2) - Gl(15)-APTEOS(3)[wt%] polymer electrolytes

In both plots, the dielectric modulus for low frequencies is almost zero. The long tail at low frequency is due to large capacitance associated with the electrode system, which confirms the non- Debye behavior of the

system. The increase in modulus spectra at higher frequencies indicates that the polymer electrolyte systems are ionic conductors and this is attributed to the bulk of the material.

The tangent loss can be calculated from the   ratio of ε' and ε'',

$$\tan u = \frac{v''}{v'}$$

The variation of tangent loss with frequency for A3 sample is shown in fig 4.
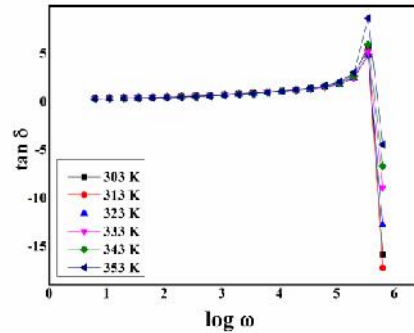

**Figure 4- Variation of tangent loss with frequency of the sample having maximum
ionic conductivity (A3) at different temperatures.**

The presence of peak in the plot represents the appearance of relaxation effect in the polymer electrolyte. It is noted that the peak is shifted to higher frequency range with temperature increases which indicates the reducing of relaxation time and this shifting of peaks is attributed to the fast segmental motion coupled with the mobile ion. The relaxation time, τ (Table 1) can be calculated from the graph using the relation,

$$\ddagger = \frac{1}{\check{S}_{peak}}$$

The dielectric relaxation over a broad frequency range is useful for the investigation of dipole relaxation in a polymer electrolyte [4].

CONCLUSION

PVA-STA based polymer electrolytes were prepared by solvent casting technique. It shows that low wt% of APTEOS in PVA (80wt%)-STA (2wt%) polymer electrolyte gives higher ionic conductivity $0.6858 \times 10^{-3} Scm^{-1}$ than the complexes. The dielectric constant of the prepared polymer samples are between -0.5 to 4.5 at 1MHz. Hence, it is concluded that the sample A3 serves as a better proton exchange membrane for fuel cell applications.

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