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Effect of TiO_2 on Chemically synthesized Polymer blend Electrolytes (PVA-PANI)

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Abstract: The electrochemical methods of energy storage and conversion are of great interest for many applications. In the present investigation, Polymer blend electrolytes doped with TiO_2 have been prepared by Solution Cast technique. The electrolytes were characterized by FTIR and Complex impedance analysis. FTIR Spectroscopic studies conforms the complexation of the dopants to Polymer. Frequency dependent conductivity values are obtained from Complex Impedance analysis. It shows that there is increase in the magnitude of conductivity for the TiO_2 doped electrolyte than pure Polymer blend electrolyte.

Keywords: *Polymer electrolyte, Poly aniline, TiO_2.*

I. INTRODUCTION

Recently there is a great demand in energy, and many researchers have tried to make effort to develop new energy resources. The development of solid polymer electrolytes with high ionic conductivity at ambient and sub-ambient temperatures has been made extensively due to its potential applications in electrochemical devices, such as high energy-density batteries, electrochromic devices and chemical sensors [1, 2]. Polymer electrolytes [PE] are among the important classes of macromolecules. These polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups [3]. The conduction in PEs takes place through two distinct events: the first is due to the charge migration of ions between the coordinate sites of the host polymer and the second is associated with the polymeric chain segmental motion [4]. The ionic conductivity of PEs is strongly affected by various factors such as (i) crystalline of the material, (ii) simultaneous cation and anion motions and (iii) the ion pair formation. These factors reduce the cationic conductivity and; therefore, act as a barrier for potential applications [5]. The polymer electrolyte should possess the following properties [6, 7, 8, 9]: (i) high ionic conductivity and high transference number; (ii) high chemical, thermal and thermal stabilities and (iii) good compatibility with the electrode. In the present study we have used Polyaniline (PANI) and polyvinyl alcohol (PVA) as host materials. Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Polyaniline is unique due to its ease of synthesis, environmental stability, and acid/base doping/dedoping chemistry. However, two major shortcomings of conductive form of polyaniline are difficult to process, since it is insoluble in common organic solvents and unstable at melting processing temperatures, that has restricted its applications and its poor mechanical properties. The shortcomings can be overcome by preparing polyaniline blends and composites that possess the mechanical properties of the insulating host matrix and the electrical properties of the conducting polyaniline.

PVA, one of the important classes of polymer electrolytes is a polar polymer. It is a semi-crystalline polymer and has very important applications due to the role of OH group and hydrogen bonds [10].

II. EXPERIMENTAL

A. Materials

Poly Aniline (C_6H_6), Hydrochloric acid (HCl) and Potassium persulphate ($K_2S_2O_8$) were purchased from Merck. Polyvinyl-alcohol and Titanium Oxide (TiO_2) were purchased from Qualigens fine Chemicals. Deionized water was used for all samples. Aniline was double distilled before used as monomer. The entire chemicals used were of analytical grade.

B. Instrumentation

Infrared spectroscopy can be used to identify the chemical composition, chain structure and physical properties (i.e., chain orientation, crystallinity, and chain conformation or chain dynamics) of the polymer electrolyte sample. A common laboratory instrument that uses this technique is a FTIR spectrometer scanning from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}. FTIR spectra of the electrolytes were recorded, using Shimadzu 8400 S FTIR spectrophotometer instrument by KBr pelletisation method. The complex impedance study was performed using the impedance analyzer Solatron1260.

C .Synthesis of electrolytes

Required amount of Aniline and PVA solutions were taken in a beaker and calculated volume of pre-aerated oxidizing agent such as PDS was added to the solution. A magnetic stirrer was used for one hour to make the solution highly homogeneous. The solution was then placed in a Petri dish and dried using microwave oven to get a thin film of polymer blend electrolyte. The same procedure was repeated with the addition of 0.02g of TiO_2 .

III. RESULTS AND DISCUSSION

A. FTIR studies

Infrared spectroscopy is one of the most widely used tools for the detection of functional groups in pure compounds and mixtures and for the compound comparison. The FTIR spectrum for PVA-PANI and PVA –PANI-TiO_2 films are shown in figures 1 and 2 respectively. The observed shifts , appearances and disappearances of vibrational band and change in the intensity of peaks indicated that there is a complex formation between PVA –PANI and PVA –PANI-TiO_2 and are tabulated in table 1.

Fig 1. FTIR spectrum of PVA-PANI film

Fig 2. FTIR spectrum of PVA-PANI –TiO_2 film

B. AC Impedance Analysis

Figure 3 and 4 show the complex impedance spectrum (i.e Nyquist plot) of PVA-PANI and PVA-PANI-TiO_2 blend polymer electrolytes at room temperature. In graph, the real and imaginary parts of the impedance of the samples are plotted in a complex plane and their frequency dispersion curves possess information about the effects of electrode – electrolyte interface, grain and grain boundary resistances etc. It show that the sample comprises of a broadened semicircle in the high frequency region followed by tail in the low frequency region. Semicircle on the high frequency is due to the bulk properties whereas, spike arises on the low frequency is due to the material-electrode interface of the material. The intercept of the semicircle with the real axis (z) gives rise to the Bulk (ionic) resistance (R_b) of the materials.

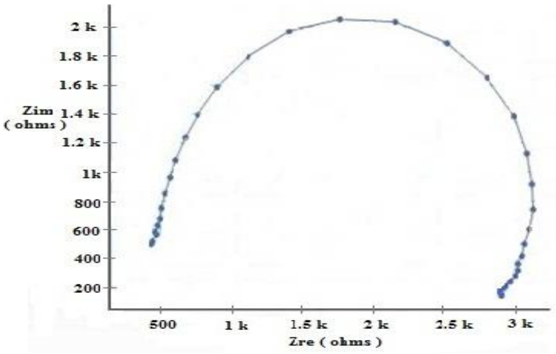

Fig 3. Nyquist plot of PVA – PANI film

Table 1.The Vibrational Assignmment of PVA – PVA and PVA – PVA - TiO_2 Electrolytes

PVA-PANI		PVA-PANI-TiO_2		
Wave number (cm^{-1})	Intensity (%)	Wave number (cm^{-1})	Intensity (%)	Assignment
		2430.30_s	43.897808	NH stretching modes
2280.50_m	68.085791	2276.99_s	29.511565	N=C=O antisymmetric stretch
2207.41_m	76.880940	2206.87_m	67.891048	C≡N stretch
2165.82_m	79.156887	2165.12_s	71.388451	N≡C stretch
1635.16_s	50.472247	1634.11_s	62.518454	NH_3 deformation
1578.89_s	39.485294	1581.06_s	38.285921	NH_2 deformation
1520.04_s	42.250823	1521.37_s	44.905959	NH_3^+ deformation
1496.09_w	31.142297	1494.80_m	40.105368	N=N-O antisymmetric stretch
1461.70_m	32.943698	1462.52_s	42.450988	N=N-O antisymmetric stretch
1377.22_s	38.910237			CH_3 deformation
		1288.80_s	63.728126	N-O stretch
1258.37_S	34.581355			C – N stretch
1198.20_s	41.602722	1195.22_s	63.678172	C – O stretch
		1142.26_s	42.887244	SO_2 symmetric stretch
1027.84_s	32.534382	1025.40_m	54.827619	C – O stretch
947.17_m	79.126874			CH_2 out-of-plane wag
		907.81_s	86.911078	CH_2 out-of-plane wag
918.18_m	76.682871			CH_2 out-of-plane wag
850.48_m	56.321749	850.43_m	80.871897	C – Cl stretch
741.71_s	32.871917	742.33_s	42.579988	CH out-of-plane deformation

687.68_{vs}	37.645956	687.08_{vs}	58.381086	OH out-of-plane deformation
617.73_{vs}	35.251878	616.03_{vs}	81.120968	OH out-of-plane deformation
523.30_{m}	63.941271	519.81_{s}	82.954358	C – C=O bend
475.21_{s}	40.145225	475.74_{s}	55.380919	C – O – C bend

vs - very strong , s- strong, vs- very strong , m- medium, w-weak

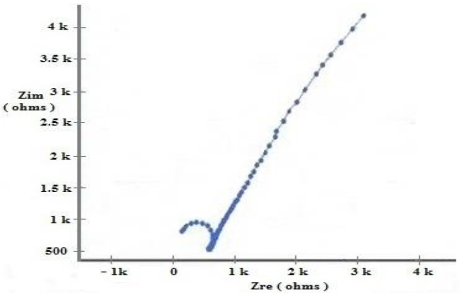

Fig 4. Nyquist plot of PVA - PVA - TiO_2 film

The semicircle moves towards the higher frequency side and diameter of the semicircle differs, which predicts the conductivity was through ions [11]. The PVA-PANI-TiO_2 sample shows the less bulk resistance value compared with PVA-PANI sample indicating higher value of the conductivity due to the increase in charge carrier. Also it has been observed from the plot that single semicircle corresponding to the parallel combination of resistance and capacitance which are present in the system. The ionic conductivity of a polymer electrolyte depends on the actual concentration of the conducting species and their mobility.

The bulk ionic conductivity has been calculated using the relation,

$$\sigma = \frac{d}{R_b A} \quad \text{s/cm}$$

Here, d is the thickness of the polymer electrolyte film, A is the surface area of the film and R_b is the bulk resistance of the electrolyte film. The bulk ionic conductivity has been calculated and tabulated in table 2

Table 2. The bulk ionic conductivity of the electrolytes

Sample	Bulk resistance of the material R_b KΩ	Thickness of the electrolyte film d cm	radius of the film, R cm	surface area of the film A cm^2	Ionic conductivity σ x 10^{-6} s/cm
PVA-PANI	2.7	0.04	0.5	0.785	18.8724
PVA-PANI-TiO2	0.5	0.04	0.5	0.785	101.912

The low ionic conductivity in a polymer complex (PVA-PANI) results from the crystalline phase that affects the mobility of ions [12]. When TiO_2 are added to polymer electrolyte , the surface groups of the TiO_2 particles may promote a local structural modifications thereby amorphous region in polymer electrolyte .This may enhance the transport of ions in membrane. Figures 5 and 6 show the varation of impedance with frequency for PVA-PANI and PVA –PANI-TiO_2 films .

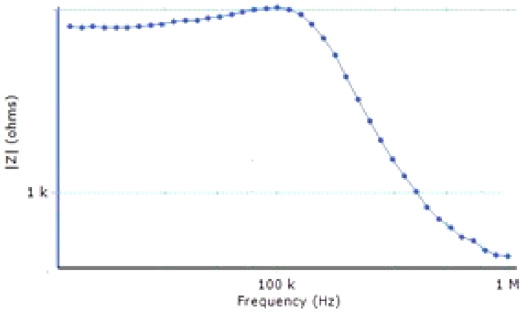

Fig 5. The variation of impedance with frequency for PVA-PANI film

Figure 5 shows that impedance is high when the frequency is low and it remains constant upto 100KHz and gradually decreases as the frequency increased above 100KHz. For PVA –PANI-TiO_2 sample (Fig 6), impedance is maximum when the frequency is very low and starts to decrease at lower frequency itself and the impedance becomes almost zero at higher frequency. Hence the conductivity is increased with increase in frequency and is maximum at higher frequency.

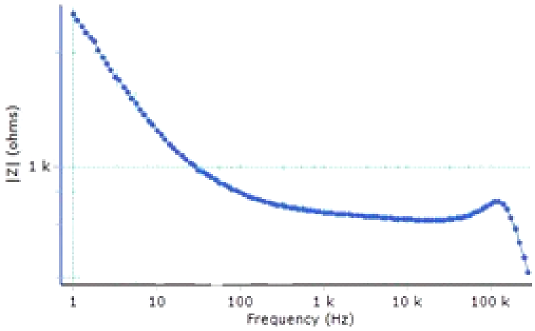

Fig 6. The variation of impedance with frequency for PVA-PANI -TiO_2 film

CONCLUSION

Polymer blend electrolytes added with TiO_2 were synthesized and the samples were characterized by FTIR and AC Impedance analysis. FTIR analysis conforms the complex formation that occurs between PVA -PANI and PVA -PANI-TiO_2. Frequency dependence of ac electrical conductivity of polymer electrolytes was studied. It infers that ionic conductivity is maximum for PVA -PANI Polymer electrolyte added with TiO_2 .

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