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Characterisation of PVA: NH_4F: ZRO_2 Composite Polymer Electrolytes

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ABSTRACT

Proton conducting polymer electrolytes have been prepared using Poly (vinyl alcohol), ammonium fluoride and nanofiller ZrO2 by the well known technique the Solution Casting Technique. Complex formation among the components of the polymer electrolytes has been confirmed by FTIR analysis. The maximum ionic conductivity has been found to be 3.4 x 10-5 Scm-1 for 85PVA:15NH4F:2ZrO2 polymer electrolyte at ambient temperature. It is found to be one order higher than the polymer electrolyte 85PVA:15NH4F. TG/DTA analysis shows the thermal stability and heat resistant. The prepared electrolyte has been subjected to morphological studies.

Introduction

Research on proton conducting polymer electrolytes has received a considerable interest because of their widespread application in fuel cells, super capacitors and electro chromic devices. The polymer electrolytes have many advantages such as leak- proof, electrochemical stability, flexibility and ease of processing into thin films of large surface area. The main disadvantage is its low ionic conductivity at ambient temperature. The incorporation of ceramic filler like SiO2, TiO2, Al2O3, BaTiO3, ZrO2 etc. to the polymer electrolytes enhances the conductivity value by one to three orders of magnitude. However the particle size and concentration of insulating matrix (nanofiller) decide the conductivity. In the present work an attempt has been made to synthesis and characterizes the composite polymer electrolytes using PVA, NH4F and ZrO2.

Experimental Technique

In the present work, electrolytes have been prepared using Poly (vinyl alcohol) PVA with average molecular weight 1,25,000 (AR grade, Sd fine CHEM-limited make), ammonium fluoride NH4F (AR grade, Merck), inorganic nanofiller ZrO2 of particle size 45nm (Aldrich, USA) and the solvent Dimethyl Sulphoxide (DMSO) by Solution casting technique. From our earlier work on PVA:NH4F, it has been observed that the 85PVA:15NH4F polymer electrolyte has the highest ionic conductivity as 6.9 x 10-6Scm-1 at ambient temperature. 1.75 mol%, 2mol%, 2.5 mol% of nanofiller ZrO2 have been added to 85PVA:15NH4F polymer electrolyte to prepare composite polymer electrolytes. The free standing nature and dryness of the prepared composite polymer electrolyte has been visually examined.

Characterisation

The composite electrolyte is subjected to FTIR analysis using SHIMADZU IR Affinity – 1 Spectrometer in the range 400 – 4000 cm-1 at room temperature. Electrical measurements have been performed on HIOKI make LCZ meter (Model 3532) in the frequency range 42Hz – 1MHz at 303K by sandwiching the electrolytes between two steel blocking electrodes. Thermo gravimetric analysis (TG) has been studied using SDT Q600 V8.3 Build 101 at a heating rate of 200 C/min in the range 00C to 8000C. The surface morphology of the polymer electrolytes have been examined with JEOL.JSM-6390 scanning electron microscope.

Results & Discussion

SEM analysis:

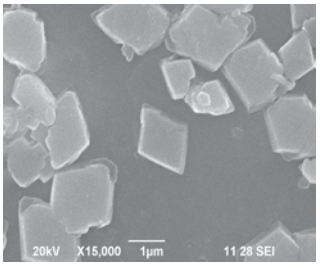

Figure 1

Figure 1 reveals the surface morphology of the polymer electrolyte 85PVA:15NH4F:2ZrO2 having maximum ionic conductivity at X15000 magnification. From the figure, it is evident that the surface of the polymer electrolyte is somewhat rough and the nanofiller ZrO2 had not undergone any chemical reaction with the polymer. From the Figure the space between the nano particles is evident. This free space forms a new kinetic path via polymer –ceramic boundaries for proton ion transport thereby enhance the ionic conductivity [1].

FTIR analysis:

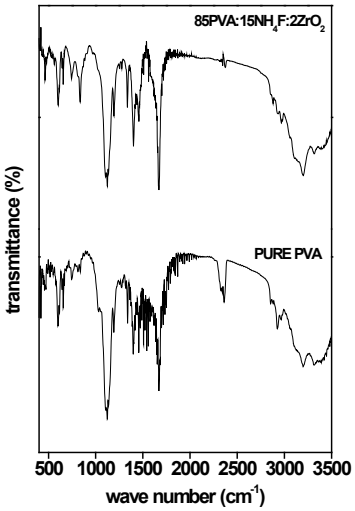

Figure 2

Figure 2 shows FTIR transmittance spectra of pure PVA and 85PVA: 15 NH4F:2ZrO2. The stretching and bending vibration of hydroxyl group (O-H) at 3317 and 1462cm-1 are the most characteristic band of pure PVA get shifted towards lower wave number at 3315 and 1459 cm-1 in the complex [2]. It gives strong indication of specific interaction of the salt NH4F, nanofiller ZrO2 and the host polymer PVA in the polymer electrolytes. The peaks at 752 and 654 cm-1 are attributed to C-S stretching vibration of the solvent DMSO [3]. It indicates the presence of trace of the solvent in the polymer electrolytes. The vibrational peaks due to the N-H wagging (out of plane), H-N-H bending and N-H stretching of NH4+ present in the salt NH4F appear at 546, 1402, 2978 and 3318 [4].They get displaced in the sample. Further the absorption peaks of ZrO2 (3400, 2283, 1634, 1122, 745 and 500 cm-1 get shifted to 3379,2262,1634,1123,746 and 485 cm-1 in the complex [5]. The addition of ZrO2 increases, amorphous nature of the polymer. The change in the frequency is due to the attachment of NH4+ (ammonium ion) to hydroxyl (O-H) group and carbonyl group (C=O) of the polymer. The increase of amorphous nature, the presence of new peaks, the shift and changes in the intensity of the peak position of FTIR spectra of doped samples confirm the complex formation among the poly-

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mer, salt and nanofiller.

Conductance spectra analysis:

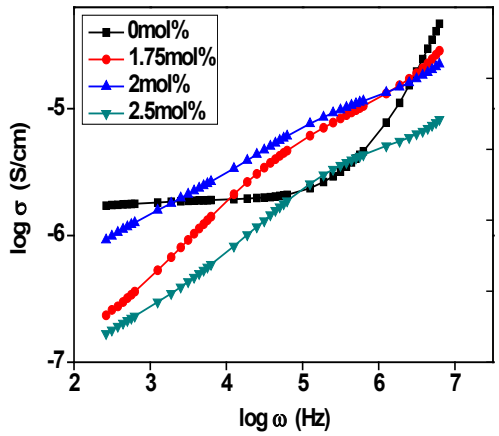

Figure3

Figure 3 shows the Conductance Spectra of 85PVA: 15NH4F, 85PVA: 15NH4F: 1.75 ZrO2, 85PVA:15NH4F:2ZrO2, and 85PVA: 15NH4F:2.5ZrO2 polymer electrolytes respectively at 303K. A typical conductance spectrum is composed of three different regions; the low frequency region describing the electrode - electrolyte polarization followed by a mid frequency plateau region and the high frequency region which represents the bulk relaxation. The extrapolation of the dc plateau region to log σ axis gives the dc conductivity value. It has been observed that the dc conductivity value increases with increase of temperature. It suggests that the free volume around the polymer chain causes the mobility of proton ions and polymer segments and hence the conductivity [6]. The maximum ionic conductivity (3.4 x 10-5 Scm-1) of 85PVA: 15NH4F: 2 ZrO2 suggests that the nanoparticles are aiding the formation of amorphous phase. The amorphous phase of the polymer network facilitates the ionic motion in the polymer network thereby enhances the ionic conductivity as confirmed by XRD, FTIR analyses.

TG/DTA Analysis:

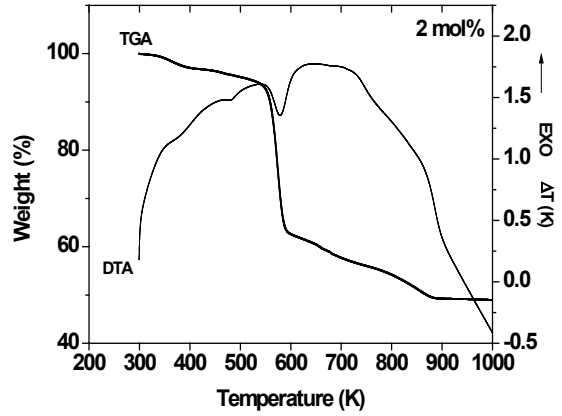

Figure 4

Figure-4 shows TG/DTA thermogram of the best conducting polymer electrolyte 85PVA:15NH4F:2ZrO2. According to the author Mishra and Rao, there are two stages of decomposition in Pure PVA and it is thermally stable upto 531K [7]. In the present study, the first decomposition occurred at 515 K followed by endothermic peaks 570 K in the DTA curve for all electrolytes respectively. The first degradation is due to decomposition of the side-chain of PVA. The second decomposition occurred at 730K followed by endothermic peaks. 572 K in the DTA curve for all samples respectively. The second degradation is due to oxidation combustion of the PVA main chain [8].

Table -1 Thermo gravimetric results in PVA-NH4F-ZrO2 polymer electrolytes

Composition	Weight loss % at temperature	
	373K	523K
85PVA:15NH_4F	4.5	13.9
85PVA:15NH_4F:1.75ZrO_2	2.3	6.2
85PVA:15NH_4F:2ZrO_2	2.1	5.5
85PVA:15NH_4F:2.5ZrO_2	3.5	8.4

The weight loss at 373K and 523K for all prepared electrolytes are shown in Table- 1. The weight loss upto 373K is probably due to the evaporation of the residual solvent and moisture present in the polymer electrolytes. The weight loss above 373K due to crystallization [9]. The polymer electrolyte 85PVA:15NH4F:2ZrO2 has weight loss 2.1% at 373K and 5.5% at 523K (Table- 1). It has been observed from the Table-1 that this polymer electrolyte has less weight loss among the prepared electrolytes. The lesser the weight loss in the sample the better it is. It suggests that the polymer electrolyte is thermally stable after incorporation of the nanofiller. Thus this electrolyte has more thermal stability & heat resistant.

Conclusions:

A new composite polymer electrolyte has been prepared by incorporating nano-sized 2 mol% of ZrO2 (45nm) into 85PVA:15NH4F polymer Complex formation among polymer, salt and nanofiller has been confirmed by FTIR studies. The maximum ionic conductivity of 3.42 X 10-5 S/cm at room temperature is attained for 85PVA:15NH4F:2ZrO2 composite polymer electrolyte. This can be explained by the miscibility between optimum content of polymer, salt and nano filler. Thermo gravimetric analysis confirms that the 85PVA:15NH4F:2ZrO2 electrolyte is thermally stable and heat resistant among the prepared polymer electrolytes.

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