

The Development of PVA Based Proton Conducting Solid Polymer Composite Electrolyte System

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ABSTRACT

In this Study the attempt was to improve the proton conductivity by dispersing the Nano sized GDC to obtain (100-x) (80PVA:20AN) (x)(GDC) Nano-composite system. X-ray diffraction (XRD) study shows that the addition of filler GDC in polymer not only reduces the intensity of the characteristic (110) peak but also broadens which is an indication of the increase in amorphousness. The Arrhenius plots for different concentrations of GDC in (80PVA:20AN) polymer blend shows the initial increase in ionic conductivity of the composite polymer electrolyte upto 20 wt% filler GDC. The proton conductivity increases with increased relative humidity within entire studied range of H₂ partial pressures.

Keywords : Nano Composite System, XRD, polymer blend, proton conductivity.

I. INTRODUCTION

Solid proton conductors are compounds containing loosely bound molecules where conductivity generally strongly depends on their state of hydration. Composite solid electrolytes are heterogeneous, multiphase, typically two-phase solid systems. The significant enhancement in ionic conductivity in LiI and other ion conducting materials on addition of submicron size particles of inert insulating second phase such as Al₂O₃, or SiO₂ is reported [1-5]. Two main aspects for understanding the conductance of composite materials are (i) the microscopic mechanism, which determines the magnitude of interfacial conductivity and (ii) the percolation theory [6,7]. These complexes are relatively inexpensive and can be easily processed as thin films for applications such as hydrogen sensors [8], electrochromic displays, and PEFC systems. During the present work, efforts were directed to prepare new proton conducting polymer electrolyte materials and

characterized for PEMFC/sensors device applications. A good number of attempts are made in the past and continuing to develop the fast solid proton conducting polymer electrolytes [9]. There is a growing interest in the use of fuel cells (FC) with hydrogen as the main fuel for stationary, mobile and transportation applications. In this context, different types of membranes based on PVA investigation are due to Nikolic et al. [10]. Water-soluble polymer, i.e. PVA used in practical applications because of its ease of preparation, excellent chemical and thermal stability along with good mechanical properties. The PVA/SiO₂ nanocomposites exhibit a significantly improvement in thermal resistance in comparison with the pure PVA [11].

During this work an attempt was made to improve further the proton conductivity of highest conductivity giving 80PVA:20AN complex polymer, the nano sized GDC was dispersed to obtain (100-x)(80PVA:20AN):(x)(GDC) nano-composite systems.

II. MATERIALS AND METHOD

Poly(vinyl alcohol) (PVA), with a degree of hydrolysis more than 99% and average molecular weight of 146000, was procured from Aldrich, USA. Ammonium nitrate (AN-(NH₄NO₃), gadolinium doped ceria (Ce_{0.8}Gd_{0.2}O₂/GDC) having particle size 100 nm, were obtained from Aldrich, USA. The double-distilled-deionized water was obtained using TKA, Germany, water purifier. The materials were Synthesized in the form of homogeneous and uniform film by solution cast technique.

The aqueous solutions with desired mole ratios of PVA:AN as (80:20), was prepared by dissolving PVA and AN separately in deionized water and then mixing them together. Later, this aqueous solution was thoroughly stirred for 8–10 h at 60–70 °C using magnetic stirrer so as to obtain the homogeneous single-phase solution. PVA is doped with ammonium nitrate and dispersed with GDC powder with compositions = (100-*x*) (80PVA:20AN):*x*(GDC), where *x* = 5, 10, 15, 20 and 25 wt%. The viscous gel mixture was then casted on the glass plate and dried for one week. The smooth and uniform films were obtained. All the prepared composite polymer electrolytes during present study were then thoroughly characterized using various analytical tools.

III. RESULTS AND DISCUSSION

X-ray Diffraction

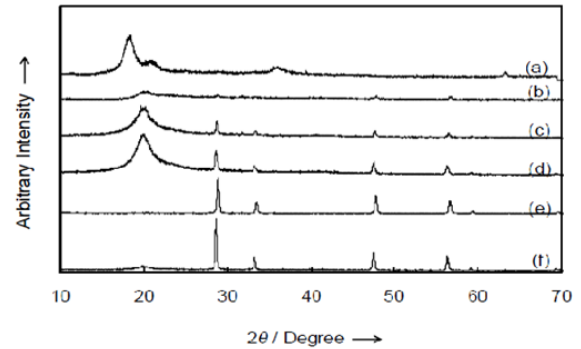


Fig. I : XRD patterns of (a) Pure PVA, (b) 95(80PVA:20AN):5GDC, (c) 90(80PVA:20AN):10GDC, (d) 85(80PVA:20AN):15GDC, (e) 80(80PVA:20AN):20GDC and (f) 75(80PVA:20AN):25GDC.

The XRD patterns of pure PVA and (100-*x*) (80PVA:20AN):(x) GDC (*x* = 5, 10, 15, 20 and 25 wt%) composite solid polymer electrolytes are shown in Fig.I.-(a) to (e) and (f), respectively.

Addition of filler GDC in polymer not only reduces the intensity of the characteristic (110) peak but also broadens, which is an indication of the increase in the degree of amorphousness. Chand et al. [12], also, reported the similar results. The interaction of the polymer chain with the filler (GDC) during the preparation of film usually increases the interlayer spacing of polymer chain and that tends to shift the diffraction peak towards lower angle [13]. But in the present case the peak shifts to higher diffraction angle suggesting decrease in inter planer distance. The characteristic peaks corresponding to GDC are clearly identified in 5wt% GDC (Fig.I(b)). The intensities of all characteristic peaks of filler GDC increases with an increase in its content in complex polymer. Evidently, the amorphousness of composite solid polymer electrolyte, in general, increases due to the addition of GDC filler as in the previous case of GDC addition. At higher concentration of filler (GDC), the GDC peak

appeared prominently due to formation of GDC clusters. The degree of amorphousness is compared in Table I.

Samples	X_C (%)
Pure PVA	40
95(80PVA:20AN):5GDC	35
90(80PVA:20AN):10GDC	30
85(80PVA:20AN):15GDC	25
80(80PVA:20AN):20GDC	17
75(80PVA:20AN):25 GDC	10

Table 1 : The degree of crystallinity obtained from XRD pattern for (100-x)(80PVA:20AN):(x) (GDC) composites.

Ionic Conductivity

Arrhenius plots for (100-x) (80PVA:20AN) : (x)(GDC) complexes when $x = 5, 10, 15, 20$ and 25 (in wt%) are shown in Fig.IV.37. All the samples obey the Arrhenius law. In this case also, the ionic conductivity of the nano composite polymer electrolyte increases with increasing the GDC filler concentration up to 20 wt%, beyond which conductivity decreases.

Furthermore, the magnitude of conductivity enhancement due to GDC addition is higher at low temperature vis-à-vis high temperature. Further, The activation energy is found to be minimum for the maximum conductivity giving composition.

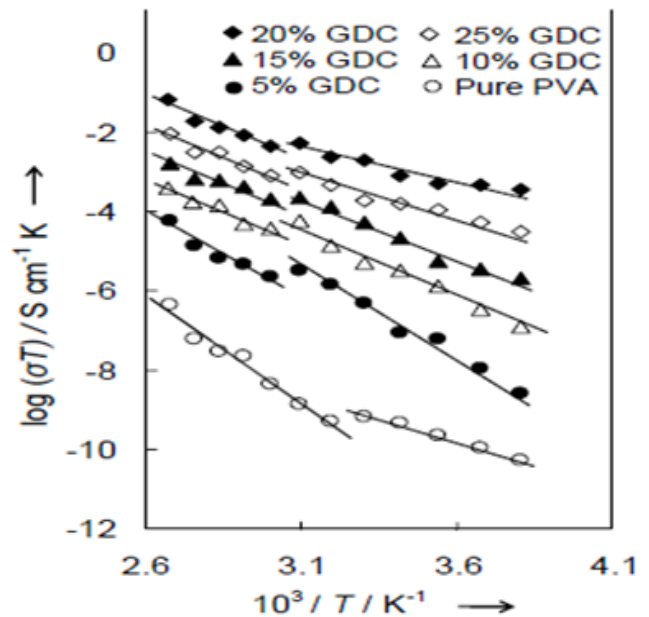


Fig.II: Arrhenius plots for different concentrations of GDC in (80PVA:20AN) polymer complex

The XRD results discussed already, revealed the dispersion of nano particles of GDC in 80PVA:20AN polymer complex. In other words, the GDC nano particle do not chemically react with polymer but are disperse uniformly in the polymer matrix. Since GDC is insoluble in PVA polymer it forms heterogeneous composite system and at about 20 wt% gave maximum conductivity (order of magnitude), the possibility of increased conductivity due to dissociation of salt is ruled out. The system under consideration is a heterogeneous i.e., there exists more or less sudden structural changes. The space charge region across the polymer/GDC interface is higher conducting compared to bulk polymer complex. The increase in conductivity up to 20 wt% of filler GDC in (PVA:AN) polymer complex is due to the increase in space charge layers in composites. The maximum conductivity at 20 wt% GDC added polymer is attributed to the percolation threshold where ion conducting paths throughout the polymer composites are optimum. Addition of filler in polymer complex beyond 20 wt% leads to aggregation of GDC particles which disrupts the proton percolating

paths across the film leading decrease in conductivity. Additionally, such aggregation of filler grains could make the long polymer chains more immobilized, leading to the decrease in the conductivity. Dissanayake et al. [14] have also reported the similar results for 80(80PVA:20AN):20GDC. The highest conducting 80(80PVA:20AN):20GDC Nano composite polymer electrolyte film was further studied in detail.

interface due to electrochemical reaction. Concurrently, more mobile charge carriers (H^+) are available for charge transport through the polymer electrolyte under external electric potential difference leading to an enhancement in conductivity.

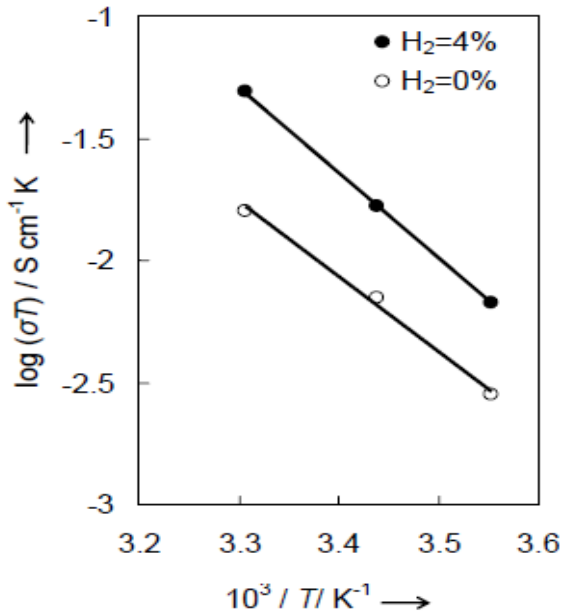


Fig. III (a) : Arrhenius plots of 80(80PVA:20AN):20(GDC) at fixed hydrogen concentration.

The Arrhenius plot for 80(80PVA:20AN):20GDC in presence of different hydrogen concentrations are shown in Fig.IIIa. In this system also the conductivity increases with an increase hydrogen concentration. Also, the proton conductivity increases, at fixed H_2 partial pressure, with an increase in relative humidity (Fig.III). The proton conductivity increases with increased relative humidity within entire studied range of H_2 partial pressures as shown in Fig.IIIb. The linear dependence of $\log(\sigma)$ on RH (%) and $\log(\sigma)$ on $\log(P_{H_2})$ are clear from Fig.III(a-c). As already discussed that the increased H_2 partial pressure at porous Pt-electrode increases H^+ concentration across Pt-electrolyte

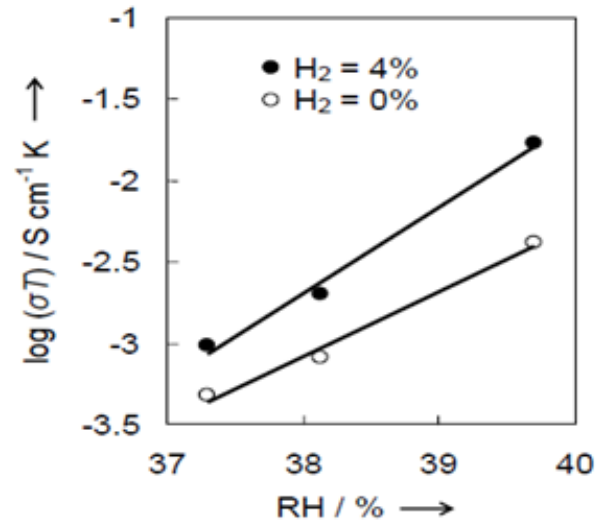


Fig. III (b): Variation of proton Conductivity with relative humidity at Constant hydrogen concentration

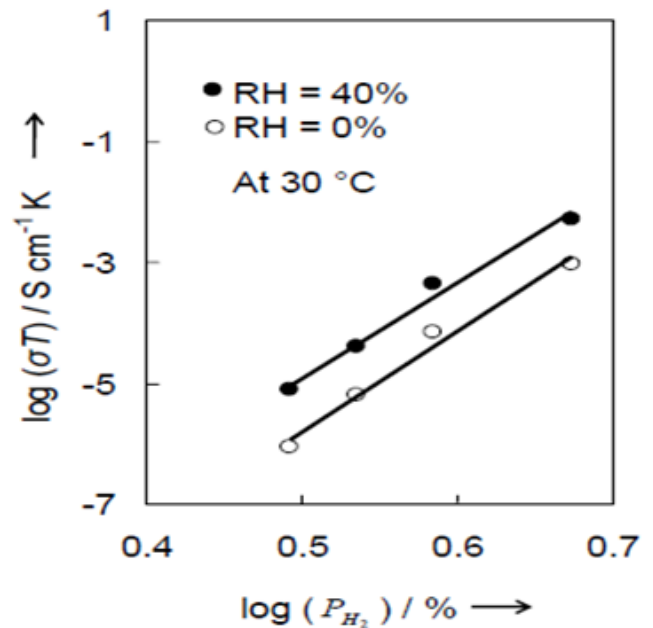


Fig.III(c): Variation of conductivity of 80(80PVA:20AN):20(GDC) with H_2 partial pressure at fixed (0.0 and 40%) relative humidity

IV. CONCLUSION

During this work a new type of proton conducting AN doped PVA and filler GDC were studied. PVA is doped with ammonium nitrate and dispersed with Gadolinium doped ceria powder with compositions = (100-x) (80PVA:20AN):x(GDC), where $x = 5, 10, 15, 20$ and 25 wt%. The XRD results revealed the dispersion of Nano particles of GDC in 80PVA:20AN polymer complex and at about 20 wt% gave maximum conductivity under normal atmospheric conditions. The ionic conductivity of the Nano composite solid polymer electrolyte initially increases with an increase in the filler GDC concentration up to 20 wt%; beyond this concentration conductivity decreases. The proton conductivity increases with increased relative humidity within entire studied range of H_2 partial pressures. Above all, PEFCs based on proton donor and filler hold the largest potential for developing low temperature PEFCs to be operated at room temperature.

V. REFERENCES

- [1]. C. C. Liang, J. Electrochem. Soc., 120 (1973) 1289.
- [2]. J. B. Wagner, Mater. Res. Bull., 15 (1980) 1691.
- [3]. K. Shahi and J. B. Wagner, Jr., J. Electrochem. Soc., 128 (1981) 6.
- [4]. O. Nakamura and J. B. Goodenough, Solid State Ionics, 7 (1982) 119.
- [5]. F. W. Poulsen, N. H. Andersen, B. Kindle and J. Scoonman, Solid State Ionics, 9/10 (1983) 131.
- [6]. T. Jow and J. B. Wagner, Jr., J. Electrochem. Soc., 135 (1988) 529.
- [7]. D. Stauffer, in Introduction to Percolation, Eds. Taylor and Francis, (London), (1985).
- [8]. R. Bouchet, E. Siebert, G. Vitter, J ElectrochemSoc 144(1997)L95-7.
- [9]. H. Pu, M. Luo and Z. Yang, Euro. Polym.J., 43 (2007) 5076.
- [10]. Z. Peng and L. X. Kong, Polym. Degrad. Stab., 92 (2007) 1061
- [11]. N. Chand, N. Rai, T. S. Natarajan and S. L. Agrawal, Fibers and Polym., 12 (2011) 438.
- [12]. Lord Raleigh, Phil. Mag. 34(1892) 481.
- [13]. M. A. K. L. Disaanayake, P. A. R. D. Jayathilaka, R. S. P. Bokalawala, I. Albinsson and B. E. Mellander, J. Power Sources, 119-121 (2003) 409
- [14]. J. Fleig and J. Maier, Solid State Ionics, 85 (1996) 9.