

Influence of TiO₂ as Filler on the Discharge Characteristics of a Proton Battery

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Received: August 31, 2015, Accepted: September 10, 2015, Available online: November 20, 2015

Abstract: Different concentrations of TiO₂ dispersed nano-composite proton conducting polymer electrolyte membranes were prepared using solution casting technique. Fourier Transform Infrared Spectroscopic analysis was carried out to determine the vibrational investigations about the prepared membranes. Variation of conductivity due to the incorporation of TiO₂ in polymer blend electrolyte was analyzed using Electrochemical Impedance Spectroscopy and the value of maximum conductivity is $2.8 \times 10^{-5} \text{ Scm}^{-1}$ for 1mol% of TiO₂ dispersed in polymer electrolytes. Wagner polarization technique has been used to determine the value of charge transport number of the composite polymer electrolytes. The electrochemical stability window of the nano-composite polymer electrolyte was analyzed using Linear Sweep Voltammetry. Fabrication of Proton battery is carried out with configuration of Zn+ZnSO₄.7H₂O+AC | Polymer electrolyte | MnO₂+AC. Discharge characteristics were investigated for polymer blend electrolytes and 1mol% TiO₂ dispersed nano-composite polymer electrolytes at constant current drain of 10 μ A. There is evidence of enhanced performance for proton battery which was constructed using 1mol% TiO₂ dispersed nano-composite polymer electrolytes compared to the blend polymer electrolytes.

Keywords: Proton battery, TiO₂, polymer electrolyte, nano-composite

1. INTRODUCTION

The field of solid polymer electrolytes played vital roles in last few decades due to their significant theoretical and experimental interest as well as practical importance for the development of electro chemical devices and energy conversion units such as batteries, fuel cells, humidity and gas sensors, electrochromic display devices, photoelectrochemical solar cells etc., [1-4]. All solid state electrochemical power sources are in need of high ionic conducting polymer electrolytes [5]. Many approaches are accomplished in order to enhance the ionic conductivity of polymer electrolytes such as polymer blending [6], binary salt systems [7]. Addition of plasticizer [8], dispersion of filler [9] are some of the ways to improve the ionic conductivity while maintaining the mechanical strength [10] which is necessary for device applications. In the present study, both blending and filler dispersion techniques are

adopted to prepare proton conducting nano-composite polymer electrolytes. Blending of poly (methyl methacrylate) [PMMA] and poly (vinyl pyrrolidone) [PVP] and dispersion of nano -size TiO₂ particles in methanesulfonic acid [MSA] doped blend polymer electrolytes were carried out. PMMA and PVP are chosen as the host polymers because both contain carbonyl groups as well as PVP possess faster ionic mobility when compared to other polymers [11,12]. MSA is described as a “green acid” due to its environmental advantages [13] and used as an ideal catalyst for esterification because of good kinetics and ease of handling. Very few researchers have focused investigation about TiO₂ dispersed nano-composite. It was reported that the magnitude of conductivity was increased with the incorporation of TiO₂ filler in poly (vinyl pyrrolidone) based host polymer and the performance of nano-composite polymer electrolyte in the electrochemical cell was also studied [14]. The effect of nano-sized TiO₂ on the conductivity and mechanical stability of PMMA based Lithium ion conducting gel polymer electrolytes was studied [15]. The transport properties and

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the ionic conductivity of TiO₂ dispersed nano-composite polymer electrolytes were improved when compared to pure PEO-LiClO₄ polymer electrolytes for Lithium ion batteries [16]. From the literature survey, it was found that dispersion of TiO₂ in the polymer host enhanced the electrical, mechanical and transport properties of the solid polymer electrolytes.

In the present work, nano-composite blend polymer electrolytes were prepared by solution casting technique and the effect due to the incorporation of TiO₂ in blend based polymer electrolytes on the vibrational, electrical and electrochemical stability property is discussed and also proton battery performance is compared with filler dispersion and without filler dispersion polymer electrolytes.

2. EXPERIMENTAL

Poly methyl methacrylate (PMMA) (M_w=15,000), poly vinyl pyrrolidone (PVP) K₃₀ (M_w=40000), N,N-Dimethyl formamide (DMF) (HIMEDIA), Methanesulfonic acid (MSA) (Sd Fine-Chemical) and Titaniumdioxide (TiO₂) of size 27.03 nm (Alfa aesar) were the materials used in the preparation of nano composite proton conducting solid polymer electrolytes. PVP was dissolved in DMF at 70°C and preheated PMMA at 70°C was added to it. MSA was added to it after 5 hours. PMMA, PVP were blended in ratio of 1:1 and the concentration of MSA was fixed as 14.04 mol%. By varying the concentrations of TiO₂, we were obtained different compositions of nanocomposite polymer electrolytes. The prepared samples were stirred for the time duration of 48 hours for the proper dispersion of TiO₂ nanoparticle in the polymer electrolyte. The formed solid polymer electrolytic solutions were transferred to the polypropylene petri dishes and kept in hot air oven at 70°C for 12 hours. The obtained free standing films were stored in vacuum desiccators for further characterization.

Fourier Transform Infrared spectra of the prepared samples were recorded using Fourier Transform Infrared spectrometer (JASCO 4100, Japan) in the wave number range between 550 and 4000 cm⁻¹. Microscopic images of the prepared sample surface were taken out using an Optical Microscope (OLYMPUS BX51M, Japan). Electrochemical measurements of the prepared samples were measured using Electrochemical Workstation (IM6 ZAHNER, Germany) within the frequency range between 100 mHz and 1 MHz at different isothermal values. AC impedance data were measured with the aid of IM6 Zahner elektrikwork station in the frequency range of 100mHz to 1MHz at different isotherms. Transport numbers were determined by placing the polymer electrolyte between two stainless steel electrodes using Wagner's polarization technique. Variation of current with respect to time was monitored by applying a DC voltage of 1 V. Linear Sweep Voltammetry, Transport number measurements and Discharge characteristics were determined using an Electrochemical analyzer (Bio Logic SP 300, France) interfaced with the computer. The decomposition potential of the polymer electrolyte was determined by means of Linear Sweep Voltammetry. The prepared polymer electrolyte was sandwiched between Stainless Steel, MnO₂ as counter and working electrode with fixed scan rate of 5 mV/sec. The applied potential to the working electrode was varied linearly in the range between 0 and 2 V and the corresponding current values were estimated. Proton batteries were constructed using configuration Cell 1 consisting of Zn+ZnSO₄.7H₂O+AC | Blend proton conducting Polymer electrolyte | MnO₂+AC and Cell 2 consisting of Zn+ZnSO₄.7H₂O+AC |

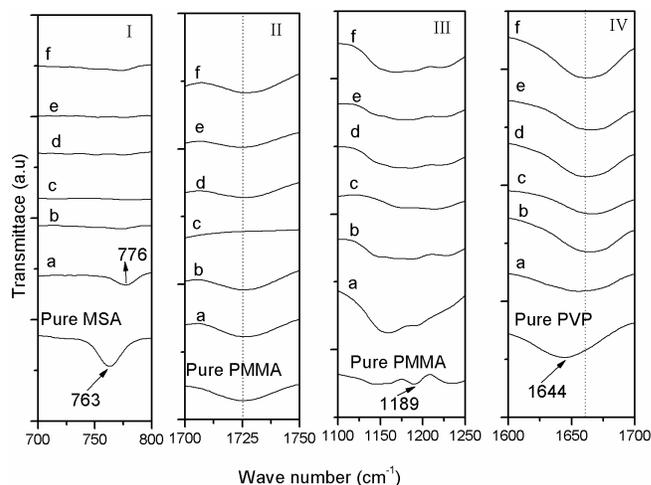


Figure 1. FTIR spectrum of : (a) 0mol% of TiO₂ (b) 0.5mol% of TiO₂ (c) 1mol% of TiO₂ (d) 1.5mol% of TiO₂ (e) 2mol% of TiO₂ (f) 2.5mol% of TiO₂

Nano composite blend polymer electrolyte | MnO₂+AC and discharge characteristics of the fabricated Proton batteries were determined.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

Fourier Transform Infrared spectroscopy was carried out to determine the stretching and bending vibrations of the prepared samples. FTIR spectra of samples are shown in Figure 1. Methanesulfonic acid can be dissolved in polymer blend matrix of PMMA/PVP by virtue of coordinative interaction between MSA and polar groups present in the polymers [17]. The appearance of characteristic peaks at 763 cm⁻¹, 981 cm⁻¹ and 1137cm⁻¹ corresponds to MSA, ν_s (C-S), ρ_{s+as}(CH₃) and ν_{as} (SO₃⁻) respectively [18]. The symmetric stretching of C-S bond in MSA is shifted from 763 to 776cm⁻¹ in polymer blend electrolyte and it is disappeared in nano composite as shown in Figure 1(I). The peaks appeared at 1725cm⁻¹ and 1189cm⁻¹ may be attributed to the stretching of C = O and C – O modes in pure PMMA, respectively [19]. There is no discrete shift in peak of C = O in PMMA is observed which is shown in Figure 1(II, III). Also, the peak corresponding to C-O is shifted in proton conducting polymer nano composites. It indicates that MSA prefers C-O group more than C=O group of PMMA interaction. An observation of intense peak at 1644 cm⁻¹ can be attributed to C=O stretching of pure PVP. The position of the observed peak is shifted which is shown in Figure 1(IV) for filler free and filler incorporated polymer electrolytes which indicates that there is an interaction between MSA and C = O group of pure PVP.

3.2. Conductance spectra analysis

Logarithmic variation of conductivity as a function of frequency for various compositions of prepared TiO₂ samples is shown in Figure 2a. At lower frequencies, the value of conductivity is found to be low and is due to the space charge polarization at the electrode-electrolyte interface. The observation of plateau part in the

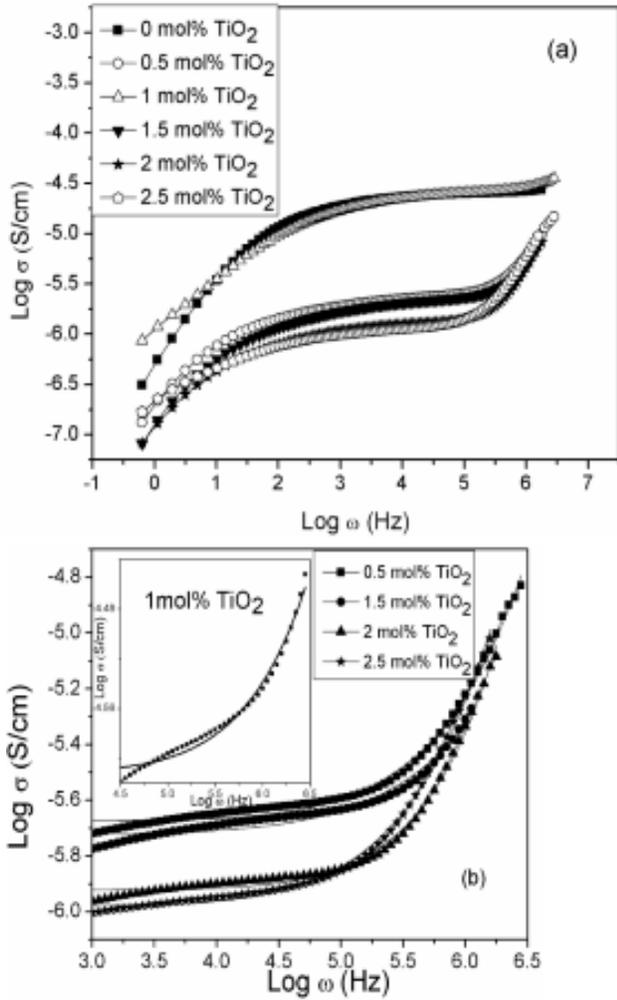


Figure 2. a. Conductance spectra for various concentration of TiO₂ dispersed proton conducting polymer electrolyte membrane, b. Nonlinear least square fitted conductance plot

mid frequency region correspond to hopping motion of the mobile ions that indicates that the charge carriers have sufficient time to hop from one site to next site. By the extrapolation of plateau region to the value of zero frequency gives the value of dc conductivity (σ_{dc}). The value of σ_{dc} obtained at ambient temperature for different concentration of TiO₂ incorporated nano composites are

given in Table 1. The incorporation of TiO₂ in the blend polymer electrolytes results in enhancement of conductivity. This is due to the lewis acid-base interaction centers present in the electrolyte which lessens ionic coupling that promote salt dissociation.

The distribution of frequency is found to be high due to coulombic interaction between charge carriers and disorder within the structure. The conductivity $\sigma(\omega)$ obeys Jonscher's power law such as $\sigma(\omega) = \sigma_{dc} + A\omega^n$ [20], where n, is the power law exponent in the range between 0 and 1 ($0 < n < 1$), A is the temperature dependent constant. The value of n is given by the Jump relaxation model which is given by [21].

$$n = \frac{\text{backhoprate}}{\text{Siterelaxationtime}} \quad (1)$$

If $n < 1$, the backward hopping is slower than the site relaxation time, whereas $n > 1$ backward hopping is faster than the site relaxation time. The parameter n is extracted from the conductance spectra by using a non-linear least square fitting procedure and is shown in Figure 2b. The n value is found to be greater than 1 for all the filler dispersed proton conducting polymer electrolytes and its values are given in Table 1. This n value shows the presence of bad site for the next hop or due to coulombic interaction between the mobile ions and is found lesser value for 1 mol% of TiO₂ dispersed membrane which denotes that the value of back hop rate is lower.

3.3. Transport number measurements

Wagner's polarization technique is used to find out the transport number of ions [22]. Figure 3 shows the time dependence of current across 1 mole % of TiO₂ dispersed nano composite polymer electrolytes. The prepared nano composite polymer electrolytes are placed in between the two Stainless Steel electrodes. At initial stage, the flow of current through the membrane is found to be large, afterwards it decreases and attained its constant value within few seconds. Transference numbers of ion and electrons are calculated using the below mentioned Eq.'s.

$$t_{ion} = \frac{I_i - I_f}{I_i} \quad (2)$$

$$t_{els} = \frac{I_f}{I_i} \quad (3)$$

where I_i is the initial current and I_f is the final current. The transport number values for ions (t_{ion}) are calculated using Eq.(2) and its value is found to be in the range between 0.93 and 0.98 for the prepared membranes. It suggested that transport of charge carri-

Table 1. Conductivity values of the prepared nano composite proton conducting polymer electrolyte membrane

Composition (PMMA:PVP = 1:1)	Conductivity (σ_{dc})	n	χ^2
42.98(PMMA:PVP):14.04MSA:0TiO ₂	2.5×10^{-5}	-	-
42.73(PMMA:PVP):14.04MSA:0.5TiO ₂	2.0×10^{-6}	1.1562	0.99
42.49(PMMA:PVP):14.02MSA:1TiO ₂	2.8×10^{-5}	1.0957	0.99
42.245(PMMA:PVP):14.01MSA:1.5TiO ₂	2.1×10^{-6}	1.1043	0.97
42.005(PMMA:PVP):13.99MSA:2TiO ₂	1.2×10^{-6}	1.2285	0.99
42.765(PMMA:PVP):13.97MSA:2.5TiO ₂	1.1×10^{-6}	1.3221	0.99

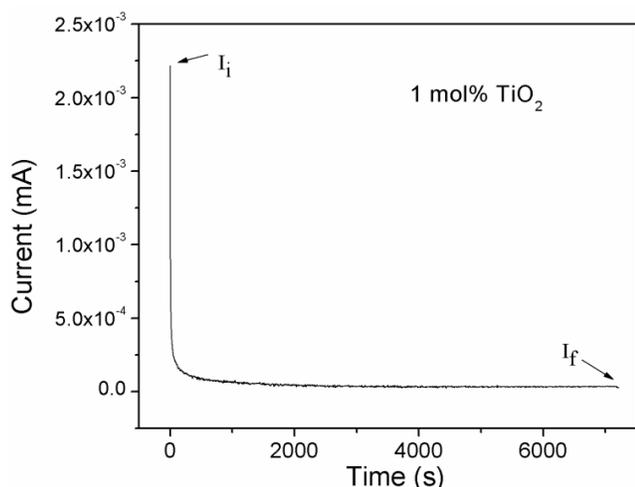


Figure 3. Polarization current Vs time plot for 1mol% of TiO_2 dispersed polymer electrolyte

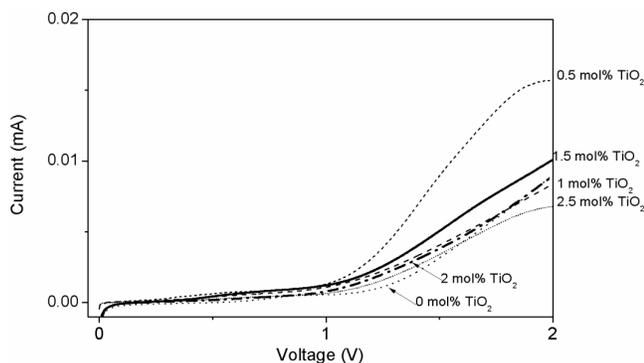


Figure 4. Electrochemical stability plot for all the prepared nano composite polymer electrolytes

er takes place in the prepared nano composite is predominantly due to the motion of ions.

3.4. Electrochemical stability

Electrochemical stability is an important parameter in the evaluation of viability of the polymer electrolyte membranes which is generally termed as Linear Sweep Voltammetry. Electrochemical stability window of the prepared nanocomposite polymer electrolyte membranes is determined with MnO_2 coated Cu foil as working electrode and stainless steel as counter electrode, respectively. Linear sweep voltammogram of prepared membrane is shown in Figure 4. It is noted that there is no obvious change of current is observed upto 1 V which may be due to the necessity of electrolyte usage in the Proton battery [23]. The corresponding voltage value of filler free and 1mol% of filler dispersed proton conducting polymer electrolyte is found to be 1.7 and 1.5 V at 0.005 mA, respectively.

3.5. Battery characterization

The construction of proton battery is carried out with the help of

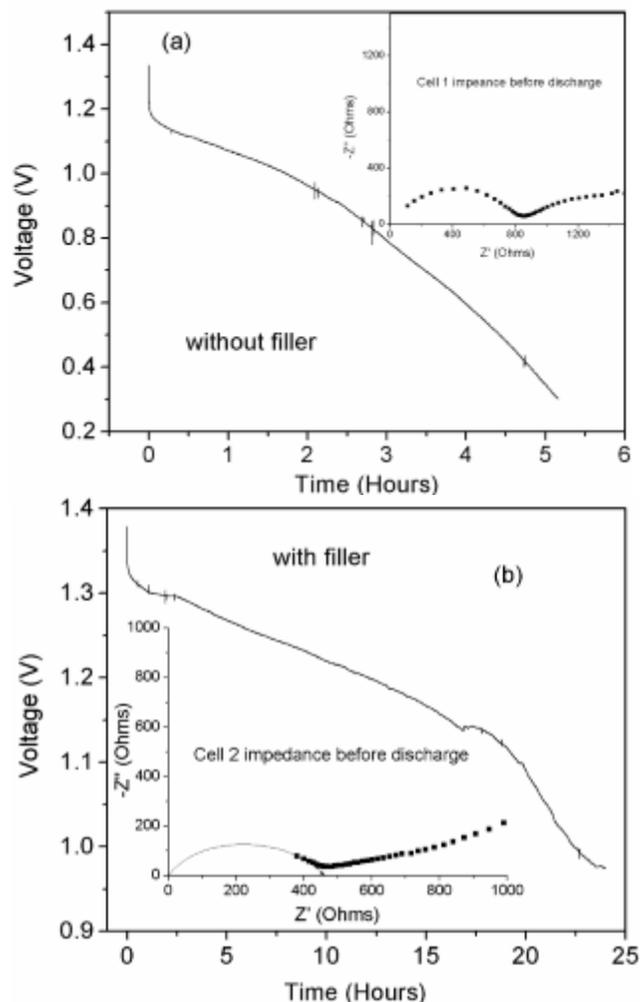


Figure 5. a. Discharge characteristics of the proton battery constructed using blend polymer electrolytes, b. Discharge characteristics of the proton battery constructed using nano composite blend polymer electrolytes.

filler free and 1mol% of TiO_2 dispersed proton conducting polymer electrolyte membrane. Proton batteries are constructed by placing a proton conducting polymer electrolyte in between the anode and the cathode pellets [24]. The anode, cathode consist of Zn (metal powder) (50wt%) + $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (40wt%) + Activated Carbon (AC) (10wt%), MnO_2 (80wt%) + Activated Carbon (AC) (20wt%). Solid blend proton conducting polymer electrolyte acts as separator 1 and Solid nano composite (1mol% TiO_2 dispersed) proton conducting polymer electrolyte as separator 2. Two proton batteries are assembled using separator 1 and separator 2 as cell 1 and cell 2. Anode-Separator-Cathode assembly is placed in between the Stainless Steel plates (Current Collectors) and it is clamped tightly to attain proper contact. Figure 5a and 5b show the discharge characteristics of proton battery for Cell 1 and Cell 2 at $10\mu\text{A}$ respectively. Cell 1 and Cell 2 attained a potential value 1V within 1.72 hours and 22.49 hours, respectively which is taken as the plateau region for the current drain of $10\mu\text{A}$. The parameters determined for the

fabricated Cells (Cell1 and Cell2) are given in Table 2. It is observed that there is improvement in electrochemical performance which is due to the incorporation of filler in the PMMA/PVP based blend polymer electrolyte membrane. Filler in the blend based polymer electrolytes may improve the chemical and physical compatibility of the electrolyte with respect to the electrodes and also it may promote the interfacial contact between electrode and electrolyte. The interfacial resistance between electrode and electrolyte is decreased for the TiO₂ dispersed polymer electrolyte when compared to the filler free polymer electrolyte which is shown in inset of figure 5(a) and 5(b).

Cell 1: Zn+ZnSO₄.7H₂O+AC | Separator 1 | MnO₂+AC
Cell 2: Zn+ZnSO₄.7H₂O+AC | Separator 2 | MnO₂+AC

4. CONCLUSIONS

TiO₂ incorporated nano composite polymer electrolyte membranes were successfully prepared using conventional solution casting technique. Complex nature is evidenced through the shifting of characteristic peaks of PMMA and PVP in the FTIR spectrum of the prepared nano composite proton conducting polymer electrolytes. The maximum conductivity value of 2.8×10^{-5} S/cm was obtained for 1mol% of TiO₂ dispersed nano composite polymer electrolyte. The ionic transference number showed that the charge transport in these polymer electrolytes was mainly due to the movement of ions. The window was found to be electrochemically stable due to the dispersion action of TiO₂. The parameters were evaluated and compared for two proton batteries constructed with blend polymer electrolytes and nano composite polymer electrolytes. The energy density of the proton battery constructed with blend polymer electrolytes and nano composite polymer electrolytes was 0.24WhKg⁻¹ and 3.04WhKg⁻¹ respectively. Due to the incorporation of filler, the discharge characteristics of the proton battery were found to be improved.

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Table 2. Cell Parameters of the constructed proton battery

Cell parameters	Cell 1	Cell 2
Cell weight/g	0.43	0.46
Effective area of the cell/cm ²	1.32	1.32
Mass of the active material/mg	104	104
Open circuit voltage/V	1.43	1.4
Current drain/μA	10	10
Time for plateau region/hours	1.72	22.49
Discharge capacity/μAh	17.2	224.9
Power density/WKg ⁻¹	0.138	0.135
Current density/ μAcm ⁻²	7.58	7.58
Energy density/WhKg ⁻¹	0.24	3.04