

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Comparison of filler free and nano composite polymer electrolyte in the discharge characteristics of proton battery

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Abstract: Filler free and nano composite polymer electrolytes were prepared by solution casting technique. The nano composite solid polymer electrolyte was prepared by incorporating Al₂O₃ filler of size 6.673nm at different compositions. Ionic conductivity measurements were performed in the frequency and temperature range of 100mHz-1MHz and 303K-373K, respectively. The conductivity of filler free and nano composite solid polymer electrolytes (NCSPE) was in the order of 10⁻⁵S/cm. Using these polymer electrolytes, proton battery was fabricated with the configuration of Zn+ZnSO₄.7H₂O+AC/ NCSPE /MnO₂+AC. The discharge characteristics were studied under constant current drain of 0.01mA. The open circuit voltage for filler free and nano composite polymer electrolyte incorporated proton battery was measured for 24 hours of duration.

Keywords: nano composite, proton battery, discharge, constant current drain.

1. Introduction:

Most of the research is devoted to find the materials forelectrochemical energy storage devices that play a tremendous role in technical applications like computers, communication devices, industrial controls, electricvehicles, space ships etc.[1]. Consequently much attention has been focused in the development of batteries, fuel cells etc. Batteries constitute an important component in the techno-economic growth. The usage of solid polymer electrolytes (SPE) in the batteries provides an added advantage that the mechanical strength enhances and favors the gain in electrochemical properties. Research has been focusing to tailor a solid polymer electrolyte possesses high ionic conductivity as well as good mechanical strength.

Blending of one or more polymers is one of the techniques to enhance the ionic conductivity. Consequently in the current work, PMMA and PVP have been made into a blend with the ratio of 50:50. Methanesulfonic acid is chosen as a proton provider. It was reported that the addition of insulating fillers in the polymer electrolytes not only enhance the ionic conductivity but also enhancement of mechanical strength of the polymer electrolytes[2]. Hence, the mechanical strength of the blend polymer electrolyte is expected to be improved by the addition of nano-sized inorganic filler ie., Al₂O₃(6.673nm).

According to the literature investigations, few reports onall solid state proton batteries have been sighted. The ionic conductivity and discharge characteristics of TiO₂ dispersed proton conducting cellulose

acetate based gel polymer electrolytes were carried out[3]. The nano composite proton conducting solid polymer electrolytes were prepared by dispersing SiO₂ in PEO matrices and the optimized membrane has been utilized for proton battery fabrication. The discharge characteristics of the assembled proton batteries were compared by varying the cathode material[4]. In the present paper, the ionic conductivity of the prepared nano composite polymer electrolytes is studied and the effect of filler on the discharge characteristics of the prepared solid polymer electrolyte is also compared.

2. Experimental:

PMMA (poly methyl methacrylate)(M_w=15,000) (Himedia), PVP (polyvinyl pyrrolidone)(K₃₀) (Himedia), MSA (Methanesulfonic acid) (SDFCL), Al₂O₃ (Aluminiumoxide) (Alfa Acer) and N,N-Dimethyl Formamide(Himedia) were used as the raw materials for the preparation of solid polymer electrolyte. Filler free and nano composite solid polymer electrolytes were prepared by mixing PMMA and PVP in suitable ratios and dissolved in DMF at 70°C under vigorous stirring for 1 day. Required amount of MSA was added to it. After 1 hour, nano-sized Al₂O₃ filler was dispersed in the electrolyte solution. Stirring was continued for another 1 day to get the homogeneous solution. Then this homogeneous solution was transferred to poly propylene dishes which were kept in oven at 70°C for complete evaporation of DMF. Then the dry polymer electrolyte was utilized for characterization. The prepared solid polymer electrolytes were listed in the table 1.

Table 1: Various compositions of filler incorporated SPEs.

Sample code	Composition (mol%)			
	PMMA	PVP	MSA	Al ₂ O ₃
AL0	42.98	42.98	14.04	0
AL1	42.475	42.475	14.05	1
AL2	41.975	41.975	14.05	2
AL3	41.48	41.48	14.04	3
AL4	40.98	40.98	14.04	4

The electrical behavior of solid polymer electrolyte was carried out using ac impedance spectroscopy. The complex impedance parameters were measured with the aid of IM6 Zahner elektrik workstation in the frequency range of 100mHz to 1MHz.

Filler free and high conducting nano-composite polymer electrolytes were utilized to fabricate a proton battery. Anode (Zn(0.5g), ZnSO₄.7H₂O(0.4g) and Activated carbon (0.1g)) and cathode (MnO₂(0.8g) and Activated carbon(0.2g)) [5,6] were made into a pellet of thickness ~ 0.4 mm and the diameter was 13 mm. The solid polymer electrolyte of appropriate size was placed in between anode and cathode. Stainless steel plate was used as a current collector which was made into an attachment with cathode and anode. The open circuit voltage and the discharge characteristics at constant current drain were studied using Biologic electrochemical workstation (Biologic SP-300, France).

3. Result and discussion:

3.1. Conductivity Analysis:

The ionic conductivity values for nanocomposite polymer electrolytes containing different concentration of Al₂O₃ are presented in the table 2. When the nano filler is incorporated in the blend based polymer electrolytes, the conductivity is not enhanced. This is due to the fact that Al₂O₃ is not attributed to the formation of high degree of amorphous nature in the polymer system[7].

Table 2: Conductivity values calculated from Cole-Cole plot and conductance spectra at ambient temperature

Sample	Conductivity (S/cm) (Cole-Cole plot)	Conductivity (S/cm) (Conductance plot)	χ^2
AL0	2.51×10^{-5}	-	-
AL1	5.79×10^{-6}	5.38×10^{-6}	0.99

AL2	1.05×10^{-5}	1.08×10^{-5}	0.99
AL3	1.90×10^{-7}	1.87×10^{-7}	0.99
AL4	2.50×10^{-6}	2.16×10^{-6}	0.98

The order of conductivity of 2 mol% Al₂O₃doped blend electrolyte is same as that of the blend electrolyte without filler content. Ionic conductivity declined on further increase of Al₂O₃ content.

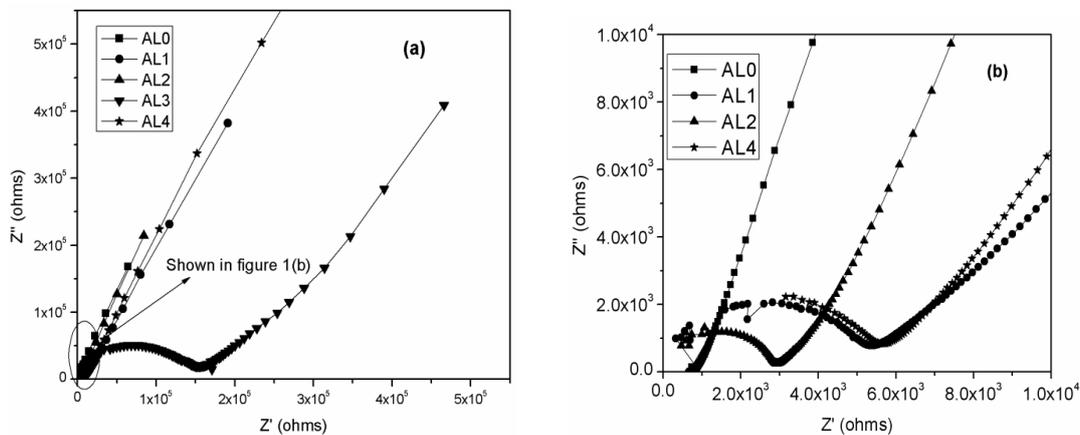


Figure 1.(a) Cole-Cole plot for the prepared filler free and nano composite solid polymer electrolytes at ambient temperature (b) Cole-Cole plot for AL0, AL1, AL2, AL4 in high frequency region.

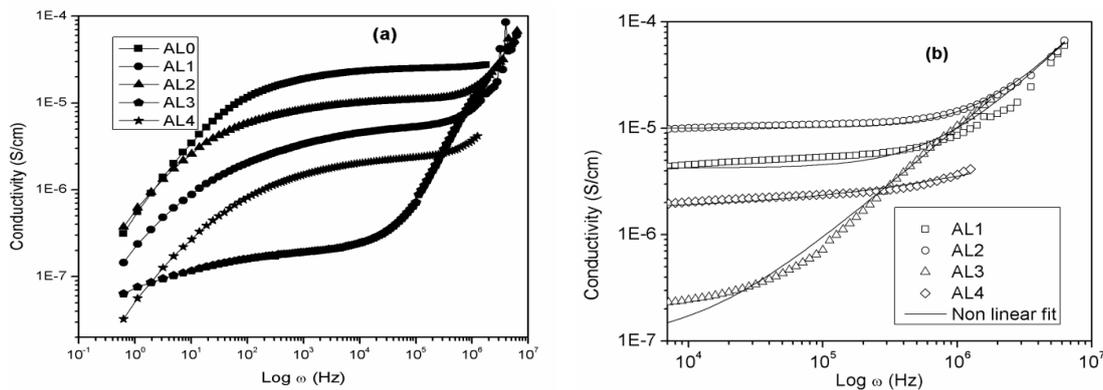


Figure 2. (a) Frequency dependent conductivity plot for filler free and nano composite solid polymer electrolytes (b) Fitted conductivity plot

The conductivity values of the composite solid polymer electrolytes can be determined by two methods. One is by Cole-Cole plot (shown in figure 1) and the other is by conductance spectrum (shown in figure 2). From the Cole-Cole plot, the conductivity values are calculated by using the formula

$$\sigma = \frac{t}{R_B A} \text{-----(1)}$$

wheret and A are the thickness and area of the polymer electrolyte. R_B is the bulk resistance which can be determined by the low frequency intercept of the semicircle or high frequency intercept of inclined line on the x-axis.

Ionic conductivity values from the conductance spectra is determined by fitting the curve using non-linear least square fit ($\sigma_{ac} = \sigma_{dc} + A\omega^n$) in the high frequency region which is shown in figure 2. The high frequency dispersion is obtained only for Al₂O₃ dispersed polymer electrolytes which correspond to the bulk relaxation phenomena[8]. The conductivity values calculated from the Cole-Cole plot and from the conductance spectraare nearly same as expected.

3.2. Open circuit voltage (OCV):

The fabrication of a proton battery is briefly explained in the experimental part. Two proton batteries are constructed. One with filler free solid polymer electrolyte (AL0) and the other with nano composite membrane (AL2) which shows high conductivity among other prepared nano composite polymer electrolyte. Figure 3 shows the open circuit voltage of two sort of proton battery as a function of time. The open circuit voltage of both the batteries is near the same for 24 hours of duration.

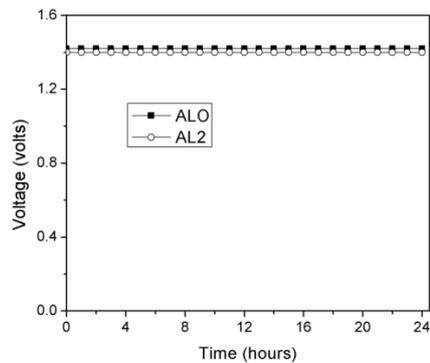


Figure 3: Open circuit voltage for proton battery constructed by without and with filler solid polymer electrolyte

3.3. Discharge characteristics:

The discharge characteristic of two sort of proton battery at constant current drain of 0.01mA is shown in figure 4 and 5. The proton battery constructed by using filler free proton conducting polymer electrolyte is discharged to cut-off potential 0.3V within 6 hours. From the figure 4, there is no plateau region is observed. The proton battery constructed by using nano composite shows the plateau region. This shows that the incorporation of inorganic nano filler in the solid polymer electrolyte enhances the electrochemical behavior of the battery.

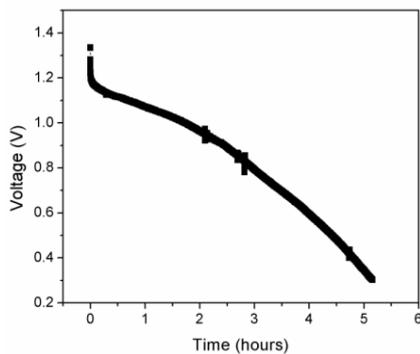


Figure 4: Discharge characteristics of proton battery fabricated by using filler free solid polymer electrolyte at constant current drain of 0.01mA

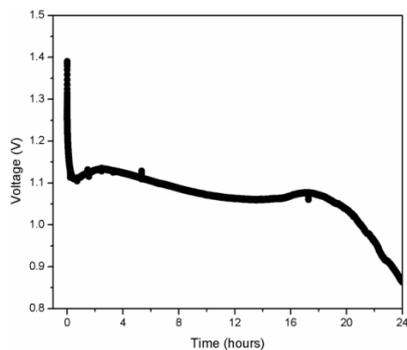


Figure 5: Discharge characteristics of proton battery fabricated by using high conducting nano composite solid polymer electrolyte at constant current drain of 0.01mA

4. Conclusion:

The proton conducting solid polymer electrolyte of with and without filler incorporation were prepared by using solution casting technique. The conductivity values of the prepared solid polymer electrolytes have been calculated by using Cole-Cole and conductance plot. The open circuit voltage for the proton battery constructed by using filler free and high conducting filler incorporated polymer membrane was monitored for 24 hours and it was 1.42V and 1.4V respectively. Even though the filler dispersed membrane show less conductivity when compared to filler free membrane, the plateau region of proton battery constructed by filler incorporated solid polymer electrolyte show large value. Discharge characteristics of proton battery which contain filler incorporated membrane are found to be performing better when compared to filler free membrane. Due to the incorporation of filler in solid polymer electrolyte, the electrochemical behavior is improved.

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