



# COMPARATIVE ELECTRICAL AND ELECTROCHEMICAL PERFORMANCE OF PROTON CONDUCTING POLYMER NANOCOMPOSITES BASED ON TiO<sub>2</sub> AND Al<sub>2</sub>O<sub>3</sub> FILLERS

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## ABSTRACT

Two different systems of nanocomposite blend solid proton conducting polymer electrolytes based on PMMA/PVP with MSA as proton provider dispersed with nano fillers such as TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are prepared by solution casting technique. The maximum conductivity value of  $2.82 \times 10^{-5}$  S/cm is observed for the 1 mol% of TiO<sub>2</sub> dispersed nanocomposite blend solid polymer electrolytes. The maximum conducting sample in each set of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> dispersed nanocomposite solid polymer electrolyte is used for the construction of proton battery as electrolyte. Electrochemical impedance value is calculated for the fresh cells. The discharge characteristics are monitored for 0.01 mA of current drain. The energy density of the proton battery constructed with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> dispersed nanocomposite polymer electrolytes are 3.16 and 2.82 Wh/Kg respectively. The cell performance of TiO<sub>2</sub> based nanocomposite polymer electrolyte found better than the Al<sub>2</sub>O<sub>3</sub> based nanocomposite polymer electrolyte.

**Key words:** Nanocomposite solid polymer electrolytes, Electrochemical stability window, Proton battery, Discharge characteristics, Electrochemical impedance.

## INTRODUCTION

The particle size and the physical nature of the dispersed particles in polymer electrolyte play a significant role<sup>1</sup>. Nowadays, polymeric nanocomposites that are composed of inorganic nanoparticles and polymeric material are of great interest because the addition of nanoparticles enhances properties such as ionic conductivity, thermal stability, mechanical strength etc. The effects of dispersing insulating ceramic filler particles such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> etc on various electrolytic properties of nanocomposite solid polymer electrolytes are investigated by various workers<sup>2,3</sup>. The uses of different active and passive fillers have their own technical highlights in the device application and also each filler has

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different significant effect in polymer electrolyte systems. Hence in the present work, electrical and electrochemical variation due to the incorporation of two different fillers ( $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) in PMMA-PVP<sub>K30</sub>-MSA based blend polymer electrolytes is discussed.

## EXPERIMENTAL

### Method

PMMA (poly methyl methacrylate) (HIMEDIA) and PVP (poly vinyl pyrrolidone) (HIMEDIA) were chosen as the host polymers. PVP<sub>K30</sub> was initially dissolved in DMF (N,N-Dimethyl formamide) (Merck) at 70°C. Then, the preheated PMMA was added. Stirring was continued for several hours to obtain a clear blend solution. Required amount of MSA (Methanesulfonic acid) (Sd-fine chem.) was added. After 24 hrs of stirring, calculated quantity of  $\text{TiO}_2$  (size-27 nm) (Alfa acer)/ $\text{Al}_2\text{O}_3$  (size-6.7 nm) was added. Finally, the obtained homogeneous nanocomposite solution was transferred to polypropylene petridishes and kept in oven for 12 hrs for complete evaporation of solvent. Proton battery construction was already discussed in ref<sup>4</sup>.

Electrical study was carried out by using the electrodes as stainless steel and the separator as the prepared nanocomposite polymer electrolytes. AC impedance data for this electrical analysis recorded using IM6 Zahner elektrik workstation, in the frequency range of 100 mHz to 1MHz at room temperature. Electrochemical study of the proton battery is carried out by using Biologic SP-300 work station.

## RESULTS AND DISCUSSION

### AC impedance analysis

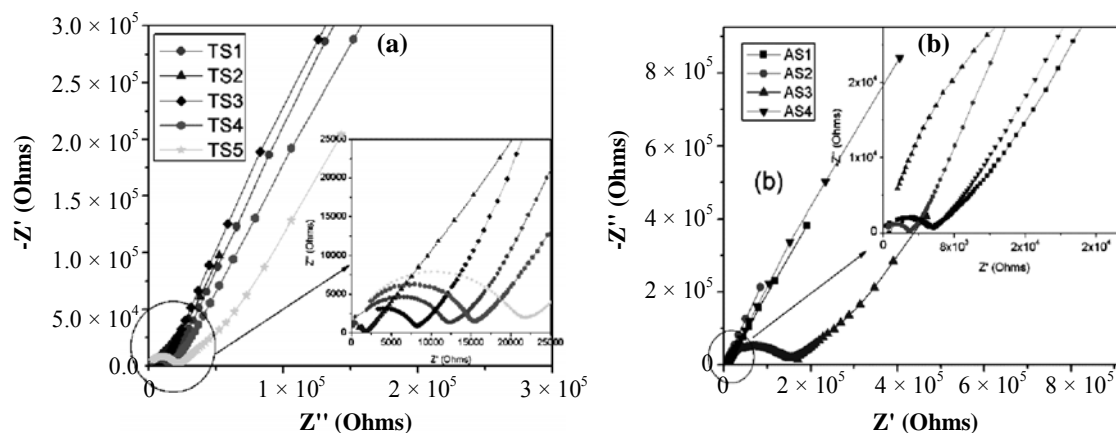
The complex impedance plot for PMMA-PVP<sub>K30</sub>-MSA- $\text{TiO}_2$ , PMMA-PVP<sub>K30</sub>-MSA- $\text{Al}_2\text{O}_3$  nanocomposite solid polymer electrolytes at different concentration of filler are shown in Figs. 1(a) and 1(b), respectively. The composition and their conductivity values from the Cole-Cole plot is given in Tables 1 and 2 for PMMA-PVP<sub>K30</sub>-MSA- $\text{TiO}_2$  and PMMA-PVP<sub>K30</sub>-MSA- $\text{Al}_2\text{O}_3$ , respectively. The Cole-Cole plot consists of both semicircular arc and spike. The bulk electrical resistance value ( $R_B$ ) is calculated from the intercept on the real part of the impedance ( $Z'$ ) axis and the conductivity value can be calculated from the relation  $\sigma = L/R_B A$  where L and A are the thickness and area of the sample respectively. From table 1 and 2, it is inferred that the conductivity value is maximum for 1 mol%  $\text{TiO}_2$  and 2 mol%  $\text{Al}_2\text{O}_3$  filler dispersed blend polymer electrolytes and it is in the order of  $10^{-5}$  S/cm.

**Table 1: Composition and conductivity values of PMMA:PVP<sub>K30</sub>:MSA:TiO<sub>2</sub> nano-composite solid polymer electrolytes**

Sample code	Compositions (mol%) (PMMA:PVP <sub>K30</sub> :MSA:TiO <sub>2</sub> )	Conductivity (S/cm) at 303 K
TS1	42.73 : 42.73 : 14.04 : 0.5	$2.10 \times 10^{-6}$
TS2	42.49 : 42.49 : 14.02 : 1	$2.82 \times 10^{-5}$
TS3	42.24: 42.24:14.02 : 1.5	$2.20 \times 10^{-6}$
TS4	42.01: 42.01 : 13.98: 2	$1.17 \times 10^{-6}$
TS5	41.77 : 41.77 : 13.96 : 2.5	$1.07 \times 10^{-6}$

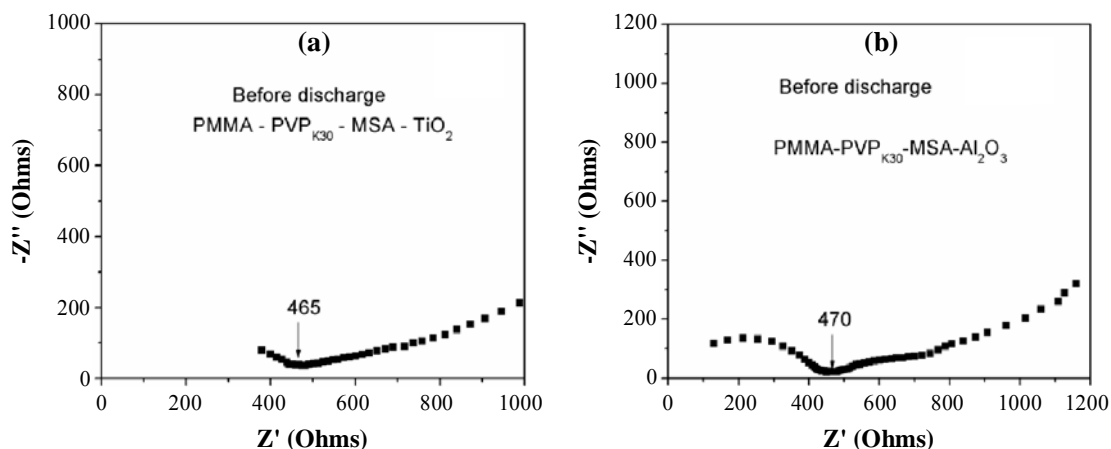
**Table 2: Composition and conductivity values of PMMA: PVP<sub>K30</sub>: MSA: Al<sub>2</sub>O<sub>3</sub> nano-composite solid polymer electrolytes**

Sample code	Compositions (mol%) (PMMA:PVP <sub>K30</sub> : MSA: Al <sub>2</sub> O <sub>3</sub> )	Conductivity (S/cm) at 303 K
AS1	42.55 : 42.55 : 13.9 : 1	$5.79 \times 10^{-6}$
AS2	42.12 : 42.12 : 13.76 : 2	$1.05 \times 10^{-5}$
AS3	41.69: 41.69:13.62 : 3	$1.90 \times 10^{-7}$
AS4	41.26: 41.26 : 13.48: 4	$2.50 \times 10^{-6}$

**Fig. 1: Cole-Cole plots for (a) PMMA-PVP<sub>K30</sub>-MSA-TiO<sub>2</sub> (b) PMMA-PVP<sub>K30</sub>-MSA-Al<sub>2</sub>O<sub>3</sub> system of nanocomposite solid polymer electrolytes**

## Electrochemical impedance spectroscopy

Primary proton batteries are constructed by using the high conducting membrane (TS2 and AS2) in each of the two different sets of nanocomposite blend solid polymer electrolytes. Fig. 2 (a) and (b) represent the electrochemical impedance of the fresh cell for the cell fabricated with TS2 (cell 1) and AS2 (cell 2), respectively. The internal resistance of the cell 1 and cell 2 are found as 465 ohms and 470 ohms respectively.

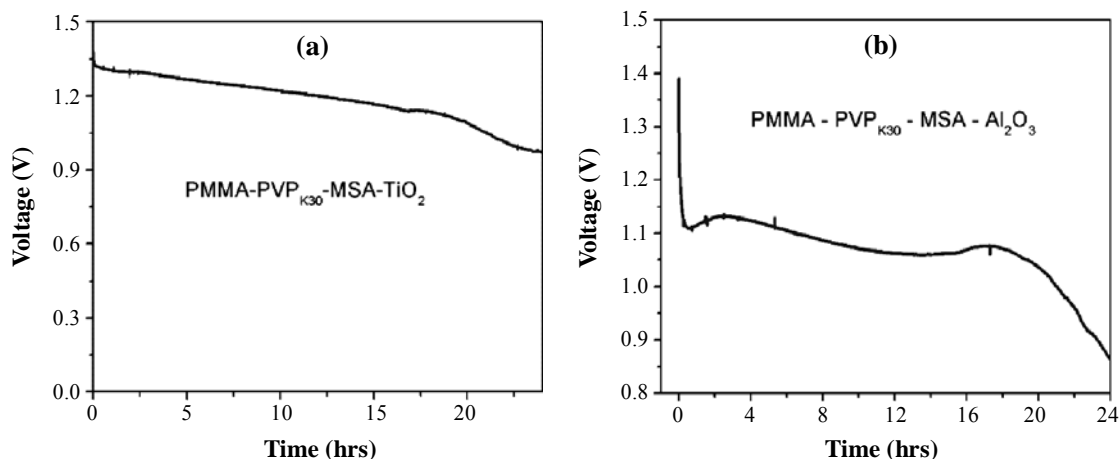


**Fig. 2: Electrochemical impedance of (a) cell 1 (b) cell 2 before discharge**

## Discharge characteristics

The discharge profile of cell 1 and cell 2 are shown in Fig. 3 (a) and (b), respectively at constant current of 0.01 mA. In the discharge profile of cell 1, the discharge pattern reaches the cut-off potential of 1 V in 23 hrs and in cell 2, the discharge pattern reaches the cut-off potential of 0.9 V in 23 hrs. From the discharge pattern, it is inferred that the discharge performance is found better for cell 1 (cell constructed with TiO<sub>2</sub> dispersed nanocomposite membrane) than cell 2 (cell constructed with Al<sub>2</sub>O<sub>3</sub> dispersed nanocomposite membrane). Even though the internal resistance of cell 1 and cell 2 are nearly equal, the discharge pattern is found better for cell 1.

The calculated energy density (from Fig 3 (a) and (b)) of the proton battery constructed with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> dispersed nanocomposite polymer electrolytes are 3.16 and 2.82 Wh/Kg, respectively. The enhanced discharge performance of the cell 1 is observed, which may be due to TiO<sub>2</sub> filler particles promote ion transport between electrode-electrolyte than the Al<sub>2</sub>O<sub>3</sub> filler particles.



**Fig. 3: Discharge pattern of (a) cell 1 (b) cell 2 at a constant current of 0.01 mA**

## CONCLUSION

Nanocomposite blend solid proton conducting polymer electrolytes are prepared with two different fillers of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  by using traditional solution casting technique. The maximum conductivity value is obtained of the order of  $10^{-5}$  S/cm for the two different systems of nanocomposite membranes. The internal resistance of the proton battery constructed with those high conducting membrane is found nearly equal. The discharge behavior is found better for the cell fabricated using  $\text{TiO}_2$  dispersed membrane.

## REFERENCES

1. M. Ravi, K. Kiran Kumar, V. Madhu Mohan and V. V. R. Narasimha Rao, *Polymer Testing*, **33**, 152 (2014).
2. M. Forsyth, D. R. Mac Farlane, A. Best, J. Adebahr, P. Jacobsson and A. J. Hill, *Solid State Ionics*, **147**, 203 (2002).
3. J. Xi, X. Qiu, S. Zheng and X. Tang, *Polymer*, **46**, 5702 (2005).
4. C. Ambika, G. Hirankumar, S. Karthickprabu and R. S. Daries Bella, *Int. J. Chem. Tech Res*, **6**, 5209 (2014).

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