Effect of TiO_2 nano-filler on ionic conductivity of poly (ethylene oxide) based gel polymer electrolyte for magnesium ion batteries

R.A. Jayarathna, H.M.J.C. Pitawala *
Faculty of Science and Technology, Uva Wellassa University of Sri Lanka

and

M.A.K.L. Dissanayake
Institute of Fundamental Studies, Hantana Road, Kandy

Introduction

Gel polymer electrolytes (GPEs) have been identified as novel materials for magnesium ion rechargeable batteries. Among different polymers, poly(ethylene oxide) (PEO) based systems are the most studied candidates due to their solvation power, complexion ability, and proper chemical structure to support ion transport directly connected with Mg^{2+} (Dissanayake *et al.*, 2012). However, ionic conductivity of PEO based polymer electrolytes at ambient temperature is not high enough for most practical applications. In order to improve the ionic conductivity, the addition of nano sized oxide fillers into the PEO-salt matrix have been regarded as the most promising method (Agrawal *et al.*, 2013). We here present the synthesis and characterization of PEO based Mg^{2+} ion conducting GPE by incorporating titanium dioxide nano filler (TiO_2).

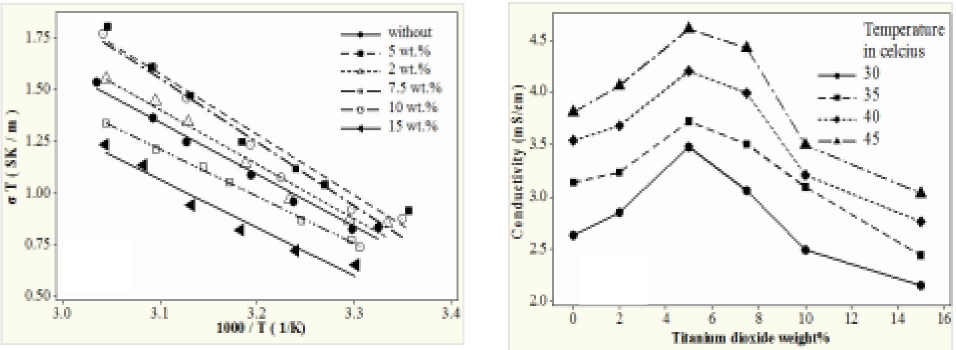
Methodology

PEO (M_w~1×10^5), magnesium triflate (MgTf) (purity>97%), ethylene carbonate (EC) (purity >99%), propylene carbonate (PC) (purity >99%) were purchased from sigma Aldrich and used as starting materials along with titanium dioxide (TiO_2) nano-filler. Prior to use, polymer, salt and TiO_2 were vacuum dried using appropriate temperatures. Nano composite polymer electrolytes were prepared by adding different amounts of TiO_2 (2,5,7.5,10,15 wt.%) in the PEO:MgTf :EC/PC (1:1) mixture with weights of 0.20 g, 0.12 g, 0.30 g and 0.30 g respectivel y. The mixtures were heated to 80 ^{0}C and magnetically stirred for 12 hours without heating until a homogenous gel was formed. The cathode film was prepared using vanadium pentoxide (V_2O_5), carbon black and polyvinylidene fluoride (PVdF) with the weight percentages of 76%, 14% and 10% respectively with the solvent of 1-methyl -1, 2-dipyrrolidine using doctor blade method.

The prepared electrolytes were characterized in order to obtain their ionic conductivity using complex impedance spectroscopy whereas electrochemical tests were performed using the cells, Mg/electrolyte/V_2O_5:C. DC polarization tests were done using both blocking (stainless steel) and non-blocking (Mg) electrodes. Microscopic images of the electrolytes were taken using the polarization microscope to investigate the change of crystallinity with the addition of nano-filler.

Results and Discussion

Figure 01(a) shows the temperature dependence of ionic conductivity for the GPEs, PEO:MgTf:EC/PC (1:1), incorporating different wt. % of nano-sized TiO2 filler. Among studied systems, highest ionic conductivity is observed for the GPE with 5 wt. % filler content. Figure 01(b) shows the variation of conductivity with different wt. % TiO2 at various temperatures (conductivity isotherms) for the PEO:MgTf:EC /PC (1:1) GPEs. This plot also shows that the 5 wt.% filler containing electrolyte has the highest ionic conductivity in the studied temperature range. A possible explanation to this effect could be the availability of extra hopping sites for migrating ionic species due to formation of Lewis acid-base type interactions of ionic species with O/OH surface groups on TiO_2 nano filler (Pitawala *et al.,* 2008).



(a) (b)

Figure 01: (a) Variation of temperature dependence of ionic conductivity for different compositions of titanium dioxide filler (b) Conductivity isotherms.

It is clear that the conductivity starts to decrease when the filler concentration exceeds 5 wt. %. This implies that excess amount of filler may reduce the solubility of Mg-salt and increase the probability of formation of ion-pairs and higher ionic aggregates thus reducing the number of free Mg^{++} ions available for ionic transport. The blocking effect due to higher concentration of TiO_2 would also contribute to this conductivity drop.

A comparison of the surface morphology of filler free and filler added (5 wt. %) GPEs shows a marked change in the polarization micrographs (results are not shown here). This is related to the increase of amorphous phase of material which favors the decrease of the crystallinity after addition of filler. The increase of the amorphous phase content would directly contribute to the observed conductivity enhancement (Mohan *et al.,* 2005).

Figure 02 shows the electrochemical test results for Mg/electrolyte/V_2O_5:C cell, when (a) filler free electrolyte and (b) electrolyte with 5 wt. % filler. The capacity of the battery calculated using these results is 43.59 mA h/g (filler free electrolyte) and 65.40 mA h/g (5 wt. % filler added electrolyte). According to these observations, due to the addition of TiO_2 nano filler into the parent electrolyte, the cell capacity has enhanced due to the increase of ionic conductivity of the GPEs as discussed.

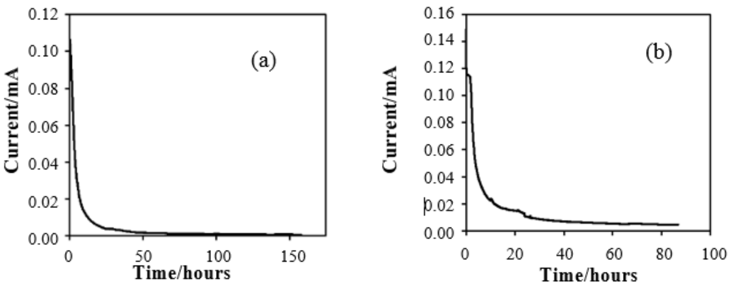


Figure 02: Electrochemical test for Mg/electrolyte/V_2O_5:C cell (a) filler free electrolyte (b) electrolyte with 5 wt.% filler.

Our DC polarization test results are summarized in Table 01. The ionic transference number has increased from 0.045 to 0.075 with the addition of 5wt. % filler into the PEO:MgTf:EC/PC (1:1) GPE.

Table 01: DC polarization test results for the electrolytes without filler and with 5 wt. % filler.

Electrolyte	Electronic transference number SS/electrolyte/SS system	Ionic transference number Mg/electrolyte/Mg system
without filler	0.005	0.045
with 5wt.% filler	0.010	0.075

Conclusion

In this work, we have studied the effect of titanium dioxide nano filler (TiO_2) on the ionic conductivity of gel polymer electrolyte based on PEO polymer. Our results show that the incorporation of titanium dioxide nano filler into PEO:MgTf: EC/PC (1:1) gel polymer electrolyte has resulted a significant enhancement of ionic conductivity with the values of 2.63 mS cm^{-1} (without filler) and 3.48 mS cm^{-1} (with 5 wt.% filler) at 30 °C. In addition, the cell consisting of electrolyte with 5wt. % filler has shown a higher capacity than the filler free electrolyte. The polarization micrographs show that the decrease of crystallinity and increase of amorphous phase content of the parent electrolyte with the addition of filler. DC polarization test results show that the conduction is predominantly due to ions rather than electrons. The possible explanation of this conductivity enhancement can be explained by the increase of the amorphous phase content of the parent electrolyte due to addition of filler. In addition, the conductivity enhancement is directly associated with surface interactions of the filler particles with ionic species providing extra ion hopping sites in the system.

Acknowledgements

The authors wish to thank Mr. C.A. Thotawattage, Research Assistant, IFS and the research team in the Condensed Matter Physics laboratory at IFS for their great support. Also the advice and guidance by Prof. G. K. R. Senadheera and Dr. V. A. Senaviratna are gratefully acknowledged.

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