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Conference Paper · January 2014

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PERFOMANCES OF TiO_2 AS CATHODE MATERIAL IN RECHARGEBLE Mg BATTERIES WITH POLYETHYLENE OXIDE BASED GEL ELECTROLYTE

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In recent years there has been an increasing interest on research and development of solid state polymeric lithium batteries. Although Lithium ion battery technology is one of the most popular and evolving modern battery technologies, it also faces several difficulties such as the growth of a passivation layer on lithium anode, high reactivity of lithium metal, limited availability of lithium as a raw material etc.,. Therefore, it has been realized that Mg^{++} ion batteries would be among the best alternatives for solving the above problems. However, reported discharge capacities of the Mg batteries comprising with quasi solid Mg^{2+} ion conducting electrolytes are quite low due to the poor conductivity of the polymeric electrolyte and the mass and the properties of the cathode material used in these Mg batteries. In this study we have explored the possibilities of using low cost, highly abundant TiO_2 as the cathode martial in rechargeable magnesium batteries fabricated with Mg^{++} ion conducting, quasi solid (gel) polymeric electrolyte based on polyethylene oxide (PEO) as the host matrix. Electrolyte was characterized by AC impedance spectroscopy, cyclic voltammetry (CV) and DC polarization method. The best ionic conductivity of the electrolyte, determined by the complex impedance measurements was 2.52×10^{-3} S/cm at room temperature for the composition of PEO (12.20 wt%), $(CF_3SO_3)_2Mg$ (14.6 wt%), EC (36.6 wt%), PC (36.6 wt%). The conductivity appears to follow the Arrhenius behavior with increasing temperature. The estimated value of Mg^+ ion transference number and total ionic transference number are found to be 0.10 and 0.98 respectively. Fabricated batteries with cell configuration $Mg/PEO:EC:PC:Mg(CF_3SO_3)_2/TiO_2$-C

Proceedings of the 14th Asian Conference on Solid State Ionics (ACSSI 2014)
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ISBN: 978-981-09-1137-9
doi:10.3850/978-981-09-1137-9_075

exhibited a discharge capacity of 270 mAh/g and 1.85 V open circuit voltage. The weight of the fabricated cathode material, TiO_2 used in these devices was approximately 1 mg.

Keywords: Mg Battery, Impedance spectroscopy, Polymeric electrolyte

1. Introduction

The energy demand is rapidly increasing with increasing global population. Therefore, the supply of energy has become the main challenge for maintaining a comfortable standard of living. Conventional energy sources derived from fossil fuels will soon be incapable of meeting the energy demand of the global population. Also, the use of fossil fuels will continue to enhance the current level of CO_2 in the atmosphere and environmental pollution. Therefore, finding alternative, environmental friendly, renewable energy sources such as solar and wind and storage devices such as batteries have become important in research and development work. Rechargeable battery technology is considered as a CO_2 emission free energy technology.

Majority of current rechargeable battery technologies are directed towards developing Li battery systems. In the view of the natural abundance of Magnesium, their low cost, low molecular weight and safety, Mg rechargeable battery system is considered to be one of the most suitable replacements for Li systems. A typical Mg battery consists of a metallic Mg anode, a Mg^{++} ion conducting electrolyte and a suitable cathode. During the charging process, Mg^{++} ions are released from the intercalation positive electrode (cathode) and metallic Mg^0 is deposited in the negative electrode (anode). Mg^{++} dissolution from the anode and intercalation into cathode happen during the discharging of the battery. Oxides are considered to be the most promising positive electrode materials for high energy density secondary Li batteries. The reason is the high degree of ionic character of metal oxygen bonds in oxides, which generally leads to high oxidizing power of the compound and hence to a high voltage of the battery. However for most Li batteries, $LiCoO_2$, V_2O_5 or MnO_2 or their derivatives have been used as the cathode material together with a liquid or gel electrolyte. The use of liquid electrolytes and rare earth materials for cathodes also limit their practical applications. Hence, developing solid or gel type electrolytes and low cost cathodic materials are still open problems with these batteries. Therefore, in this study we have explored the possibilities of developing a Mg^{++} ion battery using a PEO based gel electrolyte and low cost TiO_2 as the cathode martial. Possible Mg^{++} insertion and deinsertion into and out of TiO_2 occurs as follows:

$$\text{Positive electrode: } TiO_2 + x\,Mg^{++} + 2xe^- \longrightarrow Mg_xTiO_2$$

$$\text{Negative electrode: } x\,Mg \longrightarrow x\,Mg^{++} + 2xe^-$$

2. Experimental

2.1. Materials

Polyethylene oxide (PEO, Avg. Mw $4x10^6$), magnesium trifluoromethane sulfonate ($Mg(CF_3SO_3)_2$) were purchased from Sigma Aldrich and propylene carbonate (PC) ethylene carbonate (EC) with purity >98% were purchased from Fluka.

2.2. Electrolyte preparation and characterization

The electrolyte used for the Mg battery was prepared according to the following recepie: 0.12 g of magnesium trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$) was dispersed in 0.3 g of propylene carbonate (PC) with 0.3 g of ethylene carbonate (EC) and the mixture was stirred well for complete dissolution. Then, 0.1 g of PEO was added to this solution and the mixture was heated up to 80°C under continuous stirring until a homogeneous viscous gel is formed. This viscous gel was then allowed to cool down to room temperature.

Total ionic conductivity of electrolyte samples was determined by using complex impedance analysis by a computer controlled Metrohm Autolab (PGATAT 128N) impedance analyzer in the frequency range between 0.1 Hz - 10 MHz. For these measurements appropriate amounts of polymer electrolytes were sandwiched between two polished stainless steel (SS) electrodes with the configuration SS/electrolyte/SS and the impedance measurements were taken from the room temperature up to 65 ^{0}C at 5^{o}C intervals.

Symmetrical cells, SS/electrolyte/SS and Mg/electrolyte/Mg were used for the DC polarization test by applying small dc voltage to estimate the total ionic transference number (t_{ion}) and the magnesium ion transference number (t_{Mg+2}) respectively. The ac complex impedance response of the Mg/electrolyte/Mg cell was also measured before and after dc polarization.

2.3. Preparation of the TiO_2 cathode

A powder mixture (0.2 g) of 89 wt% TiO_2, (0.025 g) of 11 wt% carbon powders, one drop of Triton-X and few drops of acetic acid were thoroughly ground with ethanol. This mixture was used to prepare the cathode pellet of 5 mm diameter and two tape thickness (24μm) pellet on Fluorine doped Tin Oxide (FTO) glass substrate and then sintered at 450 °C for 45 minutes. The weight of the prepared

TiO_2 electrode was 1 mg. The weight of the magnesium pellet used as the anode was 0.07 g.

2.4. Fabrication of the Mg/Electrolyte/TiO_2-C/FTO Cell.

A cleaned pellet of metallic magnesium was used as the anode. The Mg/PEO:EC:PC:$Mg(CF_3SO_3)_2$/TiO_2-C/FTO cell was assembled by sandwiching the gel electrolyte in between the magnesium anode and the TiO_2 cathode.

2.5. Characterization of the cell

In order to characterize the cells the discharge capacity of the Mg/Electrolyte/TiO_2-C/FTO cells was monitored by applying a constant load of 60 kΩ.

3. Results and discussion

3.1 Electrolyte characterization

The ionic conductivity of the gel polymer electrolyte was calculated using the relation

$$\sigma = l / R_b A \quad (1)$$

where l is the thickness of the electrolyte sample, A is the contact area between the electrolyte and the stainless steel electrode and R_b is the resistance determined from impedance spectra. Room temperature ionic conductivity is found to be 2.52×10^{-3} S/cm. As shown in Figure 1, the temperature dependence of the conductivity follows the classical Arrhenius equation,

$$\sigma = \sigma_o \exp(-E_a/RT). \quad (2)$$

Magnesium transference number (t_{Mg+2}) was measured using the dc and ac measurements suggested in the literature [1] by using the relation.

$$t_{Mg+2} = \frac{I_s(\Delta V - R_o I_o)}{I_o(\Delta V - R_s I_s)} \quad (3)$$

Where I_0 and I_S are the initial and final steady state currents of Mg/electrolyte/Mg (Fig.2) and R_0 and R_S are the Mg/electrolyte/Mg cell resistance before and after the dc polarization respectively. Evaluated Mg^{++} ion transference number for the gel electrolyte is found to be 0.10 indicating the Mg^{++} contribution to the electrolyte.

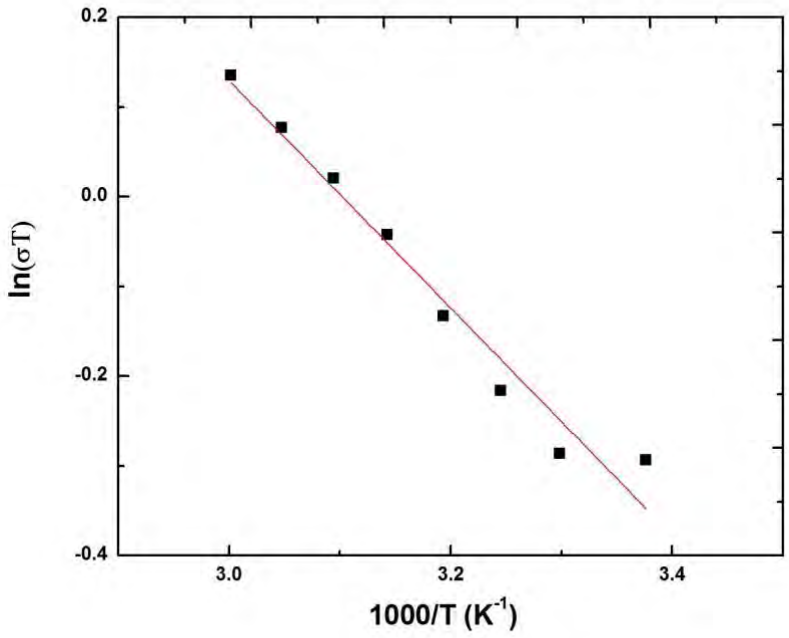

Figure 1. Temperature dependence of the ionic conductivity of the PEO based electrolyte PEO:EC:PC: $Mg(CF_3SO_3)_2$ in logarithm scale.

The results of the DC polarization test taken with Mg/Electrolyte/Mg symmetrical cell and applying a DC voltage of 1.5 V is shown in Figure 2.

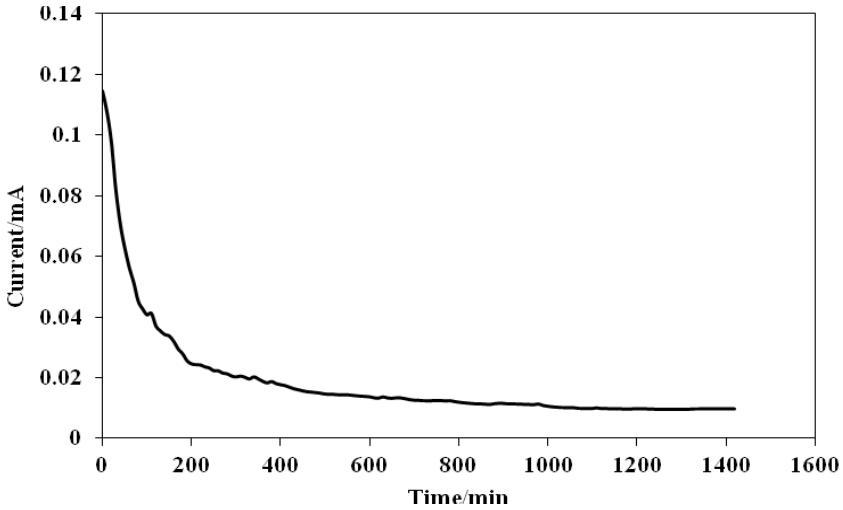

Figure 2. Variation of dc polarization current as a function of time for Mg/EC:PC:PEO:Mgtf/Mg

The total ionic transference number was determined by the DC polarization test using the symmetrical cell SS/electrolyte/SS and according to the equation

$$t_{ion} = I_i - I_f / I_i \quad (4)$$

where I_i is the initial current and I_f is the final residual current. In this method the dc polarization current was monitored as a function of time (Fig.3). Calculated value was found to be 0.985 showing that the ionic conductivity in the gel electrolyte is dominant and the electronic conductivity is negligible.

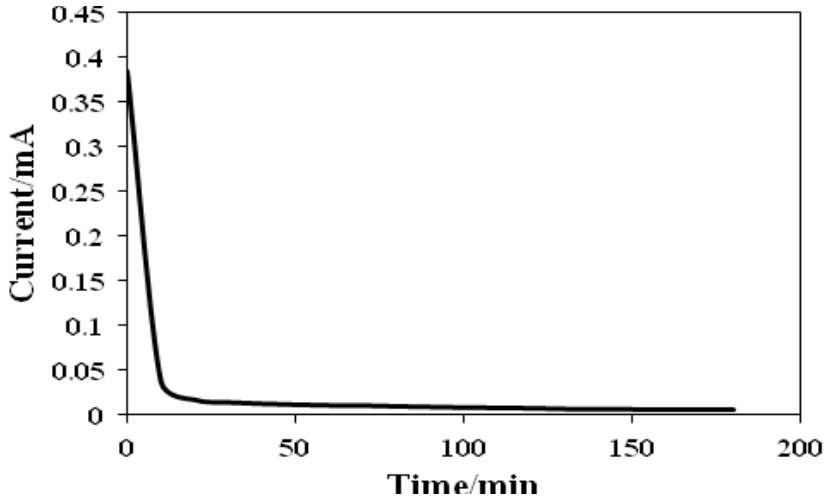

Figure 3. Variation of polarization current as a function of time for SS/EC:PC:PEO:Mgtf/SS

3.2. Mg/electrolyte/ TiO_2-C cell

The open circuit voltage of the Mg/Electrolyte/TiO_2-C battery was monitored for the first 24 hours until it became stabilized. Initial increase of voltage was observed during the first 2 hours after assembling the cell which was subsequently stabilized at 1.82 V. This value remained essentially constant up to nearly 30 hours (Figure 4)

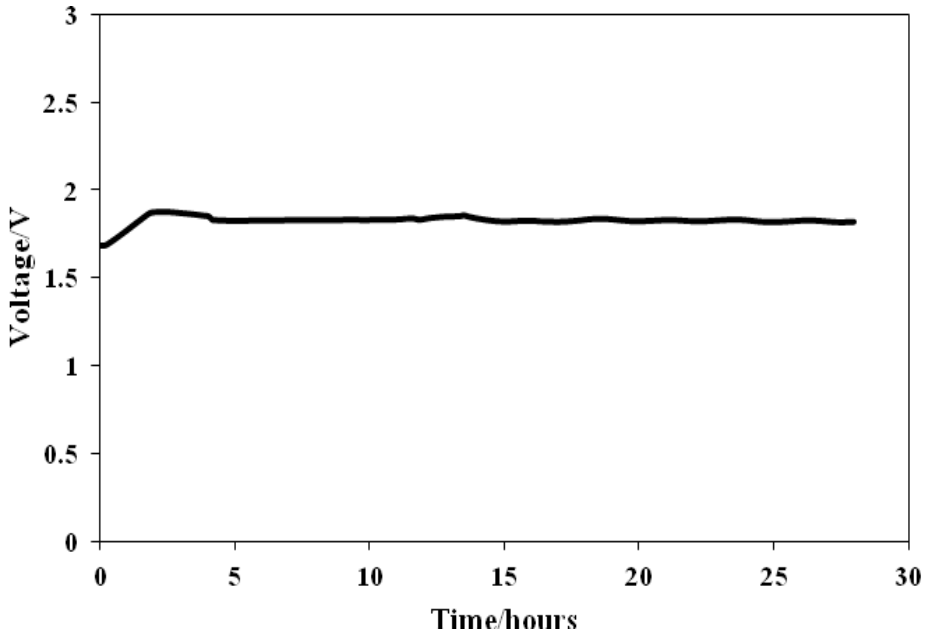

Figure 4. Open circuit voltage of Mg/ PEO:EC:PC: $Mg(CF_3SO_3)_2$/TiO_2-C/FTO cell during 24 hours of storage.

Fig.5. shows the discharge characteristics of the cell Mg/Electrolyte/TiO_2-C for a constant load of 60 kΩ. It shows that the discharge was sustained for nearly 25 hours for 60 kΩ. The value of the discharge capacity was evaluated by integrating the area under the curve of figure 5 according to

$$C = \frac{\int_0^t I(t)dt}{M} \tag{5}$$

where M is the mass of the active material (TiO_2) in the cathode. Estimated discharge capacity of the cell is 270 mAh/g.

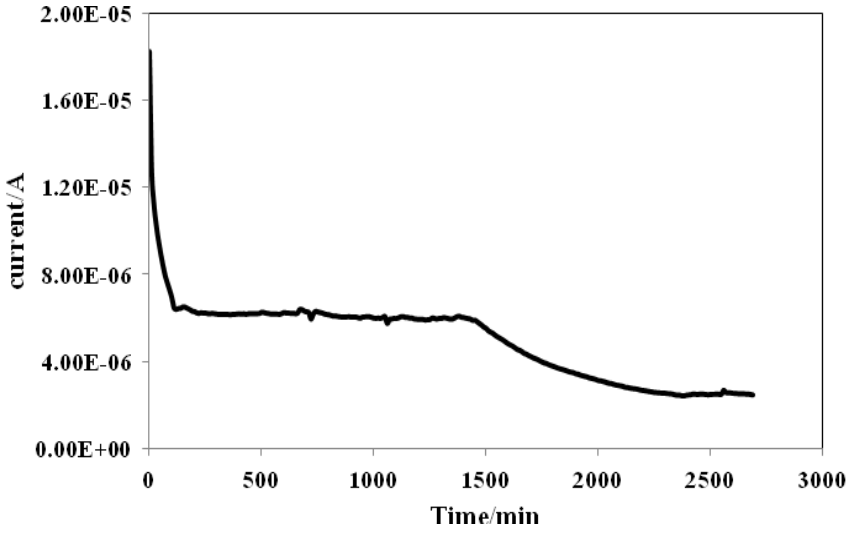

Figure 5. Constant load discharge characteristics of the cell Mg/PEO:EC:PC: $Mg(CF_3SO_3)_2/TiO_2$-C/FTO under 60 kΩ load.

Fig. 6 shows typical charge and discharge curves of the Mg/PEO:EC:PC: $Mg(CF_3SO_3)_2/TiO_2$-C cell under constant current. The data show stable charge-discharge cycles.

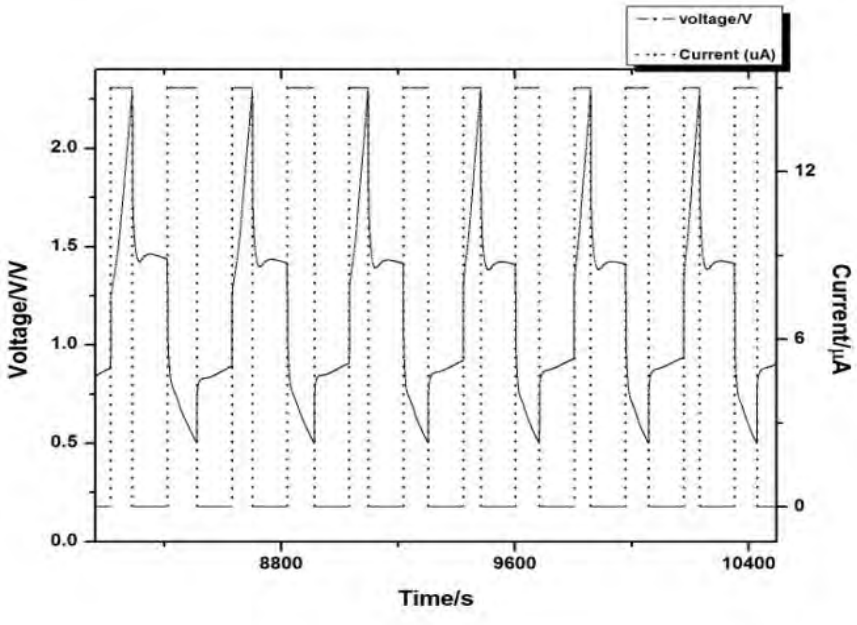

Figure 6. Charge - discharge curves of a Mg/PEO:EC:PC:$Mg(CF_3SO_3)_2/TiO_2$-C/FTO cell at room temperature.

4. Conclusion

PEO:EC:PC: $Mg(CF_3SO_3)_2$ gel polymer electrolyte was synthesized and characterized. It shows predominantly ionic nature with negligible electronic conductivity. Mg^{++} ionic transference number is about 0.10. Mg batteries were fabricated with this gel polymer electrolyte and low cost TiO_2 cathode. The discharge capacity of these Mg cells is 270 mA/g. These results show that magnesium polymeric electrolyte offers and interesting alternative to lithium systems for room temperature solid sate batteries. On the other hand the conventional cathode materials such as $LiCoO_2$, V_2O and MnO_2 used in lithium batteries can be substituted with low cost TiO_2 in Mg batteries can be done with the lost cost heavily available materials like TiO_2 effectively.

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