

INVESTIGATIONS ON MAGNESIUM POLYMER ELECTROLYTES

AROCKIYASWAMY, M SAKTHIVEL, R PARVATHAKUMARI, A SIVASHANMUGAM AND S GOPUKUMAR

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

Synthesis and characterization of Polyethylene Oxide (PEO) blended with Magnesium salts viz, $MgCl_2$, $Mg(ClO_4)_2$ are presented in this paper. Microstructural characterization was done using Fourier Transform Infra red spectroscopy (FTIR). AC impedance Technique was used for electrical characterization of the prepared polymer electrolytes. Discharge behaviour of Magnesium button cells assembled using the above polymer electrolytes are discussed in terms of capacity output. Preliminary investigations reveal the possibility of fabricating Magnesium Polymer batteries.

Keywords: Polyethylene oxide, magnesium salts, $MgCl_2$ and $Mg(ClO_4)_2$

INTRODUCTION

Magnesium (Mg) is an interesting anode battery material with more advantages like high standard potential (-2.37 V), low cost, good low temperature performance due to their exothermic corrosion reaction during discharge etc. On the other hand, solid polymer electrolytes have many advantages in comparison to conventional organic, inorganic or liquid electrolytes. These polymer electrolytes have advantages like

- * Thin film forming property
- * Good processability
- * Flexibility
- * Light Weight
- * Elasticity
- * Transparency
- * High ionic conductivity
- * Wide potential window
- * Kinetically stable
- * Moderate temperature (343 to 423 K)

Hence, it is provoking to fabricate and study the performance of a battery system combining magnesium and solid polymer electrolyte like PEO blended with magnesium salts. In the present study we want to look at the effect of solid polymer electrolyte on the performance of the solid state magnesium

battery. We report herein a comprehensive investigation carried out on polyethylene oxide (PEO) with a magnesium salt as a possible solid polymer electrolyte in solid state magnesium batteries. In this work the synthesis, structural and electrical characterization are described regarding new polymeric electrolytes for magnesium batteries on the basis of polyether blend polyethylene oxide (PEO).

EXPERIMENTAL

Preparation of anode

Mg AZ 31 alloy sheets with 1.5 mm thickness was used as anode. The Mg sheets were cut into pieces to get 2 x 4 cm² size of flat anode. Then, a hole is made by drillers on one corner of the Flat electrode. Then the hole is riveted with silver rivet which acts as current collecting points. A flexible copper wire is soldered over the rivet. The rivets as well as the riveted area of the anode was marked with araldite so as to eliminate the bimetallic corrosion of magnesium. The anode was cleaned before it is used.

Preparation of cathode

The cathode mixture containing Manganese oxide, Acetylene black and Teflon (binder) of appropriate proportions are mixed uniformly. The cathode mixture was spread over the mesh and covered with tissue paper and pressed at an optimized pressure.

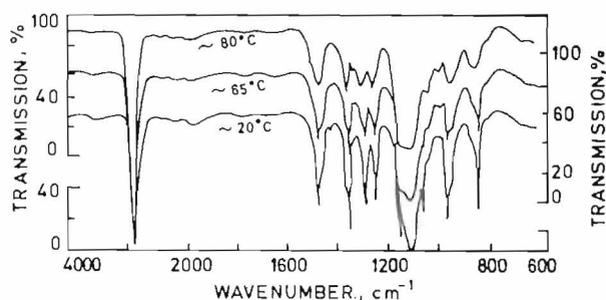


Fig. 1: FTIR absorption spectra of PEO

Preparation of polymer electrolyte film

Poly(ethylene oxide) (PEO) with average molecular weight, 5,000,000 g/mol, Propylene Carbonate (PC) and Magnesium chloride (MgCl₂). Magnesium perchlorate (MgClO₄)₂ were purchased from Aldrich, and used without further purification.

The polymer salt complexes were obtained by dissolving the polymers in acetonitrile (90/10) by volume, subsequent evaporation of the solvent and drying the samples under high vacuum conditions until constant sample weight was achieved. Films were then obtained by casting the dispersion over Teflon plates. These were subsequently dried under vacuum for 48 h.

Infrared spectra were collected on a Nicolet 520 FTIR system at 2 cm⁻¹ resolution. Sodium chloride plates were used as windows for the polymer complexes and Lithium salts.

Conductivity measurements of the prepared polymer films were carried out using a Hewlett-Packard model 4192 AC impedance analyser coupled to a computer, in the frequency range 100 KHz to 10 Hz. The conductivity measurements were made at room temperature.

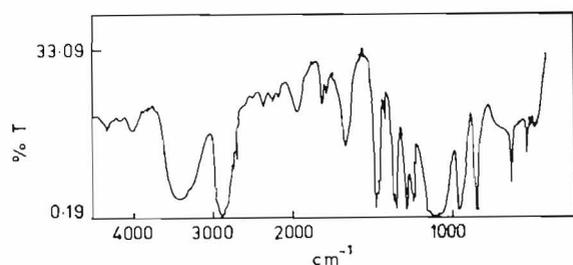


Fig. 2: FTIR absorption spectra of sample Mg₁ showing the effect of complexation on CH₂ modes of PEO

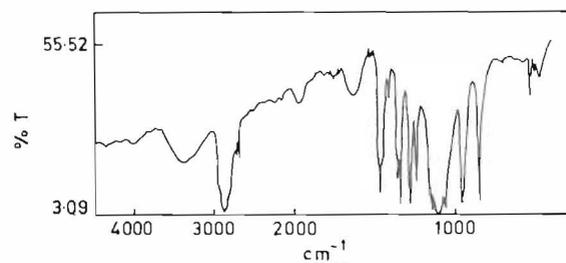


Fig. 3: FTIR absorption spectra of sample Mg₂ showing the effect of complexation on CH₂ modes of PEO

Cell assembly

The cell was constructed as Mg/(PEO)₈ Mg(Cl₂)/MnO₂. The Polymer film was placed between the anode and the cathode mixture, the whole structure was then sealed. The open circuit voltage was measured with the help of a voltmeter.

RESULTS AND DISCUSSION

Microstructural Characterization

Magnesium salt incorporation into PEO is capable of producing co-ordination compounds, this co-ordination being more favoured the larger the size of the anion of the corresponding salt [22]. The Magnesium salts used in this work, Mg(ClO₄)₂ and MgCl₂, possess an anion of great dimensions so that the co-ordination takes place between the oxygens of the polyethers and the magnesium ion, and no free crystalline magnesium salt exists.

It has been known that the degree of solvation and the influence of the anion properties on the morphology of the polymer significantly affect the spectral feature of polymer electrolytes.

An overview of the FTIR spectra (Transmittance vs wavenumber) between 400 and 4500 cm⁻¹ for PEO and the polymer electrolyte complexes Mg₁, Mg₂, Mg₃ is presented

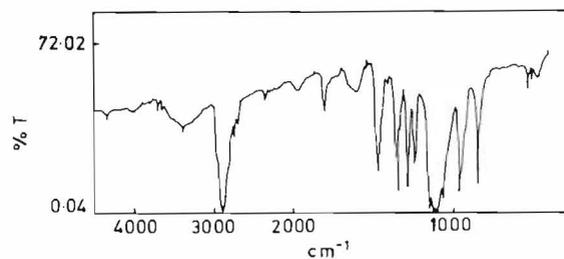


Fig. 4: FTIR absorption spectra of sample Mg₃ showing the effect of complexation on CH₂ modes of PEO

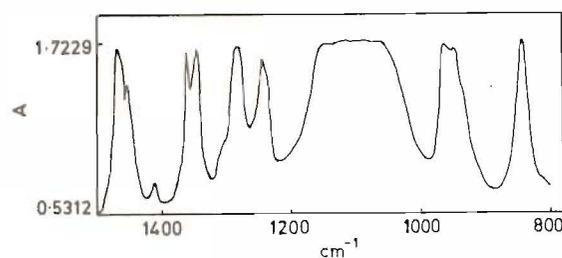


Fig. 5: FTIR absorption spectra of sample Mg_1

in Figs. 1-4 respectively, and the FTIR spectra (Absorbance vs wavenumber) between 800 and 1500 cm^{-1} for the complexes Mg_1 , Mg_2 and Mg_3 is presented in Fig. 5-7 respectively. The vibrational spectrum of PEO has been extensively studied [23-28] and the detailed assignments are reported in [23].

Relating to the Propylene carbonate effect, it has to be pointed out that plasticized complexes show a spectra which matches that of the unplasticized one. Absorptions assigned to the methylene group (CH_2) unit occurs in three different regions. These include the strong band at 2900 cm^{-1} (Symmetric and anti-symmetric stretching modes) and the less intense but similarly shaped, bands at about 1460 cm^{-1} (asymmetric CH_2 bending) and 843 cm^{-1} (CH_2 rocking). The strong band at 1108 cm^{-1} (C-O-C stretching) is strongly affected by cation complexation, but is in a region rich in absorptions due to the anion.

It has been described [29] that this band shifts to lower wave numbers when salt is added. In our case this displacement is from 1108 cm^{-1} observed for pure PEO to 1102-1113 cm^{-1} when it is complexed with the salt. This displacement for complexes Mg_1 , Mg_2 , Mg_3 are 1104 cm^{-1} , 1102.9 cm^{-1} and 1113 cm^{-1} respectively.

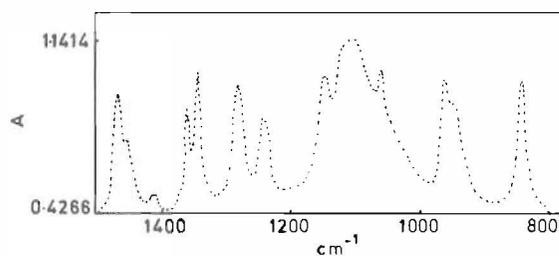


Fig. 6: FTIR absorption spectra of sample Mg_2

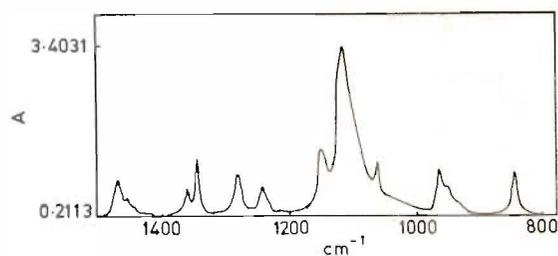


Fig. 7: FTIR absorption spectra of sample Mg_3

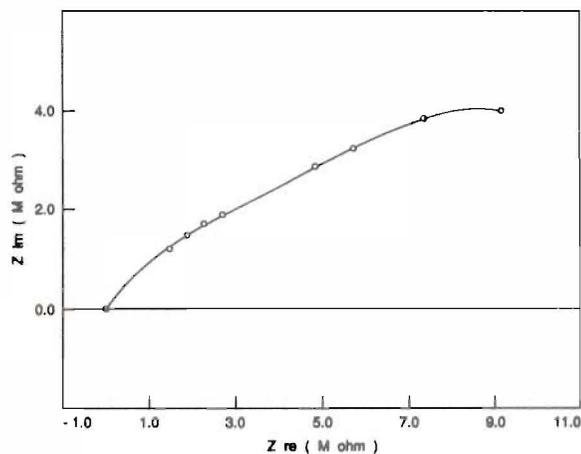


Fig. 8: Impedance spectroscopy analysis of the sample Mg_1 at room temperature

The C-H stretching band centered at about 2900 cm^{-1} is again quite sensitive to the extent of magnesium salt complexation, are the bending and rocking modes around 1460 and 843 cm^{-1} respectively, being the band splitting into two or more components. Due to magnesium salt complexation, the C-H stretching band is shifted from 2900 cm^{-1} for pure PEO to 2889.7 cm^{-1} , 2887.2 cm^{-1} and 2.887.2 cm^{-1} for complexes Mg_1 , Mg_2 and Mg_3 respectively and the asymmetric CH_2 bending is shifted from 1460 cm^{-1} to 1466.6 cm^{-1} , 1466.9 cm^{-1} and 1466.6 cm^{-1} for complexes Mg_1 , Mg_2 and Mg_3 respectively.

TABLE I: Ionic conductivity of the samples

Temperature	Samples	Conductivity S/cm
Room temp	Mg_1	2.2791×10^{-4}
Room temp	Mg_2	1.4306×10^{-7}
Room temp	Mg_3	2.3090×10^{-5}

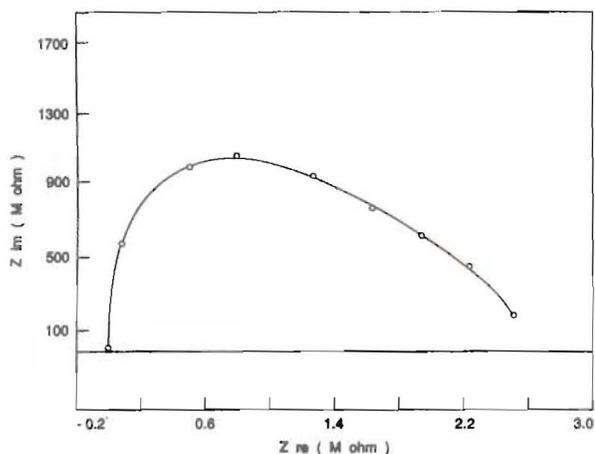


Fig. 9: Impedance spectroscopy analysis of the sample Mg_2 at room temperature

Relating to the C-H rocking mode absorption, the band is again shifted from the value of 843 cm^{-1} observed for PEO to 842.5 cm^{-1} , 842.8 cm^{-1} and 842.8 cm^{-1} for complexes Mg_1 , Mg_2 and Mg_3 respectively.

Electrical characterization

Electrical characterization was achieved by means of complex impedance spectroscopy applied to the different samples in the form of films are placed between blocking magnesium electrodes. Analyses were conducted at room temperature, the results obtained can be seen in Table I. Figs. 8,9 and 10 give the corresponding impedance plane for the complexes Mg_1 , Mg_2 and Mg_3 samples respectively. At room temperature, the arcs are observed to be more open, the ion conduction values being obtained from their intercepts on the abscissa. The behaviour is generalised in all plasticizer free samples. The impedance plane consists of an arc and an inclined straight line at low frequencies whose slope does not tend to vary as a function of Temperature.

Each of these spectral regions represents a physical zone in the configurations used and which, in all cases, consisted of an electrolyte placed between two magnesium electrodes. Under these conditions the half-circle representing the resistance of the Electrolyte and the sloped straight line (if present) indicates the resistance against ion passage through the electrode- electrolyte interface. Nevertheless, as in our case we are examining electrolytes with blocking electrodes there exists neither an ion source nor sink, which triggers a

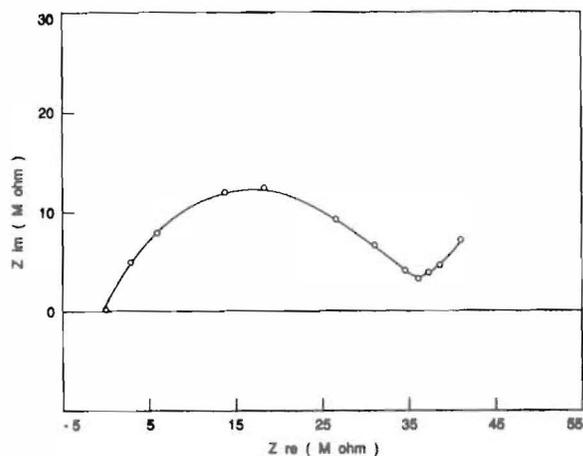


Fig. 10: Impedance spectroscopy analysis of the sample Mg_3 at room temperature

polarisation phenomenon in the electrolyte, as a consequence of the electric field applied (i.e. ion enrichment at the electrolyte face and ion depletion at the opposite face), together with a negative charge on the electrode surface (opposing the positive charge of the electrolyte) and its respective negative charge on the surface of the counter electrode. The double charge layer at each interface possesses infinite resistance against charge bearing ion transfer through the interface, which on the impedance plane, would translate into a straightline practically parallel to the ordinate similar to the one obtained in the case of a condenser.

CONCLUSION

The following conclusions obtained

- * Magnesium based polymer electrolyte involving PEO indicates complex formation as evidenced by FTIR studies
- * A C impedance studies on the prepared magnesium polymer electrolyte films are in the order of electrolyte samples Mg_1 , Mg_2 and Mg_3 and their conductivity values are 2.2791×10^{-4} , 1.403×10^{-7} and 2.309×10^{-5} respectively.
- * Preliminary studies on the polymer electrolyte films such as the assembling of an all-solid state magnesium cell with an OCV of 1.85 V.

REFERENCES

1. P King, *J Electrochem Soc*, **110** (1963) 113
2. A Fry, *U S Patent*, **2**, 712, 564 July (1953)
3. Mchubb, *U S Patent*, **2**, 934, 583 April (1960)
4. P V Wright, *Brit Polymer J*, **7** (1975) 319
5. M B Armand, J M Chabagno and M Duclot, *Second International Meeting on Solid Electrolytes*, St Andrews, Scotland, Extended Absts (Sept 1978)
6. C A Vincent, *Prog Solid State Chem*, **17** (1987) 145
7. D E Fenton, J M Parker and P V Wright, *Polymer*, **14** (1973) 589
8. P V Wright, *J Polymer Sci Polym Phys*, **14** (1976) 955
9. M Minier, C Berthier and W Gorecki, *J Physique*, **11** (1984) 307
10. C C Lee and P V Wright, *Polymer*, **23** (1982) 681
11. D R Payne and P V Wright, *Polymer*, **23** (1982) 690
12. J E Weston and B C H Steele, *Solid Ionics*, **7** (1982) 75
13. Dupon, B L Papke, M A Ratner, D H Whitmore and D F Shriver, *J Amer Chem Soc*, **104** (1982) 6247
14. A G Einset, W S Schlindwein, R J Latham, R G Linford and R. Pynenburg, *J Electrochem Soc*, (to be published)
15. P G Bruce, F Krok and C A Vincent, *Solid State Ionics*, **27** (1988) 81
16. R Huq and G C Farrington, *Solid State Ionics*, **28-30** (1988) 990
17. R Huq and G C Farrington, *J Electrochem Soc*, **135** (1988) 524
18. R Huq, M A Salzberg and G C Farrington, *J Electrochem Soc*, **136** (1989) 1250
19. R J Hoffman, R C Winterton and T D Gregory, *U S Patent* **4**, 894, 302 (1990).
20. R E Dueber, J M Fleetwodd and P G Dickens, *Solid State Ionics*, **50** (1992) 329
21. F Joho, P Novak, O Haas and R Nesper, *Chimia*, **47** (1993) 288
22. M Armand, *Solid State Ionics*, **9-10** (1983) 745
23. T Yoshihara, H Tadokoro and S Murahashi, *J Chem Phys*, **41** (1964) 2902
24. W H T Davidson, *J Chem Soc*, (1995) 3270
25. T Miyazawa, K Fukushima and Y Ideguchi, *J Chem Phys*, **37** (1962) 2764
26. A Miyake, *J Amer Chem Soc*, **82** (1960) 3040
27. M Shimomura, Y Tanabe, Y Watanabe and M Kobayashi, *Polymer*, **31** (1990) 1411
28. V M Da Costa, T G Fiske and L B Coleman, *J Chem Phys*, **101** (1994) 2764
29. S J Wen, T J Richardson, D I Ganthous, K A Striebel, P N Ross and E J Cairns, *J Electroanal Chem*, **408** (1996) 113