



SOLID STATE ELECTROCHEMICAL CELLS BASED ON PEO-Mg(ClO₄)₂ POLYMER ELECTROLYTE AND Mg/Cu ELECTRODES

**L.R.A.K. BANDARA, M.A.K.L. DISSANAYAKE, M.A. CAREEM
AND V. AMALASHWARAN**

Department of Physics, Faculty of Science, University of Peradeniya, Sri Lanka

ABSTRACT

Polymer electrolytes are of great interest mainly due to their possible application in advanced high-energy electrochemical devices such as batteries/fuel cells, electrochromic display devices, smart windows and photo-electrochemical solar cells. Many of the solid state electrochemical cells that are being used or being developed at present are based on Li⁺ ion conductors, which are more expensive and less stable. Magnesium ion conducting solid polymer electrolytes have the advantage of low cost and the cells based on these electrolytes allow the use of the more stable magnesium metal as an electrode material. It is, therefore, interesting to study characteristics of Mg²⁺ ion based solid state cells.

In this work, we report the results of studies on polymer electrolyte films with different compositions prepared by complexing PEO with Mg(ClO₄)₂ and plasticized with ethylene carbonate (EC). These polymer electrolyte films have been prepared by the solvent-cast method. DC polarization technique and Differential Scanning Calorimetry (DSC) have been employed for studying the complexation of the salts with the polymer and the plasticizer. The AC conductivity measurements have been made in these plasticized polymer electrolyte systems in the temperature range from 25 to 110 °C. The conductivity of the system with maximum conductivity was found to vary from 10⁻⁴ to 10⁻³ ohm⁻¹ cm⁻¹ within the above temperature range and the maximum conductivity of 6.43H10⁻⁴ S cm⁻¹ at room temperature was found for the sample with composition Mg(ClO₄)₂[0.5PEO+0.5EC]₁₀. The transference number suggests that the charge transport in these polymer electrolyte systems is mainly due to ions, with a negligible contribution from electrons. The conductivity vs. temperature behaviour is found to be of VTF type for all the complexes studied over the entire temperature range. The amorphous nature of the studied system was further confirmed by the DSC results.

Solid state primary cells have been fabricated by using the polymer film with maximum conductivity as the electrolyte and Cu and Mg as electrodes. The performances of these cells have been studied by constant load discharge characteristics. The open circuit voltage (V_{OC}) and the short circuit current (I_{SC}) for the cell configuration Cu(+)/Mg(ClO₄)₂[0.5PEO+0.5EC]₁₀/Mg(-) were found to be 1.36 V and 1.63 mA respectively. The capacity of the cell was found to be 3.01 mAh. The magnesium ion conducting polymeric electrolytes offer an interesting alternative to lithium systems for room temperature solid state battery systems.

1. INTRODUCTION

Polymer electrolytes are a group of salt complexed polymers with relatively high ionic conductivity, at the best 10⁻³ (Ωcm)⁻¹. This is many orders of magnitudes larger than that of uncomplexed polymers, which are more or less non-conducting¹. This field of research has been extremely active due to its possible application in advanced high-energy electrochemical devices, i.e., batteries/fuel cells, electrochromic display devices/smart windows, and photo-electrochemical solar cells, all requiring an electrolyte². The advantages of polymer electrolytes compared with other electrolytes (liquid, crystalline or glassy) are their superior

mechanical properties, such as high flexibility in combination with stability, and their lack of volatile and toxic components³.

Poly (ethylene Oxide) (PEO) is an excellent host for many alkali metal salts, and the resulting PEO-salt complexes are ionic conductors⁴. Research in polymer electrolytes has almost exclusively been focussed on electrochemical cells. Solid state electrochemical cells have many advantages over conventional aqueous cells due to absence of liquid leakage or gassing, lightweight, rugged structure and the possibilities of making thin film micro batteries of flexible size and shape and operation over a wide temperature range.

Many of the solid state cells based on polymer electrolytes that are being used or being developed at present are mainly based on Li^+ ion conductors, which are expensive and chemically unstable. Of the metals not widely studied, magnesium is one of particular interest. Its diagonal relationship in the periodic table with lithium, is shown for example by the similarity in their ionic radii (for Li^+ 68 pm and for Mg^{2+} 65 pm).

The analogous PEO/magnesium salt complexes are of considerable interest because of the divalent charge and the consequent increase in anion to cation ratio of 2:1. On the other hand, magnesium ion conducting solid polymer electrolytes have the advantage of low cost and the cells based on these electrolytes have the possibility of using magnesium metal as an electrode material. It is, therefore interesting to study characteristics of Mg^{+2} ion based solid state cells. Recent work on several promising solid magnesium ion conductors and cells based on these materials can be found in literature⁵. In this paper, we report the polarization and discharge characteristics of thin film solid state primary cells using the plasticized polymer, $\text{Mg}(\text{ClO}_4)_2[0.5\text{PEO}+0.5\text{EC}]_{10}$ as the electrolyte and Cu and Mg as electrodes.

2. EXPERIMENTAL

Commercially available Poly(ethylene Oxide) (PEO) (Aldrich: $\text{MW} \approx 4 \times 10^6$) and $\text{Mg}(\text{ClO}_4)_2$ (Aldrich, 99%) were dried for 12 hours at 50 °C and 100 °C respectively before use. Ethylene carbonate (EC) (Aldrich) was used as the plasticizer, under very dry conditions. The solvent casting technique has been used in which PEO, the metal salt and the plasticizer were dissolved in acetonitrile (Aldrich, 99%).

Several different composition ratios were studied in order to find the best ambient temperature conductivity. The starting materials were weighed and mechanically stirred for 24 h to create a homogeneous solution. After dissolving, the solution was cast on glass retaining Teflon plates in the open laboratory, but protected from dust. The solvent was allowed to dry at room temperature before final drying in a vacuum oven. The resulting polymer electrolyte membranes were transparent and free from air bubbles and pinholes. Films typically 50-150 μm thick, were further dried under vacuum at about 60 °C to remove the last traces of solvent. Disc shaped samples with a diameter of about 1.2 cm were used for the AC impedance and polarization measurements.

The ionic conductivity was measured using the complex impedance technique from 25 to 110 °C using spring-pressed stainless steel electrodes. Measurements were done in the frequency range of 1 Hz to 10^5 Hz using a Solatron SI1260 impedance analyzer with a signal of 20 mV. The complex impedance plots for all the samples consisted of only a spike due to electrode/electrolyte interface. The ionic transference number (t_{ion}) measurements of the electrolytes were carried out using the DC polarization method. The thermal behaviours of the samples were investigated using a Perkin Elmer Pyris1 microcomputer controlled DSC instrument over the temperature range -100 to +200 °C, at 20 °C/min.

A thin film of the plasticized polymer electrolyte with composition $\text{Mg}(\text{ClO}_4)_2[0.5\text{PEO}+0.5\text{EC}]_{10}$ having the maximum conductivity was used as the solid electrolyte in the electrochemical primary cells with the configuration:



Cells were fabricated by mechanically pressing two perfectly cleaned Mg and Cu foils against the electrolyte film. A schematic diagram of a cell is shown in Fig. 1. Discharge characteristics of the cells were studied under constant load conditions. Current and voltages were measured using a Keithley model 177 microvolt digital multimeter with 0.1 μA and 0.1 mV sensitivities.

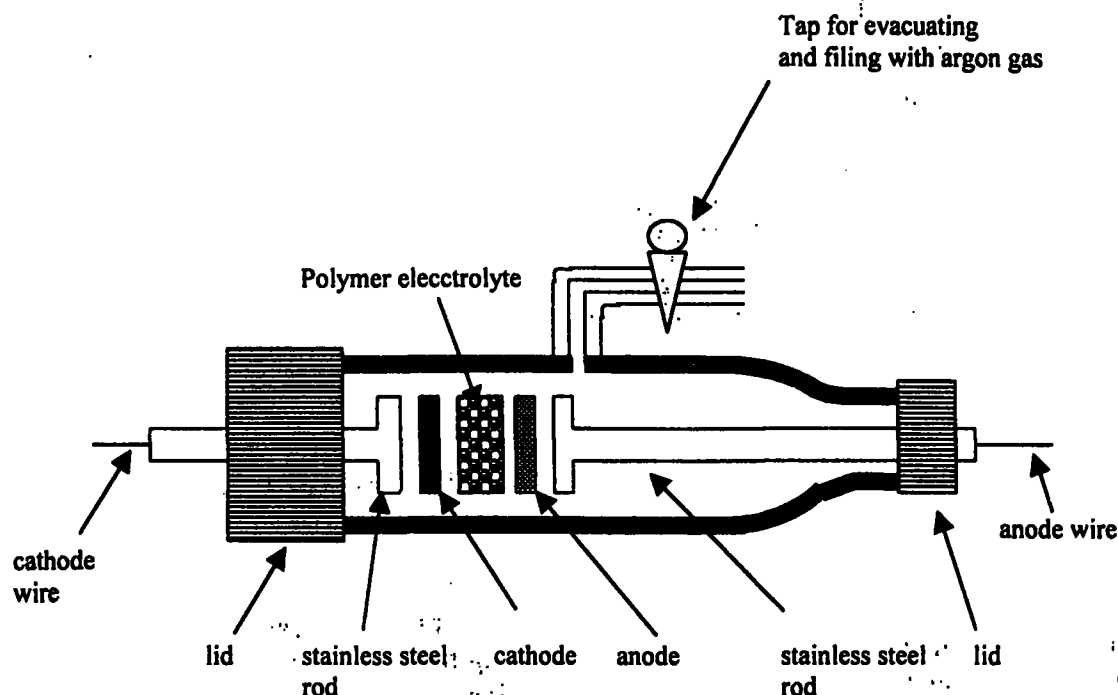


Fig. 1. Schematic diagram of the electrochemical cell, $\text{Cu (+) / Mg(ClO}_4)_2 [0.5\text{PEO}+0.5\text{EC}]_{10} / \text{Mg (-)}$ assembled in a special type of sample holder, made of glass.

3. RESULTS AND DISCUSSION

Polymer electrolytes for commercial applications should possess high ionic conductivity over a wide temperature range. The most successful approach to increasing the ionic conductivity of the polymer electrolytes, especially at low temperatures, seems to be by addition of various plasticizers⁶. The ionic conductivity of the plasticized polymer electrolyte with composition $\text{Mg(ClO}_4)_2 [0.5\text{PEO}+0.5\text{EC}]_{10}$ was $6.43 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C . Without any plasticizer, the electrolyte with composition $\text{Mg(ClO}_4)_2 [\text{PEO}]_{10}$ showed the conductivity of $7.31 \times 10^{-5} \text{ S cm}^{-1}$ at the same temperature. The ionic conductivity increases as the plasticizer content increases, but in the case of PEO/EC, a serious loss of mechanical stability is experienced as the plasticizer level is increased, because EC (and other polar solvents) dissolve PEO.

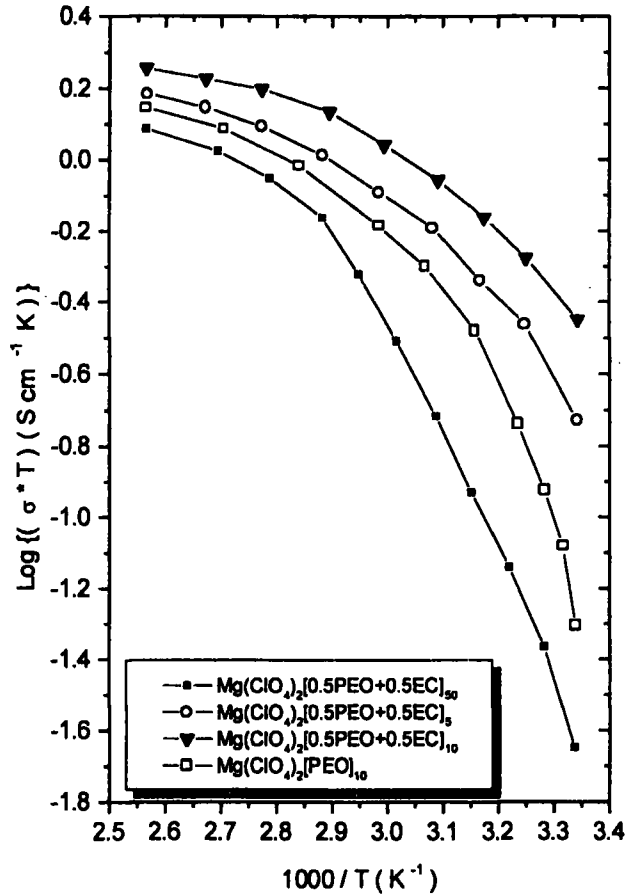


Fig. 2 Temperature dependence of the conductivity of PEO-EC-Mg(ClO₄)₂ solid polymer electrolyte systems with various compositions.

A selection of conductivity results for each electrolyte system is shown, in an Arrhenius plot fashion, in Fig. 2. The curvature of the Arrhenius plots, is clearly evident at higher temperatures for all the electrolytes investigated, implying that the conductivity can be described by the familiar Vogel-Tamman-Fulcher (VTF) equation,

$$\sigma = AT^{-1/2} \exp \left[-E_a / (T - T_0) \right] \quad (2)$$

where E_a is a pseudo activation energy, T_0 is related to the experimentally measured glass transition temperature. A is a pre-exponential factor, proportional to the carrier concentration.

Generally, following a well-known trend, as the salt concentration increases the conductivity of the electrolyte reaches a maximum and then decreases. The presence of the conductivity maximum is indicative of two competing effects occurring as the salt concentration is raised: the increases of both the concentration of charge carriers (ions) and that of the viscosity of the medium. In addition, at high salt concentration and especially in the case of electrolytes having a low dielectric constant, ionic association is likely to play a significant role in determining the number of the mobile charge carriers in the electrolyte. From the plots of Fig. 2, it can be seen that the conductivity of the samples falls off significantly as the salt concentration increases. The conductivity of the system with maximum conductivity was found to vary from 10^{-4} to 10^{-3} ohm⁻¹ cm⁻¹ within the temperature range 25 to 110 °C and the maximum conductivity of 6.43×10^{-4} S cm⁻¹ at room temperature was found for the sample with composition Mg(ClO₄)₂[0.5PEO+0.5EC]₁₀. Without the

plastisizer, the ionic conductivity of the electrolyte, $\text{Mg}(\text{ClO}_4)_2[\text{PEO}]_{10}$ at room temperature, was $8.33 \times 10^{-5} \text{ S cm}^{-1}$.

According to the DSC data, there are no higher melting endotherms that could be associated with a crystalline complex of PEO and the magnesium metal. This evidence, combined with the results of initial variable temperature studies indicates that these electrolytes are amorphous. It has been accepted that the amorphous regions are responsible for the ionic conductivity of polymer/salt complex films.

The results of the dc polarization measurements on a sample sandwiched between the stainless steel blocking electrodes and taken under 1 V bias voltage, at 70°C , are shown in Fig. 3. The transference numbers calculate from the polarization data are $t_{\text{ion}} \approx 0.92$ and $t_e \approx 0.08$. The transference numbers suggests that the charge transport in these polymer electrolyte systems is mainly due to ions, with a negligible contribution from electrons.

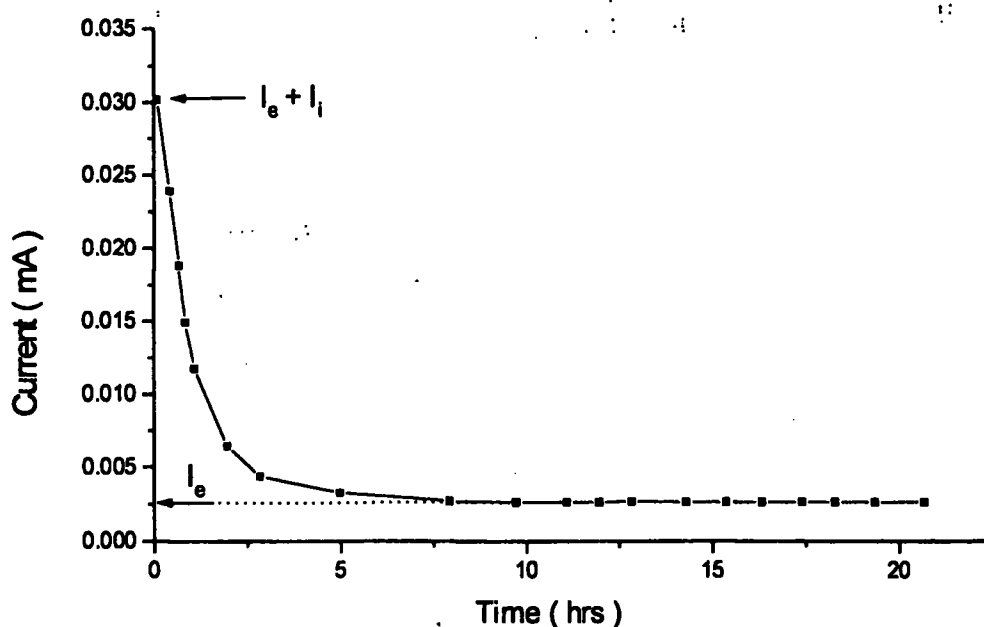


Fig. 3 Current vs. Time plot for the electrolyte $(\text{MgClO}_4)_2[0.5\text{PEO}+0.5\text{EC}]_{10}$ taken from dc polarization measurements at 70°C .

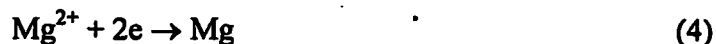
The all solid state cell concept has been explored both for primary and secondary battery designs with attractive prospects. Indeed, notable advances in primary battery technology in recent years are related to use of gel electrolytes and to development of new cell types. Solid state primary cells can provide a very long life operation at low currents.

During the discharge process of the $\text{Cu}(+) / \text{Mg}(\text{ClO}_4)_2[0.5\text{PEO}+0.5\text{EC}]_{10} / \text{Mg}(-)$ cell, the charge transfer reactions at the respective electrodes can be represented as follows:

At the Mg anode, oxidation takes place via the reaction,



The Mg^{2+} ions would migrate through the electrolyte to the Cu cathode and a thin layer of metallic magnesium is formed at the electrolyte/ Cu interface according to the reaction:



Therefore the overall cell reaction during the discharge process would give rise to a depletion of the Mg electrolyte and deposition of metallic magnesium at electrolyte/Cu interface.

The performances of these polymer based solid electrochemical cells have been studied by the discharge characteristics at different loads. The open circuit voltage (V_{OC}) and the short circuit current (I_{SC}) for the cell configuration $Cu(+)/Mg(ClO_4)_2[0.5PEO+0.5EC]_{10}/Mg(-)$ were found to be 1.36 V and 1.63 mA respectively. Fig. 4 shows the discharge curves for 10 k Ω and 5 k Ω load resistors. The average current during the discharge was about 0.13 mA and 0.78 mA respectively. Based on these values the capacity of the cell is estimated to be 3.01 mAh assuming a discharge time of 54 hours.

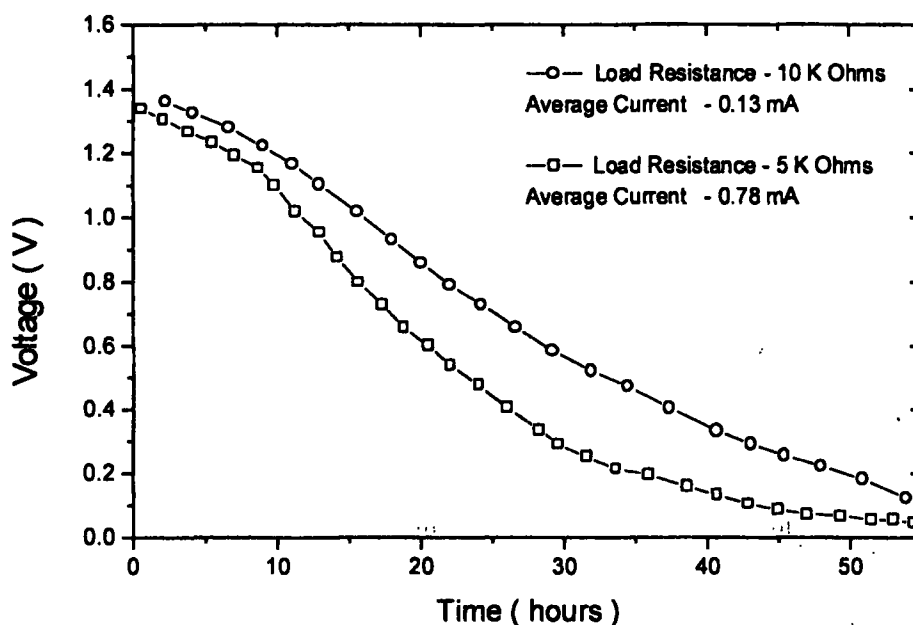


Fig. 4 Discharge curves for the cell $Cu(+)/Mg(ClO_4)_2[0.5PEO+0.5EC]_{10}/Mg(-)$ under constant load.

The internal resistance of the cell was found to be ≈ 200 k Ω and showed increase with the time of discharge. The performance of the cell is severely affected by the deposition of a magnesium layer on the copper electrode. This layer is probably responsible for the drop in voltage of the cell, as both electrodes effectively becomes Mg as time goes. It disturbs the stability and hence the long terms durability.

ACKNOWLEDGEMENTS

Authors wish to thank the International Science Programs, Uppsala University, Sweden for providing equipment and training, and to the University of Peradeniya for financial assistance.

REFERENCES

1. Farrington, G.C., Huq, R., Koksang, R. and Tonder, P.E., Influence of plasticizers on the electrochemical and chemical stability of a Li^+ polymer electrolyte, *Solid State Ionics*, **57**, 277-283 (1992).
2. Gray, F.M., *Solid Polymer Electrolytes: Fundamentals and Technological applications*, 1st edition, 1, VCH Publishers, New York (1991).

3. Croce, F., Passerini, S. Selvaggi, A. and Scrosati, B., Properties and applications of Lithium ion-conducting polymers, *Solid State Ionics*, **40/41**, 375-379 (1990).
4. MacCallum, J.R., Tomlin, A.S. and Vincent C.A., An investigation of the conducting species in polymer electrolytes, *Eur. Polym. J.*, **22**, 787-791 (1986).
5. Patrick A., Glasse M., Latham R. and Linford R., Novel solid state polymeric batteries, *Solid State Ionics*, **18/19**, 1063-1067 (1986).
6. Bandara, L.R.A.K., Dissanayake, M.A.K.L., Mellander, B.-E., Ionic conductivity of plasticized (PEO)-LiCF₃SO₃ electrolytes, *Electrochimica Acta*, **43**, 1447-1451 (1998).