# Electrochemical Studies on Poly(Ethylene Oxide) Based Gel-Polymer Electrolytes for Magnesium-Ion Batteries

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Abstract. Research and development works in the field of multi-valent metal-ion batteries are intensified these days because of the abundance of multi-valent elements such as magnesium, aluminum, calcium and so on in the Earth's crust. Magnesium-ion batteries are particularly important, because they have high theoretical volumetric capacity (3832 mAh cm<sup>-3</sup>) compared to that of wellknown lithium-ion batteries (2062 mAh cm<sup>-3</sup>). However, there are potential challenges, typically, designing suitable electrolytes with sufficient ambient temperature ionic conductivities is a major challenge. In this work, a set of gel-polymer electrolytes based on poly (ethylene oxide) (PEO) host polymer and magnesium acetate (Mg(CH<sub>3</sub>COO)<sub>2</sub>) ionic salt have been synthesized and characterized by electrochemical impedance spectroscopy (EIS), DC polarization and linear sweep voltammetry (LSV) techniques. Among the compositions studied in this work, the optimized PEO-Mg(CH<sub>3</sub>COO)<sub>2</sub>-EC-PC electrolyte (6:14:40:40 wt.%) showed an ambient temperature ionic conductivity of 6.1x 10<sup>-5</sup> S cm<sup>-1</sup>. Ionic conductivity vs inverse temperature showed Arrhenius behavior with almost same activation energies (0.15 - 0.18 eV) for all the compositions. DC polarization studies performed with stainless steel blocking electrodes under an externally applied voltage of 1V showed that the highest conducting composition is dominantly an ionic conductor with an ionic transference number of 0.99. The electronic contribution to conductivity was found to be almost negligible, which is desirable to avoid short circuits within the cell. The LSV test on highest conducting composition revealed that the electrochemical stability window of these electrolytes is about 2.2 volts.

## Introduction

Due to the limited availability and ever increasing prices of lithium based raw materials, present day battery research efforts are focused on so-called batteries beyond lithium-ion. Typically, multi-valent metal-ion batteries are heavily investigated these days because of the relatively high abundance of multi-valent elements such as magnesium, aluminum, calcium and so on in the Earth's crust [1-3]. Magnesium-ion batteries (MIBs) are becoming more and more popular in the R&D level, because they have high theoretical volumetric capacity (3832 mAh cm<sup>-3</sup>) compared to that of lithium-ion batteries (2062 mAh cm<sup>-3</sup>) [2, 4-6]. Apart from the natural abundancy, divalent Mg<sup>2+</sup> ions are favorable for efficient charging/discharging processes. Magnesium is less reactive than lithium with oxygen and water and could be handled in open air with minimum hazards. Further, ionic size of Mg<sup>2+</sup> (144 pm) is almost comparable to that of Li<sup>+</sup> (152 pm) and hence insertion compounds used in lithium-ion batteries can also be used for MIBs [2]. However, as in many other secondary battery systems, designing suitable electrolytes with sufficient ambient temperature ionic conductivities, suitable electrochemical and mechanical stabilities, is a major challenge in the field of MIBs.

Due to several advantages such as ease of fabrication as thin films, flexibility to accommodate volume changes of the electrodes during charging/discharging processes, cheapest raw materials, good interfacial stability and so on, polymer electrolytes are highly preferred for secondary batteries [7-8]. There are a few works done on polymer electrolytes for MIBs, but the quasi-solid state gel-polymer electrolytes (GPEs) are in the early stages of investigation as far as MIBs as concerned [3, 5-6, 9-11].

Poly (ethylene oxide) (PEO) is a very commonly used polymer host for synthesizing polymer electrolytes for secondary batteries. In this work, PEO-magnesium acetate based GPEs have been synthesized and characterized for applications in MIBs. Acetate anion (CH<sub>3</sub>COO<sup>--</sup>) is almost double in size compared to that of Mg<sup>2+</sup> and hence cationic contribution to conductivity could be enhanced in these GPEs. It has been found that the best conducting composition, PEO-Mg(CH<sub>3</sub>COO)<sub>2</sub>-EC-PC (6:14:40:40 wt.%), showed an ambient temperature ionic conductivity in the order of  $10^{-5}$  S cm<sup>-1</sup>.

## **Materials and Methods**

Five different compositions of PEO-Mg(CH<sub>3</sub>COO)<sub>2</sub>-EC-PC GPEs have been synthesized as listed in Table 1. PEO, Mg(CH<sub>3</sub>COO)<sub>2</sub>, EC and PC, all purchased from Sigma-Aldrich, are the polymer host, ionic salt, plasticizer and the solvent, respectively. Magnesium acetate, Mg(CH<sub>3</sub>COO)<sub>2</sub>, was vacuum dried for 8 hours at 50 °C prior to use as it is a highly hygroscopic material. All the other chemicals were used as received. For the synthesis of GPEs, required amount of Mg(CH<sub>3</sub>COO)<sub>2</sub>, EC and PC were magnetically stirred at room temperature for 3 hours, then the required amount of PEO was added and stirred again for 5 hours at 75 °C until a clear homogenous gel sample was obtained.

Metrohm Autolab (PGSTAT 128N) impedance analyzer in the frequency range from 1 Hz to 0.1 MHz was used for impedance measurements on disc shaped samples sandwiched between two spring-loaded stainless steel blocking electrodes (SS/GPE/SS) separated by an insulating spacer. The temperature of the samples was varied from 25 to 75 °C and the impedance data were recorded at 10 °C intervals on heating. The ionic conductivity of each samples were estimated by finding the bulk resistances in the respective Nyquist plots. DC polarization test was performed at room temperature on best conducting sample under an applied voltage of 1V with a scan rate of 5 mV s<sup>-1</sup>; stainless steel (SS) blocking electrodes were used to assemble the cell. The electrochemical window of the best conducting sample was found from the linear sweep voltammetry (LSV) studies performed with a scan rate of 5 mV s<sup>-1</sup> for a cell configuration of SS/GPE/SS.

Sample	PEO (wt.%)	Mg(CH <sub>3</sub> COO) <sub>2</sub> (wt.%)	EC (wt.%)	PC (wt.%)
Α	14	06	40	40
В	12	08	40	40
С	10	10	40	40
D	08	12	40	40
Ε	06	14	40	40

Table 1. Sample compositions of five different PEO-Mg acetate based GPEs synthesized in this work.

## **Results and Discussion**

Five different compositions, A, B, C, D and E were synthesized by systematically varying the ether oxygen (EO)/Mg<sup>2+</sup> ratio as summarized in Table 1. In all these samples, both plasticizer EC and the liquid solvent PC were kept fixed at 40 wt.%. Electrochemical impedance spectroscopic (EIS) data were recorded by using Metrohm Autolab (PGSTAT 128N) impedance analyzer with an applied ac signal of 10 mV in the frequency range of 1 Hz to 0.1 MHz. EIS is a powerful technique used to study the electrochemical properties of the electrolytes and also the properties of electrolyte/electrode interfaces. EIS is used as one of the major techniques to study electrolytes and electrolyte/electrode interfaces in almost all types of secondary battery systems [1-10]. Nyquist plot representation of the EIS spectra at ambient temperature are shown in Fig.1a for all the compositions. Nyquist plots usually consist of a semi-circle in the high frequency region followed by a spike in the low frequency region. The intercept of the low frequency end of the semi-circle with the X-axis gives rise to the bulk

resistance  $(r_b)$  of the electrolytes. By using the bulk resistance values extracted from the respective Nyquist plots, the ionic conductivity values ( $\sigma$ ) were calculated using equation (1).



Fig. 1 (a) Nyquist plots at RT, and (b)  $\sigma$  vs 1/T plots, for PEO-Mg(CH<sub>3</sub>COO)<sub>2</sub>-EC-PC gel-polymer electrolyte samples, A, B, C, D and E.

 $\sigma = t/r_b A$ 

where A is the cross-sectional area and t is the thickness of the electrolyte sample sandwiched between stainless steel blocking electrodes with the help of a non-conducting spacer.

As shown in Fig.1a, the radii of the semi-circles systematically decrease from samples A to E with the increase of the magnesium acetate salt content. Lowest bulk resistance at ambient temperature is observed for sample E leading to highest conductivity among all the samples studied in this work. Our attempts to synthesize samples with salt concentration higher than 14 wt.% was not successful due to the segregation of ionic species. On the other hand, gel formation was not possible for samples with PEO concentration higher than 14 wt.%. As listed in Table 2, ambient temperature ionic conductivity is in the order of 10<sup>-5</sup> S cm<sup>-1</sup> for all the compositions studied in this work and the highest ambient temperature ionic conductivity of 6.1 x 10<sup>-5</sup> S cm<sup>-1</sup> was observed for sample E. Increase in conductivity with salt content can be attributed to the increased concentration of mobile ions. Mg<sup>2+</sup> ions are favourable to have better ionic conductivities, because they are divalent charge carriers. Magnesium acetate is advantageous, because the size of acetate anion (CH<sub>3</sub>COO<sup>--</sup>) is almost double compared to that of Mg<sup>2+</sup> cations and hence cationic contribution to the ionic conductivity can be enhanced. There are a couple of reports in the literature on magnesium acetate based electrolytes for MIBs [1, 12]. Typically, Kadir et. al. [12] reported almost same ambient temperature ionic conductivity of 1.12 x 10<sup>-5</sup> S cm<sup>-1</sup> for a potato starch - magnesium acetate based biopolymer electrolyte incorporated with an ionic liquid. In 2011, Hashmi et.al.[13] also studied an ionic liquid mediated PEO based GPE system for MIBs and reported a room temperature ionic conductivity of 5.6 x 10<sup>-4</sup> S cm<sup>-1</sup>.

Conductivity variation with inverse temperature ( $\sigma$  vs 1/T) is shown in Fig.1b. All these GPE samples show Arrhenius behavior of conductivity variation with inverse temperature satisfying the Arrhenius equation given in (2).

$$\sigma(T) = \sigma_0 \, e^{-E_a/kT} \tag{2}$$

where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy and k is the Boltzmann constant.

There are a few other  $Mg^{2+}$  ion conducting GPE systems reported in the literature which also showed Arrhenius behavior of conductivity variation with inverse temperature [1, 6, 13]. From the slopes of the respective ln  $\sigma$  vs 1/T plots shown in Fig.1b, activation energies and the pre-exponential factors have been calculated for each and every composition (A to E) and are tabulated in Table 2 along with ambient temperature ionic conductivities. It has been found that the activation energies are almost the same varying between 0.15 to 0.18 eV for all the GPEs studied in this work; a clear evidence that the activation process is primarily controlled by the concentrations of EC and PC rather than that of the polymer host and/or the magnesium-acetate ionic salt. As can be noticed in Fig.1b, conductivity increases with temperature, which would be mainly due to the increase in free volume and segmental flexibility within the polymer chains leading to increased mobility of ionic species.

Sample	σ <sub>RT</sub> (S cm <sup>-1</sup> )	σ <sub>0</sub> (S cm <sup>-1</sup> )	Ea (eV)
Α	1.4 x 10 <sup>-5</sup>	1.1 x 10 <sup>-2</sup>	0.17
В	1.8 x 10 <sup>-5</sup>	0.7 x 10 <sup>-2</sup>	0.15
С	3.6 x 10 <sup>-5</sup>	4.6 x 10 <sup>-2</sup>	0.18
D	4.3 x 10 <sup>-5</sup>	2.6 x 10 <sup>-2</sup>	0.16
Е	6.1 x 10 <sup>-5</sup>	3.9 x 10 <sup>-2</sup>	0.17

Table 2. Conductivity at ambient temperature ( $\sigma_{RT}$ ), pre-exponential factor ( $\sigma_0$ ) and the activation energy ( $E_a$ ) of PEO-magnesium acetate based GPEs.

In order to differentiate the ionic and/or electronic contributions to the conductivity, DC polarization analysis was carried out by applying a constant DC voltage of 1 V across the SS/GPE/SS cell and the resulting current vs time plot is shown in Fig.2a for sample E; the highest conducting composition. Current was measured with time for about 12 hours and a sudden drop of current to almost zero within a few minutes indicates that the electrolyte is a dominant ionic conductor. The estimated ionic transference number is,  $t_{ion} = 0.99$ , which is almost close to unity as expected and hence the electronic contribution to conductivity is insignificant. After all, this is one of the important requirements for an efficient electrolyte to avoid short circuits within the cell. LSV data was also recorded on sample E (Fig.2b). From the LSV data, the electrochemical stability window (ESW) of the highest conducting composition (sample E) was determined as 2.2 V.



Fig. 2 (a) DC polarization curve measured under an applied DC voltage of 1 V, and (b) LSV curve; both recorded with a scan rate of 5 mV s<sup>-1</sup> in the configuration SS/GPE/SS for the highest conducting composition; sample E.

#### Conclusion

Among a set of PEO-Mg acetate based GPEs studied in this work, the optimized PEO-Mg(CH<sub>3</sub>COO)<sub>2</sub>-EC-PC composition (6:14:40:40 wt.%) showed an ambient temperature conductivity of  $6.1 \times 10^{-5}$  S cm<sup>-1</sup>. Conductivity vs inverse temperature showed Arrhenius behavior with almost same activation energies for all the compositions. DC polarization studies revealed that the highest conducting composition is dominantly an ionic conductor with an ionic transference number of 0.99. The electronic contribution to conductivity was found to be almost negligible, which is desirable to avoid short circuits within the cell. The LSV test showed that the electrochemical stability window of the highest conducting composition is about 2.2 volts. The size of acetate anion (CH<sub>3</sub>COO<sup>--</sup>) is almost double compared to that of Mg<sup>2+</sup> cations and hence anionic mobility will be minimized in these electrolyte systems.

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