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Citation: AIP Conference Proceedings 1711, 050003 (2016); doi: 10.1063/1.4941629
View online: http://dx.doi.org/10.1063/1.4941629
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1711?ver=pdfcov
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Ionic Transport and Electrochemical Stability of PVDF-HFP Based Gel Polymer Electrolytes

A. Rosdi\textsuperscript{a)}, N. H. Zainoi\textsuperscript{b)} and Z. Osman\textsuperscript{c)}

Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

\textsuperscript{a)} atiq.ngah@yahoo.com
\textsuperscript{b)} husna.zai87@gmail.com
\textsuperscript{c)} Corresponding author: zurinaosman@um.edu.my

Abstract. The gel polymer electrolytes (GPEs) samples consisting of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), ethylene carbonate (EC) and propylene carbonate (PC) with different concentrations of magnesium triflate salt, Mg\textsubscript{2}+\textsubscript{3}O\textsubscript{3} were prepared using the solution casting technique. The ionic conductivity of the GPEs was studied by using a.c impedance spectroscopy and the sample containing 20 wt% salt exhibited the highest conductivity of 5.11 \times 10^{-3} \text{ S cm}^{-1}. Ionic transport number of the GPEs shows that the samples contain ionic species as main charge carrier while cationic transport number for the highest conducting sample was found to be 0.27. The electrochemical properties of the GPEs were studied using Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV). The GPEs show high electrochemical stability ~3.5V (versus Mg\textsuperscript{2+}/Mg) where the highest conducting sample exhibited the highest stability.

INTRODUCTION

Polymer electrolyte has been one of the main topics in the research and development of rechargeable batteries to fulfill high demand of users since three decades ago [1]. Currently, gel polymer electrolytes (GPEs) have attracted interest in this field of research, as the most suitable candidate to replace solid electrolytes and liquid electrolytes for the safe fabrication of battery, due to their advantages [2]. Gel polymer electrolyte is comprised of liquid electrolytes and polymer hosts, where the host polymer provides mechanical stability and easy film formation, meanwhile salt solutions are remain in the polymeric structure to enable the ionic conduction process [3]. In this work, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) has been used as a polymer host in the GPE samples containing magnesium triflate salt as ion provider. PVDF-HFP satisfies the two major properties such as high conductivity and good mechanical strength, due to its co-existence of crystalline PVDF-HFP [4]. Additionally, magnesium salt seems to have more advantages towards the cost effective due to its natural abundance, more stable and safe technology for large scale applications rather than lithium salt [5-6]. Magnesium also has capabilities closed to the lithium batteries such as low electrochemical equivalence (12.15 g equiv\textsuperscript{-1}) and negative electrode potential [7]. Moreover, magnesium ions are possible to replace lithium ions as the charge carrier in gel polymer electrolytes, due to its ionic radii that closed to lithium ions. It was reported that the reversibility of Mg\textsuperscript{2+} and Mg electrode occurs in GPE for the purpose of rechargeable battery [8]. The addition of plasticizers, such as ethylene carbonate (EC) and propylene carbonate (PC) to the GPE helps in solvating the salt and acts as a conducting path. The plasticizers also decreases the glass transition temperature of the polymer by softening the polymer backbone, thus increase the ionic conductivity [9-11].

In this present study, the effect of different concentrations of magnesium triflate (MgCF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} on the ionic conductivity was investigated by using a.c impedance spectroscopy. The transport number measurements were also performed on the GPE samples. The electrochemical window stability was then studied by linear sweep voltammetry (LSV) and cyclic voltammetry (CV).
**EXPERIMENTAL METHODS**

**Preparation of Gel Polymer Electrolytes Sample**

Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), molecular weight of 400,000 g/mol, from Aldrich was used as a host polymer, ethylene carbonate (EC) from Fluka and propylene carbonate (PC) from Aldrich were used as plasticizing solvents, magnesium triflate, \((\text{Mg(CF}_3\text{SO}_3))_2\) was used as a dopant salt and tetrahydrofuran (THF) from Fluka was used as a solvent. PVDF-HFP and \((\text{Mg(CF}_3\text{SO}_3))_2\) salt were dried at 70 °C for 24 h under vacuum (< 10⁻³ Torr) prior to their use.

A fixed amount of PVDF-HFP was dissolved in THF and the mixture was stirred and heated until the solution turned into a clear and homogeneous mixture. After complete dissolution, \((\text{Mg(CF}_3\text{SO}_3))_2\) salt and a mixture of EC and PC (with a fixed mass ratio of 2:1) were added to the polymer solution. The solution was then stirred and heated continuously for several hours until a homogenous solution was obtained.

In this work, the gel polymer electrolyte samples were prepared by varying the salt concentration from 5 wt% to 30 wt%. The GPE samples were obtained by casting the solution onto glass petri-dishes and the solvent was left to evaporate slowly at room temperature. The plasticized PVDF-HFP film without salt was also prepared as a reference.

**Ionic Conductivity Studies**

The ionic conductivity studies of the GPE samples were conducted by using HIOKI 3533 LCR impedance spectroscopy analyzer that interfaced with a computer in the frequency range from 10 Hz to 200 KHz. The GPE samples were sandwiched between two stainless steel electrodes. The value of bulk resistance \(R_b\) was obtained from Cole-Cole plot. The ionic conductivity can be obtained by using equation:

\[
\sigma = \frac{t}{R_b A}
\]

where \(t\) is the thickness of the GPE films and \(A\) is the contact area between the electrodes and electrolyte.

**Transport Number Studies**

The ionic transport number was measured using a direct current (DC) polarization method as proposed by Watanabe et al. [12]. The sample was sandwiched with the configuration of SS|GPE|SS, where SS is the stainless steel that acts as blocking electrodes. The current was monitored as a function of time on the application of fixed voltage of 0.3V across the GPE sample. The value of ionic transport number can be determined by using the equation:

\[
T_{\text{ion}} = t_T - \frac{t_e}{t_T}
\]

where \(t_e\) and \(t_T\) are the electronic and total current, respectively.

Meanwhile, the cationic transport number was evaluated by the method that proposed by Evans et al. [13] using the combination of DC polarization method and AC impedance spectroscopy. The cells were polarized by applying fixed voltage of 0.3V and subsequently initial and final currents were recorded. The cells were subjected to AC impedance spectroscopy before and after polarization. The \(\text{Mg}^{2+}\) transport number, \(t_+\) values were then determined using the equation:

\[
t_+ = \frac{t_s}{t_0} \left( \frac{\Delta V - R_s I_s}{\Delta V - R_0 I_0} \right)
\]

where \(t_0\) and \(t_s\) are the initial current and final current, respectively. \(R_0\) and \(R_s\) are the cell resistances before and after polarization, respectively.
Linear Sweep Voltammetry (LSV)

LSV studies were conducted by using WPG 100e system performed on a SS|GPE|Mg cell to estimate electrochemical window stability using voltage range from – 4 V to 4 V with scan rate of 5 mV/s⁻¹.

Cyclic Voltammetry (CV)

CV was performed using a potentiostat/galvanostat on symmetrical cell of Mg|GPE|Mg to investigate the electrochemical behaviour of the GPE sample at the interface between electrode and electrolyte.

RESULTS AND DISCUSSION

Ionic Conductivity Studies

<table>
<thead>
<tr>
<th>Amount of salt (wt.%)</th>
<th>Conductivity (S/cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.70 × 10⁻⁴</td>
</tr>
<tr>
<td>10</td>
<td>1.68 × 10⁻³</td>
</tr>
<tr>
<td>15</td>
<td>3.73 × 10⁻³</td>
</tr>
<tr>
<td>20</td>
<td>5.11 × 10⁻³</td>
</tr>
<tr>
<td>25</td>
<td>4.46 × 10⁻³</td>
</tr>
<tr>
<td>30</td>
<td>3.88 × 10⁻³</td>
</tr>
</tbody>
</table>

Table 1 lists the conductivity values for GPE samples containing magnesium triflate salt at room temperature. It was observed that the optimum conductivity value of 5.11 × 10⁻³ S/cm⁻¹ was obtained from the sample containing 20 wt% (Mg(CF₃SO₃))₂ salt. The increase in the ionic conductivity with salt content is related to the increase of the number of free ions. However, the ionic conductivity decreases as more than 20 wt% of salt were added to the samples. This is due to the aggregation of ions and caused the formation of ion clusters, thus reducing the number of charge carriers [14-15].

Transport Number Studies

The ionic transport number for samples containing 10 wt%, 20 wt% and 30 wt% salt has been evaluated using the DC polarization method. Figure 1 shows the trends of current as a function of time until it reached a constant value. By using Eq. (2), the value of ionic transport number was calculated as suggested by Pandey et al. [7]. The values obtained were found to be > 0.98. This result indicates that the major charge carriers in the GPE samples are ions. Effect of ion-ion and polymer-ion interactions on the microscopic parameter might also influenced the value of high ionic transport number [16].

The cationic transport number of these GPE samples was also calculated by using Eq. (3). The cell resistances before and after polarization were obtained from impedance plots while the initial and final currents were obtained from the current-time plot as shown in Fig. 2. The intercept at the high-frequency region of the impedance plot corresponds to the resistance of electrolyte. It can be observed that the resistance of electrolyte remained at about the same value, suggesting that the composition of the GPE samples did not change even after polarization. On the contrary, the diameter of the semicircle at the low-frequency region has formed from the total resistance of the cell. Upon the polarization, the value of the total cell resistance has increased, indicating that the passivation layer is formed. The values of Mg²⁺ transport number were calculated as 0.11, 0.27 and 0.20 for samples containing 10 wt%, 20 wt% and 30 wt% of Mg(CF₃SO₃)₂ salt, respectively. These values suggest a major contribution of triflate anion towards the conductivity mechanisms of the GPE samples.
FIGURE 1. Normalized current versus time for GPE samples containing (a) 10 wt% (b) 20 wt% (c) 30 wt% of Mg(CF$_3$SO$_3$)$_2$

FIGURE 2. DC Polarization current curve for GPE sample containing 20 wt% salt as a function of time. Inset graph shows the impedance plot (a) before polarization and (b) after polarization.

Linear Sweep Voltammetry (LSV) Analysis

The electrochemical stability studies of the GPE films can be evaluated by using LSV which is recorded on SS|GPE|Mg. The current-voltage response curves of GPE samples containing 10 wt%, 20 wt% and 30 wt% of Mg(CF$_3$SO$_3$)$_2$ salt are shown in Fig. 3. The range of the voltage stability can be observed between -3.5 to 3.5 V (versus Mg$^{2+}$/Mg) for all samples, which can be assigned to the decomposition voltages of the polymer electrolytes. This result suggests that the synthesized GPE film could be applicable for the high voltage cathode materials with Mg intercalations. Therefore, these values of voltage stability show that the GPE samples are suitable to be used as electrolyte in magnesium battery [2].
FIGURE 3. Linear sweep voltammetry of the cells prepared with the GPE samples containing (a) 10 wt% (b) 20 wt% and (c) 30 wt% of Mg(CF$_3$SO$_3$)$_2$

Cyclic Voltammetry (CV) Analysis

FIGURE 4. Cyclic voltammetry of GPE sample containing 20 wt% salt with symmetrical cell of Mg|GPE|Mg

In addition, the electrochemical stability test of the highest conducting sample was performed on symmetrical cell of Mg|GPE|Mg at room temperature by using cyclic voltammetry. Figure 4 presents the CV curves for four cycles of Mg|GPE|Mg cell. There are two main features can be observed from the curves:
1. The peak current tends to decrease with the increase in cycle number and remains constant in third and fourth cycle.

2. The subsequent sweeps nearly overlapping with symmetric anodic and cathodic sweeps

The redox peaks corresponding to anodic oxidation at 2.5 V and cathodic reduction at -2.5 V occurred versus Mg$^{2+}$/Mg. The peak current tends to decrease during the initial cycles may due to formation of passivation layer on electrode and stabilize afterwards. On cycling, there is no substantial change in the redox peak voltages and the overlapping of the subsequent sweeps indicates that the charge transfer reaction at the interface between the GPE sample and magnesium metal is reversible and the GPE is able to support reversible redox process [17].

CONCLUSIONS

The highest room temperature conductivity of $5.11 \times 10^{-3}$ S cm$^{-1}$ was obtained from GPE sample containing 20 wt% Mg($\text{CF}_2\text{SO}_3$)$_2$ salt. The ionic transport number revealed that the charge carriers in the GPE samples are mainly due to ions. The Mg$^{2+}$ ions transport number of the highest conducting sample was found to be 0.27. The electrochemical properties of GPE samples display stability up to 3.5 V. Cyclic voltammetry shown the GPE able to support the reversible redox process thus suggested the GPE can provide better cycle stability for operation in magnesium battery.

ACKNOWLEDGEMENTS

Authors would like to thank the Ministry of Higher Education Malaysia and University of Malaya for the grant, FP003-2013B.

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