PMMA-LiBOB Gel Polymer Electrolytes in Lithium-Oxygen Cell

M Z Kufian, A K Arof*, S. Ramesh
Center for Ionics University of Malaya, Physics Department, University of Malaya, 50603 Kuala Lumpur

*Corresponding author’s email: akarof@um.edu.my

Abstract. In this study, gel polymer electrolytes (GPEs) have been prepared using PMMA, lithium bis(oxalato)borate, (LiBOB) and tetraethylene glycol dimethyl ether, (TEGDME) as polymer host, ion source and solvent, respectively. PMMA-LiBOB-TEGDME GPEs were used using electrical impedance spectroscopy, Fourier-transform infrared spectroscopy, linear sweep voltammetry, transference number and also charge-discharge measurement. The highest conductivity is achieved by the 15 wt.% LiBOB- 32.69 wt. % PMMA-52.31 wt. %TEGDME GPE with the conductivity value of 1.71 mS cm\(^{-1}\). From the FTIR deconvolution of selected GPE, the highest ionic conductivity of GPE is contributed by the 64% of the free ion. The Li-ion transference number for the highest conducting GPE is 0.38. The GPEs are stable up to 4.2 V (vs.Li/Li\(^+\)) suggesting suitability for the application in the lithium-oxygen battery. The capacity is 447 mAh g\(^{-1}\) at the first discharge cycle.

Keywords: Lithium-oxygen cell, LiBOB, PMMA, TEGDME, conductivity

1. Introduction
A lithium-oxygen battery is one of the satisfactory candidates to replace the traditional lithium-ion battery since its high energy density of ~11.5 kWh kg\(^{-1}\) compared to fossil fuels [1]. The three components in a lithium-oxygen cell are lithium metal, electrolyte and air cathode [2]. Generally, the electrolyte was liquid electrolyte due to the highest ionic conductivity [3-5]. Apart from that, the liquid electrolyte has several disadvantages such as volatile, flammable and leakage[6]. To overcome these problems, a new design of the electrolyte system without scarifying the ionic conductivity of the electrolyte is very important. Gel polymer electrolytes (GPEs) are the suitable candidate to replace the liquid electrolyte in the battery system. From the literature [7-9], the ionic conductivity of GPEs in ranges ~ 10\(^{-3}\) S cm\(^{-1}\) which are comparable with a conductivity of the liquid electrolyte. Our previous work reported [10] that by using polyacrylonitrile (PAN)-LiBOB GPE obtained the highest conductivity and also discharge capacity of 0.12×10\(^{-3}\) S cm\(^{-1}\) and 187 mAh g\(^{-1}\), respectively. In this work, we are using poly(methyl methacrylate) (PMMA) as polymer host, LiBOB as lithium-ion donor and TEGDME as the solvent. LiBOB was selected due to the bigger size of anion perhaps it can improve the lithium-ion transference number [11,12]. While PMMA was selected due to stable against nucleophilic Li:O\(_2\) attack [13]. To understand the Li\(^+\) ion interaction of LiBOB in PMMA-TEGDME GPEs, a structural analysis which is FTIR has been carried out. In the electrochemical analysis, conductivity measurement,
transference number, and LSV were tested. Charge-discharge measurement using the highest conductivity of LiBOB-PMMA-TEGDME GPE as an electrolyte was tested to determine the suitability of the GPE in the lithium-oxygen cell.

2. Methods

2.1. Preparation of GPEs
PMMA and LiBOB were heated and vacuum at 60 °C inside a vacuum oven for 4 hours before used to remove moisture content. TEGDME solvent was added with molecular sieves (d = 4 Å). The TEGDME solvent with containing molecular sieves was vacuumed until bubbles disappeared. The TEGDME solution was stored in an inert gas (argon gas) to make the solution in an inert environment. Various wt.% of LiBOB was added in 0.8g TEGDME solution and stirred until completely dissolved. Table 1 was shown the weight of PMMA and salt materials used for preparing PMMA-LiBOB-TEGDME GPEs. Then, 0.5 g PMMA was added and continuously stirred and heated at 80 °C to make a gel polymer solution. The gel polymer solution was cast in glass petri dish and pressed it using a clean glass plate to make a gel polymer electrolyte film. The GPEs was stored in the inert gas environment for future characterizations.

| Composition                  | PMMA (g) | LIBOB (g) |
|------------------------------|----------|-----------|
| 100 wt.% PMMA                | 0.5      | 0.000     |
| 5.0 wt.% LiBOB-36.52 wt.% PMMA-58.44 wt.% TEGDME | 0.5 | 0.0690 |
| 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME | 0.5 | 0.2294 |
| 20 wt.% LiBOB-30.77 wt.% PMMA-49.23 wt.% TEGDME | 0.5 | 0.3250 |
| 25 wt.% LiBOB-28.85 wt.% PMMA-46.15 wt.% TEGDME | 0.5 | 0.4333 |
| 30 wt.% LiBOB-26.92 wt.% PMMA-43.08 wt.% TEGDME | 0.5 | 0.5571 |

2.2. Characterizations of GPEs

2.2.1. Electrical Impedance Spectroscopy (EIS)
The conductivity of the GPEs was measured using the computerized LCR meter (HIOKI model IM3570) in the frequency range from 1 MHz to 50 Hz. The thickness of GPEs was measured using a micrometer gauge. The conductivity of the samples was calculated from Equation 1.

$$\sigma = \frac{t}{AR_B}$$

where \(t\), \(R_B\) and \(A\) are thickness (cm), bulk resistance and area of the electrolyte film, respectively. The ionic conductivity measurement of the GPEs was taken from room temperature until 120 °C.

2.2.2. Fourier transform infrared (FTIR) spectroscopy
The effect on the structure of salt concentration for PMMA-LiBOB GPEs system can be determined by using FTIR spectroscopy. FTIR spectroscopy was carried out using the Thermo Scientific model Nicolet iS10 in the absorbance mode between 2100 and 700 cm\(^{-1}\) with resolution 1 cm\(^{-1}\). The IR bands were also deconvoluted using the OMNIC software. Holomb et al. [11] reported free BOB\(^–\) ions could be identified at various wavenumbers on the IR spectrum: 1804, 1780, 1273, 1200, 1096, 986 and 703 cm\(^{-1}\). In this work, the out-of-phase carbonyl (C=O) stretching [\(\nu_{out}(C=O)\)] mode of LiBOB with free BOB\(^–\) ions and Li\(^+\)···BOB\(^–\) ion pairs located at 1804 and 1828 cm\(^{-1}\) respectively were investigated. From this information in above, the area percentage of free ions (%FI) was calculated using Equation 2.
\[
\% FI = \frac{A_{FI}}{A_{FI} + A_{IP}} \times 100\%
\]  

(2)

where \(A_{FI}\) and \(A_{IP}\) refer to the areas of free ions and ion pairs respectively. The values of the areas were obtained directly from OMNIC software.

2.2.3. Transference number \((T_{Li^+})\)

Bruce & Vincent methods were selected to measure the lithium-ion transference number. Lithium metal foil was selected as a non-blocking electrode. The GPEs were sandwiched between two non-blocking electrodes and was done inside a glove box with argon environment. An impedance measurement was taken before and after the polarization. The polarization was done by applying a small constant potential (10 mV) on an electrolyte between non-blocking lithium electrodes. The transference number for the lithium-ion can be calculated using equation (6) below:

\[
t_{Li} = \frac{I_{ss}(V - I_{ss}R_{ss})}{I_0(V - I_{ss}R_{ss})}
\]

(3)

where \(t_{Li}\), \(V\), \(R_0\), and \(R_{ss}\) are lithium transference number, applied potential, initial resistance of the passivation layer and resistance of the passivation layer (steady state), respectively.

2.2.4. Linear sweep voltammetry \((LSV)\)

LSV was carried out by using two electrodes system to measure electrochemical window \((ECW)\) of the GPEs. Stainless steel \((SS)\) and lithium metal were selected as working and a counter electrode respectively. The GPEs was sandwiched in between working and counter electrode. Open circuit voltage \((OCV)\) of the LSV configuration was measure before LSV measurement start. Electrochemical analyzer brand from CH Instrument (model: 600E) was used. The measurement was set from an initial voltage which is this case is OCV value.

2.2.5 Fabrication of lithium-oxygen cell

Super P and polyvinylidene difluoride \((PVDF)\) in a weight ratio of 80:20 was selected for preparing lithium air cathode. 20 wt.% of PVDF was dissolved in N-Methyl-2-pyrrolidone \((NMP)\) solvent and stirred and heat at 80 °C to obtain a uniform transparent solution, then put the super p into the solution and stirring for overnight. The slurry solution was coated on the surface of Toray carbon paper by using a brush technique. The Toray carbon paper was dried and vacuum at 120 °C for overnight. The weight of the Toray carbon paper was weighed before and after the coating in order to calculate the mass of the electrode active materials. Cells were assembled in a glove box filled with pure argon. The GPE was sandwiched in between air cathode and lithium metal electrode. The charge-discharge tests were conducted using battery cycler \((Neware, China)\) with cut-off voltages of 2.0–4.2 V at a constant current density of 0.02 mA cm\(^{-2}\).

3. Results and Discussion

The ionic conductivity behavior of PMMA–LiBOB GPEs system was shown in Figure 3. The conductivity of GPE LiBOB salt is 6.76\(\times\)10\(^{-5}\) S cm\(^{-1}\). The ionic conductivity was ascertained to increase with the LiBOB salt content up to 15 wt.% LiBOB salt with the value of 1.71\(\times\)10\(^{-3}\) S cm\(^{-1}\). The increment of the ionic conductivity value may be due to the increasing number of free ion. This will be further discussed in the FTIR deconvolution analysis. The conductivity dropped due to the association of ion to form aggregate ions.
Figure 1. Variation of conductivity as a function LiBOB salt

Figure 2 presents the FTIR spectra of pristine PMMA and various concentrations of PMMA-LiBOB GPEs in the region between 700 and 2100 cm$^{-1}$. Bands due to the pristine PMMA (Figure 2a) were observed at 748 (CH$_2$ rocking modes), 840 (C-O), 983 (CH$_2$ wagging modes), 1143 (CH$_2$ twisting), 1239 (C–O-C bending vibration), 1722 (C=O band) and 2951 cm$^{-1}$ (C-O-C). Theerthagiri et al. [14] have also reported that bands at 745, 839, 974, 1142, 1230, 1439, 1730, and 2951 cm$^{-1}$ are found in the PMMA based polymer film. Several changes can be observed from the FTIR spectrum indicated that there are interactions between Li$^+$ ion from LiBOB salt and PMMA. The C=O band of PMMA salt was observed to shift from 1722 (GPE without salt) to 1733 cm$^{-1}$ with an addition of a various amount of LiBOB. The peak at 1189 cm$^{-1}$ belongs to C-O-C group also shifted to the 1198 cm$^{-1}$ as LiBOB content increased. A similar observation was also observed at peak 1482 cm$^{-1}$ which are dedicated to CH$_2$ scissoring mode. From these results, confirmed that interactions occurred in PMMA-LiBOB GPEs.

The FTIR spectrum was deconvoluted in order to resolve the hidden bands that might be contributed to the polymer-salt interactions. Figure 3 shows the FTIR deconvolution of the 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% at the region between 1760 and 1850 cm$^{-1}$. TEGDME all samples. The deconvoluted bands are correspond following the report of Holomb et al.[11]. The presence of free ions can be observed from a strong band appeared. However, another three bands at 1812, 1819 and 1829 cm$^{-1}$ are due to the contact ions of LiBOB salt. The percentages of free and contact ions can be calculated from the ratio of the respective area to the total area of the deconvolution bands. Table 2 lists the percentage of free and contact ions of the PMMA based GPEs with various concentrations of LiBOB. Our previous work reported that the highest ionic conductivity of LiBOB-PVDF electrolyte also gave the highest percentage of free ion 66% [15].

![Graph](image_url)

**Table 2.** Area percentage of free and contact ions of the PMMA – LiBOB gel electrolyte

| LiBOB Salt(wt.%) | % Free ions | % Contact ions |
|------------------|-------------|---------------|
| 5                | 56          | 44            |
| 15               | 64          | 36            |
| 20               | 62          | 38            |
| 25               | 55          | 45            |
| 30               | 57          | 36            |
Figure 2. FTIR spectra of (a) Pristine PMMA, (b) 0 wt.% (c) 5 wt.% (d) 15 wt.% (e) 20 wt.% (f) 25 wt.% and (g) 30 wt.% of LiBOB salt and (h) TEGDME solvent

Figure 3. Deconvolution of 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME
The ECW of the GPE containing 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME was measured on a stainless steel electrode from open circuit voltage to 6.0 V, as shown in Figure 5. From the graph, the GPE started to oxidize slowly from 4.2 V and then sharply increased at 4.7 V. This LSV value is reasonable and was reported in the literature[9]. The result indicates that the GPE is suitable to be applied in energy devices such as a lithium-oxygen battery.

Figure 4. Potential window stability of 15 wt.% LIBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME GPE

Figure 5. (a) DC polarization with an applied voltage of 10 mV and (b) Nyquist plot before and after DC polarization of 15 wt.% LIBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME GPE
Figure 6. Charge and discharge profile of the lithium-oxygen cell using 15 wt.% LIBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME GPE performed using a current of 0.02 mA cm$^{-2}$ at (a) 1$^{st}$, (b) 3$^{rd}$ and (c) 15$^{th}$ cycles.

Lithium-ion transference number of GPE containing 15 wt.% LIBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME GPE was used to sandwich between lithium metal non-blocking electrodes. The transference number, $T_{\text{Li}^+}$ was evaluated by dc polarization measurement in conjunction with ac impedance spectroscopy reported by Evans et al.\cite{16}. DC polarization measurements were carried out to determine the initial, $I_o$ and steady-state, $I_s$ currents by applying a dc voltage of 10 mV across the sample. Impedance spectroscopy was used to determine the film resistances before, $R_o$ and after, $R_s$ the dc polarization measurement. Transference number, $T_{\text{Li}^+}$ of the GPE sample was calculated from Equation 3 as mentioned. The transference number, $T_{\text{Li}^+}$ of 15 wt.% LIBOB-32.96 wt.% PMMA-52.04
wt.% TEGDME GPE is 0.38. Previous studies reported the transference number of LiBOB based salt in the range of 0.25 to 0.46 [17, 18].

Figure 6 shows the charge and discharge performance of lithium-oxygen cell using 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME GPE at 1st, 3rd and 15th cycles. The discharge capacity at the 1st and 3rd cycles were 447 and 40 mAh g⁻¹ respectively. The discharge capacity keeps decreasing on the increasing number of cycles. From the charge and discharge curve as well, we can determine the value of overpotential. From Figure 6 (a) – (c) is shown that the values of overpotential keep increased with increasing the number of cycles. According to Elia and Hassoun[19], the increasing the overpotential with the cycle number may be due to the insulating nature of lithium peroxide that covering in a large amount of carbon electrode surface upon full discharge.

4. Conclusion

FTIR results indicated that there are interactions of the PMMA-LiBOB-TEGDME system. The highest conductivity was achieved by the 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME electrolyte. This is parallel to the highest free ion percentages of 64% also obtained by the GPE containing 15 wt.% LiBOB. The potential window stability of 15 wt.% LiBOB-32.96 wt.% PMMA – 52.04 wt.% TEGDME was observed up to 4.2 V. The Li⁺ ion transference number is 0.38. Lithium–oxygen cell gives the discharge capacity of 447 mAh g⁻¹ in the first cycle.

References
[1] Christensen J, Albertus P, Sanchez-Carrera R. S, Lohmann T, Kozinsky B, Liedtke R, Ahmed J and Kojic A 2012 159 R1
[2] Abraham K M and Jiang Z 1996 Journal of the Electrochemical Society 143(1)1-5
[3] Simonetti E, Carewska M, Carfi D, Moreno M, Francesco M D, Appetecchi M, and Simonetti G B 2017 Electrochimica Acta 235 323
[4] Moreno M, Simonetti E, Appetecchi G B, Carewska M, Montanino M, Kim M, Loeffler N and Passerini S 2017 Journal of the Electrochemical Society 164 A6026
[5] Suo L, Hu S Y, Li H, Armand M and Chen, L Q, 2013 Nature Communications 4
[6] Li Q, Chen J, Fan L, Kong X and Lu Y 2016 Green Energy & Environment 1 18
[7] Arof A K, Jun H K, Sim L N and Kufian M Z and Sahraoui 2013 Optical Materials 135
[8] Ma Y, Gao L B, Yang G X, You X Y and Yang J 2016 Colloids and Surfaces a-Physicochemical and Engineering Aspects 502 130
[9] Li W Y, Pang Y, Liu J Y, Liu G H, Wang Y G and Xia Y Y 2017 Rsc Advances 7 23494
[10] Kufian M Z and Arof A K 2014 Materials Technology 29 A114
[11] Holomb R, Xu W, Markusson H, Johansson P and Jacobsson P 2006 Journal of Physical Chemistry A 1100 11467
[12] Kaskhedikar N, Karatas Y, Cui G, Maier J and Wiemhofer H D 2011 Journal of Materials Chemistry 21 11838
[13] Amanchukwu C V, Harding J R, Shao-Horn Y and Hammond P T 2015 Chemistry of Materials 27 550
[14] Theerthagiri J, Senthil R A, Buraidah M H and Madhavan J 2015 Ionics 21 2889
[15] Arof A K, Amirudin S, Yusof S Z and Noor I M 2014 Physical Chemistry Chemical Physics 6 1856
[16] Evans J, Vincent C A and Bruce P G 1987 Polymer 28 2324
[17] Sumathipala H, Hassoun J, Panero S and Scrosati B 2007 Ionics 13 281
[18] Kufian M Z, Aziz M F, Shukur M F, Rahim A S, Ariffin N E, Shuhaimi N E A, Majid S R, Yahya R and Arof A K 2012 Solid State Ionics 208 36
[19] Elia G A and Hassoun J 2015 Scientific Reports 5
Acknowledgments
We gratefully acknowledge the funding support from the University Malaya, PPP Grant No.: PG011-2013B and High Impact Research Grant (No. J-00000-73555) and University of Malaya, Grant No.: RP003C-13AFR.