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## PMMA-LiBOB Gel Polymer Electrolytes in Lithium-Oxygen Cell

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# PMMA-LiBOB Gel Polymer Electrolytes in Lithium-Oxygen Cell

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**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 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  $1.71 \text{ mS cm}^{-1}$ . 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<sup>+</sup>) suggesting suitability for the application in the lithium-oxygen battery. The capacity is 447 mAh g<sup>-1</sup> 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  $\sim 11.5 \text{ kWh kg}^{-1}$  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  $\sim 10^{-3} \text{ S cm}^{-1}$  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  $0.12 \times 10^{-3} \text{ Scm}^{-1}$  and  $187 \text{ mAh g}^{-1}$ , 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<sub>2</sub>O<sub>2</sub> attack [13]. To understand the Li<sup>+</sup> 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 ( $d = 4 \text{ \AA}$ ). 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.

**Table 1.** PMMA-LiBOB-TEGDME

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.

$$\sigma = \frac{t}{AR_b} \quad (1)$$

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  $\text{cm}^{-1}$  with resolution 1  $\text{cm}^{-1}$ . The IR bands were also deconvoluted using the OMNIC software. Holomb *et al.* [11] reported free BOB<sup>-</sup> ions could be identified at various wavenumbers on the IR spectrum: 1804, 1780, 1273, 1200, 1096, 986 and 703  $\text{cm}^{-1}$ . In this work, the out-of-phase carbonyl (C=O) stretching [ $\nu_{np}(\text{C=O})$ ] mode of LiBOB with free BOB<sup>-</sup> ions and  $\text{Li}^+\cdots\text{BOB}^-$  ion pairs located at 1804 and 1828  $\text{cm}^{-1}$  respectively were investigated. From this information in above, the area percentage of free ions (%FI) was calculated using Equation 2.

$$\%FI = \frac{A_{FI}}{A_{FI} + A_{IP}} \times 100\% \quad (2)$$

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:

$$t_{Li} = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})} \quad (3)$$

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)

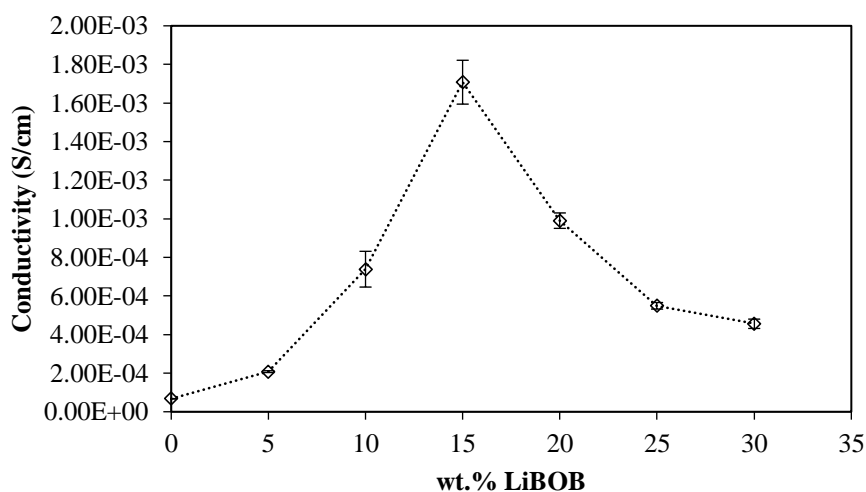
LSV was carried out by using two electrodes system to measure electrochemical window (ECW) of the GPEs. Stainless steel (SS) and lithium metal were selected as working and a counter electrode respectively. The GPEs was sandwiched in between working and counter electrode. Open circuit voltage (OCV) of 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<sup>-2</sup>.

## 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  $6.76 \times 10^{-5} \text{ Scm}^{-1}$ . The ionic conductivity was ascertained to increase with the LiBOB salt content up to 15 wt.% LiBOB salt with the value of  $1.71 \times 10^{-3} \text{ S cm}^{-1}$ . 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.



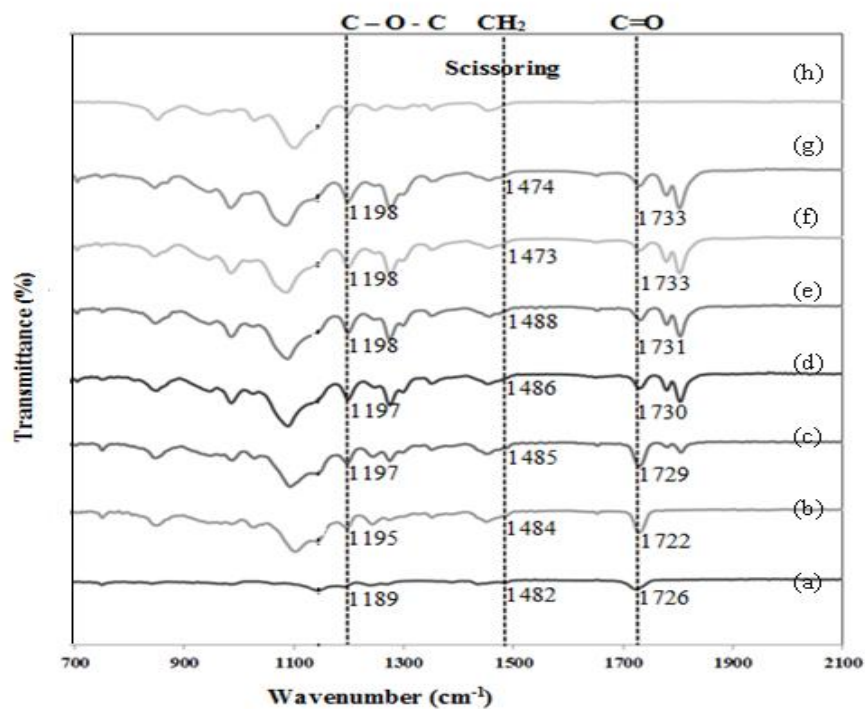
**Figure 1.** Variation of conductivity as a function LiBOB salt

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

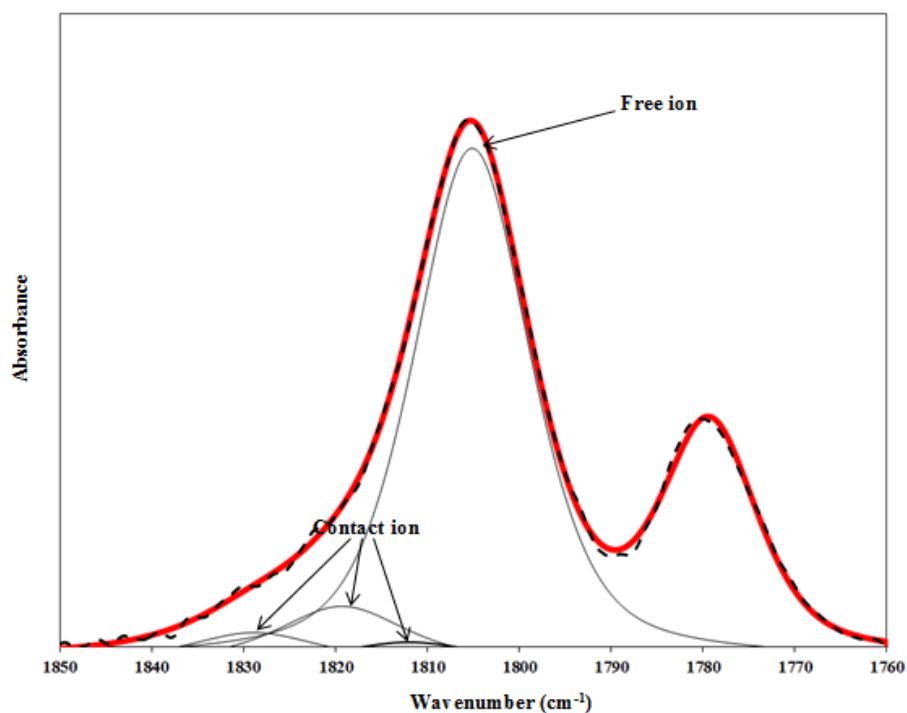
The FTIR spectrum was deconvoluted in order to resolve the hidden bands that might be contributed to the polymer-salt interactions. Figure 3 shows the FTIR deconvolution of the 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% at the region between 1760 and 1850  $\text{cm}^{-1}$ . TEGDME all samples. The deconvoluted 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  $\text{cm}^{-1}$  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].

**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

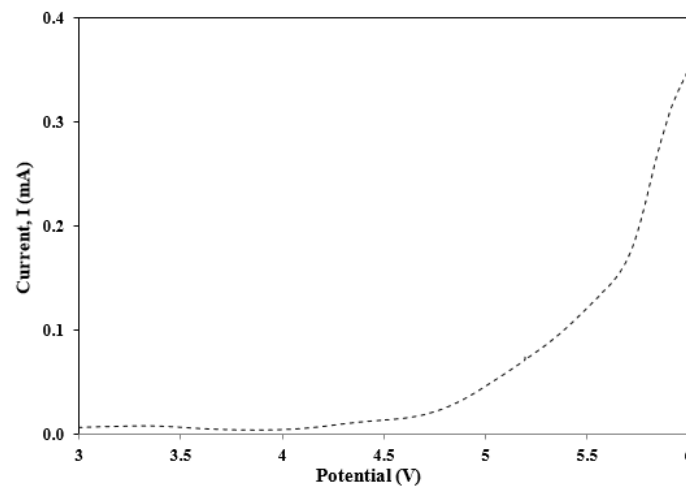


**Figure 2.** FTIR spectra of (a) Pristine PMMA, (b) 0 wt.% (c) 5 wt.% (d) 15 wt.% (e) 20 wt.% (f) 25 wt.% and (g) 30 wt.% of LiBOB salt and (h) TEGDME solvent

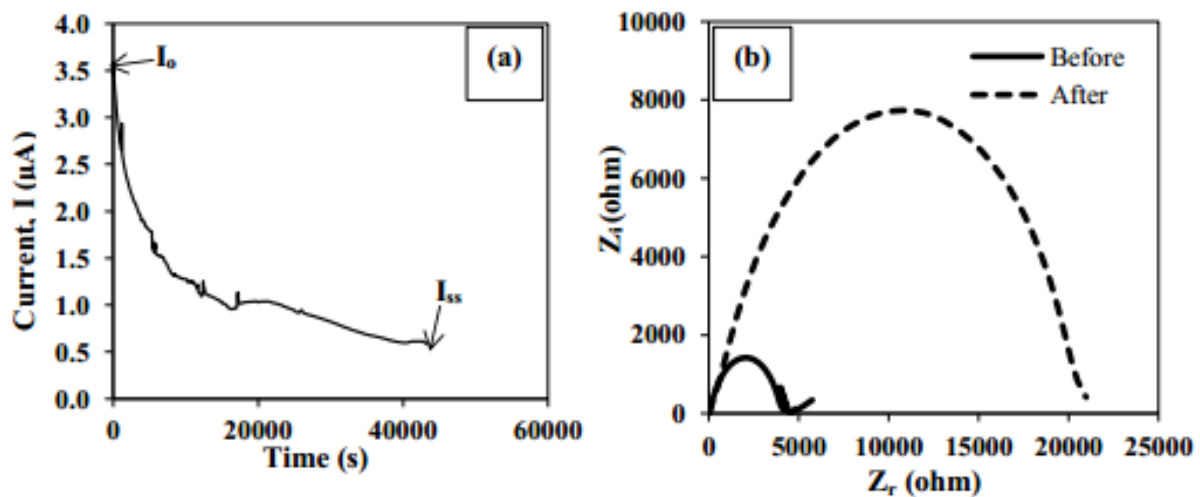


**Figure 3.** Deconvolution of 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME

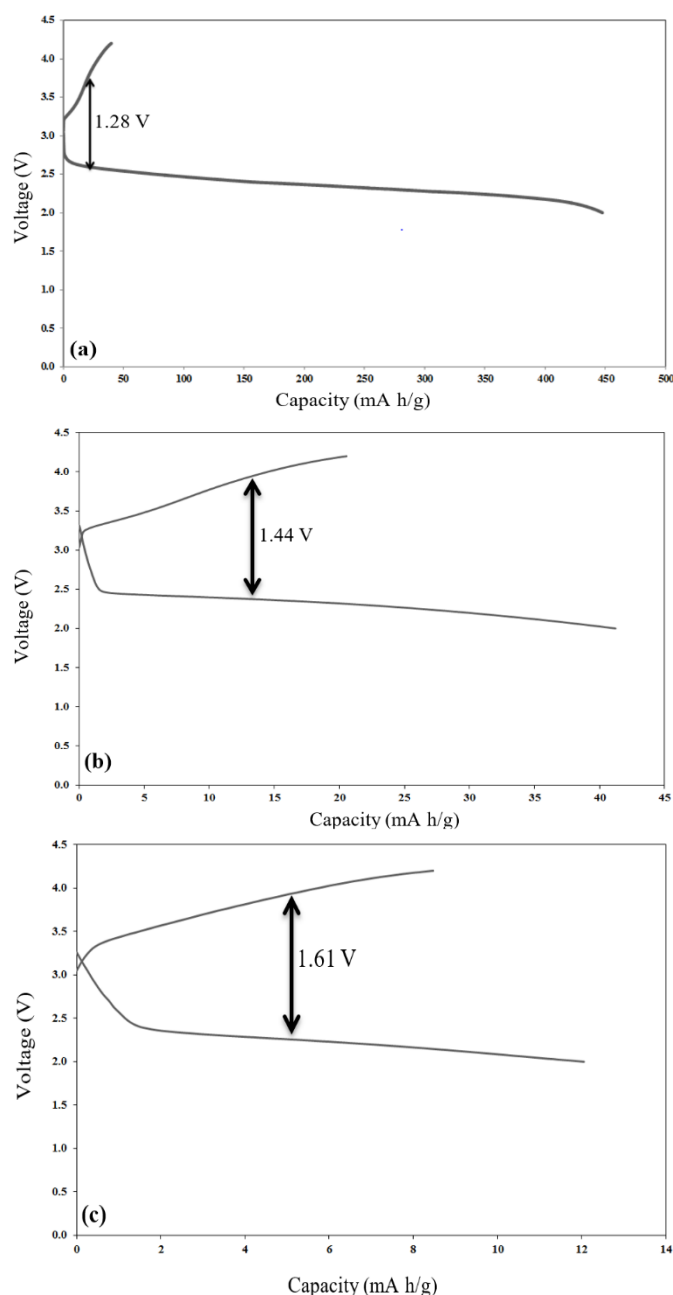
The ECW of the GPE containing 15 wt.% LiBOB-32.96 wt.% PMMA-52.04 wt.% TEGDME was measured on a stainless steel electrode from open circuit voltage to 6.0 V, as shown in Figure 5. From the graph, the GPE started to oxidize slowly from 4.2 V and then sharply increased at 4.7 V. This LSV value is reasonable 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  $0.02 \text{ mA cm}^{-2}$  at (a) 1<sup>st</sup>, (b) 3<sup>rd</sup> and (c) 15<sup>th</sup> 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.*[16]. DC polarization measurements were carried out to determine the initial,  $I_0$  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 1<sup>st</sup>, 3<sup>rd</sup> and 15<sup>th</sup> cycles. The discharge capacity at the 1<sup>st</sup> and 3<sup>rd</sup> cycles were 447 and 40 mAh g<sup>-1</sup> 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<sup>+</sup> ion transference number is 0.38. Lithium–oxygen cell gives the discharge capacity of 447 mAh g<sup>-1</sup> in the first cycle.

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