Int. J. Electrochem. Sci., 8 **(2013)** 7320 - 7326

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Studies on Cellulose Acetate-LiBOB Polymer Gel Electrolytes

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Received: 20 February 2013 / *Accepted:* 29 March 2013 / *Published:* 1 May 2013

Liquid electrolytes were prepared by dissolving different amounts of lithium bis(oxalato) borate (LiBOB) in γ-butyrolactone (GBL) solvents. Upon addition of 0.8 M LiBOB in GBL solvent, this liquid electrolyte showed room temperature ionic conductivity of 4.79 mS cm^{-1}. In order to prepare polymer gel electrolytes (PGE), 1 to 6 wt.% cellulose acetate (CA) was added into this optimum liquid electrolyte composition. The highest room temperature conductivity obtained for the PGE system was 5.36 mS cm^{-1} for sample containing 2 wt.% CA. Temperature dependent conductivity data revealed the CA-LiBOB polymer gel electrolyte obeys an Arrhenius rule implying that this PGE could operate at intermediate and high temperature conditions. Moreover, linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements confirmed this PGE system also exhibits excellent electrochemical stability. Thus, the CA-LiBOB -based PGE could be a promising candidate as an electrolyte particularly in lithium batteries application.

Keywords: Gel electrolytes, Cellulose acetate, LiBOB, Conductivity, Electrochemical stability

1. INTRODUCTION

Efforts have been done to improve recent lithium batteries technology in order to fulfill several important criteria such as economical production, environmental and safety regulations, energy capacity and power density. In the case of electrolyte types in the lithium batteries, substitution of common liquid electrolytes with solid or polymer gel electrolyte systems is extensively carried out [1-5].

The scientific studies of solid polymer electrolytes (SPEs) have been paid much attention in rechargeable lithium batteries due to the risk deficiency of liquid electrolytes leakage and design flexibility [6]. However, these SPEs have the major drawback in which possess the low ionic conductivity at ambient temperature due to the high crystalline inherent in their complexes. In addition, SPEs have poor electrode-electrolyte contact compared to liquid electrolytes. Therefore, recent studies have been targeted towards the identifications of new electrolyte materials and other alternative systems to solve the problems of solid and liquid phase electrolytes. Polymer gel electrolytes (PGEs) have been developed to overcome these problems seeing that properties of PGEs are in comparable with those of solid and liquid electrolytes.

Polymer gel electrolytes (PGEs) belong to the salt-solvent-polymer hybrid system are generally prepared by immobilizing the salt solution with a suitable polymer matrix. The solvent is retained in these electrolytes, and thus helps the ionic conduction process [7]. Moreover, PGEs are well known to have good physical properties that can maintain superior electrodes-electrolyte interfacial contact during battery fabrication processes.

A number of salt used in commercial Li batteries do not meet the criteria as a good electrolyte especially in thermal stability at high temperature, conceivably affect the cyclic performance of the batteries itself. For example, $LiPF_6$ salt is extensively used in lithium battery industries because it can provide large electric conductivity of the electrolyte; however it is chemically and thermally not very stable. $LiPF_6$ often undergoes the decomposition process [8]:

$$LiPF_6 \rightarrow LiF + PF_5 \qquad \text{(Eq. 1)}$$

This process will reduce the number of free Li^+ ions for charge transportation [9]. The hydolisis of decomposition product PF_5, a strong lewis acid may produce HF in electrolyte [10]. In addition, PF_5 is able to initiate the polymerization of cyclic ethers and degrade the performance of Li battries [11]. Alternatively, LiBOB can be a promising candidate used in lithium electrolyte since it has advantages of wide potential window, hydrogen and fluorine free, and good thermal stability [12]. Moreover, LiBOB-based electrolyte also contributes to high ionic conductivity (10^{-3} S cm^{-1}) [13,14].

In this work, liquid electrolytes consist of various LiBOB concentrations in a solvent of γ-butyrolactone were prepared. To prepare PGEs, different wt.% of CA was added into the selected optimum liquid electrolyte. CA is chosen due to its excellent properties as a polymeric gelling agent as well as it has heteroatom (oxygen atom) that possesses lone pair electrons in facilitating ionic conduction [15]. The highest conducting PGE sample was characterized through linear sweep voltammetry (LSV) and cyclic voltammetry (CV) in order to prove its electrochemical stability. To the best of our knowledge, this is the first report on CA-LiBOB polymer gel electrolyte system.

2. EXPERIMENTAL

LiBOB salt (HSC), GBL (Merck) and CA with an acetyl content of 39.8% wt.% (Aldrich) were used as received. Different amount of LiBOB were added into the GBL. Liquid electrolytes concentrations of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 M LiBOB in GBL solvents were prepared by stirring each mixture at room temperature until a homogenous solution were obtained. Then, six samples of PGE were prepared. LiBOB with amount of 3.10 g was dissolved in 20 mL GBL (equivalent to 0.8 M LiBOB in GBL). As a polymeric gelling agent, CA was added to the 0.8 M LiBOB liquid electrolyte with different weight ratios in order to convert the liquid electrolytes into gels. The mixture was stirred at room temperature until the solution was homogenized and no visible of CA-agglomerates.

Electrochemical impedance spectroscopy (EIS) was measured using the HIOKI 3532-50 LCR Hi Tester interfaced to a computer with a frequency range between 100 Hz and 1 MHz. The imaginary part, Z_i of impedance was plotted against its real part (Z_r). Horizontal and vertical axes of the plot having the same scales, therefore bulk resistance, R_b of the sample was obtained from the intercept of the plot with the real impedance axis, Z_r. Ionic conductivity, σ of the samples was then calculated using the equation:

$$\sigma = t / (R_b A) \qquad \text{(Eq. 2)}$$

where t is the distance between the electrodes (cm) and A is the contact area between the electrolyte and the electrodes (cm^2).

In order to investigate its electrochemical behaviour of the PGE, the sample containing 2 wt.% of CA was characterized by linear sweep voltammetry and cyclic voltammetry. Both measurements were performed using the Wonatech Automatic Battery Cycler with three electrodes system. Stainless steel (SS) was used as working electrode while Li foil was used as reference and counter electrodes.

3. RESULTS AND DISCUSSION

One of the important criteria to be an electrolyte for lithium battery application, it should possess the ionic conductivity in the range of 10^{-1} to 10^{-3} S cm^{-1}. Figure 1 presents the plot of conductivity versus LiBOB salt content in the GBL-LiBOB system of liquid electrolytes at room temperature (303 K). It can apparently be observed that the conductivity increases steeply from 0.2 M to 0.8 M LiBOB concentration with ionic conductivity of 4.79 mS cm^{-1}. A steep increase of conductivity conceivably attributed to an increase in the number of available free mobile ions. Upon dissociation, LiBOB salt (C_4BO_8Li [16]) provides free Li^+ ions, which take part in the conduction process and thus the ionic conductivity increase [15]. For that reason, 0.8 M LiBOB liquid electrolyte is chosen as the optimum composition in preparing PGE in the next step because it presents the highest free Li^+ ions.

However, the conductivity in between 0.8 M to 1.0 M only marginally increases. This indicates that ion aggregates are also formed due to the presence of a large number of ions [7], therefore the occurrence of partial formation of neutral cation-anion pairs that do not contribute to the conduction process. The gradually higher rate of increase in conductivity by addition 1.0 M to 1.2 M LiBOB is the result of re-dissociation of ion-pairs to form a single or triplets ions which again take part in the ion transport and reach the maximum conductivity at 1.2 M of LiBOB concentration. Upon increasing the salt concentration greater than 1.2 M LiBOB, the conductivity decreases from 6.59 mS cm^{-1} (1.2 M) to 4.95 mS cm^{-1} (1.4 M) due to the formation of ion aggregate at high salt concentrations which do not help in the ionic conduction process.

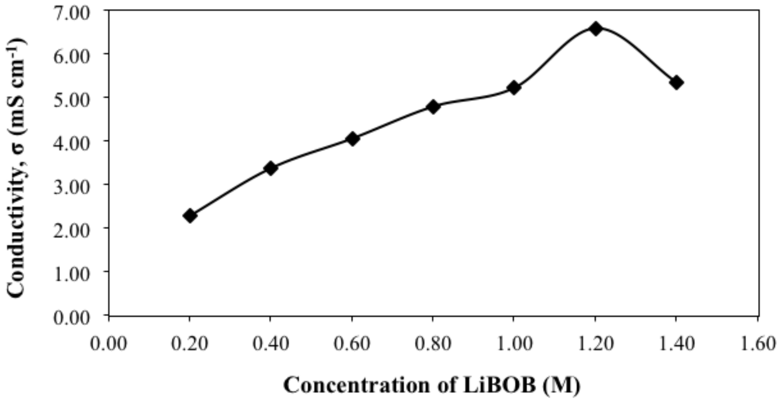

Figure 1. Conductivity of liquid electrolytes as a function of LiBOB salt concentration

The variation of conductivity with CA concentration at room temperature for PGE containing CA in the 0.8 M solution of LiBOB in GBL is depicted in Figure 2. The conductivity of PGE is observed to increase with the addition of CA, reaches a maximum value of 5.36 mS cm^{-1} at 2 wt.% CA and then decreases to a value of 3.87 mS cm^{-1} at 6 wt. % CA. Effect of adding CA as a polymer to the liquid electrolyte system can be explained through the "Breathing Polymeric Chain Model" [17], according to this model, the polymeric gel is considered to consist of dissociated ions, ion-pairs, solvent and polymeric chains. This model explained that when polymer is added to a liquid electrolyte, there is an increase in pressure of surrounding system volume due to the polymer chain 'breathes' (opens or folds) occupying different volumes [18]. Therefore, this phenomenon has risen to localized pressure change or fluctuations of surrounding volume. This pressure wave assists the ionic pair dissociation resulting in an increase the number of mobile ions as a charge carrier in PGE system thus increase the conductivity of electrolytes. When the CA concentration is high (> 2 wt.% CA) resulting in a decrease in conductivity. The conductivity tends to decline with further addition of CA due to ion association dominated in the bulk [19] thus decreased the free mobile ions available to take part in the conduction process. In addition, it is assumed that there a competing between free ions to move at the microscopic level [17].

Figure 3 depicts the temperature dependence of conductivity for the sample containing 2 wt.% of CA in the temperature range of 303 to 373 K. The plot shows that the conductivity of PGE system increases with increasing temperature and reaches the highest value of 10 mS cm^{-1} at 373 K. This proves that PGE with LiBOB salt is thermally stable and can operate at high temperature. Value of regression is close to unity implying that the entire points lie on straight line [20] that verifies that the variation of ionic conductivity with temperature obeys an Arrhenius-type thermally activated process

[21]. Thus, it indicates that there is no phase transition of polymer matrix [22]. Moreover, polymer matrix will not experience the change in dynamic conformational [21] and Li^+ ions might migrate through the conduction path formed by the lattice structure of cellulose acetate chains.

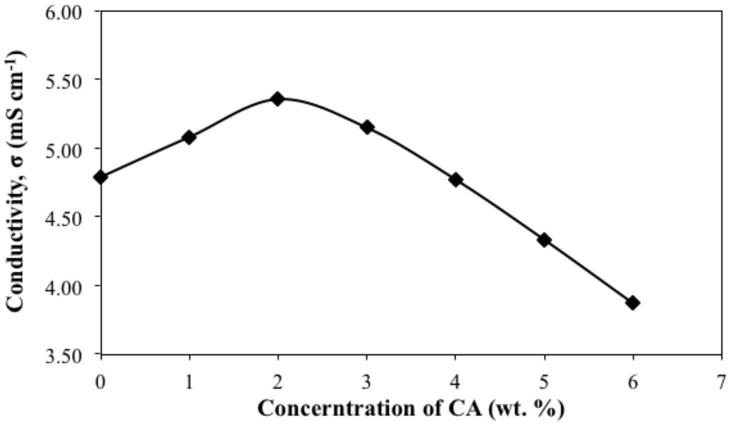

Figure 2. Variation conductivity as a function of CA concentration for PGE

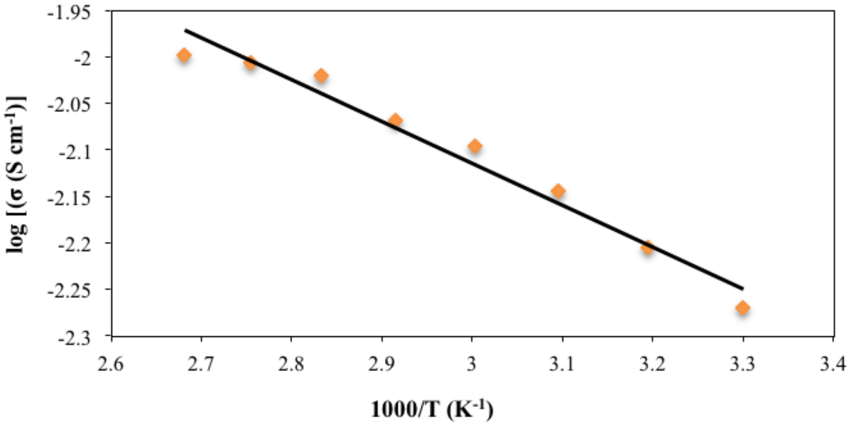

Figure 3. Conductivity-temperature dependence of 2 wt.% CA-LiBOB-based PGE

Another important criterion on selecting electrolytes for application in lithium batteries is good electrochemical stability window. The electrochemical stability window of PGE containing 2 wt.% CA is determined by means of LSV of an inert electrode with a constant 5 mV s^{-1} scan rate. The current response of the working electrode is shown in Figure 4. From the plot of current versus voltage, current flow of the PGE is almost constant until the applied voltage swept to further value and reached a voltage breakdown of the PGE at 4.7 V. On increasing the voltage beyond 4.7 V, the current that is related to the PGE steadily increases. This implies that 4.7 V represents the electrochemical stability window or anodic stability of GBL-0.8 M LiBOB-2 wt.% CA polymer gel electrolyte. Kufian et al. [23] also reported the same value of decomposition voltage for PMMA-EC-PC-LiBOB electrolyte system.

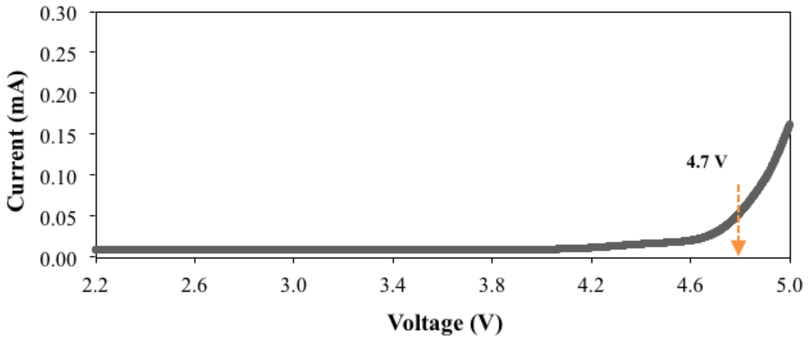

Figure 4. Linear sweep voltammetry curve of the highest conducting PGE sample

Figure 5 demonstrates the cyclic voltammogram 5 mV s^{-1} sweep rate of PGE. The area of first and second cycle are identical, therefore it can be concluded that the tiny reactions are reversible [12]. The good repeatability of CV curves will also contribute a good cyclic performance of Li batteries.

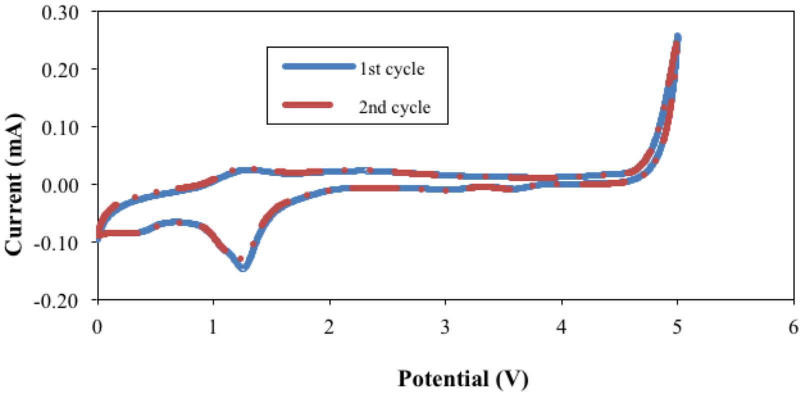

Figure 5. Cyclic voltammogram of PGE at the scan rate of 5 mV s^{-1}

4. CONCLUSION

The conductivity of PGE increased on addition of CA and achieved the highest ionic conductivity of 5.36 mS cm^{-1} upon addition of 2 wt.% CA. This has proven that by addition of CA polymeric gelling agent, it could enhance the ionic conductivity of the electrolyte. The study of conductivity-temperature dependence showed that this PGE obeys the Arrhenius behaviour and could be desirable electrolytes for lithium batteries that would be able to operate at elevated temperatures. LSV and CV results demonstrated that LiBOB-GBL-CA electrolyte system exhibited good electrochemical stability since it reached a high voltage breakdown at 4.7 V. Therefore, the CA-LiBOB –based PGE could be a promising candidate as an electrolyte particularly in lithium batteries application.

ACKNOWLEDGEMENT

This work is supported by Ministry of Higher Education of Malaysia (MOHE) for Research Grant Scheme. The authors would like to express their gratitude to i-MADE Lab, Institute of Science, and Faculty of Applied Sciences, UiTM for their support in providing research facilities to carry out this research. SZZA would like to thank MOHE and UiTM for the scholarship funding.

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