Short communication

Electrochemical studies on epoxidised natural rubber-based gel polymer electrolytes for lithium–air cells

S.N. Mohamed, N.A. Johari, A.M.M. Ali, M.K. Harun, M.Z.A. Yahya *

Ionic Materials & Devices (iMADE) Research Laboratory, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

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ABSTRACT

Gel polymer electrolyte films comprised of 50% epoxidised natural rubber polymer host, lithium triflate salt ($LiCF_3SO_3$), and ethylene carbonate (EC) or propylene carbonate (PC) plasticizer are prepared using the solution-casting technique. AC impedance studies show that the electrical conductivity of the electrolytes is dependent on both the salt and plasticizer concentrations. The highest room temperature conductivity of $4.92 \times 10^{-4}\,S\,cm^{-1}$ is achieved when 10 wt.% propylene carbonate is introduced into the system containing 1.0 g 50% epoxidised natural rubber polymer doped with 35 wt.% $LiCF_3SO_3$. Conductivity studies of these polymer electrolytes are carried out at various temperatures and are found to obey the Vogel–Tamman–Fulcher (VTF) rule. The highest conducting plasticized sample is used as a gelled electrolyte for lithium–air cells.

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1. Introduction

The research and development of solid polymer electrolytes (SPEs) has received a great deal of attention due to the usefulness of these materials in a variety of applications, including lithium batteries [1]. The main drawbacks of these electrolytes are low ionic conductivity at room temperature and poor electrode–electrolyte contact compared with liquid electrolytes. Although the latter are able to produce high conductivity, they have poor mechanical properties and face the risk of leakage as well as a safety hazard particularly in the case of an internal short [2]. Recent studies have been targetted towards the identification of new electrolyte materials and other alternative systems to solve these problems with solid and liquid phase electrolytes. Gel polymer electrolytes (GPEs) have been identified as promising substitutes for SPEs and liquid electrolytes in battery systems.

Previous reports have indicated that several types of polymer-based electrolyte might be suitable for use in GPEs. These include: biomaterial-based polymers such as chitosan [3], cellulose [4] and natural rubber [5]. Modified natural rubber (NR) has a low glass transition temperature, T_g, soft elastomer characteristics at room temperature, and good elasticity and adhesion properties [6]. Such characteristics allow rubber to form a free-standing film, as well as to provide good contact between the electrode and the electrolyte. Thus rubber is an excellent base material for the further development of GPE systems [5]. In the work presented here, the prospects of lithium polymer electrolytes based on a 50% epoxidised NR polymer (ENR-50) are investigated.

Various methods have been employed to enhance the performance of polymer electrolytes, such as blending [7], addition of ceramic fillers [8], and plasticization [9]. The addition of plasticizers to a polymer host structure, as in the formation of GPE systems, leads to improved ionic conductivity [10]. Recently, Kumutha and Alias [11] reported enhanced ionic conductivity when plasticizer was added to a 30% methyl grafted NR (MG30)–$LiCF_3SO_3$ electrolyte system. According to Cowie and Spence [12], plasticizers assist in the dissolution and dissociation of salts, which increases the number of mobile charges.

The lithium–air cell is unique because the cathode active material, oxygen, is not stored in the battery, but instead is accessed directly from the environment. The theoretical open-circuit voltage (OCV) of the lithium–air cell at standard state is approximately 3.45 V, which is higher than that of metal–air batteries. In practice, the OCV of the lithium–air cell is 2.8–3.0 V, mainly due to the mixed potentials exhibited by the lithium anode and the air cathode [13,14]. Kuboki et al. [15] reported the performance of lithium–air primary batteries using a 1 M $LiClO_4$ EC/PC in a liquid electrolyte. In general, the use of a liquid lithium electrolyte results in corrosion of the lithium electrode due to its chemical reaction with water, resulting from vaporization of the electrolyte and hydrolysis of the anode [15,16]. The corrosion product is usually in the form of LiOH, which can saturate the electrolyte and precipitates at the cathode. This precipitation impedes the oxygen reduction reaction on the cathode, thereby limiting the efficiency of the battery. With this

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* Corresponding author. Tel.: +603 5544 4496; fax: +603 5544 4562.
E-mail address: mzay@salam.uitm.edu.my (M.Z.A. Yahya).

concern in mind, the possibility of using GPE gel films as a conducting medium in the lithium–air primary cell is explored in this study.

The work reports the results of electrical conductivity measurements performed on non-plasticized and plasticized ENR-50-based polymer electrolytes doped with lithium triflate. The latter solutions of GPE prepared by the solution-casting technique are mixed using different concentrations of salt and plasticizers with the goal of obtaining the highest conductivity gel. Propylene carbonate (PC) and ethylene carbonate (EC) are used as plasticizers to determine which better enhances the electrical conductivity of the electrolyte. The optimized GPE film is then used to fabricate lithium–air primary cells. The discharge curves of the cells are plotted and analyzed to understand the performance and discharge characteristics of the films.

2. Experimental

2.1. Electrolyte preparation

ENR-50 (Rubber Research Institute of Malaysia), tetrahydrofuran (THF; Merck) and $LiCF_3SO_3$ (LiTf; Aldrich) were used as starting materials for the preparation of films. ENR-50 stock solutions were prepared by dissolving the polymer in THF under continuously stirring with a magnetic bar. To determine the salt concentration that yielded the highest conductivity, different amounts of LiTf salt were mixed in different beakers that each contained 1.0 g ENR-50. The solutions were stirred for several hours at room temperature, and then poured into glass petri dishes and left to dry at ambient temperature. Free-standing gelled films were obtained after all the THF solvent had evaporated. The films were dried in a vacuum oven for 24 h at 60 °C, and then stored in an argon-filled MBRAUN glove-box ($O_2 < 0.1$ ppm; $H_2O < 0.1$ ppm) to prevent the absorption of moisture. The highest ENR-50-salt conducting sample was used to prepare gelled ENR-50-salt films by adding different amounts of EC and PC (both from Aldrich) plasticizer from 10 to 50 wt.%, respectively.

2.2. Electrolyte characterization

Impedance spectroscopy was performed on each sample using a HIOKI 3531 – 01 LCR Hi – Tester interfaced with a computer over the frequency range of 100 Hz to 1 MHz. The impedance test for each sample was carried out between 303 K (room temperature) and 383 K.

2.3. Cell fabrication

A commercial manganese (Mn)-catalyzed fibrous carbon–air electrode (Electro-Chem-Technic, UK) with an active area of $3.142 \, cm^2$, weighing 0.188 g with a thickness of 0.5 mm, was cut into a circular shape with a small additional portion for the positive terminal. The air-side of the electrode was coated with a gas-permeable, hydrophobic Teflon layer. Films of gelled electrolytes (area: $3.80 \, cm^2$ and thickness: 0.12 mm) with the highest conductivity were sandwiched between lithium metal (Aldrich) (weight: 2.6 g) and the air cathode. The assembly was supported by a nickel-plated mesh that acted as a current collector in a coin-type cell holder. The total weight of each cell was 5.54 g. All operations were carried out in a glove-box to avoid exposure to moisture.

2.4. Cell characterization

The discharge characteristics of the cells were measured by means of a AUTOLAB PGSTAT302 potentiostat–galvanostat system.
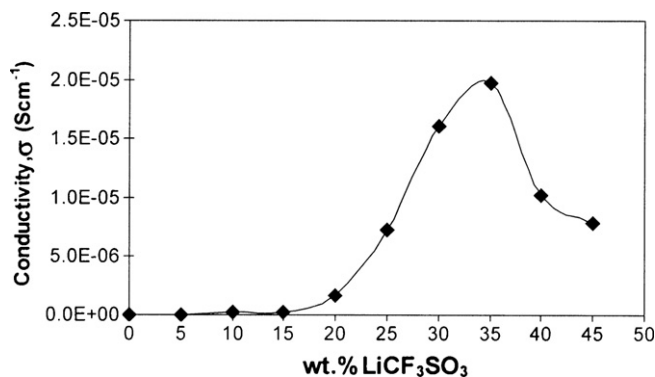

Fig. 1. Dependence of conductivity $LiCF_3SO_3$ content.

The cells were discharged using a constant current of 1.0 mA. Cell characterizations was performed at room temperature (30 °C).

3. Results and discussion

3.1. Electrolyte characterization

Before the addition of plasticizer, the highest conductivity achieved was $1.98 \times 10^{-5} \, S \, cm^{-1}$ at room temperature when 35 wt.% of $LiCF_3SO_3$ salt was introduced to non-plasticized ENR-50 (Fig. 1). Note that the ionic conductivity of the polymer electrolyte increases with increasing $LiCF_3SO_3$ concentration up to 35 wt.%, after which the conductivity decreases. This slow increase in ionic conductivity at lower salt concentrations may be attributed to an increase in the number of available free mobile ions. Upon dissociation, $LiCF_3SO_3$ provides free Li^+ ions, which take part in the conduction process and give rise to an increase in conductivity. The presence of mobile ions also raises the amorphous state of the ENR-50 through favourable free volume, and therefore facilitates the ion migration processes. According to Mellander and Albinson [17], the variation in polymer conductivity is due to ion association and dissociation. The decrease in conductivity at higher concentrations is probably caused by the formation of ion aggregates, which decrease the number of free mobile ions available to take part in the conduction process. Majid and Arof [18] have reported that the ion concentration can be determined using the Rice and Roth model [18]. Calculated values are presented in Table 1.

The GPEs with EC or PC plasticizers have higher conductivity than those without plasticizers (Table 1). The plasticized sample containing 10 wt.% PC exhibits the highest electrical conductiv-

Table 1
Transport parameters of non-plasticized and plasticized systems

| Sample	Plasticizer	Conductivity ($S \, cm^{-1}$) at 303 K	Ion concentration, η (cm^{-3})
ENR 50 + 15% $LiCF_3SO_3$	–	2.22×10^{-7}	1.12×10^{17}
ENR 50 + 25% $LiCF_3SO_3$	–	7.10×10^{-6}	1.66×10^{19}
ENR 50 + 35% $LiCF_3SO_3$	–	1.98×10^{-5}	5.52×10^{20}
ENR 50 + 35% $LiCF_3SO_3$	10% EC	5.61×10^{-5}	9.42×10^{20}
	20% EC	2.41×10^{-4}	7.50×10^{21}
	30% EC	6.50×10^{-5}	3.32×10^{21}
	40% EC	4.29×10^{-5}	8.10×10^{20}
	50% EC	3.35×10^{-5}	6.43×10^{20}
ENR 50 + 35% $LiCF_3SO_3$	10% PC	4.92×10^{-4}	9.01×10^{22}
	20% PC	8.99×10^{-5}	5.15×10^{21}
	30% PC	6.67×10^{-5}	4.03×10^{21}
	40% PC	5.83×10^{-5}	1.22×10^{21}
	50% PC	4.23×10^{-5}	7.84×10^{20}
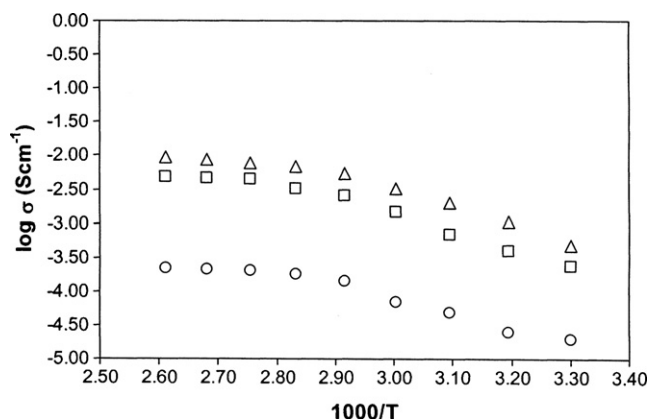
Fig. 2. Variation of conductivity of non-plasticized and plasticized samples as function of temperature. ($\bigcirc$): ENR-50 with 35 wt.% LiTf; ($\square$): 35 wt.% LiTf + 20 wt.% EC; ($\triangle$): 35 wt.% LiTf + 10 wt.% PC.

Fig. 3. Frequency dependence of real part (ε') of dielectric constant. ($\bigcirc$): ENR-50 with 35 wt.% LiTf; ($\square$): 35 wt.% LiTf + 20 wt.% EC; ($\triangle$): 35 wt.% LiTf + 10 wt.% PC.

ity, namely, 4.92×10^{-4} S cm^{-1}. The physicochemical properties of these plasticizers, such as their high dielectric constants (EC, $\varepsilon_{25} = 85.1$; PC, $\varepsilon_{25} = 69.0$) and the low freezing point of PC ($-49\,^\circ$C) make them promising candidates for enhancing the conductivity and performance of GPEs. The plasticizers enhance conductivity in polymer electrolytes by several different mechanisms. It is believed that the high dielectric constant of these plasticizers increases the number of mobile ions by weakening the coulombic force between the anions and cations of the salt [19], thereby resulting in higher dissociation. The plasticizers also reduce the viscosity of the polymer electrolyte, thus facilitating the movement of the charge carriers along the polymer backbone and enhancing conductivity. The addition of the plasticizer has also been reported to reduce the crystallinity of the complexes, leading to better ionic conductivity [20]. In this work, the addition of PC as the plasticizer results in better conductivity than that of EC for the entire temperature range studied, despite the fact that EC has a higher dielectric constant. A possible reason for this is that EC is solid at room temperature whereas PC has a low freezing point. The solid state of EC at room temperature might limit the dissociation of the salt, thereby reducing the number of mobile ions [21].

A conductivity–temperature (σ vs. T) dependence study was carried out in order to understand the conduction mechanism within the temperature range of 303–383 K. A plot of $\log \sigma$ vs. $10^3/T$ for the non-plasticized and plasticized systems is shown in Fig. 2. The conductivity of both the non-plasticized and plasticized systems increases with increasing temperature. The PC sample with the highest conductivity exhibits the highest electrical conductivity at all temperatures compared with those containing EC and the non-plasticized samples. The non-linearity of the conductivity with temperature indicates that ion transport in this polymer obeys the Vogel–Tamman–Fulcher rule, which describes the conductivity based on the free-volume model [22]. This implies that the samples have become more amorphous. The presence of the plasticizer causes the entropy configuration of ENR-50 to favours the provision of more free volume where the ions can move easily through the plasticizer rich phase. This behaviour is in agreement with the conductivity results in Table 1. The increase in the volume of the amorphous phase in the highly conducting plasticized samples implies that the amorphous phase of the polymer electrolytes facilitates fast Li$^+$ motion in the polymer network. In addition, it provides a larger free volume upon temperature increase [3].

The conductivity of polymer electrolytes can be further understood by studying their dielectric constant. Fig. 3 shows the change in the value of the dielectric constant, ε', in the frequency range
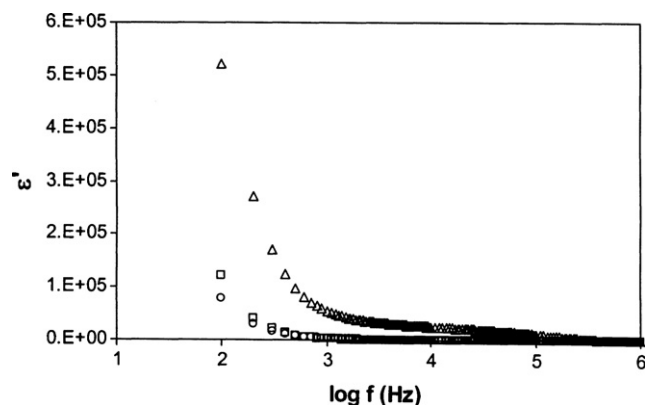
of 100 Hz to 1 MHz for non-plasticized and plasticized polymer electrolyte systems. The graph shows that the presence of salt and plasticizer at certain concentrations causes an increase in the dielectric constant at lower frequencies. Since impedance at low frequencies is due to the Faradaic reaction, the impedance is directly dependent on concentration of free ions available. Therefore, these results are in accordance with the findings presented in Table 1, that indicate that the highest conductivity is achieved with samples containing the highest concentration of free ions (10 wt.% PC).

3.2. Cell characterization

The discharge characteristics of lithium–air primary cells are plotted in Fig. 4. The cells were fabricated using the plasticized films with the highest electrical conductivity as the electrolytes. The cells were discharged at a constant current of 1.0 mA at room temperature (30 $^\circ$C). A discharge capacity of 61 and 55 mAh is observed for PC (cell A) and EC (cell B) plasticized systems, respectively. The mid-point voltage of both cells at a current of 1.0 mA is around 2.7 V for cell A and 2.5 V for cell. Therefore, the specific energy of cells A and B is 29.7 and 24.8 Wh kg^{-1} for (entire cell weight), respectively. This means that the specific power obtained for cells A and B is 0.49 and 0.45 W kg^{-1} (entire cell weight), respectively. The EC plasticized system (cell B) shows a lower capacity than the PC plasticized system (cell A) partially because of its lower lithium ion conductivity. This is in agreement with the data that show the conductivity of the ENR50-LiTf electrolyte plasticized with PC to be higher than that of ENR50-LiTf electrolyte plasticized with EC. Fur-
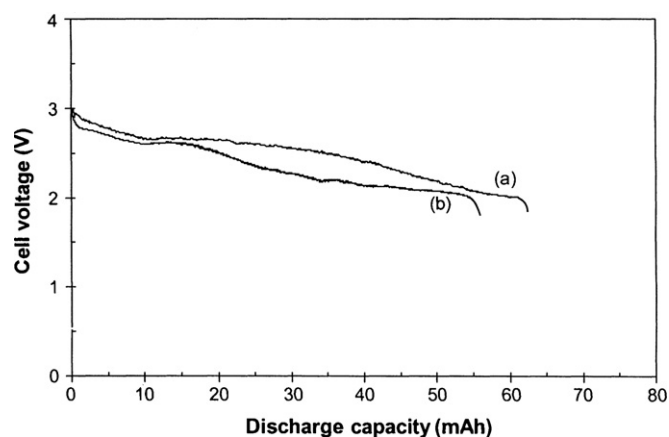

Fig. 4. Discharge capacity of lithium–air primary cells using: (a) ENR-50-LiTf-PC and (b) ENR-50-LiTf-EC electrolytes. (I = 1.0 mA; 30 $^\circ$C; in air).

thermore, the performance can be explained by considering the deposition of $Li_2O_{(s)}$ in a carbon-based air electrode. The overall cell reaction during discharge appears to be $4Li_{(s)} + O_{2(g)} \leftrightarrow 2Li_2O_{(s)}$ [23] due to the lower oxygen concentration in the GPE. Therefore, the formation of $Li_2O_{(s)}$ during the discharge process may prevent a continuous reaction between the electrode and the electrolyte, particularly in electrolytes with lower ion concentrations.

4. Conclusions

Investigations have shows that PC plasticized systems have higher conductivity than both EC plasticized and non-plasticized systems. The highest conductivity achieved is $4.92 \times 10^{-4}\,S\,cm^{-1}$ at room temperature when 10 wt.% of PC is introduced into the highest conducting non-plasticized system. The electrochemical properties of lithium–air cells demonstrate a discharge capacity of 61 and 55 mAh for PC and EC plasticized systems, respectively. The specific energy of cell A, made with PC plasticized GPE, and of cell B, made with EC plasiticized GPE, is 29.7 and 24.8 Wh kg^{-1} (entire cell weight) respectively. Additionally, the specific power obtained for cells A and B is 0.49 and 0.45 W kg^{-1} (entire cell weight), respectively. Since the electrolyte properties of ENR50-LiTf-PC are superior to those of ENR50-LiTf-EC, the electrochemical performance of a lithium–air cell fabricated with the former electrolyte is slightly higher.

Acknowledgement

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