



Development of membranes and a study of their interfaces for rechargeable lithium–air battery

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ABSTRACT

This paper describes an investigation with an objective to screen and select high performance membrane materials for a working, rechargeable lithium–air battery. Membrane laminates comprising glass–ceramic (GC) and polymer–ceramic (PC) membranes were assembled, evaluated and analyzed. A superionic conducting GC membrane with a chemical composition of $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ ($x = 0.5$) was used. Polymer membranes comprising of PC(BN), PC(AlN), PC(Si_3N_4) and PC(Li_2O) electrochemically coupled the GC membrane with the lithium anode. The cell and membrane laminates were characterized by determining cell conductivity, open circuit voltage and carrier concentration and its mobility. The measurements identified Li_2O and BN as suitable dopants in polymer matrix which catalyzed anodic charge transfer reaction, formed stable SEI layer and provided high lithium ion conductivity.

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1. Introduction

Lithium–air battery is a promising future generation of environmentally sustainable power source [1,2]. A Li–air cell can be fabricated by electrochemical coupling of lithium anode and carbon-based air cathode [3]. The Li–air cell provides a high practical voltage, which translates into higher power and specific energy (13.0 kWh kg^{-1} of lithium) as compared to any other metal–air electrochemical system. The Li–air cell reactions and associated electrochemical potentials are shown by equations (i) and (ii).



Lithium metal and oxygen are consumed during the discharge, and lithium oxide or lithium peroxide is formed depending upon whether the reaction (i) or (ii) is carried out. The cell can operate at high Coulombic efficiencies provided there is a minimal parasitic cell reaction among the cell components. An important factor for achieving the high Coulombic efficiency is the formation of a protective layer on the highly reactive lithium metal anode.

Abraham and Jiang [4], about 12 years ago, demonstrated the first practical non-aqueous rechargeable Li–oxygen battery cell. Their cell design employed a Li ion conducting gel polymer electrolyte (membrane) derived from either polyacrylonitrile or poly(vinylidene difluoride) polymer. In this cell, the membrane

served not only its usual role of an ion-transporting and electronically insulating separator between the Li anode and the carbon cathode, but also enabled the construction of a laminate type cell with inlets and outlets for the transport of oxygen during its operation. The cell exhibited good capacity versus discharge rate but its rechargeability was limited, attributed in part to the limited cycle life of the Li anode. Following this early investigation, several studies have been reported to improve the performance of Li–air battery. Abraham et al. [5] suggested the use of gel electrolytes with non-volatile liquid plasticizers. Doble et al. [6] reported a study of the use of catalysts to enhance the rate capability and capacity utilization of the oxygen electrode. Kuboki et al. [7] investigated ionic liquids in Li–air cells to increase the overall stability and performance of the battery. Beattie et al. [8] investigated high capacity composite carbon cathodes to increase energy density. Ogasawara et al. [9] demonstrated rechargeability of Li– O_2 cells starting with the formation of Li_2O_2 in the cathode with or without catalyst. Visco et al. [10] reported electrochemical performance of a working Li–air cell and suggested that a development of Li–air cells may lead to an energy density of 1000 Wh kg^{-1} or 1000 Wh L^{-1} . All these prior investigations used liquid electrolytes to electrochemically couple lithium and air-cathode. For the first time Kumar et al. [11,12] reported the fabrication and performance of an all-solid-state, rechargeable Li– O_2 cells; however, with limited cell capacity (0.002 mAh). The low temperature operation and rechargeability of the Li–air cell can be achieved by reducing charge-transfer resistance at lithium–electrolyte interface and also by forming a solid electrolyte interface (SEI) layer at the lithium surface. Prior studies [13,14] have addressed these issues at cell level and showed that reduction of charge-transfer resistance and long-term stability can

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be achieved through an addition of a ceramic phase in PEO-based polymer matrix. In a report, Appetecchi et al. [15] have suggested that cell preparation procedure and environment play a major role in the stability of the lithium–polymer electrolyte interface; however, their investigation was limited at only high temperature (90 °C).

An all solid-state Li–air cell provides advantages of increased cell stability, wider operational temperature range, ruggedness, safety and potentially longer cycle and shelf lives. This investigation is dedicated to identifying and developing cell components which can facilitate manufacturing of all solid-state Li–air cells. This investigation is centered around the use of superionically conducting glass–ceramic (GC) membrane because it addresses issues associated with the use of metallic lithium as anode such as parasitic reactions and dendritic shorts leading to cell failure. The objective of the paper is to develop a membrane laminate using GC and PC materials which can: (i) enhance ionic conductivity, (ii) catalyze anodic ($\text{Li}^0 \rightarrow \text{Li}^+ + \text{e}^-$) reaction, and (iii) electrochemically couple lithium with air cathode.

2. Experimental

2.1. Synthesis of glass–ceramic membrane

A GC membrane was prepared from the raw materials to yield a material with chemical composition of $0.8\text{Li}_2\text{O} \cdot 0.25\text{Al}_2\text{O}_3 \cdot 1.5\text{GeO}_2 \cdot 1.5\text{P}_2\text{O}_5$ (LAGP). A 40-g batch of this composition was prepared by using reagent grade chemicals such as Li_2CO_3 (Alfa Aesar), Al_2O_3 (Sigma–Aldrich), GeO_2 (Alfa Aesar), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Acros Organics). Raw materials in specified proportion were weighed, mixed and milled in a high energy milling machine for 30 min to homogenize the mixture. The homogeneous mixture was transferred to a platinum crucible for melting in a high temperature electric furnace. Initially, the furnace was heated to 450 °C at the rate of 1°C min^{-1} and held at this temperature for 1 h to decompose and release the volatile components from the batch. Subsequently, the furnace temperature was raised to 1350 °C at the rate of 1°C min^{-1} to melt the components and form a homogeneous glass. The melting temperature of 1350 °C was maintained for 2 h. Subsequently; homogeneous, viscous glass melt was poured onto a flat stainless steel (SS) plate at room temperature and pressed by another steel plate to yield <1 mm thick transparent glass sheets. The pressed glass sheets were annealed at 500 °C for 2 h to release the thermal stresses and then allowed to cool to room temperature. These annealed specimens remained in the glassy state as observed by visual inspection. The annealed glass was then ground to fine powder by using high energy mill and pelletized under a high pressure (>490 MPa) to obtain <0.04 cm thick and 1.1 cm diameter pellets. The glass pellets were crystallized at 850 °C for 12 h to obtain the GC electrolyte (membrane) with high ionic conductivity [16–18]. The density and porosity of GC membrane were 3.13 g cm^{-3} and 1.64%, respectively.

2.2. Processing of polymer–ceramic membrane

A polymer complex comprising of poly(ethylene) oxide (PEO) (m.w. 200,000, Union Carbide) and $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ (3M) (LiBETI), was used as Li^+ ion conducting host matrix. Nanosize boron nitride (BN, 5–20 nm), aluminum nitride (AlN, <100 nm), and silicon nitride (Si_3N_4 , <50 nm) and lithium oxide (Li_2O) were used as ceramic dopants. All the materials were weighed inside a dry box maintained with argon atmosphere (<50 ppm of oxygen and <88 ppm moisture). Dried PEO and LiBETI in ratio 8.5:1 were mixed with 1 wt% of each BN, AlN, Si_3N_4 and Li_2O in an energy milling machine (SPEX SamplePrep, 8000M, Mixer/Mill, Metuchen, NJ, USA) for

30 min. The weighed materials were transferred into a metallic jar and taken out from the dry box for high energy milling (Spex, 8000M) to obtain a homogenous mixture. After milling, 300 mg of the specimen was loaded into a die in the dry box and heated for 10 min at 95 °C and pressed with 490 MPa pressure into a polymer–ceramic (PC) disc membrane. The PC membrane was removed from die after it was cooled down to $\sim 27^\circ\text{C}$. Thus, PC specimens in the form of discs (11 mm dia and 1–1.3 mm thick) were obtained. The PC membranes, viz., PEO:LiBETI(8.5:1)–1 wt% BN, PEO:LiBETI(8.5:1)–1 wt% AlN, PEO:LiBETI(8.5:1)–1 wt% Si_3N_4 and PEO:LiBETI(8.5:1)–1 wt% Li_2O hereafter abbreviated as PC(BN), PC(AlN), PC(Si_3N_4) and PC(Li_2O), respectively, were stiff and free standing.

2.3. Cleaning of lithium metal strip

The oil soaked Li metal strip was cleaned by using a naphthalene solution and mechanically scrubbed to remove oxide deposit on the surface of Li during its storage, and immediately used to form a cell characterized in this investigation.

2.4. Preparation of carbon–GC composite solid cathode

An O_2 /air-cathode was prepared using nickel mesh, carbon black (acetylene 50% compressed), water soluble Teflon (TE-3859) and GC powder. In a 1-g batch of carbon black (25 wt%) and GC powder (75 wt%), 8 mL deionized water and 0.5 mL Teflon were used to obtain a soft mass which was spread on both sides of the nickel mesh and sandwiched between two SS plates. The assembled sandwich was pressed with 294 MPa pressure, dried at 100 °C overnight and sintered at 320 °C for 20 min in argon atmosphere. The cathode was used to fabricate cells with different configurations mentioned in the paper.

2.5. Aluminum foil

A thin Al foil (Ultra aluminum foil, Durable Packaging International, Wheeling, IL 60090, USA) was used to cover the lithium surface and prevent SS electrodes from direct contact during AC impedance measurement. It was observed that Al foil covered the lithium surface very effectively and yielded reproducible AC impedance data.

2.6. Electrical conductivity measurement

All the cells in this study were placed in between two SS electrodes and then tightened in a Macor[®] glass-ceramic cell fixture. The cell fixture was then transferred to an air-tight glass jar fitted with electrical leads for electrochemical characterization of cells. The electrical conductivity of each specimen was measured by the AC impedance technique in the 0 to 117 °C temperature range. For the AC impedance technique a Solartron 1260 impedance analyzer with 1287 electrochemical interface was used to obtain impedance data in the $0.1\text{--}10^6$ Hz frequency range.

3. Results and discussion

3.1. Electrochemical characterization of solid-state GC and PC membranes

3.1.1. Au/GC/Au cell

A typical AC impedance spectra of gold coated GC membrane (Au/GC/Au) at room temperature ($23 \pm 1^\circ\text{C}$) is shown in Fig. 1. The spectra shows two intersections ($R_1 = 282 \Omega$ and $R_2 = 394 \Omega$) on real Z' axis forming a semicircle centered around 1×10^5 Hz, part of which is overlapped on experimentally measured data

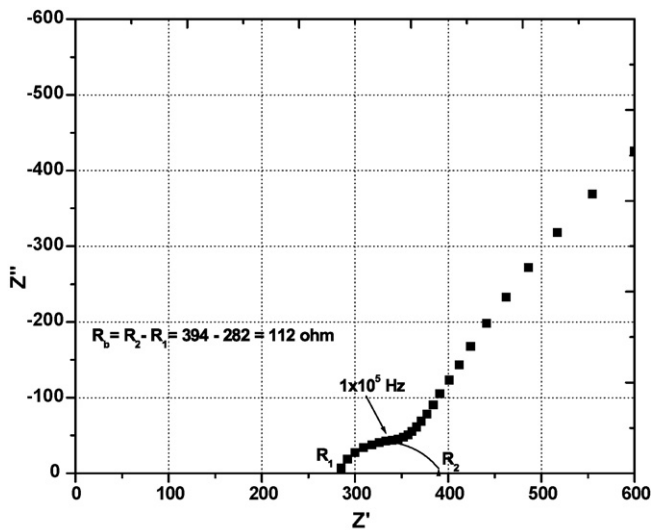


Fig. 1. Nyquist plot of gold coated LAGP (GC) at room temperature ($23 \pm 1^\circ\text{C}$) measured with SS electrodes.

points. The first intersection (R_1) is interpreted as circuit resistance external to the specimen and is related to electrolyte-electrode or contact resistance. The difference between first and second intersection ($R_2 - R_1$) is interpreted as electrolyte bulk resistance ($R_b = R_2 - R_1 = 112 \Omega$) and this resistance includes contribution of the grains and grain boundaries contained in the GC matrix. The R_b at a particular temperature is normalized with respect to the thickness and cross-sectional area to obtain the conductivity of the specimen [19]. By this method, calculated conductivity of the GC membrane was $\sim 4.48 \times 10^{-3} \text{ S cm}^{-1}$ at 23°C and $\sim 4 \text{ S cm}^{-1}$ at 310°C , the highest conductivity value achieved for any solid lithium ion conductor [18]. A solid electrolyte with ionic conductivity of this magnitude – comparable to the ionic conductivity of liquid electrolyte – seems very promising to fabricate a practical electrochemical device. But, in a real electrochemical device the electrolyte (GC) must be coupled to anode and cathode without gold coating.

3.1.2. Al/Li/GC/cathode cell

Fig. 2 shows the Nyquist plot of Al/Li/GC/cathode cell (a progress towards a real Li–air cell using GC membrane as electrolyte) at room temperature ($23 \pm 1^\circ\text{C}$). The plot of Fig. 2 shows two

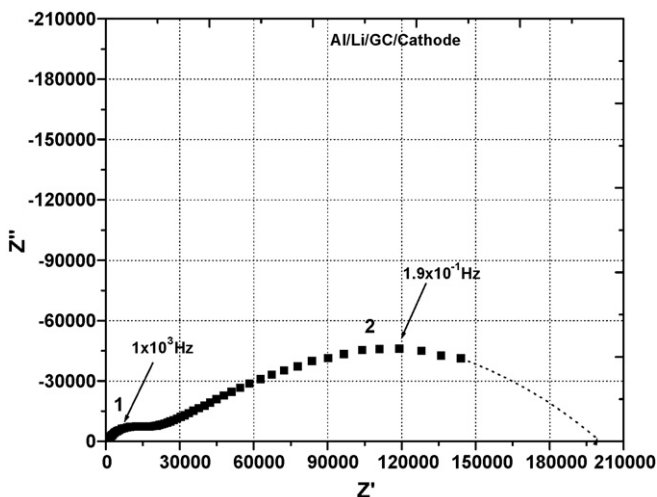


Fig. 2. Nyquist plot of Al/Li/GC/cathode cell, using GC as electrolyte, Li as anode and carbon–GC composite as cathode and measured at room temperature ($23 \pm 1^\circ\text{C}$) with SS electrodes.

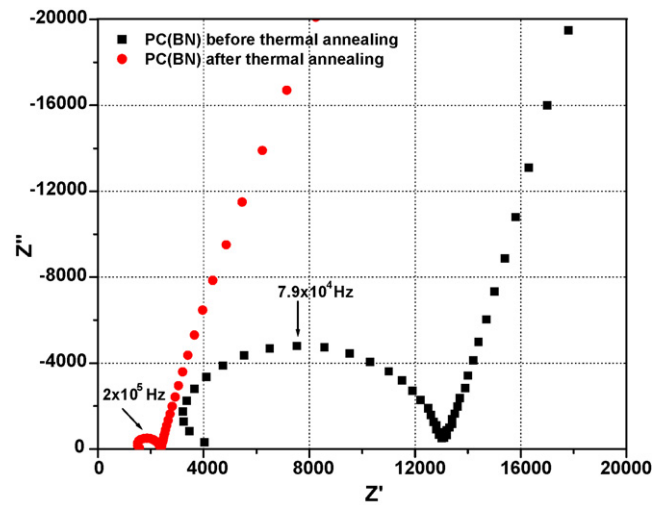


Fig. 3. Nyquist plot of PC(BN) membrane before and after thermal annealing measured at room temperature ($23 \pm 1^\circ\text{C}$) with SS electrodes.

depressed semicircles: the first centered on $1 \times 10^3 \text{ Hz}$ and the second one at $1.9 \times 10^{-1} \text{ Hz}$. The first semicircle is attributed to the resistance and capacitance of the bulk electrolyte (Fig. 1). The second semicircle resulted from the charge transfer resistance and capacitance developed at the interface of GC and lithium. The resistances associated with first and second semicircle are $\sim 22,740$ and $\sim 197,210 \Omega$, respectively, with a total resistance of cell being $\sim 219,950 \Omega$. The cell resistance was too high to form a practical lithium–air cell. Lithium metal and cathode possess high conductivity ($10^0\text{--}10^3 \text{ S cm}^{-1}$). Therefore, over three orders of magnitude increase in the conductivity of the Al/Li/GC/cathode cell over Au/GC/Au must be attributed to Li–GC and GC–cathode interfacial resistances. This observation suggests that these large interfacial resistances must be minimized to fabricate a practical, working lithium–air cell. Thus, to effectively couple the GC membrane to Li and air–cathode, one must use either a liquid electrolyte or some other membrane material which can reduce the interfacial resistances. The focus of the present investigation was to develop solid-state cells.

To reduce the aforementioned interfacial resistances a number of PC composite electrolytes were considered and investigated. The basis for selecting the PC electrolytes was to achieve: (i) low cell resistance, (ii) effectiveness to couple GC membrane to lithium and air–cathode, (iii) minimize the lithium–electrolyte interface resistance, and (iv) provide stable SEI at the lithium surface. The PC(BN), was chosen to achieve the aforementioned goals whose electrochemical performance with other PC materials is presented in Section 3.2.

3.1.3. Effect of annealing on the conductivity of PEO:LiBETI(8.5:1)–BN membrane

Fig. 3 shows the Nyquist plot of PC(BN) membrane with blocking electrodes (SS) at room temperature ($23 \pm 1^\circ\text{C}$) measured before and after thermal annealing at 117°C for 12 h. After thermal annealing the frequency at which the semicircles are centered shifted from 7.9×10^4 to $2.0 \times 10^5 \text{ Hz}$. Furthermore, after thermal annealing the magnitude of both resistive and capacitive components in PC(BN) specimen were reduced as can be seen from the comparison of two curves in Fig. 3. The value of bulk resistances for PC(BN) membrane before and after thermal annealing was 9844 and 827Ω , respectively. After thermal annealing the bulk resistance of PC(BN) membrane was decreased by a factor of about 12. Therefore, it is clear that the thermal annealing significantly lowers bulk resistance of PC(BN) membrane. A similar observation in a polymer–ceramic

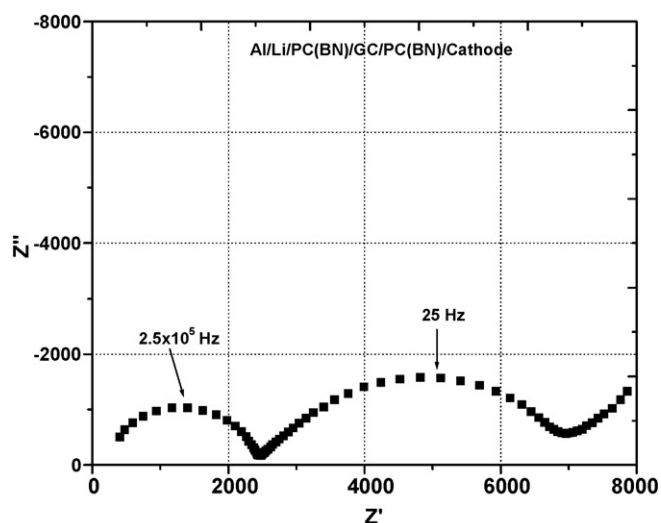


Fig. 4. Nyquist plot of Al/Li/PC(BN)/GC/PC(BN)/cathode cell using PC(BN) membrane as an electrolyte to couple GC membrane to lithium and air-cathode at room temperature ($23 \pm 1^\circ\text{C}$).

composite electrolyte containing PEO:LiBETI and Al_2O_3 has been reported earlier [19]. Thus, the thermal annealing is critical to stabilize the structure of the electrolyte and minimize bulk resistance. It was inferred that the use of PC(BN) membrane in between GC membrane and the two electrodes (Li and air-cathode) may reduce the large interfacial resistance associated with electrolyte and electrodes. The effectiveness of a PC(BN) membrane in reducing the interfacial resistances is presented in next section.

3.1.4. Al/Li/PC(BN)/GC/PC(BN)/cathode

Fig. 4 shows the Nyquist plot of Al/Li/PC(BN)/GC/PC(BN)/cathode cell (basically a working Li–air cell using PC(BN)/GC/PC(BN) laminate as the membrane) at room temperature ($23 \pm 1^\circ\text{C}$). The spectra show two distinct semicircles, similar to Li/GC/cathode cell presented in Fig. 2. In Fig. 4 the first and second semicircle are centered around 2.5×10^5 and 25 Hz, respectively. The first semicircle is attributed to the resistance and capacitance of the PC(BN)/GC/PC(BN) membrane laminate. The second semicircle is related to the charge transfer resistance and capacitance at the PC(BN) membrane and electrodes interfaces. The resistances associated with first and second semicircle are ~ 2205 and $\sim 4802 \Omega$, respectively. Two PC(BN) layers and one GC membrane were used to fabricate the Al/Li/PC(BN)/GC/PC(BN)/Cathode cell. The combined bulk resistance should be $\sim 1766 \Omega$ (Figs. 1 and 3) which is close to the bulk resistance ($\sim 2205 \Omega$) of Li–air cell (first semicircle of Fig. 4). The sum total resistance of these two semicircles is the resistance of the cell is $\sim 7007 \Omega$. After comparison of Figs. 2 and 4, it is clear that cell resistance decreased by a factor of over 31 upon introducing the PC(BN) membranes in between GC membrane and the two electrodes. Furthermore, it is important to mention that with this combination Li–air cell was fully functional and showed good rechargeability without use of any liquid or gel electrolyte [11,12]. The functioning of a working solid-state Li–air cell is attributed to the use of a PC(BN) membrane that electrochemically couples the GC membrane to the lithium and air-cathode. This observation led us to search for other PC membranes which may further help in achieving goals for fabricating a solid-state, rechargeable lithium–air cell.

3.2. Lithium–PC interface stability

In search of a PC membrane which may further lower the cell resistance and improve long-term cell stability, four

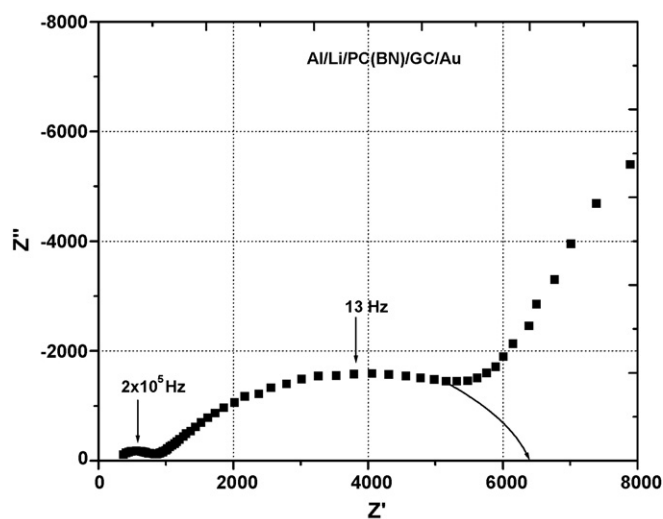


Fig. 5. Nyquist plot of Al/Li/PC(BN)/GC/Au cell using PC(BN) membrane as an electrolyte to couple GC membrane to anode at room temperature ($23 \pm 1^\circ\text{C}$).

cells: (i) Al/Li/PC(BN)/GC/Au, (ii) Al/Li/PC(AlN)/GC/Au, (iii) Al/Li/PC(Si_3N_4)/GC/Au, and (iv) Al/Li/PC(Li_2O)/GC/Au, were fabricated and characterized. In order to simplify the cell configuration, use of a cathode was avoided. The cathode side of the GC electrolyte was gold (Au) coated to isolate the Li–PC interface. It should be noted that the interfaces susceptible to major thermal and environmental degradation during this investigation were Li–PC(BN)/AlN/ Si_3N_4 / Li_2O) only. The interface between the cathode and PC(BN)/GC was found to be thermally and environmentally very stable (results not shown), and by addition of this part into full Li–air cell, it added only a few hundred ohms to the total cell resistance. Al foil was used to protect the lithium surface from reacting with the SS electrode. The results obtained in this investigation with Al foil were compared with the results obtained without Al foil in prior investigations [11,12,14], and it was concluded that Al foil helped improve cell stability. The role of Al foil in electrochemical stabilization of the cell is still under investigation.

Fig. 5 shows the Nyquist plot of Al/Li/PC(BN)/GC/Au cell – basically a half Li–air cell – at room temperature ($23 \pm 1^\circ\text{C}$). The spectra show two distinct semicircles, similar to Al/Li/PC(BN)/GC/PC(BN)/cathode Li–air cell presented in Fig. 4. In Fig. 5 the first and second semicircle are centered around 2×10^5 and 13 Hz, respectively. The first semicircle is attributed to the resistance and capacitance of the PC(BN)/GC membrane laminate. The second semicircle is related to the charge transfer resistance ($\text{Li}^0 \rightarrow \text{Li}^+ + \text{e}^-$) and capacitance at the PC(BN) membrane and lithium interfaces. The resistances associated with first and second semicircle are ~ 494 and $\sim 5525 \Omega$, respectively, with the total resistance of the cell equal to $\sim 6019 \Omega$. After comparison of Figs. 4 and 5, it is clear that addition of an extra PC(BN) layer add only few hundred ohms to the bulk resistance of the cell and major characteristics of the cell remain unchanged.

Fig. 6 shows temperature dependent cell conductivity of all four cells namely: (i) Al/Li/PC(BN)/GC/Au, (ii) Al/Li/PC(AlN)/GC/Au, (iii) Al/Li/PC(Si_3N_4)/GC/Au, and (iv) Al/Li/PC(Li_2O)/GC/Au, in the temperature region 0 – 97°C after 16 h of cell assembly. All four cells were thermally annealed at 117°C for 12 h before temperature dependant conductivity measurement. As can be seen from the plots in Fig. 6, the conductivities of the cells are very close at this point in time in the aging experiment. The difference in cell conductivity may be attributed to the type of ceramic dopant [14], because it is only the ceramic dopant which differed from one PC to another. At this point in the investigation, conductivity of individual cells

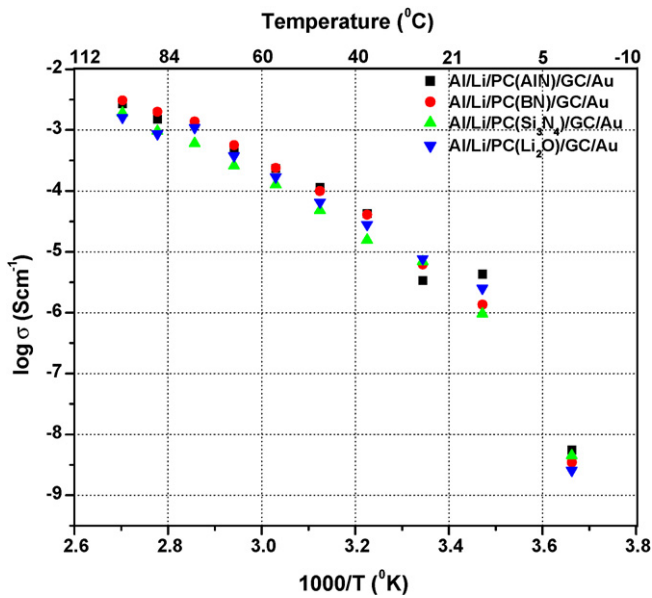


Fig. 6. Temperature dependent cell conductivity of (a) Al/Li/PC(AIN)/GC/Au, (b) Al/Li/PC(BN)/GC/Au, (c) Al/Li/PC(Si₃N₄)/GC/Au, and (d) Al/Li/PC(Li₂O)/GC/Au cells in the temperature range 0–97 °C after thermal annealing at 117 °C for 12 h.

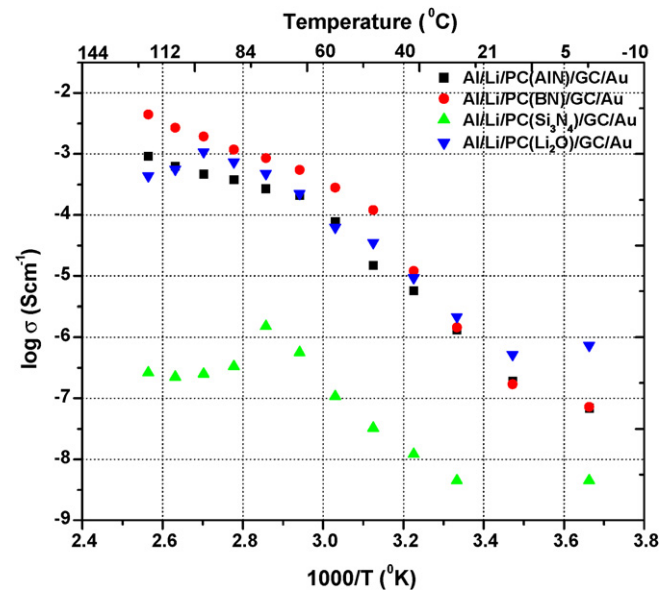


Fig. 7. Temperature dependent conductivity of (a) Al/Li/PC(AIN)/GC/Au, (b) Al/Li/PC(BN)/GC/Au, (c) Al/Li/PC(Si₃N₄)/GC/Au, and (d) Al/Li/PC(Li₂O)/GC/Au cells in the temperature range 0–117 °C after 570 h of cell assembly.

may be considered as base conductivity of the cell as initially cell degradation (16 h after cell assembly) may be neglected. To illustrate and differentiate the roles of ceramic dopants in various PCs in forming SEI layers on lithium electrode, the conductivity of the cells was monitored with respect to aging time.

Table 1 shows time dependent interfacial resistance (R_i), and total cell resistance (R_t), of all the four cells at room temperature ($23 \pm 1^\circ\text{C}$). After 30 h of aging, the Al/Li/PC(BN)/GC/Au cell shows the least R_i value ($R_i = 6893 \Omega$), followed by Al/Li/PC(Li₂O)/GC/Au ($R_i = 6992 \Omega$), Al/Li/PC(AIN)/GC/Au ($R_i = 9628 \Omega$), and Al/Li/PC(Si₃N₄)/GC/Au ($R_i = 12,207 \Omega$) cells. Thereafter, resistances of all the four cells kept on changing. The percentage increase in resistance for the cell Al/Li/PC(AIN)/GC/Au, Al/Li/PC(BN)/GC/Au, Al/Li/PC(Si₃N₄)/GC/Au, and Al/Li/PC(Li₂O)/GC/Au after 570 h of cell storage at room temperature are 332, 145, 190 and 124%, respectively. Furthermore, at the end of 1848 h only two cells, namely Al/Li/PC(BN)/GC/Au and Al/Li/PC(Li₂O)/GC/Au, were in acceptable state (impedance data could be measured with confidence) (Table 1). It was found that the values of interfacial resistances exhibited by all the four cells are much larger than their respective bulk resistances. In fact the total cell resistance is dominated by interfacial cell resistance (Table 1). It is noted that the lithium–electrolyte interfacial resistance is the primary source of cell resistance. The large interfacial resistance may have origi-

nated from any of the following sources: (i) formation of SEI layer on the lithium surface, and (ii) different charge-transfer reaction kinetics [14] catalyzed by AlN, BN, Si₃N₄, and Li₂O dopants at the lithium–electrolyte interface. The formation of SEI layer and catalysis of charge-transfer reaction are cell history and temperature dependent.

The charge transfer catalysis and SEI layer will affect the number of charge carriers and their mobility in the cells. The formation and characteristics of the SEI layer can be evaluated from the temperature dependant cell conductivity.

Fig. 7 shows cell conductivity of all the four cells after 570 h of cell storage in the temperature region 0–117 °C. The highest cell conductivity at higher temperature (35–117 °C) is noted from the Al/Li/PC(BN)/GC/Au cell. The Al/Li/PC(Si₃N₄)/GC/Au cell deteriorated to the extent that its conductivity values were lower by orders of magnitude over the entire temperature range. The low temperature conductivity values of the Al/Li/PC(Li₂O)/GC/Au cell were superior to the Al/Li/PC(BN)/GC/Au cell. But at higher temperatures its conductivity is lower than that of the Al/Li/PC(BN)/GC/Au cell. The performance of the Al/Li/PC(AIN)/GC/Au cell is comparable to Al/Li/PC(Li₂O)/GC/Au and Al/Li/PC(BN)/GC/Au cells.

Fig. 8 shows the temperature dependent OCV of all the four cells in the temperature range 0–117 °C after 570 h of aging at room temperature. The fabricated cells must display certain OCVs

Table 1

Time dependent electrochemical parameters of cell 1–4 at room temperature, where R_i = interface resistance, $R_t = (R_b + R_i)$ = total cell resistance.

Time (h)	1. Al/Li/PC(AIN)/LAGP/Au		2. Al/Li/PC(BN)/LAGP/Au		3. Al/Li/PC(Si ₃ N ₄)/LAGP/Au		4. Al/Li/PC(Li ₂ O)/LAGP/Au	
	R_i (Ω)	R_t (Ω)	R_i (Ω)	R_t (Ω)	R_i (Ω)	R_t (Ω)	R_i (Ω)	R_t (Ω)
30	9,628	10,327	6,610	6,893	12,207	12,737	6,992	15,332
72	–	–	7,029	7,551	9,638	10,066	–	–
96	–	–	6,423	7,000	10,710	11,436	6,858	10,568
240	13,369	27,169	6,214	6,821	11,547	12,687	6,866	12,476
336	17,830	33,030	7,324	8,039	13,815	14,935	6,453	11,733
408	32,012	45,312	11,226	11,995	15,134	17,014	10,097	17,137
504	37,878	58,478	9,594	10,425	24,177	30,127	9,904	17,234
624	87,087	122,287	13,258	14,110	–	–	15,745	17,405
672	–	–	9,492	10,349	–	–	84,052	88,272
696	106,000	112,980	10,175	11,225	–	–	97,58	11,358
1344	–	–	38,775	41,925	–	–	34,710	37,120
1848	–	–	33,027	38,297	–	–	94,824	100,204

Table 2
Time dependent cell conductivity, σ_{cell} ($\mu\text{S cm}^{-1}$); number of charge carrier, n_i ; charge carrier mobility, μ_i ($\text{cm V}^{-1} \text{s}^{-1}$) of cell 1–4 measured at room temperature.

Electrochemical cell	After 240 h of cell storage			After 336 h of cell storage		
	σ_{cell}	$n_i (\times 10^{16})$	$\mu_i (\times 10^{-3})$	σ_{cell}	$n_i (\times 10^{16})$	$\mu_i (\times 10^{-3})$
1. Al/Li/PC(AlN)/LAGP/Au	3.12	1.05	1.86	2.62	0.67	2.43
2. Al/Li/PC(BN)/LAGP/Au	12.40	0.70	11.10	10.60	0.43	15.40
3. Al/Li/PC(Si ₃ N ₄)/LAGP/Au	3.94	0.40	6.07	3.18	0.08	25.30
4. Al/Li/PC(Li ₂ O)/LAGP/Au	4.27	1.17	2.29	4.58	0.64	4.49

depending on: (i) the difference in the work function between the two electrodes (here Li or Al/Li and Au metals), (ii) temperature, and (iii) electrochemical coupling between the two electrodes. All four cells show different temperature dependent OCV characteristics (Fig. 8). In the Al/Li/PC(AlN)/GC/Au cell, OCV remains constant (2.0 V) up to 60 °C then gradually increases to about 2.6 V and remains stable up to 118 °C. Al/Li/PC(BN)/GC/Au cell shows a continuous increase from 0.7 to 1.7 V with increase in temperature. In the Al/Li/PC(Si₃N₄)/GC/Au cell, OCV increases from 0.3 to 1.6 V up to 60 °C and then decreases to about 1.2 V. The OCV of Al/Li/PC(Li₂O)/GC/Au cell, remains constant at about 1.8 V from 0 to 117 °C.

The number of charge carriers and their mobility were measured at room temperature after 240 and 336 h of cell aging using a technique reported earlier [20] and the results are presented in Table 2. Table 2 also lists the value of the cell conductivity at the room temperature. From Table 2 it is evident that Al/Li/PC(BN)/GC/Au cell has a moderate number of charge carriers but its conductivity and mobility are the highest among the four cells. It is important to note here that the only variable is the ceramic dopant in the PEO:LiBETI polymer matrix which is in contact with lithium metal. Therefore, the change in number of charge carriers and its mobility during cell aging may be attributed to (a) transfer of Li⁺ ion from lithium anode to PCs layer and (b) accumulation of Li⁺ ions on ceramic particles doped in the PC host.

The results shown in Figs. 7 and 8, and Table 2 may be explained on the basis of SEI layer formation and the ability of the PCs to catalyze charge transfer reaction. The SEI layer may be thicker and less conductive at lower temperatures. At higher temperature its con-

ductivity may increase allowing better electrochemical coupling and thus higher OCV. Thermodynamically, an increase in temperature should reduce OCV. Thus, the temperature dependent change in OCV is largely dominated by the electrochemical coupling and the SEI layer formation.

4. Summary and conclusions

This paper described an investigation which was conducted with an objective to select and optimize components for a working, rechargeable lithium–air cell. A major goal of the investigation was to identify suitable ceramic dopants in an ionically conducting polymer matrix so as to: (i) catalyze anodic charge transfer reaction ($\text{Li}^0 \rightarrow \text{Li}^+ + \text{e}^-$), (ii) form a stable SEI layer at the lithium surface to enhance rechargeability, and (iii) provide high lithium ion conductivity across a broader temperature range.

Membrane laminates comprising of GC and PC materials were fabricated and characterized. The use of PC material was essential to reduce cell impedance and enhance electrochemical compatibility with lithium. Polymeric membranes comprising of PC(BN), PC(Li₂O), PC(Si₃N₄) and PC(AlN) electrochemically coupled the GC membrane with lithium anode. The PC formulations were evaluated by measuring cell conductivity, open circuit voltage, and carrier concentration and its mobility. These measurements allowed identification of Li₂O and BN as suitable dopants as they met the goals established for this investigation. For low temperature application Li₂O was determined to be more effective, whereas BN was preferable for the high temperature performance of the cells.

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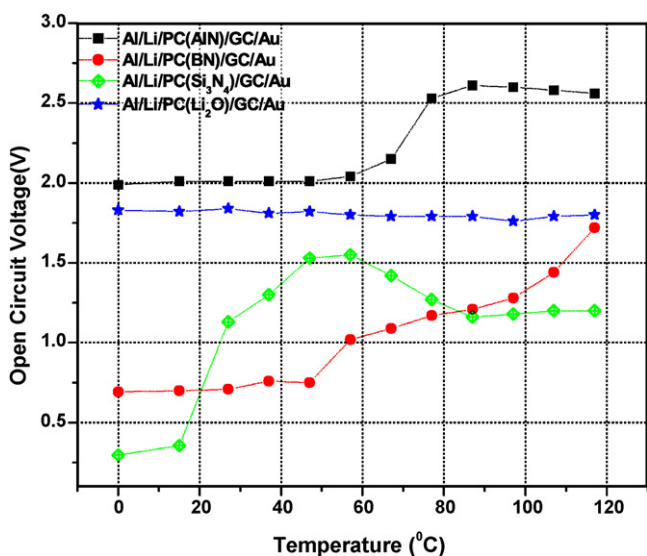


Fig. 8. Temperature dependent open circuit voltage (OCV) of (a) Al/Li/PC(AlN)/GC/Au, (b) Al/Li/PC(BN)/GC/Au, (c) Al/Li/PC(Si₃N₄)/GC/Au, and (d) Al/Li/PC(Li₂O)/GC/Au cells in the temperature range 0–117 °C after 570 h of cell assembly.

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