Oxygen-selective immobilized liquid membranes for operation of lithium-air batteries in ambient air

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ABSTRACT

In this work, nonaqueous electrolyte-based Li-air batteries with an O_2-selective membrane have been developed for operation in ambient air of 20–30% relative humidity (RH). The O_2 gas is continuously supplied through a membrane barrier layer at the interface of the cathode and ambient air. The membrane allows O_2 to permeate through while blocking moisture. Such membranes can be prepared by loading O_2-selective silicone oils into porous supports such as porous metal sheets and Teflon (PTFE) films. It was found that the silicone oil of high viscosity shows better performance. The immobilized silicone oil membrane in the porous PTFE film enabled the Li-air batteries with carbon black air electrodes to operate in ambient air (at 20% RH) for 16.3 days with a specific capacity of 789 mAh g^{-1} carbon and a specific energy of 2182 Wh kg^{-1} carbon. Its performance is much better than a reference battery assembled with a commercial, porous PTFE diffusion membranes as the moisture barrier layer on the cathode, which only had a discharge time of 5.5 days corresponding to a specific capacity of 267 mAh g^{-1} carbon and a specific energy of 704 Wh kg^{-1} carbon. The Li-air battery with the present selective membrane barrier layer even showed better performance in ambient air operation (20% RH) than the reference battery tested in the dry air box (<1% RH).

1. Introduction

A Li-air battery is a promising candidate as a portable power source, due to its highest theoretical specific energy (11,972 Wh kg^{-1}) among all the known electrochemical couples [1]. The demand for primary Li-air batteries is a potential large market, especially in rural and remote locations where the recharge of a battery is impossible. In these applications, the primary batteries should have long life time and high capacity. In a primary Li-air battery, the lithium anode is electrochemically coupled to atmospheric oxygen through an air cathode. Compared to Li-ion batteries, Li-air batteries have higher energy density because the active cathode material O_2 is available from ambient air and does not need to be stored in the battery [2]. Abraham and Jiang first reported that the main discharge reaction in a nonaqueous Li-air battery resulted in the formation of Li_2O_2 [3].

$$2Li + O_2 = Li_2O_2 \quad E_0 = 3.10\,V \qquad (1)$$

Since Abraham and Jiang's discovery [3], extensive research on Li-air batteries has been conducted [1,4–7]. However, there are still several critical problems to be solved before the Li-air battery can

be applied for practical application in ambient air condition [2–6]. The first is ubiquitous moisture (about 1% in volume) in air may penetrate into the battery with O_2 and corrode the Li anode due to the reaction with Li, and then cause fast failure of the battery and serious safety problems.

$$2Li + 2H_2O = 2LiOH + H_2 \qquad (2)$$

The second is the deposition of Li_2O_2 or Li_2O on the cathode surface. The third is the insufficient amount of O_2 for electrode reaction at high discharge rates due to the limited O_2 solubility in the electrolyte. Among these problems, the most urgent one to be resolved is to prevent the reaction of Li anode with moisture from the ambient air. Even trace amount of moisture may cause poor battery performance and serious safety issues.

A continuous supply of dry air is essential to obtain high performance of a Li-air battery. Currently, Li-air batteries under research are mainly operated in a pure O_2 environment or dry air condition [3–7]. Continuous supply of dry O_2 from ambient air is still a big problem. A promising method to solve this problem is to use a membrane that is selective to O_2 while preventing moisture from entering the battery. This is challenging because O_2 and H_2O cannot be separated by bulk or Knudsen diffusion due to the higher diffusivity of H_2O than O_2 and smaller kinetic diameter of H_2O than O_2. Current air dehydration membranes [8] are water selective, which cannot selectively provide oxygen directly to the battery.

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There is very little available literature on O_2 selective membranes. Reynolds et al. [9] prepared immobilized polyperflurocarbon liquid into a polymer Celgard 2500 porous substrate and obtained O_2 permeance of 1.7×10^{-10} mol m^{-2} s^{-1} Pa^{-1} and O_2/H_2O selectivity of 3.9. The membrane exhibited O_2/H_2O selectivity, but the O_2 permeance was low. This will prevent the battery from discharging at high current density due to limited O_2 supply. Also, no data is available about application of this membrane in real Li-air batteries for ambient operation.

In this paper, we report for the first time that an O_2-selective membrane with high O_2 permeability can be obtained by immobilizing an O_2 selective liquid into a porous metal or PTFE substrate. These membranes can significantly improve the performance of Li-air batteries operated in ambient air with 20–30% RH. An immobilized liquid membrane is usually composed of a porous support and a liquid that is selective to a specific target molecule. The selectivity is due to higher solubility and/or diffusivity of the selected molecule than that of the rejected molecules. For O_2-selective/water barrier membranes, a promising candidate for the O_2-selective liquid is silicone oil. Silicone oil has been used as an O_2 carrier in bioreactors [10]. Poncelet et al. [11] found that silicone oil has solubility to oxygen of ~6 mmol dm^{-3}, 20-fold higher than that of oxygen in water. Furthermore, silicone oil is non-volatile and stable, which is necessary for long-term battery storage and operation. The other important component of immobilized liquid membrane is a porous supporting substrate with suitable porosity and thickness so that sufficient O_2 diffusion channels and permeation flux can be obtained. The substrate should also have intimate contact with the immobilized liquid so that defects, such as pinholes that form across the membrane, are minimized. In this work, four kinds of substrates, namely a porous metal sheet, a surface modified porous metal sheet, a commercial PTFE sheet, and a silicalite/porous metal membrane substrate, were evaluated with various silicone oils. These membranes were assembled in Li-air batteries and the discharge performance of the batteries was investigated.

2. Experimental

The structures of immobilized liquid membranes are illustrated in Fig. 1, where Fig. 1(a and b) shows the membrane of liquid immobilized in a homogenous, porous substrate sheet and in the metal substrate sheet being coated with a hydrophobic silicalite membrane on one side, respectively. The O_2-selective silicone oil is held
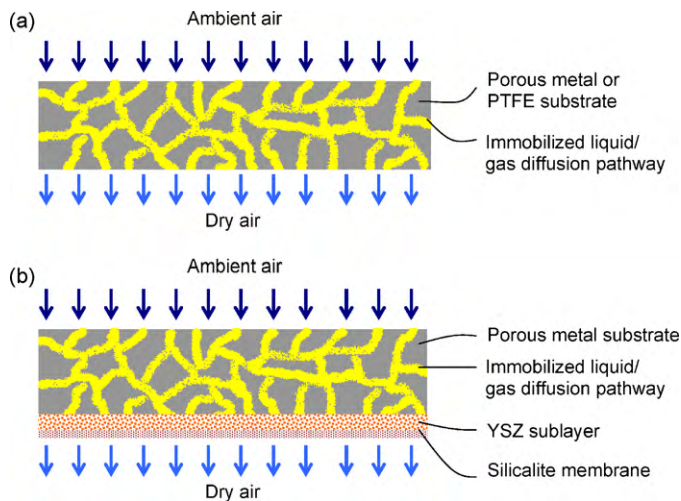
within pores of the durable, thin, and porous metal substrate sheet by capillary force. The porous metal sheet of uniform pore structures at micrometer and sub-micrometer level has been prepared in house by a proprietary process, because the conventional metal foams are very weak, thick, and have too large pores. The immobilized liquid membranes are characterized and tested to evaluate their effects on the discharge performance of Li-air batteries in ambient air environment.

2.1. Preparation of membranes

The silicone oils used for the membrane preparation are Dow Corning 200 fluids (polydimethylsiloxane, PDMS, viscosity 10,000 and 100,000 centistokes (cst)) and Shin-Etsu DM-fluid (dimethylpolysiloxane, viscosity 100,000 cst). Both silicone oils are colorless, non-volatile, and have high O_2 solubility. For example, at 220 °C, the DM-fluid has a vapor pressure no higher than 1 Torr. Saturated O_2 solubility (Bunsen coefficient) in the DM-fluid at 20 °C and one atmosphere pressure is 28% by volume.

2.1.1. Immobilized liquid membrane in porous metal and surface-modified porous metal substrates
(1) Porous metal substrate

A porous metallic Ni substrate was prepared by a proprietary process recently developed at PNNL. The substrate was made by a tape-casting process followed by thermal treatment. The advantage of using tape-casting is the ease of scale up so that larger substrate sheets can be obtained. As shown in Fig. 2, the substrate had a very smooth surface, uniform pore structure across the thickness, and good mechanical strength. The sub-
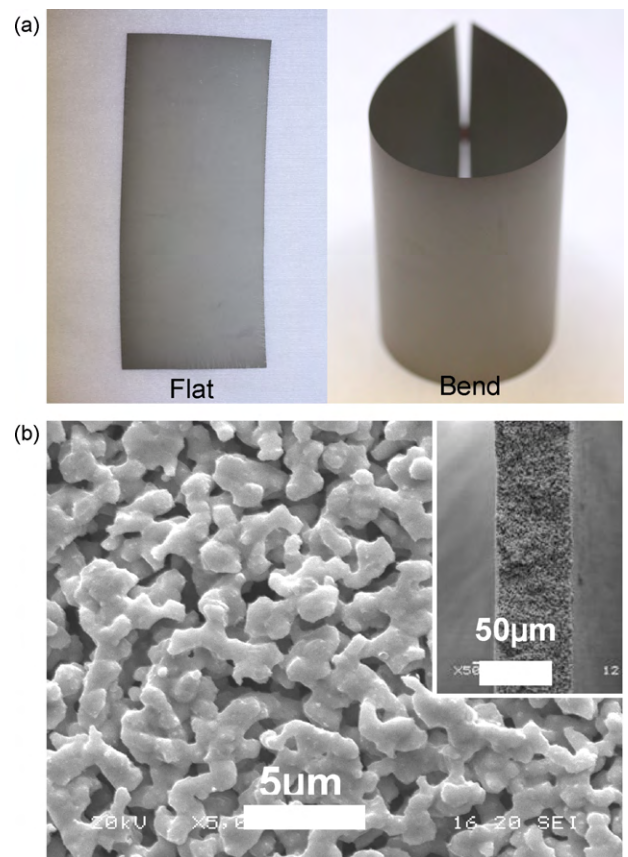

Fig. 1. Schematic of two kinds of O_2 membrane structures. (a) Liquid immobilized in homogeneous porous substrate, and (b) liquid immobilized in silicalite membrane-coated porous metal substrate (asymmetrical).

Fig. 2. Texture of new porous metal substrate sheet used in this work. (a) Photograph of a porous metal substrate, and (b) SEM surface image of the porous metal substrate with the cross-section image in the inset.
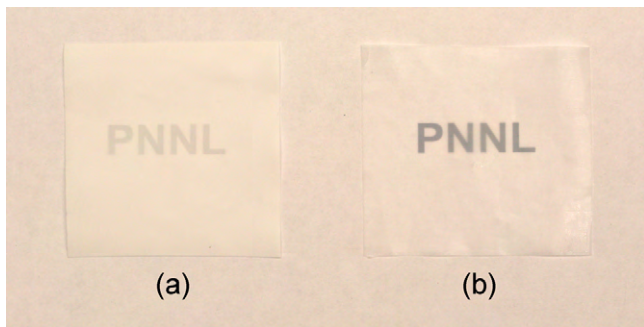
Fig. 3. Photographs of PTFE film before (a) and after (b) loading of silicone oil.

Fig. 4. Experimental setup for air permeability measurements.

strate used in this work generally had a thickness of 50 μm, mean pore size of ∼1 μm, and controllable porosity of 30–50%.

(2) Surface-modified porous metal substrate

An evaporation–deposition method was used to modify the Ni substrate surface to make it hydrophobic in order to further enhance adhesion between the silicone oil and the Ni supporting matrix. The procedure was similar to that reported in literature [12]. Briefly, fresh Ni substrate was treated in PDMS (Dow Corning, viscosity 5000 cst) vapor at 235 °C for 4 h. The substrate became very hydrophobic after treatment and an increase of water contact angle from 0° to 125 ± 1° was observed on the substrate surface.

(3) Loading of oil into porous metal substrate

Silicone oils with various viscosities were loaded into the fresh metal substrate and surface-modified metal substrate. The loading was conducted in vacuum at various temperatures. Generally, the porous metal substrate was submerged in silicon oil in a horizontal position and the oil container was put under 300 mm Hg vacuum to remove bubbles trapped in metal pores so that silicone oil could fill the pores. After loading, the porous metal substrate was taken out of the oil and excess oil on the surface was wiped off. Calculation based on the weight gain suggests that about 50–66% (vol.) of the metal substrate pores was occupied by the silicone oil.

2.1.2. Immobilized liquid membrane in PTFE substrate

Silicone oils were also immobilized into a commercial Mupor PTFE membrane (from Interstate Specialty Products) with a thickness of 102 μm and a pore size 2 μm. Silicone oil with viscosity of 100,000 cst was soaked into the PTFE pores at room temperatures. The PTFE membrane film was too soft to be self-supported. It was difficult to handle during the liquid immobilization process. Specifically, 50 ml of silicone oil was contained in a 200 ml glass petri dish. The PTFE substrate (5 cm × 5 cm in size) was then placed horizontally on the surface of the silicone oil. Another 50 ml of silicone oil was poured on top of the PTFE substrate. The petri dish was then placed in a vacuum oven at 300 mm Hg to remove air trapped in the PTFE pores. The oil-loaded PTFE substrate was then taken out from the oil, and the excess oil was wiped off. The PTFE substrate appeared to be transparent (Fig. 3(b)) after the oil loading, instead of white color before oil loading (Fig. 3(a)), indicating even distribution of the silicone oil in the entire PTFE sheet.

2.1.3. Immoblized liquid membrane in silicalite/porous metal substrate

The silicalite/porous metal substrate was prepared by growing a thin layer of silicalite membrane on one side of the metal substrate (Fig. 1(b)). First, one side of the metal substrate was coated with a layer of yttria-stabilized-zirconia (YSZ) particles (particles size of ∼200 nm) by screen printing as an intermediate layer between metal substrate and silicalite membrane. Second, home-

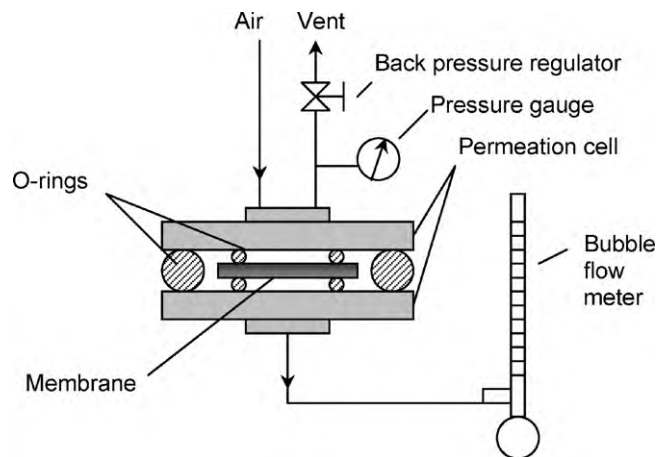made silicalite seed crystals with size of ∼100 nm were coated on the YSZ layer using a spin coater (WS-400B-6NPP-LITE, Laurell) at 1500 rpm. Third, a crystal growth precursor was prepared by mixing 5.65 ml tetrapropylammonium hydroxide (TPAOH, Aldrich), 10.2 ml tetraethyl orthosilicate (TEOS, Sigma–Aldrich) and 60 ml H_2O at 50 °C for 2 h. Fourth, hydrothermal growth of the seeded substrate was conducted at 180 °C for 2 h. Finally, the silicalite-coated metal substrate was taken out, rinsed with D.I. water, dried at 100 °C for 8 h and heated at 400 °C in a 2% (vol.) O_2/N_2 gas environment for 4 h to remove the template TPA to free the zeolite pores.

The idea was that a silicalite membrane with well defined pore size of 0.54 nm × 0.57 nm would let oxygen diffuse through while constraining the leakage of silicone oil from the metal pores for prolonged battery operation. To prepare this kind of liquid-immobilized membrane, the silicalite/porous metal substrate was placed in a vacuum oven with its silicalite-coated side facing downwards. Only the porous metal side was covered with the silicone oil. The substrate was exposed to vacuum at 300 mm Hg at room temperature for 3 h. Excessive silicone oil was wiped off from the metal surface after vacuuming. The silicalite surface was kept clean without contacting silicone oil.

2.2. Membrane characterization

Scanning electron microscopy (SEM, JEOL JSM-5900) was used to observe the morphology of substrates and membranes.

The gas permeability of selected membranes was tested using a home-made gas permeation cell. As shown in Fig. 4, air was introduced into the feed side of the permeation cell. The pressure of air was controlled with a back pressure regulator and measured with a precise pressure gauge (Omega DPG7010). Flow rate of the air diffusing through the membrane was measured using a bubble flow meter. The air permeance was calculated with the following equation:

$$P_i = \frac{F_i}{A_m \cdot \Delta P_i} \quad (3)$$

where F_i is the permeation flow rate of gas i (mol s^{-1}), A_m is the membrane surface area (m^2), and ΔP_i is the partial pressure differential of gas i (Pa).

2.3. Preparation of air electrodes

Carbon air electrodes were prepared following a similar procedure as described in our previous papers [13]. Darco® G-60
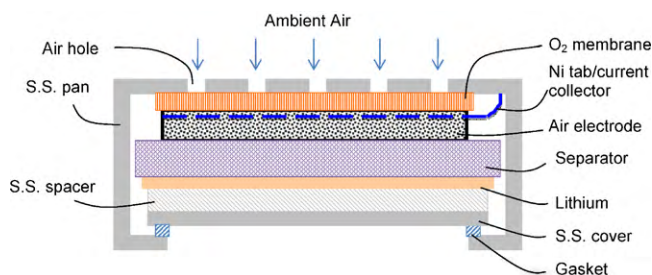
Fig. 5. Schematic layout of an assembled Li-air coin-type battery.

Fig. 6. SEM cross-section image of silicalite membrane grown on YSZ sub-layer supported on porous metal substrate.

activated carbon (from American Notir) or Ketjen black EC600JD carbon (from Akzo Nobel) was mixed with nano MnO_x powder (from QuantumSphere, Inc.) and Dupont Teflon® PTFE 30B fluoropolymer resin aqueous dispersion (containing 60 wt% of 0.05–0.5 μm PTFE resin particles suspended in water) in aqueous solution. After drying, the mixture was cold pressed onto a 40 mesh Ni screen with a Gore PTFE diffusion film slightly laminated at the carbon side as the air-facing side. The composition of carbon, catalyst and binder in the air electrode from Darco carbon (referred as "DC air electrode" in this paper) was 89.5%, 2.5% and 8.0% by weight, respectively. The composition of carbon, catalyst and binder in the air electrode from Ketjen black carbon (referred as "KB air electrode" in this paper) was 86.6%, 2.5% and 10.9% by weight, respectively. The thicknesses of air electrodes were 0.36 mm and 1.00 mm for the DC air electrode and KB air electrode, respectively. Then, the DC and KB air electrode sheets were die-cut into circular disks with a small piece of Ni tab. The air electrode disks have a diameter of 1.59 cm and an area of 1.98 cm^2.

The carbon in the air electrode acts as the electronically conductive agent and supporting material for catalysts. The high surface area of carbon can be active for oxygen reduction by itself. The porous structure of the carbon hosts Li_2O_2/Li_2O product formed during the discharge process. From these perspectives, the carbon loading should be as high as possible. On the other hand, certain void space in the cathode is necessary to host the electrolyte solution and assure diffusion transport of reactants not become a rate-limiting factor. There should be an optimum carbon loading. The optimum carbon loading will be a strong function of the carbon material, electrolyte, catalysts, and cell design. In this work, we focus on evaluation of the membrane performance by fixing the battery material properties. It is expected that for a given membrane, the energy capacity can be further enhanced by optimizing the cathode materials and structures.

2.4. Li-air coin cell assembly

The schematic structure of the assembled coin cells is shown in Fig. 5. Coin cell kits of 2325 type were purchased from Canada National Research Council (CNRC) and the cell pans were machine-drilled 19 Ø1.0 mm holes which were evenly distributed on the cell pans for air to pass through. The procedure for assembling the testing coin cells was as follows. The electrode disks were connected onto the coin cell pans by spot-welding the Ni tab onto the hole-drilled pans, dried at around 80 °C under vacuum overnight, and then stored inside a glove box filled with purified argon, in which the moisture and O_2 content were both less than 1 ppm. The O_2 membrane was placed between the pan with holes and the air electrode disk from which the originally laminated Gore PTFE diffusion membrane was peeled off. As a comparison, where no O_2 membrane was used, the Gore PTFE membrane was maintained at the air electrode surface. Then a piece of separator (diameter 1.91 cm, Whatman® GF/D glass microfiber filter paper) was placed onto the air electrode, an appropriate amount of electrolyte (1.0 M

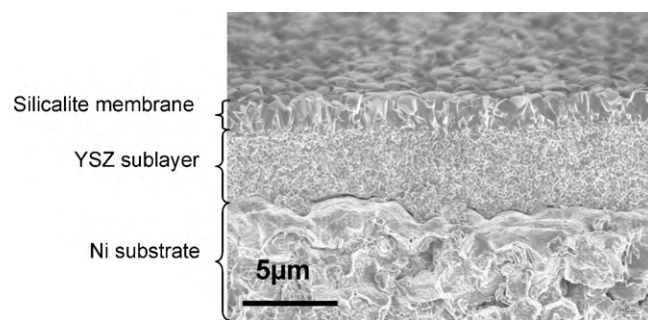lithium bis(trifluoromethanesulfonyl)imide in ethylene carbonate and propylene carbonate at a weight ratio of 1:1) was added onto the separator, then a piece of lithium disk (diameter 1.59 cm and thickness 0.50 mm), a stainless steel spacer with a thickness of 0.86 mm from CNRC, and a coin cell cover with a polypropylene gasket were placed in sequence. Finally the whole assembly was crimped on a pneumatic coin cell crimper purchased from CNRC at a gas pressure of 200 psi. The cells using the DC air electrode and KB air electrode are named as battery A series and battery B series, respectively.

2.5. Cell testing

Li-air coin cells were tested either in ambient air with 20 or 30% RH or in a dry box filled with dry air (<1% RH) and connected to an Arbin BT-2000 Battery Tester. The variation in ambient air humidity (20% or 30% RH) was due to the testing of the batteries in different months of a year. The cells were exposed to the testing-environment air for 30 min and then tested by discharging at a constant current of 0.05 mA cm^{-2} to 2.0 V. The batteries with the originally laminated Gore PTFE membrane were tested in ambient air and dry air environment as a comparison. For each kind of membrane structure and/or composition, duplicate membrane samples were prepared and assembled as two to four battery cells. These cells were tested in parallel under the same conditions. Variations or artifacts could be caused by the membrane preparation itself, battery assembly, and testing failure. The representative performance data are presented in the paper.

3. Results and discussions

3.1. SEM/AFM observation

3.1.1. Immobilized liquid membrane in porous metal substrate

AFM observation of porous metal substrate before and after loading of silicone oil was conducted. The metal surface roughness decreased significantly after oil filling, indicating the occupation of the pores in the porous metal substrate by the silicone oil.

3.1.2. Silicalite/porous metal substrate

The silicalite membrane was grown on the top of the YSZ sublayer that was supported on a porous metal substrate. Compared to the metal substrate of average pore size of 1 μm, the YSZ sublayer coating reduced the pore size to about 200 nm, which made the seed coating easier. The SEM surface analysis confirmed full coverage of the YSZ sub-layer surface by the zeolite membrane. The SEM cross-section image (Fig. 6) shows a silicalite membrane thickness of 1–2 μm and the YSZ coating of 3–4 μm. The intimate contact between the silicalite membrane and YSZ sub-layer

Table 1
Air permeance of porous metal substrate and selected membranes.

Sample	Air permeance (mol m^{-2} s^{-1} Pa^{-1})
Fresh porous metal sheet	2.85×10^{-4}
Silicalite membrane grown on the porous metal sheet	1.58×10^{-6}
Silicon oil loaded into the porous metal sheet that was modified to hydrophobic	1.62×10^{-6}

is clearly observed. The XRD pattern of this membrane indicated a pure silicalite crystal phase.

3.2. Gas permeation

Table 1 shows the dry air permeance of the fresh porous metal substrate, silicalite-coated porous metal substrate, and porous metal substrate filled with Dow Corning 100,000 cst silicone oil measured at room temperature (22 °C). The fresh metal substrate has a high air permeance of 2.85×10^{-4} mol m^{-2} s^{-1} Pa^{-1}, indicating its good permeability to be used as supporting matrix for liquid membranes. The silicalite-coated and the silicone oil-filled metal substrate have the air permeance of two orders of magnitude lower than that of the fresh metal substrate, which indicated good coverage of the metal substrate pores by the molecular separation membrane material.

The silicone oil-loaded porous metal substrate was further tested for air separation functions under various conditions. It was found that this membrane had an O_2/H_2O separation factor of 1.5–3.6 and a relatively high O_2 permeance of 2×10^{-7}–1.5×10^{-6} mol m^{-2} s^{-1} Pa^{-1} at room temperature. It should be noted that the O_2/H_2O selective factor and permeance of the membrane varied with the permeation test conditions. The actual gas-separation conditions on the permeate side under battery operation, such as O_2 partial pressure gradient across the membrane, is not known and can be complicated due to the electrolyte solvent vaporization. These O_2/H_2O selective factors and permeance values are only indicative to the membrane gas-separation characteristic and may not be the same during the ambient operation of the Li-air battery. It was also found that N_2 cannot be separated using this type of membranes. So, effect of N_2 on the performance of Li-air batteries was not screened out in this study. It is known that N_2 can slowly react with Li metal. However, the reaction rate of N_2 with Li is dynamically very slow. We think the effect of N_2 on the Li battery performance is negligible in this work.

3.3. Battery performance

Fig. 7 shows typical discharge curves of the batteries assembled with the DC air electrode and selected O_2 membranes of liquid immobilized in the porous metal substrate (A2) and in the PDMS-treated porous metal substrate (A4) in ambient air of 30% RH. Compared with the batteries containing the same air electrode
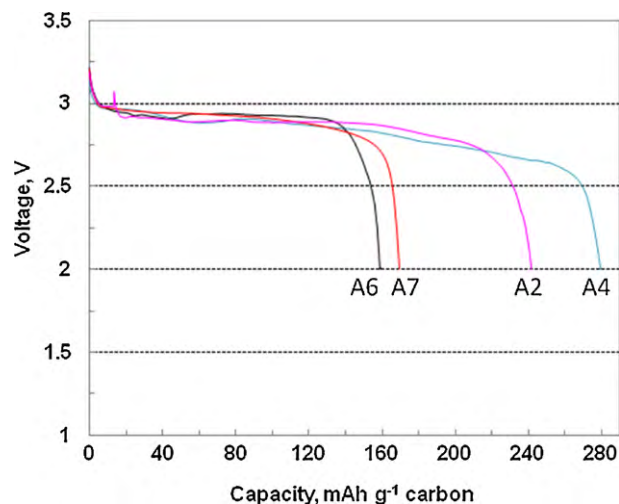

Fig. 7. Discharge curves of Li-air batteries assembled with DC air electrode and different membranes. Tested in ambient air with 30% RH: Dow Corning silicone oil-immobilized in porous metal sheet (A2) and in PDMS-treated porous metal sheet (A4), commercial Gore PTFE diffusion membrane directly laminated on the DC air electrode (A6). The control cell: battery with the commercial PTFE membrane in dry air of <1% RH (A7).
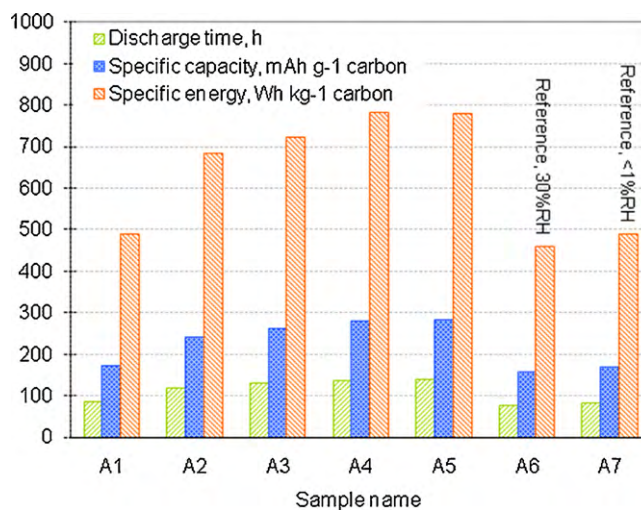

Fig. 8. Comparison of battery performances with different membranes listed in Table 2 and Fig. 7.

but with originally laminated Gore PTFE diffusion membrane that were tested in the same ambient air (A6) and in the dry air condition (A7), both A2 and A4 had better performance. The important experimental conditions for this set of battery runs are listed in Table 2. The discharge performance data (discharge time, specific capacity and specific energy) of the batteries with the immobilized liquid membranes are summarized and plotted in Fig. 8. It is seen

Table 2
Preparation of O_2-selective immobilized liquid membranes and testing conditions of Li-air batteries with DC air electrode.

Number	Substrate	Liquid	Liquid viscosity (cst)	Liquid loading temperature (°C)	Test condition
A1	Porous metal	DC200[a]	10,000	25	Ambient air with 30% RH
A2	Porous metal	DC200	100,000	25	Ambient air with 30% RH
A3	Porous metal	DC200	100,000	220	Ambient air with 30% RH
A4	PDMS-treated porous metal	DC200	100,000	25	Ambient air with 30% RH
A5	PDMS-treated porous metal	DC200	100,000	220	Ambient air with 30% RH
A6	Porous Gore PTFE	N/A	N/A	N/A	Ambient air with 30% RH
A7	Porous Gore PTFE	N/A	N/A	N/A	Dry air (<1% RH)

[a] DC200 means Dow Corning 200 fluid (silicone oil).

that all the O_2 membranes comprising the silicone oil of higher viscosity immobilized in the porous metal substrates (A2 and A3) and in the PDMS-treated porous metal substrate (A4 and A5) have substantially improved the battery discharge performance. The battery cells A2–A5 all exhibited longer discharge time and higher specific capacity/specific energy than the reference cells (A6 and A7) equipped with the Gore PTFE diffusion membrane. It is noted that for this particular set of the DC air cathode attached with the Gore PTFE membrane, testing in the dry box (A7) showed only slightly better performance that testing in the ambient air of 30% RH (A6). It is postulated that the gas diffusion rate through this macro-porous PTFE membrane was too fast and the carbon material was even sensitive to trace amounts of moisture that was present in the dry box.

When comparing the Li-air batteries with O_2 membranes of fresh porous metal substrates loaded with different silicone oils (A1 versus A2 and A3), it can be seen that the membrane loaded with the silicone oil of higher viscosity is much better than the membrane with the silicone oil of lower viscosity. This may be explained by effective reduction of the moisture penetration into the battery with the high viscosity oil. The membranes A2 and A3 loaded with the same silicone oil but at two different immobilization temperatures (25 °C versus 220 °C) do not show much difference in the battery performance, indicating that influence of the immobilization temperature on the membrane performance is limited.

The membranes comprising the silicone oil loaded into the surface-modified porous metal substrate (A4 and A5) gave consistently better discharge performance than the membranes using the untreated porous metal substrate (A2 and A3). This suggests that enhancement of the porous metal surface hydrophobicity indeed improves the membrane quality. The battery performances of A4 and A5 look similar, which suggests that the immobilization temperature has little impact on the membrane performance. This observation is consistent with the above comparison with the untreated porous metal substrate. It is more convenient and cost-effective to load the silicone oil into the substrate at room temperature than at higher temperatures. Thus, the present membrane preparation can be readily scaled up in future for large-scale production.

Fig. 9 compares discharge curves of the batteries assembled with the same KB air electrode but different membrane barriers. The important experimental conditions are given in Table 3. B1 and B2 membranes were prepared with different porous substrates by using the same oil immobilization conditions. The silicalite-coated porous metal substrate and commercial Mupor porous PTFE film were used for preparation membrane B1 and B2, respectively. For comparison purposes, the batteries made of the same cathode material with originally laminated Gore PTFE diffusion membrane were tested in the ambient air (B3) together with B1 and B2, and tested in the dry air box condition (B4) as well. The spikes on the discharge curves of the batteries with the membrane B1 and B2 were caused by the power outage during the lengthy discharge process. The down-direction peaks on the discharge curves are probably related to the O_2 deficiency in the inner side of the air electrode because of the thick air electrode (ca. 1 mm). The slow wetting of the electrolyte to the formed Li_2O/Li_2O_2 during discharge may also cause the increase of the internal resistance. Once these factors
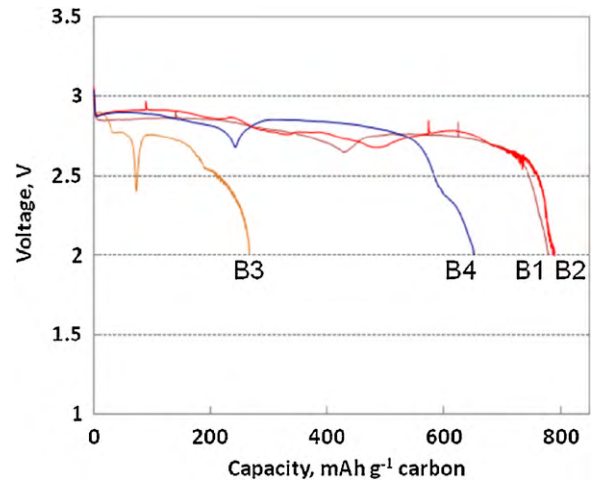

Fig. 9. Discharge curves of Li-air batteries assembled with KB air electrode and different membranes. Tested in ambient air with 20% RH: Dow Corning silicone oil loading in silicalite/porous metal substrate (B1) and Shin-Etsu silicone oil loaded in commercial Mupor PTFE diffusion membrane (B2), commercial Gore PTFE diffusion membrane (B3). The control cell: battery with the commercial PTFE membrane in dry air of <1% RH (B4).
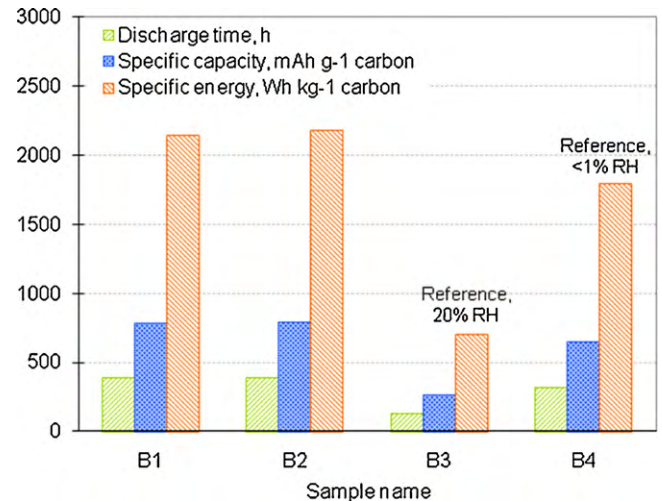

Fig. 10. Comparison of battery performances with membranes listed in Table 3 and Fig. 9.

were balanced, the cell voltage increased again, and the discharge process continued until the end.

The discharge performance data (discharge time, specific capacity and specific energy) of all the batteries with the KB air electrode are summarized and plotted in Fig. 10. It is seen that both immobilized liquid oil O_2 membranes (B1 and B2) have much longer discharge time, higher specific capacity and specific energy than the reference battery with the PTFE membrane in the ambient condition (B3). The batteries with the new membranes even show better performances than the control run of the battery with the PTFE membrane in <1% dry air environment. The membrane B1 has the

Table 3
Preparation of O_2-selective immobilized liquid membranes and testing conditions of Li-air batteries with KB air electrode.

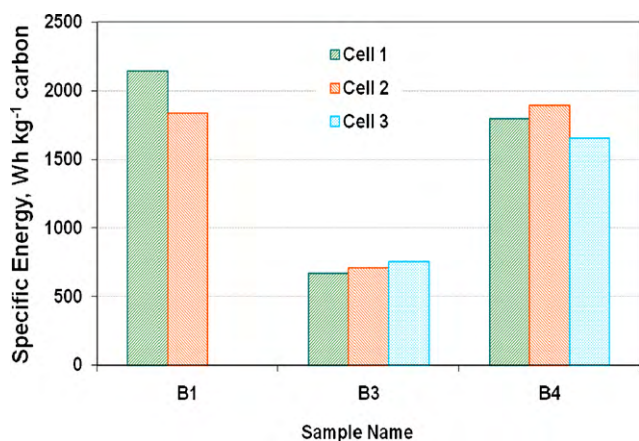| Number	Substrate	Liquid	Liquid viscosity (cst)	Liquid loading temperature (°C)	Test condition
B1	Silicalite/porous metal	DC200	100,000	25	Ambient air with 20% RH
B2	Mupor PM3T	Shin-Etsu silicone oil	100,000	25	Ambient air with 20% RH
B3	Gore PTFE	N/A	N/A	N/A	Ambient air with 20% RH
B4	Gore PTFE	N/A	N/A	N/A	In dry air (<1% RH)

Fig. 11. Reproducibility of specific energy for typical battery assembly and testing. B1, batteries equipped with a new membrane (Dow Corning silicone oil loading in silicalite/porous metal substrate) and tested in ambient air of 20% RH. B3, batteries with commercial Gore PTFE diffusion membrane tested in ambient air of 20% RH. B4, the same battery with the PTFE membrane and tested in dry air of <1% RH.

silicalite zeolite membrane as one additional barrier layer to the immobilized oil. The similar results of both liquid membrane B1 and B2 indicate that the membranes were effective in blocking the penetration of moisture from ambient air into the Li-air batteries and may also prevent loss of the electrolyte solvent from evaporation. The ultimate discharge performance is limited by the cathode structure and reaction rather than by the membrane itself.

Reproducibility of the battery cell performance is illustrated by Fig. 11. The B1 membrane was assembled as two duplicate coil cells. They were tested in parallel under the ambient conditions of 20% RH. Six duplicate cells were assembled with the reference Gore PTFE membrane. Three of them (B3) were tested under the ambient conditions of 20% RH together with the B1 cells, while the other three (B4) were tested in the dry box (1% RH), All those cells were tested in the same batch. The variation in the performance among duplicate cells was insignificant relative to the large difference among batteries equipped with new and reference membranes.

There are two possible ways to reduce the moisture impact on the Li-air battery performance. One way is to reduce diffusivity of both H_2O and O_2, which would also minimize the solvent loss from the battery into ambient air due to evaporation. In this way, the serious oxygen polarization or starvation for the electrode reaction will occur if the oxygen diffusion rate is too slow relative to the current discharge. The other way is to use a membrane that is selective to O_2 over H_2O. From point of view of just O_2 transport, the second way is preferred and requires high O_2/H_2O selectivity. Practically, a balanced approach between the diffusivity reduction and O_2/H_2O selectivity enhancement was sought by this study.

The battery performance obtained with the immobilized silicone oil membrane is considered resulting from the reduced O_2 and H_2O diffusivity and selectivity to O_2 over H_2O through the membrane. The diffusivity of molecule in liquid is much lower than in gas phase medium. So the O_2 and H_2O diffusivity can be significantly reduced by using the silicone oil membrane. The O_2/H_2O selectivity in the silicone oil membrane can be attributed to the solution–diffusion mechanism, in which the selectivity can be expressed as:

$$\alpha_{O_2/H_2O} = \frac{S_{O_2} \cdot D_{O_2}}{S_{H_2O} \cdot D_{H_2O}} \tag{4}$$

The membrane selectivity (α_{O_2/H_2O} at feed O_2/H_2O molar ratio of 1) is enhanced by the higher O_2 solubility (S_{O_2}) [11] and/or dif-

fusivity [14] (D_{O_2}) than H_2O solubility (S_{H_2O}) and diffusivity (D_{H_2O}) in silicone oil. Usually, the diffusivity in a liquid phase is few orders of magnitude lower than the gas diffusion in a porous medium. The immobilized liquid membrane needs to be thin enough so that adequate O_2 supply is assured for discharge at high current rate.

The porous metal substrate used in this study has a thickness of ~50 μm. The thickness is controllable by adjusting the manufacturing procedure so that substrate with thickness of 25–1000 μm can be obtained. By immobilizing the silicone oil membrane in the pores of the metal substrate with various thicknesses, the liquid membrane thickness can be adjusted to meet specific application requirements. In this work, silicone oil is used to demonstrate the membrane design concept. In principle, any O_2-selective liquid can be loaded into the porous metal substrate as O_2/H_2O selective membrane.

4. Conclusions

The O_2 membranes comprising silicone oil-immobilized in four types of porous substrates, i.e., fresh porous metal sheet, surface-modified porous metal sheet, silicalite membrane-coated porous metal sheet, commercial porous PTFE film, enable operation of the nonaqueous electrolyte-based Li-air batteries in ambient air conditions. The batteries equipped with these new membranes even showed much higher capacity and specific energy under the ambient air conditions at RH of 20–30% than the control battery made of the same material with a commercial PTFE diffusion membrane tested under the dry air box conditions (<1% RH). The new membrane materials and structures invented in this work are effective in blocking the moisture penetration into the Li-air batteries while allowing oxygen permeate through, and may prevent loss of the electrolyte solvent from evaporation. These membranes can be readily prepared and are very promising for practical production of large-size membrane sheets at low costs. They are applicable to any primary or rechargeable metal-air batteries that are sensitive to moisture.

References

[1] R.E. Williford, J.G. Zhang, J. Power Sources 194 (2009) 1164.
[2] I. Kowalczk, J. Read, M. Salomon, Pure Appl. Chem. 79 (2007) 851.
[3] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (1996) 1.
[4] D. Linden, T. Reddy, Handbook of Batteries, 3rd ed., McGraw-Hill, New York, 2001, p. 38.50.
[5] S.S. Zhang, D. Foster, J. Read, J. Power Sources 195 (2010) 1235.
[6] W. Xu, J. Xiao, J. Zhang, D. Wang, J.-G. Zhang, J. Electrochem. Soc. 156 (2009) A773.
[7] X.H. Yang, Y.Y. Xia, J. Solid State Electrochem. 14 (2010) 109.
[8] F.L. Coan, J.A. Jensvold, U.S. Patent 7,294,174.
[9] T.A. Reynolds, D.J. Brose, M.N. Golovin, U.S. Patent 5,985,475.
[10] R. Leung, D. Poncelet, R.J. Neufeld, J. Chem. Tech. Biotechnol. 68 (1997) 37.
[11] D. Poncelet, R. Leung, L. Centomo, R.J. Neufeld, J. Chem. Tech. Biotechnol. 57 (1993) 253.
[12] J. Yuan, X. Liu, O. Akbulut, J. Hu, S. Suib, J. Kong, F. Stellacci, Nat. Nanotechnol. 3 (2008) 332.
[13] J. Xiao, D. Wang, W. Xu, R.E. Williford, J. Liu, J.-G. Zhang, J. Electrochem. Soc. 157 (2010) A487.
[14] E. Dumont, Y. Andres, P. Le Cloirec, Chem. Eng. Sci. 61 (2006) 5612.