



Ambient operation of Li/Air batteries

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ABSTRACT

In this work, Li/air batteries based on nonaqueous electrolytes were investigated in ambient conditions (with an oxygen partial pressure of 0.21 atm and relative humidity of ~20%). A heat-sealable polymer membrane was used as both an oxygen-diffusion membrane and as a moisture barrier for Li/air batteries. The membrane also can minimize the evaporation of the electrolyte from the batteries. Li/air batteries with this membrane can operate in ambient conditions for more than one month with a specific energy of 362 Wh kg⁻¹, based on the total weight of the battery including its packaging. Among various carbon sources used in this work, Li/air batteries using Ketjenblack (KB) carbon-based air electrodes exhibited the highest specific energy. However, KB-based air electrodes expanded significantly and absorbed much more electrolyte than electrodes made from other carbon sources. The weight distribution of a typical Li/air battery using the KB-based air electrode was dominated by the electrolyte (~70%). Lithium metal anodes and KB-carbon account for only 5.12% and 5.78% of the battery weight, respectively. We also found that only ~20% of the mesopore volume of the air electrode was occupied by reaction products after discharge. To further improve the specific energy of the Li/air batteries, the microstructure of the carbon electrode needs to be further improved to absorb much less electrolyte while still holding significant amounts of reaction products.

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1. Introduction

Metal/air batteries have much higher specific energies than most currently available primary and rechargeable batteries [1,2]. They are unique in that the cathode active material is not stored in the battery. Instead, oxygen from the environment is reduced by catalytic surfaces inside the air electrode, forming either an oxide or peroxide ion that further reacts with cationic species in the electrolyte. The Li/O₂ couple is especially attractive because it has the potential for the highest specific energy among all the known electrochemical couples. When only the lithium weight is considered (oxygen will be absorbed from the surrounding air environment), the Li/air battery has a specific energy of 11,972 Wh kg⁻¹. However, water vapor corrosion of anode materials has hindered development of Li/air batteries for practical applications [3].

Two approaches used to overcome the water corrosion problem have been reported in the literature. One approach is to operate Li/air batteries in a nonaqueous electrolyte. Abraham and Jiang [2,4] first reported a Li/O₂ battery based on a nonaqueous electrolyte in 1996. Since then, several groups have conducted extensive work

and have documented the effects of various factors on the performance of Li/air batteries [5–12]. Although a lithium anode is stable in a nonaqueous electrolyte, most of the lithium/air batteries cited above were investigated in a pure oxygen environment because penetration of moisture from the ambient environment will quickly corrode a lithium electrode. Another approach to protect the lithium electrode is to use a glass electrolyte (such as LISCON glass (Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂) made by Ohara Inc. of Japan). However, this glass is not stable when in contact with lithium metal. Visco et al. [13,14] of Polyplus Battery Company first solved this problem by depositing a solid-state interfacial layer (Cu₃N, Lipon, etc.) between the lithium metal and the LISCON glass, thus forming a protected lithium electrode. Li/air batteries using this protected lithium electrode can operate in both aqueous and nonaqueous electrolytes. Recently, several groups [15,16] used an organic electrolyte as the interfacial layer between the lithium metal and the LISCON glass, thereby forming a triple electrolyte structure (organic electrolyte/LISCON glass/aqueous electrolyte). A high discharge capacity per gram of carbon has been reported using this structure because the reaction product (i.e., LiOH) of this battery is soluble in the aqueous based electrolytes [16].

Both nonaqueous and aqueous electrolyte-based Li/air batteries have similar theoretical specific energies (near 12,000 Wh kg⁻¹) when only the lithium weight is considered. The practical specific energies of these batteries are largely reduced when other components of the batteries (e.g., the electrolyte and packaging) are

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considered, even if oxygen can still be absorbed from the environment. Zheng et al. [17] simulated both aqueous and nonaqueous electrolyte-based Li/air batteries where the total weight of the lithium, the carbon-based air electrode, and the electrolyte were considered. Their analysis showed that the maximum theoretical capacities of the cells are 435 mAh g^{-1} and 940 mAh g^{-1} for Li/air batteries with aqueous and nonaqueous based-electrolytes, respectively. The corresponding specific energies for aqueous and nonaqueous-based Li/air batteries are 1300 Wh kg^{-1} and 2790 Wh kg^{-1} , respectively. The main difference between these two kinds of Li/air batteries originates from the fact that the solvent is consumed in aqueous electrolyte-based Li/air batteries, but it is not consumed in the nonaqueous electrolyte-based Li/air batteries.

Because the air electrode plays a critical role in the operation of Li/air batteries, most of the previous work on these batteries have reported the specific capacity (mAh g^{-1}) of the battery based on the weight of carbon in the air electrode instead of the weight of the complete battery [8,10,11]. Many of the high specific values were reported with a very low carbon loading when the batteries were tested in a pure oxygen environment (where the oxygen pressure is larger than 1 atm). These studies have established a solid foundation for the effects of various components on the performance of the Li/air batteries. However, the integration of these components into a high-performance Li/air battery is still a significant challenge. As with many new technologies, a combination of the individually optimized components may not necessarily lead to an optimized device configuration. To fully realize the potential of Li/air batteries, the structure of the air electrode (its material selection, porosity and thickness) and the complete battery (including the air electrode, electrolyte, separator, current collector, lithium metal anode, package, etc.) need to be further optimized. The performance of Li/air batteries in ambient conditions (with an oxygen partial pressure of only 0.21 atm) also needs to be investigated because the capacity of these batteries is only about one-fifth of that obtained in a pure oxygen environment [6]. Moisture in the ambient environment also strongly affects the performance of Li/air batteries. In recently reported work [18], we found that the capacities of Li/air batteries were proportional to both the specific capacity per unit weight of the carbon source (mAh g^{-1}) and the carbon loading per unit area (g cm^{-2}). Therefore, the product of these two parameters (i.e., the area-specific capacity [mAh cm^{-2}]), was introduced to optimize the performance of the air electrode.

In this work, we report for the first time the specific energy of complete Li/air batteries (including packaging) with nonaqueous electrolytes operated in ambient conditions. Various factors (including the selection of oxygen-diffusion membranes, preparation of air electrodes, and battery-assembly procedures) will be reported. The weight distribution of a complete Li/air battery will be analyzed. The approaches that could be taken to further improve the performance of Li/air batteries will also be discussed.

2. Experimental

2.1. Preparation of carbon-based air electrodes

50 g of Ketjenblack® EC-600JD (KB) (Nobel Polymer Chemicals, Chicago, IL) was soaked in 600 mL of deionized water in a beaker for about 15 min. The slurry was then mechanically mixed for 30 min. A catalyst consisting of 1.3 g of Nano-MnO_x powder (Quantum Sphere Inc., Santa Ana, CA) was added to a beaker containing 20 mL of deionized water, and the mixture was ultra-sonicated for 20 min. The catalyst dispersion was added to the water-soaked carbon slowly while stirring actively. A suspension of 15 g of PTFE (TE-3859, DuPont fluoropolymer dispersion in water, 60% solids) was then added to the mixture and stirred for another hour. The mix-

ture was then filtered and dried in an oven at 95°C overnight. The weight ratio of KB and PTFE after drying was 85:15. The dried carbon mixture was then fed into a stainless steel calender machine with a vertically orientated roller. The calender pressure and speed were optimized for film preparation. The best carbon films were obtained under a pressure of 80 psi. The thickness of the carbon film was $\sim 0.7\text{--}0.8 \text{ mm}$. Nickel mesh (29.6 or 17.1 mg cm^{-2} , Gerard Daniel Worldwide) was used as the current collector for the air electrode. To reduce the contact resistance between the nickel mesh and the carbon, the nickel mesh was sprayed with conductive paint (Acheson EB-020A), air dried, and then cured at 150°C for about 5 min. The nickel mesh was then laminated onto the carbon sheet to act as a current collector. To reduce the ingress of moisture from the atmosphere, a porous PTFE film (3- μm thick, W.L. Gore & Associates, Inc., Elkton, MD) was laminated to the front side of the air electrode (facing the air supply) in some of the batteries.

2.2. Assembly of lithium/air pouch cells

Four generations of Li/air cells were assembled as shown in Fig. 1(a)–(d). The KB activated carbon sheets with nickel-mesh current collectors prepared above were used as air electrodes. Glass-fiber filter paper GF/C (Aldrich) or Celgard 5500 (Celgard Inc.) membrane was used as a separator. Lithium metal foil 0.5-mm-thick (Honjo Metal Co., Ltd., Japan) with a copper mesh current collector was used as the anode. The electrolytes were 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in propylene carbonate (PC)/ethylene carbonate (EC) (in a 1:1 ratio by wt) with or without 20 wt% 1,2-dimethoxyethane (DME). All cells were assembled in an argon-filled glove box (MBraun Inc., Stratham, NH) with the moisture and oxygen content held at less than 1 ppm.

Generation-1 (G1) cells (see Fig. 1(a)) were coin cells prepared using Type-2325 cell kits from CNRC, Canada. The cells had a diameter of 23 mm and a thickness of 2.5 mm. The positive pans of the kits have $19 \times \text{Ø}1.0\text{-mm}$ holes that are evenly distributed for air distribution. On each cell, the small tab on the circular electrode was spot welded onto the positive pan to ensure good electrical connection. Generation-2 (G2) cells (see Fig. 1(b)) were single-side pouch cells with $16 \times \text{Ø}3.0\text{-mm}$ air diffusion holes. These cells were prepared by stacking the lithium foil, the separator, and the electrolyte-soaked air electrode. The active area of the air electrode was 16 cm^2 . Generation-3 (G3) cells (see Fig. 1(c)) used polyethylene as the oxygen-diffusion window. A high-density polyethylene (HDPE) film (20- μm -thick, Blue Ridge Films, Inc., Virginia) was laminated in a frame made of aluminum/polymer laminate (Nippon Inc., Japan). The active window of the double-sided pouch cell was $4 \text{ cm} \times 4 \text{ cm}$ with two air electrodes and a polymer film window on the sides of the cells. The oxygen-permeable HDPE film was heat-sealed to the inner layer of the metal/polymer laminate.

Generation-4 (G4) cells (see Fig. 1(d)) used a heat-sealable polymer (Melinex® 301H, DuPont Teijin Films, Wilmington, DE) as both the packaging and oxygen-diffusion membrane. Melinex® 301H (referred as ML hereafter) is a bilayer membrane with a biaxially oriented polyethylene terephthalate (PET) layer, and a terephthalate/isophthalate copolyester of ethylene glycol thermal bonding layer. Thermal bonding was achieved by applying heat and pressure at $140\text{--}200^\circ\text{C}$. The thickness of the ML varied from $12.7 \mu\text{m}$ to $30 \mu\text{m}$. The oxygen permeability of various polymer membranes was measured using a Mocon permeation system (MOCON Inc., Minneapolis, MN). A schematic of a typical G4 cell with polymer membranes is shown in Fig. 2. The cell consists of a 0.5-mm-thick lithium foil ($4 \text{ cm} \times 4 \text{ cm}$), fully wrapped by a separator (glass fiber filter paper GF/C or Celgard 5550). A copper mesh was pressed into the lithium foil and extended to the outside of the cell as the anode current collector. Two carbon-based air electrodes ($4.6\text{-cm} \times 4.6\text{-cm}$ square, 0.7-mm-thick) were stacked on the outside of the

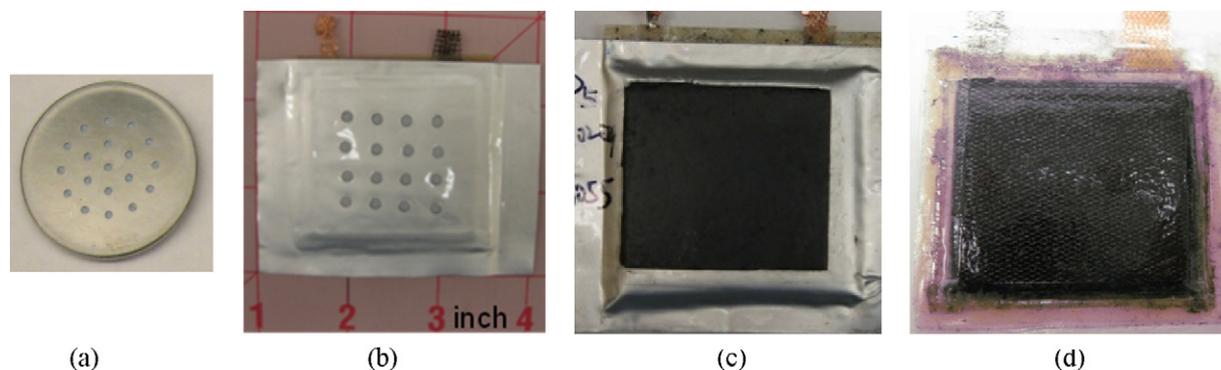


Fig. 1. Photos of Li/air batteries operated in ambient environment. (a) G1 cell design, which is a 2325 coin cell: diameter = 2.3 cm; (b) G2 cell design, which is a single-sided pouch cell (4 cm × 4 cm) with diffusion holes; (c) G3 cell design, which is a double-sided pouch cell with low permeability polymer window (4 cm × 4 cm); (d) G4 cell design, which is a double-sided pouch cell with low-permeability polymer window (4.6 cm × 4.6 cm).

separators to form an air electrode/separator/lithium/separator/air electrode stack (or dry-cell stack). Nickel mesh was pre-laminated onto the carbon electrode as a current collector. The dry-cell stacks were fully soaked in the selected electrolytes for more than 2 h, and then heat sealed in ML (20- μm -thick) or other polymer (such as HDPE) membranes.

After the Li/air cells were assembled, they were stored in an argon-filled glove box overnight and then tested in ambient conditions with an oxygen partial pressure of 0.21 atm and an average relative humidity of $\sim 20\%$ as measured by a Dickson Handheld Temperature/Humidity/Dew Point Monitor. The electrochemical performance of the cells was measured by an Arbin BT-2000 Battery Tester (Arbin Instruments Inc., College Station, TX). The cells were exposed to ambient air for 30 min and then discharged at a constant current of 0.05 mA cm^{-2} to 2.0 V. The cell voltages then were maintained at 2 V until the current was less than 0.01 mA cm^{-2} .

3. Results and discussion

The G1 cells (coin cells) prepared in this work have been used to select and optimize various components (including electrolyte, carbon, separator, oxygen-selective/diffusion membrane, etc.). The results obtained based on these coin cells have been published elsewhere [9,18–20]. The results obtained from the pouch cells (see Fig. 1(b)–(d)) are reported in this paper.

The initial pouch type Li/air cells (G2) had leaking problems because the gas diffusion membrane (PTFE) did not seal well with the metal/polymer laminations. The diffused moisture reacted with the lithium metal and led to gas generation ($2\text{H}_2\text{O} + 2\text{Li} = 2\text{LiOH} + \text{H}_2\uparrow$). Fig. 3 shows a cell that has expanded because of gas formation (H_2 release) after discharge in ambient conditions.

To minimize the gas-generation problem associated with moisture diffusion during ambient operation of Li/air batteries, completely sealed Li/air cells with an oxygen-diffusion mem-

brane were developed. For long-term operation of a primary Li/air battery (such as for 30 days), only a small amount of oxygen flow is required to maintain its small discharge current (such as 0.05 mA cm^{-2}). Therefore, it is possible to use a low-oxygen-permeability membrane as the package for the battery. The appropriate low-permeability membrane also may act as a good barrier to minimize moisture diffusion into the battery and electrolyte diffusion out of the battery, and therefore maintain normal operation of the battery during the specified operating lifetime. Assuming a Li/air cell has a 0.5-mm-thick, lithium metal foil as the anode, and that the reaction of 20% of the lithium metal with moisture will lead to cell failure, then the required maximum water vapor permeation rate ($\text{g mm}^{-2} \text{ day}^{-1}$) corresponding to various operation lifetimes can be calculated. For example, for a Li/air battery operated in an ambient environment for 5 days with less than 20% lithium loss, the maximum water vapor penetration has to be less than $3.23 \times 10^{-4} \text{ g mm}^{-2} \text{ s}^{-1}$. For a 12.7- μm -thick membrane, water vapor permeability of the film has to be less than $1.4 \text{ g mm}^{-2} \text{ day}^{-1}$. On the other hand, the minimum oxygen permeability coefficient ($\text{cm}^3 \text{ mm}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$) required at various current densities also can be calculated. For example, to maintain a current density of 0.05 mA cm^{-2} , the required oxygen-diffusion rate through the membrane is at least $1.08 \times 10^{-7} \text{ mole m}^{-2} \text{ s}^{-1}$. Here we have assumed that the reaction product is 100% Li_2O_2 , which was the dominant reaction

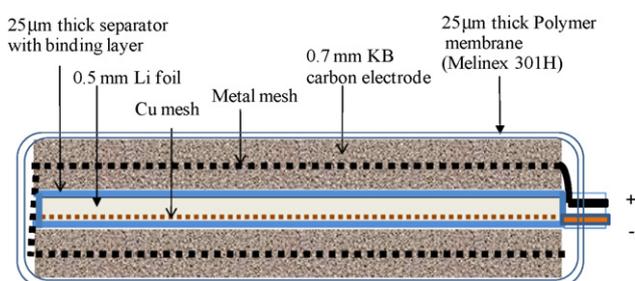


Fig. 2. Schematic of a typical G4 cell with polymer membranes.



Fig. 3. Expansion of a G2 cell after discharge in ambient conditions.

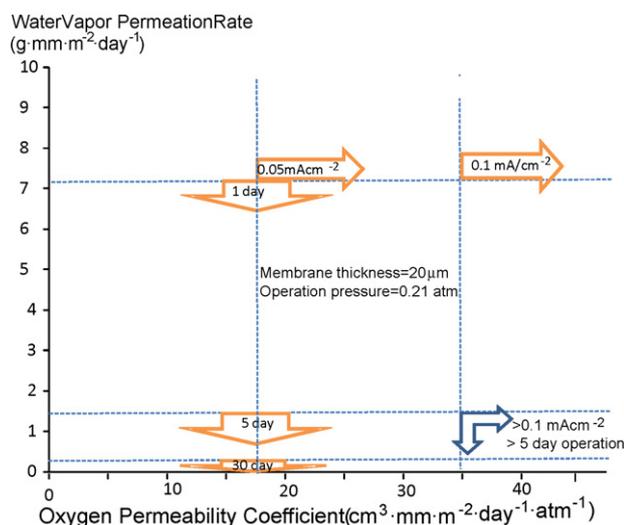


Fig. 4. Operation time and current density for Li/air batteries using a gas-diffusion membrane with different water vapor permeation rate and oxygen permeability coefficient. The following assumptions have been used in the calculation. The product of Li/O₂ reaction is 100% Li₂O₂; reaction of 20% lithium with moisture will lead to the battery failure.

product observed in our recent nuclear magnetic resonance experiment. If the membrane thickness is 20 µm thick and the operation pressure is 0.21 atm, the membrane has to have an oxygen permeability coefficient of larger than 17.5 cm³ mm m⁻² day⁻¹ atm⁻¹. If the reaction product is 100% Li₂O, the required minimum oxygen flow will be 5.4 × 10⁻⁸ mole m⁻² s⁻¹ and the required oxygen permeability coefficient of membrane needs to be larger than 8.8 cm³ mm m⁻² day⁻¹ atm⁻¹. For the given materials with the specific water vapor permeation rate and oxygen permeability coefficient, the thickness of the membrane can be adjusted to satisfy a given application. The results of these calculations are summarized in Fig. 4.

Table 1 compares the required minimum oxygen flow rates (see column 5) at various current densities and measured oxygen flow rates (see columns 6 and 7) for selected polymer membranes. One example of an oxygen-permeable membrane (which is also heat-sealable) is a PET-based ML membrane. The table shows that high-density polyethylene can provide enough oxygen flow at a current density of 0.05–0.1 mA cm⁻². It also suggests that 20-µm-thick ML cannot provide enough oxygen flow for Li/oxygen reactions at the given current densities. For example, 20-µm-thick ML can only provide approximately 7.2% of the required oxygen flux for a current density of 0.05 mA cm⁻². Both HDPE and heat-sealable ML have been used to prepare the double side pouch cells (G3 and G4). Surprisingly, however, the results from tests of these pouch cells demonstrated that 20-µm-thick ML is the best choice as an oxygen-diffusion membrane when tested at a current den-

Table 2
Key characteristics of initial samples.

Cell	Packaging material	Dry cell (g)	Electrolyte (g)	DME left (%) after vacuum extraction	Capacity (mAh)
#1	Blue-HDPE	3.816	1.726	3.8	250
#2	Blue-HDPE	3.439	1.883	7.0	243
#3	Blue-HDPE	3.842	1.990	9.9	237
#4	ML	3.355	1.725	3.9	224

sity of 0.05 mA cm⁻² in the ambient environment. We believe that this discrepancy is the result of altered gas diffusion properties of polymer membranes (ML in this case) when they were soaked with the electrolyte used in the Li/air batteries. In other words, when ML absorbed the electrolyte, its internal pore size may expand and its oxygen-diffusion coefficient may be much larger than those measured in the dry conditions used in standard permeability tests. The details of the pouch cell tests are described. On the other hand, HDPE-based, oxygen-diffusion membranes exhibited shorter lifetimes related to their larger moisture permeabilities.

A series of double-sided pouch cells were prepared. The package material for cells #1, #2, and #3 was a 46-µm-thick HDPE membrane (Blueridge Films, Inc.) sealed on a metal-polymer laminate (silver bag) frame. The package material for cell #4 was a 20-µm-thick, heat-sealable PET (MELINEX® 301H) membrane with no frame. In these initial cells, air electrodes were prepared using DARCO® G-60 carbon with 15% PTFE binder. The separator was CELGARD®-5550. To ensure the integrity of the cells during the subsequent assembly process, some dry cells were bonded by carefully wrapping with cotton thread to maintain contact between the layers. Other parameters of the cells have been described in the experimental section. The electrolyte was 1 M LiTFSI in EC/PC (1:1) mixed with 20 wt% DME. After soaking with electrolyte, the cells were kept under vacuum for 30 min to evacuate the DME. Addition of 20% DME in the cells during soaking can help fully wet the cells. The extraction of DME was expected to reduce the electrolyte weight and generate more gas-flow paths to facilitate oxygen-diffusion. The soaked cells then were sealed with selected package materials. The key parameters for these initial cells are listed in Table 2, which shows that some DME (3.8–9.9%) was still left inside the cells after vacuum extraction. These cells have been tested in the ambient environment (RH ~ 20%) for 14–16 days with no gas release like those shown in Fig. 3. The discharge voltages as a function of capacities of these Li/air cells are shown in Fig. 5. DARCO® G-60 carbon has a lower mesopore volume than KB carbon. Therefore, the Li/air cells using DARCO® G-60 carbon electrodes have much lower expected capacities than those using KB-based carbon electrodes. Although these cells used different package materials, their average performance was very similar when tested in ambient conditions.

Further investigation of pouch cells with KB-based air electrodes indicated that double-sided pouch cells with an HDPE membrane

Table 1
Comparison of required oxygen flow rate at various current densities and measured oxygen flow rate in selected polymer membranes.

Membrane	Current density (mA cm ⁻²)	Film thickness (µm)	Oxygen partial pressure (atm)	Required minimum O ₂ flow (mol m ⁻² s ⁻¹)	Membrane O ₂ flow at 25 °C/0.21 atm (mol m ⁻² s ⁻¹)	Measured O ₂ permeability of membrane (cm ³ m ⁻² day ⁻¹ atm ⁻¹)
ML ^a	0.1	20	0.21	2.16 × 10 ⁻⁷	7.79 × 10 ⁻⁹	71.8
ML ^a	0.05	20	0.21	1.08 × 10 ⁻⁷	7.79 × 10 ⁻⁹	71.8
ML ^a	0.05	30	0.21	1.08 × 10 ⁻⁷	5.25 × 10 ⁻⁹	48.4
MSE-HDPE ^b	0.1	25	0.21	2.16 × 10 ⁻⁷	5.67 × 10 ⁻⁷	5224
Blue-HDPE ^c	0.1	50	0.21	2.16 × 10 ⁻⁷	6.36 × 10 ⁻⁷	5857
MSE-HDPE ^b	0.05	50	0.21	1.08 × 10 ⁻⁷	2.80 × 10 ⁻⁷	2577
Blue-HDPE ^c	0.05	46	0.21	1.08 × 10 ⁻⁷	5.49 × 10 ⁻⁷	5055

^a Melinex® 301H, DuPont Teijin Films.

^b Mid South Extrusion, Inc.

^c Blueridge Films, Inc.

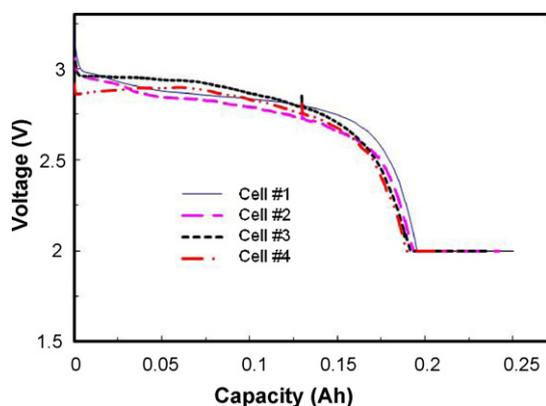


Fig. 5. Voltage profiles as a function of discharge capacities for Li/air pouch cells. Solid line is for the sample #1; long dash/short dash line is for the sample #2; dash line is for the sample #3; dash/dot line is for the sample #4.

have shorter lifetimes than those prepared with a 20- μm -thick ML membrane. This difference can be attributed to higher moisture diffusion through HDPE membranes. However, Li/air cells packaged in a thicker ML membrane (30 μm) had a much shorter lifetime (less than a day). This can be attributed to an insufficient oxygen flux through the membrane, which cannot sustain a continuous Li/O₂ reaction for the given current density. Considering all of these factors, a 20- μm -thick ML membrane was used in most of the cells in the subsequent investigations.

More double-sided pouch cells with two KB-based air electrodes were prepared. The air electrode films composed of 85% KB and 15% PTFE (4.0 cm \times 4.0 cm) were laminated with a nickel mesh (coated with electro-conductive paint) with a tab extending from the mesh. The total thickness of the air electrode with the nickel mesh was 0.8 mm. The air electrode had a carbon loading of 14.9 mg cm⁻². The separator was glass fiber filter paper GF/C from Aldrich (4.0 cm \times 4.0 cm). The anode was 3.8-cm \times 3.8-cm and 0.5-mm-thick lithium metal pressed onto a copper mesh current collector. The four edges of this dry-cell pack were sealed with heat-sealable tape. The total weight of the dry cell was 2.421 g. After the dry cell was assembled, 5.8 g of electrolyte (1.0 M LiTFSI in PC/EC (1:1 wt)+20% DME) was added to the cell slowly and evenly distributed onto the dry cell. After all of the electrolyte was absorbed, we weighed the cell again and found that the total electrolyte weight absorbed by the cell was 5.758 g. The cell soaked with electrolyte was quickly sealed in a package of 20- μm -thick ML membrane. The total weight of the complete cell was 8.387 g after sealing. The open-circuit voltage of the cell was 3.084 V, and the cell resistance was less than 0.1 ohm. The cell then was removed from the argon-filled glove box and tested in open air where the RH was about 20%. The discharge profile of the cell is shown in Fig. 6. The cell was discharged at a current density of 0.05 mA cm⁻² (surface area). When the cell voltage reached the low voltage limit of 2 V, the cell was discharged at a constant voltage of 2 V until its current density was less than 0.01 mA cm⁻². The open circuit voltage of the cell increased to \sim 2.8 V at the end of the discharge as shown in Fig. 6. It has been discharged in the ambient environment for 33 days with a capacity of 1185.4 mAh. The specific energy of the complete cell (including the package) was 362 Wh kg⁻¹.

To further improve the performance of Li/air batteries, a model has been established to analyze the effect of various components on the performance of practical Li/air batteries. Fig. 7 shows the weight distribution of all of the components in a typical G4 Li/air cell prepared in this work. In previously published papers, most theoretical work predicted the performance of Li/air batteries based on the weight of only the lithium metal or only the weight of the carbon (a few recent reports also included the binder and catalyst).

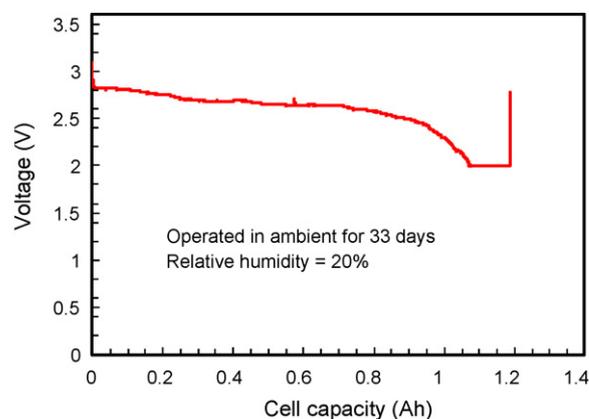


Fig. 6. The voltage profile as a function of capacity for a Li/air cell. The specific energy of the complete cell (including the package) was 362 Wh kg⁻¹.

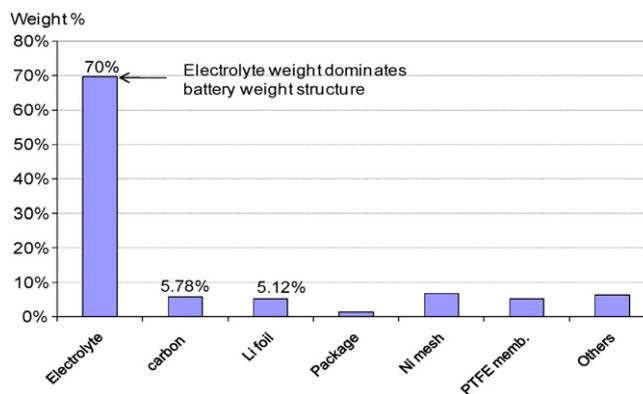


Fig. 7. Weight distribution in a practical Li/air battery.

However, the weight distribution of practical Li/air batteries given in Fig. 7 shows that both the lithium anode and the carbon occupy less than 6 percent of the total battery weight. The weight of the nickel mesh (cathode current collector) alone is greater (6.7%) than those of the lithium and carbon. Therefore, it is important to find a better cathode current collector to increase the specific energy of Li/air batteries. In the current battery design, the package/oxygen-diffusion membrane occupies less than 2% of total weight of the battery. The most important finding shown in Fig. 7 is that the electrolyte occupies nearly 70% of the battery weight. As a comparison, the electrolyte normally occupies only 10–20% of the weight in lithium-ion batteries. Although the weight distribution of the Li/air batteries depends on the specific design of the battery, the general pattern of the weight distribution should be similar. To increase the specific energy of practical Li/air batteries, one of the main challenges is to reduce the weight of the electrolyte while maintaining high capacities.

The main structure and performance parameters of the above battery are analyzed further as shown in Table 3. It shows that

Table 3
Key parameters in a practical Li/air battery.

Dry air electrode porosity (%)	88.7
Carbon mesopore volume (cm ³ /g)	4.95
Mesopore expansion efficiency (%)	87.0
% of pore volume occupied by Li ₂ O ₂	20.3
Lithium utilization (%)	68.5
Capacity (Ah)	1.12
Carbon based capacity (mAh/g)	2340
Nominal voltage (V)	2.67
Specific energy (Wh kg ⁻¹)	362

lithium utilization in the given sample is near 70%, which is very close to its practical limit. This is also an indication that the selected oxygen-diffusion membrane (20- μm -thick ML) provided good protection for the battery, and the corrosion of the lithium metal by moisture was minimal during the discharge process.

Because KB carbon has a very high mesopore volume of $4.95\text{ cm}^3/\text{g}$, the dry cell has a very large porosity (88.7%). After soaking with electrolyte, the thickness of the air electrode increased 87%. The large increase in the thickness of electrode after it was soaked with electrolyte is one of the main reasons that KB-based air electrodes absorbed nearly twice as much electrolyte as our initial estimate based on its initial thickness and porosity. This is also the main reason for the reduced practical specific energy of Li/air batteries. For the battery shown in Fig. 6, the specific capacity based on the carbon weight alone is 2340 mAh/g. This value is very high considering that the battery was operated in an ambient with an oxygen partial pressure of only 0.21 atm and a relative humidity of 20%. Although the excellent specific capacity based on the weight of an individual component (KB carbon) has been demonstrated, this same component absorbs much more electrolyte than other kinds of carbons. This is a good example that the individually optimized components may not be the best choice for the complete devices. To further improve the performance of Li/air batteries, a better carbon source that has a good balance between mesopore volume and electrolyte absorption needs to be found.

Several reports [21] and our own investigations have shown that the capacity of carbon-based air electrodes increases with the mesopore volume of the carbon, but it is not very sensitive to the bulk porosity of the carbon electrode. In other words, expansion of mesopores during electrolyte soaking generated the majority of the three-phase regions required for the Li/O₂ reaction. In practice, inter-particle spaces (bulk porosity) and mesopore spaces in an air electrode are similar to the artery and capillary in a living organism. Oxygen and lithium ions are transported through inter-particle spaces (i.e., rely on bulk porosity of electrode), but the final lithium/oxygen reaction occurs mainly in the mesopore spaces within the carbon particles. To reflect this phenomenon, we have introduced carbon mesopore volume in our model. After soaking in liquid electrolyte, these mesopores will fully expand to form a three-phase region to facilitate the lithium/oxygen reaction. Consequently, the reaction byproduct will partially occupy these spaces after reaction. In fact, only ~20% of the mesopore space was occupied by reaction byproducts as shown in Table 3. Although KB has a large pore volume ($4.95\text{ cm}^3/\text{g}$), not all of the volume can be utilized for the lithium/oxygen reaction. If the pore size is too small, its reactant entry into the pore will be blocked quickly by initial reaction products. If the pore size is too large, most of volume will become inactive after the internal active surface of the pore is fully covered by a critical thickness of reaction products. These large pores also will absorb a large amount of electrolyte, which further increases the weight of Li/air batteries. A nanostructured carbon with a large mesopore volume and an optimized pore size may lead to the better use of carbons, less electrolyte absorption, and a significant improvement on the specific energy of Li/air batteries.

4. Conclusions

Ambient operation of Li/air batteries based on nonaqueous electrolytes was investigated in this work. Most Li/air batteries investigated in the literature have been tested in a pure oxygen environment with an oxygen pressure greater than 1 atm and with no exposure to moisture. The ambient condition used in this work has a low oxygen partial pressure of 0.21 atm and a relative humidity of ~20%. Both of these conditions are known to be detrimental

to the performance of Li/air batteries. For long-term, low-discharge rate operation, it is possible to use a low-permeability membrane to operate Li/air batteries at ambient conditions. Among several polymer membranes evaluated in this work, 20- μm -thick Melinex® 301H (ML) has been identified as the best choice to be used as both an oxygen-diffusion membrane and a moisture barrier. In addition, it also serves as the packaging material for the Li/air batteries. Li/air batteries with this heat-sealable polymer membrane were operated in ambient conditions for more than a month with a specific energy of 362 Wh kg^{-1} based on the total weight of the Li/air battery. We found that Li/air batteries with KB-based air electrodes have the best specific capacity (2340 mAh/g) based on the weight of carbon alone. However, KB carbon expands significantly after being soaked with electrolyte. It also absorbs much more electrolyte than other carbon materials, consequently leading to a large increase in battery weight and a corresponding decrease in the specific energy of Li/air batteries. A detailed analysis of the weight distribution for a complete Li/air battery revealed that the weight of Li/air batteries was dominated by the weight of electrolyte (~70%) when KB-based carbon electrolyte was used. The lithium metal anode and KB carbon occupy only 5.12% and 5.78% of the total battery weight, respectively. We also found that only ~20% of the mesopore volume of the air electrode is occupied by reaction products. To further increase the specific capacity of Li/air batteries, nanostructured carbons with a large mesopore volume and optimized pore size are required to reduce their electrolyte absorption but still maintain their capability to retain a large amount of the reaction products.

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References

- [1] D. Linden, T. Reddy (Eds.), *Handbook of Batteries*, 3rd ed., McGraw Hill, New York, 2001, p. 38.2.
- [2] K.M. Abraham, Z. Jiang, *J. Electrochem. Soc.* 143 (1996) 1.
- [3] E.L. Littauer, K.C. Tsai, *J. Electrochem. Soc.* 124 (1977) 850.
- [4] K.M. Abraham, Z. Jiang, *U.S. Pat.* 5,510,209,1996.
- [5] J. Read, *J. Electrochem. Soc.* 149 (2002) A1190.
- [6] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, D. Foster, *J. Electrochem. Soc.* 150 (2003) A1351.
- [7] J. Read, *J. Electrochem. Soc.* 153 (2006) A96.
- [8] S.D. Beattie, D.M. Manolescu, S.L. Blair, *J. Electrochem. Soc.* 156 (2009) A44.
- [9] W. Xu, J. Xiao, J. Zhang, D. Wang, J.-G. Zhang, *J. Electrochem. Soc.* 156 (2009) A773.
- [10] T. Shiga, H. Nakano, H. Imagawa, *US 2008/0299456 A1*, Dec. 4, 2008.
- [11] S.S. Zhang, D. Foster, J. Read, *J. Power Sources* (2009), doi:10.1016/j.jpowsour.2009.08.088.
- [12] R.E. Williford, J.-G. Zhang, *J. Power Sources* 194 (2009) 1164.
- [13] S.J. Visco, E. Nimon, L.C. De Jonghe, B. Katz, M.-Y. Chu, *Abs. 396, IMLB 12 Meeting*, 2004, The Electrochemical Society, Inc.
- [14] S.J. Visco, B.D. Katz, Y.S. Nimon, L.D. Dejonghe, *US Patent 7,282,295* (2007).
- [15] I. Kowalczyk, J. Read, M. Salomon, *Pure Appl. Chem.* 79 (2007) 851.
- [16] Y. Wang, H. Zhou, *J. Power Sources* 195 (2010) 358.
- [17] J.P. Zheng, R.Y. Liang, M. Hendrickson, E.J. Plichta, *J. Electrochem. Soc.* 155 (2008) A432.
- [18] J. Xiao, D. Wang, W. Xu, D. Wang, Ralph E. Williford, J. Liu, J.-G. Zhang, *J. Electrochem. Soc.*, 157 (2010), in press.
- [19] W. Xu, J. Xiao, D. Wang, J. Zhang, J.-G. Zhang, *Electrochem. Solid-State Lett.*, 13 (2010), in press.
- [20] J. Xiao, W. Xu, D. Wang, J.-G. Zhang, *J. Electrochem. Soc.* 157 (2010), in press.
- [21] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, *J. Power Sources* 146 (2005) 766–769.