Li-air batteries: A classic example of limitations owing to solubilities*

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Abstract: A review is presented of the present state-of-the-art of Li-air cells and batteries. We examine the properties of this unique system in terms of the effects of solubilities of reactants and products in both nonaqueous (aprotic) and aqueous electrolyte solutions. Definite trends are observed, such as increasing cell-specific energy and capacity as both the oxygen solubility increases and viscosity decreases in organic solvents, but quantitative analyses are limited owing to the complex relations between solubility, solution viscosity, oxygen diffusion, and electrolytic conductivity. Adding to this complex relation is the dependence of the nature of the carbon-based air cathode (surface area and pore volume) upon practical specific capacities, which can be realized with Li-air cells that far exceed the specific energies and capacities of all present commercial metal-air and Li-ion cells and batteries.

Keywords: solubility; Bunsen coefficient; Li-air batteries; organic solvents; nonaqueous solvents.

INTRODUCTION

The applications for high-energy, high-capacity batteries have enormous impact on various programs for mobile electronic equipment for both commercial and military applications. Metal-air batteries (e.g., Zn-air, Al-air), which are aqueous systems, have been studied for many years [1] since their specific capacities (mAh/g) are extremely high. The reason for these high specific capacities is that the cathodic reactant, O_2 from air, does not have to be stored in special containers such as high-pressure steel vessels, thus significantly reducing the total mass of the battery. However, since these are aqueous systems, their specific energies (Wh/kg) are generally low owing to their low theoretical and operating cell potentials under 2 V and the moderate molecular masses of the anodic reactants. The concept of replacing Zn or Al with Li offers significant advantages owing to the high potential of the Li anode and the low molecular mass of Li.

The concept of a Li-air battery was introduced by researchers at Lockheed [2–4] who proposed the use of an aqueous alkaline solution for the electrolyte solution. Problems relating to low efficiency owing to the parasitic reaction of Li with water and major safety concerns owing to excess H_2 formation from this parasitic reaction led to the abandonment of this concept in the 1980s. In 1996, Abraham and Jiang [5,6] proposed replacing the aqueous electrolyte with a nonaqueous polymer electrolyte, which led to advanced studies by Read et al. [7–10], Dobley et al. [11], and Kuboki et al. [12] who em-

ployed *liquid* aprotic organic solvents for the electrolyte solution. In developing Li-air cells and batteries (commonly referred to as a Li-air semi-fuel cell) based on an organic electrolyte solution, a number of obvious limitations still have to be addressed, which include the prevention of ingress of water from the atmosphere into the cell via the fuel cell air electrode, resulting in reaction with metallic Li posing a serious safety problem, limitations owing to the solubility of O_2 in the electrolyte solutions, and the precipitation of Li oxides in the porous cathode structure.

Li-air semi-fuel cells are basically composed of a metallic Li anode and an air (O_2) fuel cell cathode. The air electrode serves to provide an interface where O_2 from air is dissolved in an electrolyte solution and catalytically reduced on the active components of the cathode, which is carbon with or without a catalyst to enhance the rate of O_2 reduction. As shown by one of us (JR) and reviewed below, a rate limitation for O_2 reduction is related to O_2 solubility and diffusion in the electrolyte solution [8,13]. In order to eliminate, or at least minimize, water ingress into the cell, one obvious approach is to construct a Li-air cell utilizing an organic solvent in which the water solubility is minimized. By utilizing an organic-based [7–12] or ionic liquid-based electrolyte solution [12,15], the products of the cell reactions involve insoluble Li_2O and Li_2O_2. For the Li-air semi-fuel cell, the overall (mixed) cell reactions in organic electrolyte solutions are

$$2Li + \tfrac{1}{2}O_2 \rightarrow Li_2O \tag{1}$$

$$2Li + O_2 \rightarrow Li_2O_2 \tag{2}$$

Because both Li_2O and Li_2O_2 are not soluble in organic electrolyte solutions, both oxides will precipitate in pores of the porous carbon-based cathode which blocks further O_2 intake and thus abruptly ends cell life (examples are shown below). Even with this "solubility" limitation, Li-air semi-fuel cells still represent a major advance since the practical achievable specific capacities and specific energies are extremely high. A comparison of specific energies for various metal-air cells is given in Table 1; the energies were calculated using Gibbs energies of formation according to the well-known equation

$$\Delta G^{o}_{reaction} = \Sigma \, \Delta G^{o}_{f} \, (products) - \Sigma \, \Delta G^{o}_{f} \, (reactants)$$

ΔG^{o}_{f} values used in our calculations were taken from ref. [14], and the results we obtained are summarized in Table 1. Theoretical values for the Li-air semi-fuel cell in aqueous solution are included in this table. The reactions in aqueous solutions are

$$2Li + \tfrac{1}{2}O_2 + 2H^+ \Leftrightarrow 2Li^+ + H_2O \tag{3}$$
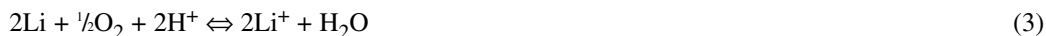
in acid solution and

$$2Li + \tfrac{1}{2}O_2 + H_2O \Leftrightarrow 2LiOH \tag{4}$$

in neutral or alkaline solutions. Although these aqueous systems do not possess the theoretical high capacities and energies as for nonaqueous solutions, their chemistry offers an interesting alternative approach to organic-based electrolyte solutions which are "cathode-limited," i.e., the end of the operational lifetime of cells based on reactions 1 and 2 is simply due to the precipitation of Li_2O and Li_2O_2 in the porous carbon-based cathode structure effectively shutting down the electrochemical reaction. In aqueous solutions, the products of reactions 3 and 4 are, to a large extent, very soluble in solution, i.e., the operational life times of these aqueous systems are "anode-limited" depending upon the amount of metallic Li used in the anode. Recent advances developed by MaxPower for stabilizing Li anodes in an aqueous environment are discussed below.

Table 1 Theoretical specific energy and capacity comparisons for selected systems.

Metal-air and Li-ion systems (organic or aqueous electrolyte solution)	OCV (V)	Specific energy (Wh/kg)	Specific capacity (mAh/g)
$2Li + \frac{1}{2}O_2 \rightarrow Li_2O$ (aprotic organic sln)	2.913	11 248[a]	3862
$Li + \frac{1}{2}O_2 \rightarrow \frac{1}{2}Li_2O_2$ (aprotic organic)	2.959	11 425[a]	3862
$2Li + \frac{1}{2}O_2 + H_2SO_4 \Leftrightarrow Li_2SO_4 + H_2O$	4.274	1091[a]	255
$2Li + \frac{1}{2}O_2 + 2HCl \Leftrightarrow 2LiCl + H_2O$	4.274	3142[a]	366
$2Li + \frac{1}{2}O_2 + H_2O \Leftrightarrow 2LiOH$	3.446	5789[a]	1681
$Al + 0.75O_2 + 1.5H_2O \rightarrow Al(OH)_3$ (aq)	2.701	4021[a]	1489
$Zn + \frac{1}{2}O_2 \rightarrow ZnO$ (aq)	1.650	1353[a]	820
$x6C + LiCoO_2 \Leftrightarrow xLiC_6 + Li_{1-x}CoO_2$	~4.2	420[b]	139

[a]The molecular mass of O_2 is not included in these calculations because O_2 is freely available from the atmosphere and therefore does not have to be stored in the battery or cell.
[b]Based on $x = 0.5$ in $Li_{1-x}CoO_2$.

THE Li-AIR CELL IN NONAQUEOUS APROTIC ELECTROLYTE SOLUTIONS

The selection of the aprotic electrolyte solution is generally governed by a number of factors such as

i. high dielectric constant to minimize ion pairing
ii. low viscosity to maximize specific conductivity
iii. solvents which minimize water solubility
iv. solvents which maximize oxygen solubility

For practical reasons, mixtures of aprotic organic solvents and blends of organic solvents with room-temperature ionic liquids (ILs) are designed to best incorporate as many of the (i–iv) features as possible, but it is difficult to include all of these features in any given pure solvent or mixture of aprotic solvents.

The properties of the air electrode also are governed by a number of factors such as

v. surface area of the catalytic activated carbon
vi. pore volume of the activated carbon
vii. nature of the binder used to fabricate free-standing air electrodes
viii. total porosity/density of the free-standing air electrode.

Table 2 summarizes the properties of selected carbons which are presently being studied for use in Li-air cells, and Fig. 1 compares the discharge behavior of Li-air cells based on Super P carbon cathodes. Figure 1 demonstrates the end-of-life of the Li-air cell owing to the precipitation of Li-oxides in the porous carbon cathode. Figure 1 also demonstrates the effect of electrode binder on discharge capacity. The electrolyte solution studied in ref. [15] was a 50/50 mixture of the ionic liquid 1-hexyl-3-methylimidazolium[PF6] and 1 mol dm^{-3} LiBF$_4$ in a 1:1 (v/o) blend of PC and DME (propylene carbonate and dimethoxymethane, respectively).

Table 2 Properties of selected carbons.

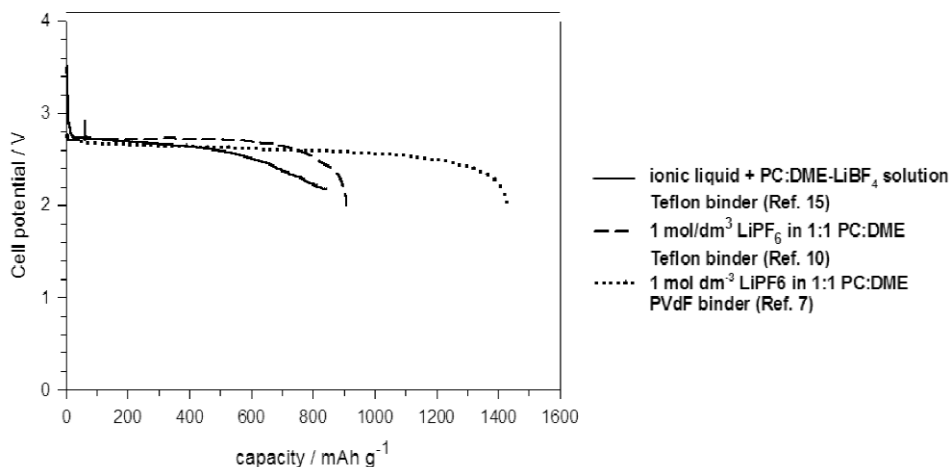| Carbon	Super P	Vulcan XC-72	Black pearls 2000
Surface area, m^2/g	62	235	1480
Particle size, nm	40	30	12
Pore volume, cm^3/g	–	0.59	3.35

Fig. 1 Discharge of Li-air cells at ~25 ℃ at 0.1 mA/cm to a 2 V cutoff.

For Super P electrodes utilizing PVdF as the binder, the pore volume (mL) to mass (g) of Super P is 4.6 mL/g compared to 1.9 mL/g for electrodes utilizing Teflon as the binder (7). The larger pore volume structure of the PVdF-based cathodes also improves the discharge capacity owing to improved transport of oxygen into the interior of the electrode.

Oxygen solubility and transport in the electrolyte solution has significant effects on both the specific capacity and rate capability of Li-air cells. Because solubility data for oxygen in solvents of interest for Li-air batteries are scarce, one of us (JR) has determined Bunsen and Ostwald coefficients for oxygen in a number of pure and mixed organic solvents [8,13], and in mixtures containing electrolyte. Table 3 reproduces the results from [8] based on solvents containing the electrolyte $LiPF_6$.

Table 3 Specific capacity of super P cathodes and electrolyte properties[a].

Electrolyte solution[b]	α	σ	η	Specific capacity
1 mol dm^{-3} LiPF$_6$ in PC:EC (1:1)	0.0482	6.5	7.73	512
1 mol dm^{-3} LiPF$_6$ in PC	0.0516	5.5	8.06	380
1 mol dm^{-3} LiPF$_6$ in PC:DME (1:1)	0.0722	13.2	2.59	999
1 mol dm^{-3} LiPF$_6$ in PC:DMC (1:1)	0.0729	9.4	3.50	652
1 mol dm^{-3} LiPF$_6$ in PC:DEC (1:1)	0.0787	6.7	4.78	1308
1 mol dm^{-3} LiPF$_6$ in PC:DME (1:2)	0.0998	15.9	1.98	1095
0.5 mol dm^{-3} LiPF$_6$ in PC:DME (1:2)	0.1218	12.2	1.19	1257

[a]Data from ref. [8] at ~25 °C. α is the Bunsen coefficient, σ is the electrolytic conductivity in units of mS/cm, and η is the viscosity in cP. The specific capacity in units of mAh/g of carbon is based on Teflon-bonded cathodes at a current density of 0.1 mA/cm^2.
[b]PC = propylene carbonate, EC = ethylene carbonate, DME = dimethoxyethane, DMC = dimethyl carbonate, and DEC = diethyl carbonate.

Table 3 clearly shows a trend in increase of specific capacity as the solubility of oxygen increases and the viscosity decreases. Figures 2 and 3 show the effect of oxygen solubility and viscosity on specific capacity at selected current densities for the Li-air cell in 1 mol dm^{-3} LiPF$_6$ in PC:DME (1:1). The same trend is observed at the various current densities although there are several deviations at the lower current densities, The trend of increasing specific capacity as α increases can be simply explained as the result of a higher concentration of oxygen in the electrolyte solution resulting in a high flux of oxygen. In addition, the trend in viscosity shown in Table 3 and Fig. 3 is identified with the dif-

fusion of oxygen in the electrolyte solution. To estimate the diffusion coefficient of oxygen, we use the Stokes–Einstein equation, which for the "stick" boundary condition (16) is given by

$$D = \frac{kT}{6\pi\eta a} \tag{5}$$

where a is the hydrodynamic radius of O_2. For 1 mol dm^{-3} $LiPF_6$ in PC:DME (1:1) and using the bond length of 121 pm for the hydrodynamic radius of O_2, a diffusion coefficient of $7.0 \cdot 10^{-6}$ cm^3/s is obtained.
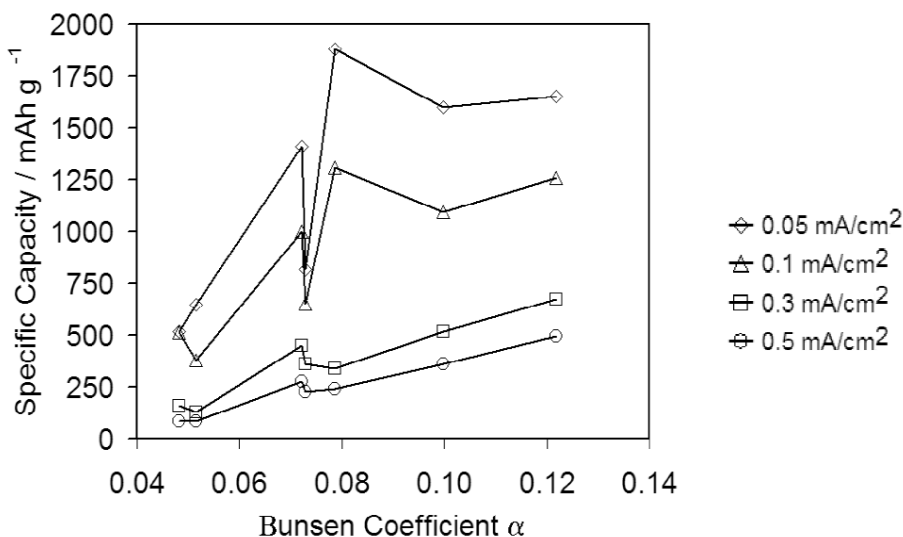

Fig. 2 Bunsen coefficient vs. specific capacity for Super P cathodes at room temperature as a function of current density [8].
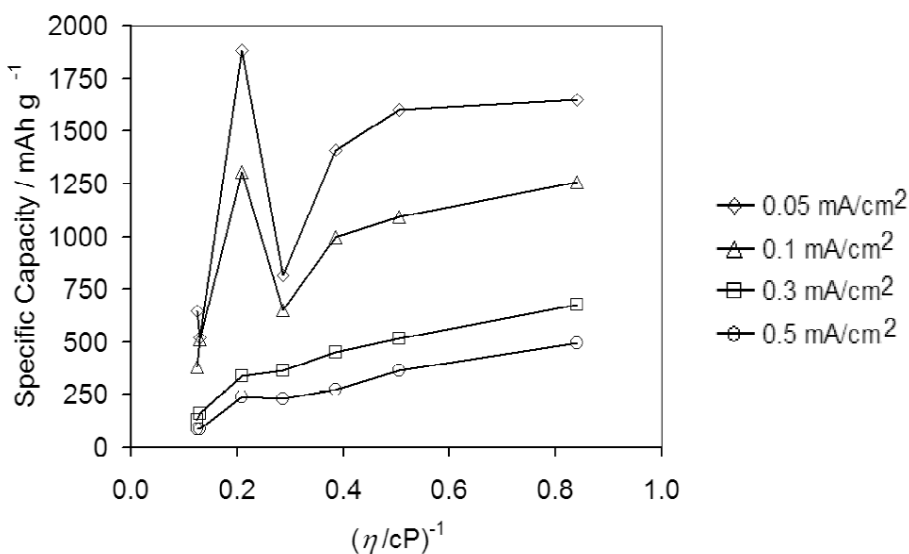

Fig. 3 Reciprocal of the solution viscosity vs. specific capacity for Super P cathodes at room temperature as a function of current density [8].

Assuming the air electrode can be treated as a semi-infinite medium, the flux, F, in units of cm^3 O_2 per unit area of electrode, cm^2 and time, s, the steady-state flux of oxygen at the side of the air electrode facing the atmosphere is given by

$$F = C_o \sqrt{Dk} \tag{6}$$

In eq. 6, C_o is the oxygen concentration at the outer surface of the air electrode and is identified with the Bunsen coefficient, D is the oxygen diffusion coefficient in the electrolyte solution, and k is the first-order rate constant which can be calculated from eq. 5 since it is known from the experimental cell discharge rate R (mA/cm^2) and the mechanism of the electrochemical reaction, e.g., for reaction 2 above, 1 cm^3 of O_2 will generate 2.4 mAh of specific capacity. The concentration of oxygen, C, at any distance x from the outer side of the air electrode to the interior of the electrode is obtained from the diffusion equation, which is given by

$$C = C_o \exp\left\{-x\sqrt{k/D}\right\} \tag{7}$$

Using the rate constant k based on mechanism [2] and replacing C_o with the Bunsen coefficient α, combining eqs. 6 and 7 for 273.2 K yields

$$C = \alpha \exp\left\{\frac{-xR}{8640\alpha D}\right\} \tag{8}$$

The typical thickness of the Super P Teflon-bonded electrode is ~0.075 cm [7,10], and from eq. 8, the calculated steady-state concentrations of O_2 within the electrode in 1 mol dm^{-3} $LiPF_6$ in PC:DME (1:1) at selected current densities are shown in Fig. 4. Since the insoluble lithium oxide reaction will form where the oxygen concentration is the greatest, which is at the atmospheric side of the cathode, it is at this outermost surface where most of the discharge products will form. This will eventually limit the maximum specific capacity that can be achieved in a Li-air cell in nonaqueous electrolyte solutions.
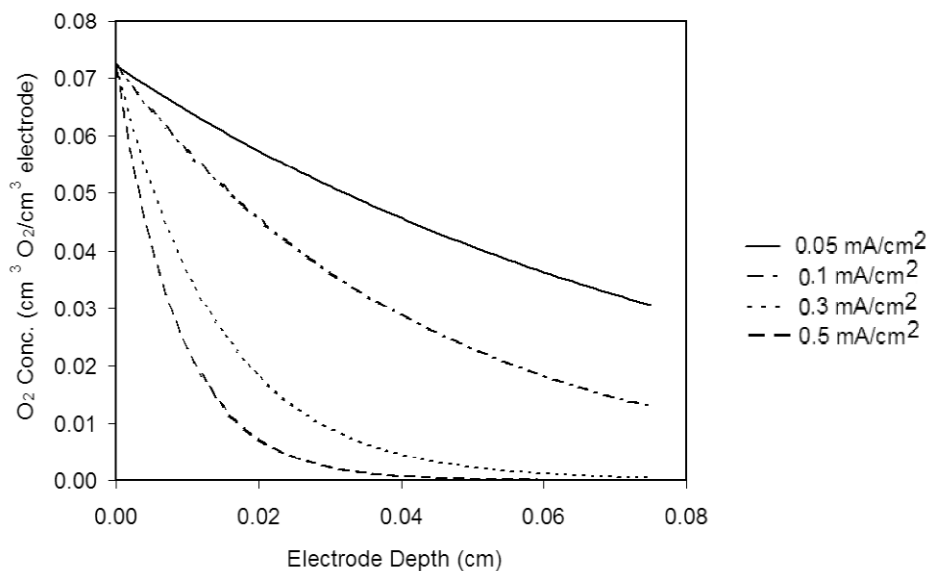

Fig. 4 Oxygen concentration as a function electrode depth for 1 mol dm^{-3} $LiPF_6$ in PC:DME (1:1). Current densities as shown.

THE Li-AIR CELL IN AQUEOUS ELECTROLYTE SOLUTIONS

While theoretical specific energies for the Li-air cell in aqueous electrolyte solutions are much lower than in nonaqueous solutions (Table 1), aqueous-based systems still represent an alternative approach for long operational life. As indicated above, the reaction (discharge) products in aqueous solution are generally highly soluble so that the aqueous-based Li-air cell is "anode-limited." In addition, Li-air cells in nonaqueous electrolyte solutions have "nominal" potentials (i.e., practical discharge potentials) of around 2.6 to 2.7 V (Fig. 1), whereas for the aqueous analog, nominal potentials are around 3.0 to 3.3 V depending upon pH and temperature as shown below. The key problem to be addressed in developing an aqueous-based Li-air cell is the complete elimination of the parasitic and dangerous reaction between metallic lithium and water.

To protect the lithium anode from reacting with water, we have been developing a new technology based on a water-stable, Li^+-conducting solid-state (LiGC) plate or "membrane". The lithium anode is protected from contact with water by this water-stable LiGC membrane as shown schematically in Fig. 5. Because this LiGC plate or membrane will react with metallic Li, an additional inert Li-stable membrane (separator) saturated with an aprotic organic electrolyte solution is inserted between the Li anode and the LiGC plate. In practice, for this Li-stable membrane, we have used a commercial microporous polyolefin membrane (25 μm thick, ~40 % porosity) and polyimide, based membranes produced by electrospinning [17] which have adjustable thicknesses from 10 to 25 μm and porosities ≥80 %.
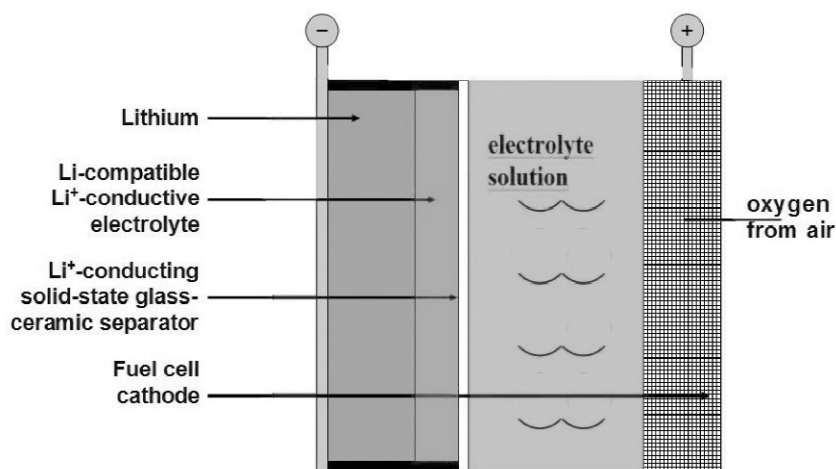

Fig. 5 Schematic of the Li-air semi-fuel cell detailing the protected Li anode.

At the heart of our technology is the solid-state Li^+-conducting ceramic material which has conductivities of 10^{-4} to 10^{-3} S/cm at ambient temperatures, excellent chemical resistance towards organic and aqueous electrolyte solutions, and high mechanical stability [18,19]. The actual compositions of these membranes are proprietary to a leading glass-ceramic manufacturing company, but they follow the general compositions shown in Table 4. Figure 6 shows the conductivity as a function of temperature for the LiGC material. In working cells and batteries, the practical resistance of this solid-state glass-ceramic material is minimized by use of very thin plates with thicknesses from 75 to 300 μm. Equation 9 is a representation of the Li-air cells under development.

Table 4 Basic composition of the LiGC membrane.[a]

Component	mol %
P_2O_5	26–55 %
SiO_2	0–15 %
$GeO_2 + TiO_2$	25–50 %
where GeO_2	0–50 %
and TiO_2	0–50 %
ZnO_2	0–10 %
M_2O_3[b]	0 < 10 %
Al_2O_3	0–15 %
Ga_2O_3	0–15 %
Li_2O	3–25 %

[a]Ref. [19].
[b]M is a lanthanide element.

$$\sigma = 29.38 \times 10^{-7046/2.3RT}$$
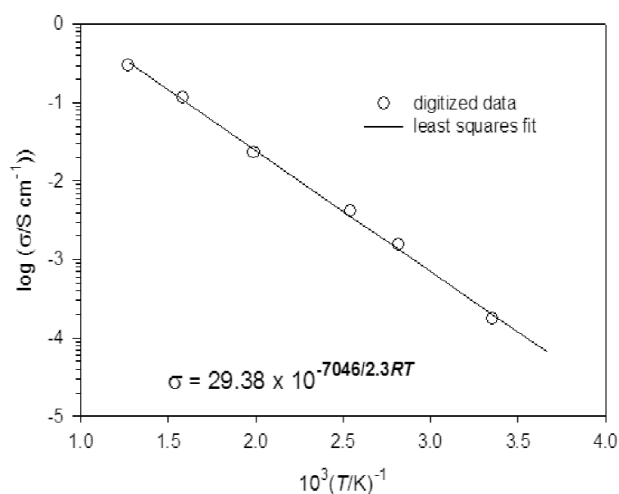
Fig. 6 Arrhenius plot of the conductivity for the LiGC membrane.

Li metal anode	Microporous membrane with organic based electrolyte solution	Li^+-conductive glass-ceramic	Organic or aqueous electrolyte solution	Air cathode	(9)

The basic structure of the fuel cell air cathode electrode for use in aqueous electrolyte solutions is a double-layer membrane consisting of a hydrophobic outer layer (typically PTFE) facing the atmosphere laminated to a porous catalytically active carbon (Table 2) layer which is soaked with the electrolyte solution. The hydrophobic layer is completely free of electrolyte solution and serves to maximize O_2 transport to the electrolyte-soaked catalytically active carbon layer which faces the electrolyte solution. A typical air cathode is around 0.05 cm thick, and about half, or ~0.025 cm, corresponds to the catalytically active layer. This thickness is thus around half that of the air cathodes used for organic electrolyte solutions as discussed above. Thick and highly porous air cathodes are required for Li-air cells in organic electrolyte solutions to maximize specific capacities which are limited by precipitation of the lithium oxide discharge products. However, in aqueous-based Li-air cells where there are no in-

soluble discharge products, highly efficient commercial air cathodes designed for aqueous H_2/O_2 fuel cells can be employed. Figures 7 and 8 [15] demonstrate this application for Li-air cells in aqueous H_2SO_4 and KOH solutions with a commercial Alupower air cathode [20]. Both figures show that the polarization of the air cathode is essentially constant with time, and that the end-of-life of the Li-air cell is due to the complete electrochemical oxidation of the Li anode. It is also noted that the nominal cell discharge potentials are 3.2 V in acid solution (Fig. 7) and 3.0 V in alkaline solution (Fig. 8). These potentials are significantly higher than those obtained with Li-air cells in organic electrolyte solutions, ~2.7 V as seen in Fig. 1.
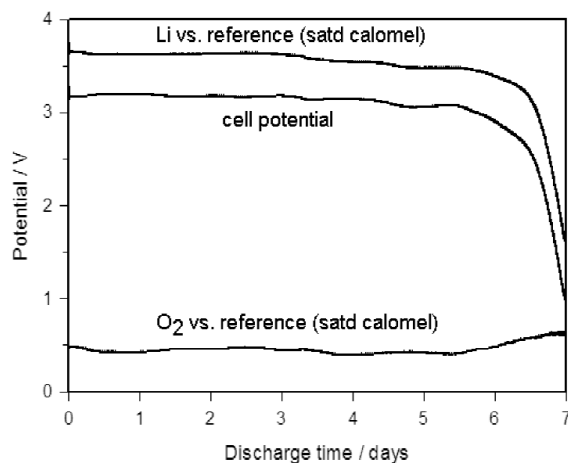

Fig. 7 Constant current discharge (0.1 mA/cm^2) of a Li-air cell at 25 °C in 5.25 mol dm^{-3} H_2SO_4 from ref. [15] (LiGC thickness is 75 μm).

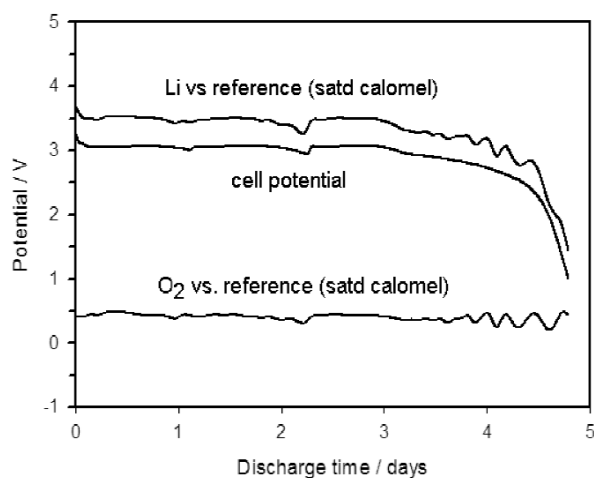**Fig. 8** Constant current discharge (0.1 mA/cm^2) of a Li-air cell at 0 °C in 3.0 mol dm^{-3} KOH from ref. [15] (LiGC thickness is 75 μm).

CONCLUSIONS

The lure of extremely high specific energy and specific capacity is the impetus for recent advanced research on Li-air batteries. In nonaqueous aprotic electrolyte solutions, the specific capacity of the Li-air

cell is limited by the precipitation of lithium oxides within the cathode and the solubility of oxygen in the electrolyte solution which affect the transport of oxygen within the interior of the air cathode. In aqueous-based electrolytes where the solubility of discharge products is not encountered, our recent research shows that these systems are an attractive alternative to organic-based Li-air systems.

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