Short communication

Primary Li-air cell development

Owen Crowther*, Benjamin Meyer, Michael Morgan, Mark Salomon**

MaxPower, Inc., 141 Christopher Lane, Harleysville, PA 19438, USA

ARTICLE INFO

ABSTRACT

In the present communication, we report on recent researches for optimizing the performance of a primary organic-based Li-air cell. These researches focus on new processing technologies for a high capacity and high rate capable carbon cathode, and the development of oxygen selective membranes based on polysiloxane and methacrylate–polysiloxane copolymers. These membranes, generally classified as silicone rubbers exhibit high permeability for oxygen and impede water transport from the atmosphere into the Li-air cell and solvent loss from the cell into the atmosphere.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Metal-air batteries based on Zn, Mg and Al anodes are a well-developed technology [1], but the use of Li anodes has long remained an elusive goal until the breakthrough study by Abraham and Jiang [2]. The innovation reported by Abraham and Jiang was based on the use of nonaqueous electrolyte solutions, and this approach was quickly followed by a number of researchers, for example those cited in Refs. [3–9]. Subsequent technology developed for Li$^+$-ion conducting glass-ceramic membranes [10] which are impervious to water allowed the Li-air technology to be expanded to include aqueous systems including a novel Li-seawater battery discussed below. The technology involves using a glass-ceramic membrane [10] to hermetically seal and protect the Li anode from water [9,11]. To demonstrate the exceptionally high specific energies and capacities theoretically available for Li-air cells in organic electrolyte solutions compared to other Li- and metal-air systems, we used critically evaluated thermodynamic data for Gibbs energies of formation from Ref. [12]. The comparisons are shown in Table 1. It is interesting to note that the aqueous Li-air cell will operate in seawater at modest discharge rates (<~0.1 mA cm^{-2}) where the O$_2$ solubility is reasonably high, generally down to depths of around 500 m. At high rates and at lower ocean depths where the O$_2$ solubility is limited, the mechanism converts to that for a Li-water cell where the cathodic reaction is the evolution of H$_2$. As shown in Table 1, the specific energy and capacity of this Li-seawater cell is higher than any other aqueous Li, Zn, Mg or Al based cell due to the fact that the molecular mass of water is not included in the calculations since water is freely available from seawater and does not have to be stored in the cell.

Given the above breakthrough concept for nonaqueous Li-air and subsequent new technologies for other Li-based systems, it is not surprising that many laboratories throughout the world, including the present laboratory, are devoting many resources to develop these high energy systems. In the present communication, we report on recent researches for optimizing the performance of a primary organic-based Li-air cell. The present communication focuses on new technologies for a high capacity carbon cathode and oxygen selective membranes to preclude water transport from the atmosphere into the Li-air cell, and solvent loss from the cell into the atmosphere.

2. Experimental

In all of the present studies we have used a 1 mol dm^{-3} LiBF$_4$ electrolyte in a 1:1 (v/v) mixture of propylene carbonate and dimethylcarbonate. PC was selected as one cosolvent due to its high dielectric constant and high boiling point, and DMC was selected as the other cosolvent because it exhibits a high solubility for O$_2$ [3,4,8]. Electrolyte grade PC and DMC were obtained from Ferro, and high purity LiBF$_4$ was obtained from Aldrich. The electrolyte solution was prepared in an argon-filled dry box.

Properties of commercial carbons used for the air electrodes are summarized in Table 2.

---

* Corresponding author. Tel.: +1 215 256 4575x108; fax: +1 215 256 1674.
** Corresponding author. Tel.: +1 215 256 4575x103; fax: +1 215 256 1674.
E-mail addresses: Owen.Crowther@MaxPowerinc.com (O. Crowther),
Mark.Salomon@MaxPowerinc.com (M. Salomon).

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

Metal-air system (organic or aqueous electrolyte solution)	OCV (V)	Specific energy (Wh kg^{-1})	Specific capacity (mAh g^{-1})
$2Li + 1/2O_2 \rightarrow Li_2O$ (aprotic organic solution)	2.913	11,248[a]	3862
$Li + 1/2O_2 \rightarrow 1/2Li_2O_2$ (aprotic organic)	2.959	11,425[a]	3862
$2Li + 1/2O_2 + H_2SO_4 \Leftrightarrow Li_2SO_4 + H_2O$	4.274	1091[a]	255
$2Li + 1/2O_2 + 2HCl \Leftrightarrow 2LiCl + H_2O$	4.274	3142[a]	366
$2Li + 1/2O_2 + H_2O \Leftrightarrow 2LiOH$	3.446	5789[a]	1681
$Al + 0.75O_2 + 1.5H_2O \rightarrow Al(OH)_3$ (aqueous)	2.701	4021[a]	1489
$Zn + 1/2O_2 \rightarrow ZnO$ (aqueous)	1.650	1353[a]	820
$2Li + H_2O$ (seawater) $\Leftrightarrow 2LiOH + 1/2H_2$	2.512	9701[b]	3862

[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] The molecular mass of H_2O is not included since it is freely available from seawater (pH 8.2) and does not have to be stored in the battery.

Table 2
Properties of common carbons for Li-air cells.

Carbon	Surface area, m^2 g^{-1}	Particle size	Pore volume, cm^3 g^{-1}
Super P	62	40 nm	~3.8
Vulcan XC-72	235	30 nm	0.59
Black Pearls 2000	1480 (10,000 m^2 L^{-1})	12 nm	2.35
Ketjen Black 300	800 (10,000 m^2 L^{-1})	<125 μm aggregates ~30 nm particle size	~3.3
Ketjen Black 600	1415 (10,000 m^2 L^{-1})	Ave. aggregate ~125 μm ~40 nm particle size	5
Shawinigan acetylene black	70	48 nm	~4.6

Air electrodes were prepared using a novel approach which we refer to as the "mineral spirits" method. The first step in this process involves preparation of the air cathode powder; in methanol, the carbon power was mixed with TE-3859 aqueous Teflon suspension and a wetting and dispersing additive followed by preliminary drying (solvent removal) at 120 °C followed by thorough drying in vacuum at 100 °C. The powder was then mixed with a small amount of mineral spirits to produce a dough which was molded into 175 cm^2 square pads. The pads were placed onto a Ni grid and pressed at 138 N cm^{-2} at 175 °C and calendered to a desired thickness between 155 and 64 μm. The method produced mechanically stable composite cathodes of high porosity with an average porosity of 85% as calculated from

$$P\% = 100 \left\{ 1 - \frac{\rho_{app}}{\rho_{true}} \right\} \tag{1}$$

In Eq. (1) P is the porosity in percent, ρ_{app} is the apparent density of the air electrode and ρ_{true} is the density of the pure components. A typical composition of the air cathode (minus the grid) is 79.1 mass% carbon, 19.8% Teflon and 1.1% wetting agent.

A number of studies to establish an optimum (baseline) air cathode were carried out to determine which carbon material will be used in advanced studies. The cells used in these studies are represented by

Li metal anode	1 mol dm^{-3} LiBF$_4$ electrolyte solution in Tonen E20 separator	Air cathode

(2)

The criteria used in producing the optimum cathode structure were the deliverable capacity at various discharge rates measured in units of mAh per gram of carbon as established by Abraham and Jiang [2]. All cells based on Eq. (2) utilized a cathode onto which we pressed a porous Teflon (Porex) membrane. The cells used in these studies were either sealed in plastic bags filled with O_2 or simply discharged in the atmosphere as discussed further below.

Once a baseline cathode structure was established, more advanced studies on a practical approach to a Li-air involving a cathode protected from the atmosphere by an O_2-selective membrane [13]. The cells used in these studies are represented by

Li metal anode	1 mol dm^{-3} LiBF$_4$ electrolyte solution In Tonen E20 separator	Protected Air cathode

(3)

A schematic of this "protected cathode" Li-air cell is shown in Fig. 1. The O_2-selective membranes used in our studies are based on compounds which exhibit high O_2 solubilities and diffusion and are applied to the outer surface of the cathode as a gel, liquid or solid hosted in an inert porous membrane such as Teflon, Celgard, or polyphenylene sulfide (PPS) [13,14]. In addition to exhibiting high O_2 solubilities, these basic materials also retard diffusion of water vapor from the atmosphere into the cell and the evaporation of organic solvents (e.g. DMC) out of the cell. A guideline for selection of highly O_2-selective materials can be found in the compilation by Battino et al. [15], and examples of materials used in our researches include perfluorocarbons, ethers, polyfluoroethers, polysiloxanes, alkylmethacrylates and silicone rubbers [13,14]. In the present study, we report results for a silicone rubber O_2-selective membrane based on two types of silicone rubbers. The first is a polysiloxane–methacrylate copolymer based on materials as received from Gelest. The rubber was prepared from a mixture of methacryloxypropyl polydimethylsiloxane of molecular mass ~5000 (29 mass%), methacryloxypropyl polydimethylsiloxane of molecular mass ~1050 (35%), N,N-dimethylacrylamide (35%), and 1% Darcur (2-hydroxy-2-methyl-1-phenyl-propan-1-one) photo initiator. These components were dissolved in 3-methyl-3-pentanol and coated onto porous films of Teflon (Porex, 101 μm thick or Dexmet, 51 μm thick), and polyphenylene sulfide

(PPS from Bondex, 45.4 μm). The coated films were placed on a conveyer with a belt speed of 213 cm min^{-1} while being exposed to a UV source with 210–315 nm wavelength range (Fusion model F300 with an LV6N conveyer) and at an average power level of 1400 mJ cm^{-2} to effect cross-linking. The total thicknesses of the UV cured silicone rubber coatings on the substrates varied between 330 and 1016 μm. A second thinner silicone rubber membrane was prepared from Semicosil 964 which is a RTV-amine obtained from Wacker Silicones. Semicosil 964 can be cured either by UV or with moisture when in contact with air. Air cathodes were prepared by
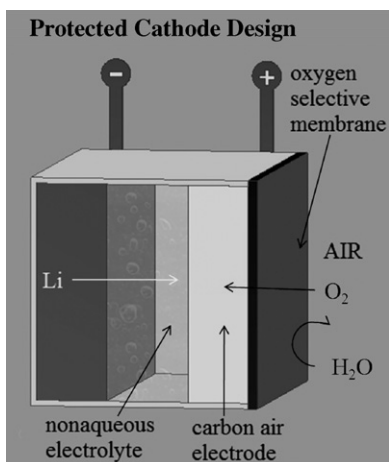
Fig. 1. Schematic of the "protected cathode" Li-air cell.

Fig. 2. Discharge performance in oxygen of baseline cathode: ○, $0.2\,mA\,cm^{-2}$; △, $0.5\,mA\,cm^{-2}$; □, $1\,mA\,cm^{-2}$; ▽, $2\,mA\,cm^{-2}$.

Table 3
Achieved capacities for curves in Figs. 2 and 3.

	Capacity ($mAh\,g^{-1}$)
Fig. 2 symbol	
○	2924
△	1007
□	409
▽	228
Fig. 3 symbol	
▲	947
▽	818
○	786
□	735
△	492
◇	453

dip coating the electrode with one side masked, and moisture cured overnight in the atmosphere at room temperature. This produced a thin (76–89 μm) hydrophobic silicone rubber membrane coated directly onto the surface of the air cathode.

The surface area of cathodes in all cells was $10\,cm^2$ and the anode (excess Li) area was comparable. The outer surface of cathodes in baseline Li-air cells, Eq. (2), were protected only with a porous Porex membrane, while cathodes for the "protected cathode" cells, Eq. (3), were protected either with a polysiloxane–methacrylate silicone rubber-coated PPS (Bondex) membrane, or with a Semicosil rubber directly coated directly onto the cathode. All cell cathodes operated as flooded cathodes, and were discharged at various rates in O_2-filled plastic bags or in the atmosphere at defined relative humidities.

3. Results and discussion

3.1. The baseline cathode

The objective for developing a baseline cathode structure was to maximize discharge rate capability and specific capacity. The variables involved in developing such a cathode include many factors such as total electrode porosity and electrolyte solution. When porosity is totally blocked by precipitation of the reaction products Li_2O_2 and Li_2O which are electronically non-conductors, oxygen saturated electrolyte solutions can no longer enter the cathode, and the Li-air cell quickly reaches its end-of-life (EOL). While precipitation within micro and macropores within the basic carbon powders are related to achievable capacities in $mAh\,g^{-1}$ [3,16,17], the EOL is not reached solely due to blocking of these pores. The finished composite cathode will also provide additional void space which is accessible to O_2-saturated electrolyte solution and catalytic sites on carbon which are available for further reduction of O_2. Ketjen Black EC600G was selected as the carbon for use in our baseline cathode cells based on its high surface area of $1415\,m^2\,g^{-1}$, small particle size of 40 nm and high volume porosity (micro + macro) of $5\,cm^3\,g^{-1}$ (see Table 2). Using this carbon to fabricate a highly stable and porous (85%) composite cathodes using our "mineral spirits method," a cathode was produced which exhibits high rate capability (Fig. 2) and high specific capacities at the EOL (Table 3).

The rate capability of this cathode as shown in Fig. 2 and Table 3 is, by comparison with the literature reports, very high. For example, at a current density of $0.1\,mA\,cm^{-2}$, the literature values for specific capacity are generally between 1500 and $2500\,mAh\,g^{-1}$ [2–9] whereas the present cathode meets and exceeds these speci-
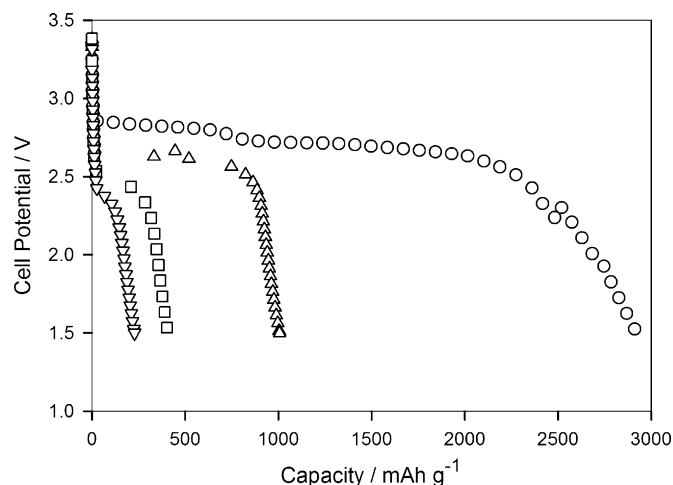
fication at twice the rate, i.e. at $0.2\,mA\,cm^{-2}$. The cathode is also capable of delivering useful capacities at rates of to $1\,mA\,cm^{-2}$. Based on these studies, this baseline cathode using Ketjen EC600G carbon was selected for advanced studies on the protected cathode design of Fig. 1 and Eq. (3).
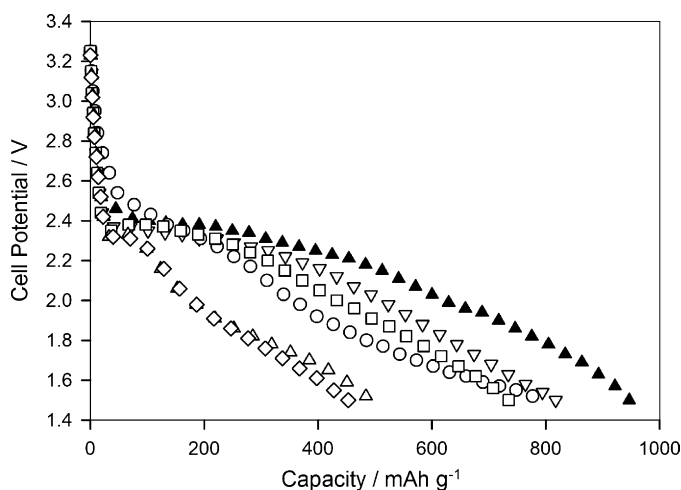

Fig. 3. Discharge performance of baseline cathodes protected with polysiloxane–methacrylate O_2-selective membranes (on PPS) of various total thicknesses: ▲, 330 μm; ▽, 432 μm; ○, Porex membrane, no protection, 102 μm; □, 889 μm; △, 432 μm; ◇, 1016 μm. Cells discharged in air at $0.1\,mA\,cm^{-2}$, room temperature and a relative humidity of 15%.
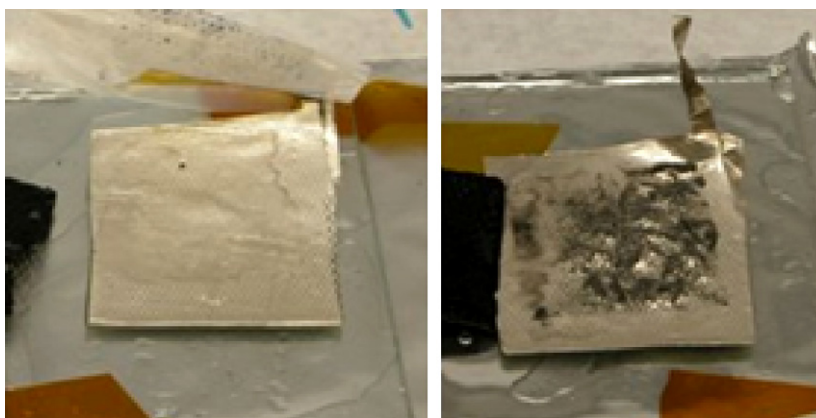
Fig. 4. Postmortem analyses of Li anodes from cells discharged in air with polysiloxane–methacrylate protected cathode cell (left) and from non-protected cell (right).

3.2. The protected cathode Li-air cell

The membranes under development are those which selectively maximize O_2 solubility and diffusion, and minimize diffusion of both water into the cell and organic solvent out of the cell. There are many materials which can be used for this purpose [13,15], and in the present study we focused materials to fabricate two silicone rubbers. Hydrophobic silicone rubber basic materials are used for contact lenses as they permit rapid transit of O_2 necessary to prevent swelling of the cornea; typical permeabilities, P, for O_2 in polydimethylsiloxane cross-linked films are $\sim$600 Barrers [18] to $\sim$200 Barrers for methacryloxypropyl terminated polydimethylsiloxane rubbers [19], and thus are effective and important candidates for use as the protective membrane covering the atmospheric side of the air electrode. The Barrer is a common unit used in the contact lens industry and represents the amount of O_2 which diffuses per second through membranes of specified thickness and O_2 pressure, and its units are 10^{-11} (cm^3 O_2) cm cm^{-2} s^{-1} mm Hg^{-1}. To emphasize the significance of these high O_2 permeability values, it is of interest to compare the O_2 permeability for the polyimide Kapton, 0.065 Barrer [20] and PET (polyethylene terephthalate), 0.01 Barrer [21], i.e. essentially five orders of magnitude smaller than those for the silicone rubbers used in the present investigations.

Fig. 3 compares the discharge performance of Li-air cells without cathode protection (Eq. (2)) and with cathodes protected with the UV cured polysiloxane–methacrylate copolymer coated onto PPS (Eq. (3)). Cells were discharged in air at 0.1 mA cm^{-2} and a relative humidity of 15%. For the thinner silicone membranes (330 and 432 μm), the protected cathode cells outperformed the baseline cell with only a porous Porex membrane pressed onto the cathode. For thicker silicone rubber membranes, performance dropped as expected, but still delivered useable capacities. Specific capacity values for the cells shown in Fig. 3 are summarized in Table 3. Fig. 4 shows photos of postmortem analyses of the anode for the cell with the 330 μm silicone rubber backing on the cathode, and the cell with only the porous Porex backing on the cathode. Analysis shows no visible corrosion on the anode from the cathode protected Li-air cell whereas visible corrosion on the anode is obvious and extensive for the unprotected Li-air cell.

Fig. 5 compares the discharge performance of a Li-air cell without cathode protection (Eq. (2)) and with a cathode protected cell with the thin 83 μm Semicosil-based silicone rubber-coated directly onto the surface of the air cathode (Eq. (3)). The cells were discharged in air at 0.2 mA cm^{-2} and a high relative humidity of 42.9%. The unprotected cathode cell died relatively quickly in this high humidity atmosphere delivering a capacity of only 151 mAh g^{-1} whereas the silicone rubber protected cell discharged
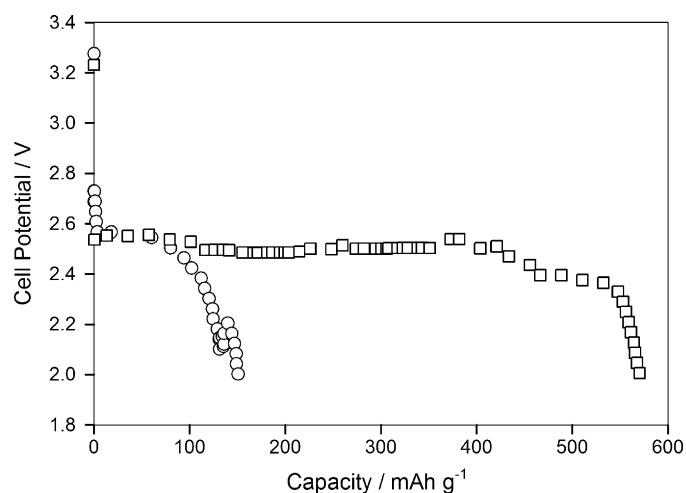

Fig. 5. Room temperature discharge performance of baseline cathodes with only Porex backing (○) and baseline cathode Protected cell with Semicosil-based O_2-selective 83 μm silicone rubber membrane coated directly onto cathode (□). Current density is 0.2 mA cm^{-2}, and relative humidity is 42.9%. Delivered capacities are 570 mAh g^{-1} for protected cell and 151 mAh g^{-1} for unprotected cell.

normally delivering a capacity of 570 mAh g^{-1} at this relatively high current density (for a Li-air cell) of 0.2 mA cm^{-2}. We attribute the large increase in performance to increased O_2 transmission through the thinner Semicosil-based silicone rubber membrane.

The diminished specific capacity of cells discharged in air at relative humidities between 15 and 43% compared to cells discharged in pure oxygen is due to several factors. A major factor is due to the low partial pressure of oxygen which results in higher overpotentials at the cathode. As the reaction products Li_2O and Li_2O_2 build up, diffusion of oxygen into the cathode decreases and the cells reach the cutoff voltage (1.5–2.0 V) prematurely. The presence of water not only results in catastrophic failure due to reaction with the Li anode in unprotected Li-air cells as seen in Figs. 3 and 5, but also due to the formation of insoluble Li_2CO_3 on the cathode [22]; the carbonate is formed due to the reaction of water and CO_2. The solubility of CO_2 in aprotic solvents and materials used to synthesize the O_2-selective membranes is very high [23], generally an order of magnitude higher than the solubility of oxygen [15].

4. Conclusion

Advanced composite cathodes for a Li-air primary cell were fabricated using a carbon with high surface area and high micro and macropore volume (Ketjen Black 600) in a process which results in a

mechanically stable and high porosity structure. The total porosity of both the basic carbon powder and the composite cathode provides additional volume to permit O_2-saturated electrolyte solution to diffuse through the porous electrode which in turn results in a more homogeneous distribution of the reaction products Li_2O_2 and Li_2O. The net result is a cathode exhibiting high specific capacity and rate capability up to around $2\,mA\,cm^{-2}$. O_2-selective membranes based on silicone rubbers applied to the outer surface of the air cathode resulted in cells with discharge behavior comparable to cells without such protection. The cells with thinner O_2-selective membranes exhibited higher specific capacities and the retardation of water into the cell was very effective. This "protected cathode" technology offers enticing challenges for future work involving Li-air and Li-seawater cells and batteries.

Acknowledgment

References

[1] D. Linden, T.B. Reddy (Eds.), Handbook of Batteries, 3rd edition, McGraw-Hill, NY, 2001.
[2] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (1996) 1.
[3] J. Read, J. Electrochem. Soc. 149 (2002) A1190.
[4] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, D. Foster, J. Electrochem. Soc. 150 (2003) A1351.
[5] A. Dobley, J. DiCarlo, K.M. Abraham, Proc. 41st Power Sources Conference, June 14-17, 2004, p. 61.
[6] J. Read, A. Pitt, Proc. 41st Power Sources Conference, June 14-17, 2004, p. 64.
[7] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, J. Power Sources 146 (2005) 766.
[8] J. Read, J. Electrochem. Soc. 153 (2006) A96.
[9] I. Kowalczk, J. Read, M. Salomon, Pure Appl. Chem. 79 (2007) 851.
[10] J. Fu, U.S. Patent 6,485,622 (November 26, 2002), and earlier patents cited therein.
[11] S.J. Visco, Y.S. Nimon, B.D. Katz, U.S. Patent 7,390,591 (June 24, 2008).
[12] A.J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Marcel Dekker, New York, 1985.
[13] MaxPower Patent pending.
[14] M. Salomon, B. Meyer, A. Driedger, D. Bansal, 216th Meeting of The Electrochemical Society, Vienna, 4–6 October, 2009 (abstract 3042).
[15] R. Battino, T.R. Rettich, T. Tominaga, J. Phys. Chem. Ref. Data 12 (1983) 163.
[16] S.S. Zhang, D. Foster, J. Read, J. Power Sources 195 (2010) 1235.
[17] C. Tran, X.-Q. Yang, D. Qu, J. Power Sources 195 (2010) 2057.
[18] I. Blurne, P.J.F. Schwering, M.H.V. Mulder, C.A. Smolders, J. Membr. Sci. 61 (1991) 85.
[19] Y.-C. Lai, W. Lang, E.T. Quinn, D.V. Ruscio, US Patent Application 2006/0142525 (June 29, 2006).
[20] L. Nicodemo, A. Marcone, T. Monetta, G. Mensitieri, F. Bellucci, J. Membr. Sci. 70 (1992) 207.
[21] R.Y.F. Liu, Y.S. Hu, D.A. Schiraldi, A. Hiltner, E. Baer, J. Appl. Polym. Sci. 94 (2004) 671.
[22] J. Ostroha, "Lithium-Air System Development" presentation at the 11th Electrochemical Power Sources R&D Symposium, July 13–16, 2009, Baltimore, MD. The presentation can be found at www.11ecpss.betterbtr.com/xThursday/TH4-LiAir%207-16-09.pdf (accessed by the present authors on August 15, 2010).
[23] P.G.T. Fogg, Carbon Dioxide in Nonaqueous Solvents at Pressures Less Than 200 kPa, in: IUPAC Solubility Data Series, vol. 50, Pergamon Press, Oxford, 1992.