J|A|C|S
ARTICLES

Published on Web 01/05/2006

Rechargeable Li_2O_2 Electrode for Lithium Batteries

Takeshi Ogasawara,[†,§] Aurélie Débart,[†] Michael Holzapfel,[‡] Petr Novák,[‡] and
Peter G. Bruce[*,†]

Contribution from the School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, U.K., and Electrochemistry Laboratory, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Received October 5, 2005; E-mail: P.G.Bruce@st-andrews.ac.uk

Abstract: Rechargeable lithium batteries represent one of the most important developments in energy storage for 100 years, with the potential to address the key problem of global warming. However, their ability to store energy is limited by the quantity of lithium that may be removed from and reinserted into the positive intercalation electrode, Li_xCoO_2, $0.5 < x < 1$ (corresponding to 140 mA·h g^{-1} of charge storage). Abandoning the intercalation electrode and allowing Li to react directly with O_2 from the air at a porous electrode increases the theoretical charge storage by a remarkable 5−10 times! Here we demonstrate two essential prerequisites for the successful operation of a rechargeable Li/O_2 battery; that the Li_2O_2 formed on discharging such an O_2 electrode is decomposed to Li and O_2 on charging (shown here by in situ mass spectrometry), with or without a catalyst, and that charge/discharge cycling is sustainable for many cycles.

Introduction

The high energy density of rechargeable lithium batteries has resulted in them becoming the dominant power source for portable electronic devices, with a market value of $2 billion per annum.[1−3] Global warming represents a major threat to humanity. Rechargeable lithium batteries have a key role to play in addressing this threat, e.g., by their use in future hybrid electric vehicles. Currently, rechargeable lithium batteries are based on a positive electrode formed from the intercalation compound $LiCoO_2$ and a graphite negative electrode. On charging, Li is removed from the $LiCoO_2$ electrode, passes across the electrolyte, and is inserted between the graphene layers in graphite; discharge reverses the process.[3] Energy storage is limited mainly by the positive electrode, which can store only 130−150 mA·h g^{-1} of charge (∼0.5Li/Co) compared with 300 mA·h g^{-1} for graphite. There is intense interest in finding ways of increasing energy storage in the positive electrode. The major effort by researchers worldwide to design and synthesize new intercalation electrodes is likely to yield improvements in energy density, but only by a factor of 2. Radically different approaches are required in order to deliver a step change in performance. A quite different approach involves dispensing with the positive intercalation electrode and reacting lithium directly with O_2 from the air. The reactants no longer have to be carried on-board the cell, and the supply of O_2 is, in principle, infinite. The use of an O_2 cathode can lead potentially to energy densities 5−10 times greater than at present!

Air cathodes are already employed in aqueous batteries, or in batteries that at least contain an aqueous electrolyte/air interface; the most well-known are probably the primary (discharge only) Zn/air and Al/air batteries.[4,5] However, the chemical/electrochemical processes in aqueous batteries involve O_2 reacting with water and hence are fundamentally different from an O_2 electrode operating in a nonaqueous lithium battery. Studies addressing the O_2 electrode in nonaqueous Li batteries have been very limited in number; most of these have focused on primary (discharge only) batteries with only a few considering rechargeability.[6,7] Such studies have demonstrated that Li_2O_2 is the dominant discharge product.[6] Here we demonstrate, using in situ mass spectrometry, that remarkably Li_2O_2 decomposes to yield Li + O_2 on electrochemical charging and that such charge/discharge cycling is sustainable for many cycles. These are essential prerequisites for the successful operation of a future rechargeable Li/O_2 battery, offering a step change in energy density.

Experimental Section

Preparation of the Cathode and Electrochemical Measurements. The electrochemical cells used to investigate cycling were based on a Swagelok design and composed of a Li metal anode, an electrolyte (1

[†] University of St. Andrews.

[‡] Paul Scherrer Institut.

[§] Present address: Mobile Energy Company, SANYO Electric Co., Ltd., 7-3-2 Ibukidai-Higashimachi, Nishi-ku, Kobe, Hyogo, 651-2242, Japan.

(1) Nazri, G. A.; Pistoia, G. *Lithium Batteries Science and Technology*; Kluwer Academic Publishers: MA, 2004.

(2) Schalkwijk, W. V.; Scrosati, B. *Advances in Lithium-Ion Batteries*; Kluwer Academic/Plenum Publishers: New York, 2002.

(3) Tarascon, J.-M.; Armand, M. *Nature* **2001**, *414*, 359−367.

(4) Linden, D. *Handbook of Batteries and Fuel Cells*; McGraw-Hill: New York, 1984.

(5) Visco, S. J.; Nimon, E. Lithium metal aqueous batteries. Presented at the 12th International Meeting on Lithium Batteries, Nara, Japan, June 27−July 2, 2004; Abstract 53.

(6) (a) Abraham, K. M.; Jiang, Z. *J. Electrochem. Soc.* **1996**, *143*, 1−5. (b) Dobley, A.; Rodriguez, R.; Abraham, K. M. High Capacity Cathodes for Lithium-Air Batteries. Presented at the 206th Meeting of the Electrochemical Society, Honolulu, HI, October 4−8, 2004; Abstract 496. (c) Dobley, A.; Morein, C.; Abraham, K. M. Cathode optimization for lithium-air batteries. Presented at the 208th Meeting of the Electrochemical Society, Los Angeles, CA, October 17, 2005; Abstract 823.

10.1021/ja056811q CCC: $33.50 © 2006 American Chemical Society

M $LiPF_6$ in propylene carbonate (Merck)) impregnated into a glass fiber separator, and a porous cathode. The cathode was formed by casting a mixture of Super S carbon (MMM), EMD (electrolytic manganese dioxide), and Kynar2801 (a copolymer based on PVDF) (mol ratios of 95:2.5:2.5) onto an Al grid. The cathode construction followed well-established procedures for porous electrodes.[8−10] The cell was gastight except for the Al grid window that exposed the porous cathode to the O_2 atmosphere. The cell was operated in 1 atm of O_2. To investigate specifically the electrochemical decomposition of Li_2O_2 on charging, electrodes were prepared by mixing ball-milled Li_2O_2 (Aldrich 90%), Super S carbon, EMD, and PTFE (Aldrich) or Kynar2810 (mol ratios of 16:80:2:2). Ball milling was carried out for 30 min under Ar resulting in Li_2O_2 with an average particle size of 100 nm. The electrodes were again incorporated into cells with Li foil and 1 M $LiPF_6$ in propylene carbonate as the electrolyte. Electrochemical measurements were performed at room temperature using a Bio-Logic Mac Pile II. Gravimetric analysis to establish O_2 loss employed a cell composed of a polypropylene pack containing a thin Li anode, a fiberglass separator soaked in electrolyte (1 M $LiPF_6$ in propylene carbonate), and the Li_2O_2 electrode described above. The polypropylene pack had holes to allow O_2 evolution.

Sample Characterization. Powder X-ray diffraction (XRD) was carried out using a STOE STADI/P diffractometer operating in transmission mode with a primary beam monochromator and position sensitive detector. Fe Kα1 radiation ($\lambda = 1.936$ Å) was employed. Examination of charged electrodes involved first disassembling the cell in the glovebox, rinsing the cathode twice with dimethyl carbonate, removing the solvent under vacuum, and then introducing the electrode into an airtight X-ray holder. Chemical analysis for Li was carried out using flame emission spectroscopy (Philips PU9400X AAS).

In situ Differential Electrochemical Mass Spectrometry (DEMS). This analysis was carried out to detect the gases generated during charging. The cell consisted of a lithium anode, electrolyte (1 M $LiPF_6$ in propylene carbonate), and the working positive electrode, as described above. The cell was purged continuously with Ar gas which flowed from the cell into the mass spectrometer carrying the evolved gases for MS analysis. The experiment setup is described in detail elsewhere.[11] The cell potential was raised in 100 mV steps from 4.2 V every 120 min, and the variation of the ion current for different m/z (mass per electron) was monitored as a function of time.

Results and Discussion

Electrochemical Cycling of a Lithium/Oxygen Battery. The variation of potential for a Swagelok cell operated in 1 atm O_2 on discharge then charge is shown in Figure 1a. The discharge potential (2.5−2.7 V) is in good agreement with that reported previously for a similar cell discharged in 1 atm of O_2 involving formation of Li_2O_2 and was confirmed by Raman spectroscopy.[6] As solid Li_2O_2 forms and fills the pores, polarization will increase, and this is presumed to be the main factor controlling termination of the discharge process. EMD is not essential for the electrode reaction to occur; however it does facilitate the process, as discussed later. EMD is also an intercalation host for Li; however, the proportion used in the electrode is small and contributes at most 16 mA·h g^{-1} to the discharge capacity. Recharging occurs at 4.2−4.4 V. Small inflections are observed at approximately 3.25 V on discharge and charge. The origin of these small features is currently under investigation by us. The feature on discharge may correspond to the small capacity expected for EMD.

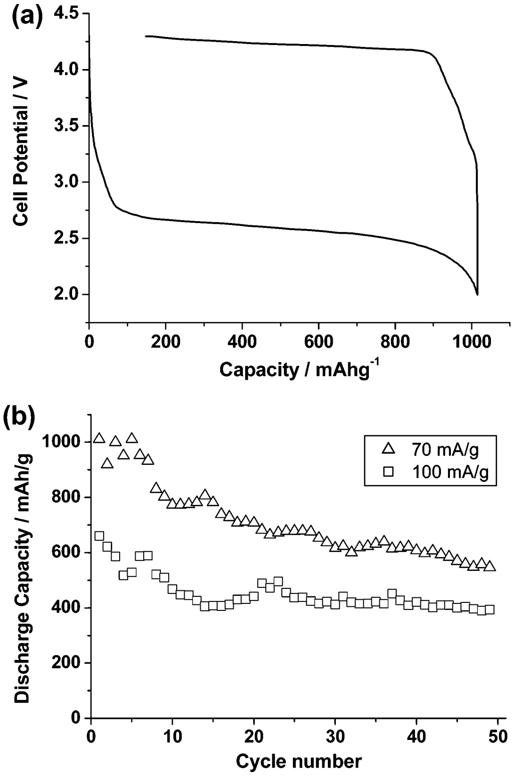

Figure 1. (a) Variation of potential on discharge then charge corresponding to the third cycle of the cell at a rate of 50 mA g^{-1}. Capacities are expressed per gram of carbon in the electrode. (b) Variation of discharge capacity with cycle number for an O_2 cathode. Rates = 70 and 100 mA·h g^{-1}. Capacities are per gram of carbon.

Figure 1b presents the discharge capacity as a function of cycle number at 70 and 100 mA g^{-1}, demonstrating, for the first time, that cycling can be sustained for many cycles.[6,7] Although the capacity does fade, the rate of fade slows, and a discharge capacity of ∼600 mA·h g^{-1} (per g of carbon) is still obtained after 50 cycles at a rate of 70 mA g^{-1}. Although inevitably less than the theoretical capacity based on $2Li + O_2 \rightarrow Li_2O_2$ (1170 mA·h g^{-1}), since the electrode requires at least a porous conductor (carbon) and a binder, and taking account of the fact that the O_2 electrode is far from optimized, these results do demonstrate that cycling is sustainable in a Li/O_2 battery.

Although the cell can be recharged, it is clear that the charging potential is significantly higher than that on discharge (Figure 1a). This could signal that recharging the cell does not involve reversing the $2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$ reaction but instead involves a quite different process, e.g., electrolyte decomposition. It is therefore important to establish whether recharging does involve the electrochemical decomposition of Li_2O_2, if the O_2 electrode is to be used as the basis of a rechargeable cell. It is known that lithium can react with a variety of transition metal oxides to form nanocomposites composed of Li_2O and the transition metal, e.g., $2Li^+ + 2e^- + CoO \leftrightarrow Li_2O + Co$.[12,13] This work demonstrated the surprising result that the formation of Li_2O is electrochemically reversible. However, such reversibility involves a stoichiometric reaction between the transition

---

(7) (a) Read, J. *J. Electrochem. Soc.* **2002**, *149*, A1190−A1195. (b) Read, J.; Mutolo, K.; Ervin, M.; Behl, W.; Wolfenstein, J.; Drieger, A.; Foster, D. *J. Electrochem. Soc.* **2003**, *150*, A1351−A1356.

(8) Richard, M. N.; Koetschau, I.; Dahn, J. R. *J. Electrochem. Soc.* **1997**, *144*, 554−557.

(9) Burchardt, T. *J. Power Sources* **2004**, *135*, 192−197.

(10) Tarascon, J.-M.; Gozdz, A. S.; Schmutz, C.; Shokoohi, F.; Warren, P. C. *Solid State Ionics* **1996**, *86−88*, 49.

(11) Ufheil, J.; Baertsch, C.; Würsig, A.; Novák, P. *Electrochim. Acta* **2005**, *50*, 1733−1738.

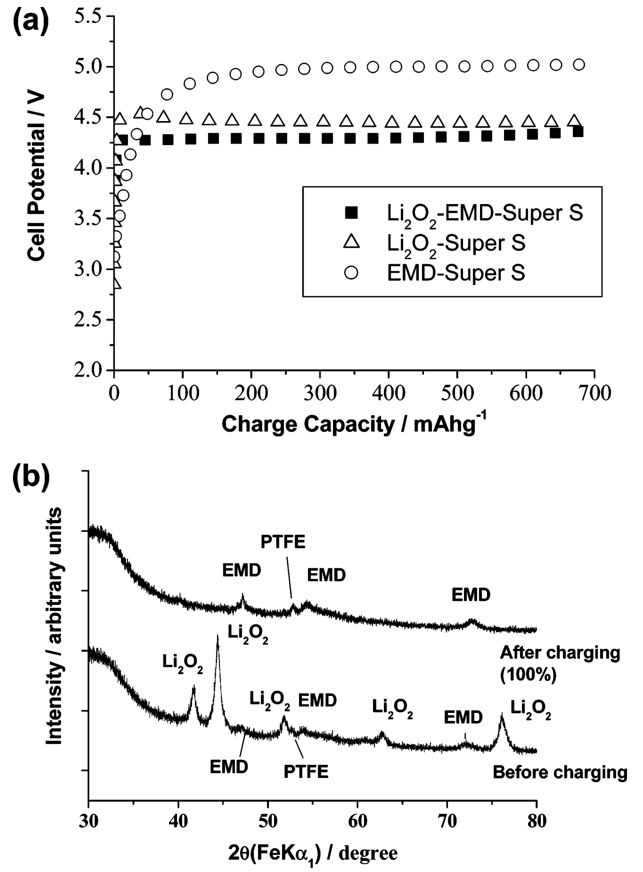

Figure 2. (a) Variation of voltage on charging cells with three different cathodes. Capacities are per gram of carbon. Charging rates were 10 mA g^{-1}. (b) Powder X-ray diffraction data for a Li_2O_2/Super S/EMD/PTFE electrode before charging and after passage of sufficient charge to decompose all the Li_2O_2.

metal and Li_2O, whereas here we demonstrate that Li_2O_2 may be decomposed electrochemically in the absence of such a reaction.

Oxidation/Decomposition of Li_2O_2. Figure 2a presents charging curves for cells containing three different cathodes, one composed of Li_2O_2/Super S/EMD/Kynar or PTFE, one from which Li_2O_2 is absent, and another from which EMD is absent. Without Li_2O_2 the potential rises to a plateau at 5.1 V, in accord with the decomposition potential for this electrolyte.[2,14] The lower voltages observed for the other two cells indicate that when Li_2O_2 is present, charging does not simply involve electrolyte decomposition. They also show that Li_2O_2 decomposition occurs without EMD but that the presence of the manganese oxide does lower the potential and is therefore an active participant, aiding the charging process. We have used several other manganese oxides, β-MnO_2, Mn_2O_3, and Mn_3O_4 as well as other transition metal oxides. All lower the charging potential. The mechanism is as yet unclear. Further work is underway to investigate the role of transition metal oxides in aiding the electrochemical reaction. We have carried out the same experiments as reported in Figure 2a using different electrolytes, including 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1 v/v) and $LiAsF_6$ in propylene carbonate, and the results are the same.

Table 1. Gravimetric Analysis of Li_2O_2 Electrodes

composition	charge removed[a]	initial weight of battery	calculated weight loss[a]	observed weight loss	difference
unit	%	g	mg	mg	%
Li_2O_2–EMD–Super S	70	4.4164	39.1	37.6	4.1
Li_2O_2–Super S	65	4.2156	37.5	37.7	0.4

[a] Based on $Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e^-$.

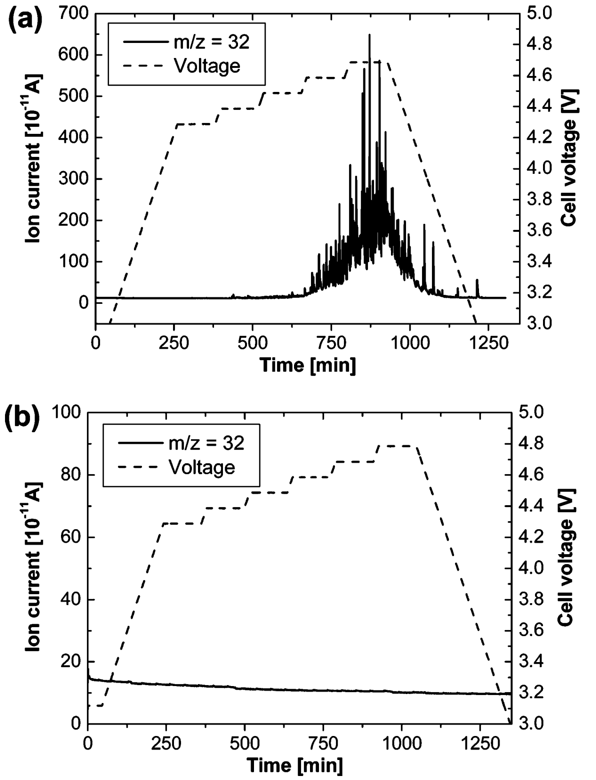

Figure 3. Variation of ion current corresponding to O_2 evolution as a function of time. The voltage was increased by 100 mV every 120 min. Electrode (a) with Li_2O_2 and (b) without Li_2O_2.

Several experiments were carried out to demonstrate electrochemical decomposition of Li_2O_2. Powder X-ray diffraction data were collected on the Li_2O_2/Super S/EMD/PTFE cathode before and after charging and are presented in Figure 2b. Sufficient change was extracted to decompose all the Li_2O_2, assuming that the reaction was $Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^-$. The results indicated that Li_2O_2 was absent at the end of charge. Chemical analysis was also carried out on the fully charged electrode and revealed a reduction in lithium content of 95.7%. An identical uncharged electrode kept at open circuit for the same length of time as the charging process showed a reduction in Li content of only 0.5%.

Although the above results indicate Li_2O_2 is removed from the electrode on charging, they do not demonstrate that the decomposition process involves the reaction $Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^-$. To address this, two experiments were carried out. The first involved gravimetric analysis of a cell before and after charging. A modified cell was employed to minimize the weight of all components other than the cathode (see Experimental Section). The cell was weighed before and after charging. The

---

(12) Poizot, S.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J.-M. *Nature* **2000**, *407*, 496–499.
(13) Obrovac, M. N.; Dunlap, R. A.; Sanderson, R. J.; Dahn, J. R. *J. Electrochem. Soc.* **2001**, *148*, A576–A588.
(14) Kanamura, K.; Okagawa, T.; Takehara, Z. *J. Power Sources* **1995**, *57*, 119–123.

results of the gravimetric analysis are presented in Table 1, for electrodes with and without EMD. On the basis of the charge passed and the assumption that all such charge corresponded only to the direct decomposition of Li_2O_2 according to the reaction $Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^-$, calculated weight losses were obtained and compared with the observed weight losses. The agreement is good (Table 1). These results provide strong evidence that the decomposition of Li_2O_2 follows the above equation.

To provide direct evidence for O_2 evolution, in situ mass spectrometry was carried out on the gases evolved during charging of the cell. The electrodes and electrolyte were identical to those used above. The experimental arrangement is summarized in the Experimental Section; full details may be found in ref 11. The cell potential was raised in 100 mV steps from 4.2 V, and at each step the evolved gases were analyzed. Significant O_2 evolution was observed above 4.5 V (Figure 3a). The amount of oxygen evolution far exceeded any other gases, by 10:1 (the next most abundant being CO_2). As a control a similar cell, devoid of Li_2O_2 but with EMD, gave no such oxygen evolution (Figure 3b).

Conclusions

In conclusion, the results reported here show that the electrochemical reaction $2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$, in a nonaqueous lithium battery with an O_2 cathode, is reversible and that charge/discharge cycling can be sustained over 10s of cycles. This provides important evidence supporting the feasibility of an O_2 electrode for rechargeable lithium batteries. However, there remain fundamental and practical issues to be addressed, including the role of EMD and other such compounds in promoting the electrode reaction, optimization of electrode porosity, structure, and composition, avoidance of H_2O or CO_2 ingress when operated in air. $LiPF_6$ in propylene carbonate may not be the best electrolyte. Ionic liquids, which are not miscible with water, may offer an attractive alternative.[15] Although practical cells may be some way off, the present results, combined with the theoretical capacities obtainable with O_2 electrodes, reinforces the view that this is an important avenue for further investigation.

Acknowledgment. P.G.B. is indebted to the Royal Society, the EU, and EPSRC for financial support. The authors also acknowledge Andreas Würsig and Werner Scheifele for their contribution to the development of the DEMS method.

JA056811Q

---

(15) Kuboki, T.; Okuyama, T.; Ohsaki, T.; Takami, N. Lithium air batteries using hydrophobic room-temperature ionic liquid electrolyte. Presented at the 12th International Meeting on Lithium Batteries, Nara, Japan, June 27–July 2, 2004; Abstract 398.