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# Characterization of the Lithium/Oxygen Organic Electrolyte Battery

**J. Read***,z

*Army Research Laboratory, Adelphi, Maryland 20783-1197, USA*

The effects that electrolyte and air cathode formulation have on discharge capacity, rate capability, and the rechargeability of the lithium/oxygen organic electrolyte cell were characterized. To characterize the effects of cell formulation on the discharge reaction, we used techniques including static and dynamic gas consumption measurements and scanning electron microscopy. It was found that electrolyte formulation has the largest effect on discharge capacity and rate capability. Electrode processing is also important in determining discharge capacity at low rate. The Brunauer-Emmett-Teller surface area of the carbon black used to prepare the air electrode is not a significant factor in determining discharge capacity. The discharge product was found to depend on both discharge rate and electrolyte formulation. This is understood in terms of the concentration of oxygen in the electrolyte during discharge.

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Metal/oxygen batteries are unique in that the cathode active material is not stored in the battery. Oxygen from the environment is reduced at a catalytic air electrode surface forming either an oxide or peroxide ion that then reacts with cationic species in the electrolyte. Metal/oxygen batteries have been developed based on Fe, Zn, Al, Mg, Ca, and Li. Most systems developed so far have been based on alkaline electrolytes with the zinc/oxygen battery in commercial use for hearing aids. The lithium/oxygen aqueous electrolyte battery has been studied but suffers from corrosion of the lithium electrode by water.[1] Abraham and Jiang[2,3] were first to report a lithium/oxygen organic electrolyte battery. The battery was shown to have an open circuit potential (OCP) close to 3 V, an operating voltage of 2.0 to 2.8 V, and with a cobalt phthalocyanine catalyzed air electrode, good coulombic efficiency upon recharge over several cycles. The discharge mechanism was determined to be primarily the deposition of $Li_2O_2$ in a carbon-based air electrode.

We studied the effects of air cathode formulation and electrolyte composition on discharge capacity, rate capability, and rechargeability. To characterize the effects of cell formulation on the discharge reaction, we used techniques including static and dynamic gas consumption measurements and scanning electron microscopy (SEM).

## Experimental

Several different air cathode formulations were used for this study. Initial formulations were a hybrid $\lambda$-$MnO_2$/carbon air cathode based on polyvinylidene fluoride-hexafluoropropylene (PVDF) binder with a plasticizer to allow lamination of the cast cathode to a current collector grid. Subsequent formulations contained only carbon and polytetrafluoroethylene (PTFE) binder.

*PVDF air cathode formulation*.—Hybrid $\lambda$-$MnO_2$/carbon air cathodes were prepared by coating acetone slurries of $\lambda$-$MnO_2$, Super P carbon black, PVDF, and dibutyl phthalate (weight ratios: 19/11/15/55) on a glass plate. Cathode films with a dried thickness averaging 250 μm were used for this study. $\lambda$-$MnO_2$ was prepared by acid digestion of $LiMn_2O_4$ spinel[4,5] in a procedure previously reported.[6] $\lambda$-$MnO_2$ was incorporated to improve rate capability and served as an internal standard for characterizing air cathode performance. The cast film was cut into 5 $cm^2$ pieces and laminated to aluminum grids treated with a carbon/binder mixture that insures low grid to cathode contact resistance. The dibutyl phthalate was removed from the laminated cathode by extraction in methanol. The finished electrodes were 42% $\lambda$-$MnO_2$, 25% Super P, and 33% PVDF.

*PTFE air cathode formulation*.—Carbon air cathodes were prepared by mixing a 10 wt % PTFE emulsion (0.05 to 0.5 μm PTFE particles in water) with either Super P carbon black manufactured by M.M.M. Carbon Belgium, Shawinigan Black acetylene black manufactured by Chevron Phillips Chemical Company (SAB), or a 3:1 mixture of Black Pearls 2000 manufactured by Cabot Corporation and SAB (BP2000/SAB). The carbons were wet with a 1:2 isopropanol/water (v/v) mixture before the PTFE emulsion was added and the paste mixed with a spatula. The paste was mixed for 2 min then placed in a foil tray to dry under vacuum at 80°C. The dried paste was ground in a blender to form a fine powder. The powder was then dry pasted onto preweighed 5 $cm^2$ aluminum grids treated with a carbon/binder mixture that insures low grid to cathode contact resistance. Cathodes were cold pressed at 4000 psi for 2 min. Several groups of cathodes were further hot pressed at 250°C and 4000 psi for 2 min to improve electrode integrity. The finished electrodes were 91% carbon black and 9% PTFE with a thickness of 800 μm.

*Electrolytes*.—Propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), diethyl carbonate (DEC), dimethyl carbonate (DMC), $\gamma$-butyrolactone ($\gamma$-BL), tetrahydrofuran (THF), and tetrahydropyran (THP) from either Ferro Corporation or Aldrich were used to prepare electrolytes. Ferro Corporation solvents were used as received while the Aldrich solvents were dried to less than 20 ppm water using a molecular sieve. Hashimoto $LiPF_6$ salt was used to prepare 1 M electrolyte solutions. Electrolytes were prepared in a glove box with $<5$ ppm oxygen and $<1$ ppm water. Where electrolyte solvent mixtures are used, solvents are in a weight ratio of 1:1 unless specified otherwise.

*Cell construction and testing*.—Cathodes were dried under vacuum at 80°C for a minimum of 2 h. Cells were designed to be cathode limited. A nickel tab was used for the anode collector and an aluminum tab for the cathode collector. Cells were constructed by placing a dried cathode, Celgard 2300 separator, and a lithium foil pressed onto nickel grid, onto a 5 $cm^2$ polypropylene block. The air cathode was bound to the separator/anode/polypropylene block using insulated nickel wires. Cells were placed in foil laminate pouches and 5 g of electrolyte were added. 100 to 150 mL of ultrapure carrier grade $O_2$ was sealed in the pouch. Cell impedance was recorded after a minimum 1 h rest.

Cells were discharged at rates of 0.05, 0.1, 0.2, 0.5, and 1.0 $mA/cm^2$ to 2 V at ambient temperature after a 3 h rest period. For cycling studies, cells were charged and discharged at 0.1 $mA/cm^2$.

*Oxygen consumption*.—Several methods were used to measure oxygen consumption. The volume of each cell was measured before and after discharge using the Archimedes principle. Using each

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* Electrochemical Society Active Member.
z E-mail: jread@arl.army.mil

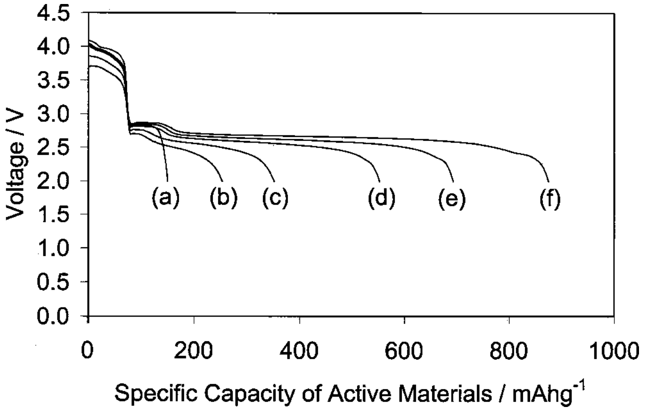

**Figure 1.** Specific capacity of active materials ($\lambda$-$MnO_2$ + Super P) in PVDF air cathodes. (a) Argon blank, (b) 1.0 mA/cm$^2$, (c) 0.5 mA/cm$^2$, (d) 0.2 mA/cm$^2$, (e) 0.1 mA/cm$^2$, and (f) 0.05 mA/cm$^2$.

cell's weight in air, corrections for pressure and temperature variations, and an estimated cell component volume, the change in oxygen volume at standard temperature and pressure (STP) was calculated. A value for mAh of discharge capacity per milliliter of oxygen consumed (mAh/mL $O_2$) was calculated for each cell discharged.

The consumption of oxygen during discharge and cycling was measured on selected cells using an apparatus that measures displacement of water. The apparatus consisted of a sealed vessel containing both the cell under study and water, a column of water connected to this vessel which is open to the atmosphere on one end, and a differential pressure sensor with one port open to the atmosphere. The output of the pressure sensor was connected to an auxiliary input of the battery cycler. The apparatus was placed in a 20°C controlled temperature chamber and equilibrated for 24 h before discharge or cycling.

## Results

As a matter of convention, the capacity of the lithium/oxygen discharge reaction for any particular cell has been normalized to the weight of carbon in the air cathode. This convention assumes that the products of the lithium/oxygen discharge reaction deposit only onto carbon. This assumption may not be true for cathodes that contain $\lambda$-$MnO_2$, as some of the discharge reaction may take place on the surface of $\lambda$-$MnO_2$.

*Rate studies (PVDF).*—Figure 1 shows the discharge behavior of the PVDF air cathode formulation in 1 M $LiPF_6$ PC:DME electrolyte at five different rates. This figure also shows a cell filled with argon instead of oxygen gas discharged at 0.1 mA/cm$^2$ to demonstrate the capacity obtained from $\lambda$-$MnO_2$ alone. Voltage is plotted *vs.* specific capacity of the active materials ($\lambda$-$MnO_2$ + Super P). Figure 2 shows the discharge behavior of Super P alone for these same cells. For this figure, the $\lambda$-$MnO_2$ capacity is removed and the remaining capacity is renormalized to the Super P weight. A value of 240 mAh/g is used for the specific capacity of the $\lambda$-$MnO_2$. Figure 3 shows the specific capacity of Super P, $\lambda$-$MnO_2$, and $\lambda$-$MnO_2$ + Super P as a function of discharge rate. The Super P specific capacity decreases dramatically as discharge rate increases while for $\lambda$-$MnO_2$ the specific capacity remains essentially constant with rate.

Figure 4, curve (a) shows how the value of mAh/mL $O_2$, from the air electrode reaction, varies with discharge rate. This curve was generated from oxygen volume measurements taken before and after discharge using the Archimedes principle. Using these values for mAh/mL $O_2$, one can calculate that the discharge product is 92% $Li_2O_2$ and 8% $Li_2O$ at 0.05 mA/cm$^2$ while it is 55% $Li_2O_2$ and 45% $Li_2O$ at 1.0 mA/cm$^2$. Oxygen volume was also measured during discharge using a displacement device. The values of mAh/mL $O_2$ determined from that data correspond well to those taken before and after discharge. During discharge, the consumption of oxygen did not start until almost all of the $\lambda$-$MnO_2$ discharge capacity was exhausted. Once oxygen consumption did start, the rate at which it was consumed is constant and independent of voltage.

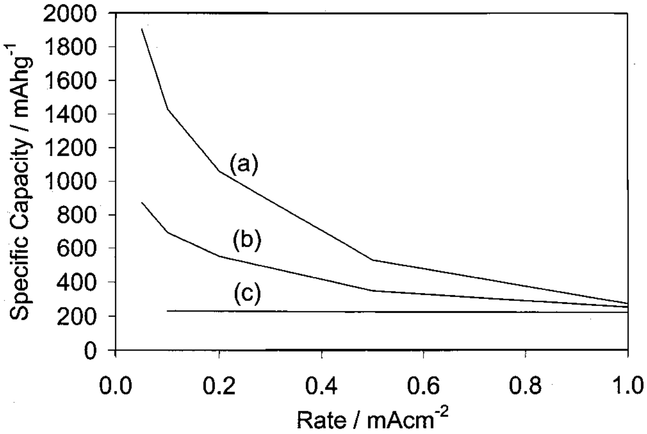

**Figure 3.** Rate curves for PVDF air cathodes (a) Super P, (b) $\lambda$-$MnO_2$ + Super P, and (c) $\lambda$-$MnO_2$.

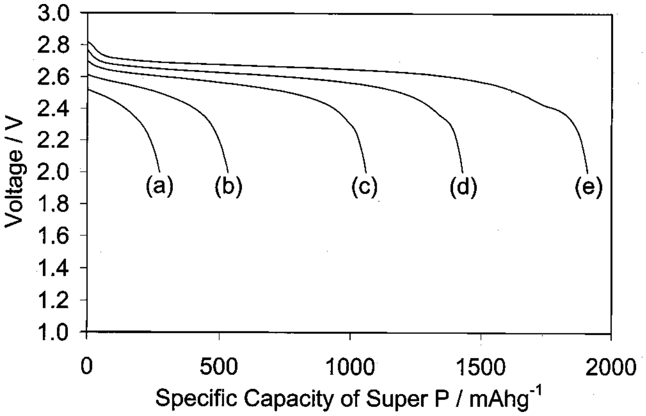

**Figure 2.** Specific capacity of Super P in PVDF air cathodes. (a) 1.0 mA/cm$^2$, (b) 0.5 mA/cm$^2$, (c) 0.2 mA/cm$^2$, (d) 0.1 mA/cm$^2$, and (e) 0.05 mA/cm$^2$.

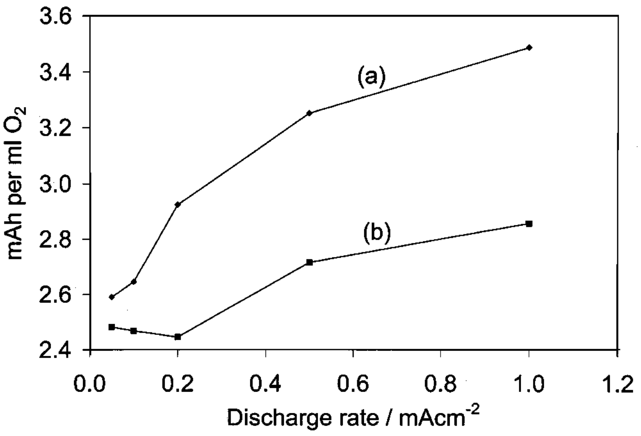

**Figure 4.** mAh/mL $O_2$ for (a) PVDF and (b) PTFE air cathodes.

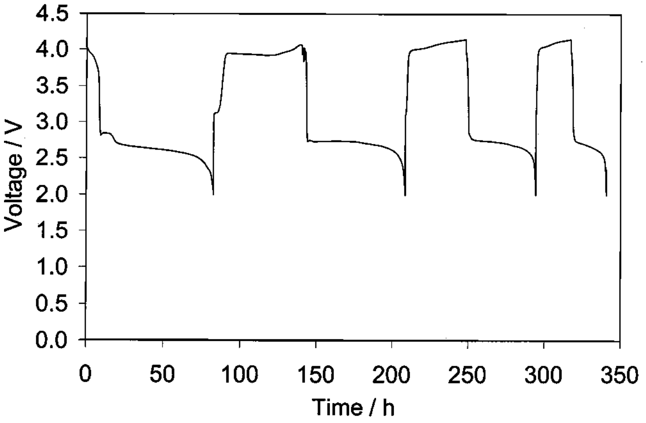

**Figure 5.** Voltage *vs.* time for PVDF air cathode cycling at 0.1 mA/cm$^2$.

*Cycling studies (PVDF).*—Figure 5 shows the cycling of a hybrid $\lambda$-$MnO_2$/carbon air cell in 1 M $LiPF_6$ PC:DME electrolyte between 4.15 and 2.0 V at 0.1 mA/cm$^2$. The cell discharges at about 2.7 V and charges at or above 4.0 V. The discharge plateaus typical of $\lambda$-$MnO_2$ disappeared after the second cycle. Cells cycled between 4.15 and 2.5 V behaved the same as those cycled between 4.15 and 2.0 V. Cells were cycled in both PC:DME and PC:DMC electrolytes.

Oxygen consumption and generation was measured during cycling in 1 M $LiPF_6$ PC:DME electrolyte between 4.15 and 2.0 V at a current density of 0.1 mA/cm$^2$. The results show $O_2$ gas being consumed during discharge and gas being generated during charge. The volume of gas consumed on discharge was within 10% of the volume of gas generated on charge for the first few cycles. As more cycles were carried out, the amount of gas generated on charge became significantly greater than that consumed on discharge. It is assumed that $O_2$ is being generated upon charge over the first few cycles, although analysis of the gas generated has not yet been performed.

*Electrolyte studies (PVDF).*—Table I shows how discharge capacity varies with electrolyte composition and discharge rate. The discharge capacity of the $\lambda$-$MnO_2$ component of the electrode is essentially constant as a function of electrolyte formulation and discharge rate and has been removed. The remaining capacity, attributable to the air electrode reaction, is normalized to the weight of Super P and is reported as mAh/g of Super P. Large performance differences are seen between the various electrolyte formulations with respect to the air electrode reaction.

Table I also shows how the value of mAh/mL $O_2$, from the air electrode reaction, varies with electrolyte formulation. A value of 2.4 for mAh/mL $O_2$ indicates the formation of $Li_2O_2$ while a value of 4.8 indicates $Li_2O$ is the discharge product. A value for percentage $Li_2O_2$ and percentage $Li_2O$ formed during discharge can be calculated from this mAh/mL $O_2$ value and is also given.

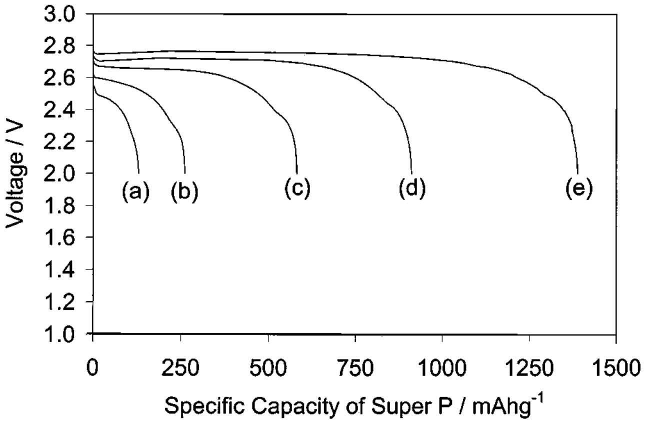

**Figure 6.** Specific capacity of Super P in PTFE air cathodes. (a) 1.0 mA/cm$^2$, (b) 0.5 mA/cm$^2$, (c) 0.2 mA/cm$^2$, (d) 0.1 mA/cm$^2$, and (e) 0.05 mA/cm$^2$.

Cell volumes were measured immediately after discharge and then 5 months after discharge to determine if any further reaction had taken place between the oxygen in the cell and lithium metal or between the electrolyte and the lithium peroxide or lithium oxide deposit. Cells were stored at ambient temperature. Cells discharged in 1 M $LiPF_6$ electrolytes of $\gamma$-BL, EC:DMC (2:1), PC:DME, and PC:THF did not gas during this period. Cells containing 1 M $LiPF_6$ EC:DMC (2:1) cycled between 4.15 to 2.0 V gained 10-15 mL in gas volume over this period. Cells containing 1 M $LiPF_6$ electrolytes of PC and PC:THP leaked after storage and could not be measured.

*Rate studies (PTFE).*—Figure 6 shows the discharge behavior of PTFE/Super P air cathodes in 1 M $LiPF_6$ PC:DME electrolyte. The cathodes used in this rate study were cold pressed at 4000 psi for 2 min. The discharge behavior is similar to the PVDF formulation with a large decrease in discharge capacity with increasing rate. The rate capability is reduced over that in the PVDF formulation (compare to Fig. 2).

Figure 4, curve (b) shows the values for mAh/mL $O_2$ consumed from these same cells. These values were calculated from volume measurements taken before and after discharge. The value for mAh/mL $O_2$ was similar to that found in the PVDF electrode at low rate but differed significantly at high rate. Oxygen consumption was also measured during discharge using the displacement device at several different discharge rates. The consumption of oxygen was constant throughout discharge regardless of cell voltage. The value for mAh/m $O_2$ calculated from least squares analysis of the oxygen volume *vs.* capacity data was within 1% of the value calculated from volume measurements taken before and after discharge using the Archimedes principle.

*Cycling studies (PTFE).*—Cells initially discharged at 0.05 mA/cm$^2$ in PC:DMC, PC:DEC, and PC:DME were recharged

**Table I. Specific capacity and mAh/mL $O_2$ for PVDF/Super P air cathodes.**

| Electrolyte formulation | Specific capacity (mAh/g) at rate (mA/cm$^2$) 1.0 | 0.2 | 0.05 | mAh/mL $O_2$ | Percent of $Li_2O_2$:$Li_2O$ |
|---|---|---|---|---|---|
| PC:$LiPF_6$ | 0 | 284 | 626 | 3.19 | 67:33 |
| $\gamma$-BL:$LiPF_6$ | 51 | 503 | 1184 | 2.84 | 82:18 |
| EC:DMC(2:1):$LiPF_6$ | 86 | 562 | 1369 | 3.06 | 72:28 |
| PC:DME:$LiPF_6$ | 280 | 1069 | 1934 | 2.48 | 97:3 |
| PC:THF:$LiPF_6$ | 328 | 1198 | 1911 | 2.22 | 100:0 |
| PC:THP:$LiPF_6$ | 192 | 899 | 1618 | leaker | leaker |

**Table II. Specific capacity and mAh/mL $O_2$ for PTFE air cathodes.**

| Carbon | Press method | Electrolyte formulation | Specific capacity (mAh/g) | mAh/mL $O_2$ |
|---|---|---|---|---|
| Super P | Hot | PC:EC:$LiPF_6$ | 380 | 2.69 |
| Super P | Hot | PC:DMC:$LiPF_6$ | 673 | 2.53 |
| Super P | Hot | PC:DME:$LiPF_6$ | 984 | 2.51 |
| Super P | Hot | PC:DEC:$LiPF_6$ | 1347 | 3.49 |
| SAB | Hot | PC:EC:$LiPF_6$ | 382 | 2.72 |
| SAB | Hot | PC:DMC:$LiPF_6$ | 736 | 3.66 |
| SAB | Hot | PC:DME:$LiPF_6$ | 764 | 2.49 |
| SAB | Hot | PC:DEC:$LiPF_6$ | 841 | 4.66 |
| BP2000:SAB | Hot | PC:EC:$LiPF_6$ | 511 | 2.73 |
| BP2000:SAB | Hot | PC:DMC:$LiPF_6$ | 626 | 3.07 |
| BP2000:SAB | Hot | PC:DME:$LiPF_6$ | 1086 | 2.47 |
| BP2000:SAB | Hot | PC:DEC:$LiPF_6$ | 1196 | 3.61 |
| Super P | Cold | PC:DEC:$LiCF_3SO_3$ | 1040 | 2.73 |
| Super P | Cold | PC:DME:$LiPF_6$ | 1388 | 2.48 |
| Super P | Cold | PC:DEC:$LiPF_6$ | 2120 | 4.02 |
| SAB | Cold | PC:DME:$LiPF_6$ | 975 | 2.49 |

at 0.05 $mA/cm^2$ to 4.15 V and gave only 1-2% of their discharge capacity back. Subsequent cycles gave even less capacity.

*Electrolyte/carbon black/process studies (PTFE)*.—Table II shows the discharge capacity per gram of carbon at 0.05 $mA/cm^2$ for PTFE cathodes prepared from three different carbon blacks. Cathodes were prepared using both the cold press and hot press methods. Five different electrolyte formulations were used with two different electrolyte salts.

Discharge capacity is most affected by the electrolyte formulation. Discharge capacity is ordered from highest too lowest as PC:DEC $>$ PC:DME $>$ PC:DMC $>$ PC:EC regardless of carbon black type or pressing method. The electrolyte salt also appears to affect discharge capacity as demonstrated by the difference between 1 M $LiCF_3SO_3$ PC:DEC and 1 M $LiPF_6$ PC:DEC. 1 M $LiPF_6$ PC:DEC consistently gives the best performance regardless of carbon black type or pressing method.

The method of electrode preparation clearly has a large effect on discharge capacity. Cold pressed electrodes performed significantly better than hot pressed electrodes regardless of carbon black type or electrolyte formulation. Two side effects of hot pressing at 250°C would be a reduction of the pore volume in the electrode and a degradation of the wetting agent (typically 6% of the PTFE weight) used in the PTFE emulsion.

The type of carbon black used has an effect on discharge capacity at 0.05 $mA/cm^2$. Each electrolyte appears to prefer a particular carbon black. PC:EC electrolyte performs best with BP2000/SAB while PC:DEC gives the highest discharge capacity with Super P. There does appear to be a specific interaction between the carbon black and the electrolyte, suggesting that wetting of the carbon black is an important factor in determining discharge capacity. The single point Brunauer-Emmett-Teller (BET) surface area reported for each carbon black, BP2000 (1475 $m^2/g$) $\gg$ SAB (75 $m^2/g$) $>$ Super P (62 $m^2/g$) cannot be used to predict the trend in discharge capacity.

Table II gives values for mAh/mL $O_2$ consumed for each cell calculated from volume measurements taken before and after discharge. The values for PC:EC and PC:DME are consistent among the three carbon black types, while for PC:DMC and PC:DEC the values appear to be erratic. When volume measurements taken one month after discharge were compared to ones taken immediately after discharge, it was found that cells discharged in PC:DMC and PC:DEC increased in volume while ones discharged in PC:EC and PC:DME did not change. This meant that the values for mAh/mL $O_2$ would be high for PC:DMC and PC:DEC and could not be trusted.

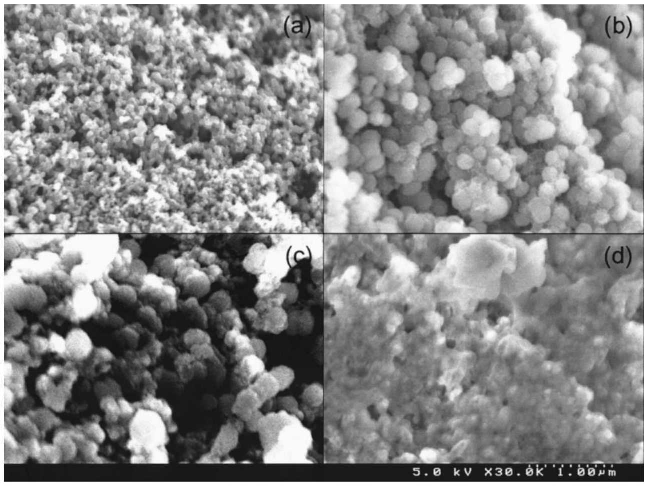

**Figure 7.** SEM micrographs of PTFE/Super P air cathodes (air side of electrode). (a) Undischarged and discharged at (b) 0.05 $mA/cm^2$, (c) 0.2 $mA/cm^2$, and (d) 1.0 $mA/cm^2$.

*SEM studies (PTFE and PVDF)*.—Figure 7 shows SEM micrographs of the airside of PTFE/Super P cathodes in PC:DME electrolyte under different discharge conditions. The individual particles of Super P are visible in the undischarged electrode with a primary particle size on the order of 50 nm. After low rate discharge at 0.05 $mA/cm^2$, the electrode surface contains spheres of $Li_2O_2/Li_2O$ discharge product with diam of 150-200 nm. After discharge at 0.2 $mA/cm^2$, the spheres on the surface appear to be larger at 300 nm and at 1.0 $mA/cm^2$ the deposit appears to be more of a film. Figure 8 shows how the deposit appears at the center of these same electrodes. The deposit in the center of the electrode is not visible at 1.0 $mA/cm^2$ and fills the pores in the center of the electrode at 0.05 $mA/cm^2$. The SEM micrographs of the lithium side of the cathode are nearly identical to those taken at the center of the cathode. The film formed on the air side of the electrode discharged at 1.0 $mA/cm^2$ appears to limit discharge in the interior of the electrode.

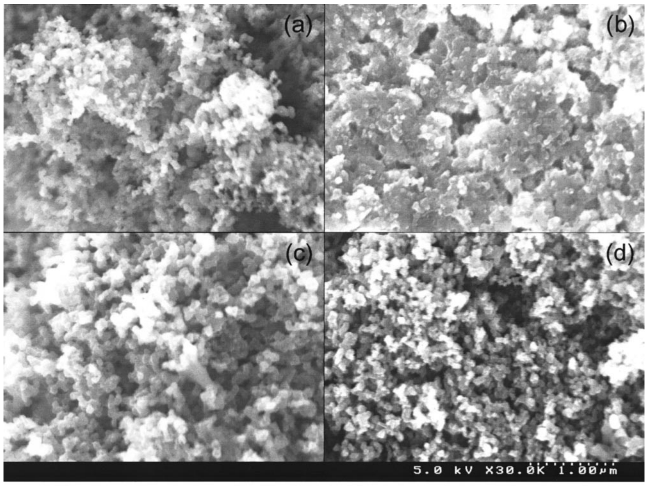

**Figure 8.** SEM micrographs of PTFE/Super P air cathodes (center of electrode). (a) Undischarged and discharged at (b) 0.05 $mA/cm^2$, (c) 0.2 $mA/cm^2$, and (d) 1.0 $mA/cm^2$.

SEM micrographs of discharged PVDF and PTFE electrodes show large differences in the amount of discharge product depending on electrolyte composition. For PTFE/Super P cells discharged in 1 M $LiPF_6$ PC:DME electrolyte at low rate, all of the pores visible in a fresh electrode appear to be filled and it is assumed that discharge ends because there are no pores left where discharge product can deposit. For PVDF/Super P cells discharged in 1 M $LiPF_6$ PC electrolyte, the deposit does not fill all of the pores in the electrode. In this case, the end of discharge might be the result of low porosity of the deposited film limiting access to the carbon black, low lithium ion conductivity through the film, or low electronic conductivity of the deposit itself.

## Discussion

The discharge reaction at the air cathode results in $Li_2O_2$ or $Li_2O$ being deposited on the carbon surfaces and in the pores of the electrode. Electrolyte formulation would be expected to influence the nature of the deposit itself as oxygen solubility, oxygen transport, and lithium ion conductivity are all defined by choice of electrolyte solvents and salts. Electrode thickness, electrode porosity, volume fraction of carbon black, and wetted surface area of carbon black should also influence where and how much deposition occurs. The effects that oxygen solubility, oxygen transport, and electrode morphology have on the deposition process should be most obvious at high rates of discharge, as under these conditions, large oxygen concentration gradients will be established in the cathode.

Electrolyte formulation has a strong influence on both discharge capacity and mAh/mL $O_2$ ratio. We try to correlate only two physical properties, oxygen solubility and lithium-ion conductivity, to the results. Oxygen solubility in the various electrolytes can be estimated from the literature for electrolytes containing the solvents PC, THF, THP, and $\gamma$-BL,[7] assuming that oxygen solubility is an additive property and that electrolyte salt has little effect on solubility. Using these estimated values, one can predict the trends in both discharge capacity and mAh/mL $O_2$. Higher oxygen solubility gives a higher discharge capacity and lower mAh/mL $O_2$ ratio, although the correlation between capacity and mAh/mL $O_2$ ratio is not perfect. Low oxygen concentration in the electrolyte would make the formation of $Li_2O$ preferred over that of $Li_2O_2$ thereby driving the mAh/mL $O_2$ ratio up from 2.4 for $Li_2O_2$ to 4.8 for $Li_2O$. Measurements of oxygen solubility on the specific electrolytes used in this study have not been performed at this time. Regardless of whether the electrode was formulated with PVDF or PTFE, Super P or BP2000, hot pressed or cold pressed, for 1 M $LiPF_6$ PC:DME, the mAh/mL $O_2$ ratio does not change at low rate. It suggests that at low rate, this ratio is only a function of electrolyte formulation. The lithium-ion conductivity for electrolytes used in this study vary from 1.5 mS/cm for 1 M $LiCF_3SO_3$ PC:DEC to 14.8 mS/cm for 1 M $LiPF_6$PC:DME. The conductivity values do not correlate with the trend in discharge capacity or mAh/mL $O_2$.

Differences in discharge capacity may also be due in part to differences in the ability of electrolyte to wet the carbon black surface. This is suggested by the PTFE air electrode data where particular electrolytes prefer specific carbons and where cold pressed electrodes that contain wetting agent perform significantly better than hot pressed electrodes. If more carbon black surface area is wet with electrolyte, more discharge capacity would be expected. The BET surface area does not correlate with discharge capacity, at least for the carbon blacks used in this study. This suggests that the surface area wetted by electrolyte is very different than the surface area determined by BET. In fact, the carbon black with the lowest BET surface area gives the highest discharge capacity at low rate.

SEM micrographs demonstrate how the deposition of discharge product is affected by electrolyte formulation. Electrodes discharged at low rate in 1 M $LiPF_6$ PC:DME have pores that are completely filled with deposit whereas cells discharged in 1 M $LiPF_6$ PC have large amounts of pore volume left. The deposits that result from the different electrolytes must therefore be different in some significant way, possibly in porosity or conductivity. One interesting observation from the SEM images of the air side of these discharged cathodes is how round and smooth the spherical deposits appear to be. The smooth nature of these deposits suggests that new discharge product deposits on the surface of older deposits. This could only occur if (*i*) $Li_2O_2$ or $Li_2O$ is partially soluble in the electrolyte, or (*ii*) the peroxide ion can migrate from the surface of the carbon black after being formed to the surface of the deposits, or (*iii*) the deposit itself is capable of catalyzing oxygen reduction.

When comparing results for PVDF and PTFE cathodes containing Super P and 1 M $LiPF_6$ PC:DME, performance differences are observed that can be related to physical differences in the air electrode formulations. The difference in specific capacity at low rate can be explained by examining the ratio between the available pore volume for $Li_2O_2/Li_2O$ deposition and the amount of carbon black in the formulation. The pore volume calculated for the PVDF air cathodes using DBP volume fraction and that calculated from electrode density in the hot pressed PTFE cathodes are almost identical at 73%. The value of pore volume (mL) to Super P weight (g) is 4.6 mL/g in PVDF cathodes and 1.9 mL/g in PTFE cathodes. If the available pore volume determines discharge capacity per gram of carbon, then the PVDF electrodes should have a discharge capacity 2.4 times that of the PTFE electrodes. The ratio observed is 2.0 (1934 mAh/g to 984 mAh/g). The calculated discharge capacity based on available pore volume and a deposit of $Li_2O_2$ with a density of 2.3 g/mL is roughly five times higher than the actual discharge capacity. This suggests that the available pore volume may only influence discharge capacity per gram of carbon black. The differences in specific capacity at higher rates could be the combination of a thicker PTFE electrode and a higher density of carbon black in that PTFE electrode. SEM micrographs show that at high rates of discharge, the surfaces of the air electrode become closed off by discharge product. Since the PTFE electrode has a higher density of carbon black at the surface, it will be more prone to this problem under high rates of discharge. The transport of oxygen into the interior of the electrode will also be more restricted when using a thicker electrode. The difference in mAh/mL $O_2$ ratio at higher discharge rates, shown in Fig. 4, can also be explained by physical differences in the air cathodes. The general trend of increasing mAh/mL $O_2$ ratio with increasing discharge rate may be related to oxygen solubility in the electrolyte. As discharge rate increases, the oxygen concentration in the electrolyte will drop, and $Li_2O$ should preferentially be formed. The fact that the $1.0\ mA/cm^2$ value for mAh/mL $O_2$ is much higher in PVDF electrodes than PTFE electrodes is most likely related to the ability of the PVDF electrode to sustain a higher rate of discharge due to a lower volume fraction of Super P. With a lower volume fraction of Super P, 8% *vs*. 20%, it is more difficult to form a continuous film at the air side of the electrode and prevent discharge of the interior. The PVDF electrode is essentially able to discharge at a lower oxygen concentration as a result of the physical properties of the electrode.

No satisfactory explanation can be given at this time for the difference in reversibility between the two formulations. The only obvious difference between the two formulations is the presence of $\lambda$-$MnO_2$ in the PVDF cathodes. The cycling capacity appears to be mainly due to the air electrode reaction. The inability to cycle at a significant capacity beyond 4-5 cycles may result from the inability to reversibly strip $Li_2O_2$ or $Li_2O$. The disappearance of the $\lambda$-$MnO_2$ discharge plateaus may indicate that the surface of the $\lambda$-$MnO_2$ is becoming passivated with discharge product from the air electrode reaction.

## Conclusions

Electrolyte formulation has the largest influence on cell performance and presumably on the nature of the deposit formed during discharge. Oxygen solubility in the electrolyte is correlated to discharge capacity. Electrolytes with high oxygen solubility result in cells with high discharge capacity and lower mAh/mL $O_2$ ratios.

From the PTFE electrode data it is apparent that particular electrolytes prefer particular carbons. One would conclude that the ability of an electrolyte to wet a particular carbon is an important factor in determining cell capacity.

The air electrode's physical properties, its thickness, porosity, and volume fraction of carbon black appear to be significant factors in determining cell performance. The discharge capacity per gram of carbon is affected directly by the ratio of pore volume to carbon black weight. The deposition of discharge product at the surface of the air electrode at high rate appears to limit discharge capacity by preventing access to the interior of the electrode. The BET surface area of the carbon black does not appear to be an important factor in determining discharge capacity, although wetted surface area may be important. The presence of $\lambda$-$MnO_2$ appears to facilitate reversibility of the air electrode reaction.

The ratio of $Li_2O_2$ to $Li_2O$ deposited is a function of discharge rate and electrolyte formulation. This can be understood from the standpoint that lower oxygen content in the electrolyte results in the preferential formation of $Li_2O$.

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