We have employed the rotating ring disk electrode (RRDE) technique to study the oxygen reduction reaction (ORR) on gold and glassy carbon electrodes in dimethyl sulfoxide (DMSO) electrolytes containing lithium salts. At the gold ring electrode at 3.0 V vs. Li/Li+ (0.1 M LiPF6) soluble superoxide radical anion undergoes oxidation to O2 under convective-diffusion conditions. For both glassy carbon and gold cathodes, typical oxygen reduction current-potential curves are sensitive to rotation speed and undergo a maximum and further electrode passivation by formation of Li2O2 while the Au ring electrode currents follow the same peak shape with detection of soluble superoxide at the ring downstream in the electrolyte solution. Unlike the behavior in acetonitrile-lithium solutions, LiO2 is more stable in DMSO and can diffuse out in solution and be detected at the ring electrode. While in cyclic voltammetry both time and potential effects are convoluted, we have carried out RRDE chrono-amperometry experiments at the disk electrode with detection of superoxide at the Au ring so that thus potential and time effects were clearly separated. The superoxide oxidation ring currents exhibit a maximum at 2.2 V due to the interplay of O2- formation by one-electron O2 reduction, Li2O2 disproportionation and two-electron O2 reduction.

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Electrochemical experiments.— Electrochemical experiments were performed in an air-tight acrylic box filled with Ar and dried with phosphorous pentoxide keeping a positive pressure by a stream of dry oxygen (see SI). The motor controller, motor and disk and ring mercury contacts in the bearing block are located outside the air-tight acrylic box and sealed with a rubber ring with a permanent flow of dry oxygen in the box. The electrochemical cell and RRDE cylinder immersed in the aprotic electrolyte were kept inside the box. This box contained the four-electrode glass cell and the electrolyte was fed from bottles filled in the glove box by a system needles and Teflon tubes without contact with the atmosphere. Large area platinum gauze was used as counter electrode in a compartment separated from the main compartment by a fritted glass.

A non-aqueous Ag/AgCl reference electrode was prepared by placing a silver wire in a fritted glass compartment filled with a 0.01 M AgNO₃ solution in acetonitrile (0.1 M of tetra butyl ammonium hexafluorophosphate was added to the solution to increase conductivity). The reference electrode was calibrated with respect to Li/Li⁺ couple, that is commonly used as reference in Li-air battery studies. Inside the argon glove box, a Ag/AgCl electrode and a 3.2 mm diameter Li wire (99.9% trace metals basis ALDRICH) were placed in a beaker filled with 0.1 LiPF₆ in DMSO and the cell potential was measured with a high impedance voltmeter obtaining 3.7 V. It is worth mentioning that the potential measured between the same electrode and Li metal in a 0.1 M LiPF₆ solution in acetonitrile was 3.23 V that is 0.47 V lower than in DMSO solution. This difference is explained by an important Li⁺ solvation energy difference between DMSO and acetonitrile. Further potential calibration was done with ferrocene in DMSO solution.

Several rotating ring disk electrode systems have been employed as shown in Table I. In all cases both disk and ring were embedded in Araldite epoxy resin cylindrical body (Ciba-Geigy).

The geometrical area of the disk electrode was in all cases 0.196 cm². The geometric collection efficiency was calculated using the Albery-Hitchman theory⁴ and experimentally verified with the Fe(CN)₆³⁻/⁴⁻ redox couple in a galvanostatic experiment. Soluble superoxide was detected at the ring electrode by convective-diffusion oxidation current at ER = 3.0 V vs Li/Li⁺ in DMSO. In previous experiments we have employed a platinum ring but a residual ring current was detected due to the electrochemical oxidation of DMSO so that a gold ring was employed in the present study (GC/Au and Au/Au RRDE).

Results and Discussion

The electrochemical behavior of the ORR in Li⁺ ion containing DMSO electrolyte shows cathodic currents that reach a peak which increases with rotating frequency but are below the convective-diffusion Levich current:⁵,⁶

\[ I_L = 1.554nFAD^{2/3}ν^{-1/6}C_{O_2} W^{1/2} \]  

where F is the Faraday constant, n the number of electrons per O₂ molecule, A the electrode geometric area, D₀₂ the O₂ diffusion coefficient in DMSO, cₐ 1.67 × 10⁻⁵ cm² s⁻¹, C₀₂ = 2.1 × 10⁻⁵ M⁻¹ the kinematic viscosity, ν = 0.0019 cm² s⁻¹, A = 0.2 cm², and W (f = 2πω) the rotation frequency in Hz. For n = 1 the expected values at 2 Hz (120 rpm) and 25 Hz (1500 rpm) are respectively 170 and 600 μA respectively.

Figures 1 and 2 depict the cyclic voltammogram of a Au and GC electrodes respectively in oxygen saturated 0.1 M LiPF₆ solution at a sweep rate of 100 mV s⁻¹ when the electrode potential was linearly scanned between 4.7 to 1.9 V at 100 mVs⁻¹. In the reducing sweep current maxima are apparent with further passivation of the electrode.

The corresponding convective-diffusion soluble superoxide oxidation current at the Au ring electrode simultaneous to the ORR are shown in the upper panels of Figures 1 and 2 for Au and GC disks electrodes respectively. Both disk and ring currents increase with rotation frequency and ring current maxima at 2.1 and 2.3 V respectively for Au and GC disk electrodes are observed (upper panel in Figs. 1 and 2). These results are consistent with previous reports.⁵,¹⁰

It should be noted from Figures 1 and 2 that glassy carbon is less reactive than gold with lower peak current at the same rotation speed. However, lower polarization and higher yield of superoxide are observed for glassy carbon. This may be due to the interaction of insoluble Li₂O₂ with the respective surfaces. On HOPG for instance the lithium peroxide deposits first at terrace edges and the surface is never totally passivated unlike gold.²⁵ The type of electrode surface may play an important role on the formation of solid insoluble lithium peroxide and surface passivation by the insulating

Table I. Geometric dimensions of RRDE used and the respective calculated and experimental collection efficiencies

<table>
<thead>
<tr>
<th>Electrode</th>
<th>r₁ (μm)</th>
<th>r₂ (μm)</th>
<th>r₃ (μm)</th>
<th>No Calc.</th>
<th>No Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC/Au</td>
<td>0.25</td>
<td>0.26</td>
<td>0.31</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Au/Au</td>
<td>0.25</td>
<td>0.26</td>
<td>0.30</td>
<td>0.29</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Figure 1. O₂ reduction polarization curve on a Au disk electrode in O₂ (1 atm) saturated 0.1 M LiPF₆ in anhydrous DMSO at W = 2, 4, 9, 16 and 25 Hz (ω = 60 W, in rpm) and scan rate of 0.1 V s⁻¹ (lower panel) and O₂⁺ oxidation Au ring currents at ER = 3 V (upper panel). A₀ = 0.2 cm².

Figure 2. Cyclic voltammogram of a GC/Au RRDE at 0.1 V s⁻¹ in O₂ (1 atm) saturated 0.1 M LiPF₆ in DMSO under convective-diffusion regime at W = 2, 4, 9, 16 and 25 Hz (ω = 60 W, in rpm) (lower panel) and O₂⁺ oxidation Au ring currents at ER = 3 V (upper panel). A₀ = 0.2 cm².
Peroxide. Possibly soluble lithium superoxide forms at the carbon surface which is not covered by lithium peroxide and thus a larger yield of soluble superoxide is collected at the ring electrode for glassy carbon.

It is noteworthy that in acetonitrile no soluble superoxide can be detected in 0.1 M lithium containing solutions with the rotating ring disk electrode; however addition of only 0.1 M DMSO to 0.1 M LiClO4 in acetonitrile yields soluble O2− which can be detected at the ring electrode due to the preferential solvation of Li+ which stabilizes soluble O2− from disproportionation.15

The ring current maxima indicates that the surface concentration of soluble O2− increases the larger the ORR overpotential and then decreases due to either disproportionate or a two electron transfer to O2 from the electrode, according to the accepted mechanism:5,9,13,26,27

\[
O_2 + Li^+ + e^- \rightarrow [O_2Li]_{surf} \quad [2]
\]

\[
[O_2Li]_{surf} + [O_2Li]_{surf} \rightarrow Li_2O_2 + O_2 \quad [3]
\]

\[
[O_2Li]_{surf} + Li^+ + e^- \rightarrow Li_2O_2 \quad [4]
\]

Since the ORR product Li2O2, is insoluble27 blocking the electron transfer at the electrode surface is observed in the reverse scan both on disk and ring electrodes. We have investigated the removal of oxygen reduced species from the electrode surface by exploring different potential windows as shown in Figure 3. When opening the potential window to 4.7 V for 10 seconds (panel A), the second potential scan shows complete recovery of both disk and Au ring currents. Panel B shows that starting the potential sweep at 3.8 V after a 10 second oxidation, subsequent lower cathodic currents are observed at disk and ring electrodes because of partly blockage by remaining oxygen reduction products on the surface. Finally, if we restrict the positive potential limit to 3 V for 10 seconds, the GC disk electrode surface is completely blocked with negligible disk and ring currents. These results are consistent with previous reports from Abraham10 and the IBM group,28 and also with recent surface morphology study by AFM on highly oriented pyrolytic graphite (HOPG).25 Electrochemical quartz crystal microbalance (EQCM) on Au and X-Ray Photoelectron Spectroscopy (XPS)29 experiments on HOPG and Au during oxygen reduction in LiPF6 in DMSO.

The oxidation and removal of LiO2 and Li2O2 and solvent and electrolyte decomposition products extends over a wide potential range30 as can be seen from the anodic current in Figure 3A due to side reactions of Li2O2 with the solvent and electrolyte salt. Therefore, in order to obtain a reproducible fresh surface for each new experiment we have applied a high oxidation over potential where most ORR species at the surface are removed. A potential larger than 4.2 V is necessary to fully oxidize surface species formed during cycling. It should be mentioned that above 4.3 V oxidation of DMSO on Au has been observed by SNIFTIRS experiments in 0.1 M LiPF6 in DMSO with detection of dimethyl sulfone.14 We have thus adopted as a pretreatment of the GC and Au surfaces an oxidation potential of 4.2 V during 60 seconds and found then reproducible cyclic voltammetry curves for the ORR in DMSO/LiPF6.

Since both potential and time are convoluted in the potential sweep experiments described, we have studied RRDE chronoamperometric transients for potential steps at the disk electrode from the positive potential limit (4.2 V) to different final electrode potentials in the ORR potential region. To our best knowledge these are the first experimental evidence of RRDE transient experiments of oxygen cathodes in lithium containing aprotic solvents.

Figures 4 and 5 depict typical disk and ring current transients for Au/Au and GC/Au electrodes RRDE electrodes at selected potentials in the ORR potential window. On both surfaces, the disk currents drop as the surface is progressively passivated by ORR insoluble products as confirmed by the mass uptake in EQCM experiments (see Figure 6 below). The ORR currents, I, can be corrected by the oxygen concentration depleted at the surface:

\[
C_{O2}^t = C_{O2}^\infty \left(1 - \frac{I}{I_{Lim}}\right) I_{Lim} \quad [5]
\]

where superscripts s and ∞ stand for surface and bulk O2 concentrations respectively, and the \(I_{Lim}\) is the respective Levich convective-diffusion limiting current at 9 Hz (540 rpm) (c.a. 720 μA.cm−2) for the two-electron O2 reduction to Li2O2.

The soluble superoxide oxidation ring currents recorded simultaneously exhibit a peak at the different disk electrode potentials which reflect the outward flux of soluble LiO2 from the disk into the electrolyte. The time evolution for these transients (c.a. >1–10 s) is much longer than the transient time for the convective-diffusion flux from disk to ring, c.a. 300 ms at 9 Hz (540 rpm)31,32 so that the transient reflects the flux on the disk surface. Notice that the ring currents are lower than the expected values from the geometric respective collection efficiency factors since most of the charge is accumulated on the
Figure 4. Chrono-amperometric transients for the reduction of O$_2$ on a RRDE Au disk electrode at 2.3, 2.2, 2.1 and 2.0 V in 0.1 M LiPF$_6$ in anhydrous DMSO at $W = 9$ Hz (540 rpm) (lower panel) and scan and O$_2^-$ oxidation Au ring transient current at $E_R = 3$ V (upper panel). $A_D = 0.2$ cm$^2$, $N_o = 0.28$. Potential step at the disk electrode from 4.2 V to the values indicated in each panel.

disk electrode surface as Li$_2$O$_2$ and detected as a mass gain in EQCM experiments.

The disk current decay corresponds to the electrochemical reduction of O$_2$ on the Au partly covered by an insoluble Li$_2$O$_2$ deposit that progressively blocks electron transfer at the surface. The ORR constant disk current decreases the higher over potential and suggests that the oxygen reduction still can proceed on a Li$_2$O$_2$ thin film but at a lower rate until a critical peroxide film thickness is reached.

The electrochemical quartz crystal microbalance (EQCM) offers the unique possibility to measure the mass deposited in comparison with the charge passed, thus enabling the distinction between different molar masses deposited per Faraday of charge. Furthermore, neutral molecules like solvent can be detected if co-deposited on the surface. In a recent communication$^{33}$ we have suggested the co-deposition of solvent from EQCM evidence of mass per electron deposited much larger than any value expected from reactions.$^{2–4}$ This has been interpreted by the uptake of strongly bound DMSO to lithium ions when Li$_2$O$_2$ is deposited from oxygen reduction in DMSO based electrolyte.

EQCM experiments show that the Li$_2$O$_2$ is in the order of micrograms per square centimeter, much larger than expected coverage for a lithium peroxide monolayer,$^{24}$ c.a. 260 μC.cm$^{-2}$ or 135 ng.cm$^{-2}$. Since lithium peroxide is an insulator, the flux of electrons from the underlying substrate across the Li$_2$O$_2$ film to the O$_2$ molecules adjacent to the surface would limit the ORR. As the poorly conducting film thickness increases charge transport through the growing Li$_2$O$_2$ film to the Li$_2$O$_2$-electrolyte interface is limited$^{15}$ and the O$_2$ current drops to zero at a critical thickness.

It is interesting to compare simultaneous disk and ring electrode current transients at potentials where O$_2$ reduction takes place. While the disk current decays monotonously, the ring current transient shows a maximum at short times. The ring currents are always a small fraction of the geometric collection efficiency so that the fraction of soluble superoxide is very small. Most of the superoxide formed by the reduction of oxygen results in the deposit of insoluble Li$_2$O$_2$ and only a small fraction can be collected at the ring electrode downstream. Furthermore, the ring peak current for the collection of superoxide ion under convective-diffusion conditions at constant disk potential exhibits a disk electrode potential dependence and goes through a maximum as shown in Figure 7. The maximum ring current at 2.2 V can be explained by the interplay between the buildup of surface O$_2^-$ concentration at the disk electrode with further bimolecular disproportionation (eqn. 3) at low cathodic over potentials or direct two electron reduction at higher over potentials:

$$O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2 \downarrow$$  

These processes are summarized in the following scheme, where $Z = 1.4554$ D$_{O_2}$/$\nu^{1/2}$ or $135$ ng.cm$^{-2}$ if $\nu$ is expressed in Hz.

While in Figures 1 and 2 the ring current shows a peak with potential, this is convoluted with time since the potential varies linearly

[6]
Figure 5. Chrono-amperometric transients for the reduction of O₂ on a RRDE GC disk electrode at 2.4, 2.35, 2.30 and 2.20 V in 0.1 M LiPF₆ in anhydrous DMSO at W = 9 Hz (540 rpm) (lower panel) and scan and O₂⁻ oxidation Au ring transient current at Eᵣ = 3 V (upper panel). A₉₀ = 0.2 cm², No = 0.32. Potential step at the disc electrode from 4.2 V to the values indicated in each panel.

Figure 6. Chrono-amperometric transients for the reduction of O₂ on a Au coated quartz disk electrode at 2.0 V in 0.1 M LiPF₆ in anhydrous DMSO (solid line) and simultaneous EQCM mass gain (Δm/A).

Figure 7. O₂⁻ oxidation Au ring current at the peak for different Au disk electrode potentials for data in Figure 4.
$Li_2O_2 + O_2$

$O_2 + Li^+ + e \rightarrow [O_2]_{DMSO}^{2-} + e + Li^+ \rightarrow Li_2O_2$

$ZW^{1/2}$

Scheme I. Scheme of reaction.

with time. It noteworthy in Figures 4 and 5 at 2.3 and 2.2 V the ring currents have dropped to zero there still is a disk current. Therefore at short times oxygen reduction results in soluble superoxide detected at the ring and insoluble lithium peroxide deposited at the disk as shown by the EQCM, but at longer times the collection of superoxide at the ring vanishes completely while the disk still records oxygen reduction cathodic current. Therefore there is a branching point as shown in the Scheme I. We, thus speculate that at longer times either dismutation or 2-electron O2 reduction prevails over the one-electron reduction to peroxide. Another possible interpretation could be that the soluble superoxide is produced at the bare electrode while oxygen reduction still takes place on the covered Li2O2 patches. The ring current is always less than the value expected for the quantitative collection of superoxide formed on the ring, i.e. $I_e N_e$, while the EQCM detects solid deposit with a mass per electron larger than 39 g per Faraday expected for Li2O2 deposit or 23 g per Faraday expected for Li2O2 and this has been interpreted as co-deposition of solvent13 which undergoes further decomposition by contact with lithium peroxide as seen from XPS evidence.9

Conclusions

We have studied the O2 reduction reaction (ORR) on gold and glassy carbon electrodes in LiPF6 electrolyte in DMSO solutions using the rotating ring disk electrode. With the Au ring soluble superoxide radical anion produced by one-electron reduction of O2 has been detected by electrochemical oxidation at 3.0 V vs. Li/Li+ in DMSO under convective-diffusion conditions. Only a small fraction of the O2 flux at the disk electrode results in soluble superoxide collected at the ring.

For both glassy carbon and gold cathodes, typical oxygen reduction current-potential curves are sensitive to rotation speed and undergo a maximum with passivation by formation of a thick Li2O2 deposit while the Au ring electrode currents follow the same peak shape with detection of superoxide at the ring downstream the electrolyte solution.

Chrono-amperometric transients at the RRDE allowed to distinguish time and potential effects on the disk and ring currents. A small fraction of the stable Li2O2 thus diffuses out in solution and is detected at the ring electrode at short times. This ring current peak shows a maximum yield of soluble superoxide which depends on the disk electrode potential.

Both the preferential solvation of Li+ in DMSO electrolyte with stabilization of soluble O2− and the disproportionation of adsorbed superoxide assisted by the conductive electrode surface are relevant to the lithium air battery technology.

Acknowledgment

Financial support from ANPCyT PICT grant No. 2037/2008 and FS-Nano 07 are greatly acknowledge. WT and AT acknowledge research scholarships from CONICET (Argentina).

Abbreviations

Cyclic Voltammetry, CV; Rotating Disk Electrode, RDE; Rotating Ring Disk Electrode, RRDE, Oxygen Reduction Reaction, ORR; Electrochemical Quartz Crystal Microbalance, EQCM.

References