In the present study, we investigated the reduction and the evolution of oxygen from lithium containing DMSO based electrolytes at gold. The number of electrons that are transferred per \( \text{O}_2 \) (\( z \)-value) during oxygen reduction depends on the structure of the electrode: Despite the presence of \( \text{Li}^{+} \), \( \text{O}_2 \) is reduced electrochemically to superoxide at smooth gold electrodes and at low overpotentials. At porous electrodes a \( z \)-value close to 2 \( e^-/\text{O}_2 \) indicates \( \text{Li}_2\text{O}_2 \)-formation even at low overpotentials. This is ascribed to a reaction of superoxide, which is catalyzed by gold-particles at open circuit. This behavior is also responsible for the non-proportionality between reduced and evolved amounts of oxygen. Furthermore, we observed a linear relationship between evolved amounts of \( \text{CO}_2 \) and reduced amounts of oxygen, indicative for electrolyte decomposition during oxygen reduction. Combined electrochemical quartz crystal microbalance (eQCMB) and Differential electrochemical mass spectroscopy (DEMS) measurements reveal that mass changes that occur in the anodic sweep are due to the evolution of \( \text{CO}_2 \), whereas oxygen evolution takes place without any mass changes. The observed mass changes (mass changes per transferred electron) are affected by convection due to the formation of soluble reduction products which observed in rotating ring disc electrode measurements.

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It is common knowledge that, in order to electrify automotive traffic, portable storage systems for electrical energy are required. For the time being lithium-ion-batteries are the most promising candidates for a real life technical application. However, due to the requirement of heavy metal oxides as cathode material their specific energy density is too low to replace current fuels.\(^1\) Due to the low weight and very negative standard potential of lithium, a lithium-oxygen battery has, in theory, a specific energy density of 13.8 \( \text{kJ/g} \) (considering the weight of the discharged state and the formation of \( \text{Li}_2\text{O}_2 \) rather than \( \text{Li}_2\text{O} \)) and a theoretical electrochemical efficiency of 90.2\% as can easily be calculated from thermodynamics\(^2,3\) (10\% of the energy is lost due to the heat flow caused by the entropy).

It is in general accepted that reduction of oxygen in \( \text{Li}^+ \)-containing organic solvents yields \( \text{Li}_2\text{O}_2 \) as a reaction product.\(^4,5\) The process of \( \text{Li}_2\text{O}_2 \) formation in DMSO seems to be unique as it involves the formation of a superoxide intermediate.\(^4,5\) This has not only been shown by CV and rotating ring disc electrode (RRDE) measurements but also by combining electrochemistry with spin-trap experiments and EPR-spectroscopy\(^6\) as well as by DEMS experiments.\(^7\) The remarkable stability of superoxide, despite the presence of \( \text{Li}^+ \)-cations, was ascribed to the large donor number of DMSO\(^4,5\) of nearly 125 \( \text{kJ/mol} \) as compared to acetonitrile with a donor number of 58.9 \( \text{kJ/mol} \).\(^8\) In the latter solvent superoxide intermediates have not been reported so far. However, whether \( \text{Li}_2\text{O}_2 \) forms via lithium induced disproportionation of superoxide or via a direct electrochemical transfer of two electrons depends also on the electrode material: At gold and low over-potentials oxygen is reduced to superoxide, whereas at rhodium direct peroxide formation takes place even at low overpotentials.\(^7\) At glassy carbon both the direct and indirect pathway of peroxide formation take place in parallel irrespective of the applied potential. The formation of superoxide and the formation of peroxide are inner sphere reactions, where the reactants need to adsorb at the electrode surface prior to any charge transfer.\(^7\) The difference in the reaction mechanism of oxygen reduction at gold and glassy carbon might explain why Li-air batteries employing gold sputtered cathodes show superior performance over those electrodes that employ carbon cathodes.\(^9,10\)

Differential electrochemical mass spectroscopy (DEMS) was employed to show that oxygen reduction in DMSO based electrolytes has a true coulombic efficiency (i.e. the ratio of reduced to evolved oxygen) of less than 100\%.\(^6,7\) Similar results were also presented by Peng et al.\(^9\) Although the authors of that particular paper did not discuss that their DEMS measurements show that more oxygen is consumed during the cathodic scan than evolved in the subsequent anodic scan the fact remains.

Electrochemical quartz crystal micro balance (eQCMB) measurements produced largely contradicting results. Jie and Uosaki found that \( z \) per transferred mol of electron 7–37 \( \text{g/mol of mass were deposited during oxygen reduction.}^{20}\) Torres et al. found 60 to 175 \( \text{g/mol} \)\(^21\) while Sharon et al. found nearly 23 \( \text{g/mol} \).\(^22\) However, in none of the aforementioned studies the potential region of oxygen evolution was discussed. Only very recently Torres et al., employing the more elaborate impedance analysis technique, found a slight decrease of mass in the potential region of oxygen evolution via eQCMB. Yet, this decrease does not account for mass changes observed in the potential region of oxygen reduction.\(^23\)

In the present study we employ RRDE and DEMS in combination with the eQCMB to gain a better understanding of the oxygen reduction and subsequent oxygen evolution from lithium containing DMSO based electrolytes. We try to resolve the different observations by eQCMB in the potential region of oxygen reduction and we discuss the potential region of oxygen evolution in detail. In addition, we will follow up on one of our own papers\(^18\) and will discuss apparently contradicting differences between smooth and porous Au-electrodes in two of our publications. At porous electrodes the number of electrons transferred per oxygen is higher than at smooth electrodes when low overpotentials are applied.\(^7,18\)

**Experimental**

**Chemicals, materials and electrolyte.**—Battery grade LiClO\(_4\) was purchased from Sigma Aldrich and was of 99.99% purity. Tetrabutyl ammonium perchlorate (TBAClO\(_4\)) was purchased from Sigma Aldrich and was of 98% purity. Extra dry DMSO stored over molecular sieves (3 Å) was obtained from Acros Organics and was of 99.7% purity. All electrodes in the present study were made from gold. Argon, oxygen and a 80:20 mixture of argon and oxygen were obtained from Air Liquide. All gases were of 99.999% purity. A mixture of 10% oxygen in 90% argon was used in RRDE measurements. This mixture was prepared by adjusting the flow of argon and oxygen correspondingly by the use of two flow metes.

Gold sputtered quartz crystals used for the eQCMB measurements were either obtained from Indomet GmbH or from Quartztechnik Dana GmbH. Crystals from the first mentioned manufacturer were used in combination with the dual thin layer cell (diameter: 14 mm, 6 MHz). Crystals from the second manufacturer were used in quartz solution (diameter: 25.4 mm, 5 MHz). The control unit used for the eQCMB measurements was purchased from Genev Instruments. This

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The electrolyte was prepared under inert gas atmosphere in an MBraun glove box. When preparing small amounts of electrolyte (10 ml) and low concentrations (0.1 M) the conducting salt and DMSO where simply mixed.

If larger quantities of electrolyte (200 ml–500 ml) with larger concentrations of LiClO₄ (0.5 M) were prepared, it was taken special care that the temperature of the electrolyte did not exceed approximately 50°C. In order to do so the amount of LiClO₄ was divided in at least 20 portions and added to the DMSO one at a time under vigorous stirring. After adding 5 portions, the electrolyte was given time to cool down to room temperature again.

A coulometric KF Titratör (C20, Metler Toledo) with a diaphragm electrode was used to determine the water content. The freshly prepared electrolyte, had a water content of 6 ppm. However, the water content increases significantly during the experiment, the water content after each measurement is given in the Results section of this paper. In experiments where the dual thin layer cell was used the water content was determined at the outlet. It is likely that the water content in these measurements increases during sampling. Therefore, the water content given for the dual thin layer cell poses a maximum value.

According to the manufacturer of the used electrolyte accumulation of DMSO affects the chemistry involved in the detection process of water. The error was estimated by adding a water standard. The error is in the range of 30%.

**Instruments.** All potentiostats and function generators used in this study were homebuilt. RRDE measurements were done with a Ring-Disk Electrode System of EG&G (i.e., the motor and control unit) while the tip comprising the disk and ring electrode was obtained from Pine Instruments. The mass spectrometer of the DEMS was a QMG 422 from Pfeiffer Vacuum.

**Reference electrode.** The reference electrode used in this study was a silver wire immersed in a solution of 0.1 M AgNO₃ in DMSO. Electrolyte contact to the working electrode was achieved by filling a Teflon tube with the silver containing solution and sealing it with a commercial, rough glass bead. The end with the glass bead was immersed into the working electrolyte, while the other open end was immersed into the silver containing solution. A drawing of the reference electrode can be found elsewhere.¹⁸

According to the values given by Gritzner et al.²⁵ the reference electrode described above has a potential of +3.89 V with respect to the Li+/Li couple.

**Dual thin layer cell.** A drawing of this particular cell type (as well as of the conventional cell) can be found in Ref. 25 In short: The dual thin layer cell comprises two compartments that are constantly flushed with electrolyte. The electrolyte enters the first compartment where the working electrode is placed and electrochemistry takes place (upper compartment). Reaction products are flushed along with the electrolyte into the second compartment (lower compartment). A porous Teflon membrane pressed on a steel frit forms a barrier between electrolyte and vacuum. Volatile reaction products evaporate through the Teflon membrane into the vacuum of the mass spectrometer and are detected according to their masses. The electrolyte then is flushed to the outlet. The flow of the electrolyte going from the first to the second compartment causes a delay between the faradaic current and the response in the ionic current. In all calculations where the ionic current was correlated to processes appearing at the working electrode this delay time was accounted for.

The reference electrode is placed at the inlet. The main counter electrode (gold) is placed at the outlet. In order to reduce electronic oscillations, a second counter electrode is placed at the inlet. The main counter electrode is connected via a resistance of 1 Ω, the second via a 1 MΩ resistance to ascertain an optimal distribution of the current.

A more detailed description of the dual thin layer cell along with its versatile applications for DEMS can be found elsewhere.²⁵–³⁰

**Conventional DEMS cell.** The conventional cell is a cylindrical glass body with a surface grinding at its lower part. The surface grinding is pressed on a gold sputtered porous Teflon membrane, which rests on a steel holder and acts as the working electrode. The steel holder features a steel frit through which volatile reaction products flow into the vacuum. The reference electrode, the counter electrode and a Teflon tube through which gas is bubbled are immersed into the electrolyte if not stated otherwise. A drawing of the cell can be found elsewhere.¹⁸,²⁵,²⁹

In the classical cell the partial pressure of oxygen at the electrode is very low because oxygen evaporates immediately at the interface between vacuum and electrolyte. The exact value of the partial pressure cannot be determined.

**RRDE measurements.** In the RRDE measurements we employed a tip with exchangeable disc electrodes and a ring electrode made from glassy carbon. The tip was purchased from Pine Instruments. To ensure that the electrochemical reaction at the ring electrode and at the applied potential takes place under diffusion limitation we reduced oxygen under the same conditions from an electrolyte of 0.5 M TBAClO₄ in DMSO. In this electrolyte oxygen is reduced quantitatively to superoxide. We checked for various potentials at the ring electrode whether the observed collection efficiency matches the theoretical collection efficiency. For a rotation speed of 2940 rpm the observed collection efficiency matches the theoretical value at a potential of −0.6 V.

**Calibration for O₂.** In order to correlate the measured ionic current for mass 32 to the amount of oxygen that actually enters the mass spectrometer, calibration is required.

In order to account for the collection efficiency of the used cells, the state of the filament and other setting of the mass spectrometer, oxygen was reduced in an electrolyte of 0.5 M TBAClO₄. It is known that oxygen in this electrolyte is reduced to superoxide.⁶,¹⁸ Therefore, the ratio of the measured ionic current for mass 32 and the faradaic current divided by Faraday’s constant gives the calibration constant K*. K* does not only account for the probabilities of ionization, fragmentation and detection but also for the probability of a compound to enter the mass spectrometer (collection efficiency). The collection efficiency of the dual thin layer cell depends on the flow rate, but also on the exact geometry of the cell that changes in each experiment, due to different forces applied to the cell. Therefore, calibration was done after each experiment (K* of the dual thin layer cell changes by roughly ±10%).

In both cells, a baseline was subtracted from the ionic currents. Therefore, the ionic current for O₂ (mass 32) appears as a negative current during oxygen reduction.

**Calibration of the eQCMB.** The quartz crystal microbalance was calibrated by electrodeposition of copper from a solution of 0.1 M CuSO₄ in 0.1 M H₂SO₄. The calibration constant for the quartz crystal in the dual thin layer cell was 313 Hz/µg and for the crystal used in stationary solution was 17.49 Hz/µg.

**Results.** Figure 1 shows a number of CV’s and MSCV’s (i.e. mass spectroscopic cyclic voltammogram) for mass 32 and 44 that are obtained when a gold sputtered Teflon membrane is used as a working electrode in the conventional cell. In this experiment an electrolyte of 0.1 M LiClO₄ in DMSO was employed. As the potential approaches −1 V, oxygen reduction is observed. This is clear from the reduction current in Figure 1A and the negative ionic current for mass 32 in Figure 1B. In the potential region of oxygen reduction both the ionic current for mass 32 and the faradaic current go through a minimum. The peak is not due to diffusion limitation: In the conventional cell the working electrode is situated at the interface between vacuum and electrolyte.
Hence, oxygen that reaches to the electrode passes into the vacuum immediately if it is not reduced electrochemically first. Therefore, in the conventional cell the flux of oxygen to the working electrode is diffusion limited all the time. The peak in Figure 1A appears because reduction products are deposited on the surface and block the electrode. When electrochemical reduction of oxygen stops, every oxygen molecule that reaches the electrode evaporates. Therefore, the ionic current for mass 32 returns to its baseline value and we observe a peak in the ionic current for mass 32 (Figure 1B) as well. This also demonstrates that the pores of the membrane are not blocked.

In the anodic sweep three peaks appear at $-0.3 \, V$, at $-0.1 \, V$ and at $0.7 \, V$ in the faradaic current. The peaks at $-0.3 \, V$ and at $-0.1 \, V$ are paralleled by oxygen evolution. Minor quantities of oxygen are also evolved during the third peak. However, in Figure 1C a more intense signal parallel to the third peak appears in the ionic current for mass 44, which is indicative for the evolution of CO$_2$.

In Figure 1, the lower potential window was successively decreased, and by doing so the amount of oxygen, reduced in each cycle, was increased. When the amount of oxygen, evolved in the following anodic sweep of each cycle, is plotted against the amount of oxygen reduced in the previous cathodic sweep, a straight line is obtained which has a slope smaller than one (c.f. Figure 2A). We have shown similar results in a previous publication, where the intercept and a positive intercept with the x-axis (c.f. Figure 2A) were indicated. The curves shown in Figure 1 were reproduced for the present paper in order to be able to show the MSCV for mass 32 (B) and 44 (C) obtained at a gold sputtered Teflon membrane in the conventional cell (porous electrode; convection only due to purging with pure oxygen).

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This peak does neither appear in Ar saturated solution (when cycling in the same potential range as in Figure 1) nor in O$_2$-saturated solution when the potential range of O$_2$ reduction was excluded. This is shown in Figure S1 and Figure S2 of the supporting information. A fragment with mass 44 is indicative for the evolution of CO$_2$. Since DMSO is the only carbon source in the system under investigation the evolution of CO$_2$ must ultimately result from electrolyte decomposition.

In Figure 2B the amount of evolved CO$_2$ is plotted against the amount of reduced oxygen during the previous cathodic sweep. From the resulting linear relationship it is obvious that electrolyte decomposition relates to oxygen reduction. It is evident from Figure 2 that the sum of the evolved amounts of oxygen and the evolved amounts of CO$_2$ do not account for the amounts of reduced oxygen. A more detailed discussion on the true columbic efficiency (e.g. the ratio of reduced to evolved amounts of oxygen) is given in the Discussion section of this paper.

According to Equation 1, it is possible to calculate the number of electrons that are transferred per reduced molecule of oxygen.

$$ z = i_t \cdot K^*/i_{32} \tag{1} $$

In Equation 1, $z$ is the number of transferred electrons in e$^-$/O$_2$, $i_t$ is the faradaic current, $i_{32}$ is the ionic current for mass 32 and $K^*$ is a calibration constant.

The z-value was calculated from the data shown in Figure 1 and the result is plotted as a function of the potential in Figure 3. In Figure 3 the z-value starts from 1.5 e$^-$/O$_2$ at $-1.5 \, V$ and increases to 2 e$^-$/O$_2$ as the potential decreases beyond $-1.2 \, V$. The z-value shown here resemble those already shown in Ref. 18. However, they differ from the z-values obtained at smooth gold electrodes, where the z-value at low overpotentials is close to 1 e$^-$/O$_2$ (vide infra).

Oxygen reduction in lithium-containing electrolytes leads to the formation of solid Li$_2$O$_2$. In addition, also decomposition products deposit on the electrode. The formation of decomposition products is indicated by the evolution of CO$_2$. In order to investigate this deposit of reduced oxygen species and decomposition products we employed the electrochemical quartz crystal microbalance technique (eQCMB).
Figure 3. Number of electrons transferred per oxygen as a function of potential. The curves shown were calculated from the data shown in Figure 1 (porous electrode). Color coding as in Figure 1.

Figure 4 shows the results that were obtained in a quiescent solution in 0.1 M LiClO₄ in DMSO. The curves shown are the average of 12 subsequent cycles in a single set up. In Figure 4A the CV and in Figure 4B the mass change is shown as a function of potential (The derivative of the deposited mass is shown because it allows a better comparison to the current). Note that there is a delay of about 250 mV between the onset of oxygen reduction (CV) and the potential at which mass deposition is observed. In the following anodic sweep a major mass change is only observed at a potential larger than 0.3 V. At this potential the evolution of oxygen has largely ceased and CO₂ evolution starts (c.f. Figure 1). No mass change is observable in the potential region of oxygen evolution (~0.7 V to 0.1 V).

Figure 4C also features the reduced quality factor Q as a function of the applied potential. Q is calculated according to Equation 2 from the two resonance frequencies \( f_1 \) and \( f_p \).

\[
Q = \frac{f_1 + f_p}{2 \cdot (f_1 - f_p)}
\]  

[2]

\( f_1 \) and \( f_p \) in Equation 2 are not the resonance frequencies of the quartz crystal itself (which has only one resonance frequency \( f_b \)) but of the BVD-equivalent circuit \(^{32}\) that describes how the quartz behaves as an electronic element in an AC-field. In practice it is difficult to measure \( f_b \), but \( f_1 \) and \( f_p \) are more easily accessible. Although the exact values of \( f_1 \), \( f_p \) and \( f_b \) differ significantly, it is possible to approximate \( \Delta f_1 \) (changes of \( f_1 \)) by \( \Delta f_p \) or \( \Delta f_b \) (changes of \( f_1 \) and \( f_p \), respectively). According to the Sauerbrey equation changes in \( f_E \) arise when the mass of the quartz crystal changes.\(^{33}\) That is also true for \( \Delta f_1 \) or \( \Delta f_p \), but changes in \( f_1 \) and \( f_p \) can also appear when the friction at the interface between electrode and electrolyte changes. \( f_1 \) is not affected by the friction and it is, therefore, necessary to check whether changes in \( f_1 \) and \( f_p \) are due to mass changes or due to friction. Changes in friction show up in changes of the reduced quality factor which can be calculated from Equation 2. A decrease in the quality factor Q indicates an increase of friction at the interface between the oscillating electrode and the electrolyte. The latter in turn signifies an altered viscosity of the matter in contact with the electrode.\(^{32}\)

Given the noise level there are no significant changes in the quality factor in the cathodic sweep. However, considerable changes occur in the anodic sweep. At about 0.3 V Q decreases and reaches a minimum at 0.49 V. The change in Q is mirrored by the first peak in the anodic sweep of the \( \text{dm/dt} \) vs. E plot. The signal in Q parallel to the second peak in the \( \text{dm/dt} \) vs. E plot is much less significant.

\[
m.p.e. = F \cdot (\text{dm/dt}) / i
\]

[3]

\( F \) is Faraday’s constant and \( \text{dm/dt} \) is the mass change. The m.p.e value is plotted as a function of the applied potential in Figure 5. The m.p.e value steadily increases as the potential becomes more negative than \(-1.15 \text{ V} \) and reaches a value of 48 g/mol·e⁻ at \(-1.35 \text{ V} \). There is no plateau at either 23 g/mol·e⁻ or 39 g/mol·e⁻ that would be expected for the quantitative deposition of lithium peroxide or lithium superoxide, respectively. The formation of the latter has been suggested previously in literature.\(^{20}\) Above \(-1.2 \text{ V} \) m.p.e values are not meaningful because the frequency change is negligible.
Figure 6. QCM and DEMS measurements combined. This was possible by using a dual thin layer cell. The electrolyte was kept in storage vessel and was bubbled with a mixture of argon and oxygen \((Ar : O_2 = 80 : 20)\) throughout the experiment. The flow rate of the electrolyte was 5 μL/s and the sweep rate was 10 mV/s. Water content max. 105 ppm. A: CV; B: MSCV for mass 32; C: MSCV for mass 44; D: MSCV for mass 29; E: First derivative of mass with respect to time as a function of applied potential (inverted y-axis); The shown curves are the average over 38 cycles. The experiment was conducted at a smooth gold electrode under convective conditions.

The missing mass change in the potential region of oxygen evolution is strange because oxygen evolution should result in the removal of solid Li₂O₂ from the electrode. The data presented in Figure 6 show that oxygen is evolved from Li₂O₂, indeed. The curves were obtained when oxygen was reduced under continuous electrolyte flow. The convection conditions in this cell are more defined than in the conventional cell\(^4,35\) and soluble reduced oxygen species are transported away. Hence, they are not available for oxygen evolution. The signal in the ionic current for mass 32 (Figure 6B) must, therefore, be due to the oxidation of species attached to the electrode. Yet, oxygen evolution comes along without mass changes (Figure 6E). A discussion on that will be given in the Discussion section of this paper.

Aside from the CV (A), the MSCV for mass 32 and 44 (B, C) and the dm/dt vs. E plot (E) Figure 6 also features the MSCV for mass 29 (D). The latter was collected to ensure that the evolution of a signal in the MSCV for mass 32 in the anodic sweep can be assigned to oxygen evolution: In principle it is conceivable that other fragments than O₂\(^+\) cause a signal for mass 32. For instance methanol, formed during electrolyte decomposition, could emulate oxygen evolution. However, organic molecules usually form a CHO\(^+\)-fragment with mass 29 as well. The absence of a signal in the MSCV for mass 29 in the potential region of oxygen evolution shows unambiguously that the signal in the MSCV for mass 32 is due to oxygen evolution.

As in Figure 4, also in Figure 6 there is a delay between onset of oxygen reduction and mass deposition. This delay correlates to a step in the CV, which is not present in the MSCV for mass 32. As was shown previously\(^7\), this step corresponds to a change in the mechanism of oxygen reduction from the indirect pathway (where superoxide is formed electrochemically and disproportionates to Li₂O₂ in the aftermath) to the direct pathway (by which peroxide is formed electrochemically). According to Equation 1 the number of electrons transferred per reduced oxygen was calculated from the ratio of the faradaic current and the ionic current for mass 32. The resulting \(z\)-values are plotted in Figure 7A as a function of the potential.

The \(z\)-values displayed in Figure 7A show again (c.f. Ref. 7) that a transition from the indirect to the direct pathway of peroxide formation takes place. This transition is responsible for the delay between oxygen reduction and mass deposition: Initially soluble superoxide is formed, which is transported away from the electrode. Only when the potential region of peroxide formation is entered the formation of a solid deposit is expected. In previous eQCMB measurements a lower than expected mass change was assigned to the formation of soluble superoxide at low over potentials.\(^36\) Indeed, when the potential of \(-1.2\) V is reached, where Figure 7A indicates that oxygen is reduced nearly entirely to peroxide, both the m.p.e. and the m.p.O₂ values, reach a plateau in Figure 7B. The m.p.e.-values in Figure 7B were calculated according to Equation 2, while the m.p.O₂-values (the mass change that is caused per reduced oxygen) were calculated according to Equation 4 from the data in Figure 6:

\[
m.p.O_2 = \left(\frac{dm}{dt}\right) \cdot \frac{K^*}{I_{32}} \tag{4}\]

In Equation 4 \(dm/dt\) is the mass change, \(I_{32}\) is the ionic current for mass 32 and \(K^*\) is the calibration constant for the dual thin layer cell. Note that the \(z\)-plot in Figure 7A differs significantly from the \(z\)-plot in Figure 3. That is, at the smooth gold electrode and at low overpotentials the \(z\)-value is close to one and experiences a steep
increase as the overpotential increases. On the other hand, when gold sputtered electrodes were used the z-value is above 1.5 $e^{-}/O_2$ in the whole potential range. These results seem to contradict each other, as in both experiments a Li-containing DMSO based electrolyte and the same electrode material was used. This difference is discussed in detail below.

From the data in Figure 6 we have also calculated the z-values for the oxygen evolution. These data are shown as a function of the applied potential in Figure 8B. To simplify comparison Figure 8A also features the faradaic current in the potential region of oxygen evolution. Oxygen evolution proceeds in two distinct peaks which we have assigned in a previous publication to the oxidation of reduced oxygen species. The lke/liest reduced oxygen species that can react at the ring electrode is superoxide. Indeed, in Figure 7A the z-value at potentials smaller than 0.03 V indicates that oxygen evolution in both peaks is due to the oxidation of peroxide. The slightly larger z-value of 2.4 $e^{-}/O_2$ in the second peak is probably due to some sort of side reaction. Recently, based on UV/vis and SERS studies, Yu and Ye have proposed that the second peak is due to the oxidation of LiO$_2$. This reaction should come along with a z-value of only one. Based on the data presented in Figure 8B we have to reject this interpretation.

At even more positive potentials than −0.16 V oxygen evolution in Figure 6 continues in a shoulder (c.f. ionic current for mass 32). The z-values are probably distorted due to parallel electrochemical processes. That is why we cannot assign the evolved oxygen to any reduced oxygen species, or give any interpretation on its origin.

Figure 9 shows RRDE-results obtained at a gold-disc electrode and a glassy carbon (GC) ring electrode. The latter was set to a potential of 0.3 V, which is well inside the potential region of Li$_2$O$_2$-oxidation. In Figure 9B the current at the disc electrode and at low rotation speeds experiences a shoulder, much alike to the one observed in Figure 6, which indicates the change from the indirect to direct pathway of peroxide formation. The shoulder in the current at the disc is paralleled by a peak in the current at the ring. This is most probably due to the formation of superoxide at the disc electrode and its subsequent oxidation at the ring electrode, as has been discussed in literature several times. However, the transition from the direct to the indirect pathway of peroxide formation has not been observed in an RRDE-measurement before. This is due to the fact that in the current study the electrolyte was not saturated with oxygen, but purged with a mixture of only 10% O$_2$ and 90% Ar. Due to the low oxygen concentration in our experiment superoxide formation enters diffusion limitation at low rotation speeds before the mechanism of oxygen reduction shifts from the indirect to the direct pathway of peroxide formation. In oxygen saturated solution or with high rotation speeds (c.f. 2940 rpm in Figure 9) the transition from the indirect to the direct pathway of peroxide formation and electrode blocking, due to the precipitation of Li$_2$O$_2$, cannot be resolved.

Figure 9 shows that the transition from the indirect to the direct pathway of peroxide formation comes along with a second peak (low rotation speeds) or a shoulder (medium rotation speeds) in the current at the ring electrode. Since decomposition products are barely oxidized at the potential that was applied to the ring electrode (0.3 V, c.f. Figure 1 and Figure 6) the second shoulder is most probably due to the oxidation of reduced oxygen species. The likeliest reduced oxygen species that can react at the ring electrode is superoxide. Despite the fact that oxygen is predominantly reduced to Li$_2$O$_2$ at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2. This is also the case in other studies which indicates that 10–20% of oxygen is reduced to superoxide. In peroxide at large overpotentials, it is still possible that a fraction of the oxygen is also reduced to superoxide. Indeed, in Figure 7A the z-value at potentials smaller −1.2 V remains somewhat below 2.
to superoxide increases significantly as the electrode is deactivated. Hence, we observe a peak in the current at the ring electrode. This interpretation is also in good agreement with the results presented by Yu and Ye who have shown by means of UV/vis spectroscopy that parallel to peroxide also a significant amount of superoxide is formed and that the share increases as the electrode is deactivated.11 RRDE-measurements in connection with potential step experiments also show that ring currents are observed irrespective to which potential the disc electrode is stepped, whereas the peak height of the ring current depends on the disc potential.13

It is the prevailing view in literature that the species that reacts at the ring electrode is superoxide.6,8,10,11 However, it is also conceivable that hindered nucleation results in the formation of dissolved LiO2−, which could react at the ring electrode. Since the value of z, which is below 2 suggests the formation of superoxide, we deem this interpretation unlikely, but it cannot be ruled out based on the presented data.

RRDE-results obtained when smaller potentials were applied to the ring electrode can be found in the supporting information (Figures S3 to S6). Even at ring potentials lower than −0.7 V, the onset potential of oxygen evolution due to Li2O2-oxidation, a second peak in the current at the ring electrode is observed. This gives further support to the idea that superoxide reacts at the ring electrode.

When oxygen is reduced via the indirect pathway of peroxide formation, Li2O2 results from chemical disproportionation of superoxide. In order to investigate whether the presence of gold at open circuit can influence this reaction we performed the following experiment. We conducted oxygen reduction in our dual thin layer cell. In the first measurement (black curve in Figure 10) we used an unaltered Teflon membrane in the lower compartment as an interface between vacuum and electrolyte. In the second measurement this membrane was replaced by a gold sputtered Teflon membrane (yellow curve in Figure 10). Figure 10 shows the CVs and the MSCVs for masses 32 and 44 for both measurements.

In Figure 10 the CV remains largely unaffected, when the Teflon membrane is changed to a gold sputtered Teflon membrane. A shoulder due to superoxide formation appears in both cases, followed by a peak when the mechanism of oxygen reduction shifts to the direct pathway of peroxide formation.

The intensity of the ionic current for both mass 32 and 44 is reduced when the Teflon membrane is changed to a gold sputtered Teflon membrane. This might be due to changes in the exact geometry of the cell setup, when the membrane is changed (the geometry might be altered, when the spacers used are compressed). However, the changes in the MSCV for mass 32 go beyond a reduced sensitivity: The shape of the MSCV in the potential region of oxygen reduction now follows the shape of the CV and features a shoulder at low overpotentials. This means that in the potential region of superoxide formation less oxygen is consumed as compared to the potential region of peroxide formation. This is not the case when a Teflon membrane is used (black curve of Figure 10): Equal amounts of oxygen are reduced regardless whether superoxide or peroxide is formed electrochemically. Since the electrochemical process is not affected by the type of membrane in the lower compartment there is bound to be another process that yields oxygen and is indeed affected by the presence of gold. One possible reaction that would result in oxygen evolution is the disproportionation of superoxide to peroxide. This reaction is slow on the timescale of a DEMS experiment when a Teflon membrane is used (otherwise the transition from z ≈ 1 e−/O2 to z ≈ 2 e−/O2 would not be observable). However, the disproportionation of superoxide could be heterogeneously catalysed by gold at open circuit potential. Notwithstanding this, also any other gold catalysed reaction in which superoxide is oxidized could cause the changes in the MSCV for mass 32 in Figure 10B. We will follow up on this in another publication that will give further support to the notion that superoxide undergoes a heterogeneous reaction at gold at open circuit potential.

**Discussion**

**Superoxide versus peroxide formation.**—It is evident from Figure 7A that the z-value increases from approximately 1 e−/O2 at low overpotential to approximately 2 e−/O2 as the potential passes −1.2 V, which indicates that oxygen is reduced to superoxide at low overpotentials and at gold electrodes. At higher overpotentials oxygen is reduced to peroxide, which has also been proposed by others.6,8,11,38,41,42,43 Also the QCMB-results support the idea that the product distribution of oxygen reduction shifts from superoxide to peroxide: In Figure 4 there is a delay of about 250 mV between the potential at which oxygen reduction starts and at which the formation of a deposit is observed. A similar delay is present in Figure 6. Since superoxide is considered soluble its formation should not result in the formation of a deposit, whereas peroxide precipitates as Li2O2. The formation of the latter causes a frequency shift. The potential at which the formation of a deposit is observed corresponds well to the potential at which z increases from 1 e−/O2 to 2 e−/O2.

**Decomposition of the electrolyte.**—The evolution of CO2 only occurs in the anodic sweep when oxygen was reduced in the previous cathodic sweep. The evolution of CO2 indicates that electrolyte decomposition takes place (c.f. Figure 1 and Figure 6). The electrochemical oxidation of the electrolyte (which is the only carbon source in the system under investigation) should not depend on the reduction of oxygen in a previous cycle. Therefore, CO2 evolution is the result of the electrochemical oxidation of decomposition products which form during oxygen reduction. The formation of decomposition products also shows up in the m.p.e.-values of the quiescent solution: Figure 5 shows that the m.p.e.-values that are observed in the potential range of peroxide formation are much larger than expected for Li2O2, which indicates the additional deposition of decomposition products. However, it needs to be pointed out that in the absence of convection most of the reduced oxygen will precipitate as Li2O2,

![Figure 10. CV (A) and MSCV for mass 32 (B) and 44 (C) obtained in the dual thin layer cell with a smooth gold electrode in the upper compartment and a gold sputtered Teflon membrane (yellow curve; rough gold electrode) or a Teflon membrane (black curve) in the lower compartment. Electrolyte: 0.5 M LiClO4 in DMSO; water content max 22 ppm; sweep rate: 10 mV/sec, flow rate: 5 μL/sec. The experiment was conducted under convective conditions.](image-url)
eventually. Hence, in addition to oxygen that is reduced to Li$_2$O$_2$ via the direct pathway also superoxide will be reduced to Li$_2$O$_2$ via the transfer of 1 electron. The expected m.p.e value for the latter reaction is 46 g/mol · e$^\cdot$. It can be expected that superoxide is present at potentials where the direct pathway of peroxide formation prevails because it was found at low overpotential and remained at least partially in front of the electrode. A distortion to higher than expected m.p.e-values in the potential range of peroxide formation is, therefore, expected. However, when the overall mass change and the total charge in the potential region of oxygen reduction is considered, then the m.p.e.-value amounts to 30 g/mol · e$^\cdot$ which is still larger than the expected 23 g/mol · e$^\cdot$ for Li$_2$O$_2$ formation.

On the other hand, an m.p.e.-value of 21.5 g/mol · e$^\cdot$ and an m.p.O$_2$-value of 42 g/mol · O$_2$ is observed under convection conditions (c.f. Figure 7B). These values correspond well to those expected for Li$_2$O$_2$ formation. This appears to contradict the notion of an additional deposition of decomposition products which we derived from the larger than expected m.p.e-values obtained in quiescent solution. However, even at high overpotentials where peroxide formation dominates not all the electrochemically reduced oxygen species precipitate as Li$_2$O$_2$ on the surface of the electrode (c.f. RRDE measurements in Figure 9). When a portion of the reduced oxygen species is transported away under convection conditions then lower than expected m.p.e- and m.p.O$_2$-values would be observed because a portion of the current is not due to the formation of a solid deposit. Hence, the fact that the observed m.p.e.-values match well those expected for Li$_2$O$_2$ formation is just a coincidence that results from the additional deposition of decomposition products and an incomplete precipitation of reduced oxygen species.

Our results appear to be in contradiction to the results presented by Sharon et al. who found m.p.e.-values that fit well to the quantitative precipitation of pure Li$_2$O$_2$. However, Sharon et al. used a cell that contained a fairly low volume of 3 ml electrolyte that was purged with oxygen throughout the experiment. Considering our results concerning superoxide formation and the influence of convection on the observed m.p.e.-values, the well fitting m.p.e.-values observed by Sharon et al. might be the result of convection caused by electrolyte purging.

Also the work of Torres et al. suggests that the exact experimental conditions have a significant effect on the observed m.p.e-value. Due to a rough morphology of the Li$_2$O$_2$ deposit solvent molecules can be entrapped in the Li$_2$O$_2$ layer which results in very large m.p.e.-values of 61 to 175 g/mol · e$^\cdot$ during oxygen reduction in DMSO based electrolytes. The formation of a rough film was confirmed by impedance analysis of the eQCMB. The experiment showed that the resistance in the BVD-equivalent circuit increases, which shows up when the friction at the electrode electrolyte interface increases. However, the experimental conditions in our study (cycling to large overpotentials) are different from those in the study of Torres et al. (step to moderate overpotentials) and different morphologies of the deposit can be expected. Notwithstanding this, it was also proposed that under the experimental conditions a reaction between Li$_2$O$_2$ and DMSO occurs that results in decomposition products. The formation of the latter was confirmed via XPS.

It is evident that interpretation of m.p.e-values is not straightforward as many effects can distort eQCMB results. If parts of the current result in the formation of soluble species parallel to the formation of a solid deposit, the m.p.e-values calculated according to Equation 3 are distorted to lower values. On the other hand electrolyte processes parallel to electrochemistry can also result in mass changes. The formation of decomposition products (this study) or voids in the deposit that entraps solvent molecules (Torres et al.) are examples for the difficulties that arise if the oxygen reduction reaction in organic solvents is investigated.

Electrolyte decomposition takes place during oxygen reduction, but since two different reduced oxygen species are formed - superoxide and peroxide - the question arises which of these species (or intermediates that arise during its formation) initiates electrolyte decomposition. No mass deposition takes place in the potential range of superoxide formation, hence, no decomposition products precipitate on the electrode, whereas parallel to Li$_2$O$_2$-formation the deposition of decomposition products is observed. Therefore, peroxide or species that form during peroxide formation are the active species that initiates electrolyte decomposition - or at least causes the formation of those decomposition products that precipitate during oxygen reduction. The formation of a deposit would be expected at low overpotentials if superoxide was the active species that initiates electrolyte decomposition. Sawyer et al. have shown previously that a solution of superoxide is stable in DMSO over weeks. This is supported by the fact that we have never observed formation of CO$_2$ after reduction of oxygen in an electrolyte of 0.1 M TBAClO$_4$ in DMSO (c.f. Figure S7). Since no mass deposition is observed above −1.2 V in our eQCMB measurements this is also true for Li$_2^+$-containing electrolytes, where the polarization of DMSO, by the large charge density of the Li$_2^+$-cation could facilitate any reaction between superoxide and DMSO. Electrolyte decomposition, therefore, takes place during peroxide formation. However, we cannot rule out that superoxide causes the formation of other decomposition products that remain in solution and are not detectable via eQCMB. Based on our results we cannot decide whether solid Li$_2$O$_2$ or any intermediate that occurs during peroxide formation initiates electrolyte decomposition. It has been suggested before that decomposition of DMSO based electrolytes occurs during oxygen reduction. However, our results might be perceived to contradict the results of others: Schroeder et al. have shown that DMSO exposed to Li$_2$O$_2$ does not undergo any decomposition. Even though DMSO exposed to solid Li$_2$O$_2$ does not undergo any decomposition this does not mean that DMSO is stable when exposed to intermediates of electrochemical peroxide formation. Another report that appears to be in contradiction to our results is the work presented by Peng et al. who conducted DEMS measurements on oxygen reduction and evolution from DMSO based electrolytes at gold electrodes. Peng et al. did not observe any CO$_2$ evolution at gold electrodes. However, the spectra presented exclude the potential range in which we observe CO$_2$ evolution. Furthermore, it is noteworthy that CO$_2$ evolution in our study takes place at the very same potential at which Peng et al. observe the evolution of CO$_2$ at carbon based electrodes (0.7 V vs Ag/Ag$^\oplus$ = 4.6 V vs Li/Li$^\oplus$). It is rather unlikely that the evolution of CO$_2$ observed by Peng et al. is due to carbon corrosion: The curves presented in Ref. 7 show that at glassy carbon similar amounts of CO$_2$ are evolved as at other electrode materials. By means of FTIR Peng et al. have shown that relatively small amounts of Li$_2$CO$_3$ and LiHCO$_3$ form when a Li$_2$O$_2$ battery is discharged that employs a DMSO based electrolyte and an oxygen electrode manufactured from gold. The amount of Li$_2$CO$_3$ and LiHCO$_3$ formed upon discharge increases significantly when the oxygen electrode is manufactured from Super-P. Model batteries are discharged with low current densities and, therefore, at low overpotentials (different from the DEMS results shown by Peng et al. where the electrode was cycled into the potential window of direct peroxide formation). Under these conditions oxygen is reduced to superoxide at gold electrodes. Li$_2$O$_2$ is formed afterwards via the chemical, lithium-induced disproportionation of superoxide where we do not observe electrolyte decomposition. However, at glassy carbon electrodes roughly 50% of oxygen is converted to peroxide via the direct, electrochemical transition of two electrons. Since we have shown that electrolyte decomposition occurs during electrochemical peroxide formation the formation of decomposition products upon discharge of batteries with carbon based electrodes is expected. The effect of the electrode material on the formation of decomposition products upon discharge of lithium oxygen batteries which was observed by Peng et al. is understandable by the results presented here and in context with the results presented in Ref. 45.

The water content of 90 ppm in the DEMS measurement of Figure 1 is relatively high. It can be excluded that trace amounts of water have an effect on the evolution of CO$_2$. In fact, this is quite likely: From the supporting information of Ref. 7 it is clear that the evolved amounts of CO$_2$ tend to increase as the water content in the electrolyte increases. However, it is not clear whether there is a
primary or secondary effect of water. In the former case water would enhances electrolyte decomposition in the latter case water would fa-
cilitate oxidation of decomposition products and, hence, would make electrolyte decomposition more visible. Notwithstanding this, CO₂ evolution is also observed at a water content of only 20 ppm.7

Without spectroscopic evidence it is hard to comment on the exact nature of the decomposition products. The fact that CO₂-evolution proceeds without further consumption of oxygen gives a hint that CO₂-moiety is preformed in the decomposition product and can be released upon electrochemical oxidation (c.f. Supporting Information and Figure S8).

Our results suggest that it is beneficial to avoid the direct pathway of peroxide formation during battery discharge. Although Figure 2 suggests that the actual amounts of oxygen that are re-evolved as CO₂ are rather small, prolonged battery operation is not possible even when only small amounts of electrolyte are decomposed in each charge-discharge cycle. However, whether it is really beneficial to favor the indirect pathway of peroxide formation depends on the stability of the electrolyte under these operation conditions. We did not observe any electrolyte decomposition when oxygen was reduced to superoxide, however, intermediates that occur during disproportionation of superoxide might be able to induce electrolyte decomposition as well.

*z*-values at gold sputtered Teflon membranes.— In Ref. 18 we have shown that oxygen reduction at a gold sputtered Teflon membrane proceeds via the transfer of more than 1.5 electrons per oxygen over the whole potential region of oxygen reduction. This appears to contradict the results presented in Figure 7A and elsewhere2 where we have shown that a transition from the direct to the indirect pathway of peroxide formation occurs as the overpotential increases. Yet, both results are reproducible: At smooth gold electrodes used in the dual thin layer cell we always observe a step in the *z*-value from close to 1 e⁻/O₂ to nearly 2 e⁻/O₂ (c.f. Ref. 7), while this step is far less pronounced when gold sputtered Teflon membranes are used as working electrode in the conventional cell (c.f. Figure 3 and Ref. 18). There is one obvious difference between the experiments of Figures 1 and 6: The partial pressure of oxygen at the electrode.

In the conventional cell with the porous electrode electrochemistry takes place at the interface between electrolyte and vacuum. At the working electrode the concentration of oxygen is very low because oxygen readily passes over into the vacuum. In the dual thin layer cell electrochemistry does not take place at the interface between electrolyte and vacuum and the concentration in front of the electrode equals the concentration of oxygen in the bulk electrolyte (as long as no O₂ is reduced electrochemically). The Tafel-slope for the formation of superoxide is 120 mV/dec, and, hence, a reduction of the concentration in oxygen by one decade will reduce the potential (i.e. increase the overpotential) at which a certain current due to superoxide formation is observed by 120 mV. At higher overpotentials the superoxide is reduced further to peroxide. The formation of lithium peroxide in the direct path is a surface limited (adsorption) process. At this point we do not know the reaction order with respect to O₂ or which reaction step is the rate limiting. However, it is not unreasonable to assume that the second electron transfer is slower than the first one, which corresponds to a Tafel slope of 40 mV. For a reaction order of one with respect to oxygen, this means that to maintain a given current at a lower O₂ concentration, the potential has to be decreased by only 40 mV per decade of concentration. In this case, the potential region of superoxide formation is much smaller in the conventional cell and is not well resolved form the potential region of peroxide formation. This might be one reason why we observe a *z*-value of 1.5 e⁻/O₂ in the conventional cell and at low overpotentials, whereas *z*-value in the conventional cell in the same potential region is close to 1 e⁻/O₂.

Another possible reason for a larger than expected *z*-value in the potential region of superoxide formation is the structure of the electrode: The thickness of the gold-layer is only 50 nm. Due to mechanical wear or due to shadowing during the sputter-process, it is likely that parts of the gold layer remain without electrical connection to the potentiostat and are, therefore, at open circuit potential. As already pointed out gold at open circuit potential causes oxygen evolution by catalysing disproportionation of superoxide to oxygen and peroxide or by some other reaction that results in the oxidation of superoxide (c.f. Figure 10).

When parts of the gold electrode under potential control are close to those parts without, then diffusion to and reaction of superoxide at these sites is fast. This causes a lower ionic current for mass 32 whereas the faradaic current remains the same. Therefore, the calculated *z*-values are larger than expected. That is, oxygen is released in a reaction that requires no net charge transfer. This effect on the *z*-values is limited to measurements in the conventional cell because only there a rough gold electrode was used this. Both the on-set potential for oxygen reduction (c.f. Figure 1 and Figure 6) and the transition potential from the indirect to the direct pathway of peroxide formation (c.f. Figure 3 and Figure 7) are shifted by 100 mV to lower potentials in the conventional cell. This is due to a Nernst shift because of the lower concentration of oxygen at the porous membrane. Therefore, it is more likely that the *z*-value of 1.5 e⁻/O₂ at low over-potentials is due to the effect of gold particles at open circuit potential than due to the effect of kinetics.

**True coulombic efficiency.—** We have shown here and elsewhere18 that there is a non-proportionality between the reduced and the evolved amounts of oxygen. We pointed out that a positive intercept with the x-axis (i.e. negative intercept with the y-axis) means that in each cycle a constant amount of the reduced oxygen is not available for oxygen evolution, while a slope smaller than one means that in addition also a certain portion of the reduced oxygen cannot be re-evolved.

In each cycle the potential passes through the region of indirect peroxide formation and, therefore, a constant amount of oxygen is reduced to superoxide. The superoxide produced in this potential region is either transported away from the electrode (due to convection, caused by purging of the electrolyte with oxygen) or undergoes a reaction under oxygen release at those parts of the gold electrode that are at open circuit. The *z*-value in the potential range of superoxide formation is then defined by the ratio of superoxide that undergoes a reaction to the superoxide that diffuses away (mind that also in the case of the gold sputtered Teflon membrane usually a minor step is observed). In either case oxygen that is reduced to superoxide cannot be evolved again in the anodic sweep. In each cycle the same amount of superoxide is formed which is not reoxidized to oxygen. Therefore, a positive intercept with the x-axis results.

As the potential region of direct, electrochemical peroxide formation is entered, electrolyte decomposition starts as well. For each carbon atom that is evolved as CO₂ in the anodic sweep at least one molecule of reduced oxygen is consumed irreversibly. This reduces the slope of the straight line in Figure 2A. CO₂ is only the end product of DMSO oxidation and it is, therefore, likely that the evolved amount of CO₂ does not represent the total amount of oxygen that is consumed due to electrolyte decomposition. In addition to electrolyte decomposition some of the reduced oxygen species will be transported away and may precipitate at locations without any electrical contact to the electrode. Both processes only consume a portion of the reduced oxygen, and reduce the slope of the straight line in Figure 2A.

It is also possible that water exerts an effect: It was shown by Andrieux et al.40 that oxygen reduction in DMSO based electrolytes and in the presence of weak acids results in the formation of H₂O₂. The formation of soluble H₂O₂ in the presence of water upon discharge of Li-air batteries was also suggested by others.35,64 The formation of soluble H₂O₂ in our study would reduce the slope in Figure 2 further. However, Andrieux et al. used acids with a much larger pka-value than water in DMSO.40 Therefore, it is not clear whether the acidity of DMSO is sufficient to initiate this reaction. Furthermore, formation of H₂O₂ comes along with the formation of LiOH (as OH⁻ is bound to precipitate as LiOH). Accumulation of LiOH from cycle to cycle should show up with an increasing loss of activity, which we do not observe.
Characteristics of the deposit.—Both Torres et al. and Jie and Uosaki who investigated oxygen reduction in an electrolyte of 0.1 M LiPF₆ in DMSO by means of eQCM did not consider the potential region of oxygen evolution.²⁰,²¹ Sharon et al. on the other hand only state that the same mass that was deposited during oxygen reduction was removed during the anodic run.²² From that it was concluded that Li₂O₂ formation was reversible. However, closer examination of the curves shown by Sharon et al. reveals that the mass changes in the anodic run are observed at potentials positive of oxygen evolution. In a more recent study also Torres et al. have pointed out that the loss of mass in the potential region of oxygen evolution does not account for the masses that were deposited during oxygen reduction and that large overpotentials are required to return to the original state of the quartz.²³

There are several phenomena in eQCM measurements that can distort the observed mass changes significantly: The formation of a deposit on the electrode has a different interaction with the electrolyte. Therefore, a non-slip plane at the interface between electrolyte and electrode can turn into a slip plane or vice versa.²⁵ In addition, different double layer structures at the electrode and the deposit can distort mass changes significantly: When ions or molecules are specifically adsorbed at the electrode (or the deposit) they will be removed once the deposit forms (or once the deposit is removed).²⁶ In the case of thick coats solvent molecules and ions can be entrapped in the formed deposit.²³ However, those effects should not only affect the mass changes during oxygen evolution but also during oxygen reduction. These effects are, therefore, not fit to explain the missing mass changes during oxygen evolution.

In eQCM studies connected to the oxidation of metal surfaces Schumacher et al. observed mass changes that were several times larger than expected from the transferred charge.²⁰,²¹ Schumacher et al. were able to assign the additional mass changes to a roughening of the metal surface. Cavities on the surface will cause electrolyte to be dragged along with the movement of the crystal which causes an additional mass load. It is important to note that the eQCM does not measure the mass that rests on top of the quartz crystal (i.e. not the entire mass of the column of electrolyte that rests on top of the crystal) but the mass of the surrounding matter that follows the shear motion of the AT-cut quartz crystals. In a similar way also Torres et al. explain larger than expected mass changes during oxygen reduction.²² We are going to elaborate in the following, why the cavity-effect described by Schumacher et al. is a reasonable explanation for the missing mass changes during oxygen evolution:

Figure 11 illustrates the mechanism we believe to be responsible for the missing mass changes in the potential region of oxygen evolution: Initially the electrode is free of any deposit (Figure 11A). As the potential region of direct, electrochemical peroxide formation is entered an inhomogeneous film of decomposition products (blue) and lithium peroxide precipitates on the electrode (Figure 11B), which results in a mass change. The deposition of decomposition products and Li₂O₂ goes on until the whole electrode is covered and oxygen reduction ceases (Figure 11C). Since the evolution of oxygen and CO₂ are two well separated processes Li₂O₂ is oxidized and removed from the electrode while a frame of decomposition products is left behind (Figure 11D). The remaining cavities in this frame are filled up with electrolyte, that is now forced to follow the oscillation movement of the crystal. Since the mass of Li₂O₂ is replaced by the mass of the electrolyte the expected mass changes are due the differences in the densities of the electrolyte and Li₂O₂, which are below the sensitivity limit. Only when the potential region of CO₂ evolution is entered (Figure 11E) a mass change is observed, because the mass of decomposition products is removed and the frame that forces the electrolyte in the cavities to follow the oscillation movement is destroyed.

In Figure 4C we have observed that initially the reduced quality factor decreases parallel to CO₂ evolution and returns to its original value once CO₂ evolution has stopped. This decrease indicates an increased friction at the interface between the electrode and the electrolyte parallel to CO₂ evolution. It is quite possible that the friction at the interface increases as the decomposition products lose contact to
the electrode. This situation is depicted in Figure 11E. Once CO₂ evolution has ceased also the reduced quality factor returns to its original value.

Conclusions

By means of DEMS it was shown that in addition to O₂ formation CO₂ evolution takes place during the anodic sweep, and that the evolved quantities of CO₂ linearly depend on the quantities of oxygen that were reduced in the previous cathodic sweep. Since DMSO is the only carbon source in the system under investigation, the evolution of CO₂ shows unambiguously that DMSO is decomposed during oxygen reduction. From the ratio of the faradaic current to the ionic current it appears to be favorable to construct batteries in such conditions. No mass deposition in eQCMB measurements is observed. How- ever, whether or not this discharge mode is really favorable and Research (FRG) for funding this work. This work is part of

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