Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

-Supplementary Information-

A new thin layer cell for battery related DEMS-experiments:

The activity of redox mediators in the Li-O_2 cell

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1.1. Relation between oxygen partial pressure and ionic current of mass 32

In the presented thin layer cell the saturation of oxygen within the electrolyte is determined through the applied partial pressure of oxygen. According to *Hernry`s Law* the equilibrium concentration of dissolved oxygen within the chosen electrolyte in the thin layer cell is proportional to the pressure. Therefore, the flux of oxygen into the mass spectrometer also has to be proportional to the oxygen pressure. To give a more detailed illustration, the concentration profile of the oxygen species within the thin layer cell is shown in Figure S 1.

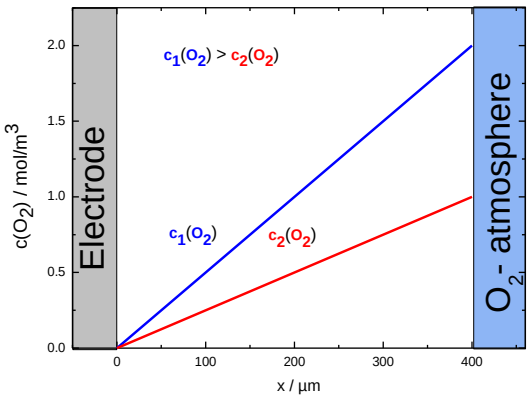

Figure S 1: Schematic representation of the oxygen concentration profile along the thickness of the working electrode compartment.

After an equilibrium phase, the concentration profile show a linear trend. At the boundary to the oxygen atmosphere the concentration of oxygen within the electrolyte is given by *Hernry`s* Law (we assume that there is an equilibrium at the gas/electrolyte interface).

$$c_{O_2} = k_H \cdot p_{O_2} \quad (1)$$

Because we are using a gold sputtered porous PTFE membrane as working electrode in all experiments, the dissolved oxygen is evaporating into the vacuum of the mass spectrometer. Therefore, the concentration of oxygen at the electrode-vacuum boundary is zero. The flux of oxygen into the mass spectrometer can be simply calculated by *Fick's first law*.

$$J_{O_2} = -D_{O_2} \cdot \frac{\partial c_{O_2}}{\partial x} \quad (2)$$

For a linear concentation profile, the term $\frac{\partial c}{\partial x}$ simplifies to $\frac{\Delta c}{\Delta x}$. Taking into account that Δx is the thickness of the working electrode compartment as shown in Figure S 1 the term , $\frac{\Delta c}{\Delta x}$. can be further simplified to $\frac{c_{O_2}}{\Delta x}$. Combining all these simplifications into eq. (1) and eq. (2) will finally lead to eq. (3).

$$J_{O_2} = -D_{O_2} \cdot \frac{k_H \cdot p_{O_2}}{\Delta x} \quad (3)$$

Eq. (3) implies a proportionality between the flux of oxygen into the vacuum of the mass spectrometer and the applied partial pressure of oxygen to saturate the electrolyte with oxygen. To test the applicability of the above equations experimentally, we varied the partial pressure of oxygen to saturate the DMSO filled thin layer cell with oxygen. Simultaneously the ionic current of mass 32 I_{32} was recorded (see Figure S 2 (a)). This ionic current is proportional to the flux of oxygen into the mass spectrometer. Indeed, we found the proportionality between I_{32} (J_{O_2}) and p_{O_2} as can be seen in Figure S 2 (b).

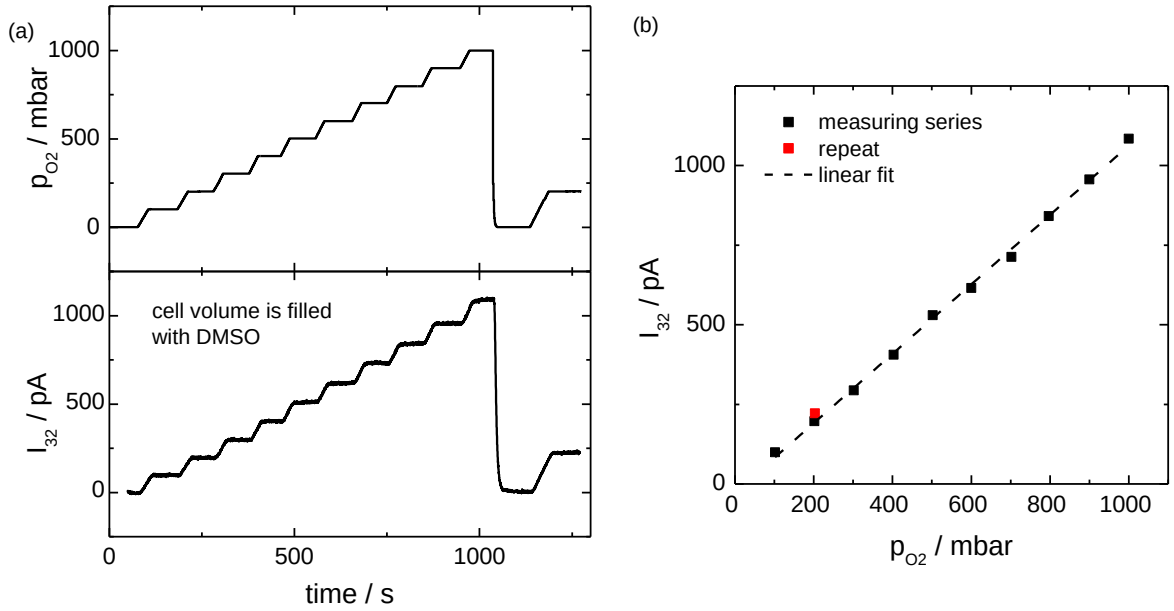

Figure S 2: (a): Applied oxygen partial pressure to saturate DMSO within the thin layer cell with oxygen (upper figure). Simultaneously recorded ionic current of mass 32 (lower figure). This figure shows the time development of both measurements. (b) Plot of the ionic current as function of the partial pressure. The ploted values were taken in the plateaus of Figure S 2 (a). In this case the thickness of the working electrode compartment was 300 µm.

1.2. Stability of TTF in deoxygenated solution

The measurement shown in Figure S 3 shows that there is no effect on the cyclic voltammetry response of TTF in a deoxygenated solution to an oxygenated solution. In the measurement in the deoxygenated solution, the potential window was also opened to -1.6 V vs $Ag|Ag^+$. Even at lower electrode potentials, TTF is not undergoing any redox processes. In addition, the absence of a CO_2 flux indicates that TTF is not undergoing a decomposition reaction, which is releasing CO_2.

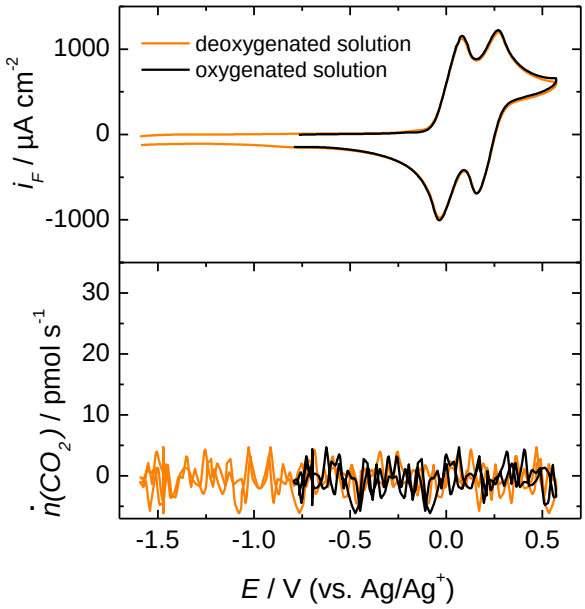

Figure S 3 CV of 10 mM TTF in a 0.5 M $LiClO_4$ in DMSO in a deoxygenated solution (orange traced) and an oxygenated solution (black traced). The lower graph shows the simultaneously recorded CO_2 flux. The measurements were performed with a sweep rate of 50 mV/s.

1.3. Determination of the number of electrons during the OER for RM containing electrolytes

During the OER, the measured faradaic current consists of three different processes:

1. Direct oxidation of Li_2O_2 on the electrocatalyst surface.
2. Oxidation of Li_2O_2 through RM^+ followed by an oxidation of RM to RM^+ on the electrocatalyst surface.

3. Oxidation of RM to RM^+ on the electrocatalyst surface, followed by a diffusion process of RM^+ into the electrolyte without oxidizing any Li_2O_2.

To determine the numbers of transferred electrons per oxygen molecule for the OER processes (first and second process), the overall faradaic current has to be corrected for the contribution of the third process. Here we will briefly describe the correction procedure choosing the TTF containing experiments shown in Figure 3 (a) of our publication as an example.

First of all, a part of the anodic sweep in the TTF containing supporting electrolytes is taken for the analysis. The measurements shown in Figure S 4 (a) differ in their lower potential limit, which was chosen in the experiment. In the black traced measurement, the lower limit was set at -0.5 V. Therefore, no ORR takes place. In the red traced measurement, the lower limit was -1.6 V. Since in the red traced measurement the potential was low enough to perform the ORR, one is able to observe all three processes, which were mentioned above, during the anodic sweep. On the other hand, the black traced measurement only contains the third process, as mentioned above. To isolate the OER processes, one can subtract the black traced measurement from the red traced measurement. The resulting current ΔI_F is shown in Figure S 4 (b). ΔI_F is further correlated with the ionic current of mass 32 to get the number of transferred electrons per oxygen molecule.

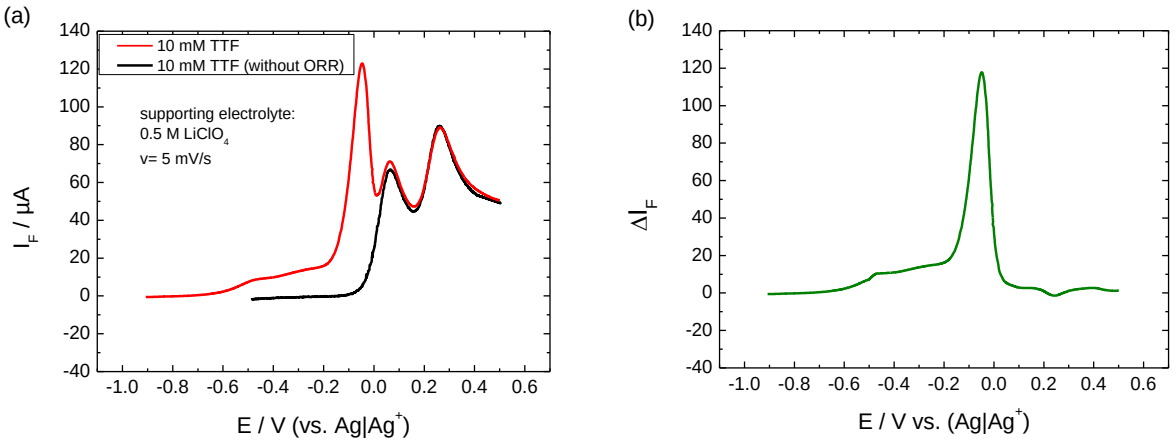

Figure S 4 (a): Extract of the anodic sweep for the TTF containing 0.5 M $LiClO_4$ in DMSO. For the red curve the potential was previously cycled into the ORR-region. In the black traced measurement the ORR potential region was avoided. (b): Current profile obtained out of the difference of the currents shown in (a).

1.4. Using TEMPO as redox mediator

2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO) was used as a redox mediator. The cyclic voltammetry and the MSCVs of mass 32 and 44 are shown in Figure S 5.It is remarkable that for the DMSO based electrolyte, we observe an irreversible TEMPO-redox system. The previous article including TEMPO as redox mediator in Li-O_2 cells were performed in Tetraglyme based electrolytes[1, 2]. Nevertheless, this experiment was used to determine the potential at which the activity of the redox mediator starts as well as the half wave potential of the TEMPO oxidation peak.

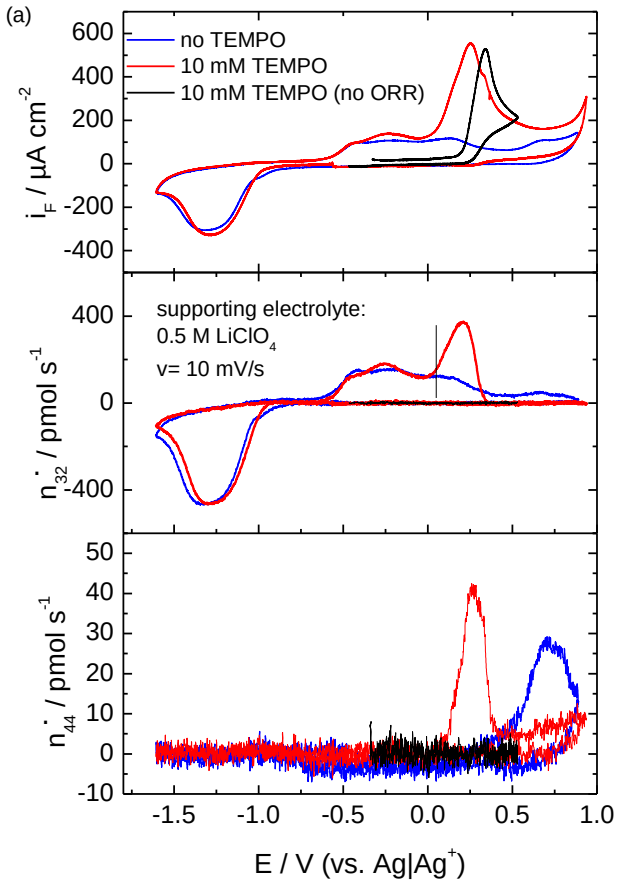

Figure S 5 (a): CVs and MSCVs on mass 32 and 44 with a sweep rate of 5 mV/s in 0.5 M LiClO4 solution in DMSO with 10 mM TEMPO (black and red trace) and without TEMPO (blue trace).

1.5. Using Fc as a redox mediator

Ferrocenium (Fc) was also used as a redox mediator. The cyclic voltammetry and the MSCVs of mass 32 and 44 are shown in Figure S 5 (a). It is well known, that the Fc^+ is very sensitive to small amounts of oxygen [3]. Therefore, the black traced measurement was performed without oxygen (system to saturate the electrolyte with gas was evacuated). For the red traced measurement, the ORR was performed under an oxygen partial pressure of 900 mbar. During the anodic sweep, at a potential of -0.5 V, the potential was kept. The tubes with the oxygen atmosphere were evacuated under potential control. Afterwards, the anodic sweep was continued. The calculated number of transferred electrons per oxygen molecule are shown in Figure S 6 (b).

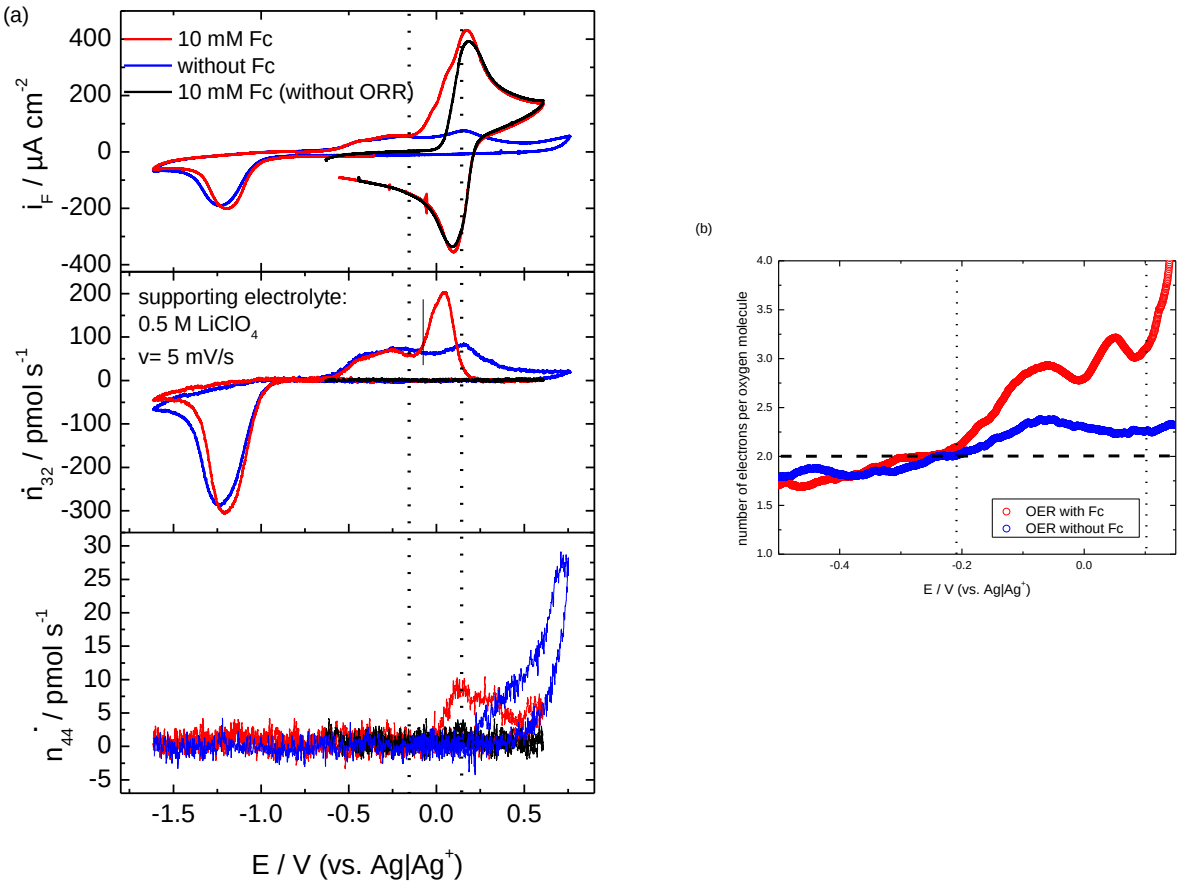

Figure S 6 (a): CVs and MSCVs on mass 32 and 44 with a sweep rate of 5 mV/s in 0.5 M $LiClO_4$ solution in DMSO with 10 mM Fc (black and red trace) and without Fc (blue trace). (b) Calculated number of transferred electrons per oxygen molecule z.

1.6. Number of transferred electrons during the ORR

The typical number of electrons, which we observe during the ORR in DMSO based electrolytes is shown in Figure S 7. Our work group previously reported about this observation [4].

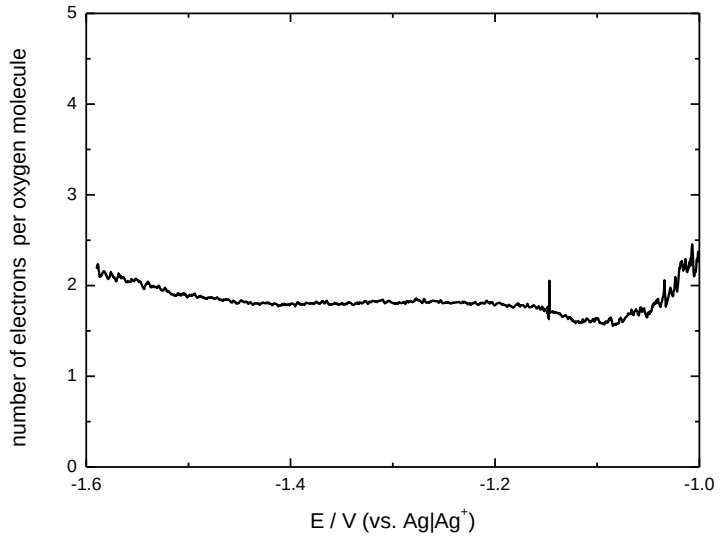

Figure S 7: Number of electrons transferred per oxygen molecule during the ORR for a 0.5 M $LiClO_4$ in DMSO.

1.7. A thermodynamic and kinetic analysis of the Li_2O_2 oxidation through a redox mediator

In our analysis, the following chemical and electrochemical reactions were considered:

$$RM \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RM^+ + e^- \tag{4}$$

$$RM^+ + Li_2O_2 \xrightarrow{k_2} RM + O_2^{\bullet -} + 2Li^+ \tag{5}$$

$$O_2^{\bullet -} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} O_2 + e^- \tag{6}$$

$$RM^+ + O_2^{\bullet -} \xrightarrow{k_4} RM + O_2 \tag{7}$$

In this reaction scheme it is reasonable to assume that the reaction (5) is the rate determining step. According to reaction (5), the O_2^- production rate can be formulated as followed:

$$\frac{d[O_2^{\bullet -}]}{dt} = k_2[Li_2O_2][RM^+] \tag{8}$$

Expressing the concentration of RM^+ through Nernst law leads to:

$$\frac{d[O_2^{\bullet -}]}{dt} = k_2[Li_2O_2][RM]\cdot e^{-(E-E^0_{RM/RM^+})F/RT} \tag{9}$$

In equation (9) E stands for the electrode potential and E^0_{RM/RM^+} for the standard potential of RM. Including the initial concentration of RM, $[RM_0]$:

$$[RM_0] = [RM] + [RM^+] \tag{10}$$

This leads to the following expression:

$$\frac{d[O_2^{\bullet -}]}{dt} = k_2[Li_2O_2][RM_o]/(1+e^{-(E-E^0_{RM/RM^+})F/RT}) \tag{11}$$

In the next step we assumed that the rate constant k_2 is given by Marcus' expression:

$$k_2 = k_{2,0}\exp\left(-\frac{(\lambda+\Delta G_0)^2}{4\lambda RT}\right) \tag{12}$$

Where λ is the reorganization energy and ΔG_0 the free enthalpy of the electron transfer.

With the help of reaction (5) ΔG_0 can be expressed as follows:

$$\Delta G_0 = -F\left(E^0_{RM+/RM} - E^0_{Li_2O_2/O_2^-}\right) = -FE_R \tag{13}$$

Combing equation (12) and (14) results in:

$$k_2 = k_{2,0}\exp\left(-\frac{\lambda}{4RT} + FE_R\left(\frac{1}{2RT} - \frac{FE_R}{4\lambda RT}\right)\right) \tag{14}$$

For DMSO one can assume a reorganization energy of 80 kcal/mol [5]. E_R is for the investigated redox mediators between 0.7 V and 1.1 V. Taking these numbers into account, one can neglect $\frac{FE_R}{4\lambda RT}$ over $\frac{1}{2RT}$. Overall expression (14) simplifies to the following expression:

$$k_2 \approx k_{2,0}\exp\left(-\frac{\lambda}{4RT} + \frac{FE_R}{2RT}\right) \tag{15}$$

If the reaction should be an inner sphere reaction, the factor $\frac{1}{2}$ in the second term of the exponent would have to be replaced by a factor α similar to that in the Butler Volmer equation.

Combing equation (11) and (15) leads to:

$$\frac{d[O_2^{\bullet -}]}{dt} = k_{2,0}\exp\left(-\frac{\lambda}{4RT} + \frac{FE_R}{2RT}\right)[Li_2O_2][RM_o]\cdot\left(1+\exp\left(\frac{-(E-E^0_{RM/RM^+})F}{RT}\right)\right)^{-1} \tag{16}$$

Taking the logarithm and summing up all constant values as *const* gives the following expression:

$$\ln\left(\frac{d[O_2^{\bullet -}]}{dt}\right) = const. + \frac{FE_R}{2RT} - \ln\left(1+\exp\left(\frac{-(E-E^0_{RM/RM^+})F}{RT}\right)\right) \tag{17}$$

Our experiments showed, that the difference $E\text{-}E^0$ is in the range between 60 mV and 200 mV. Therefore, the 1 in the right hand side logarithm term of equation (17) can be excluded giving the following equation:

$$\ln\left(\frac{d[O_2^{\bullet -}]}{dt}\right) = const. + \frac{FE_R}{2RT} - \frac{-(E-E^0_{RM/RM^+})F}{RT} \tag{18}$$

$$\frac{RT}{F}\ln\left(\frac{d\left[O_2^{\bullet-}\right]}{dt}\right) = const2. + \frac{1}{2}E^0_{RM/RM^+} + (E - E^0_{RM/RM^+}) \qquad (19)$$

147 In equation (19) the expression for E_R, defined in equations (13) and (14), was used. The
148 resulting term $-\frac{E^0_{Li_2O_2/O_2^-}}{2}$ was included into *const*. giving *const*2..
149 To explain the trend shown in Figure 5, equation (19) was rearranged as followed:

$$E = \frac{1}{2}E^0_{RM/RM^+} + const2. + \ln\left(\frac{d\left[O_2^{\bullet-}\right]}{dt}\right)_E \frac{RT}{F} \qquad (20)$$

150 The term $\ln\left(\frac{d\left[O_2^{\bullet-}\right]}{dt}\right)_E$ is constant, due to our determination of E: E is the potential at which
151 the oxygen flux into the mass spectrometer in the RM-containing experiment is increased over
152 5 pmol s^{-1} above that observed in the measurement in the supporting electrolyte. If one assumes
153 that the chemical side reactions of O_2^- are negligible, O_2^- will be oxidized by a following
154 electrochemical reaction resulting into the oxygen flux into the mass spectrometer. Thus, E in
155 formula (19) is the same as the used E_{onset} within the discussion of the underlying paper of this
156 supporting information.
157 All in all, our combination of the Marcus‘ expression as well as a Nernstian behavior for the
158 examined oxidation of the Li_2O_2 by a redox mediator shows that one would expect in a plot of
159 E_{onset} as a function of the redox potential of the redox mediator a slope of 0.5.
160

1.8. The effect of the surface roughness on the ORR at Au-electrodes

To examine the roughness effect of Au-surfaces on the ORR DEMS studies in a doual thin layer cell were performed (for details towards the experiment see [6]). A polycrystalline Au electrode with a roughness factor (RF) of 1 was used as a working electrode. After the measurements in a 0.5 M $LiClO_4$ O_2-saturated DMSO electrolyte the surface of the electrode was roughened to a RF of 3 and the measurement in a 0.5 M $LiClO_4$ O_2-saturated DMSO electrolyte was repeated. The RF values were determined by a method described by Trasatti and Petrii [7]. The experimental data is shown in Figure S 7.

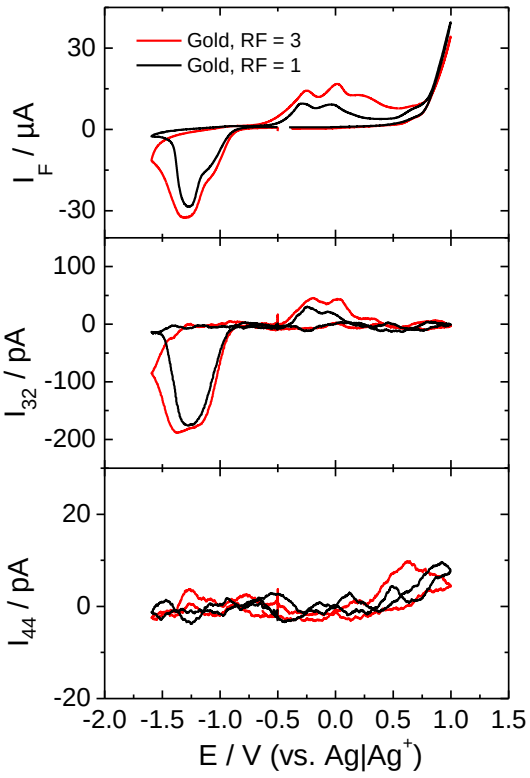

Figure S 8: DEMS study of Au-electrodes with two different roughness factors (RF). In red: RF= 3 and in blue RF=1. The figure shows the cyclic voltammetry data (top), the ionic current of mass 32 (middle) and the ionic current of mass 44 (bottom).

The experimental data show, that the shape of the ORR is influenced by the different roughness factors. The transferred charge in the ORR is higher for the rougher surface. This is because the rougher surface is able to uptake more Li_2O_2 before the poisoning of the electrode starts, because of its higher surface area. This result show that the slightly different shapes of the ORR

region within the underlying main manuscript could be explained through different roughness factors of the sputtered Au-electrodes.

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[3] J. P. Hurvois and C. Moinet, *Journal of Organometallic Chemistry*, **690**, 1829 (2005).
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[5] B. Zhuang and Z.-G. Wang, *The Journal of Physical Chemistry B*, **120**, 6373 (2016).
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