

QCM study of ORR-OER and in-situ study of a redox mediator in DMSO for Li-O₂ batteries

Supporting information

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The solubility of LiO₂ in DMSO was studied by using a rotating ring-disk electrode (RRDE), both disk ($\phi = 4.57$ mm) and disk electrodes ($\phi_{\text{inner}} = 4.93$ and $\phi_{\text{outer}} = 5.38$) were made of platinum (Pine Instruments, E7R8-SN14205). For these experiments a cyclic voltammogram was applied on the disk, while the ring was kept at a constant potential of +2.9 V vs. Li⁺/Li. The cyclic voltammogram on the disk had a lower vertex potential of +2 V vs. Li⁺/Li and an upper vertex potential of +4.1 V vs. Li⁺/Li and a scan rate of 50 mV s⁻¹ was applied. The rotation speed of the RRDE was kept constant at 1000 rpm. As reference electrode a silver wire was immersed in a glass tube with a porous glass frit, filled with 0.1 M AgNO₃ (Chempur) and 1 M LiTf₂N (IoLiTec) in DMSO (anhydrous, Sigma-Aldrich). The potential difference of the reference electrode was measured vs. a lithium wire in the electrolyte of interest and the potential in this work was corrected using this difference (3.62 V). A platinum coil was used as counter electrode. As electrolyte an oxygen saturated DMSO solution was used with 0.1 M LiTf₂N. Oxygen reduction starts on the disk during the negative scan at approx. +2.7 V vs. Li⁺/Li (Figure S1). Despite the fact that the RRDE is rotating at 1000 rpm, no limiting current plateau was observed. The lack of a plateau, which is replaced by a broad peak, can be understood by the deposition of an insoluble electrically insulating reduction product (Li₂O₂) which begins to block the availability of oxygen to reach the electrochemical interface and thereby prevents the realization of a plateau limiting current during the experiment.²¹ Another important observation is the oxidative current on the ring at a potential of +2.9 V vs. Li⁺/Li. At this potential it is known from experiments in quiescent electrolytes, that oxidation of the superoxide is under mass transport control and Li₂O₂ does not yet oxidize at this potential (Figure 3). Therefore it can be concluded that the oxidative current on the ring is due to the oxidation of soluble stabilized lithium superoxide (LiO_{2(sol)}) species which are transported to the ring interface.

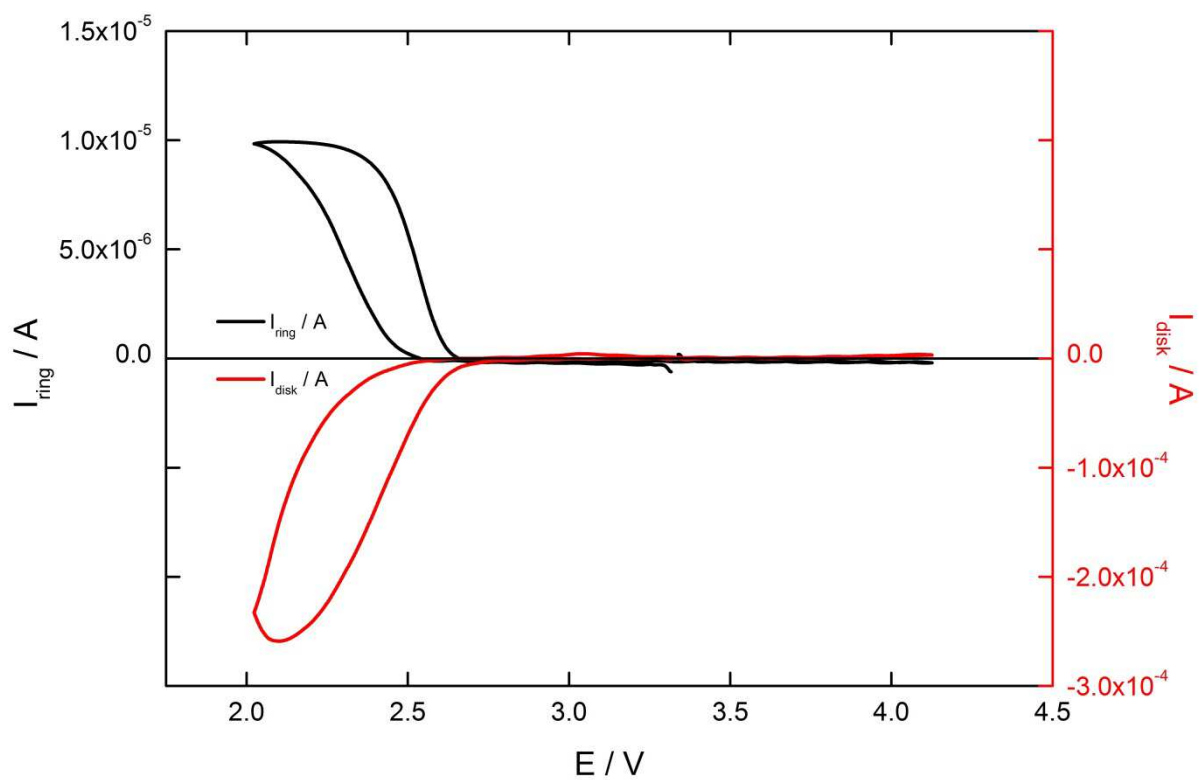


Fig. S 1 Disk (red) and ring (black) currents recorded in 0.1 M LiTf₂N in DMSO solution saturated with oxygen gas at 25 °C. The RRDE rotates at a constant speed of 1000 rpm. The disk current was generated by applying a cyclic voltammogram with a scan rate of 50 mV s⁻¹ and the ring was kept at a constant potential of +2.9 V vs. Li⁺/Li.