Influence of Mg^{2+} on the ORR and OER in the Ionic Liquid BMP-TFSI

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A major issue in the development of rechargeable Mg-air batteries is the reversibility of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) during discharge and charge of the battery. Ionic liquids such as 1-butyl-1-methylpyrrolidinium bis-(trifluoromethanesulfonyl) imide (BMP-TFSI) are promising candidates as electrolytes due to their low vapor pressure, high ionic conductivity and wide electrochemical potential window. Therefore, we investigated the ORR and OER in BMP-TFSI on glassy carbon (GC) electrodes, focusing on the effect of the electrode potential and of added Mg^{2+} ions on the reversibility and on the product distribution.

The ORR/OER in BMP-TFSI and 0.1 M Mg-$TFSI_2$/BMP-TFSI electrolytes was studied by cyclic voltammetry and potential step measurements on glassy carbon (GC) electrodes. The measurements were performed in a dual thin-layer flow cell [1] equipped with a non-porous thin (10 µm) Teflon membrane allowing for differential electrochemical mass spectrometry (DEMS), which was employed to monitor the oxygen consumption and oxygen evolution. DEMS measurements performed on a GC electrode under a flow of O_2-saturated BMP-TFSI show two distinct mass transport limited currents levels at ca. -0.4 and -1.2 V (vs. Mg/MgO), the one at -1.2 V being about twice as high as the other one. The O_2 consumption, however, is identical in both cases, indicating a change in the number of electrons per O_2 molecule from 1 to 2, i.e., a transition in the ORR selectivity from superoxide (O_2^-) to peroxide (O_2^{2-}) formation. The ORR in Mg^{2+} containing BMP-TFSI proceeds via two peaks in the first negative-going scan. Decreasing currents in the following scans indicate a rapid passivation of the electrode surface. After excursions to -1.4 V, a reversible small O_2 consumption/release appears, which is attributed to superoxide formation/oxidation.

References

[1] Schnaidt, J.; Beckord, S.; Engstfeld, A.K.; Klein, J.; Brimaud, S.; Behm, R.J. A combined UHV-STM-flow cell set-up for electrochemical/electrocatalytic studies of structurally well-defined UHV prepared model electrodes. *Phys.Chem.Chem.Phys*. **2017**, 19, 4166-4178.