O₂ Reduction on a Au Film Electrode in an Ionic Liquid in the Absence and Presence of Mg²⁺ Ions: Product Formation and Adlayer Dynamics

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ABSTRACT

Aiming at a detailed understanding of the interaction between an ionic liquid, O₂ and electrodes in Mg-air batteries we performed a combined differential electrochemical mass spectrometry (DEMS) and in situ infrared spectroscopy model study on the interaction between the ionic liquid (IL) 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (BMP-TFSI) and a gold film electrode in the presence and absence of O₂ and Mg²⁺ ions in the potential range relevant for the oxygen reduction and evolution reaction (ORR and OER). Detailed information on the dynamic exchange of adsorbed ions, on the stability /decomposition of the ionic liquid, and on the activity / selectivity / reversibility of the ORR is derived from measurements performed under potentiodynamic and potentiostatic conditions.

In neat BMP-TFSI, we find the dynamics of the potential induced exchange of adsorbed ions to depend significantly on the exchange direction. In the presence of O₂, the anions formed in the ORR distinctly affect the adsorption characteristics of the IL ions, and the exchange dynamics. Furthermore, the ORR changes from reduction to superoxide anions at moderate potentials to reduction to peroxide anion at more negative potentials. In the additional presence of Mg²⁺ ions, dominant magnesium peroxide and oxide formation result in an irreversible ORR, in contrast to the requirements of an efficient re-chargeable Mg-air battery. In addition, these ions result in the increasing formation of a blocking adlayer, reducing the coverage of adsorbed IL species.

Keywords: Adsorption, Desorption, Dynamics, ORR, Au, Ionic Liquid, BMP-TFSI, Mg²⁺, DEMS, ATR-FTIRS

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