

Oxygen Reduction and Oxygen Evolution on Well-defined Co- and Fe-containing Mixed Oxide Cathodes for Zn-Air Batteries – A Surface Science and Electrochemical Model Study

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Dedicated to the occasion of the 70th birthday of Prof. Juan Feliu,

The performance of structurally and chemically well-defined single-crystalline cobalt- and iron-containing mixed oxide thin film model electrodes as bifunctional catalyst in the oxygen reduction and oxygen evolution reactions (ORR and OER) was investigated and compared with those of unary CoO(111) and Fe₃O₄(001) oxides in a combined surface science and electrochemistry approach. Pure and mixed cobalt- and iron- containing film electrodes were prepared by vapor deposition in an O₂ atmosphere and characterized under ultrahigh vacuum (UHV) conditions by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). Electro-chemical/catalytic measurements were performed in an electrochemical cell directly coupled to the UHV system. XPS measurements of mixed binary oxides with different Co:Fe atomic ratios reveal solely Co²⁺ and Fe³⁺ states, pointing to a CoFe₂O₄ in combination with excess Co or Fe either in a CoO or a Fe₂O₃ phase. For the CoFe₂O₄/CoO binary metal oxide electrodes the base CVs in 0.5 M KOH show clear differences compared to Fe₃O₄(001) and the CoFe₂O₄/Fe₂O₃ electrodes at potentials > 0.5 V, reflecting the formation Co²⁺ to Co³⁺ transition. The mixed cobalt- and iron-containing thin film electrodes show a higher overpotential for the OER than pristine CoO(111); it is, however significantly lower compared to magnetite Fe₃O₄(001). Together with changes in the ORR performance Fe doping is found to lower the overall efficiency as bifunctional catalyst, as compared to the pure Co oxide CoO(111) and Co₃O₄(111) electrodes, but it is much higher compared to that of a pristine Fe₃O₄(001) electrode.

Keywords: Bifunctional Catalyst, Zn-air batteries, Oxygen Reduction, Oxygen Evolution, Co Oxide, Model Electrodes

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