



UNIVERSITY OF GOTHENBURG

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
NATURAL SCIENCE, SPECIALISING IN CHEMISTRY

MECHANISTIC INSIGHTS INTO TRANSITION METAL
OXIDE CATALYZED WATER OXIDATION

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Abstract

A binuclear mechanism was proposed and evaluated by means of Density Functional Theory calculations. The central reaction steps were found to be the oxidation of the transition metal TM-OH moieties to TM=O and the subsequent intramolecular O-O bond formation between two TM=O groups. These steps were employed as descriptors for the performance of a set of 3d transition metal oxides studied in a $\text{MgO}_x(\text{OH})_y$ test rig embedding. Two classes of oxygen evolution reaction (OER) catalysts were found to emerge at the TyrOH/TyrO \bullet reference potential. The first class, referred to as [+/-], which contains Mn(III-V), Co(II-IV) and Ni(II-IV), shows an endothermic oxidation step combined with exothermic O-O bond formation. The members of this class were argued to be active towards the (OER), i.e. the oxy moieties desorb spontaneously as O $_2$ at the expense of high overpotentials. The second class, called [-/+], comprising V(III-V), Cr(III-V) and Fe(II-IV), was found to show opposite behavior. Thus, poor performance is expected due to a highly unfavorable O-O bond formation step. Improved performance was predicted by mixing [+/-] with [-/+] transition metal oxides. Intermediate behavior, meaning oxidation of the TM-OH moiety to TM=O at the TyrOH/TyrO \bullet potential combined with a thermoneutral O-O bond formation, is found for Ir(III-V) and Mn(II-IV). While the former displays high activity towards the water oxidation reaction the latter is argued to be inactive due to unfavorable kinetics. The idea of mixing transition metal oxides was generalized for mixed oxidation state systems and evaluated for a Mn(II-IV) Mn(III-V) system. Improved performance was found suggesting, that this reaction path is relevant for the (OER). The generality of the mechanism was shown by direct comparison with experimental findings on iridium oxide and RuO $_2$.