

Ligand-field/redox potential correlation in Co-Fe oxides investigated by 2p3d resonant inelastic X-ray emission spectroscopy

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Development of new anode materials based on earth abundant transition metals for water splitting is strategically important for industrial and large-scale applications.¹ Especially significant has been the development of mixed-metal oxides, where a synergistic effect has been found in many cases resulting in dramatic improvement of the catalytic performance of the material.²⁻³ Nevertheless, we still lack of understanding of these observed synergistic effects. Specifically, the Co₃O₄ spinel structure has shown a high catalytic activity for OER reactions and can be further improved by substitution of Fe into Co₃O₄ at varying concentrations.³ Here, we studied a series of Fe substituted Co spinels with different Co/Fe ratios, using 2p3d resonant inelastic X-ray scattering spectroscopy (RIXS). This technique allows to characterize the electronic structure of the Co frontier orbitals, which should be responsible for the redox properties of the material, by interrogating the d-d transitions, including spin-forbidden transitions, which are very weak, broad, or completely silent in other spectroscopies.⁴ Analysis of the spectra in combination with ligand-field theory (LFT) calculations, allowed us to assign the different features to d-d transitions of each Co site in the spinel. The measured 2p3d RIXS allows to clearly differentiate the degree of spinel inversion as the Fe loading in the Co spinel increases. Interestingly, we have found a strong correlation between the lowest energy transfer feature (~0.5eV), assigned to the T_d Co²⁺ site, and the potential of the pre-catalytic wave, which indicates that the Fe content modulates the ligand-field splitting of the Co, and consequently the redox potential of the material. This study describes how 2p3d RIXS can be used to investigate in detail the electronic structure of electrocatalysts, being one of the first examples to provide evidence of the modulation of the electronic structure of the Co by Fe doping, even at low-doping levels, and how this modulation is correlated to the redox potential of the material.

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