## Role of the surface orientation, termination and transformations on the OER activity of spinel and perovskite anode materials Rossitza Pentcheva

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The development and improvement of catalysts for chemical energy conversion such as (photo-) electrocatalytic water splitting requires mechanistic understanding of the reactions at the solid-liquid interface at the atomic/molecular level. Based on density functional theory (DFT) calculations with a Hubbard U term, we focus on the oxygen evolution reaction (OER) activity of iron, cobalt and nickel containing spinels [1-3] and perovskites [4-5]. This allows us to disentangle the role of structural motifs, surface orientation and termination. Analysis of the underlying electronic and magnetic properties reveals dynamic variation of oxidation state during OER with marked differences in the degree of localization for spinels vs. perovskites. Octahedral Co at the (001) surface emerges as a potential active site with the lowest overpotentials. Considering solvation in an implicit solvent model, reveals an overall enhancement of the overpotential due to stronger binding of intermediates, but the relative trends remain unchanged [2]. Last but not least, we elucidate the effect of a surface transformation to an oxyhydroxide layer at the perovskite surface and identify important distinctions for different surface facets [5].

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Fig. 1. OER at the pristine and doped  $Co_3O_4(001)$  surface [2]. The side views with spin density of the potential determining steps at the B and A terminations, respectively, indicate differences in valence state of the surface cations during OER. Note also the formation of a hydrogen bond to the surface for \*OOH at the A layer. Volcano plot of  $-\eta$  as a function of the binding energy difference of \*O and \*OH including also the results for  $Co_xNi_{1-x}Fe_2O_4(001)$  [1].

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