Ab initio study of doped NiOOH surfaces for electro-oxidation of organic molecules

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Chemicals are mainly synthetized from fossil fuel-derived precursors. One big challenge of our century is to replace these precursors with more renewable ones, for example with biomass-derived precursors. 5-hydroxymethylfurfural (HMF) can be extracted from cellulose or hemi-cellulose and can be electro-oxidized into 2,5-furandicarboxylic acid (FDCA). FDCA can replace terephthalic acid for the synthesis of polyethylene terephthalate (PET). Nickel oxyhydroxide (NiOOH) surfaces are well-known as efficient anode materials for water electro-oxidation during the oxygen evolution reaction (OER) and are also promising for HMF to FDCA electro-oxidation. The efficiency of this electrode is experimentally shown to be enhanced with metal-doping for OER and electro-oxidation of HMF. In the present work, we perform a Density Functional Theory (DFT) investigation of the impact of metal-doping on the electrochemical reactivity of NiOOH surfaces. Based on experimental studies and the literature of metal-doping for OER, we chose to dope NiOOH with 6 different metals: Co, Cu, Fe, Ga, Mn and Sc. Periodic Density Functional Theory (using VASP, and the PBE-dDsC functional) computations of the relative stability of the relevant bulk of nickel hydroxide ($Ni(OH)_2$) and NiOOH were performed with a doping density from 0% to 25%. The relative stabilities of NiOOH and doped-NiOOH surfaces were calculated at the same level of theory. The effect of the electrochemical potential was modeled by grand-canonical DFT (GC-DFT) in conjunction with the linearized Poisson-Boltzmann equation.

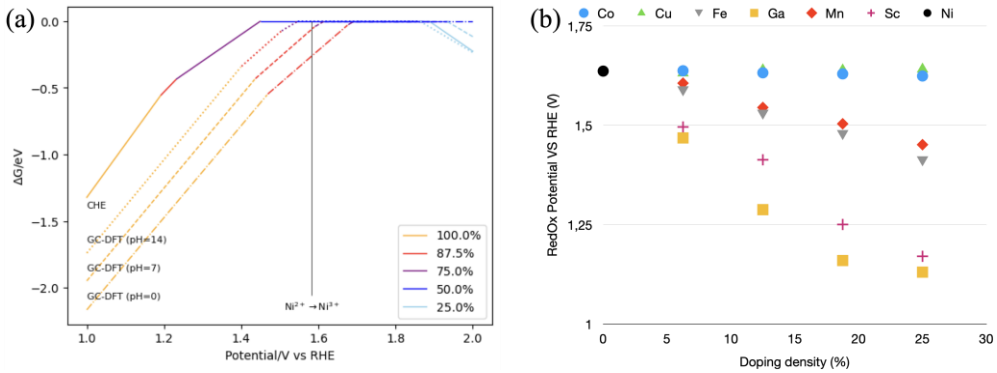

Figure 1. (a) Relative stability of hydrated NiOOH surfaces with CHE and GC-DFT methods; (b) Red/Ox potential of $NiOOH/Ni(OH)_2$ bulks with a doping density from 0% to 25% in Co, Cu, Fe, Ga, Mn and Sc.

Figure 1a shows the most stable hydrogen coverage of pure NiOOH surface as a function of the electrochemical potential at computational hydrogen electrode (CHE) and GC-DFT levels. Taking the electrochemical potential explicitly into account via GC-DFT has a significant impact on the results and shows that at the studied potential (HMF electro-oxidation at ~1.5 V) the hydrogen coverage is between 50 and 87.5% and depends on pH. The evolution of the Red/Ox potential of $NiOOH/Ni(OH)_2$ with an changing doping density is shown in Figure 1b. Three behaviors are observed out: Co, Cu have no impact, Fe, Mn linearly decrease the potential with an increase of doping, while Ga and Sc strongly destabilized bulk structure of doped-$Ni(OH)_2$. The impact of the doping on the surface state (H-coverage) and the electro-oxidation of HMF will be presented to illustrate the effect of tuning the electrocatalyst on its activity.

Keywords: DFT, electrochemistry, surface, doping

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