Comparative DFT+U and HSE Study of the Oxygen Evolution Electrocatalysis on Perovskite Oxides

The most common method for incorporating strong electron correlations is either to apply the Hubbard U correction on top of standard density functional theory calculations (DFT) or to use hybrid functionals. In this study, we elucidate the sensitivity of the Hubbard U correction in the PBE+U functional and the amount of exact exchange, α, in the hybrid HSE functional on the structural stability, catalytic activity and electronic conductivity of pure and doped perovskite oxides, ABO3, (A = La, Ca, Sr and Ba, B = Cr, Mn, Fe, Co, Ni and Cu) for oxygen evolution electrocatalysis. We find a strong dependence of heat of formations and reaction overpotentials for a range of U = 0, 3 and 5 eV and α = 0, 0.15, 0.25, 0.35 values investigated in this study, which we attribute primarily to changes in the oxidation state of B cations. If the valence of B cations in the perovskite and reference oxide is the same, then the U- and α dependence is very small. On the other hand, if the valences are different then heat of formations can change by as much as 1 eV. As the oxidation state of a surface metal ion depends on adsorbed intermediate and nature of the element, similar differences in energies appear in the calculated reaction overpotentials for oxygen evolution. The large U and α dependence sets serious constraints on the use of DFT+U and HSE methods for assessing stabilities and catalytic activities of perovskite oxides. In addition, the large α dependence raises the question whether HSE calculations can improve sufficiently the accuracy of DFT+U results for multi-step electrochemical reactions to justify the excess computational cost. Although we have investigated only one particular class of catalysts and one electrochemical reaction, the results of this study can expectedly be generalized to other strongly correlated systems in which the oxidation state of the surface changes during reaction. The influence of U on the electronic conductivity is significant only in cases where it qualitatively changes the electronic structure, e.g. opening the band-gap. From a combinatorial analysis on pure and doped oxides, we identify electronically conductive catalysts classified according to different electron conduction types: intrinsic conductivity (Fe4+, Co3+(intermediate spin, IS) and Ni3+), electron polaron hopping (along Mn3+-O-Mn4+ chains) and charge transport through holes in the valence band.

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