Trends in Ab Initio Oxygen Reduction Reaction Energetics of LaBO₃ (B = Mn, Fe, Co, and Ni) for Solid Oxide Fuel Cells

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Trends in Ab Initio Oxygen Reduction Reaction Energetics of LaBO₃ (B=Mn, Fe, Co, and Ni) for Solid Oxide Fuel Cells

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There is significant interest in lowering the SOFC operating temperatures to reduce degradation rates and material costs. However, at lower temperatures the contribution to the solid oxide fuel cell overpotential from the cathodic oxygen reduction reaction (ORR) is expected to become increasingly important, particularly as other sources of voltage loss are reduced (e.g., by making thinner and less resistive electrolyte films)[1]. The ORR at oxide surfaces is quite complex, with many possible pathways. To get help design new and more optimal materials, it is not only important to gain fundamental insight into the details of particular systems, but also necessary to find simple descriptors for the reaction process that can aid the search for new materials.

In this study we attempt to find a descriptor for the ORR in terms of fundamental properties of oxide electronic structure. In the absence of well established ORR data, we use a series of calculated energies that are expected to play a dominant role in the ORR (these we call “proxy” energies). Density functional theory (DFT) simulations are performed to calculate a series of ORR proxy energies such as surface oxygen binding, hopping, vacancy, and dissociation energies for LaBO₃ systems (B= Mn, Fe, Co, and Ni). A treatment of the O₂ gas [2] and the DFT+U method [3] are applied to increase the accuracy of the calculated energetics vs. experiments [4]. We first explored the d-band center, commonly used in transition metal catalysts as an ORR descriptor [5], but it did not provide a clear correlation with the calculated ORR proxy energetics. However, we have observed these proxy energies are linearly correlated with the O p-band center. Figure 1 shows the BO₂ surface O above B site energies as a function of the O p-band center. Each point corresponds to different B metal cations at different Ueff values (those with the same color are for the same B metal cation), and the filled symbols represent the optimal Ueff energies of different B’s.

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References

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Figure 1: LaBO₃ (001) BO₂ surface O above B (symbols with solid lines) for various B cation and Ueff’s vs. O p-band center. The filled symbols represent the optimal Ueff energies of different B’s.