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Trends in *Ab Initio* Oxygen Reduction Reaction Energetics of LaBO_3 (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 the 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 LaBO_3 systems (B= Mn, Fe, Co, and Ni). A treatment of the O_2 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 energetics are linearly correlated with the O *p*-band center. Figure 1 shows the BO_2 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 U_{eff} values (those with the same color are for the same B metal cation), and the filled symbols represent the optimal U_{eff} (taken from fits in Ref. [2]) data of a specific B. The use of the optimal U_{eff} has been shown in Ref [4] to give better energetic accuracy than GGA for LaBO_3 oxygen vacancy formation and formation energies. The linear relationship between LaBO_3 surface ORR energetics and O *p*-band center can be understood based on a rigid band model, in which the energetics are related to electron interchange between the O *p*-band and the Fermi energy level of the system. The existence of the linear relationship between the O *p*-band center and the investigated LaBO_3 ORR energetics suggests the O *p*-band center, or equivalently, the O surface binding energy, could be a valuable descriptor for LaBO_3 ORR activity (the later has been shown in Ref. [6] to be correlated with the catalytic activity of MO_x binary transition metal oxides). The establishment of simple descriptors for the LaBO_3 ORR in this work will be further tested to establish correlation with reported experimental activity data in literature, including other promising perovskite materials

for solid oxide fuel cell cathodes such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF), $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO), and $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_{3-\delta}$ (SSC).

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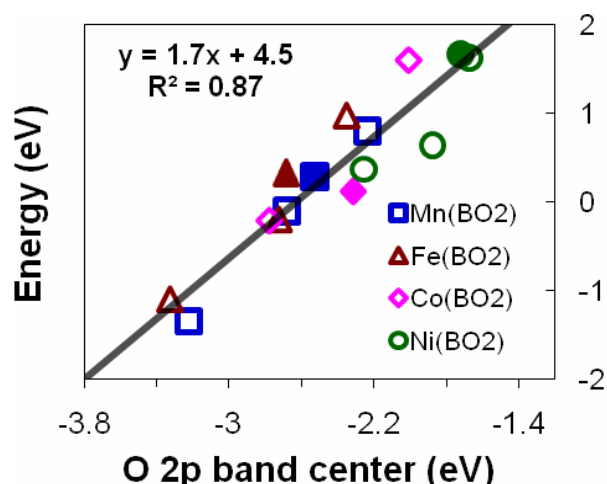


Figure 1: LaBO_3 (001) BO_2 surface O above B (symbols with solid lines) for various B cation and U_{eff} 's vs. O *p*-band center. The filled symbols represent the optimal U_{eff} energies of different B's.

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