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

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The perovskite type lanthanum strontium transition metal oxides (La, Sr)BO₃ (B=Mn, Fe, Co, and Ni) and closely related alloys are frequently explored as the cathode materials for solid oxide fuel cells (SOFCs) due to their ability to catalyze the oxygen reduction reaction (ORR), as well as low cost, high temperature stability and good electronic/ionic conductivity. The ORR contribution to the overpotential is expected to become increasingly important as other sources of voltage loss are reduced (e.g., by the making thinner and less resistive electrolyte films) and as researchers push to lower the SOFC operating temperatures to reduce degradation rates and material costs [1]. The complex ORR mechanisms are still poorly understood, including the rate-limiting steps and how different transition metal cations alter the catalytic properties. We are using density functional theory (DFT) simulations to obtain surface oxygen binding, hopping, vacancy, and dissociation energies to understand the trends vs. transition metal types. Careful treatment of the O₂ gas [2] and application of the DFT+U method [3] (which corrects for the self interaction errors in the strongly correlated transition metal oxides) increase the accuracy of our study. Initial work is focused on the undoped LaBO₃ systems and {001} BO₂ surfaces. Surfaces are simulated with a LaBO₃ 8-layer slab (2x2x4 perovskite supercell) under periodic boundary conditions.

One of the issues of the DFT+U approach is the selection of U_eff (defined as U in [4], where U is the on-site Coulomb repulsion and J is the Hund’s exchange interaction). When U_eff fits to empirical data, the value can vary depending on the material properties that are fitted (band gaps, redox energetics, etc.). Nonetheless, it has been observed that errors in the LaBO₃ ORR relevant energetics can be greatly improved if an appropriate U_eff is applied [5]. To understand the ORR energetic trends vs. U_eff and how U_eff modifies the electronic structure, we have explored a wide range of U_eff (0–7 eV) for each LaBO₃ system. Our results suggest that adding U_eff stabilizes the reduction process [5] and that the barrier of charge transfer between the oxygen center can be understood based on a rigid band model, in which the energetics are related to electron interchange between solids and O₂ molecules is not included in our energetic investigation due to the complexity of the calculations. Nonetheless, the existence of the linear relationship between O_p band center and the investigated LaBO₃ ORR energetics suggests the O_p band center, or equivalently, the O surface binding energy, could be a valuable descriptor for ORR activity.

While tests of the commonly used d-band center as the descriptor for metal catalysts did not provide a clear correlation with the calculated energetics, we have observed the ORR energetics for all materials and U_eff are linearly correlated with the O_p band center. Figure 1 shows the surface oxygen vacancy formation energies and O above surface B site adsorption energies as a function of the O_p band center. Each point corresponds to different B metal cations and/or different U_eff values. The linear relationship between LaBO₃ 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 oxygen p-band and the Fermi energy level of the system. It is noted that the barrier of charge transfer between solids and O₂ molecules is not included in our energetic investigation due to the complexity of the calculations. Nonetheless, the existence of the linear relationship between O_p band center and the investigated LaBO₃ ORR energetics suggests the O_p band center, or equivalently, the O surface binding energy, could be a valuable descriptor for ORR activity.

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References

The ORR process at oxide surfaces is inherently complex with many possible pathways. To get directions towards new and more optimal materials, it is not only important to gain fundamental insight into the details of a single system, but preferably to find fundamental intrinsic descriptors for the reaction process that can aid the search for new materials. Our detailed and systematic study of ab initio surface reaction energetics of fundamental reaction processes as oxygen adsorption, hopping, splitting and vacancy formation energies provides an excellent starting point for the search of descriptors that are likely to correlate with the ORR activity.

Figure 1: LaBO₃ (001) BO₂ surface oxygen vacancy formation and O-B adsorption energies for various B cation and U_eff’s vs. O_p band center.