

**Towards accurate *ab-initio* prediction of ORR/OER activity of LaBO<sub>3</sub> (B=Cr,Mn) Perovskites – role of Hubbard *U* and stable surface coverage**

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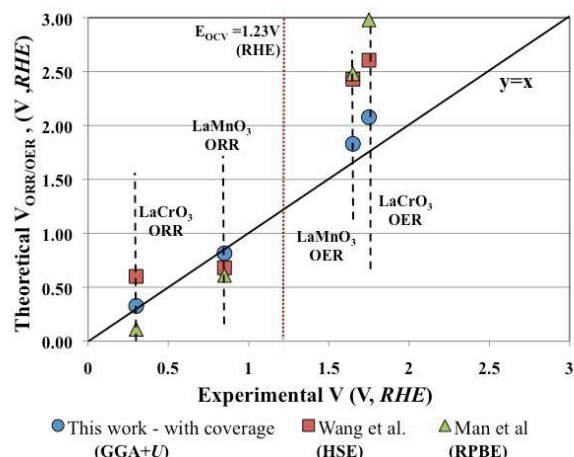
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Achieving faster kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in the aqueous alkaline conditions is crucial to the development of electrochemical devices and processes such as alkaline fuel cells or water electrolysis for hydrogen production. Complex oxides such as transition metal perovskites are promising catalysts and there is a significant interest in using simulations to help design better materials. However, modeling of ORR/OER on perovskite oxides is challenging due to the electronic structure of the transition metal, possible surface reconstructions, and potentially complex surface coverages. Previous *ab-initio* simulations of the ORR<sup>1</sup> and OER<sup>2</sup> on transition metal oxide surfaces have considered a simple approximation of pristine (001)-BO<sub>2</sub>-terminated surfaces. Their predicted voltages from these simplified surface models often deviate more than 0.5V compared to the experimental voltages<sup>3,4</sup>. In this study we use DFT with GGA+*U* (treating the electronic structure of transition metal), to predict the ORR, OER voltages. We further include the (voltage-dependent) thermodynamically stable surface coverage in aqueous environment in the modeling. The results show that including GGA+*U* and surface coverage effect together can play a critical role in correctly estimating the relative binding energies of reactive intermediates of ORR, OER. This predicts the overpotentials within 0.3V of experimental reported voltages.

Calculations were performed with Density Functional Theory (DFT+*U* approach) as implemented in the Vienna Ab-initio Simulation Package (VASP)<sup>5</sup> with the generalized gradient approximation (GGA) (PW-91 version)<sup>6</sup> and *U<sub>eff</sub>* from Wang et al<sup>7</sup>. Ionic cores were represented by the PAW method. A 2x2x1 k-point mesh for (2x2x4) 80-atom cell and a 450 eV plane-wave energy cut-off were used. Thermodynamic stability of different adsorbates (\*O, \*OH, \*OOH, \*H, \*H<sub>2</sub>O, \*HOOH) were studied on the surfaces of LaCrO<sub>3</sub> and LaMnO<sub>3</sub> by calculating their Gibb's free energy of formation in aqueous alkaline conditions (*p*O<sub>2</sub>=1 bar, pH=14, T=298K) as a function of external potential *vs.* Reversible Hydrogen Electrode (*RHE*). Surface coverage with lowest free energy predicted the most stable surface species (at the given external potential). The ORR and OER mechanisms were studied using a Computational Standard Hydrogen Electrode<sup>8</sup> method to construct potential energy surfaces. Energies of different reaction intermediates for ORR/OER were calculated in the presence of the thermodynamically most stable species (as spectator sites).

Figure 1 compares the theoretical (predicted) ORR and OER voltages (*vs. RHE*) on LaMnO<sub>3</sub> and LaCrO<sub>3</sub> (from this work, Wang et al.<sup>1</sup>, Man et al.<sup>2</sup>) to experimental voltages from Suntivich et al.<sup>3,4</sup> Although this is a small sample, it appears that the GGA+*U* voltages including the surface coverage effects are in better agreement with experimental voltages than

previous studies.



**Figure 1** Predicted working voltages for ORR and OER, from theory (*V<sub>OC</sub>*, relative to *RHE*) *vs.* experimental working voltages (*vs. RHE*) from Suntivich et al.<sup>3,4</sup> for LaBO<sub>3</sub> (B=Cr,Mn). The theoretically predicted voltages are from this work (GGA+*U* functional, with and without self-consistent coverage), Mann et al. (RPBE, bare surface) and Wang et al. (HSE06). Line *y=x* denotes perfect match for comparison. For the case of LaCrO<sub>3</sub> the experimental ORR voltage is estimated to be approximately 0.3V for the case of thin-films<sup>9</sup>.

In summary, we have performed GGA+*U* calculations, including voltage-dependent stable surface coverage, to predict the ORR and OER voltages on LaBO<sub>3</sub> (B=Mn,Cr). We find that the voltages predicted agree within 0.3V accuracy with the experimental results<sup>3,4</sup>, which for these cases is an improvement over previous studies<sup>1,2</sup>. We show that the inclusion of *U* makes the transition metal less oxophilic and thereby weakens the binding strength of surface intermediates for transition metal oxides, which, based on the scaling relationships<sup>2</sup>, improves the OER overpotentials by ~0.3 and ~0.5V for LaCrO<sub>3</sub> and LaMnO<sub>3</sub> respectively. Further including coverage effect improves the LaCrO<sub>3</sub> and LaMnO<sub>3</sub> OER potential by ~0.5V and ~0.2V respectively. This study demonstrates a possible future path for accurate predictions of ORR, OER activities of complex oxide catalysts from first principles.

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