

The Role of Oxygen Vacancies in The Oxygen Evolution Reaction on Barium Titanate (001) surfaces: A DFT+*U* study

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Abstract

Oxygen-deficient oxide perovskites have been shown to be efficient bifunctional oxygen electro-catalysts.¹ Adsorption energies of the oxygenated species involved in the threshold steps of the oxygen evolution/oxygen reduction reactions (OER/ORR) are related to the overpotential (η) needed for these to occur.^{2,3} We present a spin-polarized DFT+*U* study on the effects of oxygen vacancies (O_{vac}) in the adsorption of HO^\bullet , HOO^\bullet and O^\bullet onto the BaO- and TiO_2 -terminated slabs representing (001) surfaces of cubic $BaTiO_3$ (cBTO).

The calculated binding energies of these species increase by ~ 0.8 eV or more in the presence of an oxygen vacancy. We attribute this to the excess electrons from the vacancy being involved in charge transfer from the surface to the oxygenated adsorbates, amplifying the ionic character of the bonds and therefore their strength.⁴

Calculations show a smaller increase in binding energy for the TiO_2 -terminated than for the BaO-terminated surface, which is related to the formation of in-gap states due to the O_{vac} excess electrons. For the former case they are found near mid-gap, compared to being near the conduction band minimum in the latter case.

The OER reaction energy profiles exhibit a moderate overpotential ranging from about 0.7-1.0 V depending on slab termination and mechanism, in fair agreement with the observed on-set potential.¹ Furthermore, in accord with the experiment¹, we were able to show that in the presence of O_{vac} calculated η value is reduced by ~ 0.2 V for the TiO_2 -terminated slab.

The O_{vac} affects binding energies of OER/ORR intermediates, which ultimately leads to surface selective enhancement of the catalytic activity of cBTO. Furthermore, oxygen vacancy promotes n-type conductivity by increasing the number of freely mobile electrons. Therefore, controlling oxygen deficiency concentration in oxide perovskites is a promising strategy for developing highly effective materials used in energy technologies based on oxygen electrocatalysis.

References:

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