Influence of atomic configuration on popular descriptors for oxygen evolution reaction on complex transition-metal oxide catalysts

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Ruddlesden-Popper (RP) oxides were demonstrated to be promising catalysts for the oxygen evolution reaction (OER) – the most kinetically hindered process in fuel cells and metal-air batteries. These oxides have a general formula of $A_{1+n}B_nO_{3n+1}$, where A is an alkali or alkali earth element, B is a transition metal, and n is the number of perovskite layers. The possibility to tune their properties by substituting different elements in the A and B sites makes RP oxides appealing for rational design of low-cost, environmentally friendly, and stable catalysts for OER.

Many studies aim to identify descriptors that can help to predict a catalyst's activity. For instance, in [1] authors performed a statistical analysis of popular descriptors such as O $2p$-band center, unoccupied $3d$ band center, M−O−M bond angle, and tolerance factor. However, these properties could depend on the distributions of elements in the crystal lattice, especially in such complex oxides as RP, where the interplay between spin, charge, lattice, and orbital degrees of freedom could give peculiar magnetic and electronic structure.
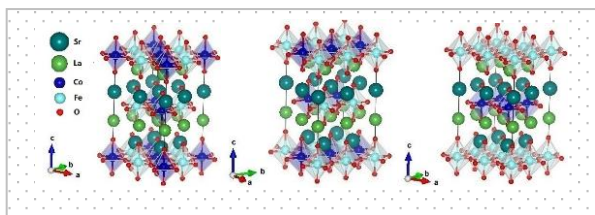

Figure 1. Various relative distributions of cobalt and iron in $LaSrCo_{1/2}Fe_{1/2}O_4$. The left structure is commonly believed to be the most energetically favorable one. The number of Fe-O-Co bridges is maximized in this structure. The number of Fe-O-Co bridges is minimized in the middle structure but there is an equal number of Co and Fe atoms in each layer. The Co and Fe layers interchange in the right structure

To understand how the distribution of elements affects electronic and magnetic properties, we performed density-functional theory (DFT) calculations of $La_{2-x}Sr_xCo_{1/2}Fe_{1/2}O_4$ (see fig. 1) with different distributions of iron and cobalt. Complex transition-metal oxides such as RP and other energy materials present a challenge for DFT calculations due to the strong electron correlation, which leads to the incorrect description of localized d- and f-electrons by standard DFT approximations. A popular low-cost solution of this problem is to add a Hubbard-like correction U to DFT. The value of U in general depends on atomic environment, and is therefore challenging to determine. To address this problem, we used ACBN0 exchange-correlation functional [2]. It allows us to calculate U self-consistently from first principles. We analyze different configurations of elements in $La_{2-x}Sr_xCo_{1/2}Fe_{1/2}O_4$. We establish that U value indeed depends on the local environment of an atom. However, even in the same local environment, U could vary by up to 3 eV due to various spin states. We identified a linear correlation between the U value and the magnetic moment of the atom. Even in the same spin state and the same local environment U value could still vary in a range of 1.5 eV due to changes in the next nearest neighbors.

We find that the distribution in A-site could also affect magnetic and electronic properties, for example, by changing the spin state of cobalt. The energy of an atomic configuration is found to strongly depend on magnetic and charge orderings. For the same Sr concentration, the most favorable spin state of Co is also found to strongly depend on the distribution of elements in both A and B sublattices. As a consequence, descriptor values such as d-band center, transition metals' band overlap, hybridization of transition metal $3d$ and oxygen $2p$ orbitals, and d-band center relative to O $2p$-band center also depend on the distribution of elements. However, the average value of these descriptors for all possible configurations reproduces the trend given by the most energetically favorable structures in $La_{2-x}Sr_xCo_{1/2}Fe_{1/2}O_4$ series.

Acknowledgements

References

[1] Hong, W. T., Welsch, R. E., & Shao-Horn, Y. (2016). Descriptors of oxygen-evolution activity for oxides: a statistical evaluation. The Journal of Physical Chemistry C, 120(1), 78-86.

[2] Agapito, L. A., Curtarolo, S., & Nardelli, M. B. (2015). Reformulation of DFT+ U as a pseudohybrid hubbard density functional for accelerated materials discovery. Physical Review X, 5(1), 011006.

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