On the O 2*p*-band center as a descriptor for the catalytic activity of complex oxides

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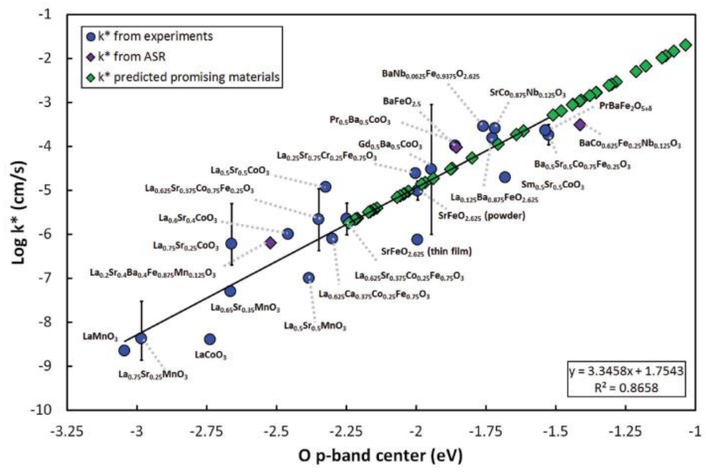
INTRODUCTION

Mechano-quantum calculations based on Density Functional Theory (DFT) play a very active role in the design of materials with catalytic activity for the dissociation of the water molecule (HER and OER reactions). A significant amount of computational effort has been dedicated to searching for electronic descriptors, i.e., numerical parameters extracted from the calculated electronic structure of the electrocatalyst material, that correlate well with the catalytic activity. [1,2] Particularly, for ABO_3 perovskites, the energy of the O 2*p*-band center is reported as a reliable electronic descriptor for the OER activity. In alkaline electrolyzers, a correlation exists between the O 2*p*-band center and the OER overpotentials. In solid oxide electrolyzers, a linear dependence has been found between the O 2*p*-band center and the oxide vacancy formation energy, the kinetics of surface oxygen exchange, or the area specific resistance. However, all these studies have mainly focused on simple ABO_3 perovskites containing only one transition metal. The $YSr_2Cu_2FeO_{7+\delta}$ system is attractive to deep into several parameters that may affect the DFT calculated O 2p-band center.

[1] Jacobs, Mayeshiba, Booske and Morgan. Advanced Energy Materials. 2018

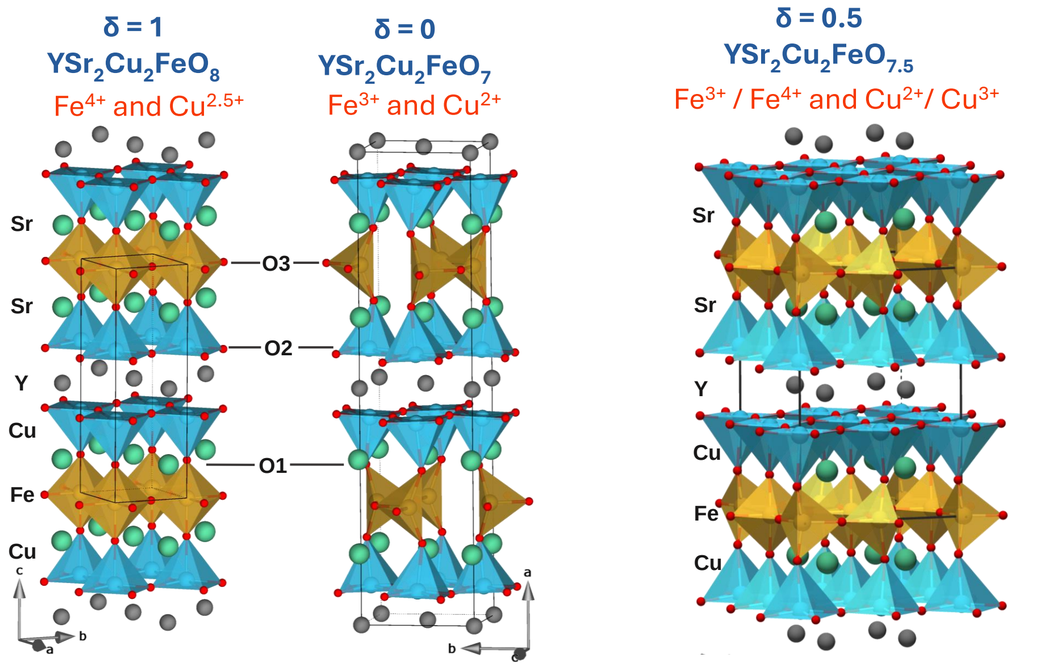
[2] Giordano, Akkiraju, Jacobs, Vivona, Morgan, and Shao-Horn. Acc. Chem. Res. 2022



Correlation between O2*p*-band center and Surface exchange coefficient [1]

OBJECTIVE

Systematic computational research is needed to analyze the feasibility of using the O 2*p*-band center as an electronic descriptor to assess the OER electrocatalytic activity of complex mixed oxides. This contribution studies the evolution of the O2*p*-band center as a function of crystal structure and composition in the layered perovskite system $YSr_2FeCu_2O_{7+\delta}$ ($0<\delta<1$).

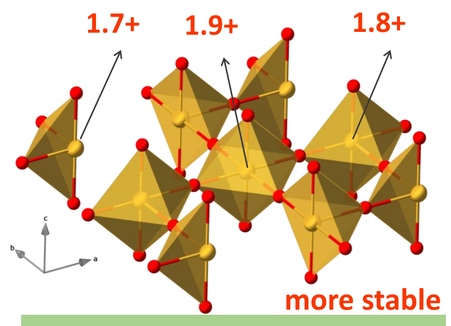


DFT METHODS

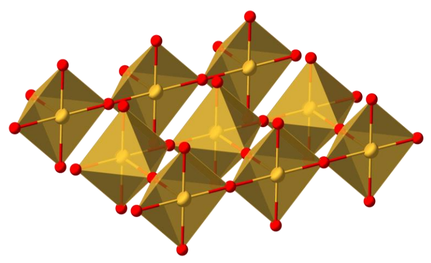
- VASP (Vienna ab-initio simulation package)
- Exchange correlation functionals: PBE-GGA (+*U*) and SCAN-metaGGA (+*U*)
- O 2*p*-band centers extracted from the calculated DOS
- Pymatgen Python library to generate crystallographic models and perform data analysis

RESULTS

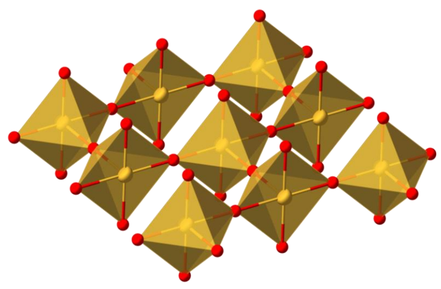
Vacancies configuration in $YSr_2FeCu_2O_{7.5}$



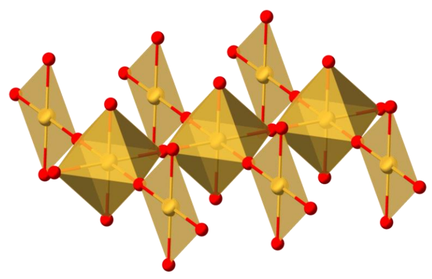
Octahedral [FeO_6]
Tetrahedral [FeO_4]
Square pyramids [FeO_5]



Square pyramids [FeO_5]



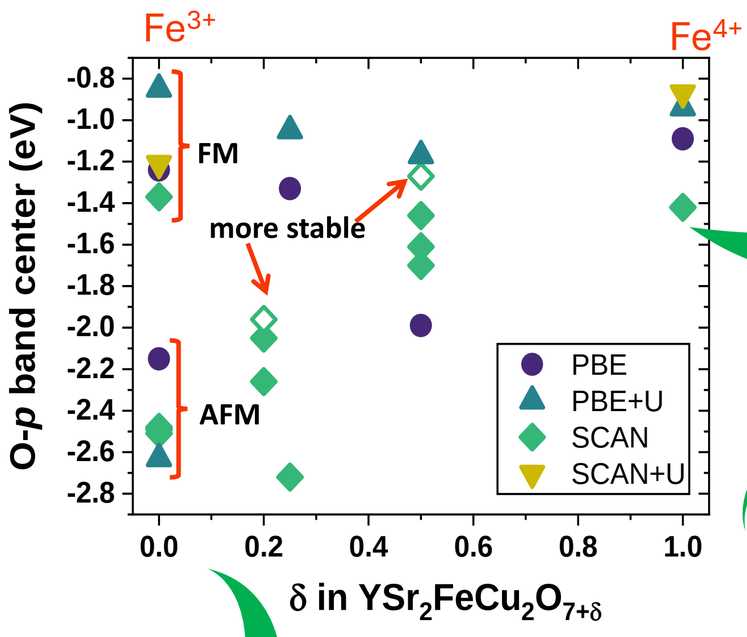
Square pyramids [FeO_5]

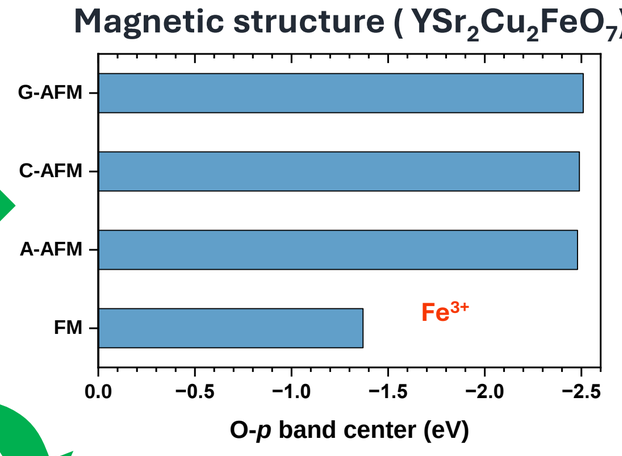


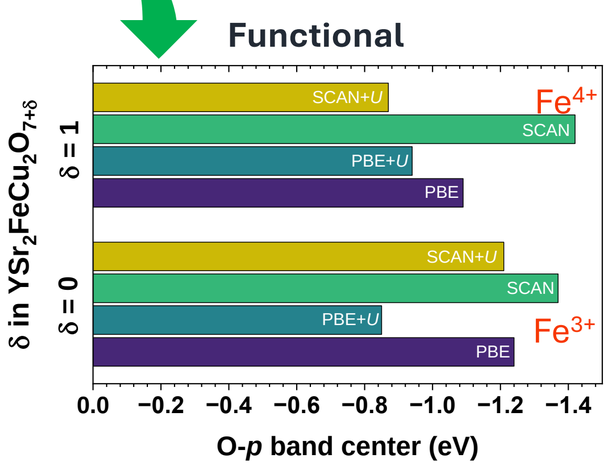
Octahedral [FeO_6]
Square planar [FeO_4]

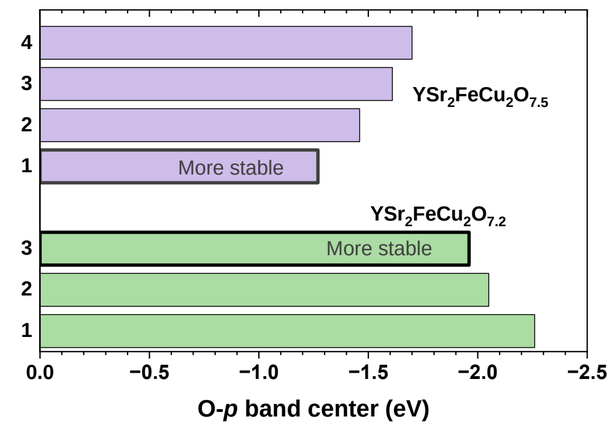
Chemical composition is the key factor, along with the combination of Cu and Fe in different oxidation states, driving the O *2p* bandwidth and its energy respect to the Fermi level. In addition, the O 2*p*-band center depends on the magnetic structure of the material, the functional used in the calculations, and the oxygen/vacancies configuration. The results show that the O 2*p*-band center values of the $YSr_2Cu_2FeO_{7+\delta}$ fall in the range of materials with high catalytic activity.

O 2*p*-band center $YSr_2FeCu_2O_{7+\delta}$ ($0<\delta<1$)









CONCLUSIONS

The O 2*p* band centers extracted from DFT calculations highly depend on the TM oxidation state. In addition, there are other factors, such as the vacancy configuration and magnetic ordering, that should also be considered. More work is needed to assess the O 2*p* band center utility as an electronic descriptor for complex transition metal oxides combining several TM ions.

FUNDING

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