Orbital and spin state effects in O_2 electrocatalysis

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Abstract: Oxygen electrocatalysis, especially Oxygen Evolution and Oxygen Reduction reactions (OER and ORR), is highly important in the development of the viable electrolyzers for water, as well as for the eventual development of viable metal-air batteries. Dioxygen, the main reactant/product of these reactions, has a ground triplet spin state, and therefore will impose additional conditions on the reaction process due to spin conservation. This talk will outline and summarize our findings on the principal desirable magnetic and orbital features of highly active OER and ORR catalysts.
Keywords: Orbital engineering, DFT, OER/ORR.

1. Introduction (11-point boldface)

During OER and ORR, because of the paramagnetic ground state of O_2, two of the four electron transfer steps required will need to have some spin selectivity, either of the electrons delivered to or extracted from the oxygen species in question. A suitable catalyst for OER should then be one where, in addition to having usable oxidation centers, the spin that needs to be evolved in producing the ground state O_2 molecule can be balanced in the catalyst, since in the overall picture spin conservation should be conserved. Similarly in ORR, the spins on paramagnetic O_2 need to be paired with opposite spin electrons in order to produce the final diamagnetic products. We find that these considerations have manifested themselves in the relative activities of highly active perovskite catalysts in recent years, where their activity differences cannot be easily explained by conductivity or thermodynamic potentials alone. We have thus outlined, in four publications[1,2,3,4], both the correlation between our calculated magnetic ground states and OER/ORR efficacy, and also the optimal orbital design parameters that should produce the best magnetic environments for OER/ORR.

2. Theoretical

All calculations were performed using periodic density functional theory (DFT) as implemented in the Vienna ab initio simulations package (VASP). A plane-wave basis set was used to represent the wavefunctions. The projected augmented wave (PAW) method developed by Blochwas used to represent the nteractions between the core electrons and valence electrons. The exchange-correlation energy was calculated within the generalised gradient approximation using the Perde-Burke-Ernzerhof functional revised for solids. A Monkhorst Pack k-point grid and a plane-wave cut-off of 400eV was used for all systems. The DFT+U approach was used to account for on-site Coulomb interactions of localised d electrons.

3. Results and discussion

The main result presented in references 1 and 2 are that among OER catalysts that are already optimized for conductivity and thermodynamics, the most active are ones where there are extended magnetic channels through the structure in the ground electronic states of the material. In addition, the presence of a larger multitude of magnetic states close in stability also correlates positively with OER activity. This is summarized on the left portion of Figure 1, which shows that the onset potential for OER among highly active perovskite species is strongly correlated to the range of magnetic accumulation on the spin centers, which is a result of not just the maximum magnetism of the centers, but of their possible degenerate electronic states in the material.

As for ORR[3], it was found that although magnetic channels helped, the absence of very many closely stable degenerate states was instead favorable for the reaction. This is rationalized in terms of electron entropy gains and losses for the electron being transferred, since for ORR electrons are moved from the catalyst to the paramagnetic oxygen; many degenerate states in the catalyst translates to a loss of electron entropy when it moves to the dioxygen. Hence, a more ferromagnetic environment (with high Curie temperature) and much less electronic degeneracy for the catalyst electron make for better ORR activity. This is illustrated in the right portion of Figure 1.

Interestingly, our analysis method of bulk perovskite magnetism has been extended to the study of the oxygen evolution in the photosynthesis process, where the PSII active enzyme uses a $CaMn_4$ oxo-cluster as the main site of oxygen evolution[5]. We were then able to describe the active site, which is very similar in structure to a small piece of cut-out from an actual perovskite, as a spin mostly ferromagnetic valve, and effectively account for the spin transitions that are required for oxygen evolution.

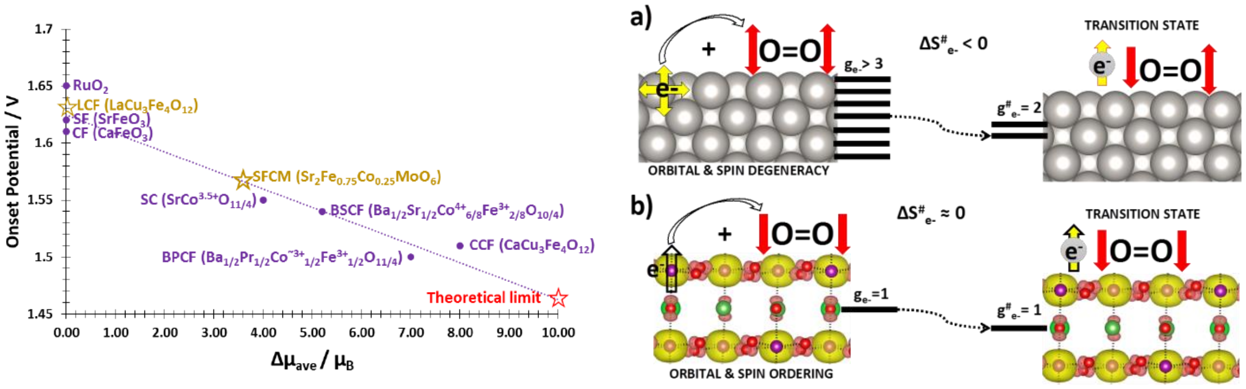

Figure 1. (Left) Correlation of extended magnetism and many degenerate electronic states with lower onset potential for OER, and hence higher activity. (Right) Loss of electron entropy in ORR electron transfer into magnetic O_2 is reduced when electron degeneracy is low in the catalyst, compared to when it is high.

4. Conclusions

The activity of highly efficient OER and ORR perovskite catalysts correlates strongly with the extended magnetism in the most stable electronic states of the catalyst. In addition, different electron entropy requirements within a catalyst exist for OER and ORR: high catalyst electron entropy favors OER, while lower catalyst electron entropy favors ORR. These considerations can then be applied when designing the best electrocatalysts.

References

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