Ferromagnetic catalysts for spin dependent OER

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Using green hydrogen as an energy vector for renewable energy can help provide a sustainable energy infrastructure. To produce green hydrogen, electrocatalytic water splitting can be used, in which H_2 and O_2 are produced from H_2O. However, the dynamics of one of its two half-reactions, the oxygen evolution reaction (OER), still pose challenges regarding the practical application of this technology. Thus, the development of an efficient catalyst for the OER can be a large step forward towards sustainable energy.

An important hurdle in the OER originates from the fact that the production of triplet O_2 is a spin-forbidden reaction as the reactants, OH^- or H_2O, are diamagnetic, but the final product, O_2, is a paramagnetic molecule with parallel spin alignment in its ground state. Recently, this was well-recognized theoretically and the use of spin selective catalysts was described as a possible way to promote the OER (figure 1 left panel). [1] Accordingly, multiple experimentalists reported a positive effect of *external* magnetic fields on OER activity of ferromagnetic catalysts. [2] However, it remains a challenge to investigate the influence of the *intrinsic* magnetic order on catalytic activity.

We use ferromagnetic $La_{0.67}Sr_{0.33}MnO_3$ epitaxial thin films as model systems for the OER to investigate the effects of *intrinsic* magnetic order. In this material, we tune the Curie temperature to be close to room temperature, which allows us to change the magnetic order of the catalyst from ferromagnetic to paramagnetic during water electrolysis by changing the temperature. We observe an increment in OER activity upon crossing the Curie temperature (figure 1 right panel). [3] To pinpoint the origin of this increment, we investigated the magnetic properties alongside the electronic structure of the catalyst while it interacts with the reactants through a combined in situ electron paramagnetic resonance spectroscopy and ambient pressure X-ray magnetic circular dichroism study. We found a clear correlation between a loss of long-range magnetic order and the change in activity, while observing no significant changes in the electronic state of the catalyst. Our study thus confirms that the OER enhancement we found on $La_{0.67}Sr_{0.33}MnO_3$ catalysts is induced by magnetic order, and that this *intrinsic* long-range order is key for a more effective OER catalysis.

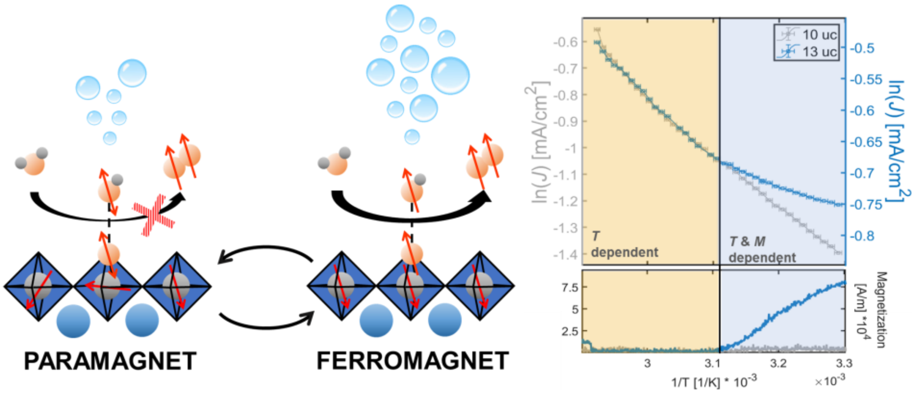

Figure 1. Left) Schematic representation of the spin dependent OER on perovskite oxide catalysts. Right) Temperature dependent OER activity displayed in an Arrhenius plot of a 10 uc (PM) and a 13 uc (FM) sample. It can be seen that for $T>T_c$ the OER activity of the FM sample is higher than expected when following the trend of the PM sample.

References

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