Combining ab-initio thermodynamics and kinetics toward the Oxygen Evolution and Reduction Mechanism on a Dual Atom Catalyst

Elisabetta INICO[1], Giovanni DI LIBERTO[1], Gianfranco PACCHIONI[1]
[1]Università degli Studi di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Via R. Cozzi 55, 20125 Milano, Italy.
** elisabetta.inico@unimib.it*

Significance and Relevance

We modeled a Dual Atom Catalyst for oxygen evolution and oxygen reduction reaction recently synthesized. Dual atom catalysts are now emerging for energy transition reactions such as water splitting. Starting from experimental data on the structure and electrochemical activity, we combined ab-initio thermodynamics and kinetics within density functional theory and combined it with the generalized Butler-Volmer formalism to understand the actual reaction mechanism.

Preferred and 2nd choice for the topic: Multiscale modeling and advanced simulation aspects
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Single Atom Catalysts (SACs) consist of isolated metal atoms stabilized on a support, maximizing the exposed active sites and showing behaviors that are reminiscent of coordination compounds[1,2] and are now widely investigated for catalytic approaches for the energy transition. Dual Atom Catalysts (DACs) are emerging as a promising frontier due to the possibility to use to catalytic centers. Starting from experimental results of the dual atom FeCo-N_3O_3@C[3], of which the structure is known, we investigate the reaction pathways for Oxygen Evolution and Oxygen Reduction Reactions (OER and ORR), providing evidence of the actual reaction mechanism which involves unconventional intermediates, that can form on single atoms.[4]

Results and Discussion

DFT calculations were conducted to simulate the Oxygen Evolution and the Oxygen Reduction on FeCo-N_3O_3@C (structure in Figure 1a). The ab initio thermodynamic approach including kinetic effects was combined with the generalized Butler-Volmer model.
Previous studies reported that on single atom catalysts OER does not follow the classical four-electrons step mechanism,[5] as alternative pathways are possible due to the formation of unconventional intermediates *OH*OH, *OH*O and O_2*.[4] In the case of DACs the picture is rather more complex due the very high number of possible adsorption configurations.

We observed that, in order to explaining the experimental results, oxygen evolution and oxygen reduction follow the same pathway. Looking the reaction in the OER direction, *OH must form on the Fe atom, and then the intermediates evolve on a bridging configuration between iron and cobalt. The adsorption of species on the cobalt site would lead to too strongly intermediated, that would poison the catalyst. The reason why the Co site does not take part in the reaction, although it is more reactive, is that it is strongly coordinated with solvent molecule. The ORR proceed similarly but in the opposite direction. Figure 1 reports a comparison between calculated and experimental polarization curves and the corresponding ORR pathway (panel b, c).

This study provides an example of the potential combination of the structural information with atomistic details, quantum chemical calculations, and activity experiments to understand the complexity of the reactivity of Dual Atom Catalysts.

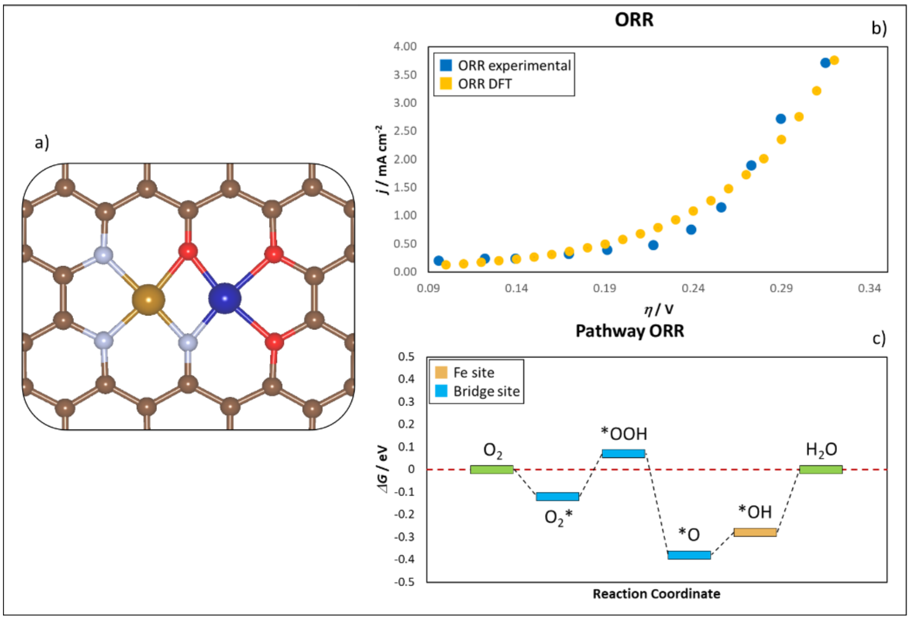

Figure 1: a) optimized structure of the FeCo-N_3O_3@C DAC. Color scheme: iron atom in gold, cobalt in blue, nitrogen in grey, oxygen in red and carbon in brown. b) polarization curves for oxygen reduction reaction. In blue the experimental curve is reported,[3] in yellow the simulated one. In panel c) the proposed pathway relative to the ORR curve in panel b) is reported.

References

1. A. Wang, J. Li, and T. Zhang, *Nat Rev Chem*, **2**, 65–81 (2018).
2. N. Cheng et al., *Nat Commun*, **7** (2016).
3. B. Tang et al., *Nature Synthesis*, **3**, 878–890 (2024).
4. I. Barlocco, L. A. Cipriano, G. Di Liberto, and G. Pacchioni, *J Catal*, **417**, 351–359 (2023).
5. R. R. Rao et al., *Energy Environ Sci*, **10**, 2626–2637 (2017).