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On the role of dopants and defects in tuning Oxygen electrocatalysis at transition metal oxide surfaces

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The production of green Hydrogen and its exploitation as fuel for electric vehicles both rely on energy conversion devices that undergo electrochemical processes involving Oxygen. In the first case, water splitting demands for efficient electrocatalyst for oxidation of water to molecular oxygen (Oxygen Evolution Reaction, OER). In the second, the oxidation of molecular hydrogen in fuel cells calls also for efficient and effective cathodes for the Oxygen Reduction Reaction (ORR).
For both OER and ORR processes the workhorse electrode materials have been noble metals as for example platinum. Concerns of costs and sustainability for a widespread deployment of electrolyzer and fuel cells have motivated an extensive research on alternative electrode materials based on transition metal oxides.
In this contribution, we discuss how OER and ORR can be catalyzed by oxides whose formula contains earth abundant or non-critical chemical elements. By applying state of the art DFT calculations, we show that the OER and ORR mechanisms for can be strongly affected by chemical modifications at the surface. In particular, we discuss the effects of oxygen vacancies in tuning both the electronic and the structural features of the exposed electrode surfaces [1, 2]. As well, we show how different possible doping elements can be very helpful in activating the electrode surface toward OER/ORR catalysis [3, 4].
Besides helping the correct understanding of experimental outcomes, our results show how the chemistry of transition metal oxide surfaces can be easily tuned for improving the electrocatalytic performance of potential electrodes for highly needed cheap and effective energy conversion devices.

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