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Design Principles for Oxygen Reduction and Evolution on Oxide Catalysts

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Driven by growing concerns about global warming and the depletion of petroleum resources, developing renewable energy production and storage technologies represent one of the major scientific challenges of the 21^{st} century. A critical element in pursuit of this quest is the discovery of efficient and cost-effective catalysts used in solar fuel production via electrochemical energy conversion processes such as oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), both of which are central to the efficiencies of directsolar and electrolytic water-splitting devices, fuel cells, and metal-air batteries. Although the Sabatier's principle provides a qualitative argument in tuning catalytic activity by varying the bond strength between catalyst surface and reactant/product (neither too strong nor too weak leading to the maximum activity at moderate bond strength), it has no predictive power to find catalysts with enhanced activity. Identifying a "design principle" that links catalyst properties to the catalytic activity is critical to accelerate the search for highly active catalysts based on abundant elements, and minimize the use of precious metals. Here we establish a molecular principle that governs the activities of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) for oxide catalysts, where the activities primarily correlate to the σ^* orbital ("e_g") occupation of surface transitionmetal cations established by systematic examination of more than ten to fifteen transitionmetal oxides. The intrinsic ORR and OER activities exhibit a volcano-shaped dependence on the e_g occupancy and the activities peak at an e_g occupancy close to unity. Our findings reflect the critical influence of the σ^* orbital on the energetics of surface reaction intermediates on surface transition metal ions such as the O_2^{2-}/OH^- displacement and the OH^- regeneration, and thus highlight the importance of surface oxide electronic structure in controlling catalytic activities. Using the established molecular principle, we further demonstrate that an alkaline earth cobalt oxide with a chemical formula of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3\delta}$ (BSCF), catalyzes the OER with intrinsic activity that is at least an order of magnitude higher than the state-of-the-art iridium oxide catalyst in basic solutions.

[1] J. Suntivich, H.A. Gasteiger, N. Yabuuchi, H. Nakanishi, J. B. Goodenough and Y. Shao-Horn, Design Principles for Oxygen Reduction Activity on Perovskite Oxide Catalysts for Fuel Cells and Metal-Air Batteries, Nature Chemistry, 3, 546–550 (2011).

[2] Jin Suntivich, Kevin J. May, Hubert A. Gasteiger, John B. Goodenough and Yang Shao-Horn, A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles, ScienceExpress, Science DOI: 10.1126/science.1212858, (2011).