OXYGEN REDUCTION REACTION

The basics of volcanoes

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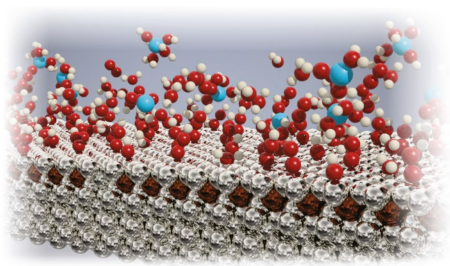

Credit: Wiley

Finding optimal oxygen reduction catalysts for fuel cells or metal–air batteries is one of the many factors that limit the practicality of the so-called hydrogen economy. These catalysts are typically platinum-based, owing to the high activity and stability of platinum in both acidic and basic media. Although the oxygen reduction reaction (ORR) mechanism on metal surfaces is well established in acid electrolytes, the mechanism in alkaline media still remains unclear. Sabatier volcano-shaped relationships, which correlate the activity of the catalyst and the binding strength of the reaction intermediates, provide a way to shed light on this issue.

Now, Ifan Stephens, María Escudero-Escribano and co-workers have elucidated the volcano relationship for platinum-based catalysts in basic media by using a combination of synthesis and electrochemical techniques. The authors have designed near-surface Cu–Pt(111) alloys with distinct affinity towards the adsorption of the *OH and *O intermediates. The effective preparation of the alloys with varying near-surface copper content up to one monolayer was verified by using angle-resolved X-ray photoelectron spectroscopy. They found that higher copper coverage correlates with an increased positive shift in the cyclic voltammetry peak associated with the adsorption of *OH or *O. This positive shift translates into a destabilization of the intermediate.

The activity of each alloy towards the ORR was obtained by using a rotating ring-disk electrode. The volcano-shaped trend exhibits a maximum activity at 0.77 monolayer copper coverage. These results suggest that the reaction in alkaline electrolyte shares the same reaction intermediates as in acid. By tuning the subsurface layers of Pt(111), a 10-fold activity enhancement is achieved relative to the pristine surface. These findings provide a key design principle for platinum-based catalysts towards the ORR in base, and may be extended to other metals.

Marçal Capdevila-Cortada

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