⯈ **ELECTROCATALYSIS**

Volcano spews out hot new catalyst

> If you assume all the charge transfer steps in the reaction involve PCET, then the thermodynamics of each step should be pH independent

Many fuel cells rely on $4H^+/4e^-$ reduction of O_2 to H_2O, the individual steps of which may involve proton-coupled electron transfer (PCET). For example, O_2 can bind a metal catalyst and be converted into a surface-bound *OOH on acceptance of H^+ and an e^-. When PCET is operative, a plot of catalytic activity versus substrate binding strength will be volcano-shaped and have a peak at the optimal binding strength. If the catalyst binds *OOH or *OH more weakly than the optimum, then these intermediates may form too slowly. Conversely, if binding is too strong then subsequent reactions become too slow. This give-and-take forms the basis of the Sabatier principle, and, with a volcano peak in sight, one can design an active catalyst by adjusting the composition of an alloy to arrive at the sweet spot for binding strength. The volcano is already mapped out for O_2 reduction mediated by Pt alloys in acid, but the reactions in alkaline waters are less well chartered. Reporting in *Angewandte Chemie International Edition*, a team led by Maria Escudero-Escribano and Ifan Stephens found that such a volcano does indeed exist in basic conditions.

Perturbing the binding strength of oxygenic intermediates to Pt(111) can be achieved by alloying it with another metal. For example, Cu is readily electro-deposited onto single crystal Pt(111), and migrates into the second layer upon annealing under H_2, as confirmed by angle resolved X-ray photoelectron spectroscopy. The Cu atoms perturb the electronic structure of the Pt catalytic sites, and cyclic voltammetry of electrodes covered with the alloys in N_2-saturated pH 13 solution (0.1 M KOH) show that introducing Cu increases the potential of a wave at ~0.6 V associated with the adsorption of *OH or *O groups. This anodic shift indicates that Cu destabilizes *OH and other intermediates, a result corroborated by density functional theory calculations.

With Pt(111)–Cu alloys of varying composition in hand, the team had materials that could bind *OH with a variety of strengths. To identify the optimal strength, the team performed voltammetry on each alloy-covered electrode in the presence of O_2, whose transport to the electrode was ensured by rotating the latter at 1600 rpm. Comparing the data for the alloys at 0.9 V versus the reversible hydrogen electrode, the alloy with 0.77 monolayer Cu emerged as the best catalyst, affording a catalytic current density of ~100 mA cm^{-2}. This catalyst binds *OH (0.1 eV) more weakly than Pt(111) does, a shift identical to that observed at pH 1. "If you assume all the charge transfer steps in the reaction involve PCET, then the thermodynamics of each step should be pH independent," explain the authors. Thus, PCET is operative not only at low pH but also at high pH, dispelling any thought of a mechanism involving proton-decoupled electron transfer and intermediates such as O_2^-.

The universality of the O_2 reduction mechanism mediated by Pt alloys means we have the design principles to improve on Pt–Ni and Pt–Co alloys presently used in vehicles. Yet, catalytic rates depend not only on a material's redox potentials and substrate binding strength, but also on variables such as local pH and stability. Moreover, specific electrolyte–intermediate interactions can also be important, and account for the higher activity of Pt(111)–Cu in KOH solution relative to that in NaOH solution, as well as the low activity of Au(100) in acid. Escudero-Escribano, Stephens and co-workers also identified other outliers — catalysts that gave data far from the two diagonal lines that define the volcano. For example, stepped Pt surfaces exhibit lower activity than Pt(111) despite binding *OH more weakly. "This suggests that there is an additional barrier to the protonation of these species on stepped surfaces, possibly associated with solvent reorganization," posit the authors. But this gap in our understanding is less important than a key remaining problem: reducing O_2 in base means that we need a catalyst to oxidize a fuel such as H_2 under similar conditions. Whatever the pH one chooses to operate at, it is only through systematic studies of cathodic and anodic reactions, as well as development of suitable ion-conducting membranes, that will we develop optimal fuel cell technologies.

David Schilter
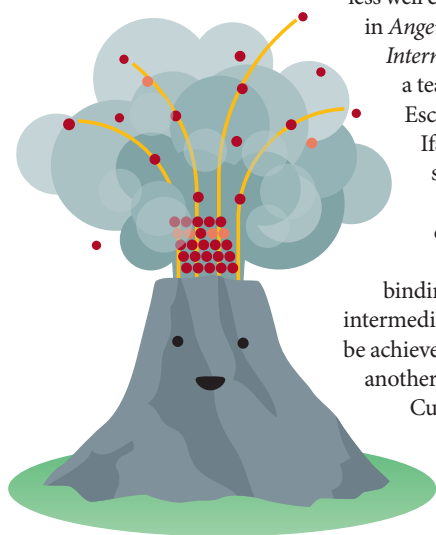
Rachael Tremlett/Macmillan Publishers Limited

ORIGINAL ARTICLE Jensen, K. D. *et al.* Elucidation of the oxygen reduction volcano in alkaline media using a copper–platinum(111) alloy. *Angew. Chem. Int. Ed.* https://doi.org/10.1002/anie.201711858 (2018)
FURTHER READING Nørskov, J. K. *et al.* Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **108**, 17886–17892 (2004).