

# BUILDING BETTER CATALYSTS FOR SPLITTING WATER

The dream of a hydrogen economy — a world run on  $H_2$  gas, free from the pollution and politics of fossil fuels — may depend on developing an energy-efficient strategy for splitting water into oxygen and hydrogen. The problem is that water bonds are very stable, requiring hefty energy inputs to break. Scientists are eagerly developing catalysts to lower the energy demands, and thus the cost, of  $H_2$  production. Yet, science still struggles with the basics, such as what structural properties make a good water-splitting catalyst. Using measurements from two APS beamlines, researchers analyzed the stability and composition of three small clusters of palladium —  $Pd_4$ ,  $Pd_6$ , and  $Pd_{17}$  — which are under investigation as potential water-splitting catalysts. They then generated structural models of the catalysts. By combining information about the identity and structure of each cluster with its catalytic activity, the researchers identified a particular Pd-Pd bond that appears to be essential for catalytic function, thus allowing scientists to design better water-splitting catalysts.

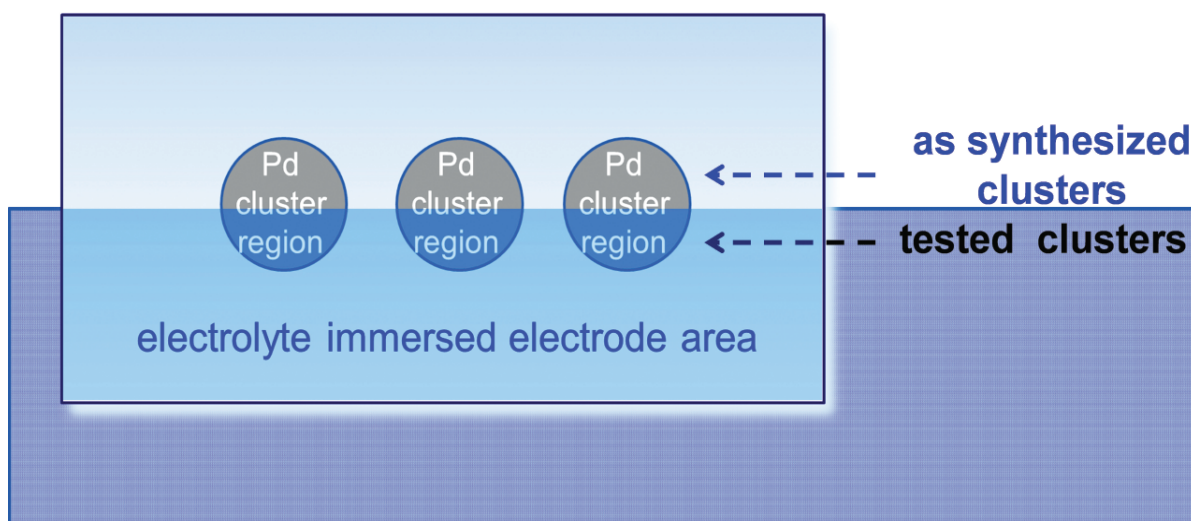


Fig. 1. A schematic of the x-ray experiment used to determine cluster stability and composition (i.e., oxidation state).

Electrochemical water splitting occurs in two distinct reactions: the hydrogen evolution reaction (HER), and the oxygen evolution reaction (OER). In this study, the researchers, from Argonne National Laboratory, the University of Birmingham (United Kingdom), and Yale University focused on the OER, which is currently the least efficient part of the water-splitting process. Past studies showed that platinum metal can catalyze OER, but those materials require a high load of the expensive metal, usually present as large nanoparticles.

In search of more cost-efficient, more energy-efficient, and more active options, the current study focuses on

palladium catalysts with sizes of less than a nanometer.

Typically, metallic catalysts are spread somewhat haphazardly onto support surfaces, resulting in unknown distributions of single atoms, clusters, and larger particles. For this study, the researchers isolated size-specific clusters by sending a molecular beam of palladium ions through a mass spectrometer, filtering out all sizes of particles except the clusters of interest:  $Pd_4$ ,  $Pd_6$ , and  $Pd_{17}$ . The clusters were then immediately deposited, separately, on an electrode consisting of a silicon wafer coated with a thin nanodiamond film (Fig. 1).

To test the catalytic prowess of the

small palladium clusters, the cathodes were dipped, halfway, into a basic solution, which is the standard medium used in OER. Then, the researchers performed voltammetry, using current as a measure of the turnover rate of the OER reaction. The current generated by the cathode containing  $Pd_4$  clusters was no better, and perhaps a little worse, than the electrode alone. However, the  $Pd_6$  and  $Pd_{17}$  clusters showed significant activity, with turnover rates that beat those from previous work on Pd metal surfaces and are comparable to those for iridium, the most active metal catalyst for OER.

The next step was to characterize the cluster samples. The researchers

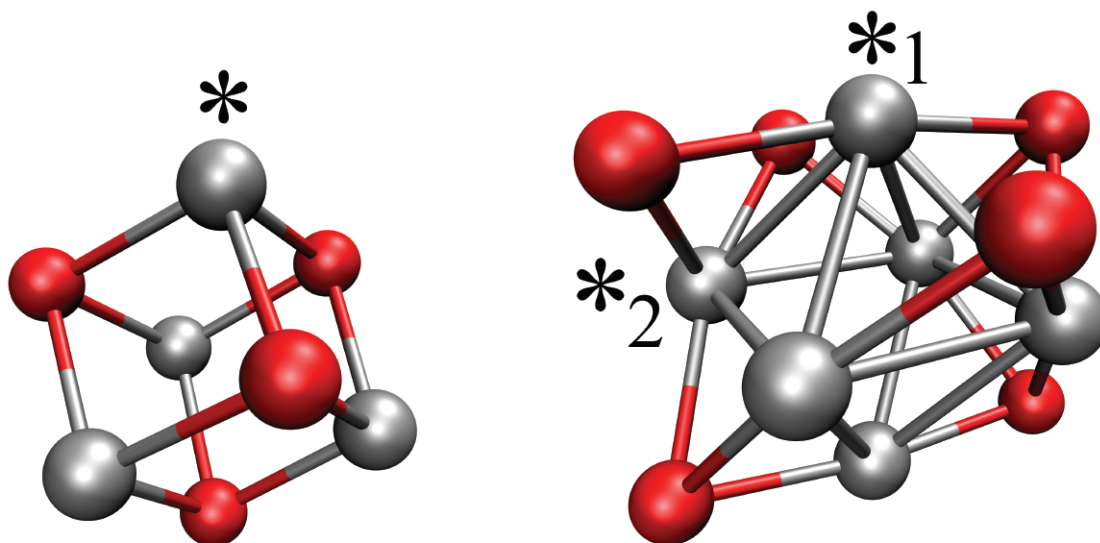


Fig. 2. Possible structures of  $\text{Pd}_4\text{O}_4$  (left) and  $\text{Pd}_6\text{O}_6$  (right) generated by density functional calculations.

brought the same cluster-coated electrodes used in the voltammetry studies to the APS for characterization by grazing incidence x-ray absorption spectroscopy (GIXAS) at MR-CAT beamline 10-ID-B and grazing incidence small angle x-ray scattering (GISAXS) at XSD beamline 12-ID-C,D.

One important observation was that immersed clusters look practically identical to those which were not subject to the water oxidation reaction, suggesting that neither catalysis nor the harsh basic environment changed the structure of the clusters. That stability is key to developing durable catalysts. The measured oxidation states of the  $\text{Pd}_4$  and  $\text{Pd}_6$  clusters was used in density functional calculations which determined, for each cluster, the structural configurations (Fig. 2) as well as the free energy for each step of the OER.

Theoretical calculations performed using the high-performance computing cluster at Argonne's Center for Nanoscale Materials suggest that bridging Pd-Pd sites are active for the oxygen evolution reaction (OER) in  $\text{Pd}_6\text{O}_6$ . Overall, a key descriptor for an efficient OER Pd catalyst is a balancing of binding energy differences with respect to liquid water for each of the important reaction intermediates (O, OH, and OOH). For these Pd clusters, OOH is more strongly bound than the other

species, resulting in the observed overpotential. DFT packages Quantum Espresso and VASP were exploited to gain this insight, along with cluster global optimization using the Birmingham Cluster Genetic Algorithm.

The researchers concluded that the pertinent difference between the clusters was the presence of particular Pd-Pd bonds in the two larger clusters, but not in the smaller cluster. They suspect that this bond may be necessary for OER catalysis, suggesting that catalytic surfaces may be hindered by inactive species. The hope is that, with the knowledge of what constitutes an active species, researchers can focus on making water-splitting catalysts using only the best clusters.

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •

12-ID-C,D • XSD • Chemistry, physics, materials science • Small-angle x-ray scattering, grazing incidence small-angle scattering, wide-angle x-ray scattering, surface diffraction • 4.5-36 keV • On-site • Accepting general users •