Hydrogen Production

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Minimizing the Use of Platinum in Hydrogen-Evolving Electrodes**

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The current use of fossil fuels to meet our energy requirements is unsustainable. Our future depends on the development of synthetic fuels, derived from renewable sources.[1] Molecular hydrogen is an attractive candidate for this purpose. Upon reacting with O_2, each mole of H_2 releases 237 kJ, with water being the only waste product. Its high energy density makes it particularly suited for automotives.[1d] However, significant barriers need to be overcome before hydrogen can be deployed as an energy carrier on a global scale.

The majority of the hydrogen produced today is derived from steam-reformed methane. Unfortunately, the methane is most often sourced from fossil reserves, and steam-reforming produces large amounts of CO_2.[1c] A more attractive method of producing hydrogen would be to split water electrochemically using an electrolyzer. In such a device, the hydrogen-evolution reaction (HER) occurs at the cathode [Eq. (1)]

$$2\,H^+ + 2\,e^- \rightarrow H_2 \tag{1}$$

and the oxygen-evolution reaction (OER) occurs at the anode [Eq. (2)].

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \tag{2}$$

The electricity could be provided from a renewable power source, such as a wind turbine or a photovoltaic. Alternatively, in a photoelectrochemical cell (PEC), light from the sun is harnessed by a semiconductor electrode, producing excited electrons and holes. These photoexcited charge carriers are used directly as reactants for the HER and the OER, circumventing the need for a separate device to provide a source of electrons.

However, in an electrolyzer or PEC, water can only be split efficiently when the electrodes are loaded with a suitable electrocatalyst. The function of the catalyst is to lower kinetic barriers, thus allowing reactions to proceed efficiently. The most active electrocatalysts for the HER and OER are Pt and RuO_x, respectively. Unfortunately, Pt and Ru are expensive and scarce. Significant efforts are being made to find alternatives based on more abundant elements.[2] In the case of the HER, promising candidates include MoS_2, W-Ni-P, W-Cu, and Ni-Fe.[3] Despite recent gains, the activity of these catalysts in their present form is insufficient for industrial applications.

In a recent publication, Esposito et al. tackle the problem with a different approach.[4] The activity of Pt for the HER is so high that large currents can be sustained with exceptionally low Pt loadings.[5] Esposito et al. demonstrate that the precious-metal content could be decreased even further. By placing a Pt monolayer on a bulk substrate of tungsten monocarbide (WC), they obtain the same HER activity as a Pt foil electrode.[4]

Similar Pt overlayer or monolayer concepts have already been explored extensively in the field of electrocatalysis.[6] For instance, materials with a Pt overlayer are the most active catalysts for the oxygen reduction reaction (ORR) in fuel cells, (the reverse of Equation (2)).[6a–f]

The successful implementation of these catalysts relies on several factors, namely that:[3d] a) the overlayer has a lower surface energy than the substrate, b) the overlayer is resistant to the formation of islands, c) the substrate and overlayer are resistant to adsorbate-induced segregation,[7] d) the catalyst is resistant to dissolution, e) the substrate is resistant to solid-state oxidation or reduction, f) the activity of the Pt overlayer is enhanced, or at least uncompromised by its interaction with the substrate.

Unfortunately, most Pt overlayer catalysts have an expensive core that is at least partially composed of a precious metal, such as Au, Pd, or a Pt alloy. In contrast, the novel feature of Esposito et al.'s new HER catalyst is that the cost of its WC core is negligible in comparison to that of the Pt group metals. According to their analysis, the catalyst structure could enable significant cost reductions to be made in preparing PECs and electrolyzers.[4]

Their density functional theory (DFT) calculations provide an explanation for the high activity of the new catalyst. The most active electrocatalysts for hydrogen evolution are

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believed to be those with a Gibbs free energy of adsorption of H, of $\Delta G_H = 0$.[8] When $\Delta G_H = 0$, both adsorption and desorption of adsorbed H are kinetically facile, leading to high catalytic turnover. Unsurprisingly, Pt meets this requirement. Esposito et al. show that when a Pt monolayer is deposited on WC, the underlying substrate has very little effect on the binding of Pt to H, relative to that of pure Pt, in which case their catalyst should also have a $\Delta G_H \approx 0$.

Esposito et al.'s surface-science experiments, taken ex situ, strongly suggest that Pt forms a monolayer structure on the surface of WC. Moreover, it appears that the surface is stable under reaction conditions, at least during the time course of their experiments.

The next step in the development of the catalyst would be to prepare it in a form that could be used in an electrolyzer or a PEC. The relatively high surface energy of WC would make small nanoparticles of the material inherently more challenging to synthesize than those of pure Pt.[9] The long-term stability of the catalyst would also need to be evaluated, especially given that WC compounds can form oxides in the harsh environment of an electrochemical cell.[10]

In summary, Esposito et al.'s work provides a new route towards decreasing the cost of hydrogen-evolving cathodes. Hopefully the current work, along with parallel progress elsewhere in the field, will lead to environmentally friendly and economically viable hydrogen production.

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