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King, Laurie A and Regmi, Yagya N (2022) Precious-metal-free catalyst could afford cost-effective green hydrogen. Chem, 8 (6). pp. 1539-1540. ISSN 2451-9294

**DOI:** <https://doi.org/10.1016/j.chempr.2022.05.012>

**Publisher:** Elsevier BV

**Version:** Accepted Version

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**Precious metal free catalyst**

**May afford cost effective**

**Green hydrogen**

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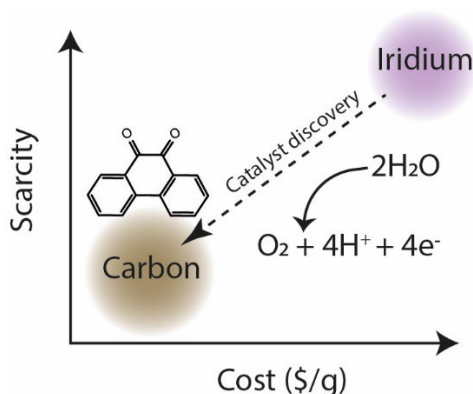
## **Summary**

Water splitting is an important technology for green hydrogen production. However, the sluggish kinetics of the anodic oxygen evolution reaction limit device performance. Furthermore, under acidic conditions, sparse and expensive iridium-based catalysts are required. Recently, in *Chem*, Lu and colleagues explore mild electrochemical oxidation treatments to transform graphite flakes into promising OER catalysts.

## **Main text**

Motivated by global energy decarbonisation, hydrogen has recently gained significant attention. Spanning grid-scale balancing, decarbonisation of petrochemical, fertiliser, steel and concrete industries, the transportation and power generation sectors, hydrogen has numerous potential applications in a Net Zero future landscape. Despite this significant promise, today, the majority of hydrogen is synthesised through fossil fuel derived chemistries resulting in carbon emissions. Net Zero targets thus require zero emission hydrogen synthesis technologies.

Electrolysis offers a pathway to store and transport renewable electricity by splitting water into hydrogen and oxygen. Hydrogen is a potential green fuel or chemical feedstock while oxygen can also be considered a valuable commodity on its own. While a plethora of technologies will undoubtedly be required to synthesise green hydrogen, today, only low temperature electrolyzers are available commercially. Specifically, both the membrane-free alkaline electrolyser technology and the proton exchange membrane electrolyser (PEM-EL) are commercially available at up to the megawatt-scale. PEM-EL is a key technology for green hydrogen offering high current densities, high energy efficiencies, a rapid response to changes in power supply and capable of mitigating gas crossover at high differential pressures.<sup>1</sup> However, due to the acidic and highly corrosive nature of PEM-ELs, beyond iridium-based oxides, very few materials have shown even limited stability or activity for the anodic oxygen evolution reaction (OER). Given the scarcity and significant fluctuations in Ir prices as observed recently, the discovery of alternative non-precious metal-based catalysts and components represents a critical challenge for PEM-EL to become a reality at the GW-scale.<sup>2</sup> Accordingly, the discovery of economic, abundant, sustainable, efficient, and stable electrocatalysts for water splitting thus represents a significant and highly desirable outcome.



**Figure 1.** Schematic representation of the quest for more abundant and cost-effective materials, such as carbon-based catalysts for acidic the oxygen evolution reaction (OER).

Recently in *Chem*, Lu and colleagues investigate oxidation treatments to transform economic and abundant graphite flakes into active catalysts for acidic OER, requiring only 270 mV overpotential to achieve 10 mA/cm<sup>2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>.<sup>3</sup> Specifically, a mild electrochemical oxidation protocol is developed using electrochemical treatments to transform inactive graphite flakes into active OER catalysts. It is interesting to observe and understand such a dynamic and structural evolution and activation in any catalyst. In particular, such activations have been observed in some very notable OER catalysts including strontium iridate (where strontium leaches to leave a highly active catalyst)<sup>4,5</sup> and nickel-iron oxyhydroxide catalysts (where the small quantities of iron from the basic electrolyte in combination with the nickel are responsible for the enhanced catalyst performance)<sup>6</sup>. Additionally, it is important to note that when such activation of a material is observed, particularly with carbon-based catalysts, experimental design must be carefully considered. For example, if an iridium-based counter electrode were used, dissolution and redeposition could be the cause of such activation. Furthermore, for an inactive carbon-based catalyst, electrochemical corrosion could result in a gradual increase in surface area. Thus, careful considerations of a multitude of factors must be considered. Accordingly, the experimental design in this study is carefully considered and the Faradaic efficiency measured, finding the material to be 99% selective to oxygen evolution under OER conditions. The authors employed a carbon-based counter electrode used throughout all experiments.

Identifying and characterising catalytic active sites remains a critical challenge in catalysis. With such information, research teams have the possibility to uncover the reaction mechanism and potentially design new and alternative catalyst motifs with enhanced catalyst activity and durability. To probe the structure of the activated catalysts, a plethora of materials characterisation techniques were deployed by Lu and colleagues.<sup>3</sup> Alongside observing an increased number of carbon defects, the highly active oxidised catalyst was shown to have a reduced crystallinity relative to graphite flakes. The identification and evolution of oxygen and carbon containing functional groups on the catalyst surface was assessed by *ex situ* X-ray photoelectron spectroscopy (XPS), *ex situ* X-ray absorption near edge structure (XANES) and *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Catalyst oxidation was confirmed whereby new oxygen containing functional groups formed and evolved on the surface of the graphite flakes as a function of potential cycling. Finally, through electrochemical assessment, the activated catalyst was shown to have a redox signature analogous to pure phenanthrenequinone. The evolution of functional groups analogous to those in phenanthrenequinone, in apparent synchronisation to the electrochemical activity, indicate the active site moieties are similar in the activated graphite. The unique nature of the catalyst structure is highlighted with a comparison to two further catalysts prepared by

alternative oxidation treatments (concentrated nitric acid, 100 °C, 25 h, and a continuous oxidation at 1 A/cm<sup>2</sup> for 5.5 h) where the harsh oxidising conditions results in very poor OER activity. Materials characterisation points to the disparity being due to the lack of quinone species in these severely oxidised samples.

Beyond activity, the stability of catalysts is critical to ascertain. Lu and colleagues utilise typical lab-based 3-electrode testing to investigate stability using 20,000 potential cycles reporting no change in catalyst-performance.<sup>3</sup> Such findings are indeed promising. However, it is important to consider that there are significant differences between 3-electrode measurements and working PEM-EL devices which utilise membrane electrode assemblies (MEAs).<sup>7</sup> Thus, to further scrutinised the catalyst performance and understand its potential for electrolyser technologies, future studies should deploy the material in an MEA for future testing.

Overall, the study by Lu and co-workers demonstrates an interesting and promising new carbon-based material for the OER under acidic conditions. Such discoveries are highly relevant and important for the field. Through extensive materials characterisations, the active site is identified as a phenanthrenequinone-like moiety. Our perspective is that the next steps for such promising materials should be further scrutinised through MEA testing to understand their relevance to the future of green hydrogen technologies.

## Acknowledgements

LAK and YNR are grateful for support from the Catalyst Hub funded by EPSRC grant reference EP/R026645/1.

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