## BIOMATERIALS/NANOMATERIALS

# COLUMN

# Hydrogen peroxide: from centralized to decentralized and clean production

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**Mario Pagliaro** is a chemistry and energy scholar based at Italy's Research Council in Palermo, Italy, where he leads a research group focusing on nanochemistry, sustainability and the bioeconomy. Rapidly approaching 10,000 citations as of early 2019, he ranks amongst Italy's most cited scientists in nanotechnology and materials science. In recognition of his "significant contributions to the chemical sciences" in 2014 he was designed Fellow of the Royal Society of Chemistry.



His work has been widely highlighted by national and international press, including by MIT Technology Review, Advanced Science News, Italy's national television, newspapers and magazines. He also serves on the advisory and editorial boards of several internationally recognized journals.

Hydrogen peroxide is a key green chemical of today's and tomorrow's global economy (1), whose current ~ 4 million tonnes yearly production forecasts to reach 6 million tonnes by 2024 (2).

Demand is driven by several new industrial uses as clean oxidant and bleaching agent. The only decomposition products of  $H_2O_2$ , indeed, are water and dioxygen.

Industrial uses for which hydrogen peroxide is in high demand include paper-making and wastewater treatment, as a reagent in the catalytic synthesis of propylene oxide, in electronics and semiconductors, mining and metal extraction, healthcare and disinfection products.

In fine chemical manufacturing, too, its use as clean and safe oxidant is being rapidly rediscovered. Diluted in ethyl ether, for example,  $H_2O_2$  is an excellent clean oxidant to selectively oxidise alcohols over sol-gel entrapped ruthenium catalyst (3).

The distributed ("on-demand") production of  $H_2O_2$  via new and cleaner routes from water or from dioxygen is highly desirable (4), especially when using today's plentiful low-cost wind and solar photovoltaic electricity (5).

Currently manufactured via the anthraquinone auto-oxidation process developed by Riedl and Pfleiderer and first industrialized in Germany in 1939 directly at large plants (1,000-1,500 tonne/day), the industrial manufacturing process starts from hydrogen, anthraquinone and air. All H<sub>2</sub> employed is obtained from methane steam reforming.

The catalytic hydrogenation of 2-ethylanthraquinone dissolved in a mixture of organic solvents takes place over a  $Pd/Al_2O_3$  heterogeneous catalyst at 45 °C under 4 atm H<sub>2</sub>. The catalyst is frequently replaced to ensure that the product mixture does not contain leached palladium because even traces of Pd can catalyze the decomposition of  $H_2O_2$  (1).

#### Hydrogen Peroxide? Reduce Oxygen at Single Pt Atoms

In 2016, Lee and co-workers in South Korea reported a single-atom catalyst comprised of platinum atoms supported on titanium nitride nanoparticles which, unlike platinum nanoparticles, predominantly produces hydrogen peroxide in the ORR, with remarkably high activity (6).

The ORR reaction at the surface of Pt nanoparticles, which typically occurs for example in PEM fuel cells cathode, follows a four electron pathway ( $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ) producing water. For the  $4e^-/4H^+$  reduction of  $O_2$ , both oxygen atoms of  $O_2$  are required to be adsorbed on surface active sites in order to cleave the strong O=O double bond, requiring at least two adjacent active Pt sites for the reduction of  $O_2$  to water.

Lee's team intuition was that isolated Pt would not be able to break the O=O bond, and the reaction would follow a two electron pathway  $(O_2 + 2H^+ + 2e^- \rightarrow H_2O_2)$  to generate hydrogen peroxide. The team thus prepared a 0.35 wt% Pt<sub>1</sub>/TiN catalyst using the incipient wetness impregnation method, and found out that the material embedding almost exclusively atomic Pt acts indeed as an efficient electrocatalyst for the reduction of  $O_2$  to  $H_2O_2(6)$ .

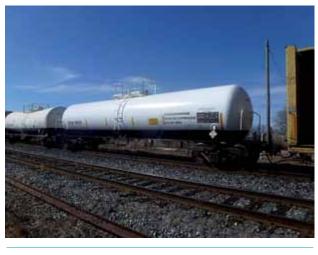
The measured electrocatalytic activity in a  $O_2$ -saturated 0.1 M HClO<sub>4</sub> solution (65% selectivity and a high mass activity of 78 A per gram Pt at an overpotential of 0.05 V) is one order of magnitude higher than the mass activity of Pt nanoparticles and three times higher than that of the best electrocatalyst then known comprised of Pt-Hg nanoparticles (26 A per gram Pt).

More recently, Lee's team replaced titanium nitride with titanium carbide (7). At 0.2 V versus RHE, the single-atom  $Pt_1$ /TiC catalyst showed ORR activity of -0.96 mA cm<sup>-2</sup> and 68% selectivity to  $H_2O_2$  alongside with markedly enhanced stability as shown by only slight reduction in current over time, and unvaried selectivity towards  $H_2O_2$  production when carrying out 1000 cycles of cyclic voltammetry in  $O_2$ -saturated solution.

Most importantly, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis of the used catalyst indicates that the single Pt atoms did not aggregate after the durability test, with XPS measurements of Ti 2p electrons after a 5000 cycle CV test showing that the TiC surface of Pt<sub>1</sub>/TiC remained unoxidised as TiC.

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**Figure 1.** A tank car transporting hydrogen peroxide by rail in a train passing through Bolton, Ontario, on April 2018. [Reproduced from wikimedia.org, under CC BY-SA 4.0 license].

Serious industrial accidents at hydrogen peroxide plants are frequent and impactful. Regardless of safety investments to mitigate risks, manufacturing  $H_2O_2$  via the anthraquinone-based process poses serious hazards due to the unstable nature of the  $H_2O_2$  molecule, widely used also as propellant, and to the concomitant presence of  $H_2$ , organic solvent and  $O_2$ , with an increased risk of explosion with increasing pressure.

Furthermore, concentrated  $H_2O_2$  is prone to explode upon interaction with organic compounds, making its and handling and transport process from large chemical plants to customers (Figure 1) an expensive and hazardous process.

The electrochemical route to  $H_2O_2$  production through the oxygen reduction reaction (ORR) is rapidly emerging as an industrially promising path.

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