Hydrogen peroxide: from centralized to decentralized and clean production

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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_2 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_2. 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_1/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 $HClO_4$ 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^{-2} 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_1/TiC remained unoxidised as TiC.

Figure 1. A tank car transporting hydrogen peroxide by rail in a train passing through Bolton, Ontario, on April 2018.
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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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