

TWO-ELECTRON WATER OXIDATION

In-situ anodic generation of hydrogen peroxide

Hydrogen peroxide is a powerful oxidizing agent with many applications. Now, a method is presented to generate it from the oxidation of water on a polytetrafluoroethylene-coated glassy carbon electrode with high efficiency.

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Hydrogen peroxide (H_2O_2) is an important oxidation reagent required for many industrial and domestic uses. Currently synthesized by the anthraquinone process, H_2O_2 is an environmentally green chemical compared to other oxidants, as it decomposes into O_2 and H_2O . An alternative synthesis is the in-situ generation of H_2O_2 by an electrochemical process. There are two ways to generate H_2O_2 electrochemically: one is by the cathodic reduction of O_2 and the other less common one is by the anodic oxidation of water. Both processes offer advantages over the anthraquinone process in terms of chemical stability, storage, transportation and ambient reaction conditions. While the reduction of oxygen to produce H_2O_2 is a well-known process that can achieve high current efficiencies, the generation of H_2O_2 from the oxidation of water is less common and in general has low current efficiencies.

Both processes generate H_2O_2 in-situ at moderate concentrations and compare favourably to the industrial anthraquinone process, which produces highly concentrated H_2O_2 and is not environmentally friendly because it uses solvent extraction methods and suffers from transportation, storage and stability safety risks¹. The electrochemical process is an environmentally friendly option, especially if it uses renewable power sources such as wind and solar to mitigate CO_2 concentration in the atmosphere by avoiding the use of fossil fuels. One of the difficulties of the anodic production of H_2O_2 by the oxidation of water is that it competes with the thermodynamically favourable oxygen evolution reaction. The two-electron water oxidation reaction method to produce hydrogen peroxide is less favourable because it occurs at more positive potentials ($E = 1.76$ V versus NHE) than the four-electron water oxidation process to form O_2 gas ($E = 1.23$ V versus NHE), where NHE is the normal hydrogen electrode. A number of catalysts have been developed to kinetically favour H_2O_2 instead of O_2 , including BiVO_4 , CaSnO_3 and ZnO . Although, in these systems the generation of hydrogen peroxide has high current efficiencies between 70%

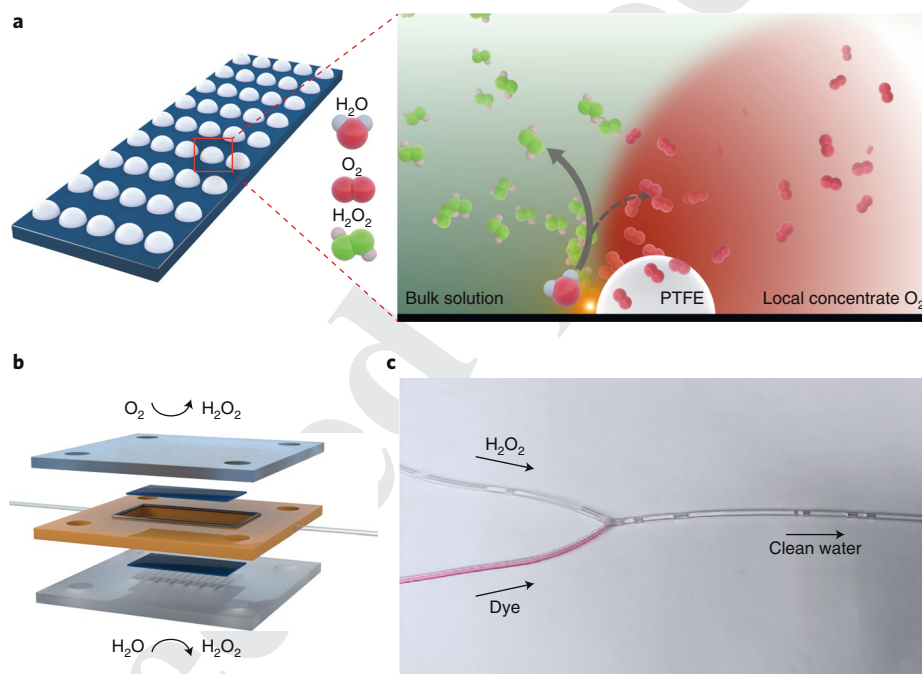


Fig. 1 | Anodic and cathodic generation of hydrogen peroxide. **a**, Glassy carbon electrode dotted with PTFE polymer for the oxidation of water. **b**, The electrode is combined with a gas diffusion electrode for the reduction of oxygen in an electrochemical flow cell. **c**, The colour of an aqueous solution contaminated with 50 ppm of red basic fuchsin dye is removed in a continuous process. Credit: Adapted with permission from ref. ⁵, Springer Nature Ltd.

and 81%, the current densities and therefore the concentrations of H_2O_2 are low^{2–4}.

Now, writing in *Nature Catalysis*, Haotian Wang, Karen Chan, Samira Siahrostami and co-workers use modified glassy carbon electrodes with hydrophobic polytetrafluoroethylene (PTFE) to confine O_2 molecules as a route to favour electrochemical water oxidation towards hydrogen peroxide⁵ (Fig. 1). The researchers point out that in the water oxidation mechanism, species such as $\cdot\text{O}$, $\cdot\text{OH}$, and $\cdot\text{OOH}$ interact with the catalytic electrode material. If the interactions are strong, OH binding leads to the formation of O_2 whereas weak interactions will slow the kinetic formation of O_2 . Weak interactions have been associated with wide band-gap

metal oxides such as ZnO , WO_3 , SnO_2 , TiO_2 , BiVO_4 and CaSnO_3 used for H_2O_2 production. The researchers propose that in order to improve the two-electron H_2O oxidation to H_2O_2 , the locally generated O_2 should increase its residence time on the electrode surface in order to increase its surface concentration. Their hypothesis is that the accumulated O_2 gas interacts with the catalysts' surface and with the intermediate oxygen species, changing the binding strength and thereby encouraging formation of H_2O_2 instead of O_2 . Their approach to achieve high- O_2 surface concentration is to coat the glassy carbon catalyst surface with hydrophobic PTFE polymers, which are dotted on the electrode surface. They demonstrate that

the selectivity of H_2O_2 production was 66% when using hydrophobic polymers deposited on glassy carbon, whereas it was only 11% on the bare glassy carbon surface. In addition, the authors report hydrogen peroxide production rates of 8.4 and 23.4 $\mu\text{mol min}^{-1} \text{cm}^{-2}$ on bare and loaded PTFE glassy carbon, respectively. This production rate is high compared to rates observed on metal oxides that are on the order of 6 $\mu\text{mol min}^{-1} \text{cm}^{-2}$ (ref. ²).

The PTFE polymer was deposited on the surface of the glassy carbon electrode in the form of dotted islands with 200–300 μm patterning, using a mask-assisted method (Fig. 1a). The polymer creates aerophilic centres around which the O_2 molecules confine and form a three-phase solid–liquid–gas interface. The PTFE prevents the quick release of O_2 , and thus provides ultra-high local O_2 concentration that the researchers propose drives the mechanism to the generation of H_2O_2 . They report that during the 10 h operation, the PTFE islands remained stable on the surface of the electrode and that the glassy carbon did not suffer oxidation up to +2.5 V versus RHE since no CO_2 was detected by gas chromatography. Typically, an experiment in 1.0 M Na_2CO_3 electrolyte produces H_2O_2 at 300 ppm concentration. An interesting approach by the researchers is

the use of a three-dimensional porous carbon fibre paper that allows them to construct an electrochemical flow cell, as depicted in Fig. 1b. This flow cell combines a gas diffusion electrode containing oxidized carbon nanotubes for the efficient two-electron O_2 reduction with a three-dimensional porous carbon fibre paper coated with PTFE polymer for the two-electron oxidation of water. The electrochemical cell continuously generates anodic and cathodic H_2O_2 with an overall Faradaic efficiency of 153% and is able to remove the colour of contaminated water in a continuous process (Fig. 1c).

Although the results of Xia et al. are remarkable, there are still questions about the long-term stability of the dotted PTFE on the glassy carbon electrodes and the explanation — which relies on density functional theory calculations — of the oxygen interaction resulting in the increased current efficiency. Future work outlined by the authors includes a more uniform and stable coating of the hydrophobic PTFE to promote long-term operations. Investigations on crystalline catalysts will allow detailed study of the mechanism and improvements to catalytic performance.

While most of the work to generate H_2O_2 electrochemically in the past decades

has been via the reduction of oxygen, the anodic route is an ambitious strategy. For this, thermodynamic restrictions need to be overcome, as oxygen evolution is the primary anodic reaction. The demonstration by this research team shows that it is possible to overcome the thermodynamic limitations by enhancing the kinetic rate of H_2O_2 production, contributing to the understanding of the role oxygen plays in the mechanism of anodic H_2O_2 generation. The process presented could lead to more environmentally friendly processes in textile, paper bleaching and chemical synthesis industries.

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