

ELECTROCATALYSIS

Oxygen caught on film

“ Kinetic modelling showed that thinner films would not only yield higher currents but also afford better protection against oxygen ”

The performance of a molecular catalyst is intimately linked to its structure. This pertains also to the structure of its environment, which might be optimized to afford protection from inhibitors without compromising transport of reactants and products to and from the site of reaction. For example, embedding a hydrogenase enzyme in a redox-active film protects it from deleterious O_2 but also lowers the rate at which H_2 can diffuse and be split into protons and electrons. This trade-off between robustness and rate has now been addressed by a team led by Christophe Léger, Vincent Fourmond and Nicolas Plumeré, who show in the *Journal of the American Chemical Society* how a film can be tolerant to O_2 yet thin enough to allow rapid H_2 splitting.

Many fuel cells involve oxidation of hydrogen, a simple reaction for

which the choice of electrocatalyst is not so simple. A particularly attractive option is an anode decorated with hydrogenases — fast H_2 -processing enzymes that are, however, deactivated by traces of oxygen that might traverse a fuel cell membrane or leak from the surroundings. Earlier work by Plumeré had tackled this sensitivity by covering an anode with nickel-iron hydrogenases in a polymeric gel featuring alkylviologens, redox-active groups that exist here in either an oxidized (AV^{2+}) or a reduced (AV^+) form. The latter is bright blue, and films greater than $100\ \mu m$ thick appear blue when under H_2 with no applied potential. When exposed to H_2/O_2 and a positive bias, enzymes near the anode split H_2 to give $2\ H^+$ and reduce $2AV^{2+}$ into $2AV^+$ groups, which are oxidized back to $2AV^{2+}$ as electrons flow to the anode. Enzymes near the surface also make $2AV^+$, but these groups are now far from the electrode and instead reduce O_2 to H_2O_2 . Some O_2 still deactivates enzymes near the surface but some of these can be reductively reactivated by AV^+ . The major flaw with these thick films is that the middle region is unused — only 0.03% of the enzymes are close enough to the anode and surrounded by sufficient oxidized viologen AV^{2+} to generate current.

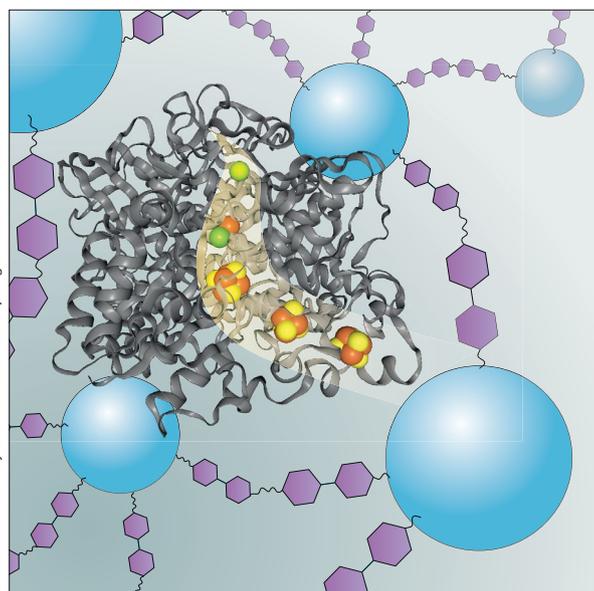
Rather than give up on their redox gel approach, the team used crosslinked viologen-appended dendrimers to prepare thinner films in which a greater fraction of the enzymes are put to work. “Kinetic modelling showed that thinner films

would not only yield higher currents but also afford better protection against oxygen,” reflects Fourmond. This surprising prediction was borne out in electrocatalysis experiments, and up to 25% of the enzymes in a $\sim 6\ \mu m$ film contribute to the anodic current when under hydrogen. The current is maintained when 5% oxygen is present, in which case a further 25% of the enzymes — those closest to the surface — are activated and harvest electrons to reduce oxygen or reactivate enzymes, such that the electrode can be active for years. The $\sim 6\ \mu m$ films are ideal in that they still have two distinct electrocatalytic and protective regions but with little unemployed enzyme in between. Even thinner films could conceivably afford higher currents by allowing more hydrogen to approach the electrode. However, in such films the two regions merge and the anode begins to compete with oxygen for the AV^+ groups generated as a result of hydrogen oxidation. Thus, the anodic current from a $3.5\ \mu m$ film does not reach a steady state because sufficient oxygen is present to deactivate the hydrogenases within minutes.

“The films were engineered further, not least in terms of increasing the rate at which enzymes get reactivated by AV^+ . Site-directed mutagenesis did the trick, to the point where steady-state currents were observed in films as thin as $3.2\ \mu m$,” notes Fourmond. This potentially novel mode of hydrogenase reactivation, as well the promising modelling-guided design of the surrounding gel, bodes well for fuel cell applications.

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