

Electrocatalysis for the generation and consumption of fuels

Efficient redox catalysis offers an important avenue in using renewable energy to process fuels. To this end, efforts in homogeneous, heterogeneous and microbial catalysis may each advance our fundamental understanding and technological capabilities.

The intermittency of renewable energy sources means that we need technologies to store energy (*Nature* **525**, 447–449; 2015). For example, electrical energy derived from renewables can be used to charge a battery or to drive an uphill chemical reaction to afford an energy-rich reduced species such as a fuel (*Nat. Mater.* **15**, 57–69; 2017). Such processes are analogous to pumping water uphill to afford a store of gravitational potential energy. The kinetic barriers associated with these reactions can be overcome with electrocatalysts — redox-active species that allow interconversion of electrical and chemical potential energy. The rate at which the conversion proceeds depends on how much electrical energy you are willing to spend. Indeed, making the fuel involves charge flowing through a circuit, and if this charge is delivered at a potential more negative than that of the equilibrium potential, then there is a corresponding energy loss.

Electrocatalysts in nature include the hydrogenases that catalyse $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$, and CO dehydrogenases, which catalyse $2\text{H}^+ + 2\text{e}^- + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$. Likewise, powered by ATP, nitrogenases reduce N_2 and protons to afford two equivalents of NH_3 and varying amounts of H_2 . These fuel-forming reactions proceed quickly, even when the enzymes operate near the equilibrium redox potentials of their respective reactions. The enzymes are thus both highly active and energy efficient, two aspects that we wish to emulate when developing synthetic homogeneous and heterogeneous catalysts. Although several of the most active electrocatalysts feature precious metals, the past decades have seen many researchers take up the challenge of developing comparably active (or even superior) base metal catalysts, which, in addition to being more sustainably and economically producible, may be less susceptible to CO poisoning.

When it comes to extracting energy from a fuel, the amount of work one can perform by oxidizing the fuel is theoretically greater when the reaction proceeds electrochemically in a fuel cell than when it involves direct combustion (*Nat. Energy* **1**, 15014; 2016). Thus, we again need to apply our knowledge of electrocatalysis when a fuel needs to be consumed. We now touch on some key developments in homogeneous, heterogeneous and

biological electrocatalysis, making reference to select articles from the Nature family of journals.

The in operando study of molecular catalysts is a powerful means to uncover reaction mechanisms and structure–function relationships (*Nat. Rev. Chem.* **1**, 0039; 2017). When species are in solution, we speak of homogeneous electrocatalysis, although this is, strictly speaking, a misnomer because polarized electrodes induce catalyst and substrate concentration gradients. The field is experiencing something of a revival in that analytical techniques are being adopted by a new generation of molecular scientists who, armed with energy-related funding, interrogate electrocatalytic enzymes or synthetic mimics thereof.

Prominent among energy-relevant redox enzymes are the FeFe and NiFe hydrogenases. The best synthetic mimics are very similar to the enzyme active sites in terms of structure, although function has yet to follow form. Efforts towards the latter include the incorporation of a redox-active ligand into a synthetic NiFe dithiolate complex, such that it undergoes protonation at the Ni centre to evolve H_2 through a pathway analogous to that of NiFe hydrogenase (*Nat. Chem.* **8**, 1054–1060; 2016).

Nitrogenase enzymes effect the 6e^- reduction of N_2 to NH_3 . Well known as a precursor to fertilizers, NH_3 is increasingly being investigated as a fuel, another which can be produced by electrocatalysis. Indeed, in contrast to the Haber–Bosch process, a recently reported Mo pincer catalyst acts on a sacrificial e^- donor and acid, under ambient N_2 pressure, to give NH_3 at room temperature (*Nat. Commun.* **8**, 14874; 2017). Only a small amount of H_2 is produced, which is encouraging as the formation of H_2 is a waste of energy here because, given the rather negative redox potentials of the e^- donors, we would want a more energy-rich product than just H_2 .

There is a disconnect between the homogeneous catalysis community and those concerned with heterogeneous catalysis. The latter community has long placed particular emphasis on the fabrication of electrodes that can operate at high current densities in real devices. For example, as early as the 1970s it was known that illuminating TiO_2 with visible light effects charge separation across a bandgap sufficiently large to oxidize H_2O and evolve O_2 ,

“
electrocatalysis
research can play
an important
part in the
interconversion
of electrical and
chemical energy
”

The anode can be connected to a Pt cathode, which, along with its alloys, is a popular and efficient catalyst for H₂ evolution. Another landmark study also described the oxidation of H₂O with photogenerated holes in a semiconductor valence band (a strategy that remains state of the art even today) (*Nat. Nanotechnol.* **11**, 1010–1019 (2016); *Nat. Rev. Chem.* **1**, 0003 (2017)) but made use of a catalyst powder suspension (*Nature* **222**, 637–638; 1979). The liberated electrons flow from the conduction band and reunite with the protons and CO₂ to give a mixture of HCO₂H, H₂CO, CH₃OH and CH₄. These two reactions — H₂O oxidation and CO₂ reduction — also proceed at polarized pairs of TiO₂ or GaP electrodes in the dark, such that these solids are not only photocatalysts but also electrocatalysts.

Alloys of Pt — including Pt–Ni (*Nat. Commun.* **8**, 15131; 2017) — are the champions of H₂ evolution, and considerable efforts have focused on matching or exceeding their activities with catalysts such as layered molybdenum disulfide. When S vacancies are introduced into the basal plane of MoS₂, one now has a material that readily accepts H⁺ and e[−] to give surface-bound H atoms, two of which couple to make H₂ (*Nat. Commun.* **8**, 15113; 2017). MoS₂ can also assume a metallic-like phase and act as a conducting wire between Ni–Co islands, which feature active sites for H₂ evolution (*Nat. Commun.* **8**, 15377; 2017), a reaction also well performed by Mo–Ni alloys (*Nat. Commun.* **8**, 15437; 2017). The islands also evolve O₂ — a job usually the domain of noble metals such as Ir or Rh. Thus, materials based on earth-abundant elements can serve as both the cathode and anode in an efficient H₂O splitting system.

Given that many metals and alloys are good electrocatalysts, one might wonder why some researchers go to the trouble of constructing low-dimensional nanostructures for catalysis. It turns out that morphology does matter — the surface of bulk Co is a poor electrocatalyst for CO₂ reduction, whereas the surface of a four-atom-thick sheet of Co is active (*Nature* **529**, 68–71; 2016). Moreover, when the latter is partially oxidized, the sheet selectively converts CO₂ into formate at a milder potential than that for any metal or metal oxide operating under similar conditions. As yet, it remains unclear how the presence of oxygen atoms improves activity, but systematic studies on the surface doping of this (and related) metal-based catalyst are likely to reveal the origin of this effect.

Far from being limited to ionic solids and metals, heterogeneous electrocatalysts can also take the form of discrete molecular species immobilized on a surface. Oxidizing a fuel is typically accompanied by reducing O₂ to H₂O, a reaction efficiently catalysed by Cu complexes of diaminotriazole. When these complexes are attached to a Au surface and then covered with a pH-sensitive H⁺-conducting lipid layer, one has a heterogeneous system in which H⁺ transfer rates can be controlled (*Nat. Mater.* **15**, 754–759; 2016). It is only when these rates are comparable to the rates of O₂ cleavage that H₂O is formed exclusively. Other conditions lead to the catalyst forming less desirable species such as H₂O₂. Molecular catalysts can also be anchored to lower dimensional

materials, with C nanotubes serving as a good support on which Co macrocycles can reduce CO₂ to CO (*Nat. Commun.* **8**, 14675; 2017). The electrocatalysis is impressive here in that it proceeds at reasonable rates while maintaining selectivity for CO formation in H₂O — very little H₂ is produced despite operating in a sea of protons.

It is perhaps unsurprising that many redox catalysts feature metal centres because their electronic states and catalytic intermediates are typically close in free energy. In this way, the system can rapidly traverse the free-energy landscape to generate the desired products. Nevertheless, the toxicities and prices of certain metal catalysts have motivated us to find out whether we can coax similar reactivity out of organics. For example, polyaromatics are reasonably good at making or reducing O₂ but are inferior to precious metals when it comes to making H₂. Although graphene itself abhors surface-bound H atoms, these are accepted by graphenes doped with heteroatom pairs separated by one C atom (*Nat. Energy* **1**, 16130; 2016). The edges of doped materials readily bind H atoms but do not easily let them go, so H₂ evolution occurs at the abundant basal plane sites.

Returning to biological catalysts, the high activities of certain redox enzymes have seen them studied as catalysts or as aspirational targets for synthetic modelling efforts. Yet, what of the organisms that express the enzymes? Bacteria can colonize biocompatible electrodes to form living films that process fuel molecules as part of their metabolism (*Nat. Rev. Chem.* **1**, 0024; 2017). Although less robust than a metal oxide catalyst such as TiO₂, bioelectrodes are inherently self-healing — they are alive, after all. One problem is that microorganisms take up a lot of space relative to the enzymes they express, such that the current densities offered by bioelectrodes may be lower than those obtained simply using electrodes decorated with the enzymes.

It was noted above that a synthetic photoelectrocatalyst can convert CO₂ to CH₄, a reaction that is also catalysed by archaea known as methanogens. But once we have CH₄, how will we oxidize it back to CO₂ when we need energy? One way would be to use microorganisms such as genetically engineered *Methanosarcina acetivorans*, which converts CH₄ to acetate by means of the enzyme methyl-coenzyme M reductase. These archaea are cultured with *Geobacter sulfurreducens*, which oxidizes acetate to CO₂ in the final step (*Nat. Commun.* **8**, 15419 (2017); *Nat. Energy* **2**, 17093 (2017)), as well as microorganisms from wastewater sludge that help oxidize acetate and produce humic acids — redox-active organic molecules that shuttle electrons from the microbes to the anode. The community operates at high Faradaic efficiency, with 90% of the electrons extracted from CH₄ finding their way to the cathode. Future work may address how we can best use these electrons to conduct a useful reduction (such as that of O₂) as part of a practical fuel cell.

The successful deployment of bioelectrodes calls for the right microorganisms — either one strain or several species harmoniously generating or consuming fuels.

Microorganisms must be welcomed by the electrode surface, which must also be able to engage in rapid e^- transfer. Overall, our understanding of microbial communities and fuel conversions will mature as more scholars — from microbiologists to materials scientists — become aware of the exciting interdisciplinary research questions in need of creative answers.

As we have seen, an electrocatalyst for the generation or consumption of a fuel can take many forms. Heterogeneous electrocatalysts have proven superior for practical applications, as is reflected in the examples

described here. But regardless of the flavour, electrocatalysis research can play an important part in the interconversion of electrical and chemical energy, with the overarching research goal being to maximize the energy efficiency of the process without sacrificing catalytic rate or stability. Many of the ground rules for designing new catalysts and optimizing experimental conditions become apparent upon studying the articles described herein. We hope that you find these past and present developments instructive, and that these studies inspire you to define the future of this exciting field.