

the eventual transition to homogenous 3',5'-linked genetic material.

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WATER ELECTROLYSIS

Divide and conquer

The electrolysis of water provides a link between electrical energy and hydrogen, a high-energy-density fuel and a versatile energy carrier, but the process is expensive. Splitting the electrolysis reaction into two steps through an electrochemical 'buffer' offers a new way to think about improving the cost and efficiency of electrolyzers.

Thomas E. Mallouk

Technologies for generating electricity from renewable resources, such as sunlight and wind, are on a steady trajectory of falling cost. Within the next decade, solar electric power is expected to reach grid parity, the point at which its cost will be equivalent (on a per-watt basis) to that of power generated from coal, nuclear fission or natural gas. This sounds like good news for a sustainable energy future — with its economic, geopolitical and environmental consequences — but there is a catch. Intermittent and fluctuating power from solar and wind are not well matched to demand, so massive energy storage (on a scale of gigawatt-hours in North America, Europe and Asia) will be needed¹. Further, electricity represents only about 20% of our energy use now, with fuels making up the balance. Although the gradual electrification of the transportation energy sector can help², fuels are essential now and will remain so well in to the future for heating, aviation and other uses. We do not yet have an economic way to make fuel from electricity; in fact, the high cost of electricity relative to fossil fuel energy reflects the thermodynamic penalty — a hefty 65% — of generating (high quality) electrical energy from (low quality) cheap heat. To go the other way and compete with the low cost of fossil fuels, one would need to start with very cheap electricity and not pay much to convert it.

One of the front-running technologies for storing electrical energy and converting it to fuel is the electrolysis of water to hydrogen and oxygen. Hydrogen can either be used directly as a fuel, converted catalytically to liquid fuels such as methanol^{3,4}, or used to make electricity in fuel cells. The latter is the reverse process of electrolytic energy storage. Electrolysis is an old and well-developed technology, the scale of which is not limited

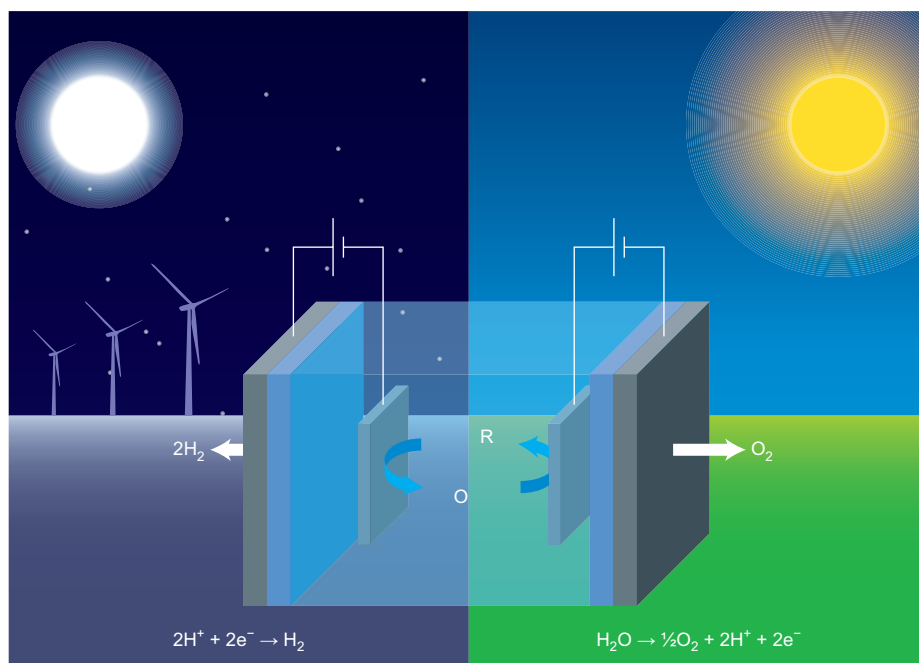


Figure 1 | A split electrolysis cell using phosphomolybdic acid to store charge. Here, phosphomolybdic acid is illustrated in its reduced and oxidized forms as R and O. This set-up allows temporal separation of the hydrogen- and oxygen-evolving half-reactions of water electrolysis. In this illustration, gas diffusion electrodes (dark grey) are separated from the aqueous R/O compartment by polymer electrolyte membranes (blue). Power for the hydrogen- and oxygen-evolving half-reactions could be derived from wind (during the night) and solar energy (during the day), respectively.

by the availability of raw materials or chemical feedstocks. However, the use of electrolysis in energy conversion is hampered by the high cost of the catalysts, membranes and hardware that comprise the electrolyser, and also by the low efficiency of the anodic half-reaction, in which water is oxidized to oxygen.

For energy storage, the best way to beat down the cost of the electrolyser is to improve

its duty cycle (the fraction of time that it is in use), which is now pinned to the solar cycle of about six hours per day with electricity made from sunlight. Writing in *Nature Chemistry*, Symes and Cronin describe a new way to split the electrolytic process in two by using the phosphomolybdate anion, $[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$, as a 'buffer' for redox equivalents⁵. Electrons and protons can

be parked on this anion during the water oxidation half-cycle of electrolysis and then freed later in the reductive half-cycle. This trick temporally separates the processes of oxygen and hydrogen evolution, which means that one reaction could run in the day (for example, with electricity from sunlight) and the other at night (with power from wind, nuclear fission and so on), as illustrated in Fig. 1. Although such light and dark power sources could be shared by a conventional electrolyser, the electrolyser would be under-utilized during the dark part of the cycle when the supply of electricity is low. In a split-electrolyser scheme, the two half-cycles can operate at different current densities, allowing a lower current to run at a smaller electrode for a longer time in the dark. The separate generation of oxygen and hydrogen also simplifies gas handling and puts less stringent demands on the membrane that separates the anode and cathode compartments of the cell.

Symes and Cronin performed proof-of-concept experiments in a water electrolysis cell to measure the energy losses incurred by splitting the process with a redox buffer. They made a phosphoric acid solution that contained both the oxidized and reduced forms of phosphomolybdic acid and electrolysed it using platinum electrodes. They recorded the potentials (relative to a reference

electrode) at which the redox buffer could be reduced and oxidized at a current density of 100 mA cm^{-2} , and also the potentials at which hydrogen and oxygen were evolved. From these measurements they could deduce that the energy lost in cycling the redox buffer was about 13% of the total energy needed for the electrolysis of water. Most of this loss could be attributed to mass-transfer resistance, suggesting that more efficient cells could be made by shortening the anode–cathode distance. Interestingly, the large size of the phosphomolybdate anion makes it impermeable to benzoylated cellulose dialysis membranes, which could be used to replace more expensive cation-exchange membranes in acidic electrolysis cells.

Despite its interesting advantages, the split cell can improve the utility of electrolysers only to the extent that complementary light and dark power sources are available. The most effective and flexible solution would be a system that can store intermittent energy as a battery does and then release it to drive an electrolyser at a steady rate. With solar energy that is available 25% of the time, such an arrangement could effectively divide the electrolyser cost by a factor of four. However, the lithium batteries that store energy in laptop computers and hybrid cars would add too much to the cost of a grid-scale electrolysis system. Flow batteries, which

perform two reversible redox reactions (for example, $\text{V}^{3+} \leftrightarrow \text{V}^{2+}$ and $\text{VO}^{2+} \leftrightarrow \text{VO}_2^+$) on opposite sides of a membrane and circulate the products in a tank, are designed for this task⁶. They are cheaper and more scalable than lithium batteries because, for stationary power applications, their weight does not really matter. However, the vanadium flow battery and others that are combinations of soluble redox couples and lithium-containing solids⁷ have as-yet unsolved problems with membranes and cyclability. The redox buffer electrolyser concept, with its membrane-friendly phosphomolybdate redox couple, is a hybrid between a flow battery and a conventional water electrolyser. When coupled to a smart grid it could provide a new capability for levelling renewable power sources and producing fuel. □

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ELECTRON MICROSCOPY

Phase transition singled out

Four-dimensional electron microscopy has been applied to the detailed characterization of metal–organic-framework nanoparticles undergoing an electronic transition. The transition characteristics of a single particle were found to differ from those of an ensemble, and also to vary from one nanoparticle to the next.

Nigel D. Browning

One of the fundamental challenges in nanotechnology is to understand and control how properties evolve as a system moves from an individual structure at the nanoscale towards the meso- and macroscale ensembles that are used in most applications. The ability to directly observe individual nanostructures and characterize their structure and composition has long been within the purview of transmission electron microscopy (TEM). The correction of spherical aberration that has progressed in TEM and in scanning-TEM (STEM) over the past 10 years to now be almost ubiquitous means that it is possible to routinely characterize nanostructures with both atomic resolution and sensitivity^{1,2}.

The development of temporal resolution in the TEM and the ability to study fast dynamics, on the other hand, has only recently come to the forefront of advances with instrumentation. It is currently defined by two different approaches in the use of photoemission sources: the single-shot dynamic TEM (DTEM, on a μs –ns timescale)³ and the stroboscopic four-dimensional electron microscopy (4D-EM, on a ps–fs timescale)⁴. In the case of DTEM, the goal is to observe on a longer timescale the irreversible structural changes that occur during nucleation and growth phenomena — the single-shot approach ensures there are enough electrons in a single pulsed beam to form a complete image of the material. In

contrast, the 4D-EM relies on a stroboscopic approach with the goal of studying very rapid reversible effects that occur during phase transitions — here, an individual pulse contains only a few electrons, and each image is therefore composed of thousands of identical charge-transfer events that are initiated by the laser pump and observed by the electron probe.

Writing in *Nature Chemistry*, Ahmed Zewail and co-workers describe⁵ how they have applied 4D-EM to reveal a wealth of new information concerning the way electronic phase transitions occur in individual nanoparticles, how the particle-to-particle variability changes the speed and magnitude of the transition, and how