The promise of protonics

Truls Norby

Fuel cells seem a good alternative to dirty and wasteful combustion. But known electrolytes — the crucial component — all have flaws. A new solid-state proton conductor suggests a solution.

Fuel cells convert chemical energy directly to electrical energy cleanly and efficiently. But materials problems have delayed good commercial products. An essential component of a fuel cell is the electrolyte — a material that conducts ions. It can be aqueous, as in the phosphoric acid and alkaline fuel cells, or molten, as in the molten carbonate fuel cell; the mobile ions in these cells are H_3O^+, OH^- and CO_3^{2-}, respectively.

A solid electrolyte is preferable because it allows sturdier, more efficient and corrosion-resistant systems to be built. The solid oxide fuel cell (SOFC) exploits the high mobility of oxygen ions, O^{2-}, in certain oxides at temperatures greater than 600 °C. Commercial SOFCs are candidates for stationary power installations and auxiliary power units in trucks. But problems with materials stability and performance at these high temperatures need to be solved. On page 910 of this issue, Haile et al.[1] describe a solid electrolyte based on a proton-conducting acidic salt, which operates in the much-sought-after intermediate temperature range.

At the lower end of the temperature scale, polymer electrolyte membranes that conduct protons (H^+) go by many names and abbreviations: polymer electrolyte membranes (PEM), proton exchange membranes (also PEM), polymer electrolyte fuel cells (PEFCs) and so on. They are neither truly solid, nor do they only conduct protons: they contain liquid-like regions of water between the polymer chains (Fig. 1a). The protons can jump between the water molecules, but mainly ride on them as H_3O^+ ions. Moreover, hydrogen bonding of additional water molecules to each proton creates drag, which slows down ion conduction. A bigger problem with these polymers is that they are fairly permeable to fuel molecules (such as hydrogen and methanol), thereby wasting energy by 'chemical short-circuit'.

To keep the water content high, PEFCs are operated below the boiling point of water, 100 °C. This requires the very best and most expensive of catalysts, platinum. And unlike SOFCs, they give off 'waste' heat at too low a temperature to be useful in, for example, domestic heating. But the flexibility and sturdiness of polymer-based fuel cells make them attractive for mobile applications. The PEFC will no doubt be used in the first fleets

Figure 1 **Fuel cells that use proton conduction.** a, **Polymer electrolyte fuel cell. The polymer membrane consists of polymer threads interspersed with aqueous regions, where H_3O^+ ion conduction — a proton (red) attached to a water molecule — occurs. Water molecules are a problem because they slow ion transfer, and require high water content in both the fuel and exhaust electrodes, which limits the operating temperature to below 100 °C. b, Fuel cell with solid-acid (CsHSO$_4$) electrolyte. At intermediate operating temperatures (150 °C to 200 °C) the loose lattice of rotating oxyanions, SO_4^{2-} ions, allows proton transfer as indicated. Haile et al.[1] have created a laboratory fuel cell using CsHSO$_4$ as the electrolyte, which operates stably between 150 °C and 160 °C.**
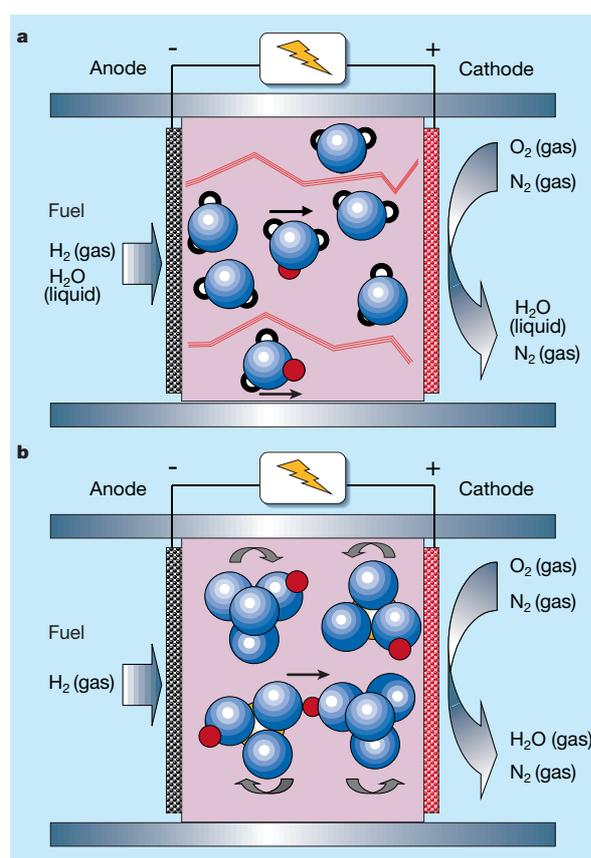
of cars powered by fuel cells. New water-replacement systems, such as imidazole ($C_3H_4N_2$), are currently being investigated in order to increase the operating temperatures of polymer electrolytes.

Given the problems with existing fuel cells, an ionic conductor working at intermediate temperatures (100–600 °C) is an ultimate goal of solid electrolyte research (often called ionics). Among the best candidates are the true proton conductors. In these there is usually no water, only lone protons bonded to oxygen ions as OH^- groups. Such compounds include hydroxides (for example, NaOH, Mg(OH)$_2$ and FeOOH) and acidic salts (such as KHSO$_4$ and KH$_2$PO$_4$). Unfortunately, most are poor proton conductors because the protons are too strongly bonded to their host oxygen ions, and they decompose or melt before the protons become mobilized.

A quarter of a century ago, a few of the acidic salts, called solid acids, were known to be good proton conductors (see ref. 2 for a review). Solid acids are compounds, such as KHSO$_4$ and CsHSO$_4$, whose chemistry and properties lie between those of a normal acid (such as H$_2$SO$_4$) and a normal salt (such as K$_2$SO$_4$). They usually consist of oxyanions, such as SO_4^{2-}, that are linked together by hydrogen bonds. It was not until the 1980s that CsHSO$_4$ was found to undergo a rather spectacular phase transition at about 140 °C during which the proton conductivity increases by almost four orders of magnitude[3].

In this higher-temperature, so-called superionic phase, the structure of CsHSO$_4$ loosens up to let the SO_4^{2-} ions rotate so that a proton on one of the oxygen ions can approach an oxygen ion on a neighbouring oxyanion, facilitating proton transfer (Fig. 1b). A structural chemist would say that the four available locations for a proton on each oxyanion have become equivalent, so that the proton can choose to occupy any one of the four. And with these protons sitting on the liberated SO_4^{2-} groups around easily

877

polarizable Cs$^+$ ions, you have the recipe for a good ionic conductor.

For a couple of decades, CsHSO$_4$ has been the model high-temperature proton conductor. But no one tested it in a real fuel cell. They may have been discouraged by its softness in the superionic phase, its solubility in water, the difficulty of synthesizing the compound with electrodes attached and the narrow operating window available (between 140 °C and its melting/decomposition temperature above 200 °C). Haile et al.[1] have now responded to the increasing clamour for intermediate-temperature solid electrolytes, and proton conductors in particular, and tried out CsHSO$_4$ in a laboratory set-up.

They made a fuel cell by sandwiching the solid acid between two electrode layers made from CsHSO$_4$ powder mixed with platinum and carbon and a volatile organic. The entire fuel cell was compressed to provide good contact between the electrolyte and electrode layers. On heating, the organic component evaporated, leaving behind a porous electrode structure with the possibility of multiple contacts between the fuel (or oxygen, at the other end of the cell), the electrolyte and the electrodes.

Next came the question of whether the solid acid electrolyte was stable when exposed to the operating conditions of the fuel cell: a temperature of 160 °C, hydrogen gas at one electrode and oxygen at the other. The laboratory fuel cell performed stably over several days, burning the world's cleanest fuel — hydrogen — and emitting the most environmentally friendly effluent, pure water.

Haile and her colleagues[1] have been studying for some time another class of proton conductors, in which the protons are not part of the structure, but merely defects dissolved in water-containing atmospheres. The breakthrough for these materials came in the early 1980s when Iwahara and co-workers showed that chemically doped SrCeO$_3$ and other perovskite-related oxides became proton-conducting in humid atmospheres and at high temperatures up to 800 °C. Iwahara demonstrated fuel cells and other devices based on a number of perovskite-related oxides, and conceived the term protonics for the rapidly expanding field of solid-state proton conductors[4].

These high-temperature perovskite conductors lose protons at high temperatures, so the optimum temperature of proton conduction is a compromise between proton concentration and mobility. The proton conductivity typically peaks at around 400–600 °C. From these temperatures and down to those of solid acids such as CsHSO$_4$ (160 °C) there is a gap in fuel-cell temperatures for which, as yet, there is no real candidate for a solid electrolyte. This is an important temperature range because it should allow good materials stability, fast

reaction kinetics, and manageable heat recovery for a wide variety of applications.

Haile et al.[1] are applying for a patent for fuel cells based on solid acid salts, but are otherwise realistically modest about their results. The CsHSO$_4$ electrolyte they used was a millimetre or more thick, whereas real applications will require micrometre-thin films to reduce the resistance of the electrolyte layer. The performance of the electrodes may also be of concern; slow charge transfer appears to cause further drops in voltage. Overall, the laboratory fuel cell delivers a modest 44 milliwatts per square centimetre, which compares unfavourably with the output of state-of-the-art PEFCs and SOFCs. More importantly, one can imagine that operation times of tens of thousands of hours will reveal degradation of the electrolyte due to creep, evaporation and reduction of sulphate in the solid acid by the fuel. From a practical

point of view, accidental overheating would melt or decompose the electrolyte and water flooding would easily dissolve it.

Nonetheless, Haile et al. have proved the concept; true solid-state proton conductors can indeed be put to work in fuel cells, and the relevance of protonics has been extended into the intermediate temperature range. If CsHSO$_4$ is not the most practical electrolyte, then there is a rich chemistry of solid acids and hydroxides with much yet to discover. ∎

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Molecular motors

Doing a rotary two-step

Mark J. Schnitzer

By spinning around, the ATP synthase converts energy from electrochemical to chemical form for storage. A cunning assay reveals intricate details of the rotation.

How do organisms power themselves? This simple question marked the start of a decades-long quest that led eventually to a rotary enzyme called ATP synthase. Using energy derived from proton gradients created during photosynthesis or respiration, this enzyme produces ATP (adenosine triphosphate) molecules — the main cellular energy store. A challenge now is to understand how ATP synthase works. It is thought to contain two rotary motors, called F$_0$ and F$_1$, which are rotationally coupled through their drive shafts. This device uses motion, in the form of 120° rotary steps by F$_1$, as an intermediate, converting energy from electrochemical through mechanical to chemical form[1]. On page 898 of this issue[2], Yasuda and colleagues describe their elegant studies of the F$_1$ motor, and show that each rotary step actually consists of two smaller substeps. More generally, their work highlights some central issues concerning energy flow in proteins.

The F$_0$ and F$_1$ motors have specialized functions (Fig. 1). The F$_0$ motor is bound to membranes of energy-generating cellular structures such as mitochondria, and channels protons through its rotor and non-rotating stator to drive rotation. Meanwhile, the stator of F$_1$ catalyses the production of ATP from ADP (adenosine diphosphate) and inorganic phosphate, provided that F$_0$ drives the F$_1$ rotor with sufficient torque

(rotary force). The catalytic sites of F$_1$ are within the three so-called β-subunits, which are arranged with tripartite symmetry in the stator. Both F$_0$ and F$_1$ can operate in reverse, and isolated F$_1$ is called the F$_1$-ATPase because, in the absence of torque from F$_0$, it hydrolyses ATP to power reverse rotation.

There is only indirect evidence that F$_0$ can drive rotation[3–5]. But rotation of F$_1$ subcomplexes has been visualized directly in vitro, by fixing the stator to a glass surface and using a micrometre-sized filament attached to the rotor's γ-subunit as a marker[6,7]. With this assay, 120° rotary steps can be detected by monitoring the movement of the filament at low ATP concentrations, such that the binding of ATP to F$_1$ is the rate-limiting event between steps[7]. The distribution of times between steps is consistent with one ATP molecule being hydrolysed per step.

Once a step begins, the time taken for the 120° turn depends on the frictional drag imposed by the filament and so on the filament's length. Drag also smoothes out any rapid fine structure within the protein's 120° movement when monitored via the filament. This obscures how rotor movements are linked to hydrolysis events, which probably occur in reverse during ATP synthesis. So, to break the speed barrier imposed by the filament, Yasuda et al.[2] have revved up the assay by using a bead with a diameter of a mere 40 nanometres as the marker. Using