

Harlingen at the University of Illinois at Urbana-Champaign have confirmed a complex order parameter in ruthenate superconductors.

"We have pretty unambiguous evidence for 'p-wave' symmetry with a complex order parameter that breaks time-reversal symmetry in this ruthenate superconductor," said Van Harlingen, a Willett Professor and head of the Department of Physics at Illinois.

Until now, this complex, odd symmetry state had been predicted by theoreticians, but not fully confirmed. Van Harlingen, Y. Maeno of Kyoto University, and their colleagues reported their latest findings in the November 24, 2006, issue of *Science* (p. 1267).

The order parameter of a superconductor characterizes the nature of the pairing interaction that forms Cooper pairs. It controls many of the superconductor's properties and provides a crucial clue to the microscopic mechanism responsible for the superconductivity.

Conventional superconductors that form Cooper pairs through phonon interactions have an "s-wave" symmetry with an isotropic order parameter. Unconventional superconductors, however, have anisotropy in either or both the phase and magnitude of the order parameter.

Ten years ago, Van Harlingen's group pioneered the Josephson interferometer technique that showed the high-temperature superconducting cuprates had "d-wave" symmetry. They are now applying the technique to a wide range of superconducting materials suspected of having unconventional symmetry.

"Our technique can directly measure phase differences in the superconducting order parameter," said Van Harlingen, who is also a member of the Frederick Seitz Materials Research Laboratory and a professor in the university's Center for Advanced Study. "This allows us to make an unambiguous determination of the pairing symmetry in unconventional superconductors," he said.

To use their interferometer technique, the researchers begin by constructing a corner Josephson junction that straddles different faces of a single crystal of the ruthenate superconductor. They then measure the magnetic-field modulation of the supercurrent that reveals the phase shift between different tunneling directions.

If all areas of a Josephson junction have the same order parameter phase, the critical current—measured as a function of applied magnetic field—will create a Fraunhofer diffraction pattern, analogous to a single-slit optical diffraction pattern. However, phase differences in the order parameter on adja-

cent crystal faces of a corner junction, or the presence of chiral domains (characterized by the direction of phase winding) along a single junction face, will result in modulated diffraction patterns.

"We observed highly modulated diffraction patterns across single edge junctions, which implies the existence of chiral domains," Van Harlingen said. Abrupt changes seen in the diffraction patterns as a function of magnetic field or time demonstrate that these domains are dynamical, changing their size or orientation.

"The presence of these domains and the distinctly different diffraction patterns observed on orthogonal faces of the same single crystal confirms the 'p-wave' triplet spin-pairing state and the complex nature of the superconducting order parameter in the ruthenate superconductors," Van Harlingen said.

### Biocatalysts Used to Enable Hydrogen Fuel Cell with No Proton Exchange Membrane

The use of hydrogen as a clean fuel faces many challenges. One problem is the design of fuel cells, which harness as electricity the energy from the reaction of  $H_2$  with  $O_2$  more efficiently than does combustion. Typical hydrogen fuel cells necessarily employ a proton-exchange membrane (PEM) to separate the anode (and highly pure  $H_2$ ) from the cathode (and  $O_2$ ) because the respective electrocatalysts (platinum or platinum with certain other metals) are not selective between  $H_2$  and

$O_2$ . Highly selective catalysts would make a PEM unnecessary and power could even be generated from very low levels of  $H_2$  in air. Recently, F.A. Armstrong, B. Friedrich, and co-researchers at the Inorganic Chemistry Laboratory, University of Oxford, United Kingdom, and the Institute of Biology/Microbiology, Humboldt University of Berlin, Germany, used catalysts found in nature to fabricate without a PEM a fuel cell that generates electricity from just 3%  $H_2$  in air, which is below the combustion limit.

As reported recently in *Chemical Communications* (p. 5033; DOI: 10.1039/b614272a), Armstrong, Friedrich, and co-researchers used a graphite anode modified with an unusual bacterial membrane-bound hydrogenase (MBH) and a graphite cathode modified with laccase—a fungal  $O_2$  reductase. Whereas many previously discovered hydrogenases are sensitive to  $O_2$ , MBH is very robust and catalytically active under ambient  $O_2$  concentrations. The MBH catalyzes the oxidation of  $H_2$  to  $2H^+$ , and laccase, which has a high selectivity for  $O_2$ , catalyzes the reduction of  $O_2$  to water. The fuel cell consists of the anode and cathode placed side by side in a tray and covered in a buffer solution, made weakly acidic to optimize both the MBH and laccase reactions.

Containing the fuel cell in a sealed tank allowed the researchers to control the composition of the atmosphere (see Figure 1). With a stationary atmosphere of 3%  $H_2$  in air, the fuel cell gave an open circuit (OC)

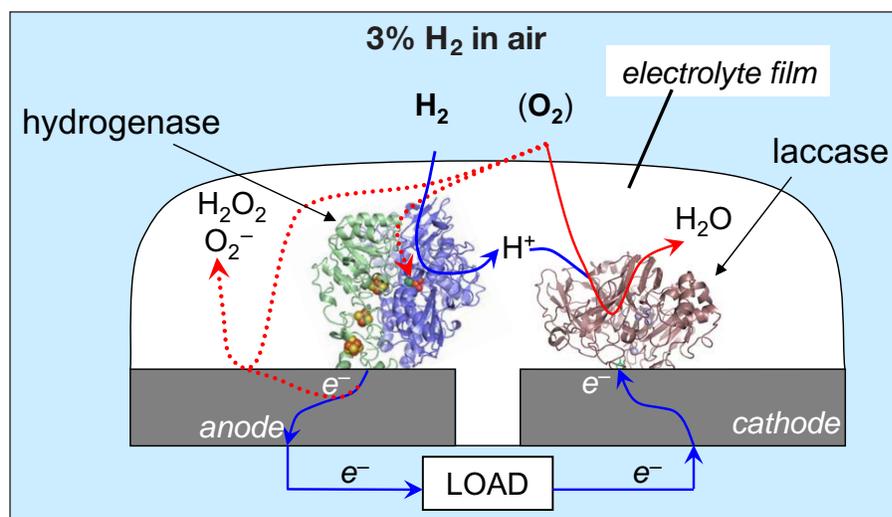


Figure 1. The fuel cell is comprised of a graphite anode modified with  $O_2$ -tolerant, membrane-bound hydrogenase (MBH) and a graphite cathode modified with high-potential fungal laccase in aqueous electrolyte exposed to an atmosphere of just 3%  $H_2$  in air. The MBH oxidizes  $H_2$  to  $H^+$  at the anode and must produce sufficient current to compete with nonproductive, that is, short-circuiting, reduction of  $O_2$  at bare areas of the electrode. In addition, the MBH must exhibit tolerance to inhibition and damage by  $O_2$  itself and by the reactive species  $O_2^-$  and  $H_2O_2$ , which are produced by the direct reduction of  $O_2$ .

voltage of  $\sim 950$  mV. A maximum power density of  $5.2 \mu\text{W cm}^{-2}$  at  $47 \text{ k}\Omega$  was recorded, which the researchers said was not surprising given that the fuel is extremely dilute ( $<30 \mu\text{M}$ ) in aqueous solution, that the electroactive coverage of the enzymes on the electrodes is low ( $<1 \text{ pmol cm}^{-2}$ ), and that the competition at the anode of noncatalytic  $\text{O}_2$  reduction with enzyme-catalyzed  $\text{H}_2$  oxidation is likely.

Acknowledging that many avenues are

open for optimization, the researchers were able to power a wristwatch for 24 h from three cells connected in series, which gave an open-circuit voltage of 2.7 V. The researchers monitored fuel cell voltage and power output as functions of time in response to changes in the atmospheric composition or applied load. Voltage drops when loads are applied to draw current but are reestablished to original values when OC conditions are restored. Flushing the

tank with  $\text{N}_2$  caused the voltage to drop to 0.2 V but introduction of 3%  $\text{H}_2$  and 0.25% ambient air in  $\text{N}_2$  resulted in an OC voltage of 1 V, although an applied load results in a rapid drop in power output. The researchers said, "The ability of MBH to catalyze  $\text{H}_2$  oxidation under low  $\text{H}_2$  concentrations perfectly reflects its physiological function in an aerobe that only occasionally encounters opportunities to use  $\text{H}_2$ ."

STEVEN TROHALAKI

### Robust, Low-Melting Inorganic Protic Salts Match Electrolytic Performance of Phosphoric Acid

Researchers J.-P. Belieres, D. Gervasio, and C.A. Angell at the Arizona State University have created a solvent-free, ionic liquid electrolyte comprised of binary ammonium salt systems that exhibit conductivities on par with phosphoric acid solutions. Electrolytes for proton exchange membrane fuel cells are typically composed of sulfonated polymers, such as Nafion, that exhibit ionic conductivity within hydrated domains. Such membranes are limited in operation to temperatures of less than  $100^\circ\text{C}$ , suffer from electro-osmotic drag, and transmit water-soluble impurities. The new ionic liquid electrolytes, announced recently in *Chemical Communications* (p. 4799; DOI: 10.1039/b611150e), are solution neutral, stable at higher temperatures, and can potentially simplify the design of proton exchange fuel cells.

The research team explored the conductivities and cell potentials of three binary ammonium salt mixtures: trifluoromethanesulfonate (triflate, Tf) + trifluoroacetate (TFAc), trifluoroacetate + nitrate, and triflate + nitrate. For each system, a complete phase diagram was determined through differential scanning calorimetry and each was found to have a eutectic melting temperature near or below  $100^\circ\text{C}$ . The electrolyte was then incorporated into a laboratory fuel cell and the cell potential was stud-

ied as function of current flow and voltage load. These results are compared with phosphoric acid and an ammonium salt with an organic cation, ethylaluminum nitrate (EAN).

Though EAN shows almost no polarization at low loads, this behavior abates at high loads due to electrode wetting problems. Most of the inorganic ammonium salts exhibit more polarization at lower loads, but remain stable through higher cell loads. However, the binary salt eutectics containing ammonium nitrate show an open circuit voltage well above that of the phosphoric acid cell, although only for a limited current range, at this time. Furthermore, the Tafel plot of the data, seen in Figure 1, demonstrates barrier-free reduction at low currents. The researchers attribute this to the low water activity of the salts. The high open cell voltages of the binary ammonium salts, shown in Figure 2, are hypothesized to be common to all protic ionic liquids with a free energy gap of 0.6 eV to 1.0 eV between the donor acid and acceptor base of the salt mixture.

Beyond the enhanced electrolytic performance of an ionic liquid membrane, a nonhydrous electrolyte allows for a greater array of catalysts and electrodes to be considered for use in a proton exchange fuel cell.

ARTHUR FELDMAN

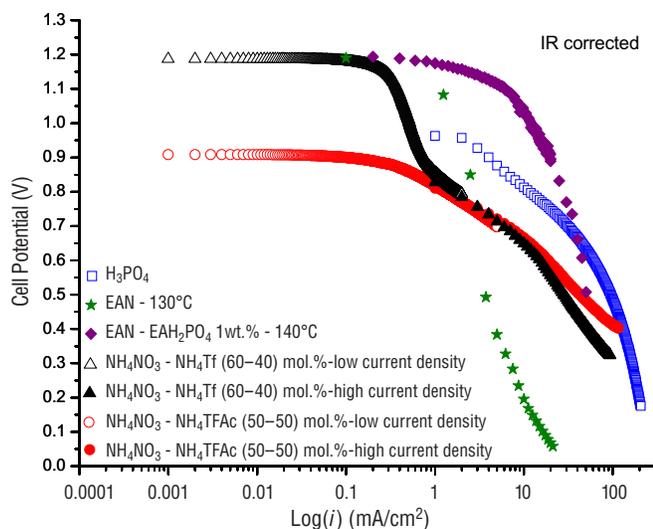


Figure 1. A Tafel plot, cell potential in volts versus log of current density, for a series of inorganic binary ammonium salts, an organic ammonium salt, and phosphoric acid. The plateau at low current density indicates barrier-free electroreduction. EAN is ethylaluminum nitrate. Reproduced with permission of The Royal Society of Chemistry.

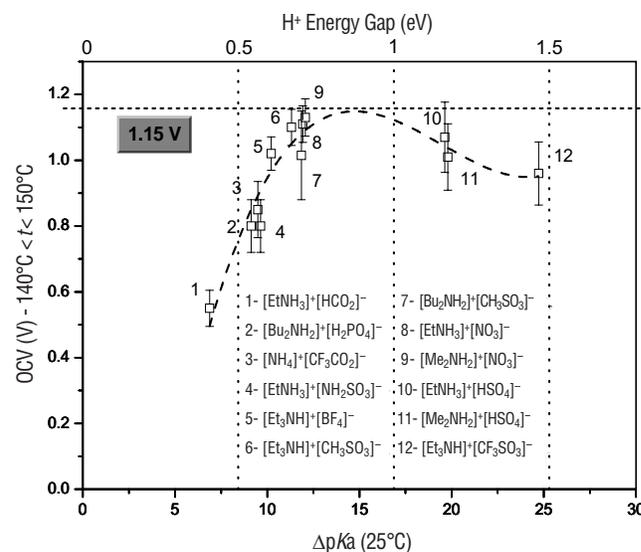


Figure 2. Open cell voltages (OCV) of several protic ionic liquids that can achieve and surpass theoretical voltages as related to the proton energy gap of the material. Reproduced with permission of The Royal Society of Chemistry.