FUEL CELLS

Hydrogen induced insulation

Coupling high ionic and low electronic conductivity in the electrolyte of low-temperature solid-oxide fuel cells remains a challenge. Now, the electronic conductivity of a perovskite electrolyte, which has high proton conductivity, is shown to be heavily suppressed when exposed to hydrogen, leading to high fuel cell performance.

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Fuel cells are capable of efficiently and cleanly converting chemical energy to electrical energy. Solid oxide fuel cells (SOFCs) are one class of such devices in which the electrolyte — the layer that separates the anode from the cathode — is a solid state metal oxide. Typically, SOFCs operating at intermediate temperatures (500–750 °C) make use of electrolytes that allow oxygen ions to move between the electrodes, but there are efforts to develop SOFCs that operate at lower temperatures (LTs; 300–500 °C) by exploiting proton-conducting electrolytes to provide the necessary ionic conductivity. Lowering the operating temperature of SOFCs provides a promising solution to transform energy conversion by allowing the use of lower-cost materials for balance-of-plant components (auxiliary equipment required in addition to the fuel cell stack) and by reducing heat exchanger size and thermal insulation requirements. Proton conductors are particularly suitable electrolytes for LT-SOFCs because they have lower energetic barriers for proton diffusion and higher ionic conductivity than oxygen-ion conductors. Yet finding materials that also have low electronic conductivity — which would prevent short-circuiting — remains a challenge. Writing in Nature, You Zhou, Shriram Ramanathan and colleagues across the USA now report an electron doping strategy to yield high-performance metal oxide perovskite proton conductors for LT-SOFCs. They achieve ionic conductivity comparable to the best performing electrolytes at similar temperatures, while minimizing deleterious electronic leakage due to a fuel-induced metal–insulator transition.

For conventional perovskite proton conductors, such as yttrium-doped BaCeO₃ and BaZrO₃, sub-valent cations (for example, Y³⁺) are used to substitute Ce⁴⁺ or Zr⁴⁺ to create oxygen vacancies (Vₒ°) in an approach termed ‘acceptor doping’ (Fig. 1a). Such vacancies are critical sites for hydrogen incorporation and transportation, which mainly occurs through the dissociative adsorption of water, leading to the formation of protonic defects (H₂O + Vₒ° + O²− → 2OH°, where O° is the lattice oxygen in the perovskite and OH° is the proton localized on the oxygen ion). Therefore, the ionic conductivity of

**Figure 1** | Electronically insulated proton-conducting perovskite for use as the electrolyte in a SOFC. **a**, Proton incorporation and conduction mechanisms in conventional perovskite proton conductors (for example, Y-doped BaZrO₃), which rely on vacancies for proton conduction. **b**, The proposed proton-conduction mechanism for H-SNO electrolyte in which hydrogen is spontaneously incorporated without the need for vacancies (for clarity, the distortion of the structure is not shown). The effective charge of the oxygen ion is shown as (2−δ)−, to reflect the reduced charge due to the ligand holes in SNO. The charges on the oxide ions are only shown explicitly on one site in each structure for clarity. **c**, Schematic showing the working principle of a SOFC using a perovskite SNO electrolyte. The electronic configuration of the Ni 3d orbitals of SNO and electron-doped H-SNO are shown on the right, demonstrating the suppression of electronic conductivity on the introduction of hydrogen. Figures adapted from ref. 2, NPG.
acceptor-doped materials is strongly related to the number of oxygen vacancies, and so the traditional way to increase ionic conductivity is to increase the concentration of oxygen vacancies in the materials. A concentration of oxygen vacancies approaching 10% is deemed very high while still maintaining the phase structure of the materials.

In their work, Zhou, Ramanathan and colleagues demonstrate a different strategy based on electron doping to incorporate hydrogen into electron conducting SmNiO₃ (SNO) to form hydrogenated SmNiO₃ (H-SNO) (Fig. 1b). No oxygen vacancies are formed upon electron doping; Ni³⁺ ions in SNO are reduced to Ni²⁺ with hydrogen incorporation (Ni³⁺ + O₂⁻ + 0.5H₂ → Ni²⁺ + HO⁻). Therefore, the concentration of protons in H-SNO is not limited by the oxygen vacancy concentration. H-SNO achieves remarkably high ionic conductivity, with the area less than one-third of the generally targeted value (0.15 Ω cm²) for an oxide electrolyte. Furthermore, H-SNO also has a very low activation energy for proton transfer of ~0.3 eV based on an H-SNO epitaxial thin film test, compared to values between 0.4 and 0.6 eV for other electrolytes, making it suitable for low-temperature SOFC applications.

Although some materials have high ionic conductivity, their utility in a fuel cell is often limited by electronic leakage when exposed to hydrogen. Electronic leakage through the electrolyte can cause the device to short-circuit and lower the efficiency; therefore ideal electrolytes couple high ionic conductivity with low electronic conductivity. As shown in Fig. 1c, SNO exhibits metallic conducting properties when exposed to air, thus at the start of the fuel cell tests, the device outputs no power as the electronically conducting SNO short-circuits the system. However, the work by Zhou, Ramanathan and colleagues demonstrates that as the SNO becomes hydrogenated, an insulating layer is formed on the side of the SNO exposed to the hydrogen fuel. Protons continue to diffuse across the electrolyte under the chemical potential gradient, but electron transport to the cathode is strongly suppressed due to carrier localization on Ni²⁺ ions. The researchers term this phenomenon a "fuel-induced filling-controlled Mott transition", the result of which is that electrons are forced to pass through the external circuit to generate electrical power.

It is unusual to find that a metallic conducting SNO perovskite can be converted to an electronically insulated phase and achieve high proton conductivity by hydrogenation. Typically, relatively few Ni³⁺ cations in perovskite oxides are reduced to Ni²⁺ by creation of oxygen vacancies under a reducing atmosphere, which can induce changes in electronic conductivity to some extent but not fully suppress the electronic conduction. The open-circuit voltage of free-standing micro-fabricated SOFCs using H-SNO as the electrolyte is close to the theoretical value calculated by the Nernst equation, which means the ionic transference number is close to unity and the electronic conduction is almost completely suppressed. Furthermore, the power density of the fuel cells, with appropriate noble metal catalysts at the electrodes, reaches 225 mW cm⁻² at 500 °C, which is comparable to the best-performing proton-conducting fuel cells.

The results reported by Zhou, Ramanathan and colleagues open a new direction for the development of high-performance proton conductors for LT-SOFCs, but also might have significance in other areas such as hydrogen generators and hydrogen pumps. The structure of the material means that the properties of the oxide could be tuned through strategies such as cation doping to adjust the length of the Ni-O bond and the Sm (or other rare earth element) repulsion to protons thereby improving the proton conductivity. However, although the researchers' preliminary results are promising, more work is needed to realize the practical utilization of this type of material. For example, the polarization resistance from the noble metal electrodes is high compared with the resistive losses from the electrolyte. Therefore, it is necessary to develop high-performance low-temperature cathodes and anodes compatible with such an electrolyte. The thermal stability of SNO also needs careful consideration because Ni may undergo exsolution from the perovskite at high temperatures (>1,000 °C) typically required for conventional fuel cell fabrication. Furthermore, the exsolution of Ni from the perovskite may also occur when pure (rather than dilute) hydrogen is used, especially under open-circuit voltage. Thus, a deliberate operation strategy should be used to keep the fuel cells under polarization conditions when exposed to pure hydrogen to maintain the oxygen gradient in H-SNO at the proper level.

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