

# Alkaline polymer electrolyte fuel cells completely free from noble metal catalysts

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In recent decades, fuel cell technology has been undergoing revolutionary developments, with fundamental progress being the replacement of electrolyte solutions with polymer electrolytes, making the device more compact in size and higher in power density. Nowadays, acidic polymer electrolytes, typically Nafion, are widely used. Despite great success, fuel cells based on acidic polyelectrolyte still depend heavily on noble metal catalysts, predominantly platinum (Pt), thus increasing the cost and hampering the widespread application of fuel cells. Here, we report a type of polymer electrolyte fuel cells (PEFC) employing a hydroxide ion-conductive polymer, quaternary ammonium polysulphone, as alkaline electrolyte and nonprecious metals, chromium-decorated nickel and silver, as the catalyst for the negative and positive electrodes, respectively. In addition to the development of a high-performance alkaline polymer electrolyte particularly suitable for fuel cells, key progress has been achieved in catalyst tailoring: The surface electronic structure of nickel has been tuned to suppress selectively the surface oxidative passivation with retained activity toward hydrogen oxidation. This report of a H<sub>2</sub>-O<sub>2</sub> PEFC completely free from noble metal catalysts in both the positive and negative electrodes represents an important advancement in the research and development of fuel cells.

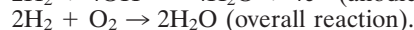
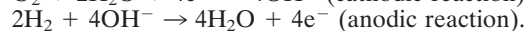
nonprecious metals | hydrogen oxidation | oxygen reduction

Fuel cells have been recognized as an alternative power-generation technique for the future in both mobile and stationary uses (1, 2). After decades of evolution, fuel cells of various types have been developed (2), such as alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC), and polymer electrolyte fuel cell (PEFC). Among them, PEFC has been the most developed one in the past 2 decades (3), featuring rapid startup and high power density particularly suitable for vehicle applications (1–3).

Compared with the aqueous electrolytes traditionally used in low-temperature fuel cells, polymer electrolytes completely eliminate the problems caused by electrolyte leakage and can effectively separate the fuels (such as hydrogen) and the oxidant (oxygen) with a thin film of a few tens of microns in thickness. For decades, the commonly used polymer electrolytes have been limited to proton exchange membranes, typically Nafion. Nowadays, many Nafion-based fuel cell systems of different sizes are being demonstrated or tested on a variety of applications across the world. Although they are promising, the Nafion-based fuel cells still face a number of obstacles to commercialization, one of which has been the severe dependence of catalysts on platinum (Pt), an expensive and scarce resource in the earth. Such dependence stems from the strong acidic nature of the proton-exchange membrane; and thermodynamically, only noble metals can be relatively stable in this corrosive environment. Despite tremendous efforts devoted to the search for non-Pt and nonprecious metal catalysts with a few interesting preliminary results reported (4–8), there has hitherto been no demonstration of PEFC completely free from noble metal catalysts in both the positive and negative electrodes.

To fundamentally get rid of the dependence on noble metal catalysts, alkaline electrolyte should be used. However, fuel cells based on aqueous alkaline electrolytes, namely AFC, have been suffering from the carbonation issue when air is used as oxidant, a fatal result of which is that the waterproof character of the gas-diffusion electrode would be broken by the K<sub>2</sub>CO<sub>3</sub> precipitate, thus causing failure of the entire fuel cell. A solution to this issue is to create a polymer version of alkaline electrolyte, because in such an alkaline polymer electrolyte (APE), the cation, usually quaternary ammonium, is attached on the polymer chain, and there is no dissociated cation in the liquid phase to form K<sub>2</sub>CO<sub>3</sub> precipitate.

The working mechanism of an APE fuel cell (APEFC) is similar but not identical to that of a Nafion-based PEFC. As illustrated in Fig. 1, at the cathode side of an APEFC, O<sub>2</sub> is reduced in the presence of H<sub>2</sub>O to produce OH<sup>−</sup>, which transfers through the hydroxide ion-conductive polymer to the anode side and reacts with H<sub>2</sub> to produce H<sub>2</sub>O.



Although the potential advantages of APEFC have long been recognized (9–12), progress has not been satisfactory. Up to now, prototypes of APEFC are still using Pt catalysts (especially in the anode) (13–19); the long-expected totally precious-metal-free APEFC has not yet appeared. This situation has been caused by the difficulties arising from both the polymer electrolyte and the catalyst aspects. The APE suitable for fuel-cell applications is still not readily available, and, in most cases, fuel-cell researchers have to develop APE by themselves. An ideal APE should be Nafion-like, namely, the polymer electrolyte should not only serve as a highly conductive and mechanically stable membrane separator but also be soluble in certain solvents so that the catalyst layer of fuel cell electrodes can be easily impregnated with the polymer electrolyte. Such a Nafion-like APE is still rare. In some reports, the membrane had to be wetted with aqueous alkaline solution to remedy the poor ionic conductivity (20–23), so the fuel cells thus made were not genuine APEFC per se. On the other hand, transferring the non-Pt catalysts from AFC to APEFC is not as straightforward as expected. Although Ag has been found to be still applicable as the cathode catalyst for oxygen reduction in APEFC (18, 19), attempts to use Ni as the anode catalyst for hydrogen oxidation failed unexpectedly and unexceptionally until now (9).

## Results and Discussion

In the present work, we report an important development in totally platinum-free APEFC on the basis of our unique ap-

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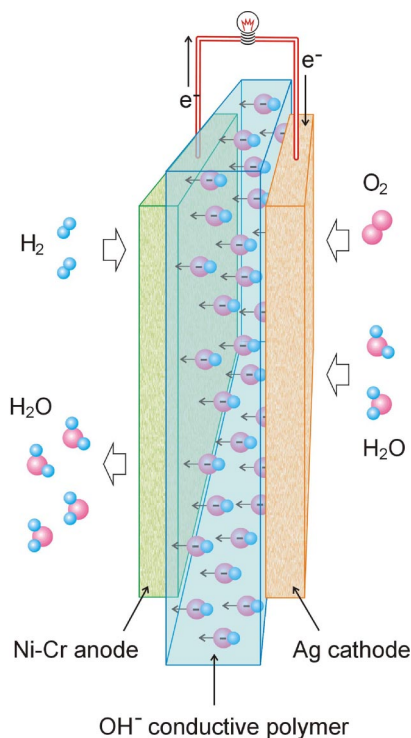
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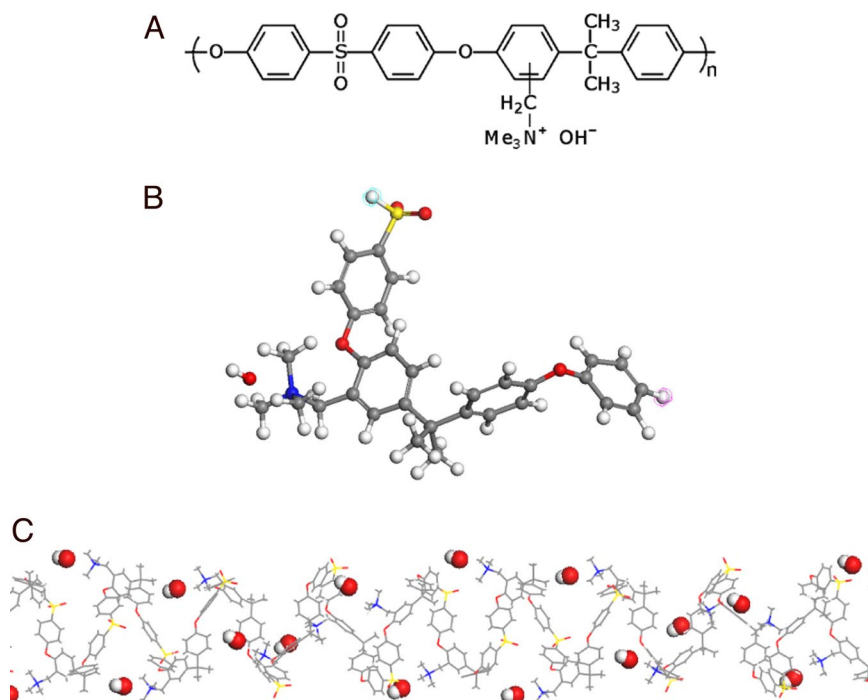
**Fig. 1.** Schematic depiction of an APEFC, consisting of a hydroxide ion-conductive polymer membrane, a Ni-catalyzed anode, and a Ag-catalyzed cathode.  $\text{O}_2$  is reduced at the cathode in the presence of  $\text{H}_2\text{O}$  to produce  $\text{OH}^-$ , which transfers to the anode and reacts with  $\text{H}_2$  to produce  $\text{H}_2\text{O}$ . Electric energy is released to the external circuit upon such conversion.

proaches in both the APE and the anode catalyst. We first successfully designed and synthesized a high-performance alkaline polymer, quaternary ammonium polysulphone (QAPS, Fig.

2), which is thermally stable up to  $120^\circ\text{C}$  [supporting information (SI) Fig. S1] and, therefore, can be used safely at  $<100^\circ\text{C}$ . The ion-exchange capacity can be regulated on demand, up to  $\approx 1$  quaternary ammonium group per structure unit (Fig. S2). Unlike the radiation-grafted membranes developed by Slade and Varcoe (24–27), our synthetic QAPS can be dissolved in certain solvents, such as *N,N*-dimethylformamide (DMF), so that it can be easily cast to membranes of required thickness and size and, also importantly, impregnated into the catalytic layers (Fig. S3). The QAPS membrane thus obtained shows a microstructure similar to that of Nafion, continuous hydrophobic networks penetrated by interlinked nanosized hydrophilic domains (Fig. S4). Such a membrane structure is advantageous in providing both high ionic conductivity ( $>10^{-2}$  S/cm at room temperature, see Fig. S5) and excellent mechanical strength ( $>1,000$  MPa in Young's modulus) and is thus suitable for fuel-cell applications.

As to the anode catalyst for hydrogen oxidation, the Ni catalysts commonly used in AFC did not work well for APEFC. It was found that, in an APEFC, the hydrogen anode made from such Ni catalysts showed an electrode potential characteristic of nickel oxides instead of the potential of a hydrogen electrode. The electrolysis method used in AFC to activate the Ni anode in a separate electrolyzer (28, 29) is, unfortunately, inapplicable for APEFC using an electrode-membrane-assembly (MEA) structure, unless a bifunctional oxygen electrode can be found. For this reason, Tanaka and coworkers (9) at Daihatsu Motors had to use hydrazine, instead of gaseous hydrogen, as the fuel for APEFC. In the present work, we succeeded in addressing this problem by tuning the surface electronic property of Ni through a combined computational and experimental study.

According to density functional theory (DFT) calculations, the impacts of H adsorption and O adsorption on the local density of states (LDOS) of the Ni surface are largely different. Whereas the H adsorption alters almost only the bottom of the *sp*-band of the Ni surface (Fig. S6A), the O adsorption predominantly changes the *d*-band (Fig. S6B); the decrease in the density of states at the Fermi level,  $\text{DOS}(E_F)$ , and the emergence of a



**Fig. 2.** The alkaline polymer electrolyte, QAPS, synthesized and used in the present work. (A) The structure unit of QAPS. (B) The stereo configuration of A, obtained from molecular dynamic (MD) simulations. (C) A MD simulation result of a QAPS chain.





may provide a practical resolution to the current predicament of hydrogen storage but, unfortunately, are unstable in acidic media) now become possible to use directly in APEFC.

## Methods

**Synthesis of APE Membrane. Polymer grafting.** The chloromethylation process of polysulphone (PS, Udel P-1700) was carried out in a 3-neck round-bottom flask with a mechanical stirrer. Ten grams of PS was dissolved in 70 mL of 1,2-dichloroethane to make a solution. After adding 1 g of zinc powder and 4 mL of trifluoroacetic acid into the solution, 20 mL of chloromethylmethylether was added drop-wise. The solution was stirred for 6–12 h at 30 °C (grafting degree was controlled by reaction time). The thus-obtained chloromethylated polysulphone (CMPS) were precipitated in methanol, washed with deionized water several times, and then dried in a vacuum oven for 24 h at 80 °C.

**Membrane preparation.** Dried CMPS powders (0.6 g) were dissolved in DMF to form a 10 wt% solution, which was then bubbled with trimethylamine gas for 0.5 h to produce QAPS. The resulting QAPS solution was cast onto a clean, flat glass plate and dried in an oven at 65 °C for 16 h and then further dried in a vacuum oven at 80 °C for 10 h. To replace the  $\text{Cl}^-$  anion in the polymer with  $\text{OH}^-$ , the QAPS membrane was immersed in 1 mol/L KOH solution for 10 h. This process was repeated 4 times to ensure a complete displacement. Finally, the OH-type QAPS membrane was repeatedly washed with deionized water until the pH of the residual water was neutral.

**Preparation of CDN Catalyst.** Acetylene black powder was wetted with ethanol and then poured into the precursor solution that was prepared by dissolving 12.13 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 0.314 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 200 mL of ultrapure water. After ultrasonic blending for 30 min, the suspension was cooled to between 0 °C and  $\approx 3$  °C under stirring; then 114 mL of 5 wt%  $\text{KBH}_4$  solution was added drop-wise into the suspension at 10 °C, followed by stirring for 30 min. The black powder thus obtained was repeatedly washed with ultrapure water

until no  $\text{Cl}^-$  could be detected. The boron-containing powder obtained was first dried in a vacuum oven at 100 °C for 4 h and cooled to room temperature. The resulting powder was placed in a glazed ceramic boat and heated under an Ar atmosphere at 120 °C for 0.5 h and then at 350 °C for 0.5 h to fully drive out boron from the catalyst. After cooling to room temperature, the CDN catalyst resulted.

**Preparation of the MEA.** OH type QAPS (ion-exchange capacity = 1.2 mmol/g) was dissolved in ethanol to make a 3 wt% ionomer solution. CDN catalyst powder was mixed with ionomer solution and sprayed on a waterproof-treated carbon paper (Toray-250) to make gas diffusion electrodes. Finally, the membrane was sandwiched between 2 gas diffusion electrodes and pressed at room temperature for 3 min under a pressure of  $500 \text{ N cm}^{-2}$ .

**DFT Calculation.** DFT calculations were performed by using the DACAPO code (www.fysik.dtu.dk/CAMPOS) with calculating parameters chosen for both the convergence in energy and relatively less-computational effort. A  $2 \times 2$ -unit cell was used to construct a 4-layer Ni(111) slab, corresponding to a 1/4-monolayer coverage of the adsorbate, and repeated in super cell geometry with successive slabs separated by a vacuum region equivalent to 6 metal layers. Adsorption was allowed on only 1 of the 2 exposed surfaces. Adsorbate and the top 2 layers of the slab were allowed to relax. The surface Brillouin zone was sampled at  $6 \times 6$  special Chadi-Cohen  $k$ -points. The Kohn-Sham 1-electron valence states were expanded in a base of plane waves with kinetic energies up to 25 Ry, and ionic cores were described by ultrasoft pseudopotentials. The exchange-correlation potential and energy were described self-consistently by using the GGA-PW91 functional.

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