Summary

Scientists from Kyushu University in Japan have invented a hydrogen fuel cell catalyst that replaces rare and expensive platinum with iron and nickel. Currently, hydrogen fuel cells, which produce electricity from hydrogen and oxygen, need platinum metal to make the reaction efficient enough for real world application but Professor Seiji Ogo and coworkers have been developing molecular catalysts that do the same job. Having already invented a cheap iron-nickel catalyst for the anode side of the fuel cell, they have now repeated their success with a similar iron-nickel catalyst for the cathode side. Professor Ogo expects this development to make hydrogen fuel cells significantly cheaper and affordable even for domestic consumers.

This research achievement has been published on October 28, 2015, in the online edition of the German academic magazine Angewandte Chemie International Edition.

This research has been carried out as a part of the research sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Grant-in-Aid for Specially Promoted Research, “New Energy Sources from Hydrogenase-Photosynthesis Models,” by Professor Seiji Ogo and his research group at the Center for Small Molecule Energy (Seiji Ogo, head of the center), Graduate School of Engineering, Kyushu University, as well as the International Institute for Carbon-Neutral Energy Research (I²CNER, Petros Sofronis, director of the institute), base of the World Premier International Research Center Initiative (WPI) established by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), and Fukuoka Industry-Academia Symphonicity.

Background

Hydrogen fuel cells generate electricity from the reaction between hydrogen and oxygen gas. Hydrogen power is expected to bring renewable energy to the forefront of energy generation. However, current fuel cells rely on rare and expensive platinum metal to make the reaction efficient enough for real world applications. They are usually too expensive for household applications.

Professor Ogo and his coworkers at Kyushu University and Kumamoto University, Japan, have tackled this problem by replacing the platinum metal with molecular catalysts. “The advantage of molecular catalysts is that we can see exactly how they work and change just one bit at a time,” Ogo explained.

In 2011 they were the first to publish a working molecular catalyst for the hydrogen-splitting anode side of the fuel cell but this catalyst still needed expensive ruthenium. “But this first attempt gave us the insights we needed so we could eventually replace the ruthenium with iron,” Ogo said. The iron-nickel hydrogen-splitting catalyst was reported in 2013 (Fig. 1) and the researchers set to work on producing a catalyst for the complementary oxygen-splitting cathode side of the cell.
“The oxygen-splitting catalyst is very similar to the hydrogen splitting catalyst,” says Ogo “which is unusual for this kind of chemistry but not so surprising for us because natural hydrogenase enzymes can split both hydrogen and oxygen too.” Ogo is referring to enzymes found in bacteria from hot springs. These enzymes are used by the bacteria to release electrons from hydrogen in nature and Ogo has long been using them as a template for his designs. “We knew natural hydrogenases could split both hydrogen and oxygen so we were sure we wouldn’t have to modify our hydrogen catalyst too much to get oxygen splitting.” In fact, they only had to exchange one set of electron-donating ligands for an even stronger ligand.

Nevertheless, the catalyst still had a surprise in store. The oxygen molecule binds side on to the iron, which has a remarkably high +4 oxidation state (Fig. 2). This is the first time such a structure has ever been isolated (Fig. 3) and Ogo believes it gives a crucial new insight into the inner workings of natural hydrogenases and for the future development of fuel cell catalysts.

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**Fig. 2. Oxygen Activation (R = CH₃ or C₂H₅)**

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**Fig. 3. Crystal Structure of Nickel (II) - Iron (IV) Peroxo Compound**

The oxygen bound catalyst can then react with hydrogen ions and electrons to produce water (Fig. 4), providing a low energy bridge between oxygen gas and water.

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**Fig. 4. Reaction from Oxygen to Water (R = CH₃ or C₂H₅)**
**Effect and Future Development**

The research group's next step is to further modify the hydrogen and oxygen splitting catalysts so they can be applied in a working fuel cell. Realization of such a fuel cell will be a crucial step the path to making fuel cells affordable enough for daily life.

**Publication**

Title: A High-valent Fe(IV)-peroxo Core Derived from O₂

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