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PRESS RELEASE (2014/5/23)

Hydrogenase S–77 — A New Frontier for Fuel Cells
(637 Times Mass Activity of Platinum)

Summary

Professor Seiji Ogo and his coworkers at Kyushu University (President, Setsuo Arikawa), Japan, have announced the application of a newly discovered hydrogenase (H_2ase) in a fuel cell which is more efficient than conventional fuel cells. The new enzyme, named H_2ase S–77, can release the electrons from hydrogen molecules and these electrons can be used in a fuel cell to generate electric current. Though H_2ases are not new, their application to the polymer electrolyte fuel cell (PEFC) has not been possible until now because they deactivate upon exposure to oxygen. H_2ase S–77, however, remains active in the presence of oxygen, which enabled Ogo and his coworkers to construct a working fuel cell with no platinum in the hydrogen anode component. An enzymatic fuel cell catalyst is a worthy goal in itself, but of particular interest was its surprising efficiency. This enzyme demonstrated a mass activity (roughly the current obtained divided by the mass of catalyst per cm^2 of electrode) that was over 600 times greater than that of platinum. Until now, platinum has far exceeded any other catalyst in terms of mass activity, resulting in the exclusive use of this rare and precious metal in commercial fuel cells. The H_2ase S–77 result, however, demonstrates that molecular catalysts could be serious contenders as a replacement for metallic platinum. Professor Ogo intends to study the working mechanism of H_2ase S–77 so that his research group can produce a stripped-down working model. Such a model would be expected to be even more efficient, as well as stable, in the hot, acidic conditions of commercial fuel cells. H_2ase S–77 was discovered by Professor Ogo and his family on an expedition to Mt. Aso, an active volcano on the island of Kyushu, Japan. He was greatly helped by his wife, Saori Ogo, and has dedicated this discovery to her, taking her first initial for the name, S–77.

This work was supported by Specially promoted Research "New Energy Sources from Hydrogenase–Photosysnthesis Models" from the Japan Society for the Promotion of Science; the Basic Research Programs CREST Type from the Japan Science and Technology Agency; and Scientific Research on Innovative Areas from MEXT.

■Background

A hydrogen–oxygen fuel cell is a promising device that generates electricity from hydrogen gas (H_2) and oxygen gas (O_2), with the formation of water (H_2O) as a waste product. Platinum is generally used as an electrode catalyst of the fuel cell. However, an alternative catalyst is necessary because platinum is scarce and expensive. Hydrogenase (H_2ase) (Note 1) is an enzyme that extracts electrons from hydrogen gas under ambient conditions. This enzyme was tested for application to a fuel cell electrode because it surpasses platinum with regard to hydrogen activation ability. However, the application of H_2ase to the fuel cell was not achieved due to its instability toward oxygen gas.

■Content

Professor Seiji Ogo and his coworkers at Kyushu University have showed that H_2ase S–77, which was found by them in Mt. Aso, an active volcano on Kyushu Island, is stable toward oxygen gas and its hydrogen activation ability surpasses that of platinum as an anode catalyst of fuel cells. H_2ase S–77 has 637 times higher mass activity (Note 2), 1.8 times higher current density (Note 3), and 1.8 times higher power density (Note 4) than platinum. These high performances are caused by the totally different mechanisms to activate (cleave) the hydrogen molecule with H_2ase S–77 between platinum (Note 5). In this work, we have succeeded in the application of high ability derived from H_2ase to polymer electrolyte fuel cell (PEFC) (Note 6).

■Effect

This achievement will facilitate the development of various hydrogenase electrodes and functional hydrogenase models.

■Future Development

Professor Seiji Ogo and his coworkers have found a new hydrogenase (Note 7) and synthesized its model complexes (*Science* **2007**, *16*, 585 and **2013**, *339*, 682). Based on the achievement of this work, they have begun the development of an artificial catalyst that surpasses the previous catalyst, which has been reported as a press release (September 6, 2011, the artificial catalyst demonstrated 1/25 performance of fuel cell with platinum catalyst) and started collaborative research with an auto manufacturer.

■Publication

Title: [NiFe]Hydrogenase from *Citrobacter* sp. S–77 Surpasses Platinum as an Electrode for H_2 Oxidation Reaction

Authors: Takahiro Matsumoto, Shigenobu Eguchi, Hidetaka Nakai, Takashi Hibino, Ki-Seok Yoon, Seiji Ogo

Journal: Angewandte Chemie International Edition
DOI: 10.1002/anie.201404701R1

【Glossary】

(Note 1) Nickel–iron hydrogenase is a natural enzyme that activates the hydrogen molecule. Its active center has nickel (Ni) and iron (Fe) atoms, which are tethered by sulfur atoms (S) of cysteine residue as shown in Figure 1. X indicates water (H_2O), hydroxide ion (OH^-) or oxide ion (O^{2-}) in a resting state, and hydride ion (H^-) in an active state.

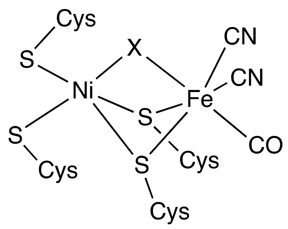

Figure 1. Active site structure of nickel–iron hydrogenase.

(Note 2) Figure 2 indicates activities of platinum and hydrogenase S–77 with regard to extraction of electrons from hydrogen gas. The horizontal axis is mass activity (current per catalyst 1 mg) and the vertical axis is iR–free over potential (subtraction of iR (resistance polarization) from observed voltage). When iR–free overvoltage is 50 mV, H_2ase S–77 has 637 times higher mass activity than platinum.

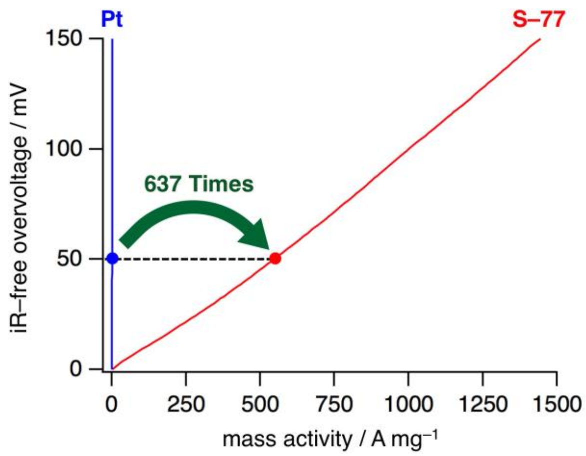

Figure 2. iR–free overvoltage *versus* mass activity.
(At an iR–free overvoltage of 50 mV, platinum: 0.859 A mg^{-1}, H_2ase S–77: 547 A mg^{-1})

(Note 3) Figure 3 indicates cell voltage *versus* current density produced from fuel cells with platinum and H_2ase S–77 as anode catalyst and platinum as cathode catalyst. The horizontal axis is current density (current per 1 cm^2) and the vertical axis is cell voltage (voltage of fuel cell).

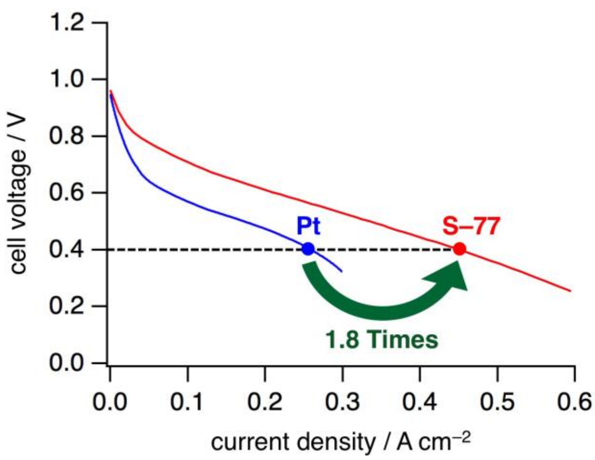

Figure 3. Cell voltage *versus* current density produced from fuel cells
with platinum and H_2ase S–77 as the anode catalyst and platinum as the cathode catalyst.

(Note 4) Figure 4 indicates power density *versus* current density produced from fuel cells with platinum and H_2ase S–77 as the anode catalyst and platinum as the cathode catalyst. The horizontal axis is current density (current per 1 cm^2) and the vertical axis is power density (product of cell voltage and current density). H_2ase S–77 has 1.8 times higher maximum power density than platinum.

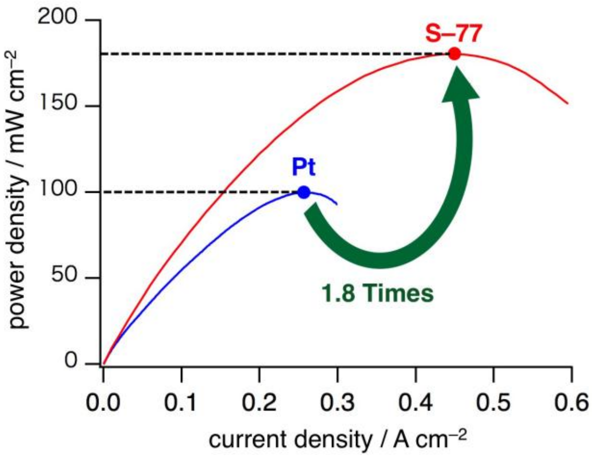

Figure 4. Power density *versus* current density produced from fuel cells with platinum and H_2ase S–77 as the anode catalyst and platinum as the cathode catalyst.

(Note 5) Figure 5 shows hydrogen activation ways with platinum and H_2ase S–77. Platinum homolytically activates (cleaves) the hydrogen molecule to produce two hydrogen radicals (H•) while H_2ase S–77 heterolytically activates the hydrogen molecule to produce hydride ion (H^-) and proton (H^+).

Figure 5. Homolytic and heterolytic activation of hydrogen molecule by platinum and H_2ase S–77.

(Note 6) Figure 6 shows electric power generated by a fuel cell with H_2ase S–77.

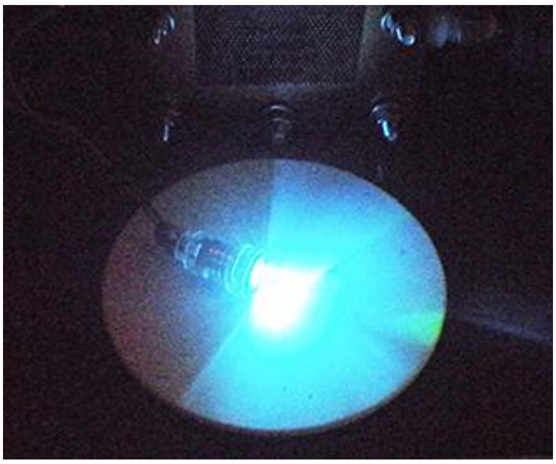

Figure 6. Electric power generated by a fuel cell with H_2ase S–77.

(Note 7) Figure 7 shows the image of finding of H_2ase S–77 from Mt. Aso.

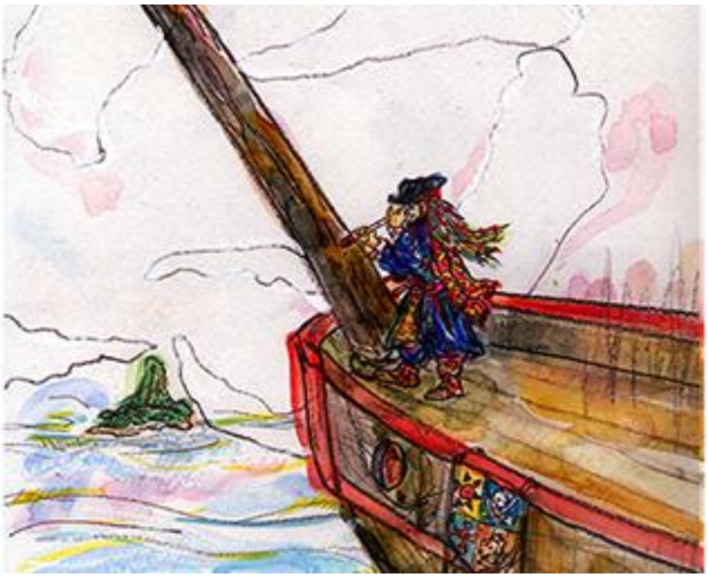

Figure 7. Image of finding of H_2ase S–77.
Selected for the cover picture of *Angewandte Chemie International Edition* (ACIE)

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