Non-platinum group metal catalysts of direct hydrazine anionic membrane fuel cells for automotive applications

A running test of a brand new fuel cell vehicle (FCV), which utilized synchrotron analysis for its development, was carried out at SPring-8 in September 2013 (Fig. 1). The power train of the vehicle, a non-platinum group metal (non-PGM) direct hydrazine fuel cell system, was designed compactly and stored under the flat floor of the vehicle.

A fuel cell can transform chemical energy into electrical energy efficiently. In a historically famous example British chemist Sir William Robert Grove successfully generated power for the first time in 1839 by supplying hydrogen and oxygen to two platinum electrodes in sulfuric acid [1].

For automotive applications, a polymer electrolyte membrane (PEM) fuel cell is recognized as a promising power source. Figure 2 shows the key concept of our research to realize a practical non-PGM fuel cell vehicle, which is called the Creation of Anionic Fuel-cell for the Earth, or CAFE for short. An anion exchange membrane fuel cell vehicle has many advantages suitable for widespread use. Since precious metals, such as platinum, are not needed at all, this system is very advantageous with respect to resources and economic considerations. Moreover, a liquid fuel, hydrazine hydrate ($N_2H_4 \cdot H_2O$), can be supplied safely using a handy polyethylene tank as well as existing infrastructure. Additionally, liquid fuel is used as a "medium" of hydrogen and electrons to realize a hydrogen society.

The principle of the anion exchange membrane fuel is compared with the proton type fuel cell in Fig. 3. Because many active transition metals dissolve in strong acidic environments, alkaline environments are better suited for non-PGM catalysts. Moreover, oxidation of a fuel is more reactive in an alkaline environment.

Fig. 1. Pt-free, zero-emission vehicle powered by a liquid-feed fuel cell.

Fig. 2. Key concept of the CAFE project to realize a practical non-PGM fuel-cell vehicle. Illustrated by Anna Tanaka.

A liquid fuel such as hydrazine hydrate is preferable as a fuel for automotive applications due to its higher energy density and handing ease. The theoretical potential (E^0) of hydrazine (N_2H_4) is as high as 1.61 V. Thus, it is expected to contribute to down-sizing because the number of cells can be decreased. Hydrazine hydrate theoretically produces nitrogen and water by their electro-oxidation reactions without CO_2 exhausts.

Metal-nitrogen-carbon type Co polypyrrol on carbon (CoPPyC) electrocatalysts have been investigated for anion-exchange membrane fuel cells [2]. Specifically, CoPPyC oxygen reduction reaction (ORR) electrocatalysts were analyzed with synchrotron X-ray radiation because it is difficult to analyze mono cluster metal center catalysts such as macrocycle materials using lab instruments. We collaborated with Dr. Nishihata's group of JAEA, Prof. Atanssov's group of the University of New Mexico, and Prof. Kasai's group of Osaka University to establish the structure-to-property correlations.

CoPPyC was synthesized from cobalt nitrate

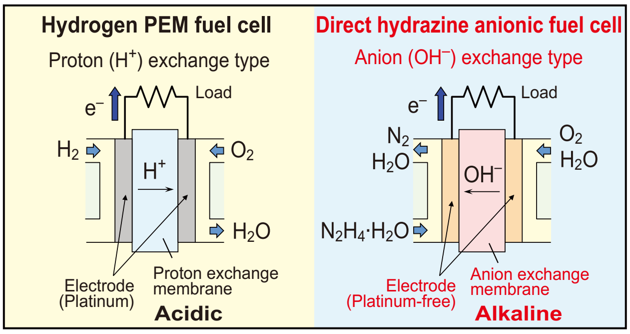

Fig. 3. Comparison of conventional fuel cell and Daihatsu fuel cell.

and PPyC. CoPPyC-A was treated in 1 M sulfuric acid to remove cobalt oxide species from CoPPyC. CoPPyC-PA was pyrolyzed and treated in 1 M sulfuric acid from CoPPyC.

In situ X-ray adsorption fine structure (XAFS) measurements at the Co *K*-edge were carried out at **BL14B2**. Oxygen-saturated alkaline electrolyte was circulated through the cell. During *in situ* XAFS analysis, potential was set at 0.1 V, –0.2 V, and –0.4 V vs. Hg/HgO reference electrode (Fig. 4(a,b)).

CoPPyC-A shows the highest coordination number initially, but after supplying an alkaline electrolyte, the coordination number and the distance to the nearest neighbor decrease. For CoPPyC-A catalyst, the coordination number decreases as the potential decreases, suggesting that the adsorbed species are removed from Co. For CoPPyC-PA catalyst, at a high potential (0.1 V), the coordination number increases from initial state, indicating that OH adsorbs stronger than O_2. As the potential decreases, so does the coordination number.

Hard X-ray photoelectron spectroscopy (HAXPES) measurements were carried out at **BL46XU** and **BL47XU** (Fig. 4(c,d)). The source X-ray energy was 7940 eV. Although the C 1*s*, N 1*s*, O 1*s*, and Co 2*p* spectra were acquired, here only the N 1*s* region is shown. CoPPyC-A and CoPPyC-PA show quite different spectral shapes: nitrogen is mainly pyrrolic in the former but pyridinic in the latter. Conversion of pyrrolic nitrogen to pyridinic occurs during pyrolysis.

The spectroscopic characterization demonstrates that the Co atom is mainly bound to pyrrolic and pyridinic nitrogens in the CoPPyC-A and CoPPyC-PA catalysts, respectively. The structure was optimized by DFT calculations. The Co-pyrrolic has a non-planar configuration, which originates from the rotational degrees of freedom along its Co–N bond and the dominant repulsive character induced between hydrogen atoms of the pyrrol trimers facing each other.

In the 20th century, fossil fuel greatly served as energy resources, and precious metals were utilized as materials of environmental protection. However, to secure these resources, territorial invasions were repeated and peace was spoiled at some locations on Earth. On the other hand, electrical energy can be generated all around the world. By confining this electrical energy in a liquid through a chemical reaction, it becomes an easy-to-use fuel, which can be used to drive a bright future with platinum-free and zero-emission vehicles. However, there are many issues that should be solved in our project, but further technical developments should be accelerated by research using synchrotron radiation.

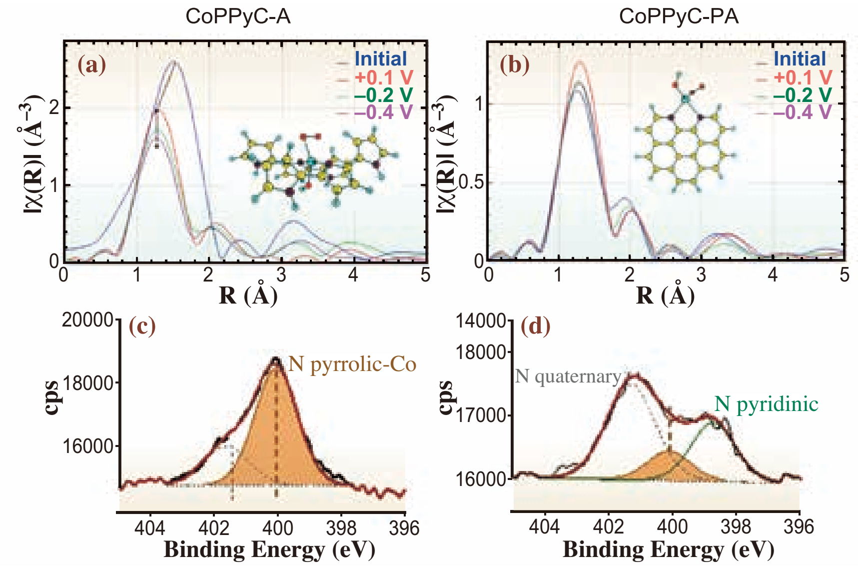

Fig. 4. Structure of CoPPyC-A and CoPPyC-PA catalysts from *in situ* XAFS and HAXPES analysis.

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