High Entropy State Pt-Ru Anode Catalyst with Completely Random Distribution

Residential fuel cell systems are expected to be widely used in the near future. Catalysts having the maximum number of Pt-Ru bondings are ideal catalysts for CO oxidation. Pt-Ru / C(RM) shows the combination of N_{Pt-Ru} / (N_{Pt-Ru} + N_{Pt-Pt}) of 0.59 ÷ 0.60 and N_{Ru-Pt} / (N_{Ru-Pt} + N_{Ru-Ru}) of 0.37 ÷ 0.40. Pt and Ru atoms were distributed with almost random distribution. Entropy tends to be the driving force at high temperature ($\Delta G = \Delta H - T\Delta S$). A high entropy state of dispersion of Pt and Ru is maintained by rapid quenching from a high temperature, resulting in the maximum number of Pt-Ru bondings. The CO tolerance of Pt-Ru / C(RM) is much higher than that of Pt-Ru / C(CM).

Residential fuel cell (PEFC: polymer electrolyte fuel cell) systems are expected to be widely used because of their efficiency of power generation as shown in Fig. 1. Generally, H_2 gas is produced from city gas composed of CH_4 by the reforming reaction. Since CO is contained in reformed H_2, the anode catalyst is deactivated by the adsorption of CO. Catalysts having the maximum number of Pt-Ru bondings are ideal catalysts for CO oxidation, but it is difficult to make such catalysts because Pt-Ru systems prefer homo-bonding owing to different stable structures. Recently we found that the quick quenching of Pt-Ru reduced at high temperature pro-

vides a CO-tolerant anode catalyst [1]. In order to count the number of Pt-Ru bondings and confirm its relation to the catalytic performance, EXAFS measurements were carried out in the Photon Factory. The energy and current of the storage ring were 2.5 GeV and 300 mA, respectively. Pt L3-edge EXAFS spectra were recorded at a BL-12C beamline. Ru K-edge EXAFS measurements were carried out at beamline NW10A of PF-AR (6.5 GeV). The sample was reduced under H_2 in the cell and the EXAFS spectra were measured without exposure to air.
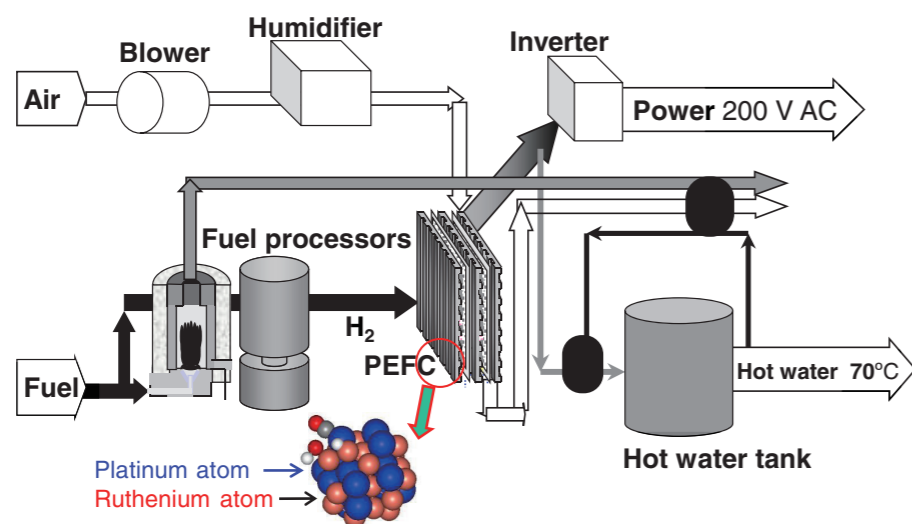
Table 1 : Ratio of coordination numbers

	N_{Pt-Ru} / (N_{Pt-Ru} + N_{Pt-Pt})	N_{Ru-Pt} / (N_{Ru-Pt} + N_{Ru-Ru})
Pt-Ru / C (RM)	0.59	0.37
Pt-Ru / C (CM)	0.44	0.32
Complete random model (Calculation)	0.60	0.40

Ratios of coordination numbers are summarized in Table 1. The molar ratio of Pt (M_{Pt}) to Ru (M_{Ru}) is 2:3. (M_{Ru} / (M_{Pt} + M_{Ru}) = 0.60 and M_{Pt} / (M_{Ru} + M_{Pt}) = 0.40). Pt has an fcc structure, while Ru has an hcp structure; therefore, bondings between like atoms were more preferably formed than were bondings between Pt-Ru bonding. The ratios of N_{Pt-Ru} / (N_{Pt-Ru} + N_{Pt-Pt}) (0.44) and N_{Ru-Pt} / (N_{Ru-Pt} + N_{Ru-Ru}) (0.32) for a commercial catalyst, Pt-Ru / C(CM), were less than those expected from a randomly mixed case. On the other hand, quick-quenched Pt-Ru/C(RM) shows the combination of N_{Pt-Ru} / (N_{Pt-Ru} + N_{Pt-Pt}) of 0.59 ÷ 0.60 and N_{Ru-Pt} / (N_{Ru-Pt} + N_{Ru-Ru}) of 0.37 ÷ 0.40. Pt and Ru atoms were distributed with almost random distribution.

Now we consider the change of entropy by alloy formation. Subscript f means the state after alloy formation, while subscript i means the state before alloy formation.

$G_i = H_i - TS_i$ $G_f = H_f - TS_f$ $G_f - G_i = H_f - H_i - T (S_f - S_i)$

Δ means the change by alloy formation (i.e. $\Delta S = S_f - S_i$). Pt and Ru atoms were mixed with molar ratio (Pt and Ru = 2 : 3).

$\Delta H = H_f(Pt-Ru) - (0.4\ H_i(Pt) + 0.6\ H_i(Ru))$

$\Delta S = k \ln (W_f) - k \ln (W_i)$

W: number of microstates in the particle, k: Boltzmann constant, l: number of atoms in Pt-Ru alloy, L: Avogadro constant

If Pt-Ru alloy consists of pure Pt nanoparticles and pure Ru nanoparticles without mixing,

$W_i = 1$ $S_i = k \ln (W_i) = k \ln 1 = 0$

When it is mixed atomically, entropy will be as follows.

$S_f(Pt-Ru) = k \ln (W_f) = k \ln (l!/((\ 0.6\ l)!\ x\ (0.4\ l)!))$

$= k\ (\ln (l!) - \ln ((0.6\ l)\ !) - \ln ((0.4\ l)!))$

$= k\ (l \ln l - l - 0.6\ l \ln (0.6\ l) + 0.6\ l - 0.4\ l \ln (0.4\ l) + 0.4\ l)$

$= k\ (l \ln l - 0.6\ l \ln (0.6\ l) - 0.4\ l \ln (0.4\ l))$

$= -k\ l\ (0.6 \ln 0.6 + 0.4 \ln 0.4)$

$\Delta S = -R\ (0.6 \ln 0.6 + 0.4 \ln 0.4)$ ($l = L$)

Entropy tends to be the driving force at high temperature ($\Delta G = \Delta H - T\Delta S$), while enthalpy is the driving force at low temperature. A high entropy state of Pt and Ru nanoparticles (random distribution) is realized at high temperature and is maintained by the rapid quenching, resulting in the maximum number of Pt-Ru bondings. This is the first report of a completely randomly distributed Pt-Ru alloy catalyst with highest entropy state. The CO tolerance of Pt-Ru / C(RM) is much higher than that of Pt-Ru / C(CM) since Pt-Ru / C(RM) has more Pt-Ru bondings.

REFERENCE

[1] T. Takeguchi, T. Yamanaka, K. Asakura, E.N. Muhamad, K. Uosaki and W. Ueda, J. Am. Chem. Soc. **134**, 14508 (2012).

BEAMLINES

BL-12C and AR-NW10A

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Figure 1: Residential fuel cell systems.