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Characteristics of a Hydrogen Concentration Cell Constituted with a Redox Pair of 2-Propanol Dehydrogenation and Acetone Hydrogenation

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A hydrogen concentration cell, constituted with a redox pair of 2-propanol dehydrogenation and acetone hydrogenation on electrode catalysts, has been studied, with which low-quality waste heat below 100 °C can be converted into electric power. The magnitudes of the open-circuit voltage (V_{OC}) of this cell were found to be dependent on the anode abilities concerned with C–H bond splitting and hydrogen spillover. The kinetical spillover capabilities of carbon-supported Pd-based composite metal catalysts were obtained separately and compared with the magnitudes of V_{OC}, whereas the catalytic dehydrogenation activities for 2-propanol were more closely related with the magnitudes of a short-circuit current (I_{SC}).

Aiming at the energy conversion of low-quality waste heat below 100 °C into electric power, a reaction couple of thermo-catalytic 2-propanol dehydrogenation (Eq. 1) and electro-catalytic acetone hydrogenation (Eqs. 2 and 3) was investigated recently:[1]

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CO + H_2, \tag{1}$$

$$H_2 \longrightarrow 2H^+ + 2e^-, \tag{2}$$

$$(CH_3)_2CO + 2H^+ + 2e^- \longrightarrow (CH_3)_2CHOH. \tag{3}$$

Another kind of novel fuel cell was proposed as a hydrogen concentration cell (Fig. 1), where the generation of a difference in the thermodynamical hydrogen activities was caused by a couple of 2-propanol dehydrogenation (H-atom generation) (Eq. 4) and its reverse reaction (H-atom consumption) between the electrodes (Eq. 5):[2]

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CO + 2(H), \tag{4}$$

$$(CH_3)_2CO + 2(H) \longrightarrow (CH_3)_2CHOH. \tag{5}$$

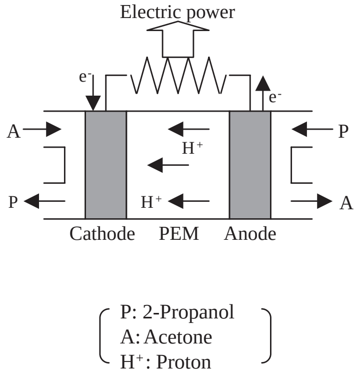

Fig. 1. Schematic diagram of a 2-propanol/acetone hydrogen concentration cell.

An electric potential between the electrodes should be induced through the couple of electro-catalytic dissociation ($(H) \longrightarrow H^+ + e^-$) and association ($H^+ + e^- \longrightarrow (H)$) together with H^+ transfer through proton exchange membrane (PEM) and e^- conduction via an outer circuit.

It was pointed out previously that the abilities of metallic species on bond splitting at the methine C–H group of 2-propanol, together with the capabilities on hydrogen spillover[3–6] toward the supporting carbon, are essentially important for this hydrogen concentration cell.[7]

Electric power can be generated by either the redox reaction between H_2 and acetone or by the H-transfer process between 2-propanol and acetone. Moreover, these two kinds of fuel cells are well complemented with each other, because the anode selectivity of hydrogen spillover becomes imperfect, often due to the accompanying formation of molecular hydrogen. Low-quality waste heat below 100 °C is not only utilized for performing the endothermic dehydrogenation reaction in the former, but also for separating 2-propanol from acetone through distillation in the latter. Consequently, a novel electric-power system of thermo–electric conversion at the temperature level of low-quality waste heat is now possible by adopting jointly the couples of hydrogen/acetone and 2-propanol/acetone (Fig. 2).[2,8]

In the present work, we attempted to elucidate the reaction characteristics, especially concerning the role of catalyst metal species, being expected at the anode, in order to improve the 2-propanol/acetone hydrogen concentration cell as a part of a thermo-regenerative fuel cell.

Experimental

Preparation of Carbon-Supported Composite Metal for 2-Propanol Dehydrogenation. In order to prepare metal fine particles as catalysts for 2-propanol dehydrogenation, such a pretreatment procedure was undertaken for the supporting material that

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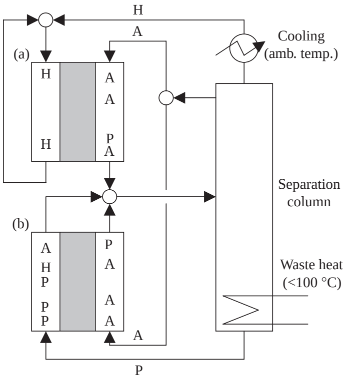


P: 2-Propanol, A: Acetone, H: Hydrogen
(a) Hydrogen/acetone fuel cell
(b) 2-Propanol/acetone concentration cell

Fig. 2. Thermally regenerative fuel cell system utilizing low-quality waste heat.

KOH-activated carbon[9] (Kansai Coke and Chemicals Co., Ltd., BET specific surface area: 3100 m^2/g) was immersed with a NaOH aqueous solution at pH 14 by stirring at room temperature for 24 h, followed by filtration, quick washing with distilled water and then evacuation at 70 °C for 10 h. Micropores of the supporting carbon thus pretreated were filled with a base only inside.[10] Overnight impregnation at room temperature with an aqueous mixed solution (100 mL) of $K_2PtCl_4/RuCl_3 \cdot 3H_2O$ or $K_2PtCl_4/FeCl_2$ or $Na_2PdCl_4/RuCl_3 \cdot 3H_2O$ or $Na_2PdCl_4/FeCl_2$ or $Na_2PdCl_4/RuCl_3 \cdot 3H_2O/FeCl_2$ at a certain ratio was followed by dropwise addition (2 mL/min) for reduction with an aqueous solution of $NaBH_4$ (900 mg/20 mL) at room temperature in a suspended state. After standing for about 15 min, the carbon-supported catalysts (5 wt % as metal) were filtered and washed with a large amount of water (1000 mL). The thus-prepared catalysts were evacuated at 70 °C overnight and kept under nitrogen until the dehydrogenation procedure of 2-propanol.

Commercially available carbon-cloth (Kuraray Chemical Co., Ltd., BET specific surface area: 2000 m^2/g), chosen as the electrode material, was impregnated at room temperature with aqueous mixed solutions of $K_2PtCl_4/RuCl_3 \cdot 3H_2O$ or $Na_2PdCl_4/RuCl_3 \cdot 3H_2O$ or $Na_2PdCl_4/FeCl_2$ or $Na_2PdCl_4/RuCl_3 \cdot 3H_2O/FeCl_2$ at a certain molar ratio (Pt/Ru = 1, Pd/Ru = 10, Pd/Fe = 14, Pd:Ru:Fe = 70:7:5), and then evacuated at 70 °C for 10 h. The impregnated carbon-cloth was reduced by gaseous hydrogen at 300 °C for 12 h, followed by filtration, washing with a large amount of water and evacuating at 70 °C for 10 h.

Reaction Procedure for 2-Propanol Dehydrogenation with Carbon-Supported Composite Metal Catalysts. Catalytic dehydrogenation proceeded under boiling and refluxing conditions in a two-necked round-bottomed flask (50 mL) with the use of carbon-supported metallic catalysts (500 mg), which were immersed in 1.25 mL of 2-propanol and set in so-called superheated liquid-film states.[11] After substituting an air atmosphere with flowing nitrogen gas, the reactor was heated by an oil bath (90 °C). The product gas was collected in a gas burette (250 mL) through a refluxing condenser cooled at 5 °C for 2 h. Both gaseous and condensed reaction products were identified gas-chromatographically by using an active-carbon column intermittently and a PEG 20M column after each reaction, respectively. The hydrogen-spillover ability toward the carbon support (η_{HYD}), which means the atomic ratio of hydrogen adsorbed on the catalyst to metallic palladium supported on the carbon material, was evaluated using the following equation:

$$\eta_{HYD} = ([\text{Acetone}] - [\text{Hydrogen gas}]) \times 2/[\text{Pd metal}]. \quad (6)$$

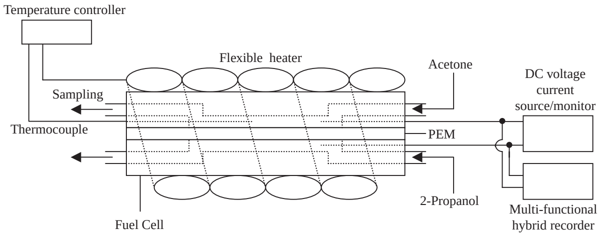


Fig. 3. Schematic diagram of the experimental setup.

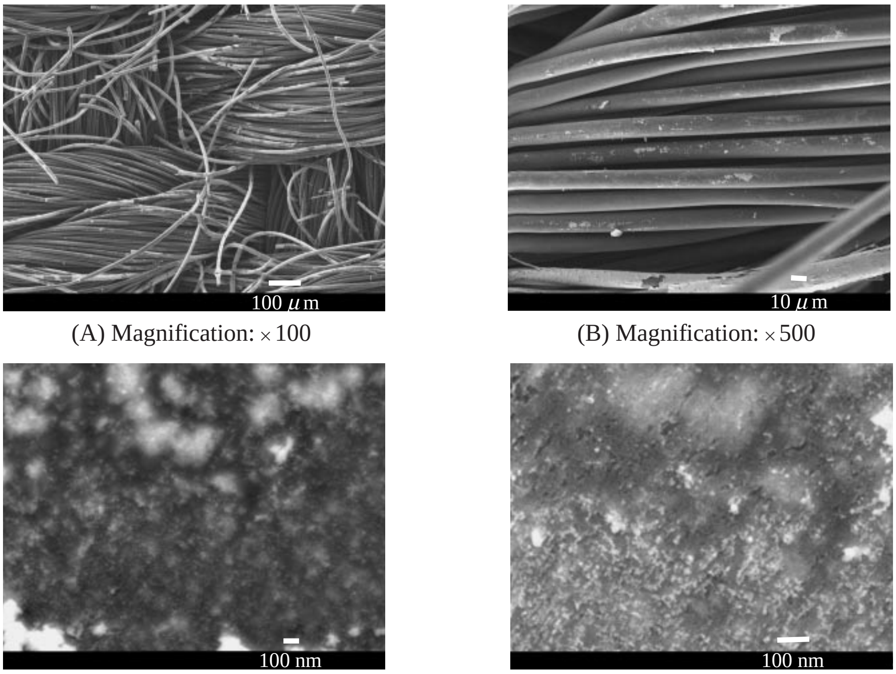
Electrochemical Measurements of *I–V* Characteristics on a 2-Propanol/Acetone Hydrogen Concentration Cell. A schematic diagram of the experimental setup is shown in Fig. 3. A commercially available DC-voltage current source/monitor (Advantest Co., Ltd., R6243) was adopted for continuous monitoring of the electric output of a hydrogen concentration cell, while a multi-functional hybrid recorder (Chino Co., Ltd., Al 3000) was used for electromotive forces as well as temperatures inside the hydrogen concentration cell. The cell, with a 2 × 2 cm^2 electrode area, was heated wholly at 60 °C by a flexible heater, equipped with a temperature controller (Iuchi Co., Ltd., TX-300). The electrode pair was separated with a polymer electrolyte membrane (Du Pont Co., Ltd., Nafion®117). An aqueous solution of acetone (10 vol %) was supplied to the cathode at a rate of 0.8 mL/min, whereas an aqueous solution of 2-propanol (50 vol %) was supplied to the anode at a rate of 0.8 mL/min.

Catalyst Characterization. Characterization of the carbon-supported metallic catalysts was performed by SEM-EDX analysis (Jeol, JSM-6700, JSM-6301), TEM analysis equipped with EELS (Jeol, JEM-2010F), and XRD analysis (Rigaku, RINT-2000).

Results and Discussion

Catalyst Characterization. Face-centered cubic (fcc) structures were confirmed by XRD spectroscopy to both Pd-based and Pt-based composite metal particles supported on a carbon-cloth. SEM analysis revealed that relatively-large metal particles (>100 nm) were grown at the outer surface, in contrast to nano-sized metal particles (<10 nm) found inside the carbon-cloth bulk (Fig. 4). The metal sizes of the latter were comparable to micro pores of the carbon-cloth. It was revealed by a SEM-EDX analysis of the Pd-based composite catalyst that large metal particles (>100 nm) consisted mainly of palladium metal, itself. On the other hand, each nano-sized metal particle (<10 nm) contained both palladium and another kind of metal species, with different atomic ratios of the particle from each other (Fig. 5).

TEM images of the Pd–Ru composite catalyst revealed the lattice lines of a metal particle to be well confirmed, as that of a single crystal (Fig. 6). The plasmon loss peaks, obtained from an EELS analysis for two of composite metal particles, were different not only from those of Pd and Ru, but also from each other (Fig. 7). Therefore, the electronic structure of these two Pd and Ru composite metal particles should be different, which the formation of an alloy at the particle level strongly suggested.



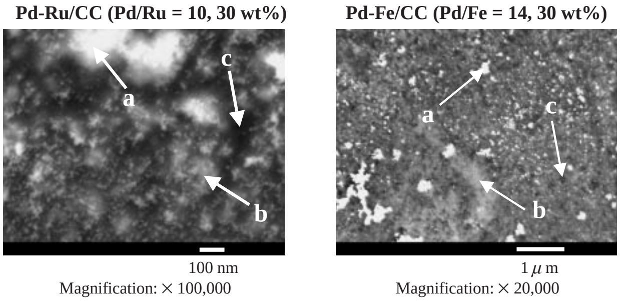
(A) Magnification: × 100 (B) Magnification: × 500

(C) Magnification: × 50,000 (D) Magnification: × 100,000

Catalyst: Pd-Ru/CC (Pd/Ru = 10, 30 wt%)

FE-SEM (JEOL Co., JSM-6700F, Accel. voltage: 5.0 kV, Beam: 10 nm ϕ)

Fig. 4. FE-SEM images of a carbon cloth-supported Pd–Ru composite catalyst.



Spot	Pd / %	Ru / %
White (a)	92.7	7.3
Gray (b)	61.1	38.9
Black (c)	64.7	35.3

Spot	Pd / %	Fe / %
White (a)	81.1	18.9
Gray (b)	50.5	49.5
Black (c)	45.7	54.3

FE-SEM (JSM-6700F, Accel. voltage: 5.0 kV, Beam: 10 nm ϕ)

Spot	Pd / %	Ru / %
White	95.0	5.0
Gray	74.9	25.1
Black	79.8	20.2

SEM(JSM-6301F, Accel. voltage: 10.0 kV)

Spot	Pd / %	Fe / %
White	95.8	4.2
Gray	75.3	24.7
Black	74.3	25.7

SEM(JSM-6301F, Accel. voltage: 15.0 kV)

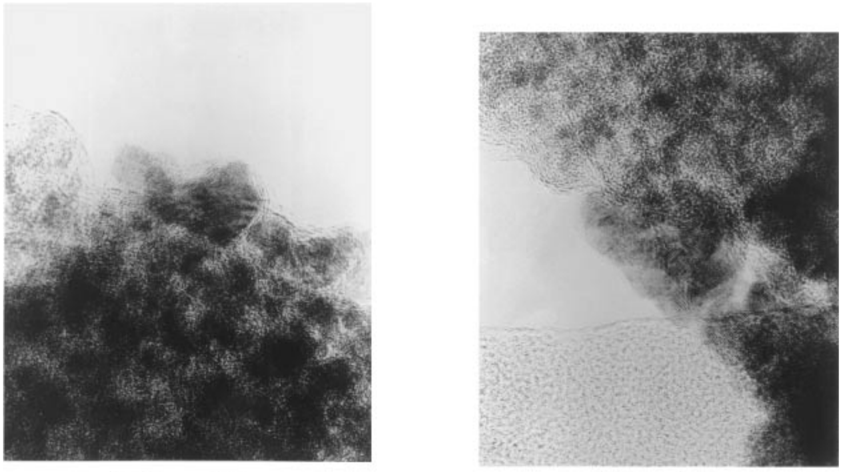
Fig. 5. FE-SEM image and EDX analyses of carbon cloth-supported composite catalysts.

Characteristics of Carbon-Supported Composite Metal Catalysts for 2-Propanol Dehydrogenation. Both Pd–Ru/C and Pd–Fe/C catalysts prepared by the co-impregnation method could demonstrate high dehydrogenation activities for 2-propanol. With regard to the hydrogen spillover ability, composite Pd–Fe catalysts were excellent, in contrast to the Fe/C catalyst, which showed little dehydrogenation activity and no spillover ability. The best performance was attained at a molar ratio of Pd/Fe = 14/1 (Fig. 8). As for composite Pd-Ru catalysts, the best 2-propanol dehydrogenation activity and hydrogen spillover ability were obtained at a molar ratio of Pd/Ru = 10/1 (Fig. 9). The Ru/C catalyst showed little hydrogen spillover ability, with hydrogen gas evolved extensively.

Palladium was a component indispensable to hydrogen spillover due to its large capability in hydrogen dissolution and migration.[13] The data concerning 2-propanol dehydrogenation and hydrogen spillover are summarized for carbon-supported Pd-based and Pt-based composite metal catalysts in Table 1.

A reaction mechanism concerning dehydrogenation of 2-propanol was previously proposed for Pt-based catalysts,[11] where oxophillic Ru or Fe species would take the role of chemisorption sites of 2-propoxide, with its methine C–H bond dissociated with adjacent Pt sites. Nanosized metallic particles of Pd (<10 nm) can provide the hydrogen spillover abilities, even in the alloy form, by transferring hydrogen from the metal bulk to the carbon support. High catalytic activities of both Pd–Ru/C and Pd–Fe/C would be ascribed to the following two reasons. One is a synergetic effect due to the combination of d^{10} and d^8 elements. The other is the size of small metal particles (<10 nm), resulting in large surface areas.

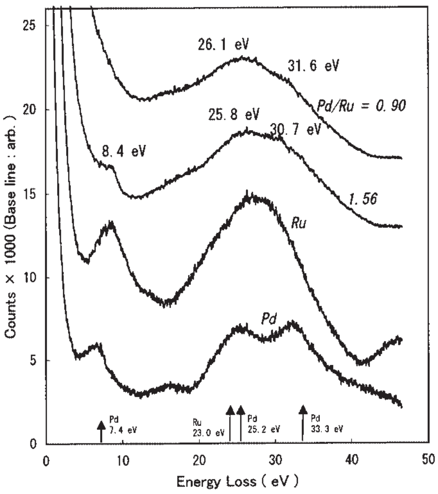
Molecular hydrogen should consist of hydrogen species derived from the O–H and C–H groups of 2-propanol. Hydrogen spillover from carbon-supported composite metal particles, prepared at molar ratios of Pd/Fe = 14/1 and Pd/Ru =



Pd/Ru = 0.90 Pd/Ru = 1.56

200kV, ×500,000, JEM-2010F(JEOL)

Fig. 6. TEM image and EDX particle composition of a carbon-supported Pd–Ru composite metal catalyst.



↑ Pd : Reference 12

Ru : Y. Murata (Prof. Emer., Univ. of Tokyo) private comm.

Fig. 7. Plasmon loss spectra of carbon-supported Pd, Ru, and Pd–Ru composite fine particles.

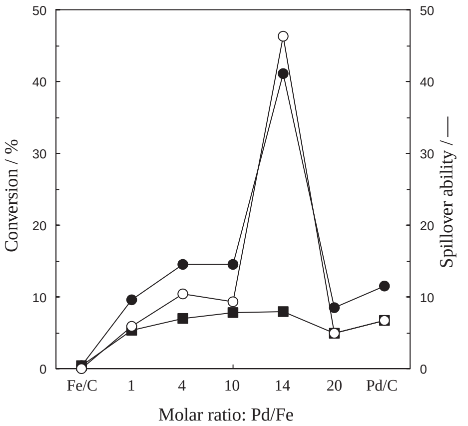


Fig. 8. Dehydrogenation and hydrogen spillover from 2-propanol after a reaction for 2 h with a co-impregnated Pd–Fe composite catalyst (5 wt %) in the liquid-film state under boiling and refluxing conditions. ●, acetone conversion; ■, gaseous hydrogen conversion; ○, spillover ability.

10/1, to the electrode could somehow provide a couple of protons and electrons efficiently.

***I–V* Characteristics on 2-Propanol/Acetone Hydrogen Concentration Cell.** Typical electrochemical performances of this 2-propanol/acetone cell were demonstrated at 60 °C with the carbon-supported Pd-based and Pt-based composite metal catalysts (Fig. 10), where the cathode and the anode were fed with 10 vol % acetone and 50 vol % 2-propanol, respectively. A linear relationship between the current and the voltage of this cell suggests that the activation and diffusion overvoltages are extremely small. Since redox reactions of both 2-propanol dehydrogenation and acetone hydrogenation can proceed on these metal catalysts by only heating, no assistance of an electric potential is required. Moreover, these electrodes are immersed with liquid substrates, without the intervention of a gaseous supply, even at high-current regions.

An important electrochemical behavior was observed with the use of a carbon-supported composite Pd–Fe catalyst for the anode, where an extraordinary larger magnitude of the open-circuit voltage (V_{OC}) than the other Pd-based catalysts was exhibited. Indeed, the hydrogen-spillover abilities of Pd-based catalysts would be inherited to their electrode performances and, consequently, sufficient hydrogen atoms or thermodynamical activities would be secured on the anode, even without current, being contrasted to Pt-based catalysts. The unique nature of the present fuel cell is originated from the catalytic realization of high stationary hydrogen concentrations or thermodynamical activities at the anode.

The short-circuit current (I_{SC}) is determined as the maximum rate of proton migration from the anode to the cathode without affording an electric voltage. Both the proton yield over the carbon-supported composite metal catalyst from 2-

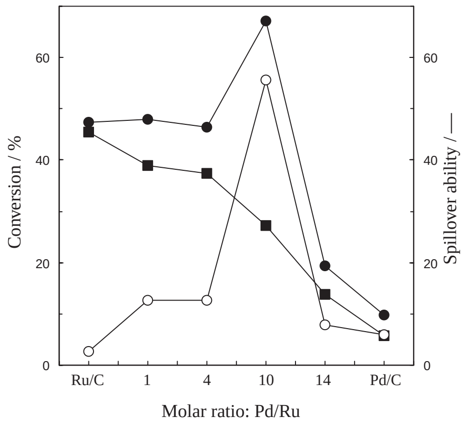


Fig. 9. Dehydrogenation and hydrogen spillover from 2-propanol after a reaction for 2 h with a co-impregnated Pd–Ru composite catalyst (5 wt %) in the liquid-film state under boiling and refluxing conditions. ●, acetone conversion; ■, gaseous hydrogen conversion; ○, spillover ability.

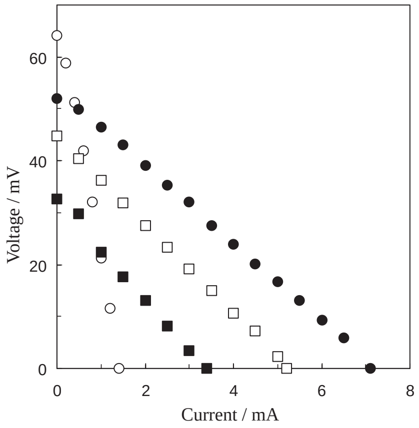


Fig. 10. Current–voltage characteristics of a 2-propanol/acetone hydrogen concentration cell with 30 wt % of Pd–Fe/C (Pd/Fe = 14) (○), Pd–Ru/C (Pd/Ru = 10) (●), Pd–Ru–Fe/C (70:7:5) (□), and Pt–Ru/C (Pt/Ru = 1) (■) at the anode. 30 wt % of Pt–Ru/C (Pt/Ru = 1) was adopted commonly at the cathode.

Table 1. 2-Propanol Dehydrogenation and Hydrogen Spillover with Carbon-Supported Composite Metal Catalysts[b)]

Catalyst metal (molar ratio)	Pt–Ru/C (1:1)	Pt–Fe/C (10:1)	Pd–Fe/C (14:1)	Pd–Ru/C (10:1)	Pd–Ru–Fe/C (70:7:5)
Acetone conversion[c)]/%	42.9	49.0	41.1	67.0	45.7
H_2 (gas) conversion[c)]/%	39.5	43.3	7.9	27.2	26.9
Spillover ability[a)]/—	4.8	7.9	46.3	55.5	26.3

a) Spillover ability: Molar ratio of H (adsorbed) = $\{([\text{Acetone}] - [H_2]) \times 2\}$ to metallic species. b) Catalyst: Prepared by co-impregnation of metallic species on activated carbon (5 metal-wt %). c) Reaction: Catalyst 500 mg/2-propanol 1.25 mL under boiling (90 °C) and refluxing (5 °C) conditions for 2 h.

Table 2. Rate Analysis on Electrode Catalysts

Anode	V_{OC}/mV	$[H]_-/[H]_+$[a)]/—	I_{SC}/mA	v[b)] $\times 10^{-8}$/mol s^{-1}
Pd–Fe/CC[c)]	64.2	87.6	1.4	0.7
Pd–Ru/CC	51.9	37.2	7.1	3.6
Pd–Ru–Fe/CC	44.8	22.7	5.2	2.6
Pt–Ru/CC	32.7	9.8	3.4	1.7

a) Nernst equation: $E = RT(\ln[H]_-/[H]_+)/nF$. b) Maximum reaction rate obtained from short-circuit current $I_{SC} = nFv$. c) CC: Carbon cloth.

propanol and the proton transfer across the electrode/membrane interface as well as inside the electrolyte bulk would be closely related to the resistance polarization of this cell, and consequently the short-circuit current.

As shown in Table 1, the catalytic activities of 2-propanol dehydrogenation and the spillover abilities of hydrogen atoms are sensitively dependent on the chemical species of the composite metal anode catalyst. Under the conditions for measuring I_{SC}, a magnitude estimation on the proton migration (v) was attempted for four kinds of anode catalysts from the correlation of $I_{SC} = nFv$, as shown in the last column of Table 2, where the observed magnitudes of I_{SC} were referred for a comparison. With regard to the open-circuit voltage (V_{OC}), the observed magnitudes for these anode catalysts are summarized in the first column of Table 2. The stationary ratios of the thermodynamical hydrogen activities between the anode and the cathode were calculated using the Nernst equation, as cited in the second column. It was revealed that the Pd–Fe/C catalyst exhibits about a 9-times larger hydrogen activity than the Pt–Ru/C catalyst. Thus, the origins of V_{OC} and I_{SC} are entirely different.

In Table 3, the rate of proton migration, estimated from I_{SC} of the Pd–Fe/CC anode, is contrasted to the thermo-catalytic reaction rate over the same composite Pd–Fe particles supported on carbon and preserved in a superheated liquid-film state with 2-propanol.[11] Since the catalytic rate of 2-propanol dehydrogenation was much larger than that of proton migration under electrocatalytic circumstances, the possibilities of an I_{SC} enhancement would be anticipated by improving proton transport through the membrane.

Table 3. Rate of Proton Migration in a Hydrogen Concentration Cell Compared to Possible Catalytic 2-Propanol Dehydrogenation

Item	Rate $/10^{-8}$ mol s^{-1}	Catalyst (Pd/Fe = 14) Load/support	Temp /°C	2-Propanol /vol %	Measurement Apparatus
H^+ Migration	0.72[a)]	30 wt %/carbon cloth	60	50	Fuel cell
2-Propanol Dehydrogenation	93.5	5 wt %/carbon granule	90	100	Liquid-film[b)]

a) Maximum reaction rate obtained from the short-circuit current, $I_{SC} = nFv$, in a fuel cell. b) Batchwise reaction: Catalyst 500 mg (Pd–Fe/C, 5 wt %-metal, Pd/Fe = 14)/substrate 1.25 mL.

Conclusion

The important role of catalyst metal species for enhancing both V_{OC} and I_{SC} at the anode was revealed in a 2-propanol/acetone hydrogen concentration cell. It seems noteworthy that the electric potential difference, given as the ratio of the thermodynamical hydrogen activities between the cathode and the anode, is the origin of the cell voltage, and is catalytically controlled. Important experimental results are as follows:

(1) 2-Propanol dehydrogenation and acetone hydrogenation proceeded so facile on the electrode catalysts that the activation overvoltages were diminished to negligible extents in contrast to that of ordinary hydrogen/oxygen fuel cells.

(2) Carbon-supported composite metal catalysts (Pd/Fe = 14 and Pd/Ru = 10 in molar ratio) could afford high dehydrogenation activities and spillover abilities toward 2-propanol.

(3) The magnitudes of V_{OC} were well related with the hydrogen spillover abilities of the anode catalysts, whereas the magnitudes of I_{SC} exhibited a close relationship with the catalytic activities for 2-propanol dehydrogenation.

In conclusion, tremendous electrochemical improvements of this hydrogen concentration cell would be attained with high catalytic dehydrogenation activities and hydrogen spillover abilities toward 2-propanol by the use of optimized anode metal species.

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