Reaction Analysis of Ethanol Electro-Oxidation on PdRu/C Catalyst at Intermediate Temperature

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To evaluate the availability of non-Pt catalysts in a direct ethanol fuel cell operating at an intermediate temperature, a PdRu/C catalyst was synthesized by a liquid phase reduction method and its catalytic activity for ethanol electro-oxidation was investigated at approximately 250°C using a single cell fabricated with CsH₂PO₄ proton-conducting solid electrolyte. Electrochemical measurement and reaction product analysis revealed that direct electro-oxidation of ethanol and hydrogen production from ethanol proceeded in parallel on PdRu/C. The PdRu/C catalyst showed high activity for hydrogen production reaction comparable to that on the PtRu/C catalyst, which results in high current density at low electrode potentials (<200 mV). C–C bond dissociation proceeded rapidly on the PdRu/C catalyst, while the subsequent oxidation of the adsorbed C₁ species may be the rate-determining step at the intermediate temperature. For further activation of the PdRu/C catalyst, activation of surface OH should be investigated.

Introduction

Direct ethanol fuel cells (DEFCs) have a high theoretical energy conversion efficiency and are promising power sources for automotive and portable applications. DEFCs also have several advantages over fuel cells with hydrogen fuel, such as ease of handling, storage, and transportation of liquid fuel, high energy density, and compactness of systems without a reformer.

Despite great efforts and numerous studies, however, DEFCs operating at low temperatures (<100°C) suffer from the slow kinetics of ethanol oxidation (Lamy *et al.*, 2001). It has been reported that the C–C bond dissociation of ethanol hardly proceeded on a Pt catalyst and the main reaction products were acetaldehyde and acetic acid (Wang *et al.*, 2006b). Therefore, the total oxidation reaction of ethanol does not occur and an efficient use of ethanol fuel has not been accomplished.

In the previous studies, we have investigated the ethanol electro-oxidation on Pt-based catalysts at an intermediate temperature (approximately 250°C) using proton-conducting solid electrolyte, cesium dihydrogen phosphate (CsH₂PO₄) (Otomo *et al.*, 2008a, 2008b; Shimada *et al.*, 2011, 2013). CsH₂PO₄ exhibits a superprotonic phase transition at ca. 230°C, leading to a stable highly conducting phase (>10^{−2} S cm^{−1}) under an appropriate amount of hu-

midity (Otomo *et al.*, 2003). From an electrochemical measurement and reaction product analysis of ethanol electro-oxidation at approximately 250°C, we have obtained the following results (Shimada *et al.*, 2011): (i) activation overpotential decreased drastically; (ii) C–C bond dissociation proceeded rapidly; and (iii) the main reaction product was CO₂. Although CH₄ was produced as a by-product on the Pt/C catalyst, it was suppressed with Ru addition to the Pt/C catalyst (i.e., PtRu/C catalyst), which suggests that activation of OH species on the catalyst surface is effective in accelerating the total oxidation of ethanol at the intermediate temperature (Shimada *et al.*, 2013). These results indicate a possibility for the efficient use of ethanol fuel with the DEFC being operated at the intermediate temperature.

Because the Pt-based catalysts, however, lead to high materials cost for DEFCs, the development of alternatives is expected. In this study, we investigated the availability of non-Pt catalysts for the DEFCs operated at the intermediate temperature. According to the investigation on the Pt-based catalysts mentioned above, the catalytic activities required for the total oxidation of ethanol are as follows: (i) C–C bond dissociation; (ii) water adsorption and the subsequent dissociation; and (iii) a charge-transfer reaction. In light of these indexes, we focused on Pd and Ru. In the literature, it is reported that (i) turnover frequencies for C–C bond dissociation of ethanol on Pd are approximately half as high as those on Pt (Ferrin *et al.*, 2009); (ii) exchange current density of the H₂ electro-oxidation reaction on Pd is comparable with that on Pt (Nørskov *et al.*, 2005); (iii) Ru exhibits a relatively high catalytic activity toward the water adsorption and dissociation reaction (Wang *et al.*, 2006a); and (iv) addition of Ru to an electrode catalyst promotes the activity of surface OH and accelerates the oxidation of surface car-

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bon species, which is known as the bifunctional mechanism (Watanabe and Motoo, 1975). Hence, we combined Pd and Ru for satisfying the three indexes of catalytic activities required for the total oxidation of ethanol mentioned earlier. Therefore, in this study, we synthesized the PdRu/C catalyst and investigated its catalytic activity for ethanol electro-oxidation at the intermediate temperature. We also discussed the reaction mechanism of ethanol electro-oxidation on the PdRu/C catalyst and compared it with that on the Pt-based catalysts.

1. Experimental

1.1 Synthesis of PdRu/C catalyst

A carbon-supported palladium ruthenium catalyst (PdRu/C; 20 wt% Pd and 20 wt% Ru) was prepared by a liquid phase reduction method using NaBH_4 (Wako Pure Chemical Industries, Ltd.) as a reducing agent. $\text{Pd}(\text{NO}_3)_2$ (Kanto Chemical Co., Inc.) was dissolved in 1 M HCl to form a yellow solution with 0.005 M Pd^{2+} . An ammonia solution (28%, v/v) was added dropwise until the yellow solution became colorless, which indicates the formation of the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ complex (Cheng *et al.*, 2010). A calculated amount of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (Strem Chemicals, Inc.) was added to the solution, and the pH value was adjusted to 10 with 1 M NaOH. An appropriate amount of a carbon support (Ketjen black, Lion Co.) was added and dispersed ultrasonically for 1 h. The suspension was reduced by the dropwise addition of 1 M NaBH_4 solution (the molar ratio of metal ion and NaBH_4 was 1:13) at 80°C under a mechanically stirred condition. After filtration, washing, and drying, the catalyst was heat-treated at 350°C in a reductive atmosphere of 1% H_2 /99% Ar for 2 h.

The synthesized catalyst was characterized with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD patterns were recorded using a SmartLab X-ray diffractometer (Rigaku Co.) with $\text{CuK}\alpha$ radiation at 40 kV and 20 mA. TEM investigation was carried out by a JEM-2100 microscope (JEOL Ltd.) operated at 200 kV.

1.2 Preparation of membrane electrode assembly

The fabrication procedure of a membrane electrode assembly (MEA) is described in our previous study (Shimada *et al.*, 2011). The composite of CsH_2PO_4 (Soekawa Chemical Co., Ltd.) and SiO_2 (Nippon Silica Industrial Co., Ltd.) was prepared by an evaporation-to-dryness method (Shigeoka *et al.*, 2004). To enhance the mechanical stability of the electrolyte, 1 wt% of SiO_2 was introduced. The obtained composite powder was pressed at 4 t cm^{-2} to form a solid electrolyte disk (diameter: 20 mm, thickness: ca. 1 mm). The synthesized PdRu/C catalyst was used for preparing a working electrode, while a commercial carbon-supported platinum catalyst (Pt/C; Pt: 46 wt%, Tanaka Kikinzoku Kogyo KK) was used for fabricating the counter and reference electrodes. An ultrasonically dispersed mixture of the catalyst powder, polytetrafluoroethylene, and water was first spread on a carbon paper (Toray Industries, Inc.) and then heated

in 1% H_2 /99% Ar at 350°C for 2 h. A saturated CsH_2PO_4 solution was infiltrated into the electrodes and then they were attached to the electrolyte disk by hot pressing at 150°C and 1 kg cm^{-2} . The reference electrode was attached to the counter-electrode side. The geometric electrode area was 0.57 cm^2 for the working and counter electrodes and 0.12 cm^2 for the reference electrode. Metal loadings on all electrodes were 2 mg cm^{-2} .

1.3 Electrochemical measurement and reaction product analysis

The MEA was set between two Pyrex glass tubes, placed in a thermostatic chamber. A gaseous mixture of ethanol (Kanto Chemical Co., Inc.), water, and argon (typical molar ratio $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}:\text{Ar} = 13:40:47$) was supplied to the working-electrode side and a gaseous mixture of H_2 and H_2O ($\text{H}_2:\text{H}_2\text{O} = 53:47$) was supplied to the counter-electrode side. Humidification was necessary to inhibit the dehydration of CsH_2PO_4 electrolyte (Otomo *et al.*, 2003). Electrochemical measurements were obtained using a half-cell configuration and a three-electrode system with Autolab PGSTAT 30 that had a frequency response analyzer module, FRA2 (Eco Chemie B. V.). The potential value reported in this study are with respect to the reversible hydrogen electrode (RHE) and they were iR corrected. The electrolyte resistance was evaluated by ac impedance spectroscopic measurements at 1 kHz.

The reaction products of ethanol electro-oxidation under steady-state polarization conditions were captured after vapor-liquid separation with a cold trap. The gaseous and liquid products were then analyzed with a gas chromatograph (GC-8A, Shimadzu Co.) equipped with a thermal conductivity detector (TCD) and a gas chromatograph (GC-14B, Shimadzu Co.) equipped with a flame ionization detector (FID), respectively.

2. Results

2.1 Characterization of PdRu/C catalyst

Figure 1 shows the XRD patterns of the PdRu/C samples before and after heat treatment at 350°C in H_2/Ar . Diffraction peaks at around 40°, 68°, and 82° correspond to the diffraction at Pd(111), Pd(220), and Pd(311) planes, respectively. In addition, a broad diffraction peak at around 44°, which is related to the Ru(101) planes, was observed in the PdRu/C sample after the heat treatment. Each diffraction peak agreed with the Joint Committee for Powder Diffraction Standards (JCPDS) data and no peak shift was observed. These results suggest that most of Pd and Ru exist in separate phases, which agrees with the previous reports of *ab initio* calculations and experiments (Curtarolo *et al.*, 2005; Fisher *et al.*, 2009). The crystallite size of the Pd nanoparticles was 5 nm after the heat treatment, which was calculated from the diffraction peak of Pd(220) using the Scherrer formula.

Figure 2 shows the TEM image of PdRu/C after the heat treatment at 350°C. It can be seen that the nanoparticles

Fig. 1 XRD patterns of the prepared PdRu/C catalyst (a) before and (b) after the annealing in 1% H_2 /99%Ar atmosphere at 350°C

Fig. 2 TEM micrograph of the prepared PdRu/C catalyst after annealing in 1% H_2 /99%Ar atmosphere at 350°C

are fully dispersed on the carbon support. The size of the nanoparticles ranges from 3 to 20 nm. Considering the peak width of the diffraction pattern shown in Figure 1, Pd may constitute the relatively larger particles and Ru may constitute the relatively smaller particles.

2.2 Electrochemical measurement and reaction products analysis of ethanol electro-oxidation

Figure 3(a) shows the current density of ethanol electro-oxidation on PdRu/C at 250°C. The onset potential was ca.130 mV, which is close to the value observed with ethanol electro-oxidation on Pt/C at 250°C (ca. 120 mV) (Shimada *et al.*, 2011). The oxidation current rose sharply in the potential range 130–300 mV, and it gradually increased at the potential higher than 300 mV. These low onset potential and high activity values in the lower-potential region indicate a small activation overpotential in the operation of DEFC.

Figure 3(b) shows the concentration of the reaction products at 250°C. The main reaction products on PdRu/C were H_2 , CO_2 , and CH_4 , while small amounts of CO , CH_3CHO , and CH_3COOH were also observed. The formation of C_1 species as the main reaction products suggests that the C–C bond dissociation reaction proceeds rapidly. The carbon-based selectivity, S_X , and C–C bond dissociation ratio, $S_{\text{C-C}}$, were calculated with Eqs. (1) and (2), respectively, and are shown in Figure 4.

Fig. 3 (a) Steady-state polarization curves of ethanol electro-oxidation on the PdRu/C catalyst at 250°C (iR -corrected). Ethanol (13 mol%)/water (40 mol%)/Ar (47 mol%); total flow rate: 45 mL min^{-1} (sccm). Filled symbol: experimental data; broken lines (curves A and B): predictions for the current density of the direct route (i_A) and the indirect route (i_B) (see text); solid line: summations of i_A and i_B (i_{total}). (b) Concentration of reaction products corresponding to the current density. Symbols: experimental data; broken lines: predictions for concentrations of H_2 (curve A) and CO_2 (curve B)

Fig. 4 Selectivity of reaction products and C–C bond dissociation ratio in ethanol electro-oxidation on the PdRu/C catalyst at 250°C. Filled symbols: product selectivity; open circles: C–C bond dissociation ratio

$$S_X = \frac{n_X C_X}{C_{\text{CO}_2} + C_{\text{CO}} + C_{\text{CH}_4} + 2C_{\text{CH}_3\text{CHO}} + 2C_{\text{CH}_3\text{COOH}}} \quad (1)$$

$$S_{\text{C-C}} = S_{\text{CO}_2} + S_{\text{CO}} + S_{\text{CH}_4} \quad (2)$$

As shown in Figure 4, approximately 70% of the C–C bond of ethanol dissociated on PdRu/C. This ratio is similar to the value for ethanol electro-oxidation on PtRu/C at the inter-

mediate temperature (Shimada *et al.*, 2013) and much higher than the value for ethanol electro-oxidation on PtRu/C at a low temperature (Wang *et al.*, 2006b).

2.3 Parallel reaction model

It can be seen in Figure 3 that CO₂ concentration increased gradually with increasing electrode potential and it followed the increase in current density at potentials higher than 300 mV. This result suggests that the electrochemical total oxidation of ethanol (Eq. (3)) proceed on PdRu/C.

In addition, high concentration of H₂ was observed at rest potential and it decreased drastically with an increase in the potential from 130 to 300 mV, which corresponds to the potential range with a sharp increase in current density. A similar result was observed in our previous study on a Pt/C catalyst (Shimada *et al.*, 2011), and it suggests that H₂ production via thermal decomposition of ethanol (Eq. (4)) and subsequent electro-oxidation of H₂ (Eq. (5)) proceed on PdRu/C at the intermediate temperature.

These observations suggest that the direct electro-oxidation of ethanol (direct route, route A) and H₂ production and subsequent electro-oxidation (indirect route, route B) proceed in parallel on PdRu/C at the intermediate temperature. To investigate the contribution of each reaction route to the total reaction, a simple model for the parallel reactions was developed and the polarization curve and reaction products were analyzed by the model, as shown in Figure 3. The details of the parallel reaction model is described in our previous paper (Otomo *et al.*, 2008a). The Butler-Volmer formulation, Eq. (6), was adopted for the relationship between the current density and the activation overpotential of the direct route. Assuming that a transfer coefficient, α , is equal to 0.5, Eq. (7) was obtained.

$$i_A = i_0 \left(\exp \left(\frac{(1-\alpha)nF\eta_{\text{act,A}}}{RT} \right) - \exp \left(-\frac{\alpha nF\eta_{\text{act,A}}}{RT} \right) \right) \quad (6)$$

$$\eta_{\text{act,A}} = \frac{RT}{\beta F} \sinh^{-1} \left(\frac{i_A}{2i_{0,A}} \right) \quad (7)$$

Similarly, the activation overpotential of the indirect route ($n = 2$) was represented as Eq. (8).

$$\eta_{\text{act,B}} = \frac{RT}{F} \sinh^{-1} \left(\frac{i_B}{2i_{0,B}} \right) \quad (8)$$

As shown in Figure 3(b), the H₂ concentration remains constant at potentials higher than 300 mV, which suggests that the rate of the indirect route is dominated by a mass-transfer

process at the higher-potential region. Therefore, a concentration overpotential should be considered for the indirect route in addition to the activation overpotential, which is represented as follows.

$$\eta_{\text{conc,B}} = \frac{RT}{2F} \ln \left(1 - \frac{i_B}{i_{\text{lim,B}}} \right) \quad (9)$$

The limiting current density of the indirect route, $i_{\text{lim,B}}$, was obtained by fitting Eq. (10) to the H₂ concentration at potentials higher than 300 mV, as shown in Figure 3(b).

$$C_{\text{H}_2} = \left(r_{\text{H}_2} \rho_{\text{metal}} - \frac{i_{\text{lim,B}}}{2F} \right) \frac{A_{\text{electrode}}}{V_{\text{out}}} \times 100 \quad (10)$$

The concentration overpotential of the direct route will be negligible because the concentration of ethanol is adequately high in comparison with H₂. Thus, the following parallel circuit model was developed and fitted to the current density shown in Figure 3(a).

$$\eta_{\text{total}} = \eta_{\text{act,A}} = \eta_{\text{act,B}} + \eta_{\text{conc,B}} \quad (11)$$

$$i_{\text{total}} = i_A + i_B \quad (12)$$

The current density and concentration of H₂ and CO₂ predicted from the parallel reaction model are plotted in Figure 3. The fitting parameters are summarized in **Table 1**. As shown in Figure 3, the proposed model well reproduces the dependence of the current density and concentrations of H₂ and CO₂ on the electrode potential.

The reaction parameters of ethanol electro-oxidation on PdRu/C were compared with those on PtRu/C, which we have reported in the previous study (Shimada *et al.*, 2013). Assuming the same parallel reaction model described above, the reaction parameters on PtRu/C were obtained and they are summarized in Table 1. It can be seen that the exchange current density of the indirect route, $i_{0,B}$, on PdRu/C is comparable to that on PtRu/C. Moreover, the H₂-production rate per mass of the catalyst at the onset potential, r_{H_2} , on PdRu/C is higher than that on PtRu/C. These results suggest that the catalytic activity of PdRu/C for the indirect route,

Table 1 Comparison of the reaction parameters of ethanol electro-oxidation at 250°C between the PdRu/C and PtRu/C catalysts (Shimada *et al.*, 2013)

Catalyst	PdRu/C	PtRu/C
Composition	Pd: 20 wt% Ru: 20 wt%	Pt: 30.2 wt% Ru: 23.5 wt%
	Separate phase	Alloy
Particle size [nm]	3–20	5
ρ_{metal} [mg cm ⁻²]	2.0	3.6
r_{H_2} [mol g _{metal} ⁻¹ s ⁻¹]	1.5×10^{-5}	9.1×10^{-6}
$i_{0,A}$ [mA cm ⁻²]	1.0	3.5
$i_{0,B}$ [mA cm ⁻²]	1.0	1.2
$i_{\text{lim,B}}$ [mA cm ⁻²]	4.5	5.3
β [—]	0.10	0.17

i.e., H_2 production and subsequent H_2 electro-oxidation, is the same or higher than that of PtRu/C. On the other hand, the exchange current density of the direct route, $i_{0,A}$ on PdRu/C is no more than 30% of that on PtRu/C. This suggests that the catalytic activity of PdRu/C for the direct route, i.e., the electrochemical total oxidation of ethanol, is inferior to that of PtRu/C, which results in the difference of CO_2 selectivity at high electrode potentials (e.g., 32% and 58% on PdRu/C and PtRu/C, respectively, at ca. 600 mV).

3. Discussion

In the previous studies, we proposed the detailed reaction mechanism of ethanol electro-oxidation on Pt-based catalysts at the intermediate temperature (Shimada *et al.*, 2011, 2013). In this section, we discuss the reaction mechanism of ethanol electro-oxidation on the PdRu/C catalyst at the intermediate temperature in comparison with those on the Pt-based catalysts.

Figure 5 shows the reaction mechanism of ethanol electro-oxidation on the Pt/C and PtRu/C catalysts at the intermediate temperature. Initially, ethanol adsorbs onto the Pt surface and the dehydrogenation reaction proceeds to form CH_xCO^* and H^* (R1). Different from the reaction at low temperature, the C–C bond dissociation reaction (R4) proceeds rapidly at the intermediate temperature and the main adsorbates on the Pt surface are C_1 species such as CH_x^* and CO^* . These adsorbates desorb into the gas phase as CH_4 and CO , or they are oxidized with OH^* to produce CO_2 . An effect of Ru addition is to promote the OH^* formation reaction (R10), which results in the acceleration of oxidation of C_1 adsorbates on Pt. On the other hand, we observed that the rapid C–C bond dissociation proceeds and the main reaction products are C_1 species such as CO_2 and CH_4 in the ethanol electro-oxidation on PdRu/C at the intermediate temperature. This indicates that the reaction mechanism of ethanol oxidation on PdRu/C is similar to that on the Pt-based catalyst. Because the PdRu/C catalyst prepared in this study consists of the separate phases of Pd and Ru, it is

expected that the reaction pathway, which is similar to that shown in Figure 5, proceeds on the Pd surface at the intermediate temperature.

In the reaction pathways shown in Figure 5, there are three branches that determine the reaction product distribution, which correspond to the reactions of adsorbates CH_xCO^* , CH_x^* , and CO^* . The branching ratios of each branch were defined by the following equations denoted as Br_I , Br_{II} , and Br_{III} , respectively, and calculated on the basis of the reaction product concentration.

$$Br_I = \frac{r_{R4}}{r_{R2} + r_{R3} + r_{R4}} \times 100 \quad (13)$$

$$Br_{II} = \frac{r_{R6}}{r_{R5} + r_{R6}} \times 100 \quad (14)$$

$$Br_{III} = \frac{r_{R8}}{r_{R7} + r_{R8}} \times 100 \quad (15)$$

All the branching ratios are equal to 100% if the total oxidation of ethanol. The branching ratios on PdRu/C and PtRu/C are compared in **Figure 6**. On PdRu/C, Br_I was comparable to that on PtRu/C, while Br_{II} and Br_{III} fell below those on PtRu/C. In addition, Br_{II} and Br_{III} on PtRu/C drastically increased with an increase in the electrode potential, while the increases of those on PdRu/C were limited. Here, Br_{II} and Br_{III} are related to reactions R6 and R8, respectively, both of which are the oxidation reactions of C_1 adsorbates by OH^* , as shown in Figure 5. The reason of the increases of Br_{II} and Br_{III} with an increase in the electrode potential is that the OH^* formation reaction (R10) is a charge-transfer reaction, and more OH^* are produced at high electrode potentials. However, the limited increases of Br_{II} and Br_{III} on PdRu/C with an increase in the electrode potential suggest that the reaction activity of OH^* was not very high and the oxidation of the adsorbed C_1 species may be the rate-determining step on PdRu/C. Indeed, in the literature, the DFT calculations point out that a reaction barrier of water dissociation on Pd is higher than that on Pt or Ru, and the surface coverage of OH adsorbate on Pd is quite small (Wang

Fig. 5 Schematic representation of proposed reaction mechanisms for ethanol electro-oxidation at approximately 250°C

Fig. 6 Branching ratios of ethanol electro-oxidation on PdRu/C and PtRu/C at 250°C. Filled symbols: branching ratios on PdRu/C; open symbols: branching ratios on PtRu/C. Circles: Br_I ; triangles: Br_{II} ; squares: Br_{III}

et al., 2006a; Phatak *et al.*, 2009; Zeinalipour-Yazdi and van Santen, 2009). There is another reason for the poor reaction activity of PdRu/C on OH* formation reaction even at high electrode potential, i.e., surface diffusion of OH* formed on the Ru surface site to the Pd surface site may be limited so that the oxidation of the C₁ adsorbates on Pd with OH* does not proceed well. This may be because the catalytic sites of Pd and Ru were not close enough because the prepared PdRu/C catalyst consists of the separate phases of Pd and Ru. Considering the above, further activation of OH* on the catalyst surface would be required to improve the CO₂ selectivity in ethanol electro-oxidation. For this purpose, it is indispensable to develop electrode catalysts that promote water adsorption and dissociation reactions (e.g., composite materials with metal oxides), as well as the preparation of fine Pd nanoparticles that are well dispersed on the catalyst support so that the OH* species formed on the composite materials such as Ru or metal oxides can diffuse to the Pd site and oxidize the adsorbates on Pd. These are the subjects of our future work.

Conclusion

In this study, a PdRu/C catalyst was synthesized by a liquid phase reduction method and its catalytic activity for ethanol electro-oxidation at the intermediate temperature (250°C) was investigated by electrochemical measurements and reaction product analysis. The characteristic features of the electro-oxidation of ethanol on the PdRu/C catalyst at the intermediate temperature are described below. (1) The onset potential of ethanol electro-oxidation on the PdRu/C catalyst was comparable to that on the Pt/C and PtRu/C catalysts, which indicates small activation overpotentials of DEFCs. (2) Direct electro-oxidation of ethanol (direct route) and H₂ production via thermal decomposition of ethanol and the subsequent H₂ electro-oxidation (indirect route) proceed in parallel. The catalytic activity of the indirect route on the PdRu/C catalyst was comparable to that on the PtRu/C catalyst, and the indirect route accounts for a large fraction of the total oxidation current on the PdRu/C catalyst. (3) Rapid C–C bond dissociation proceeds on the PdRu/C catalyst, while the subsequent oxidation of the adsorbed C₁ species may be the rate-determining step. These observations suggest the possibility for an efficient use of ethanol fuel on the PdRu/C catalyst at the intermediate temperature. On the other hand, suppression of the by-product formation and acceleration of the total oxidation reaction of ethanol remain a challenge. Further development of an electrode catalyst promoting water adsorption and dissociation should be investigated in the future work.

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Nomenclature

$A_{\text{electrode}}$	= electrode area	[cm ²]
Br	= branching ratio	[%]
C_X	= concentration of product X	[mol%]
F	= Faraday constant	[C mol ⁻¹]
i	= current density	[mA cm ⁻²]
i_0	= exchange current density	[mA cm ⁻²]
i_{lim}	= limiting current density	[mA cm ⁻²]
n	= number of transferred electrons	[—]
n_X	= number of carbon atoms in molecule X	[—]
R	= gas constant	[J mol ⁻¹ K ⁻¹]
r_{H_2}	= H ₂ production rate per mass of catalyst	[mol g ⁻¹ s ⁻¹]
r_{Rj}	= reaction rate of reaction Rj	[mol cm ⁻² s ⁻¹]
$S_{\text{C-C}}$	= C–C bond dissociation ratio	[%]
S_X	= selectivity of product X	[%]
α	= transfer coefficient	[—]
β	= transfer coefficient (= αn)	[—]
η	= overpotential	[V]
ρ_{metal}	= metal loading on electrode	[g cm ⁻²]

Subscripts

A	= direct route of ethanol electro-oxidation
act	= activation overpotential
B	= indirect route of ethanol electro-oxidation
conc	= concentration overpotential
total	= total overpotential or total current density

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