

Preparation and Electrochemical Activities of Pt–Ti Alloy PEFC Electrocatalysts

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Titanium is one of the most stable materials, remaining undissolved under strongly acidic polymer electrolyte fuel cell (PEFC) conditions. Nanocrystalline Pt–Ti alloy electrocatalysts with a catalyst grain size of several nanometers have been successfully prepared by the colloidal and sol-gel method, characterized by X-ray diffraction, field-emission scanning electron microscope, scanning transmission electron microscope, energy-dispersive X-ray analysis, and X-ray photoelectron spectroscopy. Electrochemical activities were evaluated by current-voltage characteristics measurements using membrane electrode assemblies for humidified H_2 fuels with or without 100 ppm CO, cyclic voltammetry, and CO-stripping voltammetry in 0.1 M HClO₄. Pt–Ti alloy electrocatalysts exhibited higher electrochemical performance than pure Pt catalyst, i.e., higher activity for oxygen reduction reactions and improved CO tolerance.

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Polymer electrolyte fuel cells (PEFCs) are considered to be promising future power sources for electric vehicles, stationary cogeneration systems, as well as portable instruments because of their environmental compatibility and high energy efficiency. However, due to their low operational temperature and the strongly acidic character of their electrolyte materials, noble metal, especially platinum, is used for electrocatalysts. These catalysts are usually dispersed as nanosized particles on conductive support like carbon black to obtain a large surface area.

Pt, widely used as electrocatalysts, exhibits one of the highest catalytic activities for the oxygen reduction reaction (ORR) among pure metals. However, the ORR is relatively slow and the activation overvoltage at the cathodes is also large, even with Pt. For higher efficiency of PEFCs, development of electrocatalysts having ORR activity much higher than pure Pt is desired.

Pure hydrogen is usually used as a PEFC fuel gas. However hydrogen-containing gas generated by steam reforming or partial oxidation of hydrocarbons or alcohols is often used as a practical fuel, because the infrastructure for the production and storage of pure hydrogen is not yet widely available. When reformed fuel gas containing a small amount of CO is used, the anodic overvoltage increases and the cell voltage becomes lower due to CO poisoning of Pt electrocatalysts.¹ Pt–Ru alloy is known as a catalyst with a high CO tolerance^{2,3} and is widely used as an electrocatalyst for PEFC anodes. However, Ru is also a noble metal like Pt and the natural resources are limited, so that alternative CO-tolerant electrocatalysts instead of Pt–Ru alloy are also needed.

Various Pt-based alloy catalysts have been investigated for PEFC cathode catalysts^{4,5} besides non-Pt alternative catalyst materials such as carbides and metal complex. To mention a few for PEFC cathode catalysts, Toda et al. reported more than 10 times higher activity of ORR for sputtered Pt alloys (with Ni, Co, and Fe) compared to pure Pt in 0.1 M HClO₄ solution at room temperature.⁶ Mukerjee et al. found enhanced electrocatalytic activity of ORR for some binary alloys between Pt and transition metals (e.g., Ni, Cr, and Co) under PEFC conditions. They attributed the activity enhancement caused by alloying to the electronic interaction to form Pt 5d band vacancies and the contraction in the Pt–Pt bond distance.⁷

It is also reported that for PEFC anode catalysts, Pt alloys such as Pt–Sn, Pt–Os, Pt–Mo,⁸⁻¹⁰ and Pt-based composite catalysts with oxides such as Pt/MoO_x and Pt/SnO_x,^{11,12} exhibit CO tolerance. Igarashi et al. reported that sputtered Pt alloys (Pt–Ni, Co, Fe, Mo)

showed high CO tolerance at room temperature in 0.1 M HClO₄.¹³ Mukerjee et al. revealed that Pt–Mo alloy showed even better CO tolerance than Pt–Ru alloy.¹⁴

While various Pt alloy catalysts have been extensively studied, most transition metals in alloys are thermochemically stable as ions and thus can dissolve in acid solution from the alloys.¹⁵ Because catalyst particles on support materials are a few nanometers in diameter, the dissolution of transition metals from the catalyst nanoparticles causes serious problems such as catalyst degradation and electrolyte poisoning. Some Pt–Pt group metal (PGM) alloys are expected to show superior durability in comparison with Pt-transition metal alloys. For example, Pt–Ir alloy showed higher ORR activity than pure Pt and it was examined as a cathode catalyst for PEFCs.¹⁶ However, the use of Pt–PGM alloys is not desired due to their limited availability.

Therefore, in order to develop alternative electrocatalysts using widely available inexpensive metals stable under strongly acidic PEFC conditions, we prepared Pt–Ti alloy electrocatalysts. Figure 1 shows a pH-potential equilibrium diagram, a so-called Pourbaix diagram,¹⁷ of the Ti–H₂O system described against the standard hydrogen electrode. The open circle indicates the cathodic condition and the dotted circle the anodic condition in PEFCs. This figure suggests that Ti is the stable material as an oxide in the practical operation environment of PEFCs. The aim of this study is therefore



Figure 1. pH-potential equilibrium (Pourbaix) diagram for the titaniumwater system at 80°C. The open circle shows cathodic condition and the dotted circle shows anodic condition in PEFCs.

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to prepare Pt–Ti alloy electrocatalysts for PEFCs and to analyze their microstructure, electronic state, and electrochemical properties under the cathodic and anodic conditions.

Experimental

Electrocatalysts supported on carbon black (CB) were prepared by colloidal¹⁸⁻²⁰ and sol-gel methods. Carbon black (Vulcan XC-72, Cabot Corp.) was dispersed in distilled water and chloroplatinic acid was added, which was then reduced by sodium hydrogen sulfite. Colloidal Pt-oxide (hydroxide) was prepared by adding hydrogen peroxide solution while adjusting the solution at pH 5 by NaOH. In this dispersion, Ti oxide (hydroxide) was additionally prepared by adding $Ti(OC_3H_7)_4$, which could be easily hydrated. Metal loading was fixed to 20% for the catalysts. The initial atomic ratio of Pt and Ti was set to 3:1, 1:1, or 1:3. Pt-Ti/C was heat-treated at temperatures between 700 and 900°C in pure hydrogen for 2 h. Pt/C was heat-treated at temperatures between 200 and 700°C in 5% H₂-N₂ for 2 h. With the notation of the catalyst samples, reducing temperature (°C) for the catalysts is shown in parenthesis throughout this study, e.g., Pt3Ti1(900) denotes the catalyst with the initial Pt-to-Ti ratio of 3:1 heat-treated at 900°C in the hydrogen atmosphere. Commercial Pt-Ru/C was also used for comparison, consisting of Pt 30.4 wt % and Ru 23.6 wt %, supplied from Tanaka Kikinzoku Kogyo.

Prepared catalysts were observed using field-emission scanning electron microscope (FESEM, Hitachi S-5200) and scanning transmission electron microscope (STEM, Hitachi HD-2200). Elemental analysis was carried out by energy-dispersive X-ray analysis (EDX, EDAX). In addition, crystallographic structure and electronic state of the prepared catalysts were characterized by X-ray diffraction (XRD, Rigaku RINT2200V) and X-ray photoelectron spectroscopy (XPS, Kratos Analytical ESCA-3400). XRD patterns for the catalysts were obtained using a Cu K α X-ray source (40 kV, 40 mA). XPS measurements were made using a Mg K α source (12 kV, 20 mA). Au was sputtered on the catalysts and binding energy was corrected using the Au $4f_{7/2}$ peak located at 84.0 eV.

Cyclic voltammetry (CV) and the rotating disk electrode (RDE) method 21,22 were applied to evaluate electrochemical characteristics of the catalysts. Electrochemical measurements were carried out in a 50 mL three-electrode cell (Hokuto Denko, HR200). A commercial glassy carbon (GC) electrode (Hokuto Denko, HR2-D1-GC5, 5 mm in diameter, 0.196 cm²), Pt-wire electrode (Hokuto Denko), and an Ag/AgCl electrode (saturated in KCl) were used as a working electrode, a counter electrode, and a reference electrode, respectively. The potential of the RDE was controlled by an automatic polarization system (Hokuto Denko, HSV-100). A 0.1 M HClO₄ solution (Sigma-Aldrich) was used as the electrolyte solution for the RDE measurements. At first, the GC electrode was polished using a suspension (Baikowski) containing Al₂O₃ particles of 0.3 µm diameter to obtain the clean GC surface and then it was ultrasonically cleaned in distilled water. The prepared catalysts (25 mg) were dispersed ultrasonically in distilled water (35 mL) to obtain a catalyst dispersion (0.71 mg_{catal} mL⁻¹). Using a micropipette, 28 μ L of the suspension was put on the GC disk electrode, and then the solvent was evaporated in vacuum at room temperature. Furthermore, 10 µL of diluted Nafion solution (5% Nafion solution/ethanol/water = 1009 $\mu L{:}10$ mL:39 mL) were put onto the GC disk electrode and the RDE was dried at 60°C for 1 h in order to obtain a welldispersed thin catalyst layer on the GC disk of the RDE. After drying, the catalyst layer was coated by a thin Nafion film with a thickness of 0.1 $\mu\text{m},$ based on the procedure reported by Watanabe et al. 22

In this study, the electrochemical active surface area was determined by the hydrogen underpotential deposition (H_{upd}) region obtained in the CV measurements. All potential values in this paper are referred to a reversible hydrogen electrode (RHE). In the CV measurements, potential cycles were applied between 0.05 and 1.2 V at a scan rate of 50 mV s⁻¹. N₂ gas was supplied for 10 min before CV

measurements to remove O2 dissolved in the HClO4 electrolyte solution and to substitute the gas phase of the cell with N₂ gas. Peaks of hydrogen adsorption and desorption on the Pt surface could be observed between 0.05 and 0.4 V. The CV measurements were started after 200 cycles to remove any contamination on the electrode. The coulombic charge of monolayer of Hund adsorbed on Pt $(Q_{\rm H})$ between 0.05 and 0.4 V in CV was then obtained. The atomic density of the Pt polycrystalline surface is 1.31 $\times~10^{15}~{\rm cm^{-2}}$ and the coulombic charge of the hydrogen monolayer, in which one hydrogen atom is adsorbed on one Pt atom, is thus 210 μ C cm⁻². Electrochemical surface area (ECSA) was therefore determined using the relation: ECSA (cm^2) $= Q_{\rm H} \,(\mu {\rm C})/210 \,(\mu {\rm C} \,{\rm cm}^{-2}).$

RDE measurement for the ORR was performed at various rotation speeds (ranging from 2700 to 900 rpm) after supplying O_2 into the electrolyte solution for 30 min. The electrode potential was swept in the negative direction from 1.1 to 0.3 V at a scan rate of 10 mV s⁻¹.

CO stripping voltammetry was separately carried out after the corresponding CV measurements. For the CO-stripping voltammetry, pure CO was supplied into the electrolyte solution for 10 min under the fixed potential at 0.05 V and then CO dissolved in the electrolyte solution was removed by supplying N_2 into the solution for 40 min. The current-potential cycle was obtained from 0.05 to 1.1 V at 10 mV s⁻¹.

For the electrochemical characterization in membraneelectrode assembly (MEA), the electrocatalyst slurry was prepared by mixing catalyst, 5% Nafion solution (Aldrich), and ethanol (catalyst/5% Nafion solution/ethanol = 0.1 g:2.33 mL:0.89 mL). The catalyst slurry was deposited by the spray-printing technique (Nordson) on hydrophobic carbon papers coated with poly-(tetrafluoroethylene) (PTFE, Electrochem) and then dried at room temperature. A Nafion membrane (DuPont, Nafion 112) was sandwiched with the catalyst-deposited carbon papers and then hotpressed at 130°C, 13 MPa to obtain an MEA. Catalyst loading was 0.2 mg cm^{-2} for the anodes and 0.4 mg cm^{-2} for the cathodes, while catalyst loading was 0.6 mg cm⁻² for the counter electrodes using commercial catalyst (Tanaka Kikinzoku Kogvo. 44.6 wt % Pt/C). The MEA prepared was fixed in a sample holder kept at 80°C in an atmospheric pressure. Single-cell testing was carried out using H₂ fuel or 100 ppm CO-H₂ fuel supplied to the anodes, while air was supplied to the cathodes. Both gases were humidified at 79.5°C so that the air and the fuel gas were almost fully saturated with water vapor at 80°C, the operational temperature of the MEAs. Ohmic resistance and nonohmic overvoltage were separately evaluated by applying the current-interrupt technique.

Results and Discussion

Characterization of catalysts.- The crystal structure of catalysts prepared via the colloidal and sol-gel method was examined by XRD. Figure 2 shows the XRD patterns of the Pt/C and Pt-Ti/C catalysts prepared in the initial Pt/Ti atomic ratio of 3:1, 1:1, and 1:3, denoted as Pt3Ti, Pt1Ti1, and Pt1Ti3, respectively. The initial ratio of Pt and Ti had been verified by inductively coupled plasma atomic emission spectrometry (ICP-AES). Figure 2 indicates that the XRD peaks of the Pt-Ti/C were shifted to higher angles than those of the Pt/C. The lattice constants calculated from the XRD peaks of (111), (200), (220), (311), and (222) are listed in Table I. The lattice constant of Pt-Ti/C was smaller than that of Pt/C (3.921 Å), indicating the formation of solid solution between Pt and Ti. The samples Pt3Ti1 and Pt1Ti1 are partly ordered to form the intermetallic compound as Pt₃Ti, exhibiting their superlattice lines. However, sample Pt1Ti3 revealed no superlattice line. In addition, the XRD pattern of Pt1Ti3 shows peaks from Ti3O5 as excess Ti exists, i.e., the presence of excess Ti led to the preferential formation of Ti₂O₅ in Pt1Ti3.

The microstructure of the prepared catalysts was observed by FESEM and STEM, and the average particle size (in diameter) was



Figure 2. XRD patterns of prepared catalysts: (a) Pt(200)/C, (b) Pt3Ti1(900)/C, (c) Pt1Ti1(900)/C, and (d) Pt1Ti3(900)/C.

obtained, as listed in Table II. STEM images, shown in Fig. 3, confirm that Pt–Ti alloy particles were dispersed on the carbon support and the particle size was ca. 5 nm diam. In addition, we can find from Table II that grain growth of catalysts was depressed by alloying Pt with Ti, even though heat-treatment temperature was relatively high, up to 900°C.

For supported alloy catalysts, their composition and uniformity should be known. Therefore, elemental compositions of individual alloy particles were analyzed using STEM-EDX. The content of Ti in the Pt–Ti alloys was ca. 15 atom %, independent of the initial Pt-to-Ti ratio of the samples. The composition was approximately uniform. Figures 4b-d show the distribution of specific elements (Pt, Ti, O) detected by STEM-EDX for the catalysts prepared, shown in Fig. 4a. Excess Ti existed as oxides of ca. 100–350 nm diameter. Ti oxides may be distributed as very thin film or in amorphous form, which could be difficult to be detected by XRD.

Catalyst	Lattice constant (Å)
Pt(200)/C	3.921 (±0.0018)
Pt3Ti1(900)/C	3.909 (±0.0013)
Pt1Ti1(900)/C	$3.905 (\pm 0.0005)$
Pt1Ti3(900)/C	3.917 (±0.0006)

Table I. Lattice constant of prepared catalysts, measured by

Table II. Particle size of catalysts measured by using FESEM.

	Catalyst						
	Pt(200)	Pt (450)	Pt(700)	Pt3Ti1 (900)	Pt1Ti1 (900)	Pt3Ti1 (900)	PtRu (TKK) ^a
Particle size (nm)	3.5	3.9	4.7	4.2	4.6	4.3	5.3

^a TKK=supplied by Tanaka Kikinzoku Kogyo.

XRD.



Figure 3. STEM micrograph of Pt–Ti alloy electrocatalysts: (a) secondary electron image and (b) transmission image.

XPS is a useful technique to analyze catalyst surfaces. However, for analyzing nanosized support catalysts, size effect in XPS measurements should be taken into account. Figure 5 summarizes binding energies of Pt 4f peak tops detected by XPS. With decreasing Pt particle size (i.e., with decreasing heat-treatment temperature), binding energy became higher. The reason for this is generally explained as being the size effects for ultrafine metal particles.²³ It was therefore necessary to eliminate the size effects in order to discuss the difference in materials characteristics. Therefore the XPS signal of Pt(700)/C was compared to that of Pt-Ti/C, because Pt(700)/C had almost the same particle size compared to Pt1Ti1(900)/C, as shown in Table II. The Pt 4f XPS spectra of Pt(700)/C and Pt1Ti1(900)/C are shown in Fig. 6. These doublet peaks were from metallic Pt but not from oxide or chloride. In comparison with Pt(700), the Pt 4f peaks of Pt1Ti1(900) were positively shifted. Figure 5 shows the binding energy of all Pt-Ti alloys ca. 0.3 eV higher than that of



Figure 4. (Color online) (a) STEM micrograph of Pt1Ti3/C electrocatalysts, and the distribution of specific elements detected by STEM-EDX: (b) Pt, (c) Ti, and (d) O.



Figure 5. Binding energies of (a) Pt $4f_{7/2}$ and (b) Pt $4f_{5/2}$ photoelectron spectra measured by XPS for various Pt-based catalysts.



Figure 6. XPS spectra of Pt 4f doublets for Pt(700) and Pt1Ti1(900) catalysts.

Pt(700). This positive shift is similar to that reported for Pt–Ti alloys by Beard and Ross.²⁴ This positive shift may indicate the increase of Pt 5d vacancies by alloying with Ti.

ORR activity analyzed by RDE.— CV was applied to calculate ECSA, and then the oxygen reduction activity of the catalyst was examined by RDE in 0.1 M HClO₄. In general, electrode reactions occurred through (*i*) diffusion of reactants to the electrode surface, (*ii*) charge transfer on the electrode surface, and (*iii*) scattering of products from the electrode surface. The slowest process is the rate-controlling step of the overall electrode reactions. An activation process can be rate-controlling if the rotation speed of the RDE is fast enough. The current depends on the rotation rate, according to the following Koutecky–Levich equation²⁵

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_{\rm lim}} = \frac{1}{I_k} + \frac{1}{0.62nFAD^{2/3}C\nu^{-1/6}\omega^{1/2}}$$
[1]

where *n* is the number of electrons involved in the ORR per O₂ molecule, *F*, *A*, *C*, and *D* are Faraday constant (C mol⁻¹), geometrical surface area of the electrode (cm²), solubility (mol cm⁻³), and the diffusion coefficient (cm² s⁻¹) of O₂, respectively, *x* is kinetic viscosity (cm² s⁻¹), ω is the rotation rate (rad s⁻¹), and I_{lim} is limiting current (mA). I_k is the kinetic current and does not depend on rotation rate. I_k values for each catalyst and the potentials were obtained by extrapolation of the Koutecky–Levich plots for $\omega^{-1/2} \rightarrow 0$. I_k was divided by ECSA calculated from CV curves. Activation-controlled current density j_k (mA cm⁻²) can be derived, and Tafel plots of j_k were obtained.

There is a considerable number of reports concerning the effects of particle size on the catalytic activity of Pt. Takasu et al. reported that with decreasing Pt particle size, the specific activity decreases and the Tafel slope increases by using Pt/GC model electrodes.²³ Watanabe et al.²⁶ insisted that catalytic activity did not depend on particle size. To examine the size effect of prepared catalysts, heat-treatment temperature was varied, Pt particle size was controlled, and ORR activity was evaluated by RDE. Figure 7 shows potential vs j_k calculated from RDE measurements, indicating that Tafel slope did not depend on Pt particle size for Pt/C heat-treated between 200 and 700°C (between 3.5 and 5 nm in diameter) under the conditions in this study. In order to avoid the influence of particle size, Pt(700) was used to compare Pt to Pt–Ti alloys for analyzing ORR activity.



Figure 7. Tafel plots for the ORR on Pt/C catalysts for various heattreatment temperatures in O₂-saturated 0.1 M HClO₄ at 25 °C. The values of j_k at each potential were determined from the Koutecky-Levich plots. The current density was normalized to ECSA measured by CV.

Figure 8 shows Tafel plots of Pt and Pt–Ti alloy catalysts. Figure 9 shows j_k at 0.85, 0.80, and 0.75 V. All Pt–Ti alloys had higher j_k than Pt, indicating improved ORR activity by alloying Pt with Ti. Pt1Ti1(900) exhibited the highest j_k . j_k of Pt1Ti1(900) was about 50% higher at 0.8 V and twice higher at 0.75 V in comparison with pure Pt. Tafel curves for smooth, polycrystalline Pt in diluted HClO₄ or H₂SO₄ solutions can be fitted to two Tafel regions: a low-current-density (LCD) region and a high-current-density (HCD) region. Tafel curves were fitted and Tafel slopes were obtained. Table III summarizes the Tafel slopes derived from Fig. 8. Tafel slopes became smaller by alloying with Ti in both regions. A smaller Tafel slope corresponds to a higher kinetic current density j_k at a given potential and thus, improved ORR activity by alloying with Ti, which leads to the difference in Tafel curves in the HCD region in



Figure 8. Tafel plots for the ORR on Pt(700), Pt3Ti1(900), Pt1Ti1(900), and Pt1Ti3(900) catalysts in O₂-saturated 0.1 M HClO₄ at 25°C. The values of j_k at each potential were determined from the Koutecky–Levich plots. The current density was normalized to ECSA measured by CV.



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Figure 9. Kinetic current densities (j_k) at 0.85, 0.80, and 0.75 V vs RHE in 0.1 M HClO₄ solution saturated with O₂. Sweep rate 10 mV/s, temperature 25°C. The current density was normalized to ECSA measured by CV.

Fig. 8. Paulus et al.²⁷ studied Pt-Ni and Pt-Co alloys and reported a similar decrease in Tafel slopes of supported alloy catalysts, which was not observed for bulk alloys. This may also suggest the importance of both the difference of ORR activity between pure Pt and Pt-Ti alloys and the influence of catalyst morphology.

CO tolerance analyzed by stripping voltammetry .--- CO stripping voltammetry was applied in 0.1 M HClO₄ to electrochemically evaluate CO tolerance of catalysts. The CO-stripping voltammograms of prepared catalysts and commercial Pt-Ru/C (Tanaka Kikinzoku Kogyo) are shown in Fig. 10. The potential of the adsorbed-CO oxidation peak of Pt1Ti1(900)/C was 0.74 V, while that of Pt(200)/C was 0.77 V. The potential of the adsorbed-CO oxidation peak of Pt-Ru/C was 0.5 V, as Pt-Ru/C is highly CO-tolerant. The CO-stripping peak potential for Pt-Ti/C showed a negative shift of 0.03 V, however, this shift was smaller than that for Pt-Ru/C (0.27 V). Pt-Ti alloys were thus considered to be slightly CO-tolerant in comparison with pure Pt.

ORR activity analyzed by single-cell tests.- Figure 11 shows the fuel cell performance of single cells with Pt-Ti alloy electrocatalysts used for cathodes and with Pt/C prepared by the colloidal method for comparison. Commercial Pt/C was used for anode catalysts. Pt loading was 0.4 mg cm⁻² for the cathode and 0.6 mg cm⁻² for the anode. The single cell was kept at 80°C in atmospheric pressure. Single-cell testing was carried out using H₂ fuel, while air was supplied to the cathodes. Both gases were humidified at 79.5°C. Figure 11 shows internal-resistance-corrected cell voltage vs current density curves for which internal ohmic losses had been removed by

Table III. Tafel slope for ORR on Pt and Pt-Ti alloy catalysts measured in 0.1 M HClO₄ at 25°C.

	Tafel slope	Tafel slope (mV dec^{-1})			
Catalyst	LCD region	HCD region			
Pt(200)	67	121			
Pt3Ti1(900)	58	99			
Pt1Ti1(900)	56	98			
Pt1Ti3(900)	58	103			



Figure 10. CO-stripping voltammograms of (a) Pt(200)/C, (b) Pt1Ti1(900)/C, and (c) commercial PtRu/C in 0.1 M $HClO_4$ solution. Sweep rate 10 mV/s, temperature 25°C.

using the current-interrupt technique. Cell voltage with Pt1Ti3 was almost the same as that with pure Pt, but cell voltage with Pt1Ti1 or Pt3Ti1 was higher than that with pure Pt. In other words, Pt1Ti1 or Pt3Ti1 showed higher ORR activities than pure Pt, consistent with the RDE results. Improved electrochemical performance by alloying with Ti is also consistent with literature.^{28,29} For Pt1Ti3, excess Ti oxides existing as Ti₃O₅ (see Fig. 2) and twice-larger catalyst layer thickness might also affect ORR activities.

CO tolerance analyzed by single-cell tests.- The fuel cell performance of single cells with the Pt-Ti alloy electrocatalysts used for the anodes was also evaluated. In this case, the commercial Pt/C was used for cathode catalysts. Pt loading was 0.6 mg cm⁻² for the cathode and 0.2 mg cm⁻² for the anode. The single cell was again kept at 80°C in atmospheric pressure. The test was carried out using pure H₂ gas or H₂ gas containing 100 ppm CO, while air was supplied to the cathodes. Both gases were humidified at 79.5°C. Cell voltage vs current density curves of the cells with Pt-Ti alloy cathode catalysts and Pt anode catalysts for the pure H₂ fuel are shown in Fig. 12. Cell voltages with the Pt-Ti alloy catalysts were lower than those with Pt. For the pure H₂ fuel, the cell voltage decreased by alloying Pt with Ti.



Figure 11. Cell voltage vs current density curves in H_2/air of the cell with cathode catalysts Pt(200)/C, Pt3Ti1(900)/C, Pt1Ti1(900), and Pt1Ti3(900)/C, operated at 80°C. The fuel and air were humidified at 80°C in atmospheric pressure. Platinum loading of the cathodes was 0.4 mg Pt cm⁻².

However, the voltage of the cell with the Pt–Ti alloy catalysts used for the anodes became higher than those with pure Pt when H_2 gas containing 100 ppm CO was supplied as shown in Fig. 13. The measurements were performed after cell voltage became stable, and the minimum cell voltages were recorded because of the cell voltage vibration phenomena by CO poisoning.³⁰ Voltage losses with Pt–Ti alloys for the H_2 fuel containing 100 ppm CO were smaller than those with Pt. Especially, voltage loss with Pt1Ti1(900)/C was eight times lower than that with Pt(200)/C at the current density of 200 mA cm⁻², i.e., CO tolerance was actually improved by alloying with Ti. However, the clear CO tolerance of Pt–Ti/C specified by the single-cell test seemed somehow inconsistent with the weak CO tolerance specified by CO-stripping voltammetry using RDE. One



Figure 12. Cell voltage vs current density curves in H_2/air of the cell with anode catalysts Pt(200)/C, Pt3Ti1(900)/C, Pt1Ti1(900), Pt1Ti3(900)/C, and PtRu/C, operated at 80°C. The fuel and air were humidified at 80°C at atmospheric pressure. Platinum loading of the anodes was 0.2 mg Pt cm⁻².



Figure 13. Cell voltage vs current density curves in 100 ppm CO-H₂/air of the cell with anode catalysts Pt(200)/C, Pt3Ti1(900)/C, Pt1Ti1(900), Pt1Ti3(900)/C, and PtRu/C, operated at 80°C. The fuel and air were humidified at 80°C at atmospheric pressure. Platinum loading of the anodes was 0.2 mg Pt cm⁻².

reason could be the difference in experimental conditions: CO-stripping voltammetry was applied using pure CO at 25 °C, while *I-V* measurements in single-cell tests were performed using 100 ppm CO at 80 °C. In addition, CO-stripping voltammetry reveals the potential for CO desorption, while *I-V* characteristics include various kinetic effects such as desorption, adsorption, shift reaction, and oxygen crossover through electrolytes.

Mechanism of ORR activity enhancement.— The results with single cells indicate that ORR activity of the prepared Pt–Ti alloy catalysts improved in comparison with Pt. Mukerjee et al.⁷ reported that a volcano relation between oxygen reduction current and the d vacancy of Pt alloys was measured by XAS. Toda et al.⁶ observed a positive binding energy (BE) shift of Pt 4f and Pt 4d spectra for Pt–Ni, Pt–Co, and Pt–Fe alloys and concluded that the positive shift was due to the increased 5d vacancy of Pt, which led to increased π electron donation from O₂ to the Pt surface, resulting in increased O₂ adsorption and weakening of the O–O bond. A positive BE shift of Pt 4f for Pt–Ti alloys was also observed by XPS (see Fig. 5 and 6), and thus the enhancement of ORR activity may also be due to increased vacancy of Pt in Pt–Ti alloys.

Another reason for the ORR activity enhancement may be the change in the Pt–Pt nearest-neighbor bond distance. Jalan and Taylor³¹ reported ORR activity was increased about three times by alloying Pt with Ti, Cr, Fe, Co, and Ni, and they suggested the Pt–Pt distance was shortened by alloying, which resulted in weakening of the O–O bond. The lattice constant of the prepared catalysts decreased by alloying with Ti (Table I), and Pt1Ti1 showed the highest ORR activity at the smallest lattice constant among the Pt–Ti alloy catalysts. Therefore, the contraction of Pt–Pt distance was also related to the ORR activity improvement for the prepared Pt–Ti alloys.

The ORR activity enhancement leads to higher cell voltages using the Pt–Ti alloy electrocatalysts, as experimentally verified in this study. However, because Pt loading for the electrodes was fixed in this study, the thickness of electrocatalyst layers increased with increasing Ti content. This could be one of the reasons for a decrease in cell voltage using the Pt1Ti3 electrocatalyst with the twicethicker electrocatalyst layer in which more sluggish mass transport may be expected. This thickness effect could also explain the decrease in cell voltage in case the Pt–Ti alloy catalysts were used as anode catalysts for (pure) H₂ fuels, if no enhancement effect of hydrogen oxidation reactions by alloying with Ti exists.

Mechanism of CO tolerance enhancement.— The prepared Pt-Ti alloy electrocatalysts were more CO-tolerant compared to pure Pt. It was reported that methanol oxidation on the Pt surfaces was promoted by the presence of an oxide (Nb₂O₅, Ta₂O₅, ZrO₂, TiO_2).¹² It was considered that oxides act as a source of OH species. In addition, Ioroi et al.¹¹ prepared the mixed Pt-MoO_x catalysts, exhibiting CO tolerance equal to the Pt-Ru alloy. They suggested a water-gas shift reaction (WGS) promoted CO oxidation by coexisting Pt and MoO_x . While excess TiO_x might affect the CO tolerance of our prepared catalysts because a part of Ti existed as TiO_x (see Fig. 2 and 4),¹¹ the enhanced CO tolerance was mainly caused by alloying, because Pt1Ti1 exhibited the highest CO tolerance while Pt1Ti3 exhibited almost the same CO tolerance as pure Pt, which was revealed by the single-cell performance tests. Igarashi et al.¹³ examined hydrogen oxidation

examined hydrogen oxidation activity for more than 40 kinds of alloy catalysts in 100 ppm CO containing hydrogen fuels. They revealed that CO coverage remained low in CO-containing fuels for Pt-Fe, Pt-Ni, Pt-Co, and Pt-Mo alloy, as well as conventional Pt-Ru, and high hydrogen oxidation activity could be maintained. In addition, electronic states of the alloy surfaces after the electrochemical measurements were examined by XPS, which revealed that the second constituent (besides Ru) was dissolved from the alloy surfaces, and Pt skin layers with increased d vacancies were formed. However, in their study,¹³ binding energy (BE) of Pt 4f for their Pt-Ti alloy was 0.3 eV negatively shifted, and Pt-Ti alloy did not show enhanced CO tolerance. This result seemed inconsistent with our study, and one of the reasons may be a difference between the bulk alloy and supported alloy and/or a difference in the catalyst preparation procedures. The BE of Pt 4f for Pt-Ti alloy catalysts was shifted to the positive direction compared with pure Pt, as shown in Fig. 5 and 6. This positive shift may be associated with the formation of d vacancies contributing to the enhanced CO tolerance. In addition, if Ti atoms existed on the alloy surfaces, they might have bonded with oxygen as TiO₂, one of the most stable compounds under PEFC conditions. It may be possible that CO tolerance was enhanced by CO oxidation on Pt neighboring Ti via, e.g., the bifunctional mechanism.^{2,3}

Conclusion

Pt-Ti alloy electrocatalysts supported on carbon black for PEFCs were prepared by the combined colloidal and sol-gel method. The oxygen reduction reaction (ORR) activity and CO tolerance of the prepared catalysts were examined using a rotating disk electrode (RDE). Pt-Ti alloy catalyst particles were ca. 4.5 nm in diameter and homogeneously dispersed on carbon black. ORR activity of Pt-Ti alloys was higher than pure Pt. ORR activity of the Pt-Ti alloy, with the initial atomic ratio of Pt and Ti set to 1:1, was enhanced about 1.5 times in comparison with pure Pt at 0.8 V. CO-stripping voltammetry revealed that the potential of the CO oxidation peak was slightly shifted to the negative potential by alloying with Ti. Prepared catalysts were evaluated in single-cell tests, re-

vealing that Pt-Ti alloys exhibited higher ORR activity and slight CO tolerance compared to pure Pt under PEFC conditions. XPS results indicated the formation of additional d vacancies in Pt by alloying with Ti, which could be one of the reasons for Pt-Ti alloy electrocatalysts exhibiting higher ORR activity and CO tolerance compared to pure Pt.

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References

- 1. R. A. Lemons, J. Power Sources, 29, 367 (1990).
- M. Watanabe and S. Motoo, J. Electroanal. Chem. Interfacial Electrochem., 60, 2. 275 (1975).
- 3. H. F. Oetjen, V. M. Schmidt, U. Stimming, and F. Trila, J. Electrochem. Soc., 143, 3838 (1996)
- 4. S. Mukerjee and S. Srinivasan, J. Electroanal. Chem., 357, 201 (1993).
- 5. E. Antolini, Mater. Chem. Phys., 78, 563 (2003).
- 6. T. Toda, H. Igarashi, H. Uchida, and M. Watanabe, J. Electrochem. Soc., 146, 3750 (1999). 7. S. Mukerjee, S. Srinivasan, M. P. Soriaga, and J. McBreen, J. Electrochem. Soc.,
- 142, 1409 (1995). 8. K. Wang, H. A. Gasteiger, N. M. Markovic, and P. N. Ross, Jr., Electrochim. Acta,
- 41, 2578 (1997). 9. B. N. Grgur, G. Zhuang, N. M. Markovic, and P. N. Ross, Jr., J. Phys. Chem. B,
- 101, 3910 (1997). 10. R. Liu, H. Iddir, Q. Fan, G. Hou, A. Bo, K. L. Ley, E. S. Smotkin, Y.-E. Sung, H.
- Kim, S. Thomas, and A. Wiekowski, J. Phys. Chem. B, 104, 3518 (2000). 11. T. Ioroi, K. Yasuda, Z. Siroma, N. Fujiwara, and Y. Miyazaki, J. Electrochem. Soc.,
- 150, A1225 (2003). 12. A. Hammett, Catal. Today, 38, 445 (1997).
- 13. H. Igarashi, T. Fujino, Y. Zhu, H. Uchida, and M. Watanabe, Phys. Chem. Chem.
- Phys., 3, 306 (2001).
 14. R. C. Urian, A. F. Gullá, and S. Mukerjee, J. Electroanal. Chem., 554-555, 307 (2003).
- 15. M. Watanabe, K. Tsurumi, T. Mizukami, T. Nakamura, and P. Stonehart, J. Electrochem. Soc., 141, 2659 (1994).
- T. Ioroi and K. Yasuda, J. Electrochem. Soc., 152, A1917 (2005).
- 17. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, New York (1974). 18. H. G. Petrow and R. Allen, U.S. Pat. 4.044,193 (1977)
- 19. M. Watanabe, M. Uchida, and S. Motoo, J. Electroanal. Chem. Interfacial Electrochem., 229, 395 (1987).
- 20. M. K. Ravikumar and A. K. Shukla, J. Electrochem. Soc., 143, 2601 (1996).
- 21. D. T. Sawyer, A. Sobkowiak, and J. L. Roberts, Jr., Electrochemistry for Chemists, 2nd ed., John Wiley & Sons, New York (1995); W. Vielstich, A. Lamm, and H. A. Gasteiger, Handbook of Fuel Cells: Fundamentals, Technology and Applications, Vol. 2, Electrocatalysis, John Wiley & Sons, West Sussex (2003); T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, J. Electrochem. Soc., 146, 1296 (1999).
- M. Watanabe, H. Igarashi, and K. Yoshioka, Electrochim. Acta, 40, 329 (1995). 23. Y. Takasu, N. Ohashi, X.-G. Zhang, Y. Murakami, H. Minagawa, S. Sato, and K.
- Yahikozawa, Electrochim. Acta, 41, 1595 (1996).
- 24. B. C. Beard and P. N. Ross, Jr., J. Electrochem, Soc., 133, 1839 (1986) A. J. Bard and L. R. Faulkner, Electrochemical Methods, Fundamentals and Ap-25.
- plications, p. 291, Wiley, New York (1980). 26. M. Watanabe, S. Saegusa, and P. Stonehart, J. Electroanal. Chem. Interfacial Elec-
- trochem., 261, 375 (1989). 27. U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, N. M.
- Markovic, and P. N. Ross, Electrochim. Acta, 47, 3787 (2002).
- 28. J. Shim, C.-R. Lee, H.-K. Lee, J.-S. Lee, and E. J. Cairns, J. Power Sources, 102, 172 (2001). 29
- L. Xiong and A. Manthiram, Electrochim. Acta, 49, 4163 (2004).
- H. Fukumoto, H. Maeda, and K. Mitsuda, Electrochemistry (Tokyo, Jpn.), 68, 794 30. (2000)
- 31. V. Jalan and E. J. Taylor, J. Electrochem. Soc., 130, 2299 (1983)