

Article

In Situ FTIR Analysis of CO-Tolerance of a Pt-Fe Alloy with Stabilized Pt Skin Layers as a Hydrogen Anode Catalyst for Polymer Electrolyte Fuel Cells

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Abstract: The CO-tolerance mechanism of a carbon-supported Pt-Fe alloy catalyst with two atomic layers of stabilized Pt-skin (Pt_{2AL}-PtFe/C) was investigated, in comparison with commercial Pt₂Ru₃/C (c-Pt₂Ru₃/C), by in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in 0.1 M HClO₄ solution at 60 °C. When 1% CO (H₂-balance) was bubbled continuously in the solution, the hydrogen oxidation reaction (HOR) activities of both catalysts decreased severely because the active sites were blocked by CO_{ad}, reaching the coverage $\theta_{CO} \approx 0.99$. The bands in the IR spectra observed on both catalysts were successfully assigned to linearly adsorbed CO (CO_L) and bridged CO (CO_B), both of which consisted of multiple components (CO_L or CO_B at terraces and step/edge sites). The Pt_{2AL}-PtFe/C catalyst lost 99% of its initial mass activity (MA) for the HOR after 30 min, whereas about 10% of the initial MA was maintained on c-Pt₂Ru₃/C after 2 h, which can be ascribed to a suppression of linearly adsorbed CO at terrace sites (CO_{L, terrace}). In contrast, the HOR activities of both catalysts with pre-adsorbed CO recovered appreciably after bubbling with CO-free pure H₂. We clarify, for the first time, that such a recovery of activity can be ascribed to an increased number of active sites by a transfer of CO_{L, terrace} to CO_{L, step/edge}, without removal of CO_{ad} from the surface. The Pt_{2AL}-PtFe/C catalyst showed a larger decrease in the band intensity of CO_{L, terrace}. A possible mechanism for the CO-tolerant HOR is also discussed.

Keywords: Pt-Fe; Pt-Ru; alloy electrocatalysts; CO-tolerance; hydrogen oxidation reaction; fuel cell; CO adsorption; FTIR

1. Introduction

For the applications of fuel cell vehicles (FCVs) and stationary cogeneration systems (FC-CG), polymer electrolyte fuel cells (PEFCs) have been actively developed. In 2014, a strategic roadmap for hydrogen and fuel cells was formulated by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade, and Industry (METI), Japan [1]. Its Phase 1 is an expansion of the scope of applications for FCVs and FC-CG to achieve dramatic energy conservation. While the number of residential PEFC systems installed has been increasing continuously in Japan and has also commenced

to increase in Europe, the reduction of the system cost is essential for larger scale commercialization, while maintaining the performance and durability.

Therefore, far, Pt-Ru alloy anode catalysts have been employed for the hydrogen oxidation reaction (HOR) to lessen the poisoning by low concentrations of CO contained in the reformat (hydrogen-rich gas produced by reforming hydrocarbons, followed by a purification). Indeed, the state-of-the-art commercial anode catalyst used in the commercial FC-CG system Ene-Farm® is nano-sized Pt₂Ru₃ dispersed on high-surface-area carbon black (c-Pt₂Ru₃/C). However, because the CO-tolerant HOR mass activity (based on the mass of both noble metals, Pt and Ru) and durability of c-Pt₂Ru₃/C are not sufficient, it is very important to develop novel anode catalysts, which would simplify the system, leading to cost reduction. As the support or co-catalyst for Pt-Ru alloys, the use of metal oxide materials has been effective in increasing the CO-tolerance [2–7]. It was found in our previous work that the CO-tolerance of Pt₂Ru₃ nanoparticles was improved by the use of an Sb-SnO₂ support, in place of the conventional carbon black support [7]. By use of in situ attenuated total reflection Fourier transform infrared reflection-adsorption spectroscopy (ATR-FTIRAS), we clarified that the adsorption states of CO were changed due to electronic modification by the Sb-SnO₂ support. Regarding the improvement of durability of c-Pt₂Ru₃/C, the instability of Ru at high potentials $E > 0.8$ V (vs. reversible hydrogen electrode, RHE) is difficult to overcome: the Ru component leaches into the electrolyte membrane, migrating and depositing at the cathode catalyst layer made from Pt or Pt-alloy. Thus, the loss of Ru reduces the cell performance by decreases in not only the CO-tolerance of the anode but also the activity for the oxygen reduction reaction (ORR) at the cathode. Hsieh et al. reported CO-tolerance of Pt shell/Ru core catalysts designed to suppress the dissolution of Ru [8], but it is expected to be difficult to completely protect Ru from dissolution.

Recently, a new Ru-free hydrogen anode catalyst has been developed in our laboratory. Carbon-supported PtCo alloy particles with two atomic layers of stabilized Pt skin (Pt_{2AL}-PtCo/C) exhibited high mass activity *MA* for the CO-tolerant HOR, together with high robustness versus air exposure [9]. Very recently, we have reported our research on the effect of the non-noble metal species *M* (*M* = Fe, Co, Ni) in Pt_{2AL}-Pt-*M*/C on CO-tolerance and the robustness by the use of channel flow electrode (CFE) method in 0.1 M HClO₄. It was found that Pt_{2AL}-PtFe/C exhibited the highest CO-tolerant HOR activity (with respect to the area-specific activity *j_s* and the *MA*). We considered the possibility that such a CO-tolerance could be ascribed to a modification of the electronic structure of the Pt-skin layer due to the presence of the alloy beneath the surface [10], but this needs to be analyzed experimentally.

In the present research, we have investigated the CO-tolerance mechanism on Pt_{2AL}-PtFe/C and c-Pt₂Ru₃/C by the use of in situ ATR-FTIRAS in 0.1 M HClO₄ at 60 °C. We, for the first time, demonstrate that the recovery of the HOR activity that occurs on these catalysts when changing the gas from CO/H₂ to pure H₂ can be ascribed to the mobility of adsorbed CO, resulting in increased numbers of active sites.

2. Results and Discussion

2.1. FTIR Analysis of CO Adsorption on Catalysts

TEM images and particle size distribution histograms of Pt_{2AL}-PtFe/C and c-Pt₂Ru₃/C (Figure 1) show that the average particle sizes and the standard deviations (σ_d) of the Pt_{2AL}-PtFe/C and c-Pt₂Ru₃/C, which were determined from 500 particles in several TEM images, were 2.9 ± 0.4 nm and 3.5 ± 0.9 nm, respectively. As reported previously [11], the Pt_{2AL}-PtFe nanoparticles were more uniform in size (smaller σ_d) and highly dispersed on the carbon black support, compared with c-Pt₂Ru₃/C.

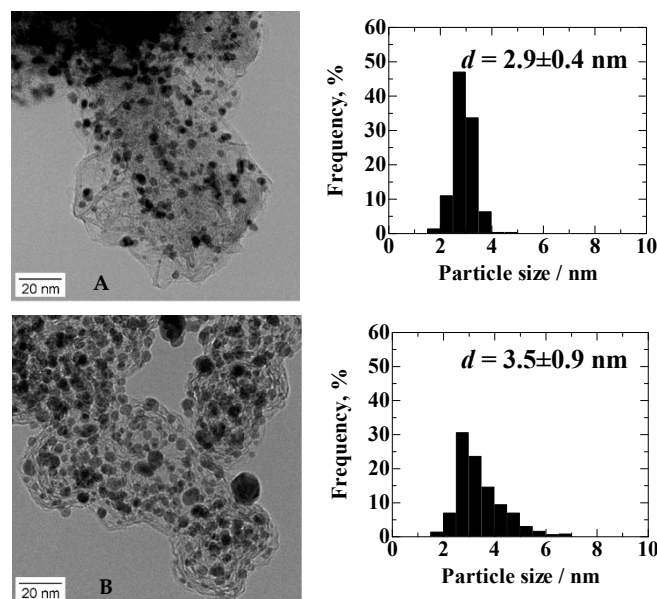


Figure 1. TEM images and particle size distribution histograms of pristine (A) Pt_{2AL}-PtFe/C and (B) c-Pt₂Ru₃/C.

By the use of an in situ FTIR cell with the attenuated total reflection configuration (ATR-FTIR) [7,12], the IR spectra on both catalysts at 0.02 V (practical operating potential in PEFCs) versus an RHE and 60 °C by bubbling 1% CO (H₂-balance) continuously in 0.1 M HClO₄ solution were measured together with the HOR current. The electrolyte solution was first saturated with pure H₂ to measure the initial HOR current and the reference IR spectrum at 0.02 V, followed by changing the gas to 1% CO/H₂. Figure 2 shows change in the HOR mass activity (MA, HOR current per unit metal mass) at 0.02 V vs. RHE during the in situ ATR-FTIR measurement of CO adsorption. The initial MA value (measured in pure H₂-saturated solution) on the Pt_{2AL}-PtFe/C catalyst (35 A g_{metal}^{−1}) was ca. 1.3 times larger than that on the c-Pt₂Ru₃/C. Such an enhancement factor in the MA for the HOR of pure H₂ on the Pt_{2AL}-PtFe/C was smaller than that (ca. 2.5 times) measured in the CFE at 70 and 90 °C [10]. This is ascribed with certainty to the fact that it is difficult for all of the catalyst particles to work effectively for the HOR, because the thickness of the catalyst layer loaded on the ATR prism corresponded to about 6.5 monolayers of the carbon black particles (to increase the signal/noise ratio of the IR spectrum), whereas the amount of the catalyst loaded in the CFE cell was ca. two monolayers of carbon black particles to obtain the HOR activity in the ideal electrochemical condition. Focusing on the changes in the MA values during CO adsorption on both catalysts in Figure 2, the CO-poisoning rate at the Pt_{2AL}-PtFe/C was rapid, losing 99% of MA after 30 min, whereas that at the c-Pt₂Ru₃/C was slower, so that about 10% of the initial MA was still maintained after 2 h. Then, the CO coverage θ_{CO} on the surface just after the in situ ATR-FTIR measurement was evaluated from the CO-stripping voltammogram in N₂-purged solution, as shown in Figure 3. The loss of MA on the Pt_{2AL}-PtFe/C catalyst is reasonably explained by the θ_{CO} value of 0.99. The value of θ_{CO} on the c-Pt₂Ru₃/C catalyst was also 0.99, but, as stated above, the HOR activity was still maintained. It is clear that the adsorbed CO (CO_{ad}) cannot be oxidized during the HOR at 0.02 V, even on c-Pt₂Ru₃/C, because the values of onset potential for the CO_{ad} oxidation on Pt_{2AL}-PtFe/C and c-Pt₂Ru₃/C were ca. 0.50 V and 0.33 V, respectively. The difference in the CO-tolerance will be discussed in more detail below.

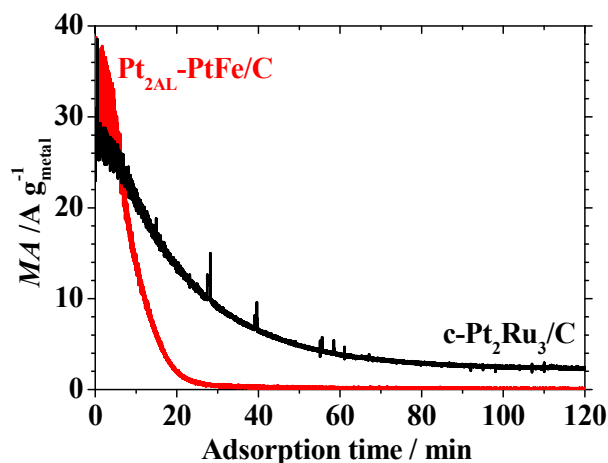


Figure 2. Change in the mass activity (MA) for the HOR at 0.02 V on Nafion-coated $\text{Pt}_{2\text{AL}}\text{-PtFe/C}$ and $\text{c-Pt}_2\text{Ru}_3/\text{C}$ electrodes at 0.02 V and 60 °C in 0.1 M HClO_4 during CO adsorption by bubbling 1% CO/H_2 .

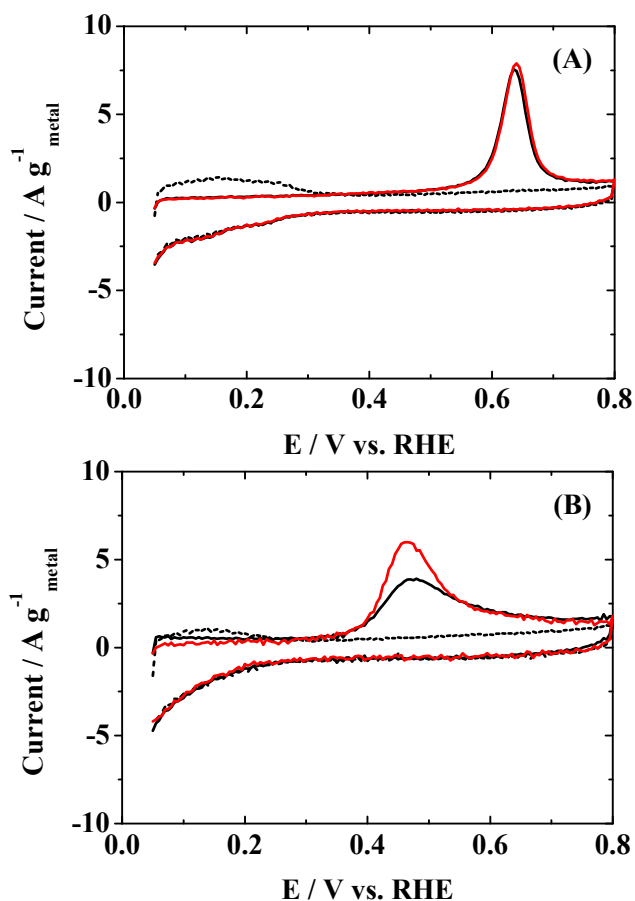


Figure 3. CO stripping voltammograms at Nafion-coated (A) $\text{Pt}_{2\text{AL}}\text{-PtFe/C}$ and (B) $\text{c-Pt}_2\text{Ru}_3/\text{C}$ electrodes measured in N_2 -purged 0.1 M HClO_4 at 60 °C and potential sweep rate of $0.02 \text{ V}\cdot\text{s}^{-1}$. Dotted lines indicate the blank CVs on the CO-free electrodes. CVs were measured at 120 min in Figure 2 (red solid line) and 90 min in Figure 7 see below (black solid line).

Figure 4 shows changes in the IR spectra observed on both catalysts during CO adsorption measured simultaneously with the HOR current shown in Figure 2. The bands observed for both catalysts around 2050–1950 cm^{-1} and 1900–1750 cm^{-1} were assigned to linearly adsorbed (on-top) CO on Pt [CO_L] and bridged CO on Pt-Pt pair sites [$\text{CO}_B(\text{Pt-Pt})$], respectively [7,12–14]. A small band around 1950 cm^{-1} on c-Pt₂Ru₃/C (see Figure 5) was assigned to CO_{ad} in a bridged configuration on Pt-Ru and/or Ru-Ru sites [CO-Ru , $\text{CO}_B(\text{Pt-Ru})$ or $\text{CO}_B(\text{Ru-Ru})$] [13].

A nearly identical CO-Ru band around 1950 to 2020 cm^{-1} at high CO coverage was reported, but it was previously assigned to on-top CO on Ru sites for Ru-decorated Pt [15]. However, based on FTIR experiments carried out by the use of size-controlled Pt, Ru, and Pt-Ru particles, Baranova et al. clearly assigned such a band to CO_{ad} bridged on Pt-Ru and/or Ru-Ru sites [16]. As has been observed for the CO adsorption process on various catalysts, the changes in the IR spectra in Figure 4 indicate that the bands consists of multiple components, which can be ascribed to CO_{ad} in slightly different configurations or environments, specifically, terraces or step/edge sites [12,13].

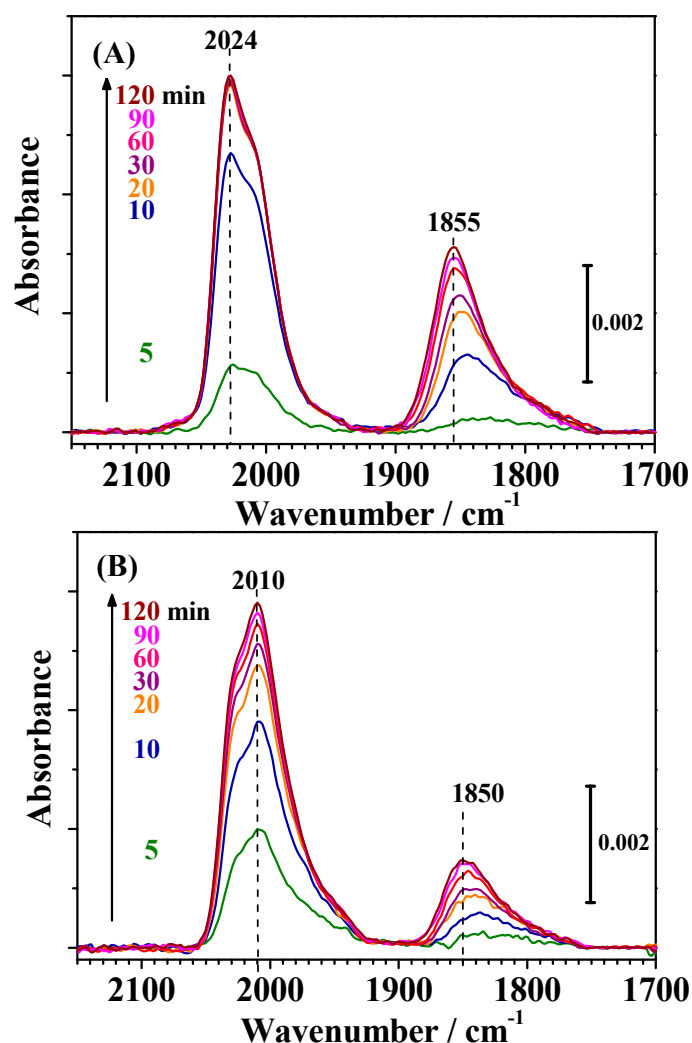


Figure 4. Changes in FTIR spectra observed on Nafion-coated (A) Pt₂AL-PtFe/C and (B) c-Pt₂Ru₃/C electrodes at 0.02 V and 60 °C during CO adsorption in 0.1 M HClO₄ with bubbling 1% CO (H₂ balance) for 120 min.

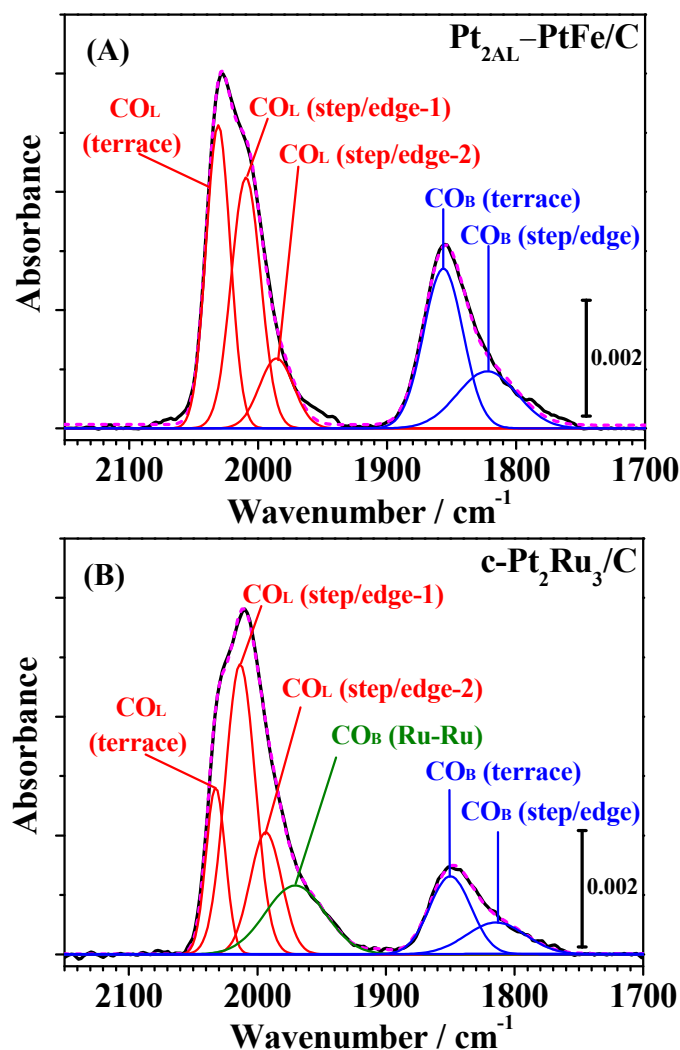


Figure 5. Deconvolution of FTIR spectra observed on (A) $\text{Pt}_{2\text{AL}}\text{-PtFe/C}$ and (B) $\text{c-Pt}_2\text{Ru}_3/\text{C}$ at 0.02 V and 60 °C after 2 h of 1% CO/H_2 gas bubbling in 0.1 M HClO_4 . The CO_L bands in the 2050–1950 cm^{-1} region were deconvoluted into three components, which were assigned to CO_L on terrace and step/edge sites, respectively. The CO_ad bridged on Pt–Ru and/or Ru–Ru sites was approximated by a broad single band with peak at 1967 cm^{-1} , which will be denoted as CO-Ru on $\text{c-Pt}_2\text{Ru}_3/\text{C}$. The CO_B bands in the 1850–1790 cm^{-1} region were also deconvoluted into two components, which were assigned to CO_B on terrace and step/edge sites. The experimental spectra in (A) and (B) were normalized to the total intensities of peaks assigned to CO_L , $I[\text{CO}_\text{L}]$; (—) experimental spectrum, (—) sum of all peaks, (—) CO_L peaks, (—) CO-Ru peaks, and (—) CO_B peaks.

Then, these bands were deconvoluted into several symmetric Gaussian peaks, and curve fitting was carried out for all spectra assuming the full width at half maximum (FWHM) to be constant and allowing the peak maxima (wavenumber) and areas to vary, as described our previous work [7,12,13]. As shown in Figure 5, the FTIR spectra on $\text{Pt}_{2\text{AL}}\text{-PtFe/C}$ and $\text{c-Pt}_2\text{Ru}_3/\text{C}$ were successfully deconvoluted into five and six components, respectively, with close correspondence between the fitted and measured spectra (see also Figure S2 in the Supplementary Materials, as another example of deconvolution of FTIR spectra measured after 1 h). The values of peak wavenumber and FWHM of all peaks are summarized in Table S1 in the Supplementary Materials. The CO_L band on $\text{c-Pt}_2\text{Ru}_3/\text{C}$ was deconvoluted into three components, i.e., CO_L on Pt terrace sites ($\text{CO}_\text{L, terrace}$, 2031 cm^{-1}) and two types of CO_L , on Pt step/edge sites ($\text{CO}_\text{L, step/edge-1}$, 2011 cm^{-1} and $\text{CO}_\text{L, step/edge-2}$, 1993 cm^{-1}). These peak wavenumbers were very close to those previously reported

for c-Pt₂Ru₃/C (same composition, but different lot number) measured at 25 °C [13]. The values of peak wavenumbers for the three types of CO_L on Pt₂AL–PtFe/C were similar to those of c-Pt₂Ru₃/C. However, the ratio of integrated intensities of CO_L components was quite different so that the intensity of CO_{L, terrace}, $I[\text{CO}_{L, \text{terrace}}]$, on c-Pt₂Ru₃/C was smaller than that for Pt₂AL–PtFe/C. With respect to the ratio $I[\text{CO}_{L, \text{step/edge}}]$ to $I[\text{CO}_{L, \text{terrace}}]$, the number of atoms on the terraces and step/edges was calculated, based on a cuboctahedral model, for simplicity, for the fcc nanoparticles Pt₂AL–PtFe with $d = 2.9$ nm and Pt₂Ru₃ with $d = 3.5$ nm. The calculation method [17,18] is shown in Section S1 in the Supplementary Materials. The number ratio of atoms at the step/edge to those at the terrace for Pt₂AL–PtFe/C was calculated to be 57% (see in Table S2), which is in accord with the percentage of $I[\text{CO}_{L, \text{step/edge}}]/I[\text{CO}_{L, \text{terrace}}]$ of 57% after CO adsorption for 2 h. In contrast, the value of $I[\text{CO}_{L, \text{step/edge}}]/I[\text{CO}_{L, \text{terrace}}]$ at c-Pt₂Ru₃/C was as large as 73%, although the number ratio of atoms at the step/edge to those at the terrace was estimated to be 45%. Hence, even at $\theta_{\text{CO}} \approx 0.99$, the adsorption of CO_L at the terrace sites was suppressed on c-Pt₂Ru₃/C. This effect of the suppression of CO_{L, terrace} will be discussed later.

The bridged CO_{ad} on Pt–Ru and/or Ru–Ru sites was approximated by a broad single band with a peak at 1967 cm^{−1}, which will be denoted as CO–Ru. The CO_B(Pt–Pt) band on both catalysts was deconvoluted into two components: CO_B on Pt–Pt pairs on terraces and step/edges. The integrated intensity of CO_B(Pt–Pt), specifically on terraces, on the Pt₂AL–PtFe/C was larger than that on c-Pt₂Ru₃/C, which is ascribed to the fact that two atomic layers of Pt-skin layers were formed on the PtFe alloy. However, it should be noted that the intensity ratio of $I[\text{CO}_B(\text{Pt–Pt})]$ to $I[\text{CO}_L]$ observed on c-Pt₂Ru₃/C in Figures 3 and 4 was larger than that reported previously [13], suggesting that a Pt-rich surface layer was formed on the present c-Pt₂Ru₃/C catalyst, while Ru sites were still present on the surface, because CO–Ru was observed. Thus, we found definite differences in the adsorption state of CO on Pt₂AL–PtFe/C and c-Pt₂Ru₃/C in the CO adsorption experiment using in situ ATR-FTIR.

2.2. FTIR Analysis of Recovery of HOR Activity on CO-Adsorbed Catalysts

It is important to note that the apparently inferior CO-tolerance of the Pt₂AL–PtFe/C catalyst is entirely inconsistent with that evaluated by the CFE [10]. Specifically, there were three differences in experimental conditions, i.e., temperatures (60 °C in the present work vs. 70 and 90 °C for the CFE experiment), CO concentrations (1% vs. 0.1%), and protocols. In the CFE experiment, CO was adsorbed on the catalysts by flowing 0.1 M HClO₄ solution saturated with 0.1% CO/H₂ for various time intervals, and the HOR activity was evaluated by a hydrodynamic voltammogram in pure H₂-saturated solution, followed by the CO-stripping voltammogram in N₂-purged solution to evaluate θ_{CO} . This protocol was employed to determine the dependence of HOR activity on θ_{CO} with a minimum change in θ_{CO} during the HOR measurement with a slow potential scan rate (1 mV·s^{−1}). Then, we adopted a similar dynamic change of the atmosphere to the present in situ ATR-FTIR measurements at 60 °C. After CO adsorption by bubbling 1% CO/H₂ for 30 min, pure H₂ was introduced to saturate the electrolyte solution, to remove dissolved CO. Lastly, the θ_{CO} values on the catalyst were evaluated by measuring the CO-stripping voltammogram.

Changes in the IR spectra during CO adsorption on both catalysts for 30 min (shown in Figure S1 in the Supplementary Materials) were, of course, nearly identical with the corresponding time intervals shown in Figure 4. As shown in Figure 6, small changes in the shape of the CO_L band were observed by the introduction of pure H₂ in the solution. The MA for the HOR on both catalysts decreased by CO adsorption similarly to the case of Figure 2, but the MA recovered appreciably just after bubbling pure H₂, as shown in Figure 7A. For example, the MA on the Pt₂AL–PtFe/C increased from only 1% of the initial value to as high as 22%. To examine the changes in the IR spectra, time courses of integrated intensities of all peaks were plotted in Figure 7B,C. When the CO-adsorbed Pt₂AL–PtFe/C catalyst was contacted with CO-free pure H₂, the $I[\text{CO}_{L, \text{terrace}}]$ decreased by ca. 20% after 60 min of H₂ bubbling, accompanied by an increase in $I[\text{CO}_{L, \text{step/edge-1}}]$ by ca. 13%. Only a slight decrease in $I[\text{CO}_{B, \text{step/edge}}]$ was seen, while $I[\text{CO}_{B, \text{terrace}}]$ was nearly unchanged. It is striking that the θ_{CO}

evaluated (solid black line in Figure 3A) was still 0.99 even after H_2 bubbling for 60 min, suggesting that the recovery of the HOR activity can be ascribed to a transfer of CO_{ad} within the surface, not by a removal of CO_{ad} from the surface. For the case of c- Pt_2Ru_3/C , the MA increased from 14% of the initial value to 52% after 60 min of H_2 bubbling, where $I[CO_{L, terrace}]$ decreased by ca. 12% with an increase in $I[CO_{L, step/edge-1}]$ by 8%. The $I[CO-Ru]$ was nearly unchanged during the recovery of the MA. A decrease in $I[CO_{B, step/edge}]$ (about 10%) was larger than that for $Pt_{2AL}-PtFe/C$. Because the value of θ_{CO} evaluated was 0.74, in accord with the remaining MA (24%) at 30 min of CO adsorption, the θ_{CO} on c- Pt_2Ru_3/C was, with certainty, unchanged even after H_2 bubbling for 60 min, similar to the case for $Pt_{2AL}-PtFe/C$.

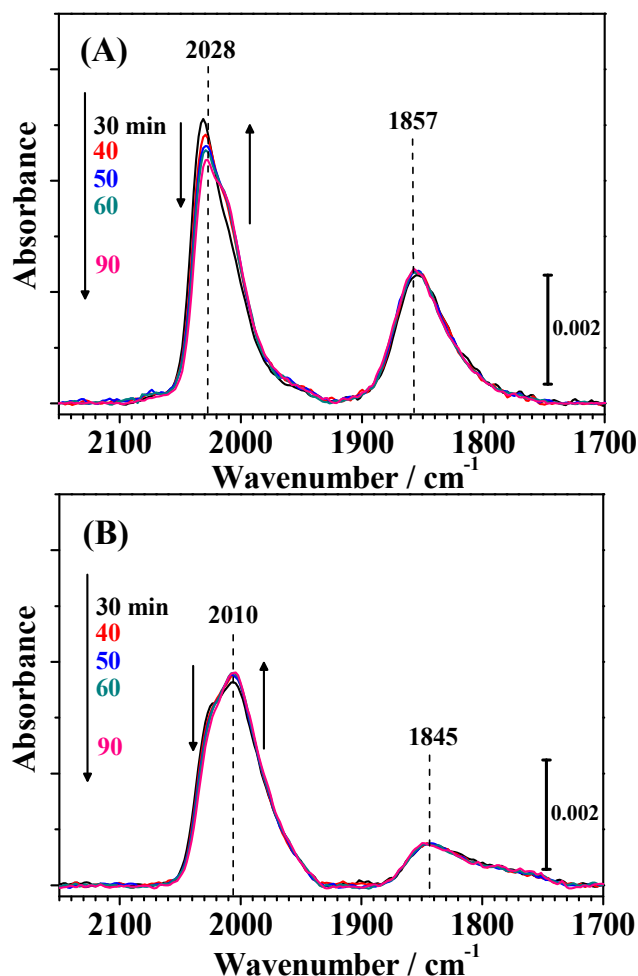


Figure 6. Changes in FTIR spectra observed on CO-adsorbed electrodes of (A) $Pt_{2AL}-PtFe/C$ and (B) c- Pt_2Ru_3/C at 0.02 V and 60 °C in 0.1 M $HClO_4$ during a recovery process of HOR by bubbling CO-free pure H_2 for 60 min (see Figure 7 below). CO was pre-adsorbed by bubbling 1% CO/H_2 for 30 min, and time intervals shown in (A) and (B) correspond to those from 30 min, at which time the gas was changed from 1% CO/H_2 to pure H_2 .

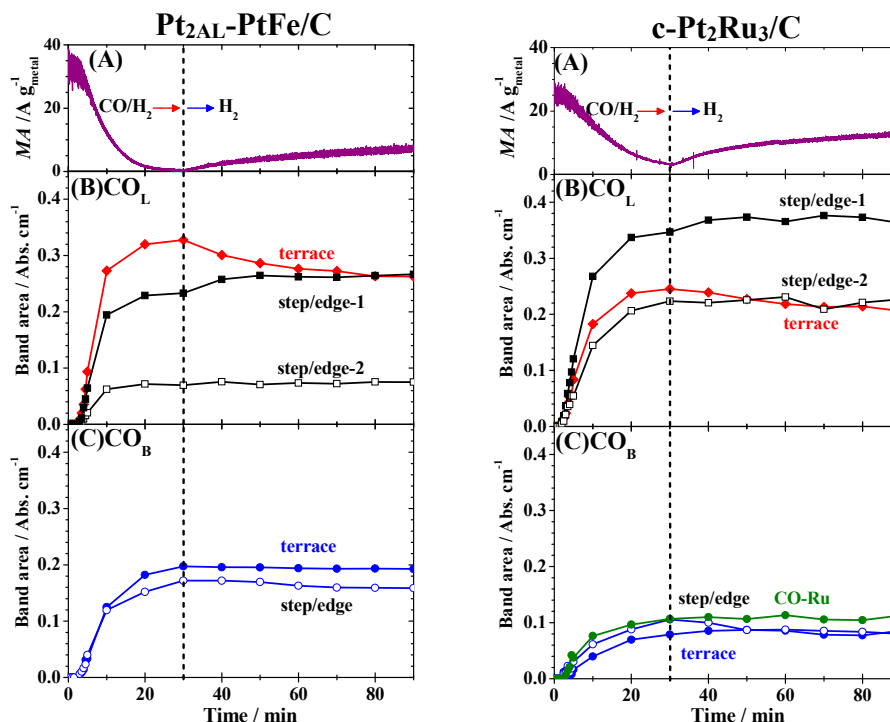
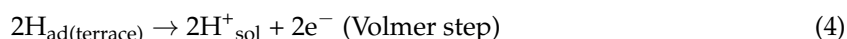
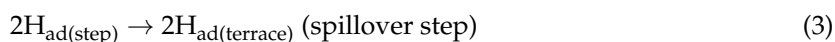
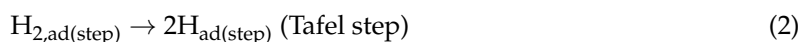


Figure 7. Time courses of the mass activity (MA) for the HOR (A) and integrated intensities of $I[\text{CO}_L]$ (B), and $I[\text{CO}_B]$ (C) observed at 0.02 V and 60 °C in 0.1 M HClO₄. First, CO was adsorbed on the working electrode at 0.02 V by bubbling 1% CO (H₂-balance) at a flow rate of 10 mL·min⁻¹ for 30 min, and CO-free pure H₂ gas was then bubbled in the solution at a flow rate 10 mL·min⁻¹ for an additional 60 min.

Here, we discuss a mechanism for the recovery of the HOR activity on CO-adsorbed catalysts by contacting with CO-free pure H₂. It has been reported for Pt₂Ru₃/C catalysts that the presence of a Pt-rich surface overlaid upon Pt-Ru alloy was essential in providing the HOR active sites by weakening the CO adsorption on Pt [13]. The Pt-rich surface of the present c-Pt₂Ru₃/C satisfies this criterion. In our previous work on the CO-tolerance of Pt₂Ru₃ nanoparticles dispersed on carbon black and Sb-SnO₂, we proposed a possible mechanism that the electronic modification (ligand effect) of Pt₂Ru₃ nanoparticles by the Sb-SnO₂ support gave rise to a weakening of the CO_{L, terrace} adsorption and suppression of CO_{L, step/edge} [7]. In ref. [19], the Pt(110) surface exhibited the highest catalytic activity for the HOR, in comparison to those for Pt(111) and Pt(100). Truncated octahedral or truncated cuboctahedral Pt-based (fcc) nanoparticles include (111) and (100) terraces, with (110)-like sites at the edges between two (111) facets. In addition, (110) steps exist on the (111) terraces. Both of these types of (110) sites can be HOR-active. Thus, we considered that, in order to improve CO-tolerant HOR activity on the Pt₂Ru₃/Sb-SnO₂ catalyst, lowering the coverage of CO_{L, step/edge} could be beneficial. However, very recently, we proposed a modified HOR mechanism [10] in which, after H₂ dissociates at the step/edges, the dissociated H atoms can “spill over” to the (111) terraces, which can accommodate larger numbers of atoms, prior to oxidative desorption:



In this mechanism, H_2 adsorbs and spontaneously dissociates at step sites due to stronger adsorption of H_2 at these sites, since H_2 cannot compete with water adsorption on the terraces. After dissociation, however, the H atoms can compete with water more successfully on the terraces, and, even though the adsorption strength would still be larger at the steps at the same coverage, at high coverage, decreased adsorption strength at the steps might allow H to move to the terraces.

This mechanism was derived to explain the orders of CO-tolerant HOR activities of various catalysts ($Pt_{2AL}-PtFe > Pt_{2AL}-PtCo > Pt_{2AL}-PtNi > PtRu > Pt$) in the CFE experiments [10]. Increased HOR activity was considered to correlate with decreased H adsorption strength on (111) terraces. However, the results shown in Figure 7 can also be well explained by this HOR mechanism. The decrease in the coverage of $CO_{L, terrace}$ would result in an increased number of active sites for reaction (4) on the terrace, assuming that the dissociation rate of H_2 were maintained at the step/edge, for example, step/edge-2. A decrease in the coverage of $CO_{B, step/edge}$ would also be beneficial for reactions (1) and (2), because two Pt active sites (Pt-Pt pair site) are formed by the desorption of one CO_B . Furthermore, the mobility of CO_{ad} would be enhanced with increasing temperature, consistent with our observation of excellent CO-tolerance for $Pt_{2AL}-PtFe/C$ at 70 and 90 °C. According to our DFT calculations on nearly all of the surfaces studied, we found that at both step edges and terraces, CO adsorption is stronger by approximately 1 eV compared with the adsorption of atomic hydrogen. Hence, as is well known, the CO concentration must be maintained at very low levels in order for H to compete effectively with CO for adsorption sites.

Even though the use of 1% CO was a very challenging condition for both $Pt_{2AL}-PtFe/C$ and $c-Pt_2Ru_3/C$, we have, for the first time, observed the recovery of the HOR activity of these CO-adsorbed catalysts (without removal of CO_{ad}) and clarified the mechanism correlated with the mobility of CO_{ad} to create HOR active sites. Such an enhanced mobility of CO_{ad} can be ascribed to a modification of the electronic structure of the Pt_{2AL} skin on PtFe alloy and the Pt-rich layer on PtRu alloy.

3. Experimental Section

The $Pt_{2AL}-PtFe/C$ catalyst (31.5 wt. % metal loading) was prepared by the use of a high surface area (specific surface area = $780\text{ m}^2\cdot\text{g}^{-1}$) carbon black support (Denka Co. Ltd., Tokyo, Japan) in the same manner as that described previously [11,20]. A commercial catalyst $c-Pt_2Ru_3/C$ (TEC61E54, 50 wt. % metal loading on high-surface-area carbon black, $800\text{ m}^2\cdot\text{g}^{-1}$, Tanaka Kikinzoku Kogyo, Japan) was used for comparison. Their microstructure was observed by transmission electron microscopy (TEM, H-9500, acceleration voltage = 200 kV, Hitachi High-Tech Co. Ltd., Tokyo, Japan).

In situ attenuated total reflection Fourier transform infrared reflection spectroscopy (ATR-FTIR) was employed to analyze the CO-tolerant mechanism at the $Pt_{2AL}-PtFe/C$ and $c-Pt_2Ru_3/C$ catalysts at 60 °C. The spectro-electrochemical cell was first reported by Ataka et al. [21], and we modified it to measure the IR spectrum on practical electrocatalysts of Pt or Pt-alloy nanoparticles supported on carbon black. Details of the experimental setup and the procedure of the ATR-FTIR can be found in our previous paper [13]: the cell used is schematically shown in Figure S3 of the Supplementary Materials. The Nafion-coated $Pt_{2AL}-PtFe/C$ ($15\text{ }\mu\text{g}_{Pt}\cdot\text{cm}^{-2}$) or $c-Pt_2Ru_3/C$ ($10\text{ }\mu\text{g}_{Pt}\cdot\text{cm}^{-2}$) layer was prepared on an Au film electrode deposited on an Si ATR prism. This amount of catalyst was chosen to ensure a high signal/noise ratio of the IR spectrum. The average thickness of Nafion was $0.013\text{ }\mu\text{m}$ and the geometric surface area of the working electrode was 1.72 cm^2 . The Nafion-coated working electrode was finally heated at 130 °C for 30 min in air. The electrolyte solution used for all experiments was 0.1 M $HClO_4$ prepared from suprapur-grade $HClO_4$ (Merck, Frankfurt, Germany) and Milli-Q water.

The ATR-FTIR measurements were carried out in a class 1000 clean room maintaining a constant temperature of 25 °C and humidity of 40% RH. A spectrometer (FTS7000, DIGILAB, Inc., Holliston, MA, USA) with an MCT detector was used. The spectral resolution was set at 4 cm^{-1} with an interferometer scan of 40 kHz. All IR spectra are displayed in absorbance units, $\log(I_0/I)$, where I_0 and I are the spectral intensities of the reference state and the sample, respectively. The reference electrode employed was an RHE. Prior to all measurements, the working electrode surface was cleaned by

repeated potential cycles of 0.05–1.00 V for Pt_{2AL}–PtFe/C and 0.05–0.80 V vs. RHE for c-Pt₂Ru₃/C at 0.05 V·s^{−1} in N₂-purged 0.1 M HClO₄. Then, we measured the initial HOR current and a reference spectrum at 0.02 V in 0.1 M HClO₄ saturated with H₂ (UHP grade, 99.9999%) with an average of 500 interferograms.

Next, we monitored the FTIR spectra (one spectrum averaged for 10 s) and HOR current on the working electrode at 0.02 V vs. RHE during CO adsorption by two protocols. The first protocol was a simple CO adsorption experiment, in which H₂ gas containing 1% CO was bubbled in the electrolyte solution at a flow rate 10 mL·min^{−1} continuously for 2 h. Such a high concentration of 1% CO was chosen to analyze the CO adsorption under an accelerated condition. The second protocol involved CO adsorption followed by purging with pure H₂ to observe the recovery process of HOR activity. CO was adsorbed on the working electrode at 0.02 V vs. RHE by bubbling 1% CO (H₂-balance) in the same manner as described above for 30 min, and CO-free pure H₂ gas was bubbled in the electrolyte solution at a flow rate 10 mL·min^{−1} for 60 min.

Immediately after the completion of the in situ ATR-FTIR measurements, the CO coverage θ_{CO} on the catalyst surface was evaluated from the CO-stripping voltammogram. After adsorption of CO at 0.02 V, the CO dissolved in 0.1 M HClO₄ was removed by bubbling N₂ gas for 30 min, followed by a potential sweep from 0.05 to 0.80 V at 0.02 V·s^{−1}. The value of θ_{CO} was defined as the ratio of the sites occupied by CO_{ad} to the CO-free electrochemically active sites,

$$\theta_{\text{CO}} = 1 - (\text{CO}Q_{\text{H}}/sQ_{\text{H}}) \quad (5)$$

where $\text{CO}Q_{\text{H}}$ and sQ_{H} are the hydrogen desorption charges with and without CO_{ad}, respectively.

4. Conclusions

The CO-tolerant HOR activities on Pt_{2AL}–PtFe/C and c-Pt₂Ru₃/C catalysts were examined by use of in situ ATR-FTIRAS in 0.1 M HClO₄ at 60 °C. In an experiment with continuous bubbling of high concentration CO (1% in H₂) at 60 °C, the CO-tolerance for Pt_{2AL}–PtFe/C was inferior to that for c-Pt₂Ru₃/C: the former lost 99% of the initial mass activity (MA) for the HOR after 30 min, whereas about 10% of the initial MA was maintained on the latter after 2 h. Based on the analysis of the IR spectra, this CO-tolerance was ascribed to the suppression of the adsorption of CO_L on terrace sites. In the second experiment, involving CO adsorption followed by introduction of CO-free H₂, the HOR activities of both catalysts with high θ_{CO} were found to recover appreciably after bubbling with pure H₂. Such a recovery of the HOR activity of CO-adsorbed catalysts can be ascribed to an increase in the number of open sites for the HOR, probably due to a transfer of CO_{L, terrace} to CO_{L, step/edge}, without removal of CO_{ad} from the surface. This result can be explained based on a modified HOR mechanism proposed recently [10]. It was suggested that the mobility of CO_{L, terrace} on Pt_{2AL}–PtFe/C might be high, compared with that on c-Pt₂Ru₃/C. Such an enhanced mobility of CO_{ad} was ascribed, with a certainty, to a modification of the electronic structure of the Pt_{2AL} skin on the PtFe alloy and the Pt-rich layer on the PtRu alloy.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/1/8/s1, Table S1: Values of peak wavenumber and the full width at half maximum (FWHM) used for the deconvolution of FTIR spectra on Pt_{2AL}–PtFe/C and c-Pt₂Ru₃/C shown Figure 5. The integrated intensity of each peak after 2 h of CO adsorption is also shown., Figure S1: Changes in FTIR spectra observed on Nafion-coated (A) Pt_{2AL}–PtFe/C and (B) c-Pt₂Ru₃/C electrodes at 0.02 V and 60 °C during CO adsorption in 0.1 M HClO₄ with bubbling 1% CO (H₂ balance) for 30 min in the experiment shown in Figure 7., Figure S2: Deconvolution of FTIR spectra observed on (A) Pt_{2AL}–PtFe/C and (B) c-Pt₂Ru₃/C at 0.02 V and 60 °C after 1 h of 1% CO/H₂ gas bubbling in 0.1 M HClO₄. Figure S3: Schematic illustration of electrochemical cell for ATR. Section S1: Calculation of the number of atoms at terraces and step/edges of a cuboctohedral Pt_{2AL}–PtFe and Pt₂Ru₃ fcc particle with the particle size d , according to the method in refs. [17,18]. Table S2: Number of atoms calculated based on a cuboctohedral shape of Pt_{2AL}–PtFe and Pt₂Ru₃ fcc nanoparticles.

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Author Contributions: This work was coordinated by Hiroyuki Uchida. Yoshiyuki Ogihara performed all measurements of in situ ATR-FTIR. Hiroshi Yano contributed to the preparation and characterization (STEM, TEM) of Pt₂AL–PtFe/C catalysts. Takahiro Matsumoto contributed to the in situ ATR-FTIR measurement. Donald A. Tryk contributed to the analysis of the CO-tolerant HOR mechanism with DFT calculations. Akihiro Iiyama contributed to the analysis of CO-tolerance. All of the authors contributed equally to the data interpretation and discussion. Yoshiyuki Ogihara prepared the manuscript, and Hiroyuki Uchida revised the final version of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. “Summary of the Strategic Road Map for Hydrogen and Fuel Cells”, by Agency for Natural Resources and Energy (June 23, 2014, METI, Japan). Available online: http://www.meti.go.jp/english/press/2014/pdf/0624_04a.pdf (accessed on 28 December, 2016).
2. Martínez-Huerta, M.V.; Rodríguez, J.L.; Tsiouvaras, N.; Peña, M.A.; Fierro, J.L.G.; Pastor, E. Novel Synthesis Method of CO-Tolerant PtRu–MoO_x Nanoparticles: Structural Characteristics and Performance for Methanol Electrooxidation. *Chem. Mater.* **2008**, *20*, 4249–4259. [[CrossRef](#)]
3. Takeguchi, T.; Kunifuji, A.; Narischat, N.; Ito, M.; Noguchi, H.; Uosaki, K.; Mukai, S.R. Ligand Effect of SnO₂ on a Pt–Ru Catalyst and the Relationship Between Bond Strength and CO Tolerance. *Catal. Sci. Technol.* **2016**, *6*, 3214–3219. [[CrossRef](#)]
4. Wang, G.; Takeguchi, T.; Muhamad, E.N.; Yamanaka, T.; Ueda, W. Effect of Addition of SnO_x to the Pt₂Ru₃/C Catalyst on CO Tolerance for the Polymer Electrolyte Fuel Cell. *J. Electrochem. Soc.* **2011**, *158*, B448–B453. [[CrossRef](#)]
5. Devaux, D.; Yano, H.; Uchida, H.; Dobois, J.-L.; Watanabe, M. Electro-Oxidation of Hydrolysed Poly-Oxymethylene-Dimethylether on PtRu Supported Catalysts. *Electrochim. Acta* **2001**, *56*, 1460–1465. [[CrossRef](#)]
6. Villullas, H.M.; Mattos-Costa, F.I.; Bulhoses, L.O.S. Electrochemical Oxidation of Methanol on Pt Nanoparticles Dispersed on RuO₂. *J. Phys. Chem. B* **2004**, *108*, 12898–12903. [[CrossRef](#)]
7. Ogihara, Y.; Yano, H.; Watanabe, M.; Iiyama, A.; Uchida, H. Effect of an Sb–SnO₂ Support on the CO-Tolerance of Pt₂Ru₃ Nanocatalysts for Residential Fuel Cells. *Catalysts* **2016**, *6*, 139. [[CrossRef](#)]
8. Hsieh, Y.C.; Zhang, Y.; Su, D.; Volkov, V.; Si, R.; Wu, L.J.; Zhu, Y.M.; An, W.; Liu, P.; He, P.; et al. Ordered Bilayer Ruthenium-Platinum Core-Shell Nanoparticles as Carbon Monoxide-Tolerant Fuel Cell Catalysts. *Nat. Commun.* **2013**, *4*, 2466. [[CrossRef](#)] [[PubMed](#)]
9. Shi, G.Y.; Yano, H.; Tryk, D.A.; Watanabe, M.; Iiyama, A.; Uchida, H. A Novel Pt–Co Alloy Hydrogen Anode Catalyst with Superlative Activity, CO-Tolerance and Robustness. *Nanoscale* **2016**, *8*, 13893–13897. [[CrossRef](#)] [[PubMed](#)]
10. Shi, G.Y.; Yano, H.; Tryk, D.A.; Watanabe, M.; Iiyama, A.; Uchida, H. Highly Active, CO-Tolerant and Robust Hydrogen Anode Catalysts: Pt–M (M = Fe, Co, and Ni) Alloys with Stabilized Pt Skin Layers. *ACS Catal.* **2017**, *7*, 267–274. [[CrossRef](#)]
11. Chiwata, M.; Yano, H.; Ogawa, S.; Watanabe, M.; Iiyama, A.; Uchida, H. Oxygen Reduction Reaction Activity of Carbon-Supported Pt–Fe, Pt–Co, and Pt–Ni Alloys with Stabilized Pt–Skin Layers. *Electrochemistry* **2016**, *84*, 133–137. [[CrossRef](#)]
12. Sato, T.; Okaya, K.; Kunimatsu, K.; Yano, H.; Watanabe, M.; Uchida, H. Effect of Particle Size and Composition on CO-Tolerance at Pt–Ru/C Catalysts Analyzed by In Situ Attenuated Total Reflection FTIR Spectroscopy. *ACS Catal.* **2012**, *2*, 450–455. [[CrossRef](#)]
13. Sato, T.; Kunimatsu, K.; Okaya, K.; Yano, H.; Watanabe, M.; Uchida, H. In situ ATR-FTIR Analysis of the CO-Tolerance Mechanism on Pt₂Ru₃/C Catalysts Prepared by the Nanocapsule Method. *Energy Environ. Sci.* **2011**, *4*, 433–438. [[CrossRef](#)]
14. Kunimatsu, K.; Sato, T.; Uchida, H.; Watanabe, M. Role of Terrace/Step Edge Sites in CO Adsorption/Oxidation on a Polycrystalline Pt Electrode Studied by In Situ ATR-FTIR Method. *Electrochim. Acta* **2008**, *53*, 6104–6110. [[CrossRef](#)]
15. Park, S.; Wieckowski, A.; Weaver, M.J. Electrochemical Infrared Characterization of CO Domains on Ruthenium-Decorated Platinum Nanoparticles. *J. Am. Chem. Soc.* **2003**, *125*, 2282–2290. [[CrossRef](#)] [[PubMed](#)]

16. Baranova, E.A.; Bock, C.; Ilin, D.; Wang, D.; MacDougall, B. Infrared spectroscopy on size-controlled synthesized Pt-based nano-catalysts. *Surf. Sci.* **2006**, *600*, 3502–3511. [[CrossRef](#)]
17. Benfield, R.E. Mean Coordination Numbers and the Non-Metal Transition in Clusters. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1107–1110. [[CrossRef](#)]
18. Okaya, K.; Yano, H.; Kakinuma, K.; Watanabe, M.; Uchida, H. Temperature Dependence of Oxygen Reduction Reaction Activity at Stabilized Pt Skin–PtCo Alloy/Graphitized Carbon Black Catalysts Prepared by a Modified Nanocapsule Method. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6982–6991. [[CrossRef](#)] [[PubMed](#)]
19. Markovic, N.M.; Grgur, B.N.; Ross, P.N. Temperature-Dependent Hydrogen Electrochemistry on Platinum Low-Index Single-Crystal Surfaces in Acid Solutions. *J. Phys. Chem. B* **1997**, *101*, 5405–5413. [[CrossRef](#)]
20. Watanabe, M.; Yano, H.; Tryk, D.A.; Uchida, H. Highly Durable and Active PtCo Alloy/Graphitized Carbon Black Cathode Catalysts by Controlled Deposition of Stabilized Pt Skin Layers. *J. Electrochem. Soc.* **2016**, *163*, F455–F463. [[CrossRef](#)]
21. Ataka, K.; Yotsuyanagi, T.; Osawa, M. Potential-Dependent Reorientation of Water Molecules at an Electrode/Electrolyte Interface Studied by Surface-Enhanced Infrared Absorption Spectroscopy. *J. Phys. Chem.* **1996**, *100*, 10664–10672. [[CrossRef](#)]



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