Supplementary Materials: 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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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-Pt_2Ru_3/C shown in Figure 5. The integrated intensities of each peak after 2 h of CO adsorption are also shown.

Peak Wavenumber (cm^{-1})		FWHM	Assignment	Peak Area (after 2 h)	
Pt_{2AL}–PtFe/C	c-Pt_2Ru_3/C	(cm^{-1})		Pt_{2AL}–PtFe/C	c-Pt_2Ru_3/C
2030	2031	20	CO_L, Pt terrace	0.120	0.070
2009	2011	25	CO_L, Pt step/edge-1	0.120	0.124
1985	1993	30	CO_L, Pt step/edge-2	0.039	0.075
-	1967	55	CO-Ru	-	0.057
1856	1850	35	CO_B, Pt terrace	0.103	0.044
1822	1821	55	CO_B, Pt step/edge	0.023	0.041

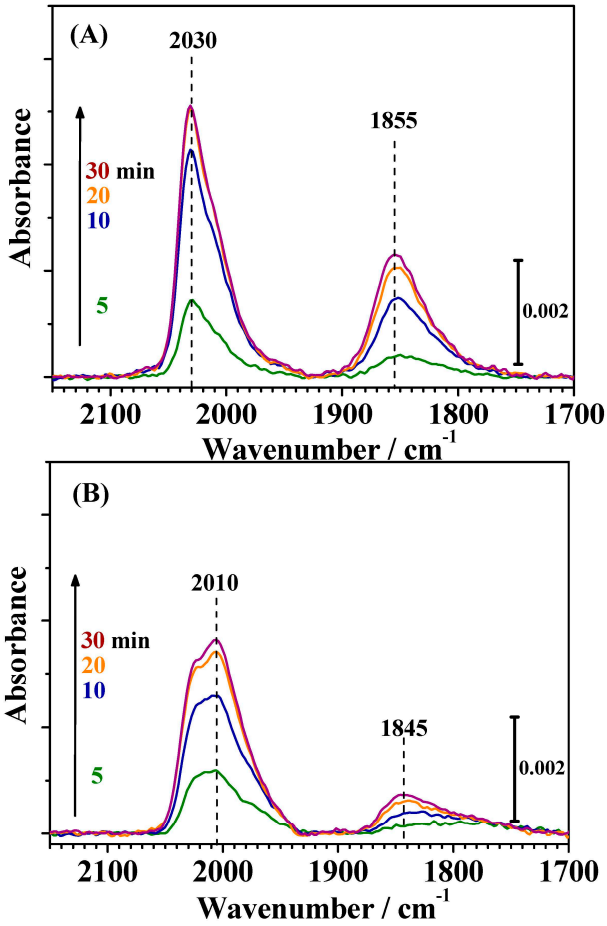

Figure S1. Changes in FTIR spectra observed on Nafion-coated (**A**) Pt_{2AL}–PtFe/C and (**B**) c-Pt_2Ru_3/C electrodes at 0.02 V and 60 °C during CO adsorption in 0.1 M $HClO_4$ with bubbling 1% CO (H_2 balance) for 30 min in the experiment shown in Figure 7.

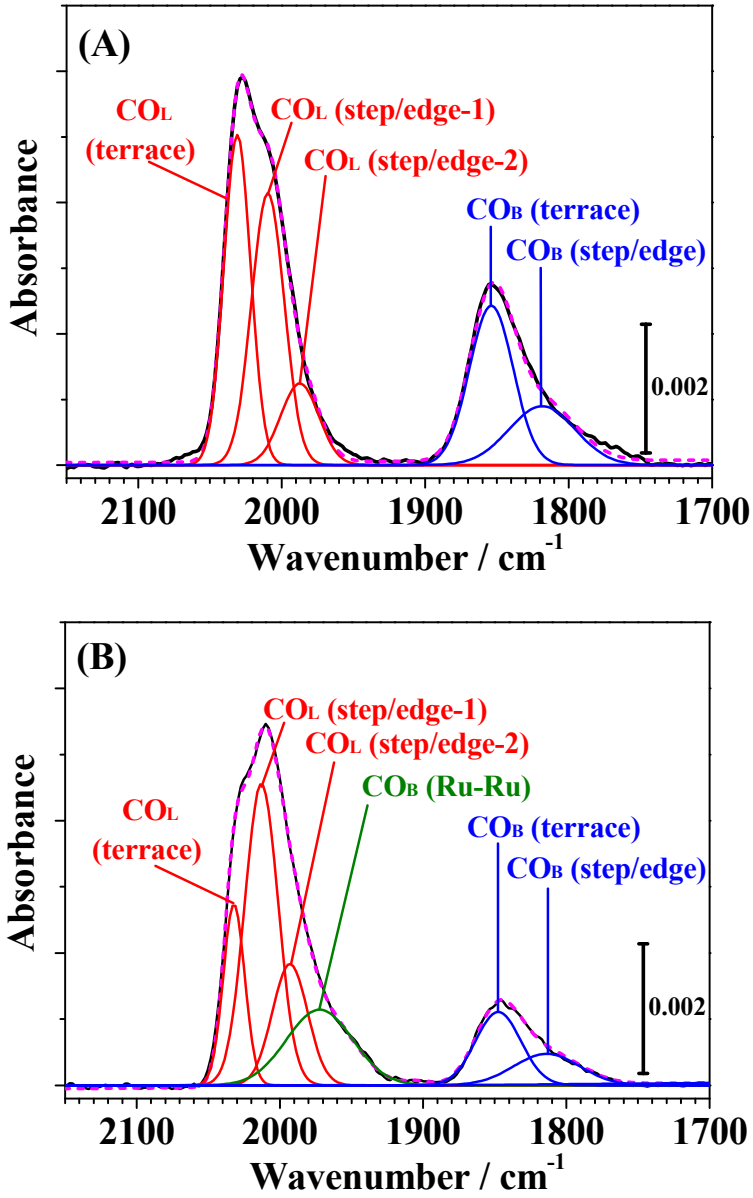

Figure S2. Deconvolution of FTIR spectra observed on (A) Pt_{2AL}–PtFe/C and (B) c-Pt_2Ru_3/C at 0.02 V and 60 °C after 1 h of 1% CO/H_2 gas bubbling in 0.1 M $HClO_4$. The experimental spectra in (A) and (B) were normalized to the total intensities of peaks assigned to CO_L, $I[CO_L]$; (-------) experimental spectrum, (——) sum of all peaks, (——) CO_L peaks, (——) CO-Ru peaks, and (——) CO_B peaks.

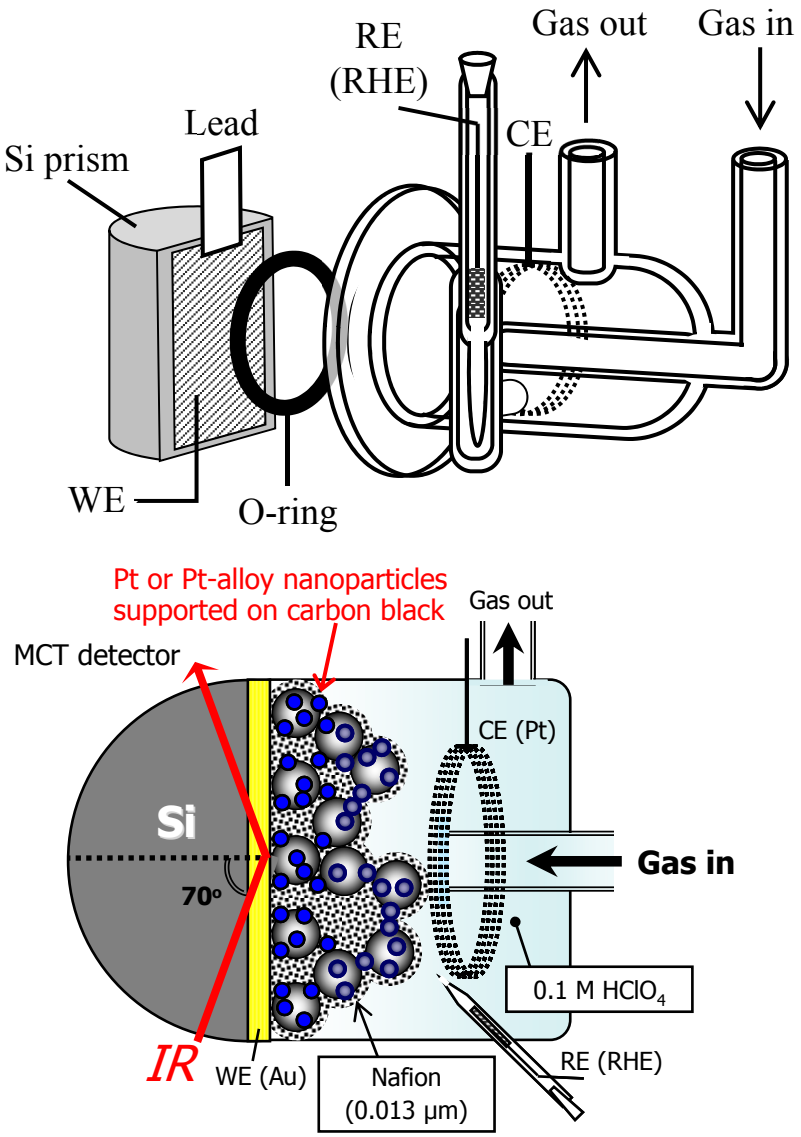

Figure S3. Schematic illustration of spectro-electrochemical cell for ATR-FTIR. Practical electrocatalysts such as Pt or Pt-alloy nanoparticles supported on carbon black (c-Pt_2Ru_3/C or Pt_{2AL}–PtFe/C in the present work) were dispersed on a gold film (ca. 100 nm thick) on the reflecting plane of a Si-ATR, followed by Nafion coating (0.013 μm). Finally, it was heat treated at 130 °C for 30 min.

S1. Calculation of the Number of Atoms at Terraces and Step/Edges of a Cubo-octohedral Pt_{2AL}–PtFe and Pt_2Ru_3 fcc Particle with Particle Size *d*, According to a Method Described Previously [17,18]

First, we calculated the number of total atoms N_{total} included in the particle with the number of atomic layers m.

$$N_{total} = (10/3)m^3 - 5m^2 + (11/3)m - 1 \quad \text{(S1)}$$

As a measure of the particle size, we calculated d for a sphere having N_{total} atoms,

$$d = a\,(3N_{total}/2\pi)^{1/3} \quad \text{(S2)}$$

where a is the lattice constant of the Pt_2Ru_3 or Pt_{2AL}–PtFe alloy.

Next, the number of surface atoms was calculated by the following equation [17].

$$N_{surface} = 10m^2 - 20m + 12 \quad \text{(S3)}$$

Then, the numbers of atoms at step/edges $N_{step/edge}$ as well as those at terraces were calculated.

$$N_{step/edge} = 12 \text{ (atoms at vertex)} + 24(m - 2) \quad \text{(S4)}$$

$$N_{terrace} = N_{surface} - N_{step/edge} \quad \text{(S5)}$$

By using an average particle size d = 2.9 nm for Pt_{2AL}–PtFe and d = 3.5 nm for Pt_2Ru_3 based on the TEM observation, we obtained the values shown below.

Table S2. Number of atoms at step/edges and terraces calculated based on a cuboctohedral shape of Pt_{2AL}–PtFe and Pt_2Ru_3 fcc nanoparticles.

Catalysts	*d* [nm]	Number of Layers, m	Number of Total Surface Atoms, $N_{surface}$	Number of Atoms at Step/Edges, $N_{step/edge}$	Number of Atoms at Terraces, $N_{terrace}$	$N_{step/edge}/N_{terrace}$
Pt_{2AL}–PtFe/C	2.9	7	362	132	230	57%
c-Pt_2Ru_3/C	3.5	8	492	156	336	45%