Electronic Supplementary Information for

Electrocatalytic hydrogenation of benzoic acids

in a proton-exchange membrane reactor

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1. General Information

Gas chromatography (GC) analyses were performed using a Shimadzu gas chromatograph (GC2014) equipped with a HP-1 (Agilent Technologies, Inc.) capillary column. Helium was used as a carrier gas for GC analyses. HPLC analyses were performed with a LC pump (LC-20 AD, Shimadzu Co.), a UV detector (SPD-20A, Shimadzu Co.), and a chiral column (OD-H 250-4.6, Daicel, Co. Inc.) under isothermal (at 25°C) conditions using respective mixture of n-hexane/IPA/TFA as a mobile phase. Galvanostatic electrolyses were carried out using a galvanostat (Hokuto Denko HABF-501A). Linear sweep voltammetry (LSV) and AC impedance measurements were performed using an electrochemical analyzer (660E, BAS. Inc.). Cathode potential changes were recorded using a voltametric data logger (VR-71, T&D Co.). XPS measurements were performed using a Quantera-SXM (ULVAC-PHI, Inc.).

2. Materials

Benzoic acid (**1a**), *p*-toluic acid (**1b**), 4-*tert*-butylbenzoic acid (**1d**), 4-(trifluoromethyl)benzoic acid (**1e**), *p*-anisic acid (**1f**), 4-fluorobenzoic acid (**1g**), cyclohexanecarboxylic acid (**2a**), 4-methylcyclohexanecarboxylic acid (*cis*- and *trans*-mixture of **2b**), 4-isopropylcyclohexanecarboxylic acid (*cis*- and *trans*-mixture of **2c**), 4-tert-butylcyclohexanecarboxylic acid (*cis*- and *trans*-mixture of **2d**), 4-(trifluoromethyl)cyclohexanecarboxylic acid (*cis*- and *trans*- mixture of **2e**), *trans*-4-methylcyclohexanecarboxylic acid (*trans*-**2b**), *trans*-4-isopropylcyclohexanecarboxylic acid (*trans*-**2c**), *trans*-4-tert-butylcyclohexanecarboxylic acid (*trans*-**2d**), *trans*-4-(trifluoromethyl)cyclohexanecarboxylic acid (*trans*-**2e**) were purchased from Tokyo Chemical Industries Co., Ltd.. 4-Isopropylbenzoic acid (**1c**), 4-methoxycyclohexanecarboxylic acid (*cis*- and *trans*-mixture of **2f**) were purchased from Sigma-Aldrich Co.. All chemicals except for 4-fluorobenzoic acid were used without further purification. 4-Fluorobenzoic acid was purified by recrystallized using a mixture of methanol and hexane. Nafion® perfluorinated membranes (Nafion® 117) was purchased from Furukawa Agency Co., Ltd.. Nafion® perfluorinated resin ionomer solution (5 *wt*.% in mixture of lower aliphatic and water, Nafion® DE521) was purchased from Sigma-Aldrich Co.. Fuel cell catalysts (TEC10E50E; platinum/Ketjenblack (EC300J) (Pt/KB; 46.1 wt.%), TECRh(ONLY)E30; rhodium/Ketjenblack (EC300J) (Rh/KB; 28.9 wt.%), TECRu(ONLY)E30; ruthenium/Ketjenblack (EC300J) (Ru/KB; 27.0 wt.%), TEC61E54; platinum-ruthenium alloy/Ketjenblack (EC300J) ($Pt_1Ru_{1.5}$/KB; Pt 30.1 wt.%, Ru 23.4 wt.%), TEC66E50; platinum-ruthenium alloy/Ketjenblack (EC300J) (Pt_1Ru_1/KB; Pt 32.6 wt.%, Ru 16.9 wt.%), and TEC62E58; platinum-ruthenium

alloy/Ketjenblack (EC300J) (Pt_1Ru_2/KB; Pt 27.2 wt.%, Ru 28.7 wt.%) were purchased from Tanaka Kikinzoku Kogyo K.K. (TKK). Carbon paper (Sigracet® GDL39BB) was purchased from SGL CARBON GmbH and used as a gas diffusion layer.

3. Preparation of MEA

MEA was fabricated with 0.5 mg cm^{-2} of metal loading amount. Fuel cell catalyst (0.2440 g), deionized water (0.2083 g), Nafion® perfluorinated resin solution, and 1-propanol (2.4270 g) were stirred in 100 mL glass beaker cell. The ionomer to carbon ratio was 0.8 : 1. This mixture and zirconia balls (diameter: 2.5 mm, 10 pieces) were added to 80 mL Teflon® vessel. The vessel was placed in a planetary rotation pot mill (LP-1, Ito Seisakusho Co.) and rotated at 200 rpm for 20 min. After the rotation, catalyst dispersion was obtained. Carbon separator used as a gas diffusion layer (2 cm x 5 cm) was coated with catalyst dispersion on one side by use of a Teflon spatula with SUS mask for 1 cm x 4 cm. After the coating, it was dried for 10 min at 60°C, and then hot-pressed (0.4 MPa, 120°C) for 1 min. Two sheets of this catalyst layer were used for anode and cathode, respectively. Nafion® perfluorinated membrane (8 cm x 10 cm) was put between anode and cathode, and their catalyst sides faced to membrane, and finally hot-pressed (0.4 MPa, 120°C) for 1 min. Pt was used as an anode catalyst material and Pt, Ru, Rh, and PtRu were used as cathode catalyst materials. The loading amount of each metal catalyst was 0.5 mg cm^{-2}.

4. Assemble of PEM Reactor and MEA

As shown in Figure S1, gold plated stainless steels, carbon separators, Teflon® gaskets, and MEA were used for the fabrication of PEM reactor and they were tightened to be in 2.0 N m by using a torque wrench with screws of M6 size. A photograph of PEM reactor system is shown in Figure S2.
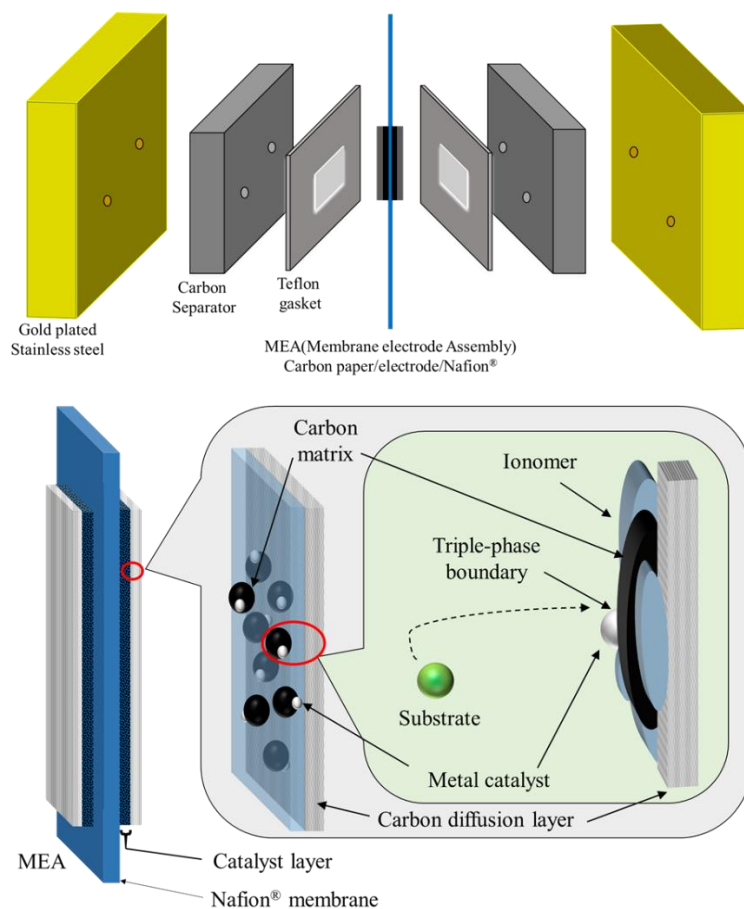
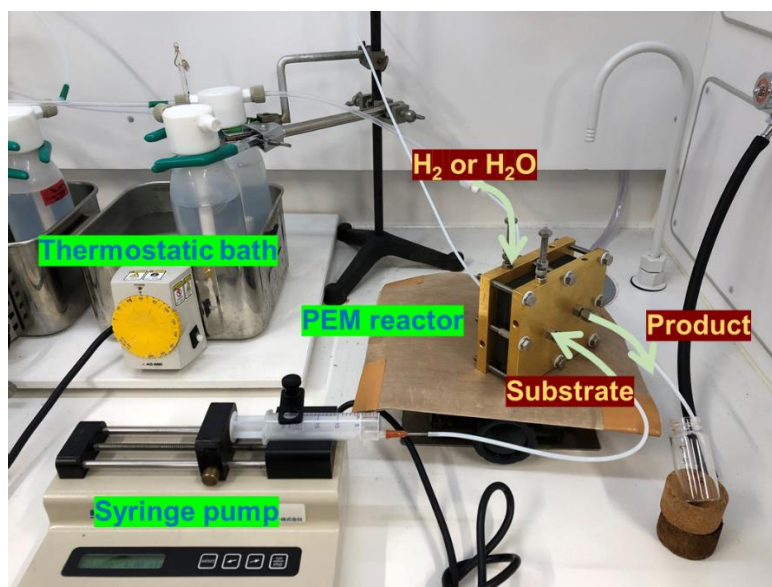**Figure S1**. Schematic drawing of a PEM reactor assembly and MEA.

Figure S2. The photograph of PEM reactor system.

5. GC and HPLC analysis

All hydrogenated products were analyzed by a gas chromatography (GC) (Shimadzu GC2014) equipped with an FID detector and an HP-1 column (Agilent Technologies, Inc.), unless otherwise stated. Helium was used as a carrier gas for GC analyses.

4-substituted cyclohexanecarboxylic acids (**2b-f**) as authentic product samples showed two peaks in their chromatograms, corresponding to *cis*- and *trans*-isomers (Figures S5, S7, S9, S11, and S13). Since the *trans*-isomer samples were available for **2b-e**, two peaks for the *cis*- and *trans*-isomers were attributed by comparison with the chromatogram of the *trans*-isomer samples (Figure S5, S7, S9, and S11). For compound **2f**, since neither isomer is commercially available, a sample with an excess of the *trans*-isomer was prepared using the method of isomerizing the *cis*-isomer to the *trans*-isomer.[1] Subsequently, this sample was used to attribute the two peaks for the *cis*- and *trans*-isomers in the chromatogram (Figure S13).

On the other hand, we employed an FID detector for GC analyses since organic compounds have molar response factors that are equal to the number of carbon atoms in their molecule in the case with an FID detector. Therefore, the *cis*-isomers have the same response factors as the corresponding *trans*-isomers, and therefore, a calibration curve for the *trans*-isomers can be used to quantify the *cis*-isomers (Figures S6, S8, S10, S12, and S14).

Because the peaks of **1g** and benzoic acid as one of the hydrogenated products overlapped in the GC measurement, HPLC was used to elucidate the current efficiency of benzoic acid for the product analysis in the hydrogenation of 4-fluorobenzoic acid (**1g**) (see Figures S15 and S16).
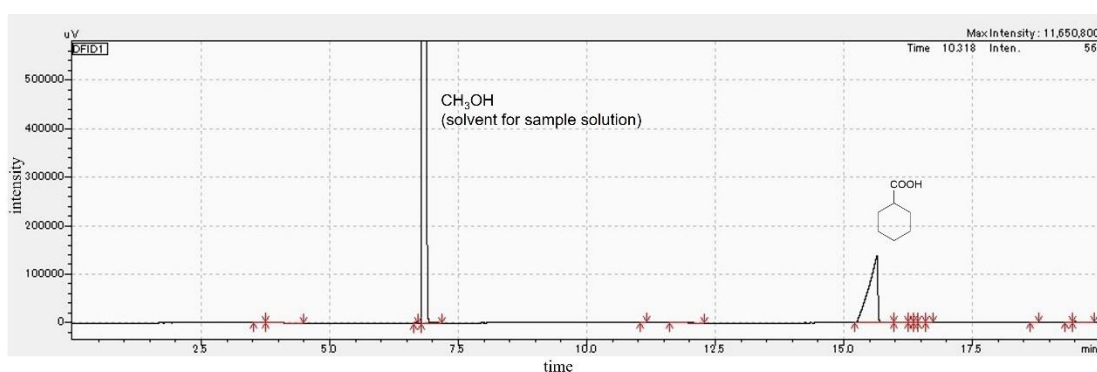

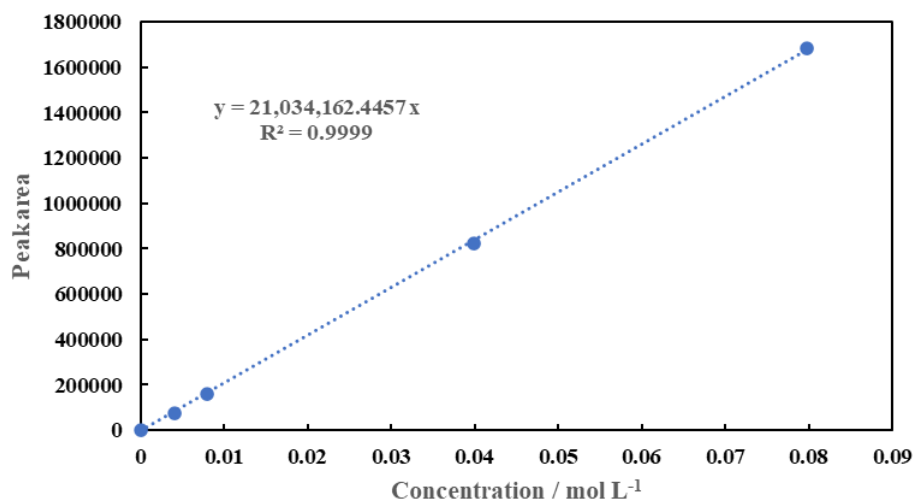**Figure S3.** GC spectrum of an authentic product sample **2a**.
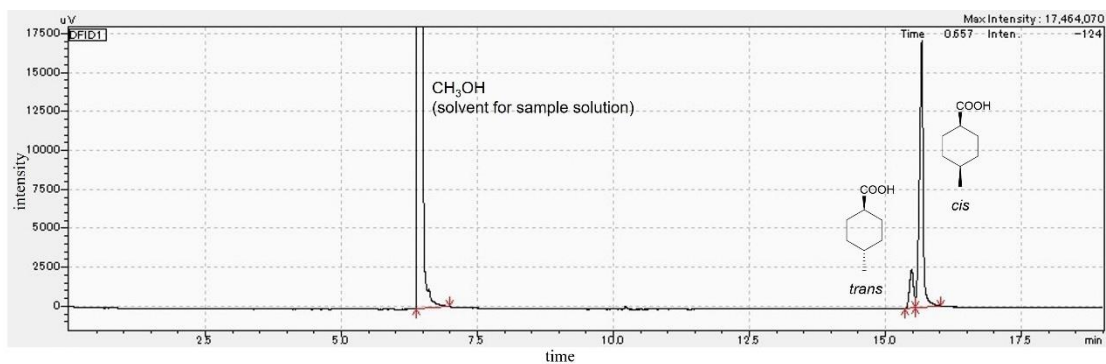
Figure S4. Calibration curve of product **2a**.

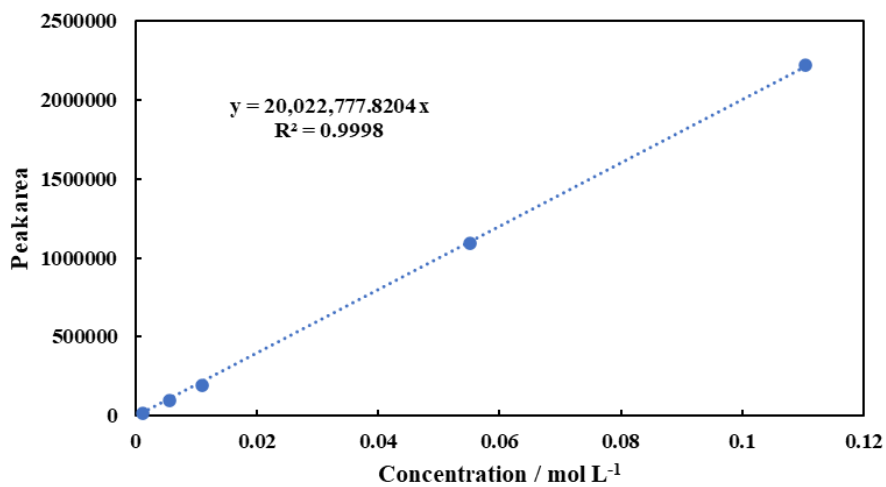**Figure S5.** GC spectrum of an authentic product sample **2b** (*cis*- and *trans*-mixture).

Figure S6. Calibration curve of product **2b**.

Figure S7. GC spectrum of an authentic product sample **2c** (*cis*- and *trans*-mixture).

$$y = 26{,}326{,}951.3802\,x$$
$$R^2 = 0.9997$$

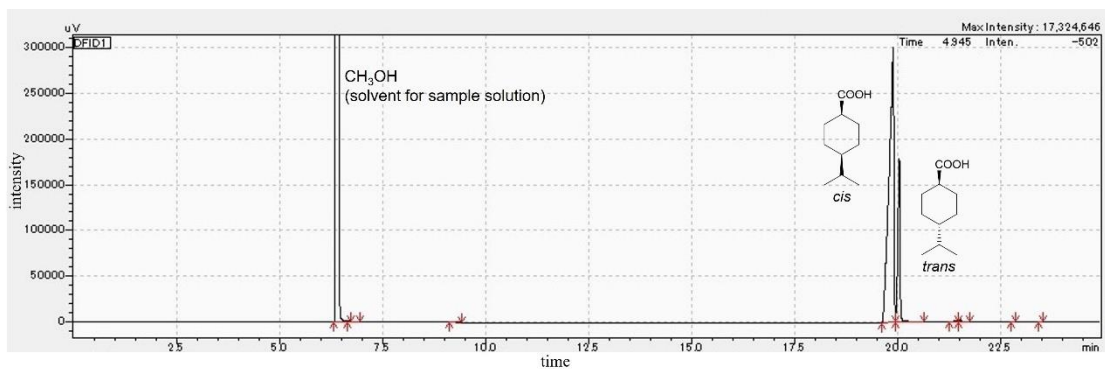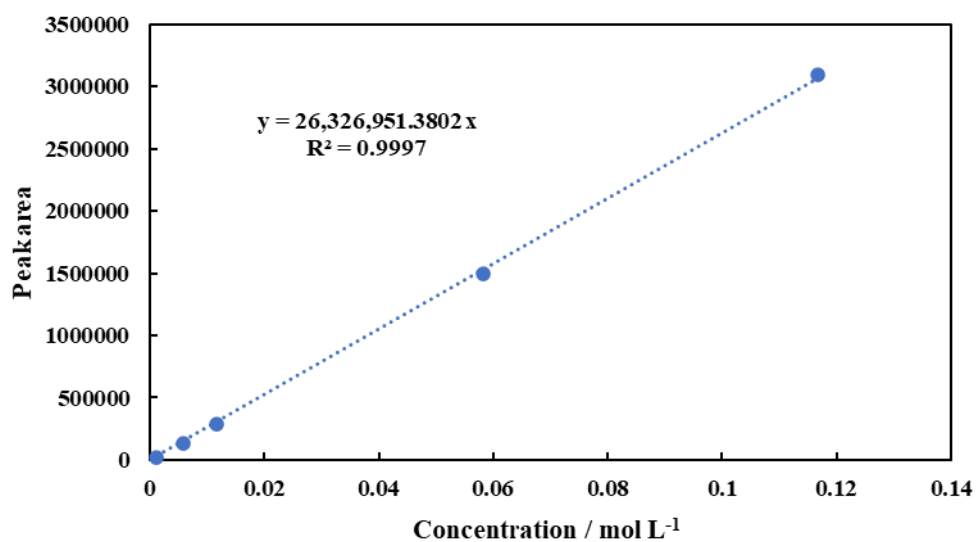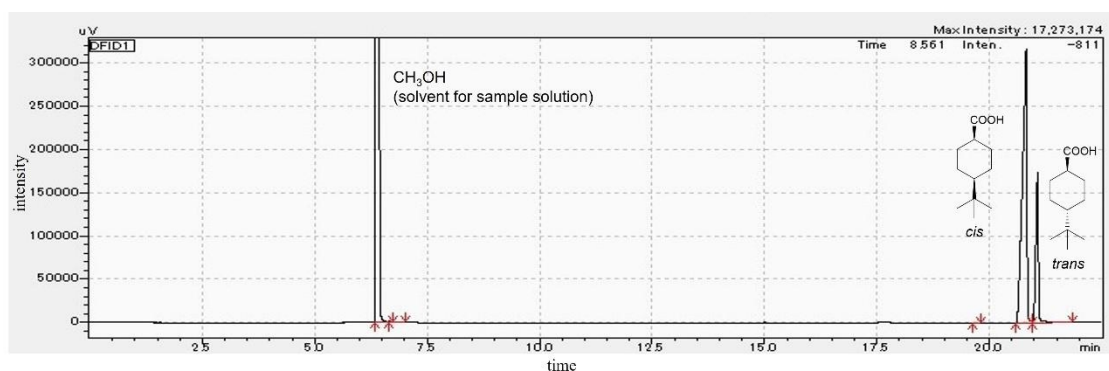**Figure S8.** Calibration curve of product **2c**.

Figure S9. GC spectrum of an authentic product sample **2d** (*cis*- and *trans*-mixture).

Figure S10. Calibration curve of product **2d**.

Figure S11. GC spectrum of an authentic product sample **2e** (*cis*- and *trans*-mixture).

Figure S12. Calibration curve of product **2e**.

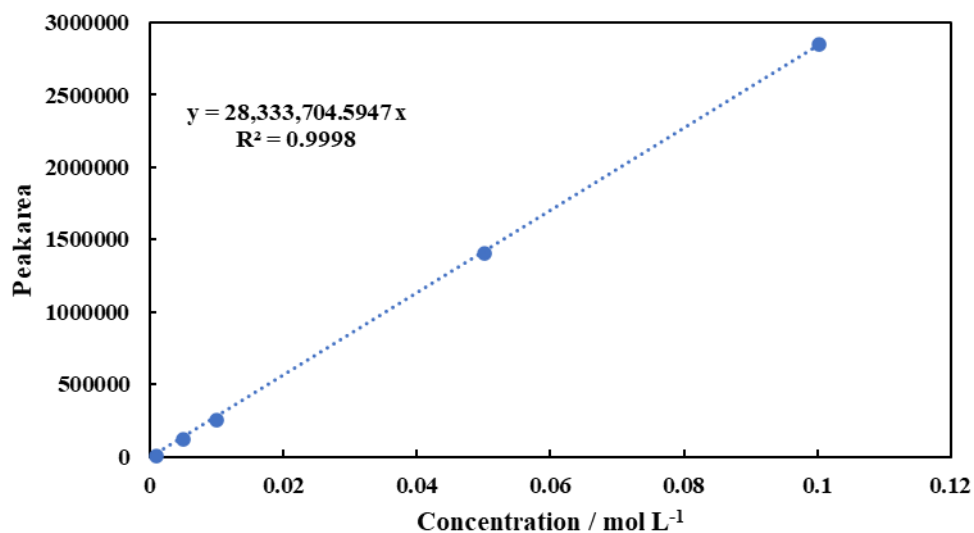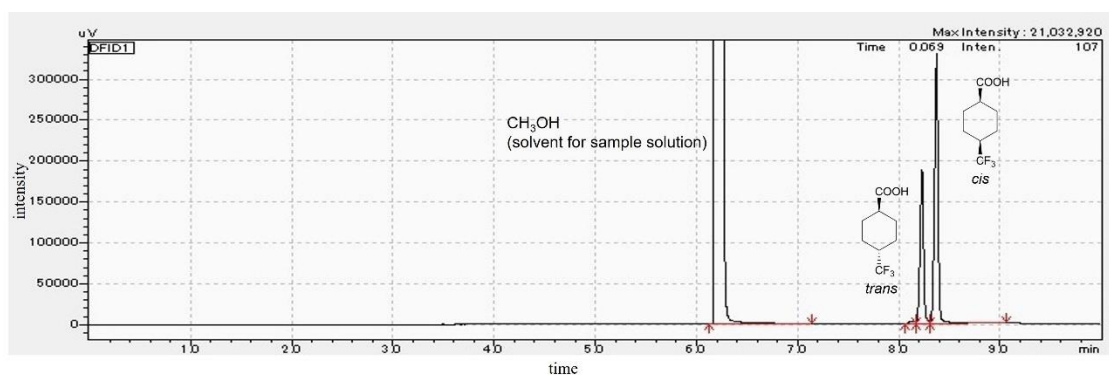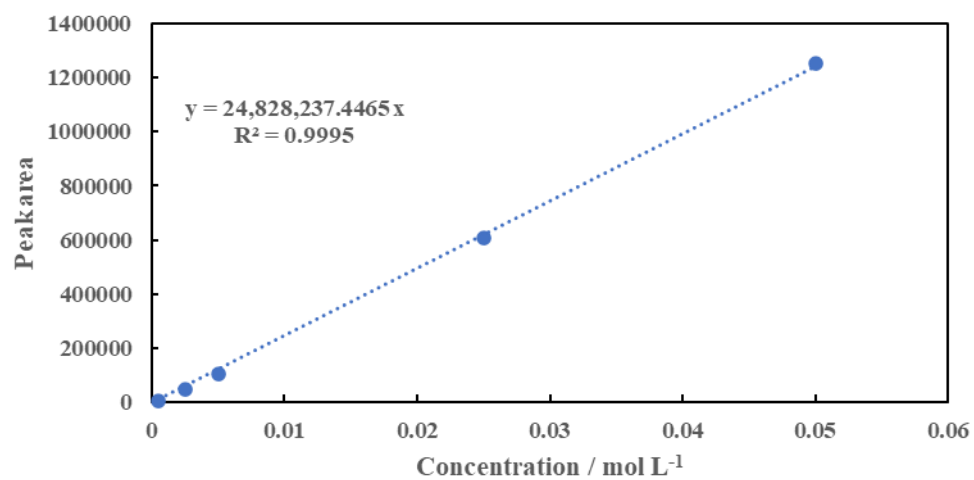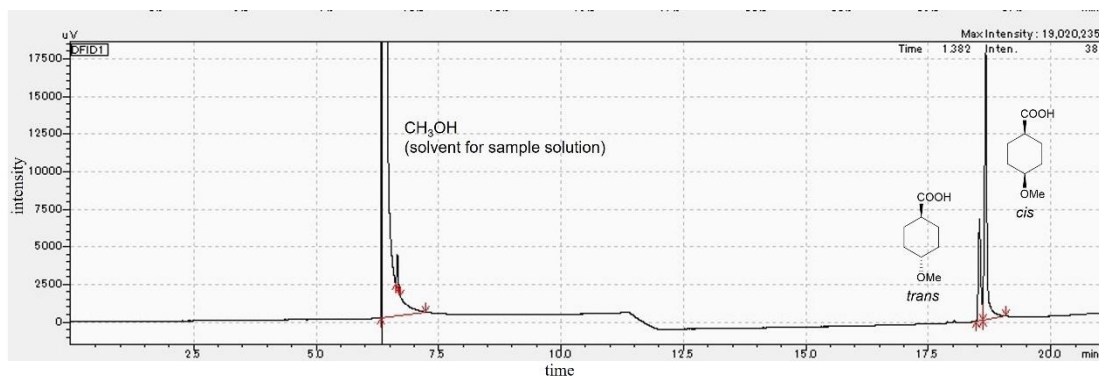**Figure S13.** GC spectrum of an authentic product sample **2f** (*cis*- and *trans*-mixture).

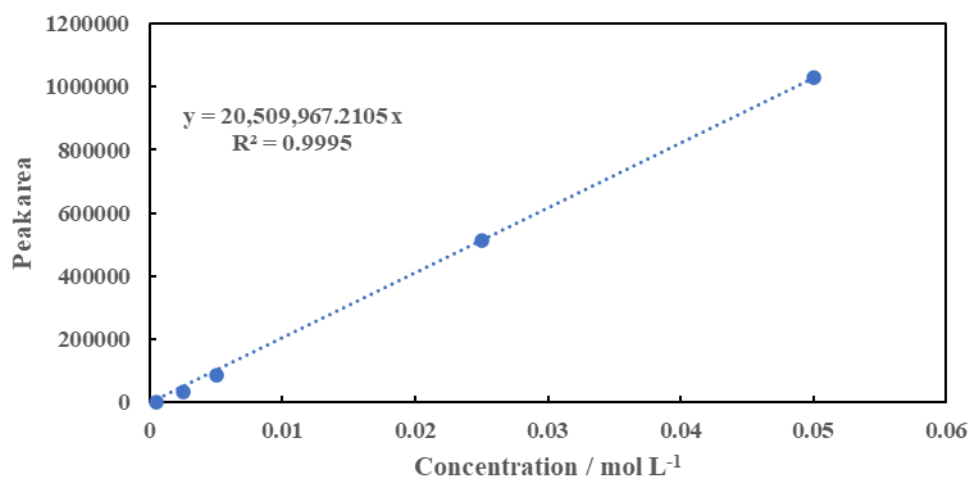

$y = 20,509,967.2105\,x$
$R^2 = 0.9995$

Figure S14. Calibration curve of product **2f**.
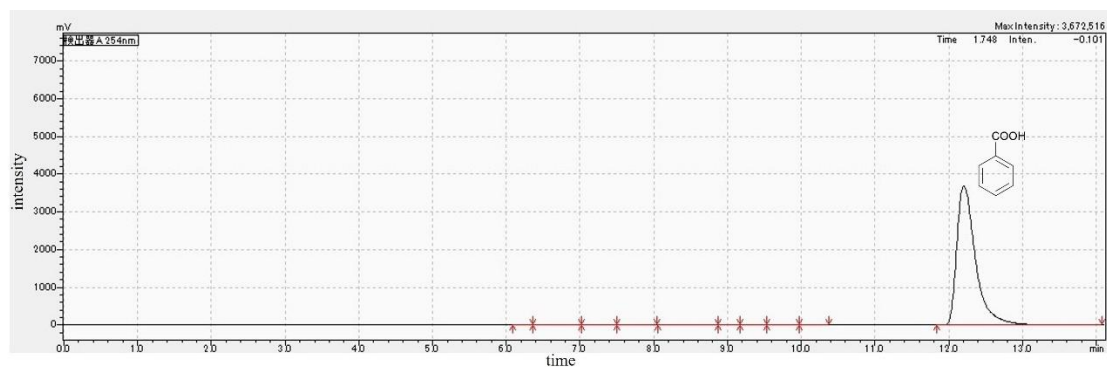

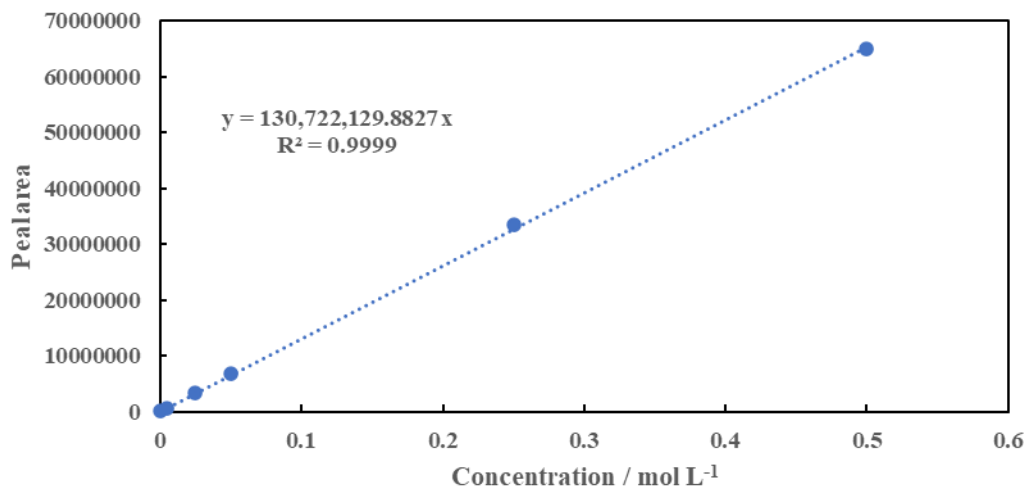**Figure S15.** HPLC spectrum of an authentic sample for benzoic acid.

Figure S16. Calibration curve of benzoic acid (HPLC).

6. AC IMP Measurements

In order to estimate IR drop in a PEM reactor, the ohmic resistance of Nafion® membrane sandwiched between anode and cathode was measured by the electrochemical impedance spectroscopy at −0.1 V *vs*. RHE from 100000 to 0.1 Hz with amplitude of 5 mV. Impedance spectra were recorded after introduction of humidified hydrogen and nitrogen gases into anodic and cathodic chambers, respectively, for 1 hour.

7. LSV Measurements

Linear sweep voltammetry (LSV) measurements for the hydrogen evolution reaction (HER) in a PEM reactor with various cathode catalysts (Pt, Ru, Rh, and PtRu) were performed using an electrochemical analyzer (660E, BAS. Inc.). To conduct Linear sweep voltammetry measurements in a PEM reactor, humidified hydrogen gas was introduced directly to the anodic chamber (flow rate of hydrogen: 100 mL min^{-1}) and electrocatalytically oxidized at Pt anode catalyst to produce protons. By this operation, anode functioned not only as the counter electrode but also as the RHE reference electrode. On the other hand, 1,4-dioxane was provided to the cathodic chamber by syringe pump (flow rate of substrate solution: 1.8 mL h^{-1}) during voltammetry measurements. The scan rate was 1 mV s^{-1}. IR drop was compensated for all voltammograms shown in Figure 4.

8. Chemical Hydrogenation of Benzoic Acid

Chemical hydrogenation was carried out in an eggplant flask. Benzoic acid (0.01 mol) was dissolved in 10 mL of 1,4-dioxane and then added 5 mg of a fuel cell catalyst

(metal/KB). The eggplant flask was evacuated and filled with hydrogen gas from a balloon in two repeating cycles. The reaction was allowed to stir under H_2 atmosphere (1 atm, balloon) at room temperature for 2 h. The catalyst was then filtered off. The yield of products was determined by GC analysis. App-TOF(Ru) was calculated by the following equation (1).

$$\text{App-TOF(Ru)} = -r(H_2) \times \frac{aw_{Ru}}{m_{catalyst} \times wt_{Ru}/100} \tag{1}$$

9. Electrocatalytic Hydrogenation of 4-Alkyl substituted Benzoic Acids with Various Cathode Catalysts

Electrocatalytic hydrogenation of 4-alkyl substituted benzoic acids was carried out in a PEM reactor with various catalyst materials (Table S1).

Table S1. Electrocatalytic hydrogenation of 4-alkyl substituted benzoic acids in a PEM reactor with various metal catalysts[a]

$$R\text{--}\langle\text{benzene}\rangle\text{--COOH} \xrightarrow[\text{Metal/KB}]{6H^+,\ 6e^-} R\text{--}\langle\text{cyclohexane}\rangle\text{--COOH}$$

1 → **2**
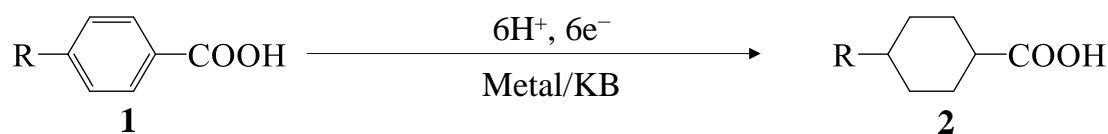
Entry	Substrate R=	Catalyst material	Current efficiency[c] (%)	cis/trans[c]
1		$Pt_1Ru_{1.5}$	>99	80/20
2	Methyl	Pt	89	78/22
3		Rh	78	87/13
4		Ru	trace	-
5		$Pt_1Ru_{1.5}$	86	70/30
6	Isopropyl	Pt	49	67/33
7		Rh	54	83/17
8		Ru	trace	-
9		$Pt_1Ru_{1.5}$	68	85/15
10	tert-Buthyl	Pt	10	81/19
11		Rh	25	90/10
12		Ru	trace	-

[a]Experimental conditions: anode catalyst, Pt (loading amount was 0.5 mg cm^{-2}); cathode catalyst, loading amount was 0.5 mg cm^{-2}; support material of catalysts, Ketjenblack EC300J; cell temperature, r.t.; concentration, 1.0 M in dioxane; coulomb number, 24 C; flow rate of hydrogen, 50 mL min^{-1}. [b]The potential values were corrected for the IR drop determined by the impedance measurement. [c]Current efficiency and *cis/trans* selectivity were determined by GC.

10. Electrocatalytic Hydrogenation of 4-Substituted Benzoic Acids at Various Current Densities

Electrocatalytic hydrogenation of 4-substituted benzoic acids was carried out at various current densities in a PEM reactor (Table S2-4).

**Table S2**. Electrocatalytic hydrogenation of *p*-toluic acid in a PEM reactor[a]
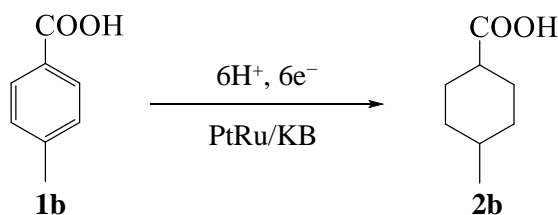
COOH   6H⁺, 6e⁻ →   COOH

$6H^+, 6e^-$

PtRu/KB

1b   **2b**

Entry	Current density / mA cm^{-2}	Flow rate / mL h^{-1}	Average cathode potential / mV *vs*. RHE[b]	Current efficiency[c] (%)	*cis/trans*[c]
1	1.5	1.8	-10	>99	80/20
2	3.0	3.6	-31	73	81/19
3	6.0	7.2	-56	48	82/18
4	12.0	14.4	-110	28	82/18

[a]Experimental conditions: anode catalyst, Pt (loading amount was 0.5 mg cm^{-2}); cathode catalyst, loading amount was 0.5 mg cm^{-2}; support material of catalysts, Ketjenblack EC300J; cell temperature, r.t.; concentration, 1 M in dioxane; coulomb number, 24 C; flow rate of hydrogen, 50 mL min^{-1}. [b]The potential values were corrected for the IR drop determined by the impedance measurement. [c]Current efficiency and *cis/trans* selectivity were determined by GC.

Table S3. Electrocatalytic hydrogenation of 4-isopropylbenzoic acid in a PEM reactor[a]
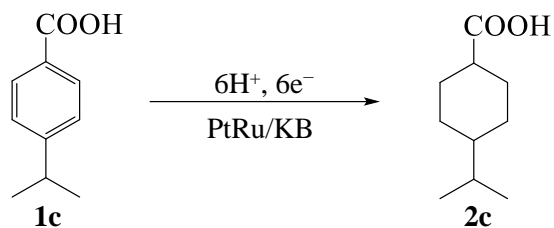
Entry	Current density / mA cm^{-2}	Flow rate / mL h^{-1}	Average cathode potential / mV *vs*. RHE[b]	Current efficiency[c] (%)	*cis/trans*[c]
1	1.5	1.8	-18	86	70/30
2	3.0	3.6	-27	36	70/30
3	6.0	7.2	-43	13	70/30
4	12.0	14.4	-66	10	72/28

[a]Experimental conditions: anode catalyst, Pt (loading amount was 0.5 mg cm^{-2}); cathode catalyst, loading amount was 0.5 mg cm^{-2}; support material of catalysts, Ketjenblack EC300J; cell temperature, r.t.; concentration, 1 M in dioxane; coulomb number, 24 C; flow rate of hydrogen, 50 mL min^{-1}. [b]The potential values were corrected for the IR drop determined by the impedance measurement. [c]Current efficiency and *cis/trans* selectivity were determined by GC.

Table S4. Electrocatalytic hydrogenation of 4-tert-buthylbenzoic acid in a PEM reactor[a]
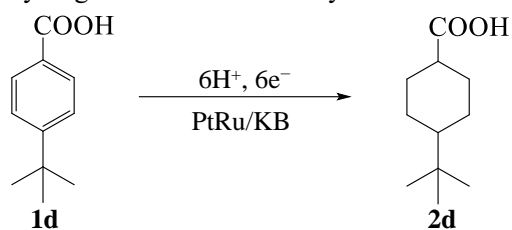
Entry	Current density / mA cm^{-2}	Flow rate / mL h^{-1}	Average cathode potential / mV *vs*. RHE[b]	Current efficiency[c] (%)	*cis/trans*[c]
1	1.5	1.8	-7	68	85/15
2	3.0	3.6	-24	47	87/13
3	6.0	7.2	-50	32	87/13
4	12.0	14.4	-70	15	86/14

[a]Experimental conditions: anode catalyst, Pt (loading amount was 0.5 mg cm^{-2}); cathode catalyst, loading amount was 0.5 mg cm^{-2}; support material of catalysts, Ketjenblack EC300J; cell temperature, r.t.; concentration, 1 M in dioxane; coulomb number, 24 C; flow rate of hydrogen, 50 mL min^{-1}. [b]The potential values were corrected for the IR drop determined by the impedance measurement. [c]Current efficiency and *cis/trans* selectivity were determined by GC.

11. Electrocatalytic Hydrogenation of BA to CCA in Combination with Water Oxidation

The electrocatalytic hydrogenation of **1a** in combination with the anodic oxidation of water was carried out. In this case, Ti separator was used for anode reaction. In addition, 0.1 M H_2SO_4 aq. was provided to anodic chamber for proton source. Temporal voltage change during the electrocatalytic hydrogenation of BA with water oxidation was also monitored (Figure S2).
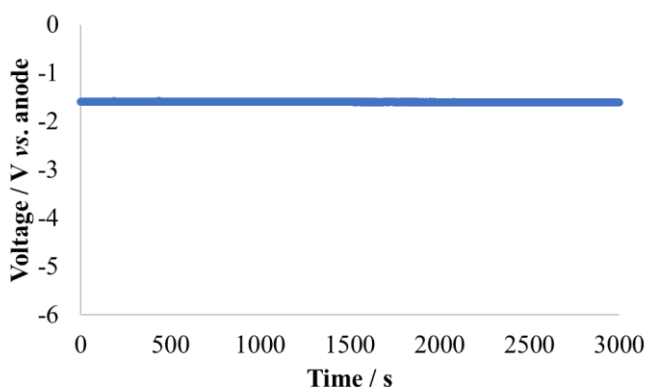

Figure S17. Temporal voltage changes in the electrocatalytic hydrogenation of BA with water oxidation.

12. Reference

1) S. Kato et. al., Method for producing *trans*-isomer of 4-substituted-cyclohexanecarboxylic acid. JP2009263336A. 2009-11-12.