

Supporting Information for

A New Approach to Stereoselective Electrocatalytic Semihydrogenation of Alkynes to Z-Alkenes Using a Proton Exchange Membrane Reactor

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General

Gas chromatography (GC) analyses were performed using a Shimadzu gas chromatograph (GC2014) equipped with a Cyclosil-B (Agilent Technologies, Inc.) or HP-1 (Agilent Technologies, Inc.) capillary column. Helium was used as a carrier gas for GC analyses. Gas chromatography - mass spectrometry (GC-MS) analyses were performed by using a Shimadzu gas chromatograph (GCMS-QP2010) equipped with a HP-1 capillary column (Agilent Technologies, Inc.). Helium was used as a carrier gas for GC-MS analyses. HPLC analyses were performed with a LC pump (LC-10 ADVP, Shimadzu Co.), a UV detector (SPD-20A, Shimadzu Co.), and a normal phase type column (Mightysil Si 60 250-4.6, Kanto Chemical, Co. Inc.) under isothermal (at 25°C) conditions using respective mixture of *n*-hexane/dichloromethane as a mobile phase. Potentiostatic and galvanostatic electrolyses were carried out using a potentiostat (Hokuto Denko HABF-501A). Cyclic voltammetry and AC impedance measurements were performed using an electrochemical analyzer (660E, BAS. Inc.).

Materials

All chemicals were used without further purification. *n*-Hexane was purchased from Kanto Chemical Co., Inc.. Methylcyclohexane and 3-hexyne-1-ol were purchased from Wako Pure Chemical Industries, Ltd. Diphenylacetylene, dichloromethane, isopropyl alcohol, 1-phenyl-1-propyne, and phenyl acetylene were purchased from Tokyo Chemical Industry Co., Ltd.. Nafion® perfluorinated membranes (Nafion® NRE212 and NRE117) and Nafion® perfluorinated resin ionomer solution (5 wt.% in mixture of lower aliphatic and water, Nafion® DE521) were purchased from Sigma-Aldrich Co.. Fuel cell catalysts (TEC10E50E; platinum/carbon (Pt/C), TECRh(ONLY)E30; rhodium/carbon (Rh/C), TECRu(ONLY)E30; ruthenium/carbon (Ru/C), and TECPd(ONLY)E30; palladium/carbon (Pd/C)) were purchased from Tanaka Kikinzoku Kogyo K.K. (TKK). Weight percent of metal in fuel cell catalysts are 46, 29, 27 and 29 wt.% for Pt/C, Rh/C, Ru/C, and Pd/C, respectively. Carbon separator used as a gas diffusion layer (Sigracet® GDL35BC) was purchased from SGL CARBON GmbH.

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. 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, Pd, Ru and Rh were used as cathode catalyst materials. The loading amount of each metal catalyst was 0.5 mg cm⁻².

Assemble of PEM reactor

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.

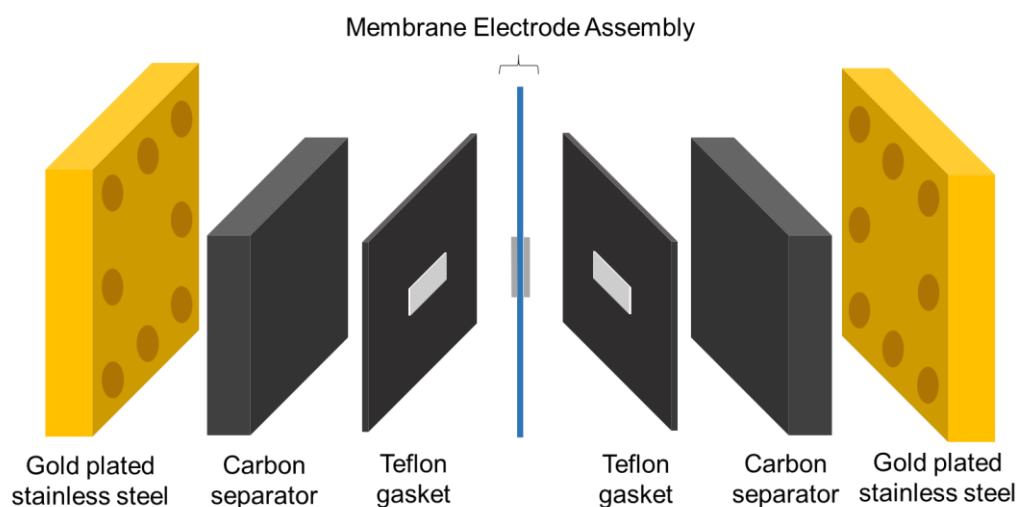


Figure S1. Schematic drawing of a PEM reactor assembly.

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. Experimental data for the resistance of Nafion[®] membrane in a PEM reactor are summarized in Table S1.

Table S1. Ohmic resistance of Nafion[®] membrane in a PEM reactor with various cathode catalyst materials^a

Cathode catalyst material	Loading amount of metal catalyst / mg cm ⁻²	Resistance of Nafion [®] membrane / Ω
Pd	0.5	0.51
Pt	0.5	0.39
Ru	0.5	0.46
Rh	0.5	0.36

^a Pt was used as an anode catalyst material. Loading amount of Pt catalyst was 0.5 mg cm⁻².

CV measurements

Cyclic voltammetry measurements for the electrocatalytic hydrogenation of diphenylacetylene (**1a**) and Z-stilbene (**2a**) in a PEM reactor with various cathode catalysts (Pd, Pt, Ru, and Rh) were performed using an electrochemical analyzer (660E, BAS. Inc.). To conduct cyclic voltammetry 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, 0.1 M substrate solutions (solvent: methylcyclohexane) were provided to the cathodic chamber by syringe pump (flow rate of substrate solution: 0.25 mL min⁻¹) during voltammetry measurements. The scan rate was 5 mV s⁻¹. IR drop was compensated for all voltammograms given in Figures 3 and S2.

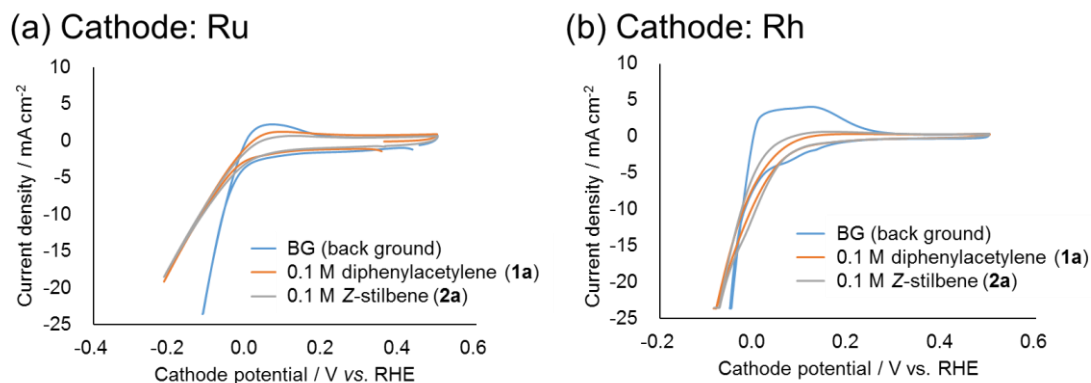


Figure S2. Cyclic voltammograms obtained with and without substrates (**1a** and **2a**) in a PEM reactor using (a) Ru and (b) Rh cathode catalysts. Solvent, methylcyclohexane; cell temperature, r.t.; flow rate of substrate solution, 0.25 mL min⁻¹; flow rate of hydrogen, 100 mL min⁻¹; IR drop was compensated.; scan rate, 5 mV s⁻¹.

Chemical hydrogenation of diphenylacetylene

Chemical hydrogenation was carried out in a two necked flask. Diphenylacetylene (0.5 mmol) was dissolved in 5 mL of methylcyclohexane and then added fuel cell catalyst, Pd/C (29 wt.%, 7 mg). The two necked flask was evacuated and filled with hydrogen gas from a balloon in two repeating cycles. The reaction was allowed to stir under H₂ atmosphere (1 atm, balloon) at room temperature for 24 h. The catalyst was then filtered off. The yield of products were determined by GC-MS and HPLC analysis.

Estimation of the standard potential of electrochemical hydrogenation reaction

The standard potential of the hydrogenation reactions (E^0 , see Table S2) was calculated from the Gibbs free energy change for this reaction (ΔG^0) according to following equation:

$$\Delta G^0 = -nFE^0$$

where n is number of moles of electrons per mole of products and F is the Faraday constant.

The Gibbs free energy change for the hydrogenation reactions was calculated from the Gibbs free energy of formation of substrates and hydrogenated products. The Gibbs free energy of formation was estimated according to the literature.¹

Table S2. The standard potential of the hydrogenation reactions

Hydrogenation reaction	Gibbs free energy change (ΔG^0) / kJ mol ⁻¹	Standard potential (E^0) / mV
1a → 2a	-148.63	770
2a → 4a	-72.52	376
4a → 1,2-Dicyclohexylethane	-169.82	147

Reference:

(1) Domalski, E. S.; Hearing, E. D. Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data.* **1993**, 22, 805.