Supplementary Information for

Electrolytic hydrogenation at 100 mA cm⁻² and 1.6 volts

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Experimental Methods

Materials

Pd (99.95%) was obtained from the Kurt J. Lesker Company as a sputtering target. Methanol (HPLC grade, \geq 99.9%), styrene (contains 4-tert-butylcatechol as the stabilizer, \geq 99%), hydrochloric acid (37 wt.%), sulfuric acid (95.0–98.0 wt.%), nitric acid (68–70 wt.%), H₂O₂ solution (30 wt.% in H₂O), isopropyl alcohol (IPA, \geq 99.5%), palladium chloride (PdCl₂, 99%), *tert*-butanol (\geq 99.7%) and dimethyl sulfoxide-d6 (DMSO-d₆) (99.9%) were purchased from Sigma-Aldrich and used as received. Furfural (98%) was purchased from Thermo Fisher Chemicals and used as received. Iridium oxide (IrO₂), 40 wt.% carbon-supported platinum (Pt/C), 40 wt.% carbon-supported palladium (Pd/C), titanium fiber felt (*ca.* 250 µm, 53–56% porosity), and carbon fiber gas diffusion layer (Sigracet 29BC) were purchased from Fuel Cell Store. Nafion membranes (NR-212) and Nafion ionomer dispersions (D520, 5 wt.%) were purchased from Ion Power.

Pd membrane preparation

Pd membranes (25 μ m) were prepared with a cold–rolling method^{1,2} from a 1/16-inch thick Pd sputtering target using an electric cold roller press (MSK-HRP-MR100A, MTI Corporation). The thickness of the membrane was measured with a Mitutoyo digital micrometer with an accuracy of ±1 μ m. The membrane was cleaned with hexane and annealed in Ar at 900 °C for 1.5 h. The annealed membranes were cleaned in a 1:1:2 (by volume) solution of HNO₃:H₂O₂:H₂O for 20 min. The membranes were then cleaned with DI water and IPA, and air dried.

Hydrogenation catalysts preparation

For styrene hydrogenation, Pd|Pd black membranes were used. Pd black was electrodeposited onto the clean Pd membrane. The electrodeposition bath was 15.9 mM PdCl₂ dissolved in 1 M HCl solution. A saturated Ag/AgCl reference electrode and a Pt plate counter electrode were used. The electrodeposition was carried out in galvanostatic mode at a current density of -3.5 mA cm⁻² (4 cm² total geometric area of the membrane) and stopped when a charge of 80 C was reached. The catalyst loading was *ca*. 6 mg cm⁻² and measured by weighing the membrane before and after electrodeposition.

Membrane electrode assembly preparation

Catalyst-coated PEMs were used in the Pd membrane electrolyzer. These PEMs have the anodic and cathodic catalyst layers pre-coated onto a Nafion NR-212 proton-exchange membrane. They were prepared with a decal method.

Specifically, to prepare the oxygen evolution catalyst layer, 60 mg IrO_2 was dispersed in 6 mL ethanol, then 360 µL Nafion ionomer solution (5 wt.%) was added. The dispersion was sonicated for 2 h to reach a uniform ink. The ink was spray-coated onto a 50 µm thick PTFE sheet (6 cm × 4 cm). The catalyst loading was measured at about 1.3 mg_{ir} cm⁻². The PTFE sheet was cut into six pieces (2 cm × 2 cm each).

To prepare the proton reduction catalyst layer, 40 mg of 40 wt.% Pt/C with 240 μ L Nafion solution was dispersed in 6 mL ethanol and spray-coated onto a PTFE sheet. The sheet was the same size as the one used for the anode. The cathode Pt loading was measured at about 0.5 mg_{Pt} cm⁻².

To decal transfer the catalysts onto the Nafion membrane, the catalyst-coated PTFE sheet was hot-pressed with the Nafion membrane at 120 °C and 50 kN for 5 min. After cooling down, the PTFE sheet was peeled off, and the catalysts remained on the Nafion membrane. This procedure was repeated for both anode and cathode.

Finally, to remove impurities, the prepared membrane was boiled in 0.5 M H₂SO₄ for 1 h.

Cell assembly of the Pd membrane electrolyzer

This work used a customized reactor with a serpentine flow field on the titanium flow plates (Fig. S1). The active area was 4 cm². Ti fiber felts were used as porous current collectors for both the anode and cathode. The sequence of cell assembly was (from anode to cathode): Ti flow plate | Ti fiber felt | IrO_2 | PEM | Pt/C | Pd foil | Pd black | Ti fiber felt | Ti flow plate. The flow plates were tightened by eight bolts with a torque of 1 N·m.

Cell assembly of the ECH electrolyzer, ECH H-cell, and Pd membrane H-cell

The ECH electrolyzer consisted of a catalyst-coated MEA with only an anode of IrO₂ (or Pt/C in the methanol permeation test) and a Pd/C gas diffusion electrode cathode. Typically, 40 mg of 40 wt.% Pd/C together with 240 μ L Nafion solution was dispersed in 6 mL ethanol and spray-coated onto a 6 cm × 4 cm Sigracet 29BC carbon fiber gas diffusion layer to form the GDE. The GDE was then cut into six pieces (2 cm × 2 cm each). The Pd loading was measured at *ca*. 0.5 mg_{Pd} cm⁻². Ti fiber felt was used as the porous current collector for the anode. The sequence of cell assembly was (from anode to cathode): Ti flow plate | Ti fiber felt | IrO₂ | PEM | Pd/C | gas diffusion layer | Ti flow plate. The flow plates were tightened by eight bolts with a torque of 1 N·m.

The ECH H-cell and membrane H-cell were assembled as per our previous reports.^{3,4} For the ECH H-cell, a Pt mesh was used as the anode, and a Pd membrane with electrodeposited Pd black facing

the hydrogenation chamber was used as the cathode. The electrolyte was a solution of methanol and 1 M HCl solution (1:1, v/v). The active geometric area of the cell was 2 cm⁻². For the membrane H-cell, a Pt mesh was used as the anode, and a Pd membrane with electrodeposited Pd black was used as the cathode. The electrolysis chamber used 7 mL of 1 M H_2SO_4 solution as the electrolyte. The active geometric area of the cell was 2 cm⁻².

Electrochemistry

All electrochemistry was conducted on a Metrohm Autolab PGSTAT302N potentiostat at room temperature. The steady-state polarization curves were measured by chronoamperometry starting from 1.25 V with a 0.05 V increase for each step. Each potential step was kept for 30 s, and the final current density was recorded. For the hydrogenation in the Pd membrane electrolyzer and ECH electrolyzer, 25 mL of DI water was circulated in the anode at a flow rate of 20 mL min⁻¹ with a multi-channel peristaltic pump. The cathode was circulated with 10 mL of reactant solution (e.g., 0.1 M styrene in methanol) at 20 mL min⁻¹ with the peristaltic pump. The styrene hydrogenation experiments were conducted galvanostatically at different current densities and concentrations.

The FE of ethylbenzene was calculated by dividing the charge that produced ethylbenzene by the total charge passed through the circuit.

$$FE = \frac{n_{EB} \times F \times 2}{j \times A \times t} \times 100\%$$

where n_{EB} is the molar of produced ethylbenzene, quantified by ¹H NMR spectroscopy; *F* is the Faradaic constant (96485 C mol⁻¹); *j* is the current density; *A* is the active geometric area of the reactor; and *t* is the reaction time. The numerator was multiplied by 2 because styrene hydrogenation is a two-electron reaction.

The EE of ethylbenzene production was calculated by dividing the reaction Gibbs free energy (ΔG_{rxn}) with the actual electric energy input to produce 1 mol ethylbenzene by the reactor. The overall reaction of the styrene hydrogenation using water as the hydrogen source is:

$$C_8H_8 + H_2O \rightarrow C_8H_{10} + \frac{1}{2}O_2 \quad \Delta G_{rxn} = +155.8 \text{ kJ mol}^{-1}$$

The EE of the reactor was thus calculated according to the following equation:

$$EE = \frac{\Delta G_{rxn} \times FE}{U \times F \times 2} \times 100\%$$

where ΔG_{rxn} is the reaction Gibbs free energy; FE is the Faradaic efficiency for ethylbenzene; *U* is the cell voltage of the cell and *F* is the Faradaic constant (96485 C mol⁻¹). The denominator was multiplied by 2 because styrene hydrogenation is a two-electron reaction.

Product quantifications

The reaction progress of styrene hydrogenation was monitored using ¹H NMR by taking 200 μ L aliquots from the hydrogenation chamber. The aliquots were diluted with 300 μ L DMSO-d₆ as the deuterated solvent. The ¹H NMR experiments were performed on a Bruker Av400 NMR spectrometer. The peaks were integrated to calculate the styrene conversion. Peaks at 7.00–7.70 ppm indicated the total amount of the phenyl ring (styrene and ethylbenzene). The quadruplet peak at 6.76 ppm came from the α -H of styrene. The triplet peak at 1.20 ppm came from the –CH₃ peak of ethylbenzene. For furfural hydrogenation, gas chromatography-mass spectrometry (GC–MS) was used to qualify the products. Aliquots of 50 μ L samples were taken each time and diluted with 1 mL dichloromethane. The GC-MS experiments were conducted on an Agilent GC–MS using an HP-5ms column and electron ionization. The samples were run using an auto-sampler with a 1 μ L injection volume and a split ratio of 20:1. The oven temperature was static at 50 °C for 1 min, ramped to 150 °C at 10 °C min⁻¹. A solvent delay of 2 min was employed.

Supplementary Figures



Fig. S1 The optical image of the palladium (Pd) membrane electrolyzer. The Pd membrane electrolyzer consists of two Ti flow plates, two Ti fiber felts as porous current collectors, a catalyst-coated PEM for water electrolysis, and a catalyst-coated Pd membrane for hydrogenation. The Ti felts, PEM, and Pd membrane are tightly assembled to form the MEA.



Fig. S2 The scanning electron microscopy (SEM) image of the Pd membrane before and after Pd black electrodeposition. a, The bare Pd membrane. b, The Pd membrane after Pd black deposition.



Fig. S3 The image of an assembled Pd membrane electrolyzer. The red alligator clip was connected to the anode of the potentiostat and the black alligator clip was connected to the cathode of the potentiostat.



Fig. S4 ¹H NMR spectra of the hydrogenation of 0.1 M styrene solution in the Pd membrane electrolyzer. The styrene peaks were diminished after 2 h, indicating nearly 100% conversion of styrene after 2 h hydrogenation in the Pd membrane electrolyzer. The peak located at 3.86 ppm belonged to the stabilizer of styrene as purchased. Current density: 50 mA cm⁻². DMSO-d₆ was used as the NMR solvent.



Fig. S5 ¹H NMR spectra of the hydrogenation of 0.1 M styrene solution in the ECH electrolyzer. The spectra only demonstrated a small conversion of styrene after 2 h. The peak located at 3.86 ppm belonged to the styrene stabilizer as purchased. Current density: 50 mA cm⁻². DMSO-d₆ was used as the NMR solvent.



Fig. S6 The impact of current density and reactant concentration in the Pd membrane electrolyzer. a, The Faradaic efficiency (FE) of ethylbenzene and reaction rate at different current densities in the Pd membrane electrolyzer. The concentration of the styrene was fixed at 0.1 M. b, The FE of ethylbenzene and the initial reaction rate at different styrene concentrations in the Pd membrane electrolyzer. The current density was fixed at 50 mA cm⁻².



Fig. S7 Electrolytic styrene hydrogenation at 50 mA cm⁻², at different concentrations. a, 0.1 M. **b,** 1 M. **c,** 5 M. **d,** Neat styrene. Experiments **a-c** used 10 mL of solution using methanol as the solvent and experiment **d** used 10 mL of neat styrene.



Fig. S8 X-ray diffraction pattern of the Pd membrane before and after hydrogen loading. The triangles indicate the reflections for metallic Pd, the circles indicate the reflections for β -PdH_x.



Fig. S9 Relationship between maximum H₂ flux through the Pd membrane, and current density. The H₂ pressure generated by the water electrolysis is calculated using the ideal gas law P = nRT/V, where *n* is the amount of H₂ generated per second, and *V* is estimated by assuming a 50 µm gap between the Nafion and Pd membrane. The local pressure between the Nafion and Pd membrane builds up as current density increases, which enhances the permeation of H₂. Consequently, the H₂ diffusion through the Pd membrane is not a rate-limiting factor below 1600 mA cm⁻² at room temperature.



Fig. S10 Hydrogenation of furfural in the Pd membrane electrolyzer. a, The composition of 10 mL 0.1 M furfural solution (dissolved in *tert*-butanol) after 3 h electrolysis in the Pd membrane electrolyzer. Current density at 50 mA cm⁻². The major products of furfural hydrogenation are furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA) and 2-methyltetrahydrofuran (MTHF). **b,** A schematic of the proposed furfural hydrogenation route in the Pd membrane electrolyzer according to the composition of the solution.

Supplementary References

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