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Supplementary Information

Supported palladium membrane reactor architecture for electrocatalytic hydrogenation

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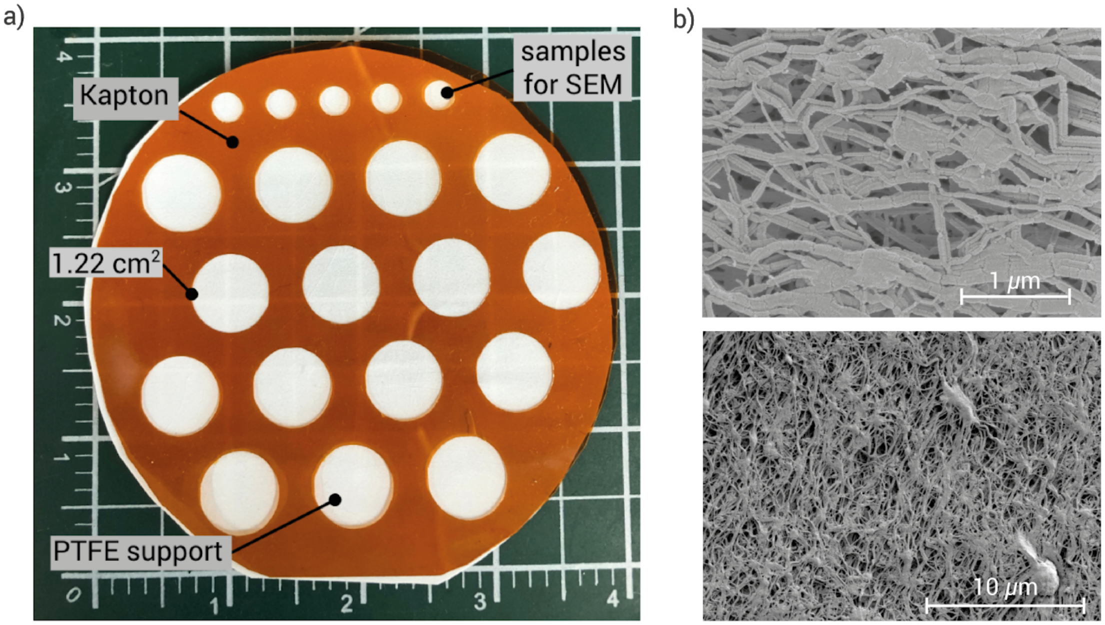


Figure S1. (a) Prepared PTFE supports attached to a Kapton mask (4″ diameter) for mechanical support. (b) SEM images of PTFE support at two magnifications. A 10 nm thick film of gold was sputtered onto the PTFE before imaging. The Tetratex PTFE support shown has a 0.05 μm pore size, 25.4 μm thickness, and 104.7 m^2/g BET surface area. Circular cutouts in the Kapton mask correspond to one testable membrane (geometric surface area = 1.22 cm^2).

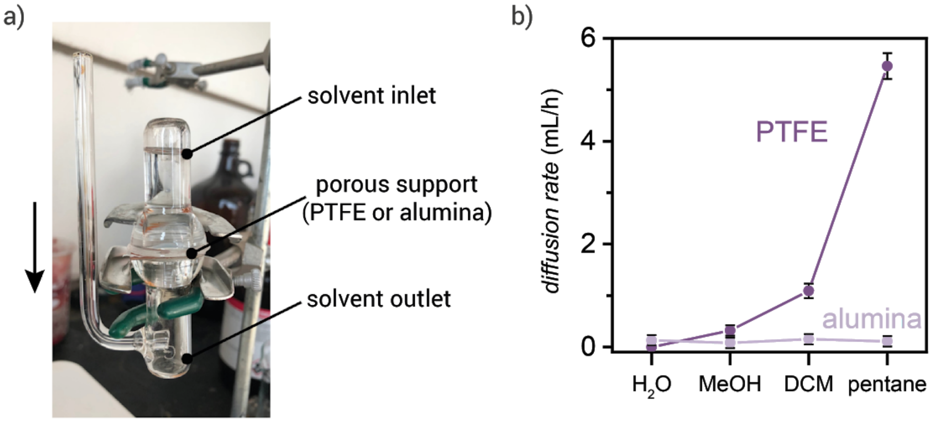


Figure S2. Liquid diffusion measurements through porous alumina supports (commonly used in gas-fed palladium membrane reactors) and porous PTFE supports (proposed for electrolytic palladium membrane reactors). (a) Photograph of experimental setup and (b) liquid diffusion rates through each support in solvents with varying polarities (H_2O being the most polar and pentane being the most non-polar). Error bars indicate standard deviations of measurements (n=6 replicates). The Tetratex PTFE and Coorstek alumina supports both have 0.1 μm pore size and 74 μm and 1 mm thicknesses, respectively.

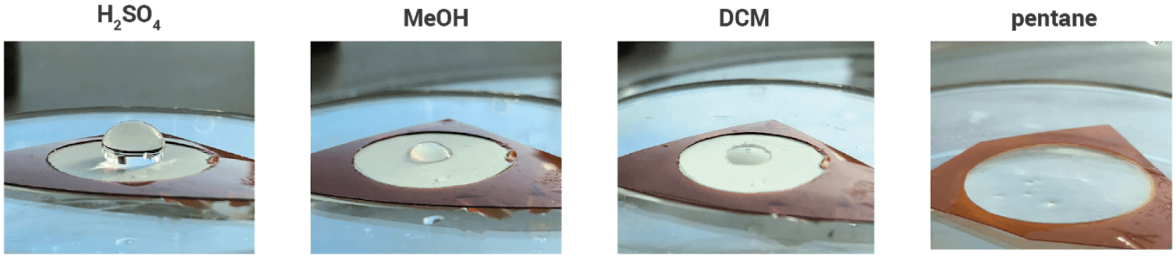


Figure S3. Solvent droplet images demonstrating the wettability of the PTFE support to solvents with varying polarities (H_2SO_4 being the most polar and pentane being the most non-polar). The Tetratex PTFE support shown has a 0.05 µm pore size and 25.4 µm thickness. The Kapton mask was attached for mechanical support.

Table S1. Liquid diffusion measurements of solvents with different polarities through alumina and through PTFE supports with different pore sizes and thicknesses.

PTFE (pore size, thickness)	Diffusion rate (mL/h)			
	H_2O	MeOH	DCM	Pentane
0.05 µm, 25.4 µm	0.0	0.25	1.1	6.7
0.1 µm, 74 µm	0.0	0.32	1.1	5.5
0.2 µm, 66 µm	0.0	0.30	1.3	7.5
Alumina (0.1 µm, 1 mm)	0.13	0.08	0.15	0.11

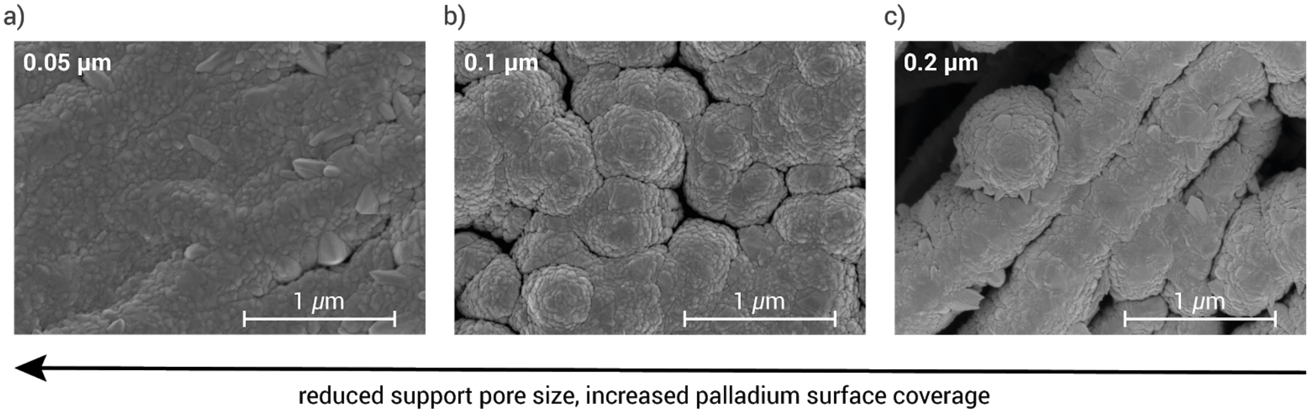


Figure S4. SEM images demonstrating relationship between palladium layer surface coverage and support pore size. 1 µm palladium sputter-deposited on Tetratex PTFE with support pore sizes (a) 0.05 µm, (b) 0.1 µm, and (c) 0.2 µm. Corresponding PTFE thicknesses are 25.4 µm, 74 µm, and 66 µm, respectively. No visible pinholes >100 nm were seen on the 0.05 µm pore size, 25.4 µm thickness PTFE support.

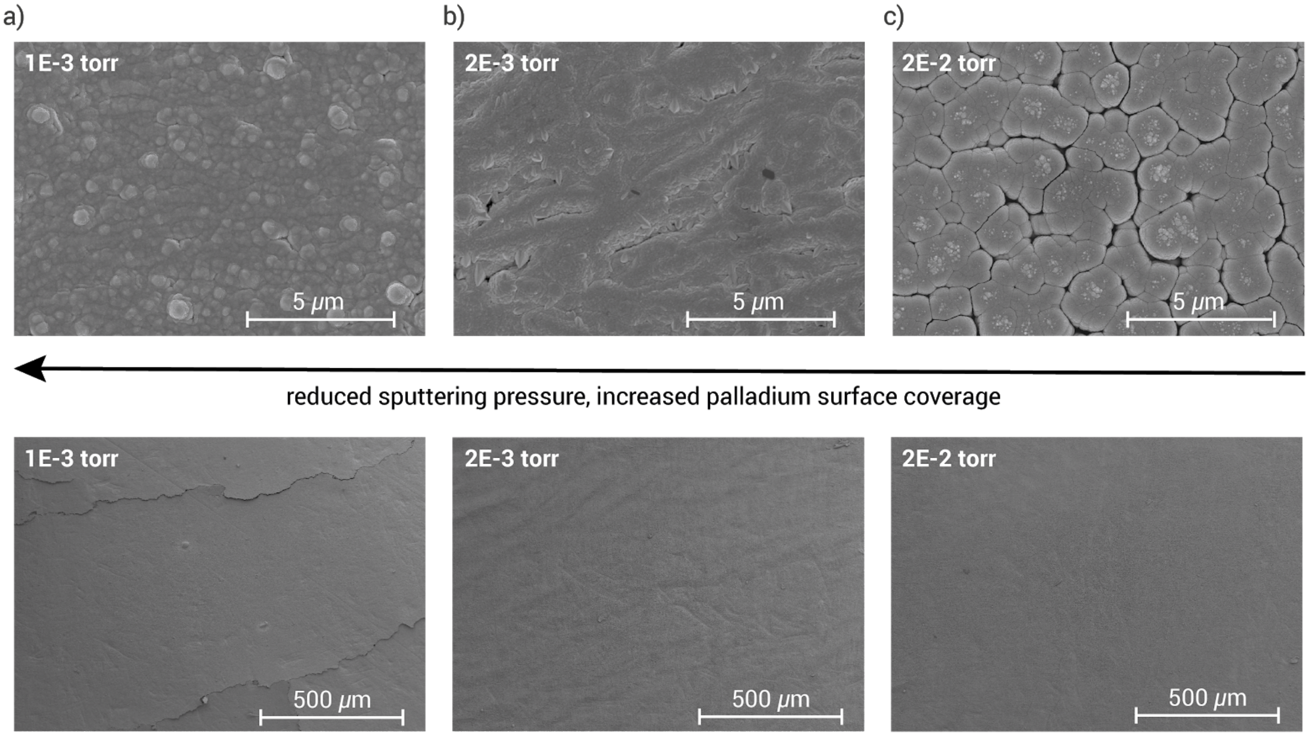


Figure S5. SEM images demonstrating the relationship between palladium layer surface coverage and sputtering pressure. ~1.5 µm palladium sputter-deposited on a 0.05 µm pore size PTFE membrane with sputtering pressures (a) 1×10^{-3} torr, (b) 2×10^{-3} torr, and (c) 2×10^{-2} torr. Both 1×10^{-3} torr and 2×10^{-3} torr sputtering pressures resulted in a continuous palladium film with no pinholes >100 nm and sputtering pressure of 2×10^{-2} torr produced a non-continuous film with columnar Pd grains. Sputtering pressure of 1×10^{-3} torr resulted in a brittle film with cracks across the entire membrane.

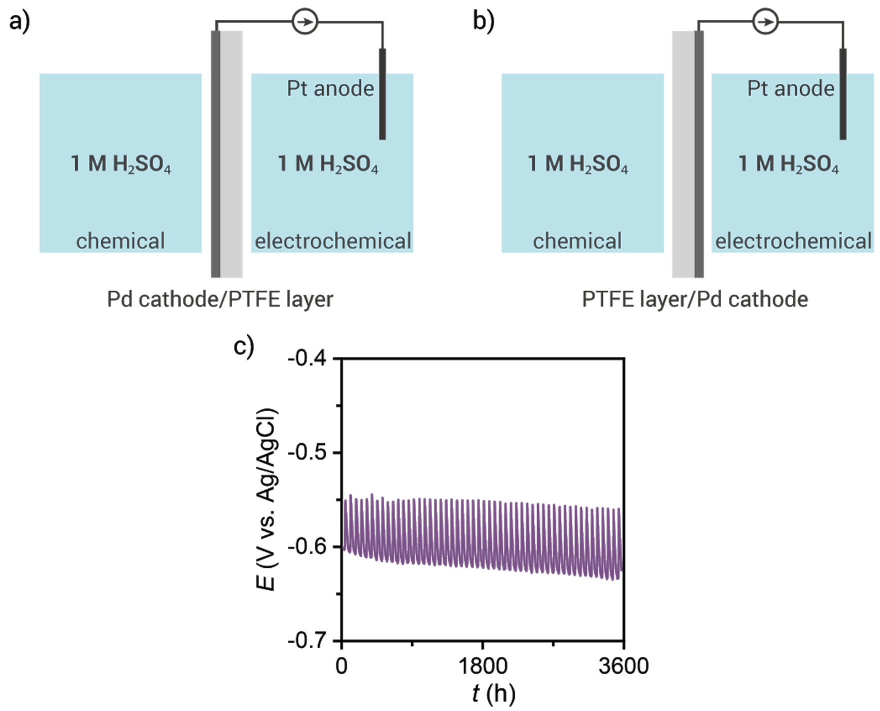


Figure S6. Electrolytic palladium membrane cell architecture with Pd/PTFE configured such that the PTFE support faced (a) the electrochemical compartments and (b) the chemical compartment.

(c) Voltage of cell for Pd/PTFE configuration shown in (b). The Pd/PTFE configuration in (a) caused a termination of program and –10 V limit (not shown). A 100 mA current was applied in both cases.

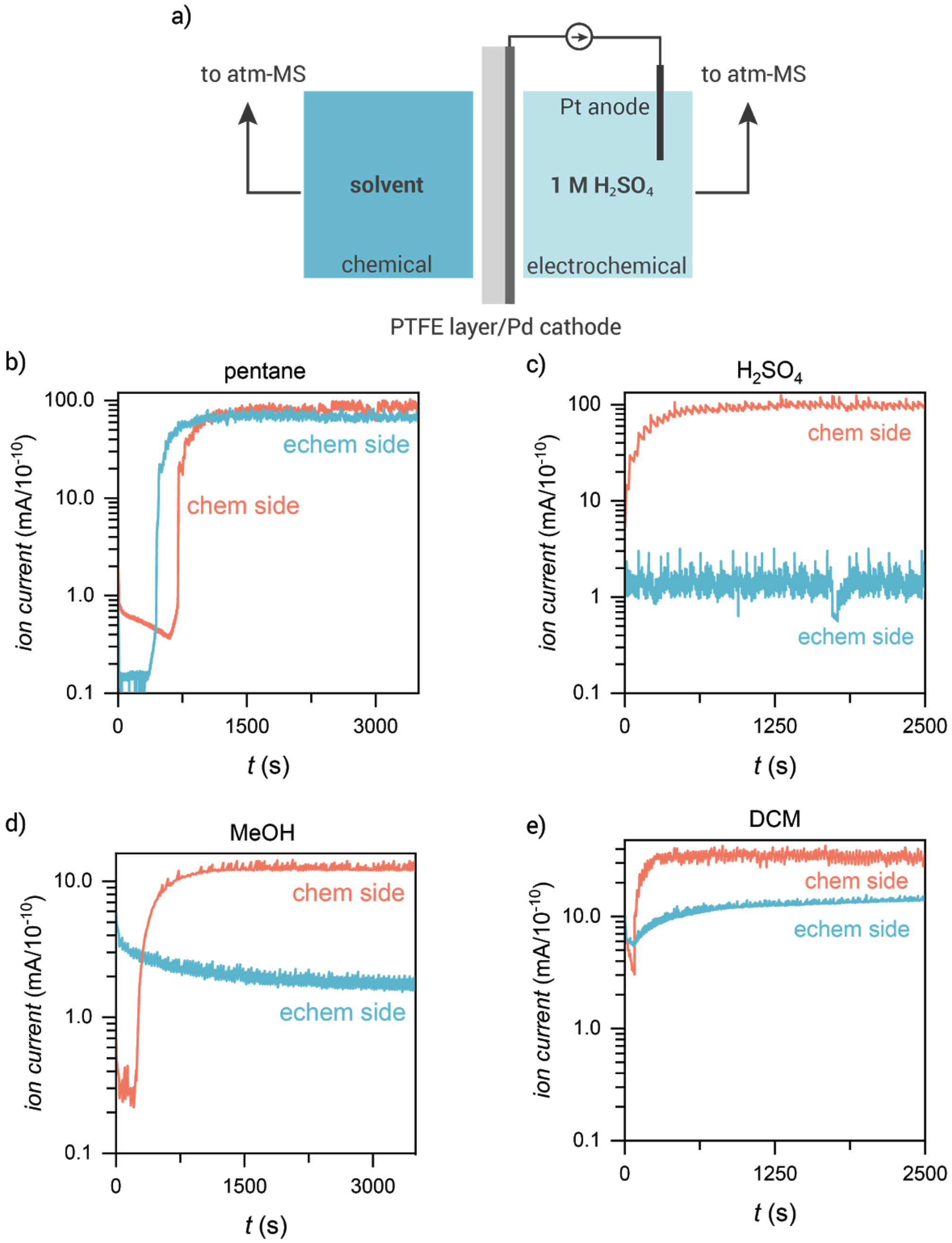


Figure S7. Hydrogen flux measurements in the electrolytic Pd/PTFE membrane reactor. (a) Cell setup for atmospheric mass spectrometer data. Ion current at 2 m/z (H_2) as a function of time in both compartments with (b) pentane, (c) H_2SO_4, (d) MeOH, and (e) DCM in the chemical compartment.
A current of 100 mA was applied at t=0–300 s. Equilibrated ion currents were used to calculate the ratio of chemical:electrochemical H_2 evolution.

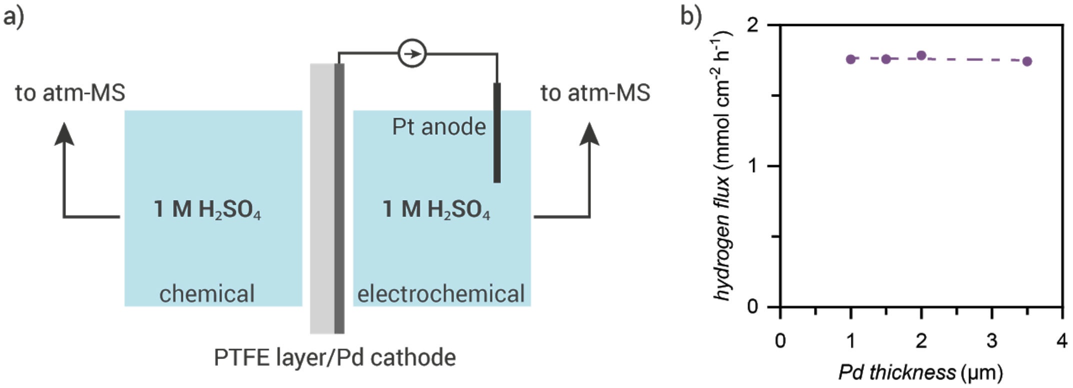


Figure S8. (a) Cell architecture and (b) measurements for hydrogen flux in the electrolytic Pd/PTFE membrane reactor for different thicknesses of Pd (1 μm, 1.5 μm, 2 μm, and 3.5 μm) with 1 M H_2SO_4 on both sides of the membrane.

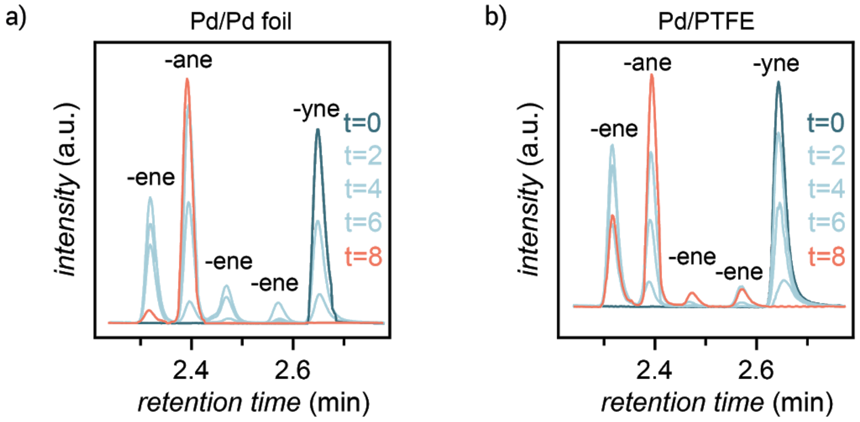


Figure S9. Gas chromatography–mass spectrometry (GC–MS) measurements of the hydrogenation reaction of 1-hexyne to 1-hexenes (labelled -ene) and *n*-hexane (labelled -ane) using (a) Pd/Pd foil and (b) Pd/PTFE membranes. Aliquots were sampled every 2 hours starting at t=0 (teal) to t=8 (orange). The reaction was run at 50 mA applied current with 1 M H_2SO_4 in the electrochemical compartments and pentane in the chemical compartment.

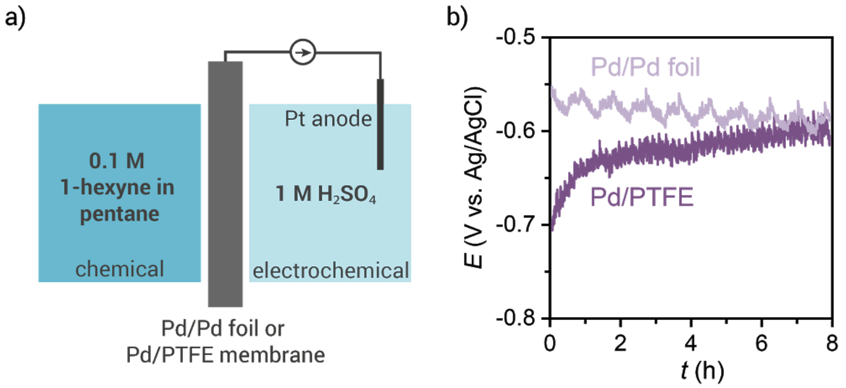
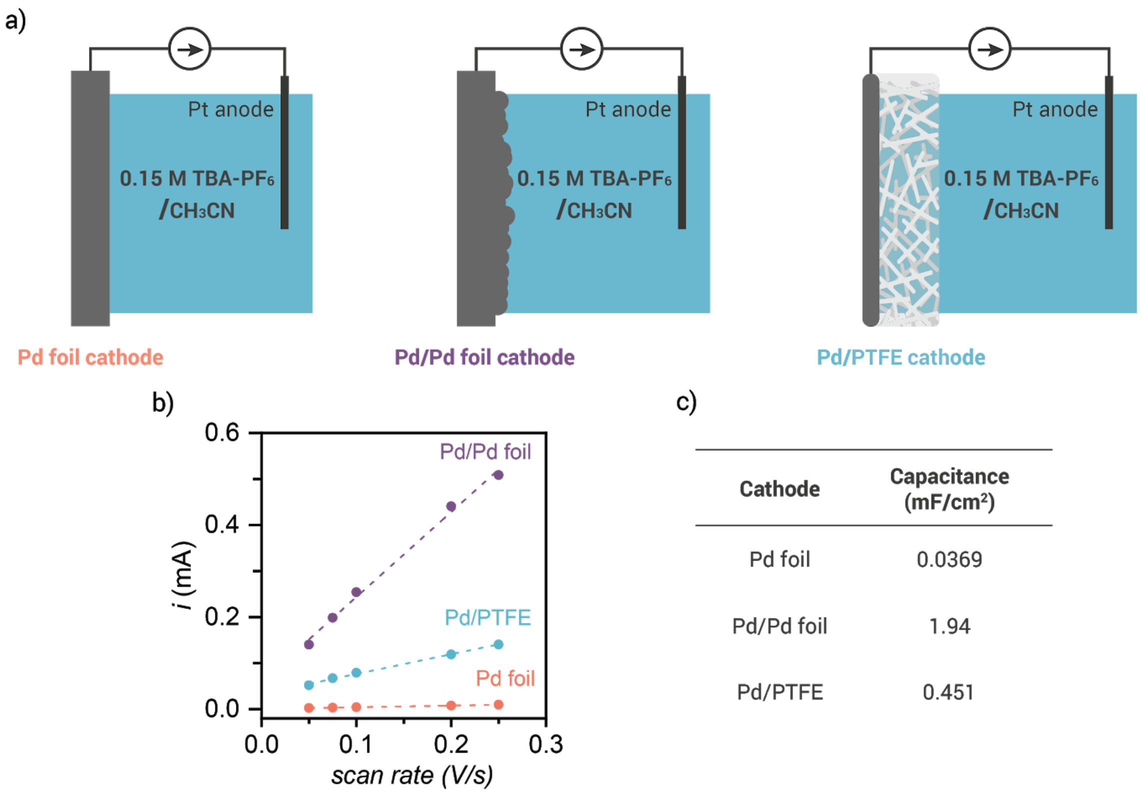


Figure S10. (a) Cell architecture and (b) voltages required to hydrogenate using Pd/Pd foil and Pd/PTFE membranes in 1-hexyne reaction. A 50 mA current was applied.



Cathode	Capacitance (mF/cm^2)
Pd foil	0.0369
Pd/Pd foil	1.94
Pd/PTFE	0.451

Figure S11. (a) Cell configurations and (b) double-layer capacitance measurements of Pd foil, Pd/Pd foil and Pd/PTFE cathodes. (c) Double-layer capacitance values calculated from measured data in (b). The dotted lines represent lines of best fit for the five data points. The geometric surface area of all cathodes was 1.22 cm^2.

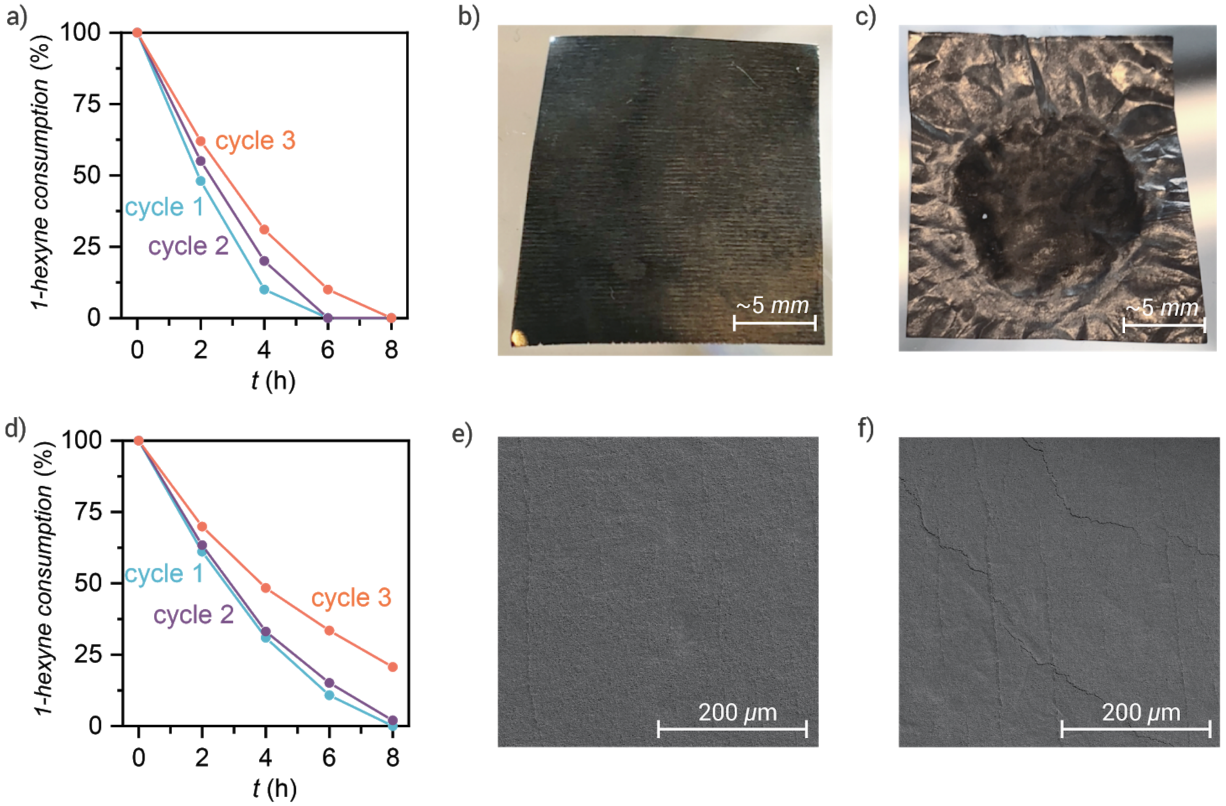


Figure S12. Stability tests for a single Pd/Pd foil (a, b, c) and Pd/PTFE membrane (d, e, f) in the electrolytic membrane reactor. (a, d) Three hydrogenation cycles of 1-hexyne in pentane for 8 hours of reaction. (b, c) Photographs of the Pd foil membrane before and after 3 cleaning/electrodeposition cycles (~9 hydrogenation cycles). A small pinhole formed in the foil during the third cleaning cycle. (e, f) SEM images of the Pd/PTFE membrane before and after 3 reaction cycles showing cracks on the membrane after the third cycle. All reactions were run at 50 mA applied current with 1 M H_2SO_4 in the electrochemical compartments.

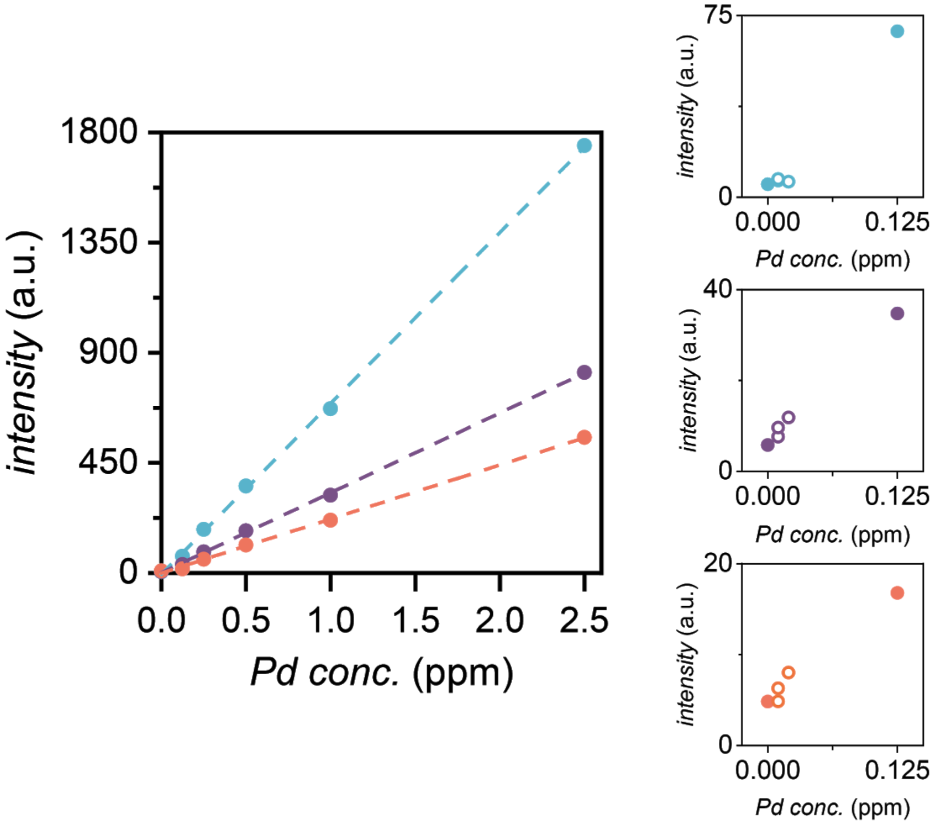


Figure S13. ICP–OES measurements after 1–3 hydrogenation cycles with the Pd/PTFE membranes (hollow dots) and calibration curves (solid dots) for three emission spectra at 361 nm (blue), 340 nm (purple), and 324 nm (orange). (a) Calibration curves used to determine sample concentration.
(b) A region between 0 and 0.125 ppm Pd concentration in which all three samples reside. A line of best fit is plotted on each of the calibration curves and was used to determine the sample concentrations.

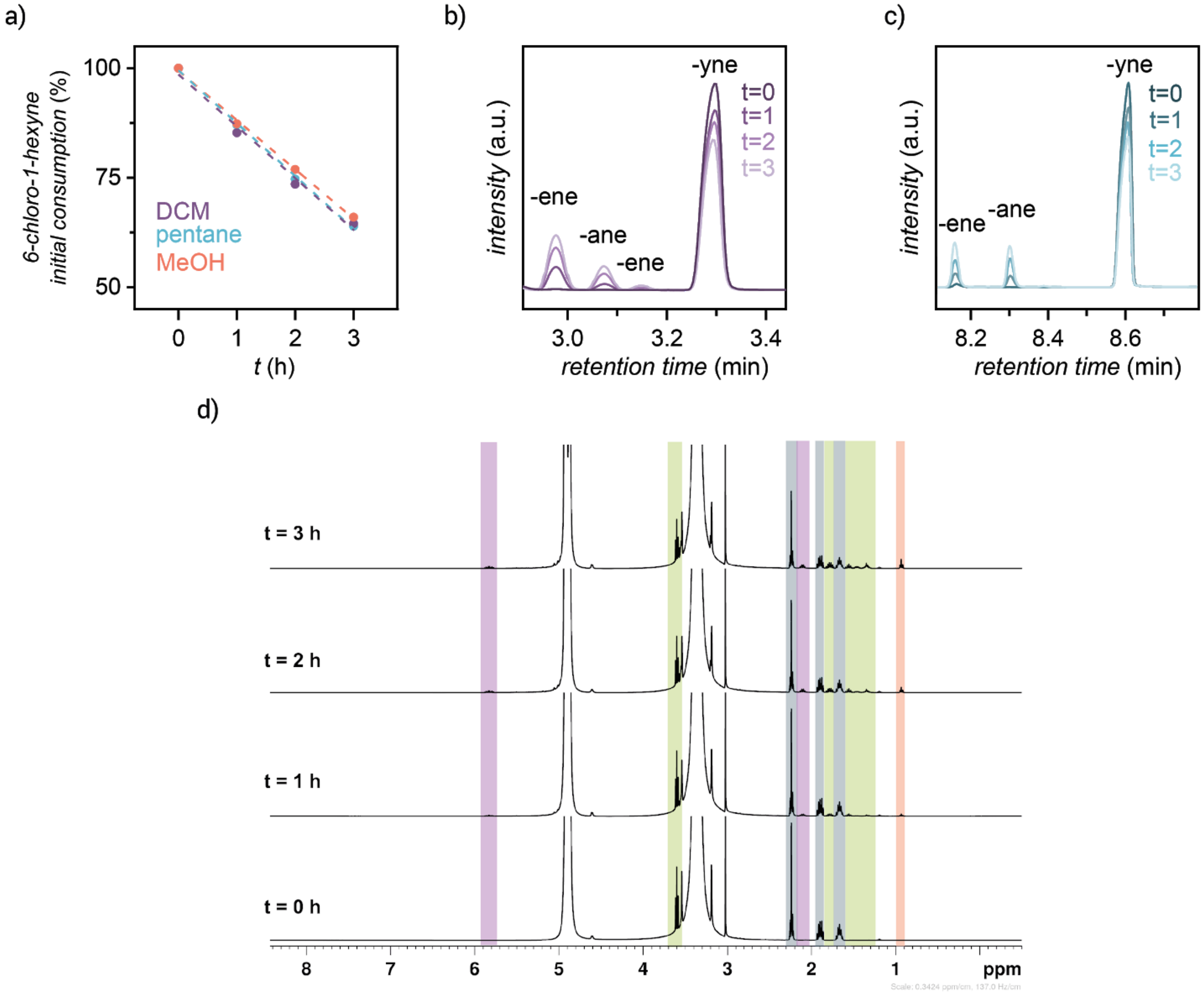


Figure S14. (a) Initial 3 hours of consumption of 6-chloro-1-hexyne in pentane, DCM, and MeOH using the Pd/Pd foil membrane. Corresponding product quantification in (b) pentane, (c) DCM, and (d) MeOH. GC–MS chromatograms in (c & d) show hydrogenation of 6-chloro-1-hexyne (labelled -yne) to 6-chloro-1-hexene (labelled -ene) and 6-chlorohexane (labelled -ane). ^{1}H NMR (25 °C, 400 MHz) in (d) shows hydrogenation of 6-chloro-1-hexyne (blue) to 6-chloro-1-hexene (purple) and 6-chlorohexane (orange). Green peaks indicate a mixture of alkyne, alkene, and alkane. A dimethylsulfone internal standard is shown as a singlet peak at ~3 ppm. A 50 mA current was applied in all cases.

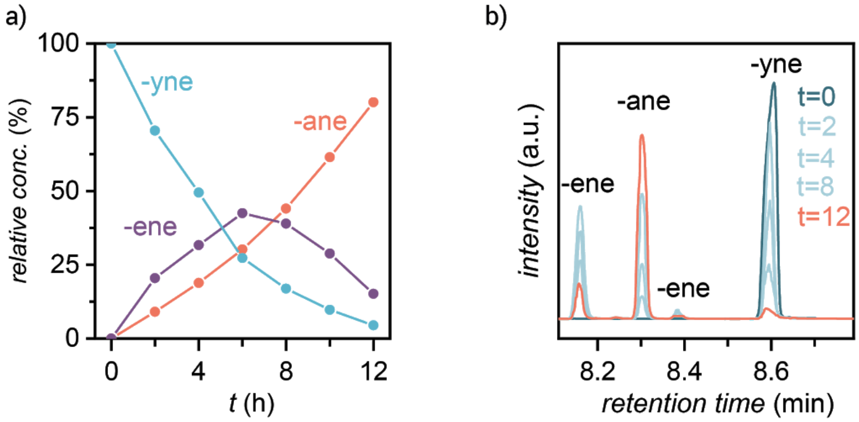


Figure S15. (a) Reaction progress and (b) GC–MS chromatograms for hydrogenation of 6-chloro-1-hexyne (labelled -yne) to 6-chloro-1-hexene (labelled -ene) and 6-chlorohexane (labelled -ane) in pentane using the Pd/PTFE membrane. A 50 mA current was applied.

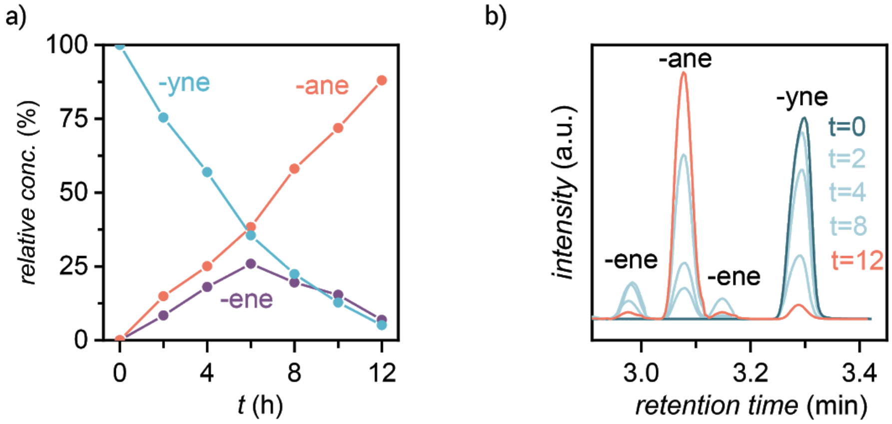


Figure S16. (a) Reaction progress and (b) GC–MS chromatograms for hydrogenation of 6-chloro-1-hexyne (labelled -yne) to 6-chloro-1-hexenes (labelled -ene) and 6-chlorohexane (labelled -ane) in DCM using the Pd/PTFE membrane. A 50 mA current was applied.

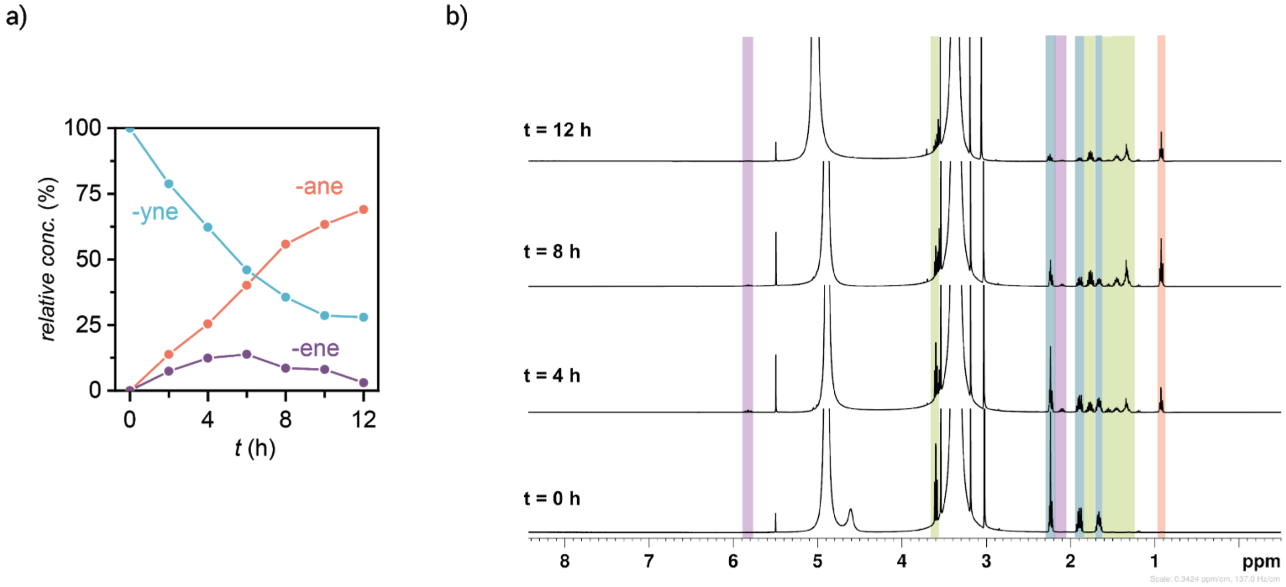


Figure S17. (a) Reaction progress and (b) ^{1}H NMR (25 °C, 400 MHz) for hydrogenation of 6-chloro-1-hexyne (blue) to 6-chloro-1-hexenes (purple) and 6-chlorohexane (orange) in MeOH using the Pd/PTFE membrane. Green peaks indicate a mixture of alkyne, alkene, and alkane. A dimethylsulfone internal standard is shown as a singlet peak at ~3 ppm. A 50 mA current was applied.

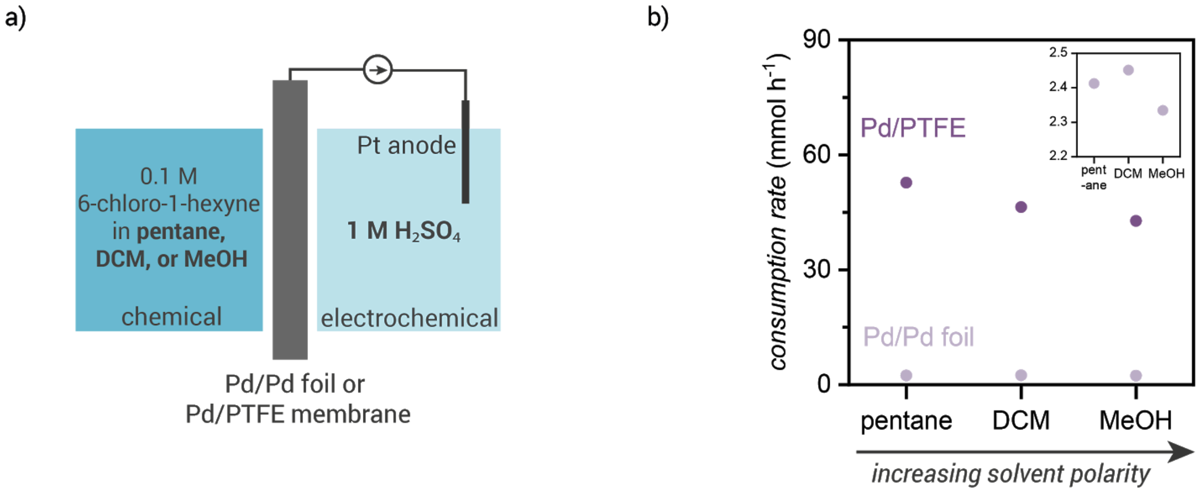


Figure S18. Normalized 6-chloro-1-hexyne hydrogenation data. (a) Cell architecture using the Pd/PTFE membrane reactor and (b) normalized 6-chloro-1-hexyne consumption rates in pentane, DCM, and MeOH with the Pd/Pd foil membrane (light purple) and Pd/PTFE membrane (dark purple). Plot inset in (b) shows small variation in Pd/Pd foil consumption rates. A 50 mA current was applied in both cases and normalized consumption rate was determined for the first three hours of reaction.

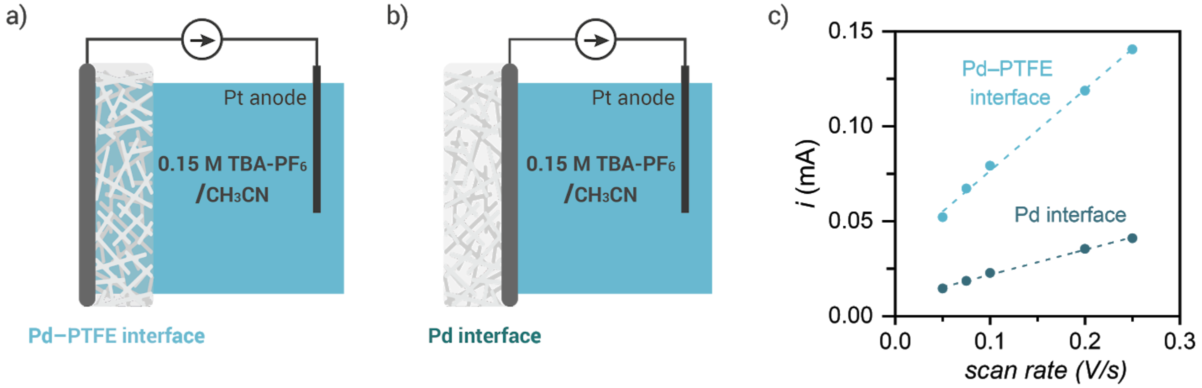


Figure S19. Measurements of electrochemical surface area (ECSA) on both sides of the Pd/PTFE membrane. Cell configurations for measurements of ECSA at (a) the Pd–PTFE interface and (b) the Pd interface. (c) Double-layer capacitance measurements using both configurations. The dotted lines represent lines of best fit for the five data points. The double-layer capacitance values of the Pd–PTFE and Pd interfaces were 0.451 mF cm^{-2} and 0.139 mF cm^{-2}, respectively. The geometric surface area of the Pd/PTFE cathode was 1.22 cm^{2}.