Supplementary Materials for

Electrochemical Reduction of CO₂ to Synthesis Gas with Controlled

CO/H₂ Ratios

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Sample preparation:

40% Pd on Vulcan carbon (Pd/C, E-Teck) was dispersed in isopropanol solution containing 0.01 wt% Nafion, with a catalyst concentration of 2 mg/mL. After sonication, a total amount of 50 μ L of Pd/C ink was deposited onto 1 cm x 3 cm rectangular glassy carbon, covering the bottom 1 cm × 1 cm area and dried in air. The resulting catalyst loading was 100 μ g Pd/C (including 40 μ g Pd and 60 μ g C).

Gas chromatography measurements

When performing CO₂RR at more negative potentials (higher current densities), the CO₂RR was shortened to 30, 15 and 10 minutes to avoid over-pressurization of gas above the electrolyte. In such way, the concentration of CO and H₂ was controlled below 1%, which was also in the concentration range when calibrating the GC. Fig. S7 shows the GC spectra of the same amount (100 μ L) of air, gas in the headspace right after the cell was sealed, and the gas in the sealed headspace after two hours. Negligible amount of O₂/N₂ was introduced during the sealing process. After two hours, there is a slight increase of the O₂/N₂ concentration, but the concentration was only 0.28%/0.77% (Table S6). The CO₂RR process was within one hour, and therefore gas leak was negligible during the reaction.

In situ X-ray absorption spectroscopy measurements

In situ X-ray absorption fine structure (XAFS) measurements were taken at the B2-2 beamline at the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory. The Pd K-edge (24350 eV) XAFS spectra were collected under electrochemical environment using the fluorescence detection method. The Pd/C catalyst was loaded over graphite papers as the working electrode. Three spectra were collected at each potential holding. The data were processed and fitted using the Ifeffit package. The Pd-Pd paths used in fitting was generated based on the crystal structure of metallic Pd and FCC PdH (NaCl structure).

In situ X-ray diffraction measurements

In-situ X-ray diffraction measurement was performed at the 17-BM beamline (λ =0.72768 Å) of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). A few drops of 40 wt% Pd/C catalyst slurry were deposited on graphite papers and used as the working electrode. Other conditions were identical to the electrochemical measurements. Two-dimensional XRD patterns were collected with a Perkin-Elmer amorphous silicon detector and the diffraction rings were integrated using the GSASII packages. The instruments parameters were calibrated using a LaB6 standard placed at the same location of the working electrode.

In situ Infrared Reflection Absorption Spectroscopy (IRRAS).

In situ IRRAS measurements were carried out with Nicolet iS50 FT-IR spectrometer equipped with an Atype MCT detector cooled with liquid nitrogen. An unpolarized light beam was used. The spectral resolution was set to 4 cm⁻¹ and 289 scans were averaged to obtain each spectrum. Spectra are reported in absorbance units defined as $A=-log(R/R_o)$, where R and R_o represent the reflected IR intensities corresponding to the sample and reference single beam spectrum respectively.

A piece of Pd foil was used as the working electrode. The Pd foil was flame-annealed and checked using cyclic voltammetry in HClO₄ prior to *in situ* IRRAS measurements. The Pd foil was held at 0.2 V while bubbling CO for 5 minutes to form a monolayer of CO. Subsequently, the foil was transferred to the IRRAS electrochemical cell to acquire IR spectrum. After that, the Pd foil was held at -0.2V for 10 minutes to allow Pd hydride formation, followed by CO bubbling, and then transferred to the cell for IR spectrum acquisition. The FTIR spectra were compared at the open circuit voltage (OCV) and 0.3 V vs. RHE, where both Pd and PdH should remain stable. Reference spectra were collected at 0.2 V vs. RHE in 0.1M HClO₄ saturated with CO.

Faradaic efficiency calculation

Faradaic efficiency of CO and H₂ is calculated based on the following equation:

$$n_{CO(g)} = C_{CO} \times 10(mL)/22400(mLmol^{-1})$$

 $n_{CO(dissolved)} = 1.774 \times 10^{-5} \times 45(mL) \times 1(g/mL)/18(gmol^{-1}) \times C_{CO}$

$$FE_{CO} = \frac{(n_{CO(g)} + n_{CO(dissolved)}) \times 2 \times 96485(Cmol^{-1})}{\int_{0}^{t} idt} \times 100\%$$

 $n_{CO(g)}$ is the CO amount in the headspace; C_{CO} is the CO concentration determined from GC; and 10mL is the headspace volume.

 $n_{CO(dissolved)}$ is the CO amount dissolved in the electrolyte, which is calculated based on the Henry's law. 1.774 × 10⁻⁵ is the molar solubility of CO in water at CO partial pressure of 1 atm at room temperature (CRC handbook); and 45mL is the electrolyte volume.

 FE_{co} is the Faradaic efficiency of CO, $96485(Cmol^{-1})$ is the Faraday Constant, 2 is the number of electrons transferred in the CO₂RR to CO, *i* (ampere) is the total current, and *t* (seconds) is the reaction time at each potential.

Faradaic efficiency of H₂ is calculated using the same equations, except for its molar solubility in water of 1.411×10^{-5} (CRC handbook)

CO/H₂ partial current density calculation

Partial current density of CO or H₂ is calculated based on the following equation:

 $j_{CO} = \frac{(n_{CO(g)} + n_{CO(dissolved)}) \times 2 \times 96485(Cmol^{-1})}{A \times t}$

where $n_{CO(g)} + n_{CO(dissolved)}$ and t have the same definitions as in the previous Faradaic efficiency calculation. A (cm²) is the geometric electrode area.

Computational Methods

The zero point energy (ZPE) correction is calculated as $ZPE = \sum_i hv_i$ where h is Planck's constant and v_i is the frequency of the ith vibrational mode of the adsorbate molecule. The vibrational modes were calculated explicitly under the frozen slab approximation. The vibrational frequencies were computed by displacing the adsorbate molecule by 0.005 Å in each of the three Cartesian directions and diagonalizing the resulting dynamical matrix. The entropies and vibrational frequencies of molecules in gas phase were taken from NIST database (http://cccbdb.nist.gov).



Figure S1. Typical cyclic voltammogram of 40wt% Pd/C in CO₂-saturated 0.5 M NaHCO₃, collected at a sweep rate of 50 mV/s.



Figure S2. LSV of Pd/C and C in CO₂-saturated 0.5 M NaHCO₃. The sweep rate was 10 mV/s.



Figure S3. Typical EXAFS fitting of Pd/C electrocatalyst (-0.05 V vs RHE) in R (a) and q (b) spaces.

Entry	Sample	Shell	R(Å)	C.N.	$\Delta E_0 (eV)$	σ^{2} (Å ²)
1	Pd foil	Pd-Pd	2.737	12.0		0.006
2	0.685V	Pd-Pd	2.732(3)	9.9(5)	1.0	0.006
3	0.300V	Pd-Pd	2.736(3)	9.0(5)	4.0	0.006
4	0.100V	Pd-Pd	2.735(3)	9.8(7)	1.0	0.007
5	0.000V	Pd-Pd	2.742(4)	9.6(9)	0.9	0.006
6	-0.050V	Pd-Pd	2.748(6)	9.7(8)	0.1	0.007
7	-0.100V	Pd-Pd	2.818(5)	9.7(9)	-6.5	0.008
8	-0.300V	Pd-Pd	2.828(4)	9.9(9)	-5.0	0.007
9	-0.500V	Pd-Pd	2.842(8)	10.7(9)	-4.3	0.007

Table S1. The *in-situ* Pd K-edge EXAFS fitting results for Pd/C electrocatalyst during the CO₂RR.



Figure S4. The raw XRD diffraction patterns of the *in situ* XRD measurements of Pd/C electrocatalyst during the CO_2RR (LSV from 0.68 to -0.56 V vs RHE from bottom to top). The time interval between each profile is 50 mV. Pd and PdH standards are presented based on the theoretical crystal structures (calculated using Mercury 3.0).

Species	Adsorption sites	BE	Adsorption sites marked on Pd(111)
Н	site-1	-0.58	
	site-2	-0.54	
	site-3	-0.03	
СО	site-1	-2.03	22
	site-2	-2.00	the particular for
	site-3	-1.40	
НОСО	site-3	-2.21	

Table S2. Binding energies (BE in eV) of H, CO and HOCO on Pd(111).

Table S3. Binding energies (BE in eV) of H, CO and HOCO on PdH(111).

Species	Adsorption	BE	Adsorption sites marked on PdH(111)	
	sites			
Н	site-1	0.12		
	site-2	0.24		
СО	site-1	-0.39		
	site-2	-0.50		
НОСО	site-2	-1.73		

Species	Adsorption	BE	Adsorption sites marked on Pd nanoparticle
	sites		
Н	site-1		
	site-2	-0.47	
	site-3	-0.59	
	site-4	-0.62	
	site-5	-0.53	3
	site-6	-0.48	
СО	site-1	-1.70	
	site-2	-2.03	6
	site-3	-2.15	
	site-4	-2.19	
	site-5	-2.12	
	site-6	-1.98	
НОСО	site-1	-2.52	
	site-7	-2.30	

Table S4. Binding energies (BE in eV) of H, CO and HOCO on Pd (Pd₃₈) nanoparticle.

Table S5. Binding energies (BE in eV) of H, CO and HOCO on PdH (Pd₃₈H₅₅) nanoparticle.

Species	Adsorption	BE	Adsorption sites marked on PdH
	sites		nanoparticle
Н	site-1	0.19	
	site-2	0.54	
	site-3	-0.31	
СО	site-1	-1.37	
	site-2	-0.79	
	site-3	-1.15	
НОСО	site-1	-1.98	
	site-2	-1.77	



Figure S5. IRRAS of Pd and PdH at OCV and 0.3V vs. RHE. Reference spectra were collected at 0.2 V vs. RHE in 0.1M HClO4 saturated with CO.



Figure S6. 40wt% Pd/C after CO_2RR at different potentials for total three hours. The inset is the particle size distribution, and the error bar is the standard deviation based on at least 300 particle counts.



Figure S7. GC spectra of the same amount of air, gas in the sealed headspace, and gas in the sealed headspace after two hours.

	area of O_2 (concentration)	area of N_2 (concentration)
Air	730 (21%)	2225 (78%)
Gas in sealed headspace	4 (0.11%)	9 (0.32%)
Gas in sealed headspace after 2 hours	10 (0.28%)	22 (0.77%)

Table S6. Integrated	l GC signals	of O_2	and N ₂ .
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