

A Unified Electrocatalytic Description of the Action of Inhibitors of Nickel Carbon Monoxide Dehydrogenase

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Supporting Information

Figure S1. CO product inhibition at -760mV.

Figure S2. Effect of cyanide on CO₂ reduction, using a lower concentration of cyanide.

Figure S3. Cyanide inhibition of the CO oxidation activity of CODHI_{Ch} observed at two different potentials.

Figure S4. Cyanate inhibition of CO₂ reduction activity of CODHI_{Ch}.

Figure S5. EPR spectra of CODHI_{Ch} at different powers and temperatures.

Figure S6. Comparison of the rates of inhibition by cyanide and sulfide.

Table S1. K_m values for CO₂ and inhibition constants for CO product inhibition, at two different potentials

Figure S1. CO product inhibition at -760mV. The CO concentration was held constant at 20% during the experiment. The percentage numbers indicate the percentage of CO₂ used in the total gas atmosphere. Argon was used to control the total gas balance. The inset figure shows the resulting Lineweaver-burk plot.

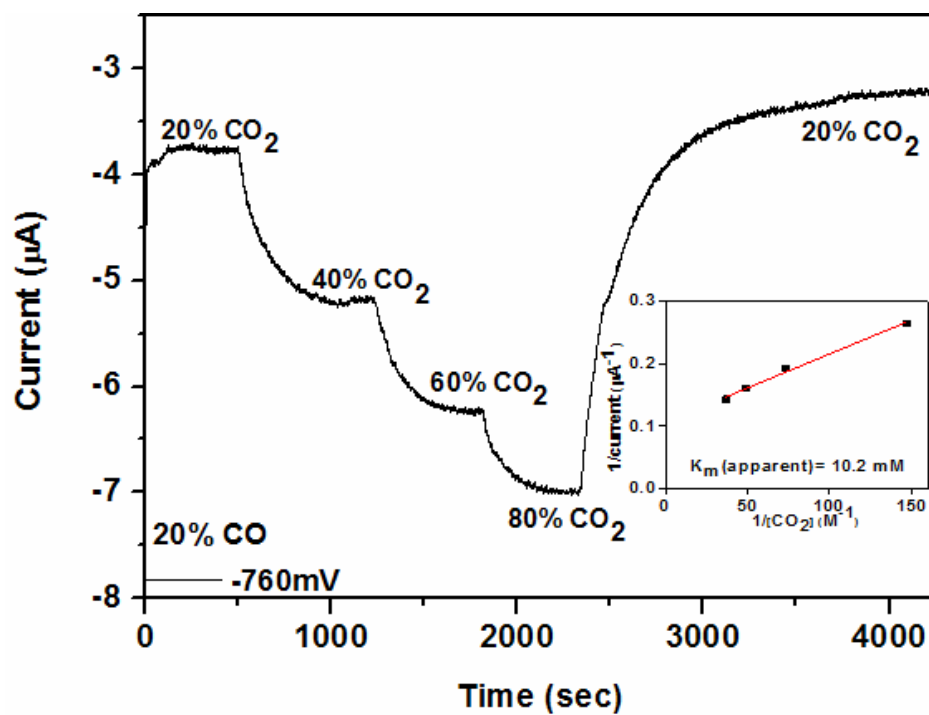


Figure S2: Cyclic voltammograms showing the potential and time dependence of inhibition of CODH I_{Ch} by cyanide at lower concentration than shown in Figure 3a. After a complete cycle, KCN was injected into the electrochemical cell at -0.74 V to give a final concentration of 0.1 mM. Experimental conditions: 25°C, 0.2 M MES buffer (pH=7.0), scan rate 1 mV s⁻¹

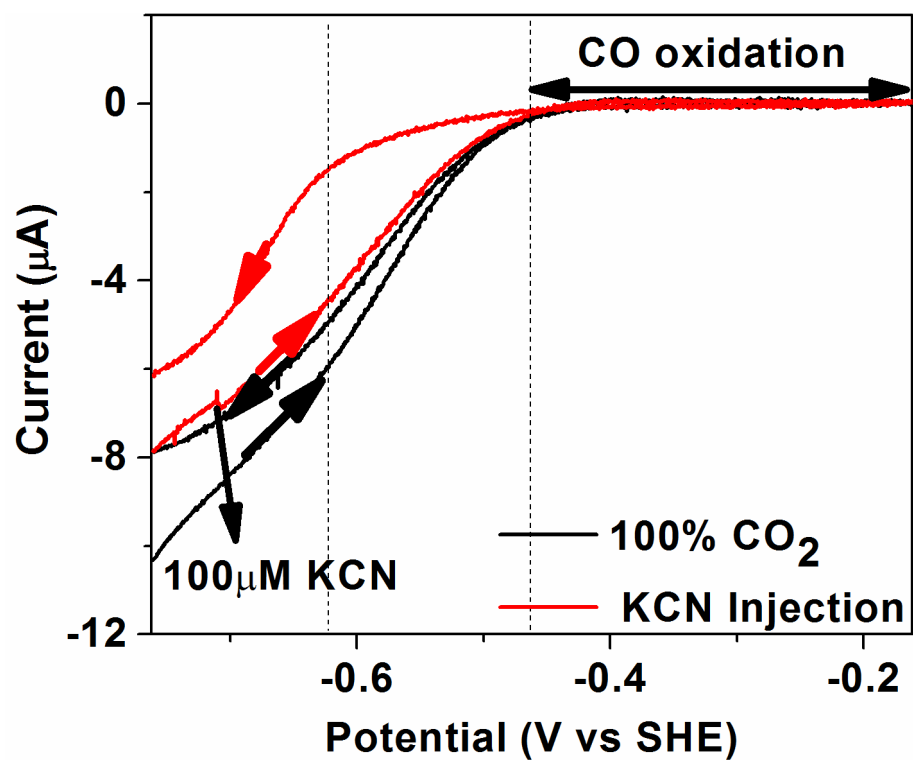


Figure S3. Inhibition of the CO oxidation activity of CODH_{Ch} by cyanide observed at two different potentials. Experimental conditions: 25°C, 0.2 M MES buffer (pH=7.0), rotation rate 3500 rpm and scan rate 1mV/sec

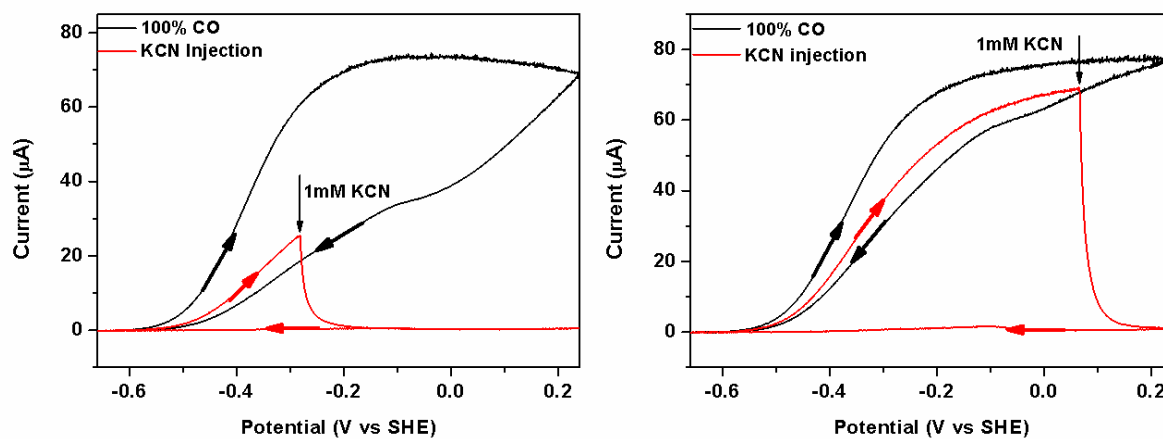


Figure S4 Inhibition of CO₂ reduction by cyanate. Different concentrations of potassium cyanate (final concentrations are shown in the figure) were added. Experimental conditions: 25°C, 0.2 M MES buffer (pH=7.0), rotation rate 3500 rpm.

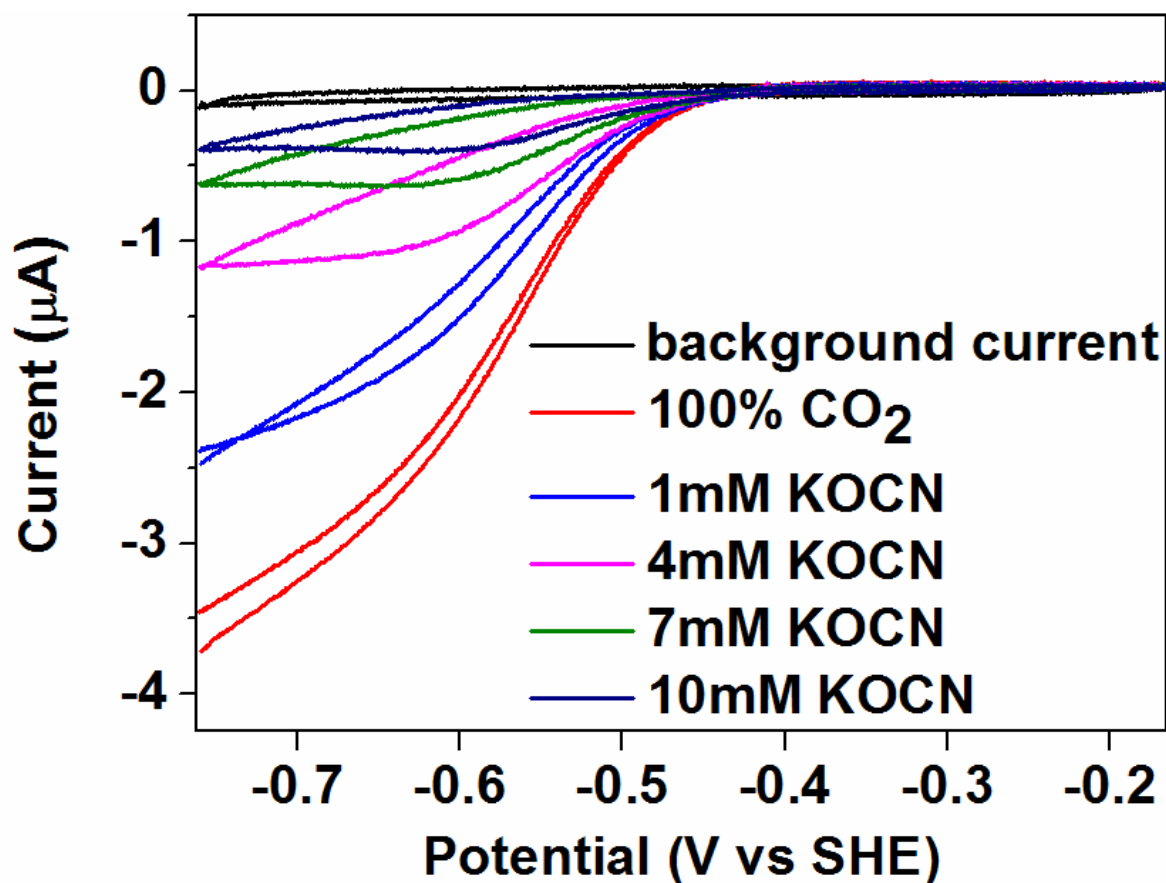


Figure S5: EPR spectra of (Left panel) CO-reduced CODH-I at 12 K: (A) Power = 41 mW; (B) Power = 5 mW. (Right panel) benzyl viologen-oxidized enzyme at (A) 10 K and 41 mW, (B) 10 K and 0.27 mW and (C) 26 K and 0.27 mW.

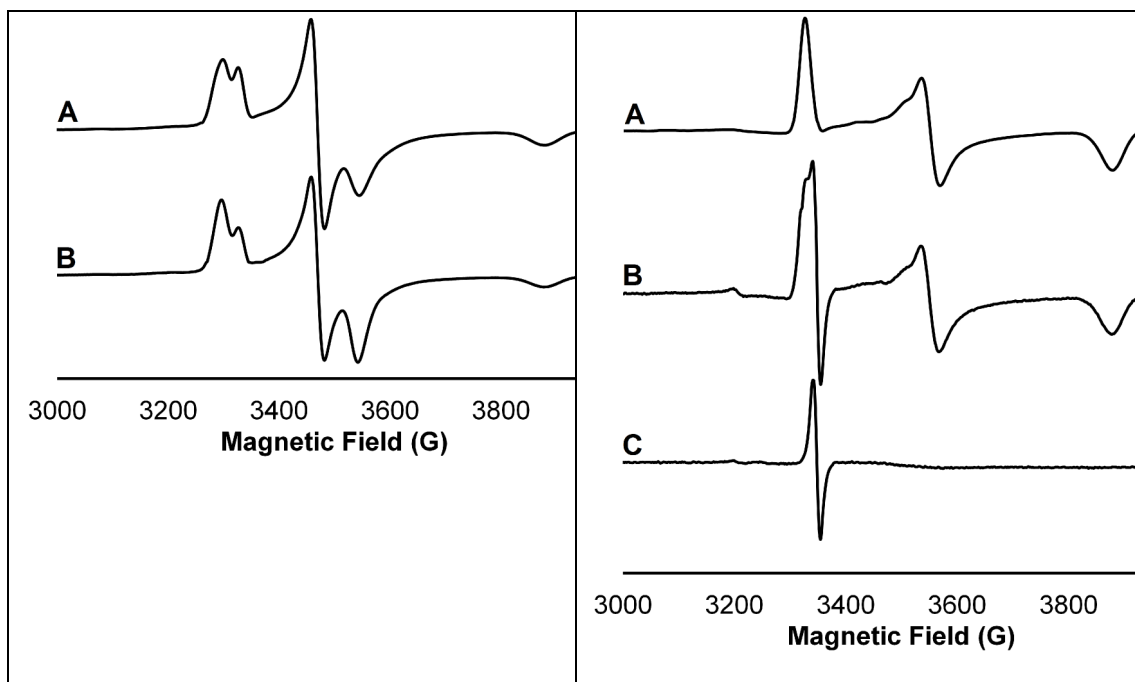


Figure S6. Comparison of the rates of inhibition by cyanide and sulfide. In each case, 1mM potassium cyanide or 1mM sodium sulfide was added at +160 mV. At this potential sulfide is a good inhibitor and binds much faster than cyanide. Experimental condition: 25°C, 0.2 M MES buffer (pH=7.0), rotation rate 3500 rpm.

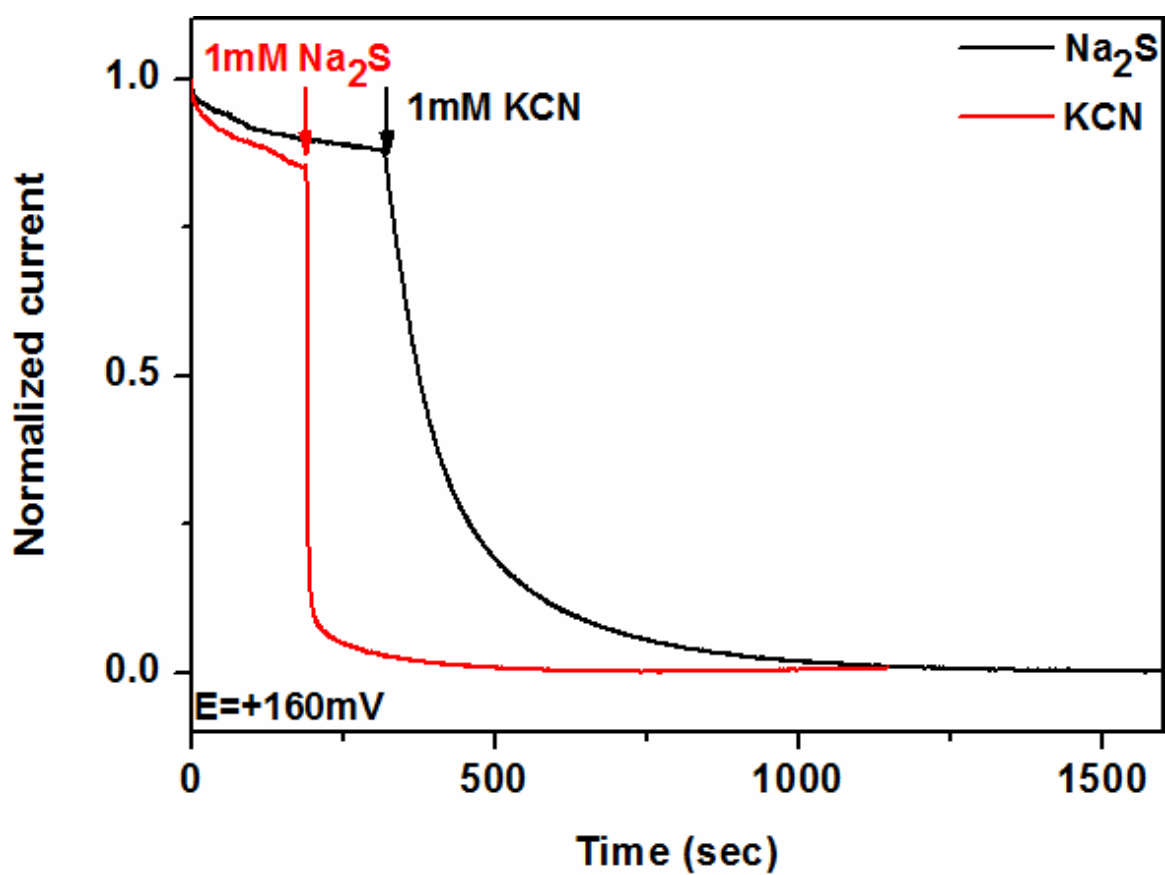


Table S1 K_m values for CO_2 and inhibition constants K_i for CO product inhibition at two different potentials

	-560 mV	-760 mV
No CO present (K_m for CO_2)	8.06 mM	7.08 mM
20% CO (apparent K_m for CO_2) (CO inhibition constant)	40.9 mM (46 μM)	10.95 mM (337 μM)