Supporting Information

Curvature-Dependent Selectivity of CO_2 Electrocatalytic Reduction on Cobalt Porphyrin Nanotubes

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1. CHE Model

The computational hydrogen electrode (CHE) model was used to model the voltage dependence of the free energy pathways and, in concert with the binding energy calculations, to find the lowest energy pathways.[1] In this model, the chemical potential of a proton–electron pair at 0 V (vs RHE) is by definition equal to one-half the chemical potential of molecular hydrogen at 101,325 Pa and at all temperatures. The chemical potential (μ) of each intermediate, calculated at 298.15 K, was varied as a function of the electrical potential (U) according to
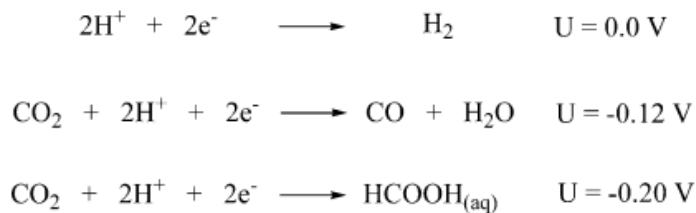
$$\mu(U) = \mu(0V) + neU,$$

where e is the elementary charge of an electron, and n is the number of proton–electron pairs consumed to form the species from CO_2. Using this method, the free energy of elementary electrochemical reaction sequences can be calculated as a function of the applied electrical potential. As the electrical potential is made more negative in the CHE, the free energies of the more reduced adsorbates will decrease by neU; thus, at a certain potential the entire pathway will become exergonic (downhill in free energy). The potential at which this occurs is referred to as the limiting potential, the elementary chemical step that dictates the limiting potential is called the potential-limiting step, and the first pathway (on each surface) to become exergonic is referred to as the lowest-energy pathway.
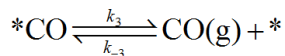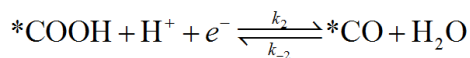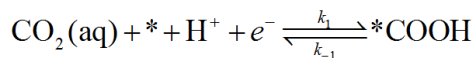
2. Equilibrium Potentials

The calculated equilibrium potentials are -0.164 V for $CO_2 + 2 \times (H^+/e^-) \rightarrow HCOOH$ and -0.153 V for $CO_2 + 2 \times (H^+/e^-) \rightarrow CO + H_2O$ (after adding -0.248 eV energy correction to CO, due to a limitation of PBE to describe the standard formation energies, as suggested by Calle-Vallejo).[2] Those numbers are in agreement with the experimental numbers of -0.12 and -0.20 V, as shown in Scheme S1.[3]

Scheme S1. HER and two $2H^+/2e^-$ CO_2ER reactions

$$2H^+ + 2e^- \longrightarrow H_2 \qquad U = 0.0 \text{ V}$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \qquad U = -0.12 \text{ V}$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH_{(aq)} \qquad U = -0.20 \text{ V}$$

3. Microkinetic Modelling

The microkinetic modeling methods utilized here[4] for CO partial current density calculations are based on the assumption that CO_2 adsorption, CO_2 protonation, COOH* protonation as well as CO* desorption are the main steps involved. The reactions can be illustrated by the following steps:

$$CO_2(aq) + * + H^+ + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} *COOH$$

$$*COOH + H^+ + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} *CO + H_2O$$

$$*CO \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CO(g) + *$$

The rate constants of step 1 and step 2, namely, the electrochemical steps, can be written as

$$k_i = A_i \left(-\frac{E_{a,i}^0}{k_B T} \right) \exp \left(-\frac{e\beta_i \left(U - U_i^0 \right)}{k_B T} \right)$$

The rate constants of step 3 can be written as

$$k_j = \gamma_j \exp \left(-\frac{E_b}{k_B T} \right)$$

The coverages and the corresponding current densities can be analyzed using a steady-state approximation. The current density for metals is calculated using $j = -22.2\,\mu C \cdot cm^{-2} \cdot TOF$. For CoPorNTs, the calculated density of the catalytically active sites are about twice as those on metals, when assuming the active sites on metal surfaces are about 5%. Therefore, the current density for CoPorNTs is presumed as $j = -44.4\,\mu C \cdot cm^{-2} \cdot TOF$.

4. Experimental Corrections of Free Molecules

For gas-phase species, the traditional PBE exchange-correlation functional fails to correctly calculate the free energy of some gas molecules.[5] Therefore, we use the experimental free energy data as a reference. The energy corrections of the crucial gaseous or liquid products discussed are listed in Table S1:

Table S1. Experimental corrections of free molecules

Free molecules	G/eV	Experimental corrections/eV	E_{ele}/eV	ZPE/eV	TS/eV
CO_2(g)	-23.190	-0.164	-23.000	0.308	0.662
H_2(g)	-6.901	-	-6.762	0.266	0.405
H_2O(l)	-14.255	-	-14.242	0.572	0.585[g]
CO(g)	-15.530	0.248	-14.806	0.136	0.612
HCOOH(g)	-29.764	-	-29.880	0.886	0.770
CH_4(g)	-23.397	0.004	-24.030	1.214	0.577
CH_3OH(l)	-29.580	-0.021	-30.222	1.364	0.742[g]
HCHO(g)	-22.046	-0.044	-22.144	0.731	0.677

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