

SUPPLEMENTARY INFORMATION

Operando electrochemical spectroscopy for CO on Cu(100) at pH 1 to 13: Validation of Grand Canonical Potential predictions

Jack H. Baricuatro^{§a*}, Soonho Kwon^{§b}, Youn-Geun Kim^a, Kyle D. Cummins^a, Saber Naserifar^b, and William A. Goddard III^{b*}

[§]First authorship is equally shared

^a*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA*

^b*Liquid Sunlight Alliance (LiSA) and Materials and Process Simulation Center (MSC), California Institute of Technology, Pasadena, California 91125, USA*

*To whom correspondence may be addressed: wag@caltech.edu, ORCID:0000-0003-0097-5716; jackhess@caltech.edu, ORCID: 0000-0002-9210-344X

TABLE OF CONTENTS

S1. Derivation of Grand Canonical Potential (GCP)

Figures and Table

- **Figure S1.** The top view of surface models with various adsorbates on Cu(100) with 2x2 supercell. The blue, white, red, and gray spheres represent Cu, H, O and C, respectively.
- **Table S1.** The GCP parameters for all surface models.
- **Figure S2.** The onset potential of CO adsorption as a function of pH; the onset potential is operationally defined as the earliest (most positive) potential at which the CO adsorption peak appears in Figure 1.
- **Figure S3.** Charge difference of $(1/2 \text{ ML CO} + 0 \text{ ML H}^*) - (1/2 \text{ ML CO} + 1/2 \text{ ML H}^*)$. The yellow and blue indicate charge accumulation and depletion, respectively. Generally, the dominant contributor to the interaction between the carbonyl and 3d-transition metal is the charge transfer from CO 5σ to $3d_{z^2}$ and the back-donation from $3d_{xz}$ to CO $2\pi^*$. In the presence of coadsorbed H^* , the donation from 5σ and the back-donation to $2\pi^*$ are reduced leading to accumulation and depletion of charge on the respective molecular orbitals in the charge difference plot.
- **Figure S4.** At pH 7 in 0.10 M KClO_4 : (a) Surface free energy diagram with various coverages of H^* , OH^* , and O^* as a function of applied potential. (b) The CO adsorption free energy as a function of U and θ_{H^*} (c) Equilibrium surface coverage of surface species as a function of potential. Figures (d-f) are analogous to (a-c) except that they pertain to pH = 13 in 0.10 M KOH.

S1. Derivation of Grand Canonical Potential (GCP)

The electrochemical half-cell is an open system in which electrons can flow in and out of the electrode during electrochemical reaction at a fixed applied potential (U) or electrochemical potential (μ_e). Therefore, the free energy should be described properly in terms of the grand canonical free energy, which is defined as,

$$G(n;U) = F(n) - ne(U_{SHE} - U) \quad (1)$$

where n is the number of electrons in the system, e is the elementary charge, F is the canonical free energy, and $U_{SHE} = \mu_{e,SHE}/e$ is reference potential, the standard hydrogen electrode (SHE) condition.

Conventional density functional theory (DFT) calculations use the canonical-ensemble algorithm with a fixed number of electrons with the Fermi energy adjusted to match the total number of electron (N) while F is minimized. In contrast, in the grand canonical DFT, the charges in the system vary during the electrochemical reaction to match to the applied potential (or μ_e), which provides a realistic description of experimental electrochemistry, but it requires more complex calculations than the canonical-ensemble algorithm.

Goddard and coworkers developed the grand canonical potential kinetics (GCP-K) formulation [ref 29] which derives the grand canonical potential (GCP) by Legendre transformation of canonical free energy.

We assume the canonical free energy quadratically depends on net charge.

$$F(n) = a(n - n_0)^2 + b(n - n_0) + c \quad (2)$$

Combining Eq. (1) and (2), we obtain the GCP,

$$G(n,U) = a(n - n_0)^2 + b(n - n_0) + c - ne(U_{SHE} - U) \quad (3)$$

For G(n,U) to be used as a thermodynamic potential, n must be equilibrated to U,

$$\frac{dG(n,U)}{dn} = 0 \quad (4)$$

$$n = -\frac{b - e(U_{SHE} - U)}{2a} + n_0 \quad (5)$$

$$G(U) = -\frac{1}{4a}(b - \mu_{e,SHE} - eU)^2 - n_0(\mu_{e,SHE} - eU) + c \quad (6)$$

The number of electrons at potential U is

$$n(U) = -\frac{1}{e} \frac{\partial GCP(U)}{\partial U} = n_0 - \frac{1}{2ae}(b - \mu_{e,SHE} + eU) \quad (7)$$

Here, b can be determined using $n(U_{PZC}) = n_0$ which leads to

$$b = \mu_{e,SHE} - eU_{PZC} \quad (8)$$

From these calculations we can obtain the differential capacitance (C_{diff}).

$$C_{diff} = \frac{\partial n}{\partial U} = -\frac{1}{2a} \quad (9)$$

The C_{diff} and Potential of Zero Charge (PZC) for various cases are tabulated in Table S1.

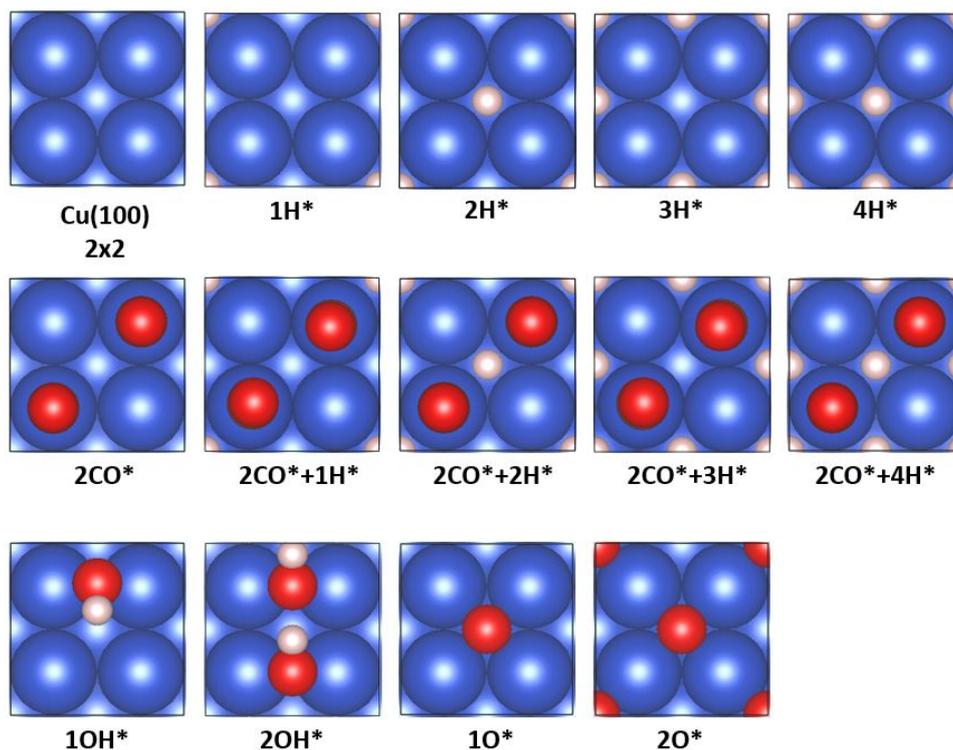


Figure S1. The top view of surface models with various adsorbates on Cu(100) with 2x2 supercell. The blue, white, red, and gray spheres represent Cu, H, O and C, respectively.

system	a [V/e]	b [V]	c [eV]	C_{diff} [F]	PZC [V vs SHE]
Cu(100)	0.683813	-4.4079	-87879.9	-0.73119	-0.39433
1H*	0.712259	-4.41647	-87895.9	-0.70199	-0.39731
2H*	0.775016	-4.46917	-87911.8	-0.64515	-0.35061
3H*	0.833455	-4.45499	-87927.7	-0.59991	-0.37531
4H*	0.84666	-4.34458	-87943.4	-0.59056	-0.47181
2CO*	1.060181	-4.56609	-89065.3	-0.47162	-0.19144
2CO*+1H*	1.064394	-4.52196	-89081	-0.46975	-0.24082
2CO*+2H*	1.054976	-4.44117	-89096.4	-0.47394	-0.33529
2CO*+3H*	1.018343	-4.31286	-89112	-0.49099	-0.4583
2CO*+4H*	1.001882	-4.23666	-89127.4	-0.49906	-0.58731
1OH*	0.69232	-4.46217	-88333.9	-0.72221	-0.35956
2OH*	0.810286	-4.66245	-88788.1	-0.61707	-0.12883
1O*	0.748503	-4.58694	-88317.6	-0.668	-0.2489
2O*	0.522081	-4.61247	-88754.9	-0.95771	-0.0808

Table S1. The GCP parameters for all surface models.

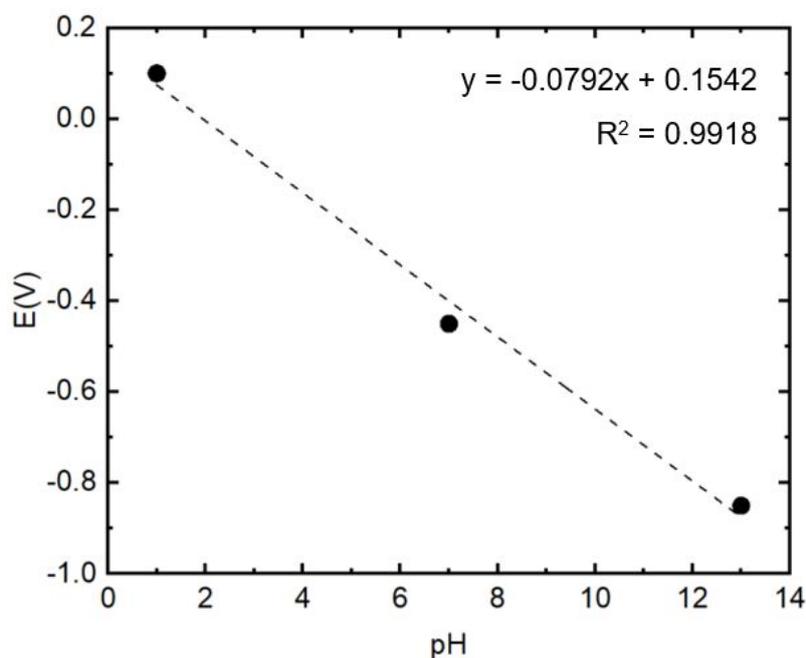


Figure S2. The onset potential of CO adsorption as a function of pH; the onset potential is operationally defined as the earliest (most positive) potential at which the CO adsorption peak appears in Figure 1.

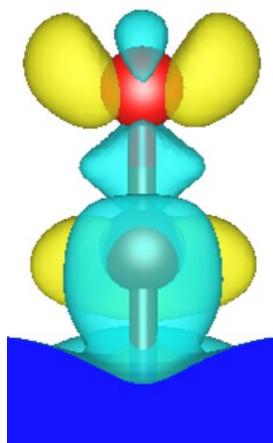


Figure S3. Charge difference of $(1/2 \text{ ML CO} + 0 \text{ ML H}^*) - (1/2 \text{ ML CO} + 1/2 \text{ ML H}^*)$. The yellow and blue indicate charge accumulation and depletion, respectively. Generally, the dominant contributor to the interaction between the carbonyl and 3d-transition metal is the charge transfer from CO 5σ to $3d_{z^2}$ and the back-donation from $3d_{xz}$ to CO $2\pi^*$. In the presence of coadsorbed H^* , the donation from 5σ and the back-donation to $2\pi^*$ are reduced leading to accumulation and depletion of charge on the respective molecular orbitals in the charge difference plot.

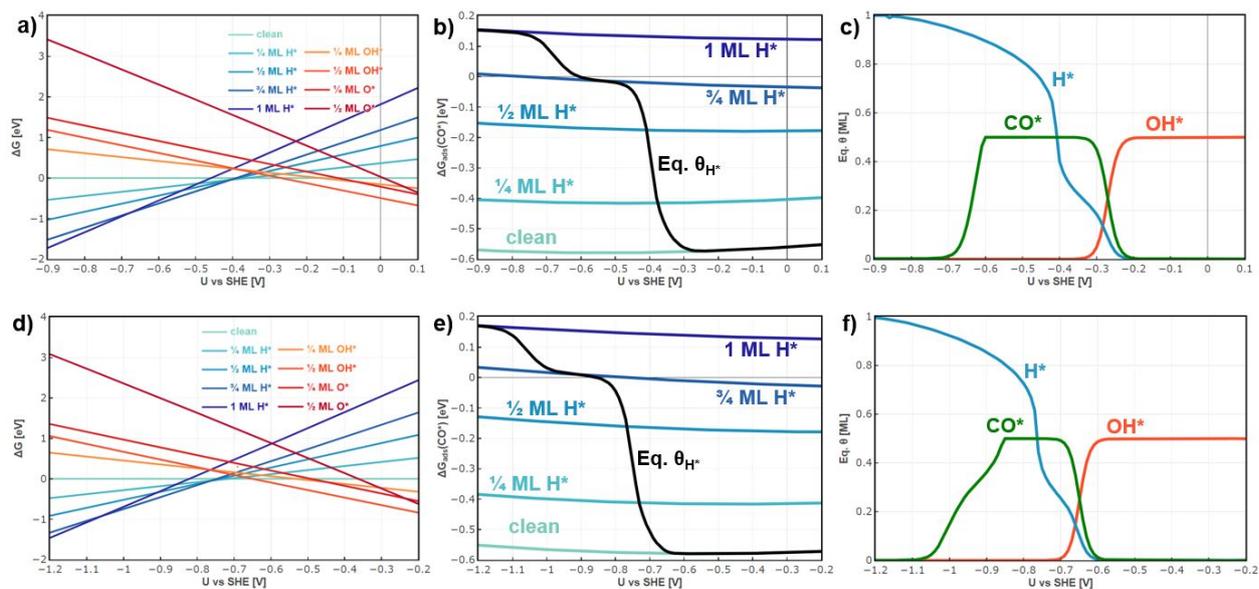


Figure S4. At pH 7 in 0.10 M KClO₄: (a) Surface free energy diagram with various coverages of H*, OH*, and O* as a function of applied potential. (b) The CO adsorption free energy as a function of U and θ_{H^*} (c) Equilibrium surface coverage of surface species as a function of potential. Figures (d-f) are analogous to (a-c) except that they pertain to pH = 13 in 0.10 M KOH.