

# Supporting information for Competition between CO<sub>2</sub> reduction and H<sub>2</sub> evolution on transition-metal electrocatalysts

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## 1 Configurations tested in DFT calculations; minima hopping methodology

In order to obtain the lowest energy configuration for each coverage of CO, a variety of initial adsorption sites were optimized and the corresponding electronic energy was calculated. Four types of adsorption sites exist on Cu(111) surface: on-top site, bridge site, three-fold fcc site and three-fold hcp site. For a  $3 \times 3 \times 3$  unit cell surface, the number of initial adsorption sites combination can be extremely large at high coverage of adsorbates, such as 3/9 ML and 4/9 ML (Figure 1). For a certain coverage of CO, the lowest energy configuration was selected. These were initially suggested by “brute intuition”.

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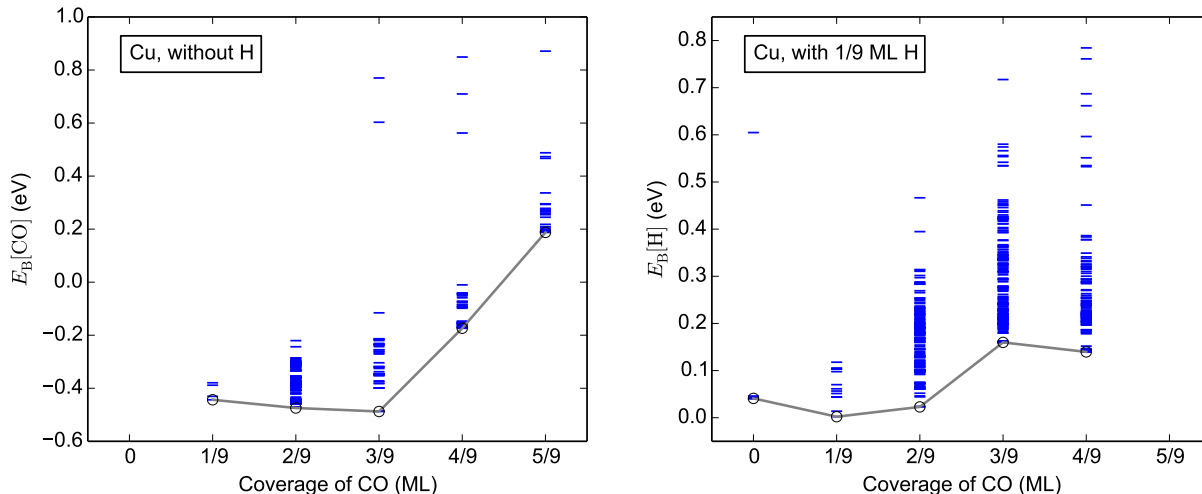


Figure S1: Energies of copper configurations. Each blue bar represents the binding energy of CO or H for one possible configuration, which was optimized within DFT. The black circle and gray line are the lowest energy configuration with a certain CO coverage, which is reported in the manuscript.

We then expanded this with a systematic constrained minima hopping method<sup>1,2</sup>. In this method, each coverage level was run in parallel in five independent runs initially at a molecular-dynamics search temperature of 2000 K. Identity-preserving Hookean constraints were implemented to maintain the identity of CO and to prevent volatilization of adsorbates, as described in reference.<sup>1</sup> All runs were continued until the molecular dynamics search temperature exceeded 4000 K, which occurs when the minima hopping algorithm is no longer finding new minima, or when at least 100 unique configurations for each coverage were identified. The lowest energy configurations of both techniques are reported in the manuscript, while all the energetic results are shown in Figures 1 and 2 for Cu and Mo, respectively.

To ensure the trend of weakening H-binding is intact on a Mo surface, the coverage-dependent calculations were also undertaken on Mo bcc(100) surface by using the above constrained minima-hopping method, with the results shown in Figure 2. We can quickly observe that the binding energy of CO is much stronger on the Mo surface and does not approach the energetic levels of Cu until coverages above 7/9 ML; second, we see only a gradual increase in the binding energy until the coverage exceeds 5/9. Therefore, we can conservatively state that the coverage is expected to be *at least* at a level of 5/9 ML. With such coverages of CO, the binding of H has been weakened

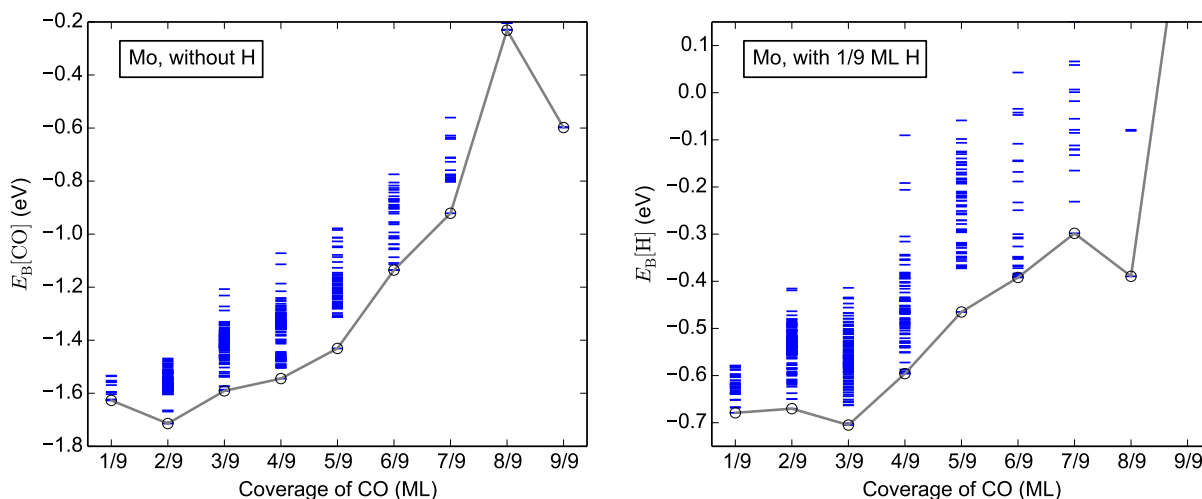


Figure S2: Energies of molybdenum configurations. Each blue bar represents the binding energy of CO or H for one possible configuration, which was optimized within DFT. The black circle and gray line are the lowest energy configuration with a certain CO coverage.

by 0.18 eV compared to that on a clean Mo surface ( $E_B[\text{H}] = -0.65$  eV when no CO adsorbed on Mo surface). This trend is very similar to what we found on Cu: a coverage of CO will weaken the binding of H. Clearly, CO adsorbs much stronger on Mo than on Cu, leading to both a stronger weakening of the H bonding and a more pronounced site blocking effect, which will counter the promotion effect caused by the H binding strength change.

## 2 Individual polarization curves of RDE

Figure 3 shows the polarization curves of positive-going sweeps in the last three cycles at 5 mV/s for Cu and Mo RDE cyclic voltammetry experiments. The average value of these curves are shown in the mainbody of the article.

## 3 Comparison of CV plots for RDE and metal sheet

As the experimental setups for RDE and metal sheet have some differences, similar CV experiments were also carried out on metal sheet to justify the reliability of the product analysis results: five cycles of 50 mV/s scan followed by five cycles of 5 mV/s scan between -0.7 V and -1.4 V

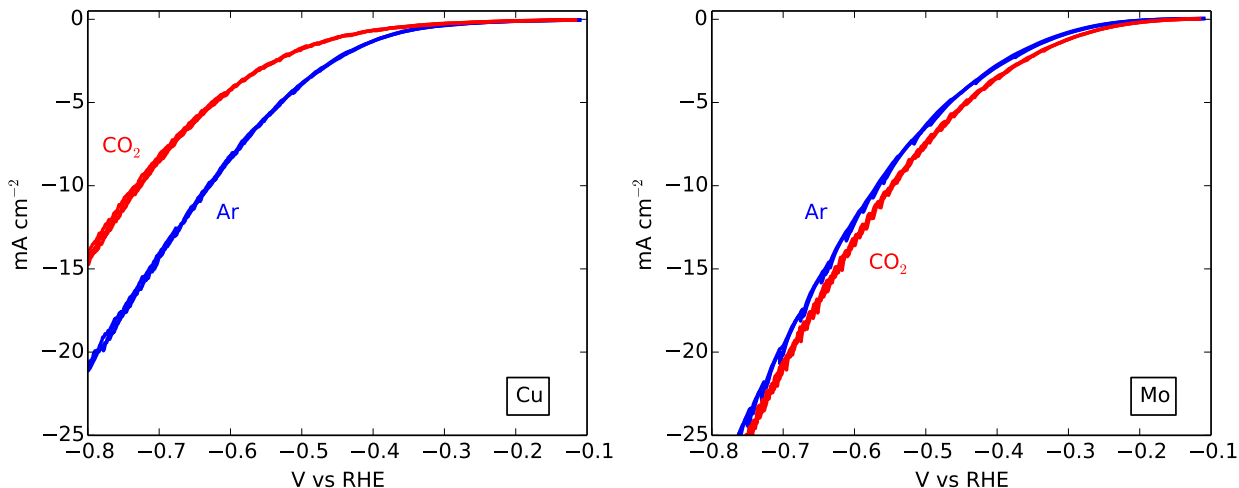


Figure S3: Individual polarization curves (positive-going) of Cu and Mo in argon versus carbon dioxide atmospheres

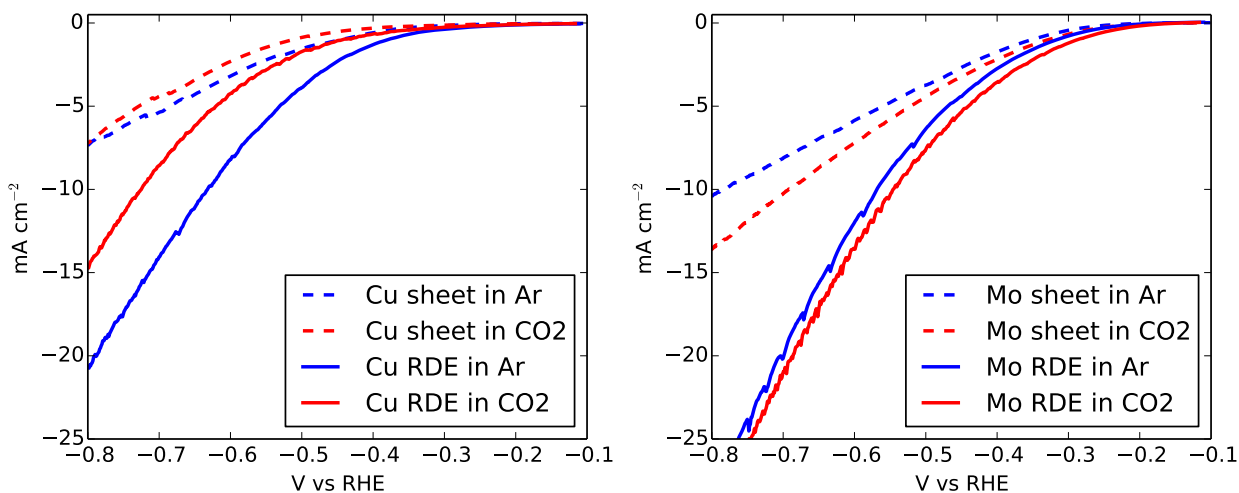


Figure S4: The polarization curves of Cu sheet, Cu RDE, Mo sheet and Mo RDE in two atmosphere. Blue is in argon and red is in  $\text{CO}_2$ .

vs Ag/AgCl (4 M KCl). The positive-going curves comparison is shown in Figure 4. Around onset potentials, the current on metal sheet is comparable to that on RDE. When the potential is more negative, the current on metal sheet is much smaller than on RDE in all cases. This is to be expected; at very negative potentials the metal sheet cannot get rid of the gas bubbles generated on its surface quickly and the actual surface area in contact with the electrolyte has been greatly reduced due to bubble blocking. Mass transport can also be expected to be less limiting in the RDE experiments. Regardless, the CO inhibition effect on HER on copper and promotion effect on HER

on molybdenum are preserved in metal sheet experiments, in agreement with the RDE data.

## 4 Pourbaix diagram

Pourbaix diagrams for both Cu and Mo are shown in Figure 5. The red lines indicate the potentials and pH's at which the electrochemical experiments were designed to take place.

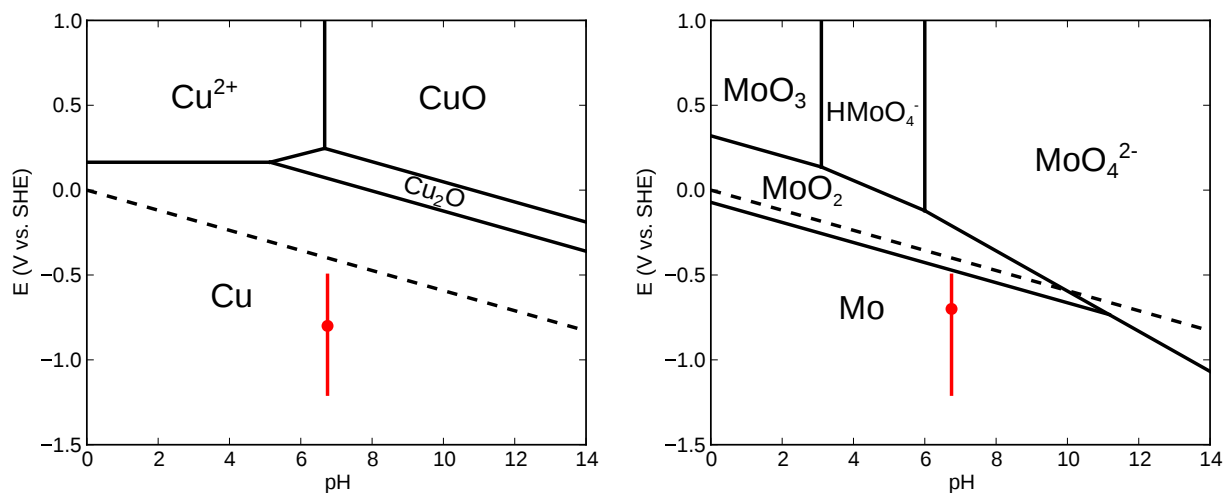


Figure S5: Pourbaix diagram of Cu and Mo (re-created).<sup>3</sup> The red lines represent the conditions where CV experiments were carried out. The red dots represent the condition when GC samples were collected. The dashed lines are the equilibrium conditions of  $\text{H}^+$  and  $\text{H}_2$ .

## References

- (1) Peterson, A. A. *Top. Catal.* **2014**, *57*, 40–53.
- (2) Goedecker, S. J. *Chem. Phys.* **2004**, *120*, 9911–9917.
- (3) Pourbaix, M. *Atlas of electrochemical equilibria in aqueous solutions*; Pergamon Press, 1966.