

Supporting Information

Mechanistic Insights into the Effect of Halide Anions on Electroreduction Pathways of CO₂ to C₁ Product at Cu/H₂O Electrochemical Interfaces

Lihui Ou*, Wanli You, Junling Jin

Model and computational details

1. Surface and solvation model

The closed-packed Cu(111) crystal planes are generally chosen as the representative surfaces for both experimental and theoretical studies due to their high selectivity to CO₂ electroreduction into hydrocarbons. Considering the complexity of real CO₂ electroreduction systems, the aqueous-phase environment is included in the present study, in which 12 explicit H₂O molecules with two relaxed bilayer structures chosen to fill up the vacuum region were used to model the solvation effect in order to better simulate the interactions between solvent and adsorbates and decrease the size of the simulated systems as much as possible in the presence of adsorbed halide anions (See Figure S1). In fact, the formation of an ordered H₂O bilayer structure in a hexagonal arrangement with 2/3 monolayer saturation coverage with respect to the surface normal had been demonstrated by X-ray absorption spectroscopy, thermal desorption spectroscopy, low-energy electron diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy along with DFT calculations in previous experimental and theoretical studies on the metal surface.¹⁻³ Our present solvation model is on the basis of the previous studies on structure and orientation of H₂O. However, many different H₂O solvation structures may also exist, which all are approximate in energy.⁴ Since all energies of interest in this study are energy differences, which are not sensitive to the accurate model of H₂O as long as the same model is consistently used and a reasonable model in a local minimum structure is chosen when calculating the energy differences. Considering the coverage is 2/3 of H₂O monolayer, thus, a (3x3) Cu(111)

*Hunan Provincial Key Laboratory of Water Treatment Functional Materials, Hunan Province Engineering Research Center of Electroplating Wastewater Reuse Technology, College of Chemistry and Materials Engineering, Hunan University of Arts and Science, Changde, 415000, China. E-mail: lihuiou@huas.edu.cn (Lihui Ou)

Electronic supplementary information (ESI) available.

slab model with nine metal atoms per layer and theoretical equilibrium lattice constant of 3.66 Å by using four metal layers was created.

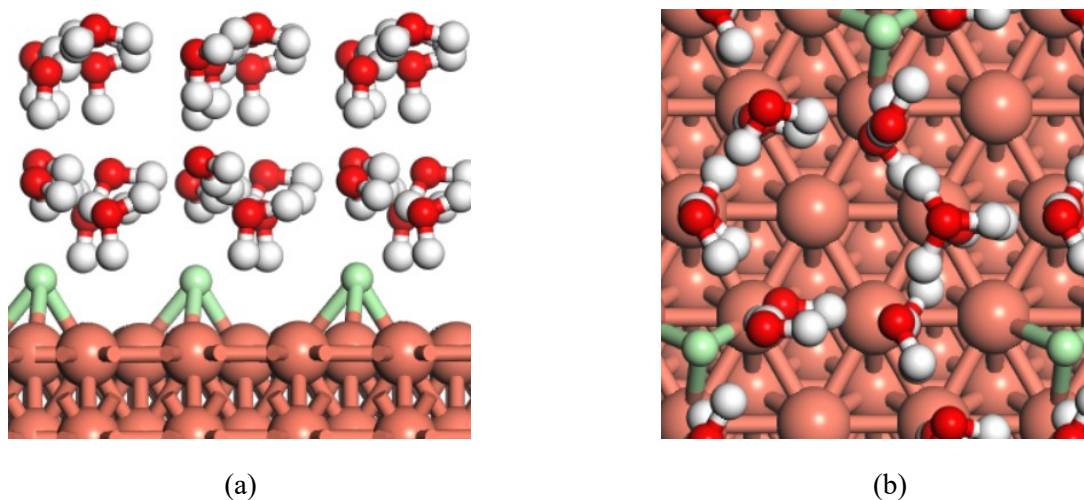


Figure S1. The solvation model at halide anions modified Cu(111)/H₂O interfaces: (a) Side view; (b) Top view.

2. Computational parameters

Using the generalized gradient approximation of the Perdew–Burke–Ernzerhof exchange correlation functional, calculations were performed in the framework of DFT.⁵ Ultrasoft pseudopotentials were employed to describe the nuclei and core electrons and the Kohn–Sam equations were self-consistently solved using a plane-wave basis set.⁶ A kinetic energy cutoff of 30 Ry and a charge-density cutoff of 300 Ry were used to make the basis set finite. The Fermi surface has been treated by the smearing technique of Methfessel–Paxton with a smearing parameter of 0.02 Ry.⁷ The PWSCF codes in Quantum ESPRESSO distribution were employed to perform all calculations.⁸ Brillouin-zone integrations were implemented using a (3×3×1) uniformly shifted k-mesh for (3×3) supercell with the special-point technique, which was tested to converge to a subset of the relative energies reported herein. A vacuum layer of 16Å was placed above the top layer of slab, which is sufficiently large to ensure that the interactions are negligible between repeated slabs in a direct normal to the surface. The Cu atoms in the bottom two layers are fixed at the theoretical bulk positions, whereas the top two layers and all adsorbates including solvent are allowed to relax to minimize the total energy of the system. Structural optimization was performed until the Cartesian force components acting on each atom were brought below 10⁻³ Ry/Bohr and the total energy was converged to within 10⁻⁵ Ry. Using the climbing image nudged elastic band (CI-NEB) method, the saddle points and minimum energy paths (MEPs) were located.^{9, 10} Zero point energy (ZPE) corrections were applied into the calculations of the

activation and reaction free energies from MEP analysis, in which density functional perturbation theory within the linear response was used to study the vibrational properties.¹¹ The ZPEs were calculated using the PHONONS code that contained in the Quantum ESPRESSO distribution.⁸

For elementary reaction step of $(A+H)^* \rightarrow AH^*$ at halide anions modified Cu(111)/H₂O interfaces, the reaction free energy is calculated based on $\Delta G_{\text{reac}} = E(AH^*) - E[(A+H)^*] + ZPE(AH^*) - ZPE(A^*) - ZPE(H^*)$, in which the asterisk (*) indicates that the species is adsorbed at halide anions modified Cu(111)/H₂O interfaces. The previous theoretical studies addressing systems in heterogeneous catalysis and surface science showed that any change of the adsorbed species including halogen atoms in entropy is negligible.¹²⁻¹⁴ Thus, the entropy change of the adsorbed species are ignored in this paper.

Löwdin population analyses of the adsorbed molecule

Table S1. The net electron gains of total, *s* and *p* orbitals of the adsorbed CO molecule at clean and halide anions modified Cu(111)/H₂O interfaces compared with isolated CO molecules

Components		Net Electron Gains (Δq)		
		Total	<i>s</i>	<i>p</i>
Clean Cu(111)	C	+0.671	-0.221	+0.892
Surface	O	+0.249	+0.011	+0.238
F ⁻ Modified Cu(111)	C	+0.517	-0.241	+0.758
Surface	O	+0.084	+0.021	+0.063
Cl ⁻ Modified	C	+0.540	-0.237	+0.777
Cu(111) Surface	O	+0.127	+0.021	+0.106
Br ⁻ Modified	C	+0.600	-0.232	+0.832
Cu(111) Surface	O	+0.201	+0.009	+0.191
I ⁻ Modified Cu(111)	C	+0.618	-0.232	+0.850
Surface	O	+0.211	-0.001	+0.212

Table S2. The net electron gains of total, *s* and *p* orbitals of the adsorbed CO₂ molecule at clean, Br and I-modified Cu(111)/H₂O interfaces compared with isolated CO₂ molecule

Components		Net Electron Gains (Δq)		
		Total	<i>s</i>	<i>p</i>
Clean Cu(111)/H ₂ O Interface	CO ₂	+0.036	+0.003	+0.033
Br ⁻ Modified Cu(111)/H ₂ O Interface	CO ₂	+1.008	+0.408	+0.600
I ⁻ Modified Cu(111)/H ₂ O Interface	CO ₂	+1.012	+0.404	+0.608

References

- 1 E. Skúlason, V. Tripković, M. E. Björketun, S. Gudmundsdóttir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jónsson and J. K. Nørskov, Modeling the Electrochemical Hydrogen Oxidation and Evolution Reactions on the basis of Density Functional Theory Calculations, *J. Phys. Chem. C*, 2010, **114**, 18182-18197.
- 2 M. A. Henderson, Interaction of Water with Solid surfaces: Fundamental Aspects Revisited, *Surf. Sci. Rep.*, 2002, **46**, 1-308.
- 3 H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelenschikov, L. G. M. Pettersson and A. Nilsson, Structure and Bonding of Water on Pt(111), *Phys. Rev. Lett.*, 2002, **89**, 276102.
- 4 S. Haq, C. Clay, G. R. Darling, G. Zimbitas and A. Hodgson, Growth of Intact Water Ice on Ru(0001) between 140 and 160 K: Experiment and Density-Functional Theory Calculations, *Phys. Rev. B*, 2006, **73**, 115414.
- 5 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 6 D. Vanderbilt, Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism, *Phys. Rev. B*, 1990, **41**, 7892-7895.
- 7 M. Methfessel and A. T. Paxton, High-Precision Sampling for Brillouin-Zone Integration in Metals. *Phys. Rev. B*, 1989, **40**, 3616-3621.
- 8 S. Baroni, A. Dal Corso, S. de Gironcoli and P. Giannozzi, PWSCF and PHONON: Plane-Wave

Pseudo-Potential Codes, <http://www.quantum-espresso.org/>, 2001.

- 9 G. Henkelman and H. Jonsson, Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points, *J. Chem. Phys.*, 2000, **113**, 9978-9985.
- 10 G. Henkelman, B. P. Uberuaga and H. Jonsson, A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths, *J. Chem. Phys.*, 2000, **113**, 9901-9904.
- 11 S. Baroni, S. Gironcolli, A. Corso and P. Giannozzi, Phonons and Related Properties of Extended Systems from Density Functional Perturbation Theory, *Rev. Mod. Phys.*, 2001, **73**, 515-562.
- 12 A. A. Peterson, F. Abild-Pederson, F. Studt J., Rossmeisl and J. K. Nørskov, How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels, *Energy Environ. Sci.*, 2010, **3**, 1311-1315.
- 13 K. Reuter and M. Scheffler, Composition, Structure, and Stability of RuO₂(110) as a Function of Oxygen Pressure, *Phys. Rev. B*, 2001, **65**, 035406.
- 14 F. Gossenberger, T. Roman and A. Groß, Equilibrium Coverage of Halides on Metal Electrodes, *Sur. Sci.*, 2015, **631**, 17-22.