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Cation-Coordinated Inner-Sphere CO₂ Electroreduction at Au-Water Interfaces

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Abstract

Electrochemical CO₂ reduction reaction (CO₂RR) is a promising technology for the clean energy economy. Numerous efforts have been devoted to enhancing the mechanistic understanding of CO₂RR from both experimental and theoretical studies. Electrolyte ions are critical for the CO₂RR, however, the role of alkali metal cations is highly controversial, and a complete free energy diagram of CO₂RR at Au-water interfaces is still missing. Here, we provide a systematic mechanism study towards CO₂RR via ab initio molecular dynamics simulations integrated with the slow-growth sampling (SG-AIMD) method. By using the SG-AIMD approach, we demonstrate that CO₂RR is facile at the inner-sphere interface in the presence of K cations, which promote the CO₂ activation with the free energy barrier of only 0.66 eV. Furthermore, the competitive hydrogen evolution reaction (HER) is inhibited by the interfacial cations with the induced kinetic blockage effect, where the rate-limiting Volmer step shows a much higher energy barrier (1.27 eV). Eventually, a comprehensive free energy diagram including both kinetics and thermodynamics of the CO₂RR to CO and the HER at the electrochemical interface is derived, which illustrates the critical role of cations on the overall performance of CO₂ electroreduction by facilitating CO₂ adsorption while suppressing the hydrogen evolution at the same time.

Introduction

The electroreduction of carbon dioxide has become one of the critical technologies of the clean energy economy, holding promise to reduce and mitigate the carbon footprint resulting from the use of chemicals and fuels.¹⁻³ Understanding the CO₂RR mechanism at the atomic level is instrumental for catalyst design and catalytic system's optimization. Theoretical approaches are promising for studying reaction mechanisms of various electrochemical reactions, including CO₂ electroreductions.⁴⁻⁹ CO₂RR on Au surfaces is of great interest to convert CO₂ to the valuable chemical (CO, a critical component of syngas).¹⁰⁻¹¹ So far, many simulations performed at solid-gas interfaces using density functional theory (DFT) focus on the thermodynamics of reaction intermediates without considering reaction kinetics.¹²⁻¹⁵ Such simplified models are insufficient to capture interfacial behaviors and evaluate atomic-scale mechanisms of electrocatalytic reactions at complex electrode-electrolyte interfaces.¹⁶⁻¹⁷

Electrolyte ions affect corrosion rates, the oxygen reduction reaction, and hydrogen evolution reaction (HER).¹⁸⁻¹⁹ Therefore, the electrochemical environment has received attention from both experimental and theoretical researchers.²⁰⁻²¹ Considering the electrocatalytic interfaces, the solvent is critical during CO₂RR over Au surfaces, since water molecules either are involved in CO₂ reduction directly or modify the solid-liquid interfacial structures affecting the

reactions indirectly.²²⁻²³ Importantly, cations in the electric double layer (EDL) region have been experimentally demonstrated to be critical to CO₂RR performance, but it is still highly controversial about the originated cation effect, thus no unified conclusion has been reached yet.²⁴⁻³¹ For instance, Koper and co-workers demonstrated that cations facilitate CO₂ reduction by coordinating the key *CO₂ reaction intermediate.²⁶ However, another recent study by Hu and co-workers concluded that the main role of cations is ascribed to the modulated local electric field, which enhances CO₂RR and suppresses the HER at the same time.²⁸ Moreover, the HER is highly competitive to the CO₂RR at Au-water interfaces and is also affected by cation identity and concentration, thereby deserving a complete atomic-scale mechanism study when CO₂ reduction performance is evaluated.³²⁻³⁴

To explore the cation effect on CO₂RR at Au-water interfaces, K cations are introduced into the simulation models to reach the negative applied potential (U = -1.17 V vs. the reversible hydrogen electrode, RHE) as discussed in our previous study.³⁵ There are several reasons to select K⁺ into the models rather than other cations (e.g., Li⁺, Na⁺, Rb⁺, Cs⁺): (1) K⁺, Rb⁺, Cs⁺ have more pronounced promotion effects on CO₂RR compared to Li⁺ and Na⁺ as measured by experiments;^{29, 36-38} (2) K⁺ is selected due to the small atomic size compared to Rb⁺ and Cs⁺ due to the limitation of model size considering the high computational cost of ab initio molecular dynamics (AIMD) simulations with an explicit modelling of the water solvent; (3) K^+ ions (similar to Cs^+), also have the significant suppression of the competitive HER as observed in recent experimental studies.³⁸⁻³⁹ For the number of cation, two K ions are mainly determined by constructing the negatively charged electrode states,³⁵ which can also be used to represent the local cation accumulation at the outer Helmholtz plane (OHP).⁴⁰ Overall, two K ions are chosen here to study the interfacial mechanisms of CO₂RR and HER at Au-water interfaces. With explicit water solvents, cations, and negatively applied potential, the model system for CO₂RR mechanistic study can be compared to the experimental condition with the commonly used aqueous electrolytes (NaHCO₃ or KHCO₃, pH = 7.0).⁴¹

By constructing a solid-liquid interface to mimic the experimental condition, besides the CO₂ activation, the full reaction pathway including CO_2 -to-CO conversion and CO desorption, is simulated via the slow growth sampling method combined with *ab initio* molecular dynamics (SG-AIMD) simulations. Afterwards, the complete free energy landscape is constructed to locate the rate-determining step (RDS), which is identified as the CO₂ activation reaction. Furthermore, HER is also considered, including both thermodynamics and reaction kinetics, to evaluate the CO₂RR at interfaces accurately. With two K cations in the interfacial region, the water dissociation is highly prohibited, thus improving the selectivity of CO₂RR at the electrochemical interface. To our best knowledge, it is the first time to address the complete free energy landscape of CO₂RR as well as the competing HER at Au-water interfaces under electrochemical conditions, which illustrates the promotion effect of cations on CO₂ reduction but the inhibition role on hydrogen evolution.

Methods

Model set-up of Au-water interfaces Atomic-scale simulations are carried out to study innersphere CO₂ electroreductions at Au-water interfaces, where potassium cations are introduced to explore the possible cation effects. Au(110) facet is chosen where the under-coordinated sites contribute to at least 20-fold higher catalytic activity compared to other surfaces (e.g. Au(100)).⁴² The (2 × 3) supercell with seven layers is constructed, and the cell size is 8.32 × 8.82×40 Å³. Besides the metal substrate, multiple explicit water layers (44 H₂O) with a density of ~1 g cm⁻³ are filled and one vacuum slab of 12 Å is left in the *z* direction to prohibit spurious periodic interactions. Two cations are introduced into the Au-water interfacial models by replacing two water molecules thus constructing the cation-containing interfaces (denoted as Au(110)-H₂O-2K).

Computational details All of the simulations are performed based on DFT via Vienna Ab-initio Simulations Package (VASP)⁴³⁻⁴⁴ where the projector augmented wave (PAW)⁴⁵⁻⁴⁶ method is used. The Perdew-Burke-Ernzerhof functional within the generalized gradient approximation framework (GGA-PBE)⁴⁷ are used to describe the electron exchange-correlation interactions. The cut-off energy is 400 eV. Bader charge analysis method is adopted to analyze the electron transfer during the elementary reactions of CO₂RR and HER.⁴⁸⁻⁴⁹

Molecular dynamics Ab initio molecular dynamics (AIMD) simulations are conducted before evaluating reaction kinetics of CO₂RR and HER at Au-water-2K interfaces, considering the dynamical feature of solvents with the hydrogen bonding network. AIMD simulations are carried out via the Nose-Hoover thermostat using the canonical ensemble (NVT) at 298 K and the time step is 1 fs.⁵⁰⁻⁵¹ A smaller time step of 0.5 fs has been tested (Figure S1), and a negligible difference is observed between 1 fs and 0.5 fs as the time step. For Au-water interfaces, 10 ps standard AIMD simulations are performed allowing the explicit H₂O molecules to reach one relatively equilibrium state, and further 30ps simulations for Au-water-2K are conducted to better describe the solvation structures of cations. During molecular dynamics, bottom four layers of Au metal substrate are fixed while the rest are fully relaxed, where the *k*-point mesh grid of ($3 \times 3 \times 1$) is used. The zero-damping method of Grimme (DFT-D3)⁵²⁻⁵³ is added to consider the dispersion corrections.

Enhanced sampling Constrained *ab initio* molecular dynamics (cAIMD) simulations with slow-growth (SG) sampling approach⁵⁴⁻⁵⁵ as implemented in VASP (SG-AIMD) are performed to evaluate the kinetic barriers of CO₂RR and HER. In this method, one suitable collective variable (CV, namely ξ) can be defined as the reaction coordinate, which is linearly changed from the initial state to final state with a transformation velocity $\dot{\xi}$. The work required to perform the transformation from initial to final states can be computed as:

$$W_{\text{initial-to-final}} = \int_{\xi(\text{initial})}^{\xi(\text{final})} \left(\frac{\partial F}{\partial \xi}\right) \cdot \dot{\xi} dt,$$

where F is the computed free energy which is evolving along with t, $\frac{\partial F}{\partial \xi}$ can be computed along cAIMD using the blue-moon ensemble with the SHAKE algorithm.⁵⁶ With the limit of infinitesimally small $\partial \xi$, the needed work (W_{initial-to-final}) corresponds to the free-energy difference between the final and initial states. In the SG sampling, a value $\partial \xi$ of 0.001 Å is used for each cAIMD step after testing the shorter step size for the "slow-growth". For elementary steps in both CO₂RR and HER, reaction barriers and reaction energies can be obtained by plotting the free energy profiles based on thermodynamic integrations.⁵⁶⁻⁵⁷

Results and discussion



Figure 1. Averaged force on various reaction intermediates (a), key representative structures including the CVs of 2.2 Å, 2.7 Å, and 4.9 Å (b), and the integrated free energy curve (c) via cAIMD simulations during CO₂ activation. CO₂ is indicated by blue-dashed circles in b. Color code: Au, golden; K, purple; C, blue; O, red; H, white.

To initiate the CO_2RR at Au-water interfaces, the inert CO_2 molecule needs to be activated, becoming an anion (CO_2^{-}) by receiving the first electron. Previous experimental studies have focused on mechanistic explorations of CO₂RR on Au surfaces, but the RDS has remained controversial.⁵⁸⁻⁶² For instance, Wuttig et al. concluded that the CO₂ adsorption with the first electron transfer is RDS by in situ surface-enhanced IR absorption spectroscopy (SEIRAS) and electrochemical kinetic studies⁵⁸, while another work by Dunwell et al. illustrated the *COOHto-*CO conversion was the RDS and their following work also discussed the possibility of *CO2-to-*COOH step being RDS.⁶⁰⁻⁶¹ Computationally, CO2RR mechanisms are usually simulated using proton-coupled-electron transfer (PCET) steps within the computational hydrogen electrode (CHE) model thereby ignoring the CO₂ activation step, which is not accessible in the solid-vacuum model. In our previous work, CO₂ activation is systematically investigated by performing SG-AIMD simulations at Au-water interfaces, where the CO₂ molecule needs to overcome a reaction barrier of 0.61 eV to adsorb on Au surfaces and the concomitant charge transfer contributes to CO2⁻ anion formation initiating the overall catalytic reactions.³⁵ To validate the reliability of SG-AIMD method, several cAIMD simulations on reaction intermediates during CO₂ activation are carried out to monitor the force convergence and evaluate the averaged force. As shown in Figure S2, all of the forces converge well within

4 ps cAIMD simulations, which further illustrates the force profile obtained here *via* the SG-AIMD sampling approach is reliable (Figure S3). Figure 1a shows the averaged force at different intermediates during CO₂ activation with key structures shown in Figure 1b, and the integrated free energy curve (Figure 1c) indicates the reaction free energy barrier is 0.61 eV, which validates the SG-AIMD approach (0.61 eV). To further determine the RDS, besides CO₂ activation, it is critical and urgent to evaluate all of the following elementary steps of CO₂RR at Au-water interfaces via SG-AIMD approach under electrochemical conditions, including *CO₂-to-*COOH, *COOH-to-*CO, and the final *CO desorption step.



Figure 2. (a) Energy profile of the $*CO_2$ -to-*COOH step in Au(110)-H₂O-2K; (b) initial and final structures (black arrows in final state indicate the proton transfer between water molecules and $*CO_2$ producing *COOH, where the involved reactive species including H, OH, and H₂O are yellow-highlighted with $*CO_2$ and *COOH shown in blue-dashed circles); (c) distance of H-O (CO₂) when producing *COOH; (d) Bader charge results of key components as a function of CV. Color code: Au, golden; K, purple; C, blue; O, red; H, white.

Different from CO₂ activation, which involves reactive species migrating from the bulk liquid region to Au surfaces, *CO₂-to-*COOH conversion occurs at the inner-sphere area along with the solvent-mediated proton transfer reaction with water as the proton donor in the pH neutral electrolyte. Before simulating the *COOH formation step, the reaction coordinate is chosen to be a collective variable (CV), representing the possible pathway of proton transfer. CV selection requires careful consideration, since it can largely affect the reaction pathway and reaction free energies. Here, the reaction collective variable during *CO₂-to-*COOH is defined as CV = R1 - R2, which is illustrated in the insert of **Figure 2a**, where the nearby water molecule is involved in the *COOH formation. With this simple CV, the reaction free energy of *CO₂-to-*COOH step is sampled via SG-AIMD simulations (**Figure 2a**), indicating that such a water-mediated proton transfer reaction shows a free energy barrier of 0.35 eV. The identified transition state (TS) is quite close to the product state, and key structures are shown in **Figure 2b**. It is predicted that the *COOH final state on Au surfaces can be stabilized by alloying or surface doping (e.g., Pd), providing stronger bindings to intermediates and enhancing the catalytic activity.⁶³⁻⁶⁵ The distance between the transferred proton and O in CO₂

is monitored during *CO₂-to-*COOH conversion (**Figure 2c**), which fluctuates but steadily decreases, demonstrating the dynamic features of interfacial structures during the formation of *COOH and OH⁻ species. Bader charge analysis results indicate that two K cations show a constant formal charge (+1.77 e) in total, and water solvents also keep almost constant charges (Figure S4). The charge distribution and fluctuation of interfacial reactive species, including Au surface, *CO₂ (*COOH), and two water molecules (1st H_{trans}, 1st OH, 2nd H_{trans}, and 2nd OH), are shown in **Figure 2d** with the illustration in **Scheme 1a**. During *COOH formation, the Au surface provides 0.27 e, where the majority (0.23 e) is transferred to *CO₂. Within two water molecules including the specified H⁺/OH⁻ species (**Figure 2d**), the 2nd H_{trans} reacts with 1st OH producing H₂O again, and 1st H_{trans} combines with *CO₂ producing *COOH, leaving 2nd OH⁻ in the final state (**Scheme 1a**). Consequently, the final state of *CO₂-to-*COOH elementary step consists of *COOH with the Bader charge of -0.34 e and OH⁻ with the charge of -0.72 e. Such a OH⁻ formation and further accumulation might increase the local pH at the electrode-electrolyte interface, which has been discussed in previous experimental work.^{34, 37}



Scheme 1. Schematic description of elementary steps including *CO₂-to*COOH step (a) and *COOH-to-*CO step (b).



Figure 3. (a) Energy profile of the *COOH-to-*CO step in Au(110)-H₂O-2K; (b) initial, TS, and final structures (OH and H₂O are yellow-highlighted, and *COOH as well as *CO are indicated by blue-dashed circles); (c) distance of H-O during proton transfer in *COOH-to-*CO step; (d) Bader charge results of key components as a function of CV. Color code: Au, golden; K, purple; C, blue; O, red; H, white.

Afterwards, the *COOH-to-*CO step proceeds with the C-O bond cleavage producing *CO on the Au surface, as shown in Scheme 1b. The PCET with water as a proton donor forms one OH⁻ at the interfacial region in the *CO₂-to-*COOH step, which can diffuse away from the interface due to the local pH gradient or being further neutralized by the buffer solution under experimental conditions.³⁴ Besides, the OH⁻ diffusion pathway is simulated at Au-water interface (Figure S5), and the small kinetic barrier (0.15 eV) indicates that OH⁻ can quickly diffuse from the inner-sphere to the outer-sphere region as compared to the following *COOHto-*CO conversion. Hence, such a hydroxyl species is replaced by one H₂O molecule to recover the neutral media condition before initiating the following reaction step. Another reason to replace the generated OH⁻ by H₂O is to maintain the similar charged state of electrode, and we observe a higher kinetic barrier for the *COOH-to-*CO conversion step with the generated OH⁻ on the less charged Au (Figure S6). Figure 3a shows the integrated free energy profile of the *COOH-to-*CO step by SG-AIMD with the CV being the C-O bond length (CV = R, insert of Figure 3a). This simple CV is selected since it provides the most favorable pathway for *CO formation as compared to those more complex CVs involving surrounding water solvents (Figure S7). The key intermediate *COOH requires 0.58 eV to overcome the energy barrier producing *CO_{atop}, and the TS is located at the C-O distance of 1.98 Å with only the bond cleavage in *COOH occurring (Figure 3b). Once the energy barrier is overcome passing through the TS, one H₂O forms via the additional proton transfer as shown in Figure 3c, indicating the continuous fluctuations similar to that observed in *CO₂-to-*COOH conversion. The possibility of *CO_{bridge} as a product is also considered, which shows a higher reaction barrier (0.67 eV) compared to *CO_{atop} (0.58 eV) (Figure S8). The local minimum states, including initial, TS, and final states, are verified by force evaluations as a function of the CV (Figure S9). As depicted in Scheme 1b, where the proton is transferred during the *COOH-to-*CO conversion with nearby water as the proton source, charge analysis is conducted to monitor the electron transfer along with C-O bond breaking (Figure 3d). Again, the K cations have a constant charge (+1.76 e), and the Au surface transfers 0.24 e to *CO when the reaction proceeds. Additionally, the proton (H_{trans}) is transferred, which combines with OH in *COOH (1stOH) producing an H₂O molecule as shown in Scheme 1b. Consequently, this *COOH-to-*CO step contributes to the almost neutral CO_{atop} (-0.07 e) and negatively charged OH⁻ (-0.66 e) at Au-water interfaces (Figure 3d).



Figure 4. (a) Energy profile of the $*CO_{atop}$ -to- $CO_{(aq)}$ step in Au(110)-H₂O-2K; (b) initial, TS, and final structures; (c) Bader charge results of key components as a function of the CV; (d) comparison of $*CO_{atop}$ and $*CO_{bridge}$ at Au-water interfaces. CO species in b and d is highlighted by the blue-dashed circle. Color code: Au, golden; K, purple; C, blue; O, red; H, white.

The last elementary step for CO₂ electroreductions at the Au-water interface is the *CO desorption from the specified Au site, which determines the efficient release of active sites, thus affecting the overall catalytic performance. Similar to the initial CO₂ activation, it is also not accessible by solid-vacuum models to evaluate the kinetic barriers of final *CO desorption. Benefiting from Au-water interfacial models, *CO desorption is monitored from the atomic level by SG-AIMD simulations, and the corresponding CV is defined as the distance between the centroid of CO and the Au site. Figure 4a shows the free energy profile of *CO_{atop} desorption with a barrier of 0.35 eV, and key structures are shown in Figure 4b. Different from previous elementary steps, where the K cations coordinate reaction intermediates with one or two K-O (CO₂) bonds, there is no short-range interaction between the CO and the cations during *CO_{atop} desorption (Figure S10 and Figure 4b). Charge analysis results (Figure 4c) illustrate that CO loses minor electrons (0.14 e), which are transferred to the surrounding species, including Au, water, and cations. Such a slight charge transfer indicates that the *CO desorption is prone to be a non-electrochemical reaction, which is in good agreement with the non-existent interaction between cations and CO (Figure S10d). As discussed above, *CO_{bridge} is possibly also produced during *COOH-to-*CO conversion, notwithstanding that a slightly higher reaction barrier (0.67 eV) needs to be overcome compared to $*CO_{atop}$ (0.58 eV). However, *CO_{bridge} is demonstrated to be quite hard to desorb from Au surfaces by SG-AIMD (Figure S11). The desorption barrier is 1.05 eV, much higher than *CO_{atop} (0.35 eV); thus, *CO_{bridge} might occupy the Au site being a spectator along with overall CO₂ electroreductions at Au-water interfaces (Figure 4d). Such a spectator phenomenon has been observed by the in situ SEIRAS study on Au surfaces, which shows *CObridge is a kinetically inert spectator with the approximate coverage of 0.2 ML.58 Therefore, combining our simulations of *CO_{bridge} and *CO_{atop} desorptions, it is predicted that on clean Au electrode surfaces the *CO_{atop} easily migrates to bridge site being as the spectator, which cannot desorb from the Au surface. When

the coverage of CO_{bridge} reaches the limit (e.g., 0.2 ML), CO_{atop} directly desorbs acting as the real active species during CO₂RR. Thus, our CO desorption study well explains the above experimental observations.

For all of the elementary steps of CO₂RR on Au with K ions, the reaction kinetic barriers are evaluated via SG-AIMD simulations, however, the variation should be estimated. To evaluate how much the calculations depend on the initial structures, SG-AIMD simulations with different initial structures are performed for elementary reactions, where the variation of the free energy barrier is calculated to be negligible (± 0.06 eV for CO₂ activation; ± 0.03 eV for *CO₂-to-*COOH; ±0.04 eV for *COOH-to-*CO; ±0.07 eV for CO desorption). The free energy profiles with key structures (initial and final states), are shown in Figure S12, with the energy barriers summarized into Table S1. These comparisons demonstrate the relatively small dependence on initial structures and insignificant errors. Overall, with 2K ions at Au-water interfaces, CO₂RR can proceed with facile kinetics. To further illustrate the cation promotion effect, we have evaluated the possibility of CO₂ activation at Au-water interface without any cation coordination. As discussed in our previous study, if there is no cation at the interfacial region, CO₂ activation cannot occur, and the sampled free energy keeps increasing without any transition state located.³⁵ As the CO₂ activation is RDS, the overall CO₂RR cannot be initiated in electrolytes without cations. During the elementary reactions of CO₂RR, K ions have relatively stable positions from the Au surfaces, and one of them is always in the inner-sphere region without being part of the surface (Figure S13). Apart from the inner-sphere cation, the other K⁺ near the Au-water interface (K2, Figure S13) should also contribute to the stabilization of key reaction intermediate (*CO₂), and much higher CO₂ activation energy barrier would be observed if there is only one cation at interface with the second one in bulk solution (Figure S14). These additional simulations demonstrate that the cation stabilizes the $*CO_2$ intermediate even though it is not in the inner-sphere region, which is in good agreement with the recent work by Choi and co-workers.⁶⁶ Therefore, we conclude that the cation role is crucial to CO₂RR by promoting the rate-determining CO₂ activation step via short-range coordination interactions (Figure S10). The cation coordination effect is further validated by the increased energy barrier during the slow-growth sampling with one K ion fixed, where there are less K-O (CO₂) coordination interactions thus contributing to slower reaction kinetics (Figure S15).



Figure 5. Complete free energy landscape of CO_2RR and competitive HER at Au-water interfaces with two K cations. The structures of TS are shown on top. The charges transferred to key intermediates (*CO₂, *COOH, *CO) are shown in the insert figure, where the charge transfer in CHE model is indicated by dashed lines. Color code: Au, golden; K, purple; C, blue; O, red; H, white.

Before constructing the free energy landscape of CO₂ reduction, the competing HER also deserves an in-depth mechanistic study at the Au-water interface. Similarly, elementary reactions during HER, including the Volmer and Heyrovsky steps, are investigated by SG-AIMD. The Tafel step is neglected since the Heyrovsky step is easier than a second Volmer step, demonstrating that HER follows the Volmer-Heyrovsky pathway but with quite high reaction barriers (0.97 eV in Volmer step; 0.79 eV in Heyrovsky step) as compared to CO₂RR (Figure S16). For the rate-determining Volmer step, both K-coordinated and K-noncoordinated H₂O molecules are considered, where similar high dissociation barriers around 1.0 eV are observed (Figure S17 and S18). Before simulating the Heyrovsky step, the OHproduced by the Volmer step is replaced by a H₂O molecule since the OH⁻ diffusion from the interface to bulk solution is kinetically facile with a quite small barrier of 0.05 eV (Figure S19). The existence of hydroxyl species at the interface prohibits the following Heyrovsky step with a much higher reaction barrier (1.31 eV) compared to the neutral Au-water interface (0.79 eV) as shown in Figure S20. Similar to the CO_2RR , the cation coverage effect on the ratedetermining water dissociation step during the HER is further explored via Au-water interfacial models with one cation at the interface and the other in the bulk electrolyte (Figure S21). With only one cation at the interface, the kinetic barrier of water dissociation is 0.80 eV, smaller than 0.97 eV with two cations at Au-water interfaces, demonstrating that the high cation coverage leads to poor HER activity via suppressing the water dissociation. Comparing with previous experimental results by Monteiro et al.,³⁹ the high near-surface cation concentration (e.g., K⁺, Cs⁺) can prohibit the HER due to the accumulation of these species at the OHP, which agrees well with our simulation results. Furthermore, it has been experimentally shown that both

cation identity and coverage effect exist in HER kinetic measurements,³⁹ deserving further theoretical simulation studies on the related promotion and/or inhibition roles.

It should be noted that the electrode potential varies along with the electron and ion transfer reaction paths due to the finite size of the simulation cell. To minimize the effect of inconstant potential, the correction method proposed by Chan and Nørskov is adopted,⁶⁷ where the solidelectrolyte interface is approximated as a capacitor with constant capacitance but varying charge and potential during the charge transfer reaction. The finite size error can be estimated by evaluating the work functions (WF) and charge distributions of two key states (e.g., initial state and TS). It is worth mentioning the WF is quite sensitive to water orientations,⁶⁸ thus additional constrained AIMD simulations are required to calculate the averaged WF. Data related to constant potential corrections are summarized in Table S2, including all of the elementary steps in both CO₂RR and HER. The maximum correction is 0.3 eV for the Volmer step, somewhat lower than that on a Pt(111) (3 × 4) cell with static water molecules of 0.5 eV,⁶⁷ but comparable to the correction (0.24 eV) reported for FeN₄-embedded graphene in a liquid electrolyte.⁶⁹ Moreover, the energy corrections from replacing OH by H₂O between reaction steps are included via the CHE model (details of the energy corrections are given in supporting information with values in Table S3).

Table 1. Summary of reaction barrier (E_a) and reaction energy (E_r) obtained in slow-growth sampling simulations, constant-potential energy corrections (ΔE_{corr}), and summarized data (free energy barrier, ΔG_b , and reaction free energy, ΔG_r) in free energy landscape including elementary steps in CO₂RR and HER. The unit is eV.

Reaction steps	Ea	Er	$\Delta E_{corr}(E_a)$	$\Delta E_{\rm corr}(E_r)$	ΔG_b	ΔG_r
CO ₂ (aq)-to-*CO ₂	0.61	0.26	0.05	-0.05	0.66	0.21
*CO ₂ -to-*COOH	0.35	0.35	0.03	-0.12	0.38	0.23
*COOH-to-*CO	0.58	0.41	-0.02	0.11	0.56	0.52
*CO desorption	0.35	0.15	-0.02	0.00	0.33	0.15
Volmer step	0.97	0.96	0.30	0.29	1.27	1.25
Heyrovsky step	0.79	0.57	0.04	0.23	0.83	0.80

Eventually, we are capable of drawing the free energy landscape of CO₂RR and HER at Auwater-2K interfaces with key TS structures shown on top (**Figure 5** and Table 1). Clearly, CO₂RR is facile, where the CO₂ activation (CO₂(aq)-to-*CO₂) is the RDS with the free energy barrier of 0.66 eV at the simulated conditions corresponding to -1.17 V_{RHE} at pH of 7. Meanwhile, the inhibited HER shows a higher energy barrier of 1.27 eV in the rate-limiting Volmer step. Therefore, under a similar electrochemical condition with two K cations at Auwater interfaces, HER is highly suppressed, but CO₂RR is facilitated. It is speculated that a high cation concentration (0.027 atom/Å² in our cell) contributes to the poor HER kinetics with a blockage effect caused by cation accumulation at interfaces, thus enhancing the selectivity of overall CO₂RR on Au surfaces. Such a kinetic blockage effect on HER is further demonstrated, and a lower water dissociation barrier (0.58 eV) is observed at the Au-water interface (0.94 eV), as shown in Figure S22 (Table S4). It should be noted that the two models show very similar work functions, when averaged over 6 ps AIMD simulations (1.88 ± 0.26 eV and 1.83 ± 0.27 eV for 2K-at-interface and 2K-in-bulk, respectively), thus almost identical applied potentials are realized. The existence of cations affects the interfacial distributions of water molecules, which can be represented by the oxygen concentration profiles in 2K-at-interface and 2K-inbulk (Figure S23). The model with 2K at the interface shows a more pronounced depletion of water molecules between the first and second solvation shells than when the K ions are in the bulk region (Figure S24). Statistical analysis of the distribution of H bonds along the z direction (Figure S25) is consistent with a recent suggestion that reduced H bond network connectivity within the EDL region inhibits the water dissociation and thus HER kinetics.⁷⁰ Very recently, experimental studies by Koper and co-workers also observed the inhibition effect of cations towards HER on Au electrodes, which is attributed to the crowded double layer with high nearsurface cation concentrations.^{33, 39} On the other hand, another study by the same group also illustrates the important role of cations on the CO₂ electroreductions, where no CO is observed on Au in solutions without metal cations.²⁶ In our simulation models, K cations are responsible for introducing the negative applied potential and the coordination role. Additionally, for innersphere CO₂ electroreductions modulated by solvents and cations, the charge transfer to key intermediates is highly different from that in CHE model (insert of Figure 5). From a computational perspective, it is significant to study various electrode-electrolyte combinations independently to differentiate the reaction parameters' promotion or inhibition effects, including cation concentration/identity, pH, and potentials in both CO₂RR and HER. In spite of the dynamic complexity of solid-liquid interfaces, decoupling these effects will contribute to the optimizations of reaction conditions for CO₂ reductions as well as hydrogen evolutions.

Conclusion

We have investigated the CO₂RR over Au surfaces from atomic-level simulations via cationcoordinated inner-sphere electroreduction. By using the SG-AIMD simulation technique, the complete free energy diagram of CO₂RR under electrochemical conditions is constructed for the first time. At Au-water interfaces with K cations, CO₂RR is facile, and CO₂ activation is the RDS with a free energy barrier of 0.66 eV. Meanwhile, HER is highly suppressed showing an energy barrier of 1.27 eV in the rate-limiting Volmer step. Our systematic molecular dynamics study indicates that CO₂RR has superior catalytic performance over the competitive HER due to the cation promotion effect. Moreover, theoretical simulations of the final *CO desorption step confirm that *CO_{atop} is the authentic active intermediate during CO₂ electroreductions while *CO_{bridge} is a kinetically inert spectator, which is in good agreement with previous experiments. Further simulations including the *CO_{bridge} as a spectator at Auwater interfaces are meaningful, which will be considered in our future work. This study motivates the development of periodic models mimicking the electrode-electrolyte interface under electrochemical conditions, which can be extended into studying various electrocatalytic reactions via AIMD simulations.

Supporting information

The Supporting Information is available free of charge, including the additional simulation models, force and free energy profiles, Bader charge analysis results, and detailed energy corrections.

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Declaration of interests

The authors declare no competing financial interests.

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Data availability

The datasets and key structures generated through theoretical simulations are available in the Zenodo database at https://doi.org/10.5281/zenodo.7474433.

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