

Unraveling the Activity and Selectivity of CO₂ Electrochemical Reduction on Single Atom Catalyst by Potential Based Scaling Relationship

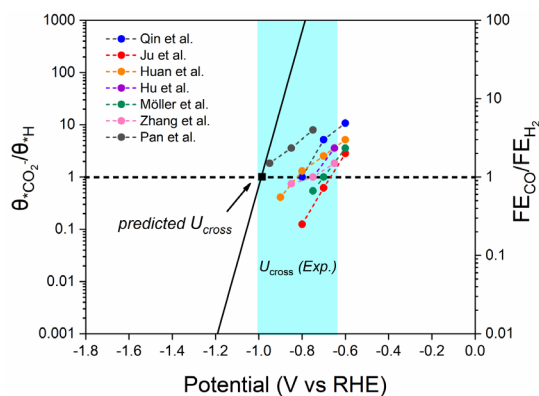
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Abstract: Achieving the fundamental understanding of electrochemical processes occurring at the complex electrode-liquid interface is a grand challenge in catalysis. Herein, to gain theoretical insights into the experimentally observed potential-dependent activity and selectivity for CO₂ reduction reaction (CO₂RR) on the popular single-iron-atom catalyst, we performed ab initio molecular dynamics (AIMD) simulation, constrained MD sampling and the thermodynamic integration to acquire the free energy profiles for the proton and electron transfer processes of CO₂ at different potentials. We have demonstrated that the adsorption of CO₂ is significantly coupled with the electron transfer from the substrate while the further protonation does not show distinct charge variation. This strongly suggest that CO₂ adsorption is potential-dependent and optimizing the electrode potential is vital to achieve the efficient activated adsorption of CO₂. We further identified a linear scaling relationship between the reaction free energy (ΔG) and the potential for key elementary steps of CO₂RR and HER, of which the slope is adsorbate-specific and not as simple as 1 eV per Volt as suggested by the traditional Computational Hydrogen Electrode (CHE) model. The derived scaling relationship can reproduce the experimental onset potential (U_{onset}) of CO₂RR, potential of the maximal CO₂-to-CO Faraday Efficiency (FE_{CO}), and the potential where $FE_{\text{CO}} = FE_{\text{H}_2}$. This suggests that our state-of-the-art model could precisely interpret the activity and selectivity of CO₂RR/HER on Fe-N₄-C catalyst under different electrode potentials. In general, our study not only provides an innovative insight into the theoretical explanation of the origin of solvation effect from the perspective of charge transfer but also emphasizes the critical role of electrode potential on theoretical consideration of catalytic activity, which offers a profound understanding of the electrochemical environment and bridges the gap between theoretical predictions and experiment results.



Introduction

Our increasing consumption of carbon-rich fossil fuels has inevitably resulted in significant emissions of green-house gases, most notably carbon dioxide (CO₂). The electrochemical CO₂ reduction (CO₂RR) has been recognized as an attractive technique for the reduction of the atmospheric concentration of CO₂ as well as the utilization of carbon resources.¹⁻⁴ Among the potential electrocatalysts in CO₂RR, the two-dimensional (2D) atomic dispersed in nitrogen-doped carbon support catalyst (TM-N-C, TM = Fe⁵⁻⁷, Co⁸, Ni⁹⁻¹¹ etc.) exhibits the excellent performance for their lower overpotentials, and high atomic efficiency, compared to the traditional metal catalysts.¹²⁻¹⁴ Extensive studies have been devoted to understanding the mechanistic nature of CO₂RR on this type of catalyst,¹⁵⁻¹⁷ however, understanding the potential-dependent selectivity has remained challenging due to difficulty in properly addressing the complexity of the electrochemical interface.^{18,19}

Density functional theory (DFT) calculation has been widely used to explore the electrochemical properties for CO₂RR on various catalyst.²⁰⁻²² By using the simple but effective Computational Hydrogen Electrode (CHE) model,²³ previous studies have suggested that the CO₂ reduction to CO on TM-N-C catalysts involves two electron-proton transfer steps and the rate-determining step (RDS) is deemed as the first step ($* + \text{CO}_2 + e^- + \text{H}^+ \rightarrow *\text{COOH}$), where the proton transfer (PT) step and electron transfer (ET) step were usually assumed to be coupled in theoretical models.²⁴⁻²⁶ However, Koper et al. pointed out that the mechanisms of CO₂ hydrogenation to *COOH intermediate are diverse for different electrocatalysts, where the PT step and ET step could be sequential as in molecular electrocatalysts besides the coupled or concerted cases.²⁷⁻³⁰ In the case of heterogeneous TM-N-C catalysts, the experimental evidence has demonstrated that the CO formation rate on Fe-N-C catalyst is independent of pH value on the NHE scale, implying that the PT may not be the rate-determining step (RDS).³¹ These evidences signify that the hydrogenation of CO₂ to *COOH probably need to be considered by decoupling the electron-proton transfer. However, in the usual practice, both overpotential (thermodynamics) and barriers (kinetics) are assumed to depend on the free energy change of the reaction intermediate before and after a coupled PCET.^{32,33} Consequently, this may not be able to give an accurate estimation of either overpotential (associated with a non-coupled ET step) or selectivity (activation barriers to form different products). For example, many reported efficient FeN_x-based single-atom catalysts for CO₂ conversion to CO

has low overpotential (less than ~ 0.2 V) with the measured onset potential (U_{onset}) at $-0.2 \sim -0.3$ V vs RHE, whereas their DFT calculations suggested that the theoretically estimated overpotential for CO formation are mostly larger than 0.50 V (i.e., the ΔG of *COOH formation).^{34–36} Similarly, this discrepancy is universal in studies of other TM-N-C catalyst (TM = Zn,³⁷ Co,³⁸ Ni,¹⁰ et.al), due to the inability to quantitatively capture the potential-dependent free energy profile from overlooking the influences of the ET-PT decoupling, inconsistent workfunction of the catalyst surface along the reaction coordinate, and the role of explicit water environment.^{39–42}

Another challenge is to unify the hydrogen evolution reaction (HER) and CO₂RR kinetics under the same theoretical framework. Since a potential significantly more negative than 0 V RHE is required in a practical CO₂RR electrolyzer, the competing HER could significantly limit the Faradaic efficiency (FE) and production rate of CO and result in low selectivity.^{43–45} As an unwanted phenomenon at low overpotential, proton (from hydronium in acidic media or water in alkaline media) would readily occupy the adsorption site and consume electron supplied from cathode, resulting a side reaction with high FE_{H_2} . It is reported that the measured FE_{H_2} rapidly rises at -0.55 V vs RHE for Fe-N-C, while the corresponding electrode potential is about -0.70 V vs RHE for Ni-N-C.⁴⁶ However, the potential-dependence of the competition between HER and CO₂RR pathways could not be quantified in the CHE-based simulation. To the best of our knowledge, there is still a lack of the theoretical insight which could quantitatively match and well explain the experimental potential-dependent activity on TM-N-C catalysts.

In addition, the solvation stabilization on different intermediate can vary hugely due to their diverse chemical nature and dipole, and hydrophilicity. Moreover, since the free energy is needed for initial, transition, and final state of a reaction step, a sufficiently thick explicit water slab is necessary to ensure proper solvation of every species involved. To address this issue, ab initio molecule dynamics (AIMD) simulation has been successfully applied to study the catalytic reactions in electrochemical environments, for it could provide the dynamic properties of electrolyte-solution interface at the quantum mechanical (QM) level.^{47–49} However, the vast configurational space of the a thick explicit water slab at an electrified surface needs very efficient and consistent sampling along the reaction coordinate, otherwise the resulted reaction free energy would be biased toward a few selected local minima configuration. In this study, we firstly explored the free energy profile for the decoupled electro-proton transfer of *COOH intermediate formation from CO₂ by employing DFT based

constrained AIMD simulation combined with thermodynamic integration (TI) method and fully explicit solvation of 20 Å thick. By introducing counterions (Na^+ , Cl^-), we are able to study the energetics of the reaction system at different charge state or applied potential. We found a linear relationship between the potential and ΔG for the first ET step where the charge-neutral linear CO_2 is reduced by Fe center to a bent CO_2^- radical. This originates in the potential-dependence of the solvation free energy of CO_2 as it transforms to a stronger H-bond acceptor inside an electrified contact bilayer of water. We have confirmed that the ET in fact occurs prior to the proton transfer during CO_2 adsorption without proceeding in a PCET fashion. In order to understand the potential-dependent competition between CO_2RR and HER, we similarly computed the free energies of $^*\text{H}$ formation from solvated proton adsorption as a function of electrode potential. We predicted that the onset potential (U_{onset}) of CO_2RR and the potential on the maximum FE_{CO} are 0.22 V and 0.49 V vs RHE, respectively, which are surprisingly consistent with the experimental observation. We further considered that the FE_{CO} is theoretically equal to FE_{H_2} at the ‘cross-over’ potential for the same ΔG between CO_2 adsorption and hydrogen adsorption, and likewise, our prediction is also in agreement with many reported experimental data. In a word, our computational results have provided a rational and detail analysis for the potential-dependent activity of CO_2RR on Fe- $\text{N}_4\text{-C}$ catalyst.

Methods

Model set-up for the electrocatalytic interface. The Fe- $\text{N}_4\text{-C}$ substrate was modeled by a single layer of four nitrogen atoms doped graphene with single atom Fe embedded in the center (Figure S1). The Fe- $\text{N}_4\text{-C}$ slab was composed of a 6×4 supercell with dimensions are $17.04 \times 14.76 \times 20.00 \text{ \AA}^3$ and was allowed to repeat periodically. The model was filled with bulk water, which contained 141 H_2O molecules and possessed an average density of $\sim 1 \text{ g/cm}^3$. The radial distribution functions (RDFs) and the coordination number (from integration of the RDFs) of O-O and O-H for validation of liquid water structure is also provided in Figure S1, which is consistent with experimentally determined results,⁵⁰ validating the proper convergence of the water structure to bulk behaviors.

DFT method details. All Born–Oppenheimer molecular dynamics (BOMD) simulations and constrained MD simulations were performed by employing CP2K/Quickstep package.⁵¹ The

electronic structure calculations are described by DFT with spin-polarized Perdew–Burke–Ernzerhof (PBE) functional and mixed double- ζ Gaussian and plane-wave (GPW) basis sets with energy cutoff of 400 Ry.⁵² The core electrons were modeled by Goedecker-Teter-Hutter (GTH) pseudopotentials with 16, 4, 5, 6, and 1 valence electrons for Fe, C, N, O, and H, respectively. The MD simulations were sampled by the canonical (NVT) ensemble employing Nose–Hoover thermostats with a time step of 1.0 fs at the target temperature of 300 K.^{53,54} In all the calculations, the DFT-D3 method proposed by Grimme et. al was adopted to better describe the non-covalent interactions.^{55,56}

Free energy calculation. In the thermodynamic integration (TI) method, the free reaction energy and kinetic barrier is obtained by applying a holonomic constraint on reaction coordinate (ζ) during MD simulations and integrating over the average unbiased force associated with the reaction coordinate,^{57,58} as is shown in eq (1),

$$\Delta A(\zeta_a, \zeta_b) = - \int_{\zeta_a}^{\zeta_b} F(\zeta) d\zeta \quad (1)$$

where $\Delta A(\zeta_a, \zeta_b)$ is the free energy difference between two reaction coordinates (ζ_a and ζ_b), $F(\zeta)$ is the averaged constrained force. For CO₂ adsorption on the single Fe stie (CO₂ + e⁻ + * = *CO₂⁻), the distance between Fe and C atoms is chosen as collective variable (CV), which is defined by eq (2),

$$CV = \zeta(r) = |\mathbf{r}_{Fe} - \mathbf{r}_C| \quad (2)$$

where r_{Fe} and r_C refer to the coordinates of Fe atom and C atom of CO₂. (Figure S3a).

For the protonation of *CO₂⁻ under acidic condition (*CO₂⁻ + H₃O⁺ = *COOH + H₂O), the CV is defined by eq (3)

$$CV = \zeta(r) = |\mathbf{r}_{O_A} - \mathbf{r}_H| - |\mathbf{r}_{O_B} - \mathbf{r}_H| \quad (3)$$

where r_{O_A} refers to the coordinate of O atom on the hydronium ion (H₃O⁺), r_{O_B} refers to the coordinate O atom of the adsorbed CO₂, and r_H refers to the coordinate of solvated proton on H₃O⁺ (Figure S3b).

For the solvated proton (H₃O⁺) adsorption on the single Fe stie under acidic condition (H₃O⁺ + e⁻ + * = *H + H₂O), the CV is defined by eq (4),

$$CV = \zeta(r) = |\mathbf{r}_{Fe} - \mathbf{r}_H| - |\mathbf{r}_O - \mathbf{r}_H| \quad (4)$$

where r_{Fe} refers to the coordinate of Fe atom, r_{O} refers to the coordinate of O atom on H_3O^+ , and r_{H} refers to the coordinate of solvated proton on H_3O^+ (Figure S3c).

Modeling the influence of applied potential. The potential of zero charge (PZC) is a crucial concept on the field of electrochemistry which can be experimentally confirmed by the measurement and regulation of surface net charge. In this case, the theoretical adjustment of surface electrode potential is applied by adding alkali metal ions (K^+ , Na^+) or halogen ions (F^- , Cl^- , et. al) into liquid layer to increase or decrease the net charge on surface. In our study, the different number of Na^+ and Cl^- were added on the liquid model (Figure S2) and AIMD simulations were further performed to equilibrate the system. The electrode potentials (Φ) of TM- N_4 -C surface were then determined by eq (5),

$$\Phi = \frac{\sigma}{C} + \Phi_{\text{PZC}} \quad (5)$$

where σ is the calculated surface net charge via Bader charge analysis,⁵⁹ C and Φ_{PZC} is the experimental capacitance of pristine graphene ($\sim 21 \mu\text{F}/\text{cm}^2$) and potential of zero charge (-0.07 V vs RHE), respectively.^{60,61} We considered the average value of potential at initial state (U_{IS}) and (U_{FS}) as the potential (U_{r}) of the reaction (i.e., $U_{\text{r}} = (U_{\text{IS}} + U_{\text{FS}})/2$). Note that here the added cations/anions serves no chemical role, and this technique has been shown to properly describe the potential-dependence of electrochemical barriers.⁶² The detailed electrode potentials, surface charges, and corresponding correction terms for each free energy profiles are provided in Table S1. A detailed discussion of the AIMD-TI method vs. the constant-potential methods is provided in Note S8.

Molecular fragment calculations. The molecular fragments are modeled using Gaussian 16 program⁶³ (Revision C.01). The geometry optimizations and potential energy surface (PES) scans are performed using PBE0 functional⁶⁴ with def2-TZVP basis sets⁶⁵ and D3 correction (Becke-Johnson damping)⁵⁶ to better account for the dispersion interactions. Molecular orbital analysis, Hirshfeld population analysis, and Mayer bond order analysis are performed using the Multiwfn program on the converged wavefunctions from DFT calculation.⁶⁶

Results and discussion

Potential-dependent CO₂ chemisorption. To understand how different applied potential influence the most concerned initial electro-proton transfer step ($* + \text{CO}_2 + e^- + \text{H}^+ \rightarrow *\text{COOH}$) in CO₂RR on Fe-N₄-C catalyst, we first construct the free energy profiles for CO₂ adsorption at different electrode potentials (Figure 1a) by TI on the equilibrated constrained AIMD trajectories. It is observed that the adsorption free energy (ΔG) is strongly dependent on the electrode potentials. Specifically, as the potential shifts negatively from +0.33 V to -0.45 V, the ΔG accordingly lowers from 0.88 eV to -0.47 eV. Similarly, the free energy barrier (ΔG^\ddagger) dramatically decreases from 0.93 eV to 0.07 eV. This indicates that the low electrode potential can facilitate the CO₂ adsorption in both thermodynamics and kinetics.

Furthermore, the locations of transition states (TS) at different potentials are displayed in Figure 1b, where the difficulty of CO₂ activation can be judged by Fe–C distance which corresponds to the reaction coordinate of the TS on the free energy profile. Under +0.33 V, the Fe–C distance at the TS is as short as 2.18 Å, indicating that the CO₂ molecule has to move very close to the catalyst surface for the full activation of CO₂. However, as the potential shifts to -0.45 V, the corresponding distance increases to 2.83 Å, indicating that the CO₂ can be activated at a farther distance from Fe, which is likely due to a higher electron density at the catalyst surface at a high overpotential.

Interestingly, we found a strong linear Brønsted-Evans-Polanyi (BEP) relationship ($R^2 = 0.997$) between ΔG and ΔG^\ddagger (Figure 1c). Likewise, Figure 1d shows that both ΔG and ΔG^\ddagger correlates decently with the electrode potential, where the R^2 are 0.969 and 0.962, respectively. Note that here the intercept corresponds to the energetics at zero potential, while the slope quantifies the potential dependence of the reaction.

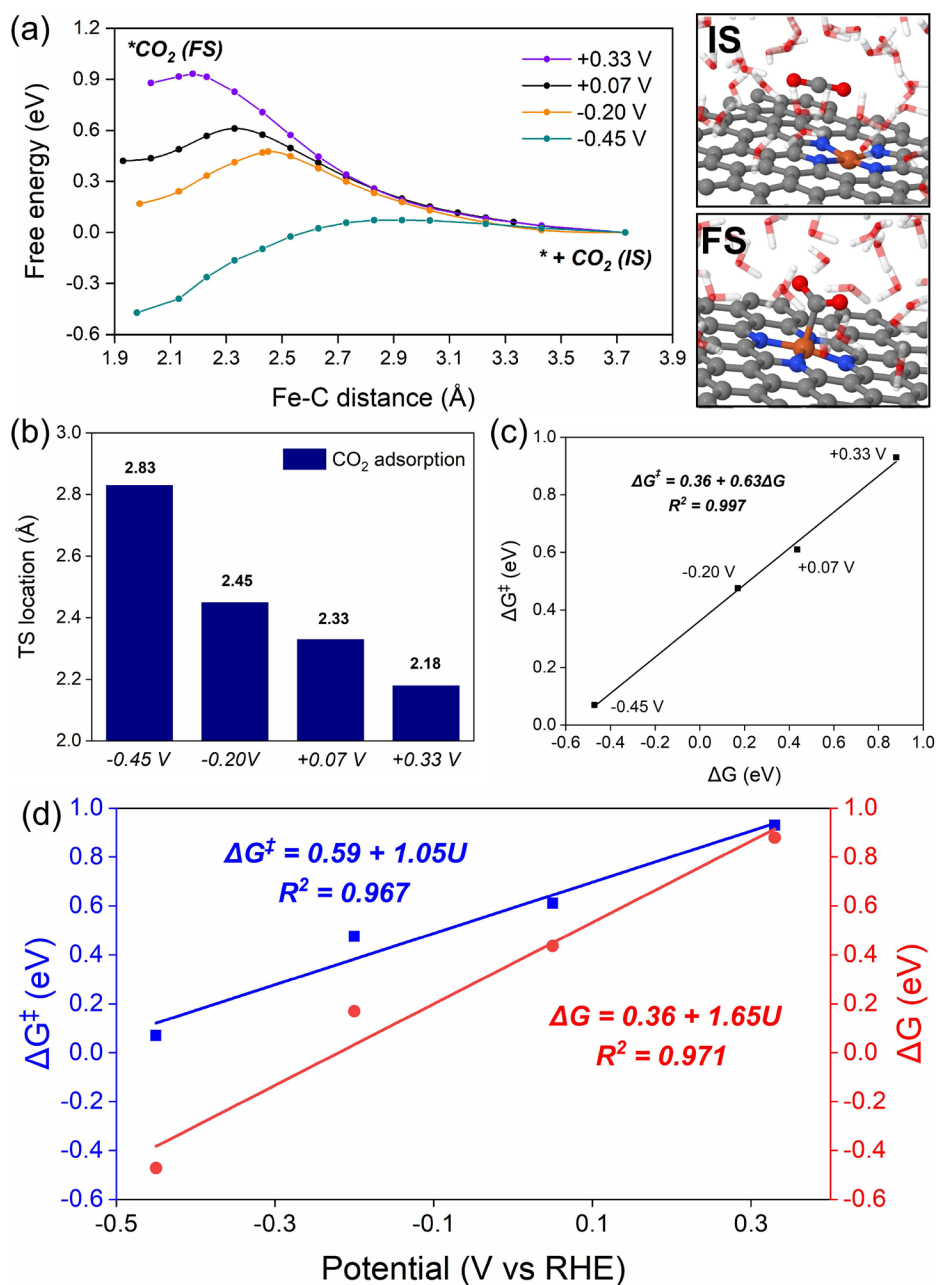


Figure 1. Potential-dependent free energetics of CO₂ adsorption at Fe-N₄-C/water interface.

(a) Free energy profiles of CO₂ adsorption at +0.33 V, +0.07 V, -0.20 V and -0.45 V vs RHE. (b) The location of transition states (TS) during adsorption at different potentials. The fitting linear relationship between (c) ΔG and ΔG^\ddagger , (d) $\Delta G/\Delta G^\ddagger$ and potential.

The potential-dependent free energy profile, the short Fe-C distance in the final state (FS), and the bending of CO₂ during the CO₂ adsorption suggest it is a chemisorption process which involves ET from the catalyst. To confirm this, we analyzed the Mulliken charge variation for the catalyst substrate and the CO₂ species along the reaction coordinate of CO₂ adsorption based on the

constrained MD simulations in Figure 2. Without surprise, both the net charges of C and O atoms show significant decrease during the adsorption process. This confirms that the neutral linear CO₂ is reduced to the bent CO₂⁻ anion where the extra electron resides in the Π* orbital as characterized by the uniform negative shift of Bader charge on C and O. However, the charge states of C and O differs in that the charge of C atom gradually decreases from ~0.48|e| to ~0.23|e| as CO₂ approaches the surface, while the O atoms experience a rapid charge transfer which take place in a very short distance (Figure 2a-b). Prior to approaching the transition state (TS), the O atoms of CO₂ experience no obvious electron transfer and even show a slight positive charge increase. But after crossing over the TS, the charge on O atom undergoes a significant negative shift by ~0.2 |e|.

Having identified the change in charge state of C and O, we further analyzed the charge variation of the catalyst substrate to understand the charge source for activating CO₂. As shown in Figure 2d, it is found that the net charge of the Fe atom shows minor change (less than ~0.2 |e|) upon CO₂ adsorption at +0.07 V, while the charge of the substrate shows significant rise (more than ~0.9 |e|). This contrast suggests that the charge transfer from the catalyst to CO₂ is mainly contributed by the charged N-doped graphene substate (as an electron reservoir), while the single Fe site remains in its initial charge state of formal oxidation state +2. These trends are also observed at -0.20 V and +0.33 V (Figure S8).

The inconsistency between charge shifts on C and on O along the reaction coordinate is likely caused by the non-simultaneity of ET and the geometric bending of the *CO₂. It can be seen in the molecular orbital (MO) diagram (Figure S10) that the HOMO and LUMO of the linear CO₂ are the s-p σ* (5σ_g) orbital and p-p π* (2π_u) orbital, respectively. When an electron is supplied to reduce it vertically, the added electron goes into the C-centered s-p σ* (5σ_g), causing a major charge shift by -0.539 |e| on C (from +0.33 to -0.209 |e|) and a minor shift by -0.230 |e| on O (from -0.165 to -0.395 |e|). The bond length of C-O only get slight elongated by 0.02 Å since the conjugate system is intact. However, when the CO₂⁻ adapts to the bent configuration, the energy level of the s-p σ* (5σ_g) and p-p π* (2π_u) switches, causing the crossover between HOMO and LUMO. As a result, the unpaired electron in bent CO₂⁻ goes to the distorted p-p π* (6a₁) orbital where the contribution from O is dominant. This induces a charge redistribution within the molecular fragment, shifting 0.202 |e| from C to O. The filling of p-p π* (6a₁) also lowers the Mayer bond order of each C-O by 0.49 and elongate the C-O by 0.08 Å compared to the IS (Table S2). This could explain the evolution of C-O

bond length along the free energy profile (Figure 2d) where the C-O bond length stays almost unchanged around 1.19 Å in the IS-TS segment and then experience a sudden jump from c.a. 1.20 Å to 1.27 Å in the TS-FS segment.

Having identified CO₂ bending to be a key process, we move on to investigate how the O-C-O angle changes along the reaction coordinate of Fe-C distance. In Figure 2e, the O-C-O stays around 175 ° in the first half of the IS-TS segment. After crossing the position corresponding to a Fe-C distance of c.a. 2.7 Å, there comes a dramatic decrease in the O-C-O angle from c.a. 170 ° to 130 °. Such trend suggest that O-C-O is a better collected variable for describing the region around the TS on the free energy surface. Hence, we reconstructed the free energy surface (Figure 2f) by using O-C-O angle as the CV for TI. Under this “bending coordinate”, the first half of the IS-TS segment forms a “cliff” on the FES since the initial ET is vertical and cause no change in the configuration of CO₂. At about 170 °, the bending process starts, and the FE profile ahead forms a smooth bump with continuous landscape free of spikes or sudden jumps. In addition, the TS locations at different potential are about the same, c.a. 140 °, which is in sharp contrast with the case in Figure 1a where the TS location exhibit a strong potential-dependence. In a word, O-C-O angle as a CV merits potential-independent and metal-independent FE landscape since it focuses on the electronic and geometric changes within the adsorbate itself. Every CV has its blind spot due to emphasis on a specific local phenomenon that it is forged with. To gain a more comprehensive understanding of the system of study, it is worth the effort to explore a variety of CVs either for sampling or for post-analysis.

From the discussions above we could conclude on the mechanism of the CO₂ adsorption on Fe-N₄-C: (i) At the IS, the linear, charge-neutral CO₂ is weakly physisorbed above the FeN₄ motif.

(ii) In the first half of the IS-TS segment, CO₂ approaches the Fe center while maintaining its charge state and configuration.

(iii) About the midpoint of the IS-TS segment (high overpotential would advance this event), the electrified catalyst surface initiates an ET to the C-centered s-p σ^* orbital in CO₂, with Fe center acting as an electron relay. The CO₂ is reduced to CO₂⁻ in a nearly vertical manner and stays in the initial configuration.

(iv) In the second half of the IS-TS segment, the CO₂⁻ starts to form coordination bond to the Fe center via C. The Fe-C formation also induces the CO₂⁻ to start bending which gradually raises the

energy level of s-p σ^* (current HOMO) while lowering the energy level of p-p π^* (current LUMO).
(v) At TS, the s-p σ^* and p-p π^* becomes degenerate, and the unpaired electron starts to cross into the p-p π^* (current HOMO) and redistribute negative charge from C to O.
(vi) In the TS-FS segment, crossover between s-p σ^* and p-p π^* takes place, reversing the LUMO and HOMO, the unpaired electron completes its crossing to p-p π^* (current HOMO) and weakens the C-O by 0.5 bond order. In this process, the catalyst surface keeps supplying electron to the C through Fe-C to replenish the loss of electron density on C due to HOMO-LUMO crossover.
(vii) At FS, the bending process ends and a bent $^*CO_2^-$ is formed.

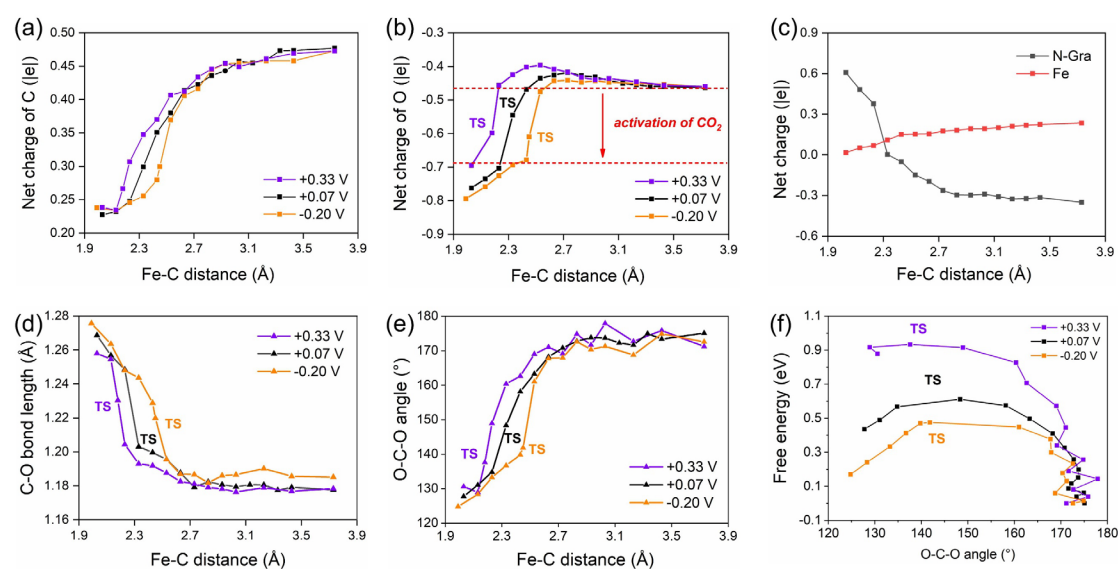


Figure 2. Exploring the mechanistic nature of CO₂ activation on Fe active site. (a) The evolution of Mulliken charge on (a) C, (b) O, and (c) Fe along the Fe-C distance coordinate, at different potentials. The evolution of (d) C-O bond length and (e) O-C-O angle along the Fe-C distance coordinate. (f) The free energy profile of CO chemisorption with O-C-O angle being the reaction coordinate. Results obtained at potential of +0.33, +0.07, and -0.20 V vs. RHE are shown.

At the end of this section, we would like to comment on the origin of the linear relationship we obtained in Figure 1. In Figure 3, we show the PES of O-C-O bending of neutral CO₂ and anionic CO₂⁻ from relaxed scan. The PES of neutral CO₂ has only one extremum at 180°, while the PES anionic CO₂⁻ has a minimum at c.a. 135°. The crossing point of the two PES is the TS of the CO₂ reduction process. Although the picture of facile ET during adsorption process is indeed similar to the case of CO₂ activation on Au and Ag surfaces reported in ref²⁰, we intend to claim that the CO₂RR mechanisms on metal catalysts and single atom catalysts (TM-N-C) are not identical, since

the latter features a more discrete d energy levels (which resembles more the macrocyclic complexes) while the former has a continuous density of state around the Fermi level (metallic property).^{15,39} By applying a positive or negative electrode potential, we are effectively shifting the PES of the initial state (neutral CO₂ + electron) downward or upward, respectively. Since the near-minimum regions of both PES have a parabolic shape, treating both PES as parabolas and analytically solving for the ΔG , ΔG^\ddagger and the TS location would yield a linear correlation between each two of them, which is what we have known as BEP relation. However, in the case of CO₂ reduction, the PES of anionic CO₂⁻ is not well approximated by a parabola due to the local minimum at 180° corresponding to the vertical reduction product of linear CO₂. Such inharmonicity and asymmetry between the PES of reactant and product causes significant deviation of the potential-dependence relation from linear behavior, especially at extreme positive or negative potentials (Figure 3c). Such relationship could be better approximated by a quadratic function with a R-square of 0.9998. However, quadratic regression could cause severe overfitting problems especially in the case of this study where the amount of data points (at different electrode potentials) is relatively small. Moreover, in the region corresponding to -1.0~0 V, the BEP relation is not significantly affected by the inharmonicity and a decent linear fitting with R² of 0.993 could be obtained. Therefore, we believe the linear potential-dependence of free energy change and barriers of the CO₂ activation process should hold in the potential window of +0.3 ~-0.7 V vs RHE.

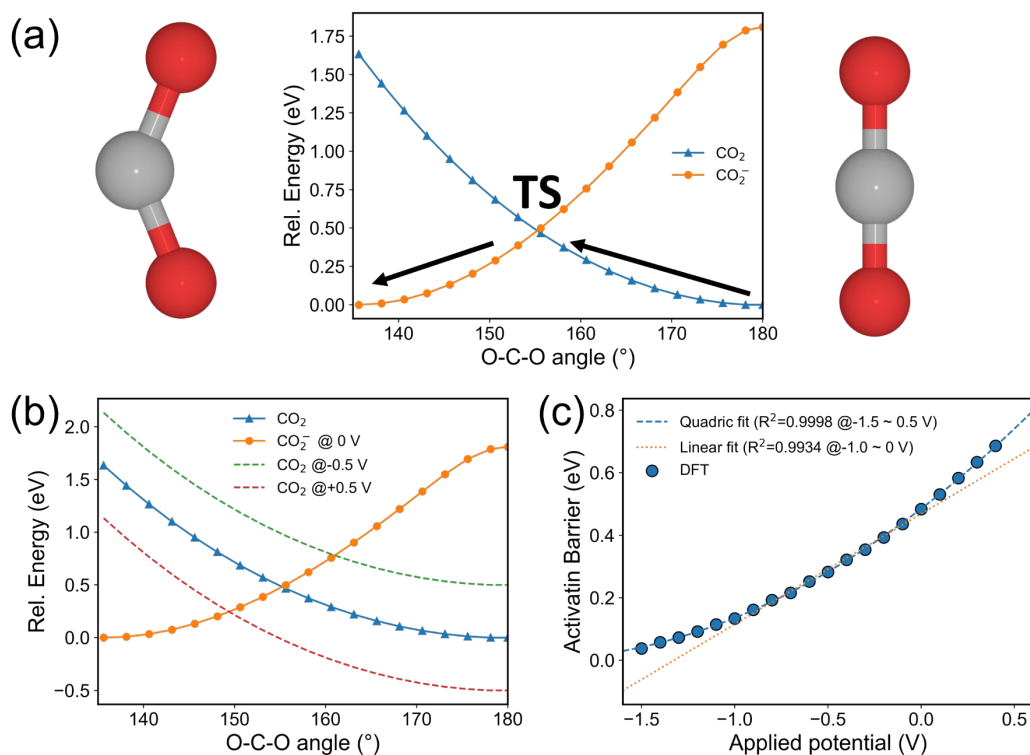


Figure 3. Potential energy surface (PES) of the CO₂ reduction. (a) PES scan of the neutral CO₂ and anionic CO₂⁻, the energy values are referenced against the global minima configurations. (b) The PES of CO₂ reduction at different potentials. (c) Relationship between the activation barrier and the applied potential (which is also $\Delta G/e$) for the CO₂ species. Two fitting methods are used, with their R-square and applicable range provided in the legend. Linear BEP is broken in the high overpotential range due to inharmonicity of the PES of CO₂⁻.

Evolution of local hydrogen bond structure during CO₂ activation. The aqueous electrocatalytic CO₂RR on Fe-N₄-C occurs in a complex environment where the water molecules could affect the energetics of adsorbate through the hydrogen bonds (H-bonds) interaction. To understand how such effect evolve along the reaction coordinate, we counted the number of H-bonds between the oxygen atoms in CO₂ and surrounding water molecules during ET step from constrained AIMD simulations, where the criteria of hydrogen bond formation between *CO₂⁻ and solvation environment are detailed in Supporting Information. As is shown in Figure 4a, the H-bonds between O in activated CO₂ and the nearby water molecules are rapidly formed once the TS is reached (Figure 4a), which suggests that the CO₂ transforms to a state that strongly interacts with its water environment. Such transformation is originated in the HOMO-LUMO crossover as discussed in the last section. To be specific, when the CO₂⁻ bend to the TS configuration, the HOMO of the molecular fragment shifts

from a symmetric non-polar s-p σ^* to a distorted, highly polar p-p π^* (Figure 4b). The crossover causes the spin density (contributed exclusively by the electron transferred from the catalyst) to redistribute to the terminal O atoms (Figure 4c) which as a result become strong H-bond acceptors. Interestingly, as the potential shifts from +0.33 V to -0.20 V, the reaction coordinate corresponding to the H-bond onset shifts accordingly as the position of TS shifts closer to the IS. In other words, the H-bond interaction exerted on CO₂ strengthens at a more negative potential, which indicate that this solvation effect during ET step is also potential-dependent, which is likely due to polarized contact water bilayer acting as stronger H-bond donors.

This can well explain that the total slope (k) of G-U relationship is not as simple as 1 eV/V on CO₂ adsorption. Since the contribution of potential-dependent solvation effect is actually included during constrained MD simulation, the reaction free energy derived by TI can be resolved into three parts, which is $\Delta G = \Delta G_{\text{chem}} + \Delta G_{\text{ele}} + \Delta G_{\text{sol}}$, where ΔG_{chem} , ΔG_{ele} , ΔG_{sol} are the chemical, electrostatic and solvation contributions for the reaction free energy, respectively. It is noted that only last two parts would be affected by the electrode potential. Therefore, the k is also can be divided into two components, i.e., $k = k_{\text{ele}} + k_{\text{sol}}$, where k_{ele} is the charge transfer number and k_{sol} is the solvation effect coefficient. The k_{ele} is calculated as ~ 1 eV/V from bader charge analysis (Table S1) and thus the k_{sol} is about 0.65 eV/V in this case.

Similar trends in H-bond formation are also observed on Co-N₄-C (Figure S13) despite very different free energetics of the CO₂ activation (Figure S9). Hence, we believe the potential-dependent solvation stabilization of activated CO₂⁻ to be a universal effect in CO₂RR on other similar TM-N-C (TM = Co, Ni, et al.) systems, independent from the nature of the metal center.

We would like to emphasize that, due to the strong solvation effect and its dynamic nature, explicit solvation is a must even for a qualitatively correct description of the FES of CO₂ activation. In fact, the chemisorbed CO₂ configuration could not be obtained at all on Fe-N₄-C using simple slab-vacuum or implicit solvation models, since the highly polar FS is not sufficiently stabilized without the directional and dynamic H-bond interactions with sufficient explicit liquid water environment. To address the vast configurational space of solvation configurations, efficient and unbiased sampling is required, otherwise the configurational entropy contribution to the reaction free energy would be inaccurate.

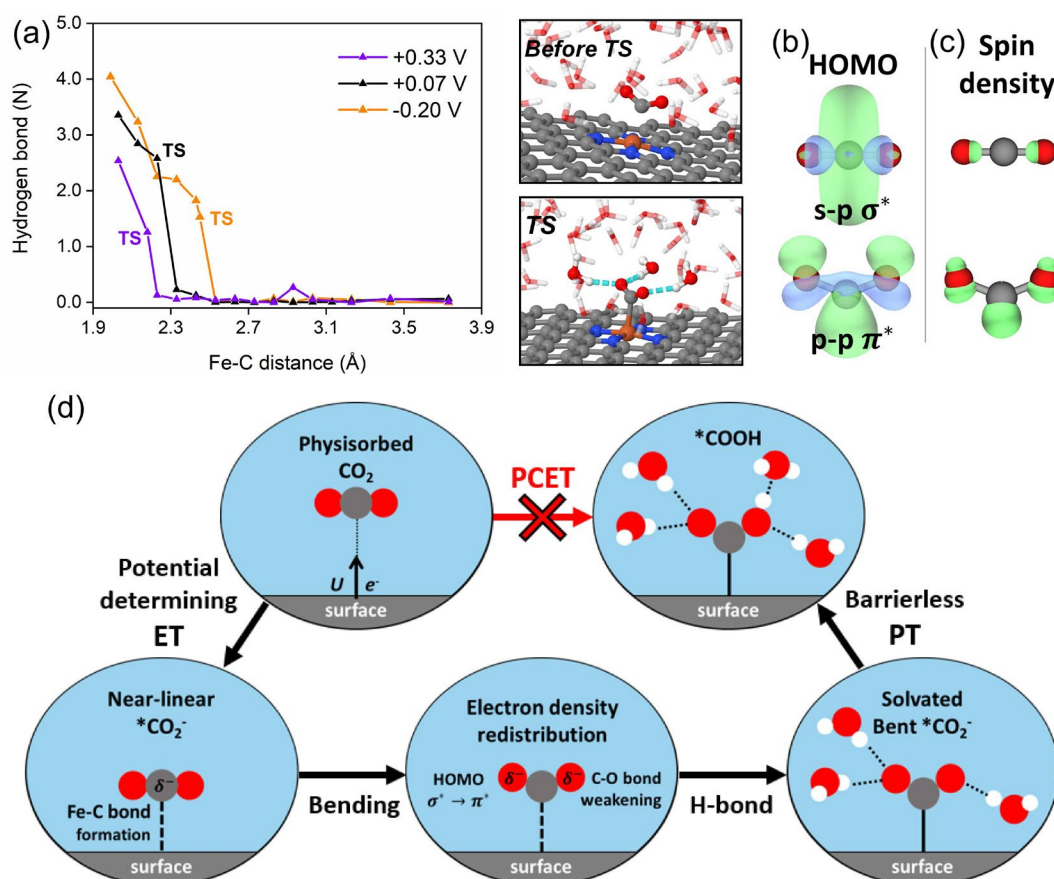


Figure 4. Solvation stabilization of the TS and a revised CO₂ activation mechanism. (a) The statistic number of hydrogen bonds between solvation environment and CO₂ reactant at different potentials on Fe-N₄-C and the snapshots of solvation environment around CO₂ before transition state (TS) and at TS. (b) HOMO and (c) spin density distribution of the CO₂⁻ anion in linear or bent configuration. (d) A revised mechanism of the CO₂ chemisorption based on the potential-dependent free energy profile and chemical bonding analysis.

Facile proton-transfer step. Above results suggest that the CO₂ adsorption is in fact coupled with the electron transfer. As the electrode potential negative shift, the TS and FS can be increasingly stabilized by the polarized water environment via H-bonds at the electrified electrode-water interface, making the CO₂ activation process both kinetically and thermodynamically favorable. However, we are not observing the spontaneous formation of the *COOH intermediate in this activation process, which could be attributed to the stronger acidity of carboxylic acid compared to that of neutral water. Therefore, we further performed constrained MD and thermodynamic integration methods to explore the protonation of *CO₂⁻ by an explicit hydronium, i.e., *CO₂⁻ + H₃O⁺ → *COOH + H₂O. Figure S15 shows the calculated free energy profiles of reaction at different

electrode potentials. It is shown that with the potential decreasing from +0.33 V to -0.19 V, the reaction free energy ($\Delta G(\text{PT})$) only slightly shifts from -0.14 eV to -0.25 eV and the process is almost barrierless. This indicates that the proton uptaking from the adjacent hydronium ion is much more facile compared to the CO_2 adsorption, which is consistent with the experimentally observed weak pH-dependence of CO_2RR rate.³¹ Moreover, the slope of the linear relation between $\Delta G(\text{PT})$ and potential is only 0.20 eV/V (Figure S15b), suggesting that level of electrode potential has less impact on PT step compared with ET step. As a result, compared to the strongly potential-dependent ET step, the PT step is probably less decisive in determining the CO_2RR activity. Additionally, the net charges of Fe adsorption site are also nearly unchanged during PT (Figure S16), implying that the Fe would similarly maintain its oxidation state during $^*\text{COOH}$ formation.⁶

The barrierless nature of the PT also cast doubt on the validity of the usual practice of treating the first ET and PT as coupled. Since the first PT experience no free energy barrier at all catalytically relevant potentials, the overpotential of CO_2 activation to $^*\text{COOH}$ will be solely determined by the first ET step and irrelevant of the PT energetics.³⁰ However, if we are to treat it as a PCET process under the computational hydrogen electrode scheme, then the contribution from PT will be included in the overpotential calculation and cause a severe underestimation (by over 200 mV in this work). The full revised mechanism, and how it differs from the traditional PCET mechanism, is provided in Figure 4d.

Competitive relationship of CO_2RR vs HER. As a major side reaction in CO_2RR , HER significantly affect the CO_2RR activity and selectivity on TM-N-C catalyst. We therefore also explored the free energy profiles (Figure 5a) of acidic HER ($\text{H}_3\text{O} + \text{e}^- = ^*\text{H} + \text{H}_2\text{O}$) at -0.16 V, -0.41 V and -0.66 V vs RHE, respectively. In order to simulating the experimental pH condition (pH 6.8 ~ 7.3) in agreement with CO_2RR , we corrected the free energy derived from thermodynamic integration and the details are presented in Note S7 and Table S3. Similar to CO_2 adsorption, the reaction free energy of solvated proton adsorption ($\Delta G(^*\text{H})$) is also strongly dependent on the electrode potential, with the $\Delta G(^*\text{H})$ gradually decreasing from 0.48 eV to -0.88 eV as the potential shifts from -0.16 V to -0.66 V. By fitting a linear scaling relationship, the slope is calculated to be 2.53 eV/V, which indicates a higher potential-dependence than the CO_2 adsorption step (1.65 eV/V). This indicates that the role of solvation could induce more potential dependent impact for the H adsorption. Interestingly, we found that the configuration of deprotonated H_2O at final state is not

as usual as previous report about metal catalyst.⁶⁷ Specifically, one hydrogen atom of H₂O is pointed to the adsorbed hydrogen rather than the O atom of H₂O from our observation (Figure 5a). This is owing to that the adsorbed H is actually negatively charged by $-0.17 |e|$ and thus have strong affinity to hydrogen atom of H₂O. It is known that the electrode potential has a huge effect to water orientation,^{68,69} which suggests that this reorientation could be influenced by potential.

Based on the scaling relationships, we could derive the theoretical onset potential by solving for the potential value at which the free energy change becomes zero (Figure 5b). As a result, the estimated onset potentials (U_{onset}) of CO₂RR and HER are -0.22 V and -0.49 V, respectively. Specifically, we could conclude that the U_{onset} of HER corresponds to the potential at which the system exhibits the highest CO Faraday Efficiency (FE_{CO}) because the afterwards the competing proton adsorption would consume the electrons, block the active sites, and hence reduce the partial current density of CO₂RR. It is worth noting that our conclusions are consistent with many previous experimental observations about the CO₂RR catalyzed by Fe-N-C, where the U_{onset} of CO₂RR is around $-0.2 \sim -0.4$ V vs RHE and the potential of maximal FE_{CO} is approximately at $-0.47 \sim -0.60$ V vs RHE (see the experimental data on Table S4).^{35,46,70-72} Conversely, the static DFT calculation results based on traditional Computational Hydrogen Electrode (CHE) model reached the incorrect estimation about the selectivity of CO₂RR/HER, i.e., HER would be prior to CO₂RR since the proton adsorption is more thermodynamically favorable (by 180 meV) than the *COOH formation on Fe-N₄-C catalyst (Figure S18).

Furthermore, we observe a crossover potential (U_{cross}) between the two scaling line in the $\Delta G-U$ curve in Figure 5b, where the $\Delta G(*\text{CO}_2^-)$ is equal to $\Delta G(*\text{H})$. At U_{cross} , the same values of ΔG suggest the equivalent coverage of $*\text{CO}_2^-$ ($\theta_{*\text{CO}_2^-}$) and $*\text{H}$ ($\theta_{*\text{H}}$) on the active sites, and thus, the similar FE for CO production and H₂ production (see SI for details). Interestingly, the U_{cross} is predicted to be -0.99 V, which also agrees with previous experimental reports ($-0.68 \sim -1.00$ V vs RHE) which are plotted together in Figure 5c. Consequently, with the three critical potentials ($U_{\text{onset}}(\text{CO}_2\text{RR}) = -0.22$ V, $U_{\text{onset}}(\text{HER}) = -0.49$ V, $U_{\text{cross}} = -0.99$ V) agreeing with experimental data semi-quantitatively, we could breakdown the potential-dependence of CO₂RR activity and selectivity on Fe-N₄-C catalyst into four major stages as illustrated in Figure 5d:

- (I) At $U > -0.22$ V, the current density and yield (including CO and H₂) would extremely low since neither CO₂ adsorption nor *H formation are thermodynamically favorable

($\Delta G(*CO_2^-) > 0$ and $\Delta G(*H) > 0$).

- (II) At $-0.22 \text{ V} > U > -0.49 \text{ V}$, the FE_{CO} would rapidly increase since the CO_2 adsorption becomes thermodynamically feasible while HER is still unfavorable ($\Delta G(*CO_2^-) < 0$ and $\Delta G(*H) > 0$).
- (III) At $-0.49 \text{ V} > U > -0.99 \text{ V}$, the FE_{CO} would peak and then gradually decrease due to a climbing FE_{H_2} of the HER side reaction and blockage of the active sites by $*H$ formation. ($\Delta G(*H) < 0$).
- (IV) At $U < -0.99 \text{ V}$, the FE_{H_2} would outcompete FE_{CO} due to a higher potential-dependence of $*H$ forming energetics ($\Delta G(*H) < \Delta G(*CO_2^-)$). This also indicates that the H_2 would be the major product at very negative electrode potential (or at a high overpotential).

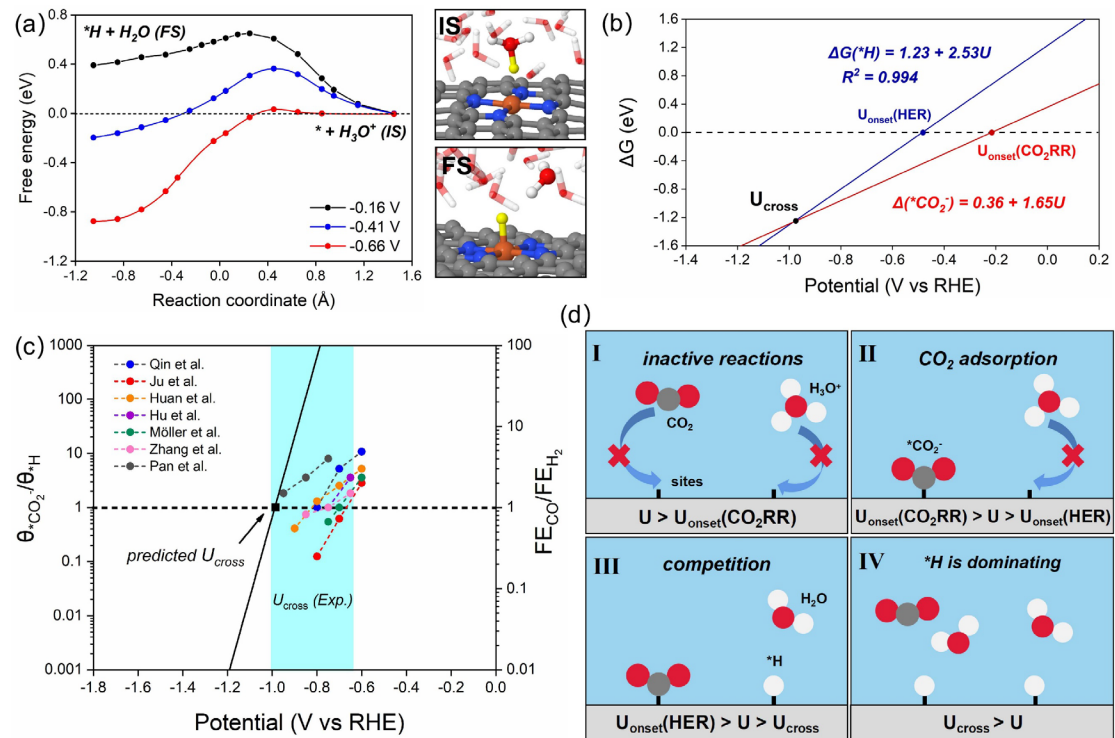


Figure 5. (a) The free energy profile of solvated proton adsorption at -0.16 V, -0.41 V and -0.66 V vs RHE. (b) The fitting linear relationship ($\Delta G-U$) between $\Delta G(*CO_2^-)$, $\Delta G(*H)$ and potential. The $U_{onset}(HER)$, $U_{onset}(CO_2RR)$ and U_{cross} correspond to the potentials at $\Delta G(*CO_2^-) = 0$, $\Delta G(*H) = 0$ and $\Delta G(*CO_2^-) = \Delta G(*H)$, respectively. (c) Comparison of theoretical U_{cross} and experimental U_{cross} . The solid black line is the relationship between $\theta_{*CO_2^-}/\theta_{*H}$ and potential, and the dotted lines are the relationships between experimental FE_{CO}/FE_{H_2} and potential from previous studies.^{34-36,38,46,70,71} The theoretical U_{cross} is the potential at $\theta_{*CO_2^-} = \theta_{*H}$, and the experimental U_{cross} is the potential at

$$FE_{CO} = FE_{H_2}.$$

Conclusion

By employing constrained AIMD simulation for configurational sampling combined with thermodynamic integration method, the free energy landscape of the key activation steps of CO₂RR and HER on Fe-N₄-C catalyst have been explored. By analyzing the charge state and geometry of the adsorbate along the reaction coordinate, and by cross-checking with a molecular fragment model, we have identified the potential determining step to be the chemisorption of CO₂ to form CO₂⁻ where the CO₂ molecule first undergoes a vertical ET to form a linear anion, and then it bends to undergo a HOMO-LUMO crossover at the TS. The TS and FS are highly polarized due to charge redistribution and are significantly stabilized by the potential-dependent solvation effect. The PT afterwards is found to be nearly barrierless and should be treated as a decoupled step and excluded from overpotential calculation. Likewise, the free energy profile of competing *H formation from hydronium has also been investigated considered at different potentials using the same sampling methods. Based on the free energetics we semi-quantitatively reproduced the experimental potential-dependent CO₂RR/HER selectivity from first principles. The main conclusions are listed below:

- (I) The CO₂ molecule first undergoes a vertical ET to form a linear anion, and then it bends to undergo a HOMO-LUMO crossover at the TS. The TS and FS are highly polarized due to charge redistribution and are significantly stabilized by the potential-dependent solvation effect. The reaction free energy (ΔG), energy barrier (ΔG^\ddagger) as well as the location of transition state (TS) are dependent on the electrode potential. The electrode potential exhibit linear scaling relationship with ΔG and ΔG^\ddagger , which is originated in the intersection between the harmonic region of the PES of neutral CO₂ and anionic CO₂⁻.
- (II) Compared to the ET step, the PT step is more thermodynamically and kinetically favorable, with no obvious free energy barrier, and the ΔG is insensitive to the electrode potential. Hence the PT should neither be rate-determining nor potential-determining in the CO₂RR process, and it should be considered decoupled from the ET to avoid underestimation of overpotential by including the potential-irrelevant thermodynamic contribution of the PT

step

- (III) The onset potential (U_{onset}) of CO₂RR, the potential at the maximal CO Faraday Efficiency (FE) and the potential at $FE_{\text{CO}} = FE_{\text{H}_2}$ (U_{cross}) could be determined on basis of the theoretically derived $\Delta G - U$ linear scaling relationships, and the results are semi-quantitatively consistent with experimental data.

In a word, our study reveals the decoupled nature of the electron and proton transfer in the CO₂ activation step, and scaling relationships whose potential-dependence vary for different reaction intermediates. The ETPT mechanism may occur to the electrocatalytic hydrogenation of aldehyde/ketone C=O in the area of electrosynthesis and oxygenated hydrocarbon conversion.^{73,74} The proposed constrained AIMD-TI method combined with fully explicit solvation, and the potential-dependent scaling relationships derived from the obtained free energy profile, could be generalized to determine the thermodynamic/kinetics properties of other electrochemical reactions on similar catalyst system and provide precise theoretical insight in line with experimental observations.

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Competing interests

The authors declare no competing financial interest.

Additional information

Supplementary information is available for this paper here

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