A unifying mechanism for cation effect modulating C1 and C2 productions from CO2 electroreduction

Electrocatalysis, whose reaction venue locates at the catalyst–electrolyte interface, is controlled by the electron transfer across the electric double layer, envisaging a mechanistic link between the electron transfer rate and the electric double layer structure. A fine example is in the CO2 reduction reaction, of which rate shows a strong dependence on the alkali metal cation (M+) identity, but there is yet to be a unified molecular picture for that. Using quantum-mechanics-based atom-scale simulation, we herein scrutinize the M+-coupling capability to possible intermediates, and establish H+-and M+-associated ET mechanisms for CH4 and CO/C2H4 formations, respectively. These theoretical scenarios are successfully underpinned by Nernstian shifts of polarization curves with the H+ or M+ concentrations and the first-order kinetics of CO/C2H4 formation on the electrode surface charge density. Our finding further rationalizes the merit of using Na+ ion-coated electrode for enhanced C2 production in terms of enhanced surface charge density.

Ever-increasing global energy demand is bringing imbalances in the natural cycles, and critically threatening our sustainability. Towards a technological breakthrough that can restore sustainable cycles by rectifying those imbalances, electrochemical CO2 reduction reaction (CO2RR) is considered promising for converting CO2 into valuable chemicals1–3, such as CO, CH4, and C2H4. Coinage-metal electrodes of Ag, Au, and Cu are known to be active towards the CO2RR4–7, on which intense research efforts have been focused8–13, while a full understanding of the CO2RR mechanism on these catalysts is still not yet at hand.

The most intriguing question is the mechanistic role of alkali metal cations (M+) at the catalyst–electrolyte interface. Opposed to the conventional view that M+ would spectate the reaction, many experimental reports have evidenced a noticeable dependence of CO2RR activity and selectivity on the M+ identity14–17, often termed a cation effect. Specifically, the selectivity trend towards the C2 product and the CO production activity trend were found to follow the order of Cs+ > Rb+ > K+ > Na+ > Li+14,15, which clearly indicate a certain mechanistic role of M+ at the rate-determining step (RDS).

Supposing the proton-coupled electron transfer (PCET) as the RDS, the origin of the cation effect was ascribed to the variation in the local pH at the interface due to the different pKa values of the buffering M+15. However, various other experiments, where no clear activity change was observed upon (bulk) pH variations, demonstrated the possibility that the RDS involves no proton transfer12,18–21. Meanwhile, Chan group suggested a mechanism for the cation effect, called a field effect22,23: the electric double layer (EDL) field formed across the Helmholtz layer would stabilize the intermediates (e.g., *CO2) via...

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adsorbate dipole-field interaction, which can be modulated by the degree of M+ accumulation at the interface. Also, using the scanning electrochemical microscopic technique, the Koper group demonstrated an absence of CO2RR activity for CO formation without M+, which led them to propose a mechanism based on a M+-complexation (or coupling) to the CO2− intermediate in conjunction with their ab initio molecular dynamics (AIMD) simulation results. Moreover, cation-dependent interfacial water structure has been exploited to understand the cation effect on the CO2RR, which yields different electric field strengths, adsorption rate, or surface-dependent solvation structure. There further exist other general discussions on the cation effect on the electrocatalytic activity, e.g., site-blocking of reactants on the electrode or surface reconstruction, albeit it has not been directly linked with the cation effect on the CO2RR.

Towards the definition of a general scheme, at the molecular level, it is thus utmostly required to establish a unified CO2RR mechanism based on a systematic assessment, which can elucidate the cation effect on the activity for the CO formation and selectivity towards C–C coupling for multcarbon products. Herein, we investigate the cation-controlled mechanism by reflecting more practical electrolysis conditions via full-equilibrium simulations and flow-type-electrolyzer experiments with gas diffusion electrodes (GDE). Using a quantum-mechanics-based multiscale simulation, offering an accurate description on the EDL structure at atom-scale, we mapped out the cation-coordinating ability to all possible intermediates and established corresponding reaction energy profiles for CO, CH4, and C2H4 productions. The suggested different nature of RDSs, either a cation-coupled electron transfer (CCET) step for CO and C2H4 productions or a PCET for CH4 production, was corroborated by our experiments widely varying the M+ concentrations and identities. Of prime interest is that the cation effect results from a cation-dependent electrode surface charge density (σ). Our mechanism further successfully accounts for recent empirical but breakthrough findings (e.g., ionomer effects), and highlights the importance of EDL engineering as the next quest for better CO2 electrolysis.

Results and discussion

To be, or not to be coordinated by a cation

To identify the chemical role of M+ during CO2RR, we first investigate atomic details of the catalyst–electrolyte interface using density functional theory in classical explicit solvent (DFT-CES) simulation. This method offers an accurate description of the electrified interface at a balanced computational cost, by mean-field coupling of a quantum mechanical description on the catalyst surface with a molecular dynamics description on the liquid structure of the electrolyte phase. Recent advances in computational simulations enable a direct investigation of the electrode-electrolyte structure, highlighting the importance of the atomic arrangement of EDL constituents (e.g., chemisorbed water, Helmholtz ions, etc.) at the buried nanoscale region, which can affect the catalytic reactions under the actual electrochemical conditions. Compared with the AIMD simulation, often used for modeling the electrochemical interfaces, the DFT-CES enables to investigate electrolyte phase dynamics with many more atoms over a more extended time-scale; multi-thousands of atoms over a few picoseconds using the DFT-CES vs. multi-hundreds of atoms over a few picoseconds using the AIMD. The availability of simulations at full length- and time-scales is critical to unambiguously confirm the possible coordinating ability of electrolyte constituents to the intermediate species since it can provide the full equilibrium-dynamic structure of the electrolyte phase without the influence of initial conditions. Most importantly, we note that the DFT-CES succeeded in unraveling the atomic origin of the famous camel-shaped behavior of the EDL capacitance, confirming its accuracy in describing the EDL structural details.

Using DFT-CES simulations, we investigate the cation-coordinating ability of 28 possible intermediate species that can be formed during the reaction paths of CO2RR (Fig. 1 and Supplementary Fig. 1); a path to form CO (Fig. 1b: blue), CH4 (Fig. 1c, green), and C2H4 via a C–C coupling step (Fig. 1d, red). Cu(100) surface, known to be active for C–C coupling reactions, was chosen as the model catalyst surface for CH4 and C2H4 formation paths, as well as Ag(111) surface for CO formation path. At two different potentials of −0.5 V vs. standard hydrogen electrode (SHE) for the potential at point of zero charge (E0,PZC) and −1.0 VSH for the interface charge of −18 μC m−2 (Supplementary Fig. 2). DFT-CES simulations identified 6 intermediate species —CO2, *COOH, *CHO, *OCCO, *OCO−, and *HOCCO— to be coordinated by a cation; herein K+ (Fig. 1a and Supplementary Figs. 3–5).

After constructing reaction paths with explicitly specifying the cation-coordinated intermediate species (as illustrated in Fig. 1b–d), we calculated the reaction free energy profile of each reaction path as shown in Fig. 2a–c (Supplementary Figs. 6 and 7 for all intermediates; see Supplementary Note 1 for the computational details). Full reaction free energy profiles suggest the kinetics of CO, CH4, and C2H4 formations, to be respectively controlled by the RDSs of

\[
\text{CO₂ + M⁺ + e⁻ → COO⁻ ↔ M} 
\]

(1)

\[
\text{CO + H⁺ + e⁻ → COH} 
\]

(2)

\[
2\text{CO + M⁺ + e⁻ → OCCO ↔ M} 
\]

(3)

Here, reaction (2) is usually termed a PCET, and thus in an analogical sense, reactions (1) and (3) can be termed a CCET.

The proposed RDSs corroborate previous experiments. Previous studies demonstrated a strong dependence of CO formation or C–C coupling rates on the cation identity, i.e., cation effect. Also, Monteiro et al. showed a lack of CO2RR activity to CO without M+, which initiated an intensive discussion about the possibility of CCET. In addition, Chan and coworkers investigated the kinetic importance of proton activity using pH control experiments. They found that the pH variation significantly changes the CH4 production rate, while the CO and C2H4 production rates are nearly unchanged on a SHE potential scale. Moreover, the reactions (1) and (3) infer a critical role of M+ in the kinetics of CO and C2H4 formation paths, and reaction (2) shows the kinetic importance of pH in the CH4 formation path.

Nature of cation-coupled electron transfer

Although the CCET is named after the PCET, there is a caveat to understand the nature of CCET in parallel to the PCET. Since cations other than a proton are much heavier than an electron, the non-adiabatic effect can no longer play a role in determining the transfer rate. Rather, it is more reasonable to consider a Born-Oppenheimer-type picture, where an electron is adiabatically transferred to the intermediate species along the reaction coordinate for the cation-coupling.

Analysis of the electronic response of the catalyst–adsorbate system during DFT-CES iterations provides valuable insight on the nature of CCET, which is indeed an adiabatic response of the electron density upon the electrolyte structure change. Figure 2d shows the change of cation coordination number (CN) to the key intermediate species of *CO2 and *OCCO, and the change of their partial charges. We find no cation-coupling at the 0th iteration step, but the electron density between the metal and the adsorbate is redistributed during iterations, which enables the cation-coupling (Fig. 2e and Supplementary Fig. 8). Projected density of states (PDOS) shows that the lowest unoccupied molecular orbital (LUMO) of the adsorbate is downshifted after the cation-coupling due to the field generated by the cation (Supplementary Fig. 9). This increases the electronic...
implies that the intermediate such as *CO2 should be reduced into metal-intermediate interface. 

The entire electron density redistribution, which is associated with the adiabatic reaction coordinate not only for the cation-coupling but for the adsorbate-binding, can be conceptualized in two different pictures; either an electronic polarization or an electron transfer from metal to adsorbate. For the *CO2 case, the former concept implies an absence of ET at the RDS; 

\[ * + CO_2 + M^+ \rightarrow *CO_2 \cdots M^+ \]  

which is followed by a subsequent fast ET. Electrostatically, the polarization induces a dipole that can be stabilized by an external field. Thus, the field effect perspective, suggested by Chan group, can be further elaborated by identifying the atomic structural details of the field that generates the field to stabilize the dipole induced at the metal-intermediate interface. 

On the other hand, the latter concept of electron transfer literally accompanies the PCET step (i.e., * + CO2 + H^+ + e^- \rightarrow *COOH), necessarily leading us to account for K^+ coupled mechanism in their RDSs, respectively. The deviation in their polarization curves and is promoted as the KOH concentration increases. The departure of j_{CD} curves in SHE and RHE scales implies that CO2RR kinetics does not simply depend on the electrode potential (i.e., * + CO2 + e^- \rightarrow *CO2), nor does its RDS accompanies the PCET step (i.e., * + CO2 + H^+ + e^- \rightarrow *COOH), reason-

Cation concentration-dependent Nernstian shifts 

To elucidate the proposed CCET mechanism, we investigated CO2-to-CO conversion on the polycrystalline Ag electrode in various concentrations of KOH electrolytes (0.01–10 M) using a flow cell reactor (see Methods, Supplementary Figs. 10 and 11). The CO2RR polarization results are provided in Fig. 3a-c (with respect to different reference potential scales; Supplementary Fig. 12 for the Faradaic efficiency (FE)). On both SHE (Fig. 3a) and reversible hydrogen electrode (RHE, Fig. 3b) scales, a partial current density of CO (j_{CD}) shows considerable deviations in their polarization curves and is promoted as the KOH concentration increases. The departure of j_{CD} curves in SHE and RHE scales implies that CO2RR kinetics does not simply depend on the electrode potential (i.e., * + CO2 + e^- \rightarrow *CO2), nor does its RDS accompanies the PCET step (i.e., * + CO2 + H^+ + e^- \rightarrow *COOH), necessarily leading us to account for K^+ coupled mechanism in their RDSs, respectively.
varied but electrolyte pH was almost untouched (Supplementary Fig. 15). With a Tafel slope of 120–130 mV dec⁻¹ for the jCO, the results support that the RDS for CO formation path is the first ET step involving the K⁺-coupling, i.e., the reaction (1). Notably, the collapse of jCO curves in the CCE scale is not a singular event that occurs limitedly on Ag electrode in the alkaline electrolyte, but can also be found in other representative electrodes for efficient CO production, e.g., Au and NiNC (Supplementary Figs. 16–19). However, the CO₂RR in acidic electrolytes is unable to be explained together due to a partial displacement of cations by the protons (or hydronium ions)⁶ (Supplementary Fig. 20).

Afterwards, the C₂H₄ formation path, which was also predicted to follow the CCET step, was investigated. Herein, instead of the CO₂RR, CO reduction reaction (CORR) was chosen as a model reaction for clearer reaction kinetic studies on a polycrystalline Cu electrode (Supplementary Fig. 21); see Supplementary Note 2 and Supplementary Figs. 22–25 for CO₂RR on the Cu electrode). CORR was also performed in various electrolytes having different pHs and K⁺ concentrations, i.e., 0.5–5 M KOH (Fig. 3d–f) and 0.5 M KOH with 0.25/2.25 M K₂CO₃ (Supplementary Figs. 26 and 27), and the partial current density of ethylene (j₂CH₂) was plotted with respect to the SHE, RHE, and CCE scales. As the jCO trend, the results exhibited a collapse of the j₂CH₂ curves on the CCE scale, but marked departures on the SHE and RHE scales, with a Tafel slope of ca. 120 mV dec⁻¹ (Fig. 3d–f). Therefore, RDS for the C₂H₄ formation of CORR is also identified as the first ET step coupled with one K⁺ transfer, i.e., the reaction (3).

On the other hand, the partial current densities of CH₄ (jCH₄), measured by CORR on the Cu electrode, are collapsed on the RHE scale, but considerable deviations can be seen on the SHE and CCE scales (Fig. 3g–i). Their Tafel slopes are ca. 120 mV dec⁻¹, indicating that RDS of the CH₄ formation from CORR is the first ET step via PCET, i.e., the reaction (2). Therefore, our experimental findings for all CO, C₂H₄, and CH₄ formation paths greatly support the DFT-CES predictions that the two formers accompany the CCET while the latter does the PCET in their RDSS.

**CCET kinetics controlled by surface charge density**

Besides the electrolyte pHs and K⁺ concentrations, CO₂RR activity or selectivity is known to be affected by the M⁺ identity, i.e., a cation...
The M+-dependent CO2RR activity was also reproduced in our experiments, performed on Ag (Supplementary Fig. 28) and Cu (Supplementary Fig. 24) electrodes. They show activity trend of Cs+ > Rb+ > K+ > Na+ > Li+ for CO and C2H4 formations but opposite trend for CH4 formation. An identical trend was also found for CORR on Cu electrode (Supplementary Fig. 29).

Cation-dependent activity change could be ascribed to the different intermediate stabilization ability of different M+ at the RDS, where the cation is coupled. However, the larger cation has a longer coordination distance, when it develops an inner-sphere interaction with the negatively charged intermediate (e.g., *COO$^-$ or *OCCO$^-$), resulting in a less coulombic stabilization of the intermediate, and thus predicting an activity trend opposite to that of the experiment.

Instead, reaction kinetic study, which can provide definite evidence on reaction mechanism, unravels that different CO or C2H4 production rates depending on the M+ identity (and its bulk concentration) are primarily attributed to different $|\sigma|$. Considering that the CCET steps of the reactions (1) and (3) govern overall CO and C2H4 production rates, respectively, the Butler-Volmer kinetics at large cathodic overpotentials yield

$$J_{CO} = \frac{n_1 F k_1 P_{CO2} C_{M^+} e^{-\alpha_c F \left(E-E^{0(1)}_{\text{Reaction(1)}}\right)/RT}}{RT} \quad (5)$$

$$J_{C2H4} = \frac{n_2 F k_2 P_{CO2} C_{M^+} e^{-\alpha_c F \left(E-E^{0(3)}_{\text{Reaction(3)}}\right)/RT}}{RT} \quad (6)$$

where $F$, $R$, and $T$ are the Faraday constant, gas constant, and temperature, respectively. $n_{1(2)}$ and $k_{1(2)}$ are the number of electrons and rate constant involved in the CO2-to-CO (or CO-to-C2H4) conversion reaction, respectively, and $P_{CO2}$ denotes the CO2 (CO) partial pressure. $E^{0(1(3))}_{\text{Reaction(1(3))}}$ are the formal reduction potential of the elementary step reaction (1) and reaction (3), respectively, and $\alpha_c$ is the cathodic charge transfer coefficient. According to the equations, the reaction rates are determined by the local cation concentration at the interface, $C_{M^+}$. Unfortunately, this parameter is not straightforwardly measurable or even defined.$^{58,59}$ Instead, it can be reasonably hypothesized that the excess cations at the EDL, which locates there to screen the electrode surface charge,
will involve in the CCET reaction. If this assumption is true, the CO and C2H4 production rates should show the first-order reaction kinetics on the $|\sigma|$ at the same $P_{\text{CO}_2}$ and $E$ on the SHE scale, because $C_{\text{M}^+}$ will be equal to or (at least) proportional to the $|\sigma|$.

The $|\sigma|$ at a certain potential ($E$) can be estimated by integrating differential capacitance ($C_{\text{diff}}$) from the $E_{\text{ZEC}}$ (Supplementary Fig. 30), using the following equation$^{59}$.

$$|\sigma| = \int_{E_{\text{ZEC}}}^{E} C_{\text{diff}} \, dE$$  \hspace{1cm} (7)

The staircase potentiostatic electrochemical impedance spectroscopy (SPEIS) reveals magnified $C_{\text{diff}}$ values as $[\text{M}^+]$ increases or cation size becomes larger (Supplementary Figs. 31 and 32), consequently leading to a wide $|\sigma|$ range, 0.001–0.304 mC cm$^{-2}$ at $-1.3$ V$_{\text{SHE}}$ for Ag electrode and 0.082–0.447 mC cm$^{-2}$ at $-1.4$ V$_{\text{SHE}}$ for Cu electrode. A correlation between $|\sigma|$ and $[\text{M}^+]$ identifies that $|\sigma|$ is proportional to $[\text{M}^+]^{0.51}$ (Fig. 4a), which agrees with the simple prediction using the Gouy-Chapman theory$^6$. Notably, their relationship greatly rationalizes the collapse of kinetically described $j_{\text{CO}}$ or $j_{\text{C2H4}}$ upon thermodynamically (or Nernstian) $\text{M}^+$ concentration-corrected potential (i.e., CCE) scale as shown in Fig. 3 (see Supplementary Note 3 for detailed discussion), inferring their RDS to be involved with the CCET path.

More evidently, both a correlation plot between $j_{\text{CO}}$ and $|\sigma|$ at $-1.3$ V$_{\text{SHE}}$ and that between $j_{\text{C2H4}}$ and $|\sigma|$ at $-1.4$ V$_{\text{SHE}}$ show a slope of unity in the logarithmic scale (Fig. 4b, c). The first-order kinetics of $j_{\text{CO}}$ and $j_{\text{C2H4}}$ on $|\sigma|$ clearly demonstrates our mechanism again that their RDSs accompany the CCET step, i.e., reactions (1) and (3). Considering that data gathered with various $\text{M}^+$ identities locates on the linear correlation curve of $j_{\text{CO}}$ and $|\sigma|$, which was plotted from all other control experiments, the changes in $|\sigma|$ mostly ascribes the changes in both $j_{\text{CO}}$ and $j_{\text{C2H4}}$. This enables us to conclude that the cation effect on CO and C2H4 formations to be controlled by the $|\sigma|$ at the electrode. However, the atomic origin of its cation-species dependence needs to be further unraveled; cation-specific interfacial solvation could play a significant role$^{13,25,29,33}$, suggesting a future research direction.

**Tuning the surface charge density for enhanced C–C coupling**

On the basis of above understandings, it can now be rationalized why great C2H4 productions have been exclusively reported so far with highly concentrated MOH electrolytes (>1 M)$^{6,31,34}$. At the same potential on the SHE scale, high pH electrolyte is not only beneficial for suppressing proton activity and consequent PCET pathways (e.g., methane and H2 formation), but also induces high $|\sigma|$, which is indisputable for stabilizing *OCCO* intermediate and thereby lowering energy cost for the C–C coupling step.

More interestingly, we can further provide a clue to a fundamental origin of modulated CO2RR activity and selectivity in the presence of ionomer at the interface, highlighted very recently with boosted C2H4 and other C2 product formations on the Nafion-coated electrode$^{25,29,33}$. In literature, these empirical findings have been deemed as a result from either high local pH (induced by accumulation of OH~ ions at the electrode–ionomer interface) and consequent high CO2 concentration or better mass transport of ionic species. Similarly, we also found 1.6 times higher $j_{\text{C2H4}}$ (0.59 mA cm$^{-2}$ at $-1.4$ V$_{\text{SHE}}$) on Nafion-coated Cu electrode during CORR (and CO2RR, Supplementary Fig. 33) in a 5 M KOH electrolyte than that on bare Cu electrode (Fig. 5a and Supplementary Fig. 34). Also, as shown in Fig. 5b, their SPEIS results verified a significantly tuned $C_{\text{diff}}$ value ($-2$ mF cm$^{-2}$) on the Nafion-coated electrode, which was ca. 1.6 times larger than that on the bare electrode ($-1.2$ mF cm$^{-2}$). Surprisingly, the $j_{\text{C2H4}}$ and estimated $|\sigma|$ values for the
Naflon-coated electrode lie exactly on a previous trend line in Fig. 4c made upon the bare Cu electrode, unveiling that fundamental origin of the boosted C2H4 production with Naflon ionomer is due to a higher |σ| and consequent promotion of the reaction (3) via the CCET pathway (Fig. 5c).

In summary, we present a CCET-based mechanism for CO2RR that identifies the role of cations in modulating the activity and selectivity during CO2RR towards CO, CH4, and C2H4 formations. Atomic- and electronic-level elucidation on the catalyst–electrolyte interfacial region, empowered by DFT-CES, helps our understanding on the nature of CCET, corroborating previous experimental findings, and mechanistic suggestions. In addition, we demonstrate distinct Nernstian shifts depending on the bulk cation concentration, and first-order kinetics on the electrode surface charge density, both of which evidence our CCET-based mechanism. Most interestingly, our kinetic study finds the cation effect results from the cation-dependent electrode surface charge density. This understanding not only accommodates past and present efforts to tune the electrochemical interfaces for improved CO2RR electrolysis (e.g., high pH operation and ionomer-coating) but also brings up a strategic discussion to maximize the electrode surface charge density for further improvements.

**Methods**

**DFT-CES simulations**

DFT-CES is a grid-based mean-field theory for the quantum mechanics/molecular mechanics (QM/MM) multiscale simulations, where the interfacial interaction is developed based on QM energetics. This is implemented in our in-house code that combines the Quantum ESPRESSO density functional theory simulation engine and LAMMPS molecular dynamics simulation engine. Full computational details can be found in Supplementary Note 1.

**Electrode preparations**

The electrodes were fabricated by an e-beam evaporator (Ulvac Inc.; deposition rate = 3 Å s⁻¹) for Ag and Au and by a sputter (Ulvac Inc.; deposition rate = 6 Å s⁻¹) for Cu at a vacuum level of 10⁻⁶–10⁻⁷ Torr. Ag (99.99%), Au (99.99%), and Cu (99.99%) targets were deposited onto polytetrafluoroethylene (PTFE) membrane as a GDE with a pore size of 450 nm, and used as a cathode for CO2 and/or CO electrolysis. Their successful preparations were investigated by the X-ray diffraction (XRD; MiniFlex 600, Rigaku) and scanning electron microscope (SEM; SU8230, Hitachi). The XRD pattern was obtained at a 40 kV accelerating voltage and a 15 mA current with a scan rate of 1° min⁻¹. The SEM and energy-dispersive X-ray spectroscopy (EDS) were taken at an acceleration voltage of 15.0 kV. The Naflon-coated Cu electrode was prepared by spraying a Naflon ink onto the Cu-PTFE electrode. The Naflon ink was prepared by mixing 2.5 mL of isopropanol and 30 μL of Naflon (5 wt%) solution, and its loading amount was set to 12.5 μg cm⁻². NiNC catalyst was prepared from NiII acetate tetrahydrate (98%, Sigma-Aldrich), phen (≥99%, Sigma-Aldrich), and ZIF-8 (ZnN4C8H12, Basolite Z1200 from Sigma-Aldrich). The precursor mixture (1 g) containing 0.5 wt% Ni with a mass ratio phen/ZIF-8 of 20/80, was
homogenized by dry ball-milling (FRITSCH Pulverisette 7 Premium) for 4 cycles of 30 min at 400 rpm, and then pyrolyzed at 1050 °C in Ar (5 N, Daedeok) for 1 h. A ZrO2 crucible with 100 zirconium oxide balls of 5 mm diameter was used for the ball-milling procedure. Atomically dispersed Ni sites stabilized upon N-doped carbon were characterized by the X-ray photoelectron spectroscopy (XPS), the extended X-ray absorption fine structure (EXAFS), and the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM; FEI: Titan™ 80–300 TEM) equipped with a fast CCD camera (Gatan, Oneview 1095). The XPS signal was collected with a Sigma Probe (Thermo VG Scientific) equipped with a micro-focused monochromator X-ray source. The EXAFS was collected in transmission mode at Pohang Accelerator Laboratory (7D-XAFS beamline) with an energy scale calibrated by Ni foil. The NINC electrode was prepared by spraying NiNC ink–4 mg catalyst, 200 μL Nafion solution (5 wt%), and 2800 μL IPA–onto a carbon paper (1 × 1 cm² active area; TGP-H-090 with a 20 wt% PTFE content Toray) with a 1 mg cm⁻² NINC. Prior to the NINC electrode fabrication, hydrophobic mesoporous layer (MPL, preventing electrolyte leakage) was additionally introduced on the carbon paper by spraying a mixture of 100 mg Ketjen black EC-300J, 100 μg PTFE (60 wt%, Sigma-Aldrich), and 20 mL IPA (99.5%, Sigma-Aldrich) with 2 mg cm⁻² Ketjen black EC-300J loading, and subsequently by heat-treatments at 513 and 613 K under N₂ atmosphere for 30 min each.

Electrochemical investigations

All electrochemical measurements were performed with a VMP-300 potentiostat (Bio-Logic). The CO₂ (4 N, Daedeok) and CO (4 N, Samjong) were electrolyzed in a home-made electrochemical flow cell (Supplementary Fig. 10)⁴⁻⁶, in which a working electrode and a saturated Ag/AgCl reference electrode (RE16, EC-Frontier) were employed as the working, counter, and reference electrodes, respectively. Prior to every single measurement, the SHE and CCE scales were calibrated against a Pt wire electrode (CE-1, EC-Frontier) were used as a reference gas. (12390-U, Supelco) was used for both TCD and FID, and Ar (99.999%) as a carrier gas.

The electrode was calibrated against a Pt wire electrode (CE-1, EC-Frontier) was used as a reference gas. All data is available in the main text or Supplementary Information. The main DFT data are available in the ioChem-BD⁶ at https://doi.org/10.1006/iochem-bd-6-162. The MD data and experimental data are available in the Zenodo at https://zenodo.org/badge/latestdoi/530912301.

References

1. Lin, S. et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water. Science 349, 1208–1213 (2015).
2. Gao, S. et al. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. Nature 529, 68–71 (2016).
3. Huang, J. E. et al. CO₂ electrolysis to multicarbon products in strong acid. Science 372, 1074–1078 (2021).
4. Back, S., Yeon, M. S. & Jung, Y. Active sites of Au and Ag nanoparticle catalysts for CO₂ electroreduction to CO. ACS Catal. 5, 5089–5096 (2015).
5. Kortlever, R., Shen, J., Schouten, K. J. P., Calle-Vallejo, F. & Koper, M. T. M. Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. J. Phys. Chem. Lett. 6, 4073–4082 (2015).
6. Dinh, C.-T. et al. CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 360, 783–787 (2018).
7. Kim, Y. et al. Time-resolved observation of C–C coupling intermediates on Cu electrodes for selective electrochemical CO₂ reduction. Energy Environ. Sci. 13, 4301–4311 (2020).
8. HorI, Y., Wakebe, H., Tsukamoto, T. & Koga, O. Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media. Electroc. Acta 39, 1833–1839 (1994).
9. HorI, Y. Electrochemical CO₂ reduction on metal electrodes. In Modern aspects of electrochemistry. Vol. 42 (Springer, 2008).
10. Lu, Q. et al. A selective and efficient electrocatalyst for carbon dioxide reduction. Nat. Commun. 5, 3242 (2014).
11. Dunwell, M. et al. Examination of near-electrode concentration gradients and kinetic impacts on the electrochemical reduction of CO₂ using surface-enhanced infrared spectroscopy. ACS Catal. 8, 3999–4008 (2018).
12. Ringe, S. et al. Double layer charging driven carbon dioxide adsorption limits the rate of electrochemical carbon dioxide reduction on gold. Nat. Commun. 11, 33 (2020).
13. Monteiro, M. C. O. et al. Absence of CO₂ electroreduction on copper, gold and silver electrodes without metal cations in solution. Nat. Catal. 4, 654–662 (2021).
14. Murata, A. & Hori, Y. Product selectivity affected by cationic species in electrochemical reduction on CO₂ and CO at a Cu electrode. Bull. Chem. Soc. Jpn. 64, 123–127 (1991).
15. Singh, M. R., Kwon, Y., Lum, Y., Ager, J. W. & Bell, A. T. Hydrolysis of electrolyte cations enhances the electrochemical reduction of CO₂ over Ag and Cu. J. Am. Chem. Soc. 138, 13006–13012 (2016).
16. Resasco, J. et al. Promoter effects of alkali metal cations on the electrochemical reduction of carbon dioxide. J. Am. Chem. Soc. 139, 11277–11287 (2017).
17. Ringe, S. et al. Understanding cation effects in electrochemical CO₂ reduction. Energy Environ. Sci. 12, 3001–3014 (2019).
18. Waegele, M. M., Gunathunge, C. M., Li, J. & Li, X. How cation-solvent interactions affect two-electron transfer electrochemical reduction of carbon dioxide. Nat. Commun. 13, 803 (2022).
19. Li, J. et al. Electrokinetic and in situ spectroscopic investigations of CO electrochemical reduction on copper. Nat. Commun. 12, 3264 (2021).
20. Chen, L. D., Urushihara, M., Chan, K. & Nørskov, J. K. Electric field effects in electrochemical CO₂ reduction. ACS Catal. 6, 7133–7139 (2016).
21. Sandberg, R. B., Montoya, J. H., Chan, K. & Nørskov, J. K. CO-CO coupling on Cu facets: Coverage, strain and field effects. Surf. Sci. 654, 56–62 (2016).
22. Gu, J. et al. Modulating electric field distribution by alkali cations for CO₂ electroreduction in strongly acidic medium. Nat. Catal. 5, 268–276 (2022).
23. Zhu, Q., Wallentine, S. K., Deng, G.-H., Rebstock, J. A. & Baker, L. R. The solvation-induced onager reaction field rather than the double-layer field controls CO₂ reduction on gold. JACS Au 2, 472–482 (2022).
24. Delley, M. F., Nichols, E. M. & Mayer, J. M. Electrolyte cation effects on interfacial acidity and electric fields. J. Phys. Chem. C 126, 8477–8488 (2022).
25. Ovalle, V. J., Hsu, Y.-S., Agrawal, N., Janik, M. J. & Waeglele, M. M. Correlating hydration free energy and specific adsorption of alkali metal cations during CO₂ electroreduction on Au. Nat. Catal. 5, 624–632 (2022).
26. Rebstock, J. A., Zhu, Q. & Baker, L. R. Comparing interfacial cation hydration at catalytic active sites and spectator sites on gold electrodes: understanding structure sensitive CO₂ reduction kinetics. Chem. Sci. 13, 7634–7643 (2022).
27. Waeglele, M. M., Gunathunge, C. M., Li, J. & Li, X. How cations affect the electric double layer and the rates and selectivity of electrocatalytic processes. J. Chem. Phys. 151, 160902 (2019).
28. Shin, S.-J. et al. On the importance of the electric double layer structure in aqueous electrocatalysis. Nat. Commun. 13, 174 (2022).
29. García de Arquer, F. P. et al. CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². Science 367, 661–666 (2020).
30. Gupta, K., Bersani, M. & Darr, J. A. Highly efficient electro-reduction of CO₂ to formic acid by nano-copper. J. Mater. Chem. A 4, 13786–13794 (2016).
31. Yan, Z., Hitt, J. L., Zeng, Z., Hickner, M. A. & Mallouk, T. E. Improving the efficiency of CO₂ electrolysis by using a bipolar membrane with a weak-acid cation exchange layer. Nat. Chem. 13, 33–40 (2021).
32. Ma, S. et al. One-step electrosynthesis of ethylene and ethanol from CO₂ in an alkaline electrolyzer. J. Power Sources 301, 219–228 (2016).
33. Kim, C. et al. Tailored catalyst microenvironments for CO₂ electroreduction to multicarbon products on copper using bilayer ionomer coatings. Nat. Energy 6, 1026–1034 (2021).
34. Deng, W., Zhang, P., Seger, B. & Gong, J. Unraveling the rate-limiting step of two-electron transfer electrochemical reduction of CO₂ over Ag and Cu. J. Am. Chem. Soc. 138, 13006–13012 (2016).
35. Gu, J. et al. Modulating electric double layer at metal-water interfaces revisited based on a charge polarization scheme. J. Chem. Phys. 149, 084705 (2018).
36. Kristoffersen, H. H. & Chan, K. Towards constant potential modeling of CO-CO coupling at liquid water-Cu(1 0 0) interfaces. J. Catal. 396, 251–260 (2021).
37. Le, J.-B., Fan, Q.-Y., Li, J.-Q. & Cheng, J. Molecular origin of negative component of Helmholtz capacitance at electrified Pt(111)/water interface. Sci. Adv. 6, eabb1219 (2020).
38. Saikon, S. & Groß, A. The electric double layer at metal-water interfaces revisited based on a charge polarization scheme. J. Chem. Phys. 149, 084705 (2018).
39. Li, X.-Y. et al. Linear correlation between water adsorption energies and volta potential differences for metal/water interfaces. J. Phys. Chem. Lett. 12, 7299–7304 (2021).
40. Le, J.-B., Fan, Q.-Y., Li, J.-Q. & Cheng, J. Molecular origin of negative component of Helmholtz capacitance at electrified Pt(111)/water interface. Sci. Adv. 6, eabb1219 (2020).
41. Malkani, A. S. et al. Understanding the electric and nonelectric field components of the cation effect on the electrochemical CO₂ reduction reaction. Sci. Adv. 6, eabd2569 (2020).
42. Soudackov, A. V. & Hammes-Schiffer, S. Probing nonadiabaticity in the proton-coupled electron transfer reaction catalyzed by soybean lipoxygenase. J. Phys. Chem. Lett. 5, 3274–3278 (2014).
43. Gauthier, J. A. et al. Facile electron transfer to CO₂ during adsorption at the metal|solution interface. J. Phys. Chem. C 123, 29278–29283 (2019).
44. Monteiro, M. C. O., Dattila, F., López, N. & Koper, M. T. M. The role of cation acidity on the competition between hydrogen evolution and CO₂ reduction on gold electrodes. J. Am. Chem. Soc. 144, 1589–1602 (2022).
45. Pérez-Gallent, E., Figueiredo, M. C., Calle-Vallejo, F. & Koper, M. T. M. Spectroscopic observation of a hydrogenated CO dimer intermediate during CO₂ reduction on Cu(100) electrodes. Angew. Chem. Int. Ed. 56, 3621–3624 (2017).
46. Liu, H., Liu, J. & Yang, B. Promotional role of a cation intermediate complex in C₂ formation from electrochemical reduction of CO₂ over Cu. ACS Catal. 11, 12336–12343 (2021).
54. Clark, T. Polarization, donor–acceptor interactions, and covalent contributions in weak interactions: a clarification. J. Mol. Model 23, 297 (2017).
55. Bard, A. J. & Faulkner, L. R. Potentials and thermodynamics of cells. In Electrochemical methods: fundamentals and applications. (John Wiley & Sons, Inc., 2001).
56. Schultz, Z. D., Shaw, S. K. & Gewirth, A. A. Potential dependent organization of water at the electrified metal–liquid Interface. J. Am. Chem. Soc. 127, 15916–15922 (2005).
57. McQuarrie, D. A. & Simon, J. D. Chemical Kinetics. In Physical chemistry: a molecular approach. (University Science Books, 1997).
58. Magnussen, O. M. & Groß, A. Toward an atomic-scale understanding of electrochemical interface structure and dynamics. J. Am. Chem. Soc. 141, 4771–4790 (2019).
59. Goyal, A. & Koper, M. T. M. The interrelated effect of cations and electrolyte pH on the hydrogen evolution reaction on gold electrodes in alkaline media. Angew. Chem. Int. Ed. 60, 13452–13462 (2021).
60. Trasatti, S. & Lust, E. The potential of zero charge. In Modern aspects of electrochemistry. Vol. 33 (Kluwer Academic/Plenum Publishers, 1999).
61. Newman, J. & Thomas-Alyea, K. E. Structure of the electric double layer. In Electrochemical systems. (John Wiley & Sons, Inc., 2004).
62. Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys.: Condens. Matter 21, 395502 (2009).
63. Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. J. Comput. Phys. 177, 1–19 (1995).
64. Dinh, C.-T., García de Arquer, F. P., Sinton, D. & Sargent, E. H. High rate, selective, and stable electroreduction of CO₂ to CO in basic and neutral media. ACS Energy Lett. 3, 2835–2840 (2018).
65. Álvarez-Moreno, M. et al. Managing the computational chemistry big data problem: The ioChem-BD platform. J. Chem. Inf. Model. 55, 95–103 (2015).
66. Shin, S.-J. et al. A unifying mechanism for cation effect modulating CI and C2 productions from CO₂ electroreduction. DFT-CES Code https://zenodo.org/badge/latestdoi/429418216 (2022).

Acknowledgements
This research was supported by the Samsung Science and Technology Foundation under Project Number SSTF-BA2101-08, the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1A5A1030054), the KIST Institutional Program, and the Korea Institute of Science and Technology Information (KISTI) National Supercomputing Center with supercomputing resources including technical support (KSC-2020-CHA-006). Experiments at PLS-II were supported in part by MSIT and POSTECH.

Author contributions
S.-J.S. and H.C. contributed equally to this work, and mainly performed the DFT-CES simulation and electrochemical experiments, respectively. H.K. and C.H.C. conceived the initial idea and supervised the project. D.H.W. prepared electrodes. S.R., H.-S.O., D.H.K., D.-H.N., and T.L. contributed to part of the experimental and computational calculations. S.-J.S., H.C., H.K., and C.H.C. wrote the manuscript with contributions from all authors.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-33199-8.

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Peer review information Nature Communications thanks Federico Dattila, Jun Cheng and the other anonymous reviewer(s) for their contribution to the peer review of this work. Peer review reports are available.

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