

Concerted Cation–Electron Transfer Mechanism for CO₂ Electroreduction

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Abstract: Converting carbon dioxide (CO₂) into valuable products is one of the most important processes for a sustainable society. Especially, the electrochemical CO₂ reduction reaction (CO₂RR) offers an effective means, but its reaction mechanism is not yet fully understood. Here, we demonstrate that concerted cation–electron transfer (CCET) is a key catalytic step in the CO₂RR to carbon monoxide.

5 The first-principles-based multiscale simulation identifies a single cation that coordinates a CO₂[−] intermediate adsorbed on Ag electrode. The CCET is experimentally verified by a collapse of the CO₂RR polarization curves upon correcting for the thermodynamic activity of the cation. As further confirmation, a kinetic study shows that the CO₂RR obeys first-order kinetics on the local cation concentration at the electric double layer (estimated by measuring the electrode surface charge). Finally,
10 this work unveils the fundamental origin of different CO₂RR activity depending on the species of alkali metal cation, and further highlights the importance of ion-pairing tendency of the cations for electrochemical interface design to achieve high-performance CO₂ electrolysis.

INTRODUCTION

As a carbon dioxide (CO₂) mitigation technology, electrochemical CO₂ reduction reaction (CO₂RR) is considered promising for converting CO₂ into valuable chemicals and fuels.¹⁻³ Among the possible products that can be formed *via* a multi-electron reduction of CO₂, two-electron-reduced carbon monoxide (CO) is of prime interest due to not only its practical importance as a constituent of a syngas,⁴ but also its mechanistic importance as a key intermediate for C–C bond coupling.⁵⁻⁷ Despite the simplicity of the CO₂RR to CO, which can be selectively catalyzed on Au or Ag surfaces,^{8,9} a full understanding of its mechanism is still not yet at hand, particularly regarding the details of the rate-determining first reduction step.¹⁰⁻¹⁴

The most intriguing and widely discussed phenomenon is the activity dependency of the CO₂RR on species of alkali metal cation in the electrolyte, often termed a “cation effect”.¹⁵ In 2016, Singh *et al.* demonstrated that the CO₂RR on the Ag surface shows an activity trend of Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺.¹⁶ Since the first reduction step was thought to occur through concerted proton–electron transfer (CPET),¹⁷⁻²⁰ they ascribed this trend to the different pKa values of alkali metal cations, which could alter the local pH at the electrochemical interface. However, little after, various other studies have indicated the possibility for a rate-determining step (RDS) involving no proton transfer.^{21,22} For example, Ringe *et al.* found a partial current density of CO (j_{CO}) to be independent of the pH even under acidic conditions.¹³ Consequently, they proposed another mechanism for the cation effect, called a “field effect”,²³ by applying an ion-size-dependent continuum surface charging model. Although the CO₂ molecule remains in a linear form without binding to uncharged Ag or Au surface based on density functional theory (DFT) calculations, the adsorption of CO₂ was found to be accompanied by a bending of the molecule driven by the non-zero net charge of the surface and the corresponding electric double layer (EDL) field under the CO₂RR conditions.^{13,23} Furthermore, the long-range electrostatic interaction between the electric field and an adsorbate dipole was attributed to stabilizing the CO₂ adsorbate more for larger cations, since they were considered to have a smaller “effective” radius (including their hydration shell), and thus could be more concentrated in the Helmholtz plane.

Beyond a continuum description, atomic level elucidations on the cation effect have also been pursued; despite that it is often called a Helmholtz “plane”, there is no actual planar object at the atomic scale. In contrast to the continuum explanation, Chen *et al.* and Resasco *et al.* proposed that cation stabilization *via* the EDL field is a more localized effect, driven by cations that directly interact with the adsorbates.^{24,25} Very recently, a more direct involvement of cations in the first reduction step of the CO₂RR was come up with by Monteiro *et al.* A possibility of cation complexation to the CO₂⁻ intermediate was suggested based on their *ab initio* molecular dynamics (AIMD) simulation results.¹⁴ Furthermore, they reported experimental results using scanning electrochemical microscopy that the CO₂RR becomes possible only if alkali metal cations exist in solution.

In a continuum of the recent efforts to unveil the cation effect, here we have theoretically and experimentally investigated the cation-controlled mechanism of electrochemical CO₂RR with reflecting more practical electrolysis conditions, *i.e.*, simulation under an actual concentration of electrolyte for a long-enough time and experiments with a flow-type device. We demonstrated that alkali metal cations co-catalyze the first reduction step of the CO₂RR through concerted cation–electron transfer (CCET). We further disclosed that the cation effect is a local colligative property, *i.e.*, the local cation concentration at the EDL mainly governs the CO₂RR kinetics, regardless of the cation species. By elucidating the atomic origin of the cation effect, our CCET-based mechanism suggests a future research direction for improving the CO₂RR electrocatalysis by tailoring the catalyst–electrolyte interphase.

20 RESULTS AND DISCUSSION

Local environment of CO₂ and COOH adsorbates

Our recently developed first-principles-based multiscale simulation, DFT in classical explicit solvents (DFT-CES),²⁶ allows the DFT calculations with including all molecular constituents of the electrolyte at the same concentration level as actual CO₂RR condition.⁴ Using the DFT-CES, we thus investigated the local environment surrounding a bent CO₂ adsorbate at the atomic level. Over the course of the

DFT-CES iterations, we found that one K^+ is coordinated to the bent CO_2 over the entire simulation time of 5 ns (**Figure 1a**) in a bidentate form (where K^+O distance is *ca.* 2.5 Å), which helps polarize an additional electron to the CO_2 adsorbate, leading its partial charge to be $-0.8 e$ (**Figure 1b**). Thus, the bent CO_2 adsorbate needs to be more appropriately labeled as $*CO_2^- \cdots K^+$ (see left panel of **Figure 1c** for its characteristic local environment). This is notable since the possibility of cation coupling to the CO_2 adsorbate, which was identified by the previous AIMD simulation using the small simulation cell performed for a short time of 2 ps,¹⁴ is confirmed from our DFT-CES simulation investigating 5-ns dynamics of actual composition of electrolyte (including both K^+ and HCO_3^-) (**Figure S1**). In addition, the formation of $*CO_2^- \cdots K^+$ is an electrochemical step with a potential-dependent thermodynamic barrier (left panel of **Figure 1d**).

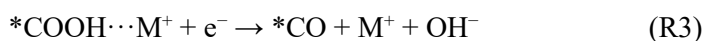
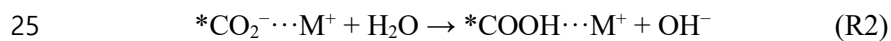
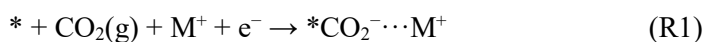
To seek for the reaction path for the subsequent proton transfer, we further investigated the local environment surrounding a $COOH$ adsorbate ($*COOH$) using the DFT-CES (right panel of **Figure 1c**). Near the $*COOH$, our simulation revealed that one K^+ is coordinated to the $O(=C)$ in a monodentate form, and one OH^- is coordinated to the HO of $*COOH$ over the entire simulation time of 5 ns (**Figure S2**). In addition, a water molecule bridges the K^+ and OH^- *via* hydrogen-bond network while exchanging the position with another water molecule during the simulation. Considering the water structure near the $*CO_2^- \cdots K^+$, where around two water molecules (which are not strongly bound) tend to bridge the K^+ and the terminal O of $*CO_2^-$ during the simulation, we conceive that the intervened water molecule between K^+ and $*CO_2^-$ will readily transfer a proton to the terminal oxygen of $*CO_2^-$. Indeed, our climbing image nudged elastic band (CI-NEB) calculation shows that the structural rearrangement from the bidentate form to the monodentate form is energetically downhill by 0.6 eV, suggesting a cation-facilitated protolysis path of water after the cation coupling to $*CO_2^-$ (right panel of **Figure 1d** and **Figure S3**).²⁷

25 Concerted cation–electron transfer

Our atomically resolved elucidations on the electrolyte structure suggest that the coordinating affinity

of K^+ to $*CO_2^-$ is a key parameter, which can determine the kinetics of the first reduction step of the CO_2RR . To unravel the role of cation more clearly, we investigated the CO_2RR activity of polycrystalline Ag electrode in an electrochemical flow cell (**Figures S4 and S5**).^{6,28} The CO_2 -to- CO conversion was measured in various concentrations of KOH electrolytes (0.01–10 M) to control the K^+ activity (**Figure 2**). The j_{CO} versus potential curves reveal that their Tafel slopes are 120–130 mV dec⁻¹, indicating the first electron transfer step to be the RDS.²⁹ On both standard hydrogen electrode (SHE) and reversible hydrogen electrode (RHE) scales, the j_{CO} shows considerable deviations in their polarization curves as the KOH concentrations are varied (**Figure 2a–b**). In both reference scales, the CO_2RR activity is enhanced by increasing KOH concentration. However, this implies that the CO_2RR kinetics does not simply depend on the electrode potential (*i.e.*, $* + CO_2 + e^- \rightarrow *CO_2^-$), nor does its RDS accompany the CPET step (*i.e.*, $* + CO_2 + H^+ + e^- \rightarrow *COOH$).³⁰ Hence, the inconsistency led us to reasonably account for the RDS to be a concerted mechanism with other species, such as K^+ , as predicted by our simulation results. Therefore, we re-plotted the polarization curves with respect to an alkali metal cation activity-corrected electrode (ACE) scale (**Figure 2c**), which is defined here as $E_{ACE} = E_{SHE} - 0.059 \times \log[M^+]$, where M^+ denotes an alkali metal cation.³¹ This plot identifies a collapse of the j_{CO} polarization curves independent of the KOH electrolyte concentration, corresponding to a Nernstian potential shift of *ca.* 60 mV per $\log[K^+]$ on the SHE scale. The same conclusion can also be obtained using 0.01 M KOH + 0–0.495 M K_2CO_3 electrolytes (**Figure S6**), in which only the K^+ activity was controlled, whereas electrolyte pH was almost untouched (**Figure S7**). Therefore, it can be concluded that changes in the CO_2RR kinetics are primarily governed by the K^+ activity, rather than electrolyte pH.^{32,33}

Gathering all findings from our simulations and experiments, we suggest the following reaction mechanism for the CO_2RR on the Ag electrode.





where (R1) is the CCET step, which is the RDS, while the proton transfer step (R2) is considered to be fast, as shown in the previous CI-NEB calculation (**Figure S3**).

Studies on chemical kinetics are useful for mechanism verification.³⁴ Following the above CCET-
5 based mechanism, the overall rate of the CO₂RR can be written as follows.

$$\text{rate} = k P_{\text{CO}_2} [\text{M}^+] \exp\left(-\frac{\Delta G_{(\text{R1})}^\ddagger - \alpha F E_{\text{SHE}}}{RT}\right) \quad (\text{Eq. 1})$$

where k , P_{CO_2} , $[\text{M}^+]$, $\Delta G_{(\text{R1})}^\ddagger$, α , and F are the rate constant, CO₂ partial pressure, cation concentration, activation energy of (R1) at $E_{\text{SHE}} = 0$ V, charge-transfer coefficient, and Faradaic constant, respectively. As the electrochemical reaction occurs at the interface, its rate needs to be governed by the local cation
10 concentration at the EDL;³⁵ however, it is not straightforwardly measurable or even defined.³⁶ Thus, we hypothesize that the excess cations at the EDL region to compensate the electrode surface charge will participate in the reaction, and the $[\text{M}^+]$ will be equal to or (at least) proportional to the magnitude of the electrode surface charge density,³⁵ $|\sigma|$. If our hypothesis is correct, this should lead to a first-order dependence of the CO₂RR rate on $|\sigma|$, and thus a linear relationship between $|\sigma|$ and j_{CO} is expected when
15 j_{CO} is measured at the same potential on the SHE scale and the same P_{CO_2} .

Then, we measured the differential capacitance (C_{diff}) of the Ag electrode in each electrolyte using staircase potentiostatic electrochemical impedance spectroscopy. The $|\sigma|$ at a certain potential (E') can be estimated by integrating C_{diff} from the potential at point of zero charge (E_{PZC} ; **Figure S8**) to the E' :³⁷⁻⁴⁰

$$|\sigma| = \left| \int_{E_{\text{PZC}}}^{E'} C_{\text{diff}} \, dE \right|. \quad (\text{Eq. 2})$$

20 The results show an increase in C_{diff} when increasing the K⁺ concentration in the electrolyte (**Figure S9**), consequently leading to a magnified $|\sigma|$ on the Ag electrode. A correlation between $|\sigma|$ and j_{CO} at -1.3 V_{SHE} identifies a linear function with a slope of unity on a log scale (**Figure 3**). Hence, the first-order dependence of j_{CO} on $|\sigma|$ was verified, evidencing the CCET-governing step described by the mechanism (R1).

Origin of the cation effect

In the context of the CCET-based mechanism for the CO₂RR, our question is then oriented to unveil the underlying fundamental origin of the cation effect, *i.e.*, activity dependency on alkali metal cation species. The CO₂ electrolysis results, measured in various alkali metal carbonate electrolytes (set to 0.05 M), revealed the CO₂RR activity trend of Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺ (**Figure S10**). This trend agrees well with other results reported in the literature.^{14,16,23} To identify whether cations other than K⁺ can also co-catalyze the CO₂RR *via* a formation of the *CO₂⁻···M⁺ intermediate, the C_{diff} of Ag electrode was also evaluated in those electrolytes (**Figure S11**). The results show a decrease in the C_{diff} value in the order of Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺, the trend of which corresponds to that of their CO₂RR activity. The relationship between the estimated $|\sigma|$ and j_{CO} values at $-1.3 \text{ V}_{\text{SHE}}$ was also greatly fit with a linear fitting line, which was derived from the data for various K⁺-based electrolytes (**Figure 3**). This result thus infers that the activity dependency of the CO₂RR on alkali metal cations, namely the cation effects, is primarily attributed to variations in the amount of excess cations at the EDL region and consequently to the different kinetics based on the mechanism (R1). Thus, k is independent of the cation species, implying that the cation effect on the CO₂RR is a local colligative effect.

The last but not the least question we are now faced with is why larger cation, such as Cs⁺, accumulates more than smaller one at the EDL. However, a full understanding of the EDL structure and energetics is extremely challenging and still remains an open question.³⁶ Therefore, possible rationales will be discussed hereafter on the basis of computational results. On the one hand, by analyzing the energetics from the AIMD simulation results, Monteiro *et al.* found that a relative stability of the cation at the electrochemical interface to that at the bulk is enhanced for larger cations.¹⁴ Such an explanation based on the thermodynamic driving force provides a good rationale for answering why larger cations can accumulate more at the EDL.

On the other hand, from our DFT-CES simulations, where $|\sigma|$ (*i.e.*, the simulation control parameter) is maintained to be same, we found that the interfacial potential drop across the EDL (which determines the electrochemical potential) decreases in the order of Li⁺ > Na⁺ > K⁺ > Cs⁺ for the 0.1 M electrolytes

(**Figures 4a** and **S12**). This result implies that, to achieve a same electrochemical potential (*i.e.*, the experimental control parameter), inducing more cathodic polarization is required for larger cations, which leads the $|\sigma|$ to show the trend of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ when measured at the same potential. When only a minimal number of cations are included to compensate for the electrode surface charge
5 (without including anions), for comparison, the interfacial potential drop shows virtually no dependence on the cation species (**Figures 4a** and **S12**). This indicates a cooperative role of cations and anions in determining the potential drop across the interface.

Smaller cations usually demonstrate stronger ion-pairing,⁴¹ which is often ascribed to their hardness.^{42–44} Our simulation results also demonstrate the formation of fewer contact ion-pairs for larger
10 cations (**Figure S13**). The loosely bound cation-anion-pairs, which are found in the electrolyte with larger cations, can better screen the charged electrode than the tightly bound ones, which are found in the electrolyte with smaller cations (**Figure 4b–c**), and thus increase C_{diff} as well as $|\sigma|$.

CONCLUSION

15 In summary, our present work affirms the coupling of alkali metal ion to the key intermediate of $^*\text{CO}_2^-$ via a short-range electrostatic interaction. It is not only demonstrated from our advanced simulation for the electrochemical interface (under more realistic conditions), but also experimentally verified from the Nernstian potential shift depending on the cation activity as well as the kinetic studies. Furthermore, the cation effect is found to originate from the difference in the local cation concentration at the EDL,
20 not from the difference in the nature of chemical interaction between cation and intermediate. Consequently, next discussion for further improving the CO_2RR electrolysis is related to identifying strategies for maximizing the local cation concentration at the EDL. Although this motivates numerous other studies, since the EDL engineering is highly complicated as multiple components and their mutual interactions are convoluted,³⁶ our finding emphasizes the importance of controlling the cation-anion-
25 pairs. To prove the suggested concept, we demonstrated that the local cation concentration can be modulated by changing the anion species at the EDL, which regulates the CO_2RR kinetics up to three-

fold (Figure S14). We thus envisage that our present elucidation of the CCET mechanism and the cation effect will trigger many other ideas to optimize the EDL characteristics for improving the CO₂RR electrolysis.

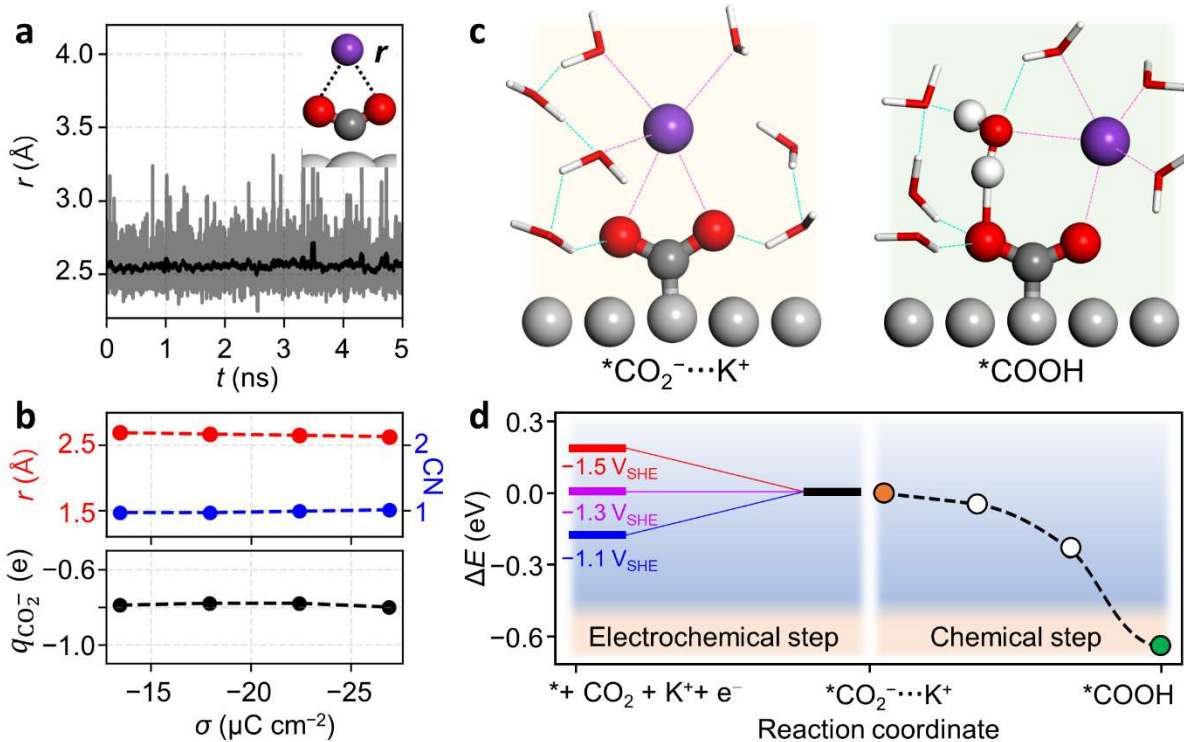


Figure 1. Local environment of the CO₂RR. **a.** Distance (r) between O of $*\text{CO}_2^-$ and K^+ with respect to time (t). The black solid line denotes a moving average of the grey line using a 0.05 ns time window. **b.** Coordination number (CN) of $*\text{CO}_2^-$ with K^+ , and the Bader charge of $*\text{CO}_2^-$ ($q_{\text{CO}_2^-}$) as a function of surface charge density, σ . **c.** Local solvation structures of the $*\text{CO}_2^-$ and $*\text{COOH}$ sampled from the DFT-CES simulations. Atoms in the quantum mechanics and molecular mechanics regions in the last DFT-CES iteration are represented using balls-and-sticks and sticks, respectively. **d.** Reaction-energy diagrams to complete the sequential electron (electrochemical step) and proton (chemical step) transfers. Potential-dependent energetics for the electrochemical step were estimated by properly referencing the chemical potentials of the electron and K^+ (see Supplementary Information). The activation energy barrier for the chemical step was calculated using the CI-NEB method. Orange- and green-filled circles denote the reactant and product states, respectively. Their atomic structures were sampled from the DFT-CES calculations and then optimized using DFT. White empty circles indicate NEB data, and ΔE is the energy difference.

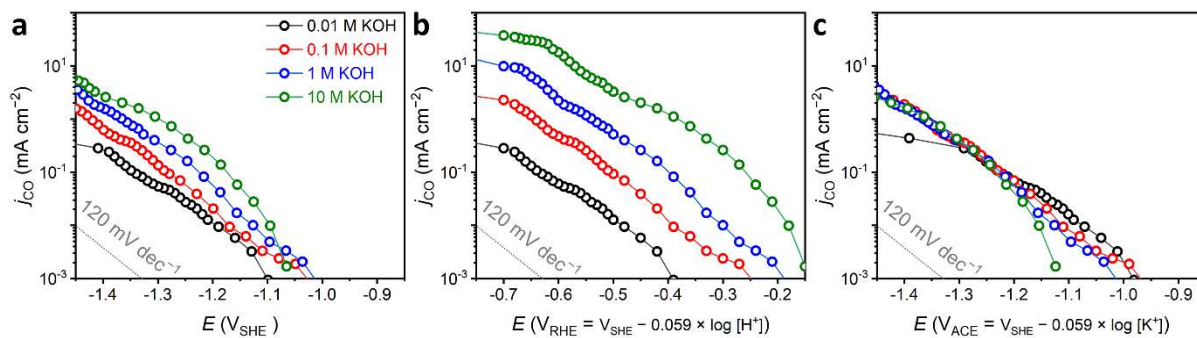


Figure 2. Electrochemical CO₂-to-CO conversion on the Ag electrode. Effect of KOH electrolyte concentration (0.01–10 M) on j_{CO} versus potential curves measured on the Ag electrode in an electrochemical flow cell. The polarization curves are plotted with respect to the **a.** SHE, **b.** RHE ($V_{\text{SHE}} - 0.059 \times \log[\text{H}^+]$), or **c.** ACE ($V_{\text{SHE}} - 0.059 \times \log[\text{K}^+]$) scales. The grey lines indicate a Tafel slope (typically plotted as an inverse function of the present polarization curve) of 120 mV dec^{-1} .

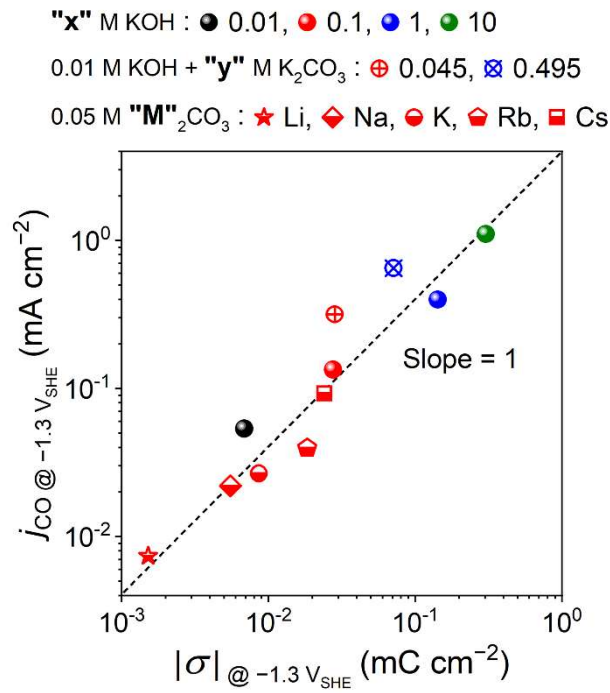


Figure 3. Kinetic study of the CO₂RR on the Ag electrode. Correlation curve between $|\sigma|$ and j_{CO} at $-1.3 \text{ V}_{\text{SHE}}$ measured in various electrolytes. The electrolytes used in the present work can be classified into three different categories: KOH electrolytes with different concentrations (filled circles); 0.01 M KOH electrolytes with additional K_2CO_3 salt (crossed circles); and various 0.05 M alkali metal carbonate electrolytes (half-filled symbols). Here, the total concentration of cation in the electrolyte and its species are distinguished by colors and symbol shapes, respectively. A guideline for the slope of one is indicated by a dashed line.

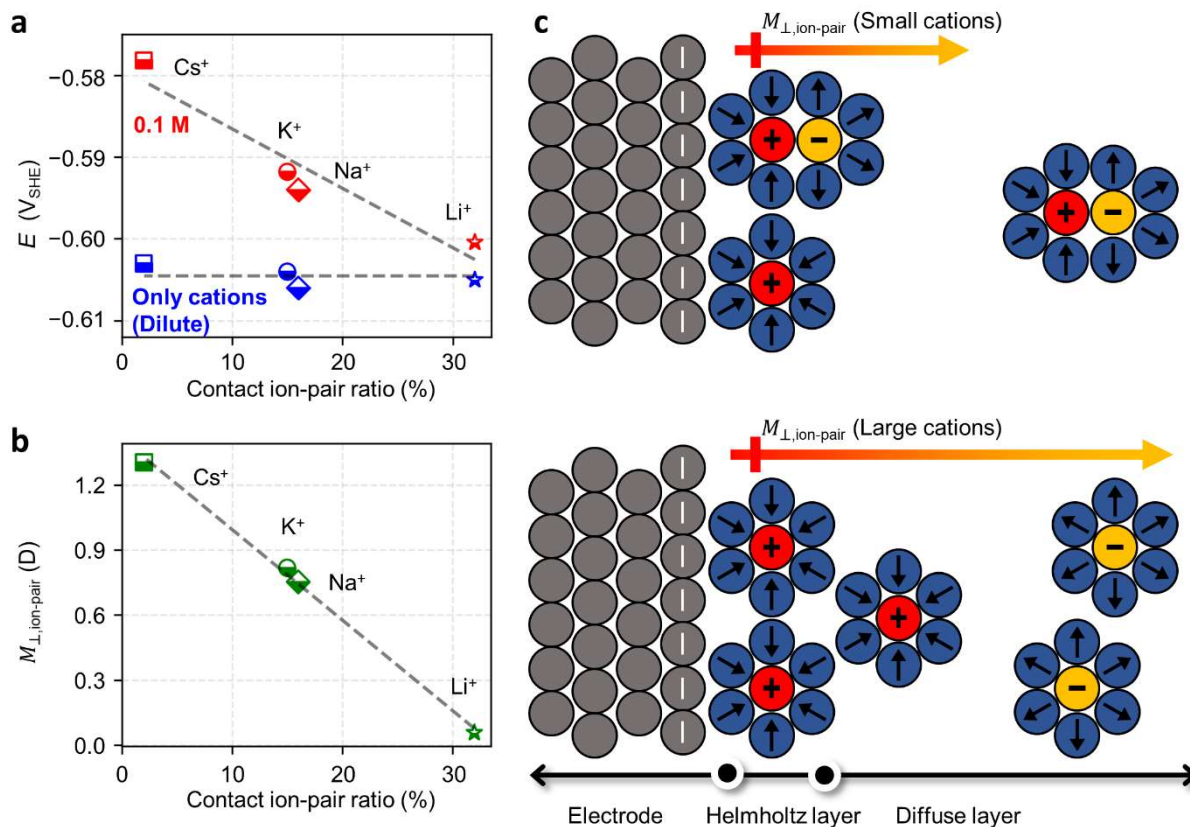


Figure 4. DFT-CES results with the different cation species. **a.** Electrode potential versus contact ion-pair ratio of each electrolyte. The electrolytes consist of 0.1 M MHCO_3 (red; M^+ is alkali metal cation) and dilute electrolyte (blue), with a surface charge density of $-14 \mu\text{C cm}^{-2}$. The dilute electrolyte only contains the minimum number of cations sufficient to compensate the charged electrode, whereas 0.1 M electrolytes have additional ion-pairs. The contact ion-pair ratio is calculated from the 0.1 M bulk electrolyte (see details in **Figure S13**). **b.** Macroscopic dipole moment of ion-pairs along the z -direction, $M_{\perp, \text{ion-pair}}$ of each electrolyte, which is calculated by subtracting the spatial charge density of ions for the dilute case from the 0.1 M case. **c.** Schematics showing the different screening ability originating from the distinct ion-pairing tendency. The red-yellow graded arrow indicates the $M_{\perp, \text{ion-pair}}$ and the blue circles with the black arrows denote water dipoles.

ASSOCIATED CONTENT

The Supporting Information is available. It includes methods and Supplementary Figures.

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Notes

The authors declare no competing financial interest.

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