Solvation-Induced Onsager Reaction Field Rather than Double Layer Field Controls CO₂ Reduction on Gold

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ABSTRACT

The selectivity and activity of the carbon dioxide reduction reaction (CO₂R) are sensitive functions of the electrolyte cation. By measuring the vibrational Stark shift of in-situ generated CO on Au in the presence of alkali cations, we quantify the total electric field present during turnover and deconvolute this field into contributions from 1) the electrochemical Stern layer and 2) the Onsager, or solvation-induced, reaction field. The magnitude of the Onsager field is shown to be on the same order as the Stern layer field (~ 10 MV/cm) but follows an opposite trend with cation, increasing from $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ \approx \text{Cs}^+$. Contrary to theoretical reports, CO₂R kinetics are not correlated with the Stern field but instead are controlled by the strength of the Onsager reaction field with Cs^+ as an exception. Spectra of interfacial water as a function of cation show that Cs^+ induces a change in the interfacial water structure correlated with a drop in CO₂R activity, highlighting the importance of cation-dependent interfacial water structure on reaction kinetics. Modeling of the interfacial Onsager reaction field for adsorbed (bent) CO₂ predicts that the magnitude of the Onsager reaction field is greater than the Stern Field. These findings show that both the Onsager reaction field and interfacial solvation structure must be explicitly considered for accurate modeling of CO₂R reaction kinetics.

Introduction

Electrocatalytic CO₂ reduction (CO₂R) has received widespread attention because it is a promising method to convert excess CO₂ in the atmosphere to industrial feedstocks. Despite numerous reports on the topic, mechanistic understanding of this process, is limited. Additionally, CO₂R kinetics are slow and must compete with H₂ evolution in aqueous electrolytes, which limits its practical application. Alkali cations are known to increase the selectivity and activity of CO₂R significantly, however, the fundamental reason for this observation is still under debate. Understanding the cation dependence would provide much needed insights to help make CO₂R economically viable.

Several explanations have been put forward regarding the effect of cations on CO₂R. To avoid confusion, we note that the terms used in this paper describing the relative size of cations, e.g. larger and smaller, are based on the crystal radii of the cations, which increases from Li^+ to Cs^+ in contrast to the solvated radii. Bell et al. propose that water molecules coordinated to larger cations possess a lower pKa.¹ They argue that this makes the interfacial pH more acidic thereby increasing the local CO₂ concentration due to bicarbonate equilibrium. The effect of local buffering has been verified experimentally,² however Xu et al. measured the local CO₂ concentration and found that it was highest for smaller cations, in contradiction to the prediction by Bell et al.³ Another consideration has been put forward by Norskov et al.^{4,5} which indicates that cations create a local electric field that can stabilize bending of CO₂ through field-dipole interactions. This interaction fosters the adsorption of CO₂ as the field in the electrochemical double layer increases.⁵ In support of this hypothesis, Chan and co-workers recently showed that multi-scale-modeling of interactions between a CO₂ dipole and the potential-dependent electric field can reproduce the observed Tafel slope for CO₂R on Au.⁶

However, at electrochemical interfaces there are multiple fields present. This includes the electric field produced by formation of the electrochemical double layer described within the Gouy-Chapman-Stern (GCS) formalism, where the electrolyte is ordered with an inner Stern layer and an outer diffuse layer.⁷⁻⁹ The ions in the electrolyte can approach the electrode but have a finite size and the distance of closest approach is known as the outer helmholtz plane (OHP). The OHP divides the Stern layer from the diffuse layer. Measuring Stark shifts for small adsorbed molecules such as CO represents a measure of the electric field present with the Stern layer, and we have recently shown that measured Stark shifts for CO on Au qualitatively match predictions from GCS theory.¹⁰ However, in addition to the Stern layer field, the absolute Stark shift will also include contributions due to the Onsager reaction field, which is induced by polarization of the electrolyte by the solute

dipole.^{11,12} This Onsager reaction field can have a similar magnitude as the field created by the double layer and should not be neglected when considering the effect of electric field on CO₂R reaction kinetics.

To yield further insight into this important question, we have directly probed the interfacial electric field during CO₂R electrocatalysis using in-situ generated CO on Au as a vibrational Stark reporter. Au electrodes display a small steady-state surface coverage of CO, which is on the order of only a few percent of a surface monolayer.^{6,13–15} This is a result of kinetics that are rate limited by CO₂ adsorption followed by rapid desorption of weakly adsorbed CO from the Au surface.^{5,6,16} To overcome this, it has been common to purge CO directly into the solution; however, these additional CO molecules act as a high intensity source of spectroscopic spectators at non-active sites. To enable direct detection of in-situ generated CO on Au in this study, the electric field is monitored using plasmon-enhanced vibrational sum frequency generation spectroscopy (VSFG) as described recently.^{10,17} Both the Stern and Onsager fields are measured as a function of applied potential in 0.1 M cation bicarbonate electrolyte with the following alkali cations: Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺.

In contradiction to predictions that larger cations induce a stronger local field in the electrochemical double layer, these measurements show that the Stern layer field reaches the highest magnitude in the presence of Li⁺ and decreases in the order Li⁺ > Na⁺ > K⁺ > Rb⁺. In contrast, the Onsager reaction field increases from Li⁺ to Rb⁺. Notably, Cs⁺ breaks the trend for both Stern layer electric field and Onsager reaction field, and analysis indicates that Cs⁺ specifically adsorbs on the Au surface. Interestingly, the CO₂R activity follows the same trend as the Onsager reaction field rather than the Stern field. Modeling of the Onsager field for adsorbed (bent) CO₂ predicts a much stronger Onsager field than Stern layer electric field, suggesting that interfacial solvation structure and its associated field play a critical role in CO₂ activation. To confirm this conclusion, we additionally measure the cation-dependent interfacial water spectra using VSFG spectroscopy. These show that Cs⁺ induces a change in the interfacial water structure correlated with a dramatic drop in CO₂R activity despite Cs⁺ displaying the strongest total (Stern + Onsager) electric field, highlighting the importance of the cation-dependent interfacial water structure on reaction kinetics.

Results

At potentials away from the potential of zero charge (PZC) an electric field is created due to the applied charge on the electrode and the oppositely charged ions in solution as shown in Figure 1a. This electric field decays as a function of distance from the electrode, and is called the double layer (DL) electric field. This field can further be broken down into contributions from an inner Stern layer electric field, and an outer diffuse layer electric field. In this paper we directly measure the Stern layer electric field as our probe is located in the Stern layer.¹⁰ At potentials relevant to CO₂R, the Stern field typically has a magnitude on the order of tens of MV/cm.

Also present for polar solutes in polarizable media is the Onsager reaction field.¹² This field occurs through interaction of the solute dipole with the surrounding solvent and ions, where the solute dipole induces image dipoles in the surrounding medium (Figure 1b). These solvent dipoles, in turn, sum to a net image dipole, or "reaction field", which can be of similar magnitude as the Stern layer field.¹¹ Notable work has been made by Dawlaty et al. to extend this model to interfaces, which are inherently asymmetric.¹¹ When it comes to CO₂ reduction, CO and other polar intermediates will experience an Onsager reaction field from the surrounding solvent and alkali cations. Both the Stern layer field and the Onsager reaction field are present at electrochemical interfaces, as shown in Figure 1c, and we will show that it is possible and important to disentangle these fields in order to separately consider their contributions to CO₂R. Here we measure these fields for the surface intermediate CO; however, because the Onsager field depends on the dipole moment and polarizability of the solvated molecule is critical to consider how this field scales to stabilize short-lived intermediates or transition states, such as adsorbed (bent) CO₂, as described below.

To begin we measure the interfacial electric field using in-situ generated CO, which resides in the Stern layer, and changes vibrational frequency in an electric field due to the vibrational Stark effect. The associated spectra are in the supporting information section 1. By measuring the vibrational frequency ($\omega(\phi)$) as a function of potential (ϕ), and with an appropriate reference frequency (ω_{ref}), we can determine the interfacial electric field ($\vec{F}(\phi)$) as shown in Equation 1.

$$\omega(\phi) = \omega_{ref} - \Delta\vec{\mu} \cdot \vec{F}(\phi) \quad (1)$$

The Stark tuning rate ($\Delta\mu$) of CO is a constant and has been measured previously.^{10,18} The choice of reference frequency is important, and allows us to separate the Stern layer electric field from the Onsager reaction field.¹⁹ In Figure 1d - f we use the CO frequency data of K⁺ as an example to show how we disentangle these two contributions to the total field. Since the net electrode charge is minimized at the PZC, the Stern layer electric field will also be at a minimum. Thus, by choosing the frequency at the PZC as our reference point (ω_{ref} in Equation 1) we can obtain the contribution of the Stern layer electric field to the total field at each potential (Figure 1d). As it is not possible to measure the in-situ generated CO frequency at the PZC

Figure 1. a) Diagram of Stern layer electric field at the electrode surface; b) Diagram of Onsager reaction field in bulk solution. The black circle represents the carbon atom in carbon monoxide, while the red circle represents the oxygen atom; c) Diagram of total field at the electrode surface with contributions from both the Onsager reaction field and the Stern layer electric field; d) Calculation of the Stern layer electric field by referencing the CO frequency under each potential to the extrapolated frequency at the PZC; e) Calculation of the Onsager reaction field by referencing the extrapolated frequency at the PZC to the frequency of CO adsorbed on Au in vacuum; f) Calculation of the total field by referencing the CO frequency under each potential to the frequency of CO adsorbed on Au in vacuum.

due to the negligible activity of CO_2R at this positive potential, the extrapolated frequency at the PZC is used. The PZC was determined by measuring the capacitance minimum with impedance spectroscopy and occurs for all alkali cations near -0.1 V vs. Ag/AgCl. The details of PZC determination are discussed in the experimental section 3, and the corresponding capacitance data is provided in the supporting information section 2. Alternatively, by referencing the extrapolated frequency at PZC to the frequency of CO adsorbed to Au in vacuum (2126 cm^{-1}), an estimate of the Onsager reaction field felt by the solvated CO reporter can be obtained (Figure 1e).^{11,20} Here we note that the magnitude of the Onsager reaction field may change with potential due to a decreasing dielectric constant. However, at fields greater than 10 MV/cm, it has been shown that the dielectric constant reaches a stable value such that Onsager field displays minimal change with applied potential.²¹ As shown in Figure 2b, most of the cations have reached the 10 MV/cm threshold near -0.3 V, so it is reasonable to assume that the observed Stark shift at more negative potentials comes mainly from the Stern layer electric field, and not from potential-induced perturbations to the Onsager reaction field. The total field present at the electrochemical interface is the sum of the Onsager and Stern fields. Consequently, while the Stern field is obtained by referencing the CO frequency under each potential to the PZC, the total field is obtained by referencing the measured frequency to the frequency of CO adsorbed to Au in vacuum (Figure 1f).

According to this method for separating individual contributions to the sum total electric field, all effects of CO solvation, including hydrogen bonding, will be combined in the Onsager reaction term. This is the result of referencing the frequency shift at the PZC to the CO frequency in vacuum such that the Onsager term includes both the polarization field plus effects of explicit solvation in aqueous electrolyte. For example, hydrogen bonding in π systems induces frequency shifts due to changes in occupancy of molecular orbitals.^{11,22,23} Although not purely a Stark effect, this is commonly quantified in terms of the equivalent field required to induce the observed frequency shift. Previous work indicates that hydrogen bonding interactions

will have a relatively minor effect on the CO vibrational frequency,^{18,24,25} compared to CN-based Stark reporters where hydrogen bonding shifts are significant.¹¹ This indicates that the Onsager reaction fields reported here are primarily the result of electrolyte polarization, although contributions from explicit solvent interactions cannot not be ignored. Although it is not possible in present measurements to fully disentangle these contributions, it is still useful to consider the electric field equivalence induced by the combination of electrolyte polarization plus solvent interactions in order to compare the effects of Onsager reaction field and Stern layer electric field on CO₂R kinetics as discussed below.

Figure 2. a) Total field strength at each applied potential; b) Stern layer electric field strength at each applied potential; c) Extrapolated CO frequency at the PZC and corresponding Onsager reaction field strength calculated as referenced to the frequency of CO adsorbed to Au in vacuum.²⁰ Error bars in panels a and b represent standard deviations from at least three experiments. Error bars in panel c are derived from error in the slope.

We apply the deconvolution method above to all alkali cations, and the calculated total electric field, Stern layer field, and Onsager reaction field, are shown in Figure 2a, b, and c, respectively. As shown in Figure 2a, these alkali cations exhibit total electric fields of similar magnitude, and Cs⁺ has the highest total field. This result is similar to the results of Weagele et al.²⁶, which show that the total field slightly increases from Li⁺ to Cs⁺. However, by deconvolution of the Stern layer electric field and Onsager field we find insightful trends. As shown in Figure 2b, at catalytic potentials the Stern layer electric field strength is largest for Li⁺, and decreases going from Li⁺ to Rb⁺, and then increases again for Cs⁺.

Figure 2c shows the Onsager contribution to the total electric field as a function of cation. Interestingly, this Onsager reaction field follows nearly the opposite trend from the Stern field, increasing with cation size from Li⁺ to Rb⁺ $\approx$ Cs⁺. We note that Cs⁺ is an anomaly in terms of the Stern layer field. Cs⁺ also deviates slightly from the observed trend in Onsager field although to a lesser extent. We attribute these observations to specific adsorption, which decreases the distance between electrode surface and OHP, and this will be discussed in greater detail below.

Disentangling these separate contributions to the total measured electric field provides important insights into the cation-dependent structure of the electrochemical double layer. For example, the Stern layer thickness, or distance from the electrode surface to the OHP, is inversely proportional to the magnitude of the Stern layer electric field at an applied potential. Because CO adsorbed on Au resides in the Stern layer, the Stark tuning slope is a sensitive function of the Stern layer thickness, which can be equated to the radius of the adsorbed (hydrated) cations. Using the slope for each cation, we determine the potential at the OHP and the size of the Stern layer using Gouy-Chapman-Stern (GCS) theory as described in the experimental section.²⁷ Table S1 in the supporting information section 3 provides the results of the GCS model using the experimentally measured slope. The calculated Stern layer thickness increases from Li⁺ to Rb⁺ and then decreases for Cs⁺, in agreement with crystal radii data, but in disagreement with bulk mobility measurements.²⁸ For all cations except Cs⁺, the calculated Stern layer thickness is slightly greater than the cation-H₂O bond distance. It indicates that the Stern thickness is approximately equal to the radius of the first hydration shell for each of the respective cations and these cations remain hydrated at interface. However, the calculated Stern layer thickness of Cs⁺ is actually less than the measured Cs⁺-H₂O distance, suggesting that Cs⁺ is partially desolvated and specifically adsorbed on the Au surface under applied potential. Specific adsorption of Cs⁺ has also been reported previously on Hg and Pt.²⁹⁻³¹ Specific adsorption also alters the polarization of the Cs⁺ cation resulting in a change to the Onsager contribution to the total electric field. The result of specific adsorption, which causes Cs⁺ to deviate from the uniform trend observed for the other cations in both the Stern and Onsager reaction fields, can be seen in Figures 2b and c, respectively.

To understand the correlation between Stern layer electric field, Stern layer thickness, Onsager reaction field, and CO₂R

Figure 3. Catalytic measurements for each cation: a) Linear sweep voltammogram (LSV). Current is normalized to the geometric area.; b) Faradaic efficiency to CO and H₂ and c) CO yield obtained after 20 minutes at -1.2 V vs Ag/AgCl. Error bars represent standard deviations from at least three replicate measurements.

kinetics, we further investigated the role of cations on the selectivity and activity of CO₂R, as shown in Figure 3. We find excellent correlation between the Onsager reaction field and the selectivity and activity. Figure 3a and b shows linear sweep voltammetry (LSV) measurements and controlled potential electrolysis (CPE) measurements, respectively, with electrolytes containing CO₂ saturated Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ bicarbonates. The current density (Figure 3a) increases from Li⁺, to Na⁺, to K⁺, but remains almost unchanged for K⁺, Rb⁺ and Cs⁺. However, the trend in CO Faradaic efficiency (FE) shows a volcano profile with Rb⁺ at the maximum (Figure 3b). Surprisingly, this trend in catalytic performance is closely correlated with the Onsager reaction field and anti-correlated with the Stern layer electric field. There is no clear correlation between the measured reaction kinetics and the total electric field, and this observation is only possible after deconvolution of the Stern and Onsager fields. Although the significant increase of CO FE from Li⁺ to Rb⁺ has been observed before, the observed decrease in the presence of Cs⁺ diverges from previous results, which reported Cs⁺ to have similar CO FE to K⁺ and Rb⁺.^{1,3} Figure 3c shows the CO production yield as a function of cation, which reflects the combined effect of current density and CO₂R selectivity. This plot highlights the significance of the cation effect, which results in a 4-fold increase in overall CO yield from Li⁺ to Rb⁺. However, Cs⁺ represents an anomaly. Below we consider the reason for this anomaly and show that this is related to the change in interfacial solvation structure induced by specific adsorption of the Cs⁺ cation as probed by the VSFG spectra of interfacial water.

Figure 4. Water spectra obtained by vibrational sum frequency generation for different alkali cations at -1.0 V vs. Ag/AgCl.

VSFG spectra of interfacial water were measured in-situ during CO₂R at -1.0 V vs. Ag/AgCl under CO₂R conditions

(Figure 4). For comparison, the control experiment done with D₂O is provided in the supporting information section 4 confirming that none of these resonant features are observed in the absence of the H₂O in the aqueous electrolyte. Three peaks are apparent at around 3350 cm⁻¹, 3600 cm⁻¹, and 3700 cm⁻¹. The peak around 3200 cm⁻¹ from "tetrahedral" or ice-like water observed at the air/water interface^{32–40} and dielectric/water interface^{41–51} is missing in the spectra shown in Figure 4. This indicates a relatively disordered water structure under applied potential at the gold electrode surface⁵². The peak at 3700 cm⁻¹ is the dangling, or free OH; however, the assignment for the other peaks is the subject of ongoing debate.^{32,33,37–39,53,53,54} It is generally considered that hydrogen bonding lowers the vibrational frequencies of water, so the water feature at 3350 cm⁻¹ can be assigned either to liquid-like³⁴ water or to a hydrogen bonding network with lower coordination compared to "tetrahedral" water around 3200 cm⁻¹,^{36,41,46} while the peak at 3600 cm⁻¹ can be attributed to more weakly hydrogen bonded or singly hydrogen bonded water.³³

Figure 5. Onsager reaction field derived from the dipole moment and polarizability as reported by Chen et al.⁵ for: a) Adsorbed CO; b) Adsorbed (bent) CO₂.

It is not the goal of the present report to provide a rigorous interpretation of these water spectra, which is the subject of ongoing work. Rather, we only comment on several marked correlations between these spectra, the Stern and Onsager contributions to total electric field, and the CO₂R reaction kinetics. First, we note that for cations Li⁺, Na⁺, K⁺, and Rb⁺, a similar overall spectrum is observed with intensity primarily at 3350 cm⁻¹ and lesser intensity at 3600 cm⁻¹. Signal is also observed in the free OH region at 3700 cm⁻¹. The water spectrum in the presence of Cs⁺ is distinct from the other four cations, consistent with the effects of specific adsorption. In this case, we observe higher intensity at 3600 cm⁻¹ and significantly diminished intensity at 3350 cm⁻¹. One possible explanation for these changes is that specific adsorption of Cs⁺ displaces the water between Au and the cations, which leads to a weaker feature for the relatively strongly hydrogen bonded water at 3350 cm⁻¹. Instead, the remaining waters residing between the cations are relatively weakly hydrogen bonded, resulting in enhanced intensity of the water feature at 3600 cm⁻¹. The disrupted hydrogen bonding network could impede effective proton shuttling^{55–58}, thus reducing CO₂R activity of Cs⁺ as discussed in more detail below. We note that $\chi^{(3)}$ will contribute to the measured water spectra due to the strong DC field present at these potentials.^{59–62} However, the spectral changes measured here for Cs⁺ cannot be explained solely by $\chi^{(3)}$ contributions because the total electric field is greatest in the presence of Cs⁺ (see Figure 2a). As such Cs⁺ should show the highest $\chi^{(3)}$ contribution from bulk water. In contrast, Cs⁺ shows a significantly diminished intensity, suggesting instead a cation-induced change in the interfacial solvation structure. To summarize, we find that the first four cations (Li⁺ to Rb⁺) display similar interfacial water structure, and CO₂R kinetics closely follow the Onsager reaction field. However, for Cs⁺ CO₂R rate is greatly diminished even though the Onsager reaction field is similar to that of Rb⁺, and this anomaly is correlated with the effect of Cs⁺ on the interfacial solvation structure.

In order to further understand the origins of the Onsager reaction field we estimate the interfacial Onsager reaction field using a relation put forth by Sorenson et al.:¹¹

$$\vec{F}_{\text{Ons}} = \frac{\vec{\mu}(1 + \zeta(\epsilon))}{16\pi\epsilon_0 a^3 - \alpha(1 + \zeta(\epsilon))} \quad (2)$$

where $\vec{\mu}$ is the solute dipole, $\zeta(\epsilon)$ is a sum of image dipoles that depends on the relative dielectric constant, a is the radius

of the cavity surrounding the dipole, and α is the solute polarizability. Figure 5 shows a 2D plot of the estimated Onsager reaction field using two free parameters, a and ϵ_r . The solute dipole and polarizability for adsorbed CO are fixed based on values reported recently by Chen et al.⁵ Figure 5a shows that this model predicts Onsager fields on the same order as measured in our experiment using reasonable values for a and ϵ_r . Interestingly, the cation dependent Onsager field strength indicates that the difference in Onsager reaction field results from cation effects on the interfacial dielectric constant. The lines in Figure 5a indicate the measured Onsager field strength for each of the 5 cations. Note that it is not possible to attribute these changes in the measured Onsager field solely to cavity size at a fixed dielectric constant, suggesting that dielectric constant at the interface is cation dependent. While the bulk dielectric constant is not significantly influenced by the electrolyte cation, the interfacial dielectric constant is known decrease and has also been shown to depend on the electrolyte cation.⁶³ The dielectric constant of a system is closely related to molecular polarizability, and we anticipate that the difference in cation polarizability contributes to the observed difference in the interfacial dielectric constant consistent with the significant increase in cation polarizability with increasing crystal radii.⁶⁴ However, determining the interfacial dielectric constant for solvent-solute systems is not trivial, especially in nanoconfined environments involving multiple species and interactions.^{65,66}

Here we have measured the Onsager contribution to the interfacial electric field experienced by CO on Au during CO₂R. To understand the observed correlation between Onsager field and CO₂R kinetics, it is important to consider the effect of field stabilization of the rate-determining transition state. Multiple studies indicate that this transition state involves the surface adsorption of bent CO₂.^{5,67,68} Consequently, it is relevant to consider the magnitude of the electric field, not for the relatively stable CO intermediate, but for the rate-determining CO₂ transition state. While exact quantification of Onsager reaction field for this species extends beyond the scope of this paper, we seek only to illustrate plausible values for this reaction field based on parameters consistent with the measured values of Onsager field reported here. Because electric field is a vector quantity, dipolar stabilization should be insensitive to the specific origins of the net field (i.e. Stern versus Onsager reaction fields); however, we find that the measured CO₂R reaction kinetics closely follow the Onsager rather than the Stern layer field. To understand this, Figure 5b shows the value for the Onsager field predicted for adsorbed CO₂. Here the dipole and polarizability for adsorbed CO₂ are based on values reported by Chen et al.,⁵ and all other parameters are kept fixed based on the fit to the measured Onsager field for CO. Again lines represent predicted values for each of the 5 cations. As shown by the scale bars in Figure 5, the Onsager reaction field predicted for bent CO₂ is nearly an order of magnitude greater than that of CO and far exceeds the Stern contribution to the total field. In the case of Rb⁺ the Stern field is ~30 MV/cm (see Figure 2b), while the Onsager field is ~150 MV/cm (see Figure 5b), approximately 5 times larger.

In light of these findings, we now consider the mechanism for cation-dependent CO₂R kinetics. Several groups have provided theoretical evidence for stabilization of adsorbed CO₂ or other polar intermediates by the interfacial electric field.^{4,5,67,68} While not always implicitly stated, this field is generally considered to come from the electrochemical double layer. However, these results suggest that the Onsager field, not the electric field in the double layer controls the kinetics of CO₂R. In our measurements the Onsager reaction field is viewed from the perspective of surface bound CO. However, the Onsager field of interest is the field induced by the transition state. This transition state is presumed to occur through a bent CO₂ molecule. In its bent state, CO₂ is predicted to have a larger dipole and polarizability than the CO Stark reporter. This is important because the interfacial Onsager Reaction field is proportional to the dipole of the solvated molecule, and polarizability can also increase the reaction field by decreasing the value of the denominator as shown in Equation 2. The resulting Onsager field will lower the transition state barrier and increase the overall reaction rate, consistent with the observation that the CO₂R activity is primarily dictated by the larger Onsager reaction field compared with the Stern layer electric field.

Although CO₂ adsorption is widely accepted as the rate-determining step for CO₂R,^{5,6,67} several studies have predicted that this step becomes trivial in the presence of electric fields on the order of 100 MV/cm.^{5,68} After field stabilization, a subsequent proton transfer likely becomes rate limiting.^{5,16,68} Involvement of a proton in the post field stabilized free energy pathway would reconcile our data showing that Rb⁺ and Cs⁺ show similar Onsager fields. However, the water structure of Rb⁺ and Cs⁺ are quite different and would likely give rise to different proton shuttling rates due to different hydrogen bonding networks.^{56,69,70} Assuming that this proton is not donated from a hydronium ion but rather transfer occurs directly from a water molecule in the cation hydration shell, proton transfer will be independent of bulk pH as confirmed experimentally.⁷¹⁻⁷³

Discussion

Overall, these data confirm that the interfacial solvation structure as well as the associated Onsager reaction field cannot be neglected when considering the kinetics of CO₂R. These findings call for additional models capable of treating solvation-mediated Onsager reaction fields and interfacial solvation structure on equal footing with the electric field produced by the electrochemical double layer. These data clearly show that although continuum models are able to predict stabilization of intermediates by an Onsager field, complete understanding of CO₂R kinetics at metal electrodes requires explicit treatment of interfacial solvation not present in continuum models, since these solvation structures result in significant changes in CO₂R kinetics as demonstrated here via direct, in-situ observation of the active Au/electrolyte interface.

Supporting Information

The supporting material contains information on the

1. Potential dependent SFG spectra of CO
2. Potential of zero charge measurements
3. Stark tuning slope and Stern layer thickness
4. VSFG spectra in the water region for NaHCO_3 in D_2O

Methods

1. Polycrystalline Au electrode preparation Two types of polycrystalline Au were used in this experiment. The Au electrodes for SFG measurements were manufactured by depositing 35 nm of Au onto round CaF_2 windows through electron beam evaporation (Denton DV-502A E-Gun Evaporator). Before the Au deposition, the CaF_2 windows were cleaned with basic Piranha ($\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ 5:1:1. Caution: Piranha solutions are caustic and should be handled with extreme care) at 80 °C for one hour. The other type of Au electrodes (referred as Cr/Au), which were used for electrochemical measurements and FE measurement, were produced with the same equipment. The difference was that a 20 nm chromium adhesion layer was deposited onto the glass substrates before another layer of 100 nm Au was deposited on the top. Before each experiment, the Cr/Au was cleaned by sonicating in ethanol for 5 mins first, followed by sonicating in copious amounts of Milli-Q water for three times.

2. Sum frequency generation measurement

The sum frequency generation system has been described previously, however, we provide a brief description here.¹⁷ The SFG system uses a Ti:Sapphire regenerative amplifire (Spectra Physics-Solstice) which outputs ~ 90 fs pulses at 800 nm with a repetition rate of 2 kHz and with an average power of 3.5 W. Seventy percent of the output is used to pump an OPA (Topas Prime) which directs the signal and idler to a non-collinear DFG stage. The remaining thirty percent is spectrally narrowed to $\sim 10 \text{ cm}^{-1}$ using an air-gap Etalon (TecOptics). The beams are incident on the sample at 56 degrees in a Kretschmann configuration. The IR beam is centered at $\sim 2100 \text{ cm}^{-1}$ in the CO region and has an energy of 3 μJ . In the water region the IR beam is centered at 2900 cm^{-1} and has an energy of 4 μJ , and a beam area of 0.032 mm^2 . The spectrally narrowed, 800 nm visible beam has an energy about 22 μJ , and a beam area of 0.128 mm^2 . When measuring the CO spectra, a potential step ranging from -0.1V to -1.3 V vs. Ag/AgCl was applied to the Au electrode, and each spectrum was collected by delaying the visible beam relative to the IR beam by ~ 850 fs, with an integration time of 1 min. For the water spectra, we integrated for 2 mins at a time delay of 500 fs.

3. Electrochemical measurements

Electrochemical measurements were made using a BioLogic SP-150 potentiostat. The electrochemical cell consisted of a Cr/Au electrode (WE), a leakless Ag/AgCl electrode (eDAQ ET072-1, RE), and a Pt mesh (CE). The electrolytes were prepared by purging 0.05 M M_2CO_3 (M=Li, Na, K, Rb, Cs, >99.9%, Sigma-Aldrich) with CO_2 (Praxair, 99.9%) for 10 mins. For linear sweep voltammetry measurement, the potential was swept from 0 V to -1.3 V vs. Ag/AgCl with a scan rate of 50 mV/s. Electrochemical impedance (EIS) measurements were taken at potentials in the range from 0.2 V to -0.6 V over a frequency range from 200 kHz to 100 mHz. The double layer capacitance was determined by fitting the EIS data with an equivalent circuit as suggested by Xie et al.⁷⁴ using ZView. Figure 6 shows the equivalent circuit used.

Figure 6. Equivalent circuit model used to fit EIS results

4. Gouy-Chapman-Stern model

The Stern layer fitting model employed in this work is a combination of Gouy-Chapman-Stern theory and Stark tuning theory. The frequency shift ($\omega(\phi) - \omega_{PZC}$) of a Stark reporter can be correlated with the potential drop ($\Delta\phi_S$) in the Stern layer by equation 3 below, where $\Delta\mu$ is the Stark tuning rate of CO ($0.7 \text{ cm}^{-1}/\text{MV}/\text{cm}$), and d_S is the Stern layer thickness. The potential drop in the Stern layer can be expressed by equation 4, where ϕ_o is the applied potential and ϕ_{OHP} is the potential at the outer Helmholtz plane (OHP). ϕ_o can be further correlated with ϕ_{OHP} by equation 5,⁷⁵ where ϵ is the dielectric constant of electrolyte in the Stern layer ($\epsilon=6$),⁷⁵ c is the concentration of cations, and z is the charge of the cation. The Stern layer thickness (d_S) and the potential at OHP (ϕ_{OHP}) can be solved from these three equations using the measured frequency of CO as an input. The calculated result is given in Table S1 in supporting information section 3. Here we note that although the same dielectric constant is employed to calculate the Stern layer thickness for the cations, employing different dielectric constants as given in Figure 5 will have only minor effects on the calculated value and does not change the trend in Stern layer thickness.

$$\omega(\phi) = \omega_{PZC} + \left(\frac{\Delta\mu}{d_S}\right) \cdot \Delta\phi_S \quad (3)$$

$$\Delta\phi_S = \phi_o - \phi_{OHP} \quad (4)$$

$$\phi_o - \phi_{OHP} = \frac{0.117d_S}{\epsilon\epsilon_0} c^{1/2} \sinh(19.4z\phi_{OHP}) \quad (5)$$

5. Faradaic efficiency measurement

The measurement process for the Faradaic efficiency of CO and H₂ has been described elsewhere,⁷⁶ but we provide a summary here. An Agilent 7890B gas chromatograph was connected to the electrochemical H-cell through a custom headspace sampling system. The H-cell has two compartments, separated by a Nafion membrane. The Nafion membrane was activated in 10% H₂SO₄ at 80 C for 10 mins before each experiment. A Pt film was used as the counter electrode, and a Ag/AgCl electrode was used as the reference electrode. The electrolyte started with 0.05 M M₂CO₃ (M=Li, Na, K, Rb, Cs). At the beginning of the measurement, the electrolyte was purged with CO₂ for 10 mins at a rate of 0.35 L/min to convert M₂CO₃ into MHCO₃ (as indicated by solution pH), and the headspace of the H-cell was filled with CO₂. During CO₂R, a constant potential, i.e. -1.2 V vs. Ag/AgCl, was applied to the Cr/Au working electrode for 20 mins by a Biologic SP-50 potentialstat, after which a gas sample from the headspace was injected into the GC. This process was repeated at least three times for each cation, and results were averaged to obtain the FE of CO and H₂.

6. Interfacial Onsager reaction field

We employ the model given by Sorenson et al.¹¹ to derive the expression of the Onsager reaction field in terms of the dipole moment, polarizability, cavity size and relative dielectric constant. The solute dipole moment at equilibrium ($\vec{m}$) can be expressed as:

$$\vec{m} = \vec{\mu} + \alpha \vec{F}_{Ons} \quad (6)$$

where $\vec{\mu}$ is the solute dipole moment, and α is the solute polarizability. Additionally, the Onsager field can be expressed as:

$$\vec{F}_{Ons} = \frac{\vec{m}(1 + \zeta(\epsilon))}{16\pi\epsilon_0 a^3} \quad (7)$$

where a is the cavity size and $\zeta(\epsilon)$ is a sum of image dipoles which depends on the relative dielectric constant. By combining equation 6 and equation 7, the expression for the Onsager field given in equation 2 can be obtained. The infinite sum ($\zeta(\epsilon)$) converges quickly, and we find that the first two terms are sufficient to reproduce the data of Sorensen et al.¹¹

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Author contributions statement

R.B. and S.W. conceived the experiments, Q.Z. conducted CPE, and LSV measurements. Q.Z. and S.W. conducted EIS and SFG Stark experiments, Q.Z., S.W. and G.D. analysed the results. Q.Z. and G.D. collected water spectra. All authors reviewed the manuscript.

Additional information

The authors declare no competing financial interests.

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