The Importance of Acid–Base Equilibria in Bicarbonate Electrolytes for CO₂ Electrochemical Reduction and CO Reoxidation Studied on Au(hkl) Electrodes

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ABSTRACT: Among heterogeneous electrocatalysts, gold comes closest to the ideal reversible electrocatalysis of CO₂ electrochemical reduction (CO2RR) to CO and, vice versa, of CO electrooxidation to CO₂ (COOR). The nature of the electrolyte has proven to crucially affect the electrocatalytic behavior of gold. Herein, we expand the understanding of the effect of the widely employed bicarbonate electrolytes on CO2RR using gold monocrystalline electrodes, detecting the CO evolved during CO2RR by selective anodic oxidation. First, we show that CO2RR to CO is facet dependent and that Au(110) is the most active surface. Additionally, we detect by in situ FTIR measurements the presence of adsorbed COtop only on the Au(110) surface. Second, we highlight the importance of acid–base equilibria for both CO2RR and COOR by varying the electrolyte (partial pressure of CO₂ and the concentration of the bicarbonate) and voltammetric parameters. In this way, we identify different regimes of surface pH and bicarbonate speciation, as a function of the current and electrolyte conditions. We reveal the importance of the acid–base bicarbonate/carbonate couple, not only as a buffering equilibrium but also as species involved in the electrochemical reactions under study.

INTRODUCTION

In the search for more efficient energy conversion technologies, the ultimate goal is to find a material that can catalyze an electrochemical process reversibly. For a given Ox/Red couple, such a material exhibits high rates for both the electrochemical reduction and oxidation with zero overpotential. Platinum is a good example of such a reversible catalyst, as it is able to catalyze reversibly H⁺/H₂ conversion, i.e., the hydrogen evolution reaction (HER) and the hydrogen evolution oxidation (HOR). Reversible catalysts have been predicted to exist for two-electron transfer reactions since such reactions typically have only a single catalytic intermediate, whose binding energy needs to be optimized. In relation to the electrocatalytic CO₂ reduction reaction (CO2RR), researchers would like to find an electrocatalyst interconverting reversibly CO₂/CO, that is, the following two-electron transfer reaction:

\[
\text{CO}_2 + 2\text{AH} + 2e^- \rightleftharpoons \text{CO} + 2\text{A}^- + \text{H}_2\text{O}
\]  

where AH is a Brønsted acid and A⁻ is its conjugated base. In neutral-alkaline media, the acid–base couple is commonly considered to be H₂O/OH⁻. However, other acid–base couples may be taken into account, e.g., H₂CO₃/HCO₃⁻, HCO₃⁻/CO₂⁻, or H₂PO₄⁻/HPO₄²⁻.

In nature there is an enzyme, the Ni-containing carbon monoxide dehydrogenase (Ni-CODH), which can catalyze in a quasi-reversible fashion the interconversion between CO₂/CO. Enzymes for the reversible conversion of CO₂ and formic acid also exist. For this latter conversion, (nearly) reversible electrocatalysts have also been identified in heterogeneous electrocatalysis and molecular electrocatalysis. However, reversible synthetic heterogeneous electrocatalysts for the CO₂/CO conversion have, to the best of our knowledge, not yet been identified. According to a computational study by Hansen et al., this is related to the existence of two intermediates (adsorbed CO and COOH) in the catalytic pathway, whose binding energies have a scaling relationship. The enzyme can break this scaling by the presence of a second coordination sphere which stabilizes COOH. Among the known metal electrocatalysts, gold has the highest activity for both CO₂ electrochemical reduction to CO (CO2RR) and CO electrooxidation (COOR). Therefore, understanding the details of the mechanism of the CO₂/CO conversion on gold, and especially the role of the electrolyte (the electrochemical “second coordination sphere”), is important for developing more efficient catalysts for CO2RR to CO.

Studies of the structure dependence of CO2RR on gold low-index monocrystalline surfaces revealed that (110) is the most active facet. The structure sensitivity trend for CO2RR to
CO on the low-index facets points to the central role of low-coordinated surface sites in CO2RR. Analogously, the Au(110) surface was measured to be the most active facet for COOR, both in acidic and alkaline media. Besides the electrode surface structure, various properties of the electrolyte (e.g., anions, cations, and pH) have been shown to play a crucial role in the electrocatalysis of the CO2RR and COOR. In particular, bicarbonate solution has been proven to lead to higher CO2RR efficiency, compared to other buffered solutions. Understandably, bicarbonate is the most widely employed electrolyte in CO2RR electrocatalysis. Aside from its buffering ability, bicarbonate can also act as a supplier of CO2 through the solution equilibrium between CO2 and bicarbonate and the role of the different species in solution are complicated by the interconnection between surface speciation and reaction rates. Recently, numerous studies have identified the importance of current-driven changes in the local environment close to the electrode surface compared to the bulk of the solution on the outcome of CO2RR.

In this study, we assess the structure and electrolyte dependence of CO2RR on monocrystalline Au(hkl) electrodes. Based on the ability of the gold electrode to selectively oxidize CO, we detect the CO produced during CO2RR by applying anodic potentials. In this way, we gain insights into the selectivity-potential trend for CO2RR in bicarbonate electrolyte through a fast semiquantitative method. Subsequently, we extend the measurements of CO2RR on Au(110) in a variety of electrolyte conditions, by changing the partial pressure of CO2 and bicarbonate concentration, and voltammetric parameters, such as the negative vertex potential and the scan rate. These electrochemical measurements of CO2RR activity together with in situ FTIR studies help us to draw a more detailed picture of the effect of bicarbonate surface speciation and equilibria not only on CO2RR but also on COOR on well-defined gold surfaces.

**Experimental Section**

**Chemicals and Materials.** Electrolytes were prepared from H2SO4 (96%, Merck Suprapur), HClO4 (70%, Merck Suprapur), KHCO3 (EmsureACS Merck), and KClO4 (99.995%, Aldrich Ultrapure) using Milli-Q water (resistivity >18.2 MΩ cm). Prior to experiments, the electrolytes were purged for 20 min with Ar (6.0 purity, Linde), CO2 (4.5 purity, Linde), or CO (4.7 purity, Linde). To obtain the selected partial pressure of CO2, the flow of CO2 and Ar was set accordingly using two mass controllers (SLAS850, Brooks Instrument).

**Experimental Procedure.** The glassware was stored overnight in a 1 L 1% KMnO4 solution. Prior to experiments, the residual KMnO4 was removed by addition of a diluted Piranha solution and the glassware was boiled in Milli-Q water for seven times. The electrochemical experiments were performed using two electrochemical cells in a three-electrode configuration at room temperature using a Bio-Logic VSP300 potentiostat. Both cells contained a coiled H2SO4 (96%, Merck Suprapur), HClO4 (70%, Merck Suprapur), KHCO3 (EmsureACS Merck), and KClO4 (99.995%, Aldrich Ultrapure) using Milli-Q water for seven times. The reference electrode was a Ag/AgCl electrode (KCl-saturated, Pine Research Instrumentation). In cell 1, the pH of the electrolyte was set accordingly using two mass controllers (SI Analytics Lab 855 Benchtop Meter), and thus, the potential was calculated according to $E_{base} = E_{Ag/AgCl} + 0.199 V + (0.059 \times pH)$.

The gold single-crystal disk electrodes ($\Theta = 1.7 \text{ mm}$) were pressed against the prism in a thin layer configuration biased at the reference potential ($E_d = 0.1 \text{ V vs RHE}$). After stabilization of the thin layer, the background spectrum was recorded at $0.1 \text{ V vs RHE}$. To minimize the disruption of the thin layer, the spectra were recorded while the potential was pulsed ($0.02 \text{ s}$) in between the selected and the reference potential. Each spectrum was obtained in reflectance mode by averaging over 100 scans with a resolution of 4 cm$^{-1}$. In this fashion, a positive (negative) band corresponds to an increase (decrease) in the transmittance at the selected potential compared to the reference. Hence, a positive (negative) band is associated with a decrease (increase) in the concentration of an IR-absorbing species on the surface and/or in the thin layer.

**Results and Discussion**

Structure Dependence of CO2RR. In this section, we will discuss the structure dependence of CO2RR to CO on the three low index planes of gold, i.e., Au(111), Au(100), and Au(110), as determined by cyclic voltammetry (CV) and chronoamperometry (CA) experiments in 0.1 M KHCO3. Our way of measuring the CO2RR electrocatalytic activity by subsequent cathodic and anodic CAs is a fast semiquantitative way to capture the structure dependence trend for CO2RR, as well as the selectivity to CO2RR vs HER as a function of the applied potential. Next, we investigated the presence of possible CO2RR reaction intermediates on Au(hkl) by means of in situ FTIR experiments.

Figure 1 A shows the cyclic voltamograms of Au(111), Au(100), and Au(110) in CO2-saturated 0.1 M KHCO3. First, the potential was scanned to negative values, where CO2 is reduced to CO, and then to positive values, where the CO formed during CO2RR is reoxidized. Under reduction

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conditions, the cathodic current measured for Au(110) is one order of magnitude larger than the current measured for Au(111) and Au(100) electrodes. However, the cathodic current is due to the contribution of two electrochemical processes, namely, CO2RR and HER. To unravel the contribution of CO2RR to the total cathodic current, the potential was scanned to values where the gold electrode is in a typical catalytic activity for all Au(hkl) planes. Notably, while for Au(111) and Au(100) n_{CO}/n_{tot} keeps increasing as a function of the more negative applied potential, for Au(110), after an initial steep increase, the n_{CO} levels out at ca. −0.6 V vs RHE and decreases at −1.0 V vs RHE. A similar trend emerges in the CVs in Figure 1 for Au(110), where the increase in the cathodic current plateaus around −4 mA cm⁻² at a potential of ca. −0.65 V vs RHE. This decrease for both n_{CO} and the cathodic current may be ascribed to a mass transport limitation in CO₂ and its consumption by the homogeneous reactions, as a response to the increase in the local alkalinity (a more detailed discussion will be given in the next section). Figure 1 B shows on the right axis the number of moles of CO divided the total number of moles of CO2RR activity as a function of the applied negative potential.

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| Figure 1. For the different Au(hkl) crystals in CO₂-saturated 0.1 M KHCO₃: (A) Cyclic voltammetry at 50 mV s⁻¹. (B) Number of moles of CO formed (left axis, full square) and number of moles of CO divided the total number of moles reduced (right axis, empty square) as a function of the applied negative potential.
Next, we investigated by in situ FTIR the presence of surface intermediates under CO2RR conditions. Figure 2 shows the p-polarized FTIR spectra recorded in CO2-saturated 0.1 M KHCO3. The background was collected at +0.1 V vs RHE, and then, the potential was gradually increased to more negative values through pulsed (0.02 s) chronoamperometry (0.0, −0.1, −0.2, −0.25, −0.3, −0.35, −0.4, −0.45, and −0.5 V vs RHE).

![Figure 2. FTIR spectra of Au(110) measured with p-polarized light in CO2-saturated 0.1 M KHCO3. The background was collected at +0.1 V vs RHE, and then, the potential was gradually increased to more negative potentials for Au(110) (Figure S5) shows the full FTIR spectra for Au(110) and Au(111). Although p-polarized light is more sensitive to the species adsorbed or close to the electrode surface, we can still observe vibration modes of species present in solution. Namely, for both Au(111) and Au(110) spectra, we detected several bands related to species in solution at 1310, 1361, 1400, 1620, and 2343 cm−1. Besides the band at 1620 cm−1 due to the OH bending of water, all the other modes are related to the bicarbonate species in the thin layer as a function of the applied negative potential. The positive band at 2343 cm−1 is due to CO2(aq) which is consumed for increasingly negative potentials. The negative-going bands at 1361 cm−1 and at 1310 cm−1 are attributed to the stretching modes of bicarbonate in solution. Initially, the concentration of bicarbonate in the thin layer increases (negative bands), but for Au(110) at a potential of −0.5 V vs RHE, bicarbonate starts being consumed (positive band). Simultaneously, carbonate is formed as shown by the positive going band at 1400 cm−1 due to the asymmetric stretching of dissolved carbonate. Furthermore, at −0.5 V vs RHE the very pronounced positive water band at 1620 cm−1 indicates the onset of water reduction. Overall, the bicarbonate surface speciation is changing as a function of the applied potential (leading to a cathodic current), being CO2 and HCO3− at low overpotential and HCO3− and CO32− at more negative potential.

Only on Au(110) at potentials more negative than −0.2 V vs RHE did we observe a band at 2100 cm−1 related to adsorbed CO. In the literature, this frequency has been attributed to CO adsorbed on top, COtop. In our study, the COtop band is a bipolar band with a Stark tuning slope of ca. 20 cm−1 V−1 (see Figure S6). The Stark tuning slope obtained in our study for COtop falls in the range (20−40 cm−1 V−1) measured for Au(hkl) during COOR. Compared to COtop previously detected on polycrystalline gold as measured in the attenuated total reflection mode (ATR), our results show a slightly different potential dependence of the COtop band. Namely, in the ATR spectra the COtop band disappears at potentials more negative than −0.1/−0.3 V vs RHE, while in our study we observed the COtop mode to potentials as negative as −0.5 V vs RHE. This different potential dependence of COtop may originate from the variations in the experimental conditions of this work compared to previous ones, i.e., the infrared technique (external vs internal reflection), reference potential (0.1 V vs RHE compared to ca. 1.0−1.2 V vs SHE), electrolyte nature (K+ compared to Na+), and electrode surface (monocrystalline compared to a high roughness Au polycrystalline surface). Finally, the FTIR measurements support the activity trend of CO2RR for Au(hkl) planes, as we detected the presence of the reaction product only on the most active surface, i.e., Au(110).

**Role of Acid–Base Equilibria in Bicarbonate Electrolyte for CO2RR and COOR.** In this section, we will investigate the role of the various acid–base equilibria present in bicarbonate electrolyte on the electrocatalysis of CO2RR and CO electrooxidation on the most active surface, Au(110). Importantly, a bicarbonate solution is a buffer system through two different acid/base equilibria. The first acid–base couple CO2/HCO3− has a pKacid = 6.3 being a good buffering agent for pH 5.3−7.3 according to

\[
\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-
\]

For higher pH 9.3−11.3, the buffering will take place through the HCO3−/CO32− equilibrium with a pKbase = 10.3 according to

\[
\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}
\]

In the bulk of the solution, the bicarbonate speciation is dictated by the bulk pH. In turn, the bulk pH of a bicarbonate electrolyte depends on the partial pressure of CO2 (pCO2) and

![Figure 3. (A) Cyclic voltammetry of Au(110) in 0.1 M KHCO3 at 50 mVs−1 for different pCO2; (B) Calculated oxidation charges obtained by integration of the CV up to 1.2 V vs RHE, after polarization to −1.2 V vs SHE and experimentally measured bulk pH from (A).](https://doi.org/10.1021/acs.langmuir.1c00703)
on the initial bicarbonate concentration. However, in aqueous electrolytes the occurrence of electrochemical processes at the electrode surface will lead to significant changes in the pH near the electrode surface. Thus, the surface pH, and as a result the bicarbonate surface speciation, will be determined by the current at the electrode. In the absence of forced convection, especially, large concentration gradients will build up between the surface and the bulk. In this case, also the kinetics of these solution reactions are important, and reaction 3 is several orders of magnitude faster than reaction 2. To investigate the effect of reaction 2 and 3 on CO2RR and CO re-electrooxidation, we will systematically change the following parameters: the partial pressure of CO2, the bulk bicarbonate concentration, and the applied cathodic potential.

Keeping the bulk concentration of bicarbonate fixed, purging the solution with different partial pressures of CO2 (P CO2) leads to different bulk pH, as the equilibrium of reaction 2 shifts to the right. Specifically, by increasing the P CO2, the pH drops, being ca. 9.0 in Ar-saturated and 6.8 in CO2-saturated 0.1 M KHCO3 (see Figure 3 B).

Figure 3 A shows the cyclic voltammograms of Au(110) in 0.1 M KHCO3 solutions purged with different P CO2. In general the cathodic current and, more precisely, the quasi-plateau in the current (j lim) observed during the cathodic scan increases with the P CO2 (see Figure S8). A more detailed discussion of the nature of j lim will be given later. Curiously, the anodic part of the CVs exhibits two oxidation waves for P CO2 \&lt;= 0.6 atm and a single oxidation peak for P CO2 > 0.6 atm. According to the oxidation peak potential, we name the peak at a potential of ca. +0.4 V vs RHE the 1st peak and the one at ca. +0.7 V vs RHE the 2nd peak. By integrating the total oxidation current (sum of the 1st and 2nd peak), we obtain the total oxidation charge (Q ox). Figure 3 B shows Q ox calculated from the CVs in 0.1 M KHCO3 solutions purged with different P CO2. The Q ox scales linearly with the P CO2, suggesting that both oxidation peaks (1st and 2nd) can be attributed to a product of CO2RR. For this reason, we investigated whether the origin of the early oxidation wave may relate to the formation of a CO2RR products beyond CO2, as proposed by Narayanan et al. During CO2RR on a gold electrode, formic acid (HCOOH) was generally detected with low Faraday efficiency (<5%). Additionally, a few reports have claimed that at more negative potential CO2 could even be reduced to methanol (CH3OH) through a path involving the formation of a formaldehyde intermediate (H2CO), as calculated by DFT. We probed whether the 1st oxidation wave in the CV of Au(110) may originate from CO2RR to any of these 1-carbon-containing products, i.e., HCOOH, CH3OH, and H2CO, by adding 10 mM of each organic molecule to a solution of 0.2 atm of CO2 in 0.1 M KHCO3 (see Figure S9). The addition of these organic molecules did not result in a net increase of any of the oxidation waves. Consequently, the duality of the oxidation wave cannot be explained in terms of CO2RR to any 1-carbon-containing molecule other than CO2.

To further probe the effect of acid–base equilibria and the nature of the two electrooxidation peaks, we performed measurements in electrolytes of different bulk bicarbonate concentrations (i.e., different buffer strength). Figure 4 displays the cyclic voltammograms of Au(110) in bicarbonate electrolytes of different concentration (0.02, 0.1, and 0.5 M) purged with Ar. In Ar-saturated electrolytes, the cathodic current is mainly due to HER and increases with the bicarbonate concentration, in agreement with bicarbonate being a viable proton donor for HER. Still, as shown by the appearance of an oxidation wave after the cathodic polarization, we measured a small COOR current. Distinctly, in Ar-purged solutions the oxidation peak potential corresponds to the 1st peak and its charge is proportional to the bulk bicarbonate concentration. During in situ FTIR experiments in Ar-saturated 0.5 M KHCO3 on Au(110), we detect the presence of CO2 at 2100 cm^-1 (see Figure S7). However, no CO2 band at 2343 cm^-1 was detected, suggesting that CO2 comes from acid/base equilibria in solution. Our results corroborates the hypothesis that bicarbonate is a source of CO2aq through the following solution equilibrium:21,22,53

\[ \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_2 + \text{OH}^- \]  

(4)

Recent first-principles molecular dynamics simulations suggest a mechanism in which HCO3- is converted into CO2 by exchange of a proton from a neighboring water molecule to bicarbonate.

Next, we investigated the effect of the negative vertex potential (and corresponding cathodic current) on the 1st and 2nd oxidation peaks. Figure 5 A shows potential opening cyclic voltammograms of Au(110) in 0.1 M KHCO3 purged with 0.2 atm of CO2. Figure 5 B displays the charge calculated from the integration of the anodic wave in (A), as the total oxidation charge, and for the 1st and 2nd peaks, separately. The peaks were fitted using an asymmetric double sigmoidal function in OriginLab. A specific potential-charge trend was observed for the two oxidation peaks. While the 2nd peak gradually increases with more negative potential until ~0.8 V vs RHE, the 1st peak only appears at a potential more negative than ~0.6 V vs RHE and keeps increasing. Interestingly, the growth of the 1st oxidation peak initiates concomitantly the appearance of the quasi-plateau in the cathodic current at ~0.6 V vs RHE. Similarly, the decrease in the 2nd oxidation peak occurs simultaneously with the increase in the cathodic current after the semi-plateau at ~0.8 V vs RHE, which is attributed to an increase in HER.

The trend observed for the oxidation peaks (1st and 2nd), by varying the P CO2, the concentration of KHCO3 and the applied cathodic potential, indicates a strong pH effect. Specifically, the growth of the 1st oxidation peak appears to emerge after the manifestation of the cathodic quasi-plateau. To have a deeper
insight into the nature of the species leading to the two well-separated anodic peaks and to the quasi-plateau in the cathodic current, we performed voltammetry at different scan rates. According to the Randles−Sevcik equation,55 for a diffusion limiting process the peak current varies linearly with the square root of the scan rate ($\nu$). From the slope of the linear fitting it is then possible to derive the diffusion coefficient $D$ (cm$^2$ s$^{-1}$) of the limiting species by rearranging the Randles−Sevcik equation (see the derivation in the Supporting Information):

$$D = \frac{s}{(2.69 \times 10^5 \times n^{3/2} \times c)^2}$$

where $s$ (A cm$^{-2}$ V$^{-0.5}$ s$^{0.5}$) is the slope, $n$ is the number of electron transferred, and $c$ (mol cm$^{-3}$) is the concentration.

To simplify the system, we controlled the effect of surface concentration gradient developing during the cathodic scan on the COOR by performing bulk COOR measurements ([CO] = 1 mM) on a Au rotating disk electrode (RDE). Figure 6 C shows voltammetry measurements of bulk COOR on Au RDE in CO-saturated 0.1 M KClO$_4$ with increasing concentration of equimolar HCO$_3^−$/CO$_3^{2−}$ at 50 mV s$^{-1}$ and 1600 rpm. We can clearly observe two different diffusion-limiting plateaus for COOR. For increasing concentration of HCO$_3^−$/CO$_3^{2−}$, the 1st plateau increases while the 2nd plateau remains constant. The increase in the 1st plateau current mirrors the increase in HCO$_3^−$/CO$_3^{2−}$ concentration, but not the concentration of OH$^−$ (i.e., pH). It is worth noticing that we used equimolar solutions of HCO$_3^−$/CO$_3^{2−}$ to minimize the increase in the bulk pH. Nonetheless, the mere addition of HCO$_3^−$ does not lead to the appearance of the 1st COOR plateau (see Figure S13). Hence, the observed rise in the 1st COOR plateau in Figure 6 C has to be ascribed to the increasing CO$_3^{2−}$ concentration.

Based on this information, we propose that the appearance of two separated bulk CO electrooxidation peaks can be attributed to reaction mechanisms mediated by two different oxygen donors. The marked pH and electrolyte dependence of the two anodic peaks leads us to ascribe the 2nd peak to COOR by H$_2$O, while the 1st peak is due to COOR by CO$_3^{2−}$. We base this on the observations that the RDE experiments of bulk COOR reveal that the 1st plateau current is proportional to the CO$_3^{2−}$ concentration (and not to OH$^−$ or HCO$_3^−$).
OH on Au(111) shows that, at a potential as low as 0.3 V vs RHE, HCO$_3^-$ rates. In Figure 7 B, we constructed a Randles−Sevcik plot of the plateau current ($j_{\text{lim}}$) as measured in (A). (C) Voltammetry of the Au(110) crystal in CO$_2$-saturated 0.1, 0.05, 0.005, and 0.0 M KHCO$_3$ and a constant concentration of K$^+$ (0.1 M, by addition of KClO$_4$) at 25 mV s$^{-1}$.

Figure 7. (A) Voltammetry of Au(110) crystal in CO$_2$-saturated 0.1 M KHCO$_3$ at different scan rates. (B) Randles−Sevcik plot of the plateau current ($j_{\text{lim}}$) as measured in (A). (C) Voltammetry of the Au(110) crystal in CO$_2$-saturated 0.1 M KHCO$_3$, 0.05, 0.005, and 0.0 M KHCO$_3$ and a constant concentration of K$^+$ (0.1 M, by addition of KClO$_4$) at 25 mV s$^{-1}$.

However, the derivation of the diffusion coefficient from the slope of the linear fitting in Figure 7 B gives a value that is two orders of magnitude lower than the diffusion coefficient of CO$_2$ (see Table S1). Most likely, the disagreement between the calculated and the theoretical diffusion coefficient of CO$_2$ is due to the interplay of homogeneous equilibria leading to consumption of CO$_2$ according to eq 2. Indeed, for each molecule of CO$_2$ being reduced, two molecules of A$^-$ (i.e., OH$^-$ or CO$_3^{2-}$) are produced according to reaction 1. Thus, CO$_2$RR can be considered as a self-inhibiting reaction; as CO$_2$RR proceeds, CO$_2$ is more and more consumed by the product of its own reduction through solution reactions. A similar plateau in the CO$_2$RR current was observed for both gold$^{25}$ and silver$^{59}$ electrodes and was ascribed to mass transport limitation in CO$_2$. Still, the CO$_2$RR current exhibits an unusual scan rate dependence; it is diffusion limited at low scan rates, but for higher scan rates, it deviates from Randles−Sevcik behavior (see Figure 7 B). Under the latter conditions, the plateau in the cathodic current disappears and the current becomes almost scan rate independent, suggesting that CO$_2$RR is not controlled any more by diffusion. Consistently, improving mass transport by forced convection has a marked effect on $j_{\text{lim}}$ at low scan rate, while its effect is more subtle for higher scan rates (see Figure S11). Even if at low scan rate under stationary conditions, the current at −1.1 V vs SHE appears to be diffusion limited, and the Koutecky−Levich analysis displays that the current is still partially kinetically controlled (see Figure S12). This latter result is in agreement with a mass transport limitation in CO$_2$RR ascribed to an “apparent” CO$_2$ flux, due to a convoluted mass transport with the kinetics of homogeneous reactions. Disentanglement of the scan rate dependence requires many more detailed experiments and presumably also kinetic simulations, which is outside of the scope of this work.

CONCLUSIONS

In summary, we investigated the structure dependence of Au(hkl) for CO$_2$RR by cyclic voltammetry, where the cathodic scan was directly followed by anodic polarization to detect by electroofoxidation the CO evolved. The Au(110) surface exhibits the highest activity for CO$_2$RR, and CO$_3^{2-}$ is the only adsorbed species detected.

By performing cyclic voltammetry on Au(110) in different bicarbonate electrolyte conditions, we revealed the importance of the current-induced changes in the surface species on
CO2RR and COOR, as sketched in Figure 8. As the cathodic reactions proceed, the surface pH increases, and CO2RR becomes mass-transport limited, resulting in a current plateau. The mass transport limitation in CO2RR exhibits an anomalous scan rate dependence, as it is the result of the interplay of the diffusion rate of different bicarbonate-related species and the kinetics of the homogeneous equilibria leading to CO2 consumption. Our results suggest that close to the species and the kinetics of the homogeneous equilibria leading to CO2, and in HER, as an available proton donor,23 while carbonate (CO3\(^2\)) participates both in CO2RR, as a supply of CO2, and in HER, as an available proton donor,23 while carbonate (CO3\(^2\)) acts as an oxygen donor in COOR. As the change of species at the electrode surface compared to the bulk may lead to the presence of new actors in the catalytic pathways, the necessity of probing in situ the local composition of the electrified interface becomes crucially important.

![Figure 8. Schematics of the current-driven changes in the surface bicarbonate speciation during cyclic voltammetry of Au(110) in CO2-containing bicarbonate electrolytes and its effect on COOR.](image)

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