Dramatic HER Suppression on Ag Electrodes via Molecular Films for Highly Selective CO₂ to CO Reduction

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ABSTRACT: The carbon dioxide reduction reaction (CO₂RR) in aqueous electrolytes suffers from efficiency loss due to the competitive hydrogen evolution reaction (HER). Developing efficient methods to suppress HER is a crucial step toward CO₂ utilization. Herein, we report the selective conversion of CO₂ to CO on planar silver electrodes with Faradaic efficiencies >99% using simple pyridinium-based additives. Similar to our previous studies on copper electrodes, the additives form an organic film which alters CO₂RR selectivity. We report electrochemical kinetic and other mechanistic data to shed light on the role of these organic layers in suppressing HER. These data suggest that hydrogen production is selectively inhibited by the growth of a hydrophobic organic layer on the silver surface that limits proton but not CO₂ mass transport at certain applied potentials. The data also point to the involvement of a proton-transfer within the rate determining step of the catalysis, instead of the commonly observed electron-transfer step for the case of planar Ag electrodes.

INTRODUCTION

While anthropogenic CO₂ emissions present a daunting societal challenge with respect to climate change, concentrated CO₂ sources also afford an attractive CO₂-recycling opportunity.¹ The electrochemical carbon dioxide reduction reaction (CO₂RR) is a catalytic process by which CO₂-recycling can be driven via renewably derived electricity, hence affording a pathway toward zero- or low-carbon chemical/fuel feedstocks.²–⁴ For such an approach to have practical utility a host of technical challenges needs to be met, with high chemical selectivity for desired C-containing products being prominent among them. The use of metallic electrodes as catalytic materials is an important strategy to facilitate the transformation of CO₂ into a range of such desirable products.⁵–⁹ Nevertheless, the mechanistic landscape of CO₂RR is complex and competing proton-coupled electron transfer (PCET) pathways can be operative; control of product selectivity remains a central issue. Approaches to rationally tune the selectivity of catalytic surfaces are needed.

Nanostructuring of metallic surfaces, to increase the number of exposed active sites, has been widely used as a strategy to prepare electrodes with improved reaction kinetics for CO₂RR.¹⁰–¹⁴ Detailed analyses of the catalytic activity as a function of the electrochemical surface area (ECSA) have suggested that nanostructuring does not alter the intrinsic activity of the active sites in any significant manner.¹⁵ This observation is in agreement with the fact that the outcome of electrochemical CO₂RR is determined by the adsorption energies of reaction intermediates,¹⁶ which are typically correlated through thermodynamic scaling relations.¹⁷ Strategies to break scaling relations and control reaction pathways to favor a single product are therefore desired.¹⁸–²⁰

In this context, molecular modifications of electrode surfaces provide an attractive approach for the electrosynthesis of desired products in CO₂RR.²¹–²⁹ Our research team has recently focused on studying the interaction of molecular films with copper electrodes to control the selectivity of CO₂RR.²⁰–³² We have disclosed that water-soluble N-substituted pyridinium-type additives undergo electrochemically induced reductive dimerization in situ, leading to the deposition of an organic film on the surface of a polycrystalline Cu electrode. As a consequence, methane generation is highly suppressed and faradaic efficiencies (FE) for C₂⁻ products can be substantially increased, up to 80%.³² Further, when such molecular films are electrodeposited onto copper-based gas diffusion electrodes, it is suggested that selective stabilization of surface intermediate *CO₂dep enhances the electrosynthesis of ethylene, with reaction rates up to 230 mA cm⁻².³¹ These electrodeposited molecular films have also demonstrated utility in the stabilization of nanostructured copper surfaces for the selective production of ethylene.³² These results with copper notwithstanding, it remains to now determine whether other metal electrodes can be similarly modified, and if so, how such additives, once deposited, may tailor the electrocatalytic profiles of these metals in the context of CO₂RR (or other reductive transformations). The simplicity of the approach offers attractive opportunities here. In addition, understanding the mechanistic basis of how such molecular films alter the CO₂RR selectivity profile may aid in the design of new organic-metal interfaces with tailored selectivities.²⁹,³¹ Studies aimed at building such understanding are complicated by the rich product profile of CO₂RR on copper electrodes. By contrast, metallic silver surfaces catalyze primarily CO₂-to-CO conversion in aqueous electrolytes, with concomitant production of H₂ and a small amount of HCOOH depending on the
potential applied.\textsuperscript{9,33} In this regard, comparing modified and unmodified silver electrodes, the former being prepared via a similar additive approach to that which we have explored with copper, provides an appealing strategy for mechanistic studies owing to the simplicity of the product profile. Herein, we explore the mechanistic basis for pyridinium-based additives to attenuate HER at organic-silver interfaces. We show that certain N-substituted pyridinium additives alter the CO\textsubscript{2}RR product profile of Ag foils by selectively inhibiting proton (HER) but not CO\textsubscript{2} reduction within a certain potential window, thereby producing CO with extremely high selectivity. A mechanistic hypothesis for this effect is proposed based on a combination of electrocatalytic, kinetic, and surface characterization studies.

RESULTS AND DISCUSSION

Selective Electroconversion of CO\textsubscript{2} to CO. Bulk electrolysis experiments were performed on a polycrystalline silver electrode with CO\textsubscript{2}-saturated 0.1 M KHCO\textsubscript{3} electrolyte (pH = 6.8) using a recently reported custom flow cell.\textsuperscript{28} Potentials were measured versus a leakless Ag/AgCl electrode and converted to the RHE scale according to the equation: \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^0_{\text{Ag/AgCl}} + 0.059 \text{ pH} \); where \( E^0_{\text{Ag/AgCl}} \) is the measured potential, \( E^0_{\text{Ag/AgCl}} = 0.1976 \text{ V at } 25{^\circ}\text{C} \), and pH is the pH value of the bulk.

In the absence of a molecular additive, bare silver electrodes produced exclusively CO, H\textsubscript{2}, and HCOOH within the tested potential range (from \(-0.80 \text{ V to } -1.20 \text{ V, Figure 1a-b, Figure S1, Table S1})

Trace CH\textsubscript{2} was detected at higher potential values, consistent with previous reports.\textsuperscript{3,2} The highest FE for CO was obtained at \(-1.10 \text{ V (FE\textsubscript{CO} = 74\%) with concomitant production of H\textsubscript{2} (FE\textsubscript{H2} = 19\%) and HCOOH (FE\textsubscript{HCOOH} = 3\%). At bias more reducing than \(-1.20 \text{ V and less negative than } -0.90 \text{ V, H\textsubscript{2} was the major product and the production of HCOOH remained constant (FE\textsubscript{HCOOH} < 5\%).}

Figure 1. (a) Faradaic efficiencies; (b) total and partial current densities obtained during CO\textsubscript{2}RR at \(-0.99 \text{ V in a CO\textsubscript{2}-saturated 0.1 M KHCO\textsubscript{3} electrolyte without or with 10 mM of either 1-Br\textsubscript{2} or 2-Cl. Chemical structure of 1-Br\textsubscript{2} (c), 2-Cl (d) and their reduction to 4,4'-b (1-Br\textsubscript{2}), 2H-(1-Br\textsubscript{2}), 4H-1, 4,4'-2 and 2H-2, respectively.

The electrocatalytic performance of Ag foils was then evaluated in the presence of molecular additives using a 10 mM solution of either 1-Br\textsubscript{2} or 2-Cl (Figure 1, Figure S2 and S3, Table S2 and S3). Similar to our previous studies with copper foils,\textsuperscript{30,31} a noticeable organic film was electrodeposited \textit{in situ} during catalysis onto the surface of the silver electrodes. Most notably, HER was completely suppressed within the range from \(-1.00 \text{ V to } -1.10 \text{ V (Figure 1a). In the presence of 1-Br\textsubscript{2}, CO\textsubscript{2} was selectively converted to CO with quantitative FE. Similar selectivities were observed when a silver electrode, previously functionalized with the organic film (by the same above-mentioned protocol), was used in bulk electrolysis experiments together with an additive-free electrolyte, confirming the role of the organic film for suppressing hydrogen production rather than solution-based pyridinium (Table S4)). In addition, the selectivity was maintained over 24 h with no detectable H\textsubscript{2}. The suppression of H\textsubscript{2} was also observed under acidic conditions at pH values as low as 4.2, in a phosphate buffer at \(-1.1 \text{ V, highlighting the robustness of these organic films (Table S5).}

This hybrid catalytic system represents the first example of a silver electrode that is completely selective (up to our detection limit) for CO\textsubscript{2}-to-CO electroconversion in pH-neutral aqueous solution.\textsuperscript{35-39} With respect to demonstrating high current densities (up to 300 mA/cm\textsuperscript{2}), silver-containing gas diffusion electrodes, derived from a Ag coordination polymer, were recently shown to produce CO at FEs >96%.\textsuperscript{40}

In the presence of molecular additive 1-Br\textsubscript{2}, the partial current density for CO \((j_{\text{CO}})\) increased by 20\% compared to bare silver (Figure 1b), indicating that the molecular film promotes the production of CO. This observation is notable, as it points to a role of the film in tuning selectivity beyond inhibition of H\textsubscript{2} evolution. Additionally, the maximum efficiency for CO is observed at a potential that is anodically shifted by 100 mV relative to that observed for bare Ag. At potentials less negative than \(-0.85 \text{ V and more reducing than } -1.30 \text{ V, H\textsubscript{2} is the predominant product, even though the partial current}
a similarly modified copper electrode. The C 1s and O 1s regions of the XPS spectrum of Ag-2 are also shifted to higher energy. We therefore suspect that the observed shift is due to a charging effect of the surface of the modified silver electrode due to its thickly insulating organic layer.

The organic films could be extracted from post-catalysis Ag electrodes using deuterated DMSO (Ag-1) and dichloromethane (Ag-2) to investigate their chemical composition by 1H NMR spectroscopy (Figure S5-S10). The 1H NMR spectrum of the extracted organic film from Ag-2 revealed the presence of only two species. As previously observed with Cu electrodes, the major species corresponds to the 4,4′-coupled dimer [Figure 1d, 4,4′-(1-Br)]2, 63%]. Interestingly, a minor constituent was unambiguously identified as tolyl-4-dihydro-pyridine (Figure 1d, 2H-2, 36%). This was further confirmed by independent synthesis of 2H-2 from the reduction of 2-Cl by Na2S2O4 in basic water and comparison with its published spectrum.

The organic film on Ag-1 proved more complex to analyze. The 1H NMR spectrum of the d6-DMSO-extracted film showed the presence of three primary species (integrated intensity ~95% of total), along with resonances associated with other trace species. Similar to Ag-2, the characteristic resonances of the previously reported 4,4′-coupled dimer [Figure 1c, 4,4′-(1-Br)]2 were observed (28% of total). Surprisingly, the corresponding 2,2′-(1-Br)2 dimeric isomer (not shown in Figure 1) was not detected, contrasting with the findings on copper electrodes. A previously unobserved set of resonances, similar to, but distinct from 4,4′-(1-Br)2, were observed. This film has been tentatively assigned as a mono-reduced 2H-(1-Br) (Figure 1c, 34%, Figure S11). The last set of resonances suggested the presence of a symmetric molecule with an aromatic:alkenyl protons ratio of 1:2. Accordingly, these resonances have been attributed to a doubly-reduced species 4H-1 (Figure 1c, 38%). Discussion of these assignments is provided in the Supporting Information. Altogether, the ratio of tertiary/quaternary amine species determined by 1H NMR spectroscopy is 3:2, in agreement with the aforementioned XPS data.

The surface of Ag-1 and Ag-2 was also analyzed ex situ by scanning electron microscopy (SEM, Figure 2, Figure S12-14) and atomic force microscopy (AFM, Figure S15) after 65 min of bulk electrolysis at −0.99 V. The SEM and AFM images of a Ag electrode in the absence of additive are relatively similar to those of Ag-1 (Figure 2a). The obtained Tafel slope in the linear region of the Tafel plot at high applied potential (157 mV/dec) is comparable to previously reported values (130–150 mV/dec), which have been assigned to a rate determining step (RDS) involving an electron transfer (ET) to CO2. In contrast, the Tafel slope obtained with Ag-1 and Ag-2 is significantly smaller (91 mV/dec and 107 mV/dec, respectively), indicating improved kinetics for the ET step to CO2. Based on the obtained values for the Tafel slope, it is difficult to unambiguously assign the RDS with Ag-1 and Ag-2. The theoretical value of the Tafel slope for the first ET or PCET as the RDS is 118 mV/dec, while the involvement of a proton transfer (PT) as the RDS results in a value of 59 mV/dec. In the non-linear region of the Tafel plot at high applied potential (Figure S16), it can be seen that the CO2RR activity decreases with increasing potential on Ag. The CO2RR reaction rate, to maintain high CO2RR selectivity.

The Organic Film Alters the Rate Determining Step. Current-voltage (Tafel) plots were probed over the potential range from −0.60 V to −1.30 V (i.e. 0.50 > η > 1.20), for bare Ag, Ag-1 and Ag-2. The Tafel analysis was performed within the linear regime as shown in Figure 3a (see also the Supporting Information). For bare Ag, the obtained Tafel slope (157 mV/dec) is comparable to previously reported values (130–150 mV/dec), which have been assigned to a rate determining step (RDS) involving an electron transfer (ET) to CO2. In contrast, the Tafel slope obtained with Ag-1 and Ag-2 is significantly smaller (91 mV/dec and 107 mV/dec, respectively), indicating improved kinetics for the ET step to CO2. Based on the obtained values for the Tafel slope, it is difficult to unambiguously assign the RDS with Ag-1 and Ag-2. The theoretical value of the Tafel slope for the first ET or PCET as the RDS is 118 mV/dec, while the involvement of a proton transfer (PT) as the RDS results in a value of 59 mV/dec. In the non-linear region of the Tafel plot at high applied potential (Figure S16), it can be seen that the CO2RR activity decreases with increasing potential on Ag. The CO2RR reaction rate, to maintain high CO2RR selectivity.
The instability of the one-electron reduced species (2-Cl)\(^{-}\), which increases its propensity for dimerization compared to (1-Br)\(^{-}\), likely contributes to the former’s efficacy in controlled film formation.

As the electrodeposition times increase, the ECSA exponentially decreases (vide infra for more discussion). We also noticed that \(j_{CO}\) and \(j_{CO}\) decrease linearly with the ECSA, showing that the intrinsic activities for CO and H\(_2\) production are constant for any electrodeposition time investigated, and are similar to bare Ag. This behavior indicates that the film does not affect the diffusion rates of proton carriers and CO\(_2\) at low overpotentials, thus keeping constant the local concentration of proton carriers and CO\(_2\) at the electrode surface, as in the case of a kinetically-controlled regime.

To shed more light on a possible involvement of a proton carrier in the RDS, the influence of the proton donor environment on the CO\(_2\)RR activity was studied.\(^{58}\) It has been previously demonstrated that the source of protons could come from HCO\(_3^-\).\(^{14,35,50,56}\) Following previous electrokinetic studies performed on mesoporous electrodes,\(^{36,41,48,50,52,56}\) we ran bulk electrolysis at \(-0.90\) \(V_{NHE}\), within the kinetic regime, while varying the concentration of HCO\(_3^-\). Acknowledging that the local concentration of HCO\(_3^-\) at the electrode interface could differ from the bulk due to the diffusion limitations through the molecular film, we have assumed that the local concentration of HCO\(_3^-\) is linearly correlated with the bulk concentration.\(^{59}\) The plot of \(\log(j_{CO})\) against \(\log[\text{HCO}_3^-]\) exhibits a slope of ca. 1.0 for Ag-1 and Ag-2, and 0 for bare Ag, indicating an approximate first order in \[\text{HCO}_3^-\] for Ag-1 and Ag-2 and a zeroth order for Ag (Figure 3b). The data available point to a rate determining step involving a proton transfer from HCO\(_3^-\) to Ag-1 or Ag-2, distinct from bare Ag.

**Site Poisoning and the Diffusion Layer Suppress HER.** To better understand the mechanism of HER suppression in the presence of the organic film, linear sweep voltammetry (LSV) measurements were recorded in an N\(_2\)-saturated 0.1 M KHCO\(_3\) electrolyte (Figure S20 and S21). Results obtained on bare Ag, Ag-1 and Ag-2 show that the onset potential for HER is shifted up to 400 mV cathodically in the presence of the organic film. Ag-1 displays the lowest HER activity, with current densities 15 times lower than Ag at \(-1.10\) V. The possibility of mass transfer limitations induced by the organic film were studied using a rotating disk electrode (RDE). On the bare Ag electrode, the HER current density increased from \(-2.2\) mA/cm\(^2\) to \(-5.6\) mA/cm\(^2\) upon increasing the rotation speed from 500 rpm to 700 rpm, implying convection mass transport limitation (Figure S22 and S23). In contrast, the HER current density remained constant for Ag-1 and Ag-2, at any rotation speed in this same range, ruling out any convection mass transfer limitation. However, the HER activities for Ag-1 and Ag-2 are 10 to 25 times lower than bare Ag, which could reflect a diffusion mass transport limitation, likely a consequence of the presence of the hydrophobic organic film.

The influence of the partial pressure of CO\(_2\) was also studied to compare bare Ag with Ag-1 and Ag-2, to determine whether a mass transport limitation due to the organic film might be operative (Figure S24 and S25). The partial pressure of CO\(_2\) (\(p_{CO2}\)) was varied between 0.2 atm and 1.0 atm, keeping a constant flow of 5 scm by using N\(_2\) as a balance gas. At \(-0.9\) \(V_{NHE}\) and \(-1.1\) \(V_{NHE}\), the plot of \(j_{CO}\) as a function of \(p_{CO2}\) gave identical traces for Ag and Ag-1, suggesting that the organic film on Ag-1 does not limit the concentration of CO\(_2\) close to the electrode surface. In contrast, the trace obtained for Ag-2 is significantly lower than for bare Ag and Ag-1, indicating that CO\(_2\) diffusion

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**Figure 3.** (a) Linear regime of the Tafel plot recorded in CO\(_2\)-saturated 0.1 M KHCO\(_3\) and (b) [HCO\(_3^-\)] dependence of the CO current density recorded at different concentrations of CO\(_2\)-saturated KHCO\(_3\) electrolyte (0.1 M, 0.33 M, 0.66 M and 1 M) at \(-0.90\) \(V_{NHE}\) for Ag (●), Ag-1 (●) and Ag-2 (●). Each data point was recorded at least two times to ensure reproducibility. Also see Figure S16 for non-linear behavior at higher applied bias.
is limited in the presence of a thicker film. These results explain the lower activity of Ag-2 for CO production in bulk electrolysis experiments compared to Ag-1. It is also worth noting that even at pCO2 as low as 0.2 atm no traces of H2 were detected with Ag-1 and Ag-2, highlighting the ability of these organics films for suppressing HER.

Related to the aforementioned experiments performed to demonstrate that CO2RR is under a kinetic regime at −0.9 V, the correlation between HER current densities and ECSA for different electrodeposition times of 2-CI were measured at −1.1 V, i.e. under the optimal conditions for CO2RR activity. The results show that the ECSA on the Ag electrode decreases exponentially with the electrodeposition time, reaching a plateau where only 40% of the area remains available (Figure S29a). Accordingly, the HER current density also decreases exponentially with the electrodeposition time (Figure S30). The correlation between the ECSA and the HER current density is shown in Figure 4 (black trace, ■, Table S10), where, in contrast to the plot shown in Figure S19, three regimes can be observed. First, the HER current density decreases linearly with the ECSA, until roughly 40% of the electrode is covered by the organic film. The current density then decreases more sharply, by ~50%, over a very small change in the ECSA. Finally, the value of the HER current density changes very slowly, even as the ECSA is further depleted to ca. 60% of the total.

The data are consistent with a scenario in which the rate of diffusion of protons through a hydrophobic film is dramatically attenuated by comparison to CO2.18 It is also possible that HER and CO2RR occur at distinct active sites56 on the silver electrode, with the hydrophobic film preferentially electrodepositing onto and inhibiting HER sites. Our available data do not unambiguously distinguish between such scenarios.

Overall, in the absence of a molecular additive, bare silver electrodes produce a mixture of primarily CO and H2 (75% CO vs 20% H2; ~5% HCOH at −0.99 V) during CO2RR. The Tafel analysis, and the zeroth and first order dependence in HCO− and CO2, respectively, are consistent with the first ET step to CO2 being the RDS, as previously observed36,38,41,48–55 Figure 5 shows a working mechanistic model for inhibition of HER on the molecularly coated Ag electrodes studied here. At potentials less negative than −1.0 V, i.e. in the kinetic regime, Tafel analysis suggests improved kinetics for CO2RR with Ag-1 and Ag-2, indicating an enhanced rate for the first ET step that activates CO2. This could be a consequence of interactions (whether direct, or from secondary sphere interactions, for example via water molecules) of the film with CO2 as it is activated and reduced on the Ag surface, analogous to previously proposed activation of CO at a Cu-film interface.31 Electrokinetic data point to the involvement of a proton transfer from HCO− within the RDS (Figure 5b). At potentials between −1.0 V to −1.2 V, the hydrophobic layer formed from the electrodeposition of the additive limits the diffusion of proton carriers to the electrode surface, but not CO2. Significantly, the production of H2 is completely suppressed, with CO being selectively generated during CO2RR. At potentials more reducing than −1.2 V, the diffusion of CO2 becomes limited, creating a depletion of the *CO2− intermediates (Figure 5c). Consequently, the production of H2 becomes more favorable. This working hypothesis warrants testing via future operando spectroscopic measurements that will aid in further characterization of the organic-silver interface.

CONCLUSIONS

We have reported on a simple and efficient method to fully suppress HER and thereby facilitate CO2RR on Ag electrodes using organic films. The films are conveniently generated at the surface of the silver electrode during bulk electrolysis by in situ reduction of pyridinium-based organic additives. Electrokinetic studies demonstrate the impact of the film on the mechanism of CO2 reduction: a proton transfer from HCO− is involved in the RDS, which is in contrast to the more typically observed electron transfer as RDS on bare Ag surfaces. Moreover, slow diffusion of proton carriers through the hydrophobic layer is responsible for a dramatic decrease in HER. Consequently, CO2 can be selectively reduced to CO, in an aqueous electrolyte, with FEs >99%. Structural changes in the additive used result in different film morphologies with distinct consequences on electrocatalysis. For example, the thick film derived from 2-CI efficiently suppresses HER but also significantly reduces CO2RR. This detrimental lowering in partial current density for CO2RR from 2-CI is eliminated when the partially covered electrode derived from 1-Br2 is used instead. The differences observed between 2-CI and 1-Br2 highlight the potential for rationally tuning electrocatalysis by functionalizing the electrode with tailored organic additives.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website.

Experimental details for bulk electrolysis experiments, surface characterization, and additional electrokinetic data (PDF)

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The authors declare no competing financial interest.

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In the presence of the molecular film, even though the interfacial concentration of HCO₃⁻ might differ from the bulk, due to the diffusion limitations through the molecular film, it is still safe to assume that the interfacial HCO₃⁻ replenished faster than it is consumed since the electrocatalytic experiments were performed in a kinetic-controlled scenario (see reference 50). To determine the order in [HCO₃⁻], we assumed that the interfacial concentration of HCO₃⁻ varies to the same extent as its bulk concentration when this is changed from 0.1 M to 1.0 M. Therefore, we used the value of the bulk concentration of [HCO₃⁻] in the corresponding kinetic plots.

TOC graphic.