Weakly Coordinating Organic Cations are Intrinsically Capable of Supporting CO₂ Reduction Catalysis

Sophia Weng, Wei Lun Toh, Yogesh Surendranath*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

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ABSTRACT: The rates and selectivity of electrochemical CO₂ reduction are known to be strongly influenced by the identity of alkali cations in the medium. However, experimentally, it remains unclear whether cation effects arise predominantly from coordinative stabilization of surface intermediates or from changes in the mean-field electrostatic environment at the interface. Herein, we show that Au- and Ag-catalyzed CO₂ reduction can occur in the presence of weakly coordinating (poly)tetraalkylammonium cations. Through competition experiments in which the catalytic activity of Au was monitored as a function of the ratio of the organic to metal cation, we identify regimes in which the organic cation exclusively controls CO₂ reduction selectivity and activity. We observe substantial CO production in this regime, suggesting that CO₂ reduction catalysis can occur in the absence of Lewis acidic cations and thus, coordinative interactions between the electrolyte cations and surface-bound intermediates are not required for CO₂ activation. For both Au and Ag, we find that tetraalkylammonium cations support catalytic activity for CO₂ reduction on par with alkali metal cations, but with distinct cation activity trends between Au and Ag. These findings support a revision in electrolyte design rules to include water-soluble organic cation salts as potential supporting electrolytes for CO₂ electrolysis.

INTRODUCTION

Electrochemical CO₂ reduction presents an attractive route for leveraging renewable electricity to drive the production of valuable fuels and commodity chemicals.1 The local electrolyte and pH environment has been found to play a critical role in dictating the rate of the CO₂ reduction reaction (CO₂RR) and in suppressing the parasitic hydrogen evolution reaction (HER).2,3 Prior work has established that aqueous CO₂RR rates and selectivity are strongly influenced by the identity of the supporting electrolyte cation, with catalytic activity increasing along the following trend: Li⁺ < Na⁺ < K⁺ < Cs⁺,4-7 Indeed, for CO₂RR studies on many different catalyst materials including Au, Ag, and Cu, it has been observed that the identity of the supporting electrolyte cation—a nominal spectator in the overall CO₂RR—can have significant effects on CO₂RR activity, with the rates varying by three-fold or greater across the series.8,9

Despite the widespread observation of cation effects on the CO₂RR, the mechanistic basis for these trends remains the subject of intense debate.9-20 Leading explanations put forward bifurcate into two broad categories: (a) cations induce changes to the mean-field electrostatic potential profile at the interface;15-18 and (b) cations are involved in coordinative chemical interactions with adsorbed reaction intermediates.11,12,19-21 The former electrostatic model postulates a sharper electrostatic potential drop in the presence of weakly hydrated cations such as Cs⁺ relative to strongly hydrated ions such as Li⁺.15 The sharper potential drop is thought to preferentially stabilize polar adsorbed CO₂⁺ relative to non-polar adsorbed H⁺ (Figure 1a, top).16 In contrast, the coordination model invokes that electrolyte cations act as Lewis acids that bind to the oxygen atoms of adsorbed CO₂⁺, thereby promoting CO₂ activation (Figure 1a, bottom).19,21 Since this coordination mode requires partial desolvation of the ion, weakly hydrated cations such as Cs⁺ are thought to interact more strongly with CO₂⁺, resulting in a larger stabilizing effect. Critically, since all alkali metal cations can, in principle, participate in both electrostatic and coordinative modes of promotion (Figure 1a), trends across them are unable to distinguish the relative influence of each. Because each mode of promotion would motivate distinct approaches to electrolyte design, addressing this knowledge gap is critical for systematic improvements to CO₂RR efficiency and selectivity.

Experimentally, CO₂ reduction has been extensively investigated in the presence of organic cations of various types, including surfactants22,23, ionomer films24-28, and cationic conjugate bases of superacids31. However, in all these studies, the organic cation is present as a minority constituent of the medium alongside either a super-stoichiometric excess of alkali metal cations for studies in neutral pH electrolytes (Figure 1b, top) or in the presence of super-stoichiometric excess of hydronium ions for studies in bulk acidic electrolyte32. Because these additives are only a minority constituent in the overall electrolyte, even if they are concentrated at the surface, it is challenging to definitively attribute CO₂ activation to these organic species versus alkali metal cations in the medium that may also be present at the surface (Figure 1b, bottom). Indeed, these systems often still display a strong sensitivity to the identity of the bulk alkali...
metal cation\textsuperscript{24}, suggesting that alkali metal cations are still significantly influencing catalysis, despite the presence of the organic additive. Further complications are introduced when bulk acidic electrolyte is used, as the interface is invariably subject to a large pH gradient during catalysis,\textsuperscript{33} obscuring the intrinsic mechanistic role of the organic cation in CO\textsubscript{2}RR selectivity and/or efficiency. Consequently, these studies do not directly address whether organic cations on their own can foster CO\textsubscript{2} reduction catalysis. In principle, the foregoing modes of promotion can be better parsed by comparing CO\textsubscript{2}RR efficiency and selectivity between alkali metal cations and far more weakly-coordinating\textsuperscript{24} organic (e.g., tetraalkylammonium) cations. If weakly-coordinating cations can foster CO\textsubscript{2} reduction in an environment where the influence of alkali metal cations is excluded, this observation would lend credence to the electrostatic promotion mechanism over the coordination mechanism.

**RESULTS AND DISCUSSION**

**Methodology for minimizing adventitious alkali metal accumulation.**

Trace alkali metal cations are common in electrochemical cells and can originate from a variety of sources. To minimize the possibility of adventitious accumulation of alkali metal cations at the working electrode interface over the course of an electrolysis experiment, we took several precautions. First, as metal-on-carbon catalysts often contain cation-exchange ionomer binders that can carry trace alkali ions as counter charges for their ionomer head groups, we opted to use gas diffusion electrodes prepared by the sputter deposition of Au and Ag on porous PTFE as our working electrodes (see SI Methods for details of electrode preparation and Figures S2-S8 for characterization). This procedure generates metal-decorated gas diffusion electrodes free from ionomer binders and corresponding adventitious alkali ions. Second, to minimize adventitious ion

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**Figure 1.** a. Depiction of the two modes of CO\textsubscript{2} activation by electrolyte cations proposed in the literature: electrostatic field-dipole stabilization of CO\textsubscript{2}\textsuperscript{*} (top) and direct coordination of CO\textsubscript{2}\textsuperscript{*} (bottom). b. Representation of the distribution of cations in an electrolyte containing majority alkali metal cations and minority organic additives. The concentration profile is depicted as a plot of cation mole fraction (χ) as a function of distance from the electrode surface (top). Molecular structures of some previously investigated organic additives are shown on the right.\textsuperscript{22,24,26,31} In such systems, the interfacial composition may differ from the bulk and is largely unknown (bottom). c. Organic cations are employed herein in vast excess relative to trace alkali metal cations (top). Tuning the bulk cation composition enables us to identify conditions that give rise to a weakly coordinating local environment in which Lewis acid-base interactions between CO\textsubscript{2}\textsuperscript{*} and electrolyte cations are inhibited (bottom). Molecular structures of the organic cations used in this study are shown on the right.
CO$_2$ reduction is observed even when organic cations are in vast excess of alkalai metal cations.

We began our investigations by establishing a baseline for CO$_2$RR catalytic activity with alkalai metal cations in our custom electrochemical cell. To this end, we compared the product selectivity of Au- and Ag-catalyzed CO$_2$ reduction in bulk CO$_2$-saturated, 0.1 M NaHCO$_3$ electrolyte (pH 6.8). Gold and silver were specifically chosen because they both display cation-dependent CO$_2$ to CO reduction activity and generate a simple product distribution consisting predominantly of CO and H$_2$. We studied the catalytic activity of both materials by coupling steady state chronopotentiometry with an in-line gas chromatograph (GC) to quantify the evolved product gases (representative raw chronopotentiograms and GC traces are shown in the SI, Figures S11-S12). For AuPTFE, at ~0.80 V (all potentials are reported relative to the reversible hydrogen electrode at pH 6.8; see SI Methods for further details), we observe a CO partial geometric current density ($i_{PCO}$) of 2.7 mA cm$^{-2}$ (Figure 2a, left plot, yellow points) corresponding to 95% faradaic efficiency (FE) (Figure 2a, right plot, yellow points), with a H$_2$ partial geometric current density ($i_{PH2}$) of 0.2 mA cm$^{-2}$ accounting for the balance current density and FE. At a more negative potential of ~1.16 V, CO$_2$RR and HER current densities rise to 6.7 mA cm$^{-2}$ and 0.9 mA cm$^{-2}$, respectively, with a monotonic increase between these potentials. Over the entire potential range canvassed, the FE for CO$_2$RR remained roughly unchanged between 90 and 95 percent (Figure 2, right), with the remainder of the faradaic balance accounted for by H$_2$: AgPTFE also displays high selectivity for CO production in 0.1 M NaHCO$_3$ electrolyte. At ~0.82 V, AgPTFE displays a $i_{PCO}$ of 0.5 mA cm$^{-2}$ (Figure 2b, left, yellow points) and a $i_{PH2}$ of 0.06 mA cm$^{-2}$ (Figure 2b, left plot, blue points), giving a CO:H$_2$ FE ratio of 91:9. The CO partial current density increases to 4.7 mA cm$^{-2}$ at a more negative applied potential of ~1.20 V with a corresponding increase in $i_{PH2}$ of 0.2 mA cm$^{-2}$. Across this potential range, the FE for CO$_2$RR remains roughly constant between 91.96% (Figure 2b, right). The high observed selectivity for CO on AuPTFE and AgPTFE in our hands is in line with literature reports of CO$_2$RR on both metals.$^{35,36}$

![Figure 2](image_url)

Figure 2. a. Partial geometric current densities (left), and faradaic efficiencies (right) for AuPTFE-catalyzed CO$_2$RR and HER in 0.1 M NaHCO$_3$ for a range of potentials. b. Partial geometric current densities (left), and faradaic efficiencies (right) for AgPTFE-catalyzed CO$_2$RR and HER in 0.1 M NaHCO$_3$. All values are the mean of three or more measurements, and error bars represent the standard error of three or more separate electrode and cell setups. Error bars that are not visible are smaller than the data point marker.

Having established the baseline activity of AuPTFE and AgPTFE in NaHCO$_3$ electrolyte we next investigated CO$_2$RR activity and selectivity in the presence of a tetraalkylammonium bicarbonate electrolyte. As a starting point for these studies, tetraethylammonium (TEA$^+$) was chosen because its ethyl groups inhibit direct Lewis acid-base coordination and it is commercially available as an electrochemical-grade aqueous solution. TEAHCOC$_3$ electrolyte was prepared by acidifying a stock solution of electrochemical-grade tetraethylammonium hydroxide (TEAOH) with CO$_2$ until the pH of the solution became neutral (see SI Methods for further details). For a AuPTFE electrode polarized to ~0.75 V in 0.1 M TEAHCOC$_3$ (pH 6.9) we observe a $i_{PCO}$ of 1.6 mA cm$^{-2}$ and $i_{PH2}$ of 0.6 mA cm$^{-2}$ (Figure 3a, left). This corresponds to a 40% decrease in $i_{PCO}$ and a four-fold increase in $i_{PH2}$ relative to the performance of AuPTFE in 0.1 M NaHCO$_3$ at the same applied potential. Upon polarization to more negative potentials, both CO and H$_2$ partial currents increase monotonically, up to a $i_{PCO}$ of 4.9 mA cm$^{-2}$ and $i_{PH2}$ of 1.8 mA cm$^{-2}$ at ~1.12 V, corresponding to a 27% decrease in $i_{PCO}$ and a two-fold increase in $i_{PH2}$ compared to NaHCO$_3$. Across the range of potentials probed, the CO:H$_2$ FE ratio remained roughly constant at 70:30 (Figure 3a, right) in favor of CO.

To see if this change in activity between NaHCO$_3$ and TEAHCOC$_3$ electrolytes is conserved for different catalyst materials, we next investigated the CO$_2$ reduction ability of...
AgPTFE in 0.1 M TEAHCO$_3$ electrolyte. At $-0.80$ V, the performance of AgPTFE in 0.1 M TEAHCO$_3$ matches that of its performance in 0.1 M NaHCO$_3$, with a $j_{CO}$ of 0.5 mA cm$^{-2}$ and $j_{H_2}$ of 0.08 mA cm$^{-2}$ (Figure 2b, left). However, at more negative potentials, $j_{CO}$ in TEAHCO$_3$ only reaches 3.0 mA cm$^{-2}$ at $-1.20$ V, corresponding to a 36% decrease relative to NaHCO$_3$. $j_{H_2}$ at more negative potentials is comparable for both NaHCO$_3$ and TEAHCO$_3$ electrolytes, reaching 0.2 mA cm$^{-2}$ at $-1.20$ V. Across this potential range, the FE for CO fluctuated between 95 and 89 percent with the balance accounted for by H$_2$ (Figure 2b, right). Although the rates of Au- and Ag-catalyzed CO$_3$RR in TEAHCO$_3$ electrolyte are diminished relative to NaHCO$_3$ electrolyte, we were intrigued by the observation of substantial CO production in this non-conventional electrolyte.

As highlighted above, trace alkali metal cations are common in aqueous electrochemical cells. To determine whether our results were affected by adventitious alkali metal contaminants, we quantified the levels of alkali metal cations in our TEAHCO$_3$ electrolyte before and after electrolysis by ICP-MS (Tables S3-S4). We found that Na$^+$ was the most abundant alkali metal cation contaminant in our 100 mM TEA$^+$ electrolyte, present at 7 ± 4 μM. Consequently, in a typical experiment in 100 mM TEA$^+$, the weakly-coordinating organic cations exceed alkali metal cations by four orders of magnitude. Despite the large excess of TEA$^+$ relative to Na$^+$, we acknowledge that the trace population of alkali cation could play an outsized role in dictating the catalytic activity of the interface. To probe the extent to which trace alkali cations are contributing to the observed CO$_3$RR activity, we prepared a series of binary electrolyte mixtures ranging from the native TEAHCO$_3$ electrolyte with a Na$^+$ mole fraction ($\chi_{Na^+}$) of $10^{-4}$ to a pure NaHCO$_3$ electrolyte ($\chi_{Na^+}$ of 1), keeping the total ionic strength constant at 100 mM. Using AuPTFE as the working electrode, we quantified catalytic activity across this electrolyte series at a constant applied potential of $-0.95$ V. Varying $\chi_{Na^+}$ from $10^{-4}$ to $10^{-3}$ leads to a 5% increase in faradaic efficiency in favor of CO$_3$RR, with another 5% increase in CO$_3$RR occurring as $\chi_{Na^+}$ increases to $10^{-2}$ and the corresponding decrease in HER faradaic efficiency that preserves the total faradaic balance close to 100% (Figure 4). The largest change in selectivity as a function of electrolyte condition occurs between $\chi_{Na^+}$ of $10^{-2}$ and 0.1, in which CO$_3$RR faradaic efficiency increases from 75% to 90%. Continuing to increase $\chi_{Na^+}$ up to 0.2 completes the smooth transition in selectivity towards the selectivity in bulk NaHCO$_3$. Although the activity trend appears to asymptote at low $\chi_{Na^+}$, the data suggest that for $\chi_{Na^+}$ between $10^{-4}$ and 0.1, (Figure 4, purple region), the catalytic activity is influenced by the presence of both Na$^+$ and TEA$^+$ at the interface. Furthermore, this observation emphasizes that in order to study the intrinsic effects of organic cations on the CO$_3$RR, the introduction of alkali cation-containing electrolytes should be avoided, as the presence of as little as 1 mM Na$^+$ may convolute measurements of catalytic activity.

As $\chi_{Na^+}$ is increased beyond 0.2, both CO$_3$RR selectivity and rate remain unchanged and matches the values observed for pure 0.1 M NaHCO$_3$ electrolyte (Figure 2a), suggesting that the interface becomes saturated in Na$^+$ once $\chi_{Na^+}$ reaches 0.2 (Figure 4, pink region). The implications of this result are two-fold. First, this observation suggests that the surface affinity of Na$^+$ is much higher than TEA$^+$, causing it to outcompete TEA$^+$ at the interface even when TEA$^+$ is in vast excess. Additionally, this observation suggests that, despite the presence of less than $10^{-4}$ mole fraction of Na$^+$ in the as-prepared 100 mM TEAHCO$_3$, the catalytic activity deviates substantially from that in pure Na$^+$, indicating that the data above in Figure 2 is at least partially reflective of CO$_3$RR activity facilitated by interfacial TEA$^+$. However, in this electrolyte, we do not observe a clear plateau in activity across a range of $\chi_{Na^+}$ conditions, preventing us from unequivocally excluding some influence from trace Na$^+$ accumulated at the interface.
Figure 4. Changes in CO and $H_2$ faradaic efficiency for AuPTFE at $-0.95$ V as Na+ mole fraction ($x_{Na^+}$) is varied from ca. $10^{-4}$ to 1. In a binary supporting electrolyte of TEAHO and NaHCO$_3$ keeping the total ionic strength constant at 0.1 M. The region highlighted in blue is the region in which catalytic activity matches that of AuPTFE in 0.1 M TEAHO. The region highlighted in pink is the transition region, in which both Na+ and TEA+ affect interfacial reactivity. The region highlighted in purple is the region in which catalytic activity matches that of AuPTFE in 0.1 M NaHCO$_3$. All values are the mean of three measurements. Error bars represent the standard error of three or more measurements with separate cell setups. Error bars that are not visible are smaller than the data point marker. For plots of partial geometric current densities as a function of electrolyte cation composition, see Figure S27.

To address the foregoing ambiguity, we examined a tetraalkylammonium polyelectrolyte. Since polyelectrolytes can be purified using size exclusion methods, we hypothesized that these electrolytes could be purified of Na+ contaminants more rigorously than electrolytes based on small-molecule organic cations such as TEA+. Additionally, polyelectrolytes may have vastly differential surface affinity relative to a small ion such as Na+, providing a greater tolerance for the latter. Poly(dimethyl diallyl) ammonium (pDDA+, $M_w = 400,000$-$500,000$ Da), a commercially available water-soluble polymer, was chosen as a model polyelectrolyte cation. As obtained, this polymer has tetraalkylammonium repeat units bearing chloride counter-ions. To generate an equivalent comparison with traditional carbonate electrolytes, we dialyzed the chloride form of pDDA+ with (NH$_4$)$_2$CO$_3$, affording the corresponding polyelectrolyte carbonate buffer. Residual (NH$_4$)$_2$CO$_3$ was removed by exhaustive dialysis against MilliQ water (full details of the dialysis, purification, and characterization of pDDAHCO$_3$ are included in the SI Methods section and Figures S9-S10). ICP-MS quantification of our polyelectrolyte immediately after dialysis shows only low micromolar quantities of alkali metal contaminants ($\pm 2$ for a 500 mM stock solution of pDDAHCO$_3$, significantly lower than that of commercial TEAOH (Table S3). Thus, in a typical experiment with 0.1 M pDDA+, the pDDA$^+$ concentration exceeds that of trace alkali metal cations by at least five orders of magnitude.

To investigate whether this electrolyte could support the CO$_2$RR at comparable rates to previously investigated electrolytes, we polarized AuPTFE working electrodes in 0.1 M pDDAHO (pH 6.8) and quantified the evolved products by gas chromatography. In pDDAHO electrolyte, AuPTFE produced a mixture of CO and $H_2$. At $-0.74$ V in pDDAHO, we measured a $j_{far}$ of 2.6 mA cm$^{-2}$, a rate comparable to that of $j_{far}$ in NaHCO$_3$ of 2.7 mA cm$^{-2}$. The rate of AuPTFE-catalyzed CO production increases at more negative potentials—albeit at a slower rate relative to other electrolytes, reaching 4.2 mA cm$^{-2}$ at $-1.07$ V (Figure 5a, yellow points). In the most extreme case, this corresponds to a 37% decrease in $j_{far}$ relative to that in NaHCO$_3$ (Figure 2a). Most strikingly, in pDDAHO electrolyte, Au-catalyzed HER is enhanced significantly relative to NaHCO$_3$ (Figure 5a, blue points). At $-0.74$ V, $j_{HER}$ is 0.9 mA cm$^{-2}$, corresponding to a nearly five-fold increase relative to $j_{HER}$ in NaHCO$_3$. The rate of HER increased faster than that of CO$_2$RR across this potential range, eventually outcompeting the rate of CO$_2$RR at a point between $-0.91$ and $-0.99$ V. Consequently, the FE for $H_2$ production increased over this potential range, beginning at 25% at $-0.75$ V and reaching 64% at $-1.07$ V (Figure 5b). Similar to our observations in TEAHO$_3$ electrolyte, use of pDAAHCO$_3$ electrolyte leads to an attenuation in CO production rate and faradaic efficiency relative to NaHCO$_3$ but nevertheless, this organic polycation is still able to support substantial CO$_2$RR activity.

We next examined CO$_2$RR on AgPTFE in pDAAHCO$_3$ electrolyte. Across the entire range of potentials tested the CO faradaic efficiency was between 98 to 100% (Figure 5d, yellow points). These faradaic efficiency values are comparable to what we measured for AgPTFE in NaHCO$_3$ electrolyte (Figure 2c). To our surprise, we observed a $j_{per}$ of 2.1 mA cm$^{-2}$ in pDAAHCO$_3$ electrolyte at $-0.76$ V, corresponding to a 4.3-fold increase relative to NaHCO$_3$. CO partial current density increased monotonically from $-0.76$ to $-1.10$ V, reaching 8.9 mA cm$^{-2}$ at $-1.10$ V (Figure 5b, yellow points), corresponding to a nearly two-fold increase in $j_{per}$ relative to NaHCO$_3$. Across this entire range, $H_2$ production was low, beginning at 0.03 mA cm$^{-2}$ at $-0.76$ V and reaching a maximum of only 0.1 mA cm$^{-2}$ at $-1.10$ V. The enhancement of CO production rate and retention of high CO selectivity for AgPTFE (Figure 5b) is at odds with the slight attenuation in rate and CO selectivity for AuPTFE (Figure 5a). While the precise origin of this divergent selectivity trend remains unclear, the high activity and selectivity for CO$_2$RR on AgPTFE in pDAAHCO$_3$ suggests that organic cations are viable electrolytes for CO$_2$-to-fuels conversion.

Figure 5. a. Partial geometric current densities (left), and faradaic efficiencies (right) for AuPTFE-catalyzed CO$_2$RR and HER in 0.1 M pDAAHCO$_3$ for a range of potentials. b. Partial geometric current densities (left), and faradaic efficiencies (right) for AgPTFE-catalyzed CO$_2$RR and HER in 0.1 M pDAAHCO$_3$. All values are the mean of three or more measurements, and error bars represent the standard error of three or more separate electrode and cell setups. Error bars that are not visible are smaller than the data point marker.
As highlighted above, pDDAHCO₃ was chosen as an example electrolyte because it could be purified by dialysis to low micromolar levels of alkali metal impurities; however, even with all precautions taken to remove alkali metal contaminants, we still observed ca. 1 μM adventitious Na⁺ in our working compartment electrolyte by post-mortem ICP-MS analysis (Table S4). To determine whether this trace alkali metal cation population is contributing to the observed CO₂RR activity, we repeated the same competition experiment above (Figure 4) with AuPTFE and varying ratios of pDDA⁺ and Na⁺. At −0.95 V, we observe that between a Na⁺ mole fraction, χ_Na⁺, of 10⁻⁵ and 0.5, the catalytic activity of Au in 0.1 M pDDAHCO₃ was largely unchanged, with CO accounting for between 56 and 61% of the overall FE (Figure 6, blue region). This observation is in stark contrast with our observation of a systematic increase in CO selectivity over the same mole fraction range in Na⁺/TEA⁺ binary electrolytes (Figure 4). We ascribe the constancy in CO/H₂ selectivity over the nominal range from 100% pDDA⁺ (χ_Na⁺ = 10⁻⁵) to 50% pDDA⁺ (χ_Na⁺ = 0.5) to an interfacial reaction environment that is fully saturated with pDDA⁺ ions such that the electrocatalytic selectivity is dictated predominantly by pDDA⁺ with negligible contribution from Na⁺ (Figure 6, blue region). For the χ_Na⁺ range between 0.5 and 0.8, we observed a 3% increase in CO selectivity suggesting that Na⁺ may be playing a minor contributing role over this range. However, we observe the largest changes in catalytic activity for electrolytes with χ_Na⁺ above 0.8. Indeed, between χ_Na⁺ of 0.9 and 0.99, we observed a 17% increase in CO faradaic efficiency, at the expense of H₂ production (Figure 6, purple region, highlighted in the top left inset). In this Na⁺ rich region, the smooth transition between the intrinsic selectivity of AuPTFE implies that catalytic activity is influenced by a combination of Na⁺ and pDDA⁺ at the interface. Critically, this analysis reveals that all previous experiments conducted in 0.1 M pDDAHCO₃ electrolyte (Figure 5) fall within the regime in which pDDA⁺ dominates catalytic activity (Figure 6, blue region). Thus, these competition experiments bolster the notion that the data in Figure 5 samples the intrinsic ability of pDDA⁺ cations to foster CO₂ reduction catalysis.

The observation that catalysis in pDDAHCO₃ electrolyte is remarkably insensitive to Na⁺ addition up to a χ_Na⁺ of 0.8 suggests that pDDA⁺ preferentially migrates and/or adsorbs to the interface under reductive polarization. A polymeric electrolyte such as pDDA⁺ may also reversibly form a thin film on the electrode surface, effectively rejecting Na⁺ ion transport to the surface. The formation of organic films—both in situ and ex situ—have been well-documented in the CO₂RR literature; however, we emphasize that all of these studies involved additives that are only sparingly soluble or completely insoluble in water. In contrast, the use of a fully water-soluble (poly)cationic in this study permitted studies across a wide range of bulk concentration ratios. While we uncover a clear ratio-independent regime for the pDDA⁺/Na⁺ binary system, a similar regime may not exist for all cations, emphasizing the importance of cation competition experiments for probing the interfacial cation micro-environment persistent under CO₂RR conditions.

Figure 6. a, Changes in CO and H₂ faradaic efficiency for AuPTFE at −0.95 V as Na⁺ mole fraction (χ_Na⁺) is varied from ca. 10⁻⁵ to 1 in a binary supporting electrolyte of pDDAHCO₃ and NaHCO₃, keeping the total ionic strength constant at 0.1 M. The region highlighted in blue is the region in which catalytic activity matches that of AuPTFE in 0.1 M pDDAHCO₃. The region highlighted in purple is the transition region, in which both Na⁺ and pDDA⁺ affect interfacial reactivity. The region highlighted in pink is the region in which catalytic activity matches that of AuPTFE in 0.1 M NaHCO₃. Inset: zoom in of the transition region in which a smooth change in catalytic activity is observed. All values are the mean of three measurements. Error bars represent the standard error of three or more measurements with separate cell setups. Error bars that are not visible are smaller than the data point marker. For plots of partial current densities as a function of electrolyte cation composition, see Figure S28.

Catalytic trends between organic and alkali cations suggest that coordination plays a minor role in CO₂ activation.

Using the above methodology, we compared the aqueous CO₂ reduction performance of AuPTFE in 0.1 M bicarbonate electrolytes containing TEA⁺ and pDDA⁺ with the performance of the same material in electrolytes containing the typically studied alkali metal cations: Li⁺, Na⁺, K⁺, and Cs⁺. At −0.97 V (see SI for full data sets for each of these electrolytes over a range of potentials and a plot of these data sets overlaid with each other, Figures S15-S20; Figure S29a), AuPTFE displays a roughly two-fold increase in j_CO across the alkali metal cation series spanning 4.9 and 4.5 mA cm⁻² in LiHCO₃ and NaHCO₃ to 10.2 mA cm⁻² in CsHCO₃ (Figure 7a, yellow bars), with a concomitant decrease in j_H₂ across the same series (Figure 7a, blue bars). These changes as a function of electrolyte cation identity are reflected in the faradaic efficiencies for CO and H₂ with the CO faradaic efficiency being the lowest in LiHCO₃ at 82% and the highest in CsHCO₃ at 97% (Figure 7a, inset). This trend in rate and selectivity for the CO₂RR is consistent with literature reports. At the same potential in TEA⁺ electrolyte, we observed a j_CO of 3 mA cm⁻² (Figure 7a), corresponding to a 40% decrease in j_CO compared to Li⁺; the alkali metal cation with the lowest j_CO of the series. In pDDA⁺ electrolyte, we observed a j_CO of 3.6 mA cm⁻² (Figure 7a), comparable to
that in TEA\textsuperscript{+}. In both TEA\textsuperscript{+} and pDDA\textsuperscript{+} electrolytes, the rate and selectivity for HER was increased relative to the alkali metal bicarbonate electrolytes (Figure 7a, inset). While a full examination of these trends is beyond the scope of this study, we note that the $j_{\text{CO}}$ for both organic cations is roughly in line with what would be expected based on their hydrated ion radius, a descriptor that has been used to rationalize trends across alkali metal cations. Irrespective of the specific reasons, we stress that the difference in $j_{\text{CO}}$ across this series of organic and alkali metal cations fall well within the range reported previously for alkali cation series alone, emphasizing that tetraalkylammonium cations are competent for supporting CO$_2$RR catalysis despite their weakly coordinating nature.

The above trends for AuPTFE are not held for AgPTFE. For Ag, at $-0.94$ V (see SI for full data sets for each of these electrolytes over a range of potentials and a plot of these data sets overlaid with each other, Figures S21-S26; Figure S29b), we observe a nearly six-fold increase in $j_{\text{CO}}$ across the alkali metal cation series from 1.0 mA cm$^{-2}$ in LiHCO$_3$ to 5.7 mA cm$^{-2}$ in CsHCO$_3$ (Figure 7b, yellow bars), corresponding to faradaic efficiencies of 82 and 101%, respectively (Figure 7b, inset). Although consistently low across the entire series, $j_{\text{CO}}$ decreased from 0.2 mA cm$^{-2}$ in LiHCO$_3$ to 0.08 mA cm$^{-2}$ in CsHCO$_3$ across this series (Figure 7b, yellow bars), corresponding to faradaic efficiencies of 16 and 1%, respectively (Figure 7b, inset). These trends are in line with the trends observed on AuPTFE: that is, $j_{\text{CO}}$ increases going down the periodic table. However, unlike for AuPTFE, the performance of AgPTFE in electrolytes with organic cations is contrary to expectations based on hydrated ion size. For AgPTFE, we found a $j_{\text{CO}}$ of 1.6 mA cm$^{-2}$, corresponding to a three-fold increase in CO partial current density relative to Li\textsuperscript{+} electrolyte. Even more striking is the observation that AgPTFE-catalyzed CO$_2$ reduction in pDDAHCO$_3$ proceeded with a $j_{\text{CO}}$ of 5.1 mA cm$^{-2}$ (Figure 7b), comparable to the most promoting alkali ion, Cs\textsuperscript{+}. Whereas activity/selectivity trends across alkali cations are generally conserved across metal surfaces, the foregoing observations suggest that this is not the case for organic cations, opening the door to designer pairings of cations and electrocatalysts for selective CO$_2$RR.

**Figure 7.** a, Steady-state partial geometric current densities and faradaic efficiencies (inset) for AuPTFE-catalyzed CO$_2$RR and HER at $-0.97$ V in bicarbonate electrolytes with varying cations. b, Steady-state partial geometric current densities and faradaic efficiencies (inset) for AgPTFE-catalyzed CO$_2$RR and HER at $-0.94$ V in bicarbonate electrolytes with varying cations. All values are the mean of three or more measurements in separate cells. Error bars represent the standard error of three or more measurements with separate cell setups. Error bars that are not visible are smaller than the data point marker.

**CONCLUSION**

Understanding the origins of cation effects is critical for developing electrolyte design principles for next-generation CO$_2$ reduction technologies. To this end, we developed a methodology for determining the intrinsic ability of organic cations to foster CO$_2$ reduction. Specifically, catalytic trends across a series of binary mixtures of organic and alkali ion electrolytes exposed regimes in which catalysis was dictated by the organic cation identity, alkali metal cation identity, or a mixture of the two (Figure 4, Figure 6). Working in the regime in which catalysis is controlled by an organic polyelectrolyte cation, pDDA\textsuperscript{+}, we find that weakly-coordinating organic cations are intrinsically capable of fostering Au\textsuperscript{+} and Ag-catalyzed CO$_2$ reduction to CO.

For Au-catalyzed CO$_2$RR, TEA\textsuperscript{+} and pDDA\textsuperscript{+} electrolytes give to CO$_2$ reduction activities that are comparable to Li\textsuperscript{+} and Na\textsuperscript{+} electrolytes, but with diminished selectivity due to enhanced H$_2$ evolution rates (Figure 7a). In contrast, for Ag-catalyzed CO$_2$RR, CO$_2$ reduction activities are comparable to Cs\textsuperscript{+} electrolytes with retention of high selectivity (Figure 7b). Importantly, across all data collected, rates of CO$_2$ reduction in alkali metal bicarbonate and tetraalkylammonium bicarbonate electrolytes are within one order of magnitude, suggesting that specific coordination to reaction intermediates plays a minor role in facilitating CO$_2$ reduction to CO. In aggregate, these findings support a revision of electrolyte design principles. Unlike metal cations, organic cations are synthetically tunable, substantially expanding the structure space available for electrolyte design. The methodology set forward here allows for detailed mechanistic investigations of electrolyte cation structure-function correlations in CO$_2$RR catalysis in this largely unexplored design space.
ASSOCIATED CONTENT

Supporting Information

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

AUTHOR INFORMATION

Corresponding Author

* Yogesh Surendranath – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0003-1016-3420; Email: yogi@mit.edu

Authors

Sophia Weng – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-9055-1732

Weilun Toh – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0001-9001-0488

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REFERENCES


Prior Work
Electrostatic Effects
Coordinative Effects
Li⁺, Na⁺, K⁺, Cs⁺

This Work
Electrostatic Effects
Coordinative Effects
Coordination-Inhibited Cations...

...can also enable CO₂ reduction