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Effect of Cations on the Electrochemical Conversion of CO₂ to CO

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We investigate the influence of electrolyte composition on the electrochemical reduction of CO₂ to CO in an electrochemical flow reactor. Specifically, we study the effect of alkali cations on the partial current densities of the two products: CO and H₂. We report that the presence of large cations such as cesium and rubidium in the electrolyte improves the partial current density for CO production. Furthermore, large cations suppress H₂ evolution, resulting in high faradaic yields for CO production. For example, with a large cation, specifically CsOH, a partial current density of 72 mA/cm² was obtained at a cathode potential of -1.62 V vs Ag/AgCl. In contrast, in the presence of a small cation, specifically sodium, a partial current density of only 49 mA/cm² was achieved at a much more negative cathode potential of -2.37 V vs Ag/AgCl, with NaBr. The effect of cation size on product selectivity for CO production can be explained by the interplay between the level of cation hydration and the extent of cation adsorption on Ag electrodes.

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Carbon dioxide (CO₂) concentrations in the atmosphere have been linked to climate change.¹ A reduction in CO₂ emissions and/or an increase in CO₂ capture may be needed to stabilize CO₂ concentrations in the atmosphere, and consequently, minimize the negative effects of CO₂ as a greenhouse gas.^{2–6} Additionally, to reduce global dependence on fossil fuels, approaches to enhance penetration of alternative energy sources need to be developed. Furthermore, uneven global distribution of oil reserves present potential energy security issues for oil importing countries (e.g., US and Europe).⁷ Natural gas to liquid (GTL) and coal to liquid (CTL) technologies are being developed to reduce dependence on imported petroleum.⁷ While GTL and CTL can provide a means of decreasing dependence on imported oil, these technologies do not address the non-renewable nature of fossil fuels. To reduce atmospheric CO₂ emissions, one technology being implemented is carbon capture and sequestration.^{5,8–10} Additionally, carbon neutral energy sources such as wind and solar are becoming increasingly important sources of energy. However, in the current infrastructure, the potential to replace traditional non-renewable sources with the aforementioned renewable sources is limited due to their intermittent nature. For example, in the US, the use of these energy sources will be limited to a maximum of $\sim 15\%$ of the US electricity supply without improved power output leveling (smart grid).¹¹ Conversion of CO₂ to useable fuels provides a means of decreasing dependence on foreign oil *via* the penetration of renewable energy sources into the transportation sector, while expanding the use of intermittent, renewable power sources (wind and solar). Because transportation is responsible for about 33% of CO₂ emissions in the United States, introducing a carbon neutral fuel would have a drastic impact on CO₂ concentrations in the atmosphere.¹²

Multiple methods (e.g., photochemical, thermochemical, and electrochemical) are being explored for the conversion of CO₂ into useful fuels. Specifically, electrochemical reduction of CO₂ combines electrical energy from a carbon neutral source with CO₂ to yield many products, including: methanol,^{13–15} formic acid,^{15–21} methane,^{15,22–25} ethylene,^{15,24–28} and carbon monoxide (CO).^{15,29–32} A broad spectrum of metal catalysts has been tested for the production of various fuels and feedstocks from CO₂ reduction.^{15,16,21,25} Carbon monoxide, which is primarily produced using Ag and Au as the catalysts, is particularly interesting as it can be combined with H₂ to yield syngas, which can be further reacted in a Fischer-Tropsch process to fuels such as methanol or “Fischer-Tropsch diesel”.^{33–35} Consequently, several reactor designs have been explored for CO production.^{30–32,36–39} As we reported earlier, the primary hurdle to the further development

of electrochemical CO₂ reduction processes lies in the challenge to simultaneously maximize energetic efficiency and throughput.⁷

Previously, we reported a flow reactor for electrochemical CO₂ conversion to formic acid.¹⁸ Using a similar reactor, we showed that amine based ionic liquid electrolytes can drastically reduce the overpotential necessary for the electrochemical reduction of CO₂ to CO, albeit at the expense of throughput.⁴⁰ Pyridine has been shown to have similar effects.^{41,42} Additionally, several researchers have shown that various alkali cations influence the selectivity for methane and ethylene on a copper electrode^{23,43} as well as formic acid and hydrogen on a mercury electrode;⁴⁴ however, little work has been published regarding the influence of electrolyte choice with the most prominent catalysts for CO₂ reduction, Ag or Au. The study of electrolytes is further complicated by effects from the electrolyte solutions on solution properties, such as conductivity, solubility and pH, which need to be de-convoluted.

To date, most efforts for the electrochemical reduction of CO₂ to CO have focused on researching different catalysts to optimize energetic efficiency and/or current density. Here we investigate in detail the influence of alkali cations (i.e., Na⁺, K⁺, Rb⁺, and Cs⁺) with three halogens (i.e., Cl⁻, Br⁻, and I⁻) and hydroxide (OH⁻) on the electrochemical reduction of CO₂ to CO with regards to current density and selectivity.

Experimental

Electrochemical cell.— A schematic of the electrochemical reactor used in this study is shown in Figure 1. A stainless steel plate and graphite plate (6 × 3 cm) served as the anode and cathode current collectors, which held the fuel cell together and provided electrical contact between the gas diffusion electrode (GDE) and an external potentiostat (PGSTAT-30, EcoChemie). The potentiostat was connected to the cell *via* banana clips which plugged directly into precisely machined 3/16” holes in the current collectors. Two 1-mm thick poly(methyl methacrylate) (PMMA) windows with precisely machined 0.5-cm wide by 2.0-cm long channels provided the electrolyte flow fields within the electrochemical reactor. A 212 Nafion membrane (DuPont) separated the two PMMA windows. The cathode current collector had a precisely machined 0.5-cm wide by 2.0-cm long by 1-cm deep window behind the GDEs to allow for the flow of gases in and out of the reactor. The anode was left open to the surroundings to allow oxygen to escape. A squeeze-action toggle plier clamp (McMaster 5062A63) held the cell together.

Electrode preparation.— The electrodes were prepared by spray-painting a Ag catalyst ink onto Sigracet “35BC”-type GDEs using a

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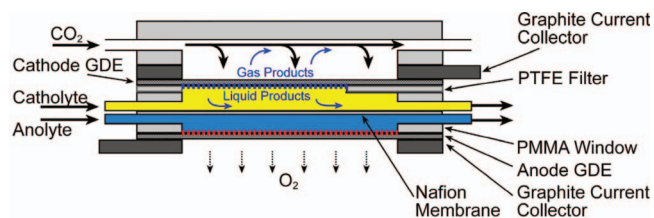


Figure 1. Schematic of an electrochemical reactor used to study the influence of various electrolyte solutions on the electrochemical reduction of CO₂ to CO.

motorized stage. A suspension of catalyst and Nafion binder with a 50/50 mixture of water and isopropyl alcohol was spray painted (Talon TG-3F spray gun) on a GDE held at 120°C. The cathode consisted of 1 mg/cm² Ag and 0.1 mg/cm² Nafion. The anode consisted of 1 mg/cm² Pt black and 0.1 mg/cm² Nafion.

Electrolyte composition.— All salts were purchased and used as provided. The following electrolyte solutions were prepared in Ultrapure water (18.2 MΩ·cm) such that the final concentrations were 1.0 M: NaCl (product # 71380, purity: 99.5%, Supplier: Fischer Scientific), KCl (P1597, 99% Sigma Aldrich), RbCl (215260, 99.8% Sigma Aldrich), CsCl (203025, 99.999% Sigma Aldrich), NaI (383112, 99.5% Sigma Aldrich), KI (P410, 99%, Fischer Scientific), RbI (251445 99.9% Sigma Aldrich), CsI (429384, 99.999% Sigma Aldrich), NaBr (460591, 99.999% Sigma Aldrich), KBr (221864, 99%, Fischer Scientific), RbBr (336149 99.7% Sigma Aldrich), CsBr (203017, 99.999% Sigma Aldrich), NaOH (221465, 97% Sigma Aldrich), KOH (44016, 90% Sigma Aldrich), RbOH (243892, 99.9% metal basis Sigma Aldrich), and CsOH (516988, 99.95% metal basis Sigma Aldrich).

Cell testing.— An Autolab potentiostat (PGSTAT-30, EcoChemie) operated in galvanostatic mode. The individual electrode potentials were measured using multimeters connected to each electrode and a Ag/AgCl reference electrode (RE-5B, BASi) in the exit stream. The cell was allowed to reach steady state for 200 s, after which, the gas flowed into a gas chromatograph (GC) (Trace GC, Thermo) for composition analysis of H₂ and CO in the affluent gas streams. For each condition tested, three GC samples were taken 90 seconds apart. The current was averaged for an additional 150 s before stepping to the next potential. All experiments were run at ambient conditions. The electrode potentials were IR corrected in Figure 2 based on conductivities found in the literature (180.1 mS/cm for NaOH, 215.3 mS/cm for KOH, 124.5 mS/cm for KBr, 84.3 mS/cm for NaCl, 108.6 mS/cm for KCl, and 122.9 mS/cm for CsCl)⁴⁵ and measured conductivities (126.3 mS/cm for RbOH, 202.2 mS/cm for CsOH, 96.4 mS/cm for NaBr, 126.3 mS/cm for RbBr, 123.5 mS/cm for CsBr, 97.4 mS/cm for NaI, 123.8 mS/cm for KI, 127.2 mS/cm for RbI, and 122.1 mS/cm for CsI). The cathode potentials were IR corrected by splitting the IR-drop 50%/50% between the anode and cathode as previously described.⁴⁶ A mass flow controller (32907-80, Cole Parmer) was used to flow CO₂ from a cylinder at 25 sccm. Also, a syringe pump (PHD 2000, Harvard Apparatus) supplied the electrolyte(s) at 0.5 mL/min. No cathode degradation was observed within the timeframe of a single experiment, however, to avoid contamination between experiments, for each electrolyte solution, a fresh cathode electrode was used and the reactor was tested at total current densities of 5, 10, 20, 40, and 80 mA/cm². In the case of iodide and bromide salt solutions (i.e., NaI, KI, RbI, CsI and NaBr, KBr, RbBr, CsBr), the electrolyte solutions were pumped between the nafion membrane and the cathode at 0.5 mL/min and a 1.0 M solution of the corresponding chloride salt solutions (i.e., NaCl, KCl, RbCl, CsCl), were pumped at 0.5 mL/min between the nafion membrane and the anode. In the case of the chloride (i.e., NaCl, KCl, RbCl, CsCl) and hydroxide (i.e., NaOH, KOH, RbOH, CsOH) salt solutions, the nafion membrane was removed as well as one of the 1 mm flow channels and the electrolyte was flowed

directly between the cathode and the anode. The affluent gas stream flowed directly into a gas chromatograph (Thermo Finnegan Trace GC) operating in the thermal conductivity detection (TCD) mode, which uses a Carboxen 1000 column (Supelco) and a He carrier gas at a flow rate of 20 SCCM. The column was held at 150°C and the TCD detector was held at 200°C. Lastly, because most of the available data regarding CO₂ reduction do not report anode potentials, the energetic efficiencies for CO₂ reduction reported here only include losses on the cathode and ignore anode and system losses.

Results and Discussion

We studied the effect of the cation size on the faradaic yield of CO₂ reduction and on the partial current densities of the products, CO and H₂. Specifically, we tested electrolyte solutions with a variety of alkali cations (i.e., Na⁺, K⁺, Rb⁺, Cs⁺) for four anions (i.e., Cl⁻, Br⁻, I⁻, OH⁻) at a concentration of 1 M in an electrochemical reactor. Figures 2a and 2b show, the partial current densities for CO (i_{CO}), the desired product, and for H₂ (i_{H_2}), the unwanted product, respectively, relative to the cathode potential for chloride, bromide, iodide, and hydroxide salts with operating currents between 5 and 80 mA. Table I shows the cathode potentials, the IR corrected cathode potentials and the faradaic efficiencies for both CO and H₂ at a total current of 80 mA.

First, we discuss the effects of different salts on CO₂ reduction (Figure 2a). *In the cases with hydroxide salts* (Figure 2a1), the partial current density for CO (i_{CO}) grew with increasing cation size with Na⁺, K⁺, Rb⁺, and Cs⁺ salts relative to the cathode potential as seen by a left shift in Figure 2a. Additionally, the overpotential necessary to achieve a fixed current output (80 mA/cm²) with high selectivity for CO was the largest with small cations as is evident by a decrease in the cathode potentials from -1.62 to -1.65 to -1.72 to -1.88 V vs Ag/AgCl with 1 M CsOH, RbOH, KOH, and NaOH electrolyte solutions, respectively. *In the case of chloride salts* (Figure 2a2), the only electrolyte which significantly changed the cathode performance was the smallest cation, Na⁺. With NaCl, at a total current density of 80 mA/cm², the product selectivity was worse as is evident by a low i_{CO} (60 mA/cm²) and the overpotential was larger as is evident by a very negative cathode potential (-1.92 V vs Ag/AgCl). For comparison sake, when using the larger cations (K⁺, Rb⁺, and Cs⁺), i_{CO} was roughly 75 mA/cm² and the cathode potential was roughly -1.85 V vs Ag/AgCl. *In the case of bromide salts* (Figure 2a3), the effect of cation size on cathode overpotential is magnified. Figure 2a3 clearly shows that with Na⁺, a much larger cathode overpotential is required with a lower i_{CO} . Furthermore, with Cs⁺, the cathode potential required

Table I. Cathode potentials, IR corrected cathode potentials and faradaic efficiencies for both CO and H₂ at 80 mA.

Salt	Potential vs. Ag/AgCl (V)		Faradaic Efficiency	
	Cathode	IR Corrected Cathode	CO	H ₂
NaCl	-1.92	-1.87	75.0	14.3
KCl	-1.88	-1.84	95.6	6.2
RbCl	-1.86	-1.83	93.6	4.7
CsCl	-1.84	-1.81	87.0	6.8
NaBr	-2.37	-2.33	60.8	21.3
KBr	-1.79	-1.76	96.6	4.5
RbBr	-1.83	-1.80	95.8	7.2
CsBr	-1.67	-1.64	93.6	1.9
NaI	-1.89	-1.81	80.8	9.7
KI	-1.70	-1.64	96.6	3.8
RbI	-1.65	-1.59	96.5	0.8
CsI	-1.62	-1.56	101.7	2.5
NaOH	-1.88	-1.86	83.0	8.7
KOH	-1.72	-1.70	96.7	4.8
RbOH	-1.65	-1.63	91.6	2.4
CsOH	-1.62	-1.60	89.8	3.8

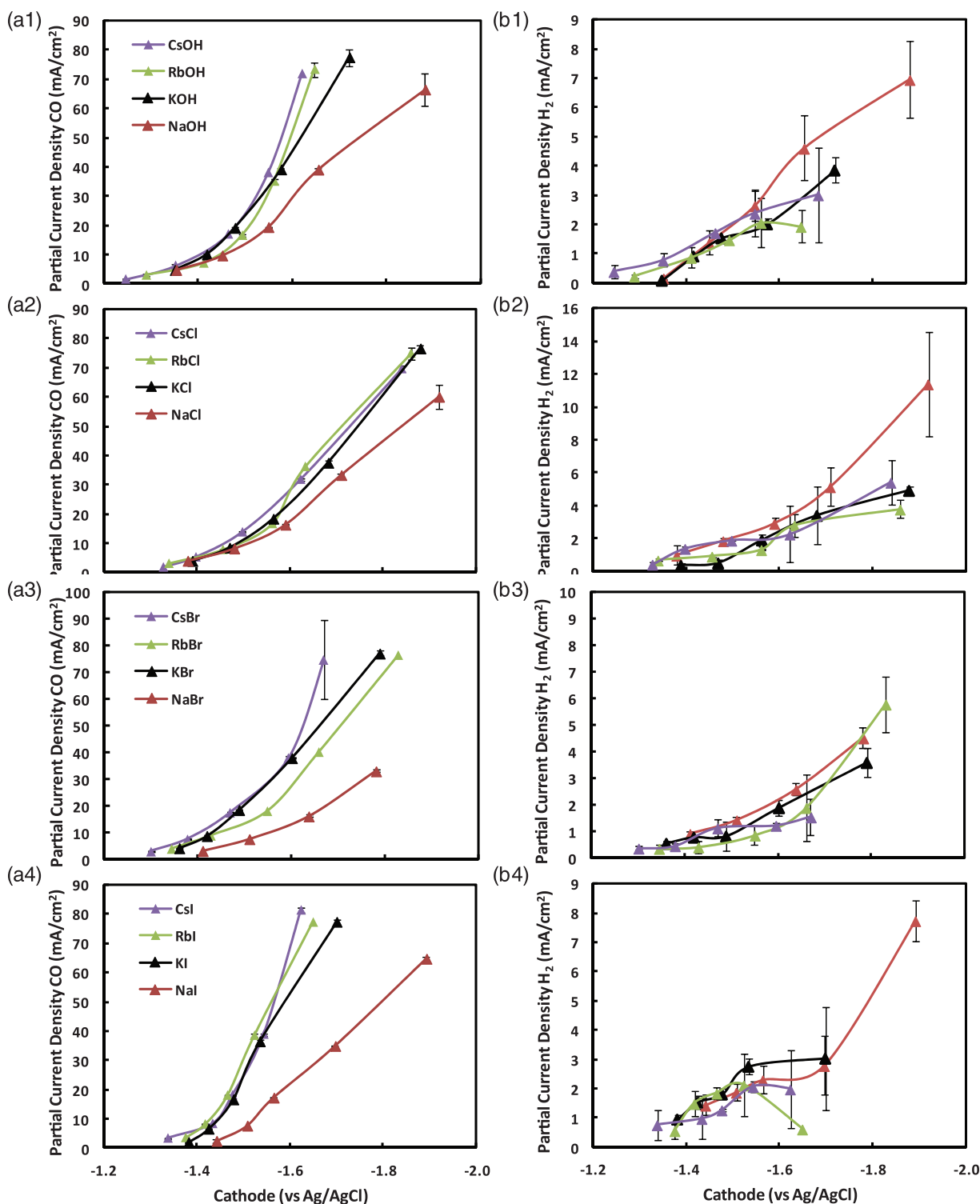


Figure 2. Partial current densities for (a) H₂, and (b) CO as well as (c) the faradaic yield for CO in 1 M (1) chloride (2) hydroxide, and (3) iodide electrolyte solutions, as a function of cathode potential. All conditions tested represent cell potentials between 2 and 3 V.

to achieve the same i_{CO} is -1.67 V vs Ag/AgCl, so less negative relative to Rb⁺ or K⁺ salts, with cathode potentials of -1.83 and -1.79 V, respectively. In the case of iodide salts (Figure 2a4), again, larger cations require smaller cathode overpotentials for the same cathode performance. The cathode potential required to achieve a fixed current output (80 mA/cm²) grew from -1.62 to -1.65 to -1.70 to -1.89 V vs Ag/AgCl with 1 M CsI, RbI, KI, and NaI electrolyte

solutions, respectively. Of note, with all four anion groups, the largest change in performance is observed with the smallest cation, Na⁺. In summary, we observed a strong trend of larger cations increasing i_{CO} and decreasing the cathode overpotential.

We also analyzed the effect of different electrolyte compositions on the undesired hydrogen evolution side reaction. The observed trends between cation size and hydrogen evolution are not as clear as the

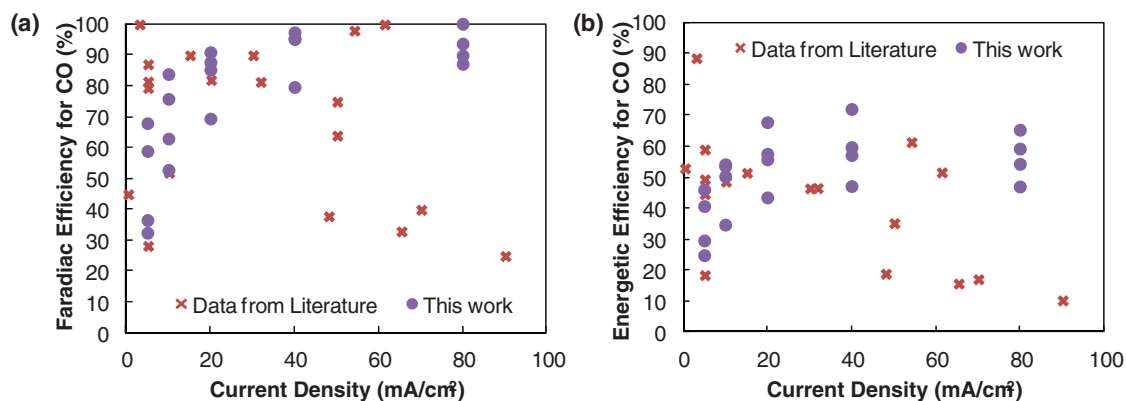


Figure 3. Comparison of the (a) faradaic and (b) energetic efficiencies for CO relative to the current densities for CO₂ reduction to carbon monoxide from literature and this work.^{15,29-31,40,58-60}

observed trends between cation size and CO production. Nonetheless, the smallest cation, Na⁺, consistently exhibited a higher partial current density for H₂ (*i*_{H2}) as seen in Figure 2b. The increase in hydrogen evolution with Na⁺ is most evident with the hydroxide, chloride and bromide anions in Figures 2b1, 2b2, and 2b3, respectively. Furthermore, the largest cations, Cs⁺ and Rb⁺, consistently exhibited a lower *i*_{H2} with the hydroxide, chloride and bromide anions. Specifically, in the case of hydroxide salts (Figure 2b1), at cathode potentials near -1.6 V vs Ag/AgCl, *i*_{H2} was 4.6 mA/cm² with Na⁺ (-1.62 V vs Ag/AgCl), 2.1 mA/cm² with Rb⁺ (-1.65), and 2.4 mA/cm² with Cs⁺ (-1.62). In the case of chloride salts (Figure 2b2), at cathode potentials near -1.9 V vs Ag/AgCl, *i*_{H2} was 11.4 mA/cm² with Na⁺ (-1.92), 3.8 mA/cm² with Rb⁺ (-1.86), and 5.4 mA/cm² with Cs⁺ (-1.84). In the case of bromide salts (Figure 2b3), at cathode potentials near -1.65 V vs Ag/AgCl, *i*_{H2} was 2.5 mA/cm² with Na⁺ (-1.64), 1.9 mA/cm² with Rb⁺ (-1.66), and 1.5 mA/cm² with Cs⁺ (-1.67). In summary, in the three aforementioned examples, we observed a strong trend that an increase in cation size led to a decrease in *i*_{H2} for comparable cathode potentials.

Effects of cation size on product selectivity, similar to what is reported here, for the electrochemical reduction of CO₂ to methane, ethylene, methanol, and formic acid, has been observed previously. For example, Hori et al. showed that large cations favor formic acid production on a mercury electrode.⁴⁴ The role of ion selection for formic acid formation is particularly interesting as this reaction has the same rate limiting step as the CO reaction, the production of an unstable anion radical intermediate, “CO₂⁻”. However, in this case, little explanation was given regarding the influence of cation size on selectivity of formic acid formation over hydrogen evolution.

One would expect that the influence of cations on CO₂ reduction is primarily controlled by ion adsorption at the electrode surface. In general, smaller cations have larger hydration powers, and consequently, have less adsorption on electrode surfaces. Ion adsorption can stabilize some reactions while suppressing others on an electrode surface. This, in turn, influences product selectivity, current density, and energetic efficiency.

In our work, the silver cathode used in the reaction is operated well below its point of zero charge (pzc), and, as a result, cation adsorption is favored on the negatively charged electrode surface, and to an increasing extent at more negative potentials.⁴⁷ Significant differences are seen in the ionic radii of the cations employed. Specifically the ionic radii of Na, K, Rb, and Cs are 102, 138, 152, and 167 pm, respectively.⁴⁸ Cations with small ionic radii have larger hydration powers (i.e., Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺).⁴⁹ Specifically, the hydration numbers Li⁺, Na⁺, K⁺ and Cs⁺ are 22, 13, 7, 6, respectively.⁵⁰ Consequently, the smaller a cation is, the smaller is its propensity to adsorb on an electrode surface.

Ions adsorbed on an electrode surface can influence reactions in several ways. Ion adsorption can block surface sites and can

thereby decrease the current density, stabilize intermediates, and modify the potential of the outer Helmholtz layer (ϕ_2) and the electrode surface.^{43,51} Because larger cations exhibit a higher propensity for adsorption on an electrode surface, the electrode potential will be expected to become more positive for larger cations (i.e., Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺).^{43,51} Maznichenko et al. validated this theory by showing that the measured overpotentials associated with the H₂ reduction reaction increased with increasing cation size (i.e., Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺).⁵² The resulting less negative ϕ_2 causes a decrease in [H⁺] at the electrode surface as described by the following equation:⁵²

$$[H^+]_{electrode} = [H^+]_{bulk} e^{-\frac{F\phi_2}{RT}} \quad [1]$$

where F is Faraday's constant, R is the gas constant, and T is the absolute temperature. Since the rate limiting step in this reaction is: $H^+ + e^- \rightarrow H\cdot$, increasing [H⁺] at the electrode surface (for example in the presence of smaller and thus more hydrated cations) increases the reaction rate and decreases the overpotentials for H₂ production.⁴⁴ As a result, H₂ production increases with decreasing cation size (Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺), as we also observed here (Figure 2a).

The second way cations influence the surface reaction is by stabilizing anions on the cathode surface.⁵³ For example, for the reaction of S₂O₈⁻² to SO₄⁻², large cations within the double layer of the cathode stabilize the reactive anion and enable much higher current densities, whereas in the discharge of H⁺ ions, cations within the double layer repel the reacting species, thereby hindering the reaction, resulting in much lower current densities.⁵⁴ Further confirming the mechanism by which large cations stabilize anions on the surface, Frumkin et al. observed an increase in the adsorption of anions on a cathode in the presence of large cations (i.e., Cs⁺), thereby showing that ion-pairing is more pronounced with larger cations, and as a result, drastically increases the interaction between cations and anions in the double layer.⁵³ While CO₂ and CO are neutral products, the rate limiting step in the reaction is: $CO_2 + e^- \rightarrow CO_2^{\cdot-}$, which forms the negatively charged “CO₂⁻” on the cathode.^{7,55,56} Cation adsorption on the cathode may stabilize “CO₂⁻” on the electrode surface through ion-pairing, thereby driving the reaction, improving the current density for a given overpotential. Ashworth et al. observed a similar trend, that cation adsorption improved the reaction kinetics of converting a neutral species with an unstable anion intermediate on the cathode.⁵⁷ Frumkin later proposed that the anion intermediate was stabilized by the cations on the electrode surface, thereby enabling higher current densities from electrolyte solutions with large cations.⁵³

Our systematic investigation of the effect of alkali cations on the electrochemical reduction of CO₂ while using a Ag electrode indicates that the cation size plays a significant role in product selectivity. Furthermore, the similar trends between this work and the aforementioned literature survey, suggest that the influence of cation

size on performance stems from cation adsorption on a cathode surface. Larger cations have a higher propensity for electrode adsorption due to their low hydration powers, whereas smaller cations are more likely to be hydrated in solution and consequently, less likely to adsorb on an electrode surface. Cations adsorbed on a cathode repel H^+ ions from the cathode. This explains the experimentally observed trend of decreased H_2 evolution when larger cations are present in the electrolyte. Additionally, cation adsorption may stabilize " CO_2^- " on the cathode surface, similar to that reported by Ashworth et al., thereby driving the reaction of CO_2 to CO. This trend was experimentally confirmed in Figure 2b.

Figure 3 reports the faradaic efficiencies and energetic efficiencies for CO production achieved in this study with the cesium salts (which performed the best) relative to state-of-the-art data reported earlier in the literature up to 100 mA/cm^2 .^{15,29–31,40,58–60} The use of a large cation, Cs^+ resulted in large improvements regarding the resultant energetic (~60%) and faradaic (~95%) efficiencies at high current densities. In particular, with a 1 M CsOH electrolyte solution, a current densities of 80 mA/cm^2 was achieved at a cathode potential of -1.62 V vs. Ag/AgCl (Figure 2). This data corresponds to a faradaic efficiency of 90% and an energetic efficiency of 65%, as seen in Figure 3. This is a significant improvement compared to state-of-the-art electrochemical reduction of CO_2 , which tend to have drastically reduced faradaic efficiencies at increased current densities.

Conclusions

Electrolyte composition influences many factors in an electrochemical reactor, including conductivity, and pH. Here, cation size of the salt in the electrolyte solution played a significant role in the electrochemical reduction of CO_2 into CO. Specifically, small cations (e.g., Na^+) favor H_2 evolution, and, consequently, have a low faradaic efficiency for CO production, whereas large cations (e.g., Rb^+ , Cs^+) favor CO production and suppress H_2 evolution, resulting in high faradaic efficiencies for CO, here up to 100%. We observed the least negative cathode potentials with the cesium salts. Here, we confirm that stronger cation hydration reduces the extent of cation specific adsorption on the cathode, which effects product selectivity and reaction rate in CO_2 reduction.^{43,51}

A major obstacle to the broader application of the electrochemical reduction of CO_2 lies in the challenge of simultaneously achieving high current densities and energetic efficiencies.⁷ Here we demonstrate a major step toward improving both the energetic efficiencies and current densities of the electrochemical reduction of CO_2 to CO on a Ag cathode. In particular, we observe a drastic improvement in the achieved resultant energetic (~60%) and faradaic (~95%) efficiencies at high current densities.

The work reported here suggests that further exploration of the effect of cations on the electrochemical conversion of CO_2 to CO, or to other products, may lead to further improvements in performance. Additionally, further exploration of anion effects on the electrochemical reduction of CO_2 may be promising, as anions influence many parameters, including product selectivity, cation adsorption (through ion-pairing), anode kinetics, and conductivity. Furthermore, alkaline solutions appeared to lead to low overpotentials (Figure 2a), but more research is needed to study the rate of carbonate formation in alkaline solutions and its role in reactor fouling.

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