

Hydrolysis of Electrolyte Cations Enhances the Electrochemical Reduction of CO₂ over Ag and Cu

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Abstract

Electrolyte cation size is known to influence the electrochemical reduction of CO_2 over metals; however, a satisfactory explanation for this phenomenon has not been developed. We report here that these effects can be attributed to a previously unrecognized consequence of cation hydrolysis occurring in vicinity of the cathode. With increasing cation size, the pK_a for cation hydrolysis decreases and is sufficiently low for hydrated K^+ , Rb^+ , and Cs^+ to serve as buffering agents. Buffering lowers the pH near the cathode leading to an increase in the local concentration of dissolved CO_2 . The consequences of these changes are an increase in cathode activity, a decrease in Faradaic efficiencies for H_2 and CH_4 and an increase in Faradaic efficiencies for CO , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ in full agreement with experimental observations for CO_2 reduction over Ag and Cu.

Introduction

An appealing option for the conversion of solar energy to fuels is the electrochemical reduction of CO₂ using water as the source of hydrogen.¹⁻³ The source of CO₂ might be the atmosphere⁴ or the sea⁵ and the desired products are compounds that can be converted to a liquid using known technologies (e.g, synthesis gas (a mixture of H₂ and CO), ethene, or ethanol).^{6,7} While much attention has been given to the discovery and development of catalysts, electrolytes, and electrolyte additives, these topics remain subjects of ongoing research.⁸ Of the various catalysts investigated to date, Ag and Au are known to be highly selective to CO and H₂, and Cu is the metal exhibiting the highest selectivity (i.e. Faradaic efficiency) to hydrocarbons and oxygenated compounds.^{9,10} Extensive work has also shown that the activity and selectivity of these catalysts can be modified by alloying,¹¹ surface restructuring,^{12,13} surface functionalization,¹⁴ solvent^{15,16} and electrolyte composition,^{17,18} pH,¹⁹ as well as temperature,²⁰ pressure,²¹ and CO₂ flowrate.⁹

Recent theoretical studies have also demonstrated that the optimal bulk pH for conducting CO₂ reduction (CO₂R) is close to 7, and that at significantly higher or lower values, the Nernstian losses become very high, resulting in a reduction of the total applied cell potential available to drive the kinetics of water oxidation at the anode and CO₂R at the cathode.²² It is also noted that for a bulk pH of 7, the pH of the electrolyte in the vicinity of the anode falls (i.e., the local electrolyte becomes acidic) and the pH in the vicinity of the cathode rises (i.e., the local electrolyte becomes basic) as the voltage applied across the cell increases. The latter effect is detrimental, since it results in a reduction of the dissolved CO₂ present as molecular CO₂ near the cathode and a corresponding rise in the concentration of HCO₃⁻ and CO₃²⁻. The decrease in CO₂ concentration near the cathode surface leads to a reduction in the Faradaic efficiency for producing C₂₊ hydrocarbons and oxygenates and an increase in the Faradaic efficiency for producing CH₄, and H₂.^{18,23}

C₂₊ products (e.g., ethene and ethanol) are preferable to C₁ products for the production of liquid fuels. However, in order to achieve the maximum selectivity to C₂₊ products and current densities of ~ 10 MA cm⁻², over Cu requires <-1 V vs RHE, in which results in significant polarization at the cathode.²² Therefore, it would be desirable to find a means for offsetting the effects of electrolyte polarization occurring near the surface of Cu cathode while maintaining a high current density and selectivity to C₂₊ products. Several investigators have shown that for a fixed applied voltage, the current density and the ratio of C₂ to C₁ products can be increased significantly by increasing the size of alkali metal cation.^{18,21,23-25} It is notable that while the effect of metal cation size on the activity of redox reactions has been known for over 45 years,^{21,26} a successful interpretation of this phenomenon has not been achieved. Eyring and coworkers²¹ ascribed the observation of increasing current density on Hg with increasing metal cation size to the higher specific adsorption of larger cations, the effect of which is to increase the potential of the outer Helmholtz plane (OHP) and thereby increase the kinetic overpotential at a fixed applied potential, as first proposed by Frumkin.²⁶ Although the effect of specific adsorption of cations

provides a qualitative explanation for the increase in the total current density (i.e. activity), the increase in the selectivity of CO₂R relative to that for the hydrogen evolution reaction (HER) with increasing cation size is beyond the scope of this theoretical interpretation. Murata and Hori noted the effects of cation size on the activity and selectivity to products formed during CO₂R over Cu.¹⁸ Frumkin's theory was used to explain the increase in CO₂R activity, whereas the increase in the ratio of C₂ to C₁ products with increasing cation size was attributed to an increase in the equilibrium values of cathode pH with increasing OHP potential determined using the Boltzmann equation. Similar explanations for the effect of cation size on the electrochemical reduction of CO₂ have been offered by other authors.^{23,24}

Recently, Janik and coworkers²⁷ have calculated the equilibrium potentials for cation adsorption on transition metal electrodes and found values ranging from -2.63 V vs NHE for Li⁺ to -2.44 V vs NHE for Cs⁺ on Ag electrode. This suggests that the specific adsorption of cations is not favorable under operating potentials of CO₂R (typically > -1.4 V vs NHE). Furthermore, Markovic and coworkers²⁸ have shown that the activity of redox reactions are affected primarily by non-covalent interactions rather than covalent interactions or specific adsorption. Based on these findings, it is evident that Frumkin's theory of increase in the OHP potential due to increase in specific adsorption (or covalent interaction) of cations is not applicable to the conditions of CO₂R. The steric effect due to cation size could possibly affect the OHP potential, and has been investigated previously using a modified Poisson-Boltzmann equation.²⁹ According to predictions of this work, variation in the size of the hydrated cation has a negligible effect on the OHP potential for the applied potentials > -1 V vs RHE. Therefore, it appears that neither specific adsorption nor steric hindrance of cations is responsible for the increase in the activity and selectivity reported for CO₂R.

Here we report a novel interpretation for the effects of metal cation size on the electrochemical reduction of CO₂ based on preferential hydrolysis of hydrated cations near the cathode surface. We show that the pK_a for hydrolysis of hydrated cations in the bulk of the electrolyte is inversely proportional to the electrostatic energy of interaction, such that the pK_a of Li⁺ and K⁺ are 13.5 and 14.6, respectively.^{30,31} Under applied potential, the cations migrating toward the cathode (negative electrode) experience an increasing electrostatic interaction, which causes a decrease in the pK_a for hydrolysis. If the pK_a of the hydrated cations is lower than the local pH, the dissociation of one of the waters of hydration releases protons thereby buffering the local pH. This effect enables the hydrated cations to buffer the electrolyte near the cathode surface offset the polarization losses associated with the increase in pH, which results in a decrease in the Nernstian losses and an increase in the kinetic overpotential for a given applied voltage. Section 1 of the Supplementary Information reviews the concept of metal ion hydrolysis and shows how the pK_a of hydrolysis can be calculated. The effects of cation hydrolysis on CO₂R are then interpreted using a multiphysics, electrochemical model²² presented in Section 2 of the Supplementary Information. This model includes the effects of ion migration, diffusion, acid-base equilibrium, gas-liquid transport of CO₂, hydrolysis of cations and the kinetics of the OER and CO₂R. The theoretical predictions are validated by comparison with the experimental

measurements of CO₂R over Ag and Cu electrodes using aqueous electrolytes containing alkali cations of different sizes.

Results and Discussion

Figures 1(a) and 1(c) show the cathodic current density versus voltage curves for Ag and Cu cathodes, respectively, in CO₂-saturated 0.1 M MHCO₃ (M = Li, Na, K, Rb, Cs) electrolytes (pH 6.8). It is evident that for a fixed potential, the current density increases 2.4 fold as the cation size increases from Li⁺ to Cs⁺ in the case of Ag, and 2.1 fold in the case of Cu. The higher current density observed for Ag at -1 V vs RHE compared to Cu is due to the higher surface roughness of the Ag foils, which were polished mechanically, whereas the Cu foils were polished electrochemically. Figures 1(a) and 1(c) also show that the electrode overpotential decreases with an increase in the cation size at a fixed current density. The influence of cation size on the Faradaic efficiencies (FEs) for CO₂R products produced on Ag and Cu cathodes at -1V vs RHE are given in Figure 1(b) and 1(d), respectively. The total Faradaic efficiency for CO₂R over Ag and Cu cathodes increases by ~15% and ~55%, respectively, as the cation size increases from Li⁺ to Cs⁺. Figure 1(d) also shows that the ratio of FEs for C₂ to C₁ hydrocarbons formed over Cu increases from 0.2 for Li⁺ to 3.3 for Cs⁺. The measured trends of CO₂R activity and selectivity are in agreement with those reported previously.^{18,23,24}

To interpret the observation reported in Figure 1, we first note that the ease with which a hydrated cation undergoes hydrolysis is given by its pK_a. Table 1 shows values of the pK_a of hydrolysis for cations in the bulk electrolyte and near Ag and Cu cathode surfaces at -1 V vs RHE. It can be seen that the pK_a for cation hydrolysis in the bulk of the electrolyte increases slightly with increasing cation size due to the decrease in the electrostatic interaction between the metal cation and the O atom of a water molecule in the hydration shell. However, the pK_a near the cathode surface decreases with increasing cation size due to the increase in the electrostatic interaction between the hydrated cation and the cathode. The increase in the electrostatic interaction is due to the increase of the surface charge at a fixed solid angle on cathode from the cation with increasing cation size (see Section 1 of the Supplementary Information). Therefore, the pK_a for cation hydrolysis increases monotonically with increasing separation distance between the cation and the cathode, such that it takes on the value in the bulk electrolyte for separation distances greater than ~ 1 nm. As the specific capacitance and hence the charge density on the surface of Ag is higher than that on Cu, the pK_a of a cation near the Ag cathode is lower than that near the Cu cathode.

We have recently shown that for a near-neutral electrolyte the pH near the cathode increases during electrochemical reduction of CO₂ with increasing applied potential.²² For example, a 0.1 M solution of KHCO₃ saturated with CO₂ at 1 bar has a bulk pH of 6.8 but the pH near the cathode surface can increase to as high as 9.5 for an applied potential of -1.15 V vs RHE.²² As can be seen from Table 1 that the hydrated K⁺, Rb⁺ and Cs⁺ ions can readily undergo hydrolysis under such conditions because their pK_a is less than 9.5, whereas Li⁺ and Na⁺ cations will not hydrolyze. Since the distribution of dissolved CO₂ between molecular CO₂ and HCO₃⁻

and CO_3^{2-} is strongly dependent on pH, a high pH leads to a reduction in the concentration of molecular CO_2 due to its rapid consumption by hydroxyl anions to form HCO_3^- and CO_3^{2-} , which occurs at much higher rates than the rate of CO_2 reduction. This is detrimental to CO_2R , since only molecular CO_2 undergoes reduction. A reduction in the pH near the cathode surface brought about by the buffering action of large alkali metal cations would cause the concentration of molecularly dissolved CO_2 to rise towards the value in the bulk electrolyte, 33 mM.

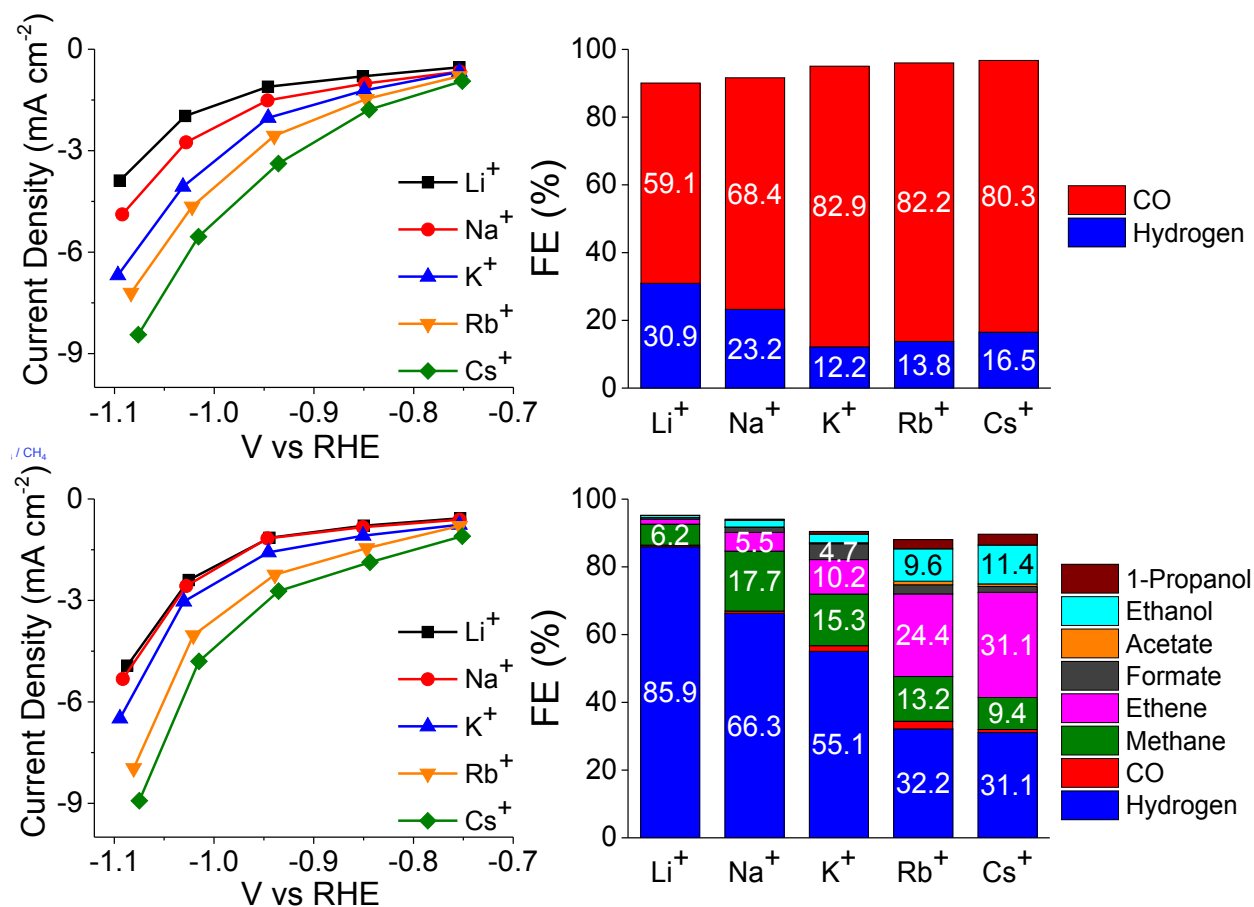


Figure 1: Influence of cation on current density and Faradaic efficiency (FE) of CO_2 reduction. (a) current densities versus applied potential on Ag cathode, (b) FEs for CO and H_2 produced over Ag at -1 V vs RHE, (c) current density versus applied potential on Cu cathode, and (d) FEs for CO_2R products produced over Cu at -1 V vs RHE in CO_2 -saturated 0.1 M MHCO_3 ($M = \text{Li, Na, K, Rb, Cs}$) electrolyte. FEs for CO_2R products produced over Ag and Cu at -1 V vs RHE are given in Table S6 and S7 of the Supplementary Information.

Table 1: pKa of hydrolysis of cations in the bulk electrolyte and near Ag and Cu cathodes at -1 V vs RHE. The pKa of hydrolysis increases linearly with the distance between the cation and the cathode. The minimum value of pKa occurs at the cathode and the maximum value at a separation distance greater than ~1 nm.

Cation	Cation Size (pm)	pKa in Bulk Electrolyte	pKa near Ag Cathode	pKa near Cu cathode
Li ⁺	69	13.6	11.64	13.16
Na ⁺	102	14.2	10.26	11.44
K ⁺	138	14.5	7.95	8.49
Rb ⁺	149	14.6	6.97	7.23
Cs ⁺	170	14.7	4.31	4.32

The effects of hydrated cation hydrolysis on CO₂R over Ag and Cu cathodes were modeled using the procedures described in Section 2 of the Supplementary Information. Figure 2 shows calculated values of pH and CO₂ concentration at the cathode, total current density and FEs of CO₂R products formed over Ag at -1 V vs RHE. Figure 2(a) shows that the cathode pH decreases from ~9 to ~7 with increasing cation size from Li⁺ to Cs⁺, in agreement with the trend in their pKa values given in Table 1. Figure 2(b) shows that the cathode CO₂ concentration increases from ~0.4 mM to ~11 mM with increasing cation size. The lower concentration of CO₂ at the cathode is due to its consumption in the CO₂R reaction to make products and in the acid-base equilibrium reactions to produce HCO₃⁻ and CO₃²⁻ anions. The CO₂ concentration is lowest at the cathode in the presence of Li⁺ and Na⁺ ions because of higher cathode pH > 8.5 that converts CO₂ to HCO₃⁻ and CO₃²⁻ anions. The increase in cathode pH and decrease in CO₂ concentration increase the polarization losses.²² Therefore, the polarization losses decrease with increasing cation size. Since the applied potential is a sum of polarization loss and kinetic overpotential, the kinetic overpotential and correspondingly the current density increase with increasing size of the cation. Figure 2(c) shows that the predicted current density increases with increasing cation size, in good quantitative agreement with what is observed in Figure 1. It can be seen that the model under-predicts the current density for Li⁺ and Na⁺ ions and over-predicts for K⁺, Rb⁺ and Cs⁺ ions. The difference between the predicted and measured current density can be ascribed to the direct dependence of CO₂ concentration and pH on the kinetics of CO₂R, an aspect that was not considered here. For example, the increase in pH may favor electrochemical reduction of CO₂³²; however, the decrease in CO₂ concentration will decrease the concentration of adsorbed CO₂⁹. The under estimation of current density for Li⁺ and Na⁺ cations may be due to the absence of a direct dependence of pH on the kinetics of CO₂ reduction for these cations, whereas the over estimation of the current density for K⁺, Rb⁺ and Cs⁺ cations may be due to the absence

of a direct dependence of CO_2 concentration on the kinetics. Figure 2(d) shows that the selectivity to CO formation over Ag increases with increasing cation size. It is important to note that the HER is only affected by the polarization loss due to pH differences between the bulk and the cathode surface, whereas the CO_2R reaction is affected by the polarization losses due to both pH and CO_2 concentration changes. Therefore, the current density for CO increases from 0.57 mA cm^{-2} for Li^+ to 4.9 mA cm^{-2} for Cs^+ , whereas the current density for H_2 increases slightly from 0.45 mA cm^{-2} for Li^+ to 0.53 mA cm^{-2} for Cs^+ . The increase in the FE for CO with increasing cation size, seen in Figure 2(d), compares very well with the measured FEs presented in Figure 1(b). We also notice that the FE for CO does not change significantly for bicarbonate electrolytes containing K^+ , Rb^+ and Cs^+ ions, which is also explained by the model.

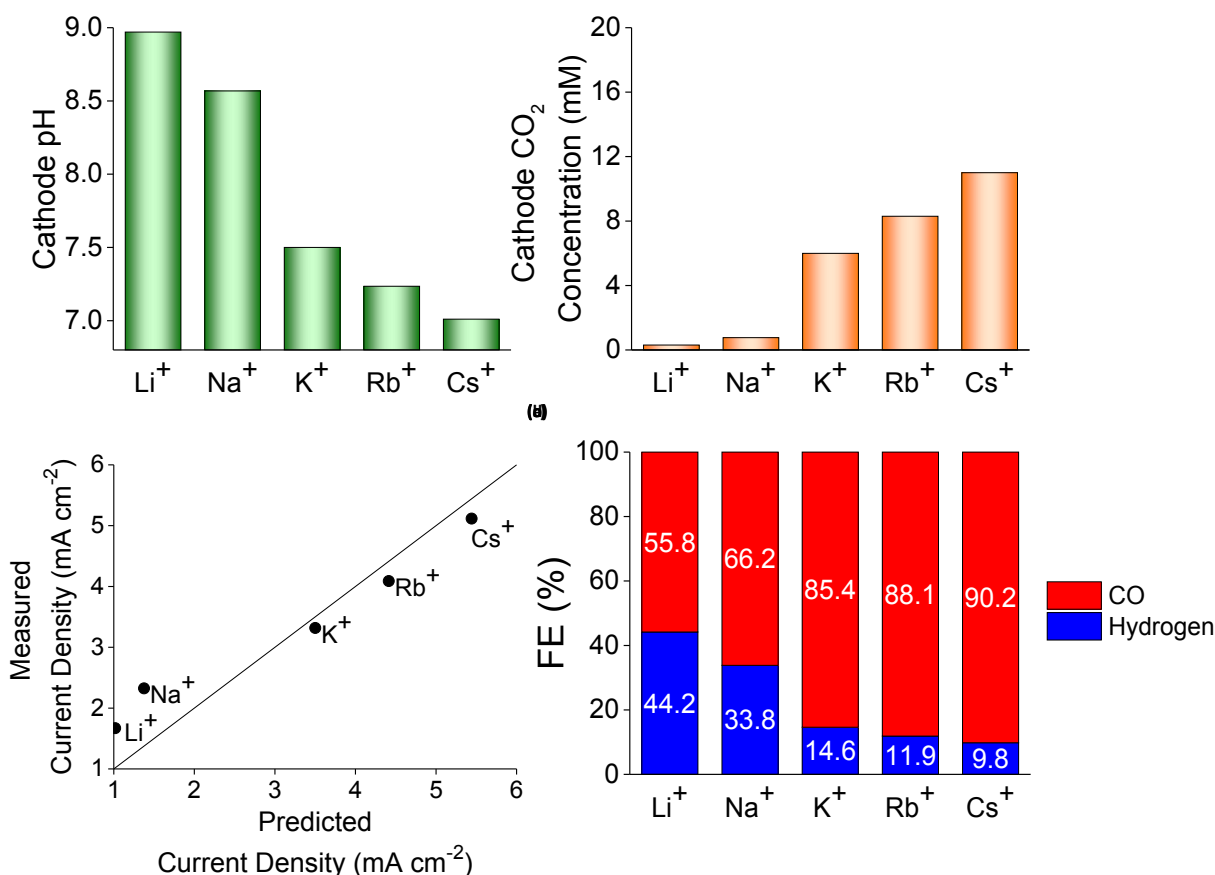


Figure 2: Calculated values of (a) cathode pH, (b) cathode CO_2 concentration (c) total current density and (d) Faradaic efficiencies (FEs) for CO and H_2 produced over Ag at -1 V vs RHE in CO_2 -saturated 0.1 M MHCO_3 ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) electrolyte.

Figure 3 shows the influence of cation size on the calculated pH and CO_2 concentration of the electrolyte near a Cu cathode, the current density, and the FEs for CO_2R products formed

over Cu at -1 V vs RHE. Figure 3(a) shows that the cathode pH decreases from ~ 8.75 to ~ 7 with increasing cation size. As the current density at -1 V vs RHE on Cu is lower than on Ag, the pH near the surface of Cu is lower for a given cation than for Ag. The surface area of the Ag foils was about 4% higher than that of the Cu foils (see *Experimental Materials and Methods* section), and consequently, the current density and polarization losses could be somewhat higher for Ag compared to Cu. With increasing cation size, the CO_2 concentration increases from ~ 0.4 mM to ~ 18 mM, as can be seen in Figure 3(b). Since the consumption of CO_2 per electron transferred is lower for the formation of hydrocarbons than CO, the concentration of CO_2 is higher on Cu than on Ag for a given cation. As the polarization loss decreases with increasing cation size, the current density in Figure 3(c) increases from ~ 1.5 mA cm^{-2} for Li^+ to ~ 3.2 mA cm^{-2} for Cs^+ . Figure 3(d) shows that the FEs for H_2 and CH_4 formation decrease, and the FEs for C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ increases with increasing cation size. The polarization loss per decade change in proton and CO_2 concentrations for formation of CO is 90 mV, C_2H_4 is 70 mV, $\text{C}_2\text{H}_5\text{OH}$ is 70 mV, CH_4 is 67.5 mV and H_2 is 60 mV. The sensitivity of current density with respect to polarization losses depends on the transfer coefficient of the reaction. Table S5 in the Supplementary Information shows that the experimentally measured transfer coefficients decrease in the order $\text{C}_2\text{H}_4 > \text{C}_2\text{H}_5\text{OH} > \text{CH}_4 \gg \text{H}_2$. Therefore, the partial current density of C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ increases significantly as compared to that for CH_4 and H_2 with increasing cation size, resulting in an increase in the FEs for C_2 hydrocarbons products but a decrease in the FEs for CH_4 and H_2 . The predicted ratio of the selectivity of C_2 to C_1 hydrocarbons increases from 0.6 for Li^+ to 3.1 for Cs^+ , agrees well with the experimental values in Figure 1(d).

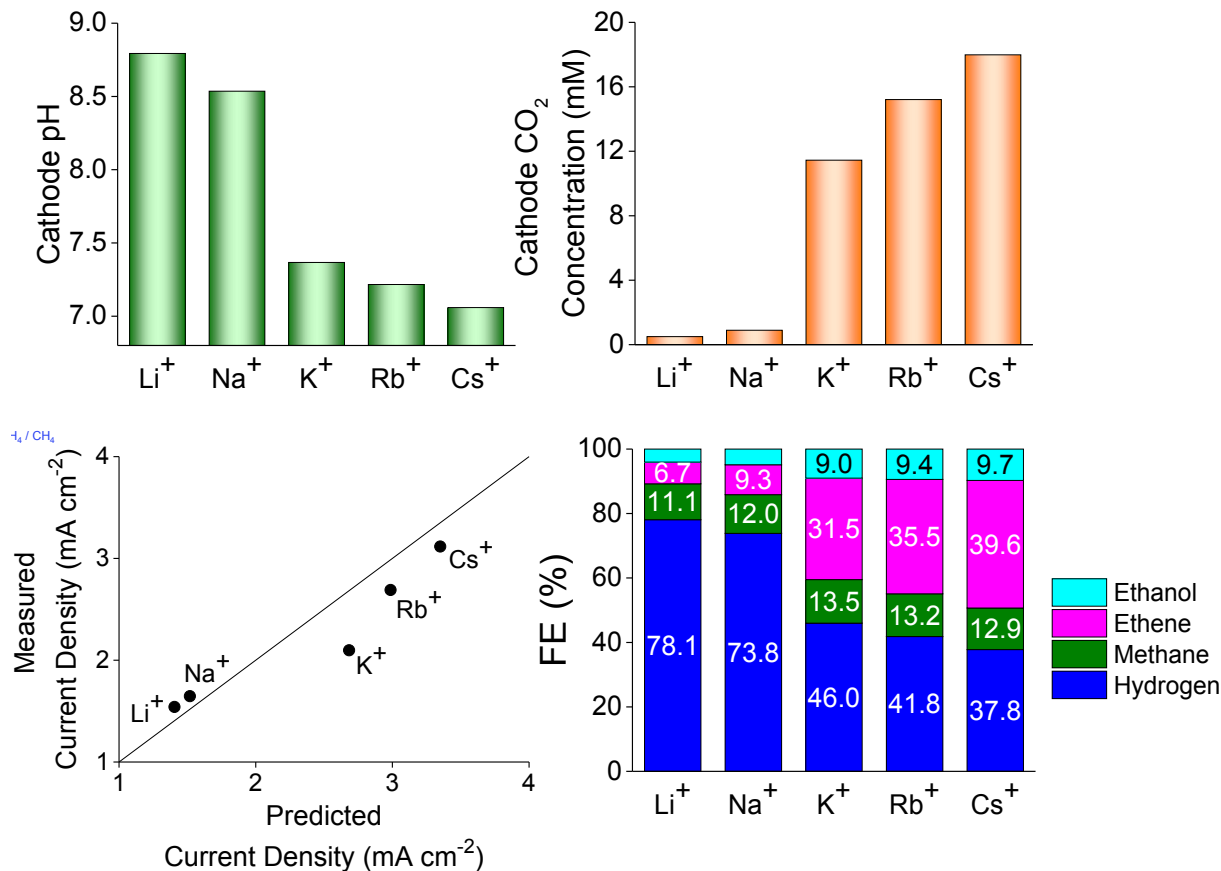


Figure 3: Calculated values of (a) cathode pH, (b) cathode CO₂ concentration (c) total current density, (d) Faradaic efficiencies (FEs) for C₂H₅OH, C₂H₄, CH₄, and H₂ produced over Cu at -1 V vs RHE in CO₂-saturated 0.1 M MHCO₃ (M = Li, Na, K, Rb, Cs) electrolyte.

The quantitative agreement between the theoretical predictions and the experimental measurements confirms that the variation in the activity and selectivity of CO₂R reactions with the cation size is due to the buffering ability of the cations in the vicinity of the cathode. The proposed effect of hydrolysis of hydrated cation is a macroscopic phenomenon which is effectively captured by our continuum model. The local buffering capability of cations should be able to increase the rate of any proton-transfer reaction. In Section 3 of the Supplementary Information we show that the current density for HER on a Ag cathode at -1 V vs RHE in 0.1 M chloride increases from ~2.5 mA cm⁻² for Li⁺ to ~4.5 mA cm⁻² for Cs⁺. The differences between the HER current densities for different cations increase with increasing applied potential as a consequence of increasing buffering at higher applied voltages. As the polarization loss is negligible at -0.7 V vs RHE, the current density for HER does not change with cation size. It is, therefore, evident that larger cations promote not only CO₂R but also HER.

For a given cation, the electrode charge density can be manipulated to control the pKa of hydrolysis. The surface charge density of the electrode at a fixed cathode potential can be

increased by increasing total cell voltage, for example, by using a high overpotential anode and a large gap between the electrodes. While this strategy would lower the electrolysis efficiency, it would increase the CO₂R activity and selectivity. The hydrated cations can promote proton-transfer only when i) the electrolyte is neither strongly acidic nor alkaline and ii) the pKa of hydrolysis is close to the local electrolyte pH. In this connection, we note that the pH near the electrode surface does not change significantly with the applied voltage in strongly alkaline medium. Since the pKa for different cations are typically less than 13, the buffering capacities of these cations are similar under alkaline conditions. Therefore, the polarization losses and thereby the kinetic overpotentials at a fixed applied potential are same for different cations. In agreement to this effect, Figure S5 in the Supplementary Information shows that the selectivity and activity for CO reduction over Cu at -1 V vs RHE in pH 13 electrolytes do not change significantly with cation size.

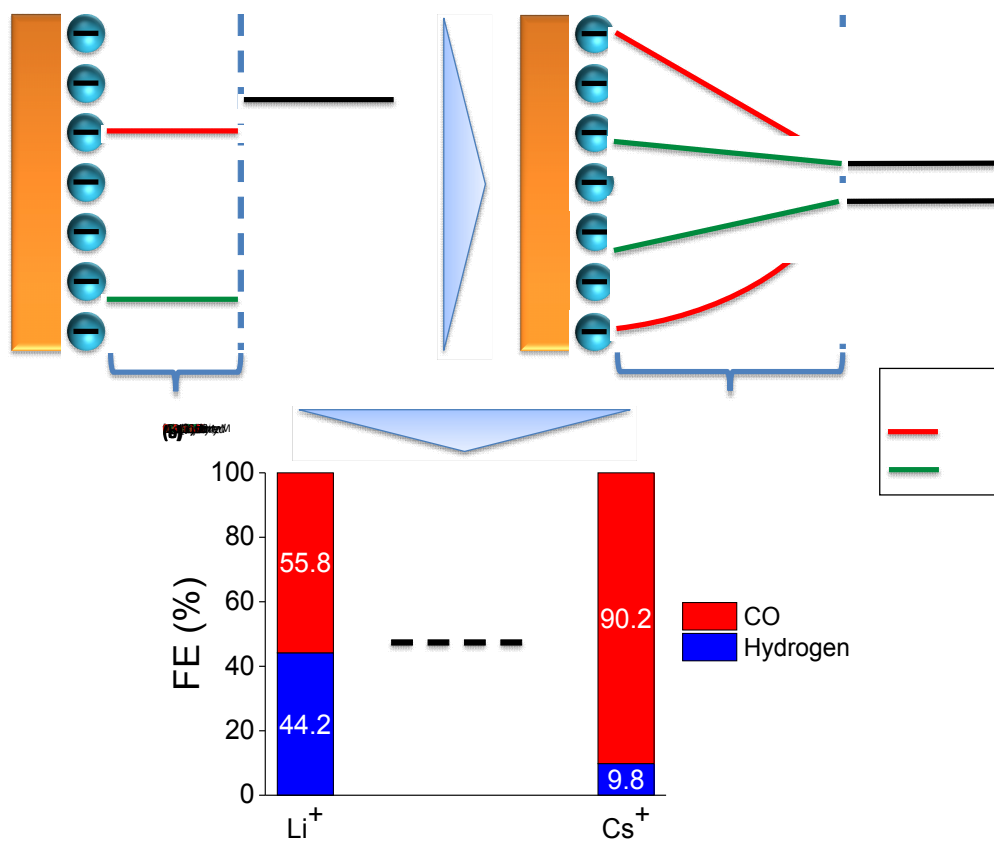


Figure 4: Effect of cation hydrolysis on the electrochemical reduction of CO₂ over Ag. (a) pKa of hydrolysis of hydrated Li⁺ and Cs⁺ inside the Helmholtz layer and in the bulk electrolyte, (b) distribution of pH and CO₂ concentration in the boundary layer. Hydrated Cs⁺ buffers the cathode to maintain the pH close to 7 and increase the CO₂ concentration, whereas hydrated Li⁺ does not buffer cathode which leads to increase in pH to 9 and decrease in CO₂ concentration to 0.4 mM. (c) FE for CO increases and for H₂ decreases with increasing cation size due to decrease in polarization.

Conclusion

The effects of cation size on the electrochemical reduction of CO₂ over catalysts such as Hg, Ag, and Cu have been reported in a number of studies over the past 45 years. Attempts to explain this phenomenon have focused on specific adsorption and steric hindrance of cations in the IHP and OHP, respectively. However, recent calculations have raised questions about the validity of these explanations, since neither specific adsorption nor steric hindrance of cations is possible under the operating conditions used for CO₂R. In this study we present an interpretation for the effects of electrolyte cations on the electrochemical reduction of CO₂ over Ag and Cu. The essence of our findings is summarized in Figure 4. We show that the hydrated alkali metal cations in the bulk of the electrolyte are stable to hydrolysis but can undergo hydrolysis in proximity to the cathode as a consequence of coulombic interactions with the negative charge on the cathode, an effect that increases linearly with increasing cathode potential. The hydrated cations act as a pH buffer near the cathode. As discussed in Section 2 of the Supplementary Information, pK_a of the hydrated cations is determined by the charge and size of cation and the charge density on the cathode. The pK_a of cations near a cathode maintained at -1 V vs RHE decreases with increasing cation size, and consequently the buffering capability decreases in the order Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺. Consequently, the pH decreases and the CO₂ concentration increases near the cathode with increasing cation size. The resulting polarization losses at the cathode causes the FEs for H₂ and CH₄ to decrease and the FEs for CO, C₂H₄, and C₂H₅OH to increase with increasing cation size. The proposed interpretation gives satisfactory quantitative agreement between experimental observations and theoretical predictions at -1.1 V vs RHE.

At less negative applied voltages, the pH of the electrolyte near the cathode rapidly falls to that of the bulk solution and the predicted pK_a of hydrolysis becomes than that of the bulk electrolyte, pH = 6.8. For instance, at -0.7 V vs RHE, the pK_a of Li⁺ is 14.4, Na⁺ is 13.6, K⁺ is 12.3, Rb⁺ is 11.8, and Cs⁺ is 10.9 over Cu. Therefore, the cations will not undergo hydrolysis at voltages more positive than -0.7 V vs RHE. We note, however, that our experimental results show that the nature of the cation also affects the current densities at low applied voltages. This effect cannot be attributed to hydrolysis of the hydrated cations near the cathode nor, as explained in the Introduction, to the specific absorption or steric hindrance of cations. It may, instead, be due to the influence of cations in stabilizing the adsorption of CO₂ at the cathode; however, this effect would need to be very strong in order to offset the very low concentration of cations relative to Ag sites at the cathode surface. Further research work is required to identify the effects of cation nature on the current density and the distribution of products observed at applied voltages of > -0.7 V. For applied voltages < -0.8 V, the effect of polarization losses is to shift the polarization curves shown in Figures 1 (a) and (c) towards more negative voltages. It is possible to plot the partial current densities against the applied potential corrected for the polarization losses (equivalently, kinetic overpotential), which should make all plots for different cations collapse into a single plot representing intrinsic kinetics of CO₂ reduction reaction.

It is noted that the hydrolysis of hydrated cations can be effective only if i) the electrolytes are neither strongly acidic nor alkaline, ii) the pKa for hydrolysis of the hydrated cation is close to the local pH of the electrolyte, and this effect will be strongest for systems in which the local concentration of the reactant (e.g., CO₂) is pH dependent. The present study further reveals that hydrolysis of hydrated cations can be used to increase the activity and selectivity of any proton-transfer reaction on any conductive electrode. Our model can be applied to any electrode for which the reaction kinetics and specific capacitance are known. The specific capacitance is used to determine the pKa for cation hydrolysis and the kinetics are needed to specify the boundary conditions for the transport equations. Based on the concept of hydrolysis, several practical strategies can be employed to increase electrocatalytic activity and selectivity by: i) increasing the local concentration of cations by tethering or physically coating anionic ionomers to the cathode, ii) decreasing the pKa of hydrolysis by increasing the cell resistance or capacitance and iii) using multi-valent cations.³³ The pKa of multi-valent cations can be computed using equation 4 of the Supplementary Information, provided that the electronegativity of cations is <1.5, which is true for alkali metal and alkali earth cations. The hydrolysis of multi-valent cations can be included in the transport equations in a similar manner to that shown for mono-valent cations in the Supplementary Information. The multi-valent cations are better for CO₂R than the mono-valent cations, as the higher positive charge on the multi-valent cations increases the polarity of OH bond in the waters of the hydration shell which makes them easier to hydrolyze. However, their application in electrolysis is limited due to their lower solubility in aqueous solutions.

Methods

Experimental Materials and Methods

Materials: Lithium carbonate ($\geq 99.998\%$ metals basis), sodium carbonate ($\geq 99.9999\%$ metals basis), potassium carbonate ($\geq 99.995\%$ metals basis), rubidium carbonate ($\geq 99.8\%$ metals basis) cesium carbonate ($\geq 99.995\%$ metals basis), lithium chloride (99.998% metals basis), sodium chloride (99.999% metals basis), potassium chloride (99.999% metals basis), rubidium chloride ($\geq 99.95\%$ metals basis), cesium chloride ($\geq 99.999\%$ metals basis), lithium hydroxide (99.95% metals basis), sodium hydroxide (99.99% metals basis), potassium hydroxide (99.99% metals basis), rubidium hydroxide solution (99.9% metals basis) and cesium hydroxide (99.95% metals basis) were purchased from Sigma Aldrich. Copper foil (99.9999% metals basis, 0.1 mm thickness) and silver foil (99.998% metals basis, 0.25 mm thickness) were purchased from Alfa Aesar. Water-based alumina fine polishing suspension (0.05 ~ 0.3 μm) and polishing cloth (Alpha-A, 8") were purchased from Ted Pella, Inc. Carbon dioxide (99.995%), nitrogen (99.999%), helium (99.999%) and hydrogen (99.999%) were purchased from Praxair. Hydrogen, helium, nitrogen, carbon dioxide gas purifiers were purchased from Valco Instruments Co. Inc. Electrolyte solutions were prepared with 18.2 M Ω deionized (DI) water obtained from a Millipore system.

Electrode and electrolyte preparation: Copper and silver foils were cut into electrodes of 2 cm by 2 cm squares and then cleaned by sonicating for 30 min in acetone, followed by isopropanol and finally in deionized water. Cu foil was electropolished in concentrated phosphoric acid at a potential of 2.0 V for 5 min with a copper foil counter electrode, followed by rinsing with DI water and drying with a stream of

nitrogen. As Ag oxidizes during electropolishing to form a layer of AgO, we chose to mechanically polish Ag foils. Ag foil was polished mechanically using an alumina suspension down to 0.05 μm on polishing cloth and then sonicated and rinsed with DI water, and dried under nitrogen. As a result of different electrode polishing procedures, the macroscopic roughness measured using AFM was 1.0400 for Ag foil and 1.0001 for Cu foil. To prepare 0.1 M of bicarbonate solution, 0.05 M of carbonate solution was sparged for 1 h with a flow of pure CO_2 at 1 bar.

Electrochemical measurements: Electrochemical measurements were carried out using a Biologic SP-300 potentiostat. Ambient pressure CO_2/CO electrolysis was carried out in a custom-made gas-tight electrochemical cell. In brief, the working electrode is parallel to the counter electrode in order to ensure a uniform potential distribution across the surface. The geometric surface area for both of the electrodes is 1 cm^2 , the volume of the anolyte and catholyte are 1.3 ml each, and the headspace volume is approximately 3 ml. A Selemion AMV anion exchange membrane was used to separate the anodic and cathodic compartments. Before conducting CO_2/CO electrolysis, the electrolyte was purged with CO_2/CO for at least 15 min to achieve an electrolyte at pH of 6.8, thereby ensuring that the solution was CO_2/CO saturated. During electrolysis, CO_2/CO was constantly bubbled through the electrolyte at a flow rate of 5 sccm to prevent depletion of CO_2/CO and to ensure constant flow of gas through the gas chromatograph. The flow rate of CO_2/CO was controlled with a mass flow controller (MKS Instrument). For all experiments, platinum foil was used as the counter electrode and Ag/AgCl electrode (leak free series) from Innovative Instruments, Inc. was used as the reference. Data were converted to the RHE reference scale using the equation:

where the pH was 6.8. To ensure the accuracy of the reference electrodes, calibration was done with a homemade reversible hydrogen electrode. Potentiostatic electrochemical impedance spectroscopy (PEIS) was used to determine the total uncompensated resistance (R_u) by applying frequencies from 10 Hz to 30 kHz at the open circuit potential. The potentiostat compensated for 85% of R_u in situ, and the last 15% was post-corrected to arrive at accurate potentials.

HER measurements with silver: The exact same electrochemical cell as the one utilized for CO_2R was employed. However, in this case, Ar was continuously bubbled through at a flow rate of 5 sccm to create an inert environment. Also, 0.1 M chloride solutions of the different cations were used as the electrolyte. Chronoamperometry was carried out to determine the current density for hydrogen evolution on a polycrystalline silver foil as a function of potential. The potential was stepped at three minute intervals to various potentials. The current density at a specific potential was calculated as the average value during the three minute interval.

Product analysis: A gas chromatograph (Agilent Technologies) equipped with a packed HaySep Q column and a Carbon column was used for analysis of gaseous products. H_2 , CO , CH_4 , C_2H_4 and C_2H_6 were detected by a pulsed-discharge, helium ionization detector (PDHID). Calibration of the gas chromatograph was carried out using calibration gas prepared by Praxair (UN 1956). During electrolysis, CO_2/CO was allowed to flow from the electrochemical cell directly into the gas sampling loop of a gas chromatograph for online gaseous product analysis, which was carried out every 25 min. For all experiments, electrolysis was allowed to proceed for 1.5 h with gas analysis done at the 10, 35, 60 and 85 min.

Liquid products were collected from the cathode and anode chambers after electrolysis and analyzed by High-Performance Liquid Chromatography (HPLC) on an UltiMate 3000 HPLC (Thermo Scientific). Vials containing liquid samples were placed in an autosampler holder and 10 μL of sample was injected

into the column. The column used was an Aminex HPX 87-H (Bio-Rad) and diluted sulfuric acid (1 mM) was used as the eluent. The temperature of the column was maintained at 60°C in a column oven, and the separated compounds were detected with a refractive index detector (RID). The expected products of CO₂R were analyzed as well by HPLC to produce a standard calibration curve at 60°C (i.e., formate, acetate, ethylene glycol, ethanol, and n-propanol).

Double-layer capacitance measurements: The double-layer capacitance values were measured utilizing methods as described by Kanan and co-workers¹³. In brief, this was done by performing cyclic voltammetry in a non-Faradaic potential regime. The exact same electrochemical cell as the one utilized for CO₂R was employed. In this case, a Nafion proton exchange membrane was used and 0.1 M HClO₄ was used as the electrolyte. Cyclic voltammetry was performed with different scan rates and the geometric current density was plotted against the scan rate. The double layer capacitance was determined by calculating the slope of this graph.

Computational Methods

The mathematical model for the electrochemical cell previously developed by Singh et al.²² was used to analyze the effects of cation size on the overall activity and selectivity of Ag and Cu cathodes. A synopsis of the model is given in the Section 2 of the Supplementary Information. The mathematical model was solved using COMSOL Multiphysics 4.3b to obtain product current densities at -1 V vs RHE in 0.1 M MHCO₃ electrolyte.

Supporting Information

Theory of hydration and hydrolysis of metal ions; prediction of partial current density; effect of cations on the hydrogen evolution reaction at neutral pH; effect of cations on the CO reduction reaction in alkaline electrolyte; effect of cation on the Faradaic Efficiency for CO₂R products produced over Ag and Cu at -1 V vs. RHE; Tables S1-S7; Figures S1-S4.

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Authors Contributions

M.R.S, Y.K, and Y.L. contributed equally to this work.

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Competing Financial Interests

Authors declare no competing financial interests.

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TOC Graphics

