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The effect of electrolyte composition on the electroreduction of CO$_2$ to CO on Ag based gas diffusion electrodes

Sumit Verma,$^a$ Xun Lu,$^a$ Sichao Ma,$^b$*c Richard I. Masel$^d$ and Paul J. A. Kenis$^a$*$^b$

Electroreduction of CO$_2$ to C$_2$-C$_3$ chemicals can be a potential strategy for utilizing CO$_2$ as a carbon feedstock. In this work, we investigate the effect of electrolyte on the electroreduction of CO$_2$ to CO on Ag based gas diffusion electrodes. Electrolyte concentration was found to play a major role in the process for the electrolytes (KOH, KCl, and KHCO$_3$) studied here. Several fold improvement in partial current densities for CO ($j_{\text{CO}}$) was observed on moving from 0.5 M to 3.0 M electrolyte solution independent of the nature of the anion. $j_{\text{CO}}$ as high as 440 mA cm$^{-2}$ with energy efficiency (EE) = 42% and 230 mA cm$^{-2}$ with EE = 54% was observed when using 3.0 M KOH. Electrochemical impedance spectroscopy showed that both the charge transfer resistance ($R_{\text{ct}}$) and the cell resistance ($R_{\text{cell}}$) decreased on moving from 0.5 M to 3.0 M KOH electrolyte. Anions were found to play an important role with respect to reducing the onset potential for CO in the order OH$^-$ < HCOO$^-$ < CO$_3^{2-}$ < Cl$^-$ < OH$^-$ < HCOO$^-$ < Cl$^-$ < CO$_3^{2-}$ at pH = 0. The decrease in $R_{\text{ct}}$ on increasing electrolyte concentration and the effect of anions on the cathode can be explained by an interplay of different interactions in the electrical double layer that can either stabilize or destabilize the rate limiting CO$_2$ radical. EMIM based ionic liquids and 1:2 Choline Cl ured based deep eutectic solvents (DES) have been used for CO$_2$ capture but exhibit low conductivity. Here, we investigate if the addition of KCl to such solutions can improve conductivity and hence $j_{\text{CO}}$. Electrolytes containing KCl in combination with EMIM Cl, Choline Cl, or DES showed a two to three fold improvement in $j_{\text{CO}}$ in comparison to those without KCl. Using such mixtures can be a strategy for integrating the process of CO$_2$ capture with CO$_2$ conversion.

Introduction

Carbon dioxide (CO$_2$) levels in the atmosphere have risen from 320 to more than 400 ppm in the past 50 years.$^1$ In a recent paper Feldman et al. provided the first experimental evidence of how rising CO$_2$ levels are affecting the Earth’s surface energy balance leading to adverse environmental impact.$^2$ Simultaneous implementation of multiple approaches has been proposed to mitigate the negative effects of high global CO$_2$ emissions.$^3$ These include switching from traditional fossil fuel power plants to renewable energy sources, increasing energy efficiency of vehicles and buildings, and the capture and sequestration of CO$_2$. Electrocatalytic conversion of CO$_2$ into value added chemicals and fuels could also be an important means of reducing CO$_2$ emissions.$^4, 4$ Depending on the catalyst, electrolyte, and reaction conditions being used,$^5, 10$ different products such as methanol (CH$_3$OH),$^{11-13}$ formic acid (HCOOH),$^{14-17}$ and carbon monoxide (CO)$^{18-25}$ are formed. Furthermore, this approach can also be used to store otherwise wasted excess energy from renewable sources when supply exceeds demand.

In this work, we focus on the electrocatalytic conversion of CO$_2$ to CO in an electrochemical flow reactor developed earlier in our group.$^{14}$ CO is an important carbon intermediate used for the production of chemicals such as acetic acid,$^{24}$ phosgene,$^{25}$ and aldehydes.$^{25}$ Furthermore, mixtures of H$_2$ and CO ("syngas") can be used to produce higher hydrocarbons and combustion fuels via the Fischer-Tropsch process.$^{27, 28}$ Although the standard reduction potential for conversion of CO$_2$ to CO is low (i.e., -0.109 V vs. SHE at pH = 0), the reaction suffers from high activation overpotential.$^{10, 29}$ The reason for such a high overpotential is often attributed to the high equilibrium potential associated with the formation of the radical intermediate CO$_2^\cdot$ during the first step of the reaction.$^{30}$ This reaction proceeds with an equilibrium potential value of -1.9 V vs. SHE.$^{21}$

Starting with the seminal work of Hori et al.$^{21}$ that pointed out Au, Ag, and Zn to be active for this reaction, a lot of cathode catalysts have been reported.$^{18, 20, 22, 23}$ In prior work, we as well as others have studied Ag catalysts with respect to the electroreduction of CO$_2$ to CO.$^{21, 34, 36}$ We have also looked at the effect of catalyst layer deposition method for electrode preparation,$^{37}$ and the effect of support materials such as TiO$_2$ on this electrochemical reaction.$^{23}$
Electrolytes have been shown to play a major role in the electroreduction of CO2 to CO. For example, Rosen et al. proposed the use of an ionic liquid electrolyte 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF4) as a co-catalyst to stabilize the radical intermediate CO2.38 CO was formed at an onset cell potential of -1.5 V, much lower than the onset potential observed when using electrolytes such as aqueous KCl, or acetonitrile (nearly -2.2 V). Sun et al. showed that the addition of ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TF2N) lowered the reduction potential and favored the formation of CO over oxalate when using Pb on the cathode.39 Zhu et al. used choline chloride (Choline Cl) to suppress hydrogen (H2) formation and lower the reduction potential of bicarbonate (HCO3-) to CO.40 However, in most of the ionic liquid related work, the partial current density for CO (jCO) was typically low (less than 5 mA cm\(^{-2}\)). This observation was attributed to the low ionic conductivity of such solutions.38 Several others have used EMIM based ionic liquids and Choline Cl based deep eutectic solvents (DES) for post combustion CO2 capture as well.41,42

In other work, Thorson et al. investigated the influence of several different alkali cations on the electroreduction of CO2 to CO.44 Analysis of the Faradaic efficiencies suggested that larger cations suppressed H2 evolution while favoring CO2 reduction. Earlier Hori et al. showed that the choice of the cation for bicarbonate electrolytes can severely change the distribution of products on Cu cathodes.45 Wu et al. reported a difference in activity and selectivity of Sn electrodes when different electrolytes such as K2SO4, KCl, or NaHCO3 were used.46

Here, we attempt to further understand the effect of electrolytes on the electroreduction of CO2 to CO. We first look at how changing the electrolyte concentration affects jCO. We then investigate the effect of anions on onset potentials and jCO for this reaction. Using electrochemical impedance spectroscopy (EIS), we try to provide mechanistic insights into the effect of electrolyte concentration and anions on the reaction. Subsequently, we design and explore a combination of EMIM Cl, Choline Cl, and a Choline Cl based DES (1:2 Choline Cl urea mixture) with KCl to develop a strategy to improve jCO for ionic liquid and DES based electrolytes by improving their conductivity. Such an electrolyte mixture can be used for integrating the process of CO2 capture with CO2 conversion.

Experimental
Preparation of electrodes
The cathodes were prepared by spraying the catalyst ink on a Sigracet 35 BC gas diffusion layer electrode (GDL) (Ion Power Inc.) using an automated air-brush setup.37 Four cathodes were made at a time. Unsupported Ag nanoparticles (< 100 nm, 99.5% trace metal basis, Sigma Aldrich) were used as the catalyst. The catalyst ink was prepared by mixing 42 mg of Ag with 1600 μL of E-pure water (> 17.9 MΩ cm), 55 μL of Nafion solution (5 wt%, Fuel Cell Earth), and 1600 μL of isopropyl alcohol. The mixture was then sonicated (Vibra-Cell ultrasonic processor, Sonics & Materials) for 20 minutes. The resulting solution was then airbrushed onto a GDL with a geometric area of 2.5 x 0.8 cm\(^2\). The actual catalyst loading was determined by weighing the GDL before and after deposition. Anodes were prepared by hand painting a mixture of 4.5 mg IrO2 non-hydrate (99.99% metals basis, Ir 84.5% min, Alfa-Aesar), 200 μL of E-pure water (> 17.9 MΩ cm), 15 μL of Nafion solution (5 wt%, Fuel Cell Earth), and 200 μL of isopropyl alcohol on a Sigracet 35 BC gas diffusion layer electrode (GDL) (Ion Power Inc.) with a geometric area of 2.5 x 0.8 cm\(^2\). Hand painting was done using a paintbrush. The GDL was weighed before and after painting to determine the actual catalyst loading. All the cathodes had a final loading of 2 ± 0.1 mg cm\(^{-2}\) Ag and all anodes had a final loading of 2 ± 0.1 mg cm\(^{-2}\) IrO2.

Preparation of electrolytes
All salts were purchased and used without any further purification. Different concentrations and compositions of electrolyte were prepared by dissolving the appropriate amount of salt in E-Pure water (> 17.9 MΩ cm) to get a final solution volume of 100 mL. The following salts were used: KCl (product number: BP366, purity: 99.0% min, supplier: Fischer Scientific), KOH (product number: P250, purity: assay 86.3%, supplier: Fischer Scientific), KHCO3 (product number: 237205, purity: 99.7% granular, supplier: Sigma Aldrich), EMIM Cl (product number: IL-0093, purity: > 98%, supplier: Iolitec), Choline Cl (product number: C1879, purity: > 98%, supplier: Sigma Aldrich), and urea (product number: 8648-04, purity: > 99%, supplier: Macron Fine Chemicals). The conductivity and pH of the electrolytes was measured using an Orion 4 star pH-conductivity meter at 20 °C when required.

Operation of electrochemical flow reactor
A slightly modified version of the flow reactor reported earlier by us was used for the electrochemical experiments.14 The only difference in the new design from the old was that we replaced the graphite current collector and the aluminium anode with a single stainless steel anode current collector. Similar to our previous design, a mass flow controller (Smart Trak 2, Sierra Instruments) was used to flow CO2 gas (S.J. Smith Welding Supply) at a set flow rate of 17 scm over the cathode GDL. High flow rates were used in order to avoid mass transfer limitations and the issue of CO2 solubility in the electrolyte. The strategy resulted in a dilution of the H2 concentration in the effluent gas stream, which helps it in being analysed accurately by a He carrier gas. A syringe pump (PHD 2000, Harvard Apparatus) was used to pump the electrolyte between the cathode and the anode at a flow rate of 0.5 mL min\(^{-1}\). A pressure controller (Cole Parmer, 00268TC) was used to maintain low pressure (14.20 psig) in the downstream of the reactor to facilitate easier transfer of the gas products formed on the cathode surface to the effluent gas stream. A potentiostat (Autolab PGSTAT-30, EcoChemie) was used to carry out the electrochemical reaction. Experiments were performed in the potentialistatic electrolysis mode and under ambient conditions. A fresh cathode and a...
fresh anode were used for all experiments. After stepping on to a potential, the current was stabilized for at least 180 seconds before the gas analysis was performed. The gaseous product stream was analysed by sampling 1 mL of the effluent gas stream diverted into the gas chromatograph (Thermo Finnigan Trace GC) operating in the thermal conductivity detection (TCD) mode, with a Carboxen 1000 column (Supelco) and Helium as the carrier gas at a flow rate of 20 SCCM. The column was held at 150 °C and the TCD detector at 200 °C. Liquid products were not analysed for this reaction. Since GDL were being used as the electrodes, fluctuations in current densities were observed due to gas bubbling. Current was averaged over a time period of 240 seconds after the gas analysis was started. A triple injection was used to average out the gaseous product peaks over time. Error bars on the different plots represent errors due to the difference in the three injections and the fluctuations in current density. Individual electrode potential was recorded by a multimeter (AMPROBE 15XP-B) connected between the electrode and the reference electrode (Ag/AgCl; 3 mol kg⁻¹ KCl, RE-5B, BASi) as shown in our previous work.⁷ The reference electrode was placed in the inlet stream of the electrolyzer to avoid the effect of any pH changes (summarized in Table S1) that occur in the flow cell as a function of electrolyte, cathode potential, and current density. All electrode potentials were converted to RHE according to the Nernst equation (E_RHE = 0.210 + E_Ag/AgCl + 0.059*pH).

**Electrochemical impedance spectroscopy**

Electrochemical impedance spectroscopy was performed on the flow cell using the frequency response module of the potentiostat (Autolab PGSTAT-30, EcoChemie). The spectrum was recorded in a potentiostatic mode at a cell potential of -2.00 V or -2.25 V. Higher potentials were not used as a significant amount of noise in the data was obtained due to gas bubbling at the GDL. Moreover, at lower cell potentials charge transfer plays a more important role than the conductivity of the electrolyte solution and hence a better understanding of kinetics can be obtained. 100 different

![Graphs](image)

*Fig. 1* Partial current density for CO as a function of (a) cell potential, (b) energy efficiency, and (c) cathode potential, as well as (d) partial current density for H₂ as a function of cathode potential for four different KOH electrolyte concentrations when using Ag nanoparticles as the cathode catalyst and IrO₂ as the anode catalyst.
frequencies (range: 10 kHz to 0.1 Hz) were used to scan the system in a logarithmic step. A single sine wave with amplitude of 10 mV was used for the sweep. The high frequency intercept on the x-axis of the Nyquist plot represents the internal resistance of the cell ($R_{\text{cell}}$), which includes the contact resistance and the solution resistance. The diameter of the semi-circle represents the charge transfer resistance ($R_{\text{ct}}$) for the reaction.

Results and discussion

Effect of electrolyte concentration

The effect of electrolyte concentration on electrochemical CO$_2$ reduction was studied by utilizing different concentrations of aqueous KOH as the electrolyte: 0.5, 1.0, 2.0, and 3.0 M (Fig. 1). Almost a four-fold improvement in $j_{\text{CO}_2}$ was observed on going from 0.5 M to 3.0 M KOH at a cell potential of -3.00 V (Fig. 1(a)). Similar trends were observed with respect to the cathode potential (Fig. 1(c)). A $j_{\text{CO}_2}$ as high as 440 mA cm$^{-2}$ was obtained at an energetic efficiency of 42% (calculated using a method described earlier$^6$), while an energy efficiency of 54% can be obtained in combination with a $j_{\text{CO}_2}$ of 230 mA cm$^{-2}$ (Fig. 1(b)). To the best of our knowledge the $j_{\text{CO}_2}$ values reported here are some of the highest reported in the literature when operating at ambient conditions. Other work showing similar current density levels (up to 300 mA cm$^{-2}$) was performed at high pressures (> 15 atm) and high overall cell potentials (more negative than -3.00 V).$^{36}$

To confirm whether the observed trend of improving $j_{\text{CO}_2}$ with increasing electrolyte concentration is a more general phenomenon, we carried out experiments with aqueous electrolytes containing different concentrations of KCl and KHCO$_3$. A similar trend of increasing $j_{\text{CO}_2}$ upon increasing electrolyte concentration was observed in all cases independent of the nature of the anion (Fig. 2). Min et al.$^{48}$ and Murata et al.$^{49}$ had earlier observed this phenomenon for KHCO$_3$. They explained this behavior by indicating that an increase in the concentration of HCO$_3^-$ ions removed OH$^-$ formed in the process thereby shifting the reaction equilibrium.

Fig. 2 Partial current density for CO and H$_2$ using 4 different electrolyte concentrations of (a, b) KCl and (c, d) KHCO$_3$ when using Ag nanoparticles as the cathode catalyst and IrO$_2$ as the anode catalyst.
to favor CO production. Although, this might be a possible explanation for the case of KHCO$_3$, our results indicate that the improvement in $j_{CO}$ is independent of the nature of the anion and therefore a more general factor might be at play here.

To gain further mechanistic insights into the observed phenomena, we performed electrochemical impedance spectroscopy on the electrochemical flow reactor at a cell potential of -2.00 V using different concentrations of KOH as the electrolyte. Increasing the electrolyte concentration leads to both a reduction in $R_{cell}$ and $R_{ct}$ (Fig. 3). The observed reduction in $R_{cell}$ can be explained by the improvement in ionic conductivity upon increasing the ion concentration of the electrolyte. Since the improvement in $j_{CO}$ was independent of the nature of the anion, the observed reduction in the $R_{ct}$ potentially could be attributed to an improved stabilization of the rate limiting CO$_2^-$ radical intermediate by a higher concentration of K$^+$ ions in the outer Helmholtz plane (OHP) of the electrical double layer. Prior work suggests that K$^+$ can act as a co-catalyst by forming ion pairs or ion bridges with the CO$_2^-$ radical thereby stabilizing it. Cations also have been shown to stabilize anionic or even neutral intermediates in a similar fashion for certain other electrocatalytic reactions. Higher concentrations of K$^+$ and OH$^-$ will lead to a more compact double layer at the electrode-electrolyte interface leading to a smaller Debye length or an OHP closer to the electrode surface. In analogous fashion, in the area of heterogeneous catalysis, alkali metal amalgams have been shown to catalyze the gas phase reduction of CO$_2$ to CO by forming complexes with the reacting CO$_2$ species.

**Effect of anions**

In many electrocatalytic reactions, the anions present in the electrolyte also play an important role. However, the role of anions in electroreduction of CO$_2$ has not been explored extensively. To study the effect of anions, we compared the i-V curves for 2.0 M KOH, 2.0 M KCl, and 2.0 M KHCO$_3$ (Fig. 4). The here observed onset potential for reduction of CO$_2$ to CO was found to vary in the order OH$^-$ (-0.13 V vs. RHE) < HCO$_3^-$ (-0.46 V vs. RHE) < Cl$^-$ (-0.60 V vs. RHE) (Fig. 4(a)), which corresponds to overpotentials of 0.02 V, 0.35 V, and 0.49 V, respectively, for these three electrolytes. An improvement in electrochemical performance while using KOH is consistent with prior work. The Faradaic efficiency and $j_{CO}$ was observed to vary in the order of OH$^-$ > HCO$_3^-$ > Cl$^-$ (Table 1). In most cases, the sum of the Faradaic efficiencies for CO and H$_2$ was > 85%. HCOOH along with minor liquid products (CH$_3$OH, C$_2$H$_5$OH), and minor gaseous products (CH$_4$) should constitute the other 15%.

Electrochemical impedance spectroscopy carried out at a cell potential of -2.25 V reveals an order of magnitude difference between the observed $R_{ct}$ values for KOH and for KCl, while the $R_{ct}$ values for HCO$_3^-$ resides in between (Fig. 5). The ratio of $R_{ct}$ between KCl and KOH (= 80) is approximately equal to the ratio of $j_{total}$ between the two at a cell potential of -2.25 V. As explained initially by Hori et al. and also demonstrated by us later, one of the most important roles of the anion is to modulate surface pH (i.e., act as a buffer), which in turn limits the availability of protons on the surface, thereby increasing the number of active sites.
available for electroreduction of CO₂ to CO. Such reasoning can help explain the higher \( I_{CO} \) and Faradaic efficiencies in the presence of OH⁻ and HCO₃⁻ anions as those parameters are directly correlated to the number of available active sites. However, the observed shift in onset potentials cannot be satisfactorily explained by the effect of pH alone. Even though H₂ evolution competes with CO₂ reduction, a few active sites should be available for CO₂ to convert to CO, and hence an onset should be seen. Analogous to these observations for CO₂ reduction, the specific adsorption of anions on the electrode surface has been shown to help stabilize or destabilize key reaction intermediates in the electrocatalytic reduction of O₂ and NO₃⁻.\(^\text{52,59}\) Smaller anions (such as OH⁻) with a large solvation shell tend to interact with the electrode surface only through electrostatic forces and are mostly located beyond the OHP (Fig. 6(a)). Weakly solvated anions (such as Cl⁻) on the other hand tend to interact directly (specific adsorption) with the electrode surface (Fig. 6(b)).\(^\text{60}\) The Gibbs free energy for adsorption of Cl⁻ on a Ag surface is more favourable (-15 kcal mol\(^{-1}\)) than Gibbs free energy for OH⁻ (-3.4 kcal mol\(^{-1}\)).\(^\text{61}\) Since specific adsorption of anions play a major role especially at low potentials,\(^\text{62}\) we anticipate that this phenomenon helps cause the observed shift in onset potential for CO₂ reduction. The presence of Cl⁻ ions on the

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<th>FE CO (%)</th>
<th>FE H₂ (%)</th>
<th>Cathode Potential (vs. RHE)</th>
<th>( I_{total} ) (mA cm(^{-2}))</th>
<th>FE CO (%)</th>
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**Fig. 5** Nyquist plot for different electrolytes obtained via electrochemical impedance spectroscopy at a cell potential of -2.25 V.

**Fig. 6** Schematic illustrations of processes in the double layer that play a role in the kinetics of CO₂ to CO conversion on a Ag cathode when using (a) KOH or (b) KCl as the electrolyte.
electrode surface may destabilize the rate limiting $\text{CO}_2^-$ species and hence limit $\text{CO}_2$ reduction. The results we report here may appear to deviate from a recent paper that highlights the $\text{Cl}^-$ anion favoring $\text{CO}$ formation to a greater extent than the $\text{HCO}_3^-$ anion.\textsuperscript{53} Moreover, the Faradaic efficiencies for $\text{CO}$ reported there when using KCl as the electrolyte (< 65%) are significantly lower than the values we observe here (> 80%) with similar electrolyte. These differences can probably be attributed to the use of a different cathode catalyst and preparation method: Airbrushed Ag nanoparticles are used in our work, as opposed to in situ AgCl-derived Ag nanocorals in the work by Hsieh et al. Similar arguments have been reported for a Cu catalyst by Lee et al.\textsuperscript{64}

Since, in our work, KOH and KHCO$_3$ tend to perform better than KCl, one might argue that $\text{CO}_3^{2-}$ or HCO$_3^-$ may be the reacting species. However, earlier work has established that $\text{CO}_2$ is the reacting species and not $\text{CO}_3^{2-}$ or HCO$_3^-$.\textsuperscript{65} At higher electrode potentials, the trends in $j_{\text{CO}}$ can be explained in terms of the higher electrolyte conductivity of KOH in comparison to the conductivity of the other electrolytes. In addition, since our electrode preparation technique involved the use of Nafion as a binder for the Ag nanoparticle catalyst, we investigated whether sulfonate adsorption plays a role in the electroreduction of $\text{CO}_2$ to CO. Three control experiments, all using a cathode comprised of 2 mg cm$^{-2}$ Ag nanoparticles on a gas diffusion electrode without Nafion and an anode comprised of 2 mg cm$^{-2}$ IrO$_2$ on a gas diffusion electrode, were performed using 2.0 M KOH, KHCO$_3$, and KCl, respectively, as the electrolyte. Removing Nafion from the cathode catalyst layer did not have a significant effect on the electrochemical performance in terms of $j_{\text{CO}}$ and onset potential when using KCl or KHCO$_3$ as the electrolyte (Fig. S1). However, when using KOH as the electrolyte, the onset cathode potential for CO dropped from -0.13 V to -0.08 V vs. RHE, which is within the error limits (mainly due to inaccuracy in pH measurements) of the $E^0$ value of -0.10 V vs. RHE for CO production. The fact that the onset is now equal to the standard potential indicates that sulfonate adsorption is important when using KOH as the electrolyte. This observation in turn supports our earlier argument that specific anion adsorption is important for determining the onset potential for the electroreduction of $\text{CO}_2$ to CO.

As shown in our earlier work,\textsuperscript{56} electrolytes also affect the

![Graphs showing current density for CO and H$_2$ using different electrolytes.](image-url)
chemistries taking place on the anode. When using KOH as the electrolyte, the O\textsubscript{2} evolution reaction takes place at the anode. As a result, the OH\textsuperscript{-} generated at the cathode has a greater chance to get consumed at the anode. Such a continuous removal of the OH\textsuperscript{-} species from the cathode can enhance CO\textsubscript{2} reduction.

Utilizing mixtures of KCl with EMIM Cl, Choline Cl, and Choline Cl based DES Imidazolium based ionic liquids and Choline Cl based deep eutectic solvents (DES) such as a 1:2 mixture of Choline Cl and urea are known to be active for CO\textsubscript{2} absorption.\textsuperscript{41-43} So, one can imagine using these solutions as electrolytes to combine CO\textsubscript{2} capture with CO\textsubscript{2} conversion. However, one of the biggest drawbacks of these solvents is that their conductivity is low, and hence they exhibit low current densities for electrochemical reactions. To improve the conductivity, we designed aqueous electrolyte mixtures comprised of 1.5 M KCl with 0.5 M of, respectively, EMIM Cl, Choline Cl, and DES (1:2 mixture of Choline Cl and urea). Since the concentration of electrolyte plays an important role in the process, the total concentration was kept constant at 2.0 M for all three mixtures. The conductivity of all three mixtures was better than the conductivity of the additives by themselves at 2.0 M concentration (Table 2). A 2 to 3 times improvement in j\textsubscript{CO} was observed for each mixture in comparison to neat 2.0 M EMIM Cl, 2.0 M Choline Cl, and 2.0 M (1:2) Choline Cl urea DES (Fig. 7, 8). These j\textsubscript{CO} values were comparable to the j\textsubscript{CO} obtained with aqueous 2.0 M KCl solution. The Faradaic efficiency for CO was greater for the mixtures when compared to the corresponding values obtained with the 2.0 M KCl electrolyte (Table 2). This is probably due to a greater stabilization of the rate limiting formation of the CO\textsubscript{2}\textsuperscript{-} intermediate by the ammonium species. However, note that at the same time the specific adsorption of ammonium species (when using EMIM\textsuperscript{+} or Choline\textsuperscript{+}) would decrease the number of active sites available for CO\textsubscript{2}\textsuperscript{-}. In addition, for j\textsubscript{CO} values greater than 100 mA cm\textsuperscript{-2}, the electrolyte conductivity starts to play an important role in the process. As a result, the mixtures exhibit j\textsubscript{CO} values similar to those observed when using 2.0 M KCl electrolyte. Since the DES combination of Choline Cl and urea mixed with KCl performs comparably to the aqueous KCl electrolyte, the strategy of mixing

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
<th>Conductivity (mS cm\textsuperscript{-1})</th>
<th>j\textsubscript{total} (mA cm\textsuperscript{-2})</th>
<th>Cathode Potential (vs. RHE)</th>
<th>FE\textsubscript{CO} (%)</th>
<th>FE\textsubscript{H\textsubscript{2}} (%)</th>
<th>Cathode Potential (vs. RHE)</th>
<th>FE\textsubscript{CO} (%)</th>
<th>FE\textsubscript{H\textsubscript{2}} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 M KCl</td>
<td>6.54</td>
<td>175</td>
<td>-0.81</td>
<td>13.7</td>
<td>77.6%</td>
<td>8.5%</td>
<td>-0.99</td>
<td>51.4</td>
<td>72.3%</td>
</tr>
<tr>
<td>2.0 M EMIM Cl</td>
<td>4.48</td>
<td>74.1</td>
<td>-0.86</td>
<td>8.0</td>
<td>91.9%</td>
<td>4.3%</td>
<td>-1.03</td>
<td>25.0</td>
<td>89.3%</td>
</tr>
<tr>
<td>1.5 M KCl + 0.5 M EMIM Cl</td>
<td>5.24</td>
<td>136</td>
<td>-0.83</td>
<td>11.5</td>
<td>82.3%</td>
<td>27.5%</td>
<td>-1.01</td>
<td>42.2</td>
<td>79.6%</td>
</tr>
<tr>
<td>2.0 M Choline Cl</td>
<td>5.92</td>
<td>74.3</td>
<td>-0.82</td>
<td>8.7</td>
<td>79.9%</td>
<td>5.9%</td>
<td>-1.00</td>
<td>27.6</td>
<td>78.0%</td>
</tr>
<tr>
<td>1.5 M KCl + 0.5 M Choline Cl</td>
<td>6.15</td>
<td>142.6</td>
<td>-0.81</td>
<td>13.6</td>
<td>86.6%</td>
<td>12.3%</td>
<td>-1.00</td>
<td>47.6</td>
<td>85.6%</td>
</tr>
<tr>
<td>2.0 M (1:2) Choline Cl Urea</td>
<td>6.45</td>
<td>34.5</td>
<td>-0.68</td>
<td>3.3</td>
<td>81.9%</td>
<td>8.9%</td>
<td>-0.83</td>
<td>11.6</td>
<td>94.1%</td>
</tr>
<tr>
<td>1.5 M KCl + 0.5 M (1:2) Choline Cl Urea</td>
<td>6.52</td>
<td>131.4</td>
<td>-0.72</td>
<td>5.2</td>
<td>81.7%</td>
<td>8.4%</td>
<td>-0.87</td>
<td>22.1</td>
<td>85.1%</td>
</tr>
</tbody>
</table>

Table 2 Total current density (j\textsubscript{total}), cathode potential and Faradaic efficiencies (FE) for both CO and H\textsubscript{2} for different mixtures of KCl with EMIM Cl, Choline Cl and 1:2 Choline Cl Urea based DES at cell potentials of -2.50 V and -2.75 V.

Fig. 8 Comparison of partial current density for (a) CO and (b) H\textsubscript{2} for different electrolytes, including deep eutectic solvents (DES), when using Ag nanoparticles as the cathode catalyst and IrO\textsubscript{2} as the anode catalyst.
DES or ionic liquids with a salt of higher conductivity can be used to combine the process of CO₂ capture and conversion.

Similar improvements in performance were also observed for mixtures of 2.5 M KCl with 0.5 M of EMIM Cl and DES (Fig. S2). However, the final combination will have to be optimized by balancing the amount of CO₂ that needs to be captured (controlled by EMIM or DES content) with the rate of conversion of CO₂ to CO (controlled by KCl). Furthermore, a rise in pH (from 6.52 to 10.02) was observed when using 1.5 M KCl + 0.5 M 1:2 Choline Cl urea DES at relatively high j<sub>CO₂</sub> (Table S1). Such a rise can have a detrimental effect on the stability of these electrolytes as the OH<sup>-</sup> abstracts the tertiary hydrogen on the ammonium ion responsible for capturing CO₂. As a consequence, the electrolyte would have to be regenerated, i.e., neutralized before recycling back to the electrolyzer.

Conclusions

Electrolyte composition is known to play an important role in electrochemical processes, and this certainly is the case for the electroreduction of CO₂ to CO on Ag studied here. We observed that increasing the concentration of the ionic species in the electrolyte (KOH, KCl, and KHCO₃) leads to an increase in j<sub>CO₂</sub> irrespective of the nature of the anion. j<sub>CO₂</sub> values as high as 440 mA cm<sup>-2</sup> were obtained when using aqueous 3.0 M KOH as the electrolyte. Both R<sub>CO₂</sub> and R<sub>dev</sub> decrease with increasing electrolyte concentration. Decrease in R<sub>CO₂</sub> indicates a larger extent of stabilization of the rate limiting CO₂ radical. Anions were also found to play a significant role in the process with the onset potential for CO formation shifting in the order OH<sup>-</sup> > HCO₃<sup>-</sup> > Cl<sup>-</sup>. Interplay of several factors such as pH, conductivity, and, more importantly, specific adsorption of certain anions on the electrode surface can be used to explain the various observed phenomena. More rigorous computational efforts or spectro-electrochemical experiments will be needed to further unravel or confirm proposed mechanisms. Deeper understanding of how electrolyte composition affects (and ideally promotes) the electroreduction of CO₂ can guide the design and associated optimum operation conditions of more efficient electrocatalytic systems.

Mixtures of KCl with, respectively, Choline Cl, EMIM Cl, or DES (1:2 mixture of Choline Cl and urea) were also explored because of their potential to enhance CO₂ absorption. Higher j<sub>CO₂</sub> values were observed when using these mixtures as the electrolyte compared to when using neat aqueous Choline Cl, EMIM Cl, or DES of equal concentration. These electrolyte mixtures hold promise to be used as a strategy to integrate the processes of CO₂ capture with CO₂ conversion.

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Notes and references
