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Direct Reduction of Carbon Dioxide to Formate in High-Gas-Capacity Ionic Liquids at Post-Transition-Metal Electrodes

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As an approach to combat the increasing emissions of carbon dioxide in the last 50 years, the sequestration of carbon dioxide gas in ionic liquids has become an attractive research area. Ionic liquids can be made that possess incredibly high molar absorption and specificity characteristics for carbon dioxide. Their high carbon dioxide solubility and specificity combined with their high inherent electrical conductivity also creates an ideal medium for the electrochemical reduction of carbon dioxide. Herein, a lesser studied ionic liquid, 1-ethyl-3-methylimidazolium trifluoroacetate, was used as both an effective carbon dioxide capture material and subsequently as an electrochemical matrix with water for the direct reduction of carbon dioxide into formate at indium, tin, and lead electrodes in good yield (ca. 3 mg$\,h^{-1}\,cm^{-2}$).

Introduction

Carbon dioxide is a well-known atmospheric pollutant.[1] In the period between 1958 and 2004, emissions from burning fossil fuels increased atmospheric carbon dioxide concentrations from 315 to 377 ppmv; the largest increase recorded in such a time period.[2] Concern that increased atmospheric CO_2 concentrations are responsible for terrestrial surface warming has lead to efforts focused on the reduction of CO_2 emissions. A possible mitigation strategy involves the capture and utilization (CCU)[3] of carbon dioxide towards value-added products, such as fuels or bulk chemicals. This strategy also combats the growing problem of energy displacement facing renewable energy sources. The energy displacement problem is that renewable energy is often generated in locations or at times that do not align with consumption demands. The conversion of this electrical energy into chemical energy in the form of energy-dense liquids allows its transport and storage for use when and where it is most required.

It is thought that the rate-determining transformation for the electrochemical reduction of carbon dioxide is the bending of the linear O=C=O molecule.[4] This step represents the formation of a highly energetically unfavorable radical anion intermediate towards reduced products. Thus, the thermodynamic potential for the formation of this radical from CO_2 is about −2.1 V versus a standard calomel electrode (SCE) in aqueous media,[4] whereas the theoretical thermodynamic reduction potential for the reduction of CO_2 to formate is only about −0.67 V versus SCE.[4] Proceeding via this free radical anion intermediate therefore represents a severe energy penalty and an alternative low-energy pathway must be traversed. This may be achieved by using proton-transfer processes and surface-bound states to lower the energy of the intermediate.

As a direct carbon dioxide reduction electrode, indium is known to produce mainly formate.[5] Hori has suggested that indium does not adsorb the intermediate radical anion strongly.[4b] This nonassociative mechanism may account for the selectivity of the heavy post-transition metals, including indium, for formate and not higher carbon products or CO.

Ionic liquids are becoming a leading technology in the area of CO_2 capture and conversion,[6] and much research has focused on the use of task-specific ionic liquids (TSILs) as highly specific storage media for large amounts of CO_2. A significant portion of these TSILs are based on the use of room-temperature ionic liquids (RTILs) that incorporate pendant alcohols and ethers,[7] amino acids,[8] or amines.[9] However, little research has been conducted into the subsequent electrochemical reduction of carbon dioxide in these environments. Non-electrochemical examples of CO_2 activation in TSILs to make formate[10] and oxazolidinones[8] have been reported. A detailed review of non-electrochemical CCU methodology in TSILs has been presented by He and co-workers.[11]

A unique set of TSILs for the absorption of CO_2 are the 1-alkyl-3-methylimidazoium acetates, which seem to be ideal ionic liquids for the sequestration of CO_2, since they can absorb up to 27 mol% CO_2[12] or equimolar quantities with the inclusion of a superbase.[13] The mechanism for this unique ability of acetate-based imidazolium ionic liquids to absorb so much carbon dioxide has been a matter of some debate. Carvalho et al. have suggested an acid–base interaction[14] between carbon dioxide (acid) and the acetate anion (base), although it appears that deprotonation of the C-2 hydrogen of the imidazolium group by the basic acetate anion is more likely to be involved.[12] This same activity is not seen for other weak acid anions.[15]

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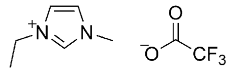
The controversy of this mechanism is highlighted in the two-step mechanism proposed by Gurau et al.,[16] in which a free carbene is formed, followed by nucleophilic attack of the carbene on the CO_2 carbon to give a C-2-bound carboxylate, which has been detected by crystallography and Raman spectroscopy.[17] As a result, acetic acid may also be formed, and has been detected by observation of its characteristic odor, although it was not detected by thermogravimetric infrared (TGA-IR) analysis.[12] It has been suggested by Cabaço et al., from computation, that acetic acid becomes complexed with another acetate anion[18] and is thus not irreversibly lost. This hypothesis also accounts for the limiting capacity of imidazolium acetates for carbon dioxide (up to a mole fraction of only 0.35), whereby the reaction is self-quenching because acetic acid produced sequesters the free acetate base.[19] To circumvent the production of a free carbene species, it has also been suggested by Cabaço et al. that, rather than being totally dissociated, the C-2 proton bond is just weakened sufficiently to allow carboxylation to occur.[18]

Most other ionic liquids absorb CO_2 by a physisorption process, whereby CO_2 is incorporated into the intermolecular spaces in the ionic liquid and leads to very little change in the lattice volume,[20] with longer alkyl chains accounting for a larger free volume and increased CO_2 solubility.[21]

Imidazolium acetate ionic liquid tends to form a solid when saturated with carbon dioxide. This represents a highly desirable situation for reversible CO_2 storage, but an unsuitable medium for its subsequent electrochemical reduction. The trifluoroacetate equivalent does not have this problem and so has an advantage in electrochemical applications. Furthermore, the incorporation of a water cosolvent, which is necessary for the formation of protonated products, greatly disfavors the chemical absorption of CO_2 in acetates, and thus, an alternative liquid must be used.[22] Recent reports for the electrochemical reduction of CO_2 in 1-butyl-3-methylimidazolium acetate[23] and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide[24] suggest that CO_2 is directly reduced to its radical anion; thus allowing further reaction to useful products, but at the cost of a high reduction potential.

Much CO_2 electrochemical reduction research has focused on the use of common commercially available alternatives such as 1-alkyl-3-methylimidazolium tetrafluoroborates, which can capture substantially less CO_2 and are also highly sensitive to water content.[6] Snuffin et al. have suggested that in the case of a BF_4^- anion it is the boron that can act as a Lewis acid for CO_2 binding[25] by substituting one fluorine for an oxygen bound carbon dioxide molecule. By substituting one of the fluorine atoms for a superior leaving group, chlorine, the binding efficiency for CO_2 is increased.

Herein, the 1-ethyl-3-methylimidazolium trifluoroacetate ([Emim][TFA]) ionic liquid is considered due to its high solubility for carbon dioxide compared with commonly used ionic liquids,[26] its compatibility with water, its high electrochemical reduction potential, and its low viscosity.[27] It has also been suggested that fluorination of the ionic-liquid anion alkyl chains in combination with the imidazolium cation can also increase the low-pressure solubility of CO_2.[28] Thus, this ionic liquid serves as a high-concentration storage medium for carbon dioxide, the storage capacity of which is largely unaffected by water to allow high-current direct reduction of carbon dioxide at an indium electrode to formate.



1-Ethyl-3-methylimidazolium trifluoroacetate

Results and Discussion

Cyclic voltammetry with an indium disc electrode in [Emim]-[TFA] (2 mL) was recorded under both argon- and carbon dioxide-saturated conditions at 5 mV s^{-1} (Figure 1). There appears to be roughly a threefold enhancement of reduction current in the CO_2-saturated case with onset at about −1.6 V versus Ag/AgCl (3 M NaCl), culminating in a peak at around −1.8 V versus Ag/AgCl (3 M NaCl). A second peak at more negative potentials is reproducibly seen in the CO_2-saturated case at about −2 V versus Ag/AgCl (3 M NaCl). This second peak is not seen in the argon-saturated case, and is thus not an ionic-liquid redox process. It is more likely that both of the reductive peaks are CO_2 reduction based, with the more negative peak being assigned as the direct reduction, at the indium electrode surface, of solvent cage sequestered CO_2. The first, more positive peak, was thought to be the C-2-bound CO_2 catalytic reduction peak, similar to that reported previously.[29] This theory was however disproven by the voltammetry of 1,3-dimethylimidazolium-2-carboxylate (10 mM), which, when added to a solution of dry [Emim][TFA], showed no change from the argon-saturated case with neither reduction peak in the CO_2-saturated case being replicated. These findings suggested that carboxylate C-2 binding, if possible, does not contribute to the CO_2 reduction current seen in the ionic-liquid saturated case. Reports in the literature confirm this hypothesis and suggest that the C-2-bound carboxylate is not possible in this ionic liquid.[18]

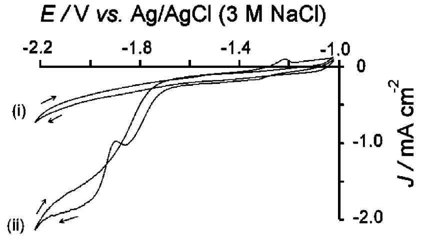


Figure 1. Cyclic voltammograms of scans at 5 mV s^{-1} for an indium working electrode and a platinum mesh counter electrode versus Ag/AgCl (3 M NaCl) in [Emim][TDA] with i) Ar or ii) CO_2 atmospheres. Only the second consecutive cyclic voltammogram is shown for clarity.

The carbon dioxide reduction evident in Figure 1 is likely to be indicative of the formation of a carbon monoxide product, or less likely the carbon dioxide radical anion intermediate proposed by Martindale and Compton.[24] No oxidative peaks were seen that were related to a reversible redox process for carbon dioxide, and so for clarity all other results are presented as linear-sweep voltammograms. The reversible couple at about −1.3 V (vs. Ag/AgCl) only appears under CO_2 saturation and was attributed to a reversible indium-based process, which was most likely the reversible formation of indium carbonate.

To form a hydrogenated product, such as formate, a proton source must be introduced, the most obvious source of which is water. Due to the physisorbtive nature of carbon dioxide with [Emim][TFA], it was hoped that the addition of a water cosolvent would have little effect on the carbon dioxide content. Thus, a sample of [Emim][TFA] (2 mL) was analyzed by cyclic voltammetry with increasing water content (Figure 2 A). For clarity only, the cathodic linear sweep portion of the second consecutive cyclic voltammogram is presented. Interestingly, with any amount of added water, the reduction now appears as only one peak instead of the two seen in dry conditions. The peak seen in the presence of water is most likely to be the direct CO_2 reduction peak. The C-2-binding mechanism under the chosen electrosynthetic conditions (2 mL ionic liquid and 1 mL water) was ruled out by the synthesis and comparison of the C-2-methylated ionic liquid [EDmim][TFA] because this ionic liquid shows an almost identical carbon dioxide reduction current and potential to that seen with the non-methylated ionic liquid (Figure 2 B). Thus, it may be concluded that the C-2 position is not catalytically active for the reduction of carbon dioxide under these conditions.

It is clear from the voltammetry results that with increasing water content the carbon dioxide signal is enhanced. This effect is likely to be due to a significant decrease in the viscosity, which accounts for faster carbon dioxide diffusion within the electrolyte medium.[29] The peak charge (Figure 2 C) for CO_2 reduction may be used to estimate the amount of CO_2 reduced on the timescale of the voltammogram. As the water content increased up to 1 mL the peak charge increased, despite the lower carbon dioxide content. This effect is, however, consistent with a dramatic decrease in solution viscosity, as found by Rodriguez and Brennecke,[30] which leads to faster diffusion of carbon dioxide to the electrode surface and an enhancement of CO_2 reduction (Figure 2 D). Conversely, when 2 mL of water was added, a dramatic decrease in peak charge was seen. The decrease in carbon dioxide content is no longer offset by the substantial decrease in viscosity. Additionally, the background water reduction process appears to be enhanced.

The addition of a water cosolvent also had a beneficial effect on the carbon dioxide reduction onset and peak potentials. Although it is true that the onset shift is likely to be due to the now competing proton reduction reaction, the shift in reduction peak is significant, 300 mV for 1 mL of water in 2 mL of [Emim][TFA].

This shift, with increasing water content, is emphasized at a low water content: a less pronounced effect is seen above 1 mL of added water in 2 mL of [Emim][TFA]. In comparison with aqueous CO_2 reduction on an indium electrode of −1.94 V (vs. Ag/AgCl, 3 M NaCl), the mixed ionic liquid/water system showed a considerably lower energy carbon dioxide reduction.

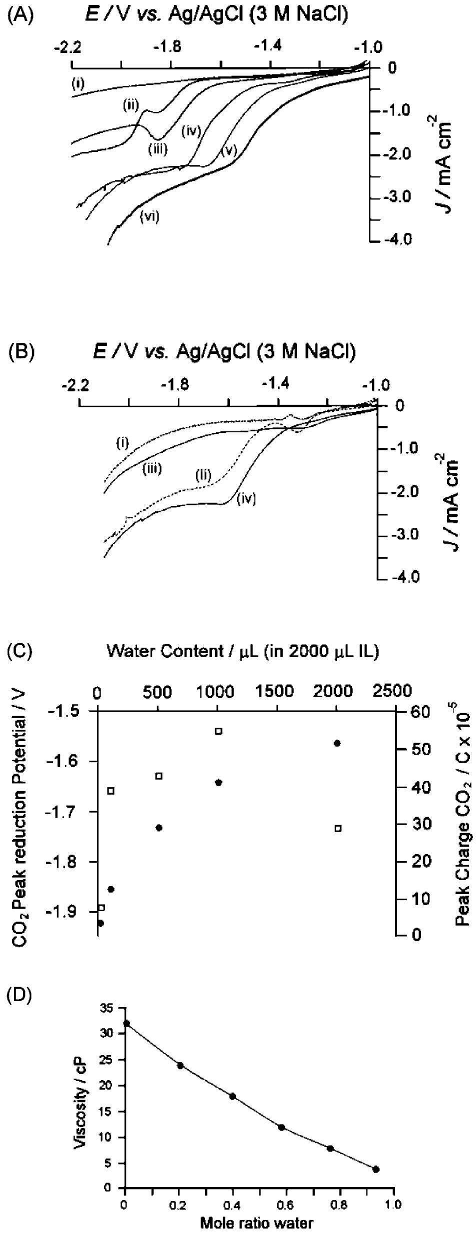


Figure 2. (A) Voltammograms of scans at 5 mV s^{-1} for an indium disc working electrode (2 mm diameter) and platinum mesh counter electrode versus Ag/AgCl (3 M NaCl) in [Emim][TFA] with an increasing percentage of distilled water co-solvent. i) Ar saturated, no water; ii) CO_2 saturated, no water; iii) CO_2 saturated, 100 μL water; iv) CO_2 saturated, 500 μL water; v) CO_2 saturated, 1 mL water; and vi) CO_2 saturated, 2 mL water. (B) Voltammograms of scans at 5 mV s^{-1} for an indium disc working electrode (2 mm diameter) and platinum mesh counter electrode versus Ag/AgCl (3 M NaCl) with 2 mL RTIL + 1 mL H_2O. i) 1,2-Dimethyl-3-ethylimidazolium trifluoroacetate ([EDmim][TFA], Ar saturated; ii) [EDmim][TFA], CO_2 saturated; iii) [Emim][TFA], Ar saturated; and iv) [Emim][TFA], CO_2 saturated. (C) Summary plot showing the variation of peak potential (circles) and peak charge (squares) with water content. (D) Viscosity decrease of the [Emim][TFA] + H_2O mixture with increasing mole fraction of H_2O (adapted from data by Rodriguez et al.[30]).

It is interesting to note that, despite the incorporation of water into the solution, the background reduction event (in the absence of CO_2) signal does not increase substantially (not shown). This can be attributed to both the high overpotential for water reduction on indium, and also the possibility of the electrode surface being blocked towards water reduction by a hydrophobic layer of bulky cations, as demonstrated in the adiponitrile process.[31]

The effect of proton concentration, [H$^+$], was also analyzed for this ionic liquid. Although the measurement and variation of pH within the ionic liquid is difficult, it was concluded that by preacidifying water before addition to the ionic liquid, an effect could be determined from additional proton content in the medium. To avoid complicated ion-pairing effects and only see the effect of added protons, trifluoroacetic acid was used to acidify deionized water to a pH of 1.2. The addition of 100 μL of cosolvent seems to have a very similar effect to that seen with regular deionized water (Figure 3 ii and iv). However, for the addition of 100 μL of water at pH 1.2, a small additional reductive feature is visible at around −1.45 V versus Ag/AgCl (3 м NaCl), which is attributed to proton reduction because it is visible in both the CO$_2$- and Ar-saturated cases, but not in the pH 6.7 case. The peak position for the reduction of carbon dioxide is not affected by increasing [H$^+$]; thus, it may be concluded that, for this electrochemical process, either reduction does not involve proton transfer or, as suggested by Schiffrin,[32] the proton donor in this case is selectively H$_2$O. However, upon the addition of 1000 μL of pH 1.2 water, the voltammograms for Ar- and CO$_2$-saturated solutions were indistinguishable (Figure 3 vii and viii). In both cases, the current rapidly increased almost immediately and a gas evolution process was observed, presumably the evolution of hydrogen. These results are to be expected because proton reduction is highly pH sensitive, with low pH heavily favoring the H$^+$ reduction process. In comparison with the voltammograms for neat [Emim][TFA] (Figure 1), about a 300 mV lower overpotential for carbon dioxide reduction is found when 1 mL of water is incorporated (ca. 18.5 м).

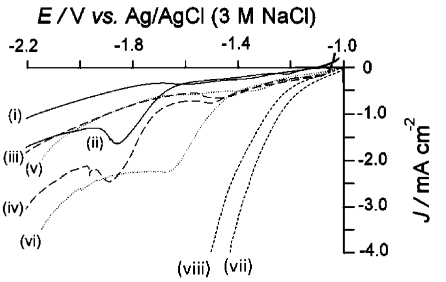


Figure 3. Voltammograms of scans at 5 mV s^{-1} for an indium working electrode and platinum mesh counter electrode versus Ag/AgCl (3 м NaCl) in [Emim][TFA] with i) 100 μL distilled water (pH 6.7) cosolvent, argon saturated; ii) 100 μL distilled water (pH 6.7) cosolvent, CO$_2$ saturated; iii) 100 μL distilled water (pH 1.2) cosolvent, argon saturated; iv) 100 μL distilled water (pH 1.2) cosolvent, CO$_2$ saturated; v) 1 mL distilled water (pH 6.7) cosolvent, argon saturated; vi) 1 mL distilled water (pH 6.7) cosolvent, CO$_2$ saturated; vii) 1 mL distilled water (pH 1.2) cosolvent, argon saturated; and viii) 1 mL distilled water (pH 1.2) cosolvent, CO$_2$ saturated.

Bulk electrolyses were carried out by using the method outlined in the Experimental Section in a solution composed of 2 mL of [Emim][TFA] and 1 mL of water (pH 1.2 or pH 6.7). The major product, formate, was detected and quantified by ^{2}H NMR spectroscopy against a 10 mм CD$_3$CN standard to give direct evidence of product conversion from CO$_2$ and without further sample treatment. Ordinarily, product determination, of non-gaseous products, from carbon dioxide reduction in ionic liquids is obtained by further conversion of an intermediate into an easily separable material, such as dimethyl carbonate.[33]

Initially, tests were conducted in the proposed solvent matrix of [Emim][TFA]/D$_2$O (2:1) to determine the detection limit and ppm shift of formate for ^{2}H NMR spectroscopy under these conditions. As well as a large and anticipated D$_2$O signal appearing at $\delta \approx 4.7$ ppm, another background signal also appeared at $\delta \approx 9.0$ ppm. This signal was assigned to a deuterium exchange reaction at the C-2 position of the imidazolium ring. This C-2 exchange signal was present in the pre- and post-electrolysis solutions with and without formate in both carbon dioxide and argon-saturated conditions. This result was unexpected, since the weak basicity of the TFA anion should limit the deprotonation of the C-2 position of the imidazolium ring.[16,34]

The C-2-exchanged deuterium signal appeared at a similar chemical shift to that expected for ᴅ-formate, but fortunately did not obscure the signal dramatically. Initially, the Faradaic efficiency for formate production in an electrolysis mixture of CO$_2$-saturated [Emim][TFA] (2 mL) and D$_2$O (1 mL) was calculated for a range of electrolyses at varying electrolysis potentials. A plot of Faradaic efficiency versus applied electrolysis potential (vs. Ag/AgCl, 3 м NaCl) is shown in Figure 4 A. This plot shows that, at more negative applied potential, the Faradaic efficiency increases dramatically between −1.55 and −1.75 V, but only a small increase is seen towards −1.95 V, with a maximum efficiency of around 90 %.

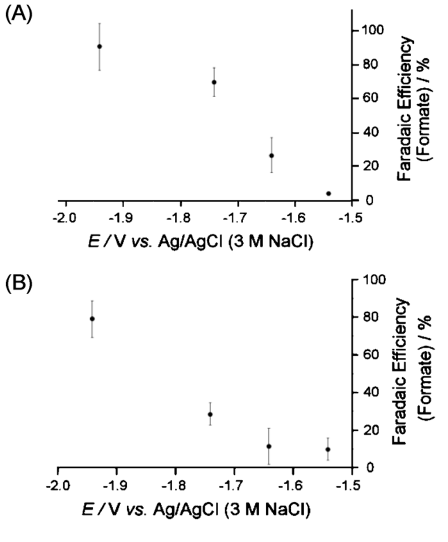


Figure 4. (A) Plot of Faradaic efficiency for formate production from CO$_2$ versus the applied potential in a solution of CO$_2$-saturated [Emim][TFA] (2 mL) and D$_2$O (1 mL; pH 6.7) at an indium working electrode, with an unfritted zinc counter electrode. (B) Plot of Faradaic efficiency for formate production from CO$_2$ versus the applied potential in a solution of CO$_2$-saturated [Emim][TFA] (2 mL) and D$_2$O (1 mL; pH 1.2) at an indium working electrode, with an unfritted zinc counter electrode.

When acidic D_2O was used, adjusted with deuterated trifluoroacetic acid to pH 1.2, Faradaic efficiencies were appreciably lower at all potentials analyzed (Figure 4B). During these electrolyses, bubbling was highly visible on the electrode surface, in contrast to that seen for pH 6.7 D_2O. It is likely that for acidic pH values proton reduction is more dominant, as expected, but does not completely destroy the formate-forming reaction. It is notable that conversions comparable to those seen in the pH 6.7 case are possible in the acidic case, but a much higher potential is required. This suggests that extra competition from proton reduction is not the entire story and a different intermediate may be generated.

When the electrolyses are carried out under the same conditions as those described previously in an argon-saturated solution, no formate is detectable. However, a new doublet appears in the ^{2}H NMR spectrum at $\delta \approx 7.5$ ppm. By comparing this signal with that of the ^{1}H NMR spectrum obtained for [Emim][TFA] in D_2O, this doublet was assigned as deuterium exchange of the C-4 and C-5 imidazolium backbone protons. These protons are not thought to be acidic, although it is possible that by applying a negative bias to the imidazolium ring, an exchange of the intermediate ring delocalized radical cation is possible under the electrolysis conditions.

To serve as a comparison with indium, tin and lead electrodes were also investigated as potential formate-forming electrodes in carbon dioxide/[Emim][TFA]/water medium. Lead is known to not only favor the reduction of carbon dioxide to formate in aqueous conditions,[35] but also to suppress the competing proton reduction reaction. Tin is very similar to indium for carbon dioxide reduction, primarily forming formate.[36]

From the voltammograms for the tin and lead electrodes (Figure 5), it is clear that the same trend in carbon dioxide reduction potential is seen as that for the indium case. With 1 mL (33%) of water added to 2 mL of [Emim][TFA], the reduction peak and onset potentials are shifted positively by +320 and +560 mV, respectively. The voltammograms on the tin electrodes under both dry and wet conditions; however, are highly inconsistent from scan to scan (Figure 5A, scans ii-a/b and iv-a/b).

The voltammograms for lead electrodes showed a similar positive shift in peak and onset potentials by +500 and +400 mV, respectively. It is possible that this shift is due to the in situ formation of a kinetically stable oxide or hydroxide, which facilitates CO_2 reduction, as seen in examples involving copper[37] and gold[38] electrodes. In both cases, the peak current densities were similar to that seen with indium working electrodes, and thus, the lead and tin electrodes were deemed synthetically viable for formate production. Other electrode materials tested were copper, silver, zinc, and stainless steel (304), of which none showed significant direct CO_2 reduction over the background proton reduction in the ionic liquid/water matrix.

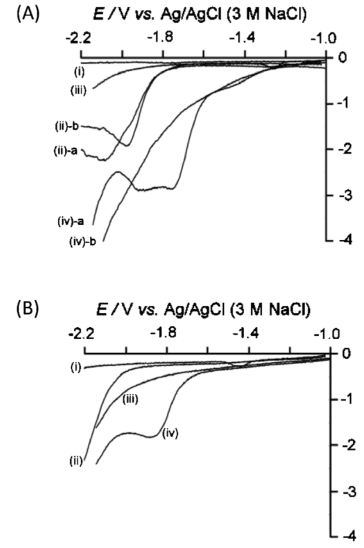


Figure 5. (A) Voltammograms of scans at 5 mV s^{-1} for a tin working electrode and platinum mesh counter electrode versus Ag/AgCl (3 M NaCl) in [Emim][TFA] with i) no distilled water, argon saturated; ii) no distilled water, CO_2 saturated; iii) 1 mL distilled water (pH 6.7) cosolvent, argon saturated; and iv) 1 mL distilled water (pH 6.7) co-solvent, CO_2 saturated; a and b represent the first and second cyclic voltammograms reported, respectively. (B) Same conditions as those described in part (A), but using a lead working electrode; all scans presented are the second consecutive cyclic voltammogram.

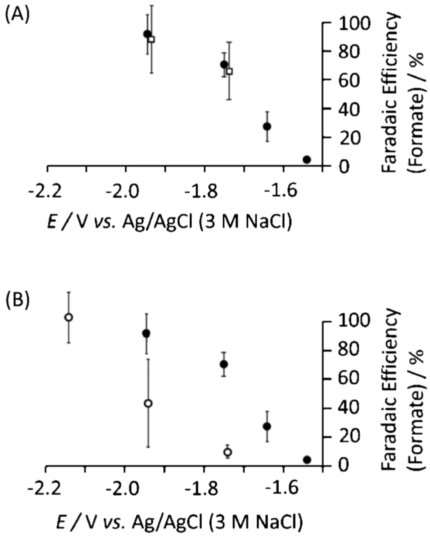


Figure 6. (A) Comparison of tin (open squares) and indium (closed circles) electrodes for the Faradaic efficiency of formate production from carbon dioxide in a matrix of 2 mL [Emim][TFA] + 1 mL D_2O (pD 6.7) at various applied potentials. (B) Comparison of lead (open circles) and indium (closed circles) electrodes for the Faradaic efficiency of formate production from carbon dioxide in a matrix of 2 mL [Emim][TFA] + 1 mL D_2O (pD 6.7) at various applied potentials.

It is no surprise that the Faradaic efficiencies found when using a tin working electrode were very similar to that seen for indium, due to their periodic similarities and their ability to make formate in aqueous solution (Figure 6A). In contrast to indium, lower applied potentials than −1.7 V versus Ag/AgCl (3 M NaCl) consistently gave negligible amounts of formate production, and thus it seems that for tin a more abrupt onset for CO_2 reduction is present. Furthermore, tin showed a greater degree of deviation in the Faradaic efficiencies, possibly owing to its unstable voltammetric profile.

Lead working electrodes showed a much higher potential for reduction to formate (Figure 6B), and appreciable Faradaic efficiencies were not evident until over −1.9 V versus Ag/AgCl (3 M NaCl). However, efficiencies quickly rose to 100% with an applied potential of −2.15 V versus Ag/AgCl (3 M NaCl); this suggested that, although lead required a higher potential for carbon dioxide reduction, it also suffered from fewer competing reactions, such as proton reduction or ionic-liquid degradation.

Conclusions

It has been demonstrated that the ionic liquid [Emim][TFA], with 33% water as a cosolvent, could act as an effective medium for the reduction of carbon dioxide to formate (up to 3 $mg\,h^{-1}\,cm^{-2}$). By deuterium labeling, the formate concentration was directly detected in the electrolysis mixture and proved to originate from carbon dioxide.

The mechanism for this high-yielding reduction of CO_2 proved not to involve a C-2-bound carboxylate intermediate, as suggested in other studies,[6,29] by comparison of voltammograms with the equivalent C-2-methylated ionic liquid. Instead, direct CO_2 reduction at the indium electrode is proposed for the reduction of carbon dioxide in this system.

In comparison to aqueous carbon dioxide reduction systems previously investigated at indium, this synthesis provided a higher current density and lower electrode potential for electrolysis. This was attributed to a stabilizing effect of the ionic liquid on the carbon dioxide intermediate and the increased solubility of carbon dioxide in the matrix.

Related metals, tin and lead, were also tested and had similar properties for formate production. Tin showed very similar behavior to that seen for indium, and lead showed an increased Faradaic efficiency for formate, but at more negative applied potentials.

Experimental Section

Synthesis of [Emim][TFA]: For the synthesis of [Emim][TFA], the literature procedure of Laali and Gettwert was followed.[39] In a 2 L round-bottomed flask, 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]; 87.972 g, 0.6 mol; Acros, 97%) was dissolved in a mixture of MeCN (600 mL) and diethyl ether (300 mL). In a separate flask, sodium trifluoroacetate (81.606 g, 0.6 mol; Sigma Aldrich, 98%) was dissolved in a solution of acetone (180 mL) and diethyl ether (180 mL). The solution of sodium trifluoroacetate was added to the solution of [Emim][Cl] and instantly formed a white emulsion. The solution was left to stir at room temperature for 2 h before being gravity filtered to remove the NaCl salt (3 times), washed with acetonitrile, and concentrated under vacuum to give the pure product, [Emim][TFA]. The product appeared as a slightly yellow viscous oil and was verified by comparison with a commercial sample (IoLiTec) by ATR-IR and ^1H NMR spectroscopy.

Synthesis of [EDmim][TFA]: The synthesis of [EDmim][TFA] was achieved through the literature synthesis of [EDmim][Br] reported by Bonhôte et al.,[40] followed by a salt exchange with NaTFA. In a 500 mL round-bottomed flask, 1-ethyl-2-methylimidazole (0.178 mol) was dissolved in freshly distilled 1,1,1-trichloroethane (200 mL). Freshly distilled bromoethane (0.566 mol) was added dropwise to this solution over 1 h. The solution was then heated at reflux for 2 h.
A white precipitate was produced and removed by filtration and dried to give [EDmim][Br] (14.00 g, 41%; confirmed by 1H NMR spectroscopy).

[EDmim][Br] (10 g, 0.052 mol) was dissolved in MeCN (90 mL) and a solution of NaTFA (0.052 mol) in MeCN (31 mL) was added. A white precipitate formed immediately; the solution was stirred for 2 h at room temperature. The white precipitate (NaBr) was removed by gravity filtration three times until a clear solution was recovered. The solvent was removed in vacuo to give [EDmim][TFA] as a waxy solid.

Voltammetry measurements: Voltammetric analysis was performed with a CHI760D electrochemical workstation from CH instruments. Cyclic voltammetry was performed at a scan rate of 5 $mV\,s^{-1}$, and all data presented represent the cathodic portion of the second consecutive voltammogram to ensure the stability of the voltammetric signal. In all cases, the first and second scans showed identical cathodic currents. All voltammetry was performed by using a 2 mm diameter indium disc working electrode, fabricated from indium shot mounted into a 2 mm Teflon tube, and connected by a copper wire on the rear. Prior to all scans, indium was etched by using 6 M HCl and polished with a lens cloth. The counter electrode was a platinum mesh and the reference electrode was an Ag/AgCl (3 M NaCl) electrode, which was highly stable, although the potential changed systematically with the composition of the electrolyte matrix. Thus, a secondary reference was employed in the form of a ferrocene redox probe which was applied to each matrix after analysis and analyzed for its electrochemical shift. All voltammograms were then replotted on a scale that reflected the true Ag/AgCl (3 M NaCl) reference electrode to compare the different solvent mixtures with each other and with aqueous solutions reported in the literature.

Procedure for carbon dioxide reduction in RTILs: Prior to use, all ionic liquids were dried under high vacuum at 40 °C over phosphorous pentoxide for 48 h to remove all traces of water before being stored under nitrogen. For each electrolysis, samples (2 mL) were removed under nitrogen and transferred to a degassed 5 mL two-necked flask. A sample (1 mL) of D_2O co-solvent was added and the solution was purged with carbon dioxide for 1 h.
Indium electrodes were prepared by pressing indium shot (Alfa Aesar, 99.9%) into a foil and pressing a copper wire into one side of the foil. The indium electrode copper wire was passed through a septa adjacent to the Ag/AgCl (3 M NaCl) reference electrode and placed into the solution, such that no copper came into contact with the solution, and an indium electrode surface area of about 2 cm^2 was formed. An unfritted zinc foil (Alfa Aesar, 99.99%) was used as the counter electrode placed into the other neck through a rubber septa. A Teflon-coated stirrer bar was inserted into the solution to ensure stirring during electrolysis. Throughout electrolysis, the headspace of the solution was purged with carbon dioxide. Electrolysis was conducted until about 20 C of charge had passed, after which the solution was collected for analysis.

Formate analysis by ^2H NMR spectroscopy: Electrolysis samples were analyzed without modification by ^2H NMR spectroscopy. ^2H NMR spectroscopy and deuterium-labeled formate was used to avoid interference from the many proton signals of the ionic liquid that would overpower the new formate signal in ^1H NMR spectroscopy. A sample (600 μL) of the electrolysis mixture was extracted, to which a 0.61 M CD_3CN (10 μL) stock solution in D_2O was added, giving 10 mM CD_3CN in the NMR sample to act as a standard. The D-formate signal was detected at $\delta \approx 9.8$ ppm, and the CD_3CN reference signal was at $\delta \approx 3.2$ ppm. By comparison of these signals, the concentration of D-formate could be extracted. Experiments were performed on a 500 MHz Bruker Avance III spectrometer equipped with a TCI (${}^{1}H/{}^{13}C/{}^{15}N//{}^{2}H$) cryoprobe by using the fully cold lock channel for direct ${}^{2}H$ detection. Samples were locked and shimmed using D_2O. The lock was disabled prior to running the experiment to take advantage of the high stability of the Ultrashield Plus magnet.

By assuming a Faradaic efficiency of 100 % and 100 % incorporation of the deuterium label, a 20 C electrolysis would generate about 35 mM of deuterium-labeled formate. Thus, the ability to detect concentrations of 10–20 mM was required for this technique. A non-electrolyzed mixture containing 10 mM D-formate and 10 mM CD_3CN was used to verify the detection efficiency of D-formate in the electrolysis mixture. For a 10 mM solution of D-formate, only 70 % was detected versus the CD_3CN standard; this had to be taken into account when quantifying electrolysis products. This discrepancy could be due to the formate signal appearing as a shoulder on the C-2 exchange signal and some signals being obscured.

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