

Carbon Dioxide Reduction in Room Temperature Ionic Liquids: The Effect of the Choice of Electrode Material, Cation, and Anion.

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Abstract

The electroreduction of carbon dioxide is systematically investigated in Room Temperature Ionic Liquids (RTILs) to establish the effect of the electrode material, the cation, and the anion on the mechanism of reduction. Silver, gold, platinum and glassy carbon macroelectrodes are investigated using cyclic voltammetry in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf₂]). On silver electrodes, a diffusion-limited reductive peak current is observed, whilst for gold, the peak current density is six times smaller. No appreciable reduction is observable on either platinum or glassy carbon. Moreover, on silver the overpotential required for reduction is reduced by *ca.* 1.5 V compared with gold. Next a cation effect and an anion effect are demonstrated on a silver electrode, with the use of the following RTILs: 1-butyl-1-methylpyrrolodinium bis(trifluoromethylsulfonyl)-imide ([Bmpyrr][NTf₂]), 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([Emim][NTf₂]), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Pmim]-[NTf₂]), and 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([Bmim][FAP]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]). The study of the anion and cation effect is enabled by the use of IL-based Ag/Ag⁺ reference electrodes, with the solvent in each reference electrode composed of the RTIL used in the primary solution. To allow direct comparison of CO₂ reduction potentials between different solvents, the cobaltocenium/cobaltocene couple is used as a standard, allowing corrected relative potentials to be reported. The peak current on silver was observed in [Bmim][NTf₂] at -1.1 V vs cobaltocenium/cobaltocene, in [Bmpyrr][NTf₂] at -1.20 V, and in [Emim][NTf₂] and [Pmim][NTf₂] at -1.50 V. Of the anions, the peak current observed in [Bmim][BF₄] occurs at a comparable potential to [Bmim][NTf₂] (-1.10 V vs cobaltocenium/cobaltocene), whilst the reduction of CO₂ in [Bmim][FAP] was observed at -1.60 V. This work provides experimental evidence that silver facilitates the inner sphere reduction of carbon dioxide, and a possible mechanism is proposed.

Introduction

Upon the application of a sufficiently cathodic potential, carbon dioxide can undergo a one electron irreversible electroreduction to a radical anion:¹



A number of products may be subsequently formed depending on the solvent, and electrode material, these include: CO, formate, methanol, methane, carbonate and oxalate.^{1,2} Because of this complexity and sensitivity, greater fundamental understanding of the electroreduction of carbon dioxide is of interest.³ In addition, increased knowledge of carbon dioxide reduction informs the development of atmospheric sensors, and provides a possible source of cheap, reactive carbon for use in organic synthesis.

Room Temperature Ionic Liquids (RTILs), which consist of a bulky, asymmetric cation and an inorganic anion,⁴ and are liquid at room temperature, have shown promise as solvents for the electroreduction of CO₂.⁵ This is due partly to the high solubility of CO₂ in a range of RTILs,⁶ and the ability to ‘tune’ the physicochemical properties of the solvent by altering its components.⁷ In particular, the use of certain anions, namely trifluoroacetate⁸ and the superbasic triazolidine,⁹ have been suggested to lower the overpotential of the reaction by chemically binding to the CO₂. Where the CO₂ is not chemically bound, such as in imidazolium tetrafluoroborates, Rosen *et. al*¹⁰ proposed that the catalysis of the reduction of carbon dioxide to carbon monoxide is a result of the cation complexing with the carbon dioxide radical anion. However, this has since been challenged in a review by Costentin *et. al*,¹¹ who proposed instead that the electrode material is likely to be the source of the lower peak potentials reported by Rosen *et. al*.¹⁰ Guirado *et. al*¹² share this view, focusing on 1-butyl-3-methylimidazolium (Bmim) and 1-ethyl-3-methylimidazolium (Emim) cations with a range of anions.

Throughout these literature reports, there is a difficulty of comparing potentials between

measurements made in different solvents. In aqueous solvents, the standard hydrogen electrode is used as the primary reference and is related to the absolute potential scale.¹³ However, in non-aqueous solvents, including RTILs, measuring the potential is less straightforward, and comparing reductive potentials across solvents is non-trivial, requiring the development of suitable reference electrodes, ideally avoiding liquid junction potentials. The above reports typically utilise electrodes optimised for aqueous systems, such as Saturated Calomel Electrodes, or pseudo-reference electrodes, instead of IL-based electrodes, which makes accurate and quantitative comparative study challenging. Ag/Ag⁺ reference electrodes were voltammetrically characterised for use in RTILs by Snook and coworkers,¹⁴ who reported a less than 1 mV drift over three weeks. They are considered the reference electrode of choice for rigorous quantitative voltammetry,¹⁵ and have since been implemented by others for this purpose.^{16–18} Snook *et. al*¹⁴ placed a silver wire in a 10 mM silver triflate/[Bmpyrr][NTf₂] solution that was contained within a pipette tip with a molecular sieve as a frit. A modified version of this reference electrode is used herein. Specifically for each RTIL used as a solvent, a reference electrode with a silver triflate solution in that ionic liquid is employed. Then, since a range of RTILs are examined in this paper, and a Ag/Ag⁺ reference electrode is likely to have different absolute potentials between different solvents,¹⁵ an internal reference, utilising a largely solvent insensitive couple is used to compare the potentials across different solvents. IUPAC recommends the ferrocene/ferrocenium redox couple,¹⁹ however on a silver electrode, an oxidative marker is not desirable, as the potentials used may oxidise the silver electrode. Therefore, the reduction of cobaltocenium (to cobaltocene), which has been shown to produce a well defined electrochemical response across a range of RTILs,²⁰ is employed herein to standardise the reference electrodes. Note that the direct inclusion of the cobaltocenium/cobaltocene couple (Cc⁺/Cc) in the solvent simultaneously with carbon dioxide reduction is avoided as this may interfere with the system under study. Hence, voltammetry of the Cc⁺/Cc couple was recorded in each solvent in the absence of CO₂, and subsequent voltammograms in the presence of CO₂ were corrected with respect to the

mid-point potential Cc^+/Cc couple, setting the formal potential to zero.

This paper reports the effect of systematically altering the electrode material, the cation, and the anion on the peak potential of the reduction of carbon dioxide using an IL-based reference electrode with an internal redox marker, and the implications this has for the proposed mechanism of reduction.

Experimental

Chemical Reagents

Silver triflate (Sigma Aldrich, $\geq 99\%$) and cobaltocenium (bis(cyclopentadienyl)cobalt(III) hexafluorophosphate, Sigma Aldrich, 98%) were used as received. Argon and carbon dioxide (99.5%) were purchased from BOC, Surrey, UK. The RTILs were prepared according to standard literature methods²¹ and kindly donated by Professor Christopher Hardacre formerly of Queen’s University, Belfast.

Electrochemical Apparatus

Electrochemical experiments (cyclic voltammetry) were conducted inside a temperature controlled Faraday cage²² using a μ Autolab II potentiostat (Metrohm, Utrecht, The Netherlands). The silver macroelectrode (3.0×10^{-4} m radius) was constructed by sealing a silver wire in glass casing with epoxy, and was polished with sandpaper (2500, 1200) prior to use. The glassy carbon macroelectrode (1.5×10^{-3} m radius, BASi Analytical, USA), was polished prior to use on white lapping pads with diamond spray (3.0, 1.0, 0.1 μm , three minutes on each size from Kemet, Kent, UK). The gold (1.2×10^{-3} m radius, IJ Cambria Scientific Ltd., UK) and platinum (8.3×10^{-4} m radius, BASi Analytical, USA) macroelectrodes were polished prior to use using a water-alumina slurry (1, 0.3, 0.05 μm , three minutes on each grade) on soft lapping pads (Buehler, Illinois).²³ A 0.5 mm platinum wire was used as a counter electrode, whilst a Ag/Ag^+ reference electrode was constructed (as described below). An

aliquot of RTIL (40 μ L, dried at < 0.2 mbar overnight) was placed in a plastic collar fixed on top of the working electrode, and a T-cell was used²⁴ to introduce the carbon dioxide, which was passed through a column of activated sieves (activated at 200 $^{\circ}$ C overnight, 4 \AA , Sigma Aldrich). A wait time of minimum 15 minutes was imposed between each experiment to ensure a stable concentration of analyte at the electrode surface.

Reference Electrodes

A reference electrode was made for each RTIL by sealing a 2 mm molecular sieve in a glass pipette, and filling with 100 μ L of RTIL overnight. The latter was then replaced with the relevant RTIL containing 20 mM silver triflate and was placed under vacuum for > 72 hours before use. A silver wire was then placed in the pipette to complete the electrode.¹⁷

Results and Discussion

This section first details the effect of altering the electrode material, considering silver, gold, platinum, and glassy carbon electrodes, on the reduction of carbon dioxide. Initial work is conducted in [Bmim][NTf₂] with the use of a platinum counter electrode and a Ag/Ag⁺ reference electrode containing 20 mM AgOTf in [Bmim][NTf₂]. A silver electrode is then used in different ILs to investigate the effect of changing the cation and the anion on the electroreduction of CO₂. A series of RTILs are used, and in each case, a reference electrode composed of 20 mM AgOTf in the chosen IL is employed. So that the peak potential of CO₂ reduction can be compared across different solvents, the voltammetry is referenced to the cobaltocenium/cobaltocene couple which is presumed to be solvent insensitive. This is followed by comparison of peak currents and potentials, to allow inferences to be drawn about the possible mechanism of reduction.

The Effect of the Electrode Material

First, the effect of different electrode materials, namely silver, gold, platinum, and glassy carbon (GC), on the reduction of carbon dioxide was investigated in [Bmim][NTf₂]. As detailed in the Experimental section, CO₂ was passed through a T-cell²⁴ containing an aliquot of the ionic liquid. Saturation with CO₂ was evidenced by observation of a stable peak current on subsequent scans, with a suitable waiting period (15 minutes) between scans to allow the concentration of CO₂ to be replenished at the electrode surface. A cyclic voltammogram (CV) was then recorded by sweeping the potential at 1 V s⁻¹ from -0.5 V to -3.0 V vs a Ag/Ag⁺ reference electrode (containing 20 mM AgOTf in [Bmim][NTf₂] and a Ag wire), as shown in Figure 1.

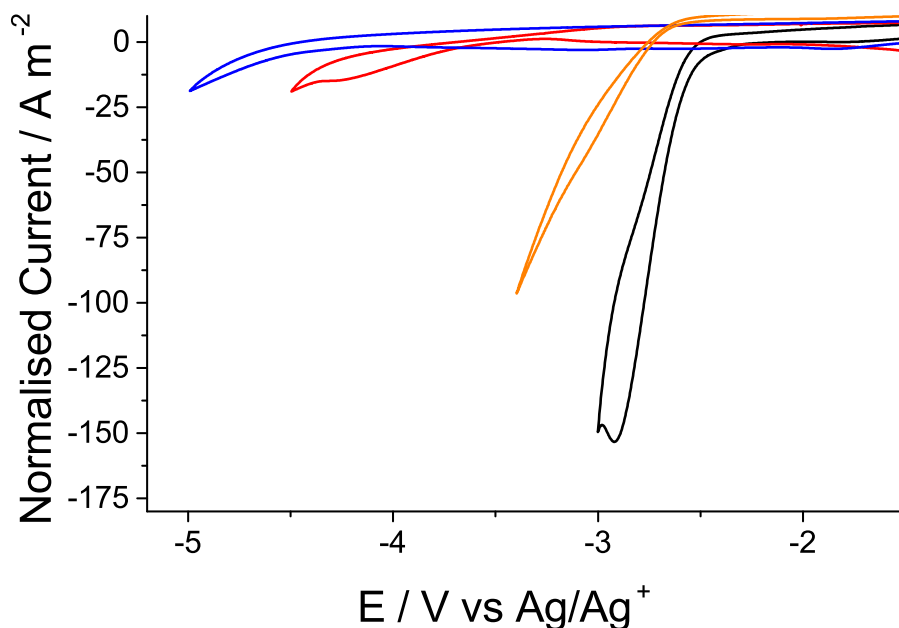


Figure 1: Cyclic Voltammogram in [Bmim][NTf₂] at 1 V s⁻¹ on silver (black), gold (red), platinum (orange) and glassy carbon (blue) macroelectrodes. The current is normalised for electrode area.

On the gold macroelectrode (red line, Figure 1), a reductive feature appears at *ca.* -4.2 V (vs Ag/Ag⁺) with a normalised peak current of *ca.* -23 A m⁻². This peak likely

corresponds to the reduction of carbon dioxide (see the Supporting Information for a Figure in the absence of CO₂). On the GC (blue line, Figure 1), no reductive features appear on the voltammogram, whilst on the Pt macroelectrode (orange line, Figure 1, Figure SI in the Supporting Information) no clear peak corresponding to the reduction of CO₂ is visible. On the silver macroelectrode, the peak current density is at its maximum at *ca.* -2.8 V vs Ag/Ag⁺, with a peak current density of approximately -150 A m⁻². This wave likely corresponds to the one electron reduction of the CO₂ to the associated radical anion, as discussed in the introduction, and as is consistent with work conducted by Guirado *et. al.*¹² CVs were then recorded across a range of scan rates (10 — 1000 mV s⁻¹, shown in Figure 2), and the peak current was found to vary linearly with the square root of the scan rate (inset, Figure 2), indicating a diffusion-limited response. The irreversible Randles-Sevcik equation (Equation 2) allows for the calculation of the concentration of CO₂.

$$\frac{i_p}{\nu^{0.5}} = 2.99 \times 10^5 AD^{0.5} C n(n' + \alpha)^{0.5} \quad (2)$$

Where A is the area of the electrode, C is the bulk concentration, n' is the number of electrons transferred before the rate determining step, i_p is the peak current, $\nu^{0.5}$ is the scan rate, and α is the transfer coefficient. In this case, the overall number of electrons (n) is assumed to be one so that n' = 0, the diffusion coefficient is set to a literature value (5.5 x 10⁻¹¹ m² s⁻¹), as provided by Reche *et. al.*¹², and α is measured to take a value of 0.63 from the Tafel slope of the experimental voltammograms in Figure 2. This provides a saturated concentration of 70 mM, consistent with other reported values in this solvent.¹² On voltammograms recorded using other electrode materials, an absent (in the case of the GC, blue line, Figure 1) or sub-diffusional response (in the case of the gold, red line, Figure 1) is observed. This indicates that on electrode materials other than silver, even at high overpotentials, the reaction is kinetically limited.

These results confirm that the enhanced reduction of CO₂ in an imidazolium RTIL pre-

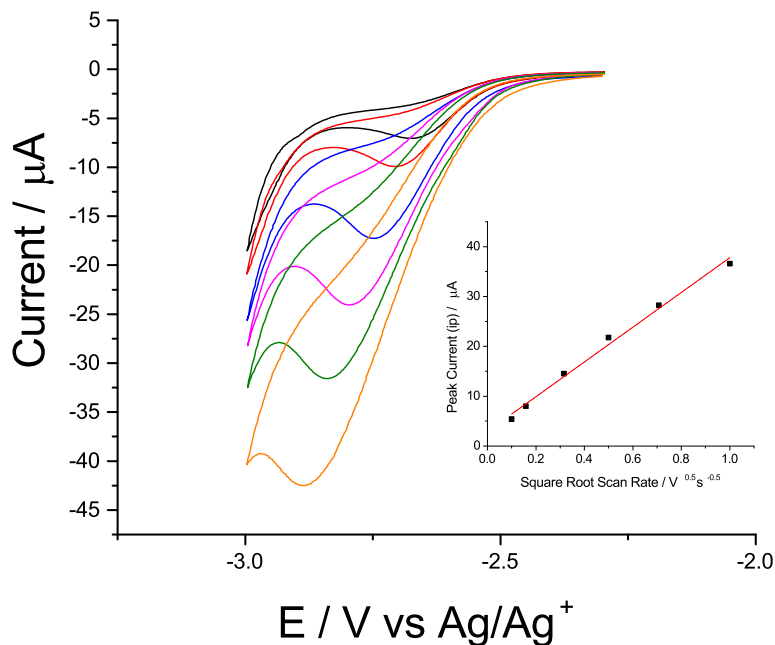
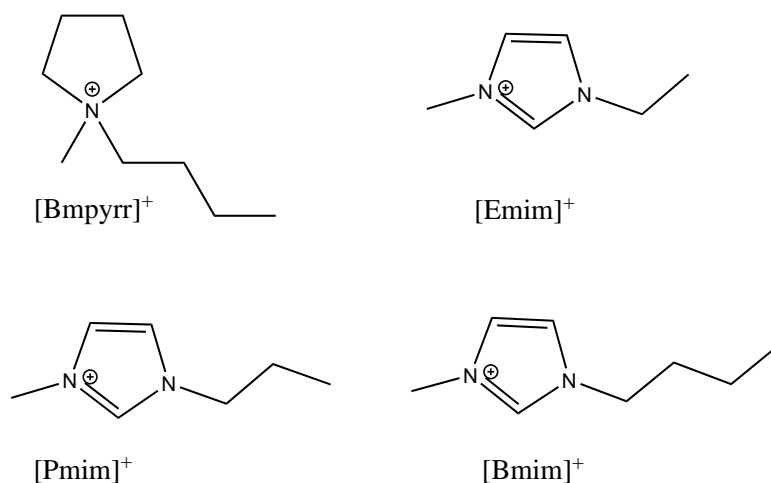


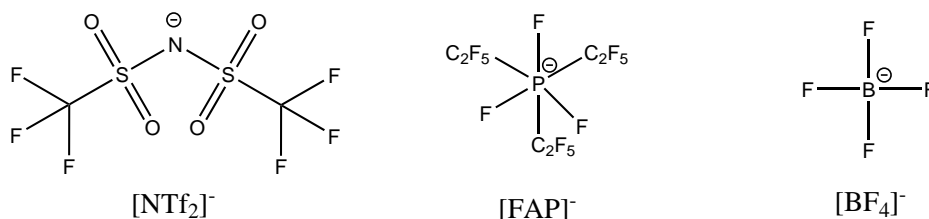
Figure 2: Cyclic Voltammogram in $[\text{Bmim}][\text{NTf}_2]$ on a silver macroelectrode, at 0.01 V s^{-1} (black), 0.025 V s^{-1} (red), 0.1 V s^{-1} (blue), 0.25 V s^{-1} (pink), 0.5 V s^{-1} (green), and 1 V s^{-1} (orange). Inset is the Randles-Sevcik plot of peak current vs square root of scan rate.

viously observed is electrode-specific. In particular, the silver surface evidently plays a significant role in catalysing the process, with other materials, such as carbon and gold, being insufficiently catalytic to observe the reduction. The role of silver is further evidenced by the normalised peak current density on silver being *ca.* six times larger than that observed on a gold electrode. The reductive wave also occurs at a *ca.* 1.5 V lower potential on silver than it does on gold. The role of silver has been conjectured before,^{11,12} but as yet has not been demonstrated. This material sensitivity also indicates that the reaction likely proceeds *via* an inner sphere pathway. This pathway is consistent with Marcus-Hush theory, which suggests a large molecular reorganisation as the neutral CO_2 molecule changes from a linear molecule to a bent structure as an electron is added to form the anion.¹ If, as is postured by Rosen *et. al.*,¹⁰ the cation forms a complex with the reduced carbon dioxide, i.e. the reduction follows an $\text{E}_{\text{irr}}\text{C}$ mechanism, the potential of the voltammetric wave would not be

sensitive to any following homogeneous or heterogeneous chemical kinetics.²⁵ (Therefore, if there are cation-specific shifts observed, it is unlikely that the $E_{irr}C$ mechanism is correct.) To assess this, alteration of the ionic components will next be considered to determine what their contribution is, if any, to the mechanism of reduction of CO_2 . A range of cations and anions were used in conjunction with a silver macroelectrode to systematically vary the solvent properties - those used in this work are presented in Figure 3. As discussed in the introduction, the reduction of carbon dioxide is hereafter reported with respect to the Cc^+/Cc couple.



Cations



Anions

Figure 3: The range of cations and anions used in this study. The cations are 1-butyl-1-methylpyrrolodinium ([Bmpyrr]⁺), 1-ethyl-3-methylimidazolium ([Emim]⁺), 1-propyl-3-methylimidazolium ([Pmim]⁺), and 1-butyl-3-methylimidazolium ([Bmim]⁺). The anions are bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻), tris(pentafluoroethyl)trifluorophosphate ([FAP]⁻), and tetrafluoroborate ([BF₄]⁻).

Converting Potentials to a Cobaltocenium/Cobaltocene Reference Electrode

As measurements in each RTIL in the subsequent subsections require the use of a Ag/Ag⁺ reference electrode based on that particular solvent, a redox marker must be employed to enable direct, albeit approximate, quantitative comparison of the reductive potentials between different solvents. As explained above, we have selected the cobaltocenium/cobaltocene redox couple with the expectation that it is relatively insensitive to the change of RTIL. Voltammetry in 10 mM cobaltocenium hexafluorophosphate was recorded by sweeping the potential from -1.2 V to -3.0 V and back to -1.2 V vs a Ag/Ag⁺. The first reductive couple, appearing at -1.7 V vs Ag/Ag⁺, corresponds to the reduction of cobaltocenium (Cc⁺) to cobaltocene (Cc).²⁴ The second reductive wave, at -2.6 V, is attributed to the reduction of the cobaltocene to the cobaltocene anion (Cc⁻).²⁶



Both reductive couples are shown in Figure 4 in [Bmim][NTf₂] (voltammograms of the other solvents studied can be found in the Supporting Information). Of the two possible redox couples, the first was chosen to act as a standard. This is due to the different possible electrochemical windows in various solvents leading to reduced visibility of the second reduction prior to decomposition of the solvent in some cases. To allow the direct comparison of all further voltammetry recorded in the presence of CO₂ by reporting each potential with reference to the Cc⁺/Cc couple, the formal potential of the first reduction was measured vs Ag/Ag⁺ in each solvent and the potential of the Cc⁺/Cc couple *separately* measured relative to the Ag/Ag⁺ couple in the relevant solvent. All voltammetry is thus reported relative to the Cc⁺/Cc couple recorded in that specific RTIL.

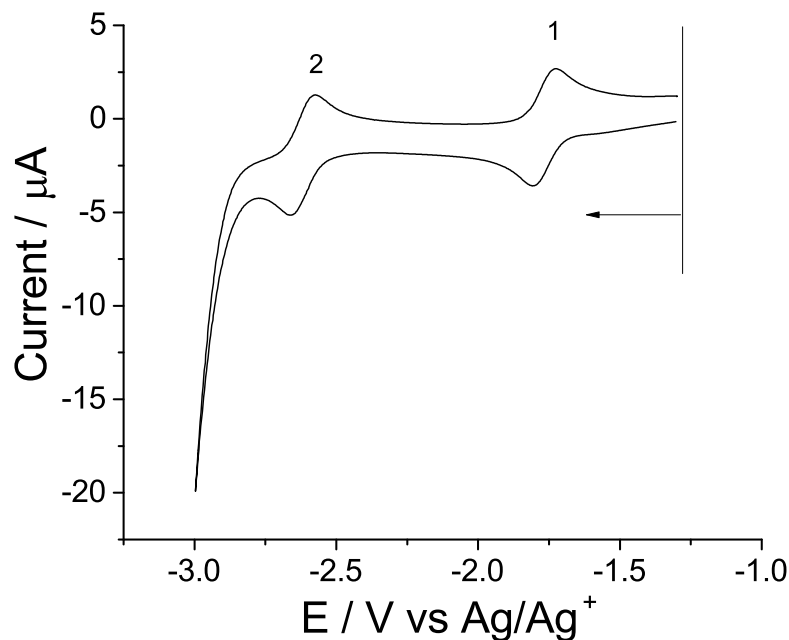


Figure 4: A cyclic voltammogram of the reduction of 10 mM cobaltocenium hexafluorophosphate on silver with a scan rate of 1 V s^{-1} (in [Bmim][NTf₂]). Peak 1 corresponds to the reduction of cobaltocenium to cobaltocene, whilst peak 2 corresponds to the reduction of cobaltocene to the cobaltocene anion.

Cation Effects of the CO₂ Reduction Potential

The effect of the cation was investigated (with a [NTf₂] anion) using 1-butyl-3-methylimidazolium ([Bmim]⁺), 1-propyl-3-methylimidazolium ([Pmim]⁺), 1-ethyl-3-methylimidazolium ([Emim]⁺), and 1-butyl-1-methylpyrrolidinium ([Bmpyrr]⁺) on a silver macroelectrode, with a platinum counter electrode, and a Ag/Ag⁺ reference, containing the same RTIL as the sample. CO₂ was then flowed through a T-cell containing an aliquot of the ionic liquid until a stable peak current was recorded on subsequent scans. A CV was recorded by sweeping the potential, at a scan rate of 1 V s^{-1} , from a potential where no Faradaic current flows, -0.4 V, to a potential more negative than the peak potential, -1.2 V. This was repeated across all solvents listed above, with the starting and turning potentials adjusted according to the solvent, as shown in Figure 5.

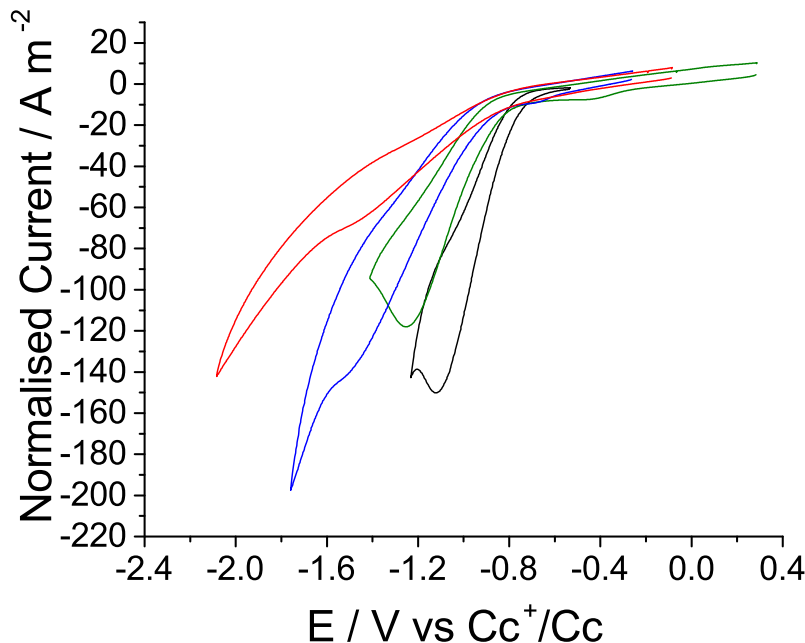


Figure 5: Cyclic Voltammograms of the reduction of carbon dioxide on silver with a scan rate of 1 V s^{-1} , reported vs a Cc^+/Cc reference, in a range of RTILs where the cation is varied. Black is $[\text{Bmim}][\text{NTf}_2]$, green $[\text{Bmpyrr}][\text{NTf}_2]$, blue $[\text{Emim}][\text{NTf}_2]$, and red $[\text{Pmim}][\text{NTf}_2]$.

All voltammetry (and therefore peak potentials) in this subsection is corrected such that it is *reported* relative to the cobaltocenium/cobaltocene couple but *measured* experimentally against a Ag/Ag^+ reference electrode. In $[\text{Bmim}][\text{NTf}_2]$, a reductive peak is observed at $-1.1 \text{ V vs Cc}^+/\text{Cc}$, with a peak current density of -160 A m^{-2} . As discussed in the previous subsection, this reductive peak is likely to correspond to the one electron reduction of CO_2 . In $[\text{Bmpyrr}][\text{NTf}_2]$, the reduction of CO_2 occurs at $-1.2 \text{ V vs Cc}^+/\text{Cc}$, with a peak current density of 120 A m^{-2} . In the modified imidazolium-based RTILs, $[\text{Emim}]$ and $[\text{Pmim}][\text{NT}_2]$, the reduction occurs at $-1.5 \text{ V vs Cc}^+/\text{Cc}$ with peak current densities of 150 and 70 A m^{-2} respectively. These voltammograms show that there is a shift in the potential of the reductive wave upon changing the cation, with the reduction occurring at the most positive potential in $[\text{Bmim}][\text{NTf}_2]$. There appears to be no discernible pattern as the chain length is decreased below four on the imidazolium cation, with the reduction in $[\text{Emim}][\text{NTf}_2]$ and

[Pmim][NTf₂] occurring at *ca.* -1.5 V vs Cc⁺/Cc. [Bmpyrr][NTf₂] possesses a 5 member ring, but unlike the imidazolium cation, lacks the ability to form the hydrogen bonds and $\pi - \pi$ interactions. In this solvent, the reduction of CO₂ occurs at *ca.* -1.2 V vs Cc⁺/Cc. These shifts suggest that the formation of a complex through the $\pi - \pi$ interaction of the imidazolium cation with the carbon dioxide intermediate is probably unlikely to be the cause of the reduction occurring at a lower overpotential. If the binding were to occur with the neutral molecule, the peak current density observed in the case of the imidazolium cations might be expected to be much greater than that of the pyrrolidinium cation. This would arise as a result of the solubility increasing as the CO₂ molecule is chemically bound by the cation at a much higher concentration than what would be observed in a non-bound interaction. The peak current densities, of 160 A m⁻² in the case of the [Bmim] based IL and 120 A m⁻² in the pyrrolidinium based IL, suggests that this is not the case. Although the variance in the potential across the cations (0.4 V) is much smaller than that observed previously on altering the electrode material (1.5 V), the cation sensitive peak potentials suggest that the reductive mechanism possibly includes a chemical step. This likely involves the cation binding to the silver surface first, where a desorption process, allowing the CO₂ molecule to access the electrode surface, precedes an irreversible reduction of the carbon dioxide, as clarified in (B) of Figure 6.

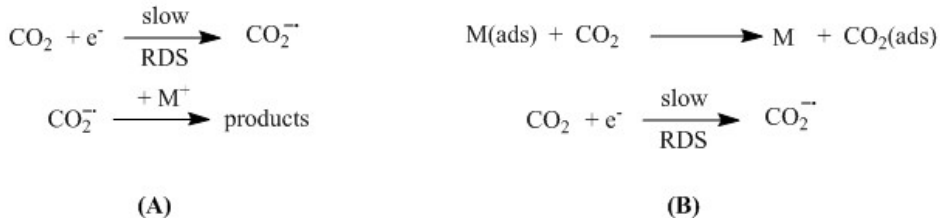


Figure 6: Two proposed mechanisms of CO₂ reduction, whereby (A) represents the mechanism previously proposed by Rosen *et. al*¹⁰ and (B) the mechanism proposed in this paper, whereby a chemical, desorption step precedes an irreversible electron transfer.

The previously proposed mechanism,¹⁰ (A) of Figure 6, suggests that the interaction with the cation (whereby the radical carbon dioxide anion interacts with the ionic liquid cation

post slow ‘irreversible’ electron transfer) is happening after the rate-determining step. If this were the case, no cation effect would be observable. As a cation effect is demonstrated, it serves to evidence the need for an alternative mechanism where the identity of the cation is significant. The peak current densities vary at most by a factor of two across this range of cations, compared with the factor of six seen between gold to silver. This further supports the notion that there is a silver-specific inner-sphere process occurring, with the desorption process from the double layer around the electrode accounting for the observed differences in the reduction potentials across cations.

Anion Effects on the CO₂ Reduction Potential

Last, the effect of varying the anion was considered, using the [Bmim]⁺ cation in each case. [Bmim][NTf₂] was investigated above, and has been included in Figure 7 (black line) for comparison purposes. As above, these voltammograms are presented with the potential scale measured versus a Ag/Ag⁺ reference electrode based on the relevant ionic liquid but corrected so as to be reported vs a Cc⁺/Cc reference electrode, and recorded at a saturated concentration of CO₂.

A CV was recorded in 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄], pink line in Figure 7) at a silver electrode by sweeping the potential from -0.4 V to -1.2 V, with a reductive feature of *ca.* 80 A m⁻² appearing at 1.05 V vs Cc⁺/Cc. The difference in peak current between the bistriflimide and tetrafluoroborate based ILs is likely to be solubility based, with the higher degree of fluorination known to promote greater solubility.²⁷ In 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([Bmim][FAP], purple line in Figure 7), a CV was recorded from -0.4 V to -1.8 V, to take into account the onset of reduction at -1.6 V vs Cc⁺/Cc. The peak current of *ca.* 20 μA (occurring at -1.6 V) is a little surprising given that FAP-based ILs have been reported to show the highest solubility of carbon dioxide of the anions presented herein.²⁸ Given this, there may be another process other than solubility contributing to the reaction, possibly the local solvent structure at the

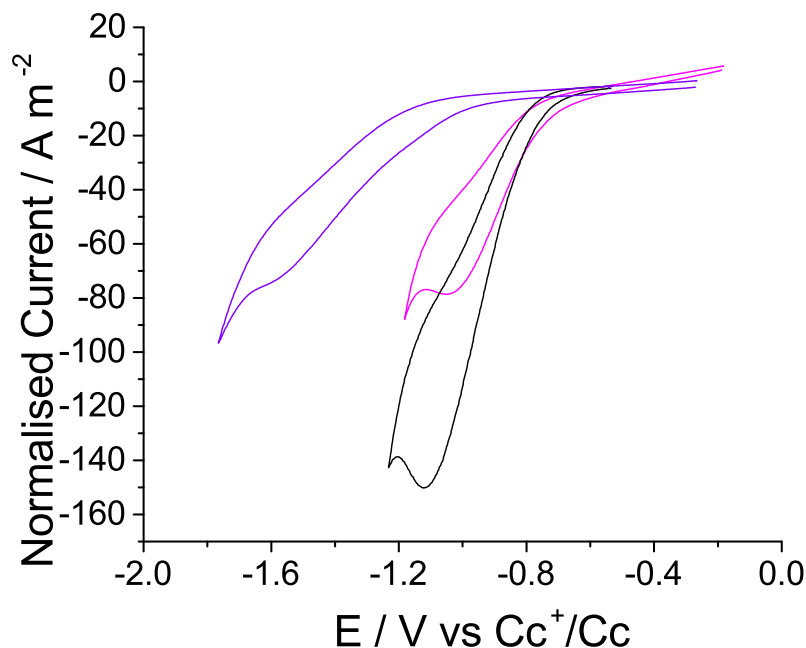


Figure 7: Cyclic Voltammograms of the reduction of carbon dioxide on silver with a scan rate of 1 V s^{-1} , with the potential scale corrected so as to be reported vs a Cc^+/Cc reference, in a range of RTILs where the anion is varied. Black is $[\text{Bmim}][\text{NTf}_2]$, pink $[\text{Bmim}][\text{BF}_4]$, and purple $[\text{Bmim}][\text{FAP}]$.

electrode interface. Once again, the differences observed in changing the anion are relatively small compared with the difference observed from altering the electrode material. This adds some credence to the suggestion that both ionic components occupy the double layer adjacent to the electrode, and must allow the carbon dioxide access to the electrode surface prior to the electron transfer occurring (in a CE type process), rather than an $E_{irr}C$ type process that sees the radical anion form a complex with the cation.

Conclusions

The paper has reported the electroreduction of CO_2 on a range of electrode materials, and with a systematically varied range of RTILs, using an IL-based reference electrode to facilitate comparison between different solvents. This work has thus demonstrated that there is a

silver-specific enhancement of CO₂ reduction in RTILs, likely an inner sphere, CE type, process involving desorption of the cation prior to electron transfer. This confirms that the imidazolium-intermediate complex formation is unlikely to play a significant role in the reduction, given that cation-specific reductive shifts in the CO₂ reduction were observed, making a E_{irr}C pathway unlikely.

Supporting Information

Three figures are included in the SI, depicting the reduction on platinum, and the reduction of cobaltocenium in a range of RTILs.

Acknowledgement

The research leading to these results has received partial funding from the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement no. [320403]. EELT thanks the Clarendon Fund and St John’s College for funding.

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Graphical TOC Entry

