

Electrochemical Carbon Dioxide Reduction in Ionic Liquids at High Pressure

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Abstract: Imidazolium ionic liquids are potentially useful solvents for both carbon dioxide reduction conversion and capture. In particular electrocatalytic CO₂ reduction has been shown to occur at low overpotentials using a 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][OTf]) and water mixed solvent. A limitation of such solvent systems is their viscosity, making it hard to maintain reasonable catalytic current densities without energy intensive stirring/agitation of the electrolyte. Here we explore the electrochemical reduction of CO₂ at high pressures (0.1 to 5.1 MPa) and demonstrate a correlation between the volume of expansion of the ionic liquid and the achieved catalytic current density. The improved electrocatalytic behaviour is proposed to be due to both the increased bulk CO₂ concentration and the improved mass transport properties of the gas-expanded ionic liquid. These initial studies at pressure represent a step towards realising an integrated CO₂ capture and utilisation system based around a common ionic liquid.

Introduction New technologies for CO₂ utilisation will be required if a circular carbon economy is to be achieved. Electrochemical CO₂ reduction is emerging as a potentially valuable form of CO₂ utilisation as it offers a route to produce useful chemical feedstocks and fuels, such as CO, HCOOH, CH₄ and C₂H₆, using renewable electrical energy. CO₂ electrocatalysis has been studied for over 35 years and in a landmark series of studies, Hori identified and categorised the activities of different metal electrodes for CO₂ reduction in aqueous electrolyte at room temperature and pressure.¹ It was shown that Au, Ag, Zn, Pd typically produce CO; Sn, In, Pd, Bi produce formate; Cu produces a mixture of CH₄ and C₂₊ products, depending on the nature of the Cu surface and the electrolyte. Since these early works numerous groups have examined routes to improve the selectivity of electrodes and to increase catalytic current densities at lower overpotentials. These have included the development of nanostructured, oxide derived, and alloy electrodes amongst others.²⁻⁵ Although significant advances have been made, the low concentration of dissolved CO₂ (34 mM) in aqueous electrolyte makes it

difficult to maintain high current densities for CO₂ reduction and competition with the hydrogen evolution reaction remains an issue-

An alternative approach to controlling activity for CO₂ reduction is through the use of non-aqueous or mixed solvents during electrolysis. In 2011 Rosen et al., reported that using a Ag cathode in a mixed ionic liquid [EMIM][BF₄] (1-ethyl-3-methylimidazolium tetra-fluoroborate) water solvent system it was possible to achieve selective reduction of CO₂ to CO with an overpotential of less than 0.2 V, significantly less than could be achieved in the absence of the ionic liquid.⁶ The high concentration of CO₂ achievable in solution (e.g. [EMIM][BF₄], concentration CO₂ = 74 mM, saturated, [EMIM][OTf] = 0.215 M, 298 K, 1 bar, ([OTf] = trifluoromethanesulfonate)),^{7,8} the good electrochemical stability and high conductivity of many common ionic liquids coupled to the proposed catalytic role of imidazolium ionic liquid/water mixtures has led to them becoming widely studied as solvents for electrochemical CO₂ reduction.⁹ In addition to being used during electrocatalysis, similar ionic liquid systems have been explored as potential CO₂ capture media.¹⁰ Therefore the intriguing possibility exists of developing integrated carbon capture and utilisation systems where the electrocatalytic reduction is carried out within the capture media. This may offer significant benefits, avoiding the need for energy intensive CO₂ release and capture agent regeneration steps, prior to utilisation.

The reason for the more positive onset potentials for CO₂ reduction using imidazolium ionic liquids is an active area of research and the complex behaviour of ionic liquid, water and CO₂ mixtures makes exact determination of the mechanisms difficult. However there is literature consensus that the mechanism of enhancement extends beyond providing a higher concentration of CO₂ in the bulk solvent.⁹ Rosen et al., proposed that the formation of a EMIM⁺-CO₂⁻ complex stabilised the initial one electron reduction product of CO₂, which has been widely proposed to be the cause of high overpotentials in many studies.^{6,11} A series of spectroscopic^{12,13} and electrochemical^{9,14} measurements have since explored the mechanism of carbon dioxide reduction in ionic liquids. Whilst some studies have found evidence supporting the possible stabilisation of reduced intermediates by the ionic liquid cation, this mechanism has also been disputed. In a study on Ag electrodes using a range of different neat room temperature ionic liquids it was proposed that the low overpotential is actually due to a silver facilitated inner-sphere reduction of CO₂, with the sensitivity of the system to the nature of the cation used a result of the need for cation desorption from the electrode surface prior to reduction.¹⁴ Supporting this mechanism is the observation that the onset for CO₂ reduction correlates with a structural transition in the double layer, with the ionic liquid structuring at the same potential regardless of the presence of the CO₂.¹² In addition to facilitating the catalytic reduction of CO₂ the ionic liquid is also proposed to suppress the hydrogen evolution reaction, particularly at low pH's where the accumulation of ionic liquid cations at the electrode surface can limit H⁺ diffusion to catalytic sites.^{9,15,16}

Although the lab based results using imidazolium ionic liquid/water mixtures as solvents for CO₂ catalysis are promising, significant barriers to their practical application exist. Studies have only reported low limiting current densities during electrolysis using both EMIM and BMIM (butyl-3-methylimidazolium) based ionic liquids indicating that mass transport of substrate to the electrode and/or transport of product away from the electrode becomes limiting. Typical diffusion coefficients for CO₂ in imidazolium ionic liquids are on the order of 10⁻¹⁰ to 10⁻¹¹ m² s⁻¹,⁸ with [EMIM][OTf] being reported to be 4.5 (±0.1)×10⁻¹¹ m² s⁻¹ (500 ppm H₂O).¹⁰ In contrast the diffusion coefficient for CO₂ in aqueous carbonate/bicarbonate solutions at room temperature and pressure is 1.59×10⁻⁹ m² s⁻¹.¹⁷ The viscous nature of many ionic liquids has been shown to be the cause of the low diffusion coefficients, with there being an inverse correlation between CO₂ diffusion coefficient and viscosity.⁸ The high viscosity is the result of both strong Van der Waals and hydrogen bonding interactions between the components of the ionic liquid/water mixture.¹⁰ Therefore in order to maintain high current densities for CO₂ reduction it will be necessary to either stir or flow a viscous solvent, likely with significant energy cost implications, or to find a way to improve the mass transport properties of the electrolyte. The viscosity of an ionic liquid can be changed through synthetic modification and using a BMIM cation with a range of different anions^{9,14} the catalytic current for CO₂ reduction has been shown to be inversely proportional to the viscosity. Similarly studies modifying the alkyl chain length of the imidazolium ion have also been carried out.⁸ The viscosity of the electrolyte can also be tuned through dilution with water.^{7,18} Electrocatalysis studies have been carried out using electrolytes with an extremely broad range of concentrations of ionic liquids, ranging from low mM (dissolved in water) to neat,⁷ in an attempt to find an optimum balance between maximising the achievable current density and the ionic liquid catalytic effect. For example using [EMIM][OTf] it was found that at > 0.64 mol% ionic liquid, some inhibition of the hydrogen evolution occurs.¹⁶ However, high levels of selectivity towards CO production were only achieved at very high concentrations (50 mol% ionic liquid). Conditions that led to a notable decrease in the maximum current for CO₂ reduction during electrochemical measurements.

Here we report the use of elevated pressures of CO₂ with [EMIM][OTf]/H₂O mixes to explore the role of pressure in providing a high local CO₂ concentration at the electrode surface, through both an increased bulk CO₂ concentration and as a result through improved mass transport properties. For many ionic liquid mixtures a large decrease in viscosity has been reported when placed under a high CO₂ pressure which correlates with the expansion of the ionic liquid.¹⁹ CO₂ expanded liquids are formed as the high pressure CO₂ dissolves leading to a volumetric expansion, with the volume of expansion dependent on the gas pressure and the liquid properties. Solvents are categorised into three different classes of CO₂ expanded liquids. Water and other solvents with low CO₂ solubility are class I, showing no significant expansion with pressure, whilst class II liquids expand greatly and have the highest gas solubility. Imidazolium ionic liquids are typically class III with CO₂, where the gas is moderately

soluble, leading to a small, but significant volume expansion (e.g. 17% volume expansion for [BMIM][BF₆] between 0.1 and 7.0 MPa).²⁰ Gas expanded ionic liquids can have distinct properties (polarity, viscosity, conductivity and acidity amongst others) that can be tuned by the CO₂ pressure²⁰ and we anticipated that the increase in volume of a CO₂ expanded [EMIM][OTf]/H₂O mix would offer both a higher bulk CO₂ concentration and an improved mass transport properties during electrocatalysis when compared to the solvent at atmospheric/low pressure.

Several groups have examined the role of CO₂ pressure with aqueous electrolytes^{21–27} and of particular note is the observation that a ~65 fold increase in current density upon going from 0.1 to 6.1 MPa of CO₂ using a Ag electrode in KHCO₃.²¹ In most cases the increased catalytic activity has been assigned to the higher CO₂ concentration at the surface of the electrode²¹ and the role of improved transport properties has not been considered. Relatively few studies have explored the role of pressure on CO₂ electrocatalysis when ionic liquids are the solvent. Zhao et al., studied the reduction of supercritical CO₂ in the presence of 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and low levels of water (2.7 to 7.5 wt%) at a Cu electrode. They observed increased current densities at a constant potential versus a Pt quasi reference electrode above the critical pressure.²⁸ Two studies have also examined the electrocatalytic CO₂ reduction to CO in an acidified [EMIM][OTf]/H₂O, with a range of water contents (90, 50 and 10 wt% water) at 1 and 3 MPa (318 K) using Zn based electrodes to produce formate.^{29–30} The initial results in [EMIM][OTf]/H₂O at two pressures is very promising, with higher current densities, and excellent selectivities towards formate at the higher pressure studied (3 MPa), demonstrating the principle of integrated capture and conversion systems using ionic liquids.²⁹ Here we have carried out a detailed examination of the role of CO₂ pressure on electrocatalytic activity on a typical ionic liquid-water mixture ([EMIM][OTf]/H₂O) using a Ag electrode to produce CO over a large range of pressures (0.1 to 5.1 MPa). Our aim is to stimulate discussion on the possible beneficial role of elevated pressures to overcome the diffusion limited currents often observed with imidazolium ionic liquid solvents. Finally, we demonstrate that a large increase in limiting current density for CO₂ reduction can be achieved even at moderate pressures (2.1 MPa), equivalent to those used in precombustion capture processes.

Experimental

[EMIM][OTf] was purchased from either Ilotec (99%) or Sigma Aldrich (≥ 98%, electrochemistry grade) and used as received. [EMIM][BF₄] (≥ 98%, electrochemistry grade) and KHCO₃ (>99.95%) were purchased from Sigma Aldrich and used as received. Milli-Q water (18.2 MΩ) was used throughout. Argon and CO₂ (CP grade) were purchased from BOC. The working electrodes for all experiments were Ag wires (Goodfellow, 99.99%). Electrodes were mechanically polished prior to use with an alumina slurry. A Pt wire counter electrode and Ag/Ag⁺ pseudo reference electrode were also

used and details of the preparation and use of the reference electrode at low and high pressure can be found in the supporting information.

In all experiments [EMIM][OTf] (3.618 mL) was added to H₂O (1.382 mL) to make 5 mL of 20 mol% (78 wt.%) [EMIM][OTf] solution. This concentration of ionic liquid in water was chosen as (i) it falls in the range most commonly studied during electrocatalysis (5-25 mol%) where water is used to decrease the viscosity and enhance conductivity (ii) we show below that at this level selectivity towards CO₂ reduction can be achieved. Low-pressure cyclic voltammogram (CV) and bulk electrolysis experiments were carried out using a sealed glass cell with the counter electrode separated from the electrolyte solution using a vycor frit. Samples were purged with either Ar or CO₂ for 20 minutes prior to experiments. Samples were not stirred during voltammetry or electrolysis studies. Gas analysis of low pressure experiments was carried out using a gas chromatography previously described.³¹

High pressure electrochemical measurements were carried out using a custom designed stainless steel cell (photo shown in Fig. 1) and filling station with recirculating pump. Full details of the high pressure apparatus can be found in the supporting information alongside Fig. S1. *Safety note, high pressure experiments require the use of equipment that is appropriately rated for the pressure and temperature regime and should only be performed by appropriately trained operators.* To study the expansion of the ionic liquid/water with pressure, a high pressure variable volume view cell that has been previously described was used.³² The ionic liquid based solvent was added to a graduated sample vial and placed in the cell. The CO₂ pressure was gradually increased, with images recorded at 0.2, 1.1, 2.6 and 5.1 MPa, following a short equilibration period. Images were analysed using image-j software to calculate the volume of expansion.

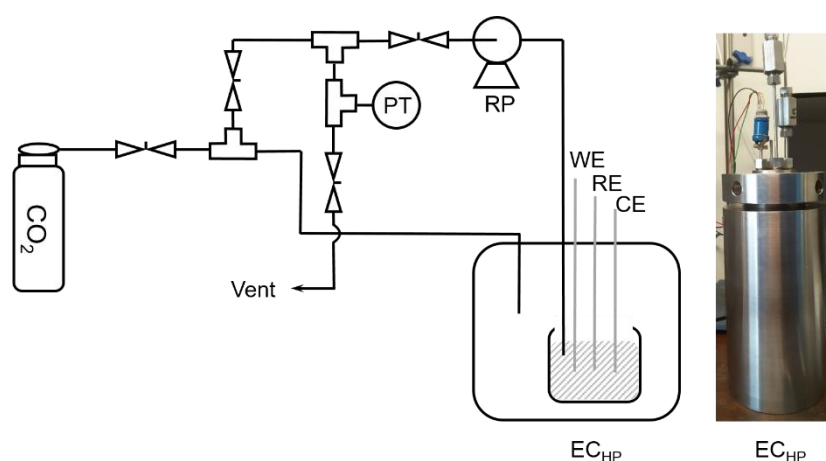


Figure 1. Schematic of the high pressure apparatus for electrochemical studies under CO₂. PT, pressure transducer; RP, reciprocating pump; EC_{HP}, high pressure electrochemical cell; WE, working electrode (Ag); RE, reference electrode (Ag/Ag⁺); CE, counter electrode (Pt). The right hand side shows a photo of the high pressure electrochemical cell.

Results and Discussion: A range of imidazolium ionic liquids have now been studied as solvents during electrocatalytic carbon dioxide reduction. Here we have focussed on [EMIM][OTf]/H₂O for a number of reasons. Firstly [EMIM][OTf] has a good electrochemical stability, with a reported electrochemical window of *ca.* 3.2 V (500 ppm H₂O).⁷ It also has a good chemical stability in the presence of H₂O, in contrast to the more commonly studied [EMIM][BF₄] which readily hydrolyses. This is a particularly important consideration for studies at high pressure where the generation of corrosive species within the stainless steel electrochemical apparatus represents a safety concern. Finally [EMIM][OTf]/H₂O mixes have been previously used as solvents for both CO₂ reduction^{7,16} and capture^{33,34} making them of interest for an integrated capture and electrochemical conversion system. CVs of [EMIM][OTf] 20 mol% in water under both N₂ and CO₂ recorded at 20 mV s⁻¹ with a silver wire working electrode are shown in Fig. 2. In the experiments shown in figures 2 and 3 the electrochemical cell is purged with a constant stream of the gas indicated and then sealed such that it has a pressure of *ca.* 0.1 MPa. Under N₂ a small current flows at potentials cathodic of -1.0 V which can be assigned to hydrogen evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). Comparison can be made to CVs recorded in a purely aqueous (0.1M KHCO₃) electrolyte (Fig. S2) which show a large current increase at potentials -1.2 V due to hydrogen evolution. It is apparent that the [EMIM][OTf] has significantly suppressed the hydrogen evolution current, likely through the passivation of the electrode surface by EMIM⁺, in-line with past studies.^{7,16} Under CO₂ an additional reduction onsets at -1.4 V which is proposed to be due to CO₂ reduction to CO ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$). Some previous work has indicated that 50 mol% or higher concentrations of [EMIM][OTf] are required to achieve selective CO₂ reduction but here we find that bulk electrolysis under CO₂ (0.1 M Pa) using only 20 mol% [EMIM][OTf] leads to CO being produced with a selectivity of 1.8:1 (CO:H₂, total Faradic efficiency 94 %, table S1). Under N₂ no CO is detected, only H₂. This represents an improvement when compared to the same experiment carried out with the more common EMIM BF₄/H₂O system (1.1:1, CO:H₂). Both ionic liquids however achieved significantly greater selectivity for CO production than the same Ag wire in a KHCO₃ electrolyte (1:16, CO:H₂, table S1). Therefore, the bulk electrolysis studies confirm that the catalytic process occurring at potentials negative of -1.4 V in the presence of [EMIM][OTf]/H₂O (20 mol% ionic liquid) is CO₂ reduction to CO.

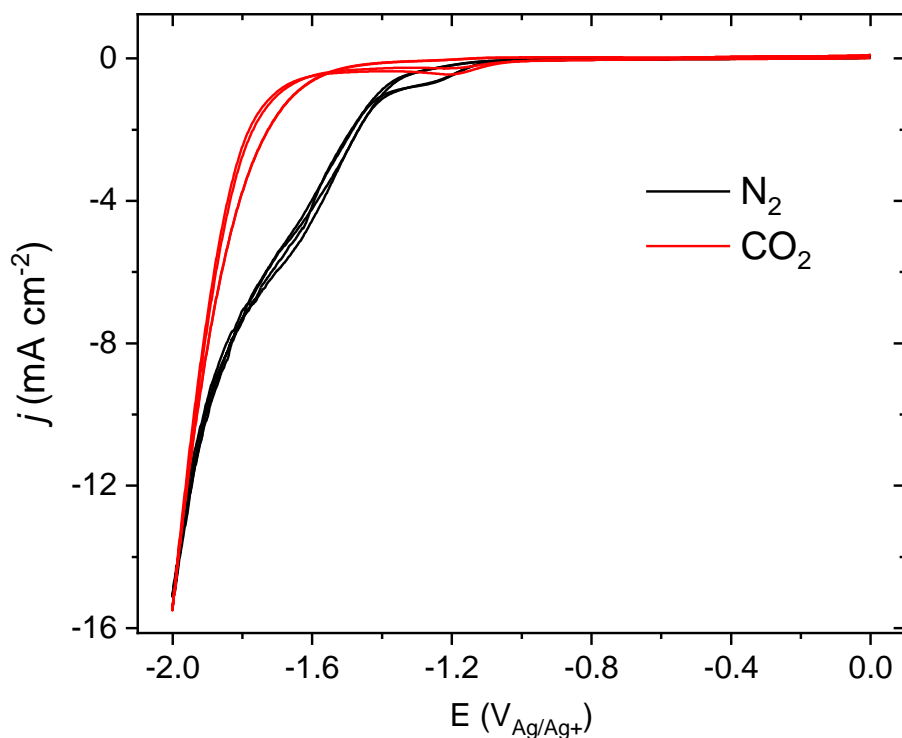


Figure 2. Two consecutive CVs using a Ag working electrode under N₂ (black) and CO₂ (red) in [EMIM][OTf]/H₂O recorded at 20 mV s⁻¹ following purging (ca. 0.1 MPa) with each gas.

At potentials negative of -1.5 V under CO₂ we see a deviation from Tafel type behaviour (Fig. S3) and a plateauing of the catalytic current density (Fig 2). This indicates either mass transport limitations (likely of CO₂ or H⁺) or that the rate of chemical steps has become limiting (i.e. the intrinsic catalytic activity of the metal electrode).³⁵ Scan rate dependent CVs under both N₂ and CO₂ for the Ag working electrode in [EMIM][OTf]/H₂O are shown in Fig. 3. As the scan rate is increased under CO₂ the maximum catalytic current due to CO₂ reduction to CO increases. However, for all scan rates, at potentials cathodic of -1.5 V we still observe a plateau current confirming that mass transport is limiting catalysis even at scan rates as high as 1 V s⁻¹. As the cell is not stirred, and we use a high concentration of ionic liquid which is likely to minimise migration effects, we are observing diffusion limited catalytic currents. Although the measured currents are much smaller (10 times approximately) in the absence of CO₂ (Fig. 3b), we also note a scan-rate dependence of the current under N₂, conditions where only the hydrogen evolution reaction will occur. Chronoamperometry data recorded of [EMIM][OTf]/H₂O in an unstirred electrochemical cell using a Ag wire electrode under low pressure CO₂ also shows a large decrease in current density with time. We record an 83% decrease within the first 60 s when a potential of -2.0 V is applied (compared to the current recorded at 0.5 s after electrolysis starts, chosen to minimise the capacitive current contribution) and a 72% loss of current in the first 60 s when a potential

of -1.6 V is applied, Fig. S4. At -2.0 and -1.6 V we are approaching similar steady state (limiting) current of only -0.24 and -0.18 mA cm⁻² 10 minutes after electrolysis starts (Fig. S5). Again this confirms that the net rate of carbon dioxide reduction is being governed by the rate at which CO₂ and/or H⁺ are reaching the electrode surface. It is therefore clear that although the [EMIM][OTf]/H₂O solvent system provides a way to gain increased selectivity, to maintain a reasonable current density for CO₂ reduction to CO under low-pressure conditions flowing or rapid stirring of the electrolyte will be required.

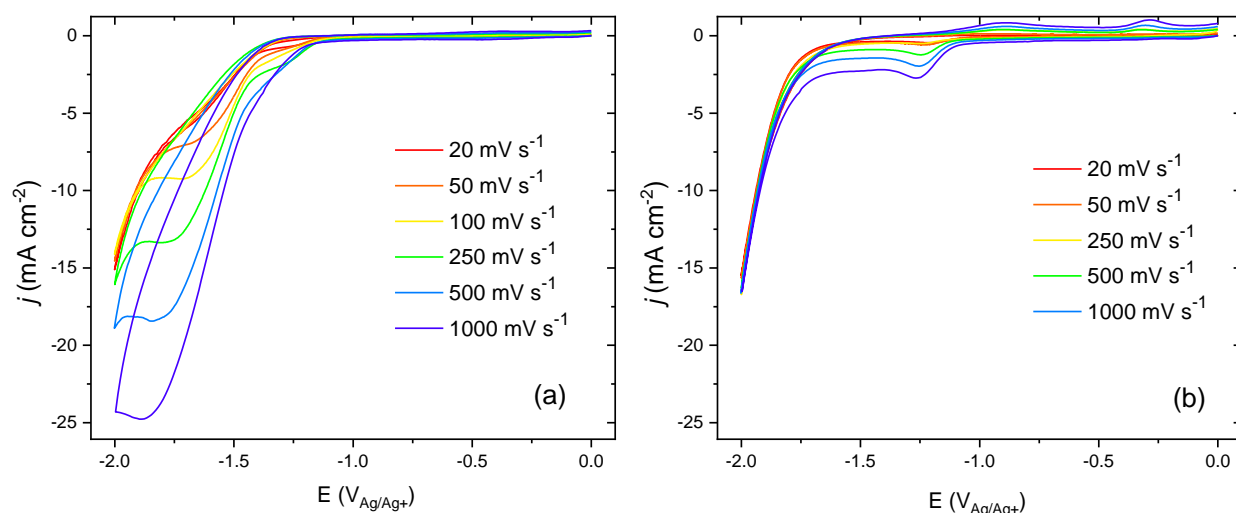


Figure 3. CVs of Ag working electrode in [EMIM][OTf]/H₂O recorded at a range of scan rates following purging (ca. 0.1 MPa) with CO₂ (a) and N₂ (b).

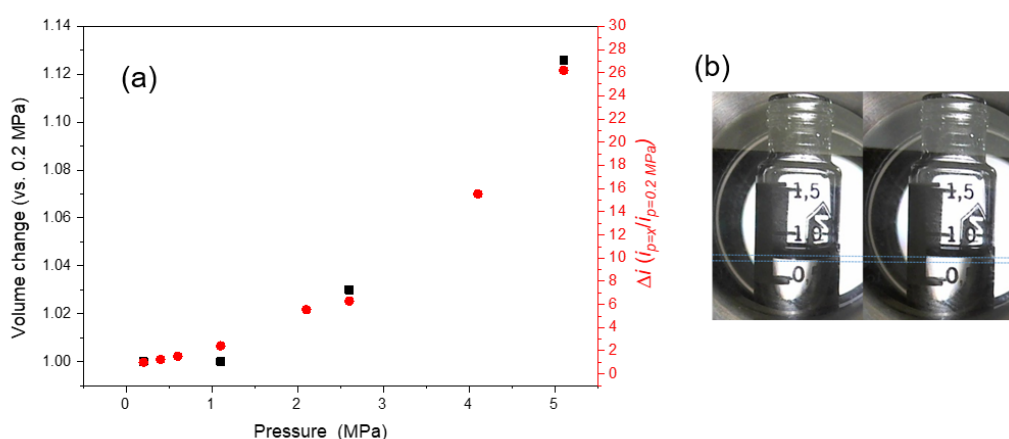


Figure 4. (a) Change in volume with CO₂ pressure at room temperature (black solid squares, left axis) and change in catalytic current (recorded at -1.50 V) with CO₂ pressure (red solid circles, right axis) using the [EMIM][OTf] electrolyte. (b) The change in volume of the [EMIM][OTf] solution is measured using a high pressure view cell with images analysed with the image-j software package.

Variable pressure studies on the ionic liquid electrolyte using a high pressure view cell have been carried out (Fig. 4) and we find that at 5.1 MPa there is a 12.6% increase in volume (compared to images recorded at 0.2 MPa). At all pressures studied (0.2 MPa to 5.1 MPa, *ca.* 294 K) distinct liquid and gas phases could be observed. The relatively small volume expansion of the ionic liquid is expected as it is widely reported that imidazolium ionic liquids form class III gas expanded ionic liquids with CO₂.³⁶ Buoyancy effect calculations for pure [EMIM][OTf] at a range of pressures showed that at higher pressures (between 1.5 and 6 MPa) the buoyancy effect caused large changes in uncorrected gravimetric measurements of CO₂ solubility,³⁷ in-line with the observed significant expansion in volume at 2.6 and 5.1 MPa seen here (Fig. 4a). We are not aware of CO₂ solubility data or volumetric change values for [EMIM][OTf] at 20 mol% (78 wt.%) in water. However previous studies on the solubility of CO₂ in pure [EMIM][OTF] at 303 K can act as an indicator with an increase from 0.13 to 1.13, 2.07 and 4.44 mol_{CO2} kg_{IL}⁻¹ occurring as the pressure was increased from 0.18 to 1.5, 2.8 and 5.4 MPa respectively.³⁷ As recent studies on the effect of the solubility of CO₂ in [EMIM][OTf] showed only a slight dependence on water content with a decrease of 10% in solubility when 10 wt% water was added (the highest water level studied)³⁴ we arrive at an estimated ~30 fold increase in dissolved CO₂ between 0.2 and 5.2 MPa here (22 wt% water), based off past studies.³⁷

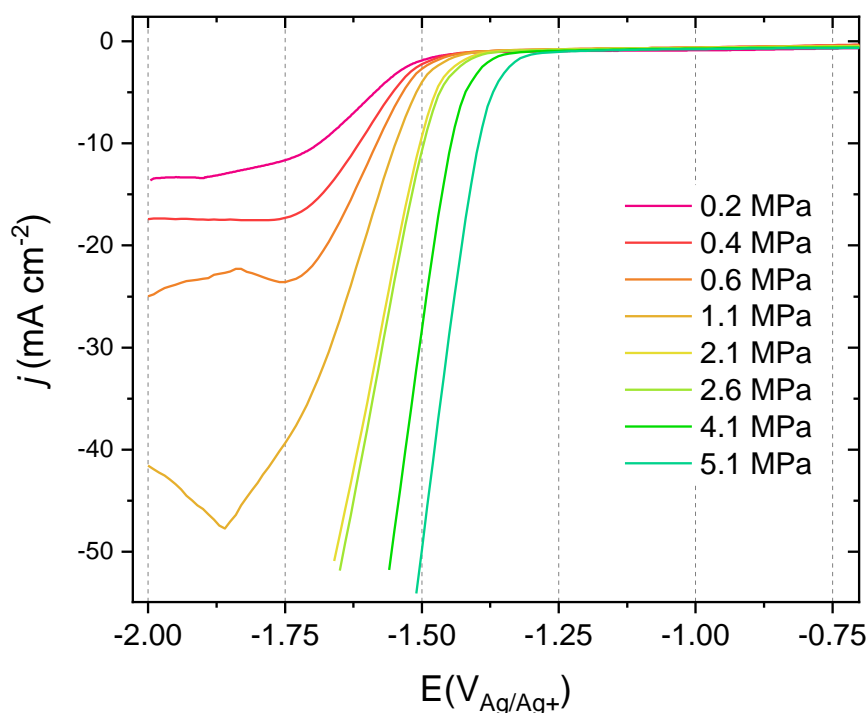


Figure 5. Linear sweep voltammograms (50 mV s^{-1}) of Ag working electrode in [EMIM][OTf]/H₂O at a range of CO₂ pressures.

Electrochemical measurements were carried out with the ionic liquid mixture at a range of CO₂ pressures (0.2 to 5.1 MPa) in a custom designed steel high pressure electrochemical cell, Fig. 5. We observe both a large increase in the electrocatalytic current for CO₂ reduction and a positive shift in the onset potential as the pressure is increased. The potential applied to reach 1.5 mA cm⁻² is used as a measure of onset potential and this decreases by ~160 mV (-1.47 to -1.31 V) between 0.2 and 5.1 MPa. Many studies have reported overpotentials for CO₂ reduction to CO in ionic liquids, however calculation of the overpotential requires knowledge of the equilibrium potential for the reduction of CO₂ to CO in the particular ionic liquid mixture under the conditions used. The Nernst equation tells us that an increase in the CO₂:CO concentration ratio by a factor of ~30 will give rise to ~44 mV change in equilibrium potential for a 2 electron reduction, assuming that the formal potential remains unchanged. The estimated shift in due to CO₂ concentration (~44 mV) is therefore significantly less than the shift in onset potential we have measured (~160 mV) here as the pressure increases from 0.2 to 5.1 MPa. The large change in onset potential could indicate a change in mechanism of CO₂ reduction at higher pressures however great caution should be exercised when interpreting the change in onset potential. Firstly, we have made use of an estimated change in dissolved CO₂ concentration and assumed the CO concentration to be non-zero and constant at all pressures. Second, such an analysis only holds if the formal potential for CO₂ reduction to CO remains unchanged with pressure. Even using atmospheric pressure of CO₂, few studies have accurately determined the standard electrode potential for CO₂ reduction for mixed water-ionic liquid solvents.³⁸ As the pressure dependence of key parameters, such as; the activity of water and the imidazolium ion (through reaction with a bicarbonate ion) as proton sources, the speciation of the dissolved CO₂ species (e.g. HCO₃⁻/CO₃²⁻, CO₂) and the ionic strength remain unknown we have no physical basis for such an assumption. Nonetheless, the magnitude of the shift in onset potential for CO₂ reduction does appear to warrant further investigation beyond this initial study.

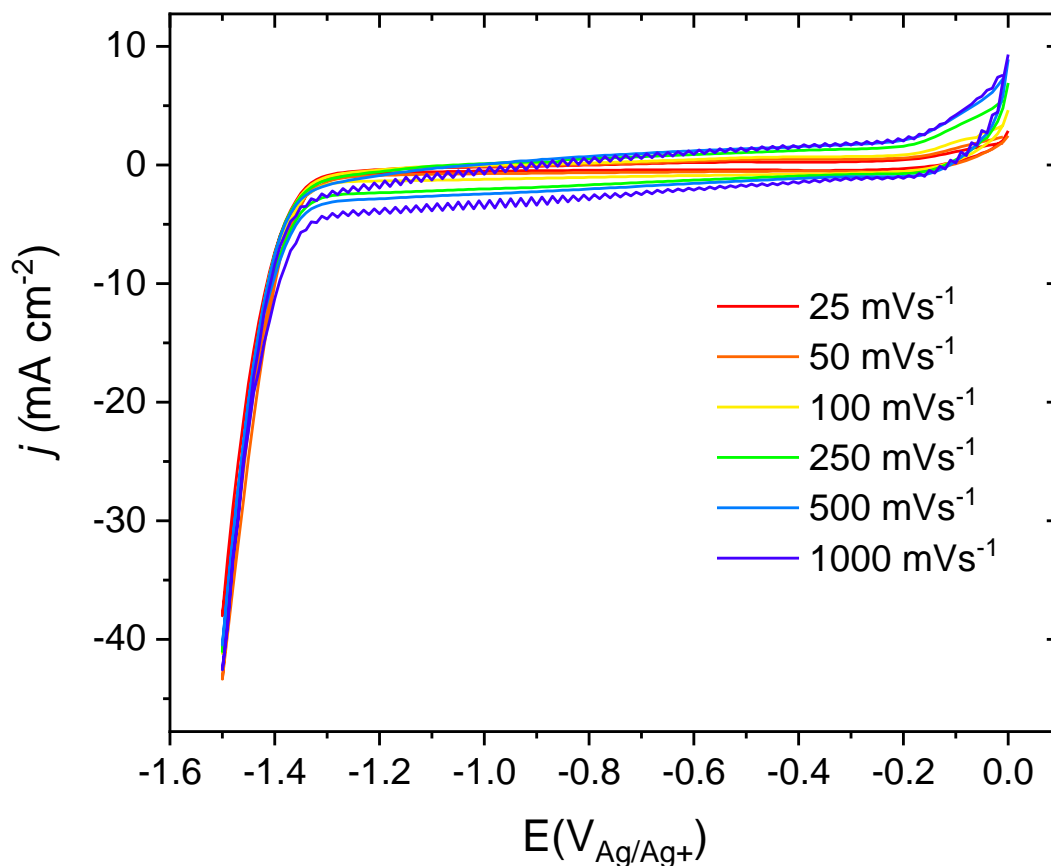


Figure 6. CVs of Ag working electrode in [EMIM][OTf]/H₂O at 5.1 MPa (CO₂) recorded at a range of scan rates.

At pressures above 2.1 MPa the currents ($< -60 \text{ mA cm}^{-2}$) became limited by the design of the electrochemical cell which uses a relatively low surface area Pt wire counter electrode. Therefore, the electrochemical window for measurements at higher pressure was limited and it was not possible to observe the potential region where the CO₂ reduction current plateaued at the highest pressure studied during linear sweep measurements recorded at 50 mVs^{-1} , Fig. 5. However from the data recorded it is clear that between 0.2 and 5.1 MPa the current for CO₂ reduction during linear sweep experiments is increasing with pressure (as measured at -1.5 V). This is expected as the measured catalytic current is anticipated to directly correlate with the increased concentration of dissolved substrate (CO₂), assuming that catalysis is not also limited by H⁺ availability.³⁵ Variable scan rate CVs recorded at 5.1 MPa (Fig. 6) show that at 5.1 MPa the current is no-longer dependent upon the scan rate in the potential window examined, this is markedly different from the results recorded in Fig. 3(a) where mass transport limitations became apparent even at very high (1 Vs^{-1}) scan rates.

Figure 4 shows there is a correlation between the measured catalytic current for CO₂ reduction and the volumetric change of the [EMIM][OTf] mixture as measured during the CV experiment at 50 mV s^{-1} .

The expanded volume of the ionic liquid is significant as in addition to the solvent containing a higher concentration of dissolved CO₂ in the bulk, volumetric expansion can also lead to changes in viscosity³⁹ of the ionic liquid solvent. Numerous studies have reported a sharp drop in solvent viscosity as the CO₂ pressure (and hence CO₂ content of the ionic liquid) increases,¹⁹ including for a imidazolium ionic liquid/methanol mixture.⁴⁰ For [EMIM][OTF]/H₂O mixtures an inverse correlation between viscosity and molar conductivity, and also between the viscosity and diffusion coefficient for CO₂, has been reported.⁷ Evaluation of the mass transfer coefficients for CO₂ reduction from the electrochemical data requires accurate knowledge of the dissolved CO₂ concentration in the bulk at the two pressures and also knowledge of the reaction order of the rate equation for CO₂ reduction with respect to both [CO₂] and [H⁺] at each pressure. This data is not obtained in this preliminary report. However from established literature it is clear that a decrease in viscosity will occur at high pressures of CO₂, which in turn leads to larger diffusion coefficients for CO₂ (and possibly H⁺). Therefore alongside the higher initial CO₂ concentration at the electrode surface, improved greater mass transfer coefficients for CO₂ (and possibly H⁺) are proposed to be the key factors behind the marked difference in the scan rate dependent data of Fig. 3a and 6.

Finally we have carried out chronoamperometry experiments at 2.1 MPa of CO₂, a pressure of CO₂, similar to what is used in previous pre-combustion capture experiments using ionic liquids.⁴¹ Two different potentials (-1.8 V and -1.5 V) have been studied, Fig S6,7. Although the chronoamperometry data shows a 69% and 68% decrease in current density within 60 s (compared to the current recorded at 0.5 s after electrolysis starts, we achieve steady state current densities in the un-stirred system of -14.5 mA cm⁻² (-1.8 V) and -13.5 mA cm⁻² (-1.5 V). This limiting current density is approximately ~ 70 greater than achieved at 0.1 MPa (Fig S5,7) demonstrating a route to achieving greatly improved current densities in ionic liquid based electrolytes without the need for extensive stirring/flowing of the electrolyte at industrially relevant pressures.

Conclusions: Imidazolium ionic liquid/water mixtures are potentially exciting solvents for electrochemical carbon dioxide reduction but an often undescribed limitation is the viscous nature of the solvent when low water contents are used. This leads to the need to either vigorously stir or flow the electrolyte, potentially an energy intensive process, in-order to maintain a reasonable current density for CO₂ reduction. Here we demonstrate that at high pressures (up to 5.1 MPa) of CO₂ very large increases in current density can be achieved both in voltammetry measurements and during prolonged electrolysis. The exact mechanism of the observed positive shift in onset potential for catalysis and the improved limiting current densities requires further investigation however, it is clear that even at moderate pressures (2.1 MPa) large improvements in electrocatalytic activity can be achieved. Alongside more detailed mechanistic research, studies that assess the energetic and economic

implications of electrocatalysis at pressure are also required. Nonetheless, ours and others⁴² initial works demonstrate the chemical feasibility of carrying out CO₂ capture and conversion in a common ionic liquid solvent.

Acknowledgements

AC thanks the EPSRC (EP/P034497/1) for financial support. This work was supported by a CO₂Chem seedcorn grant.

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