Efficient electrocatalytic CO₂ reduction driven by ionic liquid buffer-like solutions

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Abstract: We show here that electrocatalysis of CO₂ reduction in aqueous electrolytes containing the ionic liquid (IL) 1-n-butyl-2,3-dimethylimidazolium acetate ([BMMIm][OAc]) and dimethyl sulfoxide (DMSO) proceeds at low overpotentials (~0.9 V vs. Ag/AgCl) at commercially-available Au electrodes, and with high selectivity for CO production (58% faradaic efficiency at ~1.6 V vs Ag/AgCl). 0.43 mol of CO₂ per mol of IL can be absorbed into the electrolyte at atmospheric pressure, forming bicarbonate and providing a constant supply of dissolved CO₂ to the surface of the electrode. We also show that electrocatalysis of CO₂ reduction in the electrolyte is facilitated by stabilization of CO₂ radical anions by the imidazolium cations of the IL and buffer-like effects with bicarbonate.

Introduction

Concerns about escalating CO₂ emissions are driving the development of new methods for capturing and utilising atmospheric CO₂. Of the methods available for activating CO₂, electrocatalytic CO₂ reduction using renewable electricity is one of the most promising.[1-5] The possible products of CO₂ electroreduction include CO, formate, methanol, methane, and ethanol.[6] CO is particularly attractive as CO₂ reduction to CO requires just two electrons,[7] and CO can be used in the water–gas shift reaction to produce H₂.[8] Fischer–Tropsch (FT) methods can then be used to convert mixtures of CO and H₂ (syngas) into synthetic petroleum and other liquid fuels.[9] Metals such as Ag and Au can electrocatalyze reduction of CO₂ to CO in aqueous media, but relatively high reduction overpotentials and low selectivity are often observed.[10] Moreover, CO₂ electroreduction in aqueous media is complicated by competitive co-electrogeneration of H₂, which reduces the faradaic efficiency for CO production.[2]

Ionic liquids (ILs – Figure 1) are salts that are liquid below 100 °C and which, due to their wide electrochemical windows and inherent conductivities, are attracting a lot of attention from electrochemists.[11, 12] In 2011, it was shown that the CO₂-reduction overpotential in aqueous electrolytes could be lowered drastically by adding the IL 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF₄], to the electrolyte, a phenomenon that was attributed to complexion of the reduced “CO₂⁻” by the IL.[13] Since that initial report, a number of authors have demonstrated that ILs can promote CO₂ electroreduction at low overpotentials and at different electrode materials.[13-21] However, the mechanism by which ILs lower reduction overpotentials has not yet been fully elucidated. It was proposed that lowering of the pH upon hydrolysis of [BF₄]⁻ increases the conversion of CO₂ to CO, while adsorption of [EMIM]⁺ cations onto the electrode hinders proton adsorption and competitive H₂ evolution.[18] Clear cation (as well as anion) effects during CO₂ electroreduction have been observed, indicating that the formation of an IL imidazolium cation-CO₂⁺ complex after an initial, rate-determining reduction step is unlikely.[22] While reduction of CO₂ in the presence of imidazolium-based ILs usually yields CO, oxalate and HCOO⁻ can also form as the nature of the IL anions and the composition of the electrode are varied.[23]

The recent literature has also revealed remarkable insights into the interactions of CO₂ with ILs. ILs containing basic anions (such as imidazolate and triazolate) or dialkylimidazolium cations (usually associated with the acetate anion) can covalently interact with CO₂, yielding carbanates and carboxylates, respectively (Scheme 1).[24, 25] It has been proposed that H⁺ ions released during the formation of imidazolium carbonates (Scheme 1B) may act as a source of H⁺ ions during electroreduction of CO₂.[26-28] It was also recently shown that in ILs containing basic anions, CO₂ capture most likely proceeds primary via the formation of bicarbonate followed by IL-CO₂ adducts, and the IL (which invariably contains some water) behaves as a buffer-like solution.[29] When dissolved in DMSO/H₂O, 1-n-butyl-2,3-dimethyl imidazolium acetate ([BMMIm][OAc]), in which no reaction of the cation with CO₂ has been detected,[25] can stabilize up to 1.70 mol dm⁻³ of free formic acid from the hydrogenation of CO₂.[6, 29]
Bicarbonate has also been implicated in the electroreduction of CO\textsubscript{2}; while it had generally been thought that dissolved CO\textsubscript{2} is the only active species during electroreduction of CO\textsubscript{2},\cite{11, 30, 31} it was recently shown that dissolved bicarbonate formed upon dissolution of CO\textsubscript{2} in aqueous media increases the concentration of CO\textsubscript{2} near Au electrodes and increases the rate of CO\textsubscript{2} electroreduction.\cite{31}

In this contribution, we show that the use of basic ILs that form buffer-like solutions in aqueous media allow electrochemical reduction of CO\textsubscript{2} at remarkably low overpotentials and with high selectivity and faradaic efficiency for CO production. Specifically, we show that mixtures of [BMIm][OAc], DMSO and water can dissolve up to 43 mol\% of CO\textsubscript{2} (27 mol\% via formation of bicarbonate and 16 mol\% via solvated CO\textsubscript{2}) at atmospheric pressure (see SI Table S2). This solution supports selective electroreduction of CO\textsubscript{2} to CO at Au electrodes at potentials as low as −1.40 V vs. Ag/AgCl. At −1.80 V vs. Ag/AgCl, faradaic efficiencies for CO formation above 98\% are observed. Addition of large amounts of water to the electrolyte favors the formation of free bicarbonate, which reduces the energy required for the electrochemical reduction of CO\textsubscript{2}, but this is accompanied by the co-electrogenation of H\textsubscript{2}, yielding syngas that could be used for the formation of liquid fuel using follow-up processing.

**Results and Discussion**

The solubility of CO\textsubscript{2} in [BMIm][OAc]/DMSO/H\textsubscript{2}O solutions was quantified using \textsuperscript{13}C-[\textsuperscript{1}H\textsubscript{NMR spectroscopy (see SI Table S2).\cite{22} By varying the water content in DMSO from 0.2 vol\% to 100\% (without DMSO) at constant IL concentration (1.0 mol dm\textsuperscript{3}) we determined that the maximum concentration of HCO\textsubscript{3}\textsuperscript{−} (0.41 mol dm\textsuperscript{3}) was obtained when the water content was 5.2 vol\% (see SI Table S2 entries 1-4 and Figure S2). When the water content was kept at 5.2\% and the concentration of IL was varied from 0.4 to 3.0 mol dm\textsuperscript{3}, the concentration of HCO\textsubscript{3}\textsuperscript{−} increased (Figure 2). That the log of the bicarbonate concentration increased as the log of the IL concentration increased can be explained by the Henderson-Hasselbalch equation, typically employed to describe buffer systems. Spectroscopy of all IL solutions revealed that the major signal was due to bicarbonate (ca. 159 ppm) and a minor signal appeared at ca. 124 ppm due to the presence of dissolved CO\textsubscript{2}. It has recently been shown that the formation of HCO\textsubscript{3}\textsuperscript{−} near electrodes can lead to high CO\textsubscript{2}-reduction efficiencies in aqueous media.\cite{31}

We explored the effects of addition of H\textsubscript{2}O to DMSO solutions containing the buffering IL on electroreduction of CO\textsubscript{2} using linear-sweep voltammetry in blank and CO\textsubscript{2}-saturated mixtures. In all electrochemical studies the IL concentration were fixed at 0.1 mol dm\textsuperscript{-3}, changing only the concentration of water in DMSO. (Figure 3). Note that the conductivity of the solution did not change significantly upon addition of varying amounts of water to the electrolyte (conductivity from 1.598 mS at 0.5 vol\% to 1.499 mS at 5 vol\% water).

The reduction onset potential (defined at the intersection point of the tangent at maximum slope of cathodic peak and the capacitive current curve) shifted anodically as the water content increased, until it reached a limit of −0.9 V at 5.2 vol\% water (Figure 3). This value is close to the theoretical value of −0.7 V vs Ag/AgCl for reduction of CO\textsubscript{2} to CO at pH 7.\cite{23} Note that the irreversible electrochemical reduction of CO\textsubscript{2} to the radical anion occurs at −1.3 V vs. the potential of the colbatoцене/colbatocinium couple in [BMIm][OAc], and −2.0 V vs. Ag/Ag\textsuperscript{+} in 0.2 mol dm\textsuperscript{3} tetraethylammonium perchlorate in DMSO.\cite{27, 34}
All electrochemical reactions were carried out in mixtures comprising (a) 0.1 mol dm\(^{-3}\) [BMMIm][OAc] in DMSO containing 0.2 vol\% H\(_2\)O, (b) 0.1 mol dm\(^{-3}\) [BMMIm][OAc] in DMSO containing 5.2 vol\% H\(_2\)O, and (c) 0.1 mol dm\(^{-3}\) [BMMIm][OAc] in H\(_2\)O. The faradaic efficiency for CO formation during electrolysis of CO\(_2\) IL solutions was determined by applying various potentials in solutions a, b and c (the potentials are shown by the vertical lines in Figure 4).

At −1.8 V, the faradaic efficiency was 98%, 91% and 2% in solutions a), b), and c), respectively (Figure 5).

Addition of water modified the reaction path, causing co-electrogeneration of H\(_2\) (and hence syngas, CO/H\(_2\), at a ratio of approximately 1:4, Figure 5c). Figure 5c) shows that 40% of the current at −1.6 V led to H\(_2\) in the solution containing no DMSO (co-generation of H\(_2\) and CO is shown by the overlapping polarisation curves in Figure 4c). The benefits of the buffer effect (keeping a constant concentration of HCO\(_3\)^−) is evident when comparing with the electrolysis performed using solution containing the non-buffering IL [BMIm][BF\(_4\)] instead of [BMMIm][OAc], in which CO was produced at very low faradaic efficiency (15% at −1.6 V vs Ag/AgCl, see Figure S5).

The high faradaic efficiency for CO electrogeneration in 0.1 mol dm\(^{-3}\) [BMMIm][OAc] in DMSO containing 0.2 vol\% H\(_2\)O at a relatively low overpotential is among the most efficient electrochemical CO\(_2\) reductions reported so far, without the need for sophisticated electrodes (see Table S1). Tafel slopes extracted from CO\(_2\) reduction polarisation curves are shown in Figure 6. Multiple Tafel slopes are visible in each case.

The Tafel slopes for CO\(_2\) reduction at low overpotentials (bco2) are 79 mV dec\(^{-1}\), 64 mV dec\(^{-1}\), and 148 mV dec\(^{-1}\) in Figures 6A-C, respectively. At high overpotentials in each solution, the Tafel slope increased dramatically (bso2), most likely due to the reaction coming under mass-transport limitations.[35, 36] In the solution containing no DMSO, a Tafel slope of 110 mV dec\(^{-1}\), which we attribute to water reduction (see also Figure 5c), was also observed (bH2O). That the CO\(_2\) reduction Tafel slope is Solution c is close to 118 mV dec\(^{-1}\) indicates that the first electron transfer to CO\(_2\) is rate limiting. In contrast, the lower CO\(_2\) reduction Tafel slopes observed when the solutions contained DMSO indicate that fast initial electron transfer to CO\(_2\) occurred in these media.
Conclusions

We hypothesise that the CO$_2^{−}$ moiety is more stabilized in the buffer solution, resulting in a consequent decrease in the onset potential, as shown in Figure 3. Carbonate (167.2 ppm) and bicarbonate (158.5 ppm) was detected in the $^{13}$C NMR spectra of the reaction mixture containing $^{13}$C-enriched CO$_2$ (see SI Figure S6) after 24 h electrolysis, indicating that the reduction proceeds preferentially via the 2e$^−$ pathway (Scheme 2).

We also note that electroreduction of CO$_2$ in non-buffering ILs occurred with higher onset potentials and current densities lower, than those obtained in this work (Table S1, entries 3-11) and even in the presence of sodium bicarbonate (see Figure S4). This suggests that the formation of bicarbonate by dissolution in the IL/DMSO/water mixture, is essential for the CO$_2$ electrochemical reduction; stabilizing the CO$_2^{−}$, by the buffered system, formed by the activation of water and CO$_2$ forming bicarbonate in solution. We also note that electroreduction of CO$_2$ in the non-buffering IL [BMMIm][BF$_4$], gives a faraday efficiency of only 15% for CO production under the same reaction conditions.

Simple IL/DMSO/H$_2$O solutions dissolve CO$_2$ at atmospheric pressure yielding, a bicarbonate buffer-like solution. The dissolved CO$_2$ can be selectively electrochemically reduced either to carbon monoxide or a syngas mixture at simple commercial Au electrodes at low overpotentials and relatively high current densities. The 1-n-butyl-2,3-dimethylimidazolium acetate/DMSO/H$_2$O solution plays multiple roles in the process, acting as CO$_2$ sorbent and producing bicarbonate that provides the stabilization of the CO$_2^{−}$. This work provides a clear evidence of the role of bicarbonate for the effective CO$_2$ reduction. This approach, employing basic ILs in solutions that can produce buffer-like solutions, open a new window of opportunities for the ambient pressure CO$_2$ capture and transformation.

Experimental Section

General methods

1,2-dimethylimidazolium and DMSO were purchased from Sigma Aldrich. n-Chlorobutane and acetic acid were purchased from Merck and used as received. Carbon dioxide was supplied by Air Liquide with purity above 99.9998%. $^{13}$CO$_2$ was supplied by Cambridge Isotope Laboratories, Inc. (13C, 99%). 1-n-butyl-2,3-dimethylimidazolium acetate ([BMMIm][OAc]) was prepared according to literature procedures from [BMMIm][Cl].

All NMR experiments were performed using a Bruker Avance 400 spectrometer, equipped with a BBO 5 mm probe with z-gradient running at 400 MHz for $^1$H and 100 MHz for $^{13}$C, or an Agilent 400 DD2 equipped with a NMR 5 mm probe with z-gradient running at 400 MHz for $^1$H and 100 MHz for $^{13}$C. The spectra were obtained at 298 K, unless otherwise specified. Chemical shifts are reported in parts per million (ppm, δ) referenced to [D$_2$]DMSO as an external reference (capillary).

Electrochemistry measurements were performed using an Autolab/PST/STAT101 potentiostats/galvanostats. The gold working electrodes used were the RDE, AU 2 mm diameter model and Pt wire were purchased from Metrohm.

For construction of the reference electrode, a silver wire previously cleaned in HNO$_3$ was inserted into an electrochemical cell containing 0.1 M aqueous HCl solution using a platinum counter electrode. A constant current of 10 mA/cm$^2$ for 1 min was
applied. During the electrodeposition of Ag / AgCl a black layer is formed. The electrodeposited electrode was immersed in KCl solution for one hour. After, the wire electrodeposited was inserted in a glass tube molten into ceramic frit molten, containing saturated solution of KCl.

The reference electrode (Ag/AgCl) were calibrated with a commercial master electrode purchased from Gamry, by chronopotentiometry analysis for 10 min once the potential maintained a difference of +/- 3 mV. The other experiments were carried out.

The electrochemical cell consisted of a flat-bottomed flask containing 4 access ports for the working, reference and counter electrodes, and another for sampling gases using a 100 μL Hamilton sampling syringe. The Pt wire counter electrode was protected from the cathodic solution using a ceramic frit embedded in a Nafion® membrane (Figure S1).

Electrochemical experiments

The central point of this study is examination of the influence of DMSO and water mixtures on the efficiency of the electrochemical reduction of CO2. Electrolyte solutions contained 0.1 mol dm−3 [BMIM][OAc] and varying proportion of DMSO and water. Control solutions were deaerated with Ar for 30 min. CO2 was then bubbled into the solution for 30 min. CO2 reduction was performed in a typical three-electrode cell (25 mL volume) in the potential range 0-2 V vs Ag/AgCl. The working electrode was a commercially-available 0.1256 cm² Au electrode, the counter electrode was a Pt wire held within a tube that was separated from the test solution using a porous ceramic frit impregnated with Nafion®, to prevent contamination with products formed at the working. An Ag/AgCl reference electrode containing saturated KCl was used as the reference electrode.

Linear sweep, Tafel plots and chronamperometry procedures are performed in a previous described solution and electrode systems. Tafel graphs are performed in an identical system previous described, however, using a counter electrode without the protective junction.

Quantification of CO2 sorption by NMR

In the CO2 sorption experiments, CO2 was bubbled through the 0.5 mL of IL solution (DMSO/H2O) in a NMR tube container for 30 min, at room temperature. The amount of CO2 sorbed was determined by 13C NMR quantitative experiments. Routine 13C NMR spectra are normally acquired under conditions that do not allow quantification, however, quantitative 13C NMR spectra can be obtained using the inverse gated decoupled experiment with a correct relaxation delay that ensures full relaxation of the 13C nuclei (typically in 40 seconds of d1 and 1024 scans). 13C quantification of the interested compounds was achieved using the integrals of the C10 carbon from the N-CH3 substituent.

Acknowledgements

The authors are grateful to FAPERGS (16/2551-0000), CNPq (465454/2014-3), and CAPES (158804/2017-01) for partial financial support.

Keywords: CO2 reduction, ionic liquid, electroreduction, buffer-like solutions, CO2 sequestration.

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A simple ionic liquid/DMSO/H$_2$O solution is able to decrease the overpotential in a commercial electrode by in situ formation of bicarbonate providing an alternative way to produce syngas from CO$_2$. Wellington D. G. Gonçalves, Marcileia Zanatta, Nathalia M. Simon, Luciane M. Rutzen, Darren A. Walsh and Jairton Dupont* Efficient electrocatalytic CO$_2$ reduction driven by ionic liquid buffer-like solutions