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FULL PAPER

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, electroreduction 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]
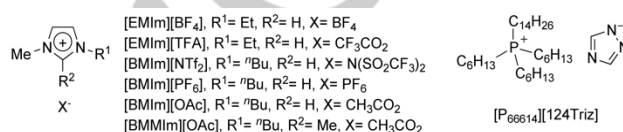

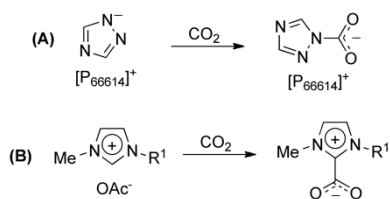**Figure 1.** Examples of ILs used as electrolytes for CO₂ reduction.

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 complexation 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 carbamates 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.[25] 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.[9, 29]

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Scheme 1. Examples of ILs used as electrolytes for CO_2 reduction that involves covalent interactions of the IL.

Figure 2. Graph of log of the bicarbonate concentration *vs*. log of the [BMMIm][OAc] concentration in IL/DMSO/H_2O mixtures. The IL was dissolved in DMSO/H_2O solution (5.2 vol% water) and CO_2 was bubbled into the solution for 30 minutes at RT. Bicarbonate concentrations were determined by integrating the ^{13}C resonances at *ca*. 159 ppm relative to that of C10 (CH_3-N) at 34 ppm (See SI Figures S2 and S3). $pH=pKa-log([IL]/[HCO_3^-])$.

Bicarbonate has also been implicated in the electroreduction of CO_2; while it had generally been thought that dissolved CO_2 is the only active species during electroreduction of CO_2,[1].[1, 30, 31] it was recently shown that dissolved bicarbonate formed upon dissolution of CO_2 in aqueous media increases the concentration of CO_2 near Au electrodes and increases the rate of CO_2 electroreduction.[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_2 at remarkably low overpotentials and with high selectivity and faradaic efficiency for CO production. Specifically, we show that mixtures of [BMMIm][OAc], DMSO and water can dissolve up to 43 mol% of CO_2 (27 mol% *via* formation of bicarbonate and 16 mol% via solvated CO_2) at atmospheric pressure (see SI Table S2). This solution supports selective electroreduction of CO_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 favours the formation of free bicarbonate, which reduces the energy required for the electrochemical reduction of CO_2, but this is accompanied by the co-electrogeneration of H_2, yielding syngas that could be used for the formation of liquid fuel using follow-on processing.

Results and Discussion

The solubility of CO_2 in [BMMIm][OAc]/DMSO/H_2O solutions was quantified using ^{13}C-[^1H] NMR spectroscopy (see SI Table S2).[32] By varying the water content in DMSO from 0.2 vol% to 100% water (without DMSO) at constant IL concentration (1.0 mol dm^{-3}) we determined that the maximum concentration of HCO_3^- (0.41 mol dm^{-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^{-3}, the concentration of HCO_3^- 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_2. It has recently been shown that the formation of HCO_3^- near electrodes can lead to high CO_2-reduction efficiencies in aqueous media.[31]
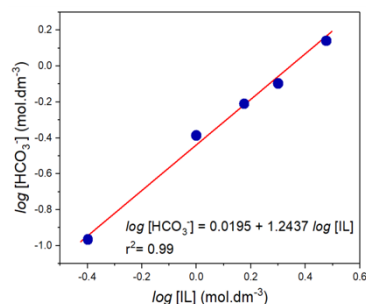
We explored the effects of addition of H_2O to DMSO solutions containing the buffering IL on electroreduction of CO_2 using linear-sweep voltammetry in blank and CO_2-saturated mixtures. In all electrochemical studies the IL concentration were fixed at 0.1 mol dm^{-3}, changing only the concentration 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).
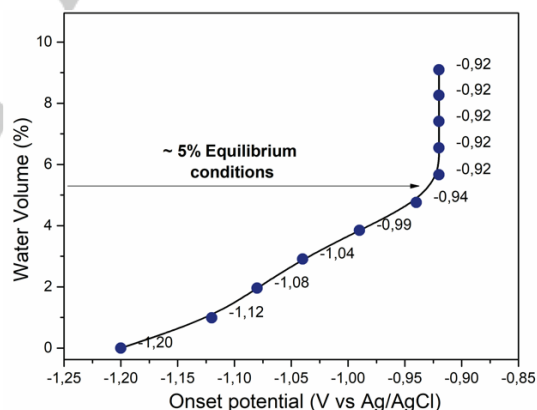

Figure 3. Onset potential for electroreduction of CO_2 at Au electrodes in 0.1 mol dm^{-3} [BMMIm][OAc] in DMSO containing increasing concentrations of H_2O.

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_2 to CO at pH 7.[2, 33] Note that the irreversible electrochemical reduction of CO_2 to the radical anion occurs at −1.3 V *vs*. the potential of the colbatocene/colbatocinium couple in [BMIm][OAc], and −2.0 V *vs*. Ag/Ag$^+$ in 0.2 mol dm^{-3} tetraethylammonium perchlorate in DMSO.[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_2O, (b) 0.1 mol dm^{-3} [BMMIm][OAc] in DMSO containing 5.2 vol% H_2O, and (c) 0.1 mol dm^{-3} [BMMIm][OAc] in H_2O. 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).
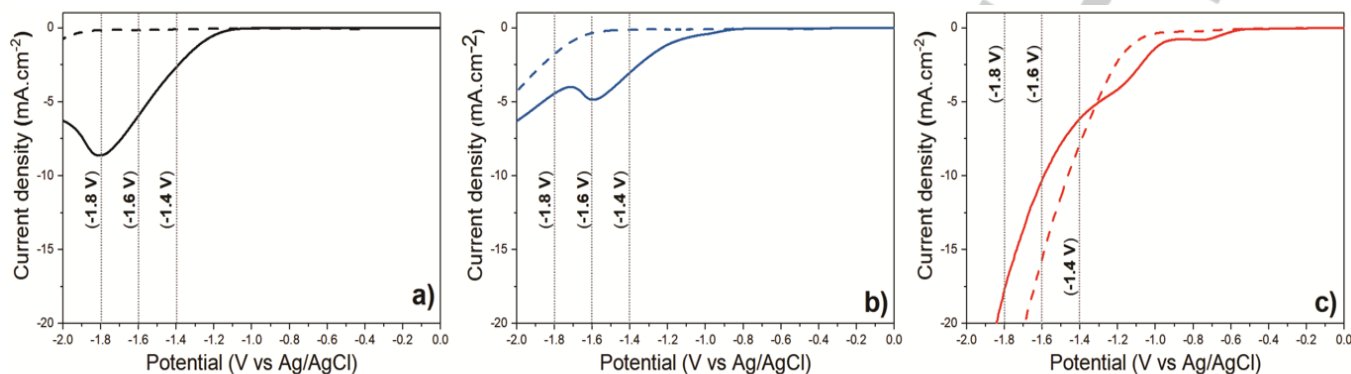

Figure 4. Linear sweep voltammetry of Au electrodes in Ar-saturated (dashed line) and CO_2-saturated (solid line) in [BMMIm][OAc] 0.1 mol dm^{-3} in a) DMSO containing 0.2 vol% H_2O, b) DMSO containing 5.2 vol% H_2O and c) H_2O. The vertical lines are the applied potentials during chronoamperometry.

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 of 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).
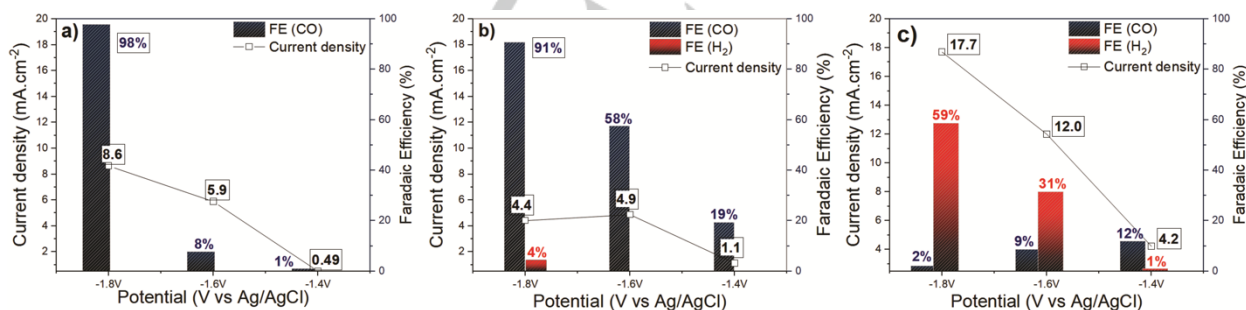

Figure 5. Chronoamperometry performance in [BMMIm][OAc] 0.1 mol dm^{-3} in a) DMSO containing 0.2 vol% H_2O, b) DMSO containing 5.2 vol% H_2O, and c) H_2O. FE is the faradaic efficiency.

The high faradaic efficiency for CO electrogeneration in 0.1 mol dm^{-3} [BMMIm][OAc] in DMSO containing 0.2 vol% H_2O 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 (b_{CO2}) 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 (b_{dif}), 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 (b_{H2O}). 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.
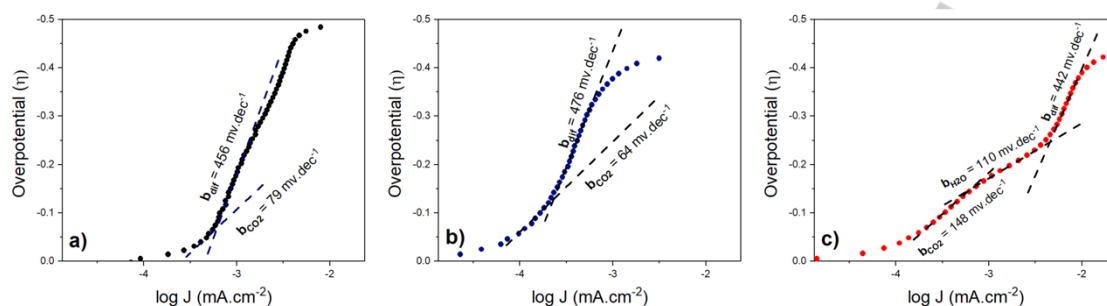
Figure 6. Polarisation curves of CO_2-saturated in [BMMIm][OAc] 0.1 mol dm^{-3} in (a) DMSO containing 0.2 vol% H_2O, (b) DMSO containing 5.2 vol% H_2O and (c) H_2O. The symbols: b_{CO_2}, b_{H_2O} and b_{dif} represent the Tafel slopes for CO_2 reduction, water reduction and diffusion step respectively.

We hypothesise that the $CO_2^{\bullet-}$ moiety is more stabilized in the buffer solution, resulting in a consequent decrease in the onset potential, as shown in Figure 3.[37-39] 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).[1]
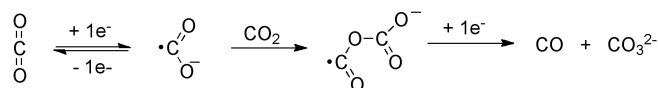
Scheme 2. Possible reaction pathways involved in the CO_2 reduction to CO in IL buffer-like solutions

Moreover, the typical signals of the imidazolium ring are intact and non-duplicated, indicating that there was no IL decomposition (compare Figures S2, S3 with S6, before and after electrochemical reaction, respectively). The origin of CO from electroreduction of CO_2 was verified by per- forming the reaction with $^{13}CO_2$ and an aqueous solution of BMMIm.OAc IL produced ^{13}CO which was detected by the appearance of a signal at mass to charge ratio (m/z) of 29 in the GC–mass spectroscopy (GC-MS) (Figure S7). Electroreduction of CO_2 in electrolytes containing 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 $CO_2^{\bullet-}$, 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 [BMIm][BF$_4$], gives a faraday efficiency of only 15% for CO production under the same reaction conditions.

Conclusions

Simple IL/DMSO/H_2O 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_2O solution plays multiple roles in the process, acting as CO_2 sorbent and producing bicarbonate that provides the stabilization of the $CO_2^{\bullet-}$. This work provides a clear evidence of the role of bicarbonate for the effective CO_2 reduction. This approach, employing basic ILs in solution 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 99.998%. $^{13}CO_2$ was supplied by Cambridge Isotope Laboratories, Inc. (13C, 99%). 1-n-butyl-2,3-dimethylimidazolium acetate ([BMMIm][OAc]) was prepared according to literature procedures [40] from ([BMMIm][Cl]).[41]

All NMR experiments were performed using a Bruker Avance 400 spectrometer, equipped with a BBO 5 mm probe with z-gradient operating at 400 MHz for 1H 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 ^1H 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$_6$]DMSO as an external reference (capillary).

Electrochemistry measurements were performed using an Autolab/PGSTAT101 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 1min 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 CO_2. Electrolyte solutions contained 0.1 mol dm^{-3} [BMMIm][OAc] and varying proportion of DMSO and water. Control solutions were deaerated with Ar for 30 min. CO_2 was then bubbled into the solution for 30 min. CO_2 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 cm^2 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 chronoamperometry procedures are performed in a previous descripted 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 CO_2 sorption by NMR

In the CO_2 sorption experiments, CO_2 was bubbled through the 0.5 mL of IL solution (DMSO/H_2O) in a NMR tube container for 30 min, at room temperature. The amount of CO_2 sorbed was determined by ^{13}C NMR quantitative experiments. Routine ^{13}C NMR spectra are normally acquired under conditions that do not allow quantification, however, quantitative ^{13}C NMR spectra can be obtained using the inverse gated decoupled experiment with a correct relaxation delay that ensures full relaxation of the ^{13}C nuclei (typically in 40 seconds of d1 and 1024 scans). ^{13}C quantification of the interested compounds was achieved using the integrals of the C10 carbon from the N-CH$_3$ substituent.

Acknowledgements

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FULL PAPER

A simple ionic liquid/DMSO/H_2O 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.
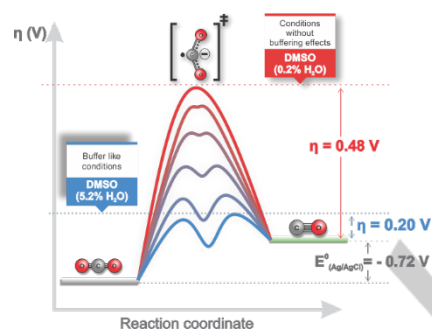
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