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CO₂ Capture and Electrochemical Conversion using Super Basic

[P₆₆₆₁₄][124Triz]

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The ionic liquid trihexyltetradecylphosphonium 1,2,4-triazolide, [P₆₆₆₁₄][124Triz], has been shown to chemisorb CO₂ through equimolar binding of the carbon dioxide with the 1,2,4-triazolide anion. This leads to a possible new low energy pathway for the electrochemical reduction of carbon dioxide to formate and syngas at low overpotentials, utilizing this reactive ionic liquid media. Herein, an electrochemical investigation of water and carbon dioxide addition to the [P₆₆₆₁₄][124Triz] on gold and platinum working electrodes is reported. Electrolysis measurements have been performed using CO₂ saturated [P₆₆₆₁₄][124Triz] based solutions at -0.9 V and -1.9 V on gold and platinum electrodes. The effect of electrode material on the formation of formate and syngas using these solutions are then presented and commented.

1 Introduction

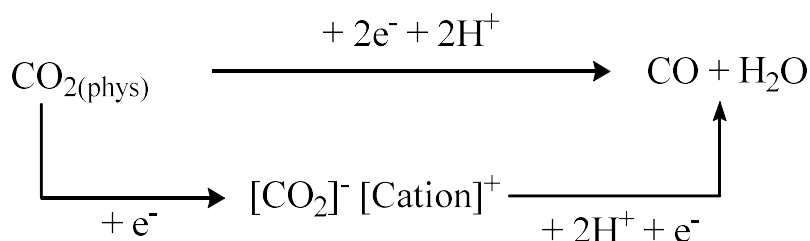
Since the industrial revolution the harnessing of fossil fuels by combustion for energy and transportation has seen atmospheric levels of CO₂ steadily rise.^{1, 2} One concern is that the rate of growth in the global CO₂ concentration in the atmosphere is associated with rising global temperatures and sea levels.³ Given the potential implications of global warming, strategies to capture and/or convert CO₂ provide the subject of much scientific endeavour.⁴

Aside from a greenhouse gas, CO₂ can be considered as an abundant, renewable and low cost C1 building block for the production of fuels or as a feedstock for industrial chemical synthesis. The synthesis of fuels is particularly attractive given the carbon neutrality of the product.

Electrochemical reduction offers a viable route to this goal owing to the potential to reduce CO₂ at high efficiencies and selectivity also with the ability to harness electrical energy from renewable sources.^{5, 6} The main barrier being the thermodynamic stability and the kinetic inertness of CO₂, due to the first electron reduction of linear CO₂ to form the bent [[•]CO₂]⁻ radical anion requiring a high reduction potential, -1.9 V vs. NHE.⁷ Attempts have been made to reduce this potential by employing various catalysts, such as recently reported reductions on Fe₃S₄ surfaces.⁸

Ionic liquids[‡] (ILs) have been employed as CO₂ capture agents and electrochemical conversion mediums due to their intrinsic ionic conductivity, wide potential windows and CO₂ solubility levels.⁹⁻
¹² ILs generally physically absorb CO₂ into the solution free volume. Reports have shown that ILs can act to stabilise the first electron reduction of the physically absorbed CO₂ by complexation of the reduction product with the IL cation.¹² This significantly reduces the energy required to form the [[•]CO₂]⁻ radical anion. Initial CO₂ electrochemical reduction experiments in ILs employed 1-alkyl-3-methylimidazolium ([C_{*n*}mim]⁺) based ILs with a range of non-coordinating anions such as [BF₄]⁻, Br⁻, Cl⁻. The electrochemically generated anion radical, [[•]CO₂]⁻, was then reacted with alcohols forming dialkyl carbonates.¹³⁻¹⁵

Further studies used hydrated ILs, to provide a source of H^+ , CO_2 physically absorbed within the IL was reduced with Ag as working electrode which enabled further reduction of the IL stabilised $[CO_2]^-$ to CO as shown in the Scheme 1.¹²

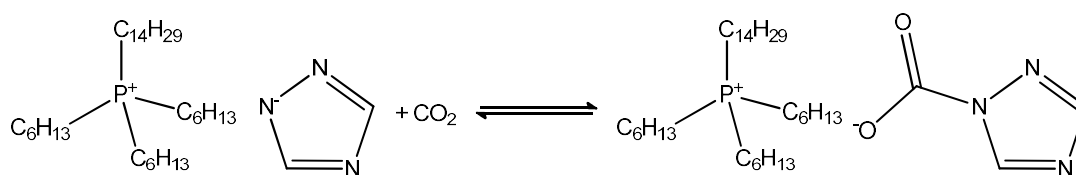


Scheme 1 – Reduction of CO_2 to CO in an IL absorbing CO_2 physically.¹²

CO_2 reduced to CO in hydrated $[C_2mim][BF_4]$ on a Ag working electrode was reported to have overpotentials as low as 0.2 V.¹² H_2 production was also suppressed due to the cation forming a monolayer on the electrode surface.¹⁶ Further improvements have been reported by employing a MoS_2 working electrode resulting in overpotentials as low as 0.054 V.¹⁷

Product selectivity has also been observed upon altering the IL anion. For example, using $[C_2mim]^+$ based ILs on Pb electrodes, oxalate is favoured in the presence of $[NTf_2]^-$ and formate favoured when $[TFA]^-$ was used.^{9, 11}

Recently, we have reported an alternative route for CO_2 reduction in ILs, by using $[P_{66614}][124Triz]$.¹⁸ $[P_{66614}][124Triz]$ is able to capture significantly more CO_2 than classical ILs like $[C_4mim][NTf_2]$ or $[C_2mim][OAc]$ due to the chemical reactivity of the 1,2,4 triazolide anion.¹⁹ The anion can chemically bind CO_2 allowing up to equimolar CO_2 capture as illustrated in the Scheme 2.¹⁹



Scheme 2 – CO_2 binding to $[124Triz]^-$ anion in the IL $[P_{66614}][124Triz]$.¹⁹

Crucially, upon binding the CO₂ geometry is altered from linear to bent. A lower energy pathway to CO₂ reduction was demonstrated in this IL that may be related to the chemical binding of the CO₂ by the anion.¹⁸ [P₆₆₆₁₄][124Triz] is also able to absorb CO₂ through physical exothermic absorption in the solution free volume driven by an entropic process of solvation. The physically absorbed CO₂ may also undergo reduction stabilised by the [P₆₆₆₁₄]⁺ cation. Formate was produced by the lower energy route at -0.7 V vs Ag/AgNO₃ with 95% Faradaic efficiency on Ag electrodes. In addition, reduction of physically absorbed CO₂ at -1.9 V vs Ag/AgNO₃ produced CO with a 41% Faradaic efficiency.¹⁸ In comparison, on using [P₆₆₆₁₄][NTf₂], which does not support chemical CO₂ binding, no product was formed at -0.7 V suggesting that the reaction occurring at this less negative potentials (*i.e.* -0.7 V) in [P₆₆₆₁₄][124Triz] is related to the reduction of chemically bound CO₂ (Scheme 2). Products were formed at -1.9 V, *i.e.* the same potential as found in [P₆₆₆₁₄][124Triz], indicating that these are formed from the reduction of physically absorbed CO₂ stabilised by the [P₆₆₆₁₄]⁺ cation (Scheme 1).¹⁸ Herein the study is expanded to investigate the influence of electrode material on CO₂ reduction potential, product distribution and Faradaic efficiency.

2 Experimental

2.1 Materials and IL synthesis

Trihexyltetradecylphosphonium chloride ([P₆₆₆₁₄]⁺Cl⁻) was received from Cytec (97.7%) and 1,2,4-triazole (98%) was purchased from Sigma–Aldrich. The Au foil (0.1 mm thick 99.9975+%) and Pt wire (0.3 mm dia, 99.99%) were purchased from Alfa Aesar. Gaseous nitrogen (99.998%) and carbon dioxide (99.99%) were obtained from BOC and passed through drying columns before contact with the IL samples. The water was purified using a Milli-Q 18.3 MΩ water system.

[P₆₆₆₁₄][124Triz] was prepared by a previously reported method²⁰ using a two step synthesis; [P₆₆₆₁₄][OH] was synthesized using an anion exchange resin from [P₆₆₆₁₄]Cl followed by addition of the superbase. The water content of the ILs was measured using a Metrohm 787 KF Titrino Karl Fischer and was found to be < 0.1 wt% for all ILs. Halide content was below the detectable limit by AgNO₃ testing.

2.2 *Electrochemical experiments*

Cyclic voltammograms (CVs) were recorded using an Ecochemie Autolab Potentiostat/Galvanostat (PGSTAT302) and carried out using a three-electrode arrangement with a Au or Pt working electrode (1.6 mm), a platinum coil as the counter electrode, and all potentials measured with respect to a 0.01 mol·L⁻¹ Ag⁺/Ag reference, with AgNO₃ dissolved in [C₄mim][NO₃] and separated from the bulk solution via a glass frit. Electrolysis experiments were carried out using a three electrode set up in a sealed 50 cm³ cell with a gas tight syringe attached. The working electrodes were a coiled Pt wire or a Au foil, a Pt coil was used as the counter electrode (contained within a counter compartment) and potentials were measured with respect to a 0.01 mol·L⁻¹ Ag⁺/Ag reference, with AgNO₃ dissolved in [C₄mim][NO₃] and separated from the bulk solution via a glass frit. A 0.1 mol·L⁻¹ [P₆₆₆₁₄][124Triz], 0.7 mol·L⁻¹ H₂O in acetonitrile solution (8 cm³) was added to the cell and bubbled with CO₂ (25 cm³ min⁻¹) for 60 min, during this time the gas syringe was gradually opened. The cell was then sealed, connected up to a potentiostat (Biologic VMP3 controlled by EC-Lab) and a potential applied to the cell for the time required to pass 10 C of charge. It should be noted that no ionic liquid decomposition or reaction was observed under any of the conditions tested in this study.

2.3 Solution phase detection

Solution samples were analysed by taking ^1H NMR spectra Bruker Avance III 600 with a DCH cryoprobe. Quantitative analysis was performed using ERETIC2 quantification tool within Topspin 3.2.

2.4 Gas Phase detection

The gas phase of the reaction was analysed using a Perkin Elmer Clarus 500 Gas chromatograph equipped with a TCD and FID (with methanizer) fitted with a packed column (stainless steel, 30 ft, 1/8 inch OD, 2.0 mm ID packed with Haysep DB 100/120 mesh). The gaseous products were transferred to the GC by connecting up the cell and injecting the contents of the gas tight syringe attached to the cell into the GC. H_2 was quantified using the TCD and CO using the FID.

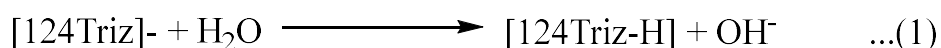
3 Results and discussion

2.1. Voltammetry Study of CO_2 reduction in $[\text{P}_{66614}][124\text{Triz}]$ using various working electrodes

CVs have been recorded at both Au and Pt electrodes in $0.1 \text{ mol}\cdot\text{L}^{-1} [\text{P}_{66614}][124\text{Triz}]$ in acetonitrile (MeCN). CVs were recorded at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ at $22 \text{ }^\circ\text{C}$. The reference electrode was a previously reported $0.01 \text{ mol}\cdot\text{L}^{-1} \text{ Ag}^+/\text{Ag}$ reference, with AgNO_3 dissolved in $[\text{C}_4\text{mim}][\text{NO}_3]$ and separated from the bulk solution *via* a glass frit.^{21, 22} $0.1 \text{ mol}\cdot\text{L}^{-1} [\text{P}_{66614}][124\text{Triz}]$ in MeCN was first saturated with argon and a baseline CV taken. Thereafter, water was added ($0.7 \text{ mol}\cdot\text{L}^{-1}$), as a source of H^+ and the influence on the CV investigated. The H^+ is required to make protonated reduction products and CO through the reaction of reduced CO_2 and H^+ (Scheme 1). Finally, the hydrated IL mixture was purged with CO_2 for 30 min and a CV taken to assess CO_2 reduction processes.

3.1.1 Au working electrode

CVs relating to the use of a polished Au working electrode (0.16 cm²) are displayed in Figure 1. The CV, after purging with Ar, is shown in blue. A small increase in reduction current is observed at *ca.* -1.1 V with a rapid increase in reduction current at *ca.* -2.0 V. Upon the addition of H₂O to the IL/MeCN mixture a small increase in current is observed at -1.0 V and a larger increase at *ca.* -1.75 V (Figure 1, red). Although the small increase in current observed at -1.0 V has a slight anodic shift compared with that observed in the Ar saturated sample (-1.1 V) this feature may be attributed to reduction of 1,2,4-triazole formed from the reaction of the [124Triz]⁻ anion and H₂O (Scheme 3).



Scheme 3 – H₂O reaction with [124Triz]⁻ anion in the [P₆₆₆₁₄][124Triz]

To test this theory 1,2,4-triazole was deliberately added to a solution of hydrated 0.1 mol·L⁻¹ [P₆₆₆₁₄][124Triz] in MeCN. The CV showed that, upon addition of 1,2,4-triazole, the current from -1.0 V increased, supporting this proposal. The presence of the small current increase at -1.1 V in the Ar saturated sample could, therefore, either be due to adventitious water or trace 1,2,4-triazole impurities from the synthesis process of [P₆₆₆₁₄][124Triz] which is synthesised from the addition of 1,2,4-triazole to [P₆₆₆₁₄][OH].

The large reduction current at -1.8 V, observed upon the addition of H₂O shows a large anodic shift compared to the onset of the large reduction current in the Ar saturated sample. This is proposed to be due to reduction of H₂O to H₂. This region also increases in current when deliberately adding 1,2,4-triazole to the electrolyte, suggesting that generation of H₂ from the reduction of 1,2,4-triazole may also contribute to this current. In addition, a small oxidative stripping peak is observed at -1.5 V following the rapid increase of current at -1.8 V, suggesting the product of reduction may interact with the electrode surface. Recent reports employing [C₄mim][BF₄] on Au surfaces have shown the

hydrogen evolution reaction to occur at *ca.* -2.0 V vs Ag/Ag⁺,²³ suggesting the use of chemically coordinating IL provides a pathway to less negative reduction potentials.

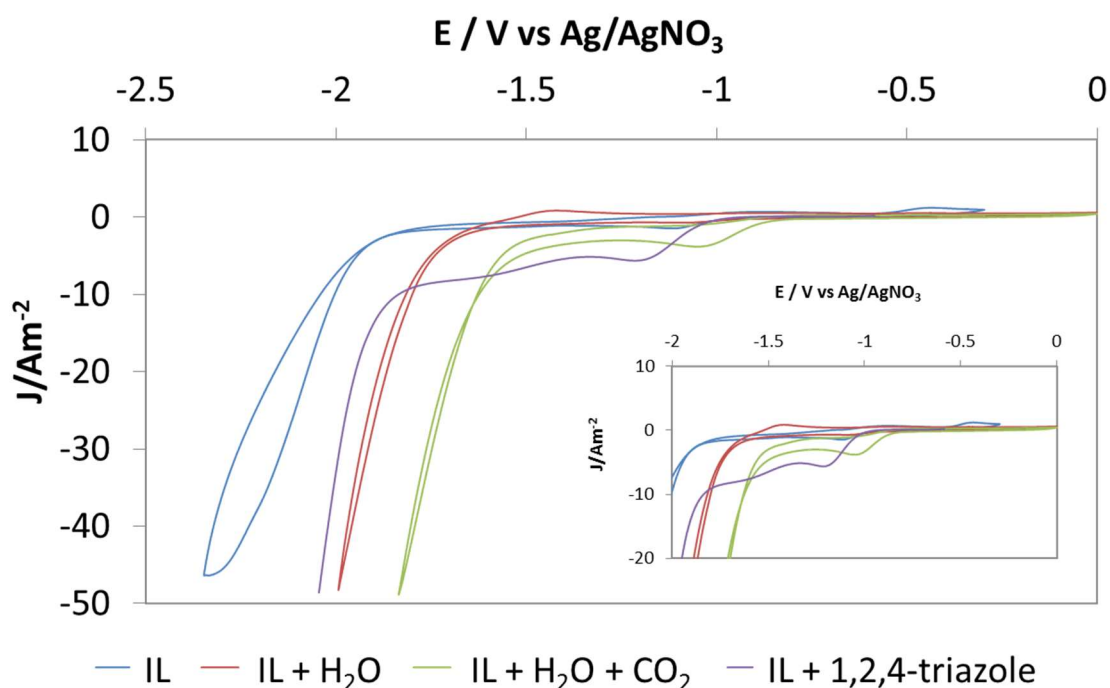
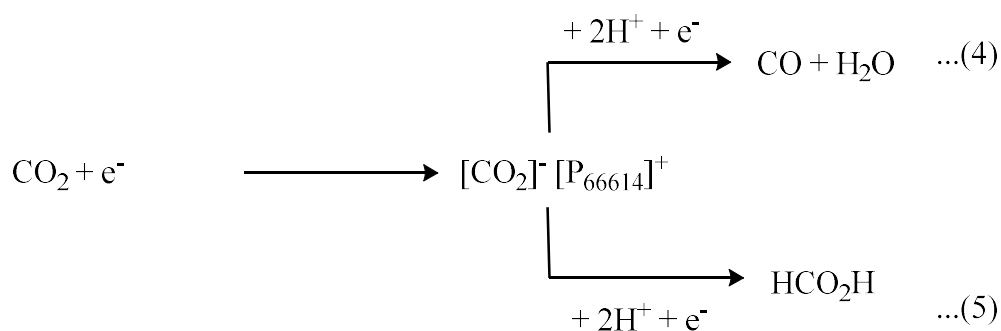
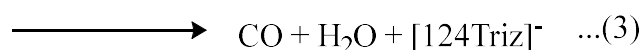
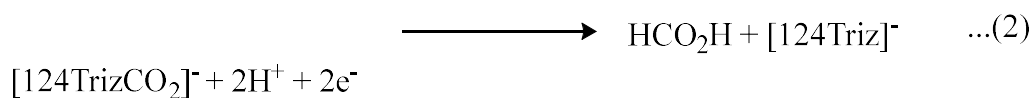


Figure 1: Cyclic voltammograms of 0.1 mol·L⁻¹ [P₆₆₆₁₄][124Triz] (IL) in acetonitrile (MeCN) at a gold electrode; (blue) IL in MeCN, (red) IL in MeCN + 0.7 mol·L⁻¹ H₂O, and (green) IL in MeCN + 0.7 mol·L⁻¹ H₂O + CO₂, IL in MeCN + 0.5 mol·L⁻¹ 1,2,4-triazole only cathodic linear sweep shown for clarity. Magnification shown inset.

Saturation of the hydrated IL mixture with CO₂ (Figure 1 green) resulted in an increase in current at -0.9 V followed by a rapid increase in current at -1.6 V. The peak at -0.9 V shows an increased current and greater anodic shift when compared to the hydrated sample. The large increase in current observed at -1.6 V shows an anodic shift on comparison to Ar saturated and hydrated samples. Previous reports on Ag electrodes have suggested reduction at less negative potentials (-0.7 V) could be assigned to the reduction of CO₂ chemically bound to the [124Triz]⁻ anion while reductions at more

negative potentials (-1.9 V) could be assigned to the reduction of physically absorbed CO₂ (Scheme 4 eqs. 2,3 and 4,5, respectively).¹⁸ The reduction of physically absorbed CO₂ at -1.6 V is in good agreement with CO₂ reduction reported on Au electrodes in [C₄mim][BF₄]. Reduction of CO₂ in [C₄mim][BF₄], an IL that only exhibits physical CO₂ absorption, on Au surface was reported at -1.8 V vs NHE (i.e. -1.6 V vs Ag/Ag⁺).²³ Interestingly, the potential for reduction of CO₂ over Au reported, herein, at -0.9 V is the lowest potential, to the best of our knowledge, reported to date using ionic liquid systems showing the potential of reactive IL to enhance the electrochemical activity.



Scheme 4 – Suggested CO₂ reduction processes occurring on the working electrode.

Assuming similar mechanisms take place at the Au electrode, this suggests that chemically bound CO₂ can be reduced at less negative potentials on Ag than Au (-0.7 V compared to -0.9 V) but reduction of physically bound CO₂ occurs at less negative potentials on Au than Ag (-1.6 V vs. -1.9 V). One plausible explanation would be that Ag is more catalytically active than the Au and, therefore, the IL is more strongly bound to the Ag electrode than the Au. This may suggest that the chemically bound CO₂ on Ag can be reduced at less negative potentials due to the increased contact with the electrode but the physically absorbed CO₂ is blocked by the IL requiring more negative potentials for reduction. Reduced binding in the Au system suggests the physically absorbed CO₂ has

easier access to the electrode and, therefore, physical adsorbed reduction occurs at a less negative potential than on Ag but reduction of the chemically adsorbed CO₂ requires a more negative potential than in the Ag system.

3.1.2 Pt working electrode

CVs relating to the use of a polished Pt working electrode (0.16 cm²) are displayed in Figure 2, the CV after purging with Ar is shown in blue. An increase in current is observed at -1.6 V followed by the start of a rapid current increase at *ca.* -2.1 V. Upon the addition of H₂O to the IL/MeCN mixture (Figure 2 red) a rapid increase in current is observed at -1.5 V with no smaller current increase observed at lower potentials. The rapid increase in current at -1.5 V shows an anodic shift and enhanced current compared to the Ar saturated sample. This peak is plausibly associated with the reduction of H₂O to H₂. On comparison with the Au electrode the reduction of H₂O to H₂ takes place at a less negative potential on Pt than Au (-1.5 V *vs.* -1.8 V). This is consistent with Pt being well known as an excellent catalyst for water splitting.

Saturating the hydrated IL mixture with CO₂ (Figure 2 green) results in a slow increase in current at -0.9 V. The increase becomes rapid at -1.4 V. The slow increase in current is plausibly due to the reduction of CO₂ bound to [124Triz]⁻ anion while the rapid increase in current is associated with the reduction of physically adsorbed CO₂.

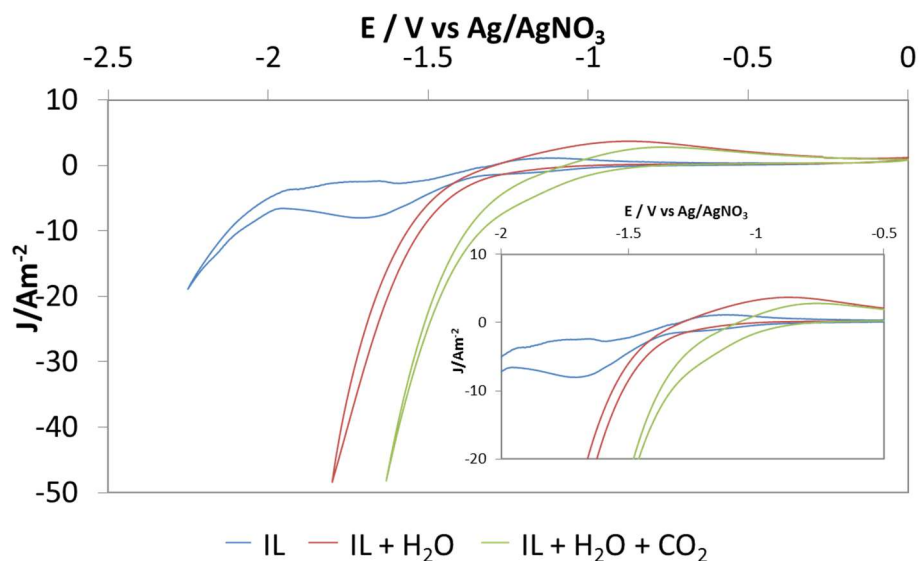
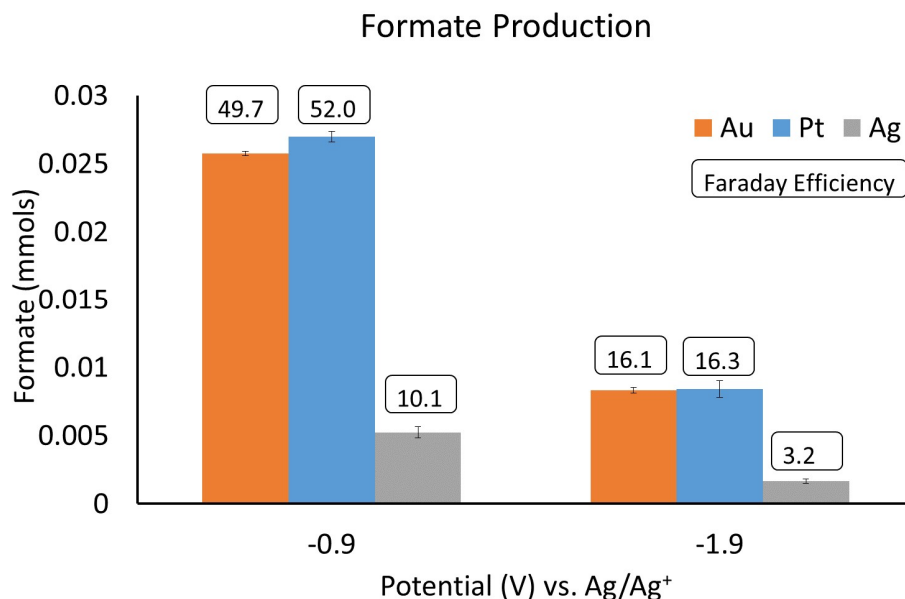


Figure 2: Cyclic voltammograms of $0.1 \text{ mol}\cdot\text{L}^{-1}$ $[\text{P}_{66614}][124\text{Triz}]$ (IL) in acetonitrile (MeCN) at a platinum electrode; (blue) IL in MeCN, (red) IL in MeCN + $0.7 \text{ mol}\cdot\text{L}^{-1}$ H_2O , and (green) IL in MeCN + $0.7 \text{ mol}\cdot\text{L}^{-1}$ H_2O + CO_2 . Magnified CVs inset.

Both Au and Pt display similar reduction potentials for CO_2 bound to the $[124\text{Triz}]^-$ anion (-0.9 V), which are more negative than reduction on Ag (-0.7 V). However, the reduction of physically bound CO_2 is less negative for Pt than Au (-1.4 V and -1.6 V respectively), both of which are less negative than Ag (-1.9 V). It is important to note that the Pt is more catalytically active than both the Au and Ag and, therefore, should show a higher activity. However, as a result of this increased activity Pt will also bind the IL more strongly than the Ag, therefore, the results suggest that a balance between activity and adsorption strength is required for CO_2 reduction at lower potentials. As CO is also formed during these experiments and the binding of CO to Pt will be much stronger than on Ag or Au, site blocking from the CO may also be contributing to the observed differences between the electrode performance.

3.2 Electrolysis Study

Electrolysis was performed in CO_2 saturated and hydrated ($0.7 \text{ mol}\cdot\text{L}^{-1}$ H_2O) $0.1 \text{ mol}\cdot\text{L}^{-1}$ $[\text{P}_{66614}][124\text{Triz}]$ in MeCN (8 cm^3). Electrolysis was continued until a fixed charge of 10 C had passed



after which the solution phase was tested by quantitative ¹H NMR and gas phase by gas chromatography (GC). The reported values for the analogous electrolysis using Ag electrodes is displayed in Figure 3. While Ag electrodes are reported to display Faradic efficiencies of 95% at -0.7 V with an applied potential of 0.17 V, electrolysis on Au and Pt at this potential resulted in no detected reduction product. Therefore, electrolysis was also performed at -1.9 V and -0.9 V to test for reduction of physical and chemical absorbed CO₂, respectively, using these electrodes. The experiments were also performed at these potentials with Ag for comparison (Figures 3 and 4), although it should be noted electrolysis at -0.9 V is not the optimum potential for formate production on Ag.

Figure 3: Quantitative ¹H NMR analysis of formate production at Au, Pt, Ag electrodes after 10 C of charge is passed. Error bars represent +/- 1.5 standard deviations. Faraday efficiency for each potential and electrode shown in boxes.

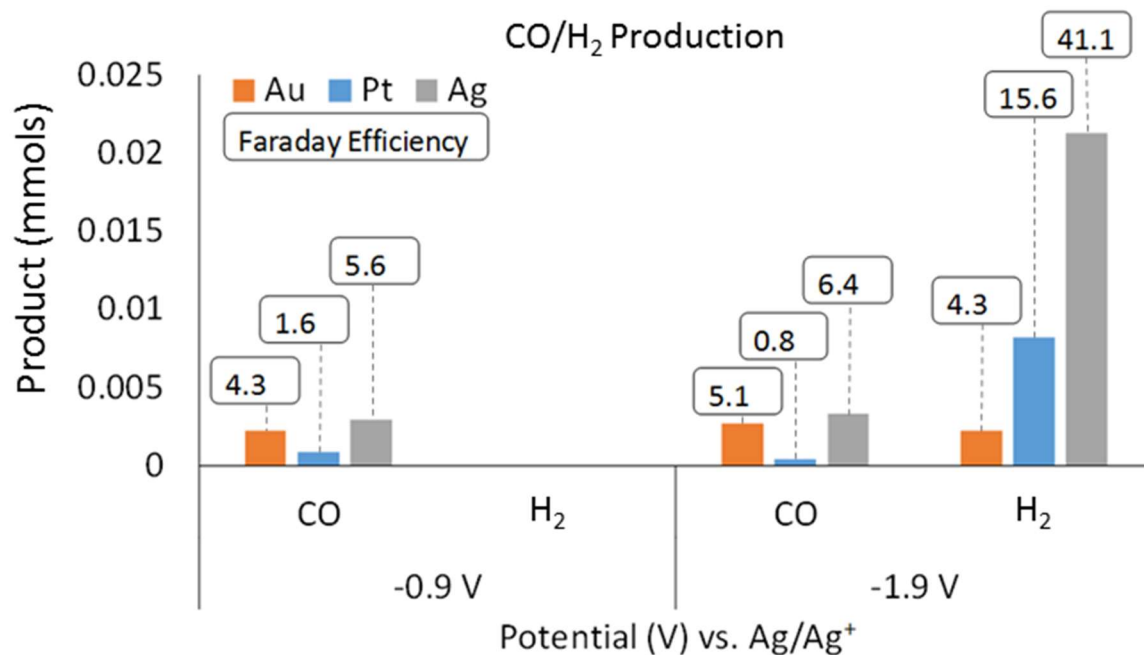


Figure 4: GC analysis of CO and H₂ production at Au, Pt, Ag electrodes after 10 C of charge is passed. Faraday efficiency (%) for each potential and electrode shown in boxes.

3.2.1 Au electrode

0.5 cm² of Au foil was employed as a working electrode. Quantitative ¹H NMR of the electrolyte after electrolysis showed the presence of formate for both investigated potentials (-0.9 V and -1.9 V). The formate produced at -0.9 V is proposed to be formed from the reduction of CO₂ bound to the [124Triz]⁻ anion (Scheme 4 eq. 2) while the formate produced at -1.9 V is proposed to be generated from the reduction of physically absorbed CO₂ stabilised by [P₆₆₆₁₄]⁺ cation (Scheme 4 eq. 5). A greater quantity of formate was detected at -0.9 V (0.026 mmol) compared with -1.9 V (0.0083 mmol) with a Faradaic efficiency of 49.7 and 16.1%, respectively. This is in contrast to previous reports using [C₂mim][TFA] whereby Faradaic efficiency for formate production increases with potential.⁹ The open circuit potential (OCP) prior to electrolysis, but after CO₂ saturation was measured at -0.45 V, suggesting an applied potential of -0.45 and -1.45 V for potential holds of -0.9 and -1.9 V, respectively. A comparison with the reported values for the analogous electrolysis using Ag electrodes is displayed in Figure 3. Electrolysis on Ag resulted in considerably less formate at both -

0.9 and -1.9 V, it should be noted the maxima for formate production is -0.7 V at which potential considerably more formate is produced than on the Au electrode.

GC analysis of the headspace gas mixture after electrolysis showed both CO and H₂ were formed with 0.0022 mmol and 0.0027 mmol of CO produced at -0.9 V and -1.9 V, respectively. This is assigned to the reduction of CO₂ bound to the [124Triz]⁻ anion (Scheme 4 eq. 3) and reduction of CO₂ stabilised by [P₆₆₆₁₄]⁺ cation (Scheme 4 eq. 4). In addition, hydrogen was only detected at -1.9 V consistent with H₂O being reduced to H₂.

3.2.2 Pt electrode

Quantitative ¹H NMR of the electrolyte after electrolysis showed a similar trend for formate production on Pt compared to Au. A greater quantity of formate was detected at -0.9 V (0.027 mmol) compared with -1.9 V (0.008 mmol) with Faradiac efficiencies of 52.0 and 16.3%, respectively. However, formate production at both potentials was not significantly different from the amount produced using the Au electrode. The OCP prior to electrolysis, but after CO₂ saturation was more negative than that previously found on Au, it was measured at -0.60 V giving smaller applied potentials of 0.3 and 1.3 V for electrolysis at -0.9 and -1.9 V, respectively. CO was detected at both -0.9 and -1.9 V; however, the amount of CO detected was significantly reduced at both potentials compared with the analogous reductions over Au and Ag. No H₂ was detected at -0.9 V while significantly more H₂ was detected at -1.9 V on Pt than Au, as expected. This corresponds with previous reports which shows the order in ability to catalyse the hydrogen evolution reaction is Pt > Au > Ag.²⁴ This in turn relates to the observed reduction potentials after the addition of H₂O on Pt, Au and Ag electrodes (-1.5,-1.8 and -1.9 V, respectively). However, more H₂ is detected for Ag electrodes at -1.9 V than over Pt this is surprising given Ag has the most negative onset potential for reduction of H₂O to H₂. Previous reports have stated the IL cation may suppress hydrogen production by blocking H₂O binding. As such, the disparity in hydrogen production may indicate a differing affinity for the cation to the three electrode surfaces, of the order Ag < Pt < Au as well as the ability

of the electrode material to activate water. As such, the production of H₂ and CO may be a balance between catalytic activity (through onset potentials) and binding energy of the reduced species.

Overall, for all three electrodes (Ag, Au and Pt) the trend in the species formed during the reduction is the same, i.e. less negative potentials favour formate whereas more negative potentials favour CO and H₂. The main difference between the electrodes is the potential at which the maxima/optimum for each species occur. For example, for formate production, on the Ag electrode this occurs at -0.7 V, which is less negative than found Au and Pt. In addition, it is clear that as the potential becomes more negative the Faradaic efficiency for the species detected decreases for all three electrodes.

4 Conclusions

We have shown the CO₂ saturated super basic IL [P₆₆₆₁₄][124Triz] can be reduced on Au and Pt electrodes to produce formate and syngas. Two reaction pathways appear to exist at -0.9 V and -1.9 V. Formate is formed in increased quantities at -0.9 V over -1.9 V on both electrode surfaces with Faradaic efficiencies of *ca.* 50 % for both electrode surfaces. The production of CO is higher on Au electrodes than Pt electrodes for both electrolysis potentials of -0.9 and -1.9 V. The production of hydrogen, only observed at -1.9 V, is *ca.* 3 times higher on Pt electrodes, enabling the ratio of CO:H₂ in the syngas mixture to be influenced by electrode choice. The reduction of physically bound CO₂ is shown to occur at similar potentials on Au electrodes to those reported for ILs that only physically absorb CO₂, such as [C₄mim][BF₄], albeit at lower Faradaic efficiencies.²³ Formate production in ionic liquids has been previously reported to occur on indium surfaces using hydrated CO₂ saturated [C₂mim][TFA].⁹ The [TFA]⁻ anion only very weakly binds to CO₂, which results in little significant activation of the CO₂ and formate production at low Faradaic efficiencies (*ca.* 10 %) at 1.55 V vs Ag/Ag⁺ rising to 90 % efficiencies at -1.95 V vs Ag/Ag⁺. The behaviour is in good agreement with our proposed onset of reduction of physically bound CO₂. In the present study, the binding of CO₂ is much stronger and, thus, formate production on Au and Pt electrodes, from the chemically bound

CO₂, is observed at applied potentials lower than any previously reported ILs. The results show the same trends as found over the previously reported Ag electrode albeit with some differences. For example, the maximum formate production is found at -0.7 V over Ag at which potential no reduction was observed on Pt and Au.

5 Acknowledgements

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6 Notes and references

‡ A table detailing ionic liquids abbreviated within the manuscript

Abbreviation	Full name
[P ₆₆₆₁₄] ⁺	trihexyltetradecylphosphonium
[C ₂ mim] ⁺	1-ethyl-3-methylimidazolium
[C ₄ mim] ⁺	1-butyl-3-methylimidazolium
[124Triz] ⁻	1,2,4-triazolide
[BF ₄] ⁻	tetrafluoroborate
[NTf ₂] ⁻	bis(trifluoromethylsulfonyl)imide
[TFA] ⁻	trifluoroacetate
[OAc] ⁻	acetate
[NO ₃] ⁻	nitrate

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