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## Experimental Considerations for Electrocatalytic CO<sub>2</sub> Reduction

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Electrocatalytic CO<sub>2</sub> reduction offers the ability to store renewable energy in the form of carbon-based fuels. Currently this process suffers from poor activity and selectivity. Unfortunately the advances in electrocatalyst development are hampered by the poor reproducibility of experimental data, even for the most basic of electrocatalysts. Here, some of the possible underlying causes of this poor reproducibility are described and discussed with the intention of providing some insights into experimental procedures and considerations needed for robust experimental investigation of CO<sub>2</sub> reduction.

## Introduction

The conversion of CO<sub>2</sub> into liquid fuels such as methanol or formic acid has the potential to “*revolutionise green energy technologies*” [1] by enabling the carbon-neutral storage of renewable energy [2-4]. While CO<sub>2</sub> can be converted to various fuels by electrochemical reduction, there are significant challenges that must be overcome before this could be considered commercially viable [4]. Unfortunately, “*no material is known to catalyse the electroreduction of CO<sub>2</sub> to fuels both efficiently and selectively*”[5].

Many metals have been examined as possible cathodes for CO<sub>2</sub> reduction in both aqueous and non-aqueous electrolytes [3, 6]. The most common metal used is Cu, and while it can reduce CO<sub>2</sub> to a wide range of hydrocarbons, its reaction selectivity is generally poor [7]. Because of this, many have investigated the effects of surface oxides [2, 8-11], crystal facets [12-14], nanoparticles [15-18] and electrode porosity [19] on the activity and selectivity of CO<sub>2</sub> reduction by Cu. While these factors are clearly important, others have highlighted that the reaction selectivity is also dependent on temperature [20-23], CO<sub>2</sub> pressure [23-26], and electrolyte buffer concentration [24, 27, 28], and thus differences in reaction selectivity are not always due to intrinsic catalytic effects [24, 29, 30]. Therefore in this paper, the effects of some experimental factors on the reaction selectivity are reviewed and discussed.

## How selective is Cu for CO<sub>2</sub> reduction ?

Cu is widely studied and often considered as the “standard” metal for CO<sub>2</sub> reduction, due to its ability to produce high amounts of many hydrocarbons [3, 6, 21]. Normally the most common hydrocarbons will be CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, with CO produced at current efficiencies of less than 10% [20, 27, 31, 32]. The formation of CO is expected as both experimental and theoretical investigations suggest that adsorbed CO is the major reaction intermediate [5, 33, 34], with this supported by the fact that electrochemical CO

reduction gives a similar product distribution to CO<sub>2</sub> reduction [27, 35]. However, despite the general agreement between the types of products found from CO<sub>2</sub> reduction at Cu cathodes, a simple survey of the literature reveals a significant differences between the current efficiencies for the major products (Table I).

**TABLE I.** Approximate current efficiency for products produced by the electrochemical reduction of CO<sub>2</sub> on Cu cathodes at -1.6 V vs AgAgCl in 0.1 M KHCO<sub>3</sub> saturated with CO<sub>2</sub>.

CH <sub>4</sub>	H <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	Reference
25	10*	4	38	[36]
40	20	5	22	[27]
15	25	5	16	[7]
5	73*	7	15	[37]
6	40	5	4	[11]
5	67	3	9	[38]
40	30	4	22	[28]

\* the current efficiency was not report and instead this has been estimated from the current efficiency going to other products

Interestingly, the current efficiency for CO reported in this selection of papers is almost constant at 3-7 %, where the range of current efficiencies for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are much larger at 5-40% and 4-38% respectively. One important note to make regarding this comparison is that the number of papers reporting CO<sub>2</sub> reduction at the some potential and in the same electrolyte for Cu cathodes is surprisingly small, but even this small set of papers suggests the selectivity of CO<sub>2</sub> reduction on Cu is not just dependent of potential and electrolyte composition. To illustrate the typical variation in current efficiency for CO<sub>2</sub> reduction on polycrystalline Cu cathodes, a set of seventeen independent experiments has been reported [39] (Figure 1), and while some of this variation can be attributed to potential (Figure 2) it is clear that significant variation in CO<sub>2</sub> current efficiency is found even when repeating the experiment under the same reaction conditions. As the typical uncertainty in the current efficiency measurements in these experiments is less than 2%, the variation in current efficiency must be caused by some as yet unknown variable.

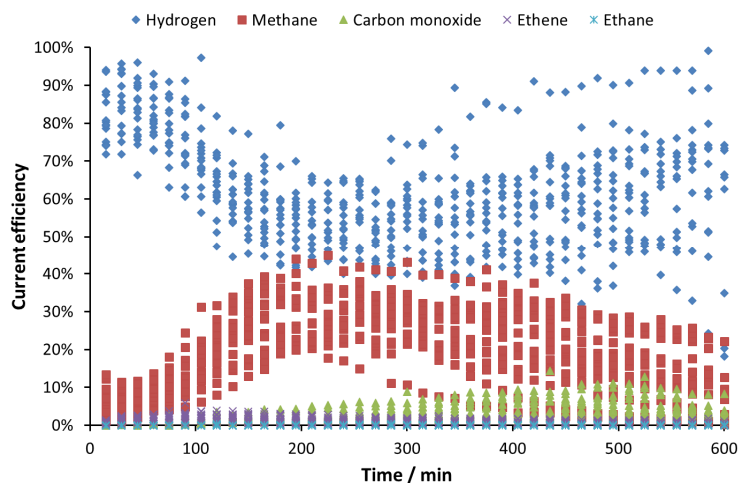


Figure 1. Current efficiency for CO<sub>2</sub> reduction on Cu cathodes measured galvanostatically at -5 mA/cm<sup>2</sup> in 0.2 M KHCO<sub>3</sub>. Adapted from [39].

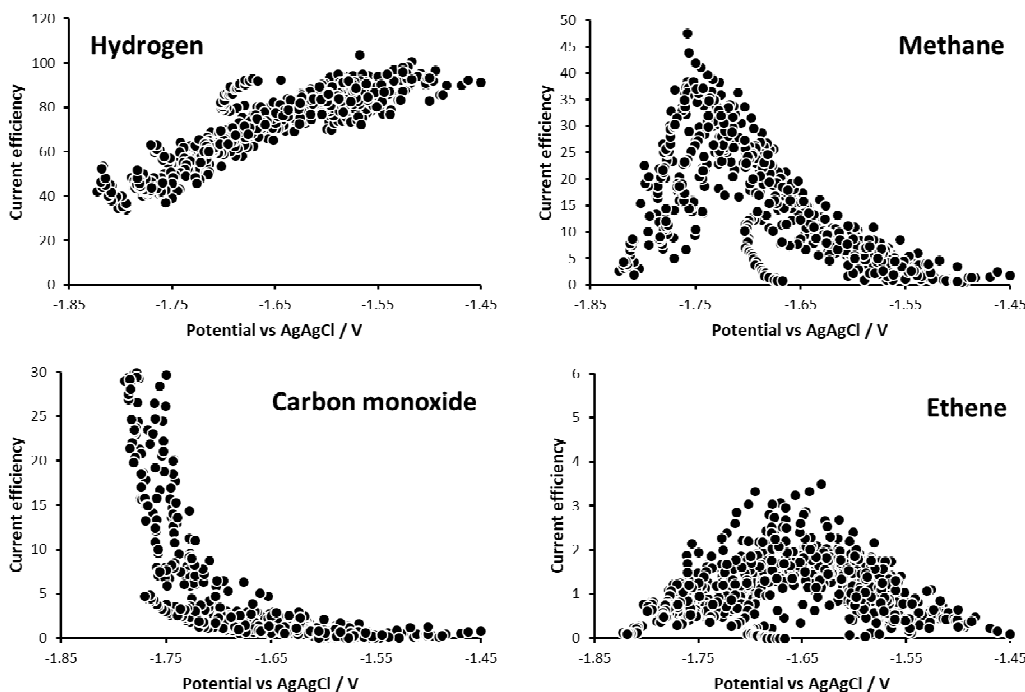


Figure 2. Current efficiency for CO<sub>2</sub> reduction products as a function of potential during galvanostatic measurements at -5 mA/cm<sup>2</sup> in 0.2 M KHCO<sub>3</sub>.

### Experimental factors that influence CO<sub>2</sub> reduction

One possible explanation for the variation in data seen in Table I and in Figure 1, could be differences in the quantity of copper oxide present on the cathode. In most cases, copper cathodes will be covered in a thin oxide layer prior to CO<sub>2</sub> reduction due to the rapid formation and growth of a native oxide layer when Cu is exposed to air [40]. While thermodynamics [41] suggest that this oxide will be reduced under typical electrocatalytic CO<sub>2</sub> reduction conditions, it has been clearly shown that a portion of this oxide or residual oxygen may remain after CO<sub>2</sub> reduction [2, 9, 42, 43]. This suggestion provides some further basis for the enhanced activity of Cu cathodes which have been intentionally oxidised prior to CO<sub>2</sub> reduction [9, 16, 44, 45], which is supported by computational investigations [10, 42, 43]. Given that Cu oxide seems to improve the activity towards ethene, uncontrolled levels of surface oxidation on Cu cathode prior to CO<sub>2</sub> reduction may be the underlying cause in the wide range of measured current efficiencies.

A second possibility of the observed selectivity variation is the differences in the hydrodynamics during CO<sub>2</sub> reduction [46]. By using a Cu rotating cylinder electrode, a strong dependence in the reaction selectivity on the mass transport rate is observed (Figure 3). This controlled study is in agreement with the results of others where electrolyte agitation was shown to alter the selectivity of CO<sub>2</sub> reduction [26, 32, 47]. As the hydrodynamics at the electrode surface will influence the local pH and CO<sub>2</sub> concentration at the cathode surface [48], it is not surprising that variations in the mass transfer rates will also alter the reaction selectivity, given the effect that pH [24, 28, 49-51] and CO<sub>2</sub> concentration [21, 22, 24, 26] has on CO<sub>2</sub> reduction. Such an effect can be

explained by the equilibrium which exists between the adsorbed CO and the CO dissolved in the electrolyte immediately adjacent to the electrode surface [52]. This adsorbed CO is the main intermediate for CO<sub>2</sub> reduction to more hydrogenated products [5, 33, 34, 52], and is bound to Cu with moderate strength [52-54]. This explains why CO can easily desorb when the electrolyte is stirred or stripped of dissolved CO [27, 55], and why the selectivity switches away from methane and ethene towards CO when the mass transfer rates are increased [26, 32, 46]. This sensitivity of the CO<sub>2</sub> reduction reaction to the hydrodynamics at the electrode surface may explain some of the significant variation in the results taken from literature (Table I), given that the hydrodynamics will vary between the different cell configurations used by research groups.

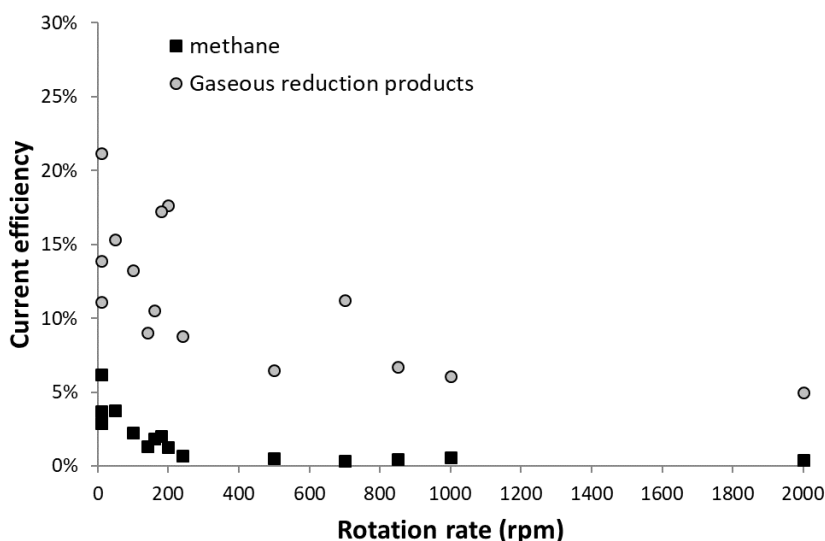


Figure 3. Current efficiency for CO<sub>2</sub> reduction products at a Cu rotating cylinder electrodes over 10 hrs of galvanostatic reduction at -5 mA/cm<sup>2</sup> in 0.2 M KHCO<sub>3</sub>.

Another possible cause for the variation in the reaction products found on Cu cathodes is the influence of deactivation or poisoning of the electrode surface. Deactivation of Cu is seen by many [24, 31, 56-62] and generally results in the hydrogen evolution reaction being promoted over CO<sub>2</sub> reduction. Currently deactivation is either ascribed to the deposition of metals from trace impurities in the electrolyte [56, 63], or the poisoning of the surface by a CO<sub>2</sub> reduction intermediate or product such as carbon [57-62, 64-67]. While both modes of deactivation are likely to occur during long-term CO<sub>2</sub> reduction, poisoning by metallic impurities present in the electrolyte does make it difficult to compare results across the literature unless such impurities are quantified by techniques such as ICP-MS.

To control the effect of poisoning, some have incorporated brief anodic treatments during the normally continuous cathodic process [66-69]. When applied to Cu cathodes, this is successful in maintaining or rejuvenating the CO<sub>2</sub> reduction activity [56, 58, 59, 61, 70, 71]. In some cases, this approach has also switched the product selectivity away from methane towards ethene [68], which suggests that the poisoning process may alter different reaction pathways in different ways. Such a shift in product selectivity has also been observed for Ag cathodes [69]. Interestingly in the case of Cu cathodes, applying

stripping cyclic voltammograms to remove these poisons seems to inhibit CO<sub>2</sub> reduction for a short period immediately after the cleaning procedure has been completed [39, 56], which suggests that a low surface coverage of poisons is necessary for CO<sub>2</sub> reduction on Cu. This differs from Au cathodes (which generally only produce H<sub>2</sub> and CO), where the CO<sub>2</sub> reduction selectivity towards CO remains high after stripping voltammetry is performed (Figure 4), suggesting that the role of deactivation and rejuvenation needs to be understood for each electrocatalyst used for CO<sub>2</sub> reduction.

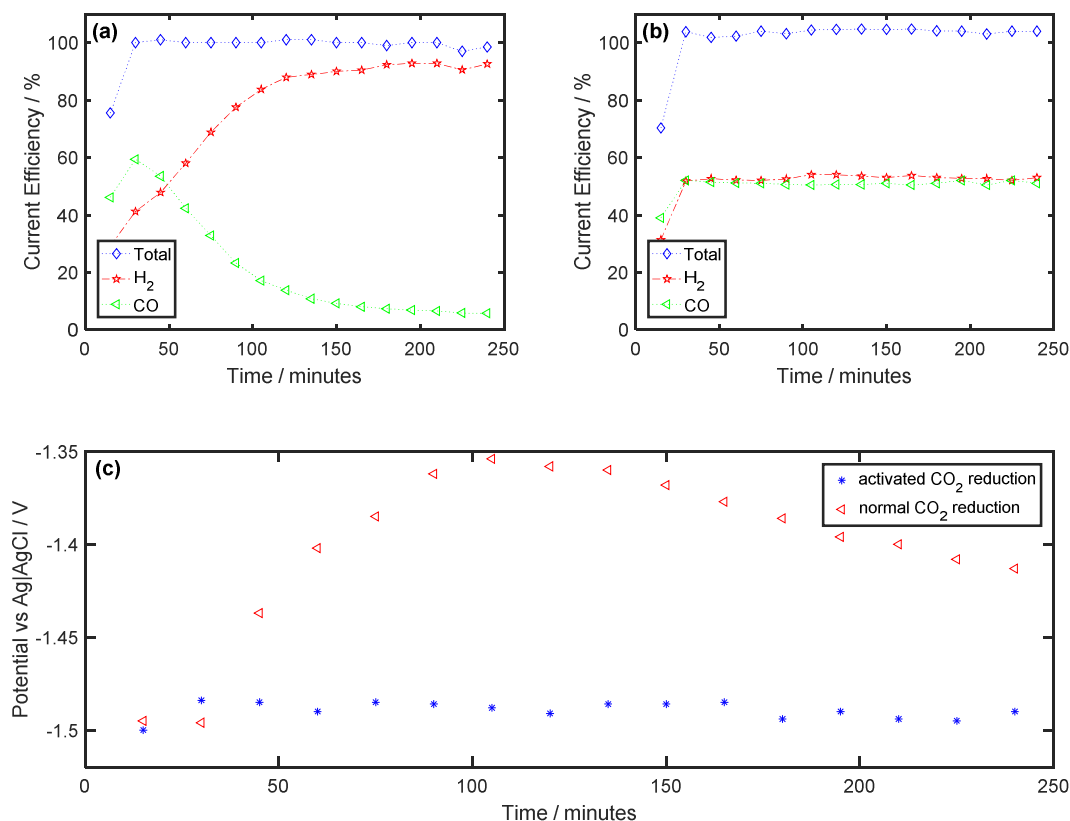


Figure 4. Current efficiency of gaseous products for CO<sub>2</sub> reduction using gold electrode in 0.2 M KHCO<sub>3</sub> (saturated with CO<sub>2</sub>) at -5 mA cm<sup>-2</sup>; (a) without treatment (b) using stripping voltammetry between -0.5 to 0.35 V at 100 mV s<sup>-1</sup> every 15 min (c) potential changes during electroreduction for both methods.

Finally, an often overlooked factor which influences electrocatalytic CO<sub>2</sub> reduction is changes to the electrolyte composition over time and the effect this has on the reaction. The most obvious change in the electrolyte is the accumulation of soluble reduction products such as formate, however the use of cation-exchange membranes such as Nafion to separate the catholyte and anolyte also can cause the ionic strength to change due to the selective transport of cations (e.g. K<sup>+</sup>) from the anolyte to the catholyte. This can be observed during CO<sub>2</sub> reduction by measuring the solution resistance over time (Figure 5).

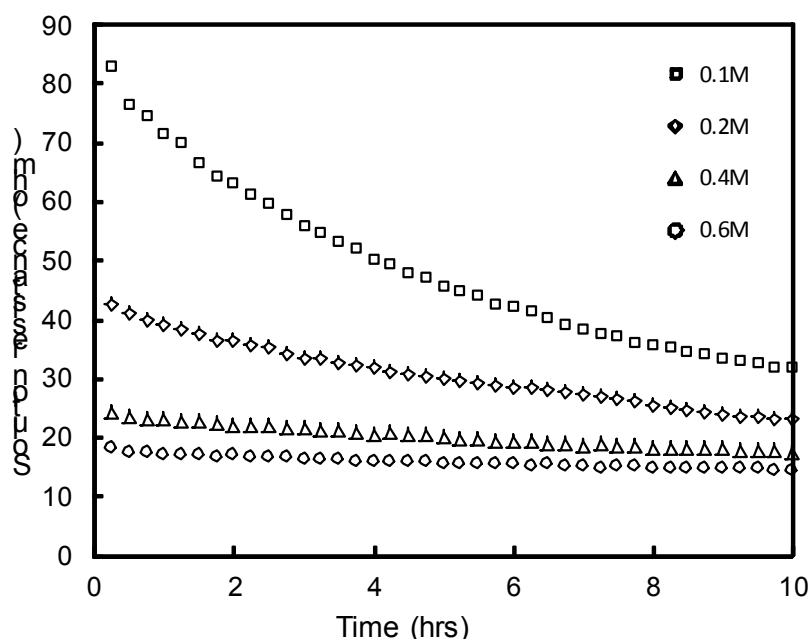


Figure 5. The solution resistance measured between a Cu cathode and a reference electrode placed in the catholyte chamber during  $\text{CO}_2$  reduction at  $-5 \text{ mA cm}^{-2}$ . The resistance was measured by EIS with the initial catholyte containing 0.1 – 0.6 M  $\text{KHCO}_3$ .

This change in  $\text{K}^+$  concentration in the catholyte chamber complicates the data analysis in two ways. Firstly the decrease in the solution resistance (the rate of which is proportional to the total cell current) makes it more difficult to correct potentials for the IR drop between the cathode and the reference electrode unless this resistance is regularly measured. Secondly, this change in the ionic strength also alters the  $\text{CO}_2$ -bicarbonate-carbonate equilibrium, with the bulk pH increasing as the ionic strength increases. This increase also results in an increased pH buffering capacity which directly influences the surface pH at the cathode during  $\text{CO}_2$  reduction [46, 48]. To further complicate matters, by comparing the calculated pH (calculated from the ionic strength) with the measured pH in the catholyte during  $\text{CO}_2$  reduction, it is clear that bulk electrolyte is not at equilibrium (Figure 6). While the differences are small on the pH scale, the fact the bulk electrolyte is not at equilibrium means that the exact  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  concentrations are not known unless additional measurements or models are employed. This effect is exacerbated when the ratio of the electrode area : electrolyte volume is increased (often high electrode area : electrolyte volume ratios are used to maximize the ability to measure low levels of reduction products dissolved in the catholyte).

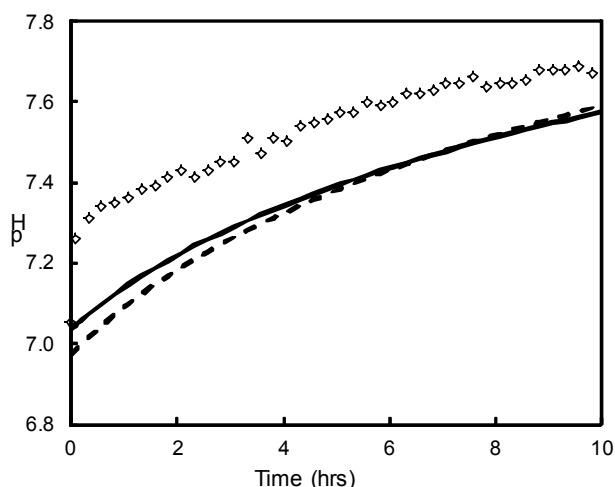


Figure 6. Comparison of the bulk pH (points) and the calculated pH (lines - assuming equilibrium) within the catholyte during CO<sub>2</sub> reduction at -20 mA cm<sup>-2</sup>. The initial catholyte contained 0.2 KHCO<sub>3</sub>. The two calculated lines represent two different models of the activity coefficients used in the pH calculations.

### Conclusions

CO<sub>2</sub> reduction is a complex reaction which is sensitive to a range of experimental parameters in addition to the choice of cathode material. This complicates the interpretation of experimental data as there is no standard conditions or experimental methods used for electrocatalytic CO<sub>2</sub> reduction [7]. In this paper the effect of residual oxygen in Cu cathodes, mass transport, deactivation and electrolyte changes are highlighted as possible aspects where better control is required in order to obtain more consistent data between different research groups and experimental set-ups.

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