Investigation into the Re-Arrangement of Copper Foams Pre- and Post-CO₂ Electrocatalysis

Jennifer Rudd, Sandra Herrnandez-Aldave, Ewa Kazimierska, Louise B. Hamdy, Odin Bain, Andrew R. Barron, Enrico Andreoli

Submitted date: 27/04/2021 • Posted date: 28/04/2021
Licence: CC BY-NC-ND 4.0
Citation information: Rudd, Jennifer; Herrnandez-Aldave, Sandra; Kazimierska, Ewa; Hamdy, Louise B.; Bain, Odin; Barron, Andrew R.; et al. (2020): Investigation into the Re-Arrangement of Copper Foams Pre- and Post-CO₂ Electrocatalysis. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.12022623.v2

The utilization of carbon dioxide is a major incentive for the growing field of carbon capture. Carbon dioxide could be an abundant building block to generate higher value products. Herein, we fabricated a porous copper electrode capable of catalyzing the reduction of carbon dioxide into higher value products such as ethylene, ethanol, and propanol. We investigated the formation of the foams under different conditions, not only analyzing their morphological and crystal structure but also documenting their performance as a catalyst. In particular, we studied the response of the foams to CO₂ electrolysis, including the effect of urea as a potential additive to enhance CO₂ catalysis. Before electrolysis, the pristine and urea-modified foam copper electrodes consisted of a mixture of cuboctahedra and dendrites. After 35-minute electrolysis, the cuboctahedra and dendrites underwent structural rearrangement affecting catalysis performance. We found that alterations in the morphology, crystallinity, and surface composition of the catalyst were conducive to the deactivation of the copper foams.
Investigation into the Re-Arrangement of Copper Foams Pre- and Post-CO$_2$ Electrocatalysis

Jennifer A. Rudd$^a$, Sandra Hernandez-Aldave$^a$, Ewa Kazimierska$^a$, Louise B. Hamdy$^a$, Odin J.E. Bain$^a$, Andrew R. Barron$^{a,b,c}$, Enrico Andreoli$^a$ *

$^a$ Energy Safety Research Institute, Swansea University, Bay Campus, Swansea, SA1 8EN, Wales, UK.
$^b$ Department of Chemistry and Department of Materials Science and Nanoengineering, Rice University, Houston, Texas 77007, USA.
$^c$ Faculty of Engineering, Universiti Teknologi Brunei, Jalan Tungku Link, Gadong BE1410, Brunei

Experimental details

Electrocatalysis experiments: CH440c (CH Instruments, USA) and Ivium-n-stat (Ivium Technologies B. V., Netherlands) potentiostat instruments were used for electrochemical measurements and electrolysis. Ivium-n-stat was used for electrochemical impedance spectroscopy for ohmic drop measurements, which was measured at a sinusoidal potential frequency of 10 kHz with 5 mV amplitude centered on the electrolysis potential (-1.6 to -1.4 V vs Ag/AgCl) just before electrolysis. A total of 85% of the measured ohmic drop was compensated for using the potentiostat control software; the remaining 15% ($R_u$) was manually adjusted for during data treatment using Ohm’s law. Due to variations in ohmic drop and current between experiments, the actual potential difference also varied from run to run. A three-electrode setup was used with a leak-free reference electrode based on Ag/AgCl in 3.4 M KCl (+0.210 V vs SHE; Innovative Instruments Inc., USA), and the counter electrode was a 2.5 cm × 5 cm piece of platinum mesh electrode (99.9% Goodfellow, UK). Potentials are converted to the reversible hydrogen electrode (RHE) scale using eq 1.

$$E_{RHE} (V) = E_{Ag/AgCl(3.4 M)} (V) + 0.210 V + (0.059 V \times \text{pH}) + iR_u$$  \hspace{1cm} (1)

The pH was measured at the start of the experiment, after bubbling CO$_2$ but prior to starting electrocatalysis. The pH of the CO$_2$-saturated bicarbonate solution was found to be 6.8.
For 35 minute electrolysis experiments a custom-made H-cell was used, constructed as described previously. The cell was filled with 3.5 mL electrolyte on the cathode side and 40 mL electrolyte on the anode side. Carbon dioxide gas was flowed into the electrolyte and maintained at a constant rate of 40 mL/min during electrolysis using a mass flow controller GFCS-010058 (Cole-Parmer, USA). Gas inlet and outlet streams were added to the cell to allow CO₂ to enter and escape while keeping the internal pressure of the cell at ambient levels. To take a gaseous measurement 2.5 mL of experimental gas exhaust was injected in the GC, of which 0.4 mL was analyzed.

Gaseous products were quantified using Agilent 7820A gas chromatograph (Agilent Technologies, UK) equipped with a thermal conductivity detector and flame ionization detector coupled to a methanizer, with argon used as the carrier gas. The following gaseous products of CO₂ electrolysis were quantified; hydrogen, carbon monoxide, methane, ethylene and ethane as well as oxygen, nitrogen and carbon dioxide. The method was also able to quantify propane, butane, pentane and hexane but these peaks were not present or near the limits of detection. The GC had two columns, HP-PLOT Q which separates hydrocarbons and CO₂, followed by HP-PLOT 5A (molecular sieve) column which separate other permanent gases. The two columns were connected by valves which could be programmed to be run in series or bypass mode. The sample peak areas were compared to calibration gases (Calgaz, USA), and quantified according to the equation below. Single point calibration was used to quantify product concentration. Linearity between hydrogen and ethylene concentration and peak area was tested using two mass flow controllers connected to a source of calibration gas and argon carrier gas, the two were mixed before injection into the GC sampling tube.

\[
\text{Faradaic Efficiency} = \frac{nF_{\text{cat}}}{1000P_{\text{T}}C_{T}}
\]
Faradaic efficiency is given in decimals, n is the number of electrons needed to reduce CO$_2$ to a given product, F is the Faraday constant (96485 Cmol$^{-1}$), Ps and Pc are the peak areas of the sample and the calibration gas respectively, $c_c$ is the calibration gas concentration in mol dm$^{-3}$, $v$ is the total volume of gas flowed through the electrolysis cell during electrolysis in cm$^3$ and $C_T$ is the total charge passed through the system during electrolysis in Coulombs.

**Characterization details**

**Characterization of copper foams made in the presence of varying HCl concentrations**

Copper foams that formed in the presence of 4 mM HCl (CF-4H) have the thinnest average wall width of 19.3 µm, whereas foams made with 73 mM HCl (CF-73H) have the widest average wall width of 29.0 µm. The 18 mM HCl foams (CF-18H) are in the middle, 26.2 µm. The pore size also varies with HCl concentration. The smallest average pore size, 38.1 µm, is observed for CF-4H. CF-18H has the largest pores, average diameter 58.6 µm, ranging from 36.5 to 70.3 µm. In contrast, CF-73H is less homogeneous than CF-18H with pore diameters ranging from 24.3 µm to 70.9 µm (these values are based on 8 measurements per foam).

![SEM images](image)

**Figure S1.** SEM images of the copper foams made in the presence of various concentrations of added HCl. a) CF-4H, b) CF-18H, c) CF-73H. The black bar at the bottom of the pictures represents 300 µm.
Table S1. Summary of the wall widths and pore sizes of various copper foams.

| Copper Foam | Wall Width (µm) | Pore Size (µm) |
|-------------|----------------|---------------|
| CF-4H       | 19.3           | 38.1          |
| CF-18H      | 26.2           | 58.6          |
| CF-18H-100U | 18.2           | 44.1          |
| CF-73H      | 29.0           | 47.6          |

Figure S2. SEM images of CF-18H a) at x3,500 and b) at x15,000 magnification. Image b) was taken of the bottom of the foam.

Figure S3. XRD of plain copper disc (black), CF-18H on copper disc (red), CF-18H on a carbon tab (blue).
Figure S4. Faradaic efficiencies of liquid products (%) vs the concentration of added HCl into the copper foam deposition bath (mM). Electrocatalysis experiments carried out at -0.81 V vs RHE in 0.1 M KHCO$_3$ electrolyte.

Table S2. Table summarizing the faradaic efficiencies of the gaseous products from electroreduction catalysis of CF-18H at -0.81 V vs RHE.

|        | Run 1 | Run 2 | Run 3 | AVG  |
|--------|-------|-------|-------|------|
| Ethylene (%) | 3.67  | 4.82  | 4.06  | 4.18 |
| Ethane (%)   | 1.40  | 2.81  | 4.87  | 3.03 |
| CO (%)       | 4.89  | 3.90  | 2.54  | 3.78 |
| H$_2$ (%)    | 56.60 | 59.96 | 52.84 | 56.47 |
**Figure S5.** SEM of CF-18H-100U. a) x75 magnification, b) x3,500 magnification of one of the “cracks” depicting the change in structure with depth. c), cuboctahedra structures interspersed with dendrites from a site below the “crack”.

**Figure S6.** XPS spectrum of CF-18H before catalysis showing no nitrogen peak in the N1s spectrum.
Figure S7. Cyclic voltammograms of copper foams in argon saturated 0.1 M HClO₄ at 0.01, 0.02, 0.05, 0.1 and 0.2 V s⁻¹. Left – cyclic voltammograms. Right – shows the sum of charging and discharging current as a function of scan rate. Top to bottom, CF-18H, CF-18H-100U, CF-18H-DCU.
**Supporting Information**

**Table S3.** Current density calculations for CF-18H and CF-18H-100U at -0.83V vs RHE.

|                      | CF-18H | CF-18H-100U |
|----------------------|--------|-------------|
| Potential vs RHE     | -0.83  | -0.83       |
| Avg Coulombs         | 4.36   | 5.58        |
| Avg current          | 0.002  | 0.003       |
| Avg current          | 2.08   | 2.66        |
| Diameter of disc     | 0.30   | 0.30        |
| Radius of disc       | 0.15   | 0.15        |
| Area                 | 0.07   | 0.07        |
| Current density      | 29.37  | 37.61       |
| Partial current density for \(n\)-propanol | 0.98  | 1.85       |

**Figure S8.** Faradaic efficiencies of liquid products (%) vs the concentration of added urea into the copper foam deposition bath (mM) all made using 18 mM HCl in the deposition bath. Electrocatalysis experiments carried out at -0.83 V vs RHE in 0.1 M KHCO₃ electrolyte. Error bars are the standard deviation from 3 measurements. The error bars on acetate are too small to depict.
Figure S9. Faradaic efficiency for observed products on CF-18H and CF-18H-100U plotted vs potential, corrected to RHE. The error bars are the standard deviation from three independent measurements. Data for acetate are provided in Figure 8 of the manuscript.
Table S4. Summary of the percentage faradaic efficiencies of all products from the CF-18H and the CF-18H-100U copper foams.

| Voltage (V) | CF-18H       | CF-18H-100U  |
|------------|--------------|--------------|
|            | -0.70 | -0.75 | -0.83 | -0.93 | -1.05 | -0.70 | -0.75 | -0.83 | -0.93 | -1.05 |
| Hydrogen   | 41.93 | 54.24 | 56.47 | 68.17 | 74.30 | 47.61 | 66.29 | 69.21 | 76.21 | 90.91 |
| CO         | 14.40 | 5.49  | 3.78  | 2.42  | 1.71  | 9.20  | 7.40  | 4.60  | 3.90  | 0.88  |
| Formate    | 12.17 | 6.90  | 6.13  | 3.37  | 2.67  | 24.73 | 5.79  | 5.92  | 3.09  | 2.42  |
| Methane    | ---   | ---   | ---   | 0.37  |       | ---   | ---   | ---   | 0.70  |       |
| Ethanol    | ---   | 1.38  | 2.79  | 0.87  | 2.51  |       | 1.75  | 3.19  | 1.07  | 1.51  |
| Acetate    | ---   | 0.43  | 0.32  | 0.17  | 0.14  |       | 0.23  | 0.70  | 0.12  | 0.07  |
| Ethylene   | ---   | 3.54  | 4.18  | 9.70  | 11.67 |       | 1.50  | 2.50  | 4.00  | 5.60  | 8.00  |
| Ethane     | ---   | 1.92  | 3.03  | 2.39  | 0.69  |       | 1.30  | 2.40  | 2.80  | 1.20  | 0.00  |
| n-Propanol | ---   | 1.51  | 3.34  | 1.64  | 1.77  |       | 2.23  | 4.93  | 1.31  | 0.89  |
| i-Propanol | ---   | 0.79  | 0.68  | 0.87  | 0.74  |       |       |       | 0.11  |       |

C3 Product total: --- 2.30 4.02 2.50 2.51 --- 2.23 4.93 1.43 0.89
C2 Products: --- 7.27 10.32 13.13 15.01 2.80 6.87 10.68 7.99 9.58
C2+C3 products: --- 9.57 14.34 15.68 17.51 2.80 9.10 15.61 9.42 10.47
C1 Products: 26.57 12.39 9.91 5.79 4.75 33.93 13.19 10.52 6.99 4.00

Figure S10. Representative NMR spectrum depicting the peaks attributed to n-PrOH, i-PrOH, EtOH, and acetate. CF-18H at -0.83 V vs RHE. The broad peak at 1.2 ppm could be due to diethyl ether but this peak alone is not enough to report the electroreduction of CO₂ to diethyl ether so no such claim has been made.
Figure S11. Faradaic efficiency vs potential for CF-18H-DCU.

Figure S12. Representative chloride 2p signal of CF-18H after 35 minutes of electrolysis at -0.83 V vs RHE.
Supporting Information

Figure S13. Copper 2p signal from CF-18H (black), CF-18H-100U (red), CF-18H-DCU (blue) after 35 minutes of electrolysis at -0.83 V vs RHE.

References

1. S. Ahn, K. Klyukin, R. J. Wakeham, J. A. Rudd, A. R. Lewis, S. Alexander, F. Carla, V. Alexandrov and E. Andreoli, ACS Catalysis, 2018, 8, 4132-4142.
Investigation into the Re-Arrangement of Copper Foams Pre- and Post-CO$_2$ Electrocatalysis

Jennifer A. Rudd$^1$, Sandra Hernandez-Aldave$^1$, Ewa Kazimierska$^1$, Louise B. Hamdy$^1$, Odin J.E. Bain$^1$, Andrew R. Barron$^{1,2}$ and Enrico Andreoli$^{1,*}$

$^1$ Energy Safety Research Institute, Swansea University, Bay Campus, Swansea, SA1 8EN, Wales, UK.
$^2$ Department of Chemistry and Department of Materials Science and Nanoengineering, Rice University, Houston, Texas 77005, USA.
$^3$ Faculty of Engineering, Universiti Teknologi Brunei, Jalan Tungku Link, Gadong BE1440, Brunei

* Correspondence: e.andreoli@swansea.ac.uk

Abstract: The utilization of carbon dioxide is a major incentive for the growing field of carbon capture. Carbon dioxide could be an abundant building block to generate higher value products. Herein, we fabricated a porous copper electrode capable of catalyzing the reduction of carbon dioxide into higher value products such as ethylene, ethanol, and propanol. We investigated the formation of the foams under different conditions, not only analyzing their morphological and crystal structure but also documenting their performance as a catalyst. In particular, we studied the response of the foams to CO$_2$ electrolysis, including the effect of urea as a potential additive to enhance CO$_2$ catalysis. Before electrolysis, the pristine and urea-modified foam copper electrodes consisted of a mixture of cuboctahedra and dendrites. After 35-minute electrolysis, the cuboctahedra and dendrites underwent structural rearrangement affecting catalysis performance. We found that alterations in the morphology, crystallinity, and surface composition of the catalyst were conducive to the deactivation of the copper foams.

Keywords: copper foam; CO$_2$ reduction; electrocatalysis; heterogeneous catalyst; modified electrodes; propanol

1. Introduction

As the concentration of carbon dioxide (CO$_2$) in the atmosphere increases daily, scientists are searching for a way to stem the tide. Carbon capture is becoming ever more efficient and has recently been commercialized by companies such as Climeworks [1, 2], and Carbon Engineering [3, 4]; however, captured CO$_2$ has marginal commercial value ($\sim$3-35 per ton) [5, 6]. Therefore, research is being carried out on the sustainable conversion of CO$_2$ into higher-value fuels and related carbon-based products, such as methane, ethylene, and propanol [7-10]. Nevertheless, it is important to note that currently only CO$_2$ obtained through direct air capture, coupled with electrochemical conversion using renewable energy can be viewed as sustainable [11].

Carbon dioxide is a stable molecule that commonly only reacts through high kinetic barriers. Therefore, a catalyst is required to promote these reactions. Copper is an important CO$_2$ reduction catalyst due to its unique properties; until 2018 it was the only metal reported capable of generating higher value products than carbon monoxide (CO) and formate from CO$_2$ in appreciable quantities [12-15]. Therefore, the use of copper as an electrocatalyst for CO$_2$ reductions is widely extended, employing solid copper surfaces [16-19], copper foil [20-23], copper nanoparticles [24-26], copper nanocrystals [27-29], or hollow copper metal–organic framework (MOF) [30-32]. However, frequently, they are sensitive to minor contaminants present in water or bicarbonate solution [33-36], requiring extensive purification of both the copper surface and reaction medium before electrocatalysis. Such pre-treatments are expensive and time-consuming, making the process industrially unviable. Moreover, a number of performance indicators must be achieved for commercialization such as 300 mA/cm$^2$ current density, low over-potentials, and high faradaic efficiency for selected products [37, 38].

Copper foams have shown good tolerance against minor contaminants as they remain active without electropolishing or scavenging the reaction solution [34, 36, 39]. The fabrication of copper foams has been previously reported, using electrodeposition. The electrodeposition using the soft templating effect of hydrogen bubbles has been used to generate highly porous copper foam structures...
on the surface of a copper disc electrode [40, 41]. Shin et al. [42] and Kim et al. [43] reported that the addition of chemical additives such as hydrochloric acid (HCl), ascorbic acid, and others could change the size and morphology of the pores. However, in order to be used as an electrocatalyst, the morphology of the microstructures and crystal facets need to be investigated, ensuring that they are optimum for CO$_2$ reduction.

The microstructures and crystal facets of copper strongly contribute to the CO$_2$ reduction mechanism and product distribution [44, 45]. Theoretical and experimental research has demonstrated that the cube-like structures such as Cu(100) facet promote the production of ethylene and the Cu(111) facet the production of methane [13]. Moreover, cube-like structures have been found to promote the formation of propanol. Propanol is an interesting CO$_2$ reduction product with current efficiencies and current densities that are commonly low due to the intrinsic complexity of C-C bond formation, [20, 46, 47] translating into high economic barriers to the commercialization of this process [48]. Kim et al. reported the development of copper nanoparticle ensembles loaded onto carbon paper which re-arranged during catalysis into cube-like particles. These particles could convert CO$_2$ into a mixture of n-propanol, acetone, and allyl alcohol with a combined faradaic efficiency of 5.9% at -0.81 V vs RHE [47]. The total current density was 12.7 mA/cm$^2$, corresponding to a partial current density $j_{n$-propanol} ~ 0.75 mA/cm$^2$. Ren et al. designed a copper catalyst with a “high surface population of defects” by electreducing anodized Cu nanoparticles, leading to nanocrystals in a rough, square shape [49]. Using this catalyst n-propanol was generated with 10.6% faradaic efficiency at -0.85 V vs RHE. Long-term electrolysis was also carried out at -0.95 V, and n-propanol could be continuously produced with a current density of $j_{n$-propanol} ~ -1.74 mA/cm$^2$ for 6 hours. Grosse et al. reported copper nanocubes that underwent structural change during catalysis [50], a small quantity of n-propanol was produced ~1.8% at -0.96 V vs RHE.

Considering the importance of the copper microstructure on CO$_2$ electroreduction, we turned our attention to the fabrication of copper foams under various conditions, aiming to tune the microstructure of the copper foam and its capabilities as an electrocatalyst. In the past, we have reported that the impregnation of a copper foam with poly(acrylamide) enhanced the production of ethylene, reaching faradaic efficiencies of 26% and an overall reduction current density of 60 mA/cm$^2$[51]. Therefore, in this work, we further investigated the addition of nitrogen-containing moieties, using urea. The addition of nitrogen-containing moieties can tune the properties of the copper catalyst to potentially give higher current densities, promote C-C bond formation, and lead to greater product selectivity [46, 52, 53]. We expected the modification of copper foam with the simplest amide, i.e., carbamide, also known as urea, could stabilize carbon monoxide adsorbed intermediates *CO on copper promoting C-C bond formation. Urea was previously used with copper [54] or to electrodeposit copper [55], but not to change the properties of the copper in the attempt to promote C-C bond formation in CO$_2$ reduction. We wanted to establish whether the addition of urea would promote the formation of n-propanol and increase the current density of copper foam catalysts. Interestingly, we found that whilst urea did not enhance selectivity for n-propanol, it instead improved the lifetime of the copper foam impacting on CO$_2$ catalysis.

**Materials and Methods**

2.1. Materials

Potassium bicarbonate (99.5%, Sigma Aldrich), Copper sulphate pentahydrate (99.9%, Sigma Aldrich), Urea (99.5%, Sigma Aldrich), Hydrochloric Acid (37.5%, Sigma Aldrich), Sulphuric acid (95-98%, Sigma Aldrich), Perchloric acid (70% ACS reagent, Sigma Aldrich), Argon gas (99.998%, BOC), Carbon dioxide gas (99.995%, BOC). All reagents were used without further purification. Deionized water with 15 MΩ.cm resistance from Merck Elix type 2 water purification system.

2.2. Copper Foam Preparation

The preparation was adapted from our previous work ACS Catalysis, 2018, 8, 5, 4132-4142 (Ahn et al. [51]). A 3 mm diameter copper rod (99.99%, Goodfellow, UK) was cut into cylindrical pieces and embedded into a polycarbonate body with Araldite epoxy (Huntsman Advanced Materials, Switzerland). The electrode was mechanically polished with 0.3 μm alumina slurry followed by rinsing
and ultrasonication in deionized water for 1 min. Copper foam was electrodeposited on the copper disc by submerging in 0.2 M CuSO$_4$, 1.5 M H$_2$SO$_4$(aq) and 4 - 73 mm HCl(aq) and applying a fixed cathodic current of 3 A cm$^{-2}$ for 15 s. Urea modified copper foam was synthesized by (i) dissolving a mass of urea corresponding to 10 - 100 mM concentration (ii) dip-coating unmodified electrodeposited copper foam in an H$_2$O solution of 100 mM concentration urea for 1 minute. The electrodeposited foams were submerged in deionized water for 5 min to remove traces of electrodeposition solution before electrochemical measurements.

The foams are denoted as follows: CF-xH, CF-18H-xU, CF-18H-DCU where CF = copper foam, xH = concentration in millimoles of HCl added to electrodeposition bath, xU = concentration in millimoles of urea added to deposition bath, DCU = dip-coated in aqueous 100 mM urea solution.

2.3. Material Characterization

Scanning electron microscopy images were taken using field emission gun scanning electron microscopy (FEG-SEM JEOL 7800F). XPS was performed using a Kratos Axis Supra (Kratos Analytical, Japan) utilizing a monochromated Al-Kα X-ray source, 15 mA emission current, magnetic hybrid lens, and slot aperture. Region scans were performed using a pass energy of 40 eV and step size of 0.1 eV. Prior to XPS analysis, the copper foams were dried in a vacuum desiccator for 24 hours. Scans were run of the copper foams after initial synthesis and again after their use as catalysts. It was possible to preclude the presence of CO$_2$ catalysis contaminants such as zinc and lead potentially deposited onto the surface from the electrolyte during electrolysis [56]. XRD measurements were carried out on a Bruker D8 Discover diffractometer with Cu-Kα source radiation (λ = 0.15418 nm). Data were recorded in the 2θ range from 35° – 100° in 0.04° increments with a step time of 0.5 seconds.

2.4. CO$_2$ Electrocatalysis

The electrocatalysis was carried out following the procedure established by Ahn et al. [51] and is detailed in full in the SI. Minor changes to the previously reported procedure are detailed here. The electrolyte solution was prepared by saturating a 0.1 M KHCO$_3$ solution with CO$_2$ by bubbling at 40 mL min$^{-1}$ for 1 hour prior to use. The pH of the solution was measured at 6.8. The electrolysis cell was saturated with CO$_2$ gas flowing at 40 mL/min for 5 min before a cathodic potential (-0.70 to -1.04 V vs RHE) was applied. Electrolysis was carried out by setting the voltage at reducing potentials for a total of 35 min. Gas headspace samples were taken from the cell using a gastight syringe for manual injection into the GC sampling loop on the 5th, 20th, and 35th minute. The electrolysis run was temporarily stopped after gas sample injection and the ohmic drop remeasured before starting the next segment. Each set of gas-phase product measurements was repeated at least three times.

2.5. Electrocatalysis Product Analysis

Liquid phase products were quantified at the end of the 35 min run using a Bruker AV-500 Nuclear Magnetic Resonance (NMR) instrument running a water suppression experiment [51]. A DMSO standard was added to the NMR tube to make a 0.1 mM concentration. Peak areas of the liquid products were then integrated and compared to the standard to obtain concentrations. Gaseous products were quantified using an Agilent 7820A gas chromatograph (Agilent Technologies, UK), equipped with a thermal conductivity detector and flame ionization detector coupled to a methanizer. A dual column setup was utilized, HP-PLOT Q and HP-PLOT 5A (Agilent Technologies, UK), for the separation of hydrocarbons and permanent gases, respectively. For full details see the supporting information.

3. Results

3.1. Effect of HCl on the copper foams

We decided to vary the hydrochloric acid (HCl) concentration and look at the effects of the different foams on CO$_2$ reduction. In our experiments, the sulfuric acid (H$_2$SO$_4$) concentration was fixed at 1.5 M and the copper sulphate concentration was 0.2 M. The HCl concentration was varied from 4 to
73 mM. These experimental conditions differ from those previously reported by Kim et al. (0.4 M CuSO₄/0.7 M H₂SO₄ [43]) and Shin et al. (0.4 M CuSO₄/1.5 M H₂SO₄/1-50 mM HCl [42]).

Scanning electron microscopy (SEM) was used to image the foams (SI Figure S1). The concentration of hydrochloric acid added to the electrodeposition bath affected the morphology of the copper foams. Shin et al. reported that increasing the concentration of HCl in the deposition bath from 1-50 mM altered the morphology of the foam walls, making them higher density [42]. Our copper foams, formed in the presence of small amounts of HCl, had thin wall widths and small pore diameters; large amounts of HCl led to thicker wall widths and larger pore diameters. This is summarized in SI Table S1.

Closer inspection of the structure of CF-18H foam (Figure 1) reveals that the top surface comprises thousands of cube-like structures, technically termed cuboctahedra [57]. Although the electrodeposition of various copper foams has previously been reported, [39, 41-43, 51, 52, 58, 59] to the best of our knowledge, no foams primarily consisting of cuboctahedra agglomerates have previously been observed. The edges of the pores comprise the same type of cuboctahedra interspersed with dendritic structures. Cuboctahedra were also found at the base of the pores (SI Figure S2). There are two different sizes of cuboctahedra, the majority are large, approximately 450 x 750 nm (width x height) in size, interspersed with smaller cuboctahedra about 250 x 250 nm. The smaller cuboctahedra are predominantly near the bottom of the pore whereas the larger ones dominate the top of the pores.

![Figure 1. SEM images of CF-18H at various magnifications. a) x300 b) x15,000 c) x35,000 magnification. These images are taken of the top portion of the foam.](image)

In order to investigate the crystal facets of the copper the foams, we have performed an ex-situ X-ray diffraction of the foams (XRD, Figure 2). XRD analyses of all of the copper foams show that both Cu metal and Cu₂O are present in the foam. The presence of millimolar concentrations of HCl during foam deposition seems not to affect the crystalline orientations of Cu⁰ formed. Compared to the Liu foams, ours contained more Cu₂O peaks corresponding to different crystalline phases. The same peaks were observed by Dutta et al. in their copper foam electrocatalysts [59]. Our foams have a high surface roughness (vide infra), which would have made them more prone to oxidation. The XRD patterns of our foams show the preferred orientation of Cu(111), with appreciable contribution from Cu(200), and Cu₃O(111)/Cu₃O(200). To preclude the Cu(111) phase coming only from the copper disc upon which the foam was grown, we also carried out XRD on the copper foam on a carbon tab. The Cu(111) peak is present in the pattern of the copper disc alone, and the copper foam on the carbon tab (SI Figure S3), confirming that the observed peak had contribution from the foam.
A preliminary CO₂ electrocatalytic activity study of the different copper foams was performed at -0.81 V vs RHE. This potential was chosen as it was the minimum overpotential required to produce appreciable quantities of n-propanol. The liquid products were analyzed, using NMR spectroscopy, to observe which foam was best at converting CO₂ to n-propanol. The effect of changing HCl content of copper foam deposition solution, on the electro-catalytic performance of copper foams is shown in SI Figure S4. At -0.81 V vs RHE adding 7 mM HCl into the copper foam deposition bath gave the best faradaic efficiency for n-propanol, about 2.4%. However, the addition of 18 mM HCl gave practically the same (within the experimental error) faradaic efficiency of n-propanol, 2.3%, and greater faradaic efficiency for ethanol production, about 3.3%. Therefore, the 18 mM HCl copper foam was used for further experiments. The gaseous products on 18 mM HCl copper foam were found to be carbon monoxide, ethylene, ethane and the by-product hydrogen (SI Table S2).

3.2. Effect of urea on the copper foams

The catalyst fabricated employing 18mM HCl CF-18H, was modified by adding urea in the foam electrodeposition bath to make CF-18H-xU (x represents the concentration in mM of urea employed). The electrodeposited foams were submerged in deionized water for 5 min to remove traces of the electrodeposition solution before electrochemical measurements. The copper foam formed from solutions with added 100 mM urea (CF-18H-100U) has a flattened and less well-defined porous structure compared to CF-18H (SI Figure S5). This indicates that urea affects the deposition of the foam possibly being integrated to form urea-modified copper foams. The wall widths between the pores range from 5.9 – 23.5μm, with an average width of 18.2 μm. The pore diameters range from 29.4 – 58.8 μm, smaller than CF-18H by 10 μm (data are summarized in SI Table S1).

In Figure 3, the top layer of CF-18H-100U is made of cuboctahedra and the lower layers comprise larger cuboctahedra interspersed with dendritic structures similar to what observed for CF-18H (Figure 1). The cuboctahedra at the surface are about 180 x 185 nm and the larger cuboctahedra at the bottom of the pores are around 300 x 300 nm. This is a similar size to those reported by Grosse et al. who grew 222 ± 47 nm copper cubes on carbon paper and copper foils [50]. The porous network spreads throughout the structure. Small cracks are observed in the urea-modified copper foam structure and are shown in detail in SI Figure S5. The structure around the crack comprises cuboctahedra interspersed with dendrites and therefore no overall change in the foam is caused as a result of the cracks.
The copper foam dip-coated in urea, CF-18H-DCU, exhibited a structure substantially like that of CF-18H confirming that no morphological changes were observed upon wetting with the urea solution. Figure 4 depicts the top, edge and bottom of a pore in CF-18H-DCU. The dendritic copper coats the copper disc electrode at the bottom of the pore, but the cuboctahedra make up most of the pore edge. The cuboctahedra at the top of the pore are approximately 650 x 850 nm (height x width). At the bottom of the pore, the cuboctahedra are smaller, about 500 x 500 nm. These cuboctahedra are comparable in size with the largest of the copper cubes tested by Grosse et al. [50] (580 nm) who demonstrated that a larger cube size leads to greater selectivity for the formation of CO$_2$ reduction products over the competing hydrogen evolution reaction. The 580 nm cube size also leads to the highest faradaic efficiency for n-propanol produced, compared to the other two cube size tested (220 and 320 nm).

The XRD analyses of urea modified foams show that peaks relating to Cu and Cu$_2$O are present in both the electrodeposited and dip-coated copper-urea foams (Figure 5). The modified foams show the preferred orientation of Cu(111), with peaks corresponding to Cu(200), Cu(311), Cu(222) and Cu$_2$O(111) also present. Comparing the two urea concentration extremes (10 and 100 mM): the ratio of Cu(111):Cu(200) is 1:0.35, Cu(111):Cu(220) is 1:0.1 and Cu(111):Cu(311) is 1:0.1 for CF-18H-10U. The ratios are slightly lower for CF-18H-100U with ratios Cu(111):Cu(200) 1:0.30, Cu(111):Cu(220) 1:0.03 and Cu(111):Cu(311) 1:0.06. This suggests that the crystal face of the copper foam does not change with the increasing concentration of urea.
The ratios of Cu(111) to Cu(200), Cu(311) and Cu(222) phases are unchanged between CF-18H-100U and CF-18H-DCU indicating that the method by which urea is impregnated into the foam does not change the copper phases present in the foam. As expected, there is little difference between the XRD of CF-18H and CF-18H-DCU. Cuprous oxide is also present in the Cu-18H-xU (x = 10-100) foams with the main component being the Cu₂O(111) phase (Figure 5).

The presence of urea on the copper surface was confirmed using X-ray photoelectron spectroscopy (XPS) and the spectra are presented in Figure 6. Nitrogen was detected in both copper foams modified with urea. There was no nitrogen in the CF-18H sample, which had no urea (SI Figure S6). The protonation state appeared to affect the binding of urea on copper. The foam CF-18H-100U deposited from acidified urea solution showed a single nitrogen signal at 400.0 eV (red dotted trace in Figure 6a) possibly corresponding to urea bound to the copper foam through nitrogen. It is known that in acidic media the carbonyl oxygen of urea is protonated [60] leaving the nitrogen-free to interact with copper. This was also observed in the case of CF-18H-DCU, though the XPS signal consisted of the convolution of two peaks at 399.8 eV and 398.9 eV (blue dotted trace in Figure 6a). The peak at 399.8 eV (purple trace) can be assigned to urea bound to copper through nitrogen, related to the 400.0 eV peak of CF-18H-100U.

**Figure 5.** XRD of 18 mM HCl copper foams with added 10 mM urea (black, in the bottom) or 100 mM urea in deposition bath (solid red, in the middle) or dip-coated from a 100 mM urea neutral aqueous solution (dotted red, at the top).

**Figure 6.** XPS spectra of the (a) nitrogen 1s signal from samples of CF-18H-DCU (top, dotted blue trace) and CF-18H-100U (bottom, dotted red trace), with fittings in solid lines. (b) Copper 2p signal from CF-18H (bottom, black), CF-18H-100U (middle, red), CF-18H-DCU urea (top, blue). (c) Copper Auger LMM peak from sample of CF-18H (bottom, black), CF-18H-100U (middle, red), CF-18H-DCU (top, blue).
The peak at 398.9 eV (green trace) is tentatively assigned to urea bound to copper through the carbonyl group [51]. The copper 2p signals are consistent for all samples and confirm the presence of copper metal (Fig. 6b). Weak satellite peaks are observed around 947 eV. These are consistent with the presence of Cu₂O, which was also observed by XRD. The most intense feature of the copper Auger signal of CF-18H-100U is found at 918.4 eV, consistent with the CF-18H copper Auger (Figure 6c). However, the Auger of CF-18H-DCU shows a stronger feature at 916.1 eV compared to 918.4 eV. The peak at 916.1 eV is dominant and indicates a surface richer in Cu₂O over Cu in the case of the dip-coated foam [61].

The electrochemical properties of the CF-18H and CF-18H-100U, in addition to the dip-coated catalyst CF-18H-DCU, were also compared. The double-layer capacitance method of determining the electrochemically active surface area was used [62]. As shown in Table 1, the copper foams have similar electrochemically active surface areas (ECSA) meaning that they are unaffected by the addition of urea in the deposition bath or dip-coating step. The foam surface area is 225 to 240 times larger than the electrode geometric surface area for the sample prepared using 18 mM HCl without and with urea, respectively. This is double that observed in our previous work, [51] and quadruple of that achieved by Dutta et al. [59]. The cyclic voltammograms and corresponding current vs scan rate plots are provided in SI Figure S7, the current density calculations in SI Table S3.

3.3. CO₂ electrocatalytic activity of foams

The CO₂ electrocatalytic activity of the copper foams deposited in the presence of different amounts of urea (CF-18H-xU) was tested at -0.83 V vs RHE. The liquid products of the urea copper foams are depicted in SI Figure S8. The faradaic efficiency increases with the concentration of urea until ~60 mM, afterwards, a plateau is observed, making CF-18H-100U the foam of choice for further study.

**Table 1. Summary of capacitance and surface area of copper foams electrodeposited with and without urea.** Applied potential -0.81 V vs RHE for CF-18H, -0.81 V vs RHE for CF-18H-100U, -0.79 V vs RHE for CF-DCU. The geometric and ECSA normalized current densities of CO₂ electrolysis at the corresponding applied potentials are also listed as j_{geometric} and j_{ECSA}, respectively.

|                     | CF-18-100U | CF-18H-100U | CF-18H-DCU |
|---------------------|------------|-------------|------------|
| Capacitance (µF)    | 447        | 474         | 472        |
| Electrochemically active surface area (cm²) | 16.0       | 16.9        | 16.9       |
| Surface roughness factor | 225        | 238         | 237        |
| j_{geometric} (mA/cm²) | 31.0       | 26.8        | 38.0       |
| j_{ECSA} (mA/cm²)   | 0.14       | 0.11        | 0.17       |

The three foams CF-18H, CF-18H-100U, and CF-18H-DCU were then tested for their activity as CO₂ reduction catalysts at various potentials in 0.1 M KHCO₃ solution while bubbling CO₂ at 40 mL/min. All products of electrocatalysis for CF-18H and CF-18H-100U are available in Figure 7 and SI Figure S9. We note that the CO₂ electrolysis experiments were affected by significant variability, as also observed in other studies [14, 15, 63]. In some instances, the values of faradaic efficiency of one material fell within the error bars of the other and vice versa. In such a case no claim could be made for either of the two catalysts, CF-18H and CF-18H-100U, performing better than the other, particularly in the case of n-propanol production (Figure 8c). However, some significant differences could be appreciated such as the CF-18H foam promoting the electroreduction of CO₂ to ethylene more effectively than the CF-18H-100U foam at -0.93 V vs RHE. Interestingly, i-propanol was generated using the CF-18H foam, albeit in small quantities – the maximum average faradaic efficiency is 0.87% at -0.93 V vs RHE (SI Table S4). This was lower for CF-18H-100U, 0.11%. A representative NMR spectrum is depicted in SI Figure S10 for CO₂ electrolysis using CF-18H at -0.83 V vs RHE.
Figure 7. Faradaic efficiencies of (a) hydrogen (b) carbon-based gas products and (c) liquid products versus potential, corrected to RHE, for copper foams CF-18H (solid lines) and CF-18H-100U (dashed lines). Data for formate are provided in SI Figure S9.

The dip-coated catalyst CF-18H-DCU demonstrated a different catalytic trend with n-propanol increasing with more negative potentials (SI Figure S11) compared to CF-18H and CF-18H-100U. For CF-18H and CF-18H-100U, the C1, C2, and C3 product distributions resulting from the electrocatalytic reduction of CO2 are shown in Figure 8. As the potential became more reductive the overall faradaic efficiency for carbon-based products decreased progressively in favor of hydrogen evolution (data are summarized in SI Table S4).

However, at more negative potentials, there was also a trade-off in the production of more C2+C3 products (ethylene + propanol) in place of C1 products. At -0.70 V vs RHE, only C1 products were detected in the form of carbon monoxide and formate, but no methane. C2 and C3 products were first observed at -0.75 V vs RHE. At -0.83 V vs RHE C2+C3 products were dominant over C1 products, a trend which continued with increasing potential. Trace amounts of methane and methanol were only observed at this potential. n-Propanol was the dominant C3 product and production peaked at -0.83 V vs RHE. i-Propanol and trace amounts of acetone were the other C3 products observed.

Figure 8. Bar chart depicting the product distribution from CO2 reduction at different electrocatalytic reduction potentials comparing CF-18H and CF-18H-100U.

3.4. Post-catalysis characterization

The CF-18H and CF-18H-100U foams were characterized after catalysis to look at their response to the applied potential. The analysis in this section is based on results gained from ex-situ measurements including SEM, XRD and XPS. SEM revealed that multiple cracks had formed both on the surface and further into the porous network of CF-18H. The cuboctahedra observed before electrolysis (Figure 1), were no longer present after 35 mins of electrolysis (Figure 9). The dendrites, a minor component in the as-prepared foams, became the only component of the foam after electrolysis, as shown in Figure 9b.
This same phenomenon was observed for CF-18H-100U. The cuboctahedra, present as the major component of the foam before electrolysis (Figure 3), are no longer present after 35 mins (Figure 9f). Therefore, we hypothesize that the copper foam responded to the process conditions of CO₂ electrolysis by re-arranging in-situ during catalysis.

XRD analysis of the copper foams after electrolysis corroborated the findings in the SEM of less crystalline materials (Figure 10). For CF-18H the peak intensity was reduced and, as can be observed in Figure 10a, the peaks are generally broader, indicative of smaller crystallite size. The rise of baseline at low diffraction angles suggests that an amorphous phase was also formed upon catalysis. Post-catalysis there was a significant increase in the relative peak intensity for Cu(200); pre-catalysis the Cu(111):Cu(200) ratio was 1:0.14, post-catalysis it was 1:0.39 with a significant loss of Cu(111) domains. There is also a small yet detectable peak at 47.5° tentatively assigned to the presence of trace amounts of CuCl(220) phase [64] (Figure 10a), which is localized on the surfaces of the foam as seen from the Cu LMM Auger spectra discussed later. Although care was taken to avoid any contamination in the CO₂ electrolysis cell, there appears to have been a trace amount of chloride ions in solution to form insoluble Cu₂O:-CuCl [64]. It follows that chloride contaminations were introduced during the electrolysis possibly due to the Ag/AgCl reference electrode and the small solution volume in the cathodic compartment (3.5 mL). Comparable changes were observed for CF-18H-100U (Figure 10b).

In line with the transition of the copper from cuboctahedra to dendrites, there is also a decrease in the Cu₂O(311) facet and an increase of Cu₂O(222). CF-18H-100U displays an increased orientation of the Cu(220) phase and a more equal spread of orientations post-electrolysis.

**Figure 9.** SEM images of CF-18H (a, b, c) and of CF-18H-100U (d, e, f) after 35 mins of CO₂ electrolysis at -0.83 V vs RHE in 0.1 M KHCO₃ and 40 mL/min CO₂.

**Figure 10.** The XRD patterns of (a) CF-18H and (b) CF-18H-100U before electrolysis (bottom black pattern) and post 35-min electrolysis (top red pattern), offset for clarity. For each material, both spectra were normalized to their respective Cu(111) peak and scaled to the ‘before electrolysis’ Cu(111) peak.
The presence of chloride contaminations was also observed in the XPS spectra of the foams after electrolysis (Figure 11). Before electrolysis, the Auger signal of CF-18H is typical for copper metal, with its most intense feature centered at 918.7 eV [65]. After 35-min electrolysis, the main feature is found to 915.6 eV, which is attributed to CuCl [66, 67]. The Cu Auger of CF-18H-100U displays similar behavior, although it retains a higher Cu metal content post-electrolysis, compared to CF-18H. Corresponding peaks were observed in the Cl 2p spectra (SI Figure S12 for a representative spectrum). Comparatively more CuCl is present in the post-catalysis XPS spectra of CF-18H than for CF-18H-100U. For CF-18H and CF-18H-100U, the Cu 2p peaks were unchanged before and after 35 minutes of electrolysis (SI Figure S13, to be compared with Figure 6b). For CF-18H-DCU, both Cu2O and copper metal are present on the surface of the foam before electrolysis, with the Cu2O Cu(LMM) becoming dominant after 35 minutes (Figure 11c).

Figure 11. Cu LMM Auger signal of (a) CF-18H (b) CF-18H-100U and (c) CF-18H-DCU before electrolysis (black signal) and post 35-minute electrolysis (red signal).

A key concern of the work was whether the urea would withstand the electrolysis conditions and remain bound to the copper foam surface. XPS analysis after 35 minutes of electrolysis was carried out to verify this. The dip-coated and non-dip-coated foams behaved differently. CF-18H-100H started with all the nitrogen in one environment at 400.3 eV (Figure 12). However, after electrolysis there were two nitrogen environments, 398.9 eV and 400.3 eV. As stated earlier in the paper, we ascribe the peak at 398.9 eV to urea bound to the copper through the carbonyl, whereas the peak at 400.3 eV is assigned to urea bound through the amine. We assume that the acid present in the formation of CF-18H-100U protonates the carbonyl oxygen of the urea [60], forcing urea to coordinate through the amine groups (giving rise to the single peak at 400.3 eV pre-catalysis).

Figure 12. Nitrogen 1s peak of (a) CF-18H-100U and (b) CF-18H-DCU. Before electrolysis (bottom black signal) and post 35-minute electrolysis (top red signal). The hypothesized integration of urea with the copper foam is depicted at the top of the figure and color-coded with XPS fittings.
In the alkaline environment during catalysis (due to proton consumption) the urea carbonyl group is de-protonated, allowing the urea to bind to copper in its preferential form, through the carbonyl group, giving rise to the peak at 398.9 eV. Some urea must continue to bind through the amine groups to leave the minor peak at 400.3 eV. In contrast, for CF-18H-DCU, urea is coated onto the copper foam from a pH 7 aqueous solution. Urea in water hydrates on both carbonyl and amine sides [68], leading to a mixture of nitrogen-bound and carbonyl-bound urea on the copper surface before electrolysis (Figure 12). After catalysis, most of the urea seems instead to be predominantly carbonyl-bound. We tentatively suggest that the difference in reactivity between CF-18H-100U and CF-18H-DCU could in part be due to the binding modes of the urea at the start and during catalysis. The complex and numerous changes observed upon electrolysis have a significant impact on the catalytic activity of the copper foams. CF-18H showed no catalytic activity for n-propanol after 2 hours of electrolysis, whereas CF-18H-100U was still active with a faradaic efficiency of about 1%.

4. Conclusions

This work describes a procedure for the fabrication of cuboctahedral porous copper electrodes under various conditions. The formation of the foams was analyzed using different concentrations of HCl during electrodeposition. It was confirmed that the concentration of HCl affects the average wall width and pore size of the foam, thereby making them respectively thicker and larger at higher HCl concentrations. The addition of urea did not significantly change the crystalline structure of the resulting urea-modified foams. Correspondingly, we did not observe a significant change in the faradaic efficiency of CO₂ conversion to n-propanol between plain and urea modified foams.

After CO₂ electrolysis, the foam changed from a cuboctahedral to a dendritic morphology, suggesting that the copper responded to CO₂ electrolysis by re-arranging in-situ during catalysis. The re-arrangement of the copper has been characterized ex-situ using SEM and corroborated with XRD. The presence of urea and its method of binding to the copper seems to have affected the catalyst response and structure-activity relationships. Indeed, pristine foams showed no catalytic activity for n-propanol after 2 hours of electrolysis, while urea-modified foams continued showing faradaic efficiencies of about 1%.

Acknowledgements: This work is part of the Reducing Industrial Carbon Emissions (RICE) and Flexible Integrated Energy Systems (FLEXIS) research operations funded by the Welsh European Funding Office (WEFO) through the Welsh Government. Financial support was also provided by the Engineering and Physical Sciences Research Council (EPSRC) through the SUSTAIN Manufacturing Hub (EP/S018107/1) and grant EP/N009525/1. The Welsh Government is also acknowledged for the Sêr Cymru II Recapturing Talent Fellowship partly funded by the EPSRC (EP/M028267/1), the European Regional Development Fund through the Welsh Government (80708) and the Ser Solar project via the Welsh Government. J.A.R. would like to acknowledge Dr Joel Loveridge for helpful NMR discussions.

References
1. Graf, F., Store and Go, Innovative large-scale energy storage technologies and Power-to-Gas concepts after Optimisation, H2020. Impact, 2018. 2018(1): p. 81-83.
2. Reisch, M., Solvay adds DuPont battery materials. C&EN Global Enterprise, 2017. 95(7): p. 14-15.
3. Keith, D.W., et al., A process for capturing CO₂ from the atmosphere. Joule, 2018. 2(8): p. 1573-1594.
4. Holmes, G., et al., Outdoor prototype results for direct atmospheric capture of carbon dioxide. Energy Procedia, 2013. 37: p. 6079-6095.
5. Zapantis, A., A. Townsend, and D. Rassool, Policy priorities to incentivise large scale deployment of CCS. Thought Leadership Report. Global CCS Institute, 2019.
6. Irlam, L., Global costs of carbon capture and storage. Global CCS Institute, 2017.
7. Voiry, D., et al., Low-dimensional catalysts for hydrogen evolution and CO₂ reduction. Nature Reviews Chemistry, 2018. 2(1): p. 1-17.
8. Rao, H., et al., Visible-light-driven methane formation from CO 2 with a molecular iron catalyst. Nature, 2017. 548(7665): p. 74-77.
9. Lu, Q. and F. Jiao, Electrochemical CO₂ reduction: Electrocatalyst, reaction mechanism, and process engineering. Nano Energy, 2016. 29: p. 439-456.
References:

10. Schrögl, R., et al., Novel carbon capture and utilisation technologies: Research and climate aspects. 2018.
11. Nørskov JK, L. A, and D. CF, Research needs towards sustainable production of fuels and chemicals. 2019.
12. Hori, Y., K. Katsuihe, and S. Shin, Production of CO and CH4 in electrochemical reduction of CO2 at metal electrodes in aqueous hydrogencarbonate solution. Chemistry Letters, 1985. 14: p. 1695-1698.
13. Hori, Y., Modern Aspects of Electrochemistry. Vol. 2. 2008, New York: Springer New York.
14. Dutta, A., et al., Beyond copper in CO2 electrolysis: effective hydrocarbon production on silver-nanofoam catalysts. ACS Catalysis, 2018. 8(9): p. 8357-8368.
15. Kuhl, K.P., et al., Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. Journal of the American Chemical Society, 2014. 136(40): p. 14107-14113.
16. Hori, Y., Electrochemical CO2 Reduction on Metal Electrodes, in Modern Aspects of Electrochemistry, C.G. Vayenas, R.E. White, and M.E. Gamboa-Aldeco, Editors. 2008, Springer New York: New York, NY. p. 89-189.
17. Hori, Y., A. Murata, and R. Takahashi, Formation of hydrocarbons in the electrochemical reduction of carbon dioxide at a copper electrode in aqueous solution. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1989. 85(8): p. 2309-2326.
18. DeWulf, D.W., T. Jin, and A.J. Bard, Electrochemical and Surface Studies of Carbon Dioxide Reduction to Methane and Ethylene at Copper Electrodes in Aqueous Solutions. Journal of Electrochemical Society, 1986. 136: p. 1686.
19. Montoya, J.H., A.A. Peterson, and J.K. Nørskov, Insights into C-C Coupling in CO2 Electroreduction on Copper Electrodes. ChemCatChem, 2013. 5(3): p. 737-742.
20. Nitopi, S., et al., Progress and Perspectives of Electrochemical CO2 Reduction on Copper in Aqueous Electrolyte. Chemical Reviews, 2019. 119(12): p. 7610-7672.
21. Lv, W., et al., Electrodeposition of nano-sized bismuth on copper foil as electrocatalyst for reduction of CO2 to formate. Applied Surface Science, 2017. 393: p. 191-196.
22. Lv, W., et al., Porous tin-based film deposited on copper foil for electrochemical reduction of carbon dioxide to formate. International Journal of Hydrogen Energy, 2016. 41(3): p. 1585-1591.
23. Lum, Y, et al., Optimizing C–C Coupling on Oxide-Derived Copper Catalysts for Electrochemical CO2 Reduction. Journal of Physical Chemistry C, 2017. 121(26): p. 14191-14203.
24. Cheng, T., H. Xiao, and W.A. Goddard, Nature of the Active Sites for CO Reduction on Copper Nanoparticles; Suggestions for Optimizing Performance. Journal of the American Chemical Society, 2017. 139(34): p. 11642-11645.
25. Kas, R., et al., Manipulating the Hydrocarbon Selectivity of Copper Nanoparticles in CO2 Electroreduction by Process Conditions. ChemElectroChem, 2015. 2(3): p. 354-358.
26. Dongare, S., N. Singh, and H. Bhunia, Electrocatalytic reduction of CO to useful chemicals on copper nanoparticles. Applied Surface Science, 2021. 537: p. 148020.
27. Huang, J, et al., Copper-comprising nanocrystals as well-defined electrocatalysts to advance electrochemical CO2 reduction. Journal of Energy Chemistry, 2021.
28. Zhang, Z, et al., Morphology-Dependent CO Reduction Kinetics and Surface Copper Species Evolution of Cu2O Nanocrystals. Journal of Physical Chemistry C, 2020. 124(39): p. 21568-21576.
29. Gorginpour, F. and H. Zali-Boeini, Synergistic effect of copper nanocrystals-nanoparticles incorporated in a porous organic polymer for the Ullmann C-O coupling reaction. Molecular Catalysis, 2021. 504: p. 111460.
30. Kung, C-W, et al., Copper Nanoparticles Installed in Metal–Organic Framework Thin Films are Electrocatalytically Competent for CO2 Reduction. ACS Energy Letters, 2017. 2(10): p. 2394-2401.
31. Kim, M.K., et al., Metal–organic framework-mediated strategy for enhanced methane production on copper nanoparticles in electrochemical CO2 reduction. Electrochimica Acta, 2019. 306: p. 28-34.
32. Rayer, A.V., et al., Electrochemical carbon dioxide reduction to isopropanol using novel carbonized copper metal organic framework derived electrodes. Journal of CO2 Utilization, 2020. 39: p. 101159.
33. Dutta, A., et al., CO2 electrolysis – Complementary operando XRD, XAS and Raman spectroscopy study on the stability of CuxO foam catalysts. Journal of Catalysis, 2020. 389: p. 592-603.
34. Klingan, K., et al., Reactivity Determinants in Electrodeposited Cu Foams for Electrochemical CO2 Reduction. ChemSusChem, 2018. 11(19): p. 3449-3459.
35. Zhong, S., et al., Efficient electrochemical transformation of CO2 to C2/C3 chemicals on benzimidazole-functionalized copper surfaces. Chemical Communications, 2018. 54(80): p. 11324-11327.
36. Kuhl, K.P., et al., New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. Energy & Environmental Science, 2012. 5(5): p. 7050-7059.
37. Jouby, M., W. Luc, and F. Jiao, General techno-economic analysis of CO2 electrolysis systems. Industrial & Engineering Chemistry Research, 2018. 57(6): p. 2165-2177.
38. Hernandez-Aldave, S. and E. Andreoli, Fundamentals of Gas Diffusion Electrodes and Electrolysers for Carbon Dioxide Utilisation: Challenges and Opportunities. Catalysts 2020. 10(6): p. 713.
39. Dutta, A., et al., Beyond Copper in CO\textsubscript{2} Electrolysis: Effective Hydrocarbon Production on Silver-Nanofoam Catalysts. ACS Catalysis, 2018. 8(9): p. 8357-8368.
40. Nikolić, N.D., et al., The effect of hydrogen co-deposition on the morphology of copper electrodeposits. II. Correlation between the properties of electrolytic solutions and the quantity of evolved hydrogen. Journal of Electroanalytical Chemistry, 2008. 621(1): p. 13-21.
41. Shin, H.C., J. Dong, and M. Liu, Nanoporous structures prepared by an electrochemical deposition process. J Advanced Materials, 2003. 15(19): p. 1610-1614.
42. Shin, H.-C. and M. Liu, Copper Foam Structures with Highly Porous Nanostructured Walls. Chemistry of Materials, 2004. 16(25): p. 5460-5464.
43. Kim, J.-H., R.-H. Kim, and H.-S. Kwon, Preparation of copper foam with 3-dimensionally interconnected spherical pore network by electrodeposition. Electrochemistry Communications, 2008. 10(8): p. 1148-1151.
44. Garza, A.J., A.T. Bell, and M. Head-Gordon, Mechanism of CO\textsubscript{2} Reduction at Copper Surfaces: Pathways to C\textsubscript{2} Products. ACS Catalysis, 2018. 8(2): p. 1490-1499.
45. Kortlever, R., et al., Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. Journal of Physical Chemistry Letters, 2015. 6(20): p. 4073-4082.
46. Han, Z., et al., CO\textsubscript{2} Reduction Selective for C\textsubscript{2} Products on Polycrystalline Copper with N-Substituted Pyridinium Additives. ACS Central Science, 2017. 3(8): p. 853-859.
47. Kim, D., et al., Copper nanoparticle ensembles for selective electroreduction of CO\textsubscript{2} to C\textsubscript{2}\textDash\textsubscript{C} products. Proceedings of the National Academy of Sciences, 2017. 114(40): p. 10560.
48. Jouyou, M., W. Luc, and F. Jiao, General Techno-Economic Analysis of CO\textsubscript{2} Electrolysis Systems. Industrial & Engineering Chemistry Research, 2018. 57(6): p. 2165-2177.
49. Ren, D., et al., Mechanistic Insights into the Enhanced Activity and Stability of Agglomerated Cu Nanocrystals for the Electrochemical Reduction of Carbon Dioxide to n-Propanol. Journal of Physical Chemistry Letters, 2016. 7(1): p. 20-24.
50. Grosse, P., et al., Dynamic Changes in the Structure, Chemical State and Catalytic Selectivity of Cu Nanocubes during CO\textsubscript{2} Electroreduction: Size and Support Effects. Angewandte Chemie International Edition, 2018. 57(21): p. 6192-6197.
51. Ahn, S., et al., Poly-Amide Modified Copper Foam Electrodes for Enhanced Electrochemical Reduction of Carbon Dioxide. ACS Catalysis, 2018. 8(5): p. 4132-4142.
52. Dutta, A., et al., Electrochemical CO\textsubscript{2} Conversion Using Skeleton (Sponge) Type of Cu Catalysts. ACS Catalysis, 2017. 7(8): p. 5431-5437.
53. Xie, M.S., et al., Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards hydrocarbons. Energy & Environmental Science, 2016. 9(5): p. 1687-1695.
54. Hao, G.L., et al., Processing and damping behaviour of porous copper. Powder Metallurgy, 2009. 52(2): p. 145-150.
55. Zhang, Q.B., A.P. Abbott, and C. Yang, Electrochemical fabrication of nanoporous copper films in choline chloride-urea deep eutectic solvent. Physical Chemistry Chemical Physics, 2015. 17(22): p. 14702-14709.
56. Wuttig, A. and Y. Surendranath, Impurity Ion Complexation Enhances Carbon Dioxide Reduction Catalysts. ACS Catalysis, 2015. 5(7): p. 4479-4484.
57. M., C.H.S., Regular Polytopes. 3rd edn. ed. 1973. Methuen: Dover Publications.
58. Shin, H.-C. and M. Liu, Copper foam structures with highly porous nanostructured walls. Chemistry of Materials, 2004. 16(25): p. 5460-5464.
59. Dutta, A., et al., Morphology Matters: Tuning the Product Distribution of CO\textsubscript{2} Electroreduction on Oxide-Derived Cu Foam Catalysts. ACS Catalysis, 2016. 6(6): p. 3804-3814.
60. Wen, N. and M.H. Brooker, Urea protonation: Raman and theoretical study. Journal of Physical Chemistry, 1993. 97(33): p. 8608-8616.
61. Biesinger, M.C., Advanced analysis of copper X-ray photoelectron spectra. Surface and Interface Analysis, 2017. 49(13): p. 1325-1334.
62. Li, C.W. and M.W. Kanan, CO\textsubscript{2} Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu2O Films. Journal of the American Chemical Society, 2012. 134(17): p. 7231-7234.
63. Morales-Guio, C.G., et al., Improved CO\textsubscript{2} reduction activity towards C\textsubscript{2}+ alcohols on a tandem gold on copper electrocatalyst. Nature Catalysis, 2018. 1(10): p. 764-771.
64. Shang, Y. and L. Guo, Nanocrystal Facets: Facet-Controlled Synthetic Strategy of Cu2O-Based Crystals for Catalysis and Sensing (Adv. Sci. 10/2015). Advanced Science, 2015. 2(10).
65. Seah, M.P., *AES: energy calibration of electron spectrometers. IV. A re-evaluation of the reference energies*. Journal of Electron Spectroscopy and Related Phenomena, 1998. 97(3): p. 235-241.

66. Gaarenstroom, S.W. and N. Winograd, *Initial and final state effects in the ESCA spectra of cadmium and silver oxides*. Journal of Chemical Physics, 1977. 67(8): p. 3500-3506.

67. Battistoni, C., et al., *An XPS and Auger study of some polynuclear copper compounds*. Inorganica Chimica Acta, 1985. 102(1): p. 1-3.

68. Lee, C., E.A. Stahlberg, and G. Fitzgerald, *Chemical structure of urea in water*. Journal of Physical Chemistry, 1995. 99(50): p. 17737-17741.
