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# Electrochemical reduction of carbon dioxide to formate in a flow cell on $CuS_x$ grown by atomic layer deposition



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## ABSTRACT

Transition metal chalcogenides (TMCs) are promising pre-catalysts for tuning the selectivity of electrochemical carbon dioxide ( $CO_{2}$ ) reduction (CO2R). Atomic layer deposition (ALD) enables well-controlled growth of thin TMC films on various gas diffusion electrodes. Herein, we have studied the CO2R performance of ALD-grown copper sulfide ( $CuS_x$ ) in a flow cell. The effects of electrode configuration, electrolyte concentration, temperature, and electrolysis time were carefully studied, combined with pre- and post-electrolysis physico-chemical analyses of the films. The unique selectivity of sulfur-doped Cu towards formate was retained with Faradaic efficiencies between 40 and 60%, but slow selectivity changes were observed over time. Major loss of sulfur was encountered during the initial 5-min reduction period, and after that, progressive formation of nanoparticles could be observed. Comparisons to ALD-grown Cu thin film and  $CuS_x$ -modified Cu foam electrodes verified the importance of sulfur and suggested that other electrocatalyst films could be easily realized with ALD.

## 1. Introduction

Low-temperature electrochemical reduction of carbon dioxide (CO<sub>2</sub>) (CO2R) is one of the Power-to-X concepts aiming to mitigate the high level of anthropogenic greenhouse gases while providing a means to store surplus energy from intermittent renewable energy sources. To electrochemically alter the stable CO<sub>2</sub> molecule, the help of active, stable, and selective catalysts is required. Here, Cu is of special interest [1], as it turns CO<sub>2</sub> into multiple products [2]. To improve the selectivity of Cu towards favoring, for example, ethylene (C2H4), oxide derivatization has been adapted [3]. The underlying mechanism is under heavy debate, but it is agreed that the oxidized Cu acts as a pre-catalyst: under reductive potentials, the oxidized Cu is unavoidably reduced to metallic Cu, causing a myriad of structural changes [4–9] that are speculated to lead to changes in selectivity, overpotential, and/or activity. In the same fashion, transition metal chalcogenides (TMCs) can be considered pre-catalysts. The potential of TMCs in hydrogen and oxygen evolution and oxygen reduction reactions has been studied, but these types of pre-catalysts have received less attention in CO2R [10]. TMCs or doping with other heteroatoms than oxygen could have different effects on the product selectivity of CO2R; thus, these modifications are also interesting research topics. Here we consider mainly sulfur modifications, which have been shown to be beneficial for formate formation. Electrochemical production of formate is closer to being economically feasible than production of  $C_2H_4$  [11].

The effects of sulfur in CO2R were initially probed in the late 90's when it was discovered that metal electrodes of Fe, Ni, Pd, Cu, and Zn, either treated with Na<sub>2</sub>S or cycled in electrolytes containing Na<sub>2</sub>S, changed their selectivity upon electrochemical reduction of CO<sub>2</sub> [12]. On Cu electrodes, especially, the formation of CH4 was suppressed while the formation of ethylene, ethanol, formate, and hydrogen all increased. Two decades later, the effects sulfur doping of Cu has on CO2R started to interest researchers more, and varying effects have been reported since. One study claims improvement in CH<sub>4</sub> formation when Ni foam is applied as a support for CuS nanosheets [13]. A comparison was made to a material that had a completely different morphology: a nanowire structure resulted in lower methane selectivity compared to CuS on Ni foam. This suggests that the improved CH<sub>4</sub> selectivity may have been due to ideal active sites being exposed in the nanosheet array rather than sulfur having a pivotal role in selectivity [13]. Most reports on sulfur doping or CuS<sub>x</sub> materials state that selectivity towards formate is astonishingly improved at the lower overpotentials [14-21], competing

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with the most selective Sn and Bi catalysts. Sn and Bi are known for the very negative potentials required to reach almost 100% formate selectivities [22], while Pd can reach >90% formate selectivities at the lowest overpotentials reported for formate generation but is notoriously quickly deactivated [23]. The potential to replace Sn, Bi, and Pd catalysts with an abundant and cheaper copper metal while also lowering the required overpotential towards formate formation provides clear motivation to further develop  $CuS_x$  catalysts and study the changes behind the  $CO_2$  reduction mechanisms. Unfortunately, most of the studies agree that sulfur leaches out of  $CuS_x$  during CO2R [16]. Yet, remarkable stability for formate production has been reported [14,19], which should again encourage more studies into these types of derivatization and how the materials could be stabilized. Sulfur has shown promise in combination with other metals such as Mo [24,25], Ag [26], Sn [27,28], and In Ref. [29].

Additionally, almost all the studies on formate production on  $CuS_x$  catalysts thus far have applied a conventional electrochemical "H-cell". We have very recently shown that a change in selectivity can take place on a Co-based supported molecular catalyst upon changing from an H-cell to a flow cell environment [30], which is why it is important to showcase the properties of sulfur-doped Cu catalysts under flow conditions that better mimic larger-scale electrolysis conditions. The effects of electrolyte concentration and temperature have also remained unexplored for sulfur-doped Cu catalysts.

Atomic layer deposition (ALD) is a simple, controllable route for forming thin film materials on complex and high surface area substrates. It has found major industrial applications in the modern semi-conductor industry. In addition, its power and possibilities are identified in emerging application areas, including the energy storage sector. We have recently demonstrated the effects of ALD thin films in Li-ion batteries [31], and its efficiency in different sections of the electrocatalysis field has been reviewed on a few occasions [32,33]. For CO2 utilization, mainly applications of ALD in photocatalytic or photo-electrocatalytic reduction reactions are demonstrated with semiconductors such as TiO<sub>2</sub> [34,35]. A few examples of low-temperature electrochemical CO<sub>2</sub> reduction are also known: thin layers of SnO2 have been deposited on CuO nanowires to yield mainly CO [36], ALD-made TiO<sub>2</sub> has been used to stabilize a molecular catalyst on the surface of an electrode for syngas formation [37], Al<sub>2</sub>O<sub>3</sub> coating on specific Cu facets has been applied to enhance ethylene formation [38], ALD-deposited  $TiO_2$  on  $MoS_2$  has been shown to produce ethanol [39], ALD has been used to create core-shell and alloy particles of Pt and Pd to enhance formate formation [40], and thin layers of sulfur-doped Sn were applied on Au nanoneedles via an ALD process and showed improved performance towards formate production [28]. To the best of our knowledge, ALD-synthesized CuSx-based CO2R catalysts have not been explored, although they have been investigated for other applications [41-43].

Herein, we demonstrate the electrocatalytic  $CO_2$  reduction on copper sulfide thin films ( $CuS_x$ ) grown by ALD directly on gas diffusion electrodes, eliminating additional spraying steps that lead to material losses. It is shown that the formate selectivity of the catalyst is retained in the flow cell under varying electrolyte and temperature conditions. Sulfur leaches out already during the initial 5 min of reduction, but changes in selectivity towards that of Cu take place within several hours. The morphology of the catalyst also changes drastically over time from a continuous thin film into cubic nanoparticles that are likely metallic Cu under reductive potential, but under ex situ post-mortem studies, they are revealed as oxides or hydroxides of Cu.  $CuS_x$  thin films were compared to ALD-modified Cu foam electrodes and an ALD-grown Cu thin film on a gas diffusion electrode to ensure that sulfur presence is the source of formate selectivity.

## 2. Experimental section

More experimental details (material storage conditions, pretreatment protocols, and product quantification details) can be found

## in the supplementary information.

## 2.1. Electrode preparation

For CuS<sub>x</sub> synthesis, a thin layer of ozone-modified single-walled carbon nanotubes (SWCNT-O<sub>3</sub>) was applied to the gas diffusion layer (GDL-CT, FuelCellsEtc) by paint brush (Badger 100G) to provide nucleation points for the CuS<sub>x</sub> film growth as well as to improve the conductivity of the catalyst layer. For this purpose, SWCNTs (OCSiAl, TUBALL<sup>TM</sup>, <1% metal impurities) were treated with ozone for 40 min to yield oxygen-functionalized nanotubes (SWCNT-O<sub>3</sub>) for increased reactivity. An ink with 2 mg of SWCNT-O3 in 3 mL of 2-propanol (Honeywell, ≥99.9% HPLC grade) was prepared by 15 min sonication in an ultrasound bath followed by vigorous stirring for 2-3 days. To gain different nanotube loadings on the GDL, different amounts of the ink were painted on an area of 2 cm  $\times$  2 cm using a template. Since the loadings were very low, the actual loading of the nanotubes on the GDLs could not be determined by weighing the electrodes before and after painting. Therefore, the loadings given here are nominal since small amounts of ink are inevitably lost during the painting (walls of the brush, template), resulting in the actual loading being slightly lower.

All thin films were deposited using a commercial, hot-wall, crossflow ALD reactor (F120, ASM Microchemistry). Nitrogen (99.999%, Linde) was used as the carrier and purge gas, and the reactor pressure during deposition was below 10 mbar.

 $Al_2O_3$  adhesion and protective layers were deposited using 10 cycles of trimethyl aluminum (TMA, Volatec Oy) and deionized water. Both precursors were evaporated from external vessels held at room temperature and delivered to the reactor by vacuum draw using needle and solenoid valves.

Copper acetylacetonate (Cu(acac)<sub>2</sub>, Sigma Aldrich) and copper bis (2,2,6,6-tetramethyl-3,5-heptanedionate) (Cu(thd)<sub>2</sub>, Volatec Oy) were used as the copper precursors for Cu<sub>2</sub>S and CuS films, respectively [44]. [45] [46]. Both precursors were evaporated in open glass boats inside the reactor. Cu(acac)<sub>2</sub> was evaporated at 135 °C, and the Cu<sub>2</sub>S films were deposited at 160 °C. Cu(thd)<sub>2</sub> was evaporated at 115 °C, and the CuS films were deposited at 130 °C. H<sub>2</sub>S (99.5 %, Linde) was used as the sulfur source. The flow rate of H<sub>2</sub>S was set to 14 sccm under continuous flow using a mass flow meter and a needle valve. H<sub>2</sub>S was pulsed into the reactor using an external solenoid valve. The H<sub>2</sub>S bottle was stored in a ventilated gas cabinet, and the H<sub>2</sub>S lines were designed to be compatible with H<sub>2</sub>S using VCR metal and ethylenepropylenediene (EPDM) polymer seals. The reactor exhaust was bubbled through an aqueous Cu(NO<sub>3</sub>)<sub>2</sub> solution to remove H<sub>2</sub>S downstream of the vacuum pump.

As a reference, metallic Cu films were deposited using the ALD process developed by Väyrynen et al. [47]. Copper bis (dimethylamino-2-propoxide) (Cu(dmap)<sub>2</sub>, synthesized in-house using a metathesis reaction between potassium dimethylamino-2-propoxide and CuCl<sub>2</sub> [48] and by isolating the product directly from the reaction mixture by sublimation), and *tert*-butyl hydrazine (TBH, EpiValence) were used as precursors. Cu(dmap)<sub>2</sub> was evaporated inside the ALD reactor at 65 °C, and TBH was held at room temperature and delivered into the reactor by vacuum draw from an external source with a needle valve. The copper films were deposited at 120 °C.

## 2.2. Electrochemical experiments and product analysis

All CO2R experiments were performed in an in-house-built flow cell (Fig. S1) comprised of three compartments: the gas compartment separated from the cathode compartment by the GDL containing the catalyst material, and the cathode and anode compartments separated by a pre-treated Nafion 115 membrane (Ion Power). Gases were bubbled into the cathode compartment at 23 mL/min from behind the GDL and directed to detection in the Agilent 990  $\mu$ -GC device through the catholyte reservoir. Catholyte and anolyte were circulated in the cell at 23 mL/min using a peristaltic pump (Watson Marlow). Leak-free Ag/AgCl

(LF-1.0-100, Innovative Instruments Inc.) acted as the reference electrode in the cathode compartment, while Ir mixed metal oxide (Ir MMO, ElectroCell) was applied as the counter electrode in the anode compartment. The potential of the reference electrode was periodically checked against a reversible hydrogen electrode (RHE) (Gaskatel). The active area of the working electrode was 4 cm<sup>2</sup>. For temperature control, the cell and all the external tubing's were insulated, and the temperature of the cell was controlled by controlling the temperature of the electrolyte reservoirs by a water bath. To validate the temperatures inside the cell, the temperature of the water bath and anolyte were measured by standard thermometers, while a thermocouple was used to measure the temperature inside the anolyte compartment of the cell.

Before CO<sub>2</sub> reduction, a potential of -1.6 V (vs. Ag/AgCl) was applied for 5 min as pre-treatment. CO<sub>2</sub> reduction was then performed by chronoamperometry (CA). Before and after CA, the uncompensated resistance was determined by measuring electrochemical impedance spectroscopy (EIS) from 20 kHz to 1 Hz at 10 mV amplitude (uncompensated resistance was determined at 1 kHz and used for *iR* correction), and a cyclic voltammogram (CV) was recorded between -0.5 V and -1.6 V (vs. Ag/AgCl). The reported current densities (J) are geometric current densities, and the potentials are reported as iR corrected unless otherwise denoted.

Gaseous products were monitored online (headspace chromatography) using the Agilent 990  $\mu$ -GC equipped with a MoleSieve 5A column for the separation and quantification of natural gases (H<sub>2</sub>, CO) and a PoraPlot U column for hydrocarbons (CH<sub>4</sub>, CO<sub>2</sub>). Ar was used as carrier gas in the first column, and He in the second column. Liquid products (the only one detected was formate) were determined by HPLC (Waters 2690) after bulk electrolysis was finished. Both catholyte and anolyte were analyzed to determine a possible crossover of liquid products. The products were separated using 5 mM H<sub>2</sub>SO<sub>4</sub> as eluent in an Aminex HPX-87H column (pH = 1–3, t = 65 °C) and detected with a refractive index detector (Waters 2414).

#### 2.3. Material characterizations

The morphologies of the materials were studied using both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. SEM images were recorded using the Tescan Mira3, equipped with an energy-dispersive X-ray detector (EDS), and the TEM images using the JEOL JEM-2800 high-throughput instrument. Raman spectra were recorded on a Horiba Jobin-Yvon/Park Systems LabRAM HR UV-NIR instrument equipped with a 633 nm laser and a Charge Coupled Device (CCD) detector. The crystallinity of the ALD films was studied by grazing incidence X-ray diffraction (GIXRD) measurements using a PANalytical X'Pert Pro MPD X-ray diffractometer. Measurements were done both on witness Si wafer pieces (incident angle 1°) and the gas diffusion electrodes (incident angle 4°) using Cu K $\alpha$  radiation ( $\lambda = 1.54$ Å). The GDL was measured before and after electrochemical CO<sub>2</sub> reduction. X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos Axis Ultra spectrometer with monochromated Al K<sub>a</sub>-radiation, a pass energy of 20 eV, an X-ray power of 75 W, and an analysis area of approximately 700  $\mu m \times 300 \, \mu m.$  The binding energy scale was based on instrument calibration, and no additional binding energy correction was applied to the data. The elemental composition was determined from peak areas of high-resolution core-level spectra after Shirley background subtraction using equipment-specific sensitivity factors.

#### 3. Results and discussion

#### 3.1. Electrode optimization

Initially, two different ALD processes based on  $Cu(acac)_2 + H_2S$  [46] and  $Cu(thd)_2 + H_2S$  [44,45], were evaluated since different chalcogenide phases are expected. The thickness of the films were varied from 5 nm to 20 nm by controlling the number of ALD cycles. A GDL with

 $0.08 \text{ mg/cm}^2$  of SWCNT-O<sub>3</sub> acted as a substrate in these initial trials. Successful growth of CuSx on the GDLs could be verified by the appearance of a gray-colored area on the GDL, as shown in Fig. S2. From SEM images (Fig. S6), it is clear that the thickness of the nanotube bundles became larger after ALD than what was before the reaction, and some material is also interconnecting the tubular structures, indicating the growth of a material on the nanotubes. Imaging from various sections of the electrode verified the even nature of the formed film. The crystal phases of the formed films were verified through XRD on films grown on witness Si wafer pieces and showing different CuS<sub>x</sub> phases: the Cu(acac)<sub>2</sub> + H<sub>2</sub>S process resulted most likely mainly in the chalcocite phase (Cu<sub>2</sub>S), while the Cu(thd)<sub>2</sub> +  $H_2S$  process resulted most likely mainly in the covellite phase (CuS) (Fig. S3), although indefinite exclusion or inclusion of other co-existing phases is not possible due to the broad nature of the reflections. Naturally, there is also a possibility for different CuSx crystallization behaviors on the GDL substrate. Later XRD experiments on GDL supports (Fig. 5), however, indicate that the phase is similar to the one observed on Si.

CO2R was performed in 0.1 M KHCO<sub>3</sub>(aq) at an applied potential of -0.89 V (vs. RHE) for 3 h on each film. The result showed almost equally low selectivity to formate on all samples (Fig. S4), which is contrary to a suggestion that the chalcogenide phase would have an influence on the selectivity [49] or that the phases on the GDLs were not so different from each other after all. However, slightly improved formate selectivity was observed for the film deposited with the Cu(acac)<sub>2</sub> + H<sub>2</sub>S process with a thickness of approximately 10 nm. Visually, the CuS<sub>x</sub> films deposited by the Cu(acac)<sub>2</sub> + H<sub>2</sub>S process were more uniform than the corresponding films synthesized with the Cu(thd)<sub>2</sub> + H<sub>2</sub>S process. Therefore, 10 nm-thick films deposited by the Cu(acac)<sub>2</sub> + H<sub>2</sub>S process with 820 ALD cycles were chosen for detailed investigations. All the following electrodes were prepared with the abovementioned process, unless otherwise denoted.

Already during initial CO2R tests, it was observed that adhesion of the material to the substrate was poor, evidenced by the uneven greenish-orange coloration of the electrodes after CA. Therefore, it was decided to explore the effects of both adhesion and protective layers of ALD-grown Al<sub>2</sub>O<sub>3</sub> to observe which configuration would prove most effective (Fig. S5). CO2R in 0.1 M KHCO<sub>3</sub>(aq) at an applied potential of -0.79 V (vs. RHE) again shows low selectivity to formate and mostly H<sub>2</sub> evolution for all the studied electrodes. None of the tested ~4 nm-thick alumina adhesion and protective layer configurations appeared to affect selectivity, but the activity was substantially lowered, indicating that too-thick layers of Al<sub>2</sub>O<sub>3</sub> will likely affect the conductivity in an undesired manner. Thus, for further tests, only one layer of Al<sub>2</sub>O<sub>3</sub> was applied to the SWCNT-O3 substrate, and the thickness of this alumina adhesion layer between the SWCNT-O3 and CuSx was decreased to roughly 1 nm (10 TMA + H<sub>2</sub>O cycles). A protective layer was deemed unnecessary, as one adhesion layer seemed to improve the adhesion issues. A more important observation was made on the relationship between formate selectivity and the amount of SWCNT-O3 on the electrode, as the CuSx catalyst on the GDL substrate without CNTs shows clearly increased selectivity towards formate formation. Therefore, the following optimization concerned finding the ideal loading of the nanotubes on the GDL support.

The nanotube loading was varied between 0.0, 0.02, 0.03, and the original loading of 0.08 mg/cm<sup>2</sup>. By optimizing the nanotube loading, as high as 60% faradaic efficiency (FE) towards formate was reached at a potential of -0.76 V (vs. RHE) (Fig. 1). As can be seen, both 0.02 and 0.03 mg/cm<sup>2</sup> loadings of SWCNT-O<sub>3</sub> on the GDL yield the highest formate selectivity and total current densities. It is to be noted here that CO<sub>2</sub> reduction using either a pristine GDL support or GDL support with 0.03 mg/cm<sup>2</sup> loading of SWCNT-O<sub>3</sub> only resulted in the production of H<sub>2</sub> at very low current densities. By observing the morphology of the electrodes with SEM (Fig. S6), it is obvious that the uniformity of carbon nanotubes is better when 0.03 mg/cm<sup>2</sup> is loaded in comparison to 0.02 mg/cm<sup>2</sup>, where some of the activated carbon of the GDL is visible while



Fig. 1. The effect of SWCNT-O<sub>3</sub> loading on CO2R activity and selectivity at ca. -0.76 V (iR corrected potential vs. RHE). SWCNT-O<sub>3</sub>: single-walled carbon nanotubes; CO2R: CO<sub>2</sub> reduction; INTE: revensible hydrogen electrode.

the first loading gives full coverage of nanotubes. Thus, the optimized catalyst electrodes for further CO2R studies contained 0.03 mg/cm<sup>2</sup> SWCNT-O<sub>3</sub>, a thin (approximately 1 nm)  $Al_2O_3$  adhesion layer, and an approximately 10 nm layer of  $CuS_x$ .

# 3.2. Studying the effects of CO2R conditions

After optimizing the electrode configuration for formate selectivity, the focus of the study was to test different CO<sub>2</sub> electrolysis conditions for these materials, including the effects of electrolyte concentration and temperature. Both the nature of the cation and the anion, as well as their concentrations, have been shown to affect CO2R [50]. Although increasing bicarbonate concentration may not always be favorable in terms of FE, the increase in current density with increasing concentration may result in beneficial settings [50-53], and therefore it is important to find optimum conditions for each catalyst and cell configuration. The electrolyte concentration was studied first. As observed in Fig. 2a, formate selectivity increases while H<sub>2</sub> selectivity decreases when going to more negative potentials in a 0.1 M KHCO<sub>3</sub>(aq) solution. In 0.5 M and 1.0 M electrolyte solutions, the FE towards formate increases steadily until, at the most negative potential applied, it decreases. The FE towards formate decreases very slightly when the concentration of the electrolyte is raised. The decrease is not, however, as dramatic as has been reported on Sn, for example [50]. An additional

product also appears as small amounts of CO are formed in the most negative potentials applied when using 0.5 M and 1.0 M KHCO<sub>3</sub>(aq) electrolyte solutions. In terms of total current density (Fig. 2b), a steady increase is observed as the electrolyte concentration increases, as is expected due to the increase in conductivity [50]. The partial current densities of H<sub>2</sub> and formate are like each other in 0.1 M and 0.5 M solutions, while H<sub>2</sub> partial current density is much higher than formate partial current density in 1.0 M KHCO<sub>3</sub>(aq) (Fig. 2c). On all the studied samples, the current density over the 60 min measurement period appears quite stable in all applied potentials, with a slight tendency to increase over time in the most negative potentials in the more concentrated electrolytes (Fig. S7). Based on these observations, 0.5 M KHCO<sub>3</sub>(aq) was chosen for further testing with varying cell temperatures.

Increasing temperature usually has myriad effects on the properties of the solution phase, and for example, H<sub>2</sub> evolution may become more favorable at slightly elevated temperatures [30]. CO<sub>2</sub> electrolysis was therefore studied at slightly elevated temperatures (30 and 40  $^{\circ}$ C) to study the effects on these materials. Selectivity between the products was not greatly changed at elevated temperatures (Fig. 3a), while total current densities steadily increased with increasing temperature (Fig. 3b). Partial current densities of H<sub>2</sub> and formate increased in magnitude such that their ratio to each other remained the same throughout the studied temperature range (Fig. 3c). When applying the more negative potentials at slightly elevated temperatures, the current density appears to increase during the 60-min measurement time (Fig. S8). This can be due to several causes: changes in the materials over time and changes in the wettability of the electrode itself over time are the most plausible suspects [30]. As is later shown, the morphology of the films does change, which can partially explain the current density increase over time. CO as an additional product starts to appear again in the more negative potentials at all the studied temperatures.

The changes in selectivity under the more reducing conditions are likely mostly explained by the Pourbaix diagram of  $CuS_x$  [16] (gradual leaching of sulfur from the structure in the form of HS<sup>-</sup> [15]), but the changes observed in morphology cannot be totally excluded. The electrodes were thoroughly characterized before and after CO<sub>2</sub> electrolysis experiments. As already mentioned, the studied ALD processes resulted in the uniform CuS<sub>x</sub> coating on carbon nanotubes, as observed by the increased diameter of nanotube bundles (SEM images in Fig. S6). The chemical composition of the electrodes was semi-quantitatively probed with EDS (Table S1) showing that before CO<sub>2</sub> reduction, the atomic percentage of sulfur present on the samples was similar from electrode to electrode, indicating good reproducibility of our approach. Cu-to-S ratio and XRD studies indicated the formation of Cu<sub>2</sub>S (Fig. S3). XRD analysis was performed on the films formed on the GDLs as well, and the diffractograms in Fig. 5c indicate the expected phase. Although the peaks are broad, their intensity is low, and the diffraction patterns of



**Fig. 2.** Effect of electrolyte concentration on CO2R product selectivity and activity. (a) FE's, (b) total current densities, and (c) partial current densities in different KHCO<sub>3</sub>(aq) concentrations. Open squares are for  $H_2$ , open triangles for HCOO<sup>-</sup>, and open circles for CO. Concentrations are indicated by the different colors in the figures. The temperature was 20–21 °C (RT) in all experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.) CO2R: CO<sub>2</sub> reduction; FE: faradaic efficiency.



**Fig. 3.** Effect of temperature on CO2R product selectivity and activity. (a) FE's, (b) total current densities and (c) partial current densities at different temperatures. Open squares are for H<sub>2</sub>, open triangles for HCOO<sup>-</sup>, and open circles for CO. Temperatures are indicated by the different colors in the figures. The concentration of KHCO<sub>3</sub>(aq) was 0.5 M in all experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.) CO2R: CO<sub>2</sub> reduction; FE: faradaic efficiency.

different phases of  $Cu_{5x}$  are quite close to each other (See, for example, diffraction patterns for  $Cu_{7}S_4$  roxbyite, ICDD PDF 00-023-0958, and for  $Cu_{31}S_{16}$  djurleite, ICDD PDF 00-034-0660).

XPS was also used to study the CuS<sub>x</sub> sample before and after CO2R. Atomic concentrations and additional spectra are provided in the Supporting Information (Table S3 and Fig. S9). Copper, sulfur, carbon, and oxygen were found on the surface before CO2R. The Cu 2p spectrum in Fig. 4a shows main peaks at roughly 932.2 eV  $(2p_{3/2})$  and 952.1 eV  $(2p_{1/2})$ <sub>2</sub>), and the sulfur 2p spectrum (Fig. 4c) shows a  $2p_{3/2}$  peak at binding energy 161.5 eV. These findings are consistent with the expected presence of copper sulfide [54]. Identification of the type of sulfide (CuS or Cu<sub>2</sub>S) is not straightforward. Additional information can be obtained from the Cu LMM Auger region (Fig. 4b) which shows a peak at kinetic energy 917.7 eV. From this, the Auger parameter (Cu 2p<sub>3/2</sub> binding energy + Cu LMM kinetic energy) is calculated to be 1849.9 eV, which would indicate the presence of Cu<sub>2</sub>S [54,55]. Although Cu<sub>2</sub>S and CuS have similar S 2p<sub>3/2</sub> binding energies, CuS should show two doublets (separated by only 0.6 eV) corresponding to mono- and disulfide arrangements in the lattice [56,57]. In our case, only one doublet is resolved. Thus, the S 2p spectrum also points towards Cu<sub>2</sub>S.

The Cu/S ratio of 1.63, calculated from the atomic concentrations in Table S3, was slightly lower than expected. This can be at least in part explained by the presence of other chemical states than sulfides. The Cu  $2p_{3/2}$  region shows a small shoulder peak at roughly 934 eV and satellite peaks between 938 and 947 eV, which can be assigned to Cu(II) species, of which at least Cu(OH)<sub>2</sub> and CuO would be possible [54]. Based on the O 1s spectrum in Fig. 4d, Cu(OH)<sub>2</sub> is more probable since it should be observed around 531.2 eV, whereas CuO would exhibit a peak below 530 eV [58]. However, a large portion of the oxygen is related to

carbon-oxygen bonding (Fig. S9 and Table S3), seen in the C 1s spectra roughly between 286 and 290 eV, making the interpretation more difficult. The presence of some metallic copper and/or Cu<sub>2</sub>O cannot be completely ruled out either since they exhibit quite similar Cu 2p binding energies as Cu<sub>2</sub>S [54]. Regarding sulfur, the 2p region shows the presence of some sulfite/sulfate with a  $2p_{3/2}$  peak at roughly 168 eV [55]. In addition, the presence of small amounts of monosulfide cannot be ruled out.

Raman spectra were also recorded (Fig. 5 and S10), but clear indications of Cu<sub>2</sub>S before CO2R could not be observed. The Raman spectra show the expected vibrations for SWCNTs (Figs. S10a-b): radial breathing modes (RBM) between 100 and 300 cm<sup>-1</sup>, carbon lattice defect-related D-peak at 1350 cm<sup>-1</sup> and graphitic lattice-related G-peak at 1590  $\text{cm}^{-1}$  [59]. CuS<sub>x</sub>-related peaks are expected to appear around  $260 \text{ cm}^{-1}$  (Cu–S vibrational mode) and  $470 \text{ cm}^{-1}$  (S–S stretching mode) [60]. Unfortunately, the RBM range of the nanotubes overlaps with the first  $CuS_x$ -related peak, which is also expected to be very weak [60] and cannot therefore be detected. In the Raman spectrum (Fig. 5a), there is no single strong peak around 470  $\text{cm}^{-1}$  but rather two weaker and broader signals detected at 440 and 490 cm<sup>-1</sup>. Either one of these could be assigned to S-S stretching vibrations, but they also match the Raman fingerprint for Cu(OH)<sub>2</sub> well [61,62]. Another weak signal at around 295 cm<sup>-1</sup> can corresponded to Cu<sup>2+</sup> oxide-related peaks or to the hydroxide [61,62]. A previous study on CuS<sub>x</sub> materials has also given rise to similar oxide-related vibrations for the sulfur-modified materials, but ascribed the vibration around 295 cm<sup>-1</sup> to the Cu-S stretching vibrations and concluded that it is in line with the presence of monosulfide  $(S^{2-})$  [15]. All other analysis methods indicate Cu<sub>2</sub>S in our case, although we cannot altogether exclude or verify the possibility of mixed



Fig. 4. X-ray photoelectron spectra of the  $CuS_x$  sample before and after CO2R: a) Cu 2p region, b) Cu LMM Auger region, c) S 2p region, and d) O 1s region. The spectra have been offset and normalized by height for better comparison. CO2R: CO<sub>2</sub> reduction.



Fig. 5. Raman spectra of the electrode after (a) ALD and (b) CO2R in the range 100–850 cm<sup>-1</sup>. (c) XRD diffractograms of the materials on the GDL-CT support after ALD and after CO2R. ALD: atomic layer deposition; CO2R: CO<sub>2</sub> reduction; XrD: X-ray diffraction; GDL-CT: gas diffusion layer.

phases. As already mentioned, the XPS also detected oxidized copper species on the surface of the electrode. In the Raman spectra taken from the substrates, the 295, 440, and 495  $\text{cm}^{-1}$  features are missing and only detected signals can be attributed to the carbon nanotubes (Figs. S10c–d).

The morphologies of the materials on the electrodes are completely changed after CO<sub>2</sub> electrolysis, where we can clearly observe the appearance of large nanoparticles on the GDLs in Fig. 6, independent of the electrolysis conditions. The distribution of the particles is quite even along the whole electrode, with some areas of more abundant agglomeration observed. The shape of the nanoparticles appears to be mainly cubic, and their size is quite large, which was later confirmed by TEM analysis (Fig. S12). EDS analysis shows that almost all the sulfur has been lost during CO<sub>2</sub> electrolysis (Table S1), and XPS results back up this finding (Fig. S9c and Table S3). After CO2R, the amounts of both copper and sulfur are largely reduced, with only a trace amount of sulfur left (Cu/S ratio  $\sim$ 20). Some potassium and fluorine are also found on the surface (see Table S3). The first one originates from residues of the used electrolyte salt, while the latter is due to the polytetrafluoroethylene (PTFE) in the GDL becoming exposed after material reorganization during CO2R. The Cu 2p spectrum in Fig. 4a shows clear changes, with a well-separated 2p3/2 peak at 934.6 eV accompanied by increased satellite peak intensity in the binding energy range of 938–947 eV. The Cu LMM Auger peak is also shifted to 916.6 eV. Based on the binding energy and Auger peak shift, we assign this peak to Cu(OH)<sub>2</sub> [54]. The O 1s spectrum in Fig. 4d shows a single peak at 531.6 eV, which also points more towards Cu(OH)<sub>2</sub> than oxides. The Cu 2p<sub>3/2</sub> peak around 932.2 eV is still observed, but since the sulfide peak in the S 2p spectrum (Fig. 4c) is not visible anymore, this could be due to either metallic Cu or Cu<sub>2</sub>O. Raman (Fig. 5b) and XRD (Fig. 5c) both confirm that the phase of the Cu is mainly oxide after the reduction reaction. It is important to note here that the phase is likely Cu under the reductive potentials during CO2R, and the formation of oxides is just the result of exposure to ambient conditions to make the postmortem analyses.

By studying the materials subjected to different times of CO2R with

EDS (see Table S1), we could confirm that the loss of sulfur takes place already after 5 min under reductive potentials. The role of sulfur in this pre-catalyst and its effects on selectivity are thus very interesting topics. Previous studies have shown that a very small amount of sulfur in the structure would be enough to cause improved formate selectivity [16], but the mechanism is under debate, as will be shortly discussed in Section 3.5. The Cu-containing phases can be detected *in situ* during CO2R by applying, for example, Raman simultaneously with applied potentials [15], but since we could not detect  $CuS_x$ -related peaks in the Raman spectra of pristine electrodes, we deemed such measurements unlikely to give valuable additional information on the material at this stage.

## 3.3. The effects of longer electrolysis times

The stability of the materials was studied under optimized conditions (0.5 M KHCO<sub>3</sub>(aq) and 40 °C) under several time intervals: 5 min reduction, or a so-called pre-treatment period, 4 h, 7 h, and 7 h + 7 h at an applied potential of -0.89 V (vs. RHE). The CA curve for the 7 h + 7 h sample and selectivity results at 4, 7, and 14 h are shown in Fig. 7. It is evident that during the initial 7 h of electrolysis, the current density continuously increases, and all the studied electrodes behave in a similar manner. As discussed previously, it could be an indication of continuous changes in the material and/or electrode wetting behavior. A gradual current density increase for sulfur-modified Cu electrocatalysts has also been reported previously without an explanation for the phenomenon [16]. Upon emptying the cell, refilling it, and continuing the electrolysis for further 7 h, a much lower but stable current is obtained. In terms of selectivity, after 4 h, formate and H<sub>2</sub> are the main components. At 7 h, trace amounts of CO begin to appear, and the CO selectivity further improves over the following 7 h. Formate selectivity would not appear to be greatly affected in the applied time frame.

What happens to the material during the initial 4–7 h? SEM images were recorded for the electrodes subjected to varying electrolysis times (Fig. S11). From 5 min to 4 h and further to 7 h, the size of the



**Fig. 6.** SEM images (25.0 kx magnification) of the electrodes after CO2R in different KHCO<sub>3</sub> concentrations (a–c) and temperatures (b, d-e). (a) 0.1 M KHCO<sub>3</sub>(aq), 21 °C; (b) 0.5 M KHCO<sub>3</sub>(aq), 21 °C; (c) 1.0 M KHCO<sub>3</sub>(aq), 21 °C; (d) 0.5 M KHCO<sub>3</sub>(aq), 30 °C; and (e) 0.5 M KHCO<sub>3</sub>(aq), 40 °C. SEM: scanning electron microscopy; CO2R: CO<sub>2 reduction.</sub>

![](_page_7_Figure_2.jpeg)

**Fig. 7.** (a) CA curves during the 7 h+7 h CO<sub>2</sub> electrolysis experiment and (b) product distribution after 4 h, 7 h, and 14 h of the CO<sub>2</sub> electrolysis experiment at an applied potential of -0.89 V (vs. RHE) in 40 °C 0.5 M KHCO<sub>3</sub>(aq). The black line + diamond symbol is for average total current density; the gray column and line + empty square symbol are for H<sub>2</sub> FE and partial current density, respectively; the orange column and line + empty triangle symbol are for formate FE and partial current density, respectively; and the blue column and line + empty circle symbol are for CO FE and partial current density, respectively. CA: chronoamperometry; RHE: reversible hydrogen electrode; FE: faradaic efficiency. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article).

nanoparticles seems to grow, and the amount of the nanoparticles seems to increase as well, according to SEM imaging. After 5 min, there is clearly some agglomeration of the material taking place, but nanoparticles are not clear from the SEM images yet. After 4 h of electrolysis, bigger nanoparticles start to appear, and after 7 h, mostly big nanoparticles (>100 nm) are observed, which appear not to grow further but mainly agglomerate more during the following 7 h of electrolysis. To gain insights into particle sizes and particle size distribution, TEM analysis was performed on the 4, 7, and 14 h samples by scratching some of the material from the electrodes (Fig. S12). Unfortunately, an unequivocal particle size analysis could not be made since the method of sample preparation removed large amounts of the activated carbon from the GDL itself, thus making statistically relevant analysis difficult. The particles are clearly mainly large (>50 nm) cubic particles, with smaller (approximately 5-7 nm) round nanoparticles attached to the bundles of the carbon nanotubes. We also hypothesized that the leaching of the sulfur from the material would progress over time, causing changes in selectivity, but as is evident in Table S1, sulfur can be considered lost only after 5 min of electroreduction, and errors in the method are too big to draw conclusions on progressive sulfur leaching.

## 3.4. ALD grown $CuS_x$ on Cu foam and ALD grown Cu thin film

To further elucidate the effects of sulfur doping and to have comparison materials, two different processes were also performed on Cu foam electrodes. In the first process, similar CuSx layers were grown on the Cu foams as had been grown on the GDL substrates, with two different pulse lengths (normal and longer). The longer pulse length was applied since the normal length seemed inadequate to form an even film on the foam. In the second process, only exposure to the H<sub>2</sub>S gas under vacuum at varying temperatures (160 and 250 °C) was performed. As can be seen from the pictures taken of the electrodes (Fig. S13), the ones with ALD-grown CuSx layers show a dark greenish color that was initially uneven but leveled after a few days of processing, while the electrode with H<sub>2</sub>S exposure at 160 °C appears unchanged, and the electrode with H<sub>2</sub>S exposure at 250 °C shows some darkening. The SEM analysis did not reveal structural damages to the processed foams in comparison to pristine Cu foam (Fig. S14), while the EDS analysis indicates that the foams with CuS<sub>x</sub> growth have a slightly higher sulfur content than those only exposed to H<sub>2</sub>S (Table S2). Raman spectra before CO<sub>2</sub> electrolysis (Fig. S16) revealed similar features already observed on the GDL electrodes: peaks that can be attributed to the oxides of Cu. When growing  $\text{CuS}_{\boldsymbol{x}}$  on the Cu foams, mainly signals related to CuO [62] are detected, while H<sub>2</sub>S exposure would appear to lead to the formation of both CuO and Cu<sub>2</sub>O [61,62], according to Raman results.

CO<sub>2</sub> reduction was performed in the previously optimized condition (0.5 M KHCO<sub>3</sub> at 40 °C), and results are presented in Figs. 8 and S15. From the FE's in Fig. 8, it is clear that all the Cu foam samples show high H<sub>2</sub> selectivity. Some previous works have also reported suppression in hydrogen evolution as a result of sulfur doping [15], but our results do not indicate such behavior but quite the opposite. In comparison to the CuS<sub>x</sub> materials on the GDL supports, the selectivity towards formate on all Cu-foam electrodes was poorer. The foams also exhibit much lower current densities (Fig. S15). When comparing the Cu foam samples with each other, small changes in selectivity can be observed: FEs towards formate and CO are almost the same on all the applied potentials on pristine Cu foam, and CO is detected in all the applied potentials. Additionally, trace amounts of CH<sub>4</sub> were detected in all the applied potentials for the pristine Cu foam sample. This trend follows quite well previous reports published about CO2R on Cu [63]. FE's towards formate are higher than those towards CO on all sulfur-treated Cu foam electrodes, and CO only appears to emerge in the more negative applied potentials. FE towards formate is not much increased in comparison to pristine Cu foam in the more positive applied potentials, but in the more negative potentials, a clear increase can be observed. CO formation is clearly suppressed, which is in agreement with literature speculations on the changes in reaction mechanisms [16]. The selectivity does not seem to depend on the temperature of the H<sub>2</sub>S exposure, as both foams show very similar selectivities. The longer pulse length, however, would appear to slightly improve the formate selectivity and decrease H<sub>2</sub> evolution on the ALD-CuSx-modified foams. The CuSx modification also suppresses CO formation more in comparison to H<sub>2</sub>S exposure, as is evident already from the FEs but more clearly from the partial current densities towards CO (Fig. S15c). After CO2R, all the electrodes exhibit Raman vibrations attributable to Cu<sub>2</sub>O (Fig. S16), a roughened surface morphology (Fig. S14), and a complete loss of sulfur (Table S2).

Additionally, thin Cu films were grown by ALD [47] on the GDL support to ensure that sulfur plays a key role instead of the applied synthesis method or support. The SEM shows evenly distributed particles of Cu on the nanotubes (Fig. S18a), and the film was verified to be Cu by XRD (Fig. S19). CO<sub>2</sub> electrolysis at 40 °C with 0.5 M KHCO<sub>3</sub>(aq) yields H<sub>2</sub> as the main product with lower and equal FEs towards formate and CO (Fig. S17). This result is very similar to the pristine Cu foam, showing that ALD can produce thin films of active Cu catalysts and that the formate selectivity of the CuS<sub>x</sub> thin films is not simply a result of the ALD process. For Cu, it has been reported that increasing the CO2R temperature favors H<sub>2</sub> evolution [64], as does increasing the concentration of the bicarbonate salt [51–53]. Our results agree with previous observations: upon changing into room temperature 0.1 M KHCO<sub>3</sub>(aq), the selectivity was lower than at higher temperatures and electrolyte

![](_page_8_Figure_2.jpeg)

**Fig. 8.** FE's for  $H_2$  (squares), CO (circles), and  $HCOO^-$  (triangles) on different Cu foam electrodes. (a) Pristine Cu foam (black), Cu foam with ALD-CuS<sub>x</sub> prepared with normal pulse length (orange with solid lines and filled symbols), and Cu foam with ALD-CuS<sub>x</sub> prepared with longer pulse length (orange with dashed lines and empty symbols). (b) Pristine Cu foam (black), Cu foam with  $H_2S$  exposure at 160 °C (green with solid lines and filled symbols), and Cu foam with  $H_2S$  exposure at 250 °C (green with dashed lines and empty symbols). FE: faradaic efficiency; (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

concentrations. The ALD-Cu film remarkably retained its morphology during a total of 3 h of CO2R with very minor changes observable (Fig. S18b), and the coverage of the film on the electrode remained good when comparing pictures from before and after CO2R (Fig. S18). As Cu is the only material capable of producing further reduced products such as ethylene and ethanol, an ALD-synthesized Cu thin film may be an interesting material for further examinations and optimizations.

#### 3.5. Discussion on the role of sulfur

In comparison to the results from previous literature reports gathered in Table S4 and to the results of the comparison materials applied here, the ALD-grown  $CuS_x$  thin films studied in flow cells retain the unique change in selectivity from CO + formate + H<sub>2</sub> to formate + H<sub>2</sub> at the lower overpotentials under varying electrolysis conditions. In a similar fashion as for the oxide derivatization, the role of sulfur is not clear. The aim of this discussion is not to directly suggest a mechanism since it would require complementary *in situ* spectroelectrochemical experiments as well as additional reduction reaction studies such as CO reduction, but rather to gather current knowledge and aim to rationalize the results obtained thus far.

Possible pathways from CO<sub>2</sub> to formic acid through electrochemical reduction are presented in Scheme S1. As mentioned, it is assumed that selectivity, activity, and overpotential are tightly associated with the binding of the intermediates [1]. Thermodynamically, the most plausible route from CO<sub>2</sub> to formic acid (HCOOH) on the formate selective catalysts is the formate intermediate (HCOO<sup>\*</sup>) pathway [65]. The formate intermediate route is usually depicted as leading to only formate formation, whereas the carboxyl intermediate route can lead to other products such as CO. The route towards formate on Cu, however, could also be the reaction between physisorbed CO<sub>2</sub> and adsorbed H<sup>\*</sup> [66].

An *in situ* Raman inspection has suggested that sulfur doping suppresses the carboxyl intermediate route, leading to improved formate formation through the formate intermediate route [15]. For Sn, it has been calculated through DFT calculations that the incorporation of small amounts of sulfur would thermodynamically favor the formation of HCOO\* intermediate [28]. Another piece of *in situ* spectroelectrochemical evidence suggests, however, that sulfur leads to stronger binding of the CO\* intermediate on sulfur-doped Cu, which poisons the surface but would allow adsorbed H\* to react with  $CO_2$  and form formate [67]. Sub-surface sulfur was speculated as the origin for changing the binding of CO\* [67], quite similarly to how sub-surface oxygen has been speculated to change the binding of intermediates on oxygen-derivatized Cu [8]. Water activation has been speculated with other metal-sulfur combinations as well [29]. On the other hand, there is

also evidence of long-range interactions between S and CO on Cu(100), which suggests a weakening of the bond strength of CO adsorbates [68]. Reduction of possible intermediates has been used as a technique to reveal possible routes from CO<sub>2</sub> to different reduced products on Cu [69]. When comparing CO<sub>2</sub> reduction to CO reduction on sulfur-doped copper, CO reduction mainly resulted in H<sub>2</sub> evolution, while CO2R showed high formate selectivity [15]. Theoretically, it has been shown that chalcogen adatoms suppress the formation of CO by either tethering CO<sub>2</sub> or transferring a hydride [70]. It is clear from our results as well that CO formation is suppressed, but some changes occurring on the electrocatalyst over time result in CO being formed again. Without detailed *in situ* spectroelectrochemical analysis of the fresh and used materials, it is difficult to speculate the reason behind this change.

One advantage of oxygen-derived Cu is said to be its favorable effects on increasing the surface roughness, leading to sites that ideally bind the intermediates to C2+ products. A study into Cu3N-derived catalysts suggests roughness is a good descriptor for selectivity changes towards C2+ products [71]. Unlike for oxide-derived Cu materials, ideally exposed surface sites for formate formation have not really been considered as the cause of the selectivity changes on sulfur-derived Cu electrocatalysts, and most reports specifically mention that mere changes in surface roughness cannot lead to the observed changes, but sulfur must play a pivotal role. The selectivity of different Cu facets towards formate has been shown to change in the order Cu(110) > Cu(111) > Cu(100) [63]. On Sn, the existence of undercoordinated sites due to the removal of sulfur from Sn has been hypothesized as a reason for the improvements in formate formation [28]. Sulfur vacancies on Cu have been speculated to lead to improvements in C<sub>3</sub> products, which would be consistent with the binding of CO\* becoming stronger to allow further reduction steps to take place [72].

#### 4. Conclusions

We have successfully deposited  $CuS_x$  thin films by ALD directly on modified and unmodified gas diffusion electrodes by using  $Cu(acac)_2 +$  $H_2S$  and  $Cu(thd)_2 + H_2S$  processes. We also showed that  $CuS_x$  materials are mainly selective in electrochemically reducing  $CO_2$  to formate in flow cell configurations and under varying electrolysis conditions. Increasing the KHCO<sub>3</sub> concentration resulted in a slight decrease in formate selectivity, while an increase in temperature did not affect the selectivity dramatically. The chemical composition of the thin films changed drastically, such that most of the sulfur was lost after only 5 min of reduction, while the changes in morphology of the thin films took place over a time frame of several hours. Measurements carried out with the reference Cu foam electrodes and Cu thin films deposited by ALD verified that sulfur plays a significant role in affecting the selectivity of Cu, but the exact mechanism still remains a mystery. Most of the literature suggests that the binding of the CO<sup>\*</sup> intermediate becomes stronger, thus poisoning these sites and suppressing the carboxylate route to CO and further reduced products. At the same time, H<sup>\*</sup> sites would not be blocked, allowing them to react with CO<sub>2</sub> to form formate. To reveal the exact reaction mechanisms of these ALD CuS<sub>x</sub> materials, thorough *in situ* characterizations combining several techniques and different sources of CO<sub>2</sub> (gas or dissolved in electrolyte) should be conducted.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

## Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtsust.2023.100575.

#### **Credit Authorship Contribution Statement**

Milla Suominen: Conceptualization, Methodology, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing. Miia Mäntymäki: Conceptualization, Methodology, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing. Miika Mattinen: Conceptualization, Methodology, Writing – Review & Editing. Jani Sainio: Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing. Matti Putkonen: Conceptualization, Writing – Review & Editing. Tanja Kallio: Conceptualization, Funding acquisition, Writing – Review & Editing.

#### References

- A. Bagger, W. Ju, A.S. Varela, P. Strasser, J. Rossmeisl, Electrochemical CO2 reduction: a classification problem, ChemPhysChem 18 (2017) 3266–3273, https://doi.org/10.1002/cphc.201700736.
- [2] Y. Hori, K. Kikuchi, S. Suzuki, Production OF CO and CH 4 in electroCHemical reduction OF CO 2 at metal electrodes in aqueous hydrogencarbonate solution, Chem. Lett. 14 (1985) 1695–1698, https://doi.org/10.1246/cl.1985.1695.
- [3] A. Eilert, F.S. Roberts, D. Friebel, A. Nilsson, Formation of copper catalysts for CO2 reduction with high ethylene/methane product ratio investigated with in situ X-ray absorption spectroscopy, J. Phys. Chem. Lett. 7 (2016) 1466–1470, https://doi. org/10.1021/acs.jpclett.6b00367.
- [4] D. Raciti, M. Mao, J.H. Park, C. Wang, Local pH effect in the CO 2 reduction reaction on high-surface-area copper electrocatalysts, J. Electrochem. Soc. 165 (2018) F799, https://doi.org/10.1149/2.0521810jes. –F804.
- [5] A. Verdaguer-Casadevall, C.W. Li, T.P. Johansson, S.B. Scott, J.T. McKeown, M. Kumar, I.E.L. Stephens, M.W. Kanan, I. Chorkendorff, Probing the active surface sites for CO reduction on oxide-derived copper electrocatalysts, J. Am. Chem. Soc. 137 (2015) 9808–9811, https://doi.org/10.1021/jacs.5b06227.
- [6] X. Feng, K. Jiang, S. Fan, M.W. Kanan, A direct grain-boundary-activity correlation for CO electroreduction on Cu nanoparticles, ACS Cent. Sci. 2 (2016) 169–174, https://doi.org/10.1021/acscentsci.6b00022.

- [7] H. Mistry, A.S. Varela, C.S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.W. Choi, K. Kisslinger, E.A. Stach, J.C. Yang, P. Strasser, B.R. Cuenya, Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene, Nat. Commun. 7 (2016), https://doi.org/10.1038/ncomms12123.
- [8] A. Eilert, F. Cavalca, F.S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E.J. Crumlin, H. Ogasawara, D. Friebel, L.G.M. Pettersson, A. Nilsson, Subsurface oxygen in oxide-derived copper electrocatalysts for carbon dioxide reduction, J. Phys. Chem. Lett. 8 (2017) 285–290, https://doi.org/10.1021/acs.jpclett.6b02273.
- [9] Q. Lei, H. Zhu, K. Song, N. Wei, L. Liu, D. Zhang, J. Yin, X. Dong, K. Yao, N. Wang, X. Li, B. Davaasuren, J. Wang, Y. Han, Investigating the origin of enhanced C2+ Selectivity in oxide-/hydroxide-derived copper electrodes during CO2Electroreduction, J. Am. Chem. Soc. 142 (2020) 4213–4222, https://doi.org/ 10.1021/jacs.9b11790.
- [10] S.M. Tan, M. Pumera, Two-dimensional materials on the rocks: positive and negative role of dopants and impurities in electrochemistry, ACS. Nano. 13 (2019) 2681–2728, https://doi.org/10.1021/acsnano.8b07795.
- [11] M. Jouny, W. Luc, F. Jiao, General techno-economic analysis of CO2 electrolysis Systems, Ind. Eng. Chem. Res. 57 (2018) 2165–2177, https://doi.org/10.1021/acs. iecr.7b03514.
- [12] K. Hara, A. Tsuneto, A. Kudo, T. Sakata, Change in the product selectivity for the electrochemical CO2 reduction by adsorption of sulfide ion on metal electrodes, J. Electroanal. Chem. 434 (1997) 239–243, https://doi.org/10.1016/S0022-0728 (97)00045-4.
- [13] Z. Zhao, X. Peng, X. Liu, X. Sun, J. Shi, L. Han, G. Li, J. Luo, Efficient and stable electroreduction of CO2 to CH4 on CuS nanosheet arrays, J. Mater. Chem. A 5 (2017) 20239–20243, https://doi.org/10.1039/c7ta05507b.
- [14] Y. Huang, Y. Deng, A.D. Handoko, G.K.L. Goh, B.S. Yeo, Rational design of sulfurdoped copper catalysts for the selective electroreduction of carbon dioxide to formate, ChemSusChem 11 (2018) 320–326, https://doi.org/10.1002/ cssc.201701314.
- [15] Y. Deng, Y. Huang, D. Ren, A.D. Handoko, Z.W. Seh, P. Hirunsit, B.S. Yeo, On the role of sulfur for the selective electrochemical reduction of CO2 to formate on CuSx catalysts, ACS Appl. Mater. Interfaces 10 (2018) 28572–28581, https://doi.org/ 10.1021/acsami.8b08428.
- [16] T. Shinagawa, G.O. Larrazábal, A.J. Martín, F. Krumeich, J. Pérez-Ramírez, Sulfurmodified copper catalysts for the electrochemical reduction of carbon dioxide to formate, ACS Catal. 8 (2018) 837–844, https://doi.org/10.1021/ acscatal.7b03161.
- [17] A.W. Kahsay, K.B. Ibrahim, M.C. Tsai, M.K. Birhanu, S.A. Chala, W.N. Su, B. J. Hwang, Selective and low overpotential electrochemical CO 2 reduction to formate on CuS decorated CuO heterostructure, Catal. Lett. 149 (2019) 860–869, https://doi.org/10.1007/s10562-019-02657-2.
- [18] G. Iijima, H. Yamaguchi, T. Inomata, H. Yoto, M. Ito, H. Masuda, Methanethiol SAMs induce reconstruction and formation of Cu+ on a Cu catalyst under electrochemical CO2 reduction, ACS Catal. 10 (2020) 15238–15249, https://doi. org/10.1021/acscatal.0c04106.
- [19] J.W. Lim, W.J. Dong, J.Y. Park, D.M. Hong, J.L. Lee, Spontaneously formed CuSxCatalysts for selective and stable electrochemical reduction of industrial CO2Gas to formate, ACS Appl. Mater. Interfaces 12 (2020) 22891–22900, https:// doi.org/10.1021/acsami.0c03606.
- [20] J. Chen, Y. Tu, Y. Zou, X. Li, J. Jiang, Morphology and composition-controllable synthesis of copper sulfide nanocrystals for electrochemical reduction of CO2 to HCOOH, Mater. Lett. 284 (2021), 128919, https://doi.org/10.1016/j. matlet.2020.128919.
- [21] T.T. Zhuang, Z.Q. Liang, A. Seifitokaldani, Y. Li, P. De Luna, T. Burdyny, F. Che, F. Meng, Y. Min, R. Quintero-Bermudez, C.T. Dinh, Y. Pang, M. Zhong, B. Zhang, J. Li, P.N. Chen, X.L. Zheng, H. Liang, W.N. Ge, B.J. Ye, D. Sinton, S.H. Yu, E. H. Sargent, Steering post-C-C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols, Nat. Catal. 1 (2018) 421–428, https://doi.org/10.1038/s41929-018-0084-7.
- [22] N. Han, P. Ding, L. He, Y. Li, Y. Li, Promises of main group metal-based nanostructured materials for electrochemical CO2 reduction to formate, Adv. Energy Mater. 10 (2020) 1–19, https://doi.org/10.1002/aenm.201902338.
- [23] D. Gao, H. Zhou, F. Cai, J. Wang, G. Wang, X. Bao, Pd-containing nanostructures for electrochemical CO2 reduction reaction, ACS Catal. 8 (2018) 1510–1519, https://doi.org/10.1021/acscatal.7b03612.
- [24] M. Asadi, B. Kumar, A. Behranginia, B.A. Rosen, A. Baskin, N. Repnin, D. Pisasale, P. Phillips, W. Zhu, R. Haasch, R.F. Klie, P. Král, J. Abiade, A. Salehi-Khojin, Robust carbon dioxide reduction on molybdenum disulphide edges, Nat. Commun. 5 (2014) 1–8, https://doi.org/10.1038/ncomms5470.
- [25] J. Xu, X. Li, W. Liu, Y. Sun, Z. Ju, T. Yao, C. Wang, H. Ju, J. Zhu, S. Wei, Y. Xie, Carbon dioxide electroreduction into syngas boosted by a partially delocalized charge in molybdenum sulfide selenide alloy monolayers, Angew. Chem. Int. Ed. 56 (2017) 9121–9125, https://doi.org/10.1002/anie.201704928.
- [26] C. Kim, H.S. Jeon, T. Eom, M.S. Jee, H. Kim, C.M. Friend, B.K. Min, Y.J. Hwang, Achieving selective and efficient electrocatalytic activity for CO2 reduction using immobilized silver nanoparticles, J. Am. Chem. Soc. 137 (2015) 13844–13850, https://doi.org/10.1021/jacs.5b06568.
- [27] F. Li, L. Chen, M. Xue, T. Williams, Y. Zhang, D.R. MacFarlane, J. Zhang, Towards a better Sn: efficient electrocatalytic reduction of CO2 to formate by Sn/SnS2 derived from SnS2 nanosheets, Nano. Energy. 31 (2017) 270–277, https://doi.org/ 10.1016/j.nanoen.2016.11.004.
- [28] X. Zheng, P. De Luna, F.P. García de Arquer, B. Zhang, N. Becknell, M.B. Ross, Y. Li, M.N. Banis, Y. Li, M. Liu, O. Voznyy, C.T. Dinh, T. Zhuang, P. Stadler, Y. Cui, X. Du, P. Yang, E.H. Sargent, Sulfur-modulated tin sites enable highly selective

#### M. Suominen et al.

electrochemical reduction of CO2 to formate, Joule 1 (2017) 794–805, https://doi.org/10.1016/j.joule.2017.09.014.

- [29] W. Ma, S. Xie, X.G. Zhang, F. Sun, J. Kang, Z. Jiang, Q. Zhang, D.Y. Wu, Y. Wang, Promoting electrocatalytic CO 2 reduction to formate via sulfur-boosting water activation on indium surfaces, Nat. Commun. 10 (2019), https://doi.org/10.1038/ s41467-019-08805-x.
- [30] M.N. Hossain, R. Khakpour, M. Busch, M. Suominen, K. Laasonen, T. Kallio, Temperature-controlled syngas production via electrochemical CO 2 reduction on a CoTPP/MWCNT composite in a flow cell, ACS Appl. Energy Mater. (2022), https:// doi.org/10.1021/acsaem.2c02873.
- [31] Z. Ahaliabadeh, V. Miikkulainen, M. Mäntymäki, S. Mousavihashemi, J. Lahtinen, Y. Lide, H. Jiang, K. Mizohata, T. Kankaanpää, T. Kallio, Understanding the stabilizing effects of nanoscale metal oxide and Li-metal oxide coatings on lithiumion battery positive electrode materials, ACS Appl. Mater. Interfaces 13 (2021) 42773–42790, https://doi.org/10.1021/acsami.1c11165.
- [32] Z. Chen, G. Zhang, J. Prakash, Y. Zheng, S. Sun, Rational design of novel catalysts with atomic layer deposition for the reduction of carbon dioxide, Adv. Energy Mater. 9 (2019) 1–26, https://doi.org/10.1002/aenm.201900889.
- [33] J. Plutnar, M. Pumera, Applications of atomic layer deposition in design of Systems for energy conversion, Small 17 (2021) 1–20, https://doi.org/10.1002/ smll.202102088.
- [34] G. Zeng, J. Qiu, Z. Li, P. Pavaskar, S.B. Cronin, CO2 reduction to methanol on TiO2passivated GaP photocatalysts, ACS Catal. 4 (2014) 3512–3516, https://doi.org/ 10.1021/cs500697w.
- [35] G. Zeng, J. Qiu, B. Hou, H. Shi, Y. Lin, M. Hettick, A. Javey, S.B. Cronin, Enhanced photocatalytic reduction of CO2 to CO through TiO2 passivation of InP in ionic liquids, Chem. Eur J. 21 (2015) 13502–13507, https://doi.org/10.1002/ chem.201501671.
- [36] M. Schreier, F. Héroguel, L. Steier, S. Ahmad, J.S. Luterbacher, M.T. Mayer, J. Luo, M. Grätzel, Solar conversion of co2 to CO using earth-abundant electrocatalysts prepared by atomic layer modification of CuO, Nat. Energy 2 (2017) 1–9, https:// doi.org/10.1038/nenergy.2017.87.
- [37] Y. Wang, S.L. Marquard, D. Wang, C. Dares, T.J. Meyer, Single-site, heterogeneous electrocatalytic reduction of CO2 in water as the solvent, ACS Energy Lett. 2 (2017) 1395–1399, https://doi.org/10.1021/acsenergylett.7b00226.
- [38] H. Li, P. Yu, R. Lei, F. Yang, P. Wen, X. Ma, G. Zeng, J. Guo, F.M. Toma, Y. Qiu, S. M. Geyer, X. Wang, T. Cheng, W.S. Drisdell, Facet-selective deposition of ultrathin Al 2 O 3 on copper nanocrystals for highly stable CO 2 electroreduction to ethylene, Angew. Chem. Int. Ed. 60 (2021) 24838–24843, https://doi.org/10.1002/anie.202109600.
- [39] F. Qi, K. Liu, D.K. Ma, F. Cai, M. Liu, Q. Xu, W. Chen, C. Qi, D. Yang, S. Huang, Dual active sites fabricated through atomic layer deposition of TiO2on MoS2nanosheet arrays for highly efficient electroreduction of CO2to ethanol, J. Mater. Chem. A 9 (2021) 6790–6796, https://doi.org/10.1039/d0ta11457j.
- [40] M. Li, S. Fu, S. Saedy, A. Rajendrakumar, F.D. Tichelaar, R. Kortlever, J.R. van Ommen, Nanostructuring Pt-Pd bimetallic electrocatalysts for CO 2 reduction using atmospheric pressure atomic layer deposition, ChemCatChem (2022), https://doi. org/10.1002/cctc.202200949.
- [41] C.S. Chen, J.H. Lin, J.H. You, C.R. Chen, Properties of Cu(thd)2 as a precursor to prepare Cu/SiO 2 catalyst using the atomic layer epitaxy technique, J. Am. Chem. Soc. 128 (2006) 15950–15951, https://doi.org/10.1021/ja063083d.
- [42] J.H. Lin, Z.Y. Zeng, Y.T. Lai, C.S. Chen, Low-temperature growth of bamboo-like multi-walled carbon nanotubes over an atomic layer epitaxy-Cu/SiO2 catalyst via metal-support interaction, RSC Adv. 3 (2013) 1808–1817, https://doi.org/ 10.1039/c2ra22591c.
- [43] H. Ali-Löytty, L. Palmolahti, M. Hannula, J. Saari, C. Goodwin, A. Nilsson, M. Valden, In situ electrochemical APXPS analysis of ALD grown Cu catalyst for CO2 reduction, in: Synchrotron Light Finl. 2021 12th, FSRUO Annu. Meet., 2021. https://researchportal.tuni.fi/en/publications/in-situ-electrochemical-apxps-an alysis-of-ald-grown-cu-catalyst-f-5.
- [44] J. Johansson, J. Kostamo, M. Karppinen, L. Niinistö, Growth of conductive copper sulfide thin films by atomic layer deposition, J. Mater. Chem. 12 (2002) 1022–1026, https://doi.org/10.1039/b105901g.
- [45] L. Reijnen, B. Meester, A. Goossens, J. Schoonman, Atomic layer deposition of CuxS for solar energy conversion, Chem. Vap. Depos. 9 (2003) 15–20, https://doi.org/ 10.1002/cvde.200290001.
- [46] N. Schneider, D. Lincot, F. Donsanti, Atomic layer deposition of copper sulfide thin films, Thin. Solid. Films. 600 (2016) 103–108, https://doi.org/10.1016/j. tsf.2016.01.015.
- [47] K. Väyrynen, K. Mizohata, J. Räisänen, D. Peeters, A. Devi, M. Ritala, M. Leskelä, Low-temperature atomic layer deposition of low-resistivity copper thin films using Cu(dmap)2 and tertiary butyl hydrazine, Chem. Mater. 29 (2017) 6502–6510, https://doi.org/10.1021/acs.chemmater.7b02098.
- [48] T.H. Baum, G. Bhandari, C. Xu, CHEMICAL VAPOR DEPOSITION PRECURSORS FOR DEPOSITION OF COPPER, 2004, US006822107B1.
- [49] C.H.M. van Oversteeg, M. Tapia Rosales, K.H. Helfferich, M. Ghiasi, J.D. Meeldijk, N.J. Firet, P. Ngene, C. de Mello Donegá, P.E. de Jongh, Copper sulfide derived nanoparticles supported on carbon for the electrochemical reduction of carbon dioxide, Catal. Today 377 (2021) 157–165, https://doi.org/10.1016/j. cattod.2020.09.020.
- [50] J. Wu, F.G. Risalvato, F.-S. Ke, P.J. Pellechia, X.-D. Zhou, Electrochemical reduction of carbon dioxide I. Effects of the electrolyte on the selectivity and

activity with Sn electrode, J. Electrochem. Soc. 159 (2012), https://doi.org/10.1149/2.049207jes. F353–F359.

- [51] R. Kas, R. Kortlever, H. Yilmaz, M.T.M. Koper, G. Mul, Manipulating the hydrocarbon selectivity of copper nanoparticles in CO2 electroreduction by process conditions, Chemelectrochem 2 (2015) 354–358, https://doi.org/10.1002/ celc.201402373.
- [52] A.S. Varela, M. Kroschel, T. Reier, P. Strasser, Controlling the selectivity of CO2 electroreduction on copper: the effect of the electrolyte concentration and the importance of the local pH, Catal. Today 260 (2016) 8–13, https://doi.org/ 10.1016/j.cattod.2015.06.009.
- [53] J. Resasco, Y. Lum, E. Clark, J.Z. Zeledon, A.T. Bell, Effects of anion identity and concentration on electrochemical reduction of CO2, Chemelectrochem 5 (2018) 1064–1072, https://doi.org/10.1002/celc.201701316.
- [54] M.C. Biesinger, Advanced analysis of copper X-ray photoelectron spectra, Surf. Interface Anal. 49 (2017) 1325–1334, https://doi.org/10.1002/sia.6239.
- [55] M.C. Biesinger, X-Ray Photoelectron Spectroscopy (XPS) Reference Pages, http:// www.xpsfitting.com/, (retrieved 5.January.2023) and references therein., (n.d.).
- [56] S.W. Goh, A.N. Buckley, R.N. Lamb, Copper(II) sulfide? Miner. Eng. 19 (2006) 204–208, https://doi.org/10.1016/j.mineng.2005.09.003.
- [57] Y. Xie, A. Riedinger, M. Prato, A. Casu, A. Genovese, P. Guardia, S. Sottini, C. Sangregorio, K. Miszta, S. Ghosh, T. Pellegrino, L. Manna, Copper sulfide nanocrystals with tunable composition by reduction of covellite nanocrystals with Cu+ ions, J. Am. Chem. Soc. 135 (2013) 17630–17637, https://doi.org/10.1021/ ja409754v.
- [58] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, Appl. Surf. Sci. 257 (2010) 887–898, https://doi.org/10.1016/j. apsusc.2010.07.086.
- [59] M.S. Dresselhaus, G. Dresselhaus, A. Jorio, A.G. Souza Filho, R. Saito, Raman spectroscopy on isolated single wall carbon nanotubes, Carbon N. Y. 40 (2002) 2043–2061, https://doi.org/10.1016/S0008-6223(02)00066-0.
- [60] A.G. Milekhin, N.A. Yeryukov, L.L. Sveshnikova, T.A. Duda, E.E. Rodyakina, V. A. Gridchin, E.S. Sheremet, D.R.T. Zahn, Combination of surface- and interferenceenhanced Raman scattering by CuS nanocrystals on nanopatterned Au structures, Beilstein J. Nanotechnol. 6 (2015) 749–754, https://doi.org/10.3762/bjnano.6.77.
- [61] H.Y.H. Chan, C.G. Takoudis, M.J. Weaver, Oxide film formation and oxygen adsorption on copper in aqueous media as probed by surface-enhanced Raman spectroscopy, J. Phys. Chem. B 103 (1999) 357–365, https://doi.org/10.1021/ jp983787c.
- [62] Y. Deng, A.D. Handoko, Y. Du, S. Xi, B.S. Yeo, In situ Raman spectroscopy of copper and copper oxide surfaces during electrochemical oxygen evolution reaction: identification of CuIII oxides as catalytically active species, ACS Catal. 6 (2016) 2473–2481, https://doi.org/10.1021/acscatal.6b00205.
- [63] Y. Huang, A.D. Handoko, P. Hirunsit, B.S. Yeo, Electrochemical reduction of CO2 using copper single-crystal surfaces: effects of CO\* coverage on the selective formation of ethylene, ACS Catal. 7 (2017) 1749–1756, https://doi.org/10.1021/ acscatal.6b03147.
- [64] S.T. Ahn, I. Abu-Baker, G.T.R. Palmore, Electroreduction of CO2 on polycrystalline copper: effect of temperature on product selectivity, Catal. Today 288 (2017) 24–29, https://doi.org/10.1016/j.cattod.2016.09.028.
- [65] J.S. Yoo, R. Christensen, T. Vegge, J.K. Nørskov, F. Studt, Theoretical insight into the trends that guide the electrochemical reduction of carbon dioxide to formic acid, ChemSusChem 9 (2016) 358–363, https://doi.org/10.1002/cssc.201501197.
- [66] T. Cheng, H. Xiao, W.A. Goddard, Reaction mechanisms for the electrochemical reduction of CO2 to CO and formate on the Cu(100) surface at 298 K from quantum mechanics free energy calculations with explicit water, J. Am. Chem. Soc. 138 (2016) 13802–13805, https://doi.org/10.1021/jacs.6b08534.
- [67] K.R. Phillips, Y. Katayama, J. Hwang, Y. Shao-Horn, Sulfide-derived copper for electrochemical conversion of CO2 to formic acid, J. Phys. Chem. Lett. 9 (2018) 4407–4412, https://doi.org/10.1021/acs.jpclett.8b01601.
- [68] X.F. Hu, C.J. Hirschmugl, Long-range metal-mediated interactions between S and CO on Cu(100), Phys. Rev. B Condens. Matter 72 (2005) 1–7, https://doi.org/ 10.1103/PhysRevB.72.205439.
- [69] S. Nitopi, E. Bertheussen, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I.E. L. Stephens, K. Chan, C. Hahn, J.K. Nørskov, T.F. Jaramillo, I. Chorkendorff, Progress and perspectives of electrochemical CO 2 reduction on copper in aqueous electrolyte, Chem. Rev. 119 (2019) 7610–7672, https://doi.org/10.1021/acs. chemrev.8b00705.
- [70] R. García-Muelas, F. Dattila, T. Shinagawa, A.J. Martín, J. Pérez-Ramírez, N. López, Origin of the selective electroreduction of carbon dioxide to formate by chalcogen modified copper, J. Phys. Chem. Lett. 9 (2018) 7153–7159, https://doi.org/ 10.1021/acs.joclett.8b03212.
- [71] M. Ebaid, K. Jiang, Z. Zhang, W.S. Drisdell, A.T. Bell, J.K. Cooper, Production of C2/C3Oxygenates from planar copper nitride-derived mesoporous copper via electrochemical reduction of CO2, Chem. Mater. 32 (2020) 3304–3311, https:// doi.org/10.1021/acs.chemmater.0c00761.
- [72] C. Peng, G. Luo, J. Zhang, M. Chen, Z. Wang, T.K. Sham, L. Zhang, Y. Li, G. Zheng, Double sulfur vacancies by lithium tuning enhance CO2 electroreduction to npropanol, Nat. Commun. 12 (2021) 1–8, https://doi.org/10.1038/s41467-021-21901-1.