



Cite this: *Energy Adv.*, 2025,  
4, 657

## *In situ* generation of Cu- and Ag–Sn alloys from metal sulfides for CO<sub>2</sub> reduction†

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Ag, Cu and Sn based electrocatalysts promise high CO<sub>2</sub> reduction kinetics and efficiencies on gas diffusion electrodes. Ag, Cu, Sn sulfide catalysts in particular may offer altered electronic properties and product selectivity, while still being easy to manufacture in scaleable synthesis routes. Comparing the CO<sub>2</sub> reduction (CO<sub>2</sub>RR) performance of Cu<sub>3</sub>SnS<sub>4</sub>, Ag<sub>3</sub>SnS<sub>4</sub>, Cu<sub>2</sub>S, SnS and Ag<sub>8</sub>SnS<sub>6</sub> at 100 mA cm<sup>-2</sup>, formate is found to be the primary CO<sub>2</sub>RR product with a faradaic efficiency of 57% for Cu<sub>3</sub>SnS<sub>4</sub> and 81% for Ag<sub>3</sub>SnS<sub>4</sub>. Characterization by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction revealed the formation of Ag<sub>3</sub>Sn and Cu<sub>3</sub>Sn alloys from the corresponding sulfide species during CO<sub>2</sub>RR. But while the Cu<sub>3</sub>Sn based electrode surface decomposed into CuO and SnO after 2 h at -100 mA cm<sup>-2</sup>, metallic Ag<sub>3</sub>Sn sites on the corresponding electrode surface could be detected by XPS after removing the surface layer. Using density functional theory, the binding energies of \*H, \*CO and \*OCHO on Cu<sub>3</sub>Sn and Ag<sub>3</sub>Sn were computed to identify possible catalytic sites. Thereby, Sn was found to render both Cu and Ag highly oxophilic resulting in strong adsorption of carboxylic functionalities, enabling formate production with a partial current density of up to 162 mA cm<sup>-2</sup>.

Received 2nd December 2024,  
Accepted 10th March 2025

DOI: 10.1039/d4ya00603h

rsc.li/energy-advances

## Introduction

CO<sub>2</sub> reduction on large scales is imperative for decreasing the impact of greenhouse gases and creating a circular carbon economy. Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) offers a selective way to recycle CO<sub>2</sub> using renewable energies. To realize this goal by obtaining high CO<sub>2</sub> conversion and energy efficiency, gas diffusion electrodes (GDE) need to be employed to avoid limitations concerning CO<sub>2</sub> mass transfer to the catalyst while operating at current densities > 100 mA cm<sup>-2</sup>.<sup>1</sup> While the catalyst material of the GDE is crucial to CO<sub>2</sub>RR and a plethora of metal chalcogenides and molecular catalysts have been tested, the application of strong reductive currents can lead to the degradation of the catalyst.<sup>2–4</sup> *In situ* X-ray absorption spectroscopy measurements have demonstrated the reduction of CuO catalysts to Cu<sup>0</sup> and SnO to Sn<sup>0</sup> and therefore, the catalytic properties of plain metal electrodes remain relevant.<sup>5,6</sup>

Nano-structuring of electrocatalysts can significantly enhance their catalytic efficiency,<sup>7–9</sup> but up-scaling such materials to industrial scales and the implementation into large electrolyzers that meet the global demand of CO<sub>2</sub> reduction, appears impractical. The *in situ* generation of catalytic sites from bulk materials under electrolytic conditions offers an alternative approach that alleviates any additional synthetic steps and demands. Recently, a Cu<sub>2</sub>SnS<sub>3</sub> and CuS composite was reported to produce formate at a partial current density of up to 240 mA cm<sup>-2</sup>, with the catalytically active species, a Cu<sub>24</sub>Sn<sub>20</sub> alloy, being generated *in situ* during electrolysis.<sup>10</sup> With Cu-based catalysts being known to be prone to corrosion,<sup>11</sup> an AgSn alloy promises a higher corrosion resistance and a lower oxophilicity. Therefore, we prepared silver tin sulfide catalysts for comparison to their respective copper tin sulfides counterparts concerning their electrocatalytic performance and corrosion stability. Previous work on AgSn-alloys explored the ideal stoichiometry for AgSn alloys with a SnO<sub>2</sub> surface for CO<sub>2</sub> reduction with Ag<sub>3</sub>Sn obtaining a partial current density for formate production of 25.4 mA cm<sup>-2</sup> at -0.8 V vs. RHE using a H-type cell.<sup>12</sup> But instead of utilizing a nanostructured core–shell-type catalyst with an Ag<sub>3</sub>Sn alloy core and a SnO surface, the corresponding Ag<sub>3</sub>SnS<sub>4</sub> sulfide material offers the possibility of generating the alloy *in situ* under electrocatalytic conditions. Here, we envisioned that transferring the previously optimized noble metal to tin ratio of 3:1 to CuSn alloys may thus lead to the optimum composition of CuSn alloys for CO<sub>2</sub>RR and allow for the

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ya00603h>



comparison of their electrocatalytic properties and stabilities with  $\text{Ag}_3\text{Sn}$ .

In the herein presented work, we prepared  $\text{Cu}_3\text{SnS}_4$ ,  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$  through mechanochemical or high-temperature synthesis to assess the  $\text{CO}_2$  reduction activity of the corresponding  $\text{Cu}_3\text{Sn}$ ,  $\text{Ag}_3\text{Sn}$  and  $\text{Ag}_8\text{Sn}$  alloys. The targeted metal sulfide stoichiometries  $\text{Cu}_3\text{SnS}_4$  and  $\text{Ag}_3\text{SnS}_4$  were found to consist of  $\text{Cu}_2\text{SnS}_3$  and  $\text{Ag}_8\text{SnS}_6$  phases respectively with an excess of amorphous  $\text{SnS}$ , thus being composite materials rather than pure metal sulfide phases. Upon reduction these mixed phases were expected to yield the previously reported ideal  $\text{Ag}_3\text{Sn}$  ratio and its  $\text{Cu}_3\text{Sn}$  analogue. For  $\text{Ag}_x\text{SnS}_y$  the corresponding alloying processes similar to  $\text{Cu}_3\text{SnS}_4$  to  $\text{Cu}_3\text{Sn}$  have not been reported yet, although  $\text{Ag}$ ,  $\text{Sn}$  are among the most prominent metals for  $\text{CO}_2\text{RR}$  catalysts.<sup>11,13</sup> The compositions of these electrodes were spectroscopically characterized after electrolysis to determine the changes in chemical speciation on the electrode surface and the bulk material. Furthermore, we evaluated the catalytic processes using density functional theory by calculating the binding energies of  $^*\text{H}$ ,  $^*\text{CO}$  and  $^*\text{OCHO}$  on  $\text{Cu}_3\text{Sn}$  and  $\text{Ag}_3\text{Sn}$ . Based on these results, possible catalytic sites and the influence of  $\text{Sn}$  are discussed, as well as the stability of the alloy surfaces under electrocatalytic conditions up to  $-300 \text{ mA cm}^{-2}$ .

## Experimental section

### Material synthesis and characterization

For synthesis of  $\text{Cu}_3\text{SnS}_4$  and  $\text{Ag}_3\text{SnS}_4$  a planetary ball mill (Fritsch, Pulverisette 7 premium line) was employed. The synthesis of  $\text{Cu}_3\text{SnS}_4$  was performed by weighing stoichiometric amounts of  $\text{Cu}_2\text{S}$  (99%, Tribotec),  $\text{SnS}$  (99%, Tribotec), and elemental sulfur (99.9%, Sigma Aldrich) for a batch size of 4 g. The reagents were added together with 24 g of 2 mm  $\text{ZrO}_2$  balls into the milling vessel under argon atmosphere. Afterwards, the reaction mixture was milled at 1100 rpm for 2 h.

$\text{Ag}_3\text{SnS}_4$  was prepared using stoichiometric amounts of  $\text{Ag}_2\text{S}$  (99%, Tribotec),  $\text{SnS}$  and  $\text{S}_0$  and 5 g of the powders were milled with 24 g of 2 mm  $\text{ZrO}_2$  balls at 1100 rpm for 2 h.  $\text{Ag}_8\text{SnS}_6$  was synthesized from the above-described powders using evacuated quartz ampules, which were gradually heated to 900 °C within 24 h, and the final temperature kept constant for 72 h. The resulting  $\text{Ag}_8\text{SnS}_6$  ingot was reduced to particulate size by ball milling the ground powder at 350 rpm for 30 min. The milled material consisted of 5 g of 2 mm sized  $\text{ZrO}_2$  balls and 200 mg of  $\text{Ag}_8\text{SnS}_6$  including 10 wt% stearic acid, which was subsequently removed by washing with isopropanol.

The identification of the catalyst materials was carried out using a Bruker Phaser D2 powder diffractometer equipped with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ) at 30 kV and 10 mA. The open crystallography database was used for the identification of the prepared materials.

The prepared electrodes were analyzed by a powder X-ray photoelectron spectroscopy using micro-focused  $\text{Al K}\alpha$  X-rays of a Nexsa G2 Surface Analysis System (ThermoFischer). The detector was 128-channel together with a 180°, double-focusing, hemispherical analyzer. The electrodes were analyzed using a band

pass energy of 50.0 eV and a 200  $\mu\text{m}$  wide analysis area; and the resulting peaks were fitted using a Shirley-type background and a Lorentzian line shape, as implemented in CasaXPS.  $\text{Ag}^0$  (99.9%, Abcr) and  $\text{Ag}_2\text{S}$  (99.9%, Abcr) powders were used as references for the measurement of the Auger parameters of silver. If indicated, additional Ar sputtering of the samples was performed for 100 s with a set cluster size of 300 and an ion energy of 6000 eV to remove surface layers.

Scanning electron microscopy images and energy dispersive X-ray spectra and maps were recorded with a Dualbeam FIB-SEM SCIO2 (ThermoFischer) equipped with a Ultimax silicon drift detector (170  $\text{mm}^2$ , Oxford Instrument) for EDX. Electron microscopy images were recorded at an acceleration voltage of 4 kV, while EDX mappings were performed at 20 kV.

### Testing electrochemical activity for $\text{CO}_2\text{RR}$

The GDE were prepared using H23C6 carbon paper (Freudenberg) and drop coated with ink containing 10 mg  $\text{mL}^{-1}$  catalyst and 20 wt% binder in respect to the resulting catalyst layer after drying. For the dispersion of the catalyst ink a 2 : 1 v/v isopropanol and water solution was sonicated for 30 min. To obtain electrodes with a loading of 3 mg  $\text{cm}^{-2}$ , the resulting ink was drop casted in 0.2 mL steps on carbon paper, which was heated to 75 °C.  $\text{Cu}_2\text{S}$  and  $\text{SnS}$  GDE as reference experiments were prepared using the reagents for the  $\text{Cu}_3\text{SnS}_4$  synthesis.

Electrocatalytic  $\text{CO}_2$  reduction experiments were performed using an in-house built electrolyzer using titanium plates as flow fields and copper current collectors.<sup>14</sup> In the assembled electrolyzer, the GDE have an active area of 2  $\text{cm}^{-2}$ , encased by PTFE gaskets, and are in contact with a catholyte chamber of a 2 mL volume. 40 mL of 1 M KOH (hyd.) ( $\geq 86.0\%$ , Fisher) was supplied as anolyte and catholyte through a Minipuls 2 pump (Gilson) at a 15  $\text{mL min}^{-1}$  flow rate. Mini HydroFlex RHE (Gaskatel) were employed as reference electrode. Nafion™ N117 (Chemours) was used as ion exchange membrane and nickel foam as anode (Goodfellow, 99.5%, porosity 95%, 1.6 mm thickness). The flow field on the cathode was passed over with 20  $\text{mL min}^{-1}$   $\text{CO}_2$  (air liquide, > 99.95 vol%) and 2  $\text{mL min}^{-1}$   $\text{N}_2$  (air liquide, 99.999%) controlled by mass flow controllers (EL-Prestige, Bronkhorst). For each experiment, two linear sweep voltammograms (LSV) were recorded before and after 2 h chronopotentiometries. LSV were measured in the potential range from 0 V to  $-1.5 \text{ V}$  vs. RHE with a scan rate of 50  $\text{mV s}^{-1}$ . If not stated otherwise, chronopotentiometries were measured with a current density of 100  $\text{mA cm}^{-2}$ , in respect to the geometric area of the electrode. The gaseous products were analyzed with an online gas chromatograph (Agilent Technologies 7820A), equipped with two columns: HP-Molsieve 5 Å 30 m, ID 0.53 mm, 25  $\mu\text{m}$  film and HPPlotQ 30 m, ID 0.53 mm, 25  $\mu\text{m}$  film, as well as a flame ionization detector (FID) and a thermal conductivity detector (TCD). The gaseous products were analyzed every 30 min by the FID-TCD and 1 mL of catholyte was sampled for liquid analysis.

The liquid samples were analyzed in a GC-MS-QP2020 gas chromatograph equipped with a HS-20 headspace analyzer and a SH-Rtx-200MS column. Since formic acid was difficult to be chromatographically separated from the solvent peaks, the

samples were derivatized using 1-propanol (HPLC grade, Sigma-Aldrich) and concentrated sulfuric acid. The samples were prepared by diluting 100  $\mu$ l sample with 300  $\mu$ l of 1 M KOH solution and to derivatize formate to propyl-formate, 100  $\mu$ l of sulfuric acid (95–97%, Sigma Aldrich) and 500  $\mu$ l of 1-propanol were added. The GC vials were then heated in the GC-MS autosampler for 20 min at 60 °C before injection. Standard dilutions of formic acid ( $\geq$ 96%, Sigma Aldrich) derivatized by this method were used as calibration standards.

### Theoretical investigations via DFT

Density functional theory (DFT) calculations were performed within the DFT formalism using VASP code<sup>15,16</sup> and the Perdew-Burke-Ernzerhof (PBE)<sup>17</sup> potential with DFT-D2 dispersion to correct for van der Waals interactions. The plane-wave energy cut-off was set to 520 eV and the  $k$ -point mesh was generated using the Monkhorst-Pack scheme with distances of 0.025 Å.  $2 \times 2 \times 2$  M<sub>3</sub>Sn (M = Ag, Cu) supercells were modelled using VESTA<sup>18</sup> and the resulting structures were relaxed using convergence criteria of  $1 \times 10^{-5}$  eV and  $2 \times 10^{-2}$  eV Å<sup>-2</sup> for electronic and ionic relaxation, respectively. After relaxation, the energy of the systems was evaluated again, using a stricter electronic convergence criterion of  $5 \times 10^{-6}$  eV and subsequently, slab models of (100), (110) and (010) planes were created with a vacuum level of 15 Å (ESI,† Fig. S20) and were again relaxed with two bottom layers being fixed in the initial positions.

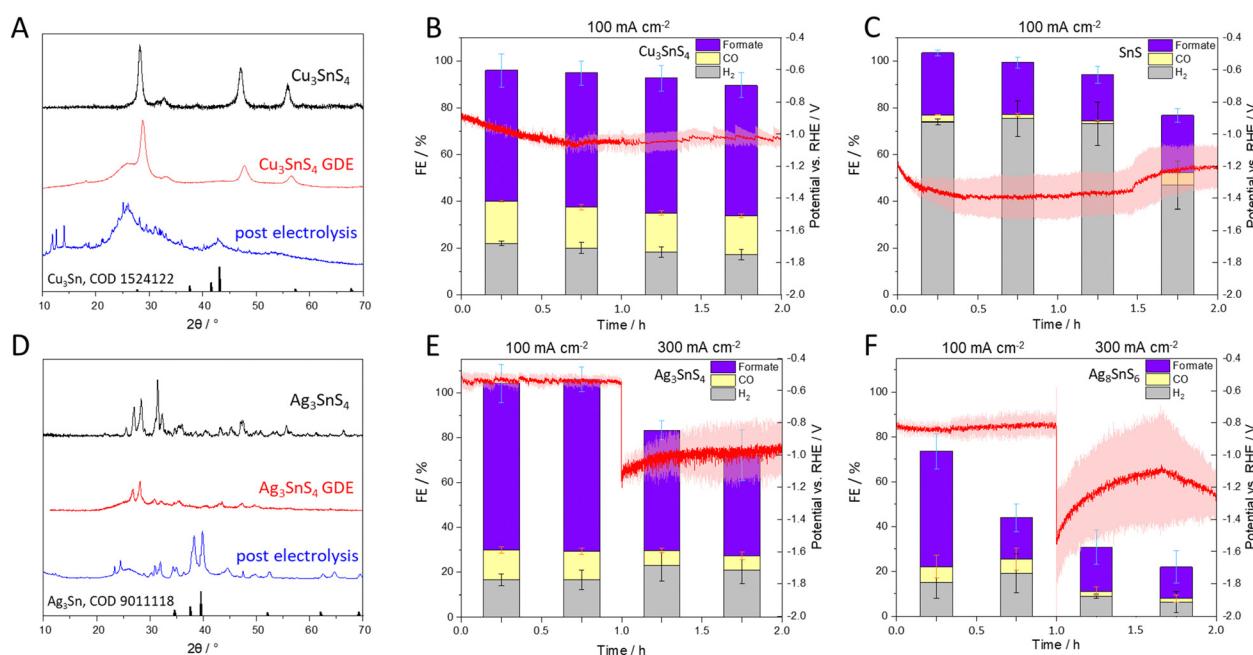
The (010) surface was the focus of the investigation due to the presence of multiple non-equivalent adsorption sites, as well as the lowest surface energy. Placing the adsorbate on the

surface resulted in surface coverage of 0.125 ML ( $1 \times 1$ ). The same numerical parameters and convergence criteria were used for supercells and pristine slabs, except for systems with \*OCHO adsorbate for which the ionic convergence criterium was increased to  $5 \times 10^{-2}$  eV Å<sup>-2</sup>. Additional details concerning the theoretical investigations are described in the ESI.†

## Results and discussion

Three metal sulfides with the stoichiometries Cu<sub>3</sub>SnS<sub>4</sub>, Ag<sub>3</sub>SnS<sub>4</sub> and Ag<sub>8</sub>SnS<sub>6</sub> were synthesized to yield upon electrochemical reduction the corresponding alloys of Cu<sub>3</sub>Sn, Ag<sub>3</sub>Sn and Ag<sub>8</sub>Sn. Here, Cu<sub>3</sub>SnS<sub>4</sub> and Ag<sub>3</sub>SnS<sub>4</sub> represent mixtures of crystalline and amorphous metal sulfide phases prepared by mechano-chemical synthesis in a planetary ball-mill from Cu<sub>2</sub>S and elemental Ag, Sn and sulfur, following previously established procedures.<sup>19,20</sup> To track the apparent stoichiometries from the initial synthesis throughout the electrode preparation, PXRD and SEM/EDX are measured of the synthesized powder, the prepared electrodes and the resulting electrode material after electrolysis in 1 M KOH and room temperature at up to 300 mA cm<sup>-2</sup>.

Fig. 1(A) depicts powder X-ray diffraction patterns of Cu<sub>3</sub>SnS<sub>4</sub> which matches the highest intensity reflexes of Cu<sub>2</sub>SnS<sub>3</sub> at 28.4°, 32.8°, 47.2° and 56.0°. EDX mappings of electrodes coated with this material find a stoichiometry of 3.16 : 1.06 : 4.0 for Cu, Sn and S (ESI,† Fig. S3), which is close to the nominal stoichiometry albeit with a slight excess of copper. The PXRD pattern is preserved after preparation of the GDE, aside from a broad reflex at 26° originating from carbon paper. (Fig. 1(C)) Post-electrolysis,



**Fig. 1** Powder X-ray diffraction patterns of Cu<sub>3</sub>SnS<sub>4</sub> (A) and Ag<sub>3</sub>SnS<sub>4</sub> (D) as synthesized displayed in black, coated on a GDE (red) and of the GDE post-electrolysis in blue. Faradaic efficiencies obtained during CO<sub>2</sub>RR for Cu<sub>3</sub>SnS<sub>4</sub> (B) and SnS at 100 mA cm<sup>-2</sup> (C) and Ag<sub>3</sub>SnS<sub>4</sub> (E) and Ag<sub>8</sub>SnS<sub>6</sub> (F) at 100 mA cm<sup>-2</sup> for 1 h and 300 mA cm<sup>-2</sup> for 1 h. CO<sub>2</sub>RR measurements were conducted in triplicates and standard deviations are depicted as ranges at the corresponding FE. The average of the corresponding electrode potentials in V referenced to RHE with IR correction are displayed in red, with the standard errors indicated as shaded areas.



the PXRD pattern of the  $\text{Cu}_3\text{SnS}_4$  GDE shows a new broad reflex at  $42.9^\circ$ , which matches the reported reflexes of a  $\text{Cu}_3\text{Sn}$  alloy, akin to the findings of Li *et al.*, who started from a  $\text{Cu}_2\text{SnS}_3$  precatalyst and obtained a  $\text{Cu}_{24}\text{Sn}_{20}$  alloy through electrolysis; as confirmed by in-operando XPS and XRD. Several other reflexes visible  $<40^\circ$  in the here prepared GDE post-electrolysis could not be clearly assigned, but as elucidated below by XPS and EDX, metal oxides and hydroxides are the most abundant species aside from  $\text{Cu}_3\text{Sn}$ .

The  $\text{Cu}_3\text{SnS}_4$  pre-catalyst has a high activity in respect to  $\text{CO}_2\text{RR}$  with an average of  $56.8 \pm 5.7\%$  formate over 2 h electrolysis,  $17.2 \pm 0.8\%$  CO and  $19.3 \pm 2.0\%$   $\text{H}_2$  at an electrode potential of  $-1.0\text{ V}$  *vs.* RHE and  $100\text{ mA cm}^{-2}$ . To ascertain whether a  $\text{CuSn}$  alloy is responsible for the observed electrochemical activity or rather Cu or Sn oxides, the starting materials  $\text{Cu}_2\text{S}$  and Sn used in the synthesis of  $\text{Cu}_3\text{SnS}_4$  were also employed as electrocatalysts. Residual sulfur in copper sulfide electrodes for  $\text{CO}_2\text{RR}$  has recently been found to reduce hydrogen evolution compared to pristine copper electrodes while producing formate with high FE.<sup>21</sup> Similarly, SnS is known to be a highly active formate producing catalyst, but with an average potential of  $-1.33\text{ V}$  *vs.* RHE and  $67.4 \pm 7.1\%$   $\text{H}_2$ ,  $\text{CO}_2\text{RR}$  performance is comparatively low (ESI,† Table S5). Together with the gradual drop in  $\text{FE}_{\text{total}}$ , SnS and its derivatives such as metallic Sn or  $\text{SnO}$  appear to not be responsible for the observed activity of  $\text{Cu}_3\text{SnS}_4$  and require nano-structuring of the electrode surface for higher FE.<sup>22</sup>  $\text{Cu}_2\text{S}$  shows an even lower performance with an average potential of  $-1.72\text{ V}$  *vs.* RHE and  $\text{FE}_{\text{HCOO}^-}$  of  $29.7 \pm 7.4\%$  and  $\text{FE}_{\text{CO}}$  of  $8.0 \pm 0.7\%$  and a decrease in  $\text{FE}_{\text{total}}$  down to  $<30\%$  after 2 h of electrolysis, likely due to corrosion. (ESI,† Fig. S1).

Under alkaline conditions, Cu based catalysts are often subjected to severe corrosion and oxidation; and we therefore synthesized and tested its more noble counterpart  $\text{Ag}_3\text{SnS}_4$ .<sup>11,23</sup> Fig. 1(D) displays the PXRD of the as prepared powder of  $\text{Ag}_3\text{SnS}_4$ , which contains  $\text{Ag}_8\text{SnS}_6$  as a crystalline phase and a stoichiometry of  $\text{Ag}_{2.56}\text{Sn}_{0.97}\text{S}_4$  based on EDX, when normalized to the sulfur content. (ESI,† Fig. S5) Post-electrolysis, the highest intensity reflexes at  $39.6^\circ$  and  $37.6^\circ$  match the reported reflexes for an  $\text{Ag}_3\text{Sn}$ , which indicates that  $\text{Ag}_3\text{SnS}_4$  is converted, similar to  $\text{Cu}_3\text{SnS}_4$ , into its corresponding alloy.<sup>10</sup>

$\text{Ag}_3\text{SnS}_4$  shows an even higher  $\text{FE}_{\text{HCOO}^-}$  than  $\text{Cu}_3\text{SnS}_4$  of initially  $81.2 \pm 2.9\%$  at  $100\text{ mA cm}^{-2}$  and  $7.6 \pm 0.7\%$  CO and  $10.8 \pm 0.4\%$   $\text{H}_2$  at  $-0.54\text{ V}$  *vs.* RHE (Fig. 1(E)). Based on the higher performance of this catalyst, the current density was increased to  $300\text{ mA cm}^{-2}$  after 1 h. An average potential of  $-1.0\text{ V}$  *vs.* RHE was recorded at  $300\text{ mA cm}^{-2}$  but  $\text{FE}_{\text{HCOO}^-}$  experienced a gradual drop from  $53.5 \pm 4.3\%$  to  $44.9 \pm 11.2\%$ . As the prepared  $\text{Ag}_3\text{SnS}_4$  also consists of  $\text{Ag}_8\text{SnS}_6$ , we synthesized the corresponding mineral phase to test whether the observed  $\text{CO}_2\text{RR}$  activity may also be obtained from an alloy with an 8:1 Ag:Sn ratio. The actual stoichiometry of the prepared GDE of  $\text{Ag}_8\text{SnS}_6$  was  $\text{Ag}_{8.9}\text{Sn}_{0.9}\text{S}_6$  (normalized to sulfur) and deviates from the expected ratio due to partial oxidation of the catalyst, as 1.1 eq. of oxygen was detected as well (ESI,† Fig. S7). During  $\text{CO}_2\text{RR}$  the  $\text{FE}_{\text{total}}$  of  $\text{Ag}_{8.9}\text{Sn}_{0.9}\text{S}_6$  drops from 73.6% with 51.6%  $\text{FE}_{\text{HCOO}^-}$  down to 43.9%  $\text{FE}_{\text{total}}$  after 1 h at  $100\text{ mA cm}^{-2}$ . The  $\text{CO}_2\text{RR}$  activity of  $\text{Ag}_{8.9}\text{Sn}_{0.9}\text{S}_6$  is significantly lower than  $\text{Ag}_3\text{SnS}_4$  and  $\text{Cu}_3\text{SnS}_4$  and after 1 h at  $300\text{ mA cm}^{-2}$ , only 14 ± 7.2%  $\text{FE}_{\text{HCOO}^-}$ , 2.1 ± 1.9%  $\text{FE}_{\text{CO}}$  and 6.2 ± 4.6%  $\text{FE}_{\text{H}_2}$  were measured. Compared

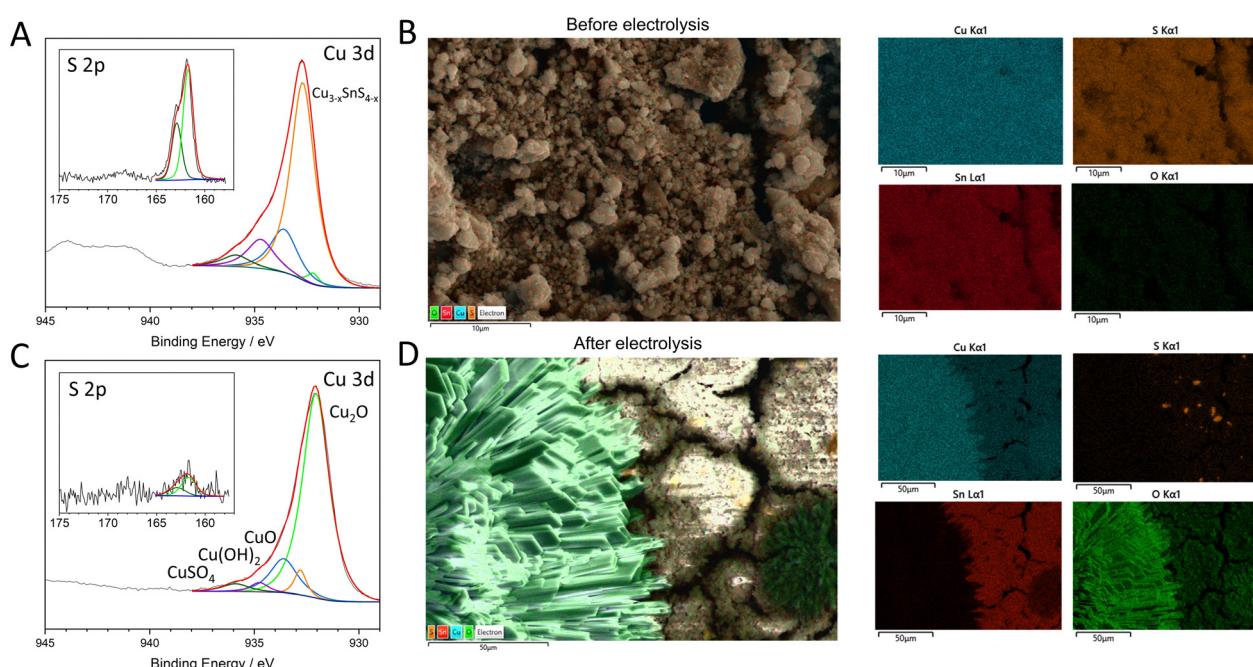


Fig. 2 XPS and EDX Imaging of  $\text{Cu}_3\text{SnS}_4$  electrode surfaces before (panel (A), (B)) and after electrolysis (C), (D) at  $100\text{ mA cm}^{-2}$ . The XPS spectra depict the Cu 3d transitions with orange peaks corresponding to metal sulfides, green to  $\text{Cu}_2\text{O}$ , purple to  $\text{Cu}(\text{OH})_2$ , CuO (blue), and dark green to  $\text{CuSO}_4$ . The corresponding S 2p regions are shown as insets. Overlays of EDX mappings before and after electrolysis (B), (D) are composed of the EDX mappings shown on the right with Cu  $\text{K}\alpha$  in blue, sulfur in orange, Sn  $\text{L}\alpha$  in red and oxygen  $\text{K}\alpha$  in green.



to  $\text{Ag}_3\text{SnS}_4$ , and especially at  $300 \text{ mA cm}^{-2}$ ,  $\text{FE}_{\text{total}}$  below 100% and a more negative electrode potential of about  $-1.3 \text{ V}$  were recorded. No additional  $\text{CO}_2\text{RR}$  products were observed using GC-MS, which may relate the parasitic currents to an inefficient restructuring process of  $\text{Ag}_{8.9}\text{Sn}_{0.9}\text{S}_6$  to an  $\text{AgSn}$  alloy or hydroxylation of the electrode surface.

### Post-mortem surface analysis

To assess changes in chemical composition on the electrode surface post electrolysis, XPS and EDX spectra were recorded for  $\text{Cu}_3\text{SnS}_4$ ,  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$ . While the as prepared  $\text{Cu}_3\text{SnS}_4$  exhibits a strong signal at  $932.7 \text{ eV}$  with 67% of the entire spectral area, small signals corresponding to  $\text{Cu}_2\text{O}$  ( $932.2 \text{ eV}$ ),  $\text{Cu}(\text{OH})_2$  ( $934.7 \text{ eV}$ ),  $\text{CuO}$  ( $933.7 \text{ eV}$ ) and  $\text{CuSO}_4$  ( $935.8 \text{ eV}$ ) are detected (Fig. 2).<sup>24</sup> High intensity S 3/2p and S 1/2p signals for metal sulfide species are measured at  $161.7 \text{ eV}$  and  $162.9 \text{ eV}$ . EDX images of the electrode surface before electrolysis similarly show a homogenous distribution of Cu, S and Sn and only traces of oxygen. (ESI,† Fig. S1) After electrolysis, 77.6% of the Sn 3d spectrum is assigned to  $\text{SnO}$  and sulfidic species only make up 4.2% of spectral intensity. The Sn 3d<sub>5/2</sub> transitions observed at  $486.3 \text{ eV}$  did not exhibit a shift in binding energies after electrolysis, which signifies an isoelectronic change from  $\text{Sn}^{2+}$  in  $\text{Cu}_3\text{SnS}_4$  to  $\text{SnO}$ . Blue colored, spherical copper oxide crystals were visible and a phase separation between  $\text{Cu}_2\text{O}$  and  $\text{SnO}$  on the electrode surface was also detected *via* EDX (Fig. 2(D)). Only traces of sulfide were detected *via* XPS and EDX. This indicates a near complete loss of sulfur during the electroreduction of  $\text{Cu}_3\text{SnS}_4$  to  $\text{Cu}_3\text{Sn}$  (Fig. 2(C), inset). Additionally, about two equivalents of Cu are leached from the electrode surface. Normalizing the Cu and O content to Sn in the EDX spectra yields a ratio of  $1.18:1.03:1$ . (ESI,† Fig. S4) While the bulk of the electrode contains an  $\text{Cu}_3\text{Sn}$  alloy according to PXRD, the surface is populated with  $\text{Cu}_2\text{O}$  and  $\text{SnO}$  species, which are likely formed after electrolysis by oxidation in air. Li *et al.* determined through

*in situ* XRD and XPS a metallic  $\text{Cu}_{24}\text{Sn}_{20}$  alloy at the surface of  $\text{Cu}_2\text{SnS}_3$  as catalytically active sites.<sup>10</sup> Similarly,  $\text{Cu}_3\text{Sn}$  is considered here to be the catalytically active species since the applied electrode potential of  $-1.2 \text{ V}$  exceeds the known stability range of copper tin sulfides, resulting in metallic phases.<sup>25</sup>

For  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$ , the extent of oxidation of the electrodes post electrolysis was expected to be diminished. However, SEM/EDX mappings of the electrodes post electrolysis showed a drastic morphological change of the electrode surface. The initial micrometer sized particles of metal sulfide were replaced by a fibrous structure consisting largely of C, O and Ag. The  $\text{Ag}_3\text{Sn}$  electrode consisted of 55.4% O, 34.5% C and 9.7% Ag and  $\text{Ag}_8\text{Sn}$  of 46.6% O, 30.2% C and 22.4% Ag (ESI,† Fig. S6 and S8). Only trace amounts of tin were detected for both electrodes. Likewise, 0.2% and 0.7% S were found for  $\text{Ag}_3\text{Sn}$  and  $\text{Ag}_8\text{Sn}$  respectively and most of the electrode surface is covered by carbonate salts. To remove the carbonate layer and allow an accurate assessment of surface of the suspected  $\text{Ag}_3\text{Sn}$  alloy, the electrodes were sonicated in HPLC water.

XPS Sn 3d spectra of the prepared electrodes show two peaks corresponding to  $\text{Sn}^{4+}$  at  $487.1 \text{ eV}$  and  $\text{Sn}^{2+}$  at  $486.2 \text{ eV}$  for both  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$  (Fig. 3(A) and (B)). The mineral  $\text{Ag}_8\text{SnS}_6$  consists of Sn with a net oxidation state of +4, but for  $\text{Ag}_8\text{SnS}_6$ , as well as  $\text{Ag}_3\text{SnS}_4$ ,  $\text{Sn}^{4+}$  only makes up 24.5 and 43.7% of the Sn 3d spectrum respectively.<sup>26</sup>  $\text{Sn}^{2+}$  is likely related to oxidation of the surface in air to  $\text{SnO}$ , although metastable  $\text{SnO}_2$  species may persist under electrocatalytic conditions.<sup>27</sup> Post electrolysis and after removal of the carbonate layer, the surface of  $\text{Ag}_3\text{Sn}$  consists of 63.1%  $\text{Sn}^{2+}$ , 33.2%  $\text{Sn}^{4+}$  and 3.7% metallic  $\text{Sn}^0$ , whereas  $\text{Ag}_8\text{Sn}$  consists of 84.7%  $\text{Sn}^{2+}$  and 13.8%  $\text{Sn}^0$  (ESI,† Fig. S12). While metallic Sn is expected for alloys, the tin oxide species present on the surface are proposed to be rapidly formed on air after removal of the surface layer. The surface of  $\text{Ag}_3\text{Sn}$  appears to be more prone to oxidation and exhibits a higher oxophilicity compared to  $\text{Ag}_8\text{Sn}$ , which may also indicate

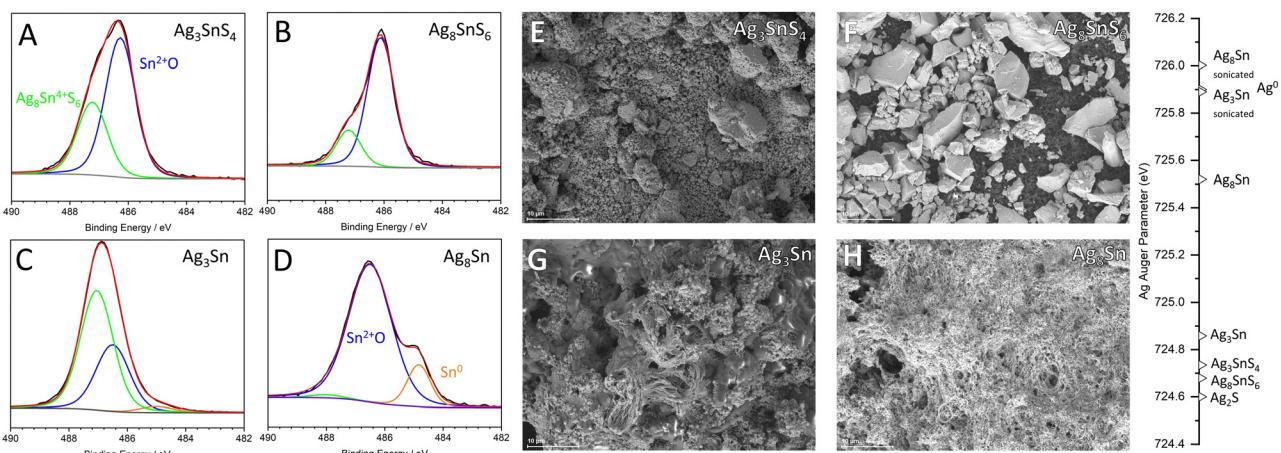


Fig. 3 X-ray photoelectron spectra in the Sn 3d region of  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$  before and after electrolysis, panel (A)–(D) respectively. The peak corresponding to Sn at a 4+ oxidation state is depicted in green, 2+ in blue and metallic tin in orange. Scanning electron microscopy images of  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$  before electrolysis (E), (F) and after electrolysis (G), (H) performed at  $100 \text{ mA cm}^{-2}$  and  $300 \text{ mA cm}^{-2}$  for 1 h each. The Auger parameters determined from the silver 3d and  $\text{M}_4\text{N}_{4.5}\text{N}_{4.5}$  transitions are indicated for the corresponding sample on the right, pre electrolysis and post electrolysis, with and without removal of the surface layers through ultrasonication.



a higher possible binding strength of carbonates and  $\text{CO}_2\text{RR}$  intermediates such as  $^*\text{OCHO}$  producing formate.<sup>28</sup> While metallic Sn was present on  $\text{Ag}_8\text{Sn}$ , for  $\text{Cu}_3\text{Sn}$  no metallic species were detected on the electrode surface by XPS. Together with the extensive morphological changes evidenced by SEM, this shows a higher corrosion stability of silver tin alloys compared to copper tin alloys.

The oxidation state of silver before and after electrolysis was tracked by determining the Auger parameter of silver 3d and  $\text{M}_4\text{N}_4,\text{N}_{4,5}$  transitions. The Auger parameters of  $\text{Ag}_3\text{SnS}_4$  and  $\text{Ag}_8\text{SnS}_6$  are initially closely centered around  $\text{Ag}^{1+}$  similar to  $\text{Ag}_2\text{S}$  at 724.6 eV and after electrolysis,  $\text{Ag}_3\text{Sn}$  is located at 724.9 eV indicating only minor changes due to electrochemical reduction.  $\text{Ag}_8\text{Sn}$  however, displays metallic character similar to  $\text{AgO}$  with 725.5 eV. After electrolysis and removal of the surface oxide layer through sonication in HPLC water for 30 s, a significantly more metallic bulk material was exposed for both silver tin materials. With 725.9 eV,  $\text{Ag}_3\text{Sn}$  now has a metallic character similar to  $\text{Ag}^0$  at 725.9 eV and  $\text{Ag}_8\text{Sn}$  to an even greater extent with 726.0 eV. A value exceeding  $\text{Ag}^0$  is surprising. However, a similar effect was observed in CuHf alloys and analogously, the shift of the Auger parameter is likely related to charge transfer of Sn to Ag, as well as a shift of the typical  $\text{CO}_2\text{RR}$  product spectrum of metallic Ag from CO to  $\text{HCOO}^-$ .<sup>29</sup> The increased metallic character of silver is also confirmed by Bader charge analysis. In both  $2 \times 2 \times 2$  supercells the surface slabs, Ag atoms exhibit a negative residual charge near Sn in comparison to metallic silver. An exception to this observation is the (010) slab, where net positively charged Ag atoms are also present (ESI,† Fig. S24).

PXRD recorded of  $\text{Ag}_8\text{SnS}_6$  after electrolysis also showed predominantly an  $\text{Ag}^0$  phase at  $38.3^\circ$  and only a minor reflection of a possible  $\text{Ag}_3\text{Sn}$  alloy at  $39.5^\circ$  (ESI,† Fig. S2). Together with the main  $\text{CO}_2\text{RR}$  product of  $\text{Ag}_8\text{SnS}_6$  still being formate – rather than CO as expected for metallic silver – an  $\text{AgSn}$  alloy appears to have formed during electrolysis. SEM analysis of the GDE surface only finds traces of Sn, which suggests a low number of possible, accessible catalytic sites consisting of Sn due to

carbonate adsorption and precipitation (ESI,† Fig. S8). The large parasitic currents observed for  $\text{CO}_2\text{RR}$  with  $\text{Ag}_8\text{Sn}_6$  might therefore be related to accumulation of carbonate layers on the electrode, aside from a possible inefficient restructuring process.

### Adsorption energies of the catalytic sites

To investigate potential compositions of the catalytic sites and whether product inhibition could occur, we calculated the adsorption energies of  $^*\text{H}$ ,  $^*\text{CO}$  and  $^*\text{OCHO}$  on the surfaces of  $\text{Cu}_3\text{Sn}$  and  $\text{Ag}_3\text{Sn}$  alloys. Thus, supercells and consequently slab models of  $\text{M}_3\text{Sn}$  ( $\text{M} = \text{Ag}, \text{Cu}$ ), characterized by an orthorhombic  $\text{Pmmn}$  structure, were considered. To describe the enhanced selectivity towards CO and formate,  $^*\text{CO}$  and  $^*\text{OCHO}$  molecules were chosen as adsorbates. Additionally, proton adsorption was also considered due to hydrogen evolution being a competing process. To assess the stability of the modelled surfaces, the surface energy  $E_{\text{surf}}$  of the slabs was evaluated (ESI,† Tables S2 and S3). The (010) surface was the focus of the investigation due to the presence of multiple non-equivalent adsorption sites, as well as the lowest surface energy.

The catalytic activity of  $\text{M}_3\text{Sn}$  materials towards particular catalytic processes is directly reflected in the energy diagrams. The changes in Gibbs free energy for various adsorbates on (010) planes of  $\text{M}_3\text{Sn}$  are depicted in Fig. 4(a)–(c). Generally,  $\Delta G$  for all processes is more exergonic in Cu-based systems compared to  $\text{Ag}_3\text{Sn}$  considering monometallic and trimetallic binding sites. The smaller radius of copper results in shorter intermetallic distances, leading to charge accumulation in smaller spaces. This promotes adsorption processes and facilitates charge transfer from the material surface to the adsorbate. Multi-metallic active sites (MM, MMM), whether in  $\text{Cu}_3\text{Sn}$  or  $\text{Ag}_3\text{Sn}$ , are overall more effective regardless of the process or adsorbate considered. This configuration likely arises from a local minimum in electron density placed between the atomic spheres of surface atoms, which is particularly significant in HER. Especially the  $\text{CuCuCu}$  active site exhibits significantly lower binding energy for  $^*\text{H}$  with  $-0.23$  eV, suitable for HER (Fig. 3(a)).<sup>30</sup> The adsorption site with

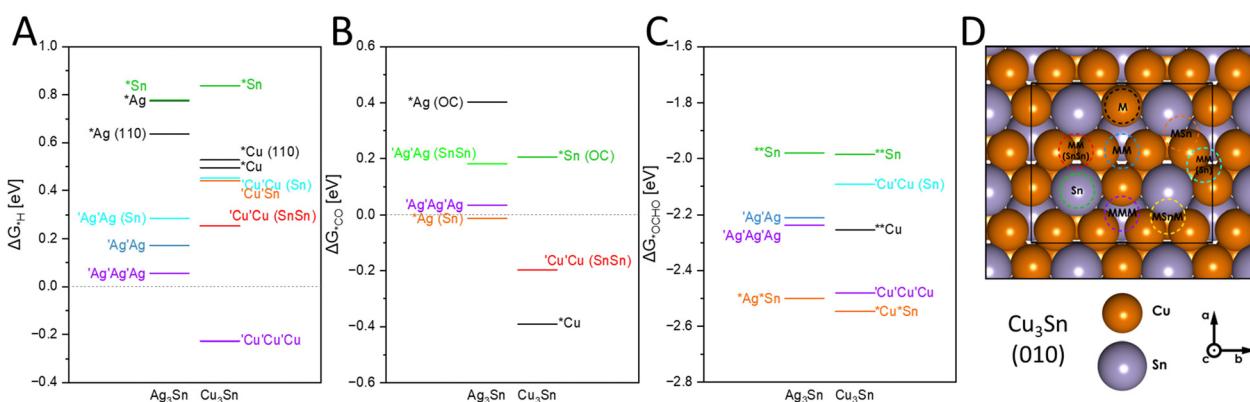


Fig. 4 Calculated Gibbs free energy of adsorption on  $\text{M}_3\text{Sn}$  (010) surfaces with panel A corresponding to  $^*\text{H}$ , panel B to  $^*\text{CO}$  and C to  $^*\text{OCHO}$ , using PBE-D2. For  $^*\text{CO}$  adsorption rotation of the adsorbent and coordination with O was observed (abbreviated as OC) and for  $^*\text{OCHO}$ , binding through both O occurred. (abbreviated as  $^*\text{O*OCH}$ ). Panel D displays the investigated binding sites on the example of  $\text{Cu}_3\text{Sn}$ , with a surface coverage of 0.125 ML ( $1 \times 1$ ). An asterisk  $*$  denotes a single bond (or close-range interaction) between an adsorbate atom/molecule and the element after the asterisk and a quotation mark indicates a more diffuse bonding interaction distributed among atoms marked with single quotation marks.



the second lowest energy, AgAgAg with 0.05 eV, already partakes in an endergonic adsorption process, followed by energetically unfavorable adsorptions at AgAg and CuCu sites with 0.17 and 0.25 eV respectively. These calculations align with the observation that  $\text{Cu}_3\text{Sn}$  produces more  $\text{H}_2$  than  $\text{Ag}_3\text{Sn}$  (19% and 11%  $\text{FE}_{\text{H}_2}$  at 100  $\text{mA cm}^{-2}$  respectively), likely at CuCuCu sites. Multi-metallic sites in the near vicinity of Sn appear unfavorable for HER with  $>0.25$  eV. Monometallic active sites, especially those involving Sn are distinctly disadvantageous for HER, consistent with other studies, where vacancies typically constitute ideal active sites for binding with an individual transition metals.<sup>31</sup>

Adsorption of CO on the (010) surface occurs overall in a more spontaneous reaction than HER (Fig. 4(b)), preferentially on monometallic Cu and Ag or CuCu ( $-0.39$ ,  $-0.01$  and  $-0.19$  eV respectively). Conversely to the observations for HER, monometallic active sites exhibit lower energies for CO adsorption. In our electrochemical experiments, a higher  $\text{FE}_{\text{CO}}$  of 17.2% was obtained with  $\text{Cu}_3\text{Sn}$ , whereas  $\text{Ag}_3\text{Sn}$  produced only 7.6% at 100  $\text{mA cm}^{-2}$ . With Cu and CuCu sites allowing for a stronger binding of  $^*\text{CO}$ , than at a monometallic Ag site,  $\text{CO}_2\text{RR}$  to CO appears favored on these Cu sites compared to Ag. It is also worth noting that in the case of  $^*\text{Sn}$  and  $^*\text{Ag}$  sites, the relaxation process resulted in molecule rotation, facilitating binding *via* oxygen. This initially led to the hypothesis that  $^*\text{OC}$  could be the preferential binding mode. However, subsequent calculations refuted this hypothesis due to the significant distances observed between the molecules and the surface (ESI,† Table S4).

The free energy of adsorption of the  $\text{CO}_2\text{RR}$  intermediate  $^*\text{OCHO}$  ranges from  $-1.9$  to  $-2.9$  eV (Fig. 4(c)) and demonstrates the high oxophilicity of  $\text{M}_3\text{Sn}$  surfaces. The energetically most favorable adsorption sites are CuSn and AgSn with  $-2.55$  and  $-2.53$  eV, as well as the trimetallic sites CuCuCu and AgAgAg with  $-2.48$  and  $-2.24$  eV respectively. Here, a beneficial influence of tin atoms in the vicinity of Cu and Ag is suggested, as evidenced by the lowest energies of bimetallic AgSn/CuSn sites. Ternary active sites follow in sequence, consistently demonstrating high activity in catalytic processes, albeit strongly favoring  $^*\text{OCHO}$  binding over  $^*\text{H}$  and  $^*\text{CO}$ . Two binding modes for  $^*\text{OCHO}$  were analyzed:  $^*\text{OCHO}$  and  $^*\text{O}^*\text{OCH}$ , with the latter mode being more prevalent on bimetallic and monometallic sites. Monodentate binding modes of  $^*\text{OCHO}$  on Ag are hypothesized to produce CO and in the here studied surfaces, the reaction pathway from the bidentate  $^*\text{O}^*\text{OCH}$  binding mode to formate is more energetically favorable after optimization (ESI,† Fig. S4).<sup>28</sup>

Overall,  $^*\text{OCHO}$  adsorption is the most spontaneous process, followed by  $^*\text{CO}$ , and least favorable for  $^*\text{H}$ , with multi-metallic active sites being highly desirable for all these processes. The presence of tin generally modulates the energetics of the adsorption towards higher energies, rendering the reactions less or even non-spontaneous in some cases, except for  $^*\text{O}^*\text{OCH}$  adsorption where bimetallic MSn sites are particularly active. The high binding affinity for  $^*\text{OCHO}$  and  $^*\text{O}^*\text{OCH}$  on  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_3\text{Sn}$  may also serve as a proxy for the binding of bicarbonate species, for which we observed extensive coverage on the electrode surfaces by EDX and XPS. The parasitic currents observed at  $-300$   $\text{mA cm}^{-2}$  could be related to increased bicarbonate binding

on the catalytic sites. A pulsed application of the applied voltage has been shown to alleviate carbonate formation and could potentially be applied to the  $\text{AgSn}$ -catalysts.<sup>32</sup>

## Conclusions

$\text{Cu}_3\text{SnS}_4$  and  $\text{Ag}_3\text{SnS}_4$  were found to be suitable precursors to the formation of  $\text{Cu}_3\text{Sn}$  and  $\text{Ag}_3\text{Sn}$  alloys through *in situ* electrochemical reduction. Both materials show a high selectivity for formate production during  $\text{CO}_2\text{RR}$  with 81%  $\text{FE}_{\text{HCOO}}$  at  $-100$   $\text{mA cm}^{-2}$ , 7%  $\text{FE}_{\text{CO}}$  and 11%  $\text{H}_2$  at  $-0.54$  V *vs.* RHE for  $\text{Ag}_3\text{Sn}$ . Sn is found to render the alloy surfaces highly oxophilic as evidenced by extensive oxidation in EDX and accumulation of carbonate on the electrode surfaces. High binding energies of up to  $-2.5$  eV for  $\text{HCOO}$  on  $\text{Cu}_3\text{Sn}$  and  $\text{Ag}_3\text{Sn}$  steer the expected  $\text{CO}_2\text{RR}$  product spectrum from  $\text{H}_2$  and CO on metallic Ag – and multicarbon compounds in the case of Cu – towards formate.

In the case of  $\text{Cu}_3\text{Sn}$ ,  $\text{Cu}_2\text{O}$  and  $\text{SnO}$  were found as separated phases on the electrode surface post-electrolysis, demonstrating an unstable alloy structure. For  $\text{Ag}_3\text{Sn}$ , the expected oxidation states of an alloy structure could be detected by XPS and PXRD after electrolysis at 300  $\text{mA cm}^{-2}$ . The gradual decrease in  $\text{FE}_{\text{HCOO}}$  at high current densities is likely caused by strong adsorption of carbonate or formate species on the catalyst surface, as evidenced by post-mortem SEM/EDX analysis and the computed binding energies. This limitation can possibly be overcome by the application of alternating currents to  $\text{Ag}_3\text{Sn}$  to reverse the excessive adsorption of carbonate on the electrode surface at current densities above  $-100$   $\text{mA cm}^{-2}$ . Future work at our laboratory is aimed at this mitigation strategy for the application of alloys for  $\text{CO}_2\text{RR}$ . Considering the high  $\text{FE}_{\text{HCOO}}$  obtained with  $\text{Ag}_3\text{Sn}$  despite its high oxophilicity and exposure to high  $\text{OH}^-$  concentrations, testing of  $\text{CO}_2\text{RR}$  activity with  $\text{O}_2$  diluted gas streams may still yield favorable results, thus showing the applicability for  $\text{CO}_2$  reduction of industrial flue gases.

Considering the vast experimental space alloying can provide, suitable binding energies can likely be tailored to the desired catalytic process.<sup>33,34</sup> The example of  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_3\text{Sn}$  demonstrates that a high oxophilicity may cause partial inhibition of the catalytic sites through carbonate adsorption or decomposition of the catalyst into *i.e.*  $\text{Cu}_2\text{O}$  and  $\text{SnO}$ . Therefore, an assessment of this property through *ab initio* methods and post-mortem spectroscopy after the application of high current densities appears necessary to select the highest performing alloy  $\text{CO}_2\text{RR}$  catalysts.

## Author contributions

Conceptualization: SAS, UPA, KjP. Formal analysis: SAS, AS, MK, AM, YH. Funding acquisition: UPA, SR. Investigation SAS, AS, MK, YW methodology SAS, AS, KP, SR. Project administration: UPA, SR, KjP, SAS resources: UPA, SR. Supervision: UPA, SR. Validation: SAS, AS, MK, AM. Visualization: SAS, MK, AM. Writing – original draft: SAS, MK, AM. Writing – review & editing SAS, AS, MK, AM, KP, UPA.

## Data availability

The datasets supporting this article have been uploaded as part of the ESI.† Further information not provided can be obtained upon request by the authors.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The work of SAS, AS, YH, YW, KP, KjP, SR and UPA was funded by grant number 03EE5104A, “CO<sub>2</sub>-Syn”, of the German Federal Ministry for Economic Affairs and Climate Action. MK and AM gratefully acknowledge Poland’s high-performance computing infrastructure PLGrid (HPC Center: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2023/016825.

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