Activation of Bimetallic AgCu Foam Electrocatalysts for Ethanol Formation from CO₂ by Selective Cu Oxidation/Reduction

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Abstract

Bimetallic AgCu metal foams (15at% Ag, 85 at% Cu) have been synthesized by means of an additive-assisted electrodeposition process using the dynamic hydrogen bubble template approach. Ag and Cu remain fully phase-segregated in the as deposited bimetallic foam exhibiting a high degree of dispersion of pure nm-sized Ag domains embedded in the Cu matrix. An activation of this bimetallic material towards ethanol formation is achieved by thermal annealing of the as deposited foam under mild conditions (200° C for 12 h). Such annealing quantitatively transforms the Cu in the bimetallic system into a mixture of crystalline Cu₂O and amorphous CuO whereas the Ag remains in its metallic state due to the thermal instability of Ag₂O above temperatures of 180° C. The selective oxidation of Cu in the bimetallic Ag₁₅Cu₈₅ catalyst goes along with an enrichment of Cu oxides on the surface of the formed mixed AgCu_xO foam.

Both *operando* X-ray diffraction and *operando* Raman spectroscopy demonstrate, however, that the oxide reduction is completed before the electrochemical CO₂ reduction sets in. The thus formed oxide-derived (OD) bimetallic Ag₁₅Cu₈₅ foam catalyst shows high selectivity towards alcohol formation with Faradaic efficiencies of $FE_{EtOH} = 33.7\%$ and $FE_{n-PrOH} = 6.9\%$ at -1.0 V and -0.9 V vs RHE, respectively. Extended electrolysis experiments (100 h) indicate a superior degradation resistance of the oxide-derived bimetallic catalyst which is ascribed to the effective suppression of the C1 hydrocarbon reaction pathway thus avoiding irreversible carbon contaminations appearing in particular during methane production.

1. Introduction

In recent years, the electrochemical conversion of environmentally harmful CO₂ into products of higher value is considered a promising and technologically feasible approach to mitigate the increase of atmospheric CO₂ [1-3] which reaches already levels above 410 ppm [4]. Because of this global threat, a paradigm shift currently drives both the energy and mobility sectors away from fossil-based (coal, oil, and natural gas) towards renewables (hydro, wind, and solar) energy sources. The chemistry sector follows this trend which will surely affect entire production chains of most commodity and fine chemicals. This so-called ‘energy transition’ can therefore be considered as a truly intersectorial challenge which calls for new transsectorial strategies. Several technologies including capture [5] and sequestration [6] have already been devised in order to reduce levels of CO₂ in the atmosphere. Amongst these, CO₂ reduction by electrochemical means [7] deserves particular attention as it can transform CO₂ directly back into synthetic fuels (so-called e-fuels) or other platform chemicals of high value [1, 2]. In particular the electrochemical co-electrolysis of water and CO₂ has the great potential to directly interlink the energy sector to the chemistry sector (see ‘Rheticus’ process as a prime example thereof) [8]. The CO₂ reduction reaction might become not only economically feasible in the future but also truly sustainable, in particular when the surplus of renewables originating from solar radiation, wind power, and hydro sources is used as energy input to drive this electrochemical CO₂ conversion. This so-called ‘power to value’ concept might, in future, become one important element among others contributing to the closing of the anthropogenic carbon cycle [3, 9, 10].

This electrocatalytic process typically relies on the oxidative splitting of water (OER: Oxygen Evolution Reaction) and the reductive conversion of CO₂ (CO₂RR: CO₂ Reduction Reaction). Oxygen (O₂) is the only product that can form on the anode side when using aqueous environments, irrespective of which anode material is used (e.g., RuO₂, IrO₂, or FeNi based systems) [11, 12]. However, a variety of different CO₂RR products are typically produced on the cathode side, [7] ranging from formate [13-15], carbon monoxide (CO) [16-27], saturated and non-saturated hydrocarbons (e.g. methane [16, 20, 28], ethylene [29-32]) to oxygenates of various chain length and energy density (e.g., methanol [20, 28, 33], ethanol [29, 34, 35], and n-propanol [34, 36]). The specific CO₂RR product distribution is mainly governed by chemical nature [7], the structure, and the morphology [30] of the electrocatalyst. Cu stands out in the group of monometallic CO₂RR catalysts [7] as it is capable to produce hydrocarbons [7, 16, 37-41] and oxygenates [32-35] of variable C-C chain length.

In particular the multi-hydrocarbon and oxygenate formation from CO₂ typically requires the balanced interaction between catalyst active sites and chemisorbed *CO (Sabatier principle), the latter being considered as the key intermediate in the CO₂RR. Such balance guarantees a sufficiently high abundance and residence time of the *CO at the reactive sites as mechanistic pre-requisites to undergo further C-C coupling and reductive hydrogenation reactions [42]. For several CO₂RR catalysts, Kuhl et al. [28] derived a Volcano like interrelation between the *CO binding strength and experimentally determined CO₂RR current densities at -0.8 V vs RHE. Au and Ag were found on the low binding energy side of the volcano curve, rationalizing the facile release of the formed CO as main product when the CO₂RR is carried out over Ag and Au. Cu was found on the high binding energy side next to the volcano maximum with the right balance of the *CO binding strength to prevent irreversible poisoning of the catalyst (e.g., as in case of Pd [13, 15]) but allowing for C-C coupling reactions.

One major drawback of the Cu catalysts is, however, their poor product selectivity [7]. One recently discussed experimental concept towards improved selectivity of C-C coupled hydrocarbons (e.g., ethylene) is based on the use of bimetallic materials consisting of a CO producer (e.g., Ag, Au, or Zn) and the C-C coupler (Cu) [29, 43-46]. A high abundance of CO is achieved, e.g. through selective CO₂RR on the Ag component in the bimetallic system. CO is subsequently transported to Cu sites in close proximity that are active for the C-C coupling. Short diffusion paths from Ag to Cu on the catalyst surface are essential for this ‘CO spillover’ concept. Further, CO₂RR efficiencies are per se improved when using AgCu bimetallics as the Ag reveals an intrinsically higher overpotential for the parasitic hydrogen evolution reaction (HER). It is the high surface concentration of chemisorbed *CO which leads to a further suppression of the HER by blocking surface sites, at least within a certain range of potentials applied [44].

In this present study, we further develop this approach by selectively activating the Cu component in the **bimetallic AgCu system** for alcohol formation. This can be achieved by thermal annealing, which leads to the selective formation of Cu oxides, whereas the Ag remains in its metallic state. **Electroreduction** of the formed oxidic Cu precursor under CO₂RR conditions transforms the bimetallic AgCu system into a C-C coupling and alcohol forming catalyst. **The latter is denoted in the following as oxide-derived (OD) Ag₁₅Cu₈₅.**

A combination of *operando* Raman spectroscopy and X-ray diffraction is used, along with TEM, STEM and so-called identical location IL-SEM imaging, to probe compositional and structural changes of the catalyst which go along with its activation for alcohol production.

For the preparation of model catalysts we apply the so-called dynamic hydrogen bubble template approach, originally developed for the electrodeposition of monometallic metal foams [47, 48], to the bimetallic AgCu system [27]. Also we will show that the use of complexing plating additives (e.g., citrate) plays a vital role for the required dispersion of the Ag in the Cu matrix.

2. Results and Discussion

2.1. Synthesis and activation of the $\text{Ag}_{15}\text{Cu}_{85}$ foam catalyst

The as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam - The bimetallic $\text{Ag}_{15}\text{Cu}_{85}$ foam catalyst (this notation refers to the bulk composition derived from the ICP-OES analysis, see Table S1) has been electrodeposited on a Cu foil substrate at $j = -3 \text{ A cm}^{-2}$ (20 sec.) using a plating bath containing 1.5 M H_2SO_4 , 20 mM CuSO_4 , 2 mM Ag_2SO_4 , and 0.1 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$. Key to this process is the hydrogen evolution reaction (HER, secondary process) that is superimposed on the metal deposition (primary process) when such high cathodic current densities are applied [30, 47, 48]. Hydrogen bubbles, which appear on the cathode during the massive HER, thereby serve as transient geometric template for the metal foaming process [30, 47, 48]. Proton consumption and water splitting (OH^- formation) lead to the appearance of pronounced pH gradients at the interface thus resulting into the deprotonation of the citric acid (10^{-1} M tri-sodium citrate di-hydrate) in the reaction boundary layer [18]. The formed citrate tends to chemisorb on the cathode thus altering the nucleation and growth characteristics of the emerging foam deposit [18]. In addition, citrate anions undergo fast chelating reactions with the Ag^+ and Cu^{2+} cations in the near electrode surface reaction boundary layer [18]. It can therefore be assumed that the actual deposition process occurs from a complexed metal ion solution produced *in situ* in the near surface electrolyte (see schematic in Fig. S1) [18]. In this present study we restrict ourselves to the discussion of one particular composition of the **bimetallic AgCu foam** catalyst containing 15 at% Ag and 85 at% Cu. Detailed compositional studies of this kind of catalysts are hampered by the fact that any changes of the bath composition (e.g., the $\text{Ag}^+ : \text{Cu}^{2+}$ ion ratio or the citrate additive concentration) will inevitably affect the Faradaic efficiencies of hydrogen production and metal deposition [27]. As a consequence of that not only the chemical composition of the deposit is altered but also its morphology on various length scales [27]. Compositional and morphological effects (e.g., pore size distribution, morphology of the pore side-walls) can therefore not be studied independently from each other when applying the dynamic hydrogen bubble approach [48] to these bimetallic systems.

Fig. 1 shows representative white-light interferometry (panel a) and SEM micrographs (panels b and c) of the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam which resembles in appearance to the pure Cu foams with their multi-level 3D architecture of interconnected pores [30, 48, 49]. A cross-sectional SEM inspection reveals a thickness of $\sim 18\ \mu\text{m}$ (see Fig. S2) of the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam. A similar bimetallic AgCu foam has recently been reported by Kottakat et al. [27] which has, however, been deposited from an additive-free plating bath and showed therefore different structural and morphological characteristics compared to the one discussed herein. The mean outermost surface pore diameter of the $\text{Ag}_{15}\text{Cu}_{85}$ foam discussed herein amounts to $\sim 25\ \mu\text{m}$. Note that these metal foams typically reveal a gradient in pore size along the surface normal due to the coalescence of hydrogen bubbles in the course of the metal deposition [30, 48]. Similar to the pure Cu metal foams deposited from an additive-free Cu plating bath [30, 48, 49], also the sidewalls of the bimetallic $\text{Ag}_{15}\text{Cu}_{85}$ foam reveal a dendritic nature with individual dendrites composed of AgCu particles having dimensions of $< 50\ \text{nm}$ (panel c). Note that individual dendrites in the pure Cu foams deposited from additive-free plating baths are composed of shaped Cu crystallites showing preferential (111) and (100) facets on their surface [49]. No such texturing is, however, visible on the bimetallic $\text{Ag}_{15}\text{Cu}_{85}$ foam. Also note that pure Cu catalysts deposited under identical plating conditions (current density, plating time) in the presence of the citrate additive do not show a well-developed foam morphology at all (Fig. S3) thus demonstrating that the presence of the citrate not only impacts the nucleation and growth of the metal deposition process but also the formation and release of the hydrogen bubbles from the electrode.

The correlation between the catalyst morphology and its composition has been achieved by means of ADF-STEM imaging (Fig. 1d) combined with EDX mapping, the latter providing information on the spatial distribution of Cu and Ag, respectively (Fig. 1e-g). The EDX analysis confirms that the electrodeposition approach yields bimetallic foams with a high degree of dispersion of Ag in the Cu matrix, which is considered as a crucial prerequisite for the intended CO ‘spillover’ concept [50]. The presence of the citric acid additive in the plating bath is found to be essential to yield a bimetallic catalyst material where the nm-sized Ag and Cu domains form a maximum of phase boundaries. By contrast, the respective metal foam deposited in the absence of citric acid resembles more a physical mixture of loosely packed Ag and Cu particles (see Fig. S4).

Activation of the $\text{Ag}_{15}\text{Cu}_{85}$ foam: ex situ XRD and XPS analysis - An activation of the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam for the selective formation of ethanol from CO_2 requires a further treatment which is typically based on an oxidation of the catalyst material. Both thermal

annealing [34, 49, 51-55] and the exposure of Cu-based catalysts to oxygen plasma [40, 56, 57] have already been demonstrated to be beneficial for the formation of oxidic catalyst precursors which, under CO₂RR conditions, reductively transform into their metallic form thereby creating those reactive sites which are actually active towards C-C coupling and the formation of alcohols [34]. In addition, the C1 hydrocarbon (methane) reaction pathway gets effectively suppressed by this oxidation/reduction cycle [34]. This side effect of the thermal treatment has been found to be particularly beneficial for the degradation stability of the CO₂RR catalysts [34]. The formation of methane via the coupled C1/C2 reaction pathway [34, 58] typically involves an undesired and irreversible carbonization of the catalyst surface [59-61].

A mild thermal annealing treatment in air at 200 °C was applied for 12 h to the as deposited Ag₁₅Cu₈₅ foam. Fig. 2a depicts representative diffraction patterns of the as deposited Ag₁₅Cu₈₅ foam, the thermally annealed one, and the catalyst after 1 h of CO₂RR at -1.0 V vs RHE (OD-Ag₁₅Cu₈₅ foam). For the sake of interpretability also the respective JCPDS reference data for *fcc* Cu, *fcc* Ag, Cu₂O and Ag₂O are presented (see also Table S1). From the XRD analysis it can be concluded that the as deposited Ag₁₅Cu₈₅ foam is composed of pure Cu and Ag phases with minor contributions originating from Cu₂O and Ag₂O. Qualitatively similar diffraction patterns of bimetallic CuAg thin films were recently reported by Clark et al. also showing peaks coinciding with those of pure *fcc* Ag and Cu [44]. In the latter case a small contribution from an AgCu surface alloying was observed. In the present case there are, however, no experimental hints in the XRD analysis for any alloying (see Table S1) in agreement with recent results by Kottakat et al. [27]. These different experimental observations can be rationalized by the particular preparation route of AgCu film formation used by Clark et al. which actually facilitates AgCu surface alloy formation [44]. The phase-segregation of Cu and Ag is indeed expected as the respective binary phase diagram indicates an immiscibility of Ag and Cu for a wide range of temperatures and compositions relevant to this study [50]. Minor oxidic components visible in the diffractogram of the as deposited sample might originate in particular at the surface of the deposit after its emersion from the metal ion containing plating bath and the subsequent drying procedure in air [30, 49].

Thermal annealing in air at 200 °C partly transforms the Cu into crystalline Cu₂O whereas the diffraction pattern of metallic Cu almost disappears. Diffraction patterns of crystalline Ag₂O are not detected due to thermal instability of the Ag₂O which decomposes at temperatures above 180 °C [62]. From the XRD analysis it can be concluded that the thermally annealed Ag₁₅Cu₈₅ is a mixed metal/oxide (AgCu_xO) composite material.

As expected, the post-electrolysis XRD analysis reveals again major contributions from metallic Cu and Ag whereas the oxidic components have almost been disappeared (see also the inset in Fig. 2a). Only trace amounts of crystalline Cu₂O can be detected which have likely been formed on the catalyst surface after the CO₂ electrolysis during exposure of the catalyst to air.

As the XRD experiment is only sensitive to bulk phases revealing long-range translational order, complementary XPS analysis has been applied being more sensitive to the chemical state of the catalyst surface. Panels b and c of Fig. 2 depict Cu2*p* and Ag3*d* core level emissions of the bimetallic catalyst material representing different stages of its preparation and use. As reference, also XPS spectra of pure Ag and Cu foil samples are provided. Obviously, Cu(II) species are already present on the as deposited foam.

This can be deduced from the satellite features on the high binding energy side of the Cu(0)/Cu(I) related Cu2*p* emission. In addition, characteristic shake-up features are visible in the XPS spectrum of the as deposited sample, thus further confirming the presence of Cu(II). Cu(II) related XPS features might originate from residuals of the complexed Cu(II) precursors which were trapped inside the metal foam after its emersion from the plating bath. Note that Cu foams deposited from a non-complexed (citric acid free) solution do not show these characteristic Cu(II) features in the XPS (Fig. S5) [49]. Further, the annealed Ag₁₅Cu₈₅ foam sample contains Cu(I) and Cu(II) species which, in this case, can be assigned to oxidic Cu as product of the thermal treatment [49]. The annealing temperature of 200 °C is, however, not high enough to induce sufficient translational order in the formed CuO phase to be detected in the XRD (Fig. 2a) in full agreement with the literature [49]. After the electrolysis, the sample contains metallic Cu as well as minor amounts of cuprous and cupric oxides. The latter can be attributed to the post-electrolysis re-oxidation of the sample when exposed to air in agreement with the XRD analysis.

Also the Ag3*d* core level emissions of the Ag₁₅Cu₈₅ foam (panel c) confirm our *ex situ* XRD analysis. After electrodeposition of the Ag₁₅Cu₈₅ foam both Ag(0) and Ag(I) species are observed in the XPS. For instance, the Ag3*d*_{5/2} peak at BE = 367.9 eV is downward-shifted by ΔBE ≈ 0.3 eV with respect to the Ag reference (BE(Ag3*d*_{5/2}) = 368.2 eV thus indicating the presence of Ag(I) species. One possible origin of the Ag(I) might be residual Ag(I) complexes trapped inside the metal foam after the deposition. Note that similar Ag(I) features appear in the photoemission spectra of pure Ag metal foams deposited from a citrate containing plating bath [18]. In accordance with the XRD analysis, the Ag3*d* core level emission of the annealed Ag₁₅Cu₈₅ foam does not show any contribution of Ag(I). This once more confirms the thermal

instability of the Ag_2O phase and the AgCu_xO composite nature after its annealing at 200°C . For the discussion of the CO_2RR product distribution (see below) it is important to note that the relative abundance of Cu and Ag on the catalyst surface differs from the respective bulk composition determined by ICP-OES and further changes in the course of the thermal oxidation/*ec* reduction treatment as evidenced by the quantitative analysis of the $\text{Cu}2p$ and the $\text{Ag}3d$ core level emissions. Their integrated intensities ($I_{\text{Cu}2p}:I_{\text{Ag}3d}$) change from 62:38 (as deposited) to 91:9 (annealed at 200°C) and 77:23 (after 1 h CO_2RR at -1.0 V vs RHE). In particular the surface of the annealed foam sample seems to be substantially enriched by (oxidic) Cu. **Basis for this quantification was the XPS data set presented in Fig. S6.**

This scenario becomes further supported by a combined HR-TEM and ADF-STEM inspection of the annealed $\text{Ag}_{15}\text{Cu}_{85}$ foam sample (Fig. 3) providing information of the spatial distribution of the metallic Ag and oxidic Cu_xO domains in the bimetallic foam. From the HR-TEM image in Fig. 3c it can be seen that the surface of the dendrite is composed of amorphous Cu_xO and crystalline Cu_2O whereas metallic Ag is found predominantly in the interior of the dendrite (see also the EDX analysis in Fig. 3h). Diameters of the Cu_xO and the metallic Ag domains in the composite are in the range of 4 - 8 nm. Spatially resolved EDX analysis combined with ADF-STEM imaging (Fig. 3) confirms a uniform dispersion of nm-sized Ag and Cu_xO domains in the bulk of the dendrite as already concluded from the EDX analysis of the as deposited sample (Fig. 1).

Activation of the $\text{Ag}_{15}\text{Cu}_{85}$ foam: operando XRD and Raman spectroscopic analysis -

Applying cathodic electrode potentials relevant for the CO_2RR leads to further structural and compositional changes in the mixed metal-oxide foam involving in particular the electro-reduction of the cupric and cuprous oxides. These compositional changes can be probed under reactive conditions by means of the *operando* XRD technique using characteristic diffraction features of the crystalline Cu_2O as fingerprint for the presence of oxidic copper (Fig. 4a). Fig. 4b depicts the normalized intensities of the (220) diffraction peak of Cu_2O as well as intensities of the Ag and Cu related to (220) and (200) reflections, respectively, as a function of the applied electrode potential. Again, crystalline CuO was not detectable in the XRD due to its amorphous state (see also Fig. 3c). The intensity of Cu_2O related diffraction peaks first increase when going from $+0.5\text{ V}$ to $+0.25\text{ V vs RHE}$ before dropping down to zero at potentials $< -0.5\text{ V vs RHE}$. Such initial rise in the normalized intensity of the Cu_2O related diffraction peaks can be attributed to the reduction of amorphous CuO to metallic Cu which proceeds via crystalline Cu_2O as an intermediate. In general, the decrease of the Cu_2O related diffraction intensity at potentials $< +0.25\text{ V vs RHE}$ is anti-correlated to the raise in the

integrated peak intensity of the metallic Cu. Fig. 4 suggests that the reduction of the oxidic Cu ‘precursor’ is already completed before the CO₂RR sets in (≈ -0.3 V vs RHE). The normalized intensity of the Ag related (220) peak remains constant, at least in the potential range relevant for the Cu oxide-metal transition ($+0.5$ V vs RHE to -0.5 V vs RHE). A certain decrease in the integrated intensity is, however, observed at potentials < -1.0 V vs RHE. One possible explanation might be a preferential leaching of the Ag component under CO₂RR/HER conditions.

Operando Raman spectroscopy further supports the conclusion on the metal-oxide transition occurring at potentials more anodic than the CO₂RR onset. Not only is this technique more sensitive to the chemical state of the catalyst surface than the XRD, it is in addition suitable to probe chemisorbed intermediates of the CO₂RR [27]. Fig. 5a shows a series of potential dependent steady-state Raman spectra covering a potential window from the open circuit potential (OCP) down to -0.9 V vs RHE. According to the literature, the vibrational modes observed at 518 and 624 cm⁻¹ originate from Cu_x(OH)_y and Cu₂O species at the catalyst surface [63]. Their peak intensities drop down to zero already at potentials $< +0.2$ V vs RHE (Fig. 5a). This value is even more positive than the oxide-metal transition probed by the *operando* XRD (Fig. 4). Differences in the observed oxide-metal transition potential might be related to technique specific. Also note that neither the *operando* XRD nor the *operando* Raman spectroscopy can exclude the presence of traces of so-called sub-surface oxygen after completion of the potential-induced oxide-metal transition [64].

CO stretching modes of chemisorbed carbon monoxide appear in the *operando* Raman spectra at applied potentials $< +0.1$ V vs RHE. The discernable Raman peaks at 2031 cm⁻², 2093 cm⁻², and 2133 cm⁻² (Fig. 5b) are due to different adsorption sites of CO chemisorbed either on metallic Cu or on Ag of the Ag₁₅Cu₈₅ foam [65, 66]. A clear improvement of the bimetallic Ag₁₅Cu₈₅ foam with regard to pure Cu catalysts is a higher abundance of chemisorbed CO at more cathodic potentials (Fig. 5c, Fig. S7). Note that the peak maximum of the integrated peak intensity of the CO stretching mode is shifted by ~ 200 mV towards more cathodic potentials in case of the thermally annealed Ag₁₅Cu₈₅ foam. A similar increased abundance of chemisorbed CO is observed for the as deposited Ag₁₅Cu₈₅ foam (Fig. 5c). This characteristic feature of the bimetallic Ag₁₅Cu₈₅ foams can be regarded as beneficial for the ethylene and the alcohol formation which require both a high abundance of chemisorbed CO on the catalyst surface [67]. The stabilization of chemisorbed CO on the catalyst surface under CO₂RR conditions can be regarded as crucial mechanistic prerequisite for any further improvement of the ethanol efficiency.

2.2 Electrochemical performance of the Ag₁₅Cu₈₅ foam catalysts

The electrocatalytic performance of the Ag₁₅Cu₈₅ foam has been evaluated by means of potential dependent electrolysis experiments (1 h duration) from CO₂-saturated 0.5 M KHCO₃ electrolytes (pH = 7.2). Results of these electrolysis experiments are shown in Fig. 6a for as deposited Ag₁₅Cu₈₅ foam. In principle, the potential dependent product distribution can be subdivided into three distinct potential regimes. In the range from -0.3 to -0.7 V vs RHE CO is the predominant CO₂RR product reaching a maximum Faradaic efficiency of FE_{CO} = 81.45% (Table S2) at -0.3 V, which corresponds to a partial CO current density of j_{CO} = - 0.24 mA cm⁻² (Table S3). It can be assumed that it is the Ag component in the as deposited Ag₁₅Cu₈₅ foam catalyst on which the CO₂RR preferentially takes place at these low overpotentials. This bimetallic catalyst outperforms pure Cu catalysts in terms of CO production at low overpotentials. One reason might be related to the almost quantitative suppression of the formate production (Fig. 6a, Table S2) which is typically produced over pure Cu electrocatalysts at these conditions (e.g. FE_{formate} = 49.2% at -0.7 V vs RHE [34]). Comparably high efficiencies of formate formation are also observed for pure Cu catalysts deposited in the presence of citrate additives (see Fig. S3 and Fig. S8 in supplementary information).

A similar effect of suppressed formate production has recently been discussed by Kottakat et al. for electrodeposited bimetallic AgCu foams [27]. In this latter case a maximum CO efficiency of ~FE_{CO} = 58.4% at -0.6 V vs RHE was reported [27]. Highest CO efficiencies at particularly low overpotentials similar to those reported herein were so far reported only for pure Au [68] or Ag [69] electrocatalysts. An example related to this present work is the pure Ag foam electrocatalyst also deposited from a citrate-containing plating bath [18]. In this latter case the FE_{CO} values did not fall below 90% within a 800 mV broad potential window ranging from -0.3 to -1.2 V vs RHE [18]. It should be emphasized, however, that the bimetallic AgCu foams are superior over the pure Ag catalyst in terms of Ag mass activity [27].

In the present case the FE_{CO} values start to drop down at potentials < -0.5 V vs RHE not only because of the HER which becomes more favored with increasing cathodic potentials, but also because of the C1 (methane) and C2 (ethylene, ethane) hydrocarbon pathways which are opened at potentials < -0.4 V and < -0.9 V vs RHE, respectively. The ethylene efficiency reaches its maximum of FE_{C₂H₄} = 36.56 % (j_{C₂H₄} = - 11.32 mA cm⁻²) at -1.1 V vs RHE. These efficiencies are comparable to those reported for Cu nano-foams [70] or Cu nano-cubes with

(100) surface orientation [71, 72]. Table S4 provides an overview on the best performing Cu-based catalysts for ethylene production. Interesting to note is that, in contrast to pure Cu foams [30], the C₂H₆ formation remains on a low level on the bimetallic catalyst within the entire potential range studied herein never exceeding 1% (Table S2).

As known from polycrystalline Cu electrocatalysts [73], methane production sets in at slightly higher overpotentials as compared to ethylene reaching on as deposited Ag₁₅Cu₈₅ a maximum of FE_{CH₄} = 25.6 % at -1.2 V vs RHE (Fig. 6a). C2 and C3 alcohol formation is negligible on the as deposited Ag₁₅Cu₈₅ foam. The n-propanol efficiencies never exceed 1% whereas a maximum ethanol efficiency of FE_{EtOH} = 4.6% (j_{EtOH} = -1.11 mA cm⁻²) is obtained at -1.0 V vs RHE. The second characteristic potential regime in the product CO₂RR distribution (< -0.7 V vs RHE) is obviously dominated by the Cu component in the as deposited Ag₁₅Cu₈₅ foam with its capability of enabling C-C coupling reactions. It can be assumed that the C-C coupling reaction benefits from the high abundance of CO inside the porous catalyst. Due to the small domain sizes of the metallic components of the as deposited Ag₁₅Cu₈₅ foam (Fig. 1, see also below discussion on Fig. 9i) the CO intermediate is rapidly transported from the Ag (CO producer) to the Cu domains (C-C coupler) either by surface diffusion ('spillover') or by diffusion through the liquid electrolyte phase inside the pores of the bimetallic foam (re-adsorption of trapped CO).

In principle, this basic concept holds true also for the thermally annealed (oxide-derived) Ag₁₅Cu₈₅ foam (Fig. 6b). The C1 and C2 hydrocarbon pathways are, however, substantially suppressed on the OD-Ag₁₅Cu₈₅ foam (Table S5). A maximum value of only FE_{C₂H₄} = 10.2% (j_{C₂H₄} = - 3.1 mA cm⁻²) is observed at -1.1 V vs RHE. Instead, ethanol is the predominant CO₂RR product at electrolysis potentials < -0.8 V vs RHE reaching a maximum value of FE_{EtOH} = 33.7% (j_{EtOH} = -8.67 mA cm⁻²) at -1.0 V vs RHE. Important to note is that the efficiency for n-propanol formation remains on a low level (e.g., FE_{n-PrOH} = 6.9%, j_{n-PrOH} = - 1.8 mA cm⁻² at -0.9 V vs RHE) thus pointing to a catalyst which is selective towards C2 alcohol formation (Table S5 and Table S6). Rahaman et al. recently reported a high alcohol efficiency for thermally annealed dendritic Cu of FE_{alcohol} = 24.8 % (j_{alcohol} = - 7.73 mA cm⁻²) at -1.0 V vs RHE [34]. The alcohol selectivity itself was, however, poor with almost equivalent efficiencies for ethanol and n-propanol [34].

The OD-Ag₁₅Cu₈₅ is currently among the best performing catalysts for the production of higher alcohols (an overview is provided in Table S7 and Table S8).

A certain drawback of the thermal annealing of the Ag₁₅Cu₈₅ foam is the decrease of the Ag (CO producer) content at the catalyst surface in the course of the thermal oxidation/ec

reduction treatment (see discussion of the XPS data). This structural and compositional alteration of the catalyst surface becomes apparent also from the CO₂RR product distribution, in particular in the low overpotential regime ranging from -0.3 V to -0.8 V vs RHE (Fig. 6b). In comparison to the as deposited sample (Fig. 6a) the Faradaic yield of CO production is substantially lower **for the oxide-derived catalyst** at lowest overpotentials, e.g. at -0.3 V vs RHE ($FE_{CO} = 37.4\%$ instead of $FE_{CO} = 81.45\%$ (as deposited)) and slightly lower at medium overpotentials, e.g. at -0.6 V vs RHE ($FE_{CO} = 52.0\%$ instead of $FE_{CO} = 60.7\%$ (as deposited)). However, the Ag content on the catalyst surface after the reduction of the oxides seems to be sufficient to substantially improve the total alcohol efficiency $FE_{alcohol}$ compared to pure Cu foams (see also discussion of Fig. 9).

Fig. 7 summarizes the suggested mechanism of alcohol formation on the bimetallic AgCu catalyst surface which is consistent with published models on alcohol formation on Cu [34]. CO forms selectively on the Ag domains and is subsequently transported to the Cu via surface diffusion ('spillover') or alternatively via CO transport through the solution phase (desorption/re-adsorption). Besides the increased abundance of CO intermediates it is the stabilization of the chemisorbed *CO on the catalyst surface which further directs the CO₂RR towards C-C coupling and alcohol formation. This stabilization is deduced from the potential dependent integrated intensity of the CO stretching mode (Fig. 5c). Its maximum is downward-shifted on the potential scale in case of the Ag₁₅Cu₈₅ foam compared to the pure Cu foam (Fig. 5c). Note that the Raman experiment does not allow for a direct comparison of the CO surface concentration on the pure Cu and the Ag₁₅Cu₈₅ foam due to differences in the surface morphology (e.g. roughness) and chemical composition of both catalyst materials.

2.3. Stability of the annealed Ag₁₅Cu₈₅ foam catalyst

Besides the CO₂RR product selectivity and activity, it is the long term stability of the catalyst which defines its overall performance. Therefore, long term CO₂ electrolysis experiments were performed at -1.0V vs RHE corresponding to the maximum ethanol efficiency in the potential dependent screening experiment (Fig. 6b). **Fig. 8 depicts the current/time transient curve (panel a) and the corresponding FE/PCD vs t plot (panel b) of a 100 h continuous electrolysis experiment. The partial current density (PCD) for ethanol formation drops down slightly from -8.4 mA/cm^2 to -7.3 mA/cm^2 thus pointing to an excellent degradation stability of the bimetallic catalyst. Note that, when the electrolysis is carried out in a discontinuous fashion, the degradation process proceeds faster (see discussion on Fig. S9 in the supplementary information).**

Structural and compositional changes upon catalyst activation via the precursor reduction and the CO₂ electrolysis itself become apparent from identical location IL-SEM analyses of the Ag₁₅Cu₈₅ foam in Fig. 9 after anneal at 200° C (panel a-b) and after 72 h of continuous CO₂ electrolysis (panel c-d). The electroreduction of the precursor and the CO₂ electrolysis at -1.0 V vs RHE leaves the mesoscopic pore structure on the μm scale fully unaffected (panel a and c) similar to what is known from Cu and Ag foams [18, 30]. Distinct structural changes are, however, visible on the nm length scale (panel b and d). After the 72 h of electrolysis (panel d) smaller particles have been evolved, most likely in the initial stage of the electrolysis where the CO₂RR is superimposed on the Cu oxide reduction (see e.g. Fig. 4). Similar morphological changes become apparent from an extended IL-analysis of the catalyst carried out at discontinuous operation mode (Fig. S10 in the supplementary information).

Combined ADF-STEM imaging and EDX mapping (Fig. 9) clearly indicate a high degree of dispersion of Ag and Cu domains. The preferential segregation of Cu in the form of cuprous and cupric oxides has disappeared under CO₂RR conditions in full agreement also with the XPS analysis.

3. Conclusions

Bimetallic Ag₁₅Cu₈₅ foam catalysts have been produced by means of an additive (citrate) assisted electrodeposition approach utilizing the dynamic hydrogen bubble template approach. Whereas the as deposited catalyst is selective towards CO at particularly low overpotentials (FE_{CO} = 81.45%, j_{CO} = -0.24 mA cm⁻² at -0.3 V vs RHE) and towards C₂H₄ at higher overpotentials (FE_{C₂H₄} = 36.56 %, j_{C₂H₄} = - 11.32 mA cm⁻² at -1.1 V vs RHE) an activation of the catalyst for selective alcohol formation is achieved by thermal annealing of the Ag₁₅Cu₈₅ at 200° C for 12 h. This treatment leads to a metal/oxide composite material consisting of metallic Ag and oxidized Cu (denoted as AgCu_xO foam), the latter being accumulated at the surface of the foam. Electroreduction of the oxidic components in the AgCu_xO precursor leads to an oxide-derived (OD) bimetallic AgCu catalyst which outperforms in terms of ethanol selectivity (FE_{EtOH} = 33.7%, j_{EtOH} = -8.67 mA cm⁻² at -1.0 V vs RHE) and durability (100 h).

A key feature of the OD-Ag₁₅Cu₈₅ foam catalyst is the high dispersion of nm-sized domains of metallic Ag (CO producer) and Cu (C-C coupler, alcohol former) in the bimetallic catalyst thus allowing for a facile transport of the CO intermediate to those Cu surface sites that are particularly active for C-C coupling and ethanol formation (CO spillover concept). The excellent performance of the OD-Ag₁₅Cu₈₅ foam catalyst is due to the synergistic effects of an

increased CO abundance at higher overpotentials and the selective activation of the Cu component by the oxide formation and its electroreduction under CO₂RR conditions.

Operando Raman spectroscopy and X-ray diffraction both clearly demonstrate that the activation (electro-reduction) of the annealed Ag₁₅Cu₈₅ foam is completed before the CO₂RR sets in.

4. Experimental Section

4.1 Chemical and Materials - Cu foils were purchased from Alfa Aesar (thickness 0.25 mm, purity $\geq 99.95\%$) and cut into pieces having dimensions of $\sim 8\text{ mm} \times 22\text{ mm}$. Prior to the electrodeposition of the CuAg foam, Cu foils were subjected to an electropolishing treatment in ortho-phosphoric acid (50w%, ACS grade, SigmaAldrich) using a two-electrode arrangement. A graphite foil thereby served as counter (cathode) and the Cu foil as working electrodes (anode), respectively. A constant potential difference of 2.0 V was applied between both electrodes for the duration of 2 min. During the electropolishing treatment, the Cu foil was gently moved in the phosphoric acid solution to remove oxygen bubbles formed upon electrode polarization on the Cu. The resulting surface morphology was characterized by means of atomic force microscopy (AFM, NanoSurf, see Fig. S11 in the supplementary information).

4.2 Electrolyte solutions – The standard plating bath for the bimetallic AgCu foam deposition was composed of 1.5 M H₂SO₄ (prepared from 96% H₂SO₄, ACS grade, Sigma-Aldrich) serving as supporting electrolyte, 20 mM CuSO₄ (Fluka), 2 mM Ag₂SO₄ (Sigma Aldrich, purity $\geq 99.5\%$), and 0.1 M Na₃C₆H₅O₇ · 2 H₂O (tri-sodium citrate di-hydrate, $>99.7\%$, Merck). For comparison purposes AgCu electroplating experiments were performed also in the additive-free bath. Furthermore also pure Cu catalysts were deposited from a plating bath in the absence of Ag containing 1.5 M H₂SO₄ (ACS grade, Sigma-Aldrich) and 20 mM CuSO₄ (Fluka). This deposition was carried out in the presence and the absence of 0.1 M Na₃C₆H₅O₇ · 2 H₂O (tri-sodium citrate di-hydrate, $>99.7\%$, Merck). See the *operando* Raman results in Fig. 5c and SEM images in Fig.S3 in the supplementary information.

The electrochemically active surface area (denoted hereinafter as ECSA) was estimated by means of cyclic voltammetry (CV) using di-methyl viologen dichloride (DMVCl₂) as reversible redox-probe following a protocol described previously [30]. Scan-rate dependent CVs were measured in aqueous 1 M Na₂SO₄ (ACS grade, Sigma-Aldrich) solution containing 10 mM DMVCl₂ (Sigma-Aldrich). The estimated ECSA of the bimetallic AgCu foams (as deposited) used herein amounts to 2.66 cm² (referring to 1 cm² geometric surface area). Note

that the ECSA further increases to 4.45 cm² after the thermal annealing. For details of the ECSA determination see Fig. S12 in the supplementary information.

All CO₂RR experiments were carried out in 0.5 M KHCO₃ (ACS grade, Sigma-Aldrich) electrolyte solutions saturated with CO₂ gas (99.999%, Carbagas, Switzerland). For blank experiments the same electrolyte was saturated with inert Ar gas.

4.3 Electrochemical experiments – The AgCu foam deposition was carried out in a glass-beaker containing 100 mL of the plating solution. For the galvanostatic deposition process, a nominal current density of $j = -3.0 \text{ A cm}^{-2}$ (referred to the geometric surface area of the Cu foil support electrode) was applied for 20 s. The three-electrode arrangement consisted of a leakless Ag/AgCl_{3M} reference electrode (RE, EDAQ), a bright Pt-foil (15mm x 5mm) serving as counter electrode (CE), and the Cu foil (substrate of the bimetallic AgCu foam) catalysts serving as working electrode (WE). The electrodeposition was performed in a face-to-face configuration (WE-CE) as indicated in Fig. S13 in the supplementary information. Note that the deposited bimetallic foam is sufficiently thick (> 15 μm) so that any contribution from the substrate to the resulting CO₂RR product distribution is excluded.

Electrodeposited bimetallic AgCu and the pure Cu foams were further activated by thermal annealing in air at 200° C for 12 h using a tube furnace (GERO Hochtemperaturofen GmbH, Germany).

All voltammetric and CO₂RR electrolysis experiments were carried out in a custom-built, air-tight glass-cell (H-type) described elsewhere [30].

Possible chloride ion cross-contaminations in the working electrolytes originating from the Ag/AgCl_{3M} reference electrode were monitored and excluded by ion exchange (IC) chromatography (Metrohm). Technical details of the CO₂RR product analysis based on online gas-chromatography and ion exchange (IC) chromatography were described elsewhere [30].

All potentials given herein are IR-corrected and referenced to the reversible hydrogen electrode (RHE) by using the following equation:

$$E_{\text{RHE}} (\text{V}) = E_{\text{Ag/AgCl(3M)}} (\text{V}) + 0.197 \text{ V} + (0.059 \text{ V} \times \text{pH})$$

4.4 Structural and compositional characterization – For the XRD analysis an STOE Stadi P system with a Cu Kα radiation source ($\lambda = 0.1540 \text{ nm}$, 40 mA) operated at 40 keV was used. XRD spectra were recorded in reflection mode (Bragg-Brentano geometry) in steps of 1° min⁻¹ with 2θ values ranging from 0 to 90 degrees. To exclude Cu diffraction peaks originating from the Cu foil support, the bimetallic foam was deposited onto a graphite substrate (99.8 %, Alfa Aesar, 0.13 mm thickness). The obtained XRD patterns were analyzed and compared to JCPDS (Joint Committee on Powder Diffraction standards) data of

polycrystalline Ag, Ag₂O, AgO, Cu, Cu₂O, and CuO (File No. 04-0783, 43-0997, 43-1038, 04-0836, 05-0667, 41-0254).

Elemental analysis of the bimetallic foams was carried out by means of inductively coupled plasma optical emission spectrometry (Agilent 5110 inductively coupled plasma optical emission spectrometry (ICP-OES)).

X-ray photoelectron spectroscopy (XPS) studies were carried out using a PHI VersaProbeII scanning XPS micro-probe (Physical Instruments AG, Germany) equipped with a monochromatic Al K α X-ray source operated at 24.8 W with a spot size of 100 μ m. Peak positions were referenced to the carbon C1s peak at 285.5 eV and curve fitting was performed using the Casa-XPS software.

The morphology of the bimetallic foams was characterized by means of Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) using a Hitachi S-3000 N Scanning Electron Microscope and a Noran SIX NSS200 energy-dispersive X-ray spectrometer. For the high-resolution identical location IL-SEM imaging a Zeiss DSM 982 instrument was used. In addition the mesoscopic surface morphology of the bimetallic AgCu foam was analyzed by means of a white light interferometry (Contour GT, Bruker).

For the transmission electron microscopy (TEM), the Ag₁₅Cu₈₅ catalyst was dispersed on a carbon coated TEM Au grid (200 mesh) after initial electrodeposition on a Cu foil substrate, followed by dispersion in absolute ethanol. For the HR-TEM imaging an FEI Tecnai F2 instrument was used with an accelerating voltage of 200 kV. Annular dark-field scanning transmission electron microscopy (ADF-STEM) in combination with EDX measurements were carried out using a FEI Titan Themis operated at 300 kV equipped with a SuperEDX detector.

4.5 Operando Raman spectroscopy - Raman spectroscopic measurements were performed using a LabRAM HR800 confocal microscope (Horiba Jobin Yvon). A large working distance objective lens (50 times magnification, 8 mm focal length) has been applied with a numerical aperture of 0.1 in order to focus a diode-pumped solid-state laser beam (excitation wavelength 632 nm, power 3 mW) on the sample. The Raman signal was collected in backscattering geometry using a home-made spectro-electrochemical cell (see Fig. S14 in the supplementary information) [74, 75].

4.6 Operando X-ray diffraction (XRD) - Operando XRD experiments (see Fig. S15 in the supplementary information) were performed at the European Synchrotron Radiation Facility ID31 high energy beamline. The 69 keV monochromatic X-ray beam was focused to the size of 5 x 20 μ m² (vertical x horizontal) at the sample position. The 2D XRD patterns were

collected with a Dectris Pilatus 2M CdTe detector. A custom made PEEK electrochemical cell consists of a Pt counter electrode, an Ag/AgCl (3 M KCl) reference electrode (EDAQ) and the sample working electrode supported on carbon paper electrically connected with an Au wire. The measurements were performed in CO₂-saturated 0.5 M KHCO₃ electrolyte and in grazing incidence geometry. The sample was first measured at OCP after the electrolyte was introduced to the cell and then at subsequently decreasing potentials in steps of 0.1 V. The resting time at each potential before the measurement was 2 min. The raw 2D diffraction patterns were radially integrated to the final 1D patterns using the pyFAI package [76]. The 1D patterns were further analyzed by integrating the characteristic peak intensities and fitting the Gaussian function to determine the FWHM.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.XXXX>

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Figure Captions

- Fig. 1: Morphological and compositional analysis of the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam deposited on a Cu foil substrate. a) White-light interferometric image of the bimetallic foam; b) and c) SEM analysis; d) ADF-STEM analysis of an individual dendrite; e) EDX mapping of the dendrite (Ag, Cu); f) spatial distribution of the Ag component; g) spatial distribution of the Cu component.
- Fig. 2: a) *Ex situ* XRD analysis of the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam, the annealed foam (12 h at 200°C), and the OD- $\text{Ag}_{15}\text{Cu}_{85}$ (after 1 h CO_2RR at -1.0 V vs RHE); b) and c) Corresponding XPS analysis of the bimetallic foam.
- Fig. 3: Structural and compositional analysis of the thermally annealed $\text{Ag}_{15}\text{Cu}_{85}$ (12 h at 200°C) metal foam; a) - c) HR-TEM micrographs of the annealed $\text{Ag}_{15}\text{Cu}_{85}$ foam; d) ADF-STEM micrograph of the annealed $\text{Ag}_{15}\text{Cu}_{85}$ foam; e) – h) EDX mapping of an isolated dendrite of the annealed $\text{Ag}_{15}\text{Cu}_{85}$ foam. The yellow square in panel g highlights the section shown in panel h. The inset in panel h depicts one-dimensional line-scans over the feature (exhibited from panel g).
- Fig. 4: *Operando* XRD experiment demonstrating the electro-reduction of Cu_2O in the annealed $\text{Ag}_{15}\text{Cu}_{85}$ foam as function of the applied electrode potential; a) Potential dependent XRD spectra; b) Integrated and normalized intensities derived from spectra shown in panel a (orange: integrated intensity of the Cu_2O (220) peak; red: integrated intensity of the Cu (200) peak; blue: integrated intensity of the Ag (220) peak).
- Fig. 5: a) **Representative** *Operando* Raman spectra of the thermally annealed $\text{Ag}_{15}\text{Cu}_{85}$ foam (12 h at 200°C) as function of the applied electrode potential; b) Enlarged section of the *operando* Raman spectrum of the thermally annealed sample at -0.2 V vs RHE focusing on the intramolecular stretching mode of chemisorbed CO demonstrating three different adsorption sites; c) Integrated intensities of Raman peaks assigned to the intramolecular CO stretching modes. **For comparison purposes also the results for the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam and for the pure Cu catalysts (deposited in the presence and absence of citrate and thermally annealed at 200°C for 12 h) are presented.**
- Fig. 6: Potential dependent CO_2RR product distribution for (a) the as deposited $\text{Ag}_{15}\text{Cu}_{85}$ foam and (b) **the (oxide-derived) OD- $\text{Ag}_{15}\text{Cu}_{85}$ foam catalyst after the annealing at 200°C .**
- Fig. 7: Proposed reaction scheme illustrating the coupling of the CO pathway and the C_2 hydrocarbon/alcohol reaction pathways.
- Fig. 8: a) Current density/time transient curve of the 100 h lasting catalyst stressing experiment at -1.0 V vs RHE (note the electrolysis current is normalized to the geometric surface area); b) **Corresponding CO_2RR product distribution focusing on the alcohols (ethanol and n-propanol).**
- Fig. 9: a) – d) Identical location (IL) SEM analysis of the catalyst before (panel a and b) and after (panel c and d) 72 h CO_2RR at -1.0 V vs RHE; e) – i) ADF-STEM micrograph and EDX mapping of a single dendrite after CO_2RR at -1.0 V vs. RHE. The yellow square in panel h highlights the section shown in panel i.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Graphical abstract