

Developing efficient electrocatalytic systems for
converting small molecules to valuable products
- From catalyst design to device implementation

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To see a thousand miles farther; Climb one more flight of the tower.

欲穷千里目，更上一层楼。

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List of abbreviations

Å	Angstrom
1D	One-dimensional
2D	Two-dimensional
Ar	Argon
AEM	Anion exchange membranes
AWE	Alkaline water electrolysis
ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectroscopy
C ₂ H ₄	Ethylene
C ₂ H ₅ OH, EtOH	Ethanol
C ₂ H ₆	Ethane
CCE	Controlled current electrolysis
CH ₃ CH ₂ CH ₂ OH	Propanol
CH ₃ OH	Methanol
CH ₄	Methane
CL	Catalyst layer
CO	Carbon monoxide
Co	Cobalt
CO ₂	Carbon dioxide
CPE	Controlled potential electrolysis
CsHCO ₃	Caesium bicarbonate
Cu	Copper
Cu ₂ O	Copper(I) oxide
CuO	Copper(II) oxide
D ₂ O	Deuterium oxide
DFT	Density functional theory
DMSO	Dimethyl sulfoxide
eCO ₂ RR	Electrochemical CO ₂ reduction reaction
EDX	Energy dispersive X-ray spectroscopy
EXAFS	Extended X-ray absorption fine structure
FE	Faraday efficiency
Fe	Iron

FID	Flame ionization detector
GC	Gas chromatography
GDE	Gas diffusion electrode
GDL	gas diffusion layer
H ₂	Hydrogen
HCOOH	Formic acid
HER	Hydrogen evolution reaction
HERFD-XANES	High energy resolution fluorescence detected XANES
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
Ir	Iridium
IrO ₂	Iridium(IV) oxide
KHCO ₃	Potassium bicarbonate
LGDL	Liquid/Gas diffusion layer
LSV	Linear sweep voltammetry
mA cm ⁻²	Current density
MEA	Membrane electrode assembly
MOF	Metal organic frameworks
N ₂	Molecular nitrogen
Ni	Nickel
NMR	Nuclear magnetic resonance
OER	Oxygen evolution reaction
OCP	Open circuit potential
OCV	Open circuit voltage
PEMWE	Proton exchange membrane water electrolysis
RHE	Reversible hydrogen electrode
RDE	Rotating disc electrode
Ru	Ruthenium
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
TCD	Thermal conductivity detector
TEA; NEt ₃	Triethylamine
UV/VIS	Ultraviolet-visible spectroscopy
XAFS	X-ray absorption fine structure

XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy

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1. Introduction

The climate crisis, environmental imperatives, and the demands of modern societies collectively drive the need for innovative technologies to efficiently harness and store renewable energy, such as wind and solar power.¹ The electrocatalytic energy conversion including the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), the CO₂ and CO reduction reaction (eCO₂RR, eCORR), and nitrogen reduction reaction (NRR) may offer a sustainable solution, converting those small molecules to value-added chemicals, sustainable fuels, and feedstocks.^{2, 3} Dating back to the 1970s, eCO₂RR research reveals complex reaction mechanisms that lead to a diverse range of products. The reaction process is coupled with multiple proton and electron transfer steps, influenced by the nature of catalyst materials.⁴ CO and HCOOH, the C₁ products generated via two-electron/proton transfer, are considered as the “low hanging fruits” for their relatively straightforward mechanism of formation.^{5, 6} Beyond two-electron reduction, selective eCO₂RR to multi-carbon products (exp. C₂H₄ and C₂H₅OH)^{7, 8} is of particular interest, as those serve as the more valuable base chemicals for industry. The critical challenge in this conversion lies in the electrochemical C-C coupling of adsorbed eCO₂RR intermediates, particularly under mild conditions.⁹ Although prior studies have identified metallic Cu as a promising candidate for C-C coupling,^{10, 11} multiple coexisting active sites should be taken into account under operational conditions, such as various crystal facets, steps, grain boundaries, edges, corners, and defects, resulting in complex structure-reactivity relationships and intricate reaction pathways.¹²

Heterogenized molecular motifs with well-defined active sites represent a potential alternative as catalysts for eCO₂RR. Their precisely defined structures could be tuned for optimizing the catalytic performance, offering opportunities to study reaction mechanisms and the structure-activity relationship.¹³ For example, coordination compounds with distinct ligands have shown significant eCO₂RR selectivity to C₁ products including CO,¹⁴ HCOOH,¹⁵ CH₄,¹⁶ as well as CH₃OH.¹⁷ More recently, Cu-based molecular complexes delivered multi-carbon products during eCO₂RR, highlighting their capability for C-C coupling. Despite these achievements, major challenges remain in the rational design of molecular catalysts for optimal activity and stability, and in the mechanistic understanding of structure-reactivity relationships. To address these, the focus of this work is placed on design, synthesis, characterization, and performance screening of a series of molecular Cu catalysts for effective C-C coupling.

Beyond the cathodic eCO₂RR, an efficient anodic process is essential for the overall electrolyzer operation. The OER stands out as a green approach, leading to O₂ as eCO₂RR by-product and supplying electrons and protons to the cathode.¹⁸ In recent years, fundamental investigations and technological development have progressed significantly in electrocatalyst design and electrolyzer implementation.

The overarching goals are to enhance cost-efficiency, performance, and long-term stability to meet commercial requirements.¹⁹ In this scenario, the development of low-noble-metal and/or non-noble-metal-based electrocatalysts based on inexpensive raw materials, as well as their utilizations in electrolysis systems (electrolyzer device and operation parameters) are of critical importance for enabling sustainable and scalable performance.¹⁹⁻²²

This dissertation focuses on the development of effective electrocatalysts eCO₂RR, encompassing both catalyst design and device implementation. In the catalyst development phase, a series of Cu(II)-phenanthroline-based molecular catalysts was synthesized and tested, achieving over 70% Faradaic efficiency toward C₂₊ products. For device-level implementation, CoNiFe metal oxides were employed as model catalysts for alkaline OER. Within this frame, the device components were systematically optimized to improve the protocol for electrode preparation, catalyst layer formulation, and the operation within the zero-gap membrane electrode assembly (MEA) electrolyzer, achieving industrially relevant current densities for both water electrolysis and eCO₂RR. For better mechanistic understanding, two *in situ* X-ray absorption spectroscopy (XAS) spectroelectrochemical cells were designed, which provide fundamental insights into dynamic phase evolution of Cu molecular catalysts under high current eCO₂RR conditions.

1.1 Basics of electrocatalytic CO₂ reduction reaction (eCO₂RR) on molecular catalysts

In this chapter, the basics of eCO₂RR will be discussed. As cathodic reaction, the eCO₂RR requires combined electron proton transfers and is coupled with anodic water oxidation (OER, eq. 1), whereas the HER (eq. 2) occurs as a cathodic side reaction.²³



Depending on the catalyst and the conditions, eCO₂RR can lead to various products. The standard equilibrium potentials (E^0) of the individual process are summarized as follows. Several pathways are occurring in parallel, leading to products distributions (see in Figure 1).⁸ These products can be used as fuels and value-added chemicals. Furthermore, the generated CO₂ emission can be re-cycled for CO₂ conversion reaction and close the loop for carbon neutrality.



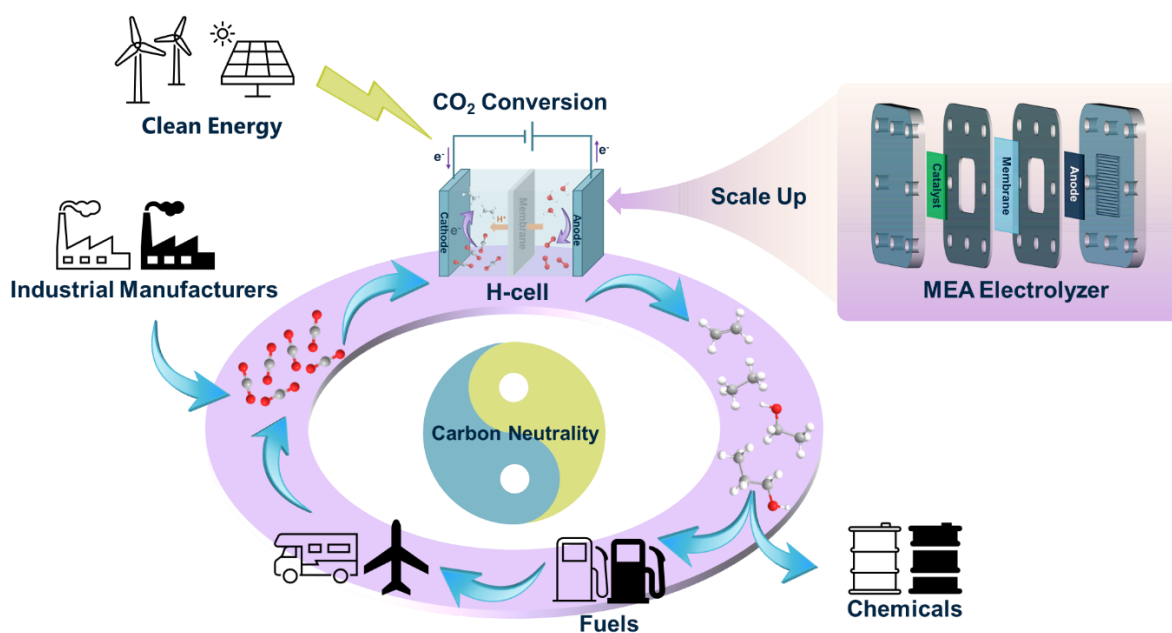
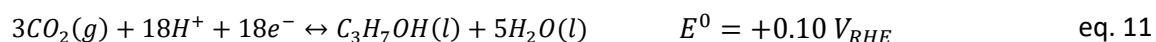
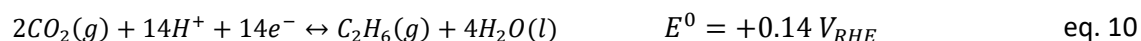
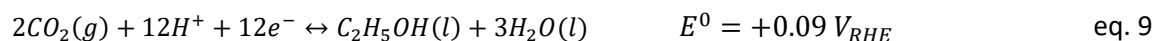
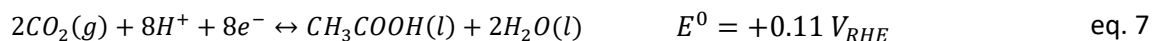


Figure 1. Concept of integrating eCO₂RR in closed carbon cycles.

To date, C₂₊ products have attracted much attention due to the market size, high value and increasing demand. C₂H₄ is a central building block for down-stream processes such as polyethylene production, the most widely used plastic globally.²³ C₂H₅OH can be used as an alternative sustainable fuel with high volumetric energy density for transportation.²³ Notably, as shown in Figure 2, Cu is unique metal catalyst that can produce a number of hydrocarbons, aldehydes and alcohols requiring more than two electrons transfers. Thus, it has ability to bind and further reduce C₁ intermediates and advance the C-C coupling process.²⁴ However, the product distribution is highly sensitive toward the structure of the Cu catalysts. In recent years, researchers have focused on investigation of Cu catalysts with various of active sites, including crystal facets, steps, grain boundaries, edges, corners and defects.⁸ However, the complex surface structure leads to difficult and unclear reaction mechanisms and structure-reactivity relationships. A further problem is pronounced HER as side reaction.

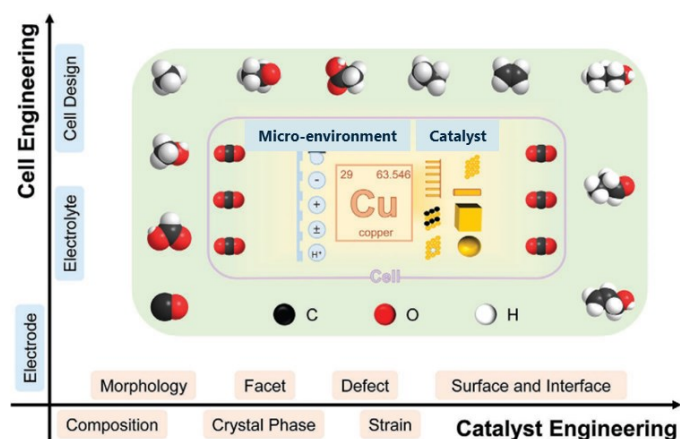


Figure 2. Catalyst and cell engineering for modulating the eCO₂RR performance of Cu-based catalysts. Figure was adapted from ref 8, with copyright permission from John Wiley and Sons.

As a crucial step for forming C₂ products during eCO₂RR, the C-C coupling process has been investigated in detail on metallic Cu surface via experimental and theoretical methods in recent years. As shown in Figure 3, the Sargent group summarized the possible pathways for multi-C products formation.²⁵

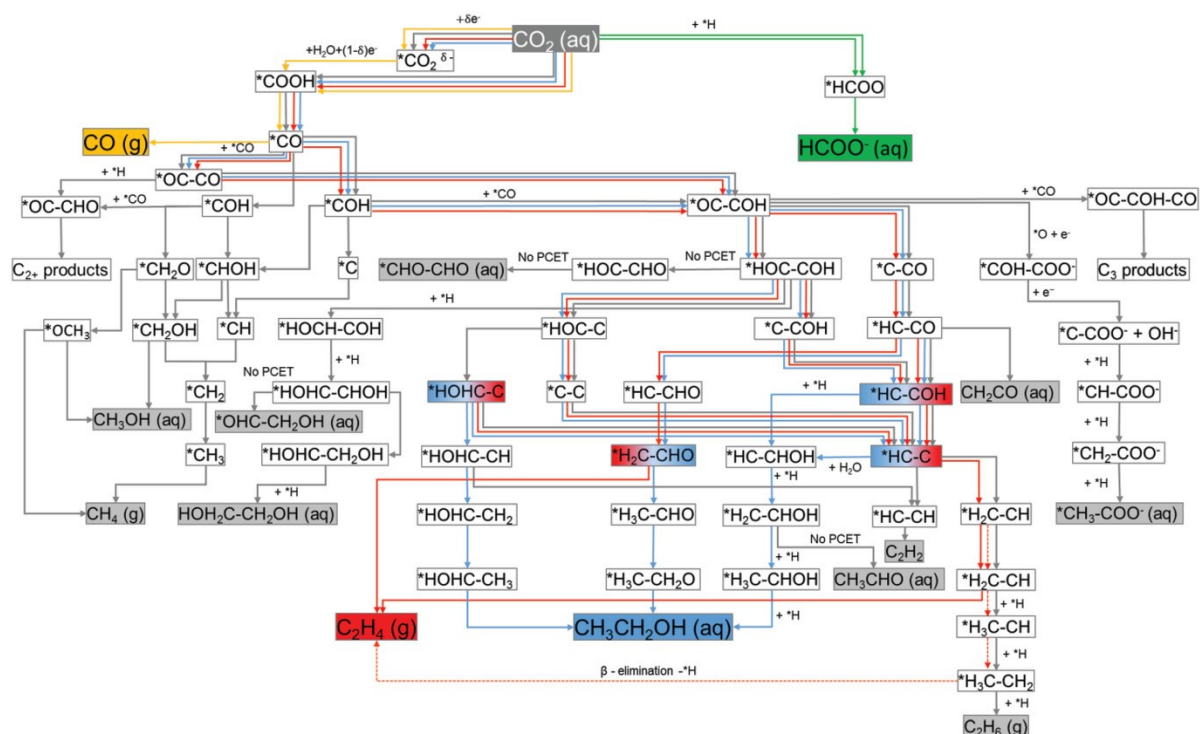


Figure 3. Summary of pathways towards eCO₂RR products. The figure was reproduced from ref 25, with copyright permission from John Wiley and Sons.

Compared to metallic catalysts with their complex product distribution, Cu molecular complexes offer well-defined active sites and can thus serve as alternatives in both homogeneous and heterogeneous eCO_2RR .¹³ The structure of molecular catalysts can be tuned for optimizing catalytic performance and

to further facilitate studies of the reaction mechanisms.¹⁴ Recently, a series of Cu-based complexes have demonstrated significant improvement for eCO₂RR to C₂ products, indicating that Cu molecular catalysts enable the coupling of C₁ intermediates toward C₂ product formation during eCO₂RR.³ Figure 4 shows four main pathways reported for Cu molecular complexes, in which CO or adsorbed *CO species derived from *COOH is considered as the key intermediate within the coupling process.²⁶⁻²⁹ Spectroscopic and computational studies have suggested the presence of further reduced and protonated intermediates including *CHO and *CH₂, for both metallic Cu and molecular Cu catalysts.³⁰ As shown in R1 to R3 in Figure 4, two of key intermediates may combine with each other in the following C-C coupling process on Cu molecular complex.^{30, 32, 33} More recently, a mechanism (R4 in Figure 4) is proposed on molecular assembly of a triphenylphosphine Cu complex that an unusual oxygen binding configuration occurs resulting in the formation of an oxalate intermediate and undergoes reductive deoxygenation to yield C₂H₄.³⁴

Several studies have suggested that the distance of Cu active sites is a crucial parameter in the formation of C₂ products during C-C coupling on Cu molecular catalysts.³⁵⁻³⁷ In the following discussion, Cu complexes are classified according to three categories: mono-, bi- and multi-nuclear Cu complexes; as well as Cu-based metal organic frameworks (MOF). The widely accepted mechanisms of C-C coupling on metallic Cu surfaces are on-surface recombination (a direct Langmuir-Hinshelwood-type mechanism) and spillover processes including on-surface diffusion or release-and-resorption of a C₁ intermediate to a nearby secondary intermediate.^{23, 38} These mechanisms are announced to play a role also for molecular systems.

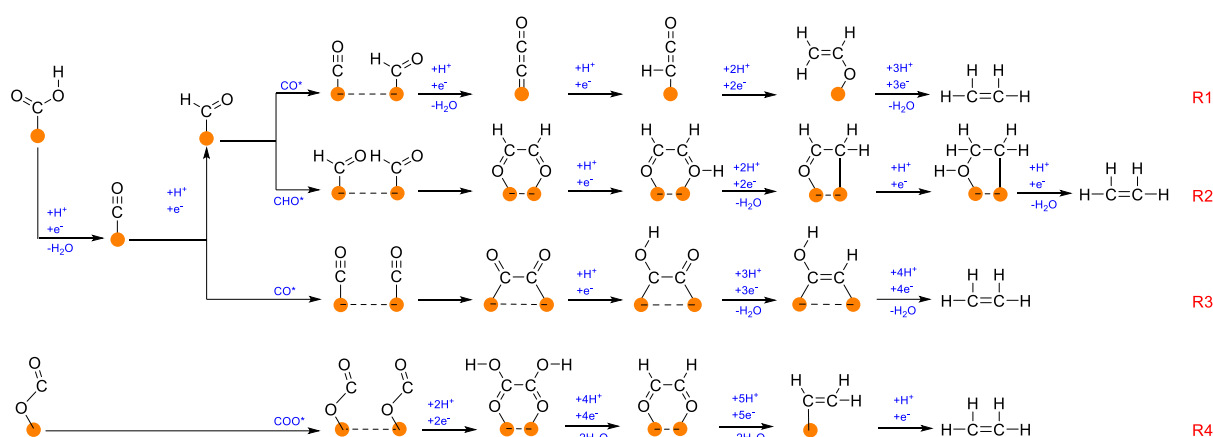


Figure 4. Selected mechanisms for C-C coupling (R1 to R4) on molecular Cu catalysts proposed in the literature. Orange circles symbolize vicinal Cu sites.^{30, 32-34}

To design and develop promising molecular catalysts for reductive CO₂ coupling, the criteria should be kept in mind: i) the capability to convert CO₂ into the key *CO intermediate; ii) a suitable binding

strength for stabilizing C_1 intermediates; and iii) a suitable distance of active sites to facilitate reductive CO_2 coupling via different pathways.

1.1.1 Mononuclear Cu complexes

In the past ten years, molecular Cu complexes have been investigated as promising catalysts for eCO_2RR , with some believed to contain mononuclear active sites. Numerous mononuclear Cu complexes have proven as excellent catalysts for CO products in eCO_2RR .¹⁴ However, recent studies on heterogenized mononuclear Cu complexes have demonstrated the formation of not only deeply reduced C_1 products like CH_4 , but also C_2 products like C_2H_4 , indicating the potential to catalyze the C-C coupling during eCO_2RR (Figure 5, **1-A** to **1-G**). Given the critical role of an appropriate $Cu\cdots Cu$ distance in C-C coupling, these results are particularly unexpected.

Wang's group was investigated Cu-porphyrin-based structure **[1-A]** (Figure 5) which serves as a notable example of a mononuclear system capable of inducing the formation of C_2 products.³⁹ By using this catalyst deposited onto a carbon fibre as working electrode, it reaches partial current densities of 13.2 mA cm^{-2} for CH_4 and 8.4 mA cm^{-2} for C_2H_4 , respectively. An absence of metallic particles was revealed from post-electrolysis (transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS)) analysis of the working electrode, supporting the hypothesis that the Cu(I)-porphyrin molecule is responsible for C_2H_4 formation. A similar complex **[1-B]** (Figure 5) with hydroxy groups positioned differently, studied by Sun et al., is a more recent work that can also yields promising results, although selectivity shifts in favour of CH_4 (51% FE for CH_4 at -1.5 V vs. RHE , 12% FE for C_2H_4).⁴⁰ It remains unclear whether the change in selectivity arises from the positioning of the OH groups and/or differences in electrolysis conditions. Later, Lan et al. investigates the influence of 2-, 3-, and 4-pyridyl substituents in comparison to the tetraphenyl-substituted parent compound **[1-C]** (Figure 5).⁴¹ As with **[1-A]** and **[1-B]**, CH_4 was generated as the main product, since the presence of pyridine substituents significantly improved CH_4 evolution, achieving up to 62% Faradaic efficiency when the pyridine nitrogen was positioned at the 3-position. Quantum chemical calculations suggested that the binding energy of the $^*COOH$ intermediate, driven by intermolecular hydrogen-bonding interactions contributed to the observed trend. Further, Kusama et al. investigated a mononuclear Cu phthalocyanine complex **[1-D]** (Figure 5), emphasizing the critical role of catalyst crystallinity.⁴² Crystalline **[1-D]** achieved a Faradaic efficiency of 25% for C_2H_4 , whereas the amorphous **[1-D]** produced negligible C_2H_4 . This result suggests that the optimal intermolecular $Cu\cdots Cu$ distance is achieved within crystalline rather than within the amorphous material.

Given these promising results, it is crucial to emphasize the identification of genuine active centers and the actual catalyst structure under operating conditions. *In situ/operando* spectroscopic

techniques are useful tools for tracking catalyst evolution during eCO₂RR. In a study by Wang and co-workers, XAS was used under eCO₂RR conditions to monitor the reversible transition between coordinated Cu ions and Cu nanoparticles.⁴³ Porphyrin-based Cu complexes may also have similar *in situ* phase transitions as those studies only reported characterizations conducted before and after eCO₂RR. Recently, Cao and co-workers reported that Cu salophen species [1-E] (Figure 5) can achieve over 100 mA cm⁻² partial current density for C₂H₄ when deployed on a gas diffusion electrode.³³ The same group investigated the Cu salan complex [1-F] (Figure 5), which exhibited comparable performance, achieving a 40 mA cm⁻² C₂H₄ partial current density.⁴⁴

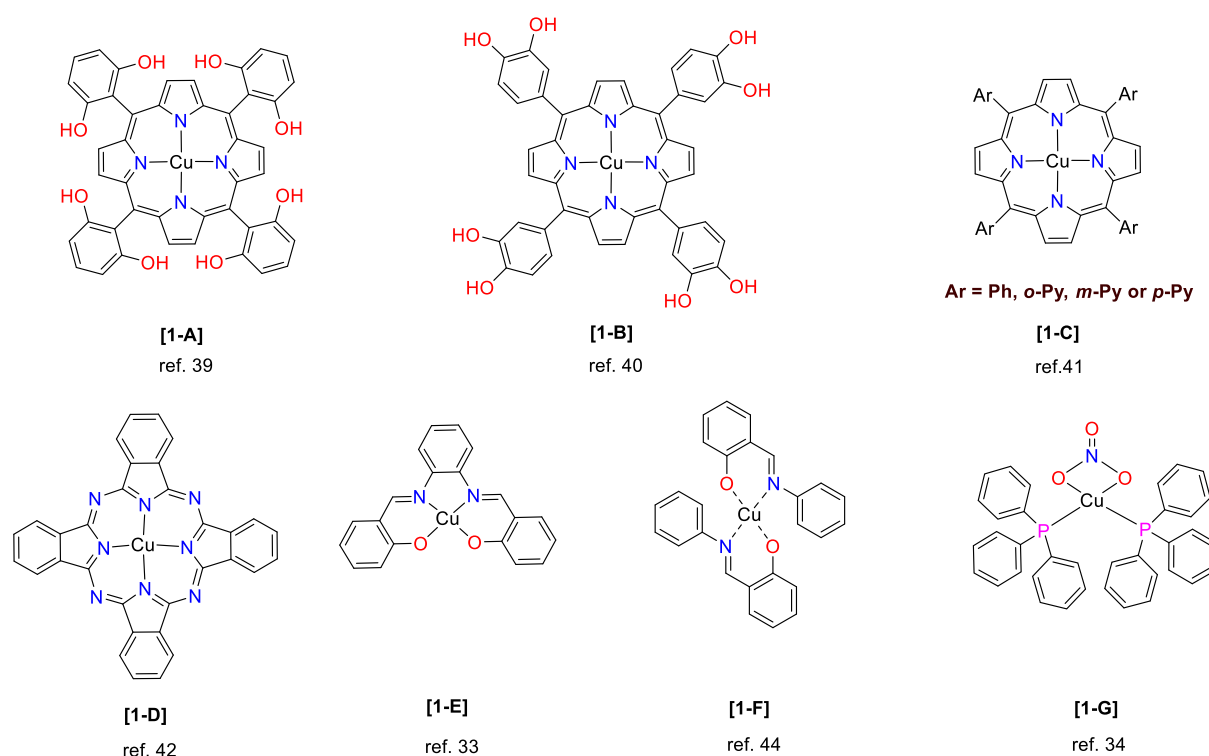


Figure 5. Mononuclear Cu catalysts for eCO₂RR reported in the literature.

A further study by Chen et al. reported another crystalline assembly of triphenylphosphine Cu complex [1-G] (Figure 5) as a catalyst precursor for eCO₂RR.³⁴ With a close 7.9 Å Cu...Cu distance in the rod-shaped nanocrystals, [1-G] exhibits an excellent *FE* of C₂ products (C₂H₄ up to 65% and EtOH up to 13%). *In situ* extended X-ray absorption fine structure (EXAFS) analysis confirmed the stable crystalline assemble during electrolysis. Based on the relatively long Cu...Cu distance, an oxalate intermediate (*OOC-*OOC) coupling process (Figure 4, R4) was proposed by the authors.

1.1.2 Bi- and multinuclear Cu complexes

Given the progress of mono Cu complexes discussed above, either intermolecular Cu...Cu dual sites or *in situ* formed CuO_x clusters can serve as active sites for that electrochemical C-C coupling on mononuclear Cu molecular catalysts. In theory, if two or more Cu sites exist in a single molecular

framework, the electrochemical C-C coupling process could be enhanced. However, precise controlling and preserving the desired Cu...Cu configuration during electrode preparation and the electrochemical reaction remains a significant challenge.

The advantage of the bidentate 1,10-phenanthroline (phen) ligand is the strong coordination with Cu ions serving as a promising candidate in preparing Cu molecular complexes. First work of my Ph.D study developed for phen-based binuclear Cu molecular catalyst **[2-A]** (Figure 6) shows promising eCO₂RR performance, achieving a 62% *FE* toward C₂ products at -1.25 V vs. RHE, only small amounts of H₂ formed.³⁵ With a short a Cu...Cu distance of 2.93 Å, the bimetallic motif within the complex was suggested as the active site for electrochemical C-C coupling. More details are shown in section 3.1. Complex **[2-B]** (Figure 6), reported by Liao et al., is a conductive binuclear Cu molecular due to a two T-shaped coordinated Cu⁺ ions linked by a direct metal-metal bond measuring 2.62 Å.³⁶ Based on *in situ* attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), a pathway involving the *COCHO intermediate was proposed for C₂H₄ formation (R1 route in Figure 4).

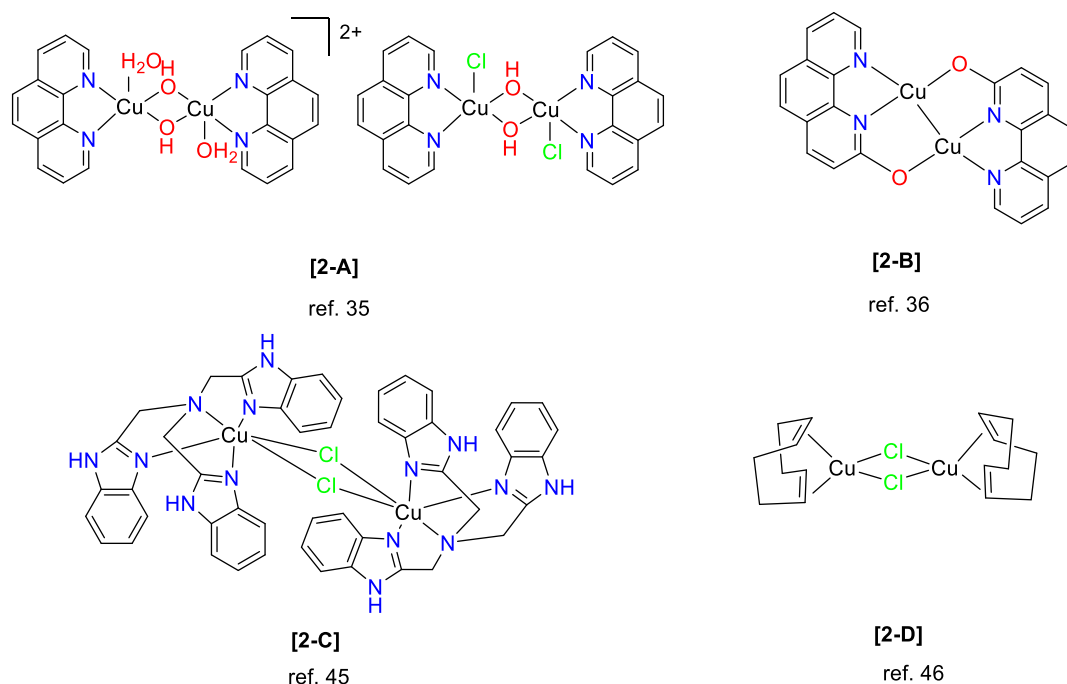


Figure 6. Binuclear Cu catalysts for eCO₂RR reported in the literature.

A study by Nam and co-workers showed that the binuclear Cu complex **[2-C]** (Figure 6) exhibits a high C₂H₄ selectivity (*FE* = 44%) but undergoes structural evolution during electrolysis, indicating that the true active sites are *in situ*-formed CuO_x clusters.⁴⁵ In a recent study by Fan and colleagues, the 1,5-cyclooctadiene (COD) ligand was utilized to synthesize binuclear complex **[2-D]** (Figure 6).⁴⁶ The complex exhibited remarkable eCO₂RR performance under acidic conditions (pH = 1), achieving a *FE* of 46% for CH₃CH₂OH and a total *FE* of 91% for C₂₊ products. Post-electrolysis analysis, including scanning

transmission electron microscopy (STEM) and both *in situ* and *ex situ* XAS, suggested that the Cu-dimer structure serves as the active site.

Complex **[3-A]** (Figure 7) was described by Lan and coworkers as trinuclear Cu catalyst.³⁰ Depending on the type of different counter anion (Cl^- , Br^- , and NO_3^-), complexes of type **[3-A]** showed different performance in eCO_2RR , in which the bromide-containing complex as the optimal one can reach a *FE* for C_2H_4 (*FE*=55%) at high current densities in a flow cell. Since the formation of CuO_x was not observed from *in situ* Raman spectroscopy, the shortest $\text{Cu}\cdots\text{Cu}$ distance of 3.3 Å in the crystal structure appears to be responsible for electrochemical C-C coupling and a pathway via $^*\text{CHO}$ intermediates (R2 route in Figure 4) was proposed by the authors. Recently, octanuclear complex **[3-B]** (Figure 7) was reported as an eCO_2RR catalyst, synthesized using the 4,7-dimethoxy-1,10-phenanthroline ligand. The ladder-like framework with $\text{Cu}\cdots\text{Cu}$ distances near 3 Å, exhibits an enhanced robustness and water insolubility compared to our previous catalyst **[2-A]**. Remarkably, **[3-B]** as a promising complex developed from my second work achieved a good eCO_2RR performance in which the *FE* of C_{2+} products reached up to 70% at 200 mA cm^{-2} current density in an MEA electrolyzer. To investigate the true active site, we performed *in situ* X-ray absorption fine structure (XAFS) and high-energy-resolution fluorescence-detected XANES (HERFD-XANES) analysis under both H-type and MEA-type spectroelectrochemical cell operating conditions, confirming the stability of Cu active centers in the kinetic region and a reversible dynamic oxidation state evolution of Cu sites under industrially relevant current densities. More details can be found in section 3.2.

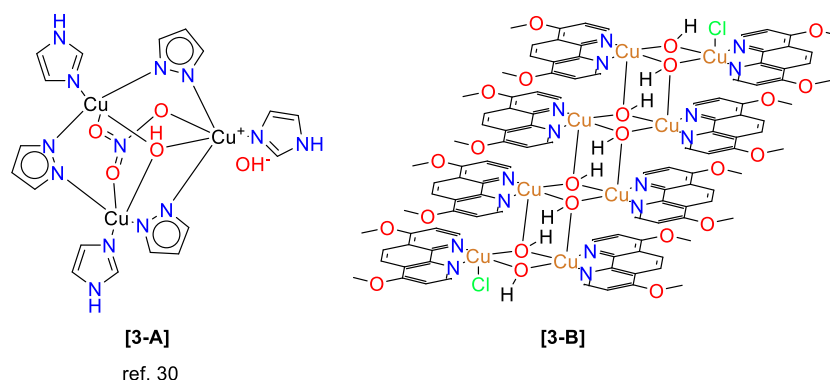


Figure 7. Multi-nuclear Cu catalysts for eCO_2RR reported in the literature.

1.1.3 Cu-based metal organic frameworks (MOF)

Similar to molecular catalysts, MOF-derived catalysts utilize metal-coordinative nodes as active sites. The potential advantages of MOFs are as follows:

- i) extended 3D structures based on molecular repeat units with well-defined active centers;
- ii) high active surface areas;

iii) densely packed active sites with uniform Cu...Cu distance.

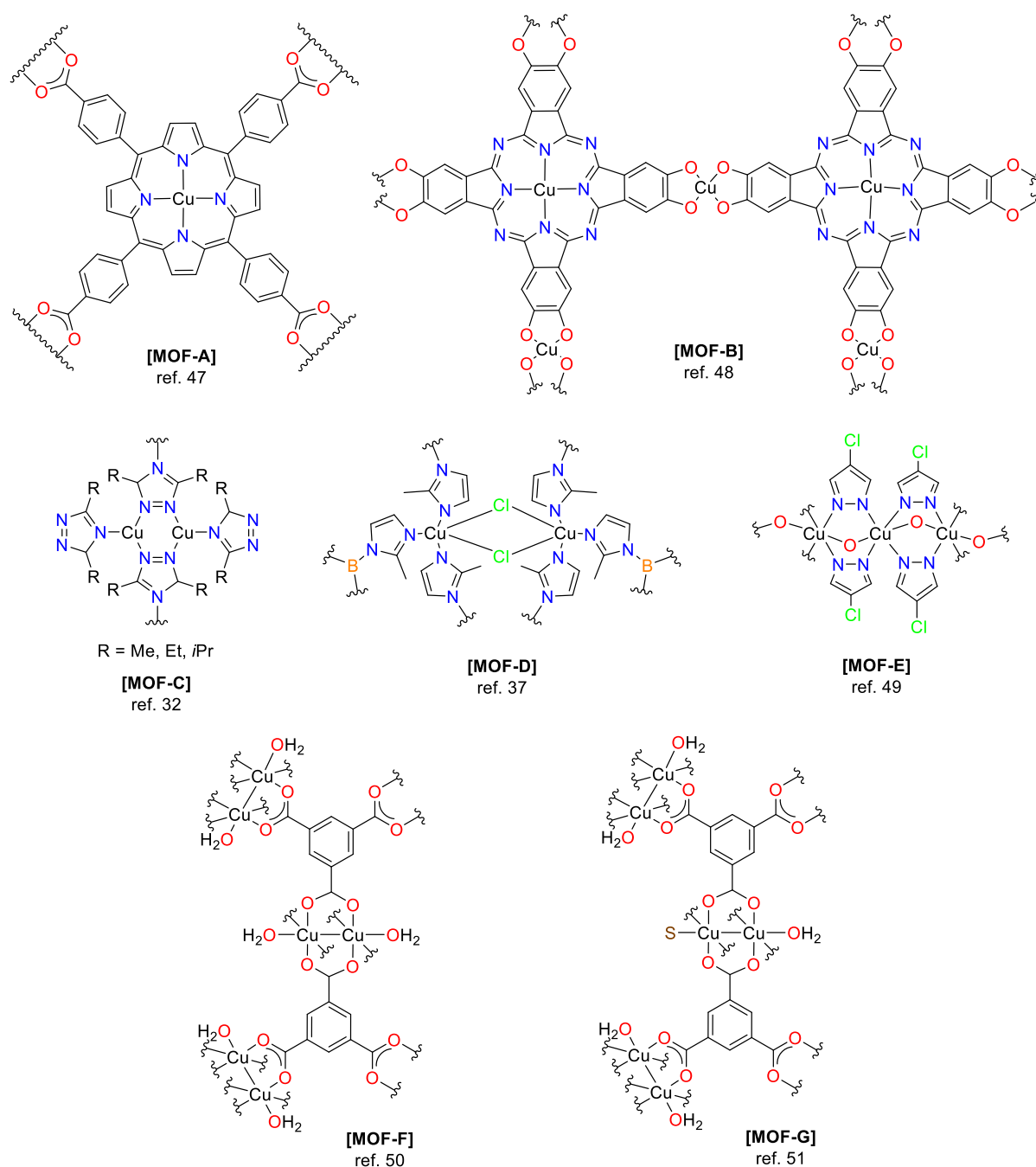


Figure 8. Summary of MOF-based Cu catalysts for eCO₂RR reported in the literature.

These properties potentially enhance electronic conductivity and facilitate reductive C-C coupling. In this context, **[MOF-A]** (Figure 8) studied by Peng et al. is derived from the tetrakis(4-carboxyphenyl)porphyrin ligand. It exhibits a promising eCO₂RR performance in which the *FE* for C₂H₄ is up to 53%, whereby impregnation of the MOF with Au nanoneedles enhanced both conductivity and catalyst performance.⁴⁷ Also, the structural stability of **[MOF-A]** was demonstrated by *operando* XAS analysis. The authors indicated that Au nanoneedles benefits both selectivity toward C₂H₄ and catalyst

stability. [MOF-B] (Figure 8) was reported by Qiu et al. and consists of hydroxylated Cu phthalocyanine and square-planar CuO_4 nodes.⁴⁸ [MOF-B] exhibits a promising selectivity toward C_2H_4 with the *FE* for C_2H_4 reaching 50% at -1.2 V vs. RHE at a current density of 7.3 mA cm^{-2} . Given the *in situ* ATR-FTIR results and density functional theory (DFT) calculations, the authors suggest that *CO spill-over to a *CHO intermediate is the C-C coupling step.

Recently, not only macrocyclic ligands turned out as promising candidates for MOF-based eCO_2RR catalysts, but smaller link nodes like azoles have also attracted attention for synthesizing MOF catalyst with high selectivity for C_2H_4 during eCO_2RR . A recent report by Zhang and co-workers indicated that the performance for eCO_2RR of 1,2,4-triazole-based Cu catalyst [MOF-C] (Figure 8) is impacted by substituent R (R = Me, Et, n-Pr) on the ligand.³² The ethyl-functionalized [MOF-C] as the optimized catalyst exhibited the best selectivity for C_2H_4 with a *FE* of 51% by using glassy carbon as the working electrode in 0.1 M KHCO_3 electrolyte. The shortest Cu...Cu distance of 3.4 Å was proposed to be responsible for the coupling process. Based on DFT calculations, C-C coupling via $\text{CO}^*\text{-CHO}^*$ and $\text{CO}^*\text{-CO}^*$ intermediates (corresponding to routes R1 and R3 in Figure 4) is suggested. [MOF-D] (Figure 8)³⁷ with two-dimensional (2D) nanosheet structure were synthesized by using 2-methyl imidazole exhibiting a low selectivity for C_2H_4 during eCO_2RR . [MOF-E] (Figure 8)⁴⁹ with one-dimensional (1D) chain structure synthesized by using 4-chloropyrazole ligands leading to high *FEs* for C_2H_4 of 60% during eCO_2RR . Trimesic acid (benzene-1,3,5-tricarboxylic acid) is a well-known ligand for designing Cu-based MOFs in recent years. The corresponding HKUST-1 type [MOF-F] (Figure 8) with covalent Cu-Cu bonds showed an excellent eCO_2RR performance with the 45% *FE* of C_2H_4 and a 200 mA cm^{-2} partial current density for C_2H_4 in a flow system.⁵⁰ Based on the structure of [MOF-F], a sulfur modified [MOF-G] (Figure 8) catalyst was recently developed, showing improved C_2H_4 selectivity with *FE* of 60%.⁵¹ However, the *in situ* XAS analysis showed that the covalent Cu-Cu bond is not stable and that Cu clusters are formed and serve as the active sites during eCO_2RR .

In summary, molecular catalysts as well as MOF-derived catalysts show similar active center configuration and C-C coupling process at the atomic level. With extended structures, MOFs may offer more active centers in a uniform distribution and improved conductivity during operation. However, the main challenges related to the stability and real active sites during eCO_2RR still need to be solved both in molecular and MOF-derived catalysts.

1.2 Fundamentals of the oxygen evolution reaction

1.2.1 Principles and significance

To further enhance the efficiency of cathodic eCO_2RR in the full electrolyzer, advancing the anodic OER presents an efficient approach to lower the cell voltage. To date, the development of the OER has

predominantly been accomplished within the context of water electrolysis, aiming at large-scale hydrogen production from renewable energy source.¹⁹ This approach can be divided into alkaline water electrolysis (AWE) and proton exchange membrane water electrolysis (PEMWE) based on the electrolyte used. In this chapter, the basics of AWE will be discussed. Compared with the widely used PEMWE, the AWE exhibits the following advantages:²¹

- i) Cost-effective and non-precious metal-based materials serve as promising catalysts under alkaline environment, offering long-term stability and electrochemical efficiency;
- ii) Corrosion issues can be significantly reduced under alkaline conditions.
- iii) The use of perfluorinated membrane can be avoided.

MEA zero gap electrolyzers enable water electrolysis for application at industrial scale. As shown in Figure 9, the MEA is composed of an ionically conductive membrane, a liquid/gas diffusion layer (LGDL), and a cathode/anode catalyst layer (CL) where noble metal-based catalysts are commonly used.²¹ The cathodic HER and anodic OER reaction under alkaline condition are as follows:



The equilibrium cell voltage (U^0) is calculated by eq. 14 and the actual cell voltage (U_{cell}) is composed of U^0 , overpotentials (η) from OER and HER, and ohmic losses (I is the current, and R_{cell} is the overall cell resistance).

$$U^0 = E_{OER}^0 - E_{HER}^0 = 1.23 V \quad \text{eq. 14}$$

$$U_{cell} = U_0 + \eta_{HER} + \eta_{OER} + IR_{cell} \quad \text{eq. 15}$$

Therefore, to minimize the η when applied in a MEA electrolyzer, it is necessary to develop effective OER/HER electrocatalysts, electrolyzer configurations, and operation parameters.

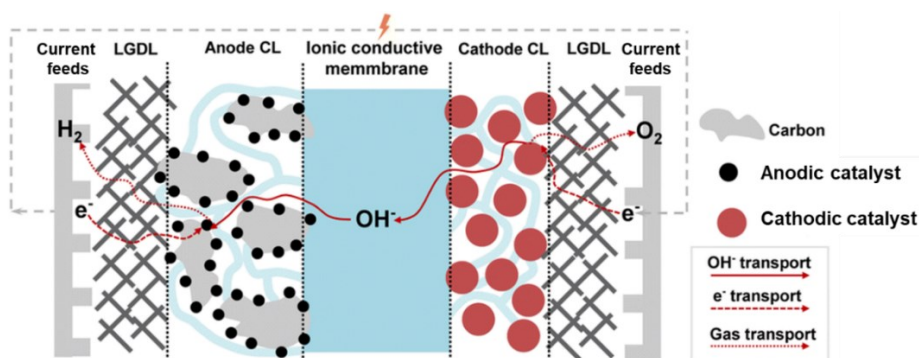


Figure 9. The MEA zero gap electrolyzer for AWE. The figure was adapted from ref 21, with copyright permission from Royal Society of Chemistry.

1.2.2 Oxygen evolution reaction (OER) catalysts for alkaline water electrolysis

Due to high cost and low natural abundance of noble metal-based catalysts, the development of cost-effective and earth abundant non-noble metal catalysts such as Co, Ni, and Fe with high active surface area and enhanced stability is of high importance.¹⁸ As indicated in Figure 10, recent studies have shown that transition metal-based catalysts with more than two metals can significantly reduce the overpotential compared with that of single metal catalysts. By involving different metals, the catalytic performance can be significantly improved by tuning the adsorption energy and electronic structure of the catalysts.⁵² The reported catalysts exhibit broad variations in their synthesis procedures, including high-temperature pyrolysis, atomic layer deposition, electrochemical deposition techniques, and incipient wetness impregnation.²

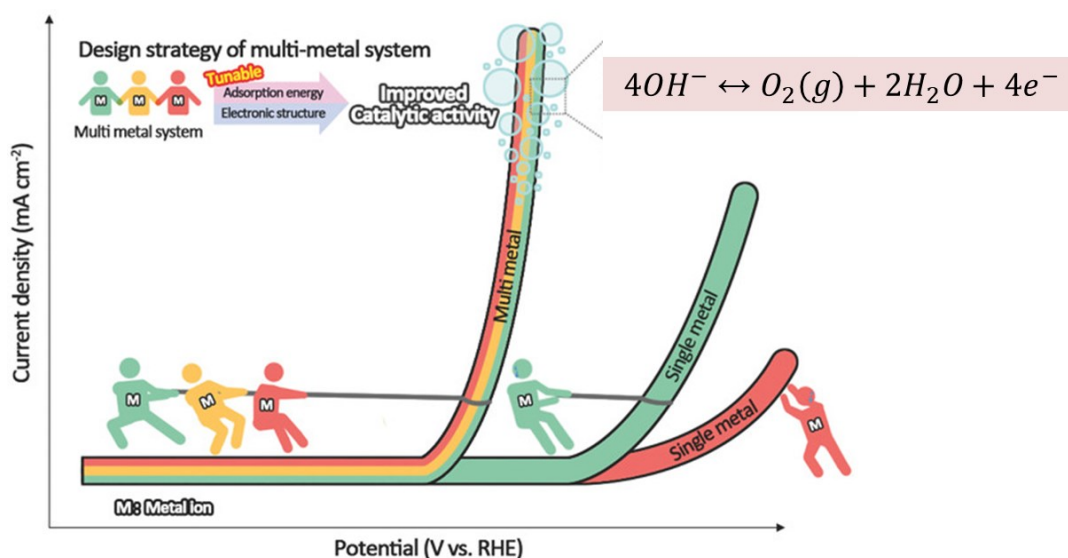


Figure 10. Strategies for the development of efficient multi-metal catalysts for the OER. The figure was adapted from ref 52, with copyright permission from John Wiley and Sons.

Among these catalysts, mixed oxides of Co, Ni, and Fe (CoNiFeO_x) exhibit promising OER performance which can be explained by a volcano-type relationship between activity and the binding energies of catalysts with oxygen intermediates, where mixed oxides of Co, Ni, and Fe are positioned near the peak of the volcano curve. Moreover, mixed metal systems have also been used to improve the stability of catalysts. For example, amorphous CoNiFeO_x shows the potential to enhance mechanical and electrochemical stability because of the disordered internal structure.⁵² However, despite significant advancements, poor electrical conductivity and limited long-term stability remain major challenges in developing highly efficient OER electrocatalysts for AWE. For this purpose, the electrolyzer assembly protocol and operation parameters could bring new opportunities.

1.3 Experimental methods

1.3.1 Testing platform and electrochemical methods

In the course of the PhD studies, a testing platform and protocol was developed for eCO₂RR research, as shown in Figure 11a, for both divided H-type cell (Figure 11b) and MEA electrolyzer (Figure 11c) configurations. The divided H-type cell is a three-electrode system (WE, CE, and RE marked in Figure 11b), and CO₂ is continuously purged through the catholyte (WE chamber) for reaction. The MEA electrolyzer is a two-electrode system, and the cathode and anode chambers were separated using an ion exchange membrane. The anolyte was circulated through the anode chamber with a certain flow rate, while humidified CO₂ was purged through the cathode chamber for reaction. One N₂ bleeding flow with defined flow rate was injected into the product stream as flow rate internal standard for products analysis (detailed in eq. 17).

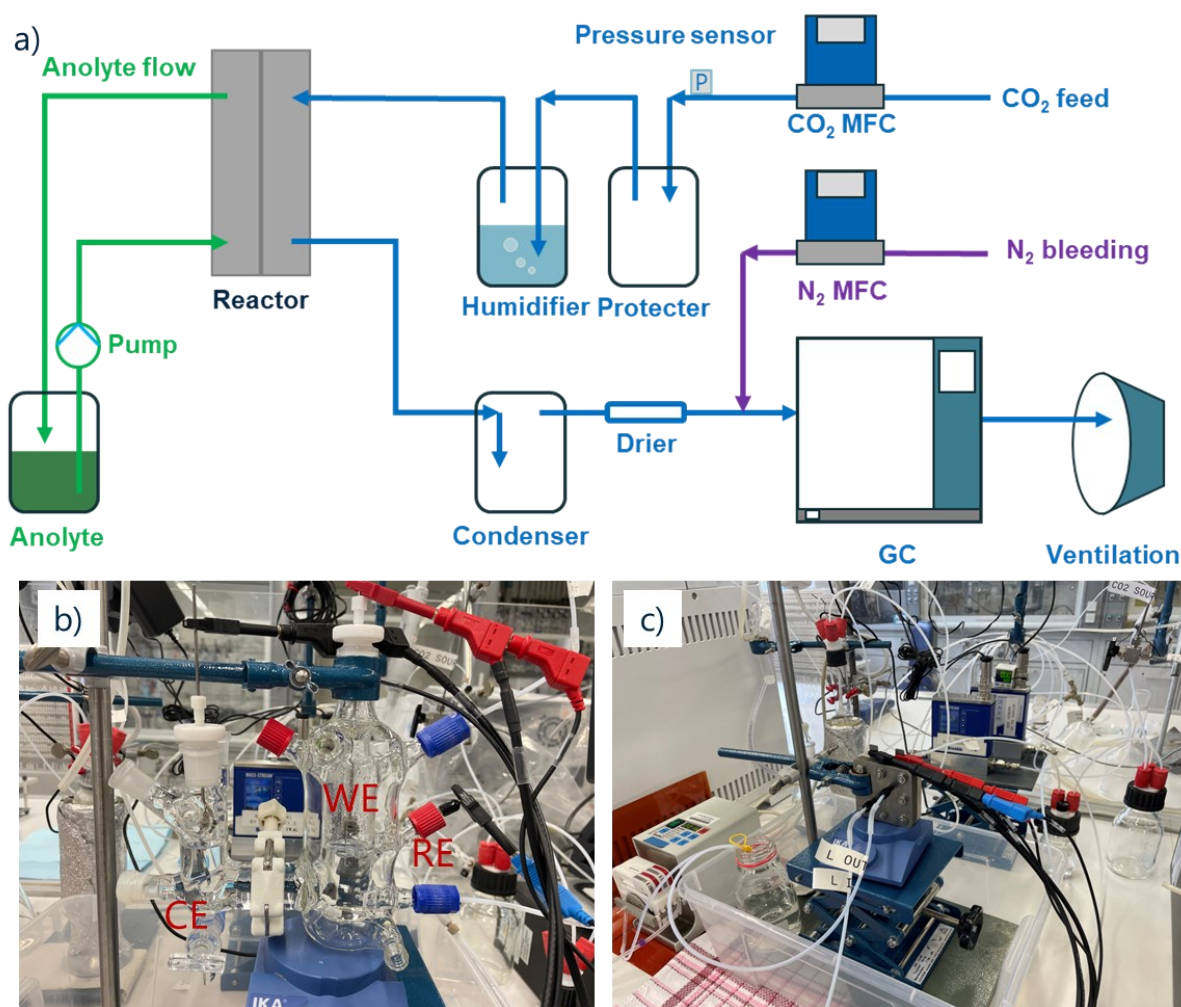


Figure 11. a) Experimental set-up for electrolysis with online quantification of gaseous products. b) H-type cell. c) MEA electrolyzer.

Electrochemical characterization in the H-type cell was performed using linear sweep voltammetry (LSV) and controlled potential electrolysis (CPE, potentiostatic electrolysis). In combination, both approaches are highly important for establishing the relationship between electrode potential (driving force), current (reaction rate), and product distribution (selectivity) in fundamental studies. On the other hand, the MEA electrolyzer with its two-electrode configuration is generally used to study the catalyst performance under practically relevant conditions (stationary conditions, high current density, galvanostatic mode).

The eCO₂RR is a proton-coupled reaction and therefore pH-dependent. Therefore, the pH value is a parameter that can be tuned for optimization of the results. When operating at different pH values, it must be kept in mind that the pH influences redox potentials measured against the reference electrode potential. In this work, the applied potential is referenced to a standard Ag/AgCl electrode (3 M KCl) and converted to the reversible hydrogen electrode (RHE) scale using eq. 16.³⁵

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.0591 \cdot \text{pH} \quad \text{eq. 16}$$

The RHE scale allows for decoupling the pH effect in proton-coupled redox reactions, thereby providing a standardized basis for comparing catalyst performance across different systems. It also enables direct calculation of the overpotential (η) required for a reaction to proceed at a specific rate.

In LSV measurements (e.g., for analysis of eCO₂RR processes), the applied potential is swept linearly at a constant rate with time (V s^{-1}) and the current is recorded as a function of the potential. Smaller onset potentials and a larger peak current density (red curve displayed in Figure 12a) in CO₂-saturated electrolyte compared to Ar-purged solution (blue curve) shows the catalytic interaction between the catalysts and CO₂ ("catalytic current"). Conducting a CPE (Figure 12b) can deliver sufficient amount of liquid and gaseous products for analysis of product distributions (see section 1.3.2).

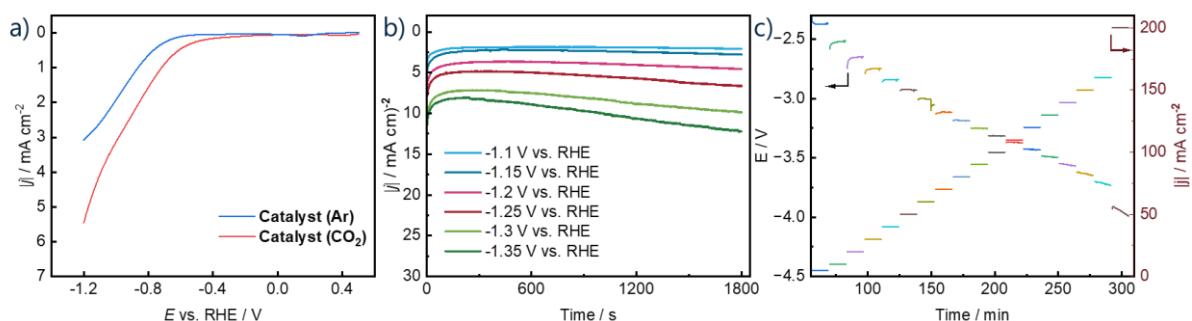


Figure 12. a) Exemplary LSVs of a catalyst-modified electrode under Ar and CO₂, respectively. b) Exemplary current-time profiles of CPEs carried out at different potentials in H-type cell. c) Typical results of CCEs in a MEA electrolyzer.

In contrast to CPE in H-type divided cells, CCE is typically deployed within eCO₂RR studies within the MEA configuration for parameter-performance correlation (Figure 12c). For this purpose, the cell voltage, impedance contributions of different cell components, and product distribution as a function of current density (and operation time) are evaluated as key performance indicators. This framework not only enables systematic optimization of cell parameters but also provides opportunities to integrate eCO₂RR with OER as the anodic half-cell reaction, paving the way for enhanced electrocatalytic efficiency and scalability.

1.3.2 Products quantification

Gaseous products quantification. The gaseous products from eCO₂RR were examined in this work using gas chromatography (GC, Agilent 6890, carrier gas: argon) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). In principle, TCD measures changes in the thermal conductivity of the carrier gas as analytes pass through the detector. The FID measures compounds based on their ability to produce ions when burned in a hydrogen-air flame. As shown exemplary in Figure 13, calibration was performed using certified gas mixtures from Air Liquide as reference standards. Area of different gaseous products are measured in GC as a linear function of concentration and the corresponding slopes are used for following *FE* calculation (eq. 17). As shown in Figure 14, TCD is equipped to analyze H₂ and CO, while FID was employed to quantify CH₄, C₂H₄, and C₂H₆. The use of certified gas mixtures and careful operation ensure a good linear correlation between the concentration and signal intensity presented by detectors, and thereby a precise quantification of the products.

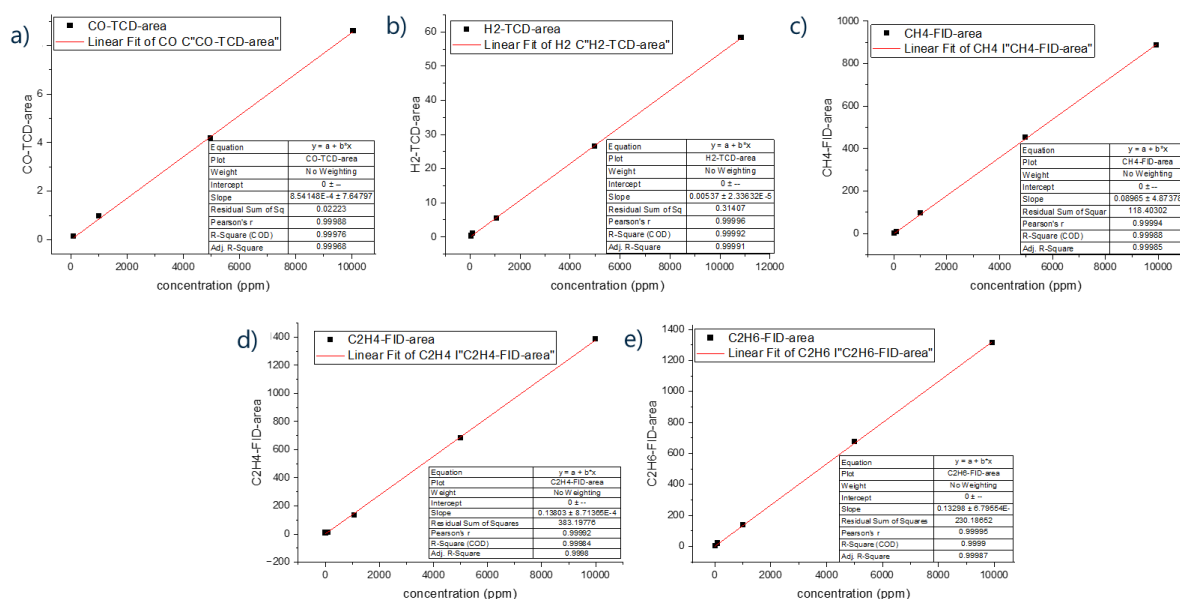


Figure 13. Exemplary GC calibration curves (measured using certified gas mixtures) used for quantification of different gaseous products.

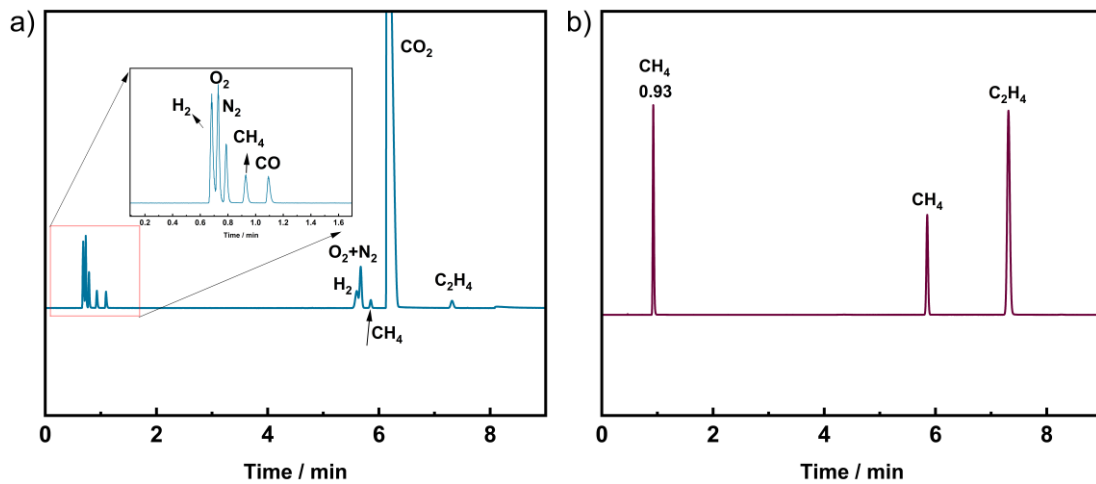


Figure 14. a) TCD and b) FID signals from GC.

Based on the volume fraction in the gas stream, the Faradaic efficiencies (FE) for a specific gaseous products x (e.g. C₂H₄) can be calculated using the following equation,³⁵

$$FE_x[\%] = \frac{p \dot{V}_{N_2} \phi_x z F}{\phi_{N_2} R T i} \cdot 100 \quad \text{eq. 17}$$

$\dot{V}_{N_2}$: the flow rate of the N₂ internal standard;

ϕ_{N_2} : volume fraction of the N₂ in the gas flow detected by GC;

ϕ_x : volume fraction of the gaseous product (i.e. C₂H₄) in the gas flow detected by GC;

p : gas pressure (1.01·10⁵ Pa);

R : gas constant (8.314 J mol K⁻¹);

T : temperature (296 K);

z : number of electrons transferred for CO₂-to- x (e.g. $z = 12$ for C₂H₄);

F : Faraday constant (96500 C mol⁻¹);

i : current recorded by the potentiostat.

Liquid products quantification. After a certain period of electrolysis, liquid samples can be collected for analysis by Proton Nuclear Magnetic Resonance (¹H NMR) spectroscopy. An example spectrum is shown in Figure 15.

By using a water pre-saturation method, the liquid products were quantified by ¹H NMR spectroscopy, employing DMSO as an internal standard (see Figure 15). FE_x was calculated using the following equation,³⁵

$$FE_x = \frac{c_x V z F}{Q} \cdot 100\% \quad \text{eq. 18}$$

c_x : the concentration of the product (e.g. HCOOH) in the liquid phase;

V : the catholyte volume;

Q : the total amount of passed electric charge for specified sampling time.

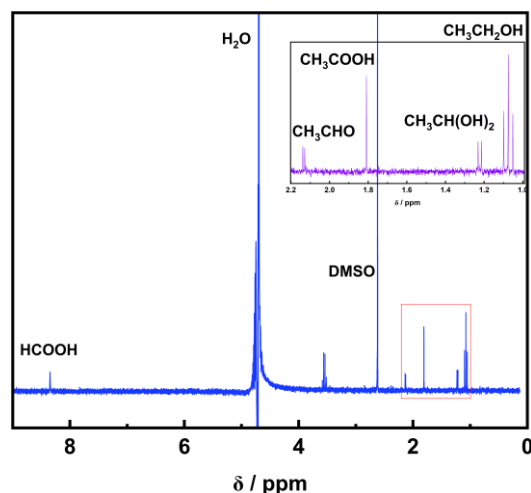


Figure 15. Exemplary ^1H NMR spectrum for quantification of liquid-phase products.

1.3.3 Spectroelectrochemical cell designs for X-ray absorption spectroscopy analysis

Previously, the characterization of eCO_2RR catalysts has predominantly depended on *ex situ* (pre- and post- electrolysis) techniques, while real-time phase evolution during electrocatalytic processes was largely overlooked. In recent years, various *in situ/operando* characterization techniques are employed to study the structural evolution of the catalyst under operating conditions and to establish relationships between reaction conditions, structure, and catalytic properties. XAS, at near edge (XANES) and extended fine structure (EXAFS), is a powerful tool that enables analysis of the electronic properties of the active site as well as the coordination environment.⁵³ A major challenges for studying molecular Cu complexes in the field of eCO_2RR is defining the true active sites, particularly for C-C coupling pathways. In this context, applying advanced *in situ/operando* XAS could help to overcome this bottleneck. For this purpose, two types of *in situ* XAS spectroelectrochemical cells and relevant analytical approach were developed in the course of this work to address the structural evolution of the molecular catalysts under eCO_2RR conditions.

***In situ* spectroelectrochemical flow cell for XAS experiments.** XAS experiments at low currents and controlled working electrode potential were carried out at the Cu K-edge at the BESSY II, XPP KMC-3 beamline. Such measurements enable monitoring of processes near the eCO_2RR onset potential under well-defined conditions. The purpose of this set-up is to mimic the reaction conditions of electrolysis in the H-type configuration. All *in situ* measurements were carried out in fluorescence mode. The *in situ* spectroelectrochemical flow cell and operating set-up are shown in Figure 16. In detail, a window covered by Kapton foil is used for beam access and fluorescence detection. The working electrode is

placed on the back side of the Kapton foil. The other part of the cell is similar to traditional flow cell equipment. Cathodic and anodic chamber are separated by a membrane and a Ag/AgCl electrode (3 M KCl solution) in cathodic chamber is used as a reference. The *in situ* XAS curves were recorded at least 2 times for analysis under different potentials and the scanning of one curve takes around 6 min.

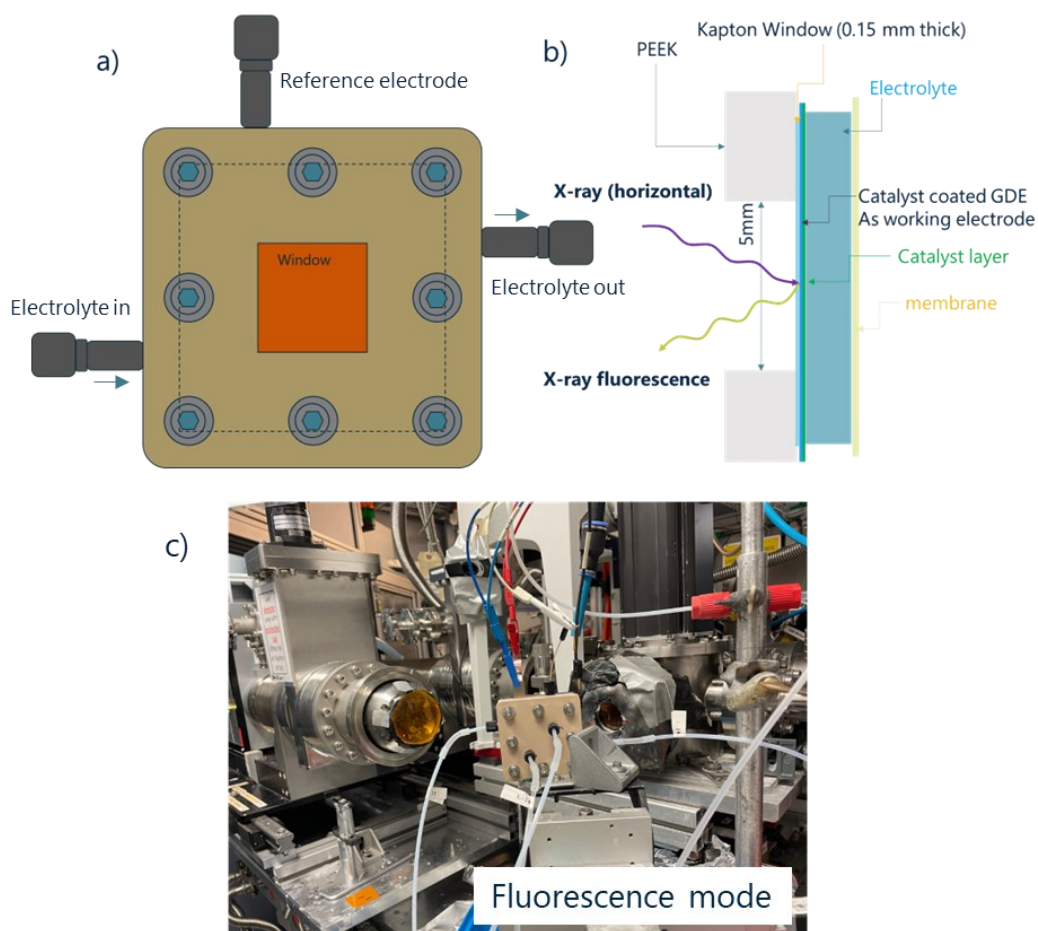


Figure 16. a,b) Schematic illustration of spectroelectrochemical flow cell designed for *in situ* XAS measurements with liquid CO₂-saturated catholytes. c) Photograph of the cell in the experimental environment at the synchrotron facility.

***In situ* MEA-type spectroelectrochemical cell for XAS experiments.** Although *in situ* XAS techniques, with an emphasis on the coordination environment, at low potentials, were performed on molecular catalysts, the dynamic structural evolution of the catalysts at industrially relevant current densities are rarely reported. Moreover, conventional XAS suffers from limitations due to the core-level lifetime broadening (~1–2 eV), making it challenging to detect the minor shift in chemical state and electronic configuration. High energy resolution fluorescence detected (HERFD)-XANES is an advanced XAS method that combines conventional XANES with an enhanced energy resolution, which can bring more detailed fundamental insights.⁵³ Incorporating this advanced technique, an *in situ* MEA-type spectroelectrochemical cell for eCO₂RR was designed for analysis of the redox state and structural

evolution of Cu catalysts at high current density under practically relevant measurement conditions (Figure 17).

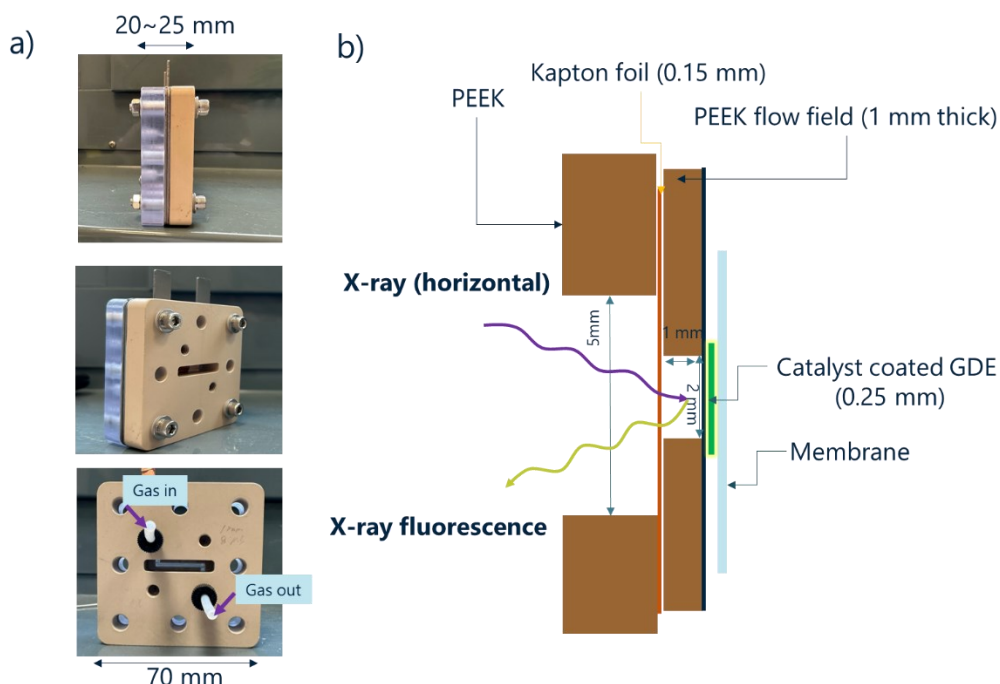


Figure 17. Photographs (a) and a schematic illustration (b) of the custom-made MEA-type spectroelectrochemical cell for XAS analysis.

The *in situ* HERFD-XAS measurements were carried out at ESRF-ID26 (Grenoble). In detail, the MEA-type spectroelectrochemical cell was developed on the basis of a traditional MEA electrolyzer. As shown in Figure 17, the window covered by Kapton foil is designed for beam access and fluorescence signal collection, and the humidified CO₂ gas paths through the flow field (single path shape) for the reaction. The membrane material is identical to standard experiments in the MEA configuration). The eCO₂RR performance of the spectroelectrochemical MEA cell was analyzed using the general gas chromatographic protocol (see Figure 13 and Figure 14) and found to be in good agreement with the standard MEA cell. Due to a lack of analytical methods on site, the liquid-phase products could not be analyzed in this series of experiments.

2. Motivation and goals

Electrocatalytic energy and chemicals conversion, such as water splitting (green hydrogen production) and the electrochemical CO₂ valorization (namely, eCO₂RR), enable the transformation of small molecules into value-added fuels and chemicals. As a cathodic process, the eCO₂RR to C₂₊ products involves a complex reaction mechanism with multiple proton- and electron-transfer steps, which are strongly influenced by the catalyst material. C₂₊ products from eCO₂RR have garnered significant interest in recent years due to their market potential and high value. Central to their formation is the C-C coupling step, which remains challenging, both in view of product selectivity and mechanistic understanding. Metallic Cu has been identified as the only metal that can efficiently catalyze conversion of CO₂ to C₂₊ products, albeit with H₂ evolution as side reaction and complex product mixtures. Therefore, new catalysts are needed to achieve specific products in rate and selectivity at low overpotential.

Molecular Cu complexes with their well-defined active sites and tuneable coordination environments hold promise as alternatives to elemental Cu, providing new possibilities for mechanistic studies and expansion of the fundamental understanding of eCO₂RR. In this context, the major goal of this thesis is to design and develop stable bi- and multinuclear copper molecular Cu compounds and to explore their potential as catalysts for eCO₂RR. Furthermore, applicability of these molecular systems under industrially relevant conditions should be tested. The specific objectives include:

- i) Achieving high selectivity and yield toward C₂₊ products while suppressing the competing hydrogen evolution reaction (HER);
- ii) Monitoring active sites under electrolysis conditions via *in situ* spectroscopy;
- iii) Evaluating their applicability under industrially relevant conditions using a membrane electrode assembly (MEA) electrolyzer at high current densities;
- iv) Establishing a scalable and straightforward synthetic route toward the molecular catalysts using inexpensive and readily available precursors.

Beyond the scope of cathodic eCO₂RR, this thesis also covers the electrolyzer implementation for performance and stability development. For eCO₂RR in electrolyzer applications, the oxygen evolution reaction (OER) at the anode, a kinetically sluggish four-electron transfer process, remains a secondary bottleneck. To overcome this challenge, a partial focus is placed upon the development and integration of cost-effective, durable, and efficient non-noble metal OER catalysts into alkaline water electrolyzers operation at industrial current densities. For this purpose, this work comprises the development of an MEA-type electrolyzers (components and procedures) and optimization of operating parameters. The specific goal is to implement in-house developed OER catalysts based on mixed metal oxides (CoNiFeO_x) into the custom-made MEA electrolyzer for performance evaluation at high stress in a practically relevant environment. Both the studies carried out on cathodic eCO₂RR and on anodic OER shall deliver

valuable contributions to the advancement of eCO₂RR and water electrolysis on the device level, both in view of fundamental understanding and practical applications.

3. Discussion of results

Following the motivation and goals, work on the development of molecular Cu complexes is described, which incorporate the phenanthroline framework as the ligand, resulting in a promising electrocatalysts for electrochemical conversion of CO_2 to C_2H_4 production in eCO_2RR (sections 3.1 and 3.2). Furthermore, a series of stable metal oxides catalyst (Co, Ni and Fe) for OER in alkaline water electrolyzer is described, with focus on application at industrial current density (section 3.3).

3.1 Heterogenized molecular electrocatalyst based on a hydroxo-bridged binuclear Cu(II) phenanthroline compound for selective reduction of CO_2 to ethylene

Molecular Cu catalysts have gained attention as promising candidates for eCO_2RR . Key feature of such catalysts is that they offer well-defined active sites, allowing for targeted structural tuning and enabling studies of unambiguous structure-activity relationships. However, in view of previously reported Cu molecular catalysts, *in situ* formation of Cu nanoclusters/particles is frequently observed, raising doubts about the real active sites responsible for the production of C_{2+} products and challenging the abovementioned benefits of molecular frameworks. Thus, it appears desirable to develop Cu-based catalysts that preserve their molecular structures under operating conditions. In this section, a heterogenized binuclear hydroxo-bridged phenanthroline Cu(II) complex (see Figure 18) is described and discussed, which exhibits a short $\text{Cu}\cdots\text{Cu}$ distance and holds promise as electrocatalyst for the formation of C_2H_4 and other C_{2+} products under eCO_2RR conditions.³⁵

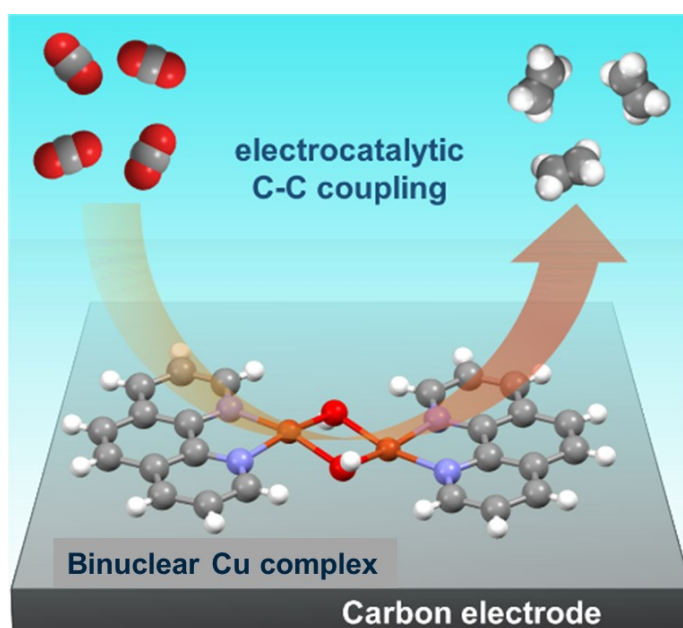


Figure 18. Electrocatalytic conversion of CO_2 to ethylene using a hydroxo-bridged phenanthroline Cu(II) complex.

In CO₂-saturated 0.1 M CsHCO₃ electrolyte, the immobilized catalyst exhibits excellent performance, in which the Faradaic efficiency for C₂⁺ products reaches up to 62%. Furthermore, it shows stable performance for more than 15 h with continuous production of C₂H₄. Comprehensive pre- and post-electrolysis characterization including X-ray photoelectron and absorption spectroscopy, scanning and transmission electron microscopy, Ultraviolet-visible spectroscopy (UV/VIS), as well as control experiments, suggest the preservation of the molecular catalyst as the true active site. The study provides a strong foundation for further exploration of structural tuning and paves the way for improved catalytic performance of Cu-based molecular electrocatalysts.

A mononuclear complex named **Cat1** was already reported by Wang's group.⁵⁴ In the system, graphene-based electrode is working electrode, and the complex is dissolved in the KHCO₃ electrolyte. The catalyst can form C₁ products in over 90% Faradaic efficiency at optimal potential. Based on this interesting work, the new binuclear hydroxo-bridged phenanthroline Cu(II) complex ([Cu₂(phen)₂(OH)₂(H₂O)₂][Cu₂(phen)₂(OH)₂Cl₂]Cl₂·6H₂O, **Cat2**, Figure 19) was proposed, which is synthesized under alkaline conditions in a straightforward fashion. In detail, the catalyst is synthesized by mixing solutions of CuCl₂ and phen in the presence of NEt₃, whereby the catalyst precipitates and can be easily filtered off. For analytical purposes, the solid can be recrystallized, although **Cat2** powder and crystals exhibit nearly the same catalytic properties. The material is composed of two different centrosymmetric complexes with different type of axial ligand (water and chloride, respectively), while the main framework is similar. The Cu···Cu distances in these complexes are 2.93 Å each.

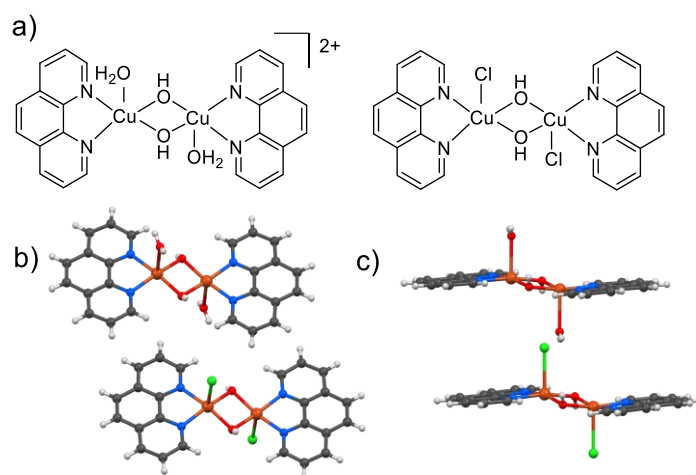


Figure 19. a) Molecular structure of **Cat2**. b,c) Molecular structures obtained from single crystal X-ray analysis (top and side view). Color code: carbon (grey), nitrogen (blue), oxygen (red), hydrogen (white), and copper (orange).

The catalytic activity of **Cat2**-modified electrodes for eCO₂RR was evaluated in a H-type divided cell (Figure 12) in CO₂-saturated bicarbonate electrolyte solution. CPE was carried out for 30 min at 6

different potentials in CO₂-saturated 0.1 M CsHCO₃ electrolyte. The product spectrum comprises gaseous products detected by gas chromatography (GC, C₂H₄, CH₄, CO, and H₂, see Figure 14) and liquid-phase products analyzed by ¹H NMR spectroscopy (HCOOH, C₂H₅OH, CH₃COOH and CH₃CHO). Figure 20a shows the relationship between product distribution and applied electrode potential, indicating that the *FE* for C₂H₄ is relatively stable across the entire potential regime. At -1.25 V vs. RHE, the maximum *FE*_{C₂H₄} is achieved with 42%, where the average current density increased to 6.3 mA cm⁻². It should be noted that the selectivity toward H₂ is always below 10% regardless of the applied potentials, revealing the ability of **Cat2** to efficiently suppress the HER. C₂H₅OH and CH₃CHO are the main liquid products with *FE* values of 12% and 6%, respectively, at -1.25 V vs. RHE working electrode potential. Compared with molecular catalysts in the literature, the present system exhibits an outstanding selectivity for C₂H₄ and exceptional HER suppression, as shown in Figure 20b. Figure 20c shows the results of the stability test that was performed for more than 15 h under continuous operation, showing stable current and production of C₂H₄.

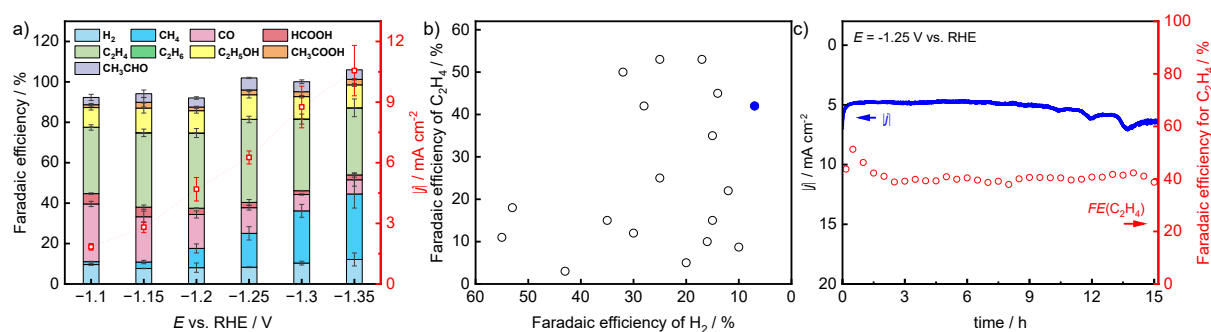


Figure 20. Electrochemical characterization of **Cat2**-modified carbon paper electrodes in CO₂-saturated aq. CsHCO₃ solution. a) *FE* for different products using **Cat2** at different working electrode potentials. b) Plot of *FE*(C₂H₄) vs. *FE*(H₂) for **Cat2** (blue symbol) and representative catalysts from the literature (Cu complexes and Cu-containing metal-organic frameworks). c) Long-term stability test of **Cat2** at -1.25 V vs. RHE.

Shown in Figure 21 is a series of pre- and post-characterization studies including XPS (Figure 21a), XAS (Figure 21b) and UV/VIS (Figure 21c) spectroscopy, with the goal to analyze the coordination environment and oxidation states of **Cat2**. In the XPS of the Cu 2p region of fresh **Cat2** powder in Figure 21a, Cu 2p_{3/2} can be split into two peaks at 934.1 eV and 932.3 eV corresponding to Cu²⁺ and Cu⁺/Cu⁰, respectively. At first glance, this result is somewhat surprising, as Cu should be in +2 oxidation state within the **Cat2** structure. As a control experiment, a **Cat2** single crystal was analyzed after different X-ray exposure times. In this control experiment, the peak of Cu⁺/Cu⁰ increases with extended exposure time. In combination with XANES and UV/VIS spectroscopy results, it can be concluded that the Cu⁺/Cu⁰ signal originates from the harsh conditions (high-energy irradiation, ultrahigh vacuum) during XPS

measurements. After electrolysis, the used electrode was analyzed again, exhibiting a similar peak position assigned to Cu^{2+} (935.0 eV) and Cu^+/Cu^0 (931.9 eV) species, whereby the presence of the Cu^+/Cu^0 signal may be related to electrolysis degradation or to X-ray induced reduction.

Figure 21b shows the XANES spectra of Cu reference samples including Cu foil, CuO, Cu_2O , as well as freshly prepared **Cat2** powder and a **Cat2**-modified carbon paper electrode after electrolysis. Fresh and post catalyst exhibit similar spectral features, in which their peak position (~ 8992 eV) of the white line closes to CuO but the edge feature is absent compared with all Cu reference. This result indicates that Cu exists in oxidation state +2 both in the fresh sample and the post-electrolysis material, whereas the coordination environment is significantly different from CuO_x .

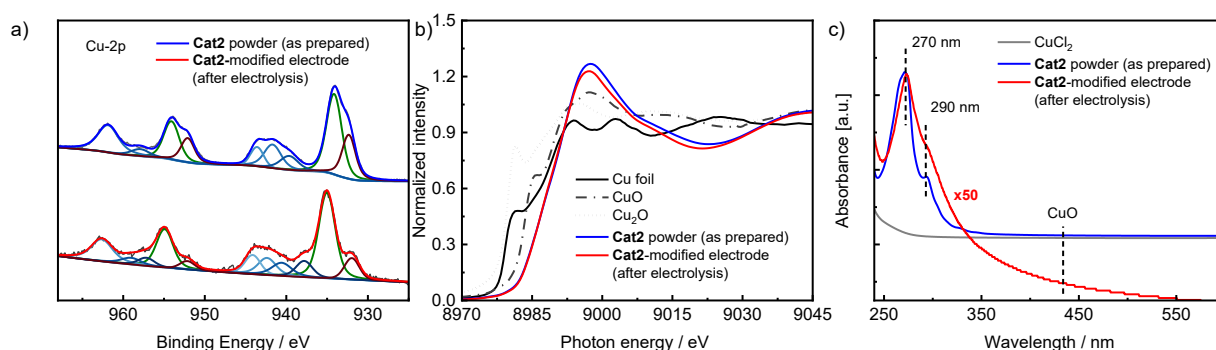


Figure 21. a) XPS analysis of **Cat2** (scans in the Cu 2p region). b) Normalized Cu K-edge XANES spectra of as-prepared **Cat2** powder and **Cat2**-modified electrode after electrolysis. c) Comparison of the UV/VIS spectra of **Cat 2** before and after electrolysis.

Further characterization via solid state DR-UV/VIS spectroscopy (Figure 21c) showed a well-defined absorption peak at ~ 270 nm with a shoulder at 290 nm, both for the fresh catalysts powder and for the used electrode. However, the latter exhibits a significantly lower intensity that can be attributed to catalyst leaching. The leaching process was also confirmed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of the electrolyte mixture and constitutes a major challenge that needs to be overcome with the development of a second-generation Cu phenanthroline electrocatalyst (see section 3.2). On the other hand, the combined results of for pre- and post-catalysts demonstrates the absence of CuO_x clusters, which was further corroborated by SEM-energy dispersive X-ray spectroscopy (SEM-EDX) analysis and Raman spectroscopy.

In summary, an easy-to-synthesize and highly promising binuclear hydroxo-bridged phenanthroline Cu(II) complex was developed, which exhibits high selectivity for CO_2 -to- C_2H_4 conversion when immobilized onto a carbon electrode. With comprehensive structural characterization, including SEM, TEM, EDX elemental mapping, XPS, and XAS, it was shown that the molecular catalyst is preserved during electrolysis, whereby reversible formation of CuO_x particles under potential bias cannot be

entirely excluded.⁴³ Furthermore, catalyst leaching into the electrolyte solution remains a challenge for long-term operation. Both issues, lack of *in situ* information and catalyst leaching, shall be addressed at the next stage with spectroelectrochemical methods and enhanced catalyst design aiming at lower water solubility, respectively.

3.2 Copper(II) Phenanthroline Catalysts for Electroreduction of CO₂ to C₂ compounds: Substitution on the Ligand Causes Structural Change of the Molecular Framework and Stability Enhancement

Based on the first study (see section 3.1), a new oligonuclear Cu(II)-dimethoxyphenanthroline complex was developed and tested as electrocatalyst for eCO₂RR. The rationale behind introducing the methoxy substituents was to

- i) study the impact of ligand modification on the catalyst structure,
- ii) modulate the electronic properties of the ligand and to test the effect on the activity of the Cu complex,
- iii) increase the hydrophobicity of the Cu complex, thereby lowering the solubility and suppressing catalyst leaching.

As a result of the ligand modification, the previously developed synthetic protocol yielded a water-insoluble coordination oligomer **Cat3** with a ladder-like molecular framework (see Figure 22). In principle, it is assumed that the product consists of a distribution of oligomers with different chain lengths. The octamer was successfully separated by crystallization and analyzed using single-crystal X-ray diffraction.

XPS and XAS spectroscopies support the Cu(II) coordination environment consisting of interconnected hydroxy-bridged binuclear units with a short Cu...Cu distance (3 Å). The catalyst exhibits excellent eCO₂RR performance, with *FE* of up to 70% for production of C₂₊ compounds. Importantly, stable performance up to 200 mA cm⁻² can be achieved in the MEA electrolyzer, which means significant progress with respect to the work presented in chapter 3.1. To fundamentally investigate the true active Cu sites in our molecular structure under operational conditions, *in situ* XAFS was carried out in a divided spectroelectrochemical cell (mimicking the reaction conditions of the H-type cell configuration). Furthermore, HERFD-XANES was conducted in a MEA-type spectroelectrochemical cell for operation at high current densities. This work not only builds an oligomeric molecular catalyst with stable coordinated Cu active sites for C₂₊ production under operating conditions but also advances *in situ* XAS analysis investigating molecular electrocatalysts at industrial current densities.

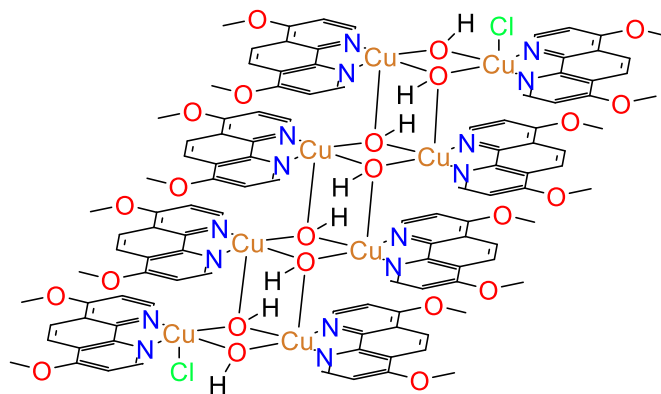


Figure 22. Molecular structure of the second-generation Cu phenanthroline complex **Cat3** (octamer fraction of the oligomer mixture).

Figure 23 reveals the electrochemical performance of **Cat3** in the H-type cell configuration. A series of CPE experiments (Figure 23a) were applied from -1.0 to -1.5 V vs. RHE in CO₂-saturated electrolyte. When applying more negative potential, CO formation decreases dramatically but formate and CH₄ generation become pronounced. C₂H₄ generation already starts at less negative potential. At -1.3 V vs. RHE, C₂H₄ becomes the predominant product with *FE* of 30%. Notably, the competing HER is less pronounced with *FE*_{H₂} of 10% over the entire applied potential region, highlighting the preference toward eCO₂RR over HER. Interestingly, **Cat3** showed outstanding electrocatalytic stability for more than 36h with constant current density and *FE*_{C₂H₄} at -1.2 V vs. RHE (Figure 23b). Figure 23c shows a comparison of the key-performance characteristics with our previous work in section 3.1. In H-cell screening, **Cat2** seems to perform better catalytic performance than that of **Cat3**. By intruding the methoxy substituents to the structure, the robustness of **Cat3** could be enhanced for operating condition in MEA electrolyzer at high current densities.

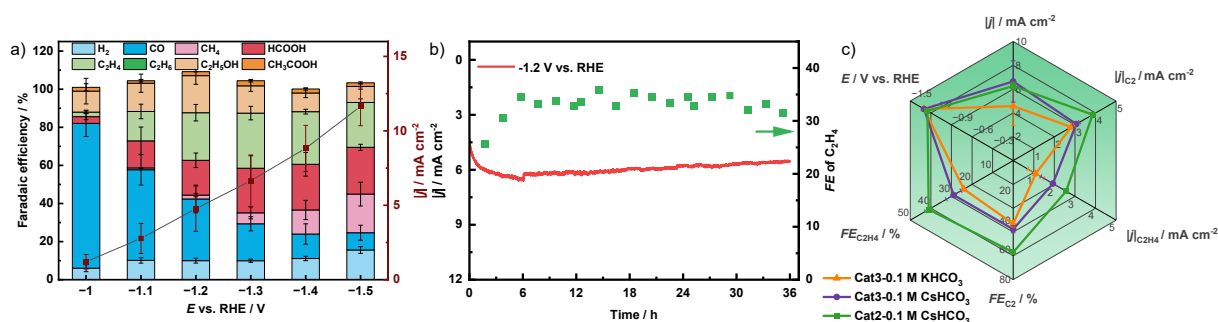


Figure 23. The electrochemical reactivity of **Cat3**-modified carbon paper. a) *FE* for different products using **Cat3** at different working electrode potentials. b) Long-term stability test of **Cat3** at -1.2 V vs. RHE. c) Comparison of eCO₂RR performance in H-cell by using **Cat2** and **Cat3** as the cathode.

It is very common that molecular Cu catalysts face structural evolution under eCO₂RR conditions, often leading to reversible or irreversible formation of CuO_x nanoparticles.⁵⁵ In view of good eCO₂RR

performance and stability for more than 36 hours in the H-cell, the dynamic changes of **Cat3** of the Cu active centers at negative bias should be tracked in order to obtain information on the true active sites. In this study, *in situ* XAS analysis was applied to monitor the behavior of **Cat3** during eCO₂RR. The spectroelectrochemical flow cell used is discussed in section 1.3.3 (see Figure 12). As shown in Figure 24, the *in situ* XAS measurements were conducted under dry conditions within the cell (catalyst-coated carbon paper), at open circuit potential (OCP), and at operating potentials from -0.9 to -1.4 V vs RHE. An aqueous CO₂-saturated 0.1 M CsHCO₃ electrolyte solution was used for these experiments and the current densities obtained at these potentials are shown in Figure 24c. As can be seen in Figures 24a and 24b, there are no significant changes for the Cu K-edge XANES (from 8970 eV to 9050 eV) and the EXAFS region (from 9030 eV to 9600 eV) across the entire potential regime, even persisting during the reverse scan from -1.4 V to -0.9 V vs. RHE, as well. Based on these results, it is suggested that the binuclear Cu motif represents the active site; in other words, the molecular structure shown in Figure 22 is responsible for the eCO₂RR performance and no observable Cu nanoparticles formed during electrolysis, at least not at low current densities.

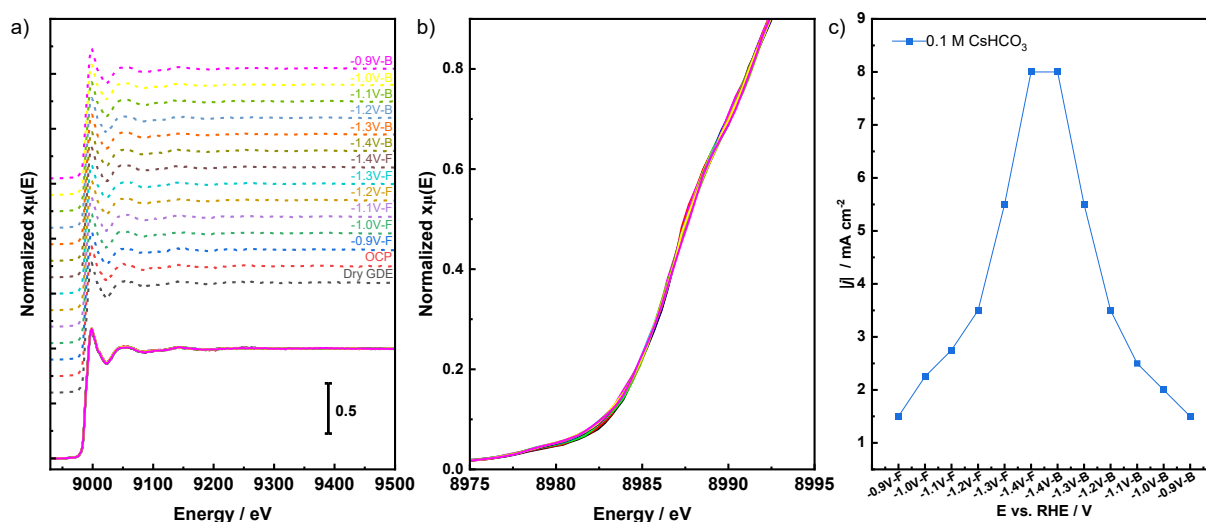


Figure 24. *In situ* XAS analysis of **Cat3**. a) XANES for **Cat3** electrocatalysts in dry form, under OCP conditions, and under eCO₂RR conditions at -0.9 V, -1.0 V, -1.1 V, -1.2 V, -1.3 V and -1.4 V vs V_{RHE} (aligning with H-cell experiments) in CO₂-saturated 0.1 M CsHCO₃ electrolyte. b) Enlarged section from Figure 24a showing *in situ* Cu K-edge spectra of **Cat3** at different potentials. c) Current densities measured during *in situ* XAS measurements.

Noteworthy, all our observations indicate that **Cat3** is significantly more robust compared to **Cat2**. More specifically, the following points speak for preservation of the molecular structure and higher stability:

- i) Catalyst leaching was not observed in the H-type cell and the color of the catalyst deposit on the electrode surface was maintained.
- ii) **Cat2** is not compatible with the more demanding MEA cell configuration, whereas **Cat3** shows strong performance under these conditions.
- iii) Significantly higher current densities could be applied without loss of performance.
- iv) No change of the Cu coordination environment was observed in the XAS spectroelectrochemical studies (Figure 24).

With these promising findings in hand **Cat3** was tested in a MEA-based electrolyzer under more demanding conditions. Figure 25a summarizes the *FEs* for different products obtained at different applied currents between 10 mA cm^{-2} to 200 mA cm^{-2} . With rising current, the cell voltage increased from 2.5 to 4 V. Moisturized CO_2 was fed to the cathode, while aq. 0.1 M CsHCO_3 was used as the anolyte. The main product is C_2H_4 with *FE* of more than 40% at 200 mA cm^{-2} and the *FE* of H_2 is lower than 20% over the entire current density regime. Similar to the results obtained from experiments in the H-type cell, $\text{C}_2\text{H}_5\text{OH}$ and CH_3COOH are the main liquid products. In view of the key-performance criteria, **Cat3** exhibit promising behavior compared with that of **Cat2**, making it as a robust catalyst especially under industrially relevant (high current) conditions (Figure 25b).

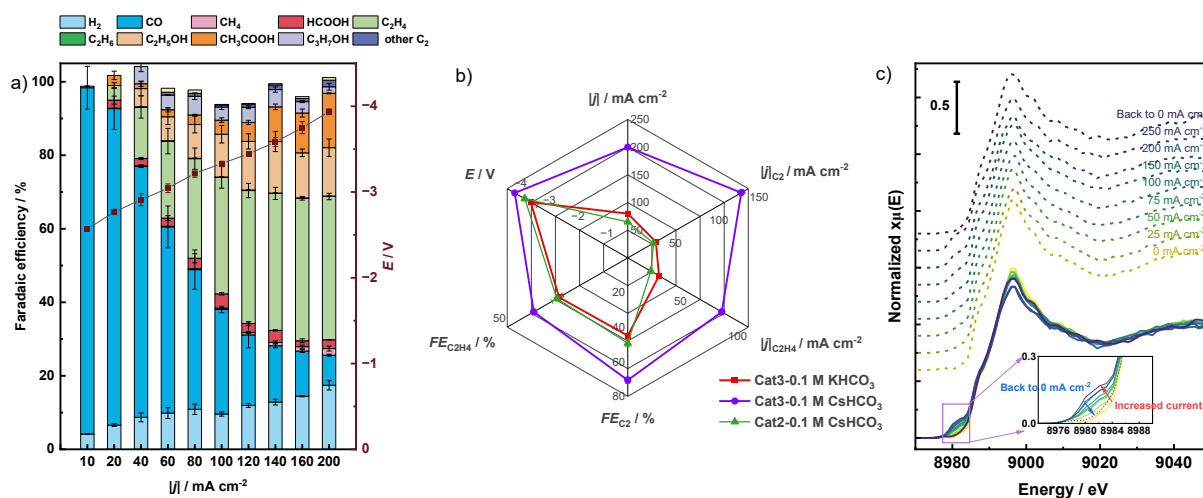


Figure 25. (Spectro)electrochemical characterization of **Cat3** in an MEA electrolyzer. a) *FE* for different products using **Cat3** at different current densities (0.1 M CsHCO_3 as the anolyte). b) Comparison of eCO_2RR key-performance criteria obtained from studies in the MEA electrolyzer by using **Cat2**- and **Cat3**-modified cathodes. c) *In situ* HERFD-XANES for **Cat3** under eCO_2RR conditions at 25, 50, 75, 100, 150, 200, 250 mA cm^{-2} and back to 0 mA cm^{-2} . The inset shows an enlargement of the indicated rectangular area.

Since the conditions during CCE in the MEA electrolyzer are much more demanding than during CPE in the H-type cell, it is necessary to revisit the analysis of the structural evolution of the catalyst. However,

conventional XAS with lower energy resolution is limited by core-level lifetime broadening, while advanced HERFD-XANES could help for tracking precise dynamic evolution for pre-edge under *in situ* conditions. Therefore, as shown in Figure 25c, *in situ* HERFD-XANES measurements were applied using a custom-designed MEA-type spectroelectrochemical cell (see Figure 12) from 0 mA cm⁻² (OCV) to industrial-level current densities (250 mA cm⁻²). A slight change of the pre-edge intensity at 8980 eV was observed when applying a more negative current density (see inset in Figure 25c). Interestingly, upon returning the MEA to zero current after electrolysis, the Cu species was re-oxidized to Cu²⁺, highlighting a distinct bias-induced reversible redox behavior of the Cu active sites during the eCO₂RR process.

In conclusion, with comprehensive *in situ* spectroscopic techniques, this study highlights the potential of **Cat3** as a highly efficient electrocatalyst for selective reduction to C₂ products in eCO₂RR under industrially relevant conditions. This work offers key insights into the *in situ* behaviour of molecular electrocatalysts, paving the way for their broader use of this approach in diverse electrochemical applications.

3.3 Pre-treated carbon additive enables reduction of metal loading in CoNiFe oxide-based OER electrocatalysts while maintaining performance

As outlined before, the OER constitutes the standard anodic half-cell reaction complementing both HER (for green hydrogen production) and eCO₂RR (for synthesis of value-added C₁ and C₂₊ compounds). Therefore, the development of low-cost and highly efficient OER electrocatalysts that enable operation at high current densities and low overpotentials plays a critical role in the industrial adoption of both water splitting and eCO₂RR. In recent years, researchers have made efforts to develop efficient non-noble metal catalytic systems with excellent activity and durability compared with that of traditional noble metal-based catalysts (IrO_x and RuO_x). Notably, the use of multi-metal catalysts, rather than single-metal ones, was shown to significantly enhance performance.⁵² Therefore, a series of Co-Ni-Fe oxides was developed and tested as OER electrocatalysts in our laboratories (Figure 26a).⁵⁶ A particular focus of the previous study was the impact of the thermal treatment conditions, namely oxygen-deficient (M), reductive (H) and aerobic (A) annealing, on the intrinsic properties affecting the OER. Furthermore, the intermetallic ratio was systematically varied and a relationship with the catalytic activity established. Among various catalysts developed, CoNiFe (2:2:1)/M (Co : Ni : Fe in a ratio 2 : 2 : 1) exhibits optimum OER performance, with an overpotential of 291 mV at 10 mA cm⁻² (η_{10}) and a Tafel slope of 32 mV dec⁻¹.⁵⁶

Although the employed metals Co, Ni, and Fe are abundant and much less expensive than the standard materials for catalysis of OER, particularly Co but also Ni are not unproblematic, as their deposits are

located in politically instable regions and their mining causes severe environmental issues.⁵⁷⁻⁵⁹ Furthermore, the increasing demand due to applications in energy storage and conversion will very likely lead to increase of cost and problems with accessibility.² Developing efficient OER catalysts with reduced metal content is therefore a worthy goal. Consequently, with the aim of lowering the metal content while maintaining the performance of the CoNiFeO_x system, Vulcan XC-72R carbon black (VC) was added in various amounts during and after synthesis, respectively (Figure 26b). Interestingly, the optimal CoNiFeO_x-VC composite shows a relatively high activity and stability at high current densities in a flow anion exchange membranes (AEM) electrolyzer under optimized electrolysis conditions. Furthermore, with comprehensive *in situ* and *ex situ* characterizations, the present study reveals important details on the oxidation states of the three metals during and after electrolysis, providing a better understanding of the OER mechanism.

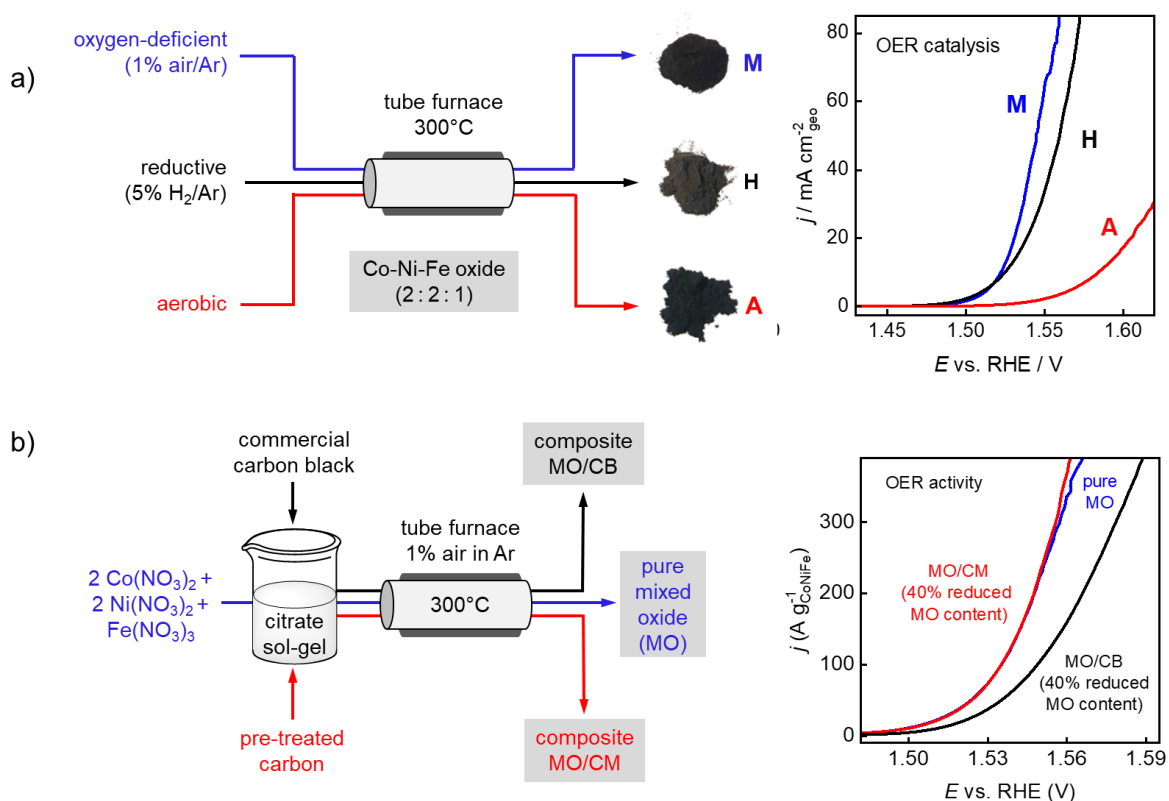


Figure 26. a) Conceptual approach for the study on the influence of the thermal treatment conditions on the electrocatalytic performance of CoNiFeO_x catalysts.⁵⁶ b) Strategy for the analysis of the influence of carbon admixture on the properties of CoNiFeO_x-based catalysts.⁶⁰

As shown in Figure 27, to meet the industrial standard of AWE, a series of experiments were carried out in a custom-made AEM electrolyzer, in which cathode and anode were separated by an AEM (Figure 9). CoNiFe (2:2:1)/M from the previous study (named as 100MO in the present study) was used as a carbon composite with optimal CoNiFeO_x-VC ratio (60 wt.% metal oxide, 40 wt.% VC). For catalyst-

coating of the electrodes, an ink was formulated and sprayed upon the surface. The resulting material 60MO/CM shows comparable OER performance when studied in preliminary experiments using a rotating disc electrode (RDE) despite “dilution” with carbon (CM refers to chemically modified carbon, namely pre-treatment with HNO_3). Interestingly, the performance of 60MO/CM was even slightly better than the pure metal oxide 100MO (see Figure 27).

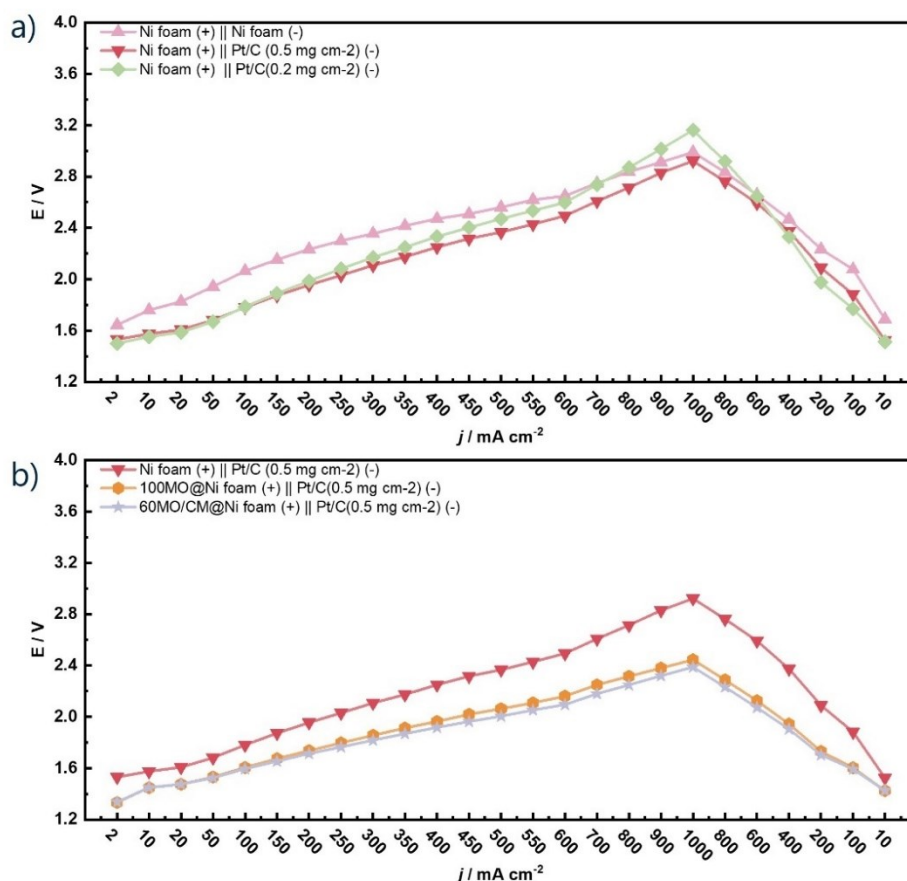


Figure 27. Load curves recorded using an AEM electrolyzer for testing the influence of different cathode materials (a) and characterizing the performance of the modified CoNiFe oxide/carbon composite catalyst.

Figure 27 shows load curves measured at different current densities using various combinations of anode and cathode materials. The influence of the cathode was examined using bare Ni-foam and varying Pt loadings on Vulcan carbon cloth electrodes. To reduce the HER overpotential, the carbon cloth with a Pt loading of 0.5 mg cm^{-2} was identified as the optimal cathode material (Figure 27a). It was observed that bare Ni-foam exhibits significantly higher overpotentials at all current densities compared to catalyst-loaded electrodes (100MO and 60MO/CM on Ni-foam) when using Pt/C ($0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) as cathode. As indicated above, the cell voltage is slightly lower when using the 60MO/CM catalyst compared to the use of 100MO (Figure 27b). Based on these promising results, 60MO/CM was subjected to a stability test, showing a stable cell voltage at around 2V for over 100h.

In summary, by optimizing the device components, and improving the protocol for electrode preparation and catalyst layer formulation, the optimal CoNiFeO_x-VC composite (60MO/CM) was investigated at high current densities in an AWE in AEM electrolyzer under industrially relevant conditions, exhibiting higher activity and stability than the carbon-free metal oxide despite reduced metal content.

4. Summary and outlook

To summarize, this dissertation explores the development of high-performance electrocatalytic systems for small molecule valorization, with a specific focus on both catalyst design and device-level implementation. For the cathodic process, electrochemical CO₂ reduction reaction (eCO₂RR), a new class of Cu-phenanthroline-based molecular complexes was designed, synthesized, and characterized. These catalysts were further evaluated in conjunction with customized electrolyzer configurations and coupled with an adaptive anodic oxygen evolution reaction (OER), targeting industrially relevant and sustainable CO₂ conversion.

In the pursuit of rational catalyst design and understanding of potential-dependent behavior, the first project focused on studies in H-type batch cell under potentiostatic conditions. A binuclear hydroxo-bridged Cu(II)-phenanthroline complex with a short Cu...Cu distance (2.93 Å) was developed as a molecular catalyst for electrochemical C-C coupling, achieving efficient ethylene formation and other interesting C₂₊ by-products. Extensive pre- and post-electrolysis characterizations confirmed that the molecular structure remained unchanged during electrocatalysis, with no observable formation of Cu (oxide) species. A major achievement is that the concurrent hydrogen evolution could be largely suppressed, with FE_{H_2} remaining below 10% across the entire analyzed potential regime. Building on these promising results, the second study focused on an improved second-generation system, namely a Cu coordination oligomer with a modified phenanthroline ligand. The new Cu(II)-4,7-methoxy-1,10-phenanthroline complex exhibits lower water solubility and excellent electrochemical stability, also achieving promising Faradaic efficiencies for C₂₊ products in the H-type batch cell.

To validate the electrocatalytic performance of these molecular systems under industrially relevant conditions, the focus was then shifted to the technological development of electrolyzer and electrolysis platforms for analysis of the molecular compounds. A continuous flow electrolysis system was established and equipped with a zero-gap membrane electrode assembly (MEA) electrolyzer. As the initial step in device and system implementation, a CoNiFeO_x-Vulcan carbon composite was deployed as a model catalyst for alkaline OER, and protocols for electrode preparation, electrolyzer assembly, and operation controlling were explored, improved, and standardized. The resulting electrocatalytic water splitting system demonstrated stable operation at current densities exceeding 400 mA cm⁻² for alkaline water splitting, with over 100 hours of durability, offering a solid technical foundation for large-scale integration and compatibility with eCO₂RR processes.

Leveraging this platform, the Cu-based molecular catalysts were tested under similar configurations, maintaining over 70% FE for C₂₊ compounds at 200 mA cm⁻². These advancements also enabled the development and validation of spectroelectrochemical cells for *in situ* X-ray absorption spectroscopy (XAS). These devices allowed for investigation of the catalytic behavior both near the onset potential

and under industrial-level current densities. Using these cells, extended X-ray absorption fine structure (EXAFS) and high-energy-resolution fluorescence-detected X-ray absorption near-edge structure (HERFD-XANES) analyses were successfully performed, enabling *in situ* monitoring of the redox behavior of the studied catalysts. As a key-result, it was found that the second-generation multinuclear Cu coordination compound resides in its molecular framework at current densities below approx. 50 mA cm⁻² in liquid electrolyte, while reversible structural transformation, likely into phenanthroline-coordinated CuO_x nanoparticles is observed at high current densities in the MEA electrolyzer. Interestingly, the molecular Cu coordination frameworks are restored when the potential bias is removed.

As an outlook regarding the eCO₂RR catalyst development, this thesis was exclusively focused on phenanthroline-based ligands. Given the electronic/geometric structure of the Cu centers plays a vital role, the impact of the ligand structure could be further investigated with additional electron-donating or withdrawing substituents. These characteristics may influence the adsorption strength and recombination kinetics of key intermediates (e.g. *CO, *CHO, and *COH), affecting the catalytic reactivity and selectivity toward the desired C-C coupling products. The other critical factor is the control of the Cu...Cu distance within molecular frameworks. Whether the spacing is intermolecular in mononuclear complexes, intramolecular in multinuclear assemblies, or embedded within MOF-derived scaffolds, its precise tuning seems essential for promoting C-C bond formation. Structural robustness under operating conditions, in combination with advanced *in situ* and *operando* material characterization techniques, will thus support a deeper understanding of structure-activity relation and could thereby help to further advance the approach presented herein.

Mechanistic understanding is further complicated by the ongoing debate over the precise nature of the key intermediates involved in C-C coupling. Whether *CO, *CHO, and/or other species dominate the coupling pathways remains an open question. Addressing this challenge calls for advanced *in situ* and *operando* spectroscopic tools, such as Raman and infrared (IR) spectroscopy, which can track intermediate adsorption and vibration under reaction conditions. These insights can be combined with quantum chemical calculations and may thereby offer distinct guidance for fine-tuning on the atomic and molecular levels.

Beyond catalyst design, further improvements in catalyst layer engineering are also necessary. Enhancing electronic conductivity, increasing accessible active site density, and enabling efficient mass transport within and across the catalyst layer are all essential steps toward high-performance systems. With this scope, the progress in device, system engineering, and operation parameters, are all critical for translating molecular catalysts into practical, scalable solutions.

Looking ahead, these directions will guide the future design of robust and scalable molecular systems for sustainable electrocatalytic valorization of carbon dioxide.

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6. Publications

The following publications form the basis for this cumulative thesis. Additional publications are listed in the appendix.

- I. **Liu, N. (First Author);** Bartling, S.; Springer, A.; Kubis, C.; Bokareva, O. S.; Salaya, E.; Sun, J.; Zhang, Z.; Wohlrab, S.; Abdel-Mageed, A. M.; Liang H-Q.; Francke R. Heterogenized Molecular Electrocatalyst Based on a Hydroxo-Bridged Binuclear Copper(II) Phenanthroline Compound for Selective Reduction of CO₂ to Ethylene. *Adv. Mater.* **2024**, 36 (6), e2309526. DOI: 10.1002/adma.202309526.
- II. **Liu, N. (First Author);** Pham, T.; Han, Y.; Yang, L., Bokareva, OS.; Bartling, S.; Springer, A.; Spannenberg, A.; Kubis, C.; Weiss, J.; Doronkin, D.; Ju, W.; Francke, R. Copper(II) Phenanthroline Catalysts for Electroreduction of CO₂ to C₂ compounds: Substitution on the Ligand Causes Structural Change of the Molecular Framework and Stability Enhancement. *Adv. Mater.* **2025**, e13702. DOI: 10.1002/adma.202513702.
- III. Pham, T.; **Liu, N.**; Bartling S.; Rockstroh, N.; Eckelt, R.; Ju, W.; Surkus, A.; Francke, R., Pre-treated carbon additive enables reduction of metal loading in CoNiFe oxide-based OER electrocatalysts while maintaining performance. *J. Catal.* **2025**, 450, 116299. DOI: 10.1016/j.jcat.2025.116299.

6.1 Heterogenized molecular electrocatalyst based on a hydroxo-bridged binuclear Cu(II) phenanthroline compound for selective reduction of CO₂ to ethylene

Na Liu (70%), Stephan Bartling, Armin Springer, Christoph Kubis, Olga S. Bokareva, Evaristo Salaya, Jiameng Sun, Zhonghua Zhang, Sebastian Wohlrab, Ali M. Abdel-Mageed, Hong-Qing Liang, and Robert Francke (10%).

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Abstract: Molecular copper catalysts have emerged as promising candidates for the electrochemical reduction of CO₂. Notable features of such systems include the ability of Cu to generate C₂₊ products and the well-defined active sites that allow for targeted structural tuning. However, the frequently observed *in situ* formation of Cu nanoclusters has undermined the advantages of the molecular frameworks. It is therefore desirable to develop Cu-based catalysts that retain their molecular structures during electrolysis. In this context, we report a heterogenized binuclear hydroxo-bridged phenanthroline Cu(II) compound with a short Cu...Cu distance as a simple yet efficient catalyst for electro-generation of ethylene and other C₂ products. In aqueous electrolyte, the catalyst demonstrates remarkable performance, with excellent Faradaic efficiency for C₂ products (62%) and minimal H₂ evolution (8%). Furthermore, it exhibits high stability, manifested by no observable degradation during 15 hours of continuous electrolysis. The preservation of the atomic distribution of the active sites throughout electrolysis is substantiated through comprehensive characterizations, including X-ray photoelectron and absorption spectroscopy, scanning and transmission electron microscopy, UV-Vis spectroscopy, as well as control experiments. These findings establish a solid foundation for further investigations into targeted structural tuning, opening new avenues for enhancing the catalytic performance of Cu-based molecular electrocatalysts.

My contribution: I developed the protocol for catalyst synthesis, was involved in structural characterization with various spectroscopic and microscopic techniques, and carried out electrochemical measurements. Furthermore, I wrote the first draft of the manuscript (70%). Robert Francke (10%) was responsible for conceptualization of the study, guided the project, and polished manuscript.

Heterogenized Molecular Electrocatalyst Based on a Hydroxo-Bridged Binuclear Copper(II) Phenanthroline Compound for Selective Reduction of CO₂ to Ethylene

Na Liu, Stephan Bartling, Armin Springer, Christoph Kubis, Olga S. Bokareva, Evaristo Salaya, Jiameng Sun, Zhonghua Zhang, Sebastian Wohlrab, Ali M. Abdel-Mageed,* Hong-Qing Liang,* and Robert Francke*

Molecular copper catalysts have emerged as promising candidates for the electrochemical reduction of CO₂. Notable features of such systems include the ability of Cu to generate C₂₊ products and the well-defined active sites that allow for targeted structural tuning. However, the frequently observed in situ formation of Cu nanoclusters has undermined the advantages of the molecular frameworks. It is therefore desirable to develop Cu-based catalysts that retain their molecular structures during electrolysis. In this context, a heterogenized binuclear hydroxo-bridged phenanthroline Cu(II) compound with a short Cu...Cu distance is reported as a simple yet efficient catalyst for electrogeneration of ethylene and other C₂ products. In an aqueous electrolyte, the catalyst demonstrates remarkable performance, with excellent Faradaic efficiency for C₂ products (62%) and minimal H₂ evolution (8%). Furthermore, it exhibits high stability, manifested by no observable degradation during 15 h of continuous electrolysis. The preservation of the atomic distribution of the active sites throughout electrolysis is substantiated through comprehensive characterizations, including X-ray photoelectron and absorption spectroscopy, scanning and transmission electron microscopy, UV–vis spectroscopy, as well as control experiments. These findings establish a solid foundation for further investigations into targeted structural tuning, opening new avenues for enhancing the catalytic performance of Cu-based molecular electrocatalysts.

1. Introduction

The valorization of carbon dioxide (CO₂) for the production of chemicals is a possible alternative to fossil feedstocks and may have the potential to contribute to the curbing of global warming caused by anthropogenic CO₂ emissions.^[1] Electrochemical reduction of carbon dioxide (eCO₂RR) has gained attention as a potential strategy for closing the carbon cycle and addressing the energy crisis while producing valuable fuels and chemicals.^[2] Of particular interest is the selective electrocatalytic reduction of CO₂ to ethylene (C₂H₄), which already finds extensive application as a C₂ building block in the chemical industry. For this reason, various methods for ethylene production using hydrocarbons as feedstock have been researched for decades.^[3] Electrocatalysts based on elemental Cu and Cu oxides, respectively, have demonstrated unique advantages in CO₂ electroreduction, as they are capable of reducing CO₂ beyond two electrons to various C₂₊ products, including hydrocarbons and alcohols.^[4] Nonetheless,

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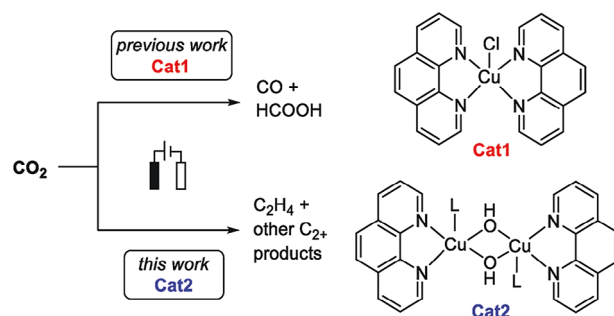
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the selectivity for C_2H_4 production is generally low to moderate due to the competing hydrogen evolution reaction (HER) and multiple reaction pathways that lead to the formation of various C_{1-3} products such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH_3OH), methane (CH_4), acetic acid (CH_3COOH), ethanol (C_2H_5OH), and *n*-propanol ($n-C_3H_7OH$).^[5]

As an alternative, molecular electrocatalysts offer well-defined active sites that i) allow for optimization of the catalytic performance via precise structural tuning, ii) facilitate studies of the reaction mechanism, and iii) enable the elaboration of unambiguous relationships between structure and catalytic activity.^[6] Previous studies have demonstrated excellent performance of molecular catalysts, particularly those based on earth-abundant metal complexes (e.g., based on Fe, Mn, Ni), for eCO_2RR .^[7] Either used as homogeneous electrocatalysts or immobilized on the cathode surface, these systems generate CO in the vast majority of cases, often with a Faradaic efficiency (FE) close to unity.^[8] The more challenging conversion to other C_1 products such as formate ($HCOO^-$)^[9] and CH_3OH ^[10] was reported much less frequently. In this context, recent studies indicate that Cu complexes could serve as catalysts for eCO_2RR to C_{2+} products.^[11] For instance, Bouwman and co-workers reported a binuclear Cu complex that selectively reduced CO_2 , instead of O_2 , from air to generate oxalate.^[12] A mechanistic study suggested that CO_2 reacted with Cu(I) sites to form a tetranuclear Cu structure with bridging oxalate anions as a critical intermediate. Brudvig, Wang and co-workers reported that a Cu–porphyrin complex with attached phenolic OH groups on carbon nanoparticles generated CH_4 and C_2H_4 with FE of 25% and 17%, respectively, at -0.98 V vs. reversible hydrogen electrode (RHE).^[13] Similarly, a Cu phthalocyanine compound immobilized on carbon black was employed for eCO_2RR , producing C_2H_4 with a FE of 25% and a partial current density of 2.8 mA cm^{-2} .^[14] More recently, a Cu-phthalocyanine-based system showed a FE of up to 70% for multicarbon products at much higher current densities.^[15] However, the same study revealed that the reconstruction (i.e., decomposition of the molecular complex) during electrolysis led to the formation of Cu nanoparticles. In view of similar reported cases,^[16] it is reasonable to assume that frequently not the Cu complex itself, but in situ formed nanoclusters surrounded by ligands serve as the real active sites responsible for the formation of C_{2+} products. The lack of stability of these catalysts seems to nullify the actual benefits of molecular catalysts, the high control of selectivity with well-defined and tunable active sites. In this context, it appears desirable to develop Cu-based catalysts that retain a molecular structure during electrolysis.

When designing new Cu-based eCO_2RR catalysts, particular attention must be paid to two aspects, namely the realization of di- or multinuclear systems that facilitate C–C coupling of adjacent CO_2 reduction intermediates and the choice of a robust and cost-effective ligand with suitable steric and electronic properties. Regarding the latter criterion, the bidentate 1,10-phenanthroline ligand (phen) stands out as an excellent choice for stabilizing bi- or multinuclear Cu ensembles. Phen features two inward-pointing nitrogen donor atoms being held juxtaposed and is therefore preorganized for strong and entropically favored metal binding.^[17] Another distinct property is the π -electron deficiency that renders phen an excellent π acceptor capable of



Scheme 1. Mono- and binuclear Cu phenanthroline complexes for CO_2RR .

stabilizing metal ions in lower oxidation states.^[18] Moreover, measurements of complex stability constants have shown that phen coordinates particularly strongly to Cu ions,^[19] making it an exciting and promising ligand for Cu-catalyzed eCO_2RR . Indeed, two recent works indicate that Cu-based systems may retain a molecular structure during electrolysis under certain circumstances. In one of these studies, Liao and co-workers presented a binuclear cuprous complex $[Cu_2(phen)_2]$ (Hophen = 1*H*-[1,10]phenanthroline-2-one) with an intramolecular Cu...Cu distance of 2.62 Å , enabling the electroreduction of CO_2 to C_2H_4 with a FE of 55% under flow conditions when the carbon working electrode was coated with the Cu complex.^[20] In the second study, Wang et al. described eCO_2RR in the presence of dissolved mononuclear complex **Cat1** (Scheme 1) in an aqueous solution using graphene-based electrodes.^[21] The system produces mainly CO, $HCOO^-$, and H_2 , with a 90% FE for C_1 products obtained at -0.6 V vs. RHE. As a result of a mechanistic study, it was suggested that **Cat1** is reversibly adsorbed on the carbon electrode, where it serves as the active site for CO_2RR . Based on this intriguing work, we propose a related binuclear hydroxo-bridged phenanthroline copper(II) complex (**Cat2**, Scheme 1) with a short Cu...Cu distance as a simple yet efficient molecular catalyst for eCO_2RR to C_2H_4 .

2. Results and Discussion

2.1. Structure of the Pristine Electrocatalyst

Compared to **Cat1** reported by Wang et al.,^[21a] which is prepared at neutral pH, our Cu phenanthroline system is synthesized under weakly alkaline conditions (see the Experimental Section and Figure S1 in the Supporting Information). As a result of the modified procedure, $[Cu_2(phen)_2(OH)_2(H_2O)_2][Cu_2(phen)_2(OH)_2Cl_2]Cl_2 \cdot 6H_2O$ (**Cat2**) is obtained, a binuclear hydroxo-bridged phenanthroline copper(II) compound, which is composed of two different centrosymmetric complexes with square pyramidal coordination (Figure 1). The main framework is the same in both Cu complexes, i.e., the divalent cation $[Cu_2(phen)_2(OH)_2]^{2+}$, in which the Cu centers are coordinated by two nitrogen atoms of one phen ligand and two oxygen atoms from the two bridging μ -hydroxo groups. The main difference between the two complexes is the type of axial ligand (water and chloride, respectively). The Cu...Cu distances in these complexes are 2.93 Å each. It can

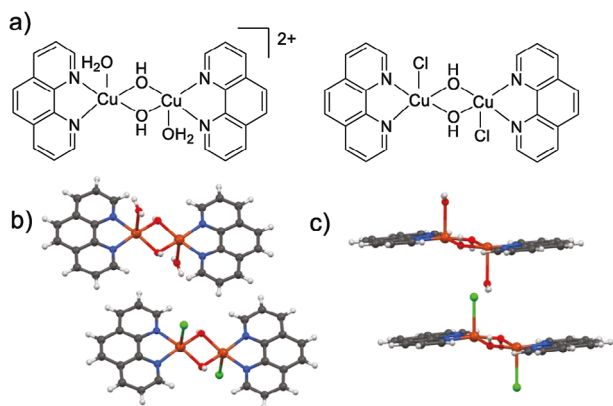


Figure 1. a) Molecular structures of the two binuclear Cu species in $[\text{Cu}_2(\text{phen})_2(\text{OH})_2(\text{H}_2\text{O})_2][\text{Cl}_2\cdot 6\text{H}_2\text{O}]$ (**Cat2**). b, c) Top and side views of the two Cu complexes (structures based on SC-XRD data, see CCDC 190413). Chloride counterions and uncoordinated water molecules are omitted for clarity. Color code: carbon (gray), nitrogen (blue), oxygen (red), hydrogen (white), and copper (orange).

be assumed that the coordinated water molecule and chloride ligand, respectively, are relatively easy to dissociate from the complex,^[22] leaving an exposed Cu–Cu site that is expected to favor carbon–carbon coupling. The structure of the as-prepared **Cat2** was confirmed by elemental analysis as well as single crystal and powder X-ray diffraction (SC-XRD and P-XRD, Figure 1 and Figure S2 (Supporting Information)).^[22]

For electrode preparation, an ink consisting of **Cat2** powder (loading: 0.5 mg cm^{-2}), graphite powder, and Nafion in a water-*i*PrOH mixture was drop-casted onto carbon paper. After drying the electrode under air, the material was analyzed using P-XRD and scanning electron microscopy (SEM), including energy dispersive X-ray (EDX) mapping (Figures S2–S4, Supporting Information). P-XRD confirmed the stability of the binuclear Cu complex within the ink, since signals corresponding to crystalline **Cat2** can still be observed. SEM shows both undefined shapes of deposits and platelet-like particles. EDX analysis suggests that the amorphous parts, having a high fluorine content, are most likely to be assigned to Nafion. Attempts to characterize the platelet structure in more detail using transmission electron microscopy (TEM) and EDX suggest that these components can be assigned to **Cat2** (Figure S5, Supporting Information).

The use of Nafion binder proved to be essential, since without this component, the catalyst could not be applied evenly to the carbon paper surface. In addition, the catalyst and the graphite particles quickly detach from the electrode during electrolysis when no binder is used.

2.2. Electrocatalytic Performance

The electrochemical CO_2 RR activity of a **Cat2**-modified electrode was examined in a gas-tight H-type divided cell using an aqueous 0.1 M cesium bicarbonate (CsHCO_3) electrolyte. Linear sweep voltammetry (LSV) curves were measured both under CO_2 and Ar atmosphere, respectively (Figure 2a). In the CO_2 -saturated electrolyte, **Cat2** exhibits a positive shift of the onset of the reductive current and a higher current density of -5.5 mA cm^{-2}

at -1.2 V vs. RHE, indicating a promising catalytic activity for CO_2 RR. Controlled potential electrolysis (CPE) was performed for 30 min at potentials between -1.35 and -1.10 V vs. RHE in a CO_2 -saturated solution. The gaseous products detected by gas chromatography (GC) were mainly C_2H_4 , CH_4 , CO , and H_2 , and the liquid-phase products analyzed by ^1H nuclear magnetic resonance (NMR) spectroscopy spectra were mainly HCOOH , $\text{C}_2\text{H}_5\text{OH}$, CH_3COOH , and CH_3CHO (Figure S6, Supporting Information). The results are summarized in Figure 2b. Interestingly, C_2H_4 is produced over the entire potential regime with relatively small variation (33–42% FE), with a maximum FE at -1.25 V . The average current density at -1.25 V is 6.3 mA cm^{-2} , which corresponds to a turnover frequency of 10.5 h^{-1} with respect to ethylene formation (assuming two hydroxo-bridged Cu centers as the active site). By contrast, CO generation is pronounced only at less negative potentials and ceases in favor of CH_4 upon increasing the driving force. Notably, the selectivity for H_2 is $\approx 10\%$ or less over the entire potential regime, highlighting the preference of **Cat2** toward CO_2 RR over HER.

Figure 2c summarizes the selectivity for H_2 , C_1 , and C_2 products at different potentials. At -1.25 V vs. RHE, the total FE for C_2 products reaches 62%, including C_2H_4 (FE = 42%), $\text{C}_2\text{H}_5\text{OH}$ (FE = 12%), CH_3CHO (FE = 6%), and CH_3COOH (FE = 2%). At the same potential, the FE for C_1 products is as low as 30% (Figure 2c). Interestingly, **Cat2** generates more C_1 products than C_2 products when using 0.1 M KHCO_3 electrolyte (Figures S7–S9, Supporting Information), consistent with previous works on Cu-catalyzed eCO_2 RR.^[23] Changing the **Cat2** loading from 0.5 to 0.75 and 0.25 mg cm^{-2} , respectively, did neither affect FE (C_2H_4) nor the ratio between C_2 and C_1 products significantly but led to a slight decrease of j in both cases (Figures S11 and S12, Supporting Information). A comparison with catalysts from the literature shows a relatively high selectivity toward C_2H_4 and an outstanding ability to suppress HER (Figure 2d, d Tables S3–S5 and Figure S36 (Supporting Information)). The stability of the catalytic system was tested in a long-term electrolysis at -1.25 V vs. RHE (Figure 2e). After a short induction period, both the current density and FE (C_2H_4) remained stable for more than 15 h of continuous operation (for details, see Figure S13 in the Supporting Information).

2.3. Post-electrolysis Characterization of the Electrocatalyst

After electrolysis at -1.25 V in CO_2 -saturated aqueous 0.1 M CsHCO_3 electrolyte, the electrode material was first characterized by SEM, TEM, and XRD (Figure 3 and Figures S14–S18 (Supporting Information)). Interestingly, an amorphous and porous composite material was formed, which, according to EDX mapping, exhibits a relatively homogeneous distribution of Cu, N, O, and C (Figure 3e,f). EDX spectroscopic analysis indicated that the chloride content decreased dramatically compared to the initial material, which can be explained by reductive dehalogenation of **Cat2** upon negative polarization of the electrode. Based on the results of scanning transmission electron microscopy (STEM) measurements and EDX mapping (see example in Figure 3), we can exclude the formation of large Cu_x/CuO_x clusters ($>2 \text{ nm}$). We were therefore interested in the environment and oxidation state in which the

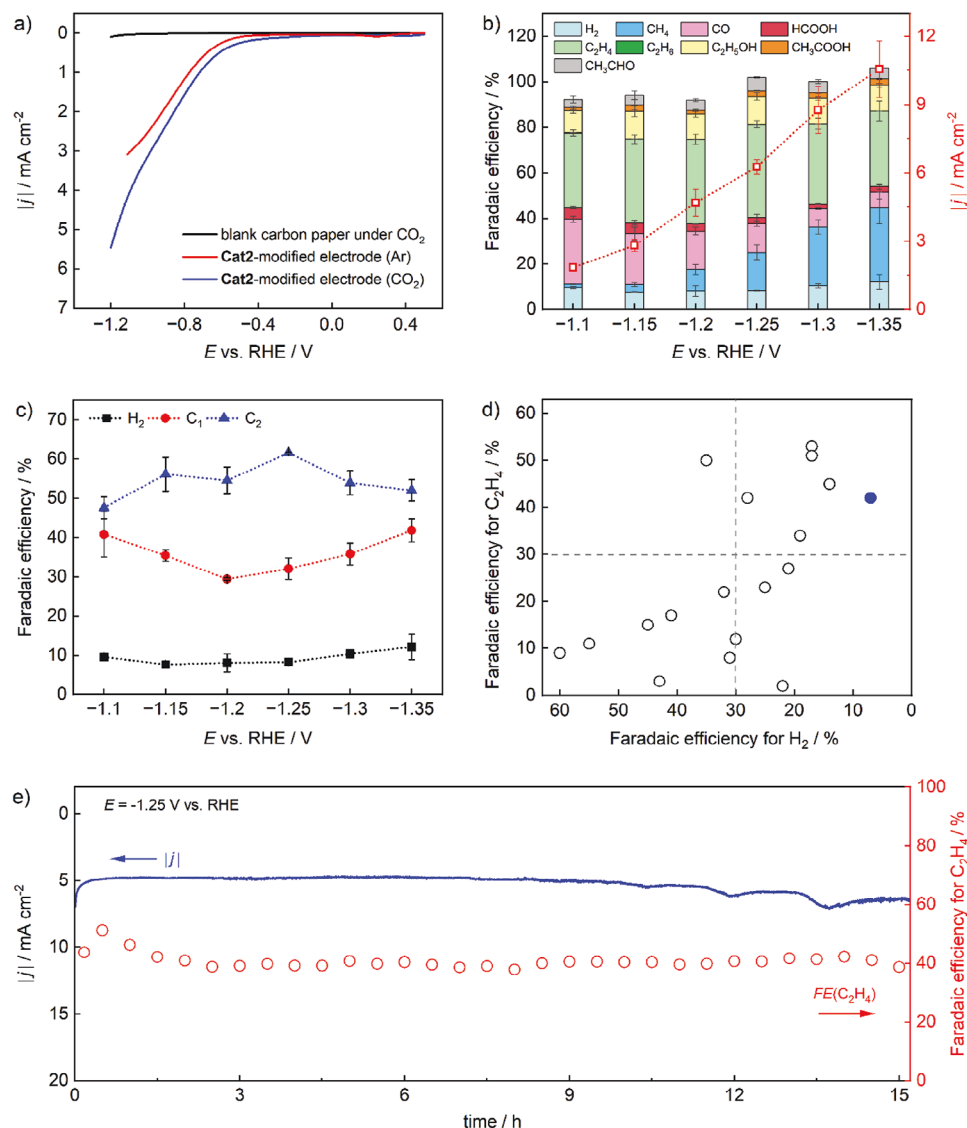


Figure 2. Electrochemical characterization of **Cat2**-modified carbon paper electrodes (aq. 0.1 M CsHCO₃ electrolyte, H-type-divided cell). a) LSVs of a **Cat2**-modified electrode under Ar (red, pH 8.9) and CO₂ (blue, pH 6.8), respectively. b) FE for different products using **Cat2** at different working electrode potentials. c) Comparison of the FEs for H₂, C₁, and C₂ products. d) Plot of FE (C₂H₄) vs. FE (H₂) for **Cat2** (blue symbol) and representative catalysts from the literature based on Cu complexes and Cu-containing metal-organic frameworks (MOFs; for details, see Tables S3 and S4 in the Supporting Information). e) Long-term stability test of **Cat2** at -1.25 V vs. RHE.

active Cu species are present and whether these change with catalysis.

As shown in Figure 4 and Figures S19–S23 (Supporting Information), the coordination environment and oxidation states of **Cat2** before and after CO₂RR were further characterized by X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and ultraviolet–visible (UV–vis) absorption analysis. In Figure 4a, the XP spectrum of the Cu 2p region for the as-prepared **Cat2** powder is shown. The strong satellite features, together with the split of Cu 2p_{3/2} into two peaks at 934.1 and 932.3 eV, suggest the presence of Cu²⁺ and Cu⁺/Cu⁰, respectively.^[24] However, Cu²⁺ is the expected oxidation state in **Cat2** (vide supra). To clarify the presence of Cu⁺/Cu⁰, reference experiments have been performed using single crystal

fragments of **Cat2** for XPS analysis. As shown in Figure 4b, the Cu 2p region suggests mainly Cu²⁺ at the beginning of the experiment. After about 1 h under X-ray radiation, Cu²⁺ is partially reduced to Cu⁺/Cu⁰, as can be seen by the growing peak/shoulder at lower binding energy. Based on X-ray absorption near edge spectroscopy (XANES) and UV–vis spectroscopy data (vide infra), we concluded that the observed Cu⁺/Cu⁰ is caused by X-ray- and/or ultrahigh-vacuum (UHV)-induced reduction during the XPS analysis and that the main oxidation state of **Cat2** is Cu²⁺. Comparison of the Cu²⁺ binding energy and satellite structure to literature data^[24] further confirms that Cu is not only coordinated to oxygen like in copper oxide (CuO), as evidenced by the structural data obtained from SC-XRD (Figure 1).

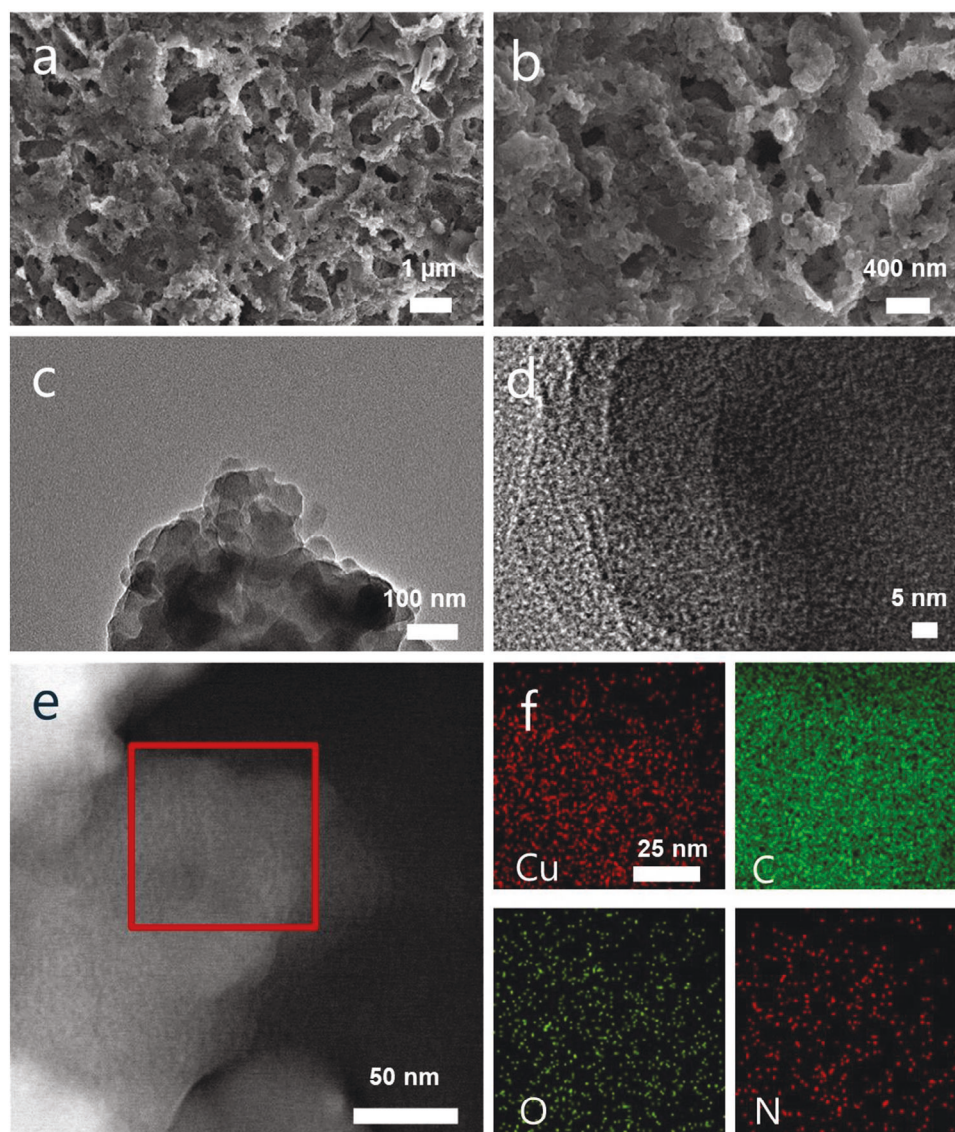


Figure 3. a,b) SEM of a **Cat2**-modified carbon paper electrode after electrolysis. c,d) TEM analysis of a **Cat2** sample after electrolysis. e) STEM analysis of a **Cat2** sample after electrolysis, including EDX mapping. f) For details of the sample preparation for TEM analysis, see Figure S18 in the Supporting Information.

After electrolysis, the **Cat2**-modified carbon paper was analyzed, showing two peaks representative for Cu^{2+} (935.0 eV) and Cu^+/Cu^0 (931.9 eV) species but with a slight shift in opposing directions and a rather low relative concentration of Cu^+/Cu^0 (10% of the total amount of Cu). The change in the chemical environment of the Cu atoms during electrolysis is probably the reason for the observed shift in the XPS peaks of the Cu^{2+} and Cu^+/Cu^0 species, as well as for the slightly different satellite peak structures of the postelectrolysis sample. The appearance of the Cu^+/Cu^0 signal may either be caused by electrolysis or, again, by X-ray-/UHV-induced reduction. It should also be noted that due to the decreased Cu content of the used electrode compared to pure **Cat2**, the survey spectra (Figure S19 (Supporting Information)) are dominated by fluorine and carbon originating from the Nafion and carbon paper (see also the XRD results shown

in Figure S14 in the Supporting Information). Additionally, for the as-synthesized **Cat2** powder, the XPS peak of Cl 2p is clearly visible at a binding energy of 197.4 eV but absent for the **Cat2**-modified electrode after electrolysis (Figure 4c). This result is consistent with the SEM and TEM elemental analysis data, confirming that the Cu–Cl bond is cleaved by cathodic reduction.

To understand the extent of change in the coordination environment of Cu species in the catalyst, we carried out X-ray absorption spectroscopy at the near (XANES) and extended (EXAFS) Cu K-edge on the fresh and spent electrocatalysts. Figure 4d shows the XANES spectra of Cu foil, CuO, Cu_2O , as well as freshly prepared **Cat2** powder and a **Cat2**-modified carbon paper electrode after electrolysis. The comparison of the spectra of both the fresh and the spent catalysts indicates distinctly different spectral features, from the Cu foil and both Cu oxide reference

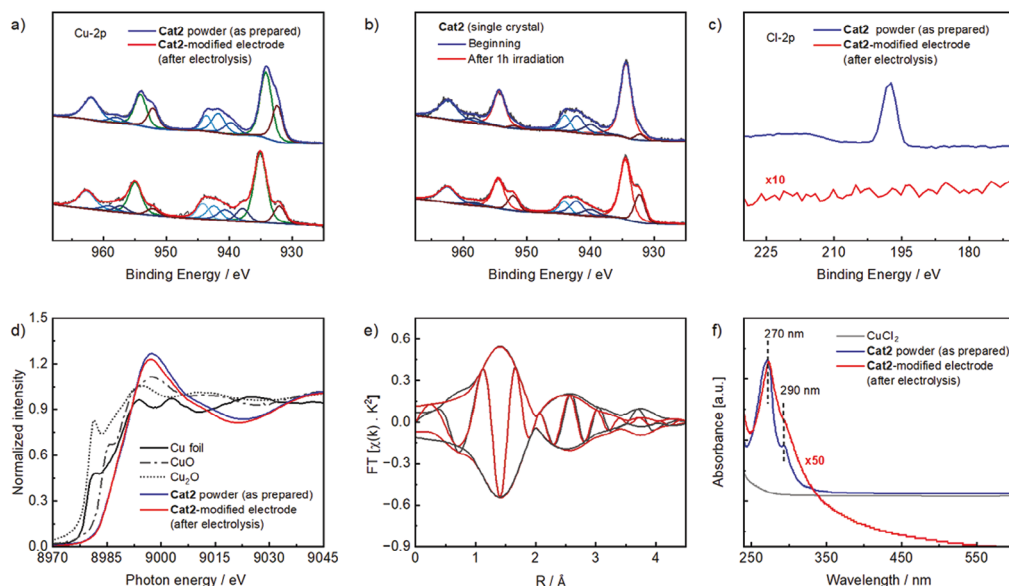


Figure 4. a–c) XPS analysis of **Cat2**. a) Scans in the Cu 2p region using the as-prepared **Cat2** powder (blue line) and a **Cat2**-modified carbon paper electrode after electrolysis (red line). b) Monitoring of the progression of the XP spectrum of an as-prepared **Cat2** during measurement in a control experiment. c) Scans in the Cl 2p region using the as-prepared **Cat2** powder (blue line) and a **Cat2**-modified carbon paper electrode after electrolysis (red line). d) Normalized Cu K-edge XANES spectra and e) Fourier transform extended X-ray absorption fine structure (EXAFS) analysis of Cu-based samples including **Cat2**. f) Comparison of the UV–vis spectra of the as-prepared **Cat2** powder and a **Cat2**-modified electrode after electrolysis.

materials. The peak position of the white line at ≈ 8992 eV, however, aligns closely with the CuO reference, whereby the characteristic edge feature at ≈ 8980 eV is absent. This finding dictates in the first place that Cu is present in an oxidized form (i.e., coordinated basically to O ligands), but also that the Cu coordination environment differs significantly from typical CuO_x clusters.^[25] Interestingly, the shape of the spectrum is largely similar to isolated Cu single sites coordinated by oxygen ligands,^[26] which points toward highly dispersed species (Cu single sites, Cu-oxo dimers, or tiny CuO_x clusters). In both cases, the spectra of the fresh and spent (i.e., after electrolysis) samples are almost identical. This striking similarity confirms that the Cu^+/Cu^0 signals in the XP spectra (Figure 4a) originate from X-ray-/UHV-induced reduction rather than from electrolysis and hints at the structural integrity of the molecular framework of **Cat2** during CO_2 conversion.

To obtain information on the coordination environment of Cu atoms and the structure of the molecular catalyst, we evaluated the EXAFS region for both the as-prepared and the electrolysis-spent samples. The fit of the EXAFS data of the fresh sample (see Fourier transform (FT)-EXAFS in Figure 4e and Table S1 in the Supporting Information) indicated backscattering at distances of 1.83 ± 0.015 , 1.94 ± 0.015 , and 2.95 ± 0.03 Å with coordination number of 1.8 ± 0.5 , 1.3 ± 0.5 , and 2.7 ± 0.5 , respectively.^[22,25] These distances can be assigned to a copper-surrounding environment consisting of oxygen, nitrogen (chlorine), and copper atoms, respectively, which agrees excellently with distances derived from the SC-XRD measurement discussed above (see structure in Figure 1). However, the coordinating Cl ligand expected at a distance of ≈ 2.2 Å,^[27] accessible via SC-XRD, could not be fitted. There is, however, a shoulder around this distance in the FT-EXAFS data, which may be related to this species (Figure 4e).

After electrolysis, the fit parameters showed similar scattering distances, but at the same time, coordination numbers are significantly smaller, and error margins are rather large (see Figure S22 and Table S1 in the Supporting Information). Here, it should be clearly stated that the signal-to-noise ratio in the post-electrolysis **Cat2**-modified electrode is not as good as in the as-prepared **Cat2** powder due to the much lower copper content.

To obtain further structural information on the catalyst, we examined pure **Cat2** and an electrolysis-spent sample of a **Cat2**-modified electrode with diffuse reflectance (DR) UV–vis spectroscopy (Figure 4f and Figure S23 (Supporting Information)). Freshly prepared pristine **Cat2** exhibits a well-defined absorption peak at ≈ 270 nm with a small shoulder at ≈ 290 nm. The postelectrolysis sample exhibits a lower intensity (scaled up by a factor of 50),^[28] but the spectrum shows very similar features. Despite the small relative changes in intensity, the peak position, as well as that of the shoulder (270 and 290 nm) and the relative ratio of the shoulder to the main peak, did not shift (change) after electrolysis, supplying additional evidence for the integrity of the atomic Cu distribution during electrolysis. Based on reported UV–vis spectra on Cu-exchanged zeolite, the observed peak would refer to isolated Cu sites coordinated by oxygen or oxygen-containing ligands (e.g., $-\text{OH}$).^[29] Additional UV–vis analysis of copper chloride (CuCl_2) salt and copper nanoparticles (Cu NPs, average diameter: 25 nm) with and without exposure to electrolysis support the assignment of the features at ≈ 270 and ≈ 290 nm to Cu^{2+} sites within the molecular framework of **Cat2** (see Figure 4f and Figure S23 in the Supporting Information). It is also important to note that based on the literature, CuO_x particles/clusters, which may form during cathodic reduction of CuCl_2 , are expected to feature a broad absorption peak ranging from 350 to 550 nm.^[30] A closer inspection reveals that intensity is gained in this

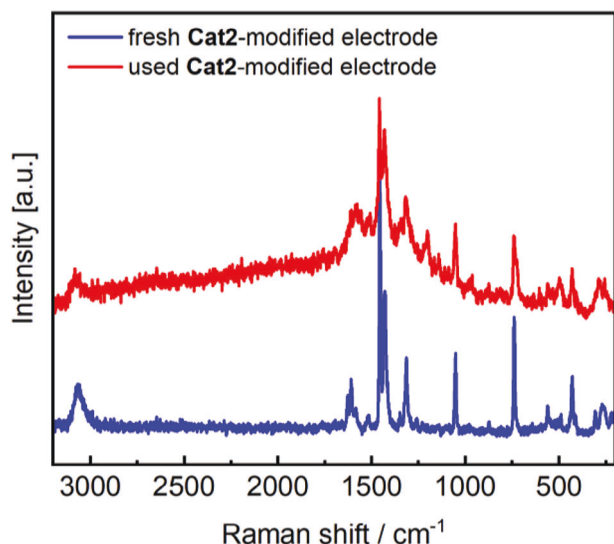


Figure 5. Comparison of Raman spectra for the **Cat2**-modified electrode before and after electrolysis (for technical details, see the Experimental Section).

region for CuCl_2 after electrolysis, which is not observed for the **Cat2**-modified electrode (Figure S23, Supporting Information). A similar increase in signal intensity can also be observed for Cu-NP-modified electrodes, which can be explained by coverage of the copper surface with an oxide layer upon exposure to air.

Taken together, the UV-vis measurements supply additional evidence against the formation of small CuO_x clusters, which agrees well with the results of SEM, TEM, XANES/EXAFS, and XPS measurements. This finding is additionally corroborated by the results of Raman spectroscopic investigations (Figure 5). The fresh **Cat2**-modified electrodes exhibit Raman bands characteristic of the binuclear Cu complexes ($429, 738, 1052, 1314, 1429, 1455, 1609, 1626, 3066 \text{ cm}^{-1}$), which was verified by control measurements on pristine **Cat2** powder and other reference materials (Figure S24, Supporting Information) as well as with density functional theory (DFT) calculations (Figure S25, Supporting Information). An assignment of respective band contributions to the Raman active vibrational modes of the **Cat2** framework compared to those for the ligand 1,10-phenanthroline was conducted based on the DFT results (Figure S25 and Table S8, Supporting Information). The Raman spectrum for the sample after electrolysis shows the same major band contributions for **Cat2** with a slight peak broadening and a decrease in intensity. In agreement with XAS, XPS, and UV-vis spectroscopic results, it can be concluded that a considerable amount of the complex **Cat2** remains intact during electrolysis. On the other hand, further evidence against the formation of significant amounts of Cu/CuO_x nanoparticles was obtained by control experiments. Broad band contributions at ≈ 527 and $\approx 622 \text{ cm}^{-1}$ are characteristic for Cu oxide materials^[31] and were also observed upon studying spent carbon paper electrodes that were modified with CuCl_2 and defined Cu/CuO_x nanoparticles (25 nm), respectively. Such features were absent in the spectrum of the **Cat2**-modified electrode after electrolysis (Figure S24, Supporting Information).

2.4. Control Experiments and Mechanistic Studies

To corroborate the interpretations discussed above and to gain a better understanding of the electrocatalysis of CO₂RR on **Cat2**-modified electrodes, a series of control experiments was performed (Table 1 and Figures S26 and S27 (Supporting Information)). First, several CPEs were carried out to ascertain the origin of carbon atoms in the gaseous products and the role of **Cat2** as a CO₂RR catalyst. Electrolysis under Ar atmosphere using a **Cat2**-modified electrode generates H₂ as the only detectable product (entry 2). A similar outcome was observed upon performing CPE in CO₂-saturated electrolyte using i) blank carbon paper electrodes (entry 3), ii) carbon paper electrodes which were modified with **Cat2**-free ink (entry 4), as well as in the presence of 1,10-phenanthroline (entry 5, no Cu salt added).

Second, the product distribution obtained with the **Cat2**-modified electrode was compared to the results obtained using carbon paper electrodes with Cu aggregates on the surface. For this purpose, **Cat2** was replaced by CuCl_2 , CuO, and Cu nanoparticles, respectively, in the ink preparation (entries 6–8). In all three cases, H₂ production is strongly enhanced, while the selectivity for C₂ products is significantly decreased. In contrast to **Cat2**, the control experiments in entries 6–8 show an inverted FE (CO):FE (HCOO[−]) ratio and formation of small quantities of *n*-PrOH.

Third, a CPE was carried out using a structural analog of **Cat2**, in which the μ -hydroxo groups are replaced by two bridging glutarate ligands (entry 9). The resulting binuclear Cu phenanthroline complex **Cat3** (see structure below in Table 1) exhibits a longer Cu...Cu distance compared to **Cat2** (8.47 Å according to SC-XRD; for details, see Figures S28–S30 in the Supporting Information).^[32] Interestingly, **Cat3**-modified electrodes exhibited a higher FE (H₂) and a lower FE (C₂H₄) within the entire studied potential regime (−1.1 to −1.35 V vs RHE, Figure S31, Supporting Information). For example, at −1.25 V, the FE for C₂ products was only 31%, while FE (C₁) and FE (H₂) increased significantly (51% and 18%, respectively).

Postelectrolysis examination of the electrolyte solution and the **Cat3**-modified electrode revealed the origin of the differences in the product distribution. The ¹H NMR spectrum of the liquid phase (Figure S32, Supporting Information) indicates the presence of glutarate but not 1,10-phenanthroline. SEM of spent **Cat3**-modified electrodes (Figures S33 and S34, Supporting Information) also showed changes in both morphology and element distribution as the complex crystals merged with the Nafion deposits on the electrode surface. In contrast to spent **Cat2** electrodes, however, a highly dispersed distribution of Cu species is clearly not obtained in spent **Cat3**. Instead, aggregates of copper are formed during electrolysis, which may be responsible for the higher FE (H₂) and the altered distribution of carbon products.^[33]

Finally, surface-enhanced infrared absorption spectroscopy spectro-electrochemical (SEIRAS-SEC) measurements were carried out in CO₂-saturated aq. 0.1 M CsHCO₃ using a thin-film Au electrode to gather information on the interaction between immobilized **Cat2** and carbon dioxide (Figure S35, Supporting Information). First, the catalyst-free electrode was examined at different potentials (0 to −1.35 V vs RHE) to check if any intermediates appeared upon the interaction between CO₂ and the Au film (Figure S35a, Supporting Information). The IR data clearly

Table 1. Control experiments on the origin of gaseous products and the nature of active sites..

Entry ^{a),b)}	Deviation from standard conditions	FE (H ₂)	FE (C ₁)	FE (CO)	FE (HCOO ⁻)	FE (C ₂)	FE (n-PrOH)
1	None	8	32	12	3	62	–
2	Ar atmosphere	70	–	–	–	–	–
3	Blank carbon paper cathode	60	–	–	–	–	–
4	Cat2 -free ink	90	–	–	–	–	–
5	1,10-phenanthroline without Cu	38	–	–	–	–	–
6	CuCl ₂ (no ligand) ^{a)}	28	43	13	19	18	2
7	CuO (no ligand) ^{a)}	29	21	5	16	37	5
8	Cu NPs ^{b)}	33	17	5	11	31	5
9	Cat3 -modified cathode	18	51	22	5	31	–

^{a)} The ink was prepared with an equimolar amount of Cu salt, but without ligand; ^{b)} Defined Cu nanoparticles (average diameter: 25 nm) were used instead of **Cat2**.

indicate that there are hardly any features related to possible reaction intermediates and show merely a change in the background with a change in potential. Repeating the experiments with a **Cat2**-modified electrode (using the same drop casting approach as for the CPE experiments), a series of vibrational features was observed that can be related to surface-active species, most probably formate-like intermediates and/or surface carbonates that are visible both in the OC/OCO (stretch/bending) regions (see Figure S35b in the Supporting Information) as well as in the C–H stretch regions (Figure S35c, Supporting Information). In particular, the significant increase of a feature at 1228 cm⁻¹ with increasingly negative potentials points toward the formation of a surface CO₂ intermediate. Presumably, it is a formate- or carboxylate-like intermediate (see the selected assignments from the literature in Table S2 in the Supporting Information for comparison). In total, these results confirm the formation of various intermediates upon the interaction of CO₂ with the immobilized molecular catalyst. However, the unambiguous assignment of the measured vibrational frequencies is not accessible from present experiments and more systematic investigations are needed, which will be part of our future endeavors.

Even though at this point there is insufficient experimental evidence of intermediates for meaningful quantum chemical modeling of the entire catalytic cycle, valuable information was obtained by means of DFT calculations on the most likely first step, the electrochemical reduction of **Cat2**. The structures of the initial species, [Cu₂(phen)₂(OH)₂(H₂O)₂]²⁺ and [Cu₂(phen)₂(OH)₂Cl₂], as well as their singly reduced forms, have been optimized. Both complexes remain stable while accommodating an additional electron, and no major structural rearrangements are observed (Figure S37, Supporting Information). The corresponding spin densities and Mulliken charges of reduced species indicate that the reduction occurs in the central unit comprised of two copper and two bridging hydroxo units. Experiments and simulations are underway to explore possible reaction pathways that depart from the reduced Cu complexes and to test possible impacts that may arise from the different axial ligands.

3. Conclusion

We have developed an electrocatalytic system based on a heterogenized binuclear hydroxo-bridged phenanthroline copper(II) compound for the selective conversion of CO₂ to C₂ products.

The molecular catalyst is easy to synthesize in one step from commercially available starting materials and was applied, together with graphite powder and Nafion binder, to carbon paper electrodes. In an aqueous CO₂-saturated solution, the modified electrodes exhibit outstanding performance with competitive selectivity for C₂H₄ (up to 42%) and minimal H₂ production (<10%). Stable performance for at least 15 h of continuous operation was demonstrated. Comprehensive structural characterization, including SEM, TEM, elemental mapping, XPS, XAS, Raman, and UV-vis spectroscopy, show a composite matrix within which the atomic distribution of copper is preserved throughout electrolysis.

Control experiments in which the molecular catalyst was replaced by Cu/CuO_x nanoparticles and Cu salts, respectively, rendered product distributions that differed strongly from that of the molecular catalyst. We therefore conclude that it is the short Cu...Cu distance within our binuclear complex and not in situ formation of Cu aggregates that is responsible for CO₂ coupling. The high selectivity for C₂ products distinguishes our catalyst from mononuclear copper phenanthroline complexes that primarily produce CO and formate.

SEIRAS-SEC experiments have provided valuable insights into the interaction between CO₂ and the electrocatalyst, as well as the presence of multiple adsorbed CO₂RR intermediates. These findings form the basis for future experimental and computational studies aimed at an improved understanding of the reaction mechanism. Further efforts to optimize the system by ligand tuning, variation of the Cu...Cu distance, and tests under flow conditions are ongoing in our laboratory.

4. Experimental Section

Materials: CuCl₂ (99%), methanol (99.8%), ethanol (99.8%), isopropanol (99.8%), and CsHCO₃ (99.99%) were purchased from Fisher Scientific. 1,10-Phenanthroline (>99.0%) was provided by Glentham Life Sciences Ltd. (UK). Glutaric acid (>99.0%) was provided by TCI Germany. Graphite powder (400 nm) was obtained from Iolitec Nanomaterials (Germany). Triethylamine (99.5%), potassium bicarbonate (99.99%), sodium carbonate (99.99%), dimethyl sulfoxide (DMSO, 99.9%), CuO (<5 μm, 98%), Cu NPs (25 nm, 99.5%), and Nafion 1100 W solution were provided by Sigma-Aldrich (Germany). Toray Carbon Paper 060 (wet-proofed) was supplied by The Fuel Cell Store (USA). Deuterium oxide (D₂O, 99.9%) was provided by Deutero GmbH (Germany). CO₂ (99.9999%) and Ar (99.9999%) were obtained from Linde AG (Germany).

Synthesis of Cat2: A solution of CuCl₂ (1 mmol) in ultrapure water (1 mL) was mixed with a solution of 1,10-phenanthroline (1 mmol) in ethanol (1 mL) under stirring at room temperature, leading to the formation of a green precipitate. After 10 min, triethylamine (10 mL) was added to the suspension under stirring, resulting in an immediate color change of the precipitate to blue. The solid was filtered off, washed with ultrapure water, and dried overnight under vacuum at 60 °C. The product was obtained as a crystalline blue solid (product yield: 200 mg, 0.15 mmol, 60%). The identity of the product was confirmed by SC-XRD, P-XRD (Figure S2, Supporting Information), and elemental analysis (measured: Cu 18.64, C 43.33, H 3.87, N 8.35, Cl 10.46; calcd.: Cu 19.13, C 43.38, H 3.94, N 8.43, Cl 10.67).

Single crystals of Cat2 were prepared by vapor diffusion crystallization (Figure S1, Supporting Information). For this purpose, solutions of CuCl₂ and 1,10-phenanthroline were mixed as described above. The green precipitate was dissolved by dropwise addition of ultrapure water, leading to a saturated solution (S-A), which was placed in a glass cylinder. A glass vial containing a solution of 100 µL triethylamine in 10 mL ultrapure (S-B) was placed inside solution S-A. The glass cylinder was closed, allowing slow mixing of S-A and S-B via vapor diffusion. Blue needle-like crystals formed slowly in S-A, which were collected after five days. The formation of Cat2 was confirmed by SC-XRD. The compound crystallized in the triclinic space group *P* $\bar{1}$ with unit cell dimensions *a* = 8.7791(15), *b* = 9.3481(16), *c* = 16.422(3) Å, *a* = 105.397(3), *b* = 99.445(3), *g* = 101.278(3)° (*T* = 110(2) K). The crystal structure was already published by Yang and co-workers (CCDC 190413).^[22]

Synthesis of Cat3: Following a previously published protocol, the product was obtained in the form of blue block-shaped crystals.^[32] The product was characterized by P-XRD (Figure S30, Supporting Information) and SC-XRD. The crystal structure was already published by Zheng et al. (CCDC 136623).^[32] SC-XRD was carried out at the same temperature (293 K) and confirmed the identity of Cat3. Furthermore, identity and purity were confirmed by elemental analysis (measured: Cu 16.02, C 52.27, H 4.23, N 7.15; calcd.: Cu 16.22, C 52.11, H 4.12, N 7.15).

Material Characterization: XRD data were collected using a Panalytical X'Pert Pro diffractometer with Cu-Kα radiation. SC-XRD was performed with a Kappa APEX II Duo diffractometer from Bruker AXS GmbH. Analysis of the copper content was performed via inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent 715-ES spectrometer. Carbon, hydrogen, and nitrogen contents were estimated through combustion analysis using a TruSpec Micro elemental analyzer (LECO Instrumente GmbH, Germany). The morphology of the electrode surface before and after electrolysis was studied with SEM using a MERLIN VP Compact (Zeiss, Germany) and TEM (FEI Titan G2 60-300) equipped with EDX. ¹H NMR spectroscopy was performed with an Avance III HD NMR400 spectrometer (Bruker). UV-vis spectra were recorded using a UV-2600i (Shimadzu) spectrometer in the range between 800 and 200 nm. For this purpose, the samples were placed in a quartz cell with a layer depth of 10 mm.

X-Ray Photoelectron Spectroscopy: The XPS measurements were performed on an ESCALAB 220iXL (Thermo Fisher Scientific) with monochromated Al Kα radiation (*E* = 1486.6 eV). Samples are prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. The measurements were performed with charge compensation using a flood electron system combining low-energy electrons and Ar⁺ ions (*p*_{Ar} = 1 × 10^{−7} mbar). The electron binding energies were referenced to the C 1s core level of carbon at 284.8 eV (C—C and C—H bonds). For quantitative analysis, the peaks were deconvoluted with Gaussian–Lorentzian curves using the software Unifit 2023. The peak areas were normalized by the transmission function of the spectrometer and the element-specific sensitivity factor of Scofield.

Electrode Preparation: The preparation of the Cat2-modified working electrode was carried out as follows: the catalyst (6 mg) and graphite powder (1.2 mg) were suspended in a mixture of 450 µL ultrapure water, 90 µL isopropanol, and 60 µL Nafion solution, followed by ultrasonication (15 min) to generate a homogeneous ink. Then, 50 µL of the ink was dropped onto a strip of carbon paper (width: 1 cm) to cover an area of 1 cm² on both sides and dried under air. Unless stated

otherwise, the catalyst loading (Cat2) of each working electrode was 0.5 mg cm^{−2}.

Electrochemical Experiments: LSV and CPE were conducted using a VIONIC potentiostat (Metrohm, Germany). All experiments were performed in a gas-tight H-type divided in a three-electrode arrangement (see Figure S6 in the Supporting Information). A platinum mesh was used as a counter electrode, and a Ag/AgCl electrode (3 M KCl solution) served as the reference. A 0.1 M CsHCO₃ solution (pH 6.8 under CO₂, pH 8.9 under Ar) served as the electrolyte. Each half-cell was filled with 17 mL of electrolyte, leaving headspace volumes of 59 mL each. Prior to each experiment, CO₂ was bubbled at a flow rate of 40 mL min^{−1} for 30 min. Current densities were calculated considering the entire immersed electrode surface area (2 cm²). Potentials measured vs. Ag/AgCl were converted to the RHE using the following relationship^[34]

$$E[\text{V vs. RHE}] = E[\text{V vs. Ag/AgCl}] \quad (1)$$

Product Quantification: Gaseous products from CPE were analyzed by GC (Agilent 6890; carrier gas: argon), calibrated using certified gas mixtures (Air Liquide) as standards. A thermal conductivity detector was used to analyze H₂ and CO, and a flame ionization detector to quantify CH₄, C₂H₄, and C₂H₆ (see exemplary chromatograms in Figure S6 in the Supporting Information). The gas mixture was separated using a parallel setup of a CP-Molsieve 5 Å porous layer open tubular (PLOT) column (Agilent, for permanent gas analysis) and a CP-PoraBOND Q PLOT column (Agilent, for CO₂ analysis). The sample was injected via a normal injection port and was split into the tandem two-column setup. The CP-Molsieve 5 Å column was used to separate the inert gases (H₂, O₂, N₂, CH₄, and CO) before the first peak (composite peak of all inert gases) eluted from the CP-PoraBOND Q column. After the first peak, CH₄, CO₂, C₂H₄, and C₂H₆ eluted from the PoraBOND Q column in sequence.

For short-term electrolysis (30 min), headspace samples were extracted with a gas-tight Hamilton syringe and injected into the GC. Short-term CPEs were repeated 3 times for each potential. For the long-term test, the H-type divided cell was connected to the CG for online analysis and a steady flow of CO₂ gas of 20 mL min^{−1} was adjusted using a mass flow controller (D-6300, Bronkhorst GmbH, Germany). In this case, the FEs for specific gaseous products *x* (e.g., C₂H₄) were calculated using the following relationship^[35]

$$FE_x [\%] = \frac{p\dot{V}\phi_x zF}{RTi} \times 100 \quad (2)$$

wherein $\dot{V}$ refers to the flow rate of the gas that is delivered to the gas chromatograph at a given sampling time (20 mL min^{−1}), ϕ_x to the volume fraction of the gaseous product (i.e., C₂H₄) in the gas flow delivered to the detector, *p* to the pressure (1.01 × 10⁵ Pa), *R* to the gas constant, *T* to the temperature (296 K), *z* to the number of electrons transferred for CO₂-to-*x* (i.e., *z* = 12 for C₂H₄), *F* to the Faraday constant, and *i* to the current recorded by the potentiostat.

The liquid products were quantified by ¹H NMR spectroscopy using a water presaturation method and DMSO as an internal standard. For sample preparation, 500 µL postelectrolysis electrolyte was mixed with 100 µL D₂O and 35 µL DMSO. FE_{*x*} was calculated using the following equation

$$FE_x [\%] = \frac{c_x V z F}{Q} \times 100 \quad (3)$$

wherein *c_x* refers to the product concentration (e.g., HCOOH) in the liquid phase, *V* to the catholyte volume (17 mL), and *Q* to the amount of passed electric charge at a given sampling time.

Assuming two hydroxo-bridged Cu atoms as the active site, the turnover frequency (TOF) with respect to ethylene formation was calculated using the following equation

$$\text{TOF (C}_2\text{H}_4) = \frac{i \times FE(\text{C}_2\text{H}_4)}{zFn_{\text{Cu-Cu}}} \quad (4)$$

wherein i is the average current during 30 min electrolysis, FE (C_2H_4) is the Faradaic efficiency for C_2H_4 , z is the number of electrons transferred for CO_2 -to- C_2H_4 ($z = 12$), and n_{Cu-Cu} is the total amount of Cu–Cu units within the catalyst loading (1.56 μ mol per electrode). The TOF (C_2H_4) values obtained at different electrode potentials are summarized in Figure S10 in the Supporting Information.

XAS Measurements: XAS experiments were carried out at the near and extended Cu K-edge at the SOLEIL Synchrotron, SAMBA beamline. Measurements were done in transmission using a Si(111) monochromator crystal and Si mirrors. The attenuation of the beam by the reaction cell was negligible due to the use of thin Kapton tape for holding the samples in the measurement holder. Data reduction and processing (background subtraction, energy correction, and normalization) of the XANES spectra were carried out using the standard Athena software from the Demeter 0.9.26 program package.^[36] Data reduction and modeling of EXAFS spectra were carried out using the XDAP software package, with standard procedures explained in detail elsewhere.^[26,37] EXAFS data were evaluated in the R -space using fixed k and R ranges (k : 3.1–8.8 $\text{\AA}^{-1}$, R : 0.0–4.5 $\text{\AA}$). The data were accordingly fitted to the shortest distances (i.e., first back-scatterer) around the Cu absorber (i.e., first Cu–Cu, Cu–O (Cu–N) scattering shells). In the evaluation, the bond length, coordination number, internal energy shift (E_0), and the mean square displacement factor (σ_0^2) were allowed to change freely within reasonable ranges based on reported values in the literature.

SEM: The samples were mounted on a heavy metal-free Al-SEM-carrier (co. PLANO, Wetzlar, Germany) with adhesive conductive carbon tape (Spectro Tabs, TED PELLA INC, Redding, USA) and coated with carbon (5.0 nm thickness) under vacuum (CCU 010 HV-Coating Unit, Co. Safematic GmbH, Zizers, Switzerland). Analysis was carried out using a field emission scanning electron microscope (MERLIN VP Compact, Co. Zeiss, Oberkochen, Germany) equipped with an energy dispersive X-ray detector (XFlash 6/30, Co. Bruker, Berlin, Germany). Representative areas of the samples were analyzed and mapped for elemental distribution based on the EDX-spectra data by QUANTAX ESPRIT Microanalysis software (version 2.0). SEM images were taken from the selected regions.

Raman Spectroscopy: Raman spectra of Cat2-modified electrodes (before/after electrolysis) were measured using a Renishaw inVia Raman microscope equipped with a 633 nm air-cooled He–Ne laser. The laser beam was focused on the sample by a $\times 50$ objective with a laser power between 0.085 and 0.17 mW to avoid damaging effects of the sample by focused high laser power. The exposure time was 25 s, with 1–3 accumulations.

All other spectra were measured by a Horiba iHR 550 Raman spectrometer equipped with a 785 nm laser (Process Instruments) with a maximum laser power of 300 mW connected to a fiber optical ball probe (MarqMetrix, 3/8" Process BallProbe). The samples were measured in the direct contact mode. The measurement parameters varied depending on the sample: laser power 50%, exposure time 0.25–3 s, 4–8 accumulations.

SEIRAS: SEIRAS was performed in a SEC cell using the attenuated total reflection (ATR) configuration. The preparation of Cat2-modified working electrodes was a modified version of a three-step process including Si prism preprocessing, chemical deposition of a Au thin film on a hemispherical Si prism, followed by spraying the electrocatalyst ink on the thin film using a spray gun.^[38] The ink was prepared as follows: Cat2 powder (6 mg) was added to a mixture of 450 μ L H_2O , 90 μ L isopropanol, and 60 μ L Nafion solution (5 wt%). After sonication, the ink was sprayed uniformly on the Au surface from ≈ 10 –15 cm distance. After drying, the prism was assembled into a homemade SEC cell as the working electrode. A Ag/AgCl electrode was used as the reference, and a Pt sheet (1 $\times$ 1 cm) as the counter electrode.

A Bruker INVENIO-S spectrometer equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen was employed for the ATR-SEIRAS-SEC measurements. All spectra were shown in absorbance ($-\log(R/R_0)$), with R and R_0 representing the sample and reference spectra, respectively. The spectral resolution was 4 cm^{-1} for all the measurements if not otherwise mentioned. In all electrochemical and spectroscopic measurements, a CHI electrochemical workstation (Model 760E, CH Instruments) was used. Before electrochemical experiments, the FT-IR chamber was continuously purged with N_2 (high purity grade) at ≈ 5 L min^{-1} for 3 h.

Then, CO_2 was purged into the $CsHCO_3$ electrolyte for 30 min. Analyses were performed at 0.0, –0.3, –0.6, –0.9, –1.1, –1.15, –1.2, –1.25, –1.3, and –1.35 V vs. RHE, respectively (2 min at each potential). Eight spectra were recorded during each interval and the averaged spectra are shown in Figure S35 (Supporting Information).

Statistical Analysis: All statistical analyses in this work were performed using the Origin 2023 software. Before data analysis, irrelevant data detection and elimination were performed on the data sets. Experimental errors for FE and average $|j|$ values were calculated as the standard error of the mean using a sample size of $n = 3$. Experimental data in bar diagrams were presented as mean values $\pm$ standard deviation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

CO_2 reduction, copper complex, electrocatalysis, ethylene, molecular catalyst

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6.2 Copper(II) Phenanthroline Catalysts for Electroreduction of CO₂ to C₂ compounds: Substitution on the Ligand Causes Structural Change of the Molecular Framework and Stability Enhancement

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Abstract: Molecular Cu catalysts have shown promise for electrochemical CO₂ reduction (eCO₂RR) to multi-carbon products. Unlike metallic Cu facets, molecular candidates offer precise control over the active site's electronic and steric configuration. However, prior studies identified critical challenges related to irreversible potential-induced formation of Cu particles, which participate in the eCO₂RR and obscure the role of molecular motifs. Based on a binuclear Cu(II) phenanthroline catalyst previously reported by us, we developed a structurally modified second generation system with enhanced stability. By introducing methoxy groups to the phenanthroline ligand, the molecular framework is changed from a binuclear complex to an oligonuclear step-like structure consisting of Cu(II) ions linked by μ_2 - and μ_3 -OH groups. When immobilized on a gas diffusion electrode, stable operation with >70% Faradaic efficiency for C₂ products was achieved at elevated current densities in an MEA electrolyzer. *In situ* XAS spectroscopy shows only negligible changes in the Cu coordination environment up to 50 mA cm⁻². When approaching 250 mA cm⁻², partial and reversible phase evolution under Cu²⁺ valence state reduction is observed, followed by phase recovery upon bias removal. The presented system combines structural robustness with adaptive redox behavior and thus shows a possible route toward implementing molecular electrocatalysts in eCO₂RR processes at industrially relevant current densities.

My contribution: I developed the protocol for catalyst synthesis, was involved in structural characterization with various spectroscopic and microscopic techniques, carried out electrochemical measurements (including the development and validation of a protocol for MEA electrolyzer studies), and wrote a major part of the manuscript (60%). Yanan Han (10%) carried out density functional theory calculations. Trang Minh Pham (10%) carried out control experiments and impedance spectroscopy analysis. Robert Francke (10%) was responsible for conceptualization of the study, guided the project, and polished the manuscript.

Heterogenized Copper(II) Phenanthroline Catalysts for Electroreduction of CO₂ to C₂ Compounds: Substitution on the Ligand Causes Structural Changes to the Molecular Framework and Stability Enhancement

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Molecular Cu catalysts have shown promise for electrochemical CO₂ reduction (eCO₂RR) to multi-carbon products. Unlike metallic Cu facets, they offer precise control over the active site's electronic and steric configuration. However, prior studies identified critical challenges related to irreversible potential-induced formation of Cu particles, which participate in the eCO₂RR and obscure the role of molecular motifs. Based on a previously reported binuclear Cu(II) phenanthroline catalyst, a structurally modified second-generation system with enhanced stability is developed. By introducing methoxy groups to the phenanthroline ligand, the molecular framework changes from a binuclear complex to an oligonuclear step-like structure consisting of Cu(II) ions linked by μ_2 - and μ_3 -OH groups. When immobilized on a gas diffusion electrode, stable operation with a Faradaic efficiency of >70% for C₂ products is achieved at elevated current densities. In situ XAS spectroscopy shows only negligible changes of the Cu coordination environment up to 50 mA cm⁻². When approaching 250 mA cm⁻², partial and reversible phase evolution occurs under Cu²⁺ valence state reduction, followed by phase recovery upon bias removal. This system combines structural robustness with adaptive redox behavior, demonstrating a route for implementing molecular electrocatalysts in eCO₂RR processes at industrial current densities.

1. Introduction

The capture and conversion of CO₂ emissions into value-added chemicals holds immense potential for closing the carbon cycle.^[1] Among various available approaches, the electrochemical CO₂ reduction reaction (eCO₂RR) has attracted significant attention due to its ability to directly utilize surplus renewable electricity for the valorization of CO₂. Depending on the employed catalyst and reaction conditions, this approach generates valuable products such as carbon monoxide (CO), formate (HCOO⁻), ethylene (C₂H₄), and various multi-carbon oxygenates.^[2] Recent advances in electrolyzer design have enabled two-electron reduction processes (i.e., CO and formate generation) to be operated under industrially relevant conditions, which could facilitate commercialization in the near future.^[2a,c] In contrast, the electrochemical synthesis of multi-carbon products (e.g., C₂H₄ and C₂H₅OH) faces persistent fundamental and

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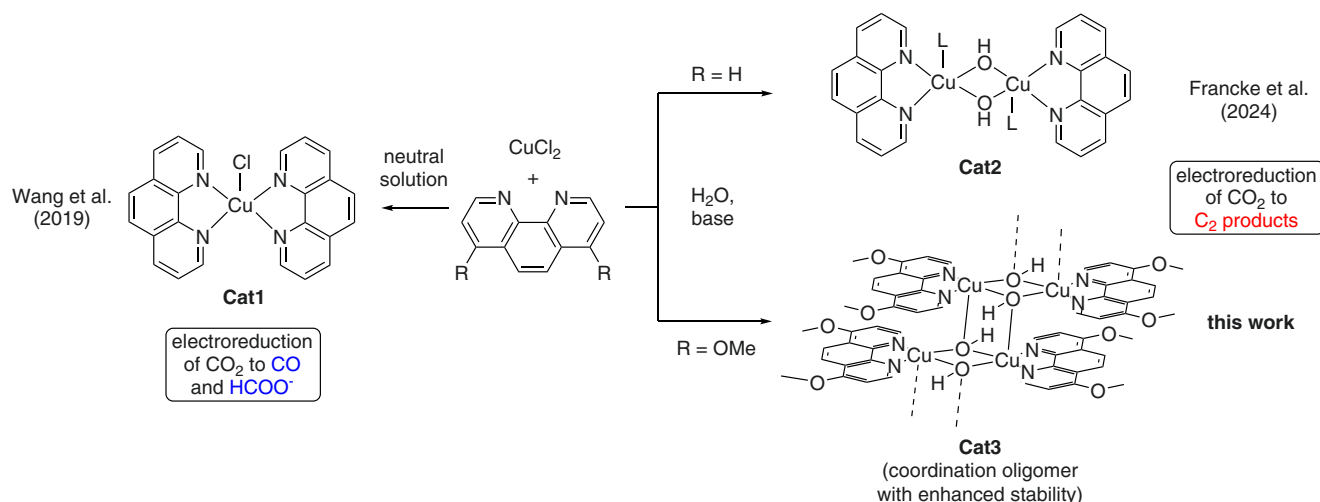
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Scheme 1. Mono, bi- and oligonuclear Cu-phen compounds as molecular catalysts for eCO_2RR .^[9a,16]

technical challenges. These hurdles arise from i) complicated reaction networks involving multiple electron transfers, protonation steps, C–O bond cleavage, and C–C coupling,^[3] ii) the complex interplay between microkinetics, mass transfer, and durability on the device level at industrially relevant current densities,^[4] and iii) structural and chemical instability of state of the art catalysts under operating conditions.^[5]

Cu-based catalysts remain the benchmark for eCO_2RR to C_{2+} products owing to their unique capability to stabilize $^*\text{CO}$ intermediates and facilitate C–C bond formation.^[6] However, the situation is complicated by various Cu sites (terraces, steps, defects) with different selectivity,^[7] while dynamic phase evolution under operating conditions often leads to a variation of the product distribution over time.^[8] Overall, these aspects lead to performance instability, hinder the mechanistic understanding, and complicate the targeted optimization strategies.

To address the challenges along the way to efficient C_{2+} production, the development of well-defined catalyst structures is a prominent strategy. In principle, such structures should enable precise elucidation of structure-performance relationships—particularly for the desired C–C coupling step—while providing opportunities for performance and durability optimization. In this regard, molecular electrocatalysts with well-defined active sites provide interesting opportunities. While many reported molecular systems have achieved high Faradaic Efficiency (FE) to CO ^[9] and HCOOH ^[10] by using earth-abundant metals such as Fe, Mn, and Co, relatively few works have demonstrated the possibility for generating C_{2+} products using molecular Cu catalysts.^[11]

The work to date highlights two critical aspects for the development of new molecular Cu catalysts for the formation of C_{2+} products. First, it appears advantageous when the molecular framework provides two or more vicinal Cu centers enabling C–C coupling between CO_2 reduction intermediates. Consequently, bi- or multinuclear Cu complexes with suitable Cu...Cu distance have shown particularly high selectivity toward C_{2+} products.^[12] Second, a robust and cost-effective ligand with suitable steric and electronic properties must be selected. The bidentate 1,10-phenanthroline ligand (phen) was identified as an excel-

lent choice for stabilizing bi- or multinuclear Cu ensembles due to strong and entropically favored binding to metal sites,^[13] an excellent π acceptor capability that stabilizes lower metal oxidation states,^[14] and a particularly high affinity to Cu ions.^[15] Both the influence of polynuclear structural motifs and the stabilizing effect of the phen ligand are well-documented by previous studies on the Cu phen system (Scheme 1). While Wang et al. have introduced Cat1 as a robust catalyst for the generation of C_1 products (CO and HCOO^- in up to 90% combined FE),^[9a] the binuclear Cat2 recently reported by us shows a strong tendency to form C_2 products.^[16] When immobilized on a carbon electrode, our easy-to-synthesize phen-based Cat2 shows 62% $\text{FE}_{\text{C}_{2+}}$ during electrolysis in an H-type divided batch cell. Structural characterization (pre- and post-electrolysis) revealed a hydroxo-bridged binuclear framework with a Cu...Cu distance of 2.93 Å. A remaining challenge in the use of Cat2 for eCO_2RR is slow leaching into the electrolyte solution, which is why stable long-term operation in a membrane-electrode assembly (MEA) electrolyzer under continuous flow conditions could not be achieved. Consequently, we aimed to develop a more stable system by modifying the phen ligand, which we achieved by introducing methoxy substituents in positions 4 and 7 (Cat3, see Scheme 1).

Herein, we present a study on the oligonuclear Cu phen compound Cat3, a distinct Cu^{2+} complex synthesized from 4,7-dimethoxy-1,10-phenanthroline and CuCl_2 using a straightforward and scalable protocol. Cat3 features hydroxo-bridged Cu centers that form a cascade-like framework. Compared to Cat2, water insolubility is achieved, accompanied by enhanced robustness under electrocatalytic conditions. Taken together, this allows for integrating Cat3 into an MEA electrolyzer for studies under technically relevant conditions. Remarkably, Cat3 achieves above 70% $\text{FE}_{\text{C}_{2+}}$ at current densities up to 200 mA cm^{-2} in the MEA electrolyzer. Stable operation was realized for 10 h with no obvious degradation in performance. To fundamentally address uncertainties about the state of our proposed molecular active Cu sites, in situ XAFS and HERFD-XANES analyses were carried out using both an H-type and an MEA-type spectroelectrochemical cell to explore different current density regions. As a result, merely negligible changes in the Cu coordination environment

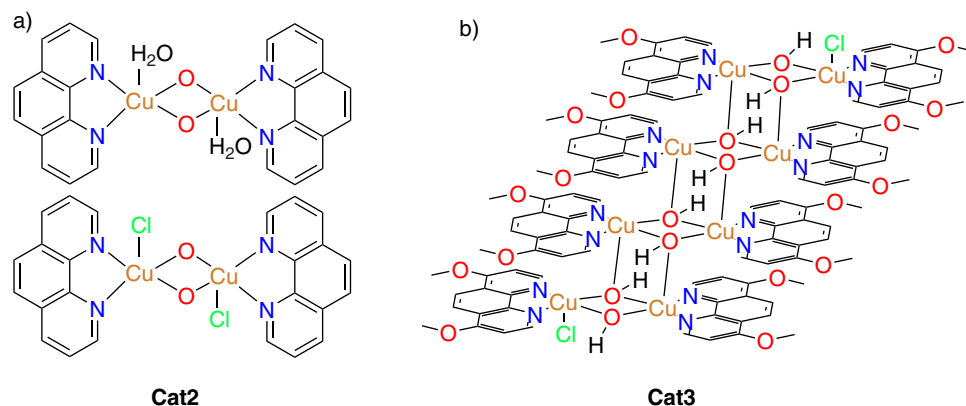


Figure 1. a) The structure of our previously reported **Cat2** and b) the core structure (coordination octamer) obtained after crystallization of **Cat3**.

were observed up to 50 mA cm^{-2} , while partial and reversible phase evolution under Cu^{2+} valence state reduction occurs when approaching 250 mA cm^{-2} . Interestingly, the initial phase recovers upon bias removal, indicating reversible adaptive redox dynamics under reaction conditions. This work not only establishes a robust molecular catalyst for the selective production of C_2 compounds, but also advances operando XAS methodologies for investigating molecular electrocatalysts under industrially relevant current densities.

2. Results and Discussion

2.1. Synthesis and Structural Characterization

Based on our previously reported protocol for the synthesis of **Cat2** (Figure 1a),^[16] three Cu catalysts with differently substituted phen ligands were prepared from CuCl_2 in alkaline solution (for details, see the Supporting Information) and screened with respect to their eCO_2RR activity. Among the derivatives evaluated, 4,7-dimethoxy-substituted phen emerged as optimal, which is why all further efforts were focused on the resulting material (**Cat3**, see Scheme 1).

The molecular structure of **Cat3** was investigated using single-crystal X-ray diffraction (SC-XRD). However, different approaches to growing single crystals unfortunately resulted in samples of limited quality, likely due to the formation of coordination oligomers of varying chain lengths. One of these oligomers could still be selectively crystallized and used for deducing the structure of the molecular core unit from the SC-XRD results. In the analyzed solid state, the Cu compound adopts an octameric architecture (Figure 1b; Figure S1, Supporting Information), in which eight Cu^{2+} ions form a cascade-like framework stabilized by μ -oxo bridges, with peripheral methoxy-substituted phenanthroline ligands and two terminal chloro ligands completing the coordination sphere. Nonetheless, due to the limited SC-XRD data quality, distinguishing between oxo ($\text{Cu}-\text{O}-\text{Cu}$) and hydroxo ($\text{Cu}-\text{OH}-\text{Cu}$) bridges, as well as precisely determining the counterions and solvent molecules, was not possible. Therefore, complementary spectroscopic and theoretical approaches were used to resolve these structural ambiguities. In this context, X-ray photoelectron spectroscopic (XPS) analysis shows the exclusive presence of oxygen within μ -hydroxo bridges and methoxy

groups (Figure S4, Supporting Information). Protonation of the bridging oxygen atoms was also probed using DFT calculations. For this purpose, the optimized structures of both the protonated and the non-protonated forms of the model dimer, tetramer, and octamer were compared to each other. The results indicate that protonation occurs preferentially on the bridging oxygen atoms, leading to a chemically reasonable model with eight protons per octamer and suggesting that protonation drives overall electronic stabilization of the coordination compound (Figure S5, Table S1, Supporting Information). X-ray absorption spectroscopy (XAS) of the as-prepared material confirms the existence of Cu in the indicated coordination environment and excludes inorganic or metallic phases (Figures S2 and S3, Supporting Information).

For the preparation of electrodes for H-cell and MEA measurements, inks consisting of **Cat3** and an ionomer in a water-*i*PrOH mixture were applied to carbon by drop casting or spray coating. To confirm the identity of the catalyst in the different states, powder and catalyst films were subjected to XPS, XAS, Raman spectroscopy, and powder XRD (P-XRD). A comparison to the results obtained from **Cat3** crystals suggests that the catalyst exists in the same structural states in all three forms (Figures S3 and S6–S10, Supporting Information).

To analyze the morphology of the crystals and the catalyst-coated electrode as well as the elemental distribution across the surface on the μm level, scanning electron microscope (SEM) measurements coupled with energy-dispersive X-ray (EDX) spectroscopy were conducted. SEM images of the studied samples display needle-like crystals, with C, N, O, and Cu species exhibiting a homogeneous distribution in the probed domains (Figures S11 and S12, Supporting Information). The nanostructure was confirmed by scanning transmission electron microscopy (STEM) at lower magnifications while a regular, yet amorphous structure was observed at higher magnifications (Figure S13, Supporting Information).

2.2. Studies in an H-type Divided Cell

The eCO_2RR activity of a **Cat3**-modified carbon paper electrode was studied in a gas-tight H-type divided cell using an aqueous 0.1 M CsHCO_3 electrolyte (Figure 2; Figures S14–S19, Supporting Information). Linear sweep voltammetry (LSV) curves

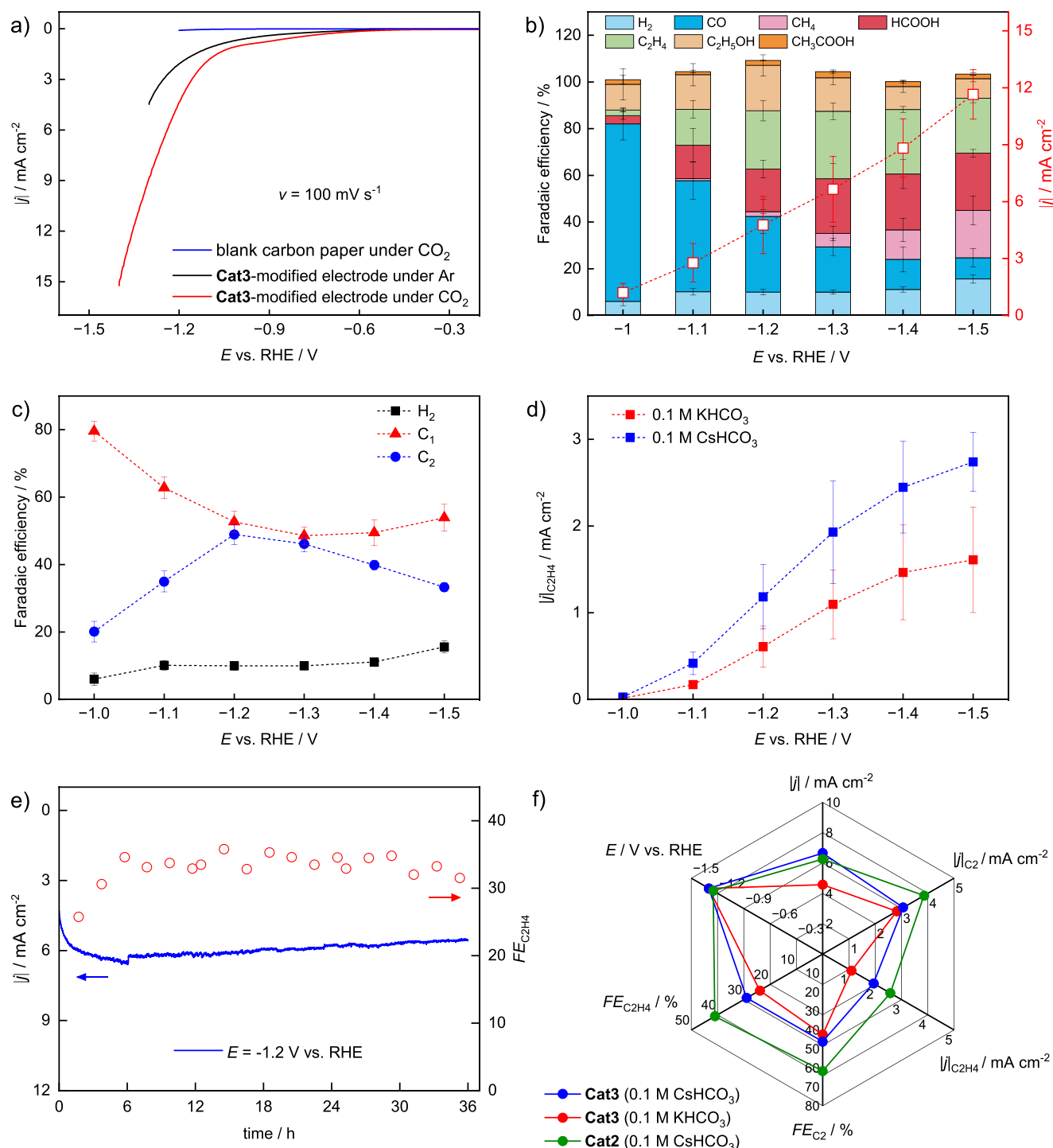


Figure 2. Electrochemical characterization of Cat3-modified carbon paper electrodes (aq. 0.1 M CsHCO₃ electrolyte, H-type-divided cell). a) LSVs of a Cat3-modified electrode under Ar (black, pH 8.9) and CO₂ (red, pH 6.8), respectively. b) Product distributions obtained upon electrolysis at different working electrode potentials using a Cat3-modified electrode. c) Comparison of the FE values for the generation of C₁ and C₂ products as well as H₂. d) Comparison of the partial current densities for C₂H₄ obtained from CPE in 0.1 M CsHCO₃ and 0.1 M KHCO₃ using a Cat3-modified electrode. e) Long-term stability test of Cat3 at -1.2 V versus RHE. f) Comparison between eCO₂RR key performance indicators showing the influence of catalyst structure (Cat2 vs. Cat3) and supporting electrolyte (CsHCO₃ vs. KHCO₃). All measurements were carried out in H-cells at the indicated working electrode potential under otherwise identical conditions.

were recorded under both CO₂ and Ar atmosphere, respectively (Figure 2a). Under CO₂, Cat3 exhibits a more positive onset potential and enhanced current density compared to the response under Ar, demonstrating promising catalytic activity.

To analyze the relationship between product distribution and working electrode potential, controlled potential electrolysis (CPE) was conducted at different potentials between −1.0 and −1.5 V versus RHE in CO₂-saturated solution (Figure 2b). While the gaseous products (mainly C₂H₄, CH₄, CO, and H₂) were detected online using a gas chromatograph (GC) after holding the potential for 14 min, the liquid-phase products (formate, ethanol, and acetate) were analyzed using ¹H NMR spectroscopy (for details, see the Supporting Information). At less negative potentials, CO generation is pronounced, but ceases in favor of formate and CH₄ as the driving force increases. C₂H₄ generation begins at −1.0 V and gains significance with increasing potential. At −1.3 V and more negative potentials, C₂H₄ becomes the predominant product, with up to 2.7 mA cm^{−2} partial current density and 30% FE. Interestingly, ethanol formation is also relatively strong with FE values up to 20%. It should be noted that FE_{H₂} remains ≈10% across the studied potential region, highlighting the preference toward eCO₂RR over HER (which is consistent with our previously reported Cat2).^[16] Analysis of the FE for H₂, C₁ and C₂ products at different potentials (Figure 2c) shows that the charge consumption for generating C₁ and C₂ products is almost equal in the range between −1.2 and −1.3 V (below and above this regime, formation of C₁ products is dominant). Control experiments with a blank carbon paper electrode as well as with CuCl₂ and Cu nanoparticle loadings show clearly different product distributions (see Figure S18, Supporting Information).

A comparison between the partial current density for C₂H₄ achieved in 0.1 M CsHCO₃ and 0.1 M KHCO₃ (2.7 and 1.6 mA cm^{−2}, both at −1.5 V) highlights the advantageous effect of Cs⁺ ions (Figure 2d), similar to our previous study on Cat2.^[16] The promoting effect of Cs⁺ ions on eCO₂RR has been reported for various electrocatalysts elsewhere. It has been ascribed to i), the weaker hydration shell compared to smaller cations, decreasing the interfacial pH and increasing local CO₂ concentration, ii), improved surface charge-dependent reaction energetics associated with the smaller hydrated ion radius, and iii), the stabilization of key eCO₂RR intermediates.^[17] The effect of Cs⁺ on the behavior of Cat3 was studied using impedance spectroscopy and is treated in detail in the SI (see Figure S20, Supporting Information; with corresponding discussion).

Noteworthy, Cat3 demonstrates exceptional electrocatalytic stability, maintaining stable FE_{C₂H₄} and nearly constant current density at −1.2 V for over 36 h of continuous operation (Figure 2e; Figures S21–S23, Supporting Information). In Figure 2f, we compare the eCO₂RR performance with the maximum FE_{C₂H₄} of Cat3 with our previous Cat2 in CsHCO₃. While Cat2 seems to outperform Cat3 in the H-cell configuration, the incorporation of the methoxy substituents significantly enhances the robustness under continuous flow conditions, enabling stable operation in an MEA electrolyzer at high current densities (vide infra). It should also be noted that in the H-cell, Cat3 exhibits significantly reduced leaching. While ICP-OES analysis of the post-electrolysis electrolyte solution revealed a Cu ion concentration of 2.5 mg mL^{−1} in the case of Cat2,^[16] only 0.03 mg mL^{−1} was found under the same conditions in the case of Cat3.

2.3. Post-Electrolysis Characterization of the Electrocatalyst

After CPE at −1.2 V in CO₂-saturated 0.1 M CsHCO₃ solution, the working electrode was analyzed using P-XRD, SEM-EDX, XPS, and XAS (Figure 3; Figures S24–S31, Supporting Information). Interestingly, P-XRD analysis of the electrode after electrolysis revealed the same reflection peaks as those of the as-prepared Cat3 electrode, indicating the preservation of crystalline domains during electrolysis. This finding is consistent with SEM results (Figures S25–S28, Supporting Information), which show microcrystalline objects on the surface (in contrast, the binuclear complex Cat2 previously investigated by us transitioned completely to the amorphous state during electrolysis).^[16] EDX mapping indicates even distributions of Cu, N, O, C, and Cl across the electrode surface. Notably, the Cl content decreased significantly after electrolysis compared with freshly prepared electrodes, indicating reductive dehalogenation of Cat3 at negative potentials (as observed for Cat2 in our previous study).

As shown in Figure 3b, XPS analysis of the pre- and the post-electrolysis materials shows two main peaks at 934.2 and 954.2 eV, accompanied by pronounced satellite features in the Cu 2p region, which can be assigned to Cu 2p_{3/2} and Cu 2p_{1/2} in the Cu²⁺ state.^[18] The peaks at lower binding energies (932.2 and 952.1 eV) are associated with Cu⁺/Cu⁰ and result from reduction through X-ray radiation under high-vacuum conditions during the measurement.^[16] This interpretation is confirmed by repeating the XPS measurement of the Cu 2p region after 1 h irradiation, whereby the Cu⁺/Cu⁰ peaks are significantly enhanced (Figure 3c). The XPS element quantification results are shown in Table S4 (Supporting Information), including the N/Cu ratio, which remains constant for the fresh and used Cat3-modified electrode, thus underlining the enhanced stability of the catalyst. In agreement with the EDX mapping results, the signal of the chloride ligand in the post-electrolysis Cl 2p scan is missing (Figure 3d), indicating reductive cleavage of Cu–Cl bonds under eCO₂RR conditions.

The oxidation state and coordination environment of the Cu species within Cat3 were examined using ex situ X-ray absorption spectroscopy (XAS, for experimental details, see the Supporting Information). Figure 3e shows the normalized Cu K-edge X-ray absorption near-edge structure (XANES) spectra of Cat3, Cu₂O, CuO, CuCl₂, and Cu nanoparticles. A comparison shows that the reference materials display clear distinctions compared to our synthesized Cat3, showing an absorption edge ≈8975 eV. Toward the higher energy region, the K-edge spectrum of Cat3, both before and after electrolysis, partially aligns with those of CuO and CuCl₂ but lacks the characteristic feature at 8986 eV. The smooth rising edge without a shoulder at 8986 eV is typical for Cu²⁺ coordinated by 5 N/O atoms confirming the SC-XRD results.^[19] This suggests that Cu in Cat3 exists predominantly in the +2 oxidation state and is coordinated by phen ligands, consistent with our previous studies.^[16] EXAFS analysis (Figure 3f) further elucidates the local structural environment around Cu atoms in Cat3. Fitting of the Fourier-transformed (FT)-EXAFS data (Figure S42, Table S5, Supporting Information) for the as-prepared powder reveals scattering contributions at distances of 1.94 ± 0.01 Å and 2.89 ± 0.02 Å with coordination numbers of 4.2 ± 0.5 for N/O and 2.2 ± 0.8 for Cu–O–Cu, respectively, in

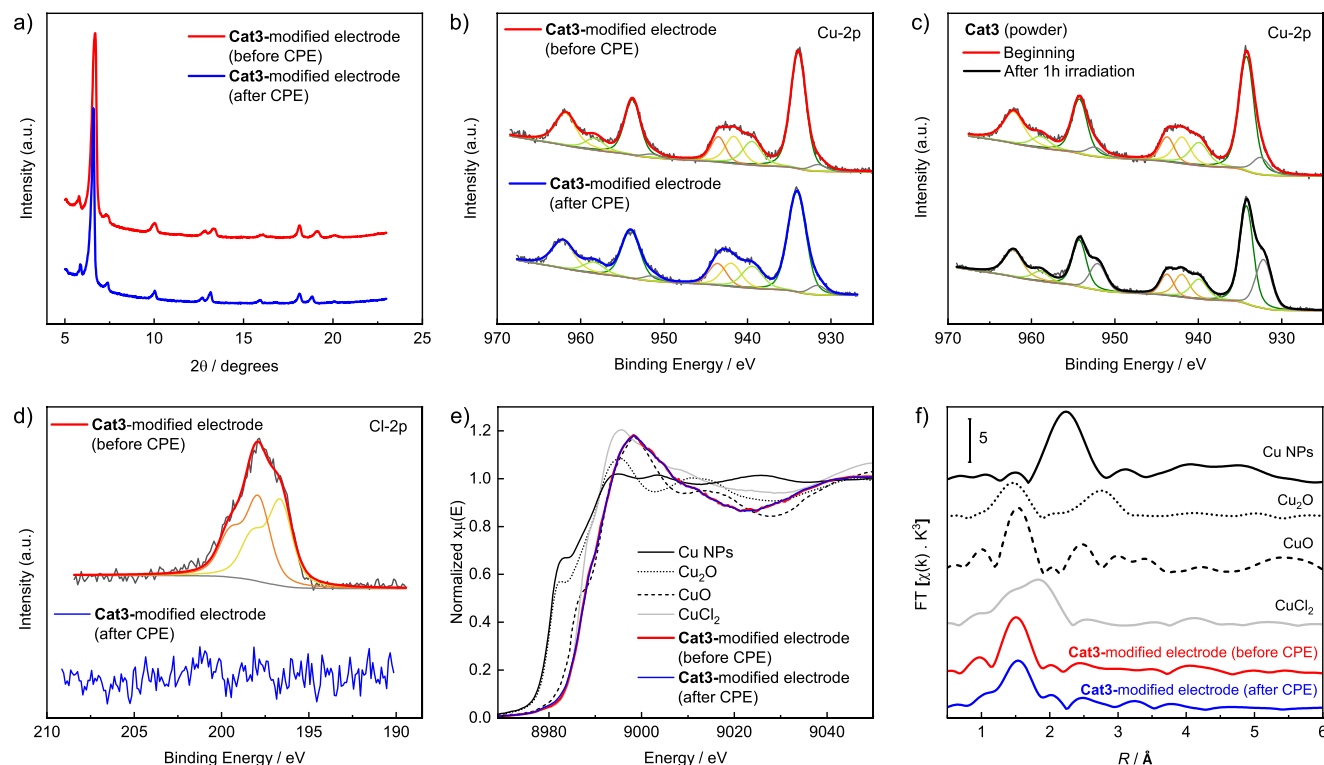


Figure 3. a) P-XRD patterns of **Cat3** after electrolysis. b–d) XPS analysis. Scans in the Cu 2p region using **Cat3**-modified carbon paper electrode before and after electrolysis, monitoring the progression of the Cu 2p spectrum of as-prepared **Cat3** powder during X-ray irradiation, and scans in the Cl 2p region. e, f) XAS analysis of **Cat3**-modified carbon paper electrode (before and after electrolysis) and of reference materials. Normalized Cu K-edge XANES spectra and Fourier transform EXAFS spectra.

agreement with our single-crystal diffraction data and DFT calculations (Figure S1 and Table S2, Supporting Information).

2.4. X-Ray Absorption Spectroelectrochemistry

Despite the high FE_{Cu} , the stable performance over 36 h in the H-cell configuration, and the good match between pre- and post-electrolysis XANES/EXAFS spectra, the progression of the molecular framework of the organometallic Cu species during electrolysis yet remains uncertain. As known from the literature, reductive demetallation of Cu complexes with a negative bias can lead to the formation of CuO_x particles.^[20] In some cases, particle formation can even be reversible, i.e., the CuO_x particles transform back into the Cu coordination compounds when the bias is removed or when the potential returns to a more positive value.^[21] This in situ phase evolution warrants special attention, particularly in determining active sites. Consequently, XAS spectroelectrochemistry (SEC) was performed under eCO_2RR conditions in a custom-made divided cell in the three-electrode configuration (Figure 4; Figure S32–S43, Supporting Information).

XAS analysis was conducted in the dry state (catalyst-sprayed carbon paper mounted in our in situ cell), in CO_2 -saturated 0.1 M CsHCO_3 solution at open-circuit potential (OCP), and at potentials ranging from -0.9 to -1.4 V versus RHE. In situ XANES spectra showing the full energy range (8850 to 9500

eV) and the enlarged pre-edge region (8970 to 8990 eV) are presented in Figure 4a. The results indicate that across the screened potential range, the Cu oxidation state and the d-orbital structure remain nearly constant. Stability of the Cu coordination environment is corroborated by the EXAFS spectra (9030 to 9600 eV) and corresponding Fourier Transformed (FT-EXAFS) profiles (Figure S33a, Supporting Information). A similar trend could be observed in control experiments (0.1 M KHCO_3 under CO_2 and 0.1 M CsHCO_3 under Ar, displayed in Figures S35 and S36, Supporting Information). The dominant scattering path observed at near 1.9 Å corresponds to Cu interactions with light atoms, such as N/O, in the first coordination shell, whereas minimal Cu–Cu scattering paths appear at ≈ 2 –4 Å, consistent with the oscillations observed in the k-space profiles (Figure S33, Supporting Information). For a more detailed comparison, wavelet-transformed EXAFS (WT-EXAFS) analyses, based on both R-space and k-space profiles, were conducted for selected samples (Figure S34, Supporting Information), confirming the absence of inorganic Cu species and preservation of the local Cu coordination environment in as-prepared **Cat3**.

For the **Cat3**-modified electrode, the primary intensity maximum appears at ≈ 1.9 Å in R-space and spans k-values from 3 to 10 Å^{−1}, corresponding to the first coordination shell while excluding the presence of reference materials such as CuO, CuCl_2 , and Cu_2O . The intensity maximum in the WT-EXAFS maps was maintained under negative bias, indicating the

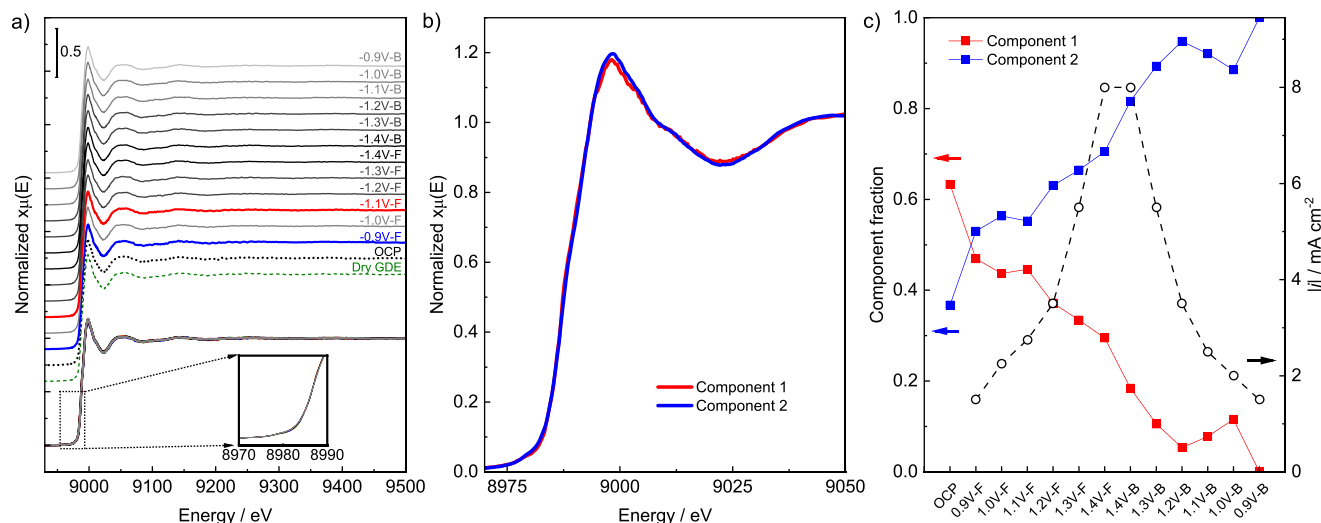


Figure 4. In situ XAS analysis of a **Cat3**-modified electrode performed in a divided SEC batch cell. a) Cu K edge XANES spectra of the electrode in dry form and in aq. CO_2 -saturated CsHCO_3 electrolyte at OCP and various potentials between -0.9 and -1.4 V versus RHE. b) The two most distinct XANES spectra within the dataset from Figure 4a obtained via multivariate curve resolution-alternating least squares (MCR-ALS). c) Component fractions corresponding to the most distinct spectra (Figure 4b) obtained via MCR-ALS, along with the corresponding current densities measured during in situ XAS analysis.

preservation of the local coordination environment around the Cu centers throughout the applied electrochemical potentials. Based on these findings, we conclude that the molecular scaffold exhibits structural stability up to -1.4 V versus RHE, which is maintained during the reverse potential scan to -0.9 V versus RHE.

To further elucidate the chemical behavior of Cu in **Cat3** under eCO_2RR conditions, multivariate curve resolution-alternating least squares (MCR-ALS) analysis was performed (Figure 4b,c). This analysis enables the deconvolution of overlapping spectral features to track subtle changes in the closer Cu coordination environment. For this purpose, the two spectra with the strongest variation, components 1 and 2, serve as internal references (Figure 4b). Notably, both profiles nearly overlap with each other, highlighting a negligible reaction-induced shift in the Cu oxidation state and coordination environment under eCO_2RR conditions. A transition to a smoother rising edge with a broader featureless white line is attributed to a very slight increase of the coordination number (Table S5, Supporting Information).^[19,22] This effect is possibly be due to reductive cleavage of the Cu–Cl bonds at the terminal Cu centers (vide supra) as well as to coordination of water and/or CO_2RR intermediates. The potential-dependent fractions of the individual components in the spectra are shown in Figure 4c along with the corresponding current densities. Starting from the OCP, the relative fraction of component 2 steadily increases at the cost of component 1, however, since the spectral components are nearly identical, the absolute change in the Cu state is minimal. Despite this gradual change, the Cu centers in **Cat3** consistently remain in the Cu^{2+} state and exhibit nearly unchanged coordination environment at low current densities. This behavior highlights the stability of the molecular framework of **Cat3**, in contrast to the dynamic restructuring observed with Cu nanoparticles under identical conditions (Figure S37, Supporting Information).

2.5. MEA Electrolyzer Studies

For testing the performance at high current density, **Cat3** was spray-coated onto carbon paper gas diffusion electrodes (GDEs) and employed in a membrane electrode assembly (MEA) electrolyzer (Figures S44–S55, Supporting Information). While the cathode was fed with a stream of water-saturated CO_2 , aq. 0.1 M CsHCO_3 was pumped through the anodic half-cell, with the applied current density ranging from 10 to 200 mA cm^{-2} (Figure 5a). The cell voltage (without IR drop correction) increases from initially 2.5 to 4 V, which is somewhat higher than reported for metallic Cu catalysts within similar cell configurations.^[5,23] At each step, the current was held constant for 15 min., followed by collection of the anolyte for liquid phase analysis by ^1H NMR spectroscopy (for details of product analysis and calculations, see the SI). The major gas-phase products are CO and C_2H_4 , while the FE for H_2 remains well below 20% across the entire current density range (Figures S46–S48, Supporting Information). Interestingly, the fraction of ethylene increases strongly with rising current density at the cost of CO formation, while the amount of CH_4 formed remains negligible. $\text{C}_2\text{H}_5\text{OH}$ and CH_3COOH were the dominant liquid products, while the fractions of HCOOH and $n\text{-PrOH}$ each remain below 10% . As a result, the FE for all C_2 products shows a steady increase with rising current density, with a maximum of 71% at 200 mA cm^{-2} (Figure S48, Supporting Information). This behavior differs from the results obtained in the H cell, where the fraction of C_2 compounds ceases in favor of CH_4 at elevated current densities (cf. Figure 2c). Furthermore, a control experiment using a GDE loaded with Cu nanoparticles shows a clearly different product distribution (see Figure S52, Supporting Information), once again highlighting the unique behavior of **Cat3**.

Analogous to the previous H-cell studies, the choice of the cation significantly impacted the C–C coupling capability of **Cat3** under MEA conditions (Figure 5b). While a maximum FE_{C_2} of

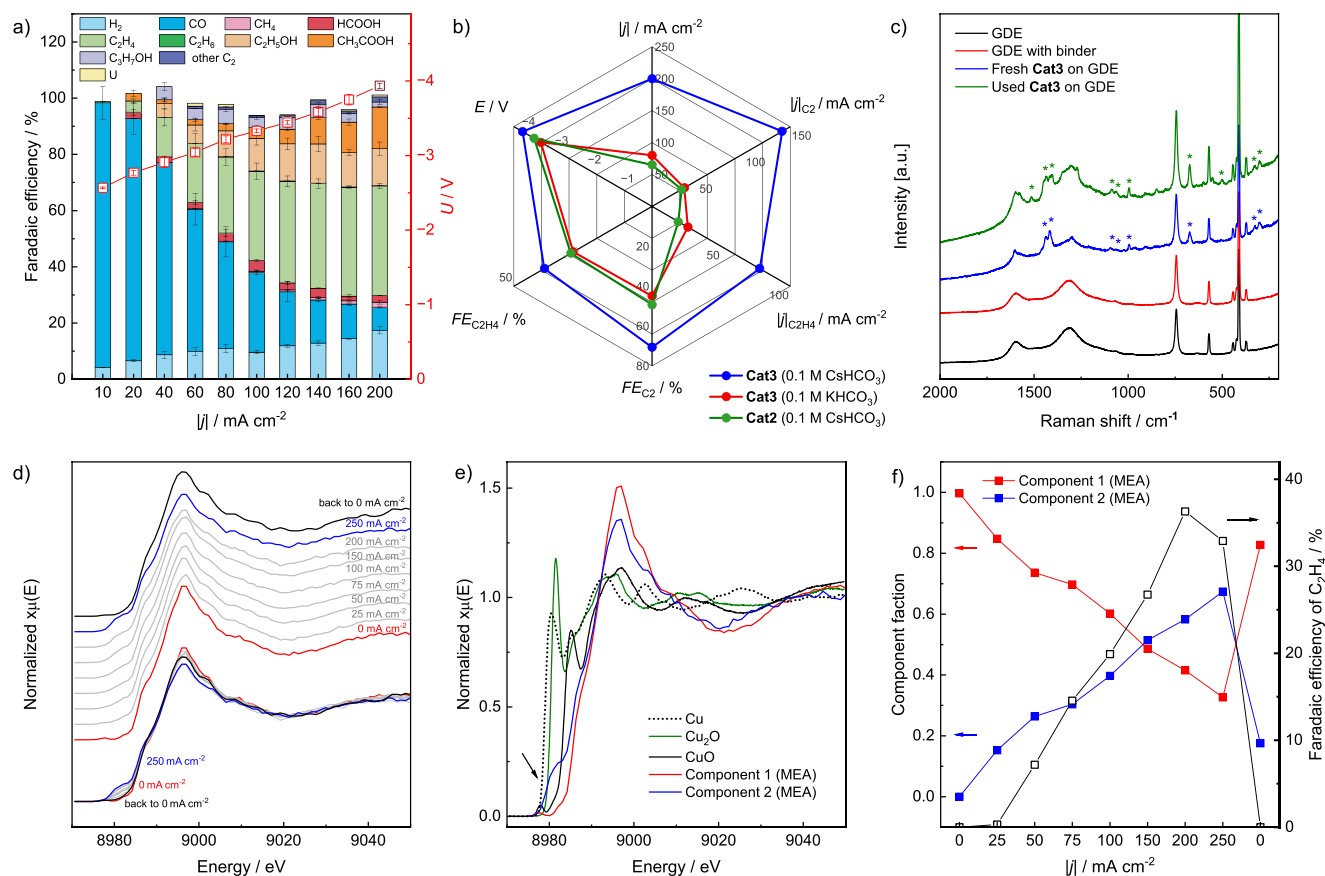


Figure 5. Electrochemical studies in an MEA electrolyzer using a **Cat3**-modified GDE (0.1 M CsHCO₃ as the anolyte). a) Relationship between current density, product distribution, and cell voltage. b) Comparison between the performance characteristics of **Cat3** and **Cat2**. c) Pre- and post-electrolysis Raman spectra of **Cat3**-modified electrode (excitation wavelength: 785 nm). Signals assigned to **Cat3** are marked with stars. d) Results of in situ Cu K-edge high-energy-resolution fluorescence-detected (HERFD) XANES analysis of a **Cat3**-modified GDE under eCO₂RR conditions at various current densities (aligning with the measurements in Figure 5a). e) Most distinct Cu K-edge HERFD-XANES spectra along with spectra of reference compounds. f) Component fractions corresponding to the most distinct Cu K-edge HERFD-XANES spectra (Figure 5e) obtained via MCR-ALS analysis. FE values for C₂H₄ are inserted for comparison.

45% is already achieved at 80 mA cm⁻² when using 0.1 M KHCO₃ as the anolyte, a steady increase to 71% is observed at current densities up to 200 mA cm⁻² when using 0.1 M CsHCO₃ (for details, see Figures S46 and S47, Supporting Information). At 80 mA cm⁻², $FE_{C_2H_4}$ remained close to 35% for over 10 h, demonstrating robust and stable performance at continuous operation (Figures S53 and S54, Supporting Information).

Noteworthy, the binuclear Cu complex **Cat2** is significantly less stable in the MEA electrolyzer under the same conditions. Due to slow catalyst leaching, this system cannot be used effectively for a longer period, which is why insoluble **Cat3** offers a clear advantage in the MEA environment. In view of C₂H₄ production rate, **Cat3** exhibits a steadily increasing turnover frequency (TOF) with rising current density, reaching 178 h⁻¹ at 200 mA cm⁻². In contrast, TOF(C₂H₄) decreases for **Cat2** when the current density rises above 50 mA cm⁻² (for details, see Figure S55, Supporting Information).

After disassembling the post-electrolysis MEA, the catalyst layer was examined and subjected to SEM, Raman spectroscopy, and TEM (Figures S56–S63, Supporting Information). Identical to the as-sprayed GDE, the coating retained its greenish

color (Figure S56, Supporting Information). SEM-EDX revealed a layer morphology similar to that of freshly prepared electrodes, whereby Cu remains evenly distributed across the surface (Figures S57–S61, Supporting Information). The Raman spectra of the fresh and the used **Cat3**-modified electrode exhibit the same characteristic bands at 302, 327, 674, 910, 995, 1096, 1304, 1418, 1438, and 1602 cm⁻¹ (Figure 5c). Additional bands at 374, 410, 441, 570, and 743 cm⁻¹ stem from the used sapphire probe and those at 1314 and 1599 cm⁻¹ from the carbon paper. The broad bands around $\approx$ 530 and 620 cm⁻¹, typical for Cu/CuO_x nanoparticles, (Figure S64, Supporting Information) are neither contained in the spectrum of the fresh nor the used electrode.

To study the structure of **Cat3** under operational conditions, in situ HERFD-XANES was carried out using a custom-made MEA-type spectroelectrochemical cell (Figure S65, Supporting Information). The HERFD-XANES technique with its exceptionally high energy resolution^[24] allows to highlight even small spectral changes related to the **Cat3** framework. The applied current density was stepwise increased from 0 mA cm⁻² (OCV) to 250 mA cm⁻². Despite nearly constant spectral features from 8990 to 9500 eV across all current densities (Figure S66, Supporting

Information), a slight but gradual increase in the pre-edge intensity at 8980 eV was observed (Figure 5d; Figure S67, Supporting Information). This growing pre-edge feature, associated with the formally forbidden 1s to 3d transition, could be tentatively attributed to structural distortion (via 3d–4p orbital mixing), weakening of metal–ligand bonds,^[25] or formation of inorganic species.^[26]

To further disentangle the hybrid/mixed phases present during the reaction, MCR-ALS analysis was applied to the MEA-derived XAS dataset and extracted two distinct spectral components, as shown in Figure 5e. Component 1 closely resembles the initial state of the catalyst, whereas component 2 represents the mixture with the highest concentration of the second phase emerging under electrochemical conditions. In component 2, Cu remains coordinated to two N/O ligands, and a Cu–Cu distance of ≈ 2.5 Å with a coordination number of 2 is observed. Approximately 35% of the Cu is estimated to be in a reduced state (Figure S68, Table S6, Supporting Information). However, the absence of a significant K-edge shift to lower energies, along with a low average Cu–Cu coordination number, and in combination with higher white line intensity comparable to standard references of Cu, Cu₂O, and CuO (Figure 5e), suggests minimal formation of inorganic Cu-based particles.

At a current density of 200 mA cm^{−2}, the sample exhibits nearly 60% component 2 (Figure 5f), comprising 35% reduced Cu moieties. This outcome corresponds to about a 20% overall reduction, and 80% of the Cu remains in the Cu²⁺ state. These observations are consistent with our linear combination analysis (LCA), where Cu⁰ is used to represent the reduced state (Figure S69, Table S7, Supporting Information). Moving to 250 mA cm^{−2}, the contribution of component 2 progressively increased, reaching $\approx 70\%$ (24.5% reduced Cu), however, causing a degradation of C₂H₄ production (Figure 5f). Interestingly, upon removal of the applied bias, a partial recovery of the Cu electronic state can be observed, both in the pre-edge region and the extended fine structure, indicating a degree of reversibility in the initial local environment of the Cu centers. Notably, K-edge profiles recorded at 200 mA cm^{−2} (Figure S70, Supporting Information), averaged over 4-min intervals (corresponding to the maximum $FE_{C_2H_4}$ yield, see Figure 5b), suggest that this structural change is potential/current-dependent, but time-independent.

3. Conclusion

Our study provides new insights into the catalysis of electrochemical CO₂ reduction with molecular Cu phenanthroline compounds. Screening of a series of differently substituted phenanthrolines revealed 4,7-dimethoxy-1,10-phenanthroline to be the most effective ligand. The resulting water-insoluble **Cat3** is a cascade-like coordination oligomer that features μ_2 - and μ_3 -hydroxo-bridged Cu centers with relatively short Cu···Cu distances. The material is readily synthesized using inexpensive building blocks and a straightforward protocol. Compared to the previously reported binuclear Cu phenanthroline compound **Cat2**, the stability of **Cat3** under electrocatalytic conditions is significantly enhanced, allowing for operation in an MEA electrolyzer at high current densities. When spray-coated onto a carbon gas diffusion electrode, **Cat3** achieves more than 70% FE_{C_2+} at 200 mA cm^{−2}, while stable performance is observed for

10 h with no obvious performance degradation. Pre- and post-electrolysis analysis by SEM and Raman spectroscopy reveal that the electrode is coated with a stable composite matrix containing homogeneously dispersed copper and no obvious formation of inorganic Cu species.

In many previous works, the decomposition of molecular Cu catalysts during eCO₂RR is reported, resulting in the formation of Cu/CuO_x particles that serve as the true active species. Conclusions regarding the type of active site should therefore be drawn with great caution and must be supported by in situ spectroscopic data. To monitor the structural evolution of **Cat3** under reaction conditions, in situ XAS was carried out under potential control in the kinetic regime using a liquid flow cell, and under galvanostatic conditions at high current densities in an MEA-type cell. While in the kinetic regime, no significant changes of the spectral features were observed, the results obtained with the MEA-SEC cell suggest gradual structural changes when increasing the current density from 50 to 250 mA cm^{−2}, i.e., reduction of the Cu oxidation state, decrease of the Cu···Cu distance, and a lowering of the Cu–N/O coordination number. However, in view of the still low Cu–Cu coordination number, absence of K-edge shift to lower energies, and high white line intensities compared to inorganic Cu reference species, no or only minimal formation of Cu/CuO_x particles is assumed. Strikingly, the original phase is largely restored upon bias removal, highlighting both the structural robustness and adaptive redox behavior of **Cat3** under harsh electrolysis conditions. While future studies will address the potential-dependent structural modifications as well as the eCO₂RR mechanism in detail, the present work highlights a possible pathway toward implementing molecular electrocatalysts in CO₂ electrolyzers for the synthesis of C₂₊ products.

4. Experimental Section

Chemicals: Copper chloride (CuCl₂, 99%), cesium bicarbonate (CsHCO₃, 99.99%), methanol (99.8%), ethanol (99.8%), and isopropanol (99.8%) were purchased from Fisher Scientific. 4,7-Dimethoxy-1,10-phenanthroline (97%) was purchased from BLD Pharmatech Ltd. (China). Triethylamine (99.5%), potassium bicarbonate (99.99%), dimethyl sulfoxide (DMSO, 99.9%), copper nanoparticles (Cu NPs, 40–60 nm, 99.5%), and Nafion 1100W solution were purchased from Sigma-Aldrich (Germany). Anode electrode (commercial IrO_x-coated gas diffusion electrode (GDE)) and Sustainion XA-9 alkaline ionomer powder, both for use in the MEA electrolyzer, were purchased from Dioxide Materials (US). Toray Carbon Paper 060 (wet-proofed), carbon gas diffusion layers (GDL, Freudenberg H23C8), and PiperION anion exchange membranes (20 microns) were obtained from The Fuel Cell Store (US). Deuterium oxide (D₂O, 99.9%) for NMR measurements was purchased from Deutero GmbH (Germany). CO₂ (99.9999%) and Ar (99.9999%) were obtained from Linde AG (Germany).

Synthesis of **Cat3:** The catalyst was synthesized according to the reported method in the previous work.^[16] A solution of 134.45 mg (1 mmol) CuCl₂ in 1 mL ultrapure water was combined with a solution of 240.60 mg (1 mmol) 4,7-dimethoxy-1,10-phenanthroline in 4 mL of ethanol under stirring at room temperature, resulting in the formation of a light green precipitate. After stirring for 10 min, 10 mL triethylamine was added to the suspension, leading to an immediate change of the precipitate color to dark green. The mixture was stirred for an additional 10 min. The precipitate was then filtered off, washed with ultrapure water, and dried overnight under vacuum at 60 °C, yielding a crystalline dark green product (yield: 300 mg). Elemental analysis: Cu 18.10, C 46.02, H 3.55, N 7.39, Cl 7.84.

Attempts to prepare high-quality single crystals of **Cat3** for SC-XRD analysis using the previously described crystallization procedure^[16] remained unsuccessful. Instead, an alternative procedure was applied, wherein **Cat3** powder (60 mg) was partially dissolved in MeOH, followed by heating to 85 °C for 12 h in an autoclave. Afterward, the mixture was allowed to cool to room temperature. Crystallization proceeded within four days. The obtained crystals were subjected to SC-XRD (see Figure S1, Supporting Information).

To confirm the identity of **Cat3** crystals, HERFD XAS (Figure S3, Supporting Information), P-XRD (Figure S8, Supporting Information), and Raman spectroscopy (Figure S9, Supporting Information) were performed. In each case, a good agreement was observed between the results of **Cat3** powder and crystalline **Cat3**.

Materials Characterization: X-ray diffraction (XRD) data were obtained using a Analytical X'Pert Pro diffractometer with Cu-K α radiation, while single-crystal XRD (SC-XRD) was carried out on a Kappa APEX II Duo diffractometer from Bruker AXS. The copper content of **Cat3** was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) with an Agilent 715-ES spectrometer. Carbon, hydrogen, and nitrogen contents were determined via combustion analysis using a TruSpec Micro elemental analyzer (LECO Instrumente GmbH, Germany). The morphology of the electrode surface, both before and after electrolysis, was examined using scanning electron microscopy (SEM) with a MERLIN VP Compact (Zeiss, Germany) equipped with EDX. ¹H nuclear magnetic resonance (NMR) spectroscopy was performed with a Bruker AVANCE 500 NEO spectrometer.

For scanning electron microscopy (SEM, field emission), the samples were mounted on a heavy metal-free Al-SEM-carrier (co. PLANO, Wetzlar, Germany) with adhesive conductive carbon tape (Spectro Tabs, TED PELLA INC, Redding, USA) and coated with carbon (5.0 nm thickness) under vacuum (CCU 010 HV-Coating Unit, Co. Safematic GmbH, Zizers, Switzerland). Analysis was carried out using a field emission scanning electron microscope (SEM, MERLIN VP Compact, Co. Zeiss, Oberkochen, Germany) equipped with an energy-dispersive X-ray (EDX) detector (XFlash 6/30, Co. Bruker, Berlin, Germany). Representative areas of the samples were analyzed and mapped for elemental distribution based on the EDX-spectra data by QUANTAX ESPRIT Microanalysis software (version 2.0). SEM-images were taken from the selected regions.

Scanning Transmission Electron Microscopy (STEM) was performed on a probe aberration-corrected JEM-ARM200F (JEOL, corrector: CEOS) at an acceleration voltage of 200 kV. A High-Angle Annular Dark Field (HAADF) and an Annular Bright Field (ABF) detector were used for imaging. The solid samples were prepared as described in the Supporting Information and deposited without any pre-treatment onto a carbon-supported Ni grid (mesh 300) and finally transferred to the microscope.

XPS (X-ray Photoelectron Spectroscopy) measurements were performed on an ESCALAB 220iXL (Thermo Fisher Scientific) with monochromated Al K α radiation ($E = 1486.6$ eV). Samples are prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. The measurements are performed with charge compensation using a flood electron system that combines low-energy electrons and Ar⁺ ions ($p_{Ar} = 1 \times 10^{-7}$ mbar). The electron binding energies are referenced to the C 1s core level of carbon at 284.8 eV (C—C and C—H bonds). For quantitative analysis, the peaks were deconvoluted with Gaussian–Lorentzian curves using the software Unifit 2023. The peak areas were normalized by the transmission function of the spectrometer and the element-specific sensitivity factor of Scofield.

Raman spectra of **Cat3**-modified electrodes (before/after electrolysis) were measured using a Renishaw inVia Raman microscope equipped with a 633 nm air-cooled He-Ne laser. For the measurement, the electrode or a spatula tip of the powdered sample was placed on a microscope slide, and the laser beam was focused on the sample using a $\times 20$ objective. The laser power was maintained at a relatively low level, ranging from 0.085 to 0.17 mW, to avoid damaging effects that may otherwise occur. The exposure time of a spectrum was 30 s with 3 accumulations. To obtain a broader cross-section of the sample, a selection of samples was analyzed using a Horiba iHR 550 Raman spectrometer equipped with a 785 nm laser source (Oxxius, maximum laser power: 864 mW) connected to a fiber opti-

cal ball probe with a sapphire lens (MarqMetrix, 3/8" Process BallProbe). The samples were measured in the direct contact mode. The measurement parameters varied depending on the sample: exposure time 10–30 s, 3 accumulations.

Electrode Preparation: For measurements in an H-cell, the electrode was prepared according to the previous work.^[16] The catalyst (6 mg) was suspended in a mixture containing 450 μ L of ultrapure water, 90 μ L of isopropanol, and 60 μ L of Nafion solution, then ultrasonicated for 15 min to produce a homogeneous ink. Next, 50 μ L of the ink was applied to a strip of carbon paper (1 cm wide) by drop-casting, covering an area of 1 cm² on both sides (resulting in 2 cm² active area in total). The electrode was then allowed to dry in air. The catalyst loading (**Cat3**) for each working electrode was 0.5 mg cm^{−2}.

For measurements in a membrane electrode assembly (MEA) electrolyzer, 40 mg of catalyst was suspended in a mixture of 3 mL ultrapure water, 600 μ L isopropanol, and 400 μ L Sustainion XA-9 alkaline ionomer solution (5 wt.% ionomer in EtOH, Dioxide Materials). The mixture was ultrasonicated to generate a homogeneous ink. Then, the ink was distributed homogeneously on the micro-porous layer of the carbon paper (Freudenberg C8H23 GDL, 25 cm² geometrical surface area) by spray coating at 60 °C, followed by air-drying for 10 min. The GDL was weighed before and after the spray-coating, and the mass difference was kept near 35 mg (on 25 cm² electrode), resulting in a catalyst loading of 1 mg cm^{−2} and ≈ 30 wt.% ionomer content in the dry as-prepared catalyst layer. From the coated GDL, pieces of 5 cm² were cut out and used as cathode for MEA measurements.

Electrochemical Experiments: Linear sweep voltammetry (LSV), controlled potential electrolysis (CPE), and controlled current electrolysis (CCE) were performed using a VIONIC potentiostat from Metrohm (Germany). CPE was carried out in an H-cell (separator: glass frit with pore size G4). A platinum plate and a Ag/AgCl electrode (3 M KCl solution) served as a counter and a reference electrode, respectively. A 0.1 M CsHCO₃ solution (pH 6.8 under CO₂, pH 8.9 under Ar) served as the electrolyte. Prior to each CPE experiment, CO₂ was bubbled at a flow rate of 40 mL min^{−1} for 30 min. Current densities were calculated based on the total immersed electrode surface area of 2 cm². Potentials measured vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) using the following relationship.^[27]

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 \text{ V} + 0.0591 \cdot \text{pH} \quad (1)$$

The MEA measurements were performed at room temperature. The spray-coated GDE was used as working electrode for eCO₂RR, and a commercial IrO_x-based electrode (from Dioxide Materials) served as the counter electrode. The cathode and anode chambers were separated using a PiperION anion exchange membrane (thickness: 20 μ m). Humidified CO₂ was purged through the cathode chamber at a flow rate of 50 sccm (room temperature), while a N₂ bleeding line (flow rate: 20 sccm) was injected after the electrolyzer, serving as the flow rate internal standard. 0.1 M CsHCO₃ solution was circulated through the anode chamber as anolyte with a flow rate of 30 sccm, using a Simdos 10 diaphragm pump.

Product Quantification: Gaseous products from CPE (H-cell) and CCE (MEA set-up) were analyzed using gas chromatography (GC, Agilent 6890) with argon as the carrier gas, calibrated using certified gas mixtures from Air Liquide as standards. A thermal conductivity detector (TCD) was used to analyze H₂ and CO, while a flame ionization detector (FID) was employed to quantify CH₄, C₂H₄, and C₂H₆. For CPE and CCE, cells were connected to the GC for online analysis by using a steady flow of CO₂ gas of 20 mL min^{−1} (H-cell) and 50 mL min^{−1} (MEA set-up), respectively. In the meantime, N₂ bleeding with a flow rate of 22 mL min^{−1} served both as an internal standard and to compensate for the CO₂ that was consumed during the reaction (for details, see Figure S44, Supporting Information). The Faradaic efficiencies (FE) for specific gaseous products x (e.g., $x = \text{C}_2\text{H}_4$) were calculated using the following equation,^[28]

$$FE_x [\%] = \frac{p V \phi_x z F}{RTi} \cdot 100 \quad (2)$$

where $\dot{V}$ refers to the flow rate of the gas delivered to the gas chromatograph at a specified sampling time with N_2 compensation, ϕ_x to the volume fraction of the gaseous product (e.g., C_2H_4) in the gas flow that was delivered to the detector, p to the pressure (1.01×10^5 Pa), R to the gas constant, T to the temperature (296 K), z to the number of electrons transferred for CO_2 -to- x (i.e., $z = 12$ for C_2H_4), F to the Faraday constant, and i to the current recorded by the potentiostat.

The liquid products were quantified by ^1H NMR spectroscopy using a water pre-saturation method and DMSO as an internal standard. For sample preparation, a 500 μL aliquot of the post-electrolysis electrolyte solution was mixed with 100 μL D_2O and 35 μL DMSO. FE_x was calculated using the following relationship,

$$FE_x [\%] = \frac{c_x V z F}{Q} \cdot 100 \quad (3)$$

wherein c_x denotes the concentration of the product (e.g. formate) in the liquid phase, V represents the catholyte volume (17 mL), and Q is the total amount of passed electric charge at the specified sampling time.

Ex Situ and In Situ X-Ray Absorption Spectroscopy (XAS) Measurements: All ex situ measurements for powder and electrode were performed in fluorescence mode. All in situ XAS measurements were carried out using either a divided spectroelectrochemical (SEC) liquid flow cell (three-electrode arrangement) or a SEC MEA cell (galvanostatic conditions) in the fluorescence mode.

For measurements in the SEC flow cell, electrode preparation follows the same procedure as in the H-cell studies (catalyst loading: 1 mg cm^{-2} with 15 wt.% Nafion ionomer, deposited on Freudenberg C2 carbon paper). The anodic and cathodic half-cells were separated by a Nafion 117 membrane. An Ag/AgCl reference electrode was placed in the cathode chamber for control of the working electrode potential. All in situ XAS measurements were carried out at the near (XANES) and extended (EXAFS) Cu K-edge at the XPP KMC-3 beamline (BESSY II). The employed flow cell is shown in Figure S32 (Supporting Information). The X-ray beam was focused to a spot size of $500 \times 500 \mu m$ at a fixed sample position. The beam energy was scanned from 8900 to 9600 eV (scan rate: 1.6 eV s^{-1}). An aqueous 0.1 M $CsHCO_3$ solution was used as both catholyte and anolyte and pumped through the half-cells at a flow rate of 20 mL min^{-1} . The catholyte was purged with CO_2 for 30 min prior to each measurement and feeding to the catholyte was continued to ensure CO_2 saturation. For every measurement at a defined potential, two in situ XAS spectra were collected. Data reduction and processing of the XANES spectra, including background subtraction, energy correction, normalization, and linear combination fitting were performed using the standard Athena software from the Demeter 0.9.26 program package.

Measurements in the SEC MEA cell (Figure S65, Supporting Information) were performed in the High-Energy-Resolution Fluorescence-Detected XAS (HERFD-XAS) mode at the ID26 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The higher harmonics were suppressed by Si-coated mirrors which operate in total reflection mode. The desired energy was selected by a Si(111) double crystal monochromator. The fluorescence X-rays were collected by an X-ray spectrometer using the (800) reflection of two spherically bent Ge crystals, and the photons were counted by a PILATUS3 100K-M detector. The monochromator energy calibration was performed by measuring Cu foil. For the HERFD-XANES measurements the monochromator energy was scanned while the spectrometer was kept fixed at the maximum of the $K\beta_{1,3}$ emission line (8903.6 eV). The assembly of the MEA SEC was carried out analogously to MEA performance characterization described above (catalyst loading: 1 mg cm^{-2} with 15 wt.% Sustanion XA-9 ionomer, sprayed on Freudenberg C2 carbon paper). The beam energy was scanned from 8900 to 9600 eV (scan rate: 11.6 eV s^{-1}). Characterization of the SEC MEA cell including analysis of the product mixture was carried out separately using the GC quantification protocol detailed above, whereby good agreement with the standard MEA electrolyzer was found. Data reduction and modelling of the EXAFS spectra were conducted using the standard Athena and Artemis software from the Demeter 0.9.26 program package. EXAFS data were analyzed in the R-space using fixed k and R ranges (2.0 –

$11.0 \text{ \AA}^{-1}$, R : 1.0 – $3.0 \text{ \AA}$). Wavelet transformations of EXAFS (WT-EXAFS) spectra were calculated using the Hama Fortran program.^[29] The Morlet wavelet was used for the analysis. The raw k^3 weighted data were added to the Hama_Fortran program for analysis. For the Multivariate Curve Resolution–Alternating Least Squares (MCR-ALS) the spectral datasets corresponding to each measurement were imported and normalized using the FASTOSH v. 1.0.8 software.^[30] To derive the pure spectra and the respective relative concentrations, the MCR-ALS Matlab toolbox^[31] integrated into FASTOSH was used.

Statistical Analysis: All statistical analyses in this work were performed using the Origin 2023 software. Before data analysis, irrelevant data detection and elimination were performed on the data sets. Experimental errors for FE and average $|j|$ values were calculated as the standard error of the mean using a sample size of $n = 3$. Experimental data in bar diagrams were presented as mean values $\pm$ standard deviation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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copper, phenanthroline, electrocatalysis, molecular catalyst, CO_2 reduction

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6.3 Pre-treated carbon additive enables reduction of metal loading in CoNiFe oxide-based OER electrocatalysts while maintaining performance

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Abstract: Mixed oxides (MO) of Co, Ni, and Fe have emerged as promising catalysts for the oxygen evolution reaction (OER) in alkaline water electrolysis (AWE). Although they are significantly cheaper than the precious metal catalysts used for proton exchange membrane (PEM) water splitting, the limited availability of Co and the exceptionally poor environmental footprint of Co and Ni mining remain challenges for scaling up AWE capacities. In this context, we present a promising approach toward reducing the metal content while preserving the catalytic performance. Based on a recent work on CoNiFeO_x OER catalysts from our group, admixture of pre-treated Vulcan carbon XC-72R (VC) at different synthesis stages in various loadings was evaluated in view of material structure and electrocatalytic activity. Attractive performance characteristics were obtained for the optimized MO-VC composite material, *e.g.*, a mass activity of 370 A gCoNiFe-1 at 1.56 V vs. RHE and a Tafel slope of 39.0 mV dec⁻¹. Stable long-term performance under practical AWE conditions was confirmed in an anion exchange membrane (AEM) electrolyzer. An understanding of the effect of carbon admixture was achieved by combining *in situ* X-ray absorption spectroscopy, analysis of the electrochemically active surface area, as well as electrochemical impedance spectroscopy. The results point toward a benign impact of carbon admixture on the electronic structure of the MO domains under potential bias.

My contribution: I developed, tested, and validated the protocol for membrane electrode assembly electrolyzer studies at industrial current densities (10%).



Research article

Pre-treated carbon additive enables reduction of metal loading in CoNiFe oxide-based OER electrocatalysts while maintaining performance

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ABSTRACT

Mixed oxides (MO) of Co, Ni, and Fe have emerged as promising catalysts for the oxygen evolution reaction (OER) in alkaline water electrolysis (AWE). Although they are significantly cheaper than the precious metal catalysts used for proton exchange membrane (PEM) water splitting, the limited availability of Co and the exceptionally poor environmental footprint of Co and Ni mining remain challenges for scaling up AWE capacities. In this context, we present a promising approach toward reducing the metal content while preserving the catalytic performance. Based on a recent work on CoNiFeO_x OER catalysts from our group, admixture of pre-treated Vulcan carbon XC-72R (VC) at different synthesis stages in various loadings was evaluated in view of material structure and electrocatalytic activity. Attractive performance characteristics were obtained for the optimized MO-VC composite material, e.g., a mass activity of 370 A g_{CoNiFe}⁻¹ at 1.56 V vs. RHE and a Tafel slope of 39.0 mV dec⁻¹. Stable long-term performance under practical AWE conditions was confirmed in an anion exchange membrane (AEM) electrolyzer. An understanding of the effect of carbon admixture was achieved by combining *in situ* X-ray absorption spectroscopy, analysis of the electrochemically active surface area, as well as electrochemical impedance spectroscopy. The results point toward a benign impact of carbon admixture on the electronic structure of the MO domains under potential bias.

1. Introduction

Hydrogen production through electrochemical water splitting powered by renewable energy is considered as one of the key building blocks in establishing a carbon-neutral economy [1–3]. Although it is the cathodic hydrogen evolution reaction (HER) that leads to the product of interest, considerable efforts are devoted to the development of catalysts for the anodic oxygen evolution reaction (OER). This is primarily caused by the slow kinetics of the four-electron OER, which represents the bottleneck of the water splitting process [4–7]. Consequently, developing OER electrocatalysts towards low overpotentials, high mass activity, and improved stability is one of the keys to further optimizing the efficiency of water electrolysis [8,9].

Compared to the already well-established proton exchange membrane (PEM) water splitting, alkaline water electrolysis (AWE) is a less prevalent but promising alternative, since instead of expensive Ir- and Ru-based catalysts, cheaper and readily available alternatives such as Co, Ni and Fe can be employed [10–13]. Recently, significant progress

has been made in the field of AWE through the development of increasingly stable anion exchange membranes (AEM), with the prospect of establishing efficient and durable AEM electrolyzers in the foreseeable future [10,14]. This development has given fresh impetus to AWE research, bringing OER electrocatalysts based on Ni, Co and Fe into the focus [15–18]. The three metals are usually applied as oxides or oxyhydroxides, with CoFeO_x, FeNiO_x and CoFeNiO_x showing particularly good OER performance [19,20]. The outstanding catalytic properties were deduced from a volcano-type relationship between activity and binding energies of oxygen intermediates, whereby mixed Co, Ni, and Fe oxides are located near the top of the volcano curve [21–23].

In a recent paper, we have presented a promising and straightforward method for preparing Co-Ni-Fe oxides as OER electrocatalysts based on a citrate sol-gel approach (Fig. 1) [24]. It was found that the key to strong catalytic performance is thermal treatment under oxygen-deficient atmosphere (M), which renders superior electrocatalytic properties compared to reductive (H) and aerobic conditions (A), respectively. A comprehensive study on the impact of the metal

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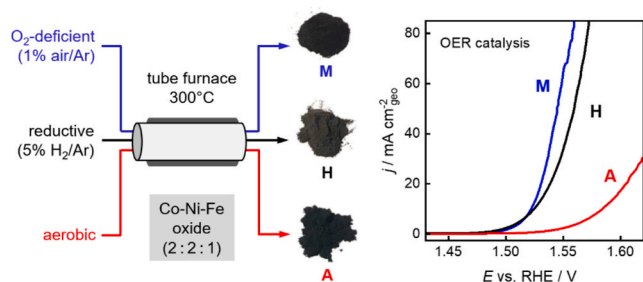


Fig. 1. Summary of our previous study on the influence of thermal treatment and metal ratio on the performance of CoNiFeO_x-based OER electrocatalysts [24].

composition showed that Co : Ni : Fe in a ratio 2 : 2 : 1 (denoted as CoNiFe (2:2:1)/M in our previous work) renders optimum performance. Using the optimized material, attractive performance characteristics were obtained, e.g., an overpotential of 291 mV at 10 mA cm⁻² (η_{10}) and a Tafel slope of 32 mV dec⁻¹. The combined results of electroanalytical studies and structural characterization suggest that performance enhancement through oxygen-deficient annealing can be mostly ascribed to a higher electrochemically active surface area, which does not significantly diminish under OER conditions in contrast to samples prepared by reductive and aerobic treatment, respectively.

Although Co-, Ni-, and Fe-based OER electrocatalysts are significantly cheaper than the precious metals used in PEM electrolysis, issues related to cost of materials are also foreseeable in the future. Thus, a shortage of the rare Co metal can be expected due to the increasing demand for production of Li ion batteries [25,26] and limited number of deposits [27]. Further issues are associated with the exceptionally poor environmental footprint of Co and Ni mining [28,29]. Consequently, reducing the metal content while minimizing the loss of performance is a worthy goal for further improvement of our CoNiFeO_x system. In this context, carbon-based materials as widespread supports for HER [30–34] and ORR [35] catalysts are interesting candidates that may enable cost-effective “dilution” of the mixed metal oxide. In fact, the use of carbon-supported OER catalysts in alkaline media has already been successfully demonstrated by others [36–40]. Depending on the materials investigated, positive properties such as excellent electrical conductivity and high porosity at a low price are usually emphasized [41]. On the other hand, a fundamental challenge is that carbon becomes thermodynamically unstable at potentials higher than its equilibrium potential of 0.207 V vs. the reversible hydrogen electrode (RHE) [42]. However, recent studies have suggested that the carbon oxidation reaction (COR) is effectively suppressed when working in alkaline environment [43] and that COR can be further reduced by combining carbon with a highly effective OER electrocatalyst (“activity–durability coincidence” of OER in the presence of COR) [44,45]. Further works demonstrate that under certain conditions, passivation can stabilize graphitic carbon kinetically [46] and that metal oxide–carbon composites can work effectively as OER electrocatalysts in AEM water electrolysis for more than 1100 h at 200 mA cm⁻² and 80 °C without performance loss [47]. In view of these encouraging findings, we opted to investigate the influence of carbon additives on the OER behavior of our CoNiFeO_x system.

Herein, we present a study on the effect of “diluting” our CoNiFeO_x electrocatalyst with Vulcan XC-72R carbon black (VC). The latter was selected as a popular material from battery and fuel cell research with excellent electrochemical properties, i.e., high electric conductivity (31 ± 5 S cm⁻¹), high purity, low sulfur contamination, good processability, and high BET surface area (207 ± 4 m² g⁻¹) [38,48–51]. In addition, VC showed good performance and particularly low susceptibility toward COR in several recent OER and ORR studies [45,48–50]. To mitigate the hydrophobicity of the material [52] and to explore potential benefits on OER performance [51] including higher surface area and better

interaction with the OER catalyst, oxidative pre-treatment of VC was applied and evaluated. A further focus of our study is the impact of the composite preparation method, whereby carbon was introduced during the sol–gel step and during ink-preparation, respectively. The effects of VC modification and composite preparation method were monitored by electroanalytical studies under RDE conditions as well as through structural characterization before and after electrolysis. Despite significant reduction of the metal content in the as-prepared materials, a stable performance was achieved. Finally, high activity and stability of the optimized CoNiFeO_x-VC composite was demonstrated at practically relevant current density in an AEM electrolyzer.

2. Results and discussion

2.1. Catalyst preparation

The composite materials studied in this work consist of a mixed CoNiFe oxide and conductive Vulcan XC-72R carbon black particles. The metal oxide component is based on the catalyst material from our previous study with best OER performance [24], CoNiFe (2:2:1)/M, whereby 2:2:1 refers to the stoichiometric ratio between the three metals and M for the oxygen-deficient thermal treatment of the catalyst precursor. The precursors were prepared from the corresponding metal nitrates in presence of citric acid using our sol–gel approach (Fig. 2) [24]. Either unmodified carbon black (CB, particle size of 20–50 nm) or carbon black pre-treated with aq. HNO₃ (CM) [53] was added to the metal nitrate solution prior to gel formation. The precursors were subjected to the same thermal treatment conditions as in the previous report (300 °C, 1 vol% air in argon).

To systematically study the impact of the reduced metal content, composites with various mass ratios between CoNiFe oxide and carbon additive were prepared (for details, see the [Experimental Section](#) and [Table S1](#) in the SI). In the following, the different materials are denoted as MO/CB or MO/CM, whereby MO refers to the mixed oxide (CoNiFe (2:2:1)/M), CB to carbon black, and CM to carbon black pre-treated with aq. HNO₃. In addition, each sample denomination contains a number *x* that represents the mass percentage of metal oxide in the material (e.g., 60MO/CM). The compositions of the materials determined by elemental analysis are summarized in [Table S2](#). After thermal treatment, inks were prepared from the MO–carbon composites and a binder, followed by deposition on the electrode surface for electrochemical studies. For comparison, catalyst series *x*MO + CB and *x*MO + CM were prepared by mixing MO with carbon particles *after* thermal treatment using a mortar. The resulting mixtures were then used for ink preparation and electrode coating under the same conditions.

2.2. Structural characterization

Structural characterization of the as-prepared composite materials was carried out using powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), scanning transmission

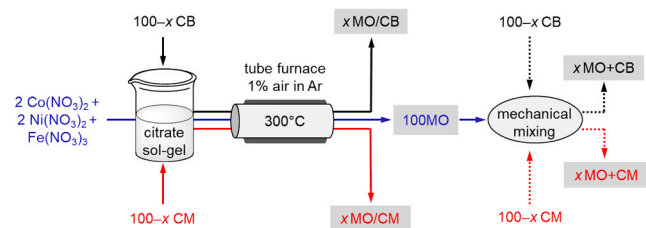


Fig. 2. Schematic illustration of the preparation of catalyst 100MO and the *x*MO/CB, *x*MO/CM, *x*MO + CB, and *x*MO + CM series. MO = metal oxide. Metal oxide content (wt. %): *x* = 100, 80, 60, 40, 20. CB = unmodified carbon black. CM = pre-treated carbon black.

electron microscopy (STEM), electron energy loss spectroscopy (EELS), Raman spectroscopy (RS), X-ray absorption spectroscopy (XAS), and Fourier transform infrared (FTIR) spectroscopy. As exemplarily shown in Fig. 3a, PXRD patterns of 100MO (corresponds to CoNiFe (2:2:1)/M in ref. [24]), 60MO/CB, and 60MO/CM exhibit similar patterns with broad diffraction peaks at 16.3° , 19.1° , and 27.3° that are typical for the (111), (200), and (220) planes of CoO, NiO, and FeO (for details, see Fig. S2). An additional peak at 11.1° occurs for the two carbon-containing samples, which indicates the presence of graphite oxide [54,55]. The presence of graphitic domains is confirmed for both the CB and the CM samples by characteristic Raman bands at 1310 cm^{-1} and 1595 cm^{-1} (Fig. S20a-b), whereby the former reflects the well-ordered bonding environment of sp^2 -hybridized carbon and the latter is caused by defects in the graphitic structure [56].

XPS was carried out to provide information about the valence states and chemical composition of the catalyst surface. Due to the strong overlap of photoelectron lines and intense Auger peaks we focus on a qualitative analysis here. For 100MO, 60MO/CB, and 60MO/CM, the Co 2p and O 1s regions are shown exemplarily in Fig. 3b and c, while the Ni 2p, Fe 2p, and C 1s regions are summarized in Fig. S7 and Table S4. The Co 2p region of the catalyst with (CM and CB) and without carbon is composed of two main peaks associated with Co $2\text{p}_{3/2}$ and Co $2\text{p}_{1/2}$ orbitals together with two intense satellite features on the high binding energy side of each peak. As discussed in our previous work [24], the

shoulders at lower binding energies are probably caused by Auger peaks of Fe and Ni which are present in this region. All catalysts show the Co $2\text{p}_{3/2}$ peak at 781.1 eV together with pronounced satellite features, which suggests the presence of Co^{2+} probably as CoO or $\text{Co}(\text{OH})_2$ [57]. However, compared to the literature dealing with monometallic oxides [57], the observed Co 2p binding energies are slightly shifted to higher values here. The interaction with other elements present in this catalyst (Ni and Fe) probably leads to this shift. The Ni 2p (mainly Ni^{2+}) and Fe 2p spectra of the three catalysts are discussed in detail in the SI.

The high-resolution scans of the O 1s regions for all three samples (Fig. 3c) show a similar shape with two main peaks at binding energies of 529.9 eV and 531.6 eV , respectively, corresponding to lattice metal–oxygen ($\text{M}-\text{O}_x$) and to metal hydroxides/defective oxides, respectively [58,59]. All samples present a much stronger signal for hydroxides/defective oxides than for lattice oxide (the presence of $\text{M}-\text{OH}$ is further confirmed for all three samples by FTIR spectroscopy, see Fig. S20c). While for samples 100MO and 60MO/CM the same binding energies are observed for both peaks, 60MO/CB shows a slightly higher binding energy for the second peak at 531.8 eV .

According to the XPS results, the impact of added carbon on the surface metal oxide composition (and valence states) seems to be negligible, which is in line with results obtained by K-edge XAS. Within the Co K edge regime, 100MO and 60MO/CM exhibit basically the same XANES profile (Fig. 3d). A similar outcome is also observed for the Ni

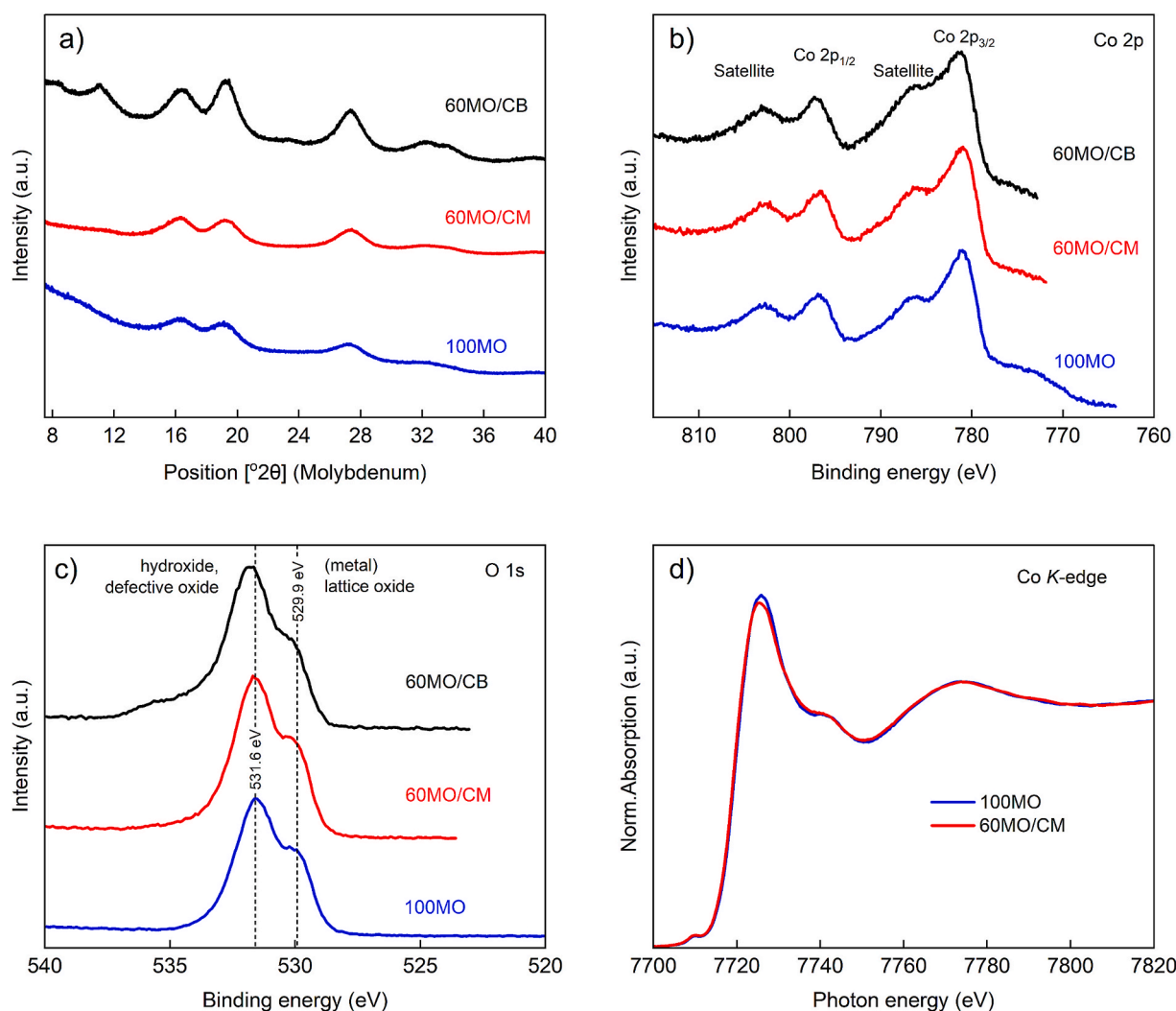


Fig. 3. Structural characterization of 100MO (blue), 60MO/CM (red), and 60MO/CB (black). (a) Powder X-ray diffraction patterns. (b) Co 2p and (c) O 1s XP spectra. (d) Co K-edge XANES analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and Fe K edge when comparing the data of 100MO and 60MO/CM (Fig. S45). The oxidation states of the three metals within both as-prepared materials are ~ 2.3 (Co), ~ 2.1 (Ni), and ~ 2.0 (Fe) according to XANES analysis (Figs. S44 and S45). Consequently, the electronic structures of the mixed metal oxide component within 60MO/CM powder seem to resemble as-prepared 100MO.

SEM analysis was performed for 60MO/CM, 60MO/CB, 60MO + CM, 60MO + CB, and 100MO (Figs. S8–S12). The samples in which the carbon particles were added only after thermal treatment (60MO + CM and 60MO + CB) show a strong segregation into different domains, which is shown exemplarily for 60MO + CB in Fig. 4a (bright domains are caused by backscattering of electrons through elements with high atomic number, here likely by Co, Ni, and Fe). In contrast, composites that were prepared by adding carbon during the sol–gel step do not show such separated domains, as exemplified for 60MO/CM in Fig. 4b.

Samples 60MO/CM and 60MO/CB were additionally examined using STEM coupled to EDX and EELS (Figs. S13–S19). The exemplary STEM image of 60MO/CM in Fig. 4c shows a homogeneous distribution of the elements Co, Ni, Fe, and C across the particle (see EDX mappings in Figs. 4e–g and S14c). Fig. 4d clearly shows nanocrystalline domains of CoNiFeO_x present on carbon. In principle, formation of a CoNiFeO_x /carbon composite could be confirmed by electron microscopic techniques, with the main structural features of the metal oxide found in 100MO being retained. A detailed discussion of the findings is provided in the SI.

Specific surface area (S) and conductivity of the as-prepared materials were investigated using BET analysis (Table S3) and impedance spectroscopy (Table S6). With higher carbon content, both the $x\text{MO}/\text{CM}$ and $x\text{MO}/\text{CB}$ series show increased S_{BET} (up to $211 \text{ m}^2 \text{ g}^{-1}$) compared to 100 MO ($80 \text{ m}^2 \text{ g}^{-1}$), although the surface-increasing effect becomes

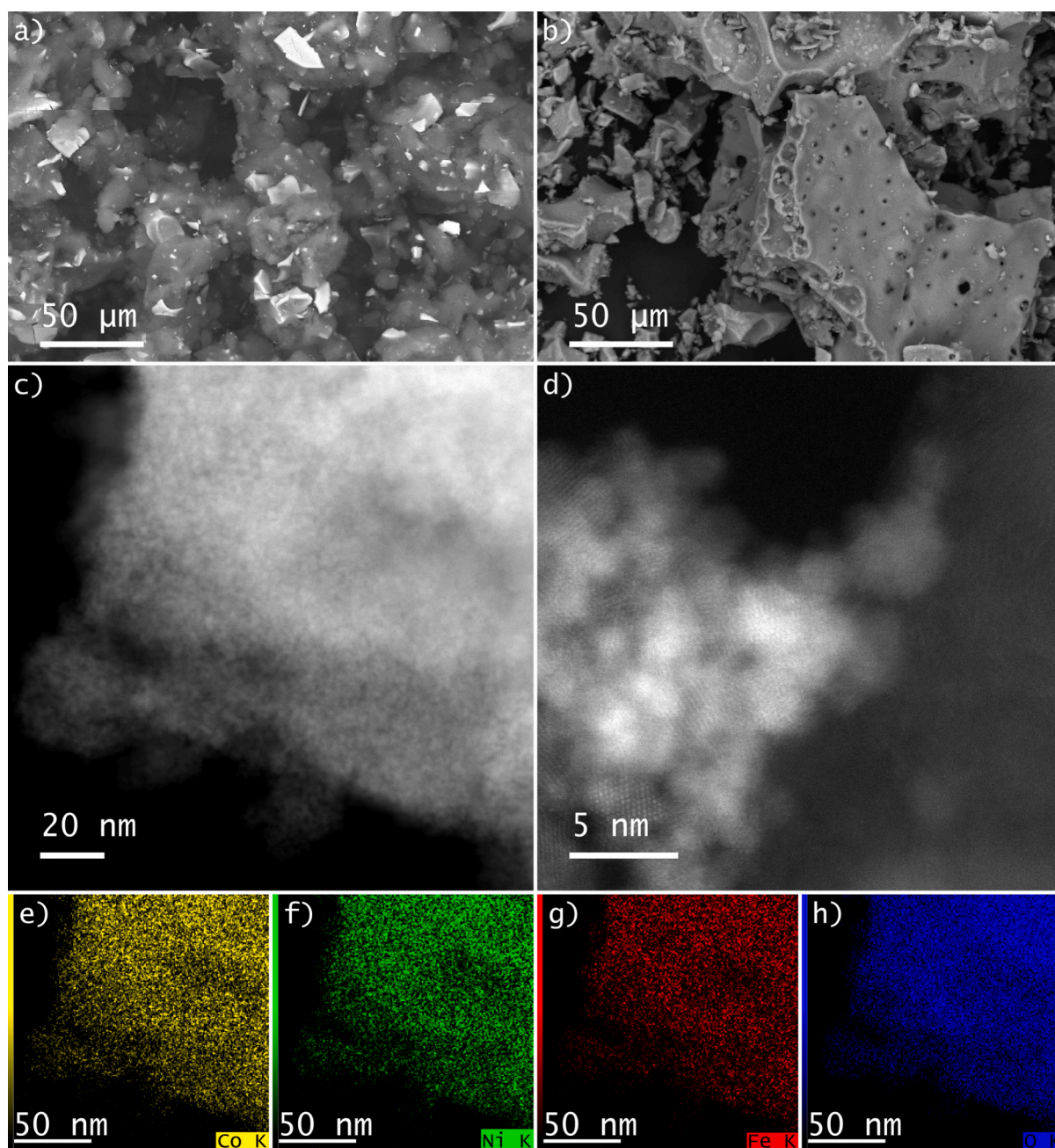


Fig. 4. Top row: SEM images of as-prepared 60MO + CM (a) and 60MO/CM (b) (BSE detector). Central row: STEM-HAADF images of 60MO/CM at different magnifications (c, d). Bottom row: EDX elemental mapping of image (c) showing the distribution of Co (e), Ni (f), Fe (g), and O (h).

significantly pronounced only below $x = 60$. Furthermore, an increase in average pore size d (up to 49 nm) and mesopore volume V_m (up to $0.56 \text{ cm}^3 \text{ g}^{-1}$) with increasing CB or CM content is clearly visible. This effect is stronger for MO-carbon composites that were prepared by mechanical mixing ($x\text{MO} + \text{CB}$ and $x\text{MO} + \text{CM}$) than for the samples that were prepared by adding carbon during the sol-gel process ($x\text{MO}/\text{CB}$ and $x\text{MO}/\text{CM}$).

The S_{BET} , V_m , and d values of selected samples, i.e., 60MO/CB, 60MO/CM, 60MO + CB, 60MO + CM, and 100MO are summarized in Table 1 along with the electrical conductivity of the as-prepared powders (for details on conductivity analysis, see the Experimental Section). A comparison of the conductivities shows that CM renders lower values than CB, which is likely due to the oxidative pre-treatment and the resulting decrease of the fraction of sp^2 -hybridized (graphitic) carbon [53]. Moreover, it becomes clear that mechanical mixing of MO and carbon particles (60MO + CB and 60MO + CM) is beneficial for conductivity compared to adding carbon during the sol-gel step (60MO/CB and 60MO/CM).

2.3. OER performance evaluation under RDE conditions

The electrocatalytic study was initiated with linear sweep voltammetry (LSV) using a glassy carbon RDE in a 1.0 M KOH electrolyte. The electrode was coated *via* drop-casting of a Nafion-containing ink (for details, see the Experimental Section). In the following, the influence of the carbon additives (CB, CM) in different mass ratios relative to MO is discussed along with the impact of the composite preparation approach (compare Fig. 2). More specifically, addition of carbon particles at the beginning of the sol-gel procedure (MO/CB and MO/CM series) is compared to mechanical mixing of as-prepared CoNiFeO_x with carbon particles using a mortar, followed by preparation of catalyst ink (MO + CB and MO + CM series). For all measurements, the same mass of $\text{CoNiFeO}_x/\text{C}$ composite was applied to the electrode surface, resulting in varying metal oxide loadings depending on the degree of “dilution” with carbon.

LSVs were recorded at 1800 rpm ($v = 1 \text{ mV s}^{-1}$) for composites with different MO content (80 %, 60 %, 40 %, and 20 %) for series MO/CB, MO/CM, MO + CB, and MO + CM. While all results are summarized in Figs. S21, S23, and S24, exemplary LSVs of 60MO/CB, 60MO/CM, 60MO + CB, and 60MO + CM are shown in Fig. 5a-b together with the LSV of pure metal oxide catalyst (100MO). Fig. 5a shows the mass specific activity related to the metal oxide content, whereas in Fig. 5b, the current density was calculated with respect to the geometrical electrode surface area. The current densities at 1.56 V vs. RHE and overpotentials at $10 \text{ mA cm}_{\text{geo}}^{-2}$ extracted from the LSVs of the four composite series are summarized in Fig. 5c. Mass specific activities, current densities and overpotentials (η_{10}) are summarized in Table S6 for all catalysts.

At first glance, a comparison of the different samples shows that most carbon composites perform significantly worse than the pure metal oxide (Fig. 5c). However, some of the “carbon-diluted” materials have a performance comparable to 100MO despite significantly lower metal content. Although 100MO renders the highest current density (Fig. 5b), catalyst 60MO/CM, for example, provides a higher mass activity

(A_{CoNiFe}^{-1}) at 1.56 V with only 60 % metal oxide content (Fig. 5a). When comparing 60MO/CM with 60MO + CM and 60MO/CB with 60MO + CB, it becomes apparent that introducing the carbon already during the sol-gel process leads to better results than only during ink preparation (Fig. 5-b). For example, the mass specific activity at 1.56 V drops by almost 80 % when replacing 60MO/CM with 60MO + CM, while η_{10} increases by more than 20 mV. A possible explanation for the superior performance of the MO/CM and MO/CB materials is that a more intimate mixing of the two components is achieved with the integrated sol-gel process and heat treatment, leading to improved contact between the MO and CM domains (see also SEM images in Fig. 4a-b, Fig. S9, and Fig. S11), and allowing the carbon to effectively contribute to current flow as conductivity-enhancing additive. Superior performance of the MO/CM and MO/CB materials is also reflected by the Tafel slopes (Fig. 5d and Fig. S25).

A further prerequisite for good performance is the chemical pre-treatment of carbon particles, as 60MO/CM performs significantly better than 60MO/CB (Fig. 5-b). This trend is also confirmed by comparing the activities and overpotentials of other congeners of the MO/CB and MO/CM series (see Fig. 5c) and the Tafel slopes in Figs. 5d and S25. A possible explanation is that the increased and more hydrophilic surface allows a stronger binding to the metal oxide during composite formation. Moreover, a sufficiently high MO content within the composite is required for good catalytic activity. While very good results can be achieved with 80MO/CM and 60MO/CM, the overpotentials and current densities are significantly worse for 40MO/CM and 20MO/CM (Fig. 5c). Finally, it should be noted that despite the good mass specific activity, the admixture of carbon does in principle decrease the geometrical LSV current density under RDE conditions (Fig. 5b). This may be attributed to a decrease of the number of active sites by “dilution” with carbon.

From Fig. 5c, it can be concluded that the group located at the top left of the diagram (60MO/CM, 80MO/CM, and 100MO) exhibits the most promising catalytic properties. Catalyst 60MO/CM represents a particularly auspicious candidate, as it achieves a high mass specific activity of $369.9 \text{ A g}_{\text{CoNiFe}}^{-1}$ at 1.56 V and a small η_{10} of 297 mV at low metal oxide content. This impression is further confirmed by chronopotentiometric profiles recorded at $10 \text{ mA cm}_{\text{geo}}^{-2}$ (Fig. 5e; further measurements are summarized in Figs. S21d, S23d, S24d, and Table S6). Again, 60MO/CM shows a behavior similar to 100MO and superior to 60MO/CB, starting at relatively low potential without significant changes within 15 min. Not surprisingly, the samples 60MO + CB and 60MO + CM show clearly inferior profiles compared to 100MO, 60MO/CM, and 60MO/CB (Fig. S21d).

Interestingly, long-term chronopotentiometric analysis at higher current density, i.e., $50 \text{ mA cm}_{\text{geo}}^{-2}$ (Fig. S28a) and $100 \text{ mA cm}_{\text{geo}}^{-2}$ (Fig. 5f), shows that 60MO/CM performs even better under high stress compared to 100MO. 60MO/CM starts at $\eta_{100} = 240 \text{ mV}$ and exhibits a stable profile with a potential increase of less than 5 mV after 7 days. In contrast, 100MO shows a stronger potential increase ($\sim 45 \text{ mV}$) after starting at a higher η_{100} value (262 mV). Since Ni foam is frequently used in AEM electrolyzers as OER catalyst support, the long-term measurement was repeated with 60MO/CB using a Ni RDE under otherwise identical conditions (Fig. 5f). Starting at a higher potential compared to the GC RDE, a similar potential was achieved after 7 days.

To further probe the performance of 60MO/CM at high stress, an on-off chronopotentiometric analysis with 3 h intervals was carried out with current densities of 10, 20, 50, and $100 \text{ mA cm}_{\text{geo}}^{-2}$ at $\omega = 1800 \text{ rpm}$ (Fig. 5g). Despite harsh conditions and strong bubble formation, the catalyst exhibits stable plateaus during the 3 h intervals. In contrast, 100MO is much less stable under these conditions, as in several trials, the experiment had to be aborted due to potential overloads at the $50 \text{ mA cm}_{\text{geo}}^{-2}$ step (see Fig. S29). In general, the potential-time profile can be affected both by catalyst degradation and by development of micro- and nanobubbles within the pores which cannot be removed by electrode

Table 1

Summary of surface areas (S_{BET}), mesopore volumes (V_m), average pore sizes (d), and conductivity values for selected materials.

Sample	S_{BET} [$\text{m}^2 \text{ g}^{-1}$]	V_m [$\text{cm}^3 \text{ g}^{-1}$]	d [nm]	conductivity [S cm^{-1}]
100MO	80.3	0.04	1.6	0
60MO + CB	106.7	0.36	49.0	28.9
60MO + CM	89.6	0.29	48.1	6.0
60MO/CB	91.1	0.17	3.3	3.3
60MO/CM	89.6	0.11	3.3	2.1

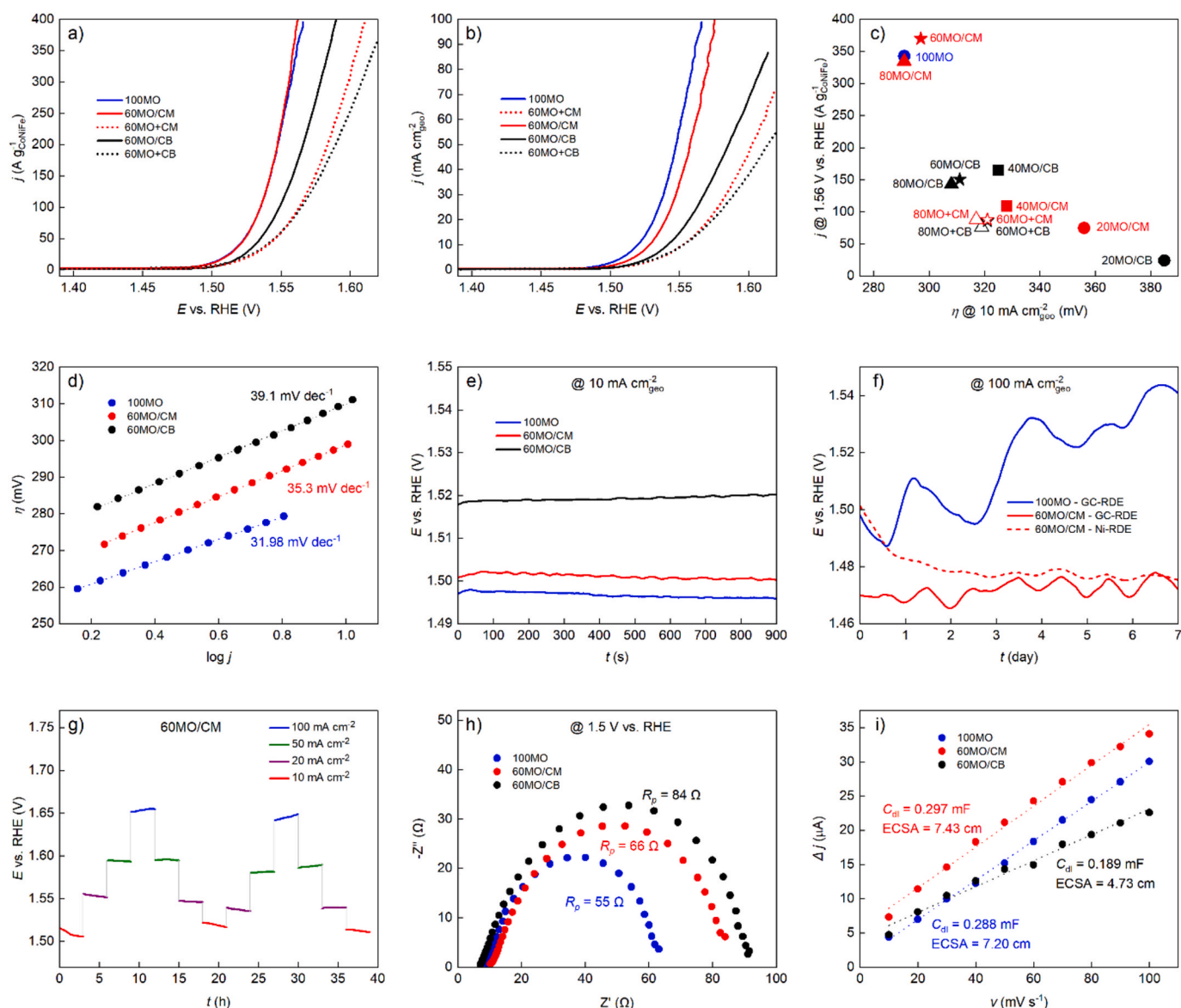


Fig. 5. (a–b) OER polarization curves measured in 1.0 M KOH solution ($v = 1 \text{ mV s}^{-1}$, $\omega = 1800 \text{ rpm}$, iR drop corrected) showing the mass activity related to metal oxide content (a) and the current density with respect to the geometrical electrode surface area (b). (c) Comparison of overpotential and mass activity between 100MO and the MO-carbon composite series. (d) Tafel plots extracted from LSVs shown in Fig. 5b. (e) Chronopotentiometric profiles recorded at $10 \text{ mA cm}^{-2}_{\text{geo}}$ ($\omega = 1800 \text{ rpm}$). (f) Chronopotentiometric stability tests recorded at $100 \text{ mA cm}^{-2}_{\text{geo}}$ for 100MO and 60MO/CM on glassy carbon and Ni RDE, respectively (all measured potentials are pH corrected). (g) Stepwise chronopotentiometric stability test carried out at 10, 20, 50, and $100 \text{ mA cm}^{-2}_{\text{geo}}$ (3 h for each step). (h) Electrochemical impedance spectra (Nyquist plots) recorded for 100MO, 60MO/CB, and 60MO/CM at 1.5 V vs. RHE. (i) Estimation of double layer capacitance (C_{dl}) and electrochemically active surface area (ECSA) via CV in the non-Faradaic regime (for details, see Figs. S22, S26, and S27).

rotation [60,61]. Based on the present data, it cannot be clearly inferred whether the superior long-term performance of 60MO/CM is due to a higher stability or to improved dissipation of gas bubbles. In view of this ambiguity, it should be noted that although RDE conditions are well suited for studying and comparing catalyst properties, the significance of the results is limited with respect to practical conditions in AEM electrolyzers [61]. Consequently, stability and performance of 60MO/CM was also evaluated in an AEM flow cell at $400 \text{ mA cm}^{-2}_{\text{geo}}$ (see Section 2.5).

To explore the origins of the observed trends, further analytical techniques were applied. Electrochemical impedance spectroscopy (EIS) at 1.5 V (Figs. 5h, S21e, S23e, and S24e) was used to determine the charge transfer resistance R_p . CV was carried out with a stationary electrode in the non-Faradaic regime (Figs. 5i, S21f, S23f, and S24f) to

determine the electrochemically active surface areas (ECSA) from the double-layer capacitance (C_{dl}). The R_p and ECSA values of 100MO, 60MO/CM, 60MO/CB, and other samples are summarized in Table S6. The Nyquist plots in Fig. 5h show the same trend as the Tafel slopes in Fig. 5d, i.e., that the charge transfer rate increases in the order $60\text{MO/CB} < 60\text{MO/CM} < 100\text{MO}$. The corresponding R_p values obtained from EIS data fitting amount to 85Ω , 66Ω , and 55Ω , indicating i) that the presence of carbon slows down OER kinetics at 1.5 V and ii), that the decelerating effect is less pronounced for CM than for CB. On the other hand, analysis of C_{dl} shows a slight increase of the ECSA for 60MO/CM compared to 100MO (7.43 cm^2 vs. 7.20 cm^2). In contrast, 60MO/CB exhibits a significantly smaller ECSA (4.73 cm^2), suggesting that the stronger catalytic performance of 60MO/CM compared to 60MO/CB could be a result of the enhanced ECSA.

The better electronic conductivity of 60MO/CM and 60MO/CB

compared to 100MO (cf. Table 1) certainly supports the rate of charge transfer and counteracts the reduction in the number of catalytically active sites. Although the oxidative carbon pre-treatment reduces the conductivity of 60MO/CM compared to 60MO/CB (2.1 S cm^{-1} vs. 3.3 S cm^{-1}), it is still significantly higher than that of poorly conducting 100MO. However, interpreting the conductivity values should be exercised with care, since conductivity measurements were performed using dry powder, while ECSA and EIS measurements were carried out in contact with the alkaline electrolyte at potential bias [62]. Under these circumstances, the differences between the electronic conductivities of the powder samples can only serve as a qualitative indication. Overall, 60MO/CM exhibits high ECSA and good conductivity, both of which may partially compensate for the lower number of active centers compared to 100MO.

2.4. Characterization of used catalysts

To better understand the structural changes which 100MO, 60MO/CM, and 60MO/CB undergo under OER conditions, additional electro-analytical and spectroscopic experiments were performed after applying $10 \text{ mA cm}^{-2}_{\text{geo}}$ for 1 h in 1.0 M KOH (RDE conditions). The first indication can be derived from the change in R_p before and after the galvanostatic measurements (Fig. S30 and Table 2). Surprisingly, the initially lowest polarization resistance of 100MO electrolysis rises by 16Ω , which corresponds to a 29 % increase. On the other hand, the R_p value of 60MO/CM increases by only 3Ω (5 %). A similarly small increase in R_p ($+2 \Omega$) is observed for 60MO/CB, albeit at a significantly higher level. As a result, the post-electrolysis R_p values of the catalysts increase in the order 60MO/CM $\approx$ 100MO < 60MO/CB.

Regarding ECSA, 60MO/CM experiences a loss of 52 %, whereas the value for 100MO decreases by only 15 %. At a first glance, this result appears surprising, as 60MO/CM shows a stable potential-time profile, while the performance of 100MO deteriorates significantly during the galvanostatic stability test (Fig. 5f). However, it must be considered that the ECSA was determined via the double layer capacitance which also contains contributions from catalytically inactive carbon domains – the ECSA does therefore not directly translate to the number of active sites. Catalyst 60MO/CB suffers a further loss of 34 % from its already low initial ECSA value. Consequently, the post-electrolysis ECSA values decrease in the order 100MO > 60MO/CM > 60MO/CB (Fig. S31 and Table 2). This finding suggests that despite the decreasing ECSA, the number of active sites and/or OER microkinetics of 60MO/CM remain stable/gradually improve under stress. In contrast, 100MO seems to deteriorate in agreement with the results of the RDE stress test at $100 \text{ mA cm}^{-2}_{\text{geo}}$ (Fig. 5f).

To analyze the structural changes that occurred under operating conditions, PXRD, SEM-EDX, STEM-EELS, XPS, and XAS measurements were performed. Compared to the pre-electrolysis PXRD results shown in Fig. 3a, used 60MO/CB and 60MO/CM show preserved but significantly broadened peaks around 16° , 19° , and 27° (Fig. 6a). In contrast, these signals vanish completely in the post-electrolysis PXRD pattern of 100MO, indicating that the material has become largely amorphous,

Table 2

Summary of changes in electrochemical properties of OER electrocatalysts after 1 h polarization at $10 \text{ mA cm}^{-2}_{\text{geo}}$ in 1.0 M KOH.

Sample	R_p before stability test ^a (Ω)	R_p after stability test ^a (Ω)	ECSA before stability test (cm^2)	ECSA after stability test (cm^2)
100MO	54.9	70.9	7.20 ± 0.07	6.13 ± 0.20
60MO/CM	66.2	69.6	7.43 ± 0.30	3.60 ± 0.12
60MO/CB	84.4	86.4	4.73 ± 0.20	3.13 ± 0.12

^a R_p measured at 1.5 V vs. RHE.

whereby minor peaks around 25° , 30° , and 32° may suggest formation of crystalline FeO and Fe_3O_4 domains [24]. Morphology changes of samples 60MO/CB and 60MO/CM according to SEM (Figs. S33–35) and STEM (Fig. S36–43) analysis are comparable to 100MO, whereby EDX mapping indicates that Co, Ni, Fe, and C retain their distribution across the surface.

After the galvanostatic tests, the sample surfaces of 100MO, 60MO/CB, and 60MO/CM were investigated again by XPS. The results for Co 2p, Ni 2p and Fe 2p are shown in Fig. 6b and Fig. S32 (all binding energies are summarized in Table S10). For all samples with (CB and CM) and without carbon, very similar XP spectra can be observed and point toward an oxidic nature of Co, Ni, and Fe after the strongly oxidizing OER conditions. Especially for Co 2p in Fig. 6b, the small satellite features together with the binding energy of the Co $2p_{3/2}$ peak around 780.3 eV indicate the presence of Co as Co_3O_4 [57]. These findings are in line with *ex situ* Co/Ni/Fe K-edge XANES data obtained from post-electrolysis 60MO/CM (Fig. S46), which indicate an increase of the Co, Ni, and Fe oxidation states from 2.3 to 3.3, from 2.0 to 2.5, and from 2.0 to 2.9, respectively.

In the O 1s region in Fig. 6c, again two main peaks at binding energies of 529.5 eV and 531.1 eV can be observed. However, in the O 1s XP spectra for 60MO/CM, the peak at 529.5 eV is weaker compared to 100MO (blue), while it almost disappears in the case of sample 60MO/CB (Fig. 6c). The addition of carbon thus seems to change the ratio of lattice oxygen to hydroxide/defective oxygen after the OER. The hydroxide peak is strongly visible for all samples before and after electrolysis.

2.5. Studies in an AEM flow electrolyzer

To approach the industrial standard of alkaline water electrolysis, further studies were carried out in a flow AEM electrolyzer, in which two electrodes were separated by an anion exchange membrane (electrolyte: 1.0 M KOH; $T = 50^\circ\text{C}$; for further details, see the Experimental Section). 60MO/CM was studied as the most promising catalyst from the RDE measurements and compared to 100MO. OER catalysts were deposited on a Ni-foam layer by air spray-coating with a mass loading of 5 mg cm^{-2} related to the geometrical electrode surface area. The influence of the cathode material was investigated by using bare Ni foam as well as different loading of Pt on Vulcan carbon cloth electrodes (Fig. S53). To minimize limitation through HER, carbon cloth with a Pt loading of 0.5 mg cm^{-2} has been identified as a suitable cathode material.

Key results are summarized in Fig. 7. Stepwise increase of current density with a time interval of 10 min for every step was used to evaluate the short-stress stability. Bare Ni foam shows significantly higher potentials at every current density compared to catalyst-loaded electrodes (100MO and 60MO/CM on Ni-foam). With ca. 600 mV, the biggest voltage gap between bare Ni foam and catalyst-loaded electrodes is achieved at $1000 \text{ mA cm}^{-2}_{\text{geo}}$. During the reverse scan, cell voltages at 800, 600, 400, 200, 100, and $10 \text{ mA cm}^{-2}_{\text{geo}}$ show significant improvement compared to the forward scan, confirming the excellent OER activity of 100MO and 60MO/CM under practically relevant conditions. Interestingly, 60MO/CM performs somewhat better than 100MO, which aligns with the RDE chronopotentiometric studies at high current density. The two samples exhibit the same potential at small current densities ($2\text{--}50 \text{ mA cm}^{-2}_{\text{geo}}$), but 60MO/CM renders 50–80 mV lower cell voltages at higher current densities. The influence of the catalyst loading on the anode was also studied (Fig. S54) and is discussed in the Supporting Information.

Long-term stability tests were carried out at $400 \text{ mA cm}^{-2}_{\text{geo}}$ with 10 intervals of 10 h each (Fig. 7b). During all intervals, the cell voltage is close to 2.0 V. Once more, 60MO/CM shows high activity and stability with little increase in cell voltage within and between the 10 h intervals. During the experiment, the starting voltage is reduced continuously for each 10 h interval. For example, the voltage at the beginning of the tenth

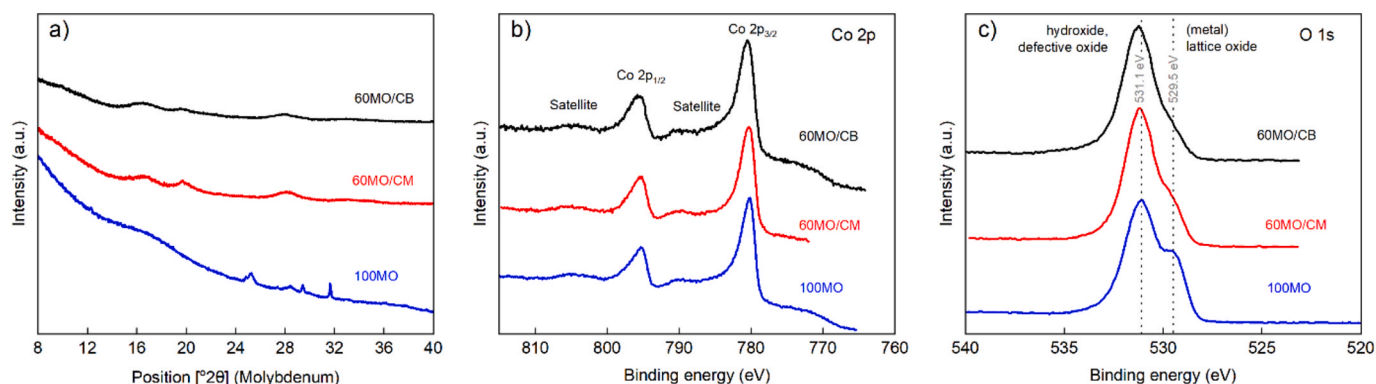


Fig. 6. (a) Powder X-ray diffraction patterns. (b) Co 2p and (c) O 1s XP spectra of 100MO, 60MO/CB, and 60MO/CM after stability tests ($10 \text{ mA cm}^{-2}_{\text{geo}}$, 1 h, 1.0 M KOH, undivided cell).

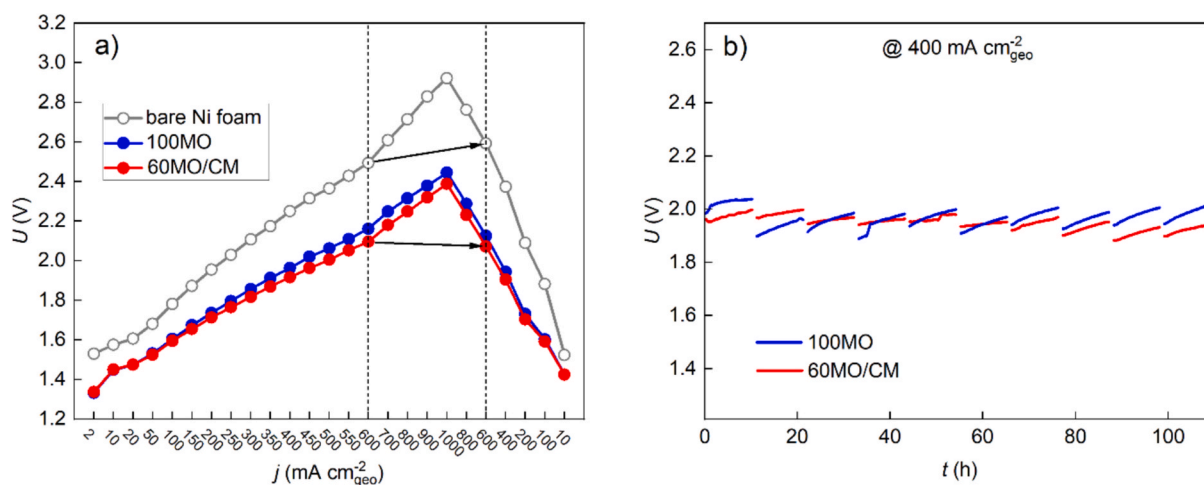


Fig. 7. Results of the flow AEM water electrolyzer studies using bare Ni foam, 100MO/CM on Ni foam, and 60MO/CM on Ni foam as the anode (1.0 M KOH, 50 °C). In all cases, Pt (0.5 mg cm^{-2}) on carbon cloth was used as the cathode. (a) Acquisition of cell voltages at various current densities from $2 \text{ mA cm}^{-2}_{\text{geo}}$ to $1000 \text{ mA cm}^{-2}_{\text{geo}}$ (10 min per each point) and step-scanning back to $10 \text{ mA cm}^{-2}_{\text{geo}}$. Arrows indicate the potential change during the reverse scan at $600 \text{ mA cm}^{-2}_{\text{geo}}$. (b) Stability experiments using 100MO and 60MO/CM, respectively, as OER catalysts at $400 \text{ mA cm}^{-2}_{\text{geo}}$.

interval is only 1.89 V and thereby 85 mV smaller compared to the first interval. In contrast, no improvement of the cell voltage is observed after 100 h of load test when 100MO is used. Moreover, compared to 60MO/CM, the pure metal oxide catalyst shows a significantly stronger potential increase during most of the 10 h intervals. Consequently, as in the step-scan experiments shown in Fig. 7a, 60MO/CM renders a better impression during long-term stability test than its carbon free counterpart 100MO.

2.6. In situ XAS analysis

To investigate the impact of CM additives on the structural evolution of CoNiFeO_x catalysts (100MO and 60MO/CM) during the OER, *in situ* XAS measurements were conducted in a custom-made spectroelectrochemical (SEC) flow cell using a carbon paper anode as catalyst support. Experimental protocols for synchrotron and electrochemical settings are detailed in the Experimental Section. To optimize fluorescence signal quality, 0.1 M KOH (instead of 1.0 M) was used as standard electrolyte, with applied potentials recalibrated to the RHE scale. Analysis was focused on the K-edge absorption profiles of Co, Ni, and Fe in the 100MO and 60MO/CM catalysts under positive electrode polarization, probing their redox dynamics during OER.

Prior to *in situ* OER studies, reference spectra were recorded for the dry catalyst layer (after ink preparation, spray coating, and electrode

mounting in the SEC cell) and for the wet state after exposing the electrode to electrolyte without potential bias (Fig. S48, Table S12). Notably, the Fe species in the 100MO and 60MO/CM materials exhibited a positive shift of the average oxidation state from 2.0 (as-prepared catalyst powder) to ~ 2.9 after spray-coating, likely caused by aerobic oxidation during the ink/spray process. In contrast, the K-edge profiles and average oxidation states for Co and Ni in 100MO and 60MO/CM remained relatively stable between the as-prepared and spray-deposited states.

Spectral evolution was analyzed at several selected critical potentials (Fig. S47) and the results are summarized in Figs. S49–S52 as well as Table S12. A comparison between the average oxidation states of 60MO/CM and 100MO at the OCP (0.76 V) as well as under OER conditions (1.61 V) is shown in Table 3. XANES spectra are shown exemplary for the Co K-edge in Fig. 8. Between 60MO/CM and 100MO, a similar progression of the mean oxidation states can be observed for Ni (from 2.3 to 2.5) and Fe (remains at ~ 3.0 , see Table 3). In contrast, there is a striking difference regarding the Co oxidation states: While 100MO shows an increase from 2.5 to 3.0, 60MO/CM exhibits significantly higher values both at the OCP (3.1) and under OER conditions (3.3).

Based on the available data and a comparison with the literature, some tentative conclusions are possible. First, Fe shows no pronounced redox activity and seems to maintain oxidation state +III over a wide potential range. Although at this point, the task of Fe in our catalytic

Table 3

Summary of average metal oxidation states by XANES analysis (for details, see the [Supporting Information](#)).

Experiment	Average oxidation states for 60MO/CM			Average oxidation states for 100MO		
	Co	Ni	Fe	Co	Ni	Fe
Analysis of as-prepared catalyst powder	2.3	2.0	2.0	2.3	2.2	2.1
<i>In situ</i> measurement at OCP (0.76 V vs. RHE)	3.1	2.3	3.0	2.5	2.3	2.9
<i>In situ</i> measurement during OER (1.61 V vs. RHE)	3.3	2.5	3.0	3.0	2.5	2.9

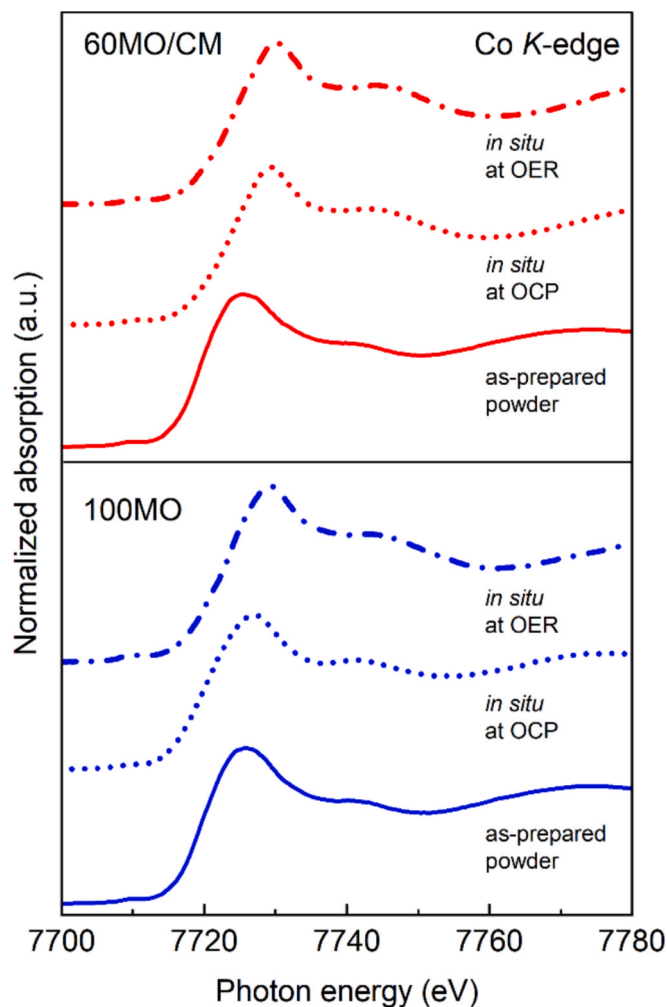


Fig. 8. *In situ* Co K-edge XANES spectra of 60MO/CM (top) and 100MO (bottom).

system cannot be unequivocally assigned, its role in mixed metal oxide OER catalysts is generally considered to be rather a performance promoter than an active site [63–65]. Second, a significant proportion of Co (IV) centers can be observed under OER conditions, while Ni is present in significantly lower oxidation states. The latter may be ascribed to the short lifetime of the Ni(IV) state [63]. Third, there is a clear difference in the redox behavior of Co between the two catalyst materials, reaching significantly higher oxidation states in 60MO/CM than in 100MO. This large difference under potential bias indicates that there is a strong influence of carbon on the electronic structure of the metal oxide, probably caused by improved charge transfer and likely influencing OER activity of the individual sites at elevated potentials.

3. Conclusion

Based on our previously reported CoNiFe oxide OER catalytic system [24], the effect of carbon black admixture and composite preparation procedure on the performance was investigated. Using RDE voltammetry and RDE chronopotentiometry, it was found that under three prerequisites, a significant reduction of metal loading is possible while maintaining high activity at low overpotentials:

1. The carbon particles must be already added during the sol–gel process and not only during ink preparation. A possible explanation is that a more intimate mixing of the two components is achieved through the sol–gel step and subsequent thermal treatment, leading to stronger interaction between metal oxide and carbon particles and allowing the carbon to effectively contribute to current flow as conductivity-enhancing additive. This rationale is supported by SEM analysis of as-prepared composites.
2. Oxidative pre-treatment of hydrophobic carbon black particles is required. A plausible explanation is that the enhanced and more hydrophilic surface enables a stronger binding to the metal oxide during composite formation.
3. A sufficiently high metal oxide content within the composite is necessary for good catalytic activity. While very good results can be achieved with 80 and 60 wt% metal oxide, activity significantly drops when reducing the content to 40 and 20 wt%, respectively.

Catalyst 60MO/CM was identified as the most promising candidate under RDE conditions: With 40 % reduced metal content, it achieved a η_{10} value of 297 mV, a mass activity of $370 \text{ A g}_{\text{CoNiFe}}^{-1}$ at 1.56 V, a Tafel slope of only 39.0 mV dec^{-1} , and negligible changes of the overpotential in long-term potentiometric measurements at $100 \text{ mA cm}_{\text{geo}}^{-2}$. A comparison between the R_p values of the catalysts before and after chronopotentiometric tests shows that 100MO experiences a strong increase in charge transfer resistance, while 60MO/CM exhibits almost no change. Interestingly, this is *not* a result of the available surface area, as the ECSA of 60MO/CM decreases more than the value of 100MO. On the other hand, the electronic structure of the metal oxide domains experiences a strong influence through the CM component under OER conditions, as demonstrated by *in situ* XANES analysis. Taken together, these observations suggest that at elevated potentials, the carbon additive has a promoting effect on OER microkinetics, enabling the effective use of the composite materials despite lower metal loading. Excellent performance of 60MO/CM was also confirmed under practically relevant conditions in an AEM flow electrolyzer. Future studies should aim at improving the mechanistic understanding, including the interplay between carbon and metal oxide domains as well as their structural changes under OER conditions.

4. Experimental section

Materials for catalyst synthesis. All chemicals were of analytical grade and used without further purification. Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from ThermoFisher GmbH (Karlsruhe, Germany). Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were obtained from Sigma-Aldrich. Vulcan carbon XC-72R (carbon black) was purchased from CABOT corporation and nitric acid (HNO_3 , ~65 %) was ordered from Fisher Scientific. Potassium hydroxide solution (KOH, 0.999–1.001 M at 20 °C) was purchased from AppliChem. Ethanol (EtOH, abs., >99.5 %) was obtained from Walter-CMP. Nafion solution (D-521) was purchased from Alfa Aesar. Throughout all experiments, deionized water was used.

Preparation of modified carbon black (CM). For oxidative carbon treatment, a reported procedure was used [53]. Vulcan carbon XC72R (2 g) was added to 90 mL of an aq. 9 M HNO_3 solution. The mixture was

stirred at room temperature for 30 min and sonicated for 1 h (120 W, 35 kHz). Then, the mixture was heated to 90 °C and stirred for 3 h (650 rpm). After allowing the suspension to cool to room temperature, the treated carbon particles were separated by centrifugation and layered with deionized water. Centrifugation and addition of water were repeated until reaching pH 7. Finally, after removal of water by centrifugation, the black powder was dried at room temperature.

Preparation of MO-carbon composites by mechanical mixing. A defined amount of CoNiFe oxide prepared according to our previously published procedure (CoNiFe (2:2:1)/M) [24], carbon black (CB) or modified carbon (CM), as well as a small amount of ethanol (200 mg MO-carbon mixture in 2 mL ethanol) were mechanically mixed in a mortar until homogeneity of the sample was achieved. The resulting mixture was then dried in an oven at 45 °C to remove the alcohol and used for catalyst ink preparation according to the procedure described below. A summary of the prepared composites including the mass ratios between MO and carbon additive is found in Table S1.

Preparation of MO-carbon composites via sol-gel synthesis. The synthesis of the composite is based on the sol-gel procedure of our previous work [24]. 12 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 12 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 6 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 30 mL deionized water using a magnetic stirrer at room temperature. A solution of 30 mmol citric acid in 30 mL deionized water was added slowly to the solution using a dropping funnel. The resulting solution was then stirred for 30 min, followed by the addition of a defined amount of carbon (CB or CM, for details see Table S1). To improve dispersion of the particles, the mixture was sonicated for 45 min. The resulting dispersion was stirred at 250 rpm for 30 min at room temperature, followed by heating to 70 °C to achieve gel formation. Heating to 110 °C for 17 h in a drying oven yielded a xerogel, which was processed into a powder by grounding in a ball mill for 10 min. The precursor material was subjected to thermal treatment in a horizontal tubular furnace (HTM Reetz) at 300 °C for 3 h under an argon/1 vol% air atmosphere ($\dot{V} = 5 \text{ mL min}^{-1}$), whereby a temperature ramp of 5 K min^{-1} was used to achieve the treatment temperature. Results of elemental analysis are provided in Table S2.

Materials characterization: Elemental analysis for carbon, hydrogen, and nitrogen was carried out using a TruSpec Micro CHNS analyzer (Leco). The metal contents of the samples were measured using ICP OES analysis which was carried out using a Varian/Agilent 715-ES spectrometer.

Powder X-ray diffraction patterns were recorded using a Stoe Stadi P transmission diffractometer equipped with a DECTRIS Mythen2 1 K detector applying $\text{Ge}(111)$ monochromatized $\text{Mo K}\alpha_1$ radiation (50 kV, 40 mA, 0.70930 Å). The samples were ground to a fine powder and placed between two plastic wraps before the measurement. Peak positions and profile were fitted with the Pseudo-Voigt function using the HighScore Plus software package (Panalytical). Phase identification was achieved by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

The XPS (X-ray Photoelectron Spectroscopy) measurements were performed on an ESCALAB 220iXL (Thermo Fisher Scientific) with monochromated $\text{Al K}\alpha$ radiation ($E = 1486.6 \text{ eV}$). Samples were prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. The measurements were performed with charge compensation using a flood electron system combining low energy electrons and Ar^+ ions ($p_{\text{Ar}} = 1 \times 10^{-7} \text{ mbar}$). The electron binding energies are referenced to the C 1s core level of carbon at 284.8 eV (C–C and C–H bonds) for 100MO, 284.5 eV for CB and 284.4 eV for CM as received from the measurement of pure CB and CM as reference samples (see Section 13 in the SI and Fig. S58 for details).

The morphology of the electrode surface before and after electrolysis was studied with electron microscopy. Scanning Electron Microscope (SEM) analysis was performed on a Thermo Fisher Scientific (Hillsboro, USA) Quattro S equipped with a Thermo Fisher Scientific UltraDry 60 M Energy Dispersive X-ray Spectrometer (EDXS) for elemental

identification.

Scanning transmission electron microscopy (STEM) investigations were carried out on a probe aberration-corrected JEM-ARM200F (JEOL, corrector: CEOS) at an accelerating voltage of 200 kV. The microscope is equipped with a JED-2300 (JEOL) energy-dispersive X-ray spectrometer (for EDX) having a silicon drift detector (dry SD60GV). EDX elemental maps are depicted after applying net count fitting using the software Analysis Station (JEOL). Electron energy-loss spectroscopy (EELS) was done with an Enfinium ER (Gatan) electron energy-loss (EEL) spectrometer. For STEM imaging, a High-Angle Annular Dark Field (HAADF) and an Annular Bright Field (ABF) detector were employed, while an Annular Dark Field (ADF) detector was used for position control during EELS acquisition. Dual EELS was performed at a camera length of 4 cm, an illumination semi angle of 27.8 mrad and a filter entrance aperture semi angle of 41.3 mrad using the low loss region for compensation of energy shifts during acquisition. The solid samples were deposited without any pre-treatment onto a holey carbon-supported Cu grid (mesh 300) and subsequently transferred to the microscope.

Specific surface areas and pore volumes were determined by N_2 physisorption measurements on a Micromeritics ASAP 2020 apparatus at -196 °C and calculated using BET and BJH methods, respectively. Catalysts were degassed at 200 °C in vacuum for 4 h before analysis. Raman measurements were carried out at an excitation wavelength of 785 nm using a HORIBA iHR550 spectrometer equipped with a sapphire ball-probe (Marq Metrix). FTIR spectra were recorded using a Bruker Alpha-FTIR spectrometer in ATR mode.

Conductivity analysis. The composite was pressed into a pellet (diameter: 10 mm, height: 1.5 mm) at a pressure of 3 kbar. The pellet was placed between two gold-plated steel disk electrodes using a spring rate of 2.4 N mm^{-1} to obtain a stack pressure of approximately 0.6 bar. Estimation of specific conductivity was done by impedance spectroscopy (amplitude: 0.05 V, frequency range: 10 kHz to 1 kHz) at open circuit potential using the TSC Battery test cell from RHD Instruments.

Electroanalytical experiments. All experiments were performed in a three-electrode arrangement using an Autolab PGSTAT 302 N (Metrohm). A glassy carbon rotating disk electrode (diameter: 3.8 mm, geometrical surface area: 0.113 cm^2) was used as the working electrode (WE). For the preparation of the coated WE, catalyst inks were prepared by dispersing 5 mg catalyst in 1 mL of a mixture of 0.1 M KOH, Nafion solution, EtOH, and H_2O (1:2:45:45 in relation to the volumes of the pure components). The ink was sonicated for 45 min at room temperature. The catalyst suspension was slowly dropped on the working electrode surface and dried for an hour under air to achieve a catalyst loading on the electrode surface area of 0.25 mg cm^{-2} . An Ag/AgCl (3 M KCl) electrode and a Pt rod were used as reference electrode (RE) and counter electrode (CE), respectively. All reported potentials are iR drop corrected. The uncompensated resistance R was determined by electrochemical impedance spectroscopy (EIS) at the open-circuit potential (OCP) from 20 kHz to 200 Hz with alternating current perturbation of 5 mV. All recorded potentials were converted to RHE.

All linear sweep voltammograms (LSVs) were recorded using a scan rate of 1 mV s^{-1} and a rotation rate of 1800 rpm. EIS analysis of the electrocatalysts was carried out at 1.50 V vs RHE, at OER onset, and at η_{10} scanning the frequency range from 10 kHz to 0.01 Hz and applying an amplitude of 5 mV. The electrochemically active surface area (ECSA) was estimated by measuring the double layer capacitance in the non-Faradaic region using cyclic voltammetry without electrode rotation (for details, see the SI).

For structural characterization of used electrodes, anodic polarization of the materials (ink preparation without Nafion) was carried out at 10 $\text{mA cm}_{\text{geo}}^{-2}$ for 1 h in a resting 1.0 M KOH electrolyte, followed by removal of the electrode from solution and rinsing with deionized water. SEM analysis was carried out directly on the electrode surface, whereas for STEM, XRD, and XPS, the catalyst material was removed from the glassy carbon disc.

Studies in alkaline flow electrolyzer. The experiments were carried out in a flow cell equipped with a catalyst-coated Ni foam current collector for the anodic (OER) reaction, an anion exchange membrane, and a Pt-loaded gas diffusion electrode for the cathodic HER process. The OER catalyst was applied to the Ni foam (Good Fellow, 60–100 PPI, 1.5 mm thickness) via spray-coating of a catalyst ink. The ink was prepared by adding 50 mg 100MO (or 60MO/CM) and 16 μL of an ethanolic 5 wt% Sustainion® XA-9 alkaline ionomer solution to 10 mL of a 3:1 (v/v) ethanol–water mixture, followed by ultrasonication at room temperature for 45 min, and resting for at least 16 h before using. The ink was applied to the Ni-foam (25 mm $\times$ 25 mm) by spray-coating at 75 °C until a catalyst loading of 5 mg cm^{-2} geometrical electrode surface area was achieved. As separator, a Fumasep anion exchange membrane (FAA-3-PK-130) was used. Prior to the experiment, the membrane was activated by storage in 1.0 M KOH solution for one hour. Depending on the experiment, two different types of gas diffusion cathodes were used. For studies with 0.2 mg cm^{-2} Pt loading, a Vulcan carbon cloth cathode (W1S1011, FuelCellStore) was used. For experiments with higher Pt loading, a Toray 060 sheet (25 mm $\times$ 25 mm) was spray-coated with an ink consisting of 7.5 mg Vulcan Carbon particles loaded with 50 % Pt (Umicore), 16 μL D-521 Nafion binder solution (Alfa Aesar), and 734 μL of a 1:1 (v/v) ethanol–water mixture until the desired loading was achieved. Electrolysis was carried out under galvanostatic conditions at 50 °C using tempered aq. 1.0 M KOH solutions as anolyte and catholyte, respectively. Anolyte and catholyte solutions were separately purged through the anode and cathode chambers, each with a flow rate of 80 mL min^{-1} .

XAS measurements. XAS K-edge spectra were recorded for Co, Ni, and Fe at BESSY II synchrotron (Helmholtz-Center Berlin, Germany) at Beamline KMC-3. The measurements were performed in transmission mode. The Co, Ni, and Fe K-edge spectra were measured from 7580 to 8290 eV, 8207 to 8922 eV, and 7009 to 8922 eV, respectively. To obtain Fe K-edge spectra, a servo system (PID controller) was needed to subtract counts coming from other elements that absorb at the same energy. Co-powder, Ni-powder, and Fe-foil were used as references, whereby the first real inflection points at 7708.4 eV (Co), 8331.6 eV (Ni), and 7111.4 eV (Fe), respectively, were used for energy calibration. Further reference materials used for Co were CoO (Co^{2+}), Co_3O_4 ($\text{Co}^{2.67+}$), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Co^{2+}). Similarly, NiO (Ni^{2+}), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Ni^{2+}), as well as Fe_3O_4 ($\text{Fe}^{2.67+}$), and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fe^{3+}) were analyzed as references for Ni and Fe K-edges, respectively (Fig. S44).

All powders for *ex situ* measurements were mixed homogeneously in a mortar with boron nitride (BN) as binder with the mass ratio of 1 : 10 (sample: binder). *In situ* measurements were carried out using a spectroelectrochemical flow cell. The OER catalyst was deposited on a carbon paper gas diffusion layer (GDL, 250 μm) at 70 °C with a mass loading of approximately 0.75 mg cm^{-2} by spray-coating with air flow. An Ag/AgCl electrode (saturated KCl, $E^0 = 0.197\text{ V}$) and a Pt-modified Vulcan carbon cloth (W1S1011, Pt loading: 0.2 mg cm^{-2} , FuelCellStore) served as the reference and the counter electrode, respectively. An anion exchange membrane (Sustainion® X37-50 Grade 60) was used as a separator. Measurements were carried out at room temperature using aq. 0.1 M KOH solutions as anolyte and catholyte (pumped separately through the anodic and cathodic half-cell with a flow rate of 20 mL min^{-1}). The back side of the working electrode was covered by a Teflon layer and orthogonally aligned to the X-ray beam.

CRediT authorship contribution statement

Trang Minh Pham: Validation, Writing – review & editing, Data curation, Investigation. **Na Liu:** Investigation. **Stephan Bartling:** Investigation, Writing – review & editing. **Nils Rockstroh:** Writing – review & editing, Investigation. **Reinhard Eckelt:** Investigation. **Wen Ju:** Conceptualization. **Annette-Enrica Surkus:** Supervision, Conceptualization, Writing – original draft, Data curation, Methodology. **Robert Francke:** Supervision, Visualization, Writing – review & editing,

Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2025.116299>.

Data availability

Data will be made available on request.

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7. Curriculum vitae

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Educational Background

2021.10-2025.10g	PhD studies in the field of electrocatalysis
Leibniz Institute for Catalysis , Rostock, Germany	Supervisor: Prof. Robert Francke
2018.09 – 2021.06	M.Sc. studies in Materials Science and Engineering
Shandong University , Jinan, China	Supervisor: Prof. Zhonghua Zhang
2014.09 - 2018.06	B.Sc. studies in Materials Science and Engineering
University of Jinan , Jinan, China	Advisor: Prof. Degang Zhao

Research Experience

- ▲ Design and synthesis of robust Cu molecular complexes for application in electrochemical CO₂ reduction reaction (eCO₂RR) to multi-carbon products.
- ▲ Dealloying fabrication of one-dimensional nanoporous nanowires as efficient electrocatalysts for energy conversion, including electrochemical water splitting (hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)).
- ▲ Design of *in situ* cells for X-ray absorption analysis (XAS) in combination with HERFD (High-Energy-Resolution-Fluorescence-Detected) and EXAFS (Extended X-ray Absorption Fine Structure) techniques.

Qualification summary

- ▲ Conceptualization and operation of electrochemical test stations (including H-type cells, various flow cell configurations/MEA electrolyzers, liquid and gas phase management, and online product analysis).

▲ Extensive experience in operation of *in situ* infrared spectroscopy (IR), scanning electronic microscopy (SEM), and X-ray absorption spectroscopic methods.

▲ Extensive experiences in structure characterization and properties analysis of materials by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS).

List of publications:

(1) **Liu, N. (First Author)**; Pham, T.; Han, Y.; Yang, L., Bokareva, OS.; Bartling, S.; Springer, A.; Spannenberg, A.; Kubis, C.; Weiss, J.; Doronkin, D.; Ju, W.; Francke, R. Copper(II) Phenanthroline Catalysts for Electoreduction of CO₂ to C₂ compounds: Substitution on the Ligand Causes Structural Change of the Molecular Framework and Stability Enhancement. *Adv. Mater.* 2025, e13702. DOI: 10.1002/adma.202513702.

(2) Pham, T.; **Liu, N.**; Bartling S.; Rockstroh, N.; Eckelt, R.; Ju, W.; Surkus, A.; Francke, R., Pre-treated carbon additive enables reduction of metal loading in CoNiFe oxide-based OER electrocatalysts while maintaining performance. *J. Catal.* 2025, 450, 116299. DOI: 10.1016/j.jcat.2025.116299.

(3) **Liu, N. (First Author)**; Ju, W.; Francke, R. Molecular copper catalysts for electro-reductive homocoupling of CO₂ towards C₂ compounds. *Current Opinion in Electrochemistry* **2025**, 49. DOI: 10.1016/j.coelec.2024.101598.

(4) **Liu, N. (First Author)**; Bartling, S.; Springer, A.; Kubis, C.; Bokareva, O. S.; Salaya, E.; Sun, J.; Zhang, Z.; Wohlrab, S.; Abdel-Mageed, A. M.; Liang H-Q.; Francke R. Heterogenized Molecular Electrocatalyst Based on a Hydroxo-Bridged Binuclear Copper(II) Phenanthroline Compound for Selective Reduction of CO(2) to Ethylene. *Advanced Materials* **2024**, 36 (6), e2309526. DOI: 10.1002/adma.202309526.

(5) **Liu, N. (First Author)**; Zhai, Z.; Yu, B.; Yang, W.; Cheng, G.; Zhang, Z. Bifunctional nanoporous ruthenium-nickel alloy nanowire electrocatalysts towards oxygen/hydrogen evolution reaction. *International Journal of Hydrogen Energy* **2022**, 47 (73), 31330-31341. DOI: 10.1016/j.ijhydene.2022.07.067.

(6) **Liu, N. (First Author)**; Yin, K.; Si, C.; Kou, T.; Zhang, Y.; Ma, W.; Zhang, Z. Hierarchically porous nickel–iridium–ruthenium–aluminum alloys with tunable compositions and electrocatalytic activities towards the oxygen/hydrogen evolution reaction in acid electrolyte. *Journal of Materials Chemistry A* **2020**, 8 (13), 6245-6255. DOI: 10.1039/d0ta00445f.

**Doktorandinnen/Doktoranden-Erklärung gemäß § 4 Absatz 1 Buchstaben g und h
der Promotionsordnung der Mathematisch-Naturwissenschaftlichen Fakultät der
Universität Rostock**

Name Liu, Na
.....
(Name, Vorname)

Anschrift Albert-Einstein Str. 29a, 18059, Rostock
.....
(Straße, PLZ, Wohnort)

Ich habe eine Dissertation zum Thema

Developing efficient electrocatalytic system for converting small molecules to valuable products.....

- From catalyst design to device implementation
.....

an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock
angefertigt. Dabei wurde ich von Frau/Herrn

Prof. Dr. Robert Francke
.....
betreut.

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