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Published in:
Electrochimica Acta

Link to article, DOI:
10.1016/j.electacta.2024.144763

Publication date:
2024

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Highlights

- Bimetallic AgCu-BTC MOFs were synthesized via fast co-precipitation employing a deprotonated BTC ligand.
- The presence of Ag in the BTC framework improved CO$_2$ reduction activity and suppressed H$_2$ evolution.
- Adjusting the relative humidity of the CO$_2$ gas stream can improve the selectivity of CO formation over H$_2$ during CO$_2$ reduction.
Investigation of Bimetallic silver-copper BTC MOF for electrochemical CO₂ reduction in Zero-gap Membrane electrode assembly (MEA) configuration

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Abstract

Bimetallic Metal-Organic Frameworks (MOFs) of silver, copper and the ligand benzene 1,3,5-tricarboxylate (AgCu-BTC MOFs), derived from Cu-BTC (HKUST-1), have been synthesized by fast co-precipitation method and investigated for CO₂ reduction reaction (CO₂RR). Three AgCu-BTC MOF variants were synthesized with varying Ag content: AgCu-1 (9.4 at. %), AgCu-2 (12.5 at. %), and AgCu-3 (16.5 at. %). A range of structural characterization techniques, including SEM-EDS, XRD, FTIR, and XPS, were utilized, revealing the formation of low-crystalline AgCu-BTC MOF with Ag⁺ in an ionic state coordinated to the BTC framework. The investigation focused on CO₂ reduction using humidified CO₂ gas with bimetallic AgCu MOFs as electrocatalysts in a zero-gap MEA setup. The setup included a gas diffusion electrode (GDE) with a Sustainion Anion exchange membrane and bicarbonate as the anolyte. Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) showed that the AgCu-3 MOF, with the highest silver content (16.5 at. %), exhibited a lower onset potential at -0.65 V vs Ag/AgCl compared to pristine Cu-BTC MOF owing to the better activity with Ag inclusion. Constant potential (CP) experiments combined with product analysis indicated that AgCu-3 MOF predominantly produced CO and H₂ as the main products, achieving a faradaic efficiency of approximately 60% for CO production and 5% for hydrogen production. Moreover, reducing the humidity level in the inlet CO₂ gas stream from 80%
to 20% RH increased CO production by 2-fold, simultaneously suppressing the HER. This reduction in humidity resulted in an increased local concentration of CO$_2$ at the catalyst site, leading to an enhanced CO$_2$RR rate. SEM and FTIR investigations after the CP experiment demonstrated the instability of the AgCu-3 MOF, revealing substantial morphological changes under humid CO$_2$ conditions.

**Keywords**

Bimetallic MOFs; CO$_2$RR; GDE half-cell; MEA configuration.

1. **Introduction**

The goal of net-zero emissions by 2050 to tackle climate change needs major innovation efforts to provide conceivable technologies for carbon capture and utilization. One ambitious challenge involves the direct conversion of atmospheric carbon dioxide into valuable chemical products using renewable sources [1]. Electrochemical conversion of CO$_2$ stands out as a compelling alternative due to its scalability to industrial levels compared to other techniques such as thermal catalysis [2,3], microbial conversion [4,5], and photocatalysis [6,7].

Effective CO$_2$ electrochemical conversion, however, faces limitations related to the activity and selectivity of the electrocatalyst. Extensive research has been dedicated to understanding the CO$_2$RR mechanisms and developing novel materials to enhance activity and selectivity [8]. Primarily, transition metals [9–11], metallic alloys [12–14], single-atom catalysts [15–17], and molecular catalysts [18–20] have been widely studied. In the past two decades, Metal-Organic Frameworks (MOFs) have been widely explored for applications in gas storage [21,22], gas separation using mixed matrix membranes [23], proton conducting material [24], gas sensing [25,26], and energy storage material [27–29]. MOFs are exciting materials for heterogeneous catalysis due to their high surface area, tailored pore structures, and coordinated metal centers that facilitate catalytic reactions [30,31]. Among the numerous MOFs, aromatic BTC (Benzene...
tricarboxylic acid) MOFs are quite interesting due to the paddle-wheel structure of their metal node, which consists of a metal dimer as the catalyst center. This metal dimer allows the formation of various carbon compounds, including carbon monoxide, methanol, and ethylene [32–35]. Albo et al. reported relatively low yield and faradaic efficiency (FE) values around 5-20% for methanol and ethanol utilizing Cu-based BTC MOF (HKUST-1) as electrocatalyst [36]. A Cu dimer in the paddle-wheel structure facilitates the formation of C-C bonds at the metal site. This unique feature is a significant advantage offered by BTC MOFs, as it enhances the activity and selectivity of C$_2$+ compounds in CO$_2$RR [37].

Interestingly, mechanistic studies have shown that introducing a second metal to form a heterometallic BTC MOF can significantly enhance CO$_2$ adsorption due to the change in electrostatic interaction strength by altering the metal atom. [38]. This has been experimentally shown by Perfecto et al., who introduced Zn(II), Ru(III), and Pd(II) as doping metals in the pristine HKUST-1. Notably, electrocatalysts based on Ru(III) bimetallic MOF achieved FE as high as 47.2% for methanol.

Besides Cu-BTC MOF, Ag-BTC MOF was reported by Shuang et al. and was employed as an efficient catalyst with 95% FE for CO$_2$ reduction to CO in an H-cell setup. The reduced activation energy for CO-forming intermediates on Ag-BTC MOF is responsible for the enhanced activity and selectivity for CO production [32]. Moreover, by combining Ag and Cu metals, AgCu binary alloys have exhibited remarkable catalysis for ethanol production due to their synergistic effect and capacity to engage in tandem reactions [39]. In this work, silver-copper AgCu-BTC MOF was successfully synthesized, and their electrocatalytic CO$_2$ reduction performance was explored.

Electrocatalytic evaluations of MOFs were generally conducted using H-cell or gas-feed flow-type electrolyzers, where the MOF electrodes were immersed in liquid electrolytes for catalytic
reactions [40,41]. The Zero-gap MEA configuration has recently garnered attention for CO$_2$ electrolysis [42]. Unlike traditional H-cell setups, this configuration reduces the inter-distance between the gas diffusion electrode (GDE) and membrane, thus reducing the overall resistance and can be operated with a humidified CO$_2$ gas stream rather than having an electrolyte at the cathode side. Furthermore, it effectively mitigates mass transport limitations, allowing for the attainment of current densities exceeding 100 mA cm$^{-2}$. This setup facilitates the investigation of (1) MOF’s selectivity for specific targeted CO$_2$ reduction products over hydrogen formation, (2) the potential influence of the absence of an aqueous electrolyte in the MEA configuration on the stability of MOF materials, and (3) the impact of variations in humidity levels in the CO$_2$ gas stream on the selectivity of CO$_2$ reduction products. The zero-gap MEA configuration offers a unique opportunity to observe how MOFs perform with gas-phase CO$_2$ reduction in this setup.

In this work, the synthesis, characterization and electrochemical testing of bimetallic AgCu-BTC MOFs with varying concentrations of Ag at.% aimed to clarify the role of silver in the BTC structure and investigated if the bimetallic Ag-Cu MOF could promote the coupling of C-C bonding, enable the selective synthesis of hydrocarbons, and suppress the competing hydrogen evolution. Further, electrochemical studies were conducted to understand the activity and selectivity of the AgCu-BTC MOF catalyst towards CO$_2$RR. The electrochemical studies were performed using a tailor-made gas-diffusion electrode half-cell setup (GDE half-cell) with bimetallic AgCu MOF-based electrode and anion exchange membrane (Sustainion), for product quantification and assess the role of humidity on the competing reactions between HER and CO$_2$RR. Finally, the morphological changes of the AgCu-BTC MOF electrode during CO$_2$RR in the gas phase and under humid conditions have been investigated by SEM-EDS and FTIR. Gaining insights into the performance of MOF-based electrodes tested in an MEA configuration is crucial.
for further developing scalable and efficient electrocatalysts for the direct electrochemical reduction of CO$_2$.

2. Material and Methods

2.1. Chemicals and Materials

All chemicals were of analytical grade and used without any further purification. Deionized water (DI water) (resistivity > 18.2 MΩ m) was used for the preparation of electrolytes. Copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$. 3H$_2$O), benzene-1,3,5-tricarboxylic acid (H$_3$BTC), silver(I) nitrate (AgNO$_3$), potassium bicarbonate (KHCO$_3$) and other common reagents like methanol, diethylamine were purchased from Sigma Aldrich, Germany. Pristine HKUST-1 MOF was obtained from MOF Technologies, United Kingdom, H23C2 carbon paper with microporous layer (MPL) treated with 40% PTFE binder was purchased from Freudenberg, Germany. Anion exchange membrane (AEM) Sustainion X-37-50 RT was purchased from Dioxide Materials, USA. GDE half-cell was purchased from GDE-cell Company, Germany, and used for all electrochemical tests.

2.2. Synthesis of bimetallic AgCu-BTC MOF

The AgCu-BTC MOF was synthesized at room temperature via a fast co-precipitation method in a procedure similar to HKUST-1 synthesis [43]. The atomic ratio of Ag and Cu was adjusted by modulating the precursor molar concentration during synthesis, as detailed in Table S1. Typically, several g of AgNO$_3$ and Cu(NO$_3$)$_2$. 3H$_2$O, depending upon the desired atomic ratio, was mixed in 75 ml of methanol using a magnetic stirrer. H$_3$BTC were added to 75 ml of methanol to prepare the ligand solution and stirred with 10 ml of diethylamine for 10 minutes. Subsequently, the completely dissolved metal solution is mixed with ligand solution to form AgCu-BTC MOF immediately. The precipitate obtained is stirred for 15 minutes and centrifuged at 4500 rpm to
collect the product. The product is repeatedly washed with ethanol to remove unreacted ligands. Finally, the product is collected in a petridish and dried in a vacuum oven at 323 K for 12 h. The resulting samples were named AgCu-1, AgCu-2, and AgCu-3 MOFs.

2.3. Analytical techniques

The morphology of the AgCu-BTC MOF samples was analyzed by Scanning Electron Microscopy (SEM), employing the Zeiss Merlin FEG-SEM operated at 2 kV-15 kV. The same SEM instrument conducted an Energy Dispersive Spectroscopy (EDS) analysis to characterize the element distribution and ratio in the samples. The MOF sample’s powder X-ray diffraction (PXRD) pattern was obtained using the Rigaku Miniflex instrument equipped with a Cu-Kα radiation source. The scanning range spanned from 5 to 60 degrees with a step size of 0.02 degrees. Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Spectrum Two FTiR spectrometer. For the assessment of the electronic states of elements within the synthesized AgCu-BTC MOF material, X-ray photoelectron spectroscopy (XPS) was performed utilizing the ESCALAB 250Xi by Thermo-scientific XPS instrument. Agilent 5977B GC/MSD instrument was employed, featuring Thermal Conductivity Detector (TCD) and Mass Spectrometry (MS) detectors for both analysis and quantification of gaseous products.

2.4. Preparation of Bimetallic MOF electrode for CO₂ reduction
The bimetallic Ag-Cu BTC MOF catalyst ink was prepared by mixing the synthesized MOF material with a 5 wt. % Nafion dispersion as an ionomer and ethanol as a solvent. This mixture was placed in a glass vial and subjected to bath ultrasonication at 350 W for 30 minutes to achieve a homogeneous slurry. Subsequently, the catalyst ink was manually coated onto H23C2 carbon paper with 5 cm x 5 cm size by airbrush spraying. During the airbrush coating process, the carbon paper was mounted onto a hot plate set at 80°C. Finally, a catalyst loading of approximately 1.0 mg cm⁻² on GDE was achieved for all the samples.

2.5. Assembly of GDE half-cell setup

![Diagram of GDE half-cell setup](image)

Fig. 1 Sketch of (a) the GDE half-cell used to study AgCu-BTC MOF and (b) the membrane-electrode assembly (MEA) in contact with the anolyte (0.5M KHCO₃). A sustainion membrane and GDL coated with AgCu-BTC MOFs are sandwiched between the Teflon and stainless steel parts.

This study employed a GDE half-cell to assess the electrochemical activity of the synthesized bimetallic AgCu-BTC MOF. This setup enables the testing of catalysts in zero-gap MEA configuration, replicating realistic mass transport conditions, and facilitates conventional three-electrode experiments [44], [45]. The cell assembly comprises a stainless steel bottom body with
a flow-field design. At the same time, the top part is composed of Teflon, and it features a 3 mm
diameter hole designed to accommodate the electrolyte, reference electrode, and counter electrode,
as illustrated in Fig. 1(a). The gas diffusion layer coated with the catalyst ink was punched into a
disk with a 3 mm diameter and placed on an uncoated carbon paper with a punch-out hole of the
same 3 mm diameter. Subsequently, a 20 mm diameter sustainion membrane was cold-pressed onto
the GDE, forming the MEA. This step ensured proper adhesion between the electrode and
membrane, reduced contact resistance, and prevented bulging due to flooding during operation.
Finally, the upper Teflon part was clamped together with the bottom part, with the membrane-
electrode assembly positioned in between. The anolyte compartment was filled with a 0.5 M
KHCO$_3$ electrolyte, allowing the MEA contact with the electrolyte. A leak-free Ag/AgCl
electrode, which was regularly tested for potential drift against a master reference electrode
(saturated calomel electrode (SCE)), was utilized as the reference electrode for all measurements,
while a Pt wire counter electrode was housed within a glass frit tube to prevent oxygen
contamination of the anolyte. During the measurements, a CO$_2$ stream with varied water content
was continuously purged into the GDE half-cell at a flow rate of 20 mL/min. The outlet of the
GDE-cell was directly connected to the GC/MS system to detect the products formed during the
CO$_2$ reduction process.

2.6. Electrochemical measurements

In all electrochemical measurements, a Gamry Reference 3000 potentiostat was used. To ensure a
proper assembly of the GDE half-cells, impedance measurements at high frequencies were
conducted before each electrochemical measurement, consistently resulting in a resistance below
100 Ohms. The electrochemical behavior of the synthesized bimetallic AgCu-BTC MOF and
HKUST-1 was investigated using cyclic voltammetry at a scan rate of 50 mV s$^{-1}$ under dry and
humid conditions. Additionally, linear sweep voltammograms (LSV) were recorded at a scan rate
of 20 mV s\(^{-1}\) to obtain polarization curves for screening the catalyst with a low onset potential. Constant Potential (CP) experiments were conducted for an hour at different applied potentials in a humid CO\(_2\) environment to observe products from CO\(_2\)RR. For comparison, HKUST-1 was also tested using the GDE half-cell for product analysis under similar conditions. In addition, constant current (CC) experiments were performed at 100 mA cm\(^{-2}\) under different %RH of CO\(_2\) gas stream to understand the influence of water on the distribution of CO\(_2\)R products.

Moreover, electrochemical surface area (ECSA) investigations were carried out to study the degradation of the MOF under electrochemical conditions. Cyclic voltammograms were obtained at several scan rates (200, 150, 100, 50, and 25 mV s\(^{-1}\)) before and after a one-hour constant potential (CP) experiment at -1.7 V vs Ag/AgCl. In addition, by plotting a peak current in the non-faradaic region \(\Delta j/2\) \((\Delta j = j\text{anodic} - j\text{cathodic})\) versus scan rate, the capacitance \(C_{dl}\) is calculated from the slope of the straight line. Freshly prepared anolyte and catalyst-coated electrodes were used for each new experiment unless otherwise specified. Equations for calculating FE and reaction rates can be found in the Supplementary Information (SI).

3. Results and Discussion
3.1. Structural characterization of AgCu-BTC MOF

AgCu-BTC MOF with different ionic radii has been synthesized to harness the synergistic effects of two dissimilar metals. The actual loading of the metal ions in the final AgCu-BTC MOF structures differs from the initially introduced silver precursor concentration and depends on the metal ions' reaction kinetics with the ligand [46]. This difference in the Ag to Cu ratio in the starting materials and the products is shown in Table S1. Typically, when synthesizing MOFs with dissimilar materials like Cu and Ag, which possess different ionic radii (Cu\(^{+2}\) – 0.73 Å and Ag\(^{+1}\) – 1.15 Å) and binding affinities to the BTC ligand, separate crystalline phases are formed. However, introducing a weak base like diethylamine (with a pKa value of 11.02) could deprotonate the organic linker, leading to an increased nucleation rate during synthesis [47]. This facilitates fast nucleation of Cu and Ag metal ions with BTC ligand forming a mixture of Ag-BTC and Cu-BTC networks in the same structure, rather than forming separate MOF phases completely. With increasing Ag precursor concentration, the colors of the sample (as shown in Fig. S1 changed from deep blue (HKUST-1) through turquoise blue (AgCu-1) to teal (AgCu-3).

Fig. 2 shows the morphologies of the AgCu-BTC MOFs in SEM micrographs, revealing irregular particles without any uniformity in the morphology. Here, a significant transformation from
octahedral structure of HKUST-1 (Fig. S2) to irregularly shaped AgCu-BTC MOF particles was due to the use of the deprotonating agent, which, in turn, facilitates the formation of combined Ag and Cu BTC framework. In Fig. S3, the EDS images of AgCu-BTC MOFs reveal a uniform distribution of silver throughout the observed area in all samples. However, as the Ag content rises from AgCu-1 to AgCu-3, EDS reveals the formation of small, nanosized Ag clusters. This ought due to the formation of localized Ag-BTC with less Cu in those areas. As shown in Table S1, the increase in the atomic weight percentage of silver is inversely related to the copper precursor content. Here, the AgCu-3 MOF has the highest Ag content among other MOF samples, around 16.5 at.%, and the rest is Cu in the MOF structure.

Fig. 3 (a) PXRD patterns of AgCu-BTC MOFs and HKUST-1 MOF, along with reference patterns (solid lines) [48]. (b) FTIR spectra of synthesized MOF particles and HKUST-1 MOF. The purple dotted lines show the location of the characteristic peaks observed for HKUST-1 MOF, and the red dotted line for additional peaks for AgCu-BTC MOFs. The PXRD patterns of the AgCu-BTC MOFs exhibited broad peaks, signifying a reduction in crystallinity, as shown in Fig. 3(a). These observed patterns have some similarity to the PXRD
pattern of HKUST-1, especially the distinct peaks observed at 2-θ values 9.6°, 10.7°, and 11.8°. This is consistent with findings from a previous study by Kwang Soo et al., where a bimetallic Ag-Cu BTC MOF, synthesized through a different route, displayed comparable initial peaks. In their study, they observed Ag nanoparticles formed within the MOF structure. This occurrence was attributed to the use of DMF as a stronger reducing agent, which reduces the silver ions to nanoparticles during the synthesis process [49]. However, in this work, the typical XRD peaks for Ag nanoparticles were not observed in the Ag-Cu MOF prepared in this work. This indicates that the fast crystallization method can prevent the formation of Ag nanoparticles. Specific peaks at 2-θ values 7° and 14° for HKUST-1 were not observed in the AgCu-BTC MOF patterns of AgCu-MOF 1 to 3. The absence of these peaks can be attributed to the formation of AgCu-BTC MOF structures characterized by low crystallinity. This phenomenon is a consequence of the fast nucleation process adopted during the synthesis. Moreover, the defects resulting from the low crystalline AgCu-BTC framework may enhance the electrochemical CO₂R activity of the catalyst by providing additional active sites and promoting improved charge transfer dynamics [50].

FTIR analysis was conducted to further analyze the structure of the AgCu-BTC MOF (Fig. 3(b)). The FTIR spectrum reveals that the AgCu-BTC MOFs do not exhibit any broad peak in the 3100-3700 cm⁻¹ range, which is typically associated with adsorbed H₂O [35]. Additionally, characteristic peaks corresponding to the C-H bending, C-O stretch and -C=O (symmetric and asymmetric bands) vibrations of the BTC ligand were observed at approximately 729 cm⁻¹, 1114 cm⁻¹ and 1300-1700 cm⁻¹, respectively, similar to the HKUST-1 structure [37,51]. The peaks from 1000-1250 cm⁻¹ generally correspond to the stretching of C-O bonds [52]. An additional vibration peak at 1050 cm⁻¹ emerged for AgCu-BTC MOFs, attributed to the C-O binding with Ag ions, for AgCu-2 and AgCu-3 MOFs (with higher loading of Ag at.%) [52,53]. Furthermore, the stretching
vibrations of the Ag-O and Cu-O bonds with carboxylate groups were identified at 480 cm\(^{-1}\) [54,55].

Fig. S4 summarizes all the XPS survey scans of all AgCu-BTC MOFs and confirms the presence of C, Ag, O, and Cu at their respective binding energies. High-resolution XPS (HRXPS) scans were conducted to elucidate these observed element’s electronic states and chemical environment.

As depicted in Fig. 4(a), the C 1s spectrum exhibits a peak for the binding energy of 284.8 eV, corresponding to C=C bonds in the BTC ligand, corrected for C calibration [32]. Notably, the O–C=O bond of the BTC ligand exhibits a binding energy of 288.2 eV for AgCu-1, 288.4 eV for
AgCu-2, and 288.3 eV for AgCu-3 MOF, which is lower than the reported value of HKUST-1 MOF (288.8 eV) [60]. This decrease in binding energy can be attributed to the presence of Ag in the BTC framework, causing a change in the bond length from Cu-O (1.98 Å) to Ag-O (2.06 Å) [55]. This change is also reflected in the decrease in binding energies of C=O in the O 1s spectrum (Fig. 4(b)), shifting from 532.1 eV in HKUST-1 to lower values in AgCu-BTC MOFs (531.3 eV for AgCu-1, 531.5 eV for AgCu-2 and 531.4 eV for AgCu-3 MOF) [49]. In the O 1s spectrum, a peak corresponding to Ag/Cu-O is observed at 532.8 eV [49,55,56]. Fig. 4(c) shows the Cu 2p spectrum with two peaks for Cu$^{2+}$ 2p3/2 at 934.2 eV and 2p1/2 at 954 eV, which aligns well with Cu$^{2+}$ in coordination with BTC ligand as reported for HKUST-1 [35]. The electronic state of Cu is predominantly in the +2 state, leading to additional satellite peaks at 939.5 eV, 943.5 eV and 962.6 eV. In Fig. 4(d), characteristic peaks of Ag$^{+1}$ valence states are observed at 368.3 eV (Ag$^{+}$ 3d5/2) and 374.2 eV (Ag$^{+}$ 3d3/2) for all AgCu-BTC MOFs, which were in agreement with PXRD and FTIR that silver is in Ag$^{+1}$ ionic state in the BTC framework rather than being present as a nanoparticles [49].

3.2. Electrochemical CO$_2$ reduction using AgCu-BTC MOF
Figure 5 illustrates cyclic voltammetry (CV) using a GDE half-cell in a MEA configuration, incorporating a Sustainion membrane (anion-exchange membrane) and 0.5 M KHCO$_3$ (anolyte) for additional details, refer to the experimental section. This experiment aims to assess the electrochemical behavior of the AgCu-BTC MOF catalyst under both humid (80% RH) and dry CO$_2$ conditions. The voltammograms of AgCu-BTC MOFs and HKUST-1 MOF in Fig. 5(a) reveal the presence of reduction peaks at -0.35 V and -0.19 V corresponding to the Cu$^{+2}$ to Cu$^{+1}$ and Cu$^{+1}$ to Cu$^0$ state transitions, respectively [57,58]. Under the humid condition, the cathodic peak intensity for Cu$^{+2}$ to Cu$^{+1}$ was still visible, while the other transition to the 0 state was suppressed. This behavior is attributed to the adsorption of water at the catalyst site in the potential range (-0.3 V to -0.5V), allowing the competitive hydrogen evolution reaction (HER) to occur [57].

The reduction peaks corresponding to Ag$^{+1}$ to Ag$^0$ usually happen at -0.19 V, thus overlapping with the Cu$^{+1}$ to Cu$^0$ transition [59]. The oxidation peak currents under dry CO$_2$ condition for all MOFs were seen at 0.22 V, owing to the desorption of CO$_2$ reduction intermediate [60]. However, these oxidation peaks shifted to lower potentials (from 0.22 V to 0.08 V) under humid CO$_2$ for MOFs with low Ag content (HKUST-1 and AgCu-1 MOF). This peak shift could be related to
Cu/Ag oxidation rather than the adsorption of CO$_2$ reduction intermediates on the MOFs. Meanwhile, the oxidation peaks for AgCu-2 and AgCu-3 MOF remain at 0.22 V, thus being attributed to CO$_2$ intermediates on these MOF catalysts.

In addition, in Fig. 5(b), the onset of hydrogen evolution reaction (HER) is observed with the increase of current density in negative potentials (< -0.2 V vs Ag/AgCl) for all MOFs [61]. HKUST-1 MOF exhibits the higher current density amongst all MOFs, showing a preference for hydrogen evolution reaction. However, the current density for HER is progressively reduced from AgCu-1 to AgCu-3 MOF samples, implying that the AgCu-3 MOF favors CO$_2$ reduction and suppresses the HER reaction.

Linear sweep voltammetry (LSV) conducted in the potential range from -0.2 to -1.8 V vs Ag/AgCl under humid CO$_2$ condition for all MOFs were shown in Fig. 6. LSV results show a decrease in onset potential for the reduction reaction with increasing Ag content in the MOF. The AgCu-3 MOF with the highest Ag content has a low onset potential of about -0.6 V vs Ag/AgCl, comparable to the literature value [35]. This is attributed to higher silver content in AgCu-3 MOF.
facilitating an increase in CO$_2$R activity rather than HER. Given the results obtained from CV and LSV, the AgCu-3 MOF catalyst with the highest silver content emerged as the best candidate for further experiments.

3.2.1. Influence of potential on product distribution

![Graph a](image1)

![Graph b](image2)

Fig. 7 (a) Faradaic efficiency (FE%) of CO and H$_2$ at various potentials (vs Ag/AgCl) for AgCu-3 MOF under humid CO$_2$ (80% RH) condition. (b) Product distribution results of AgCu-3 at 100 mA/cm$^2$ in various humidity conditions.

Based on the results from CV and LSV measurements, constant potential (CP) and current (CC) experiments were conducted on the most active AgCu-3 MOF to get information on the carbon reduction products formed during CO$_2$RR. The CP experiments were conducted over an hour, involving product analysis with a gas chromatograph at regular intervals to observe the selectivity of the product with respect to the applied potential under humid CO$_2$ (80% RH) condition. The primary products observed were CO and H$_2$ (syngas), and their FE at different potentials are depicted in Fig. 7(a). The maximum FE (CO + H$_2$) obtained is around 70% at -1.8 V vs RHE potential with AgCu-3 MOF, as seen in Fig.7(a). FE values for hydrogen were reduced to 5% at high negative potentials, and the catalyst was more selective towards CO production. A notable portion of the current density employed in the reaction seems to be consumed by other parasitic
reactions, such as MOF degradation and salt formation, rather than contributing to the desired product formation [62]. Thus, the total FE value in our system never reached 100%. However, in Fig. S5(a), it was observed that in addition to the increase in the rate of CO production with higher applied negative potentials, the hydrogen production rate also increased due to the excess availability of water at the catalyst site during these experiments with 80% RH CO₂ gas stream.

Generally, copper-based MOFs can produce other C₁ and C₂ products, as reported in the literature [35]. Therefore, a comparison was made between the HKUST-1 and AgCu-3 MOFs at -1.7 V vs Ag/AgCl under humid CO₂ condition (Fig. S5(b)). The AgCu-3 MOF yielded approximately 6.9 µmol s⁻¹ cm⁻² more CO than the HKUST-1 MOF, which produced only 4.2 µmol s⁻¹ cm⁻² of CO. Consistent with the CV observations, HKUST-1 generated more H₂ compared to the AgCu-3 MOF. Interestingly, only syngas (CO + H₂) were observed when the catalyst contained copper and silver. Even with HKUST-1, no other gaseous products like ethylene were identified in the zero-gap MEA configuration. This phenomenon could be attributed to the local pH changes (high >9 pH under these conditions) in the zero-gap MEA configuration as observed for other design configurations, which significantly influences intermediates that determine product formation [63,64].

3.2.2. Influence of water on product formation

AgCu-3 MOF catalyst was tested under various humidity levels in a constant current experiment at 100 mA/cm², as shown in Fig. 7(b). The results revealed an increase in CO production rates with decreasing humidity from only 6.2 µmol s⁻¹ cm⁻² at 80% RH to 13 µmol s⁻¹ cm⁻² at 20% RH. Moreover, the decrease in water content in the gas stream also suppresses H₂, thereby increasing the local concentration of CO₂ and leading to an enhanced CO₂RR rate. This approach to reducing the RH of the CO₂ gas stream is beneficial at the system level to improve the CO₂RR selectivity.
Moreover, in both CP and CC experiments, no visible liquid droplets were observed coming from the cell; thus, no liquid products were reported.

### 3.2.3. MOF degradation under electrochemical conditions

Fig. 8 (a) Calculated ECSA values were plotted for AgCu-3 MOF catalyst before and after the CP experiment at -1.7 V vs Ag/AgCl. (b) FTIR of the AgCu-3 MOF catalyst before and after the CP experiment at -1.7 V vs Ag/AgCl for an hour.

To assess the chemical stability of the MOF under electrochemical conditions, ECSA and FTIR analyses were conducted before and after subjecting the MOF electrode to a constant potential of -1.7 V vs Ag/AgCl for an hour under humid CO₂ conditions. The capacitance value of the AgCu-3 MOF catalyst increased from 5.63 µF cm⁻² to 84.5 µF cm⁻² after the constant potential experiment, indicating chemical changes to the catalyst, as shown in Fig. 8(a). SEM and EDS images of the AgCu-3 MOF catalyst before and after the ECSA experiment are presented in Fig. S6, indicating considerable changes in the catalyst’s morphology. Additionally, the FTIR spectrum revealed characteristic peaks of the AgCu-3 MOF before and after the constant potential experiment, as shown in Fig. 8(b). The significant peaks corresponding to the vibrations of the BTC ligand were observed at approximately 729 cm⁻¹, 1114 cm⁻¹ and 1300-1700 cm⁻¹ with lower peak intensity [37,51]. The absence of stretching vibrations of the Ag-O and Cu-O bonds at 480
cm⁻¹ corroborates that the MOF degrades under electrochemical conditions [59]. It is most likely that the increase in local pH at higher negative potentials threatens the structural stability of MOFs. Zheng et al. conducted experimental demonstrations of this phenomenon on Co-ZiF-67 MOF, showing that during electrochemical reactions, OH⁻ ions produced rapidly displace the coordinated linkers away from the metal nodes, forming Co-hydroxides [65]. This is considered the underlying cause of AgCu-3 MOF catalyst’s rapid morphological and structural changes.

4. Conclusion

This study explores the synthesis and electrocatalytic performance of an AgCu-BTC MOF in an MEA configuration using a GDE half-cell. Three AgCu-BTC MOFs with increasing silver content were synthesized and characterized. Despite the MOF’s nanosized, less crystalline structure with ionic silver, AgCu-3 exhibited a lower onset potential at -0.65 V vs Ag/AgCl than other catalysts and HKUST-1 in LSV. CO and H₂ were primary reduction products, achieving a total faradaic efficiency of nearly 70%. AgCu-3 demonstrated higher CO production (65% FE) and suppressed hydrogen evolution compared to HKUST-1.

Additionally, water plays a crucial role in product distribution; when reducing the relative humidity of the CO₂ gas stream to 20%, AgCu-3 MOF doubled the rate of CO production and suppressed hydrogen evolution. A post-electrochemical experiment investigation confirms that the AgCu-3 MOF experienced structural degradation under electrochemical reduction due to their chemical instability and potential increase in local pH. This work provides insights into MOF electrocatalysis, highlighting the significance of water in both product formation and reaction rates, thereby paving the way for future advancements in the field of MOF electrocatalyst for CO₂RR application.

CRediT authorship contribution statement
Ashwin Nambi: Conceptualization, Data collection, Writing – original draft. Athanasios Chatzitakis: Conceptualization, Formal analysis, Laboratory support and Writing – review and editing. Unni Olsbye: Review and MOF synthesis advice. Johan Hejlm: Review and Electrochemistry advice. Yujie Zhao: Formal analysis, Writing – review and editing. Andreas Kaiser: Supervision, Writing – review & editing, funding acquisition.

Declaration of Competing Interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the Innovation Fund Denmark (Grant number 5157-00008A). We also acknowledge the support from Villum Foundation (Villum Experiment project Addlight, grant no. 40975), Nordic Energy Research (CCU-NET project, grant no.100766) and from the EU cost action CA22147 “EU4MOF”.


References


Declaration of interests

☒ 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.

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