The impact of nitrogen oxides on electrochemical carbon dioxide reduction

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The electroreduction of carbon dioxide offers a promising avenue to produce valuable fuels and chemicals using greenhouse gas carbon dioxide as the carbon feedstock. Because industrial carbon dioxide point sources often contain numerous contaminants, such as nitrogen oxides, understanding the potential impact of contaminants on carbon dioxide electrolysis is crucial for practical applications. Herein, we investigate the impact of various nitrogen oxides, including nitric oxide, nitrogen dioxide, and nitrous oxide, on carbon dioxide electroreduction on three model electrocatalysts (i.e., copper, silver, and tin). We demonstrate that the presence of nitrogen oxides (up to 0.83%) in the carbon dioxide feed leads to a considerable Faradaic efficiency loss in carbon dioxide electroreduction, which is caused by the preferential electroreduction of nitrogen oxides over carbon dioxide. The primary products of nitrogen oxides electroreduction include nitrous oxide, nitrogen, hydroxylamine, and ammonia. Despite the loss in Faradaic efficiency, the electrocatalysts exhibit similar carbon dioxide reduction performances once a pure carbon dioxide feed is restored, indicating a negligible long-term impact of nitrogen oxides on the catalytic properties of the model catalysts.

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The electrochemical CO$_2$ reduction (CO$_2$RR) provides a promising, sustainable avenue to generate value-added fuels and chemicals from greenhouse gas CO$_2$. Depending on the choice of electrocatalyst, CO$_2$ can be converted into a variety of single-carbon (C$_1$; e.g., carbon monoxide, formic acid, methanol, and methane) and multi-carbon (C$_2$; e.g., ethylene, ethanol, acetate, and n-propanol) products with tremendous market potentials. While CO$_2$RR is being actively studied, most studies are conducted using highly pure CO$_2$ feed. For commercial applications, the most commonly available CO$_2$ sources are industrial point sources, such as chemical and power plants; however, CO$_2$ gas emitted from these sources often contain a variety of contaminants, such as sulfur oxides (SO$_x$), nitrogen oxides (NO$_x$), O$_2$, and volatile organic compounds (VOC) and potential in CO$_2$ electroreduction (CO$_2$RR). While CO$_2$RR is being actively studied, most studies are conducted using highly pure CO$_2$ feed. For commercial applications, the most commonly available CO$_2$ sources are industrial point sources, such as chemical and power plants; however, CO$_2$ gas emitted from these sources often contain a variety of contaminants, such as sulfur oxides (SO$_x$), nitrogen oxides (NO$_x$), O$_2$, and volatile organic compounds (VOC) and potential in CO$_2$ electroreduction (CO$_2$RR). When CO$_2$RR is being actively studied, most studies are conducted using highly pure CO$_2$ feed. For commercial applications, the most commonly available CO$_2$ sources are industrial point sources, such as chemical and power plants; however, CO$_2$ gas emitted from these sources often contain a variety of contaminants, such as sulfur oxides (SO$_x$), nitrogen oxides (NO$_x$), O$_2$, and volatile organic compounds (VOC) and potential in CO$_2$ electroreduction (CO$_2$RR). CO$_2$RR in a conventional batch cell. Furthermore, less than or equal to 1667 ppm of NO$_2$ has shown to be either beneficial or neutral, and greater than 1667 ppm of NO$_2$ has shown to be detrimental in CO$_2$RR, mainly due to a reduction in pH of the electrolyte, also on Cu catalysts in a conventional batch cell. However, the behavior of various NO$_x$ impurities in CO$_2$RR at industrially relevant high current densities (>100 mA cm$^{-2}$) has not been explored yet. In this work, we investigate the influence of NO$_2$ (i.e., NO, NO$_2$, and N$_2$O) in CO$_2$RR using a three-compartment flow cell. Three model electrocatalysts, including copper (Cu), silver (Ag), and tin (Sn), are selected to represent the most studied catalysts for C$_2$ products, carbon monoxide (CO), and formate, respectively. Most NO$_x$ contaminants in the CO$_2$ feed significantly reduce the CO$_2$RR FE because the electrochemical reduction of NO$_x$ occurs at much more positive potentials than CO$_2$RR (Fig. 1b). NO and NO$_2$ impurities have more severe impacts on CO$_2$RR FE than N$_2$O, likely due to the greater number of electrons required in the NO$_x$ reactions. Despite the loss of CO$_2$RR FE, none of the three catalysts exhibits a significant change of product selectivity after removing the NO$_x$ impurity from the CO$_2$ stream obtained from point sources.

![Fig. 1 CO$_2$ electrolysis technology using industrial CO$_2$ point sources.](https://doi.org/10.1038/s41467-020-19731-8)
CO₂ feed. Moreover, we employ gas chromatography (GC), spectrophotometry, and flow electrochemical mass spectrometry (FEMS) to analyze the products of electroreduction of NO, the dominant component of NOₓ in industrial point sources, in which the major products are ammonia (NH₃), hydroxylamine (NH₂OH), N₂, and N₂O. Investigation of the effect of different concentrations of NO in CO₂RR shows that NOₓ at typical concentrations in flue gases is compatible with CO₂RR.

**Results and Discussion**

Electrodes were prepared by loading commercial Cu, Ag, and Sn particles on a gas diffusion layer (GDL), a microporous carbon paper which provides mechanical support, electrical conductivity, and hydrophobicity. Scanning electron microscopy (SEM) images of the as-prepared electrodes confirm a uniform deposition of metal nanoparticles on GDL, covering the majority of the GDL surface (Supplementary Fig. 1). Electrochemical experiment was performed in a three-compartment flow cell, in which CO₂ gas is directly fed to the electrode-electrolyte interface, enabling CO₂RR at high current densities (Supplementary Fig. 2). NOₓ impurities were mixed with CO₂ gas feed prior to entering the flow cell. As the concentration of NOₓ in typical exhaust streams may be as high as ~3,000 ppm (i.e., 0.3 vol. %)¹³, conservative streams of 83.3% CO₂, 15.87% Ar, and 0.83% NOₓ were used for most studies. To keep the CO₂ partial pressure constant during the introduction of NOₓ, which contains Ar, CO₂ partial pressure was maintained at 0.83 bar throughout the study by using a mixture of 83.3% CO₂ and 16.7% Ar when NOₓ was not introduced.

**Impact of NOₓ impurities on CO₂ electroreduction.** The influence of NO in CO₂RR on Cu, Ag, and Sn catalysts was first evaluated at a constant current density of 100 mA cm⁻² (Fig. 2a–c). The CO₂RR experiment was performed by switching the gas feed from 83.3% CO₂ and 16.7% Ar (0–0.5 h) to 83.3% CO₂ 15.87% Ar, and 0.83% NO (green region; 0.5–1 h) and back to 83.3% CO₂ and 16.7% Ar (1–3 h). With 83.3% CO₂ and 16.7% Ar, before exposure to NO, Cu catalyst produced a wide range of C₁ (i.e., methane, CO, and formate) and C₂₊ (i.e., ethylene, ethanol, acetate, and propanol) products. In the cases of Ag and Sn catalysts, the major products were CO and formate, respectively. The observed CO₂RR selectivity of the Cu, Ag, and Sn catalysts was consistent with the previous reports⁶,⁷. When 0.83% NO was introduced at t = 0.5 h, the total CO₂RR FE decreased noticeably on all three catalysts (Fig. 2a–c). On average, the losses in CO₂RR FE accounted for 33.9, 29.6, and 27.9% on Cu, Ag, and Sn, respectively (Fig. 2d), which is likely due to the preferential reduction of NO over CO₂. Assuming NO is fully converted to NH₃, conversions of NO during CO₂RR are between 48% and 60% (Supplementary Table 5). As shown in Fig. 1b, the standard potentials of NORR are much more positive than those of CO₂RR. For instance, the standard potential of NORR to N₂ is 1.68 V vs. RHE, while the standard potentials of CO₂RR are between ~0.250 and 0.169 V vs. RHE. Cyclic voltammetry (CV) measurements under CO₂ with 0.83% NO also confirmed that NORR is more favorable than CO₂RR on Cu, Ag, and Sn catalysts (Supplementary Fig. 3). On all three catalysts, onset potentials and cathodic currents shifted to more positive potentials when 0.83% NO was introduced to the CO₂ stream. CV measurements under different concentrations of NO in Ar also confirmed more positive onset potentials of NORR than CO₂RR and showed that NORR at 0.83% NO is mass transport limited (Supplementary Fig. 4). After restoring 83.3% CO₂ and 16.7% Ar, the CO₂RR performance and the total CO₂RR FE on all three catalysts quickly recovered and were stable for additional 2 h of electrolysis. No obvious change in selectivity was observed for any of the three catalysts, suggesting that the exposure to NO did not alter the catalyst property in any significant way. There is a slight increase in H₂ FE over time (Fig. 2a–c), but it is likely due to the slow flooding of the electrode (Supplementary Fig. 5)⁴⁴.

To obtain insight on the influence of NOₓ in CO₂RR at typical concentrations of NOₓ in point sources, we evaluated the effect of 0.083% and 0.0083% NO, representing the typical NOₓ concentrations in flue gases and flue gases after NOₓ removal processes⁷², respectively, in CO₂RR (Fig. 2d). Although the losses in FE at 0.83% NO were detrimental, the effect of NO was less severe at 0.083%, with less than 5% losses in FE, and negligible at 0.0083% NO. Therefore, NO at typical concentrations of NOₓ in flue gases is compatible with CO₂RR, although complete removal of NOₓ is desired to maximize CO₂RR FE.

NOₓ is another major contaminant in industrial CO₂ point sources (5–10% of NOₓ), and a substantial amount of N₂O may also be formed as a byproduct during the NOₓ removal process²²,²³, Thus, we further investigated the influence of NO₂ and N₂O on CO₂RR on Cu, Ag, and Sn catalysts following the similar experimental procedure to the NO experiment. When 0.83% NO₂ was introduced at t = 0.5 h (yellow region), the CO₂RR FE decreased on all three catalysts (Fig. 3a). The decrease in the total FE was 30.8, 25.6, and 22.9% on Cu, Ag, and Sn catalysts, respectively. Similarly, when 0.83% N₂O was introduced (blue region), the total CO₂RR FE decreased by 11.4, 10.2, and 1.4% on Cu, Ag, and Sn catalysts, respectively (Fig. 3b). Distinct from Cu and Ag catalysts, Sn catalyst did not show a significant loss of the CO₂RR FE in the presence of N₂O, which is likely due to the poor activity of Sn for N₂ORR. Sn catalysts maintain a high CO₂RR FE over the course of 3 h of electrolysis, suggesting the resistive feature of Sn catalyst to N₂O impurity. As shown in Fig. 1b, standard potentials of NOₓ and N₂O are also more positive than those of CO₂RR, and therefore, we attribute the loss of the CO₂RR FE to the preferential reduction of NOₓ and N₂O over CO₂, which is further supported by the CV study (Supplementary Figs. 8–11). When a pure CO₂ feed was restored, the total CO₂RR FE on all three catalysts quickly recovered, suggesting that the exposure of NO and N₂O does not affect the property of the catalysts.

A comparison of the losses in FE due to the various NOₓ impurities is presented in Fig. 3c. NO and NO₂ show greater losses in FE than N₂O on all three catalysts, likely due to the greater number of electrons required in the reactions. As will be discussed in the following section, the main products of N₂ORR are NH₃ and NH₂OH, which require 5 and 3 electrons, respectively, while the main product of CO₂RR is N₂, which only requires 2 electrons. Given that all NOₓ readily reacts at the catalyst surface, the same amount of NO and NO₂ consume more electrons than N₂O, causing greater losses in CO₂RR FE. Among all the catalysts, the Cu catalyst suffers the largest FE loss on all NOₓ impurities, followed by Ag and Sn catalysts. Indeed, Cu has been demonstrated as one of the most active metals for the electroreduction of NO²⁶ and N₂O²⁵, in which Cu achieved high FE in N₂OORR to N₂ at relatively low overpotentials. The results suggest that Cu is an effective electrocatalyst for NO₂ reduction, which may be further explored in future studies.

Furthermore, pH was measured at the outlet of the electrolyzer at different time points (i.e., before, during, and after NOₓ introduction) to investigate the effect of NOₓ on the electrolyte pH (Supplementary Fig. 12). The measured pH shows that the presence of NO and N₂O has a negligible effect on the pH, while the presence of NO₂ slightly decreases the pH by 0.03. Although NO₂ hydrolyzes to produce nitric acid and nitrous acid²⁷, the effect on pH is very small, possibly due to the small amount of NO₂ in the gas feed, rapid reaction of NO₂ at the catalyst surface.
which prevents NO\textsubscript{2} from penetrating to the bulk electrolyte, and a flowing electrolyte which is constantly replenished.

**Identification of NO\textsubscript{x} reduction products.** The electrochemical reduction products of NO, the major component of NO\textsubscript{x} in industrial point sources, were further investigated. As NH\textsubscript{3}, NH\textsubbox{2}OH, N\textsubscript{2}, and N\textsubscript{2}O have been suggested as the main products in NORR\textsuperscript{26,28,29}, NH\textsubscript{3} and NH\textsubbox{2}OH were detected via spectrophotometry (Supplementary Figs. 13 and 14), and N\textsubscript{2} was detected via GC (Supplementary Fig. 15). We note that the concentration of N\textsubscript{2}O in the gas product stream was below the detection limit of GC, suggesting that N\textsubscript{2}O FE was below 2% FE.

**Fig. 2 CO\textsubscript{2} electroreduction performance in the presence of NO.** Faradaic efficiency and applied potential vs. time on (a) Cu, (b) Ag, and (c) Sn catalysts at a constant current density of 100 mA cm\textsuperscript{−2} in 1 M KHCO\textsubscript{3} for 3 h. Gas feeds were 83.3% CO\textsubscript{2} and 16.7% Ar, and 83.3% CO\textsubscript{2}, 15.87% Ar, and 0.83% NO (green). 0.83% NO was introduced at 0.5 h for 0.5 h. Corresponding Faradaic efficiencies are provided in Supplementary Tables 2–4. (d) Effect of different concentrations of NO in CO\textsubscript{2} electroreduction on Cu, Ag, and Sn catalysts. 0.083% and 0.0083% represent the typical NO\textsubscript{x} concentrations in flue gases and flue gases after NO\textsubscript{x} removal processes, respectively. Corresponding Faradaic efficiencies are provided in Supplementary Table 6. Error bars represent the standard deviation of three independent measurements.

**Fig. 3 CO\textsubscript{2} electroreduction performance in the presence of NO\textsubscript{2} and N\textsubscript{2}O.** CO\textsubscript{2} electroreduction Faradaic efficiency, excluding hydrogen Faradaic efficiency, vs. time with the introduction of (a) 0.83% NO\textsubscript{2} (yellow) and (b) 0.83% N\textsubscript{2}O (blue) on Cu, Ag, and Sn catalysts at a constant current density of 100 mA cm\textsuperscript{−2} in 1 M KHCO\textsubscript{3} for 3 h. Gas feeds were 83.3% CO\textsubscript{2} and 16.7% Ar, and 83.3% CO\textsubscript{2} and 15.87% Ar with 0.83% NO\textsubscript{2} or 0.83% N\textsubscript{2}O. NO\textsubscript{2} and N\textsubscript{2}O were introduced at \( t = 0.5 \) h for 0.5 h. Corresponding Faradaic efficiencies are provided in Supplementary Figs. 6 and 7, and Supplementary Tables 7–12. (c) Loss in Faradaic efficiency during CO\textsubscript{2} electroreduction from the introduction of 0.83% NO, 0.83% NO\textsubscript{2}, and 0.83% N\textsubscript{2}O on Cu, Ag, and Sn catalysts. Corresponding Faradaic efficiencies are provided in Supplementary Table 13. Error bars represent the standard deviation of three independent measurements.
Schematic of Faradaic efficiency of NO electroreduction products produced during electrolysis with 83.3% CO₂, 15.87% Ar, and 0.83% NO on Cu, Ag, and Sn catalysts at a constant current density of 100 mA cm⁻² in 1 M KHCO₃ for 3 h. Corresponding Faradaic efficiencies are provided in Supplementary Table 14. Error bars represent the standard deviation of three independent measurements. (b) Schematic of flow electrochemical mass spectrometry (FEMS) setup. (c) Measured current density vs. time, and deconvoluted MS signal vs. time for m/z = 2, m/z = 17, (d) m/z = 28, m/z = 30, and m/z = 44 from FEMS on Cu catalyst in 1 M KHCO₃ with 0.83% NO in Ar. −0.90 V vs. RHE was applied for approximately 2 min starting at t = 1.5 min. NORR products have been deconvoluted using the mass spectra of individual products shown in Supplementary Fig. 17. Additional information is provided in the Methods section and Supplementary Figs. 18 and 19.

on all three catalysts. As shown in Fig. 4a, NORR product selectivity varied among different catalysts. Cu primarily produced NH₃ and N₂ with no NH₂OH. Ag produced a mixture of NORR products, and Sn primarily produced NH₂OH. These observations are consistent with previous reports, in which Cu has been demonstrated as an effective catalyst for NORR to NH₃, N₂, and N₂O, which was difficult to measure via GC, was clearly observed in FEMS, suggesting that N₂O is one of the NORR products. NH₂OH was not detected in FEMS, because it is nonvolatile. Similarly, FEMS results also suggest the formation of N₂ and N₂O on Ag and Sn catalysts (Supplementary Figs. 20–25). However, the formation of NH₃ was observed only on Ag and not on Sn, likely due to the small amount of NH₃ produced on Sn. Collectively, NH₃, NH₂OH, N₂, and N₂O have been determined as the NORR products. The analysis of the NORR products further confirms that the loss in CO₂RR FE is due to the preferential reduction of NO over CO₂.

In the case of N₂ORR, a substantial amount of N₂ was quantified with a GC (Supplementary Fig. 26). While the losses of CO₂RR FE were 11.4%, 10.2%, and 1.4% on Cu, Ag, and Sn catalysts, respectively, the amounts of N₂ detected were 8.2%, 7.3%, and 0.5% of the total FE, respectively, accounting for the majority of the loss in the CO₂RR FE. Small amount of N₂ detected on Sn catalyst demonstrates the resistive nature of Sn catalyst in N₂ORR.

Characterization of catalyst structures in the presence of NOₓ.

X-ray photoelectron spectroscopy (XPS) measurements were conducted to reveal the influence of NOₓ on the surface electronic
structure and the chemical environment of the catalysts. The samples were obtained at various points of the CO2RR experiment, including before exposure to NOx, after exposure to NOx, and at the end of 3-h electrolysis. As shown in Fig. 5a, the Cu and Sn electrodes before the exposure to NOx did not show any noticeable peak in N 1s XPS measurements. In contrast, Ag showed two distinct peaks at 400.5 eV and 398.5 eV, which can be attributed to polyvinylpyrrolidone (PVP), a surfactant used in the nanoparticle synthesis. The XPS measurements obtained after the NO exposure (t = 1 h) exhibited new N 1s peaks on Cu and Sn electrodes (Fig. 5b). The peaks at 401.4 eV, 400.2 eV, and 398.2 eV can be assigned to graphitic, pyrrolic, and pyridinic N, respectively, suggesting that incorporated N atoms mainly interact with carbon in GDL rather than metal catalysts (metal nitride peaks typically observed near 397 eV). The XPS measurements obtained after 3-h electrolysis show that the N 1s signal was not detected on the Cu and Sn electrodes, whereas the XPS measurements for the Ag electrode clearly shows the N 1s signal, which is due to the presence of PVP on the surface of Ag catalyst (Supplementary Fig. 30). Conversely, when the same experiment was repeated with GDL without any catalyst, N species was still detected, confirming the incorporation of N into GDL (Supplementary Fig. 30). Experiments using NO2 and N2O show similar incorporation of N into GDL (Supplementary Fig. 30).

To probe the influence of NOx impurity on the oxidation state of the Cu catalyst, we conducted X-ray absorption spectroscopy (XAS) measurements using a customized XAS batch cell (Supplementary Fig. 31). Because of the toxicity of the NOx gases, we did not use the NOx gases directly at the synchrotron X-ray beamline but conducted XAS experiments with the electrodes taken out of the electrolyzer at 1 h (after exposure to NOx for 0.5 h) during CO2RR experiments (Fig. 2a-c and Supplementary Figs. 6 and 7). The Cu K-edge X-ray absorption near-edge spectroscopy (XANES) spectra of the Cu catalyst after the NO exposure show a similar spectrum of the Cu2O standard, suggesting an average Cu oxidation state of +1 (Fig. 5c). Extended X-ray absorption fine structure (EXAFS) result shows that the NO-exposed Cu sample contains a mixture of Cu and Cu2O (Fig. 5d). Slight oxidation of Cu is likely due to the exposure of the sample in the air during sample handling. After a constant current density of 5 mA cm2 was applied under CO2RR condition, the Cu catalyst was quickly reduced to metallic Cu, suggesting that a small amount of current is sufficient to fully reduce the Cu catalyst under CO2RR conditions. Cu foil, Cu2O, and CuO were used as references.

Fig. 5 Evaluation of the influence of NO on the catalyst structure. XPS measurements of Cu, Ag, and Sn electrodes (a) before (t = 0 h) and (b) after exposure to 0.83% NO (t = 1 h) during CO2 electrolysis. Corresponding XPS data is provided in Supplementary Fig. 27 and Supplementary Table 15. Cu K-edge (c) XANES and (d) EXAFS spectra of spent Cu catalyst after exposure to 0.83% NO during CO2 electrolysis. Cu foil, Cu2O, and CuO were used as references.
Moreover, ex-situ SEM images were obtained at various points of the experiment to evaluate the impact of NOx on the catalyst morphology. SEM images of the spent catalysts after the exposure to NOx impurities (t = 1 h and 3 h) exhibit minimal changes in Cu and Ag catalysts (Supplementary Figs. 1, 34, and 35). Although an increase in particle size was observed in the case of Sn catalysts (Supplementary Figs. 1 and 36), the Sn sample obtained after 1 h of CO2 electrolysis in the absence of NOx also showed a similar increase in particle size (Supplementary Fig. 37). The Sn particles likely aggregated to lower the surface energy under CO2RR condition regardless of NOx, and therefore, NOx impurities are not the primary cause of the size change of the Sn particles during CO2RR. These results suggest that the presence of NOx during CO2RR has a negligible impact on the catalyst morphology.

Conclusions
In summary, we investigated the influence of various NOx (i.e., NO, NO2, and N2O) in CO2RR on Cu, Ag, and Sn catalysts in a flow cell. The presence of NOx impurities reduced the CO2RR FE due to the preferential reduction of NOx over CO2. The impact of NO and NO2 is more severe than that of N2O in CO2RR due to the greater number of molecules involved in NORR and NO2RR compared to N2ORR. The major NORR products are NH3, NH2OH, N2, and N2O in which the selectivity varies among different catalysts, whereas N2O is primarily reduced to N2. Despite the loss of CO2RR FE, a small amount of NOx in the CO2 feed does not alter the metallic nature of the catalyst under CO2RR conditions as demonstrated by the XPS and XAS measurements. Furthermore, although high concentrations of NOx may be detrimental to CO2RR, NOx at typical concentrations of flue gases is compatible with CO2RR, causing small losses in CO2RR FE. NOx removal process, which is a relatively mature technology, may also be employed to ensure CO2RR operation at maximum efficiency. This work not only demonstrates the effect of a trace amount of NOx impurities that are often present in the industrial CO2 point sources on the most commonly studied metal catalysts, but also offers new insights on the electrochemical reduction of NOx, which has rarely been explored in the literature.

Methods

Electrode preparation. Commercial Cu (25 nm, Sigma-Aldrich), Ag (<100 nm, 99.5%, Sigma-Aldrich), and Sn (0.1 μm, Alfa Aesar) particles were used as cathode catalysts (Supplementary Fig. 2). The electrode area was 1 cm² and the distance between the electrode and the membrane was 0.15 cm. A FAA-3-hydroxide exchange membrane (Fumatech) was used to separate electrolyte in the anode and the cathode chamber. 1 M KOH was prepared by dissolving 3 mg of the catalyst and 20 μL of NaF (5 weight % in 50/50 water and isopropanol) in 3 mL of isopropanol. The catalyst ink was sonicated for at least 30 min, and 0.25 mg cm⁻² of the catalyst was drop casted onto a Sigracet 29 BC GDL (Fuel Cell Store).

Flow cell electrolysis. The electrochemical measurements were conducted in a three-compartment flow cell with channel dimensions of 2 cm by 0.5 cm by 0.15 cm (Supplementary Fig. 2). The electrode area was 1 cm² and the distance between the electrode and the membrane was 0.15 cm. A FAA-3-hydroxide exchange membrane (Fumatech) was used to separate electrolyte in the anode and the cathode chamber. 1 M KOH was prepared by dissolving 3 mg of the catalyst and 20 μL of NaF (5 weight % in 50/50 water and isopropanol) in 3 mL of isopropanol. The catalyst ink was sonicated for at least 30 min, and 0.25 mg cm⁻² of the catalyst was drop casted onto a Sigracet 29 BC GDL (Fuel Cell Store).

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Flow electrochemical mass spectrometry (FEMS). An identical flow cell with an entrance for the MS probe at the top of the gas channel was used for the FEMS measurement (Supplementary Fig. 16). The probe consisted of a PEEK capillary with an inner diameter of 0.25 mm and an outer diameter of 0.5 mm. The MS probe was connected to the outlet of the flow cell. A 100% CO2 with 3.2 mL min⁻¹ of 5% NO/Ar (Matheson) was used as a gas source. The gas sample was loaded to 0.5 mL Haysep D column connected to a thermal conductivity detector (TCD) and a flame ionization detector (FID). Ar was used as a carrier gas with a flow rate of 19 mL min⁻¹ and 1 mL of sample was automatically loaded to the column. The gas sample was loaded to 0.5 mL Haysep D pre-column connected to 2 m MolSieve 5 A column at 0.05 min. At 0.490 min, any molecule remaining in the Haysep D precolumn was backflushed out to vent. At 2.150 min, the gas sample was automatically loaded to 2 m Haysep D column. The column temperature was maintained at 35°C for 2.950 min, increased to 210°C at 40°C min⁻¹, and maintained at 210°C until the end of the analysis. A typical GC analyses of potential CO2RR products, N2, NO, and N2O are provided in Supplementary Fig. 38. 2% H2, 98% Ar (Keengas, 99.999%), 1% CH4, 0.25% C2H6, 0.25% C3H6, 0.25% C3H8 (Sigma-Aldrich) was used as an internal standard for CH4, CH3OH, CH3COOH, and CH3CN deconvolution. Next, the contributions from CO2 to m/z 17 signal was subtracted from the observed m/z 17 signal to obtain the chromatogram of potential CO2RR products.

Product quantification. The gas products were analyzed via a multiple gas analyzer no. 5 gas chromatography system (SRI Instruments) equipped with a MolSieve 5 A column connected to a thermal conductivity detector (TCD) and a flame ionization detector (FID). Ar was used as a carrier gas with a flow rate of 19 mL min⁻¹ and 1 mL of sample was automatically loaded to the column. The gas sample was loaded to 0.5 m Haysep D pre-column connected to 2 m MolSieve 5 A column at 0.05 min. At 0.490 min, any molecule remaining in the Haysep D precolumn was backflushed out to vent. At 2.150 min, the gas sample was automatically loaded to 2 m Haysep D column. The column temperature was maintained at 35°C for 2.950 min, increased to 210°C at 40°C min⁻¹, and maintained at 210°C until the end of the analysis. A typical GC analyses of potential CO2RR products, N2, NO, and N2O are provided in Supplementary Fig. 38. 2% H2, 98% Ar (Keengas, 99.999%), 1% CH4, 0.25% C2H6, 0.25% C3H6, 0.25% C3H8 (Sigma-Aldrich) was used as an internal standard for CH4, CH3OH, CH3COOH, and CH3CN deconvolution. Next, the contributions from CO2 to m/z 17 signal was subtracted from the observed m/z 17 signal to obtain the chromatogram of potential CO2RR products.
Dinh, C. T. et al. CO$_2$ electroreduction to ethylene via hydroxide-mediated reference electrode, respectively. 1 M KHCO$_3$ was used as an electrolyte and CO$_2$ measurements (Supplementary Fig. 31). The electrodes were exposed to air for ~20 min. 304 stainless steel, with a Kapton was used as a separator. The electrodes were quickly transported to the XPS equipment (K-alpha Alpha X-ray photoelectron spectrometer system, Thermo Fisher Scientific) after drying in the vacuum oven for 5 min. The electrodes were exposed to air for less than 20 min. High-resolution XPS measurements were obtained at pass energy of 20 eV with a step size of 0.1 eV. Flood gun was turned on. Cu 2p, Ag 3d, and Sn 3d were scanned 10 times while N 1s was scanned 30 times. Four different spots were scanned and averaged. All peaks were fitted using Thermo Advantage software with adventitious carbon referenced to the C 1s peak at 284.8 eV. XAS measurement was performed at the BID-Beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory (BNL). The electrodes were taken out of the electrolyzer at 1 h (after exposure to NOx for 0.5 h) during a 100 mA cm$^{-2}$ constant current CO$_2$RR experiment with the introduction of NO$_x$ (Fig. 2a–c and Supplementary Figs. 6 and 7). In the case of NO$_x$, the samples were exposed to 0.23% NO$_2$ instead due to the availability of the gas at the time of the experiment. The electrodes were quickly transported to the Brookhaven National Laboratory (New York, USA) and were loaded into a XAS batch cell, which was fabricated from Telfon and 304 stainless steel, with a Kapton film window for high transmissivity for X-ray measurements (Supplementary Fig. S1). The electrodes were exposed to air for ~20 min while the measurements were performed. Cu 2p and Ag/AgCl were used as a counter and a reference electrode, respectively. 1 M KHC$_2$O$_4$ was used as an electrolyte and CO$_2$ was flowed at 10 mL min$^{-1}$. XAS data were analyzed using the IFEFFIT package, which included ATHENA and ARTEMIS$^{45}$. 

Data availability
All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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Author contributions
F.J. supervised the whole project. B.K. and F.J. designed the experiments and collectively wrote the paper. B.K. conducted the electrochemical and XPS measurements. B.K. and W.C. prepared electrodes. B.K. and B.H. performed the FEMS study. H.S. conducted the SEM measurements. H.S., E.J., and S.O. performed the XAS experiments. All authors commented on the manuscript.

Competing interests
The authors declare no competing interests.

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