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SO₂-induced Selectivity Change in CO₂ Electroreduction

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Abstract

Electrochemical conversion of carbon dioxide (CO₂) to value-added chemicals has attracted much attention in recent years as a potential alternative to fossil resources. Although significant works have studied the influence of impurities in the electrolyte (e.g. metal ions), few studies have been performed to understand the influence of gaseous impurities in CO₂ electroreduction. Herein, we study the effects of sulfur dioxide (SO₂) on Ag-, Sn-, and Cucatalyzed CO₂ electrolysis in a flow-cell electrolyzer in near-neutral electrolyte, representing a broad range of CO_2 reduction catalysts. We show that the presence of SO_2 impurity reduces the efficiency of converting CO₂ due to the preferential reduction of SO₂. In the case of Ag and Sn, the effect of SO_2 impurity was reversible and the catalytic activities of both catalysts were recovered. On the contrary, a shift in selectivity toward formate accompanied with a suppression of multi-carbon (C₂₊) products was observed on Cu catalyst, demonstrating that Cu is highly sensitive to SO₂ impurity. Our results suggest that CO₂ obtained from direct air capture technologies or biorefineries could be more suitable for Cu-catalyzed CO₂ electrolysis as these CO₂ sources would be relatively cleaner (SO₂-free) than fossil-derived sources such as power plants and can be directly coupled with distributed renewable energy sources such as wind and solar.

1. Introduction

 The electrochemical production of value-added chemicals using carbon dioxide (CO₂) as the carbon source has attracted much attention in recent years and has been motivated by ever increasing CO₂ emission and anticipated cheap electricity prices derived from renewable energy sources.¹ These efforts include fundamental investigation combining experimental and computational studies to establish design principles for the rational design of catalysts,² novel synthesis approaches for constructing high surface area materials with specified active sites,^{3,4} and reactor engineering to design practical devices.⁵⁻⁸ In the latter case, the recent development of flow-cell electrolyzers,⁸⁻¹⁰ in which catalysts are positioned on a well-engineered electrodeelectrolyte interface allowing gaseous reactant to be fed from one side while electrolyte is fed on the other, has enabled the electrochemical conversion of CO₂ at practical rates of reaction that cannot be achieved with typical batch reactors, further pushing this technology toward commercialization.

Critical to the development of CO_2 electrolysis technologies is also the key understanding of potential sources of impurities in the incoming feed (e.g. electrolyte and CO_2), as well as the identification of potential mechanisms for performance degradation. It has been well studied that trace impurities in the electrolyte such as metal ions (e.g. Fe^{2+} and Zn^{2+})¹¹ can dramatically degrade CO_2 reduction performance where the catalytic surface can be irreversibly altered through the deposition of these metal ions under reducing potentials, shifting selectivities toward undesirable products.¹² Strategies such as pre-electrolysis using sacrificial electrodes,¹² pretreatment of the electrolyte with metal-chelexing resin,¹³ and designing catalysts where the catalytic surface can reconstruct under operating conditions¹⁴ have been proposed to overcome these challenges. Overall, the electrolyte most likely needs to be relatively pure and free of residual metal ions for commercial electrochemical conversion of CO_2 . On the contrary, the effect of gaseous impurities in the CO_2 feed has barely been studied¹⁵, and further work is necessary to elucidate the impact of such impurities on the performance in CO_2 electrolysis.

The CO₂ feedstock for commercial CO₂ electrolysis can be obtained from direct air capture^{16,17} or point sources such as power plants or chemical facilities.^{18,19} The former is currently an area of intensive research due to the advantage of not being geographically limited; however, such technology has not yet been fully commercialized and still under pilot plant development. The latter accounts for a large fraction of anthropogenic CO₂ emissions with the current state-of-the-art CO₂ capture technology being amine-based absorption technologies. However, the exhaust streams from point sources such as power plants contain impurities such as SO_x, NO_x, or volatile organic compounds.²⁰ Although current carbon capture processes can purify these exhaust streams using energy intensive processes involving series of scrubbing and separating units, it is critical to understand how these impurities affect CO₂ electrolysis to establish engineering criteria. To the best of our knowledge, majority of CO₂ research to date uses highly pure CO₂ gas as reactant and little is known on the effect of gaseous impurities.

Herein, we study the influence of sulfur dioxide (SO_2) in the electrochemical conversion of CO_2 in a flow-cell electrolyzer. Three different catalysts, silver (Ag), tin (Sn), and copper (Cu) as selective catalysts for producing carbon monoxide (CO), formate, and multi-carbon (C_{2+}) products, respectively, are investigated as these materials are the most commonly studied in CO_2

electrolysis (Figure 1).¹¹ The catalysts are examined for CO₂ reduction free of SO₂ impurity, during the presence of SO₂, and finally after SO₂ exposure to determine if the gaseous impurity has an irreversible effect on the catalytic performance. The CO₂ reduction products are tracked over the course of electrolysis and ex-situ surface characterization is conducted at various time points during operation to elucidate the underpinning of catalytic change. The results show that the presence of SO₂ impurity in the incoming CO₂ feed reduces the efficiency of converting CO₂ due to the preferential reduction of SO₂, as it is thermodynamically more favorable to reduce SO₂ than CO₂. In the case of Ag and Sn catalysts, SO₂ impurity does not change the CO₂ reduction product selectivities and full recovery of the catalytic activities can be observed after the catalysts were subjected to SO₂. However, in the case of the Cu catalyst, SO₂ impurity has an irreversible, detrimental effect as the overall selectivity is shifted toward formate while suppressing the formation of C₂₊ products. Characterization and computational efforts indicate that the formation of copper(I) sulfide (Cu₂S) is likely responsible for the change in selectivity for Cu-catalyzed CO₂ electrolysis.



Figure 1. Schematic of CO₂ electrolyzer and potential feed sources.

2. Results and Discussion

Initial Characterization and Experimental Procedures

Commercial Ag, Sn, and Cu nanoparticles, representing a broad range of CO₂ reduction catalysts, were loaded on a gas-diffusion layer (GDL) with a catalyst loading of 0.3 mg cm⁻² using a drop-casting method as previously described.²¹ Scanning electron microscopy (SEM) images (Figure S1) show the well-dispersed nature of the nanoparticles on the GDL and the porosity of the catalyst layer, which is critical for maintaining the electrode-electrolyte interface by allowing facile transport of gaseous reactants and products to and away from the catalytic surface. Powder X-ray diffraction (PXRD) (Figure S2) of the as-purchased nanoparticles reveals the phase purity of the nanoparticles. In the case of Sn and Cu nanoparticles, the presence of oxidized Sn and Cu in the form of SnO and Cu₂O, respectively, is apparent. The surface composition of the as-prepared electrodes was analyzed using ex-situ X-ray photoelectron spectroscopy (XPS) (Figure S3). In the case of Sn and Cu, the surfaces are partially-oxidized, most likely from air exposure during sample handling. The as-deposited nanoparticles were analyzed for the influence of SO₂ on CO₂ electroreduction in a three compartment flow-cell electrolyzer (Figure S4) with two compartments for the anolyte and catholyte and one compartment for the gaseous reactants and products. Although previous studies have shown that conducting CO_2 electrolysis in alkaline electrolytes (e.g. KOH) has improvement in CO₂ reduction performances,^{8,21,22} CO₂ strongly reacts with hydroxide (OH⁻) to form a bicarbonate/carbonate (KHCO₃⁻/CO₃²⁻) mixture, which degrades the electrolyte and reduces the efficiency of CO₂ utilization.^{9,23} Therefore, CO₂ electrolysis experiments were conducted in near-neutral conditions in 1.0 M potassium bicarbonate (KHCO₃) solution. A syringe pump was used to accurately control the feed rate of SO₂ gas into the CO₂ feed before entering the flow-cell electrolyzer, and electrolysis was conducted in the constant current mode. In short, pure CO_2 was initially fed for 30 minutes, then SO_2 was introduced into the CO_2 feed for a duration of 30 minutes, and then the SO₂ feed was stopped for the remainder of the electrolysis. The gaseous products were quantified by an in-line gas-chromatography (GC) during operation while liquid products were collected and analyzed using nuclear magnetic resonance (NMR). Depending on the source, the concentration of SO₂ in flue gas is ~ 100 ppm ($\sim 0.01\%$); however, SO₂ concentration can be as high as ~10000 ppm (~1%) in concentrated CO₂ streams that have not been desulfurized.²⁰ As a conservative limit, a stream of 1% SO₂ was chosen for initial studies.

Influence of SO₂ on Ag and Sn-catalyzed CO₂ electroreduction

The influence of SO₂ on CO₂ (CO₂ + SO₂) electroreduction was first studied on Ag and Sn catalysts, as these materials are widely studied and commercial devices are currently being developed for the selective electrochemical conversion of CO₂ to CO and formic acid.^{24,25} As shown in Figure 2, when pure CO₂ was initially fed, indeed high selectivities (>85%) toward CO and formate, respectively, were achieved on Ag and Sn catalysts in near-neutral electrolyte. The fluctuation in voltage is due to the accumulation of gas products as bubbles and eventual flush out of the catholyte chamber. However, when both catalysts were subjected to a stream of 1% SO₂ (Figure 2, red region), the total Faradaic efficiencies toward CO₂ reduction products decreased, and the remaining charge balance is likely attributed to the reduction of SO₂ since it is thermodynamically more favorable to reduce SO₂ than CO₂ (e.g. SO₂ + 4H⁺ + 4e⁻ \rightarrow S + 2H₂O E^o = 0.50 V, CO₂ + 2H⁺ + 2e⁻ \rightarrow CO + H₂O E^o = -0.11 V, CO₂ + 2H⁺ + 2e⁻ \rightarrow HCOOH E^o = -0.25 V). There is also a large overpotential to drive SO₂ reduction under CO₂ electrolysis conditions. Previous ultra-high vacuum studies have also indicated the facile adsorption of SO₂ near room

temperature.^{26,27} To further elucidate the adsorption of SO₂ compared to CO₂, Gibbs free energy of adsorption as well as binding energies were calculated (Table S3), and calculations indeed show that SO_2 adsorption is stronger on all surfaces (Ag, Sn, and Cu) compared to that of CO_2 . This further suggests the preferential reduction of SO₂ over CO₂. XPS measurements confirmed the reduction of SO₂ toward the formation of metal sulfide species (Figures S5&6, Table S4), and XPS measurements at each time point were obtained from separate electrolysis experiments with new electrodes operating at different electrolysis durations. Based on the peak positions at 161.7 and 161.6 eV, the metal sulfides were identified as Ag₂S and SnS₂ with surface concentrations of ~35.6 at.% and ~3.3 at.% on Ag and Sn catalysts, respectively.²⁸⁻³⁰ Sulfite (SO₃²⁻) and sulfate (SO₄²⁻) were also detected. The former is likely formed during sample handling from residual surface metal oxides reacting with SO_2 in the presence of water when no potential is applied, and the latter is likely formed from the natural oxidation of metal sulfides.³¹ The observed shifts in Ag peak position to lower binding energies are likely due to the presence of S species, since Ag has a lower electronegativity than S (S: 2.59, and Ag: 1.87).^{32,33} On the contrary, the shifts in Sn peak position are due to different concentration of tin oxides (SnO/SnO₂) in each sample as Sn rapidly oxidizes in air during sample handling. Due to the resolution of the spectrometer, accurately differentiating these two oxides is difficult. The formation of surface metal sulfides (Ag₂S and SnS₂) was also confirmed with high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and electron energy loss spectrum (EELS) imaging (Figures S7&8), which shows S species positioned near the edges of the particles. Bright field (BF)-transmission electron microscopy (TEM) imaging and the corresponding selected area electron diffraction (SAED) indeed show the formation of SnS_2 (Figure S8f). In the case of Ag (Figure S7f), diffraction patterns associated with Ag_2S was not observed, indicating that structure of Ag_2S is likely amorphous. This observation was further confirmed with high resolution (HR)-TEM (Figure S9), showing an amorphous layer on the surface of the Ag catalyst. For all TEM work, FAA ionomer binder was used instead of Nafion, as Nafion has sulfonic functional groups that would convolute the detection of S species associated to the metal sulfides. SEM images (Figures S10&11), after 1 hour of electrolysis with both catalysts subjected to a feed of 1% SO₂ for 30 minutes, show the formation of bulky particles with smooth surfaces, a common characteristic of metal sulfides. Future work using density functional theory (DFT) can provide additional insight on the mechanism of metal sulfide formation during CO₂ electrolysis. It must be noted, that the exact surface characteristic under reaction condition remains unclear due to the lack of in-situ surface sensitive methods and the limitation of ex-situ measurements. Gas chromatography-mass spectrometry (GC-MS) was also employed to detect other possible sulfur-containing species; however, the only sulfurcontaining species detected was unreacted SO_2 . It is likely that other residual species were produced below the detection limit and cannot be easily detected by GC-MS or NMR.



Figure 2. Performance of $CO_2 + SO_2$ electrolysis over (a) Ag and (b) Sn catalysts at constant current density of 100 mA cm⁻² in 1M KHCO₃ over the span of 3 hours. Corresponding Faradaic efficiencies can be found in Supporting Information (Tables S1&2).

Interestingly, when the feed of SO_2 was stopped, the CO_2 reduction performances recovered on both catalysts, and in the case of Sn, a slight improvement in formate Faradaic efficiency was observed. A recent study has suggested that doping Sn surfaces with sulfur (S) atoms, and then selectively removing S atoms can create highly active undercoordinated Sn sites for improved CO₂ reduction to formate.³⁰ Thermodynamically, Ag₂S and SnS₂ are not stable under CO₂ electrolysis conditions, and this was confirmed with post-reaction XPS that shows a decrease in metal sulfides (Table S4). Particle aggregation can be seen in post-reaction SEM images, which is likely due to surface rearrangement from the reduction of metal sulfides (Figures S10&S11). The $SO_2 + CO_2$ experiments suggest that the presence of small amounts of metal sulfides (Ag₂S and SnS₂) on Ag and Sn catalysts do not shift the CO₂ reduction product selectivities, as the dominant CO₂ reduction products remained as CO and formate, respectively. However, the reduction of the total CO_2 Faradaic efficiency indicates that SO_2 impurity can reduce the efficiency of converting CO₂, since the reduction of SO₂ is more favorable than CO₂. Sn catalyst was also examined under longer SO_2 exposure (Figure S12), and a plateauing of total Faradaic efficiency was observed (\sim 50%), suggesting a steady-state competitive reaction between SO₂ and CO₂ reduction. To further understand the effect of SO₂ near flue gas concentrations, both Ag and Sn catalysts were subjected to 0.01% SO₂ (Figure S13), and the results show that SO₂ at lower concentration does not significantly affect CO_2 electroreduction performances for both catalysts.

Influence of SO₂ on Cu-catalyzed CO₂ electroreduction

Next, $CO_2 + SO_2$ electroreduction experiments were performed on Cu catalyst to study the influence of SO₂ on Cu-catalyzed CO₂ reduction, as Cu is the only monometallic material that can reduce CO₂ to high-value C₂₊ products with appreciable selectivities. As shown in Figure 3a, indeed Cu can convert CO₂ to an array of products including CO, formate, ethylene (C₂H₄), ethanol (EtOH), n-propanol (PrOH), and a small amount of acetate and methane (CH₄). Long-term CO₂ electrolysis over Cu catalyst demonstrates a stable performance of converting CO₂ to C₂₊ products (Figure S14). When the Cu catalyst was subjected to 1% SO₂ (Figure 3a, red region), as similar to

both Ag and Sn catalysts, the total CO2 reduction Faradaic efficiency decreased, likely due to preferential reduction of SO₂. Interestingly, the CO₂ reduction product selectivity shifted, and formate became the dominant CO_2 reduction product, while the other CO_2 reduction products were suppressed. XPS analysis (Figures 3b&c) shows the formation of metal sulfide (Table S4) after one hour of electrolysis and the peak position at ~162.0 eV was assigned to Cu₂S with a surface concentration of ~12 at.%.³⁴ This peak assignment was also verified with commercial Cu₂S and copper(II) sulfide (CuS) particles (Figure S15). Again, sulfite and sulfate were also detected likely due to sample handling. Unreacted SO₂ was the only sulfur-containing compound that was detected with GC-MS; however, there is likely residual compounds produced under the detection limit. The formation of aggregated bulky-like particles after 1 hour of electrolysis, subjected to a feed of 1% SO₂ for 30 minutes, can be seen (Figure S16), and this observation was further confirmed with BF-TEM imaging (Figure 3d). The corresponding SAED pattern shows the presence of residual Cu₂S, metallic Cu, and CuO that was likely formed from air exposure during sample handling. Similar to the Ag and Sn catalysts, HAADF-STEM and the corresponding EELS imaging (Figure 3e-j) reveal highly disperse S species positioned near the edges of the particles, suggesting that formation of Cu₂S likely resides near the surface. This observation was also confirmed with HR-TEM imaging and the corresponding fast Fourier transform (FTT) pattern (Figure S17), also showing the formation of Cu₂S near the particle surface. Additional HAADF-STEM and EELS mapping can be found in the Supporting Information (Figure S18). Again, FAA ionomer binder was used instead of Nafion for TEM work. On the as-prepared Cu catalyst, there were no S species detected (Figure S19). The utilization of FAA ionomer showed a similar trend in $CO_2 + SO_2$ electroreduction as Nafion, and thus, the ionomer is likely not the cause of the observed shift in selectivity (Figure S20). Again, the exact surface characteristic under reaction condition remains unclear due to the lack of in-situ surface sensitive methods to examine Cu particles under CO₂ electrolysis conditions while operating at high current densities. However, Chorkendorff, Jaramillo, and co-workers very recently demonstrated that the surface structure of polycrystalline Cu thin film is fully converted to the metallic phase under CO electroreduction conditions by using in-situ grazing incident X-ray diffraction with a synchrotron radiation source.³⁵ Future work employing similar techniques could further elucidate the surface structure of Cu in the presence of SO₂ under CO₂ electrolysis conditions, and this will gain additional insight on the formation of surface Cu₂S.



Figure 3. (a) Performance of Cu catalyst at constant current density of 100 mA cm⁻² in 1M KHCO₃ with a 1% SO₂ feed over the span of 5 hours. Corresponding Faradaic efficiencies can be found in Supporting Information (Table S5). XPS spectrum of (b) Cu and (c) S region at various time points. (d) BF-TEM image. Inset: SAED pattern, (e-f) HAADF-STEM images, and (g-j) EELS mapping of Cu catalyst after 1 hour of electrolysis in $CO_2 + SO_2$ experiment, subjected to a 1% SO₂ feed for 30 minutes.

Interestingly, when the SO₂ feed was stopped, formate remained as the dominant CO₂ reduction product, and an incremental recovery was observed as the selectivity toward CO production slowly increased, followed by C_2H_4 production. Mechanistically, this observation is consistent with literature as it is well known that the pathway toward C_{2+} products goes through a CO intermediate on Cu-catalyzed CO₂ electroreduction, while the pathway toward formate is a dead-end.³⁶ Therefore, the observed trend in recovery is CO followed by C_{2+} products. In addition, an enhancement in hydrogen evolution was also observed during and after SO₂ injection. Similar to Ag₂S and SnS₂, Cu₂S is also thermodynamically unstable under CO₂ electrolysis conditions. However, even after 5 hours of electrolysis, Cu₂S was still detected on the Cu surface (Figures 3c & S21), indicating that the reduction of Cu₂S is kinetically slow. The presence of Cu₂S may be the reason for the inability of the Cu catalyst to recover its initial performance, and the observation in the current study is consistent with previous works that have shown that S-modified nanostructured Cu catalysts can selectively convert CO₂ to formate.^{37,38} In addition, commercial Cu₂S particles were also examined and the dominant CO₂ reduction product was formate (Figure S22), further supporting that surface Cu₂S is likely responsible for the change in selectivity.

To further probe the sensitivity of the Cu catalyst toward SO₂ impurity, similar experiments were conducted with lower SO₂ concentrations (0.1% and 0.01%). In both cases, a shift in selectivity toward formate was observed (Figures S23&24), and XPS measurements confirmed the presence of Cu₂S (Table S6). With lower SO₂ concentrations, there was a relatively faster rate of recovery; however full recovery was not achieved even after 5 hours of electrolysis. Again, an incremental recovery of CO followed by C_{2+} products can be seen. A recovery up to ~10% and ~5% for CO and C_2H_4 Faradaic efficiencies, respectively, was achieved in 0.1% SO₂ after 5 hours. At lower concentration of 0.01% SO₂, the recovery of CO and C₂H₄ quickly plateaued to those same Faradaic efficiencies, and no further improvement was observed. Post-reaction XPS analysis after 5 hours electrolysis shows similar Cu₂S composition on both catalytic surfaces after 0.1% and 0.01% SO₂ treatments (Table S6), suggesting that there may be residual surface Cu₂S that are stable under CO₂ electrolysis conditions. In an attempt to recover the initial performance after 1% SO₂, the flow-cell electrolyzer was operated at 1 A cm⁻² for 30 minute under Ar to locally generate a high-flux of hydrogen to potentially reduce the metal sulfides (Figure S25). Although slight improvements were observed, a full recovery was not achieved, and post-reaction XPS analysis also indicated the presence of Cu_2S (Table S6). These observations suggest that Cu catalysts are sensitive to SO₂ and that residual Cu₂S on the catalytic surface may dramatically impact the CO₂ electroreduction performance. Therefore, it is concluded that the CO₂ gas feed must be relatively pure (SO₂-free) for Cu-catalyzed CO₂ electrolysis.

Density Functional Theory Calculations

To further gain insight on the shift in selectivity, DFT calculations were performed on S modified Ag, Sn, and Cu catalysts, and the surfaces were modeled as S-doped Ag(111), Sn(111), and Cu(111), respectively. The binding energies of the hydrogen evolution reaction intermediate (e.g. *H) and CO₂ reduction intermediates for CO production (e.g. *COOH) and formate production (e.g. *OCHO) were calculated on clean and S-doped surfaces (Table S7). The DFT optimized geometries on Cu(111) and S-doped Cu(111) (Figure 4) show that *H prefers to bind at a hollow site; *COOH binds at a top site via C atom and *OCHO binds at top sites via two O atoms. The binding geometries of these intermediates on undoped and S-doped (111) surfaces of Ag and Sn were also found to be similar to those on Cu(111). It is noted that *OCHO is relatively more stable than the *COOH intermediate on all surfaces and the stability of *OCHO increases in the order: Sn(111) > Ag(111) > Cu(111).



Figure 4. DFT optimized binding configurations of (a) *H, (b) *COOH, and (c) *OCHO on Cu(111), (d) *H, (e) *COOH and (f) *OCHO on S-doped Cu(111), and (g) *H, (h) *COOH, and (i) *OCHO on Cu₂S(100). Blue: Cu, yellow: S, red: O, brown: C and white: H.

The binding energies (Table S7) show that *OCHO is more stable than *COOH by 1.25 eV, 1.35 eV and 1.13 eV on Ag(111), Sn(111) and Cu(111), respectively. In contrast, the *OCHO stability over *COOH (0.62 eV) decreases on S-doped Ag(111) compared to Ag(111). However, the *OCHO stability over *COOH increases on S-doped Sn(111) (1.54 eV) and S-doped Cu(111) (1.23 eV) compared to Sn(111) and Cu(111), respectively. To account for the formation of Cu₂S as experimentally observed, further DFT calculations were performed to calculate binding energies of *H, *COOH and *OCHO (Figure 4) on the Cu₂S(100) surface that has mixed Cu and S surface termination. Consistent with the prediction on S-doped Cu(111), the results show that the *OCHO stability over *COOH (1.24 eV; Table S7) is enhanced on Cu₂S(100) compared to Cu(111). In summary, the DFT calculations predict that surface S atoms on Cu surfaces selectively stabilize

*OCHO, and thus the formation of formate is promoted as in agreement with the experimental observations. A similar promotional effect on the formate selectivity is predicted on S-doped Sn (111). However, such promotion is not predicted on S-doped Ag(111) since the *OCHO stability over *COOH is less on S-doped Ag(111) than on Ag(111). It must be noted that there is a discrepancy between experimental and computational predication on the Ag catalyst as DFT predicts that formate is more favorable than CO formation; while experimentally, CO was observed as the major CO₂ reduction product. A similar discrepancy is also highlighted in a recent work by Bohra *et al.*³⁹ However, by incorporating solvation effects on transition states and surface coverage of *H, *COOH and *OCHO, they successfully demonstrated the promotion of CO over formate formation on the Ag surface. Future work should also focus on exploring these effects on Sn- and Cu- catalyzed CO₂ reduction.

3. Conclusions and Outlook

In summary, the influence of SO₂ impurity on Ag, Sn, and Cu-catalyzed CO₂ electrolysis was studied in a flow-cell electrolyzer. The results show that the presence of SO₂ impurity reduces the efficiency of converting CO₂ as the reduction of SO₂ is thermodynamically more favorable. In the case of Ag and Sn, full recovery was observed after both catalysts were subjected to SO₂ and the selectivities of converting CO₂ to CO and formate were preserved, respectively. However, in the case of Cu, the catalytic performance was highly sensitive to SO₂ and a shift in selectivity toward formate, accompanied by a suppression of C₂₊ products, was observed. Computational efforts suggest that residual Cu₂S formed on the surface, as confirmed with XPS characterization, is likely responsible for the shift in selectivity.

Our experimental observations further motivate the development of direct air capture (DAC) technologies as the CO₂ feedstock from these sources would be relatively cleaner than that obtained from fossil-burning point sources such as power plants and chemical facilities. The main challenge is the capture and concentration of CO₂ from a dilute source, the air. Although DAC technologies has yet been fully commercialized and previous cost estimation has indicated that these technologies are too expensive (>\$600 per ton of CO₂) to be practical,⁴⁰ small pilot-plant facilities, such as the Climeworks AG facility in Switzerland with the ability to capture 900 tons of CO₂ annually,⁴¹ are currently being developed. A recent work by Keith and co-workers provided the first comprehensive cost breakdown of a DAC facility, estimating the cost to be between \$94 and \$232 per ton of CO₂.¹⁷ Another advantage of DAC is that it is not geographically limited, and thus, this technology can be coupled with distributed renewable energy sources that is expected to be inexpensive in the near future.¹

Lastly, additional work should also focus on studying the influence of NO_x as well as O₂ impurities in CO₂/CO electrolysis. Although the concentration of NO_x and O₂ may be trace amount in the CO₂ feed, these impurities may also have detrimental effect on CO₂/CO electrolysis as demonstrated by the current SO₂ study. Similarly, both NO_x and O₂ could co-adsorb on the catalytic sites under reducing potentials or interact with the electrolyte, potentially altering the local environment or surface structure and consequently influencing catalytic performance. In particular, it has been hypothesized that subsurface oxygen atoms in Cu-catalyzed CO₂/CO electroreduction may potentially enhance the formation of C₂₊ products,⁴² and it would be interesting to determine if adsorbed oxygen species can influence the catalytic performance. Thus,

future work should focus on further understanding the influence of these gaseous impurities on CO_2/CO electroreduction activity.

4. Experimental Setup

Electrode preparation

Commercial Ag (<100 nm, 99.5%) and Cu (25nm) powders were purchased from Sigma Aldrich. Commercial Sn (0.1 micron), IrO₂ (99.99%), Cu₂S (99.5%), and CuS (99.8%) powders were purchased from Alfa Aesar. The catalyst inks were prepared by mixing 25 mg of metal particles, 20 μ l of Nafion solution (5 wt.% in 50/50 water and isopropanol) and 3 ml of isopropanol. After the catalyst inks were sonicated for at least 30 minutes prior to drop casting, 0.3 mg cm⁻² of the metal particles were drop casted onto a Sigracet 29 BC GDL (Fuel Cell Store). Ag, Sn, and Cu electrodes were used as cathodes while IrO₂ electrodes were used as anodes.

CO₂ electrolysis in flow-cell electrolyzer

The electrochemical measurements were conducted in a three chamber flow-cell electrolyzer with channel dimensions of 2 cm \times 0.5 cm \times 0.15 cm. 1M KHCO₃ (99.95%, Sigma Aldrich) was fed to the catholyte and anolyte chamber at ~1 ml min⁻¹ with peristaltic pumps. CO₂ was fed to the flow-cell at 17 sccm via a Brooks GF40 mass flow controller while SO₂ was fed from a syringe via a syringe pump (Cole-Parmer) at 0.17, 0.017, and 0.0017 sccm. To obtain SO₂ gas, a H-cell was continuously purged with SO₂ (Matheson Gas) for 30 minutes and then a 10 mL gas-tight syringe (#1010, Hamilton Company) was used to extract the gas. The cathode and anode chambers were separated by a FAA-3 hydroxide exchange membrane (Fumatech). The backpressure of the gas in the gas chamber was controlled via a backpressure controller (Cole-Parmer).

Chronopotentiometry experiments were conducted via an Autolab PG128N. The half-cell potentials were measured using an external Ag/AgCl reference electrode (Pine Research). The resistance between the cathode and reference electrode was determined using the current-interrupt technique prior to electrolysis, and the measured applied potential was iR-corrected after electrolysis. The gas products were sampled directly to a Multiple Gas Analyzer #5 gas chromatography system (SRI Instruments) equipped with a Molseive 5A and a HaveSep D columns connected to a thermal conductivity detector (TCD) and a flame ionization detector (FID). The electrolytes containing liquid products were collected at the exit of the flow cell for 200 seconds and were analyzed using ¹H NMR with water suppression using a pre-saturation method (Bruker AVIII 600 MHz NMR spectrometer). 500 µl of collected sample was mixed with 100 µl of D₂O containing 25 ppm (m/m) dimethyl sulphoxide (99.9%, Alfa Aesar) as the internal standard. To prevent SO₂ from entering the GC during SO₂ injection, a base trap was positioned between the outlet of the flow-cell electrolyzer gas chamber and the inlet of the GC. Ar was fed at 15 sccm through a tee-connector to push the gas products along with unreacted CO_2 through the base trap before entering the GC for quantification. In order to detect potential sulfur-containing products, the outlet gas stream from the electrolyzer was connected to a gas tight batch cell and was continuously purged. A gas-tight syringe (Hamilton Company) was used to draw and inject

the gas sample into an integrated GC-MS (Aglient 59771A) system equipped with a DB-FFAP column and a mass spectrometry system. The mass fragmentation patterns were compared to those of the National Institute of Standards and Technology (NIST) database. As for the catalyst recovery, a National Instrument power source (RMX-4121) was used to achieve a current density of 1 A cm⁻². After 30 minutes of electrolysis under Ar, the flow-cell electrolyzer was disassembled, the cathode was quickly dried due to severe flooding, and new anode was replaced prior to CO_2 electrolysis.

Material characterization

PXRD was conducted using Cu K $_{\alpha}$ radiation source (Bruker D8 Discover diffractometer). SEM images were obtained from Auriga 60 CrossBeam. XPS was performed with a K-Alpha Xray Photoelectron Spectrometer System (Thermo Fisher Scientific). All peaks were fitted with Thermo Avantage software with the C 1s signal calibrated to 284.8 eV.

For TEM characterization, the samples were thoroughly washed with DI water immediately after reaction to remove the residual electrolyte and then gently abraded from the GDL support to acquire particles for the TEM experiment. In order to distinguish the sulfur atoms that correspond to Cu₂S, FAA ionomer binder was used instead of Nafion binder, since Nafion has sulfonic functional groups. Bright field (BF), high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction pattern (SAED) were performed with a transmission electron microscope (JEM-2100F, JEOL) at an acceleration voltage of 200 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and electron energy loss spectrum (EELS) were obtained on a Hitachi HD2700C STEM with a probe aberration corrector.

Computational methods

Spin polarized periodic density functional theory $(DFT)^{43,44}$ calculations were performed at the GGA level within the PAW-PW91 formalism^{45,46} using the Vienna Ab-Initio Simulation Package (VASP) code.^{47,48} The total energy calculations were performed using a 3 × 3 × 1 Monkhorst-Pack grid⁴⁹ and a plane wave cut-off energy of 400 eV.

Cu(111), Ag(111) and Sn(111) surfaces were modeled using a four layer 3×3 surface slabs. One surface Cu, Ag, and Sn atom was replaced with a S atom to model S-doped Cu(111), Ag(111) and Sn(111) surfaces, respectively. A vacuum layer of ~15 Å thick was added in the slab cell along the direction perpendicular to the surface to minimize the artificial interactions between the surface and its periodic images. During geometry optimization, atoms in the bottom two layers were fixed and all other atoms including adsorbates were allowed to relax until the force on each ion was smaller than 0.02 eV/Å. The binding energy (BE) of an adsorbate was calculated as:

$$BE_{(adsorbate)} = E_{(slab + adsorbate)} - E_{(slab)} - E_{(adsorbate)}$$

where $E_{(slab + adsorbate)}$, $E_{(slab)}$ and $E_{(adsorbate)}$ are the total energy of slab with adsorbate, the energy of clean slab and the energy of adsorbate in the gas phase, respectively. E(H) is taken as one-half the total energy of the H₂ molecule during the calculation of hydrogen binding energy.

The free energy of adsorption of SO₂ and CO₂ on Cu(111), Ag(111), and Sn(111) at T = 298.15 K was calculated as:

 $\Delta G_{ad} = G_{(slab + adsorbate)} - G_{(slab)} - G_{(adsorbate)}$

where $G = E(DFT) + ZPE - T\Delta S$. E(DFT) is the total energy obtained from DFT calculations, ZPE and T ΔS are zero point energy and entropic contributions, respectively. The DFT calculations were performed to calculate ZPE of adsorbed species. ZPE and T ΔS values of gas phase species were taken from NIST database.

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Supporting Information

Schematic of flow-cell electrolyzer, SEM and TEM images, XPS analysis, tables of Faradaic efficiencies, and theoretical calculations

References

- Haegel, N. M.; Margolis, R.; Buonassisi, T.; Feldman, D.; Froitzheim, A.; Garabedian, R.; Green, M.; Glunz, S.; Henning, H. M.; Holder, B.; Kaizuka, I.; Kroposki, B.; Matsubara, K.; Niki, S.; Sakurai, K.; Schindler, R. A.; Tumas, W.; Weber, E. R.; Wilson, G.; Woodhouse, M.; Kurtz, S. *Science* 2017, *356*, 141.
- (2) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I. B.; Norskov, J. K.; Jaramillo, T. F. *Science* **2017**, *355* eaad4998.
- (3) Lu, Q.; Rosen, J.; Zhou, Y.; Hutchings, G. S.; Kimmel, Y. C.; Chen, J. G. G.; Jiao, F. *Nature Communications* **2014**, *5* 3242.
- (4) Rosen, J.; Hutchings, G. S.; Lu, Q.; Forest, R. V.; Moore, A.; Jiao, F. *ACS Catalysis* **2015**, *5*, 4586.
- (5) Ripatti, D. S.; Veltman, T. R.; Kanan, M. W. Joule **2019**, *3*, 240.
- (6) Delacourt, C.; Ridgway, P. L.; Kerr, J. B.; Newman, J. *Journal of the Electrochemical Society* **2008**, *155*, B42.
- (7) Kim, B.; Hillman, F.; Ariyoshi, M.; Fujikawa, S.; Kenis, P. J. A. *Journal of Power Sources* **2016**, *312*, 192.
- (8) Verma, S.; Lu, X.; Ma, S. C.; Masel, R. I.; Kenis, P. J. A. *Physical Chemistry Chemical Physics* **2016**, *18*, 7075.
- (9) Verma, S.; Hamasaki, Y.; Kim, C.; Huang, W. X.; Lu, S.; Jhong, H. R. M.; Gewirth, A. A.; Fujigaya, T.; Nakashima, N.; Kenis, P. J. A. *ACS Energy Letters* **2018**, *3*, 193.
- (10) Ma, S. C.; Sadakiyo, M.; Luo, R.; Heima, M.; Yamauchi, M.; Kenis, P. J. A. *Journal of Power Sources* **2016**, *301*, 219.
- (11) Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. *Electrochimica Acta* 1994, 39, 1833.

2		
3	(12)	Hori, Y.; Konishi, H.; Futamura, T.; Murata, A.; Koga, O.; Sakurai, H.; Oguma, K.
4		Electrochimica Acta 2005 50 5354
5	(13)	Wuttig A · Surendranath V ACS Catalysis 2015 5 4479
6	(13) (14)	Weng $7 \cdot 7$ hang $Y \cdot W_U = V S \cdot H_{UO} = S I \cdot I_{iang} I B \cdot I_{iu} = W \cdot H_{e} G I \cdot I_{iang} = V V \cdot I_{iang} = V \cdot V$
7	(14)	Weng, Z., Zhang, A., Wu, T. S., Huo, S. J., Jiang, J. D., Liu, W., He, O. J., Liang, T. T., Weng, H. J. And and the Chamin Intermetion of Edition 2017 , 54 , 12125
8		Wang, H. L. Angewandte Chemie-International Edition 2017, 30, 13135.
9	(15)	Zhai, Y. M.; Chiachiarelli, L.; Sridhar, N. ECS Transactions 2009, 19, 1.
10	(16)	Sanz-Perez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Chemical Reviews 2016,
11		116, 11840.
12	(17)	Keith, D. W.; Holmes, G.; Angelo, D. S.; Heidel, K. Joule 2018, 2, 1573.
13	(18)	Kovtsoumpa E I Bergins C Kakaras E Journal of Supercritical Fluids 2018 132 3
14	(10)	Wi X M \cdot Vi V S \cdot Oin 7 \cdot Thang 7 X In 12th International Conference on
15	(1))	Creambourg Car Control Technologies Chat 12: Divon T. Horzog H. Twinning S.
10		Eda 2014: Val 62 m 1220
17	$\langle \mathbf{a} \rangle$	Eas. 2014 , $v01$, 05 , $p1539$.
10	(20)	Last, G. V.; Schmick, M. I. Identification and Selection of Major Carbon Dioxide Stream
20		Compositions, 2011.
20	(21)	Lv, J. J.; Jouny, M.; Luc, W.; Zhu, W. L.; Zhu, J. J.; Jiao, F. Advanced Materials 2018, 30
27		1803111.
23	(22)	Dinh, C. T.; Burdyny, T.; Kibria, M. G.; Seifitokaldani, A.; Gabardo, C. M.; de Arquer, F.
24		P. G. Kiani, A. Edwards, J. P. De Luna, P. Bushuvev, O. S. Zou, C. O. Ouintero-
25		Bermudez R · Pang V I · Sinton D · Sargent F H Science 2018 360 783
26	(22)	Dinh C. T. do Arguer E. D. C. Sinton, D. Sorgent E. H. ACS Evenue Lettors 2019, 2
27	(23)	Dinni, C. T., de Arquer, F. F. G., Sinton, D., Sargent, E. H. ACS Energy Letters 2010, 5,
28		
29	(24)	Liu, Z. C.; Yang, H. Z.; Kutz, R.; Masel, R. I. Journal of the Electrochemical Society
30		2018 , <i>1</i> 65, J3371.
31	(25)	Yang, H. Z.; Kaczur, J. J.; Sajjad, S. D.; Masel, R. I. ECS Transactions 2017, 77, 1425.
32	(26)	Haase, J. Journal of Physics-Condensed Matter 1997, 9, 3647.
33	(27)	Rodriguez, J. A.; Jirsak, T.; Chaturvedi, S.; Hrbek, J. Journal of the American Chemical
34		Society 1998 , 120, 11149.
35	(28)	Ghafoor S · Ata S · Mahmood N · Arshad S N Scientific Reports 2017 7255
36	(20)	Hota G: Idage S B: Khilar K C Colloids and Surfaces a Physicochemical and
37	(29)	Fusing Arrests 2007, 202, 5
38	(20)	Engineering Aspecis 2007, 295, 5.
39	(30)	Zheng, X. L.; De Luna, P.; de Arquer, F. P. G.; Zhang, B.; Becknell, N.; Ross, M. B.; L1,
40		Y. F.; Banis, M. N.; Li, Y. Z.; Liu, M.; Voznyy, O.; Dinh, C. T.; Zhuang, T. T.; Stadler,
41		P.; Cui, Y.; Du, X. W.; Yang, P. D.; Sargent, E. H. Joule 2017, 1, 794.
42	(31)	Aastrup, T.; Wadsak, M.; Leygraf, C.; Schreiner, M. Journal of the Electrochemical
43		Society 2000, 147, 2543.
44	(32)	Mann J B · Meek T L · Knight E T · Capitani J F · Allen L C Journal of the
45	(0=)	American Chemical Society 2000 122 5132
40	(33)	Allen I. C. Journal of the American Chamical Society 1080 111 0003
48	(33)	Via V: Diadingar A: Drate M: Conv. A: Consuma A: Cuardia D: Sottini S:
49	(34)	Ale, T., Kledinger, A., Flato, M., Casu, A., Genovese, A., Guardia, F., Sounni, S.,
50		Sangregorio, C.; Miszta, K.; Ghosh, S.; Pellegrino, I.; Manna, L. Journal of the American
51		<i>Chemical Society</i> 2013 , <i>135</i> , 17630.
52	(35)	Scott, S. B.; Hogg, T. V.; Landers, A. T.; Maagaard, T.; Bertheussen, E.; Lin, J. C.; Davis,
53		R. C.; Beeman, J. W.; Higgins, D.; Drisdell, W. S.; Hahn, C.; Mehta, A.; Seger, B.;
54		Jaramillo, T. F.; Chorkendorff, I. Acs Energy Letters 2019, 4, 803.
55	(36)	Ren. D.: Fong. J. H.: Yeo, B. S. Nature Communications 2018 9 925
56	()	, , - <u>0,</u> ,,
57		
58		15
59		
60		ACS Paragon Plus Environment

- (37) Shinagawa, T.; Larrazabal, G. O.; Martin, A. J.; Krumeich, F.; Perez-Ramirez, J. ACS *Catalysis* **2018**, *8*, 837.
- (38) Deng, Y. L.; Huang, Y.; Ren, D.; Handoko, A. D.; Seh, Z. W.; Hirunsit, P.; Yeo, B. S. ACS Applied Materials & Interfaces 2018, 10, 28572.
- (39) Bohra, D.; Ledezma-Yanez, I.; Li, G. N.; de Jong, W.; Pidko, E. A.; Smith, W. A. *Angewandte Chemie-International Edition* **2019**, *58*, 1345.
- (40) Lackner, K. S.; Brennan, S.; Matter, J. M.; Park, A. H. A.; Wright, A.; van der Zwaan, B. *Proceedings of the National Academy of Sciences of the United States of America* **2012**, *109*, 13156.
- (41) www.climeworks.com

- (42) Eilert, A.; Cavalca, F.; Roberts, F. S.; Osterwalder, J.; Liu, C.; Favaro, M.; Crumlin, E. J.; Ogasawara, H.; Friebel, D.; Pettersson, L. G. M.; Nilsson, A. *Journal of Physical Chemistry Letters* **2017**, *8*, 285.
- (43) Hohenberg, P.; Kohn, W. *Physical Review B* **1964**, *136*, B864.
- (44) Kohn, W.; Sham, L. J. Physical Review 1965, 140, A1133.
- (45) Blochl, P. E. Physical Review B 1994, 50, 17953.
- (46) Perdew, J. P.; Wang, Y. Physical Review B 1992, 45, 13244.
- (47) Kresse, G.; Furthmuller, J. Computational Materials Science 1996, 6, 15.
- (48) Kresse, G.; Hafner, J. *Physical Review B* **1993**, *48*, 13115.
- (49) Monkhorst, H. J.; Pack, J. D. *Physical Review B* 1976, 13, 5188.

TOC Figure:

Carbon

Dioxide

Cu

Sulfur Dioxide





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