

#### Electrocatalysis

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# **Brass and Bronze as Effective CO<sub>2</sub> Reduction Electrocatalysts**

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**Abstract:** Electrochemically reducing  $CO_2$  into fuels using renewable electricity is a contemporary global challenge that requires significant advances in catalyst design. Photodeposition techniques were used to screen ternary alloys of Cu-Zn-Sn, which includes brass and bronze, for the electrocatalytic reduction of  $CO_2$  to CO and formate. This analysis identified  $Cu_{0.2}Zn_{0.4}Sn_{0.4}$  and  $Cu_{0.2}Sn_{0.8}$  to be capable of reaching Faradaic efficiencies of > 80 % for CO and formate formation, respectively, and capable of achieving partial current densities of 3 mA cm<sup>-2</sup> at an overpotential of merely 200 mV.

he electrolytic reduction of  $CO_2$  is a potential means of utilizing cheap renewable electricity to produce fuels, chemicals, and plastics while mitigating  $CO_2$  emissions.<sup>[1–3]</sup> The electrolytic production of CO and formate are among the easier products to produce from  $CO_2$ , with CO being particularly appealing because it can potentially be used as a fuel or as an intermediate for further synthesis.<sup>[4]</sup> The challenge is to develop an electrocatalyst capable of converting  $CO_2$  into CO and formate with high efficiency and selectivity for prolonged time periods.<sup>[5,6]</sup>

State-of-the-art CO<sub>2</sub>-to-CO heterogeneous electrocatalysts include oxide-derived gold,<sup>[7]</sup> nanostructured gold,<sup>[8]</sup> and nanostructured silver electrodes<sup>[9,10]</sup> that achieve partial current densities for CO formation ( $j_{CO}$ ) of 7, 40, and 3 mA cm<sup>-2</sup>, respectively, at overpotentials of 300 mV. We note that homogeneous electrocatalysts are also capable of achieving selective CO evolution.<sup>[11,12]</sup> The formation of formate from CO<sub>2</sub> is most effective at carbon-supported palladium: A current density for formate production ( $j_{HCOOH}$ ) of 1 mA cm<sup>-2</sup> can be achieved at an overpotential of merely 50 mV.<sup>[13]</sup> A growing number of non-noble metal CO<sub>2</sub> reduction electrocatalysts have been unearthed (for example, Co nanolayers,<sup>[14]</sup> WSe<sub>2</sub> nanoflakes,<sup>[15]</sup> Bi nanoflower catalyst<sup>[16]</sup>), but the performance of earth-abundant electrocatalysts is confined to low current densities (for example, Zn, Sn,

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Pb)<sup>[17]</sup> or by high rates of competitive hydrogen formation (Ni, Fe) in the absence of expensive ionic liquids.

Alloys offer the opportunity to tune the surface properties of electrocatalysts to optimize catalytic activity.<sup>[18–27]</sup> It has been shown, for example, that the activity of AuCu nanoparticles is three-fold higher than that of gold catalysts,<sup>[23]</sup> and that CuIn alloys can form CO with high selectivity.<sup>[22]</sup> A Pd-Sn alloy was reported to mediate the exclusive formation of formate at an overpotential of 0.26 V that cannot be achieved by any single metal.<sup>[18]</sup>

Despite these promising results, very few alloys of exclusively earth-abundant elements have been tested for CO<sub>2</sub> reduction electrocatalysis. We disclose here the discovery that the Cu-Zn-Sn compositional phase space is capable of mediating efficient electrocatalytic reduction of CO<sub>2</sub> to CO and formate. We tested these three earth abundant metals because: 1) the M-CO bonding strengths for pure phases of each of Cu, Zn, and Sn are compatible with CO and HCOOH evolution (Supporting Information, Figure S1); and 2) Cu-Zn, Cu-Sn, and Cu-Zn-Sn comprise the widely known alloys brass, bronze, and white bronze, respectively. We therefore prepared 21 films where the relative Cu, Zn, and Sn contents were changed in 20% increments (Figure 1a) by electrochemically reducing the corresponding mixed-metal oxide films prepared by photodeposition techniques.<sup>[22, 28-30]</sup> An analysis of each film revealed that the compositions  $Zn_{0.8}Sn_{0.2}$  and  $Cu_{0.2}Sn_{0.8}$  produce HCOOH with high selectivity and efficiency, and that Cu<sub>0.2</sub>Zn<sub>0.4</sub>Sn<sub>0.4</sub> is an effective CO<sub>2</sub> to CO electrocatalyst. These three catalysts were capable of achieving partial current densities of about 3 mA cm<sup>-2</sup> at a modest overpotential of 200 mV, which are among the highest values reported to date for earth abundant metal CO<sub>2</sub> electrocatalysts.

A series of 21 electrocatalysts were synthesized by dropcasting onto a titanium substrate a 0.6-mL aliquot drawn from a 4.8-mL methanolic solution containing 0.1-a-b mmol CuCl<sub>2</sub>, *a* mmol of ZnCl<sub>2</sub>, and *b* mmol of SnCl<sub>2</sub>. Each film was then exposed to near-infrared (NIR) radiation for 1 h. This succession of deposition and irradiation steps were repeated 7 times prior to a final 12-h exposure to NIR radiation. Each film was then immersed in a 0.5 m NaHCO<sub>3</sub> electrolyte solution in a three-electrode cell configuration and reduced at steady negative bias (-0.5 V vs. RHE) for 1 h prior to film characterization and electrocatalyst testing.

The absence of chloride ligands in the as-prepared films was confirmed by X-ray fluorescence (XRF) spectroscopy (Supporting Information, Figure S2). An XRF analysis of the films showed a relative metal content that did not change substantially before or after the electrochemical reduction step. The scanning electron microscope (SEM) image of a prototypical as-prepared sample,  $Cu_{0.33}Zn_{0.33}Sn_{0.33}$ , shows a full coverage of metal oxide nanoparticles (Figure 2 a).

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**Figure 1.** a) Compositional diagram for the Cu<sub>x</sub>Zn<sub>y</sub>Sn<sub>1-x-y</sub> alloys evaluated in this study. 21 different compositions were evaluated where the metal content was changed in 20% increments. b) Powder X-ray diffractrograms for copper, Cu<sub>0.8</sub>Zn<sub>0.1</sub>Sn<sub>0.1</sub>, Cu<sub>0.6</sub>Sn<sub>0.4</sub>, Cu<sub>0.4</sub>Sn<sub>0.6</sub>, Cu<sub>0.4</sub>Zn<sub>0.2</sub>Sn<sub>0.4</sub>, Cu<sub>0.2</sub>Zn<sub>0.4</sub>Sn<sub>0.4</sub>, Cu<sub>0.4</sub>Zn<sub>0.6</sub>, Zn<sub>0.6</sub>Sn<sub>0.4</sub>, and tin samples. These compositions, which are indicated by the colored circles in (a), represent the different solid-state phases of these alloys.



**Figure 2.** a) SEM image and b)–d) energy-dispersive X-ray (EDX) spectroscopic elemental mapping of a film  $Cu_{0.33}Zn_{0.33}Sn_{0.33}$  on titanium.

Elemental mapping of the electrochemically reduced films were measured by energy-dispersive X-ray (EDX) spectroscopy to confirm a uniform distribution of copper, zinc and tin across the films (Figures 2b–d).

The alloying for each of the ternary films was confirmed by benchmarking the powder X-ray diffraction (XRD) diffractograms against the pure metallic films and known alloys. The diffractograms for films of Cu,  $Cu_{0.8}Zn_{0.1}Sn_{0.1}$ ,

 $Cu_{0.6}Sn_{0.4}, Cu_{0.4}Sn_{0.6}, Cu_{0.4}Zn_{0.2}Sn_{0.4}, Cu_{0.2}Zn_{0.4}Sn_{0.4}, Cu_{0.2}Zn_{0.6}$ Cu<sub>0.4</sub>Zn<sub>0.6</sub>, Zn<sub>0.6</sub>Sn<sub>0.4</sub>, and Sn presented in Figure 1b were selected because they represent the different alloy phases indicated in Figure 1a. The main crystalline phase of samples with >70% Cu (for example,  $Cu_{0.8}Zn_{0.1}Sn_{0.1}$ ) was similar to metallic copper. This observation is presumably because zinc and tin atoms can both be incorporated into the lattice of copper, which exists in the same crystalline form as brass and bronze. When the relative copper content is less than 70% with a tin content higher than 10%, the base-centered monoclinic crystalline phase of η-bronze (pdf number: 045-1488) is present, for example, the Cu<sub>0.6</sub>Sn<sub>0.4</sub> sample is characterized by a prominent signal at  $30.1^{\circ}$  and  $43.0^{\circ}$ corresponding to η-bronze and an attenuated copper signal. For the binary Cu-Zn alloys, where the Cu ratio is below 50%, peaks characteristic of  $\gamma$ -brass (pdf number: 045-1488) are observed at 35.1°, 38.0°, and 43.3°. Mixtures of η-bronze and metallic tin were detected for films where the copper content was 10-30% and a tin content below 10%. Samples with a copper content of < 10% did not alloy and only mixtures of metallic zinc and metallic tin were detected. Alloys of zinc and tin at room temperature are not known.

The efficacy of CO<sub>2</sub> reduction was evaluated for each of the films by measuring the Faradaic efficiencies and partial current densities of all products in the three-electrode cell. The Faradaic efficiency of one single product (H<sub>2</sub>, CO, or HCOOH) is defined as  $FE_X$ , where  $X = H_2$ , CO, or HCOOH. The electrolyte for these experiments, 0.5 M KHCO<sub>3</sub>, was prepurged with  $CO_2$  for 1 h prior to catalysis. Each sample was subjected to 4 h of electrolysis. Gas-phase products H<sub>2</sub> and CO were detected in real-time by gas chromatography, while liquid products such as formic acid were sampled and measured every hour by <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy and calibrated against the total charge passed during the experiment. The catalytic activities were found to be stable over this 4 h testing period (Supporting Information, Figure S3). The data reported in Figure 3 shows the GC measurement 1 h into the reaction, while the NMR data was recorded during the first two hours of electrolysis. Titanium is comparably inert towards CO<sub>2</sub> reduction (catalytic onset ca. -0.8 V) and was used as the support for all studies. All of the mixed-metal films tested in this study displayed an onset of catalysis at ca. -0.4 V, and thus the catalytic activities of the alloys were benchmarked at a potential of -0.7 V. The contributions from the substrate are nominal and CO<sub>2</sub> reduction is favored at this potential.<sup>[22]</sup>

Electrocatalysis experiments at -0.7 V on the pure metallic copper coatings produced hydrogen almost exclusively (>95%), while zinc produced a small fraction of CO (ca. 20%) at a modest current density. Tin yields high selectivity of HCOOH at this potential but at a low  $j_{\rm HCOOH}$  of 0.5 mA cm<sup>-2</sup>. The screening of the ternary films, summarized in Figure 3, clearly suggest a synergistic effect between the metals because the activities of the alloys are distinctively higher than those of the pure metal electrodes. We gleaned the following structure–property relationships from this catalyst screening:

1) Tin appears to suppress hydrogen production in favor of CO or HCOOH production (the  $j_{\text{total}}$  and FE<sub>H<sub>2</sub></sub> of ternary

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**Figure 3.** a) Hydrogen evolution Faradaic efficiency (FE<sub>H2</sub>); b) total current density (*j*<sub>total</sub>), c) CO evolution Faradaic efficiency (FE<sub>co</sub>), d) HCOOH evolution faradaic efficiency (FE<sub>HCOOH</sub>), e) CO evolution partial current density (*j*<sub>CO</sub>), and f) HCOOH evolution partial current density (*j*<sub>HCOOH</sub>) for films of Cu<sub>x</sub>Zn<sub>y</sub>Sn<sub>1-x-y</sub> (where *x*=0, 0.2, 0.4, 0.6, 0.8, and 1, and y=0, 0.2, 0.4, 0.6, 0.8, and 1; where  $0 \le x + y \le 1$ ).

alloys decrease monotonously with higher tin concentrations);

- Ternary alloys containing <20% tin did not produce formate, and the H<sub>2</sub>:CO ratio of products ranged from 5– 70% (a range that meets the requirements of most industrially relevant uses for syngas<sup>[31]</sup>);
- Ternary alloys with at least 20% of each metal favors CO evolution (Figure 3c), and a higher relative concentration of Zn to Cu is favorable. The champion CO<sub>2</sub> to CO catalyst measured here was Cu<sub>0.2</sub>Zn<sub>0.4</sub>Sn<sub>0.4</sub>;
- Binary alloys Sn-M (where M = Cu or Zn) showed inferior CO<sub>2</sub>-to-CO activities relative to ternary samples containing the same amounts of tin;
- 5) Binary alloys with higher quantities of tin favor HCOOH formation

The catalysts were then tested on a carbon cloth support to facilitate higher current densities. Approximately 0.02 mmol cm<sup>-2</sup> of catalyst was coated on the carbon cloth by drop-casting. Electrochemical surface area testing showed that the capacitance on carbon cloth was 50–100 times larger than that measured on the titanium substrate (Supporting Information, Figure S4). XRF and XRD measurements confirmed that the metal ratios and crystalline structures of the alloys were similar to those measured for the samples deposited on the titanium supports (Supporting Information, Figure S5).

The Cu<sub>x</sub>Zn<sub>y</sub>Sn<sub>1-x-y</sub> samples were found to exhibit much larger current densities on the carbon cloth (Figure 4). The Cu<sub>0.2</sub>Zn<sub>0.4</sub>Sn<sub>0.4</sub> sample, for example, produced a current density at -0.7 V vs. RHE of 13 mA cm<sup>-2</sup> (compare 3.4 mA cm<sup>-2</sup> on Ti). The FE<sub>CO</sub> also increased to 86% from the 45% measured on the planar support at -0.4 V vs. RHE. This observation cannot be explained exclusively by the enhanced surface area given that the  $j_{H_2}$  was nearly constant and only the  $j_{CO}$  increased. The current density measured for the Cu<sub>0.2</sub>Sn<sub>0.8</sub> sample also increased 4-fold when deposited on the carbon cloth support, with a FE<sub>HCOOH</sub> evolution of about 85% at -0.35 V vs. RHE.



**Figure 4.** a) Cyclic voltammograms (scan rate = 100 mVs<sup>-1</sup>) recorded on  $Cu_{0.2}Zn_{0.4}Sn_{0.4}$  deposited on titanium and carbon cloth support. b) The  $FE_{CO}$  measured for the  $Cu_{0.2}Zn_{0.4}Sn_{0.4}$  samples on the two supports. c) Cyclic voltammograms recorded on  $Cu_{0.2}Sn_{0.8}$  deposited on Ti and carbon cloth. d) The *j*<sub>total</sub> and FE<sub>HCOOH</sub> value for  $Cu_{0.2}Sn_{0.8}$ subjected to electrolysis at -0.35 V for 4 h.

In conclusion, we have reported the systematic screening of Cu-Zn-Sn ternary alloys widely known as bronze and brass for CO<sub>2</sub> electrocatalysis. The electrochemical testing of a range of compositions for these samples provides clear regions of higher CO and HCOOH evolution activities, and the Cu<sub>0.2</sub>Zn<sub>0.4</sub>Sn<sub>0.4</sub> and Cu<sub>0.2</sub>Sn<sub>0.8</sub> samples stand out as particularly efficient CO<sub>2</sub> to CO and HCOOH electrocatalysts. The partial current densities for these complex mixtures reach current densities higher than those of the constituent metals. Combining the catalysts with high-surface-area supports reduced the CO<sub>2</sub> reduction overpotential by about 400 mV compared with that measured on planar supports. This method revealed a means of identifying new candidate materials to be considered for study in electrolyzer flow cells.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** brass  $\cdot$  bronze  $\cdot$  CO evolution  $\cdot$  CO<sub>2</sub> reduction  $\cdot$  HCOOH evolution

- B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C. P. Kubiak, Annu. Rev. Phys. Chem. 2012, 63, 541-569.
- [2] C. Costentin, M. Robert, J.-M. Saveant, Chem. Soc. Rev. 2013, 42, 2423-2436.
- [3] A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, et al., *Chem. Rev.* 2013, 113, 6621–6658.
- [4] S. Verma, B. Kim, H.-R. M. Jhong, S. Ma, P. J. A. Kenis, *Nature* 2014, 508, 1972–1979.
- [5] J. Qiao, Y. Liu, F. Hong, J. Zhang, Chem. Soc. Rev. 2014, 43, 631– 675.
- [6] K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Energy Environ. Sci.* 2012, 5, 7050.
- [7] Y. Chen, C. W. Li, M. W. Kanan, J. Am. Chem. Soc. 2012, 134, 19969–19972.
- [8] M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C. T. Dinh, F. Fan, C. Cao, et al., *Nature* 2016, 537, 382–386.
- [9] Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen, F. Jiao, *Nat. Commun.* **2014**, *5*, 3242; DOI: https://doi.org/ 10.1038/ncomms4242.
- [10] M. Ma, B. J. Trześniewski, J. Xie, W. A. Smith, Angew. Chem. Int. Ed. 2016, 55, 9748–9752; Angew. Chem. 2016, 128, 9900–9904.
- [11] C. Costentin, S. Drouet, M. Robert, J.-M. Saveant, *Science* 2012, 338, 90-94.

- [12] N. X. M. Elgrishi, M. B. Chambers, X. Wang, M. Fontecave, *Chem. Soc. Rev.* 2017, 46, 761–796.
- [13] X. Min, M. W. Kanan, J. Am. Chem. Soc. 2015, 137, 4701-4708.
- [14] S. Gao, Y. Lin, X. Jiao, Y. Sun, Q. Luo, W. Zhang, D. Li, J. Yang, Y. Xie, *Nature* 2016, 529, 68–71.
- [15] M. Asadi, K. Kim, C. Liu, A. V. Addepalli, P. Abbasi, P. Yasaei, P. Phillips, A. Behranginia, J. M. Cerrato, R. Haasch, et al., *Science* 2016, 353, 467–470.
- [16] J. L. DiMeglio, J. Rosenthal, J. Am. Chem. Soc. 2013, 135, 8798– 8801.
- [17] Y. Hori, Mod. Aspects Electrochem. 2008, 42, 89-189.
- [18] X. Bai, W. Chen, C. Zhao, S. Li, Y. Song, R. Ge, W. Wei, Y. Sun, Angew. Chem. Int. Ed. 2017, 56, 12219–12223; Angew. Chem. 2017, 129, 12387–12391.
- [19] D. Ren, B. S.-H. Ang, B. S. Yeo, ACS Catal. 2016, 6, 8239-8247.
- [20] D. A. Torelli, S. A. Francis, J. C. Crompton, A. Javier, J. R. Thompson, B. S. Brunschwig, M. P. Soriaga, N. S. Lewis, ACS Catal. 2016, 6, 2100-2104.
- [21] R. Reske, M. Duca, M. Oezaslan, K. J. P. Schouten, M. T. M. Koper, P. Strasser, J. Phys. Chem. Lett. 2013, 4, 2410–2413.
- [22] J. He, K. E. Dettelbach, D. A. Salvatore, T. Li, C. P. Berlinguette, *Angew. Chem. Int. Ed.* 2017, 56, 6068–6072; *Angew. Chem.* 2017, 129, 6164–6168.
- [23] S. Rasul, D. H. Anjum, A. Jedidi, Y. Minenkov, L. Cavallo, K. Takanabe, Angew. Chem. Int. Ed. 2015, 54, 2146–2150; Angew. Chem. 2015, 127, 2174–2178.
- [24] D. Kim, J. Resasco, Y. Yu, A. M. Asiri, P. Yang, *Nat. Commun.* 2014, 5, 4948; DOI: https://doi.org/10.1038/ncomms5948.
- [25] S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. T. Haasch, J. I. Gold, M. Yamauchi, P. J. A. Kenis, J. Am. Chem. Soc. 2017, 139, 47-50.
- [26] D. Kim, C. Xie, N. Becknell, Y. Yu, M. Karamad, K. Chan, E. J. Crumlin, J. K. Nørskov, P. Yang, J. Am. Chem. Soc. 2017, 139, 8329–8336.
- [27] S. Zhang, P. Kang, M. Bakir, A. M. Lapides, C. J. Dares, T. J. Meyer, Proc. Natl. Acad. Sci. USA 2015, 112, 15809–15814.
- [28] R. D. L. Smith, M. S. Prevot, R. D. Fagan, Z. Zhang, P. A. Sedach, M. K. J. Siu, S. Trudel, C. P. Berlinguette, *Science* 2013, 340, 60-63.
- [29] R. D. L. Smith, M. S. Prévot, R. D. Fagan, S. Trudel, C. P. Berlinguette, J. Am. Chem. Soc. 2013, 135, 11580–11586.
- [30] D. A. Salvatore, K. E. Dettelbach, J. R. Hudkins, C. P. Berlinguette, *Sci. Adv.* 2015, *1*, e1400215–e1400215.
- [31] Ratios of 0.6H<sub>2</sub>:CO for Fischer–Tropsch reactors, 2H<sub>2</sub>:CO for methanol synthesis, and 0.3–1H<sub>2</sub>:CO for syngas fermentation listed in: S. R. Foit, I. C. Vinke, L. G. J. de Haart, R.-A. Eichel, *Angew. Chem. Int. Ed.* 2017, 56, 5402–5411; *Angew. Chem.* 2017, 129, 5488–5498.

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## **Communications**

### *Electrocatalysis* J. He, K. E. Dettelbach, A. Huang, C. P. Berlinguette\* \_\_\_\_\_

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