Article

Electrochemical Reduction of CO\textsubscript{2} to CO on Hydrophobic Zn Foam Rod in a Microchannel Electrochemical Reactor

Chunxiao Zhang \textsuperscript{1,\#}, Shenglin Yan \textsuperscript{1,\#}, Jing Lin \textsuperscript{1}, Qing Hu \textsuperscript{1}, Juhua Zhong \textsuperscript{2,*}, Bo Zhang \textsuperscript{3,*} and Zhenmin Cheng \textsuperscript{1,*}

1 State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China; chunxiaozhangaa@163.com (C.Z.); 15926513572@163.com (S.Y.); y20190883@mail.ecust.edu.cn (J.L.); y20200029@mail.ecust.edu.cn (Q.H.)
2 Physics Department, School of Science, East China University of Science and Technology, Shanghai 200237, China
3 State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200438, China
* Correspondence: jzhong@ecust.edu.cn (J.Z.); bozhang@fudan.edu.cn (B.Z.); zmcheng@ecust.edu.cn (Z.C.)

Abstract: Due to CO\textsubscript{2} mass transfer limitation as well as the competition of hydrogen evolution reaction in electroreduction of CO\textsubscript{2} in the aqueous electrolyte, Zn-based electrodes normally exhibit unsatisfying selectivity for CO production, especially at high potentials. In this work, we introduced a zinc myristate (Zn [(CH\textsubscript{3})\textsubscript{12}COO\textsubscript{2}) hydrophobic layer on the surface of zinc foam electrode by an electrodeposition method. The obtained hydrophobic zinc foam electrode showed a high Faradaic efficiency (FE) of 91.8% for CO at ~1.9 V (vs. saturated calomel electrode, SCE), which was a remarkable improvement over zinc foam (FE\textsubscript{CO} = 81.87\%) at the same potentials. The high roughness of the hydrophobic layer has greatly increased the active surface area and CO\textsubscript{2} mass transfer performance by providing abundant gas-liquid-solid contacting area. This work shows adding a hydrophobic layer on the surface of the catalyst is an effective way to improve the electrochemical CO\textsubscript{2} reduction performance.

Keywords: hydrophobic zinc foam; CO\textsubscript{2} mass transfer; faradaic efficiency; electrochemical CO\textsubscript{2} reduction

1. Introduction

The electrochemical conversion of CO\textsubscript{2} to industrially valuable compounds under mild conditions has been considered as a promising way to turn wastes into treasures [1,2]. Therefore, the transformation and utilization of CO\textsubscript{2} has become the focus of research for researchers. Numerous materials have been identified to be able to reduce CO\textsubscript{2} in liquid electrolytes, whereas how to improve catalyst activity and product selectivity still needs to be explored in depth. The activity is usually restricted by inefficient catalysts and low CO\textsubscript{2} solubility in neutral pH electrolytes. The inferior product selectivity is the result of multiple proton-coupled multiple-electron transfer (PCET) processes and the competitive hydrogen evolution reaction (HER) [3]. Based on that, finding a catalyst with excellent performance, suppressing HER, and improving CO\textsubscript{2} mass transfer have been the directions for many researchers.

Some researchers [4–7] have found that Au and Ag possess high CO selectivity in the CO\textsubscript{2} electrochemical reduction reaction (CO\textsubscript{2}ERR), however, these two metals are not suitable for widespread industrial application due to their high price. Zn-based materials as a non-precious metal get a lot of attention due to good CO selectivity from CO\textsubscript{2} [3,8,9]. Many studies get highly efficient catalysts by changing the surface structure of the Zn-based catalyst [3,10–12]. Yu et al. [11] prepared a porous Zn electrode on zinc flake using an electrodeposition method from Zn(NO\textsubscript{3})\textsubscript{2}, and this catalyst exhibited a good CO\textsubscript{2} electroreduction performance with a CO Faradaic efficiency (FE\textsubscript{CO}) of about 80% at ~1.1 V...
(vs. RHE). Guo et al. [13] fabricated a fiber zinc-like catalyst, achieving high electrochemical activity and a FE\textsubscript{CO} of 73% at −1.2 V (vs. RHE).

The CO\textsubscript{2} mass transfer limitation leads to the low current density and poor efficiency of CO\textsubscript{2} reduction [14]. Researchers have made a lot of efforts on how to weaken the mass transfer limitation of CO\textsubscript{2}. For example, the gas diffusion electrode was designed to enhance the mass transfer between the gas-liquid-solid interface [15]. Not only that, adding the hydrophobic layer on the surface of catalyst is also an effective way to increase the CO\textsubscript{2} mass transfer [16,17].

Recently, the microchannel reactor has obtained the attention of many scientific researchers due to its remarkable mass and heat transfer performance [18,19]. The application of the microchannel reactor in the CO\textsubscript{2} ERR can increase the mass transfer of CO\textsubscript{2}, thereby increasing the selectivity of the required products [20].

In this work, we prepared a hydrophobic zinc foam to improve the activity of the electrode. Inspired by Liu et al. [21], the cerium myristate superhydrophobic layer was added to magnesium alloy to enhance corrosion resistance and Yang et al. [22] improved corrosion inhibition by preparing a super-hydrophobic nickel film on copper substrate. After electrodeposition for different time (0.5, 5, and 10 min), we get catalysts with different degrees of hydrophobicity. CO\textsubscript{2} ERR is a gas-consumption reaction, and occurs at the liquid-solid interface, where the transfer of proton, electrons, and CO\textsubscript{2} molecules is carried out [23–25]. Hydrophobic zinc foam can therefore increase the concentration of CO\textsubscript{2} at the electrode interface, improve the mass transfer of CO\textsubscript{2} [16], and weaken the hydrogen evolution reaction [26].

2. Materials and Methods

2.1. Materials and Chemicals

Zinc rod (99.99%, 1.0 mm in diameter), potassium Bicarbonate (99.99%, Macklin, Shanghai, China), sulfuric acid (95.0–98.0%, Sinopharm Reagent, Shanghai, China), ethanol (99.5%, Sinopharm Reagent), ammonium sulfate (≥99.0%, Sinopharm Reagent, Shanghai, China), zinc sulfate heptahydrate (99.995%, Aladdin, Shanghai, China), myristic acid (≥99.5%, Macklin, Shanghai, China), and zinc nitrate hexahydrate (≥99.0%, Damas-beta, Shanghai, China). Platinum gauze (Pt315) and sandpaper (5000 mesh) were purchased from Tianjin ida. Saturated calomel electrode (CHI150, SCE) was acquired from CH instruments. All of the solutions were prepared using ultrapure water. A CHI660E electrochemical workstation (CH Instruments, Shanghai, China) was used to conduct all of the electrochemical processes.

2.2. Preparation of Zinc Foam and Hydrophobic Zinc Foam

Two high-purity zinc rods were first mechanically polished utilizing sand paper, followed by sonication in 0.5 M H\textsubscript{2}SO\textsubscript{4}, ethanol and pure water in sequence for 10 s, 5 min, and 5 min, respectively, to remove surface impurities. Then, the two zinc rods as work electrode and counter electrode were immersed in the electrolyte, which contains 1.5 M (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and 0.1 M ZnSO\textsubscript{4}·7H\textsubscript{2}O. Later, the electrodeposition was conducted at −1 A cm\textsuperscript{−2} for 0.5 min under a DC workstation. Then, the obtained zinc foam electrodes were rinsed with deionized water and put in a vacuum drying oven to dry overnight.

Zinc foam was used as anode and zinc rod was used as cathode to prepare the hydrophobic zinc foam (denoted as “HPB/Zn”). Additionally, 0.04 M myristic acid (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{12}COOH) and 0.01 M Zn (NO\textsubscript{3})\textsubscript{2}·6(H\textsubscript{2}O) as surface chemical modifier were added to the anhydrous ethanol under constant stirring until dissolved. Then, a DC voltage of −30 V was applied to the two electrodes. The electrodeposition time was set to 0.5, 5, and 10 min to prepare the HPB/Zn−1, HPB/Zn−2, HPB/Zn−3, respectively. After that, the electrodes were rinsed with distilled water and dried in a vacuum oven to dry the whole night. Schematic diagrams of the electrodeposition process of zinc foam and hydrophobic zinc foam were shown in Figure 1.
2.3. Electrocatalytic Tests and Product Inspection

CO$_2$ERR was conducted in a single-chamber and three-electrode membrane microchannel reactor consisting of a pre-mixing section (5.0 m circular microchannels with an inner diameter of 1.0 mm used to pre-saturate CO$_2$ in the electrolyte) and a reaction section (cylindrical cation exchange membrane tube, Nafion 117) with the working electrode located in the center of the Nafion 117 membrane tube (Figure 2). The electrolyte, which acts as both catholyte and anolyte at the same time, was separated by the Nafion 117 membrane tube (Dupont). The Nafion117 membrane was selected in this research due to its high proton conductivity, good mechanical strength, electrochemical and chemical stability. The function of the membrane is to separate the anode and cathode chambers, prevent cathode reduction products from being oxidized, prevent the mixing of the gas products of the anode and the cathode, carry out the proton transfer to make the reaction between the poles proceed smoothly, and maintain the battery circuit. The SCE and Pt gauze worked as the reference electrode and counter electrode, respectively. Before each experiment with Zn-based catalysts, the CO$_2$ from a gas cylinder was mixed with 0.1 M KHCO$_3$ and then passed into a 5-m-long polyethylene pre-mixing tube for full pre-saturation (gas and liquid flow rate were 20 and 10 mL min$^{-1}$, respectively. Then, the pre-saturated electrolyte was passed into the microchannel for the electrochemical test, the carbon dioxide bubbles directly contact the catalyst in the microchannel to reduce the contact distance and improve the mass transfer. The experiments were performed under a constant pressure condition with a potential range of $-1.5$ to $-2.5$ V, the potentials were measured against SCE. Gaseous products were detected by an online gas chromatograph (Synpec M3000) equipped with a thermal conductivity detector (TCD).
3. Results and Discussion

3.1. Characterization of the Electrode

The scanning electron microscopy (SEM) images of zinc foam were shown in Figure 3. As shown in the images, the zinc foam showed numerous honeycomb holes. After magnifying the pore wall, it can be found that the pore wall was composed of many crisscrossed sheet-like Zn. This rough surface structure can increase the active surface area of the catalyst, which was in favor of accelerating the rate of CO$_2$ERR at low potential [20].

Figure 3. SEM images of the electrode of (a,b) zinc foam.

Figure 4 showed the SEM image of the HPB/Zn electrodes with different electrodeposition times, which demonstrated that the hydrophobic layer was successfully grown on the zinc foam electrode, and gradually increased with the increasing deposition time. In the picture, it is not difficult to find that the pore size of HPB/Zn$-3$ was smaller than that of HPB/Zn$-1$. Judging from the law that has been obtained, we can guess that if the electrodeposition time continues to increase, the pore size of the electrode will continue to decrease, resulting in a reduction in active surface area, which ultimately leads to a lower selectivity of the CO product. Therefore, this work did not continue to study the electrode obtained with a longer deposition time.
the zinc foam had the same internal structure. Table 1 showed the contact angles (CA) for different hydrophobic electrodes. The zinc foam reached a hydrophilic state, with the CA of almost zero. The HPB/Zn−3 showed the largest CA of 147° compared with HPB/Zn−1 and HPB/Zn−2. The CA results proved that just a small part of the hydrophobic surface was wetted by the electrolyte, thus the CO₂ gas was trapped between the surface of the hydrophobic electrode and electrolyte, forming a large number of three-phase interfaces [26], which is consistent with the results displayed in the SEM images.

Table 1. Hydrophobic results of catalysts for different electrodeposited times.

| Electrodeposition Time | 0       | 0.5 min | 5 min  | 10 min  |
|------------------------|---------|---------|--------|---------|
| Hydrophobic result      | All infiltrated |
| Water contact angle     | Almost zero | 136° | 141° | 149° |

Figure 4. SEM images of the electrodes of (a,b) HPB/Zn−1, (c,d) HPB/Zn−2, (e,f) HPB/Zn−3.

However, the smaller pore size may mean a lower CO₂ERR reaction rate and poorer CO product selectivity. Under high magnification, it could be seen that the HPB/Zn and the zinc foam had the same internal structure. Table 1 showed the contact angles (CA) for different hydrophobic electrodes. The zinc foam reached a hydrophilic state, with the CA of almost zero. The HPB/Zn−3 showed the largest CA of 147° compared with HPB/Zn−1 and HPB/Zn−2. The CA results proved that just a small part of the hydrophobic surface was wetted by the electrolyte, thus the CO₂ gas was trapped between the surface of the hydrophobic electrode and electrolyte, forming a large number of three-phase interfaces [26], which is consistent with the results displayed in the SEM images.

Table 1. Hydrophobic results of catalysts for different electrodeposited times.

| Electrodeposition Time | 0       | 0.5 min | 5 min  | 10 min  |
|------------------------|---------|---------|--------|---------|
| Hydrophobic result      | All infiltrated |
| Water contact angle     | Almost zero | 136° | 141° | 149° |
3.2. The Formation Mechanism of the Hydrophobic Layer

Figure 1a showed the formation mechanism of zinc foam. After power up, zinc ions moved to the cathode and were reduced to zinc on the zinc rod. At the same time, the free H\(^+\) ions near the cathode discharged to form H\(_2\) made the zinc foam have a loose and porous structure. The reaction formulas of the cathode are as follows:

\[
\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad (1)
\]

\[
\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow \quad (2)
\]

Figure 1b showed the formation mechanism of hydrophobic zinc foam. At first, the CH\(_3\)(CH\(_2\))\(_{12}\)COOH ionized to form lots of free H\(^+\) ions and CH\(_3\)(CH\(_2\))\(_{12}\)COO\(^-\) ions. At the same time, the free H\(^+\) ions around the surface of cathode got electrons to produce H\(_2\) and then separated from the system, leaving abundant CH\(_3\)(CH\(_2\))\(_{12}\)COO\(^-\) [21]. CH\(_3\)(CH\(_2\))\(_{12}\)COO\(^-\) moved to the anode under the imposed DC voltage between the two electrodes and reacted with the zinc ions (Zn\(^{2+}\)) to generate the zinc myristate (Zn(CH\(_3\)(CH\(_2\))\(_{12}\)COO)\(_2\)) on zinc foam electrode. The presence of low-free-energy functional groups of -CH\(_2\) and -CH\(_3\), and the loose morphology led to the hydrophobic zinc foam with excellent hydrophobic property [22]. The reaction formula of the anode is as follows:

\[
\text{Zn} - 2e^- \rightarrow \text{Zn}^{2+} \quad (3)
\]

\[
\text{Zn}^{2+} + 2\text{CH}_3(\text{CH}_2)_{12}\text{COOH} \rightarrow \text{Zn}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_2 + 2\text{H}^+ \quad (4)
\]

3.3. Performance on CO\(_2\) Reduction

To find out the influence of electrodes wettability on the CO\(_2\)ERR performance, the performance of zinc foam and HPB/Zn were experimented in a microchannel electrochemical device. As shown in Figure 5a, the HPB/Zn showed a higher selectivity for CO production (FE\(_\text{CO} \geq 80\%\)) at −1.5~−2.5 V (vs. SCE) compared with zinc foam. The highest FE\(_\text{CO}\) of HPB/Zn=1, HPB/Zn=2, and HPB/Zn=3 were 91.8%, 91.8%, and 90.12%, respectively, at −1.9 V (vs. SCE). However, the zinc foam electrode showed a lower selectivity for CO production (FE\(_\text{CO} = 81.87\%\), at −1.9 V vs. SCE). When the potential was below −1.7 V (vs. SCE), FE\(_\text{CO}\) of zinc foam began to decrease, but the hydrophobic zinc foam still maintained relatively stable at high potential. The hydrophobic zinc foam improved the selectivity of CO as it can facilitate the transport of CO\(_2\) gas to the catalyst layer through the gas phase, reduce the distance of the liquid electrolyte required for the diffusion of CO\(_2\) gas to the catalyst layer, which accelerated the transport of CO\(_2\) to the catalyst and increased the steady concentration of CO\(_2\) near the catalyst [27]. The decreased selectivity of CO on zinc foam electrode at high potential may be ascribed to the insufficient supply of CO\(_2\). The FE\(_\text{H}_2\) of HPB/Zn=1, HPB/Zn=2, and HPB/Zn=3 were shown in Figure 5b. The lower FE\(_\text{H}_2\) compared to the zinc foam electrode, which means that the hydrogen evolution reaction was greatly suppressed after hydrophobic modification. HPB/Zn=1 showed the highest FE\(_\text{CO}\) compared with the other three catalysts at a potential range between −1.5 and −2.5 V (vs. SCE) (Figure 5c). The high efficiency of HPB/Zn=1 can be probably ascribed to its unique morphology and excellent hydrophobic effect. The hydrophobic surface inhibited the HER and created rich three-phase contact points that provided sufficient CO\(_2\) [23].

For hydrophilic electrodes, the side reaction of hydrogen reduction is dominant at high current density, as the direct HER is more kinetically favorable than CO\(_2\) reduction and the concentration is much larger than the dissolved CO\(_2\) [28]. As shown in Figure 5c, the hydrophobic zinc foam successfully suppressed the hydrogen evolution reaction at a relatively high current density. The FE\(_\text{CO} = 88.46\%\) at −13 mA cm\(^{-2}\), whereas FE\(_\text{CO}\) of zinc foam was only 69.98\%, which further illustrated the beneficial effects of hydrophobic modification. To assess the long-term performance of HPB/Zn=1 electrode, a 10 h stability test was conducted at −1.9 V (vs. SCE). As shown in Figure 5d, the current density was stable at −6 mA cm\(^{-2}\) and the FE\(_\text{CO} (=91\%)\) remained essentially unchanged over 10 h. This result showed that the catalyst layer is stable throughout the long-term test.
Let us assume the presence of gaseous reactant inside the electrode layer, leading to an insufficient electrical contact between the HPB/Zn electrode and the electrolyte solution. To verify this guess, we compared the electrochemically active surface area (ECSA) of zinc foam and hydrophobic zinc foam. The ECSA and the electrochemical double-layer capacitance is in proportion, which represents the area of an electrode that is wetted and accessible to the electrolyte [27] and can be measured by cyclic voltammetry (CV) [29]. The experiment was carried out in the N2-saturated 0.1 M KHCO3 electrolyte solution. The scan rates were 25, 50, 75, 100, 125, 150, 175, and 200 mV/s, respectively. The scanning voltage range was −1.15~−1.3 V (vs. Ag/AgCl). In this voltage range, there is no redox reaction and electron transfer, only the charge and discharge of the electric double layer on the electrode surface occurs. The results of CV were shown in Figure 6.

The double-layer charging current was plotted against the scan rate and the slope of the linear regression gave the double-layer capacitance, as shown in Figure 7a. The capacitances of the hydrophobic zinc foam were all lower than the zinc foam, for example, the capacitance of HPB/Zn−1 is 0.25 mF cm−2, which was almost half of the zinc foam (0.468 mF cm−2). These decreased capacitances were attributed to the reduced interfacial area between the solid catalytic surface and liquid electrolyte solution, supporting the idea of its increased triple-phase reaction interfaces. Figure 7b indicates that the HPB/Zn electrodes had a smaller charge-transfer resistance (Rct), the Rct order of these electrodes was 2.8 Ω (HPB/Zn−1) < 3.1 Ω (HPB/Zn−2) < 12.9 Ω (HPB/Zn−3) < 21.5 Ω (zinc foam). This conclusion was in connection with a faster mass transfer of the CO2, which was consistent with former results [26].
The double-layer charging current was plotted against the scan rate and the slope of the linear regression gave the double-layer capacitance, as shown in Figure 7a. The capacitances of the hydrophobic zinc foam were all lower than the zinc foam, for example, the capacitance of \( \text{HPB/Zn}^{-1} \) is 0.25 mF cm\(^{-2}\), which was almost half of the zinc foam (0.468 mF cm\(^{-2}\)). These decreased capacitances were attributed to the reduced interfacial area between the solid catalytic surface and liquid electrolyte solution, supporting the idea of its increased triple-phase reaction interfaces. Figure 7b indicates that the HPB/Zn electrodes had a smaller charge-transfer resistance (\( R_{ct} \)), the \( R_{ct} \) order of these electrodes was 
\[
2.8 \, \Omega (\text{HPB/Zn}^{-1}) < 3.1 \, \Omega (\text{HPB/Zn}^{-2}) < 12.9 \, \Omega (\text{HPB/Zn}^{-3}) < 21.5 \, \Omega (\text{zinc foam})
\]
This conclusion was in connection with a faster mass transfer of the CO\(_2\), which was consistent with former results [26].

4. Conclusions

To sum up, we successfully prepared hydrophobic zinc foam electrodes by the electrodeposition method, which exhibited high CO selectivity. The FE\(_{\text{CO}}\) can reach 91.8% at a potential of \(-1.9\) V (vs. SCE) with a current density of \(-5.16\) mA cm\(^{-2}\). Under relatively
higher current density (−13 mA cm⁻²), it could still achieve high FE_{CO} of 88.46%. A long-term stability test on the hydrophobic electrode found that the current density kept steady over 10 h in −1.9 V vs. SCE. The improved electrocatalytic selectivity of electrode was due to the enlarged number of triple-phase active sites at the electrode-electrolyte interface. This study provides a feasible way to improve the selectivity of CO₂ electrochemical reduction by tuning the wettability.

Author Contributions: Conceptualization, J.L. and Q.H.; methodology, S.Y.; investigation, J.Z.; supervision, Z.C. and B.Z.; data curation, C.Z.; writing—original draft preparation, C.Z.; writing—review and editing, S.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data collected in this study are contained within the article.

Conflicts of Interest: There are no conflicts to declare.

References

1. Park, G.; Hong, S.; Choi, M.; Lee, S.; Lee, J. Au on highly hydrophobic carbon substrate for improved selective CO production from CO₂ in gas-phase electrolytic cell. *Catal. Today* 2020, 355, 340–346. [CrossRef]

2. Zhai, P.; Gu, X.; Wei, Y.; Zuo, J.; Chen, Q.; Liu, W.; Jiang, H.; Wang, X.; Gong, Y. Enhanced mass transfer in three-dimensional single-atom nickel catalyst with open-pore structure for highly efficient CO₂ electrolysis. *J. Energy Chem.* 2021, 62, 43–50. [CrossRef]

3. Luo, W.; Zhang, J.; Li, M.; Züttel, A. Boosting CO Production in Electrocatalytic CO₂ Reduction on Highly Porous Zn Catalysts. *ACS Catal.* 2019, 9, 3783–3791. [CrossRef]

4. Chen, Y.; Li, C.W.; Kanan, M.W. Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Soc.* 2012, 134, 19969–19972. [CrossRef]

5. Li, Y.; Chen, C.; Cao, R.; Pan, Z.; He, H.; Zhou, K. Dual-atom Ag₂/graphene catalyst for efficient electroreduction of CO₂ to CO. *Appl. Catal. B Environ.* 2020, 268, 118747. [CrossRef]

6. Jee, M.S.; Jeon, H.S.; Kim, C.; Lee, H.; Koh, J.H.; Cho, J.; Min, B.K.; Hwang, Y.J. Enhancement in carbon dioxide activity and stability on nanostructured silver electrode and the role of oxygen. *Appl. Catal. B Environ.* 2016, 180, 372–378. [CrossRef]

7. Koh, J.H.; Jeon, H.S.; Jee, M.S.; Nursanto, E.B.; Lee, H.; Hwang, Y.J.; Min, B.K. Oxygen Plasma Induced Hierarchically Structured Gold Electrocatalyst for Selective Reduction of Carbon Dioxide to Carbon Monoxide. *J. Phys. Chem. C* 2014, 119, 883–889. [CrossRef]

8. Rosen, J.; Hutchings, G.S.; Lu, Q.; Forest, R.V.; Moore, A.; Jiao, F. Electrodeposited Zn Dendrites with Enhanced CO Selectivity for Electrocatalytic CO₂ Reduction. *ACS Catal.* 2015, 5, 4586–4591. [CrossRef]

9. Jiang, X.; Cai, F.; Gao, D.; Dong, J.; Miao, S.; Wang, G.; Bao, X. Electrocatalytic reduction of carbon dioxide over reduced nanoporous zinc oxide. *Electrochem. Commun.* 2016, 68, 67–70. [CrossRef]

10. Xiao, J.; Gao, M.R.; Liu, S.; Luo, J.L. Hexagonal Zn Nanoplates Enclosed by Zn (100) and Zn (002) Facets for Highly Selective CO₂ Electroreduction to CO. *ACS Appl. Mater. Interfaces* 2020, 12, 31431–31438. [CrossRef]

11. Lu, Y.; Han, B.; Tian, C.; Wu, J.; Geng, D.; Wang, D. Efficient electrocatalytic reduction of CO₂ to CO on an electrodeposited Zn porous network. *Electrochem. Commun.* 2018, 97, 87–90. [CrossRef]

12. Xiang, Q.; Li, F.; Wang, J.; Chen, W.; Miao, Q.; Zhang, Q.; Tao, P.; Song, C.; Shang, W.; Zhu, H.; et al. Heterostructure of ZnO Nanosheets/Zn with a Highly Enhanced Edge Surface for Efficient CO₂ Electrocatalytic Reduction to CO. *ACS Appl. Mater. Interfaces* 2021, 13, 10837–10844. [CrossRef]

13. Guo, M.; Li, X.; Huang, Y.; Li, L.; Li, J.; Lu, Y.; Xu, Y.; Zhang, L. CO₂-Induced Fibrous Zn Catalyst Promotes Electrochemical Reduction of CO₂ to CO. *Catalysts* 2021, 11, 477. [CrossRef]

14. Raciti, D.; Mao, M.; Park, J.H.; Wang, C. Mass transfer effects in CO₂ reduction on Cu nanowire electrocatalysts. *Catal. Sci. Technol.* 2018, 8, 2364–2369. [CrossRef]

15. Vennekoeijer, J.B.; Sengpiel, R.; Wessling, M. Beyond the catalyst: How electrode and reactor design determine the product spectrum during electrochemical CO₂ reduction. *Chem. Eng. J.* 2019, 364, 89–101. [CrossRef]

16. Wakerley, D.; Lamaison, S.; Oznam, F.; Menguy, N.; Mercier, D.; Marcus, P.; Fontecave, M.; Mougel, V. Bio-inspired hydrophobicity promotes CO₂ reduction on a Cu surface. *Nat. Mater.* 2019, 18, 1222–1227. [CrossRef]

17. Li, A.; Cao, Q.; Zhou, G.; Schmidt, B.; Zhu, W.; Yuan, X.; Huo, H.; Gong, J.; Antonietti, M. Three-Phase Photocatalysis for the Enhanced Selectivity and Activity of CO₂ Reduction on a Hydrophilic Surface. *Angew. Chem.* 2019, 58, 14549–14555. [CrossRef] [PubMed]
18. Lin, J.; Tian, J.; Cheng, X.; Tan, J.; Wan, S.; Lin, J.; Wang, Y. Propane ammoxidation over MoVTeNb oxide catalyst in a microchannel reactor. *AIChE J.* 2018, 64, 4002–4008. [CrossRef]

19. Yue, J.; Chen, G.; Yuan, Q.; Luo, L.; Gonthier, Y. Hydrodynamics and mass transfer characteristics in gas–liquid flow through a rectangular microchannel. *Chem. Eng. Sci.* 2007, 62, 2096–2108. [CrossRef]

20. Zhang, F.; Chen, C.; Tang, Y.; Cheng, Z. CO₂ reduction in a microchannel electrochemical reactor with gas-liquid segmented flow. *Chem. Eng. J.* 2020, 392, 124798. [CrossRef]

21. Liu, Y.; Xue, J.; Luo, D.; Wang, H.; Gong, X.; Han, Z.; Ren, L. One-step fabrication of biomimetic superhydrophobic surface by electrodeposition on magnesium alloy and its corrosion inhibition. *J. Colloid Interface Sci.* 2017, 491, 313–320. [CrossRef] [PubMed]

22. Yang, Z.; Liu, X.; Tian, Y. Fabrication of super-hydrophobic nickel film on copper substrate with improved corrosion inhibition by electrodeposition process. *Colloid Surf. A* 2019, 560, 205–212. [CrossRef]

23. Lv, K.; Teng, C.; Shi, M.; Yuan, Y.; Zhu, Y.; Wang, J.; Kong, Z.; Lu, X.; Zhu, Y. Hydrophobic and Electronic Properties of the E-MoS₂ Nanosheets Induced by FAS for the CO₂ Electroreduction to Syngas with a Wide Range of CO/H₂ Ratios. *Adv. Funct. Mater.* 2018, 28, 1802339. [CrossRef]

24. Weekes, D.M.; Salvatore, D.A.; Reyes, A.; Huang, A.; Berlinguette, C.P. Electrolytic CO₂ Reduction in a Flow Cell. *Acc. Chem. Res.* 2018, 51, 910–918. [CrossRef]

25. Cai, Z.; Zhang, Y.; Zhao, Y.; Wu, Y.; Xu, W.; Wen, X.; Zhong, Y.; Zhang, Y.; Liu, W.; Wang, H.; et al. Selectivity regulation of CO₂ electroreduction through contact interface engineering on superwetting Cu nanoarray electrodes. *Nano Res.* 2018, 12, 345–349. [CrossRef]

26. Yue, P.; Fu, Q.; Li, J.; Zhang, L.; Xing, L.; Kang, Z.; Liao, Q.; Zhu, X. Triple-phase electrocatalysis for the enhanced CO₂ reduction to HCOOH on a hydrophobic surface. *Chem. Eng. J.* 2021, 405, 126975. [CrossRef]

27. Xing, Z.; Hu, L.; Ripatti, D.S.; Hu, X.; Feng, X. Enhancing carbon dioxide gas-diffusion electrolysis by creating a hydrophobic catalyst microenvironment. *Nat. Commun.* 2021, 12, 136. [CrossRef]

28. Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* 2014, 43, 631–675. [CrossRef]

29. Waszczyk, P.; Zelenay, P.; Sobkowski, J. Surface interaction of benzoic acid with a copper electrode. *Electrochim. Acta* 1995, 40, 5. [CrossRef]