

Article

Electrochemical Reduction of Gaseous CO₂ at Low-Intermediate Temperatures Using a Solid Acid Membrane Cell

Jae Young Kim ^{1,*} and Duck Hyun Youn ^{2,*} 

¹ Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea

² Department of Chemical Engineering, Department of Integrative Engineering for Hydrogen Safety, Kangwon National University, Chuncheon 24341, Republic of Korea

* Correspondence: jaeykim@kricr.re.kr (J.Y.K.); youndh@kangwon.ac.kr (D.H.Y.)

Abstract: In this study, the electrochemical reduction of gaseous carbon dioxide (CO₂) at low-intermediate temperatures (~250 °C) using a solid acid membrane cell was demonstrated, for the first time. Compared to solid oxide fuel cells, which operate at higher temperatures (>600 °C), this system can utilize the advantage of gaseous CO₂ reduction, while being considerably more simply implemented. A Cu-based electrocatalyst was developed as a cathode side catalyst for electrochemical reduction of gaseous CO₂ and specifically demonstrated its efficacy to produce hydrocarbons and liquid fuels. The result is significant in terms of resolving the challenges associated with producing hydrocarbons and liquid fuels from CO₂ reduction. The present study introduced the novel system with the solid acid membrane cell and the Cu-based catalyst for electrochemically reducing gaseous CO₂. This system showed a new possibility for electrochemical reduction of gaseous CO₂, as it operates at lower temperatures, produces hydrocarbons and liquid fuels and has plenty of room for improvement.

Keywords: carbon dioxide; electrochemical reduction; gas phase; solid acids; low temperatures



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1. Introduction

Carbon dioxide (CO₂) reduction has attracted enormous attention as a solution for the utilization of CO₂, a greenhouse gas [1,2]. CO₂ is an abundant and inexpensive carbon source for generating fuels and useful chemical products. The reduction of CO₂ is a fundamental step of artificial photosynthesis, making it an important technology for a renewable energy-reliant society [3,4]. When compared to other CO₂ reduction methods, electrochemical CO₂ reduction has one advantage: it can be biased by the external voltage, allowing the reaction to take on multiple forms as different voltages are applied [5,6]. Recent reviews have focused on not only potential catalysts for the electrochemical reduction of CO₂ [7–9], but also electrodes, reactor configurations, and techno-economic analysis [10–13].

Some studies have investigated the electrochemical reduction of CO₂ in gaseous and aqueous phases, but, to the best of our knowledge, there have been very few studies on the electrochemical reduction of CO₂ in the gas phase. Gas phase CO₂ reduction has some definite merits, compared to aqueous phase CO₂ reduction, due to the high capacity of CO₂ and the absence of the competitive H₂O reduction reaction. For that reason, studies have recently been conducted to understand the detailed sides of electrochemical reduction of gaseous CO₂ and to develop more feasible systems for it [14–18].

Interestingly, most techniques for the electrochemical reduction of gaseous CO₂ have utilized solid oxide fuel cells (SOFCs) at very high temperatures (>600 °C) [19,20]. Furthermore, mainly aqueous CO₂ has been investigated for electrochemical reduction at ambient temperature [21–24]. Herein, we report the first ever electrochemical reduction of gaseous CO₂ using a solid acid membrane cell at low-intermediate temperatures (150–250 °C). This system can utilize the benefits of gaseous CO₂ reduction, including the high capacity of

CO₂ and absence of the competitive H₂O reduction reaction, and can be realized much more easily, compared to SOFCs, which operate at higher temperatures. The system is described schematically in Figure 1. A solid acid membrane cell contains three parts: the proton conducting membrane (solid acid), the anode, and the cathode. Gaseous hydrogen and CO₂ are oxidized and reduced at each electrode, respectively. Protons move from the anode side to the cathode side through the membrane as a result of hydrogen oxidation.

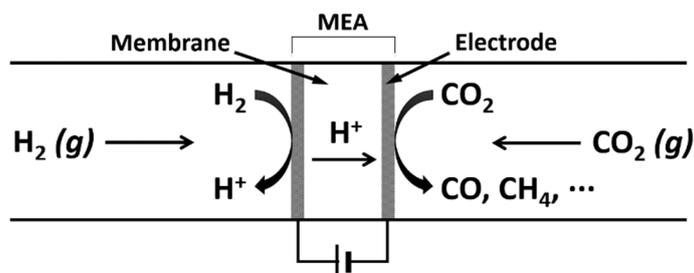


Figure 1. Schematic of a solid acid membrane cell for electrochemical reduction of gaseous CO₂. Gaseous hydrogen and CO₂ oxidized and reduced, respectively, at each electrode. Protons move from the anode side to the cathode side through the membrane as a result of hydrogen oxidation.

Cesium dihydrogen phosphate (CsH₂PO₄), a representative of superprotonic solid acids, was selected for this approach, owing to its high proton conductivity in the solid state. Superprotonic solid acids (MH_nXO₄, M = Na, K, Cs, X = P, S, and Se) are known for their high solid-state anhydrous proton conductivities at temperatures above their superprotonic transition temperature [25,26]. For CsH₂PO₄, the superprotonic transition temperature is ~241 °C [27,28]. The material exhibits a proton conductivity of ~10⁻² S/cm above this temperature, owing to transition to a highly disordered cubic structure.

The anode and cathode side catalysts chosen for hydrogen oxidation and CO₂ reduction were platinum (Pt) and Copper (Cu), respectively. Cu is one of the most efficient electrocatalysts for CO₂ reduction [29,30]. In the present study, Cu showed its efficacy to produce hydrocarbons and liquid fuels from electrochemical CO₂ reduction using a solid acid membrane cell. It is one of the first reported results by the present study, and it has some significance in terms of resolving the difficulty of producing hydrocarbons and liquid fuels from CO₂ reduction.

2. Results

2.1. Characterization of the Solid Acid Membrane

First, CsH₂PO₄ was readily synthesized by a simple precipitation method, and its crystal structure was confirmed by X-ray diffraction (XRD) patterns (Figure S1, reference: JCPDS Card No. 76-1836) [25,31], and electrochemical impedance spectroscopy (EIS) was used to determine its proton conductivity (Figure 2A). The detailed test conditions are described in the experimental section. The conductivity was determined to be ~10⁻² S·cm⁻², which was consistent with the well-known value of CsH₂PO₄ [25].

Figure 2B shows the typical current density–voltage curves for the Pt/CsH₂PO₄/Cu and Pt/CsH₂PO₄/Pt membrane electrode assemblies (MEAs) at 250 °C supplied with humid (0.4 atm H₂O) hydrogen and CO₂ to its anode and cathode sides, respectively. The current increased exponentially as larger amounts of bias voltage were applied. For the Pt/CsH₂PO₄/Cu, the current rapidly began to increase at 0.5 V. This could be due to the activation of electrochemical reduction reactions [19]. Various CO₂ reduction products formed, competing with proton reduction. The Pt/CsH₂PO₄/Pt current density–voltage curve, which had Pt as its cathode side catalyst, was also recorded (black solid line of Figure 2B). The properties were slightly different at voltages > 0.5 V. The curve for the Pt/CsH₂PO₄/Cu had an exponential shape, whereas that of the Pt/CsH₂PO₄/Pt had a linear shape. This was probably due to the nature of the electrochemical CO₂ reduction products. As discussed later, CO (carbon monoxide) was the major product for the

Pt/CsH₂PO₄/Pt, while several kinds of products (CO, CH₄, C₂H₆, C₂H₄, C₂H₂, CH₃OH, HCOOH) were somewhat evenly observed for the Pt/CsH₂PO₄/Cu (Tables S3 and S4). Various reaction pathways could be one reason for the various inflection points of the current density–voltage curves. In the current system, hydrogen was also produced via proton reduction. There have been investigations into different approaches for inhibiting proton reduction.

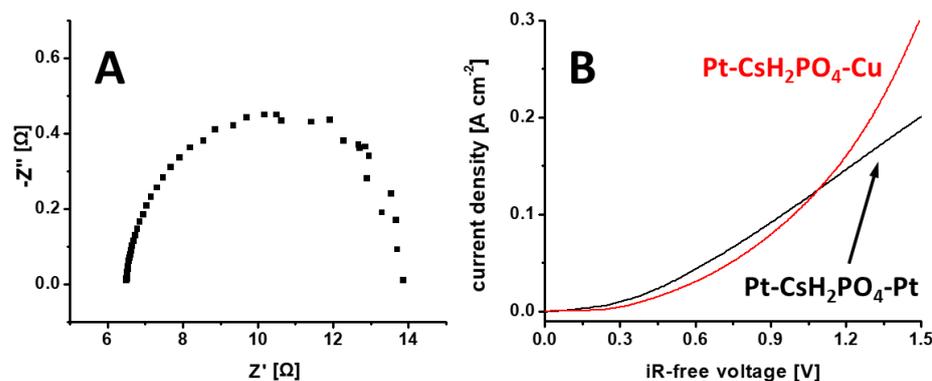


Figure 2. (A): Impedance spectrum for the Pt/CsH₂PO₄/Cu MEA for determining the proton conductivity (surface area: 1 cm², thickness: 0.06 mm); (B): Current density–voltage curves for the Pt/CsH₂PO₄/Cu and Pt/CsH₂PO₄/Pt MEAs recorded under the same environment for the analysis of CO₂ reduction products (H₂/CO₂ (0.4 atm H₂O for both), 250 °C, scan rate: 10 mV·s^{−1}).

2.2. Analysis of CO₂ Reduction Products

The products from the electrochemical reduction of gaseous CO₂ were analyzed using the Pt/CsH₂PO₄/Cu and Pt/CsH₂PO₄/Pt MEAs under −2 V constant cell voltage for time durations ranging from 0 to 130 min. Tables S3 and S4 display the detailed information of the products, including the results in terms of mol per area and Faradaic efficiency. As shown in Table S3, some major products (CO and CH₄) and minor products (C₂H₆, C₂H₄, C₂H₂, CH₃OH, and HCOOH) were detected for the Pt/CsH₂PO₄/Cu. For the Pt/CsH₂PO₄/Pt, CO was predominantly detected, and minor products, such as C₂H₄, C₂H₂, and CH₃OH, were not detected (Table S4). The result was significant for resolving the challenges associated with generating hydrocarbons and liquid fuels from CO₂ reduction.

Figure 3A shows the evolution of the two major products (CO and CH₄). The tendencies for Pt/CsH₂PO₄/Cu and Pt/CsH₂PO₄/Pt exhibited a substantial difference. A significant amount of CH₄ was evolved for the Pt/CsH₂PO₄/Cu, compared to CO. On the other hand, CH₄ evolution was negligible for the Pt/CsH₂PO₄/Pt, whereas CO accounted for most of the products. The tendency was more clearly revealed when Faradaic efficiencies were compared (Figure 3B). The Faradaic efficiency of CH₄ increased by about 10 times when the cathode electrocatalyst was changed from Pt to Cu. Other hydrocarbons (C₂H₄ and C₂H₂) evolved only for the Pt/CsH₂PO₄/Cu (Table S3). According to these results, Cu was a better electrocatalyst for hydrocarbon production than CO, and Pt could hardly promote hydrocarbon production. Furthermore, the present study is the first to report the electrochemical reduction of CO₂ using a solid acid membrane cell, producing CO, methanol, acetic acid, and various hydrocarbon products. According to previous studies, the possible mechanism could involve adsorbed anion radical CO₂[−] as an intermediate [32,33]. When CO₂ is reduced to radical CO₂[−] through a mono-electron transfer at Cu, the radical is adsorbed at the surface of Cu. Unlike Pt, Cu suppresses proton reduction to increase the production of hydrocarbons rather than H₂ or CO.

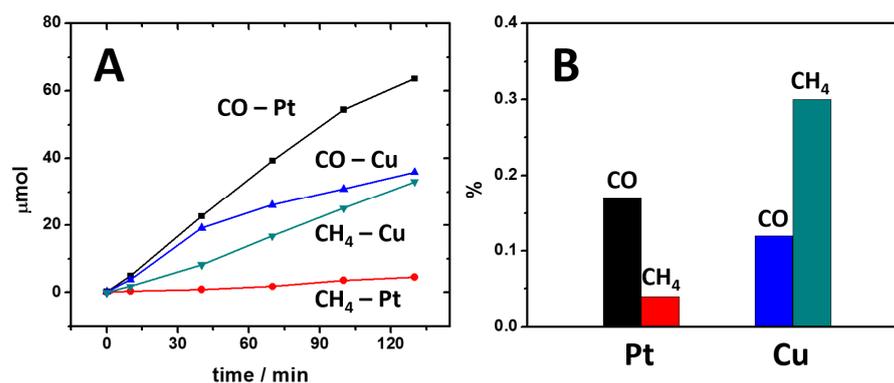


Figure 3. (A): Evolution curves for the two major products (CO and CH₄) from the electrochemical reduction of gaseous CO₂ with the Pt/CsH₂PO₄/Cu and Pt/CsH₂PO₄/Pt MEAs (surface area: 1 cm², thickness: 0.06 mm); (B): Comparison diagram (Faradaic efficiency) for the two major products (CO and CH₄) from the electrochemical reduction of gaseous CO₂ with the Pt/CsH₂PO₄/Cu and Pt/CsH₂PO₄/Pt MEAs (H₂/CO₂ (0.4 atm H₂O for both), 250 °C).

The stability of the Pt/CsH₂PO₄/Cu was investigated, as shown in Figure S2. The current density was recorded at a -2 V constant cell voltage during the electrochemical reduction of CO₂. The current density maintained its original value of ~ 100 mA cm⁻² for up to 6 h, demonstrating the good stability of the CsH₂PO₄ cell.

3. Discussion

According to the results, it was shown that a solid acid membrane cell operating at low-intermediate temperatures (~ 250 °C) could implement the novel system for electrochemically reducing gaseous CO₂. The solid acid membrane cell became more feasible with H₂ and Cu, because H₂ and Cu are representative of proton source and catalyst for hydrocarbon production, respectively. A Cu-based electrocatalyst was prepared as the cathode side catalyst of the cell and demonstrated its efficacy in producing hydrocarbons (CH₄, C₂H₆, C₂H₄, and C₂H₂) and liquid fuels (CH₃OH and HCOOH). It is worth noting that liquid fuels have hardly been observed as products of electrochemical reduction of gaseous CO₂ owing to the high operating temperatures of SOFCs (>600 °C) [1,19,20], but the temperature with the current cell could be reduced to ~ 250 °C, allowing for liquid fuels, such as CH₃OH and HCOOH, to be observed with Cu as the cathode side catalyst.

On the other hand, the overall Faradaic Efficiency remained in low values and there are some possible reasons for this; competitive proton reduction, large catalytic particle size, and weak triple phase boundaries (boundaries among catalytic particles and electrolyte and reactant gas). To solve this problem, reducing catalytic particle size is the first possible solution so that the active catalytic area for CO₂ reduction can be enlarged. Including this approach, attempts have been made to increase the overall efficiency.

4. Materials and Methods

4.1. MEA Synthesis

The CsH₂PO₄ was synthesized from a stoichiometric mixture of cesium carbonate (99.5% Cs₂CO₃, Fisher Scientific, Pittsburgh, PA, USA) and o-phosphoric acid (85% H₃PO₄, Fisher Scientific, Pittsburgh, PA, USA) in an aqueous solution. After 48 h of stirring, excess amounts of methanol were added to the solution to precipitate CsH₂PO₄. The precipitate was filtered and dried. To fabricate MEA with CsH₂PO₄, the mixtures of catalyst powders and CsH₂PO₄ were prepared (Table S1). In detail, the catalyst powder (Pt or Cu) of 0.4 mg and CsH₂PO₄ of 1.2 mg were dispersed in 2-propanol of 3 mL to be dropped on carbon paper (TGP-H-060, Toray, Tokyo, Japan). The target amount was 0.4 mg/cm² for the Pt or Cu catalyst and 1.2 mg/cm² for CsH₂PO₄. The carbon paper was cut into a circle (diameter ~ 1.3 cm) before dropping the mixture so that the electrode (carbon paper coated with the catalyst-CsH₂PO₄ mixture) could be placed in a die for pressing. To fabricate an MEA

pellet, the MEA components were placed in a die in the following order: the anode, 0.5 g of CsH_2PO_4 , and the cathode before pressing (20 MPa, 5 min). The thickness of the pellet was ~ 0.06 mm. Electrical contact was made using silver epoxy and wires at each side of the MEA pellet. The final cell had an active surface area of 1 cm^2 .

4.2. Electrochemical CO_2 Reduction

The MEA was placed in the cell designed to feed gases to each side of the MEA separately (Figure 1). The solid acid membrane cell and 2 input lines of ~ 25 cm for each anode/cathode side (~ 50 cm in total) were buried in the tubular furnace and the system temperature was controlled within the furnace. The temperature was ramped up to the target temperature ($250 \text{ }^\circ\text{C}$) at $2 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under dry argon. Humid hydrogen and CO_2 ($0.4 \text{ atm H}_2\text{O}$) started to flow to the anode and cathode sides of the MEA, respectively, after the system had reached the target temperature. All electrochemical measurements were carried out using a Metrohm Autolab PGSTAT128 potentiostat. AC impedance spectra were recorded at the open circuit voltage (OCV) of the cell and an AC potential frequency range of $100,000\text{--}0.1 \text{ Hz}$ with an amplitude of 10 mV . Linear sweep voltammetry (LSV) was performed at a $10 \text{ mV}\cdot\text{s}^{-1}$ scan rate. For analysis of the CO_2 reduction products, the cathode chamber was filled with CO_2 before closing the inlet and outlet ports. We applied a -2 V constant cell voltage for various time durations during the electrochemical reduction of CO_2 . The CO_2 reduction products were analyzed by gas chromatography (GC, GC-2014, Shimadzu Scientific Instruments Inc., Columbia, MD, USA) and GC-MS. The Faradaic efficiency of the CO_2 reduction products was calculated using the following equation: Faradaic efficiency [%] = (moles of the product produced for the time duration) \times (number of electrons required to produce one molecule of the product via CO_2 reduction) $\times 100\%$ / (moles of electrons passing through the cell for the time duration). The number of electrons required to produce one molecule of each product is shown in Table S2.

5. Conclusions

In conclusion, the solid acid membrane cell was introduced for the first time as a novel electrochemical system for gaseous CO_2 reduction. It was demonstrated that a solid acid membrane cell could be utilized for electrochemically reducing gaseous CO_2 , operating at low-intermediate temperatures ($\sim 250 \text{ }^\circ\text{C}$). A Cu-based electrocatalyst was successfully prepared as the cathode side catalyst of the cell and demonstrated that it was particularly effective at producing hydrocarbons (CH_4 , C_2H_6 , C_2H_4 , and C_2H_2) and liquid fuels (CH_3OH and HCOOH). The result is significant in terms of resolving the challenges associated with producing hydrocarbons and liquid fuels from CO_2 reduction. These results indicate that the electrochemical reduction of gaseous CO_2 using a solid acid membrane cell is a promising approach for utilizing CO_2 and obtaining useful gas products. This work is the first known example of such a CO_2 reduction approach. On the other hand, the overall efficiency remained in low values. Some attempts have been made to inhibit proton reduction and increase the overall efficiency. There is plenty of room for improvement.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12121504/s1>, Figure S1: X-ray diffraction pattern of the synthesized CsH_2PO_4 ; Figure S2: Current density–time curve for the Pt/ CsH_2PO_4 /Cu with -2 V constant cell voltage for the time duration during which CO_2 was electrochemically reduced; Table S1: Composition of the mixture to be deposited on the carbon paper to fabricate the Pt-based or Cu-based electrode for the membrane-electrode assembly (MEA) with CsH_2PO_4 ; Table S2: Number of electrons required to produce one molecule of each product via CO_2 reduction; Table S3: Produced concentration [$\mu\text{mol}/\text{cm}^2$] and Faradaic efficiency (F.E. [%]) of the products from the electrochemical reduction of gaseous CO_2 with the Pt- CsH_2PO_4 -Cu MEA; Table S4: Produced concentration [$\mu\text{mol}/\text{cm}^2$] and Faradaic efficiency (F.E. [%]) of the products from the electrochemical reduction of gaseous CO_2 with the Pt- CsH_2PO_4 -Cu MEA.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Spinner, N.S.; Vega, J.A.; Mustain, W.E. Recent progress in the electrochemical conversion and utilization of CO₂. *Catal. Sci. Technol.* **2012**, *2*, 19–28. [[CrossRef](#)]
2. Studt, F.; Sharafutdinov, I.; Abild-Pederson, F.; Elkjar, C.F.; Hummelshøj, J.S.; Dahl, S.; Chorkendorff, I.; Norskov, J.K. Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* **2014**, *6*, 320–324. [[CrossRef](#)] [[PubMed](#)]
3. Tachibana, Y.; Vayssieres, L.; Durrant, J.R. Artificial photosynthesis for solar water-splitting. *Nat. Photonics* **2012**, *6*, 511–518. [[CrossRef](#)]
4. Bard, A.J.; Fox, M.A. Artificial Photosynthesis: Solar splitting of water to hydrogen and oxygen. *Acc. Chem. Res.* **1995**, *28*, 141–145. [[CrossRef](#)]
5. Shibata, M.; Yoshida, K.; Furuya, N. Electrochemical synthesis of urea at gas-diffusion electrodes: IV. Simultaneous reduction of carbon dioxide and nitrate ions with various metal catalysts. *J. Electrochem. Soc.* **1998**, *145*, 2348–2353. [[CrossRef](#)]
6. Azuma, M.; Hashimoto, K.; Hiramoto, M.; Watanabe, M.; Sakata, T. Electrochemical reduction of carbon dioxide on various metal electrodes in low-temperature aqueous KHCO₃ media. *J. Electrochem. Soc.* **1990**, *37*, 1772–1778. [[CrossRef](#)]
7. Saveant, J.-M. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chem. Rev.* **2008**, *108*, 2348–2378. [[CrossRef](#)] [[PubMed](#)]
8. Costentin, C.; Robert, M.; Saveant, J.-M. Catalysis of the electrochemical reduction of carbon dioxide. *Chem. Soc. Rev.* **2013**, *42*, 2423–2436. [[CrossRef](#)] [[PubMed](#)]
9. Benson, E.E.; Kubiak, C.P.; Sathrum, A.J.; Smieja, J.M. Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels. *Chem. Soc. Rev.* **2009**, *38*, 89–99. [[CrossRef](#)]
10. Díaz-Sainz, G.; Alvarez-Guerra, M.; Irabien, A. Continuous electrochemical reduction of CO₂ to formate: Comparative study of the influence of the electrode configuration with Sn and Bi-based electrocatalysts. *Molecules* **2020**, *25*, 4457. [[CrossRef](#)] [[PubMed](#)]
11. Yaasshikaa, P.R.; Kumar, P.S.; Varjani, S.J.; Saravanan, A. A review on photochemical, biochemical and electrochemical transformation of CO₂ into value-added products. *J. CO₂ Util.* **2019**, *33*, 131–147. [[CrossRef](#)]
12. Zhang, W.; Hu, Y.; Ma, L.; Zhu, G.; Wang, Y.; Xue, X.; Chen, R.; Yang, S.; Jin, Z. Progress and perspective of electrocatalytic CO₂ reduction for renewable carbonaceous fuels and chemicals. *Adv. Sci.* **2018**, *5*, 1700275. [[CrossRef](#)] [[PubMed](#)]
13. Martín, A.J.; Larrazábal, G.O.; Pérez-Ramírez, J. Towards sustainable fuels and chemicals through the electrochemical reduction of CO₂: Lessons from water electrolysis. *Green Chem.* **2015**, *17*, 5114–5130. [[CrossRef](#)]
14. Yang, H.; Kaczur, J.J.; Sajjad, S.D.; Masel, R.I. Electrochemical conversion of CO₂ to formic acid utilizing Sustainion™ membranes. *J. CO₂ Util.* **2017**, *20*, 208–217. [[CrossRef](#)]
15. Lee, W.; Kim, Y.E.; Youn, M.H.; Jeong, S.K.; Park, K.T. Catholyte-free electrocatalytic CO₂ reduction to formate. *Angew. Chem. Int. Ed.* **2018**, *57*, 6883–6887. [[CrossRef](#)] [[PubMed](#)]
16. Xia, C.; Zhu, P.; Jiang, Q.; Pan, Y.; Liang, W.; Stavitski, E.; Alshareef, H.N.; Wang, H. Continuous production of pure liquid fuel solutions via electrocatalytic CO₂ reduction using solid-electrolyte devices. *Nat. Energy* **2019**, *4*, 776–785. [[CrossRef](#)]
17. Díaz-Sainz, G.; Alvarez-Guerra, M.; Solla-Gullón, J.; García-Cruz, L.; Montiel, V.; Irabien, A. Gas-liquid-solid reaction system for CO₂ electroreduction to formate without using supporting electrolyte. *AIChE J.* **2020**, *66*, e16299. [[CrossRef](#)]
18. Díaz-Sainz, G.; Alvarez-Guerra, M.; Irabien, A. Continuous electroreduction of CO₂ towards formate in gas-phase operation at high current densities with an anion exchange membrane. *J. CO₂ Util.* **2022**, *56*, 101822. [[CrossRef](#)]
19. Xie, K.; Zhang, Y.; Meng, G.; Irvine, J.T.S. Electrochemical reduction of CO₂ in a proton conducting solid oxide electrolyser. *J. Mater. Chem.* **2011**, *21*, 195–198. [[CrossRef](#)]
20. Xie, K.; Zhang, Y.; Meng, G.; Irvine, J.T.S. Direct synthesis of methane from CO₂/H₂O in an oxygen-ion conducting solid oxide electrolyser. *Energy Environ. Sci.* **2011**, *4*, 2218–2222. [[CrossRef](#)]
21. Li, C.W.; Kanan, M.W. CO₂ reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu₂O films. *J. Am. Chem. Soc.* **2012**, *134*, 7231–7234. [[CrossRef](#)] [[PubMed](#)]

22. Lu, Q.; Rosen, J.; Zhou, Y.; Hutchings, G.S.; Kimmel, Y.C.; Chen, J.G.; Jiao, F. A selective and efficient electrocatalyst for carbon dioxide reduction. *Nat. Commun.* **2014**, *5*, 3242. [[CrossRef](#)]
23. Kuhl, K.P.; Cave, E.R.; Abram, D.N.; Jaramillo, T.F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **2012**, *5*, 7050–7059. [[CrossRef](#)]
24. DiMeglio, J.L.; Rosenthal, J. Selective conversion of CO₂ to CO with high efficiency using an inexpensive bismuth-based electrocatalyst. *J. Am. Chem. Soc.* **2013**, *135*, 8798–8801. [[CrossRef](#)]
25. Cho, S.K.; Fan, F.-R.; Bard, A.J. Electrochemical vapor deposition of semiconductors from gas phase with a solid membrane cell. *J. Am. Chem. Soc.* **2015**, *137*, 6638–6642. [[CrossRef](#)] [[PubMed](#)]
26. Devanathan, R. Recent developments in proton exchange membranes for fuel cells. *Energy Environ. Sci.* **2008**, *1*, 101–119. [[CrossRef](#)]
27. Haile, S.M.; Boysen, D.A.; Chisholm, C.R.I.; Merle, R.B. Solid acids as fuel cell electrolytes. *Nature* **2001**, *410*, 910–913. [[CrossRef](#)]
28. Chisholm, C.R.; Jang, Y.H.; Haile, S.M.; Goddard, W.A., III. Superprotonic phase transition of CsHSO₄: A molecular dynamics simulation study. *Phys. Rev. B* **2005**, *72*, 134103. [[CrossRef](#)]
29. Hori, Y.; Kikuchi, K.; Suzuki, S. Production of CO and CH₄ in electrochemical reduction of CO₂ at metal electrodes in aqueous hydrogencarbonate solution. *Chem. Lett.* **1985**, *14*, 1695–1698. [[CrossRef](#)]
30. Hori, Y.; Kikuchi, K.; Murata, A.; Suzuki, S. Production of methane and ethylene in electrochemical reduction of carbon dioxide at copper electrode in aqueous hydrogencarbonate solution. *Chem. Lett.* **1986**, *15*, 897–898. [[CrossRef](#)]
31. Varga, A.; Brunelli, N.A.; Louie, M.W.; Giapis, K.P.; Haile, S.M. Composite nanostructured solid-acid fuel-cell electrodes via electrospray deposition. *J. Mater. Chem.* **2010**, *20*, 6309–6315. [[CrossRef](#)]
32. Vassiliev, Y.B.; Bagotzky, V.S.; Osetrova, N.V.; Khazova, O.A.; Mayorova, N.A. Electroreduction of carbon dioxide. Part. I. The mechanism and kinetics of electroreduction of CO₂ in aqueous solutions on metals with high and moderate hydrogen overvoltages. *J. Electroanal. Chem.* **1985**, *189*, 271. [[CrossRef](#)]
33. Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media. *Electrochim. Acta* **1994**, *39*, 1833–1839. [[CrossRef](#)]