Electrochemical CO₂ reduction: electrocatalyst, reaction mechanism, and process engineering

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Abstract

Carbon dioxide (CO₂) emission from fossil fuel utilization poses a potential threat to global climate. Recent development in electrochemical CO₂ reduction opens up new possibilities of utilization of CO₂ as a carbon feedstock for fuel generation and commodity chemicals. This article reviewed progress related to electrochemical CO₂ reduction in the past few years, with a focus on new development of CO₂ reduction electrocatalysts, mechanistic understanding of CO₂ electro-reduction reaction, and process engineering efforts in CO₂ electrolyzers. Additionally, critical issues associated with current state-of-art systems were identified and potential directions for future studies were discussed. The article aims at providing the community a timely review of recent technical achievements as well as inspiring new ideas towards a practical CO₂ electrolysis technology.

1. Introduction to electrochemical CO₂ reduction

The increasing greenhouse gas CO₂ concentration level in atmosphere raises serious concerns on fossil fuel based energy supply.[1-3] Renewable energy sources, such as solar, wind, hydro, and waves, are being considered as potential alternatives because they are more environmentally-friendly, sustainable, and carbon-neutral.[4-8] Utilization of renewable energy at a large scale, however, is challenging due to their intermittence.[4, 7, 8] Unlike traditional power sources with a steady power output, power generation from renewable sources varies significantly over time and often mismatches the energy demand, posing serious threats to the electrical power grid. A potential solution to address the mismatch is an energy storage mechanism that can store excess energy temporarily and release the stored energy when required, enabling the load shift in the grid.[5, 9-14] Considering the extremely large scale of electrical grid, the energy carrier of the proposed storage system must be cheap, easy for storage and transportation, and compatible with current energy infrastructure. An appealing idea is a carbon-based electro-fuel produced from abundant sources, such as CO₂ and H₂O, using renewable energy as energy input.[15-19] The term of “electro-fuel” refers to liquid fuels that are produced by electrochemical means. The overall scheme is outlined in Figure 1, where an electrochemical reactor, such as an electrolyzer, is powered by electricity generated from renewable sources to drive an energy uphill process that converts CO₂ and H₂O into electro-fuels. The resulting electro-fuels can be easily stored, distributed, and used to power transportation and other human activities through the existing infrastructure. CO₂ and H₂O generated during the consumption of electro-fuels are captured and fed back to the reactor to close the loop.

Figure 1. An overall schematic of electro-fuel enabled energy storage to migrate the mismatch between renewable energy generation (photovoltaic as an example) and energy demand.

As CO_2 is a fully oxidized and thermodynamically stable molecule, CO_2 utilization via electrolysis approach in aqueous electrolytes imposes several major technical challenges.[15-19] The key step to convert CO_2 into an electro-fuel is the chemical transformation of CO_2 molecule into reduced carbon species, which is a difficult process due to the poor kinetics of CO_2 electroreduction. In the past decades, CO_2 reduction has been studied intensively using thermochemical, electrochemical, and photochemical methods.[15, 19-23] For thermochemical CO_2 conversion through a reforming process, it requires not only high reaction temperatures and pressures, but also an equivalent amount of hydrogen as the reducing agent, which is energetically problematic in implementing to large scale applications.[16, 22] In the case of photochemical processes, a few systems have been reported to be photocatalytically active for CO_2 reduction, while the selectivity and/or production rate of these systems are far too low to be economically valid.[19, 21] On the contrary, electrochemical CO_2 reduction becomes more attractive because it has a few characteristic advantages compared to other approaches.[17, 23-25] For example, the reaction can be conducted at ambient conditions with the reaction rate easily controlled by tuning the external bias (*i.e.* overpotential). The products are produced at different electrodes, enabling natural separation using individual reaction chambers, which minimizes the cost associated with post-reaction separation processes.

Figure 2. A typical schematic of an ion-conducting membrane based CO_2 electrolyzer.

In a typical CO_2 electrolyzer, anode and cathode are placed in two chambers separated with an ion conducting membrane. At anode, water is oxidized to molecular oxygen, whereas CO_2 is reduced to reduced carbon pieces at cathode (Figure 2). Because it is a thermodynamic uphill reaction, an external bias is required to drive the overall reaction. The thermodynamic potential to drive one-electron CO_2 reduction to $\text{CO}_2^{\cdot-}$ is -1.90V vs. SHE (standard hydrogen electrode), making the reaction highly energetic and unfavorable. In contrast, proton-assisted electron transfer processes are more favorable with an E (electromotive force) in the range of -0.2 to -0.6 V vs. SHE (Table 1). While the proton-assisted processes can lead to a wide range of CO_2 -derived products, it makes the selective production of desired chemicals very challenging because of the similarity of redox potentials for all the reaction pathways. The situation becomes

even worse in an aqueous electrolyte based CO₂ electrolyzer, due to the severe side reaction of hydrogen evolution occurring at a similar potential (Table 1) and competing with CO₂ reduction at the cathode side. Therefore, a CO₂ reduction electrocatalyst that can selectively produce desired chemicals while suppressing undesired side-reactions is essential to achieve a highly efficient system for electro-fuel generation using CO₂ as the carbon source.

Reaction	E (V) vs. SHE
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.41
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{C} + 2\text{H}_2\text{O}$	-0.20
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24

Table 1. Standard redox potentials for CO₂ electrolysis related reactions.

Figure 3. An outline of three major categories of electrocatalysts for CO₂ reduction.

The majority of existing CO₂ reduction electrocatalysts can be divided into three groups: metallic, non-metallic, and molecular catalysts (Figure 3).[15, 17, 26-42] Early studies in electrochemical CO₂ reduction focused primarily on polycrystalline monometallic catalysts, because they are structurally simple, easy to handle, and robust, making them attractive candidates for fundamental studies.[43] Based on the primary CO₂ reduction product, monometallic catalysts can be further divided into several subgroups: CO selective metals (e.g., Au, Ag, and Zn), formate selective metals (e.g., Sn, In, and Pb), and hydrogen selective metals (e.g., Fe, Ni, and Pt). Among all the monometallic catalysts, Cu exhibits a distinct catalytic ability to produce a wide range of CO₂ reduction products, including CO, formate, ethanol, and ethylene.[43, 44] Catalysts beyond bulk monometallics, such as nanostructured metallics,[26-29] ion-modified metallics,[30-33, 45] bimetallics,[34-36, 46] and non-metallic materials,[37-42, 47] have also been recently demonstrated as promising catalysts for CO₂ reduction. They represent new trends and opportunities in electrochemical CO₂ conversion.

This review article aims at providing an overview of recent progress associated with CO₂ electrolysis, including heterogeneous electrocatalyst development, reaction mechanism studies, and process design and engineering, following by discussions of future opportunities. It should be noted that homogeneous molecular catalysts are also interesting candidates for CO₂ electroreduction,[15, 17] although this article covers primarily heterogeneous systems.

2. State-of-art CO₂ reduction electrocatalysts

Bulk metals have been studied intensively as CO₂ reduction electrocatalysts over the past few decades.[43, 44, 48-55] The properties of bulk metallic CO₂ reduction catalysts have been reviewed in detail by Hori and examined by Jaramillo research group with modern techniques.[43, 44] In light of those fundamental studies, recent efforts have been devoted to the development of high-performance electrocatalysts with advanced structures or new reaction sites that possess attractive qualities over bulk catalysts.[26]

2.1 Nanostructured metallic catalysts

Nanostructured materials usually provide much more surface active sites than bulk materials because of their enhanced surface areas. More importantly, the nanostructured catalyst surfaces usually contain a large portion of edge/low-coordinated sites, which may exhibit very different catalytic behavior from that of flat surface/fully coordinated sites in bulk counterparts.

Figure 4. (a) Scanning electron micrograph (SEM) of np-Ag surface. (b) Overpotential vs CO production partial current density on polycrystalline silver and np-Ag. Reproduced with permission from Ref. 27.

Lu *et al.* developed a dealloy process to synthesize nanoporous Ag (np-Ag) catalyst for reducing CO₂ to CO from an Al₈₀Ag₂₀ solid solution precursor.[27] The np-Ag exhibited a monolithic structure and highly curved inner surfaces (Figure 4a). In electrochemical characterizations for CO₂RR, the resulting catalytic material achieved an exceptionally high activity of approximately 20 mA cm^{-2} with over 90 % selectivity at a mediocre overpotential of about 0.5 V in aqueous

electrolyte (Figure 4b), which set the new benchmark performance for Ag-based electrocatalysts. It was discovered that the Tafel behavior of np-Ag surface showed a significantly smaller slope than that of polycrystalline Ag surface, which means np-Ag requires less driving force (*i.e.* potential) to improve reaction rate (*i.e.* current density), indicating the intrinsically better activity of np-Ag surface (Figure 4b). This conclusion was supported by differentiating the contribution from electrode surface area showing the specific activity of np-Ag was at least 20 times higher than that of the polycrystalline Ag surface. To reveal the mechanistic difference of np-Ag surface, this research group further conducted fundamental kinetic and density functional theory (DFT) based theoretical studies, which would be discussed in following section.

Figure 5. SEM of (a) AgCl layer grown on polycrystalline Ag foil and (b) Ag nano-corals. (c) Soft X-ray photoelectron spectroscopy (sXPS) of AgCl and Ag nano-corals. (d) Tafel plot at different overpotentials η as a function with the CO partial current density j_{CO} , on Ag foil and Ag nanocorals. Reproduced with permission from Ref. 33.

Hsieh *et al.* suggested that the performance of nanoporous Ag surface might be further improved by introducing a chloride anions modification.[33] In their work, the authors prepared Ag nano-corals, which was similar to np-Ag in morphology, from electrochemical reduction of AgCl layer grown on the surface of polycrystalline Ag foil (Figure 5a-b). Using synchrotron X-ray

photoelectron spectroscopy (XPS) analysis, the authors found Cl forms a stable chemically bonded thin layer on the surface of Ag nano-corals in the Cl^- state (Figure 5c). Such Cl^- bonded Ag nano-corals exhibited a comparable performance to np-Ag in reducing CO_2 to CO with similar improved Tafel behavior (Figure 5d).[27] After electrochemical surface area measurement, the specific activity of Cl^- bonded Ag nano-corals surface was found to be 32 times higher than that of the polycrystalline Ag surface. The authors believed the surface bonded Cl^- played an important role in CO_2RR because such enhancement was significantly reduced in the Cl^- removed control sample. Although the origin of this enhancement in CO_2RR was unclear, the author claimed that a detailed mechanistic study of the CO_2 reduction reaction was undergoing using Ag electrodes modified by different halides.

Figure 6. Top down (a) and cross sectional (b) SEM images of a Au-IO thin film. Specific activity for CO (c) and H_2 (d) evolution for 0.5, 1.6, 2.7 μm thick Au-IO samples evaluated in CO_2 -saturated 0.1 M KHCO_3 electrolyte, pH 6.7. Error bars represent standard deviations of three independently synthesized Au-IO samples for each thickness. Reproduced with permission from Ref. 53.

The nanoporous structure was also implemented on Au material to achieve improved performance in CO_2RR to CO. Very recently, Hall *et al.* reported ordered Au inverse opal (Au-IO) thin films with a series thickness from templating 200 nm polystyrene spheres (Figure 6a-b).[56] The resulting Au-IO electrodes exhibited high specific performance, which was inversely proportional to film thickness due to the more difficult mass transportation in thicker electrodes (Figure 6c). The authors also found the HER activity was better suppressed in thicker samples

and behaved as plateau in the potential window where CO₂RR was raised (Figure 6d). They concluded that the competition HER can be significantly influenced by electrolyte pH rise that was caused by mass transportation due to CO evolving and electrode thickness.

Zhu *et al.* performed a theoretical and experimental modeling combined study based on Au nanoparticles (Au NPs).[57] The authors synthesized a series Au NPs with different particle sizes of 4, 6, 8, and 10 nm. These particles were aggregated by smaller crystallites with dimensions of about 2.0, 2.3, 4.0, and 5.9 nm, respectively. In electrochemical characterizations for CO₂RR, the 8 nm Au NPs showed a better gravimetric performance than other larger or smaller counterparts. The authors conducted DFT investigations on different crystal faces and Au cluster composed by 13 Au atoms, suggesting that 1) the edge sites on Au NP surfaces favor CO₂ reduction and 2) the corner sites favor the HER. By examining the relationship between the density of surface sites favoring CO₂RR and the Au cluster size, it was found that the 8 nm Au NPs with a 4 nm crystallite dimension were small enough to provide a near-optimum number of edge sites that were particularly active for CO₂RR with a minimization of corner sites active for the HER. As a result, such catalytic material was able to achieve about 3 A g⁻¹ CO production current density and a near 100% faradaic efficiency with overpotential of less than 0.5 V (Figure 7).

Figure 7. Potential-dependent (a) faradaic efficiency and (b) mass activities of the different Au NPs on electrocatalytic reduction of CO₂ to CO. Reproduced with permission from Ref. 54.

In order to achieve a more cost-effective electrocatalyst for CO₂RR, Rosen *et al.* developed a nanostructured Zn material to selective reduce CO₂ to CO with high activity.[28] The dendritic Zn electrode can be synthesized using a simple electrochemical deposition process (Figure 8a). In CO₂RR test, such electrodes were able to achieve an activity comparable to the state-of-the-art Ag or Au catalysts with few hundreds millivolts more energy penalty (Figure 8b) but many orders more cost-effectiveness. Moreover, the authors also showed the dendritic Zn surface was able to suppress the competing HER much better than a flat polycrystalline surface. Because Zn is not a noble metal such as Ag or Au, the surface valence state under reaction conditions should be probed in order to establish a true surface-activity relationship. The authors employed *in-situ* X-ray adsorption spectroscopy (XAS) technique to study the Zn dendrite in *operando* conditions, which would be discussed in the following section.

Figure 8. (a) A typical SEM image for a Zn dendrite catalyst. (b) CO faradaic efficiency, and (c) CO current density for bulk and dendritic Zn electrocatalysts. Reproduced with permission from Ref. 28.

Also using electrochemical deposition, DiMeglio *et al.* synthesized a rosebud-type Bi thin film on a glassy carbon electrode (GCE) and characterized its CO₂ reduction activity in an ionic liquid containing electrolyte (Figure 9a).[58] Surprisingly, Bi, which was a formate selective catalyst in aqueous electrolyte, became a CO selective catalyst in the ionic liquid containing electrolyte. The enhancement of activity after the introducing ionic liquid was evident. A current density of approximately 4 mA cm⁻² was achieved with a CO efficiency of approximately 93 % at -1.95 V vs SCE in the ionic liquid containing electrolyte (Figure 9b). This research group recently expanded this technique to more metals such as Sn, Sb and Pb to reduce CO₂ to CO.[59] However, their exhibited performance was less than that of Bi. It is quite interesting to see that the ionic liquid containing electrolyte being able to change the selectivity of metals (Bi, Sn and Pb) from formate to CO.

Figure 9. (a) SEM image of an electrochemically deposited Bi thin film. (b) CV traces recorded for Bi-deposited and bare GCEs in MeCN that contained 20 mM EMIM-BF₄. Inset: Bi-deposited GCE in MeCN without the ionic liquid. Reproduced with permission from Ref. 55.

2.2 Oxide-derived catalysts

The intentional oxidation and reduction of metallic electrodes is a method frequently employed in recent to create active surface sites for CO₂RR. It was first reported by Frese that an oxidized and *in-situ* reduced Cu electrodes during CO₂RR showed improved methanol production over an untreated polycrystalline Cu.[60] Li *et al.* further implemented this method and performed a systematic study on the correlation between oxidation temperature and activity.[31] Their results showed that the enhanced performance in reducing CO₂ was proportional to the annealing temperature and time in which the oxide derived Cu (OD-Cu) was prepared. As the highest activity achieved at thermal treatment at 500 °C for 12 h in air, the resulting Cu electrode developed a nanowire structure with coarse surface within *in-situ* reduction in CO₂RR (Figure 10a). The catalytic activity and selectivity showed significantly improvement from a polycrystalline Cu counterpart (Figure 10b). The possible mechanism was further explored in a later work by the same group, which will be discussed in the following section.

Figure 10. (a) SEM image of a polycrystalline Cu foil annealed at 500 °C for 12 h. (b) The corresponding faradaic efficiencies for the production of CO and HCO₂H as a function of applied potentials. Reproduced with permission from Ref. 31.

This principle was successfully applied to Au materials with a different oxidation route. Chen *et al.* prepared oxide derived Au (OD-Au) electrodes by oxidizing Au foils using AC bias anodic oxidation and subsequent electrochemical reduction at constant potential.[61] The resulting electrodes exhibited a thick layer (~1 μm) of Au nanoparticles on the surface (Figure 11a) and much enhanced CO production than untreated polycrystalline Au with lower onset potential (Figure 11b). The authors also performed kinetic studies to reveal the intrinsically improved CO₂RR mechanism on OD-Au surface, which will be discussed in the following section.

Figure 11. (a) SEM image of the surface of oxide-derived Au nanoparticle film. (b) CO production partial current density versus overpotential on oxide-derived Au and polycrystalline Au. Reproduced with permission from Ref. 57.

Zhang *et al.* showed the enhanced CO₂ reduction activity to formate production on Sn/SnO_x electrode prepared from SnO₂ nanoparticles *in-situ* reduced in CO₂RR (Figure 12a).[62] The authors showed that the SnO₂ particle size played a major role in CO₂RR in tuning the surface-species binding energy, and a maximum CO₂RR activity could be achieved using 5 nm particles. Chen *et al.* examined the performance of electrodeposited Sn/SnO_x nanoclusters as CO₂ reduction catalysts.[30] The authors showed the role of SnO_x was likely to help stabilize the reaction intermediate. Compared to polycrystalline Sn, the higher density Sn/SnO_x sites were able to enhance the catalyst performance with higher selectivity and current density (Figure 12b) and to suppress the hydrogen evolution.

Figure 12. (a) Dependence of total current densities and faradaic efficiencies on the applied electrolysis potential for formate production on reduced nano-SnO₂ (~5 nm) loaded on carbon black (~30 nm). (b) Comparison of CO₂ reduction catalysis for Sn foil and *in-situ* deposited Sn/SnO_x thin-film electrodes for the faradiac efficiency of CO and HCO₂H production at various applied potentials. Reproduced with permission from Refs. 30 and 58.

2.3 Non-metallic catalysts

Figure 13. Comparison of CO formation performance at different overpotentials. Bulk MoS₂ and Ag nanoparticles (Ag NPs) results were taken from the present study where electrochemical experiments were performed in similar conditions. Reproduced with permission from Ref. 39.

The molybdenum-terminated edge of MoS₂ material is known to be active in hydrogen evolution due to its optimal binding strength to hydrogen. Recently, Asadi *et al.* discovered such reaction site is also efficient in reducing CO₂ to CO in an ionic liquid modified electrolyte.[39] Simply using commercial bulk Mo₂S materials in a 96 mol% H₂O + 4 mol% EMIM-BF₄ electrolyte, the authors achieved an equivalent or better reaction activity even comparing with state-of-the-art metallic CO selective catalysts (Figure 13). DFT calculation was used to explore the reaction site and the origin of the high activity of Mo₂S. The authors first assigned the reaction sites to the edge atoms because their spin-polarized projected density of states (PDOS) near E_f was approximately twice larger than that of the bulk atoms. In the next step, the authors excluded edge S atoms being the reaction sites due to their much less reactive *p* orbitals. Finally, they found the near E_f PDOS of Mo edge atoms was primarily dominated by *d*-orbital electron states. The *d*-band center of Mo edge atoms was closer to Fermi energy level than that of Ag, and this was considered as the reason of high activity of Mo₂S. To back up the calculations however, studies using well-defined experimental model are highly desired.

Carbon is a widely studied electrocatalytic material for many important reactions but was rarely examined in CO₂RR. Recently Kumar *et al.* observed the first CO₂RR selective to CO on nitrogen incorporated carbon nanofiber catalyst in also ionic liquid (EMIM-BF₄) modified electrolyte.[40] The carbon nanofibers were synthesized by electrospinning polyacrylnitrile (PAN) precursor fibers followed by carbonization treatment. The X-ray photoelectron spectroscopy (XPS) study showed three different nitrogen species existing on the carbon fiber surface: pyridinic, quaternary and nitrogen oxide. The nitrogen species were believed to be crucial in CO₂RR as the authors found negligible CO production on nitrogen-free control samples. Combining with XPS and activity characterizations, the authors proposed the effective reaction sites of this carbon nanofiber catalyst were the charged carbon atoms due to the

presence of nitrogen and described the reaction process as in Figure 14. Similar to Mo_2S , this system was also very sensitive to the concentration of EMIM-BF_4 .

Figure 1. Schematic of CO_2RR to CO on nitrogen incorporated carbon nanofiber surface in ionic liquid modified electrolyte. An intermediate (EMIM- CO_2 complex) was firstly formed. The complex was absorbed on the reduced carbon atoms in a following step and be further reduced to CO. Reproduced with permission from Ref. 40.

Figure 15. (a) Cathodic linear sweep voltammetry scans at 50 mV/s in a CO_2 -saturated aqueous 0.1 M KHCO_3 solution. (b) Plot of Faradaic efficiencies for formate production vs applied potential at CNT/GC, NCNT/GC, and PEI-NCNT/GC electrodes. Reproduced with permission from Ref. 59.

Zhang *et al.* demonstrated the nitrogen modified carbon material could also be applied as catalytic materials for reducing CO_2 to formate in pure aqueous electrolyte.[63] In their recent work, the authors used ammonia plasma to dope nitrogen elements to a commercial carbon nanotube material (NCNT) and found its significantly boosted performance comparing with bare carbon nanotube (CNT) (Figure 15a). In addition, a polyethylenimine (PEI) layer was introduced to the material surface because of its high adsorption to CO_2 . The PEI coated NCNT (PEI-NCNT) further enhanced the activity and selectivity of CO_2RR (Figure 15b), making the electrode performance comparable to their previously reported metal based Sn/ SnO_x electrodes.

Figure 16. (a) CO product yields of N-C, M-N-C and Au foil and their electrolysis selectivity to (b) CO, (c) H_2 and (d) CH_4 . Reproduced with permission from Ref. 38.

Varela *et al.* doped transition metal Fe and Mn into nitrogen modified carbon material in the purpose to improve CO_2RR in aqueous electrolyte.[38] Different than NCNT or PEI-NCNT, the nitrogen modified porous carbon (N-C) and their metal doped counterparts (M-N-C) the authors prepared in this work was selective to reduce CO_2 to CO instead of formate. As the results shown in Figure 16a-b, all M-N-C materials exhibited similar selectivity to CO and H_2 in the studied potential window. The CO partial current density was comparable to a polycrystalline Au foil

(benchmark CO catalyst in bulk materials) at potentials less than 0.8 V (Figure 16c). The FeMn-N-C and Fe-N-C materials showed some CH₄ conversion (Figure 16d) that was not observed on Mn-N-C or N-C. The authors believed it was due to different CO adsorption energy altered by surface metal elements.

Another nitrogen modified the carbon material recently investigated for CO₂RR was nitrogen-doped nanodiamond (NDD). In this work, Liu *et al.* synthesized NDD by chemical vapor deposition of NDD film onto Si wire template prepared from photolithography (Figure 17a).[37] In CO₂RR characterization using aqueous electrolyte, NDD electrode showed over 77% faradaic efficiency towards acetate production and about 14% towards formate formation at a potential between -0.8 to -1 V (Figure 17b). Although the conversion rate is relatively small ($\sim 1 \text{ mA cm}^{-2}$ at -1 V), the results are exciting because it is the first time report of an electrocatalyst being able to reduce CO₂ to a single C₂ product with such high selectivity. Moreover, such material can provide a platform to study C-C coupling of CO₂RR, which is highly desired for the design of advanced catalysts to convert CO₂ into more value-added chemicals.

Figure 27. (a) SEM image of NDD and (b) its Faradaic efficiency for acetate and formate production for electrochemical reduction of CO₂ at -0.55 to -1.30 V (CO₂ saturated 0.5 M NaHCO₃ solution). Reproduced with permission from Ref. 37.

2.4 Future opportunities

As great progress has been achieved in CO₂ reduction to C₁ products (CO and formate), future direction lies in developing advanced electrocatalysts to reduce CO₂ to more value-added chemicals, such as C₂-C₄ products. It is a very challenging task because 1) no known single element is able to reduce CO₂ to C₂-C₄ products in a selective manner; 2) The reaction mechanism of CO₂RR, including reaction paths, reaction intermediates, *etc.*, is still unclear. Consequently, electrocatalysts beyond monometallic systems with a comprehensive understanding of reaction mechanism become extremely important to achieve next-generation CO₂RR catalysts. Research on bimetallic or carbon supported metal catalysts would be a natural direction to pursue due to the beneficial synergy effect may resulting from the combination of

selected elements. The unique reactions sites arises from morphology and structure control (e.g. highly curved surface and oxide-derived surface) should be further explored and integrated.

3. Reaction mechanism of electrochemical CO₂ reduction

A key barrier in developing active, selective and stable electrocatalysts for CO₂RR is the lack of fundamental understanding of surface-mediated electrochemical reactions. The wide variety of possible products and number of electrons transferred ranging from CO (2e) and HCOOH (2e) up to CH₃CH₂CH₂OH (18e) in the electrochemical CO₂ reduction reaction (CO₂RR) poses significant challenges in elucidating reaction mechanisms. Therefore, a good understanding of how CO₂RR proceeds on catalytic materials is a rational step to demystify the mechanism of CO₂RR.

3.1 Kinetic studies and their limitations

Figure 18. Electrokinetics of CO₂ reduction to CO on oxide-derived Au. CO production partial current density vs (a) potential on oxide-derived Au and polycrystalline Au, (b) sodium bicarbonate concentration at constant potential, and (c) CO₂ partial pressure at constant potential. (d) Proposed mechanisms for CO₂ reduction to CO on polycrystalline Au and oxide-derived Au. Reproduced with permission from Ref. 57.

Electrokinetic studies have been performed in electrochemical CO₂ reduction.[29, 61] For example, Chen *et al.* performed kinetic characterizations on OD-Au catalysts, including Tafel analysis and reaction order dependency study.[61] As shown in Figure 18a, the Tafel slope of OD-Au (56 $\text{mV}\cdot\text{dec}^{-1}$) exhibited a dramatic decrease from that of polycrystalline Au (114 $\text{mV}\cdot\text{dec}^{-1}$), proving its intrinsically better performance. Assuming that the coverage of reaction

intermediates was negligible, the Tafel slope of polycrystalline Au indicated a rate-determining initial e^- transfer process, while the Tafel slope of OD-Au was indicative of an initial e^- pre-equilibrium prior to a rate-determining chemical step. This results revealed the improvement of OD-Au was likely due to its better capability to stabilize $\text{CO}_2^{\cdot-}$, the intermediate resulting from initial e^- transfer, than polycrystalline Au. Correlating with earlier studies conducted by Hori *et al.*, [43] and the first order dependence on both CO_2 and HCO_3^- concentration (Figure 18b-c), the authors proposed possible reaction mechanisms for polycrystalline Au and OD-Au (Figure 18d), pointing out HCO_3^- was the proton donor in CO_2RR .

Figure 19. Mechanistic insights from Tafel analysis. (A) Tafel plot for n-Cu/C and copper foil, with linear fit at low current densities demonstrating that these catalysts show Tafel slopes of 60 ± 4.2 and 86 ± 4.6 mV/decade, respectively. (B) Methanation current density as a function of partial pressure of CO_2 at -1.25 V, showing that methanation current density has a 2.03 ± 0.08 order dependence on the partial pressure of CO_2 at lower CO_2 partial pressures. (C) Proposed mechanism for the electrochemical reduction of CO_2 to methane, including the rate-limiting step (RLS). Reproduced with permission from Ref. 60.

Manthiram *et al.* studied the kinetic behaviors of their glassy carbon supported copper nanoparticle electrodes in CO_2RR to CH_4 . [64] The n-Cu/C also showed Tafel slope change to about $60 \text{ mV}\cdot\text{dec}^{-1}$ from above $86 \text{ mV}\cdot\text{dec}^{-1}$ of polycrystalline Cu foil (Figure 19a), indicating a fast one e^- transfer process before a rate-limiting non-electrochemical step (assuming the coverage of reaction intermediates was small). The reaction order of the methenation current on CO_2 concentration was found to be an unusual number of two (Figure 19b) while CO_2RR on copper foil was often assumed to proceed with a first-order dependence on CO_2 in aqueous electrolytes. Combining these two pieces of information, the authors proposed a mechanism of CO_2RR to CH_4 on n-Cu/C materials as described in Figure 19c. CO_2 **1** reacts in a one electron-transfer pre-equilibrium step to form a surface adsorbed $\text{CO}_2^{\cdot-}$ radical **2**; The adsorbed $\text{CO}_2^{\cdot-}$

radical **2** is proposed to undergo rate-limiting carbon-oxygen coupling with a Lewis acid CO_2 molecule from solution to form a $\text{CO}_2\text{-CO}_2^{\cdot-}$ adduct **3**, which is further reduced and protonated to form adsorbed CO **4** and eventually CH_4 **5**.

A comprehensive analysis on the nanostructured Ag catalysts was performed by Rosen *et al.* The authors found that the reaction order studies could be significantly influenced by electrolyte pH change due to different CO_2 and HCO_3^- concentrations.[29] They proposed that such studies have to be conducted under constant overpotential (*i.e.* constant value with respect to RHE scale) instead of constant potential with respect to reference electrode (Figure 20). In this way, the concentration of H^+ , an important reactant in CO_2RR , can be kept at a constant value, leaving the CO_2 or HCO_3^- concentration as the only variable.

Figure 20. CO production partial current density of nanoporous Ag vs CO_2 partial pressure at (a) constant potential and (b) constant overpotential. CO production partial current density of nanoporous Ag vs HCO_3^- concentration at (c) constant potential and (d) constant overpotential. Reproduced with permission from Ref. 29.

While electrokinetic study is definitely a powerful tool to probe CO_2RR mechanism, it is tricky to perform a well-defined electrokinetic study in reality. For example, while Tafel analysis is a

useful indicator of the rate-limiting step for reactions involving electron transfer, the slope is dependent on many factors other than the kinetic exponent of the electrons, such as the presence of adsorbates due to complex of the CO₂RR nature or the mass transport effect in complicated electrode structure. In addition, for fixed overpotential (*i.e.* driving force) studies, the deviation of product and/or reactant concentration from standard conditions may shift the equilibrium potential from the thermodynamic predicted value.

3.2 *In-situ* and *in-operando* spectroscopy

Figure 21. (a) Schematic of in-situ ATR-IR study of CO₂RR on a Sn/SnO_x film deposited on ZnSe ATR crystal. (b) Proposed Mechanism for CO₂RR to formate on Sn/SnO_x materials. Reproduced with permission from Ref. 61.

Baruch *et al.* employed an *in-situ* attenuated total reflectance infrared spectroscopy (ATR-IR) to perform a real time examination of CO₂RR interface at Sn electrodes.[65] The working electrode was a Sn film deposited onto ZnSe crystal using ion beam sputtering (Figure 21a) and the crystal was fitted into a custom-made three-electrode electrochemical cell. Combining both electrochemical and spectroscopic techniques, the authors found a tin oxide layer was formed on tin electrode under electrolysis conditions although thermodynamics predicted the most stable

phase was metallic. This finding pointed out that those metastable oxides must be taken into account in order to understand the electroactive nature of the tin interface. The *in-situ* ATR-IR spectra also showed the evidence of carbonate absorption on the Sn/SnO_x film during CO₂RR. Correlating with Tafel studies conducted by Chen *et al.* and Kapusta *et al.*, [30, 66] the authors proposed a mechanism for CO₂RR to formate which considered the surface-bound carbonate species as an important reaction intermediate and ruled out the formation CO₂^{•-} radical (Figure 21b).

In order to reveal the true valence state of electrocatalysts at *operando* conditions of CO₂RR, Rosen *et al.* designed an electrochemical cell that allowed the *in-situ* XAS study of their dendritic Zn electrodes.[28] The X-ray absorption near-edge spectroscopy (XANES) results collected at -0.5, -0.7, -0.9, and -1.1 V are shown in Figure 22a. It is clear that the Zn K-edge of electrode operated at -0.5 V has a significant shift toward the binding energy for Zn²⁺, suggesting that Zn dendrite was fully oxidized to Zn²⁺ within electrolysis. A continuous change of Zn oxidation state can be clearly seen in the XANES results at *operando* conditions (Figure 22b). In contrast, at potentials more negative than -0.7 V, Zn dendrite electrodes remained Zn⁰, and no obvious K-edge shift can be observed, indicating a likely stable operating window for the Zn dendrite catalyst.

Figure 22. *In-situ* XANES data for dendritic Zn electrodes operated at (a) various potentials for one hour and (b) -0.5 V at *operando* condition. Data for bulk Zn and ZnO are also included for comparison. Reproduced with permission from Ref. 28.

3.3 Grain boundary-activity correlation

In the purpose of establishing a structure-activity correlation of OD-Cu, Verdaguer-Casadevall *et al.* examined the microstructure and the adsorbate binding thermodynamic of this material.[67] TEM nanodiffraction study revealed the most important feature of OD-Cu that the material is composed of irregularly shaped, 100–300 nm grains that are joined by grain boundaries (GB) in a dense polycrystalline network (Figures 23a, b). The distribution of GBs is ~37% low energy twin boundaries and the rest randomly oriented or nontwin coincident site lattice boundaries. The authors further employed temperature-programmed desorption (TPD) technique to probe the

binding strength of CO, an important intermediate and product in CO₂RR. As the result shown in Figures 23c-d, OD-Cu prepared from oxidation at 500 °C (OD-Cu-500) exhibited a high-temperature feature centered at 275 K that is clearly absent from the profile for regular polycrystalline Cu foil. According to microkinetic modeling of CO binding to Cu surfaces with different binding sites and porosities, this high-temperature feature was attributed to the presence of a strong CO binding site with binding energy of ~67 kJ/mol. In the earlier work conducted by Li *et al.*, it was found that the performance of CO₂RR on OD-Cu was proportional to the oxidation temperature.[31] If correlating with this work, such enhancement can be more intrinsically associated to the higher surface density of GBs or stronger CO binding sites created from sample preparation at higher oxidation temperatures.

Figure 23. (a) TEM image of OD-Cu-500 with overlaid boundaries constructed from orientation mapping data. Yellow line: randomly oriented boundaries. Red line: twin boundaries. (b) Image quality map of OD-Cu-500 constructed from TEM electron diffraction data. (c-d) TPD profile of a polycrystalline Cu foil and OD-Cu-500. Experimental data (solid black lines) and fit resulting from microkinetic simulations (dashed red lines). The dotted green lines indicate the central position of the low-index facets and stepped sites in polycrystalline Cu. Reproduced with permission from Ref. 63.

Similar grain boundary-activity correlation was also observed on Au materials. Feng *et al.* deposited grain-boundary-rich Au nanoparticles onto carbon nanotube substrate (Au/CNT) using e-beam evaporation technique (Figure 24a).[68] A series of Au/CNTs with less GB surface

densities were also achieved for comparison by introducing a post thermal annealing process without significant change in geometry (Figures 24b-d). In CO₂RR characterization, the specific CO partial current density and its faradaic efficiency of Au/CNT electrodes were found to be proportional to the density of GB (Figures 24e, f). More interestingly, the relationship between the specific j_{CO} and GB surface density was even linear at low overpotentials (Figure 24g) where mass transport was less of an issue. Because all Au/CNT electrodes shared a very similar Au surface area as well as surface faceting, this result suggests that the GB surface terminations are responsible for most of the CO₂ reduction activity when mass transport is less of an issue.

Figure 24. (a-d) TEM images of as-deposited and annealed Au nanoparticles on CNT. The arrows indicate grain boundaries in the nanoparticles. (e) Specific current density for CO production (j_{CO}) vs. potential. (f) Faradaic efficiency for CO production vs. potential. (g) Correlation between specific j_{CO} and GB surface density at low overpotentials. Reproduced with permission from Ref. 64.

3.4 Future opportunities

CO₂RR is complex in nature. Although some progress has been made in fundamental understandings, detailed mechanistic insights into CO₂RR, especially reaction pathways towards C₂-C₄ products, are still limited partly because of the insufficient knowledge regarding to reaction intermediates. Developing *in-situ* and surface sensitive techniques to probe the reaction interface at *operando* conditions would be highly desired in demystifying the true CO₂RR pathways and associated intermediates. Well-defined experimental modelling studies with controllable catalyst structure and surface would be appreciable to reveal electrokinetics and structure-activity relationship. Based on those, density functional theory (DFT) calculation could be a very useful tool to understand reaction mechanism at molecular level and to predict better electrocatalytic surfaces. The interplay of *in-situ/operando* spectroscopy, experimental modelling

and DFT calculation can be a powerful combination for future CO₂RR studies to achieve next-level high-performance.

4. Design and engineering of CO₂ electrolysis process

A well design and engineered electrochemical process for CO₂ electrolysis is equally (if not more) important as a highly efficient electrocatalyst because it often dominates the ultimate performance of the system. Unlike the intensive investigations in catalyst development, very limited studies have been performed to investigate the complete process of CO₂ electrolysis. Rather than reviewing each individual process design in recent literature, an overview of major considerations and technical challenges in CO₂ electrolysis are provided.

4.1 Choice of electrolyte

In previous studies, both aqueous and non-aqueous electrolytes have been investigated for CO₂ electrolysis.[15, 17, 69-72] For aqueous electrolytes, the most commonly used electrolyte is a 0.1M – 0.5M NaHCO₃ or KHCO₃ solution with a pH value of 7 after CO₂ saturation.[15, 26, 43] The pH value is considered for CO₂ electrolysis due to the suppression of undesired hydrogen evolution reaction. The bicarbonate electrolyte also acts as a buffer to maintain the pH value at the electrode surface. Additionally, bicarbonate is relatively cheap, easy to handle, and environmentally friendly, making it a popular choice for CO₂ electrolysis studies in a typical two-compartment electrochemical cell.

Aqueous electrolytes other than bicarbonate have also been studied.[71-75] Both Lister and Kenis studied the influences of electrolyte in CO₂ electrolysis and concluded that a KOH electrolyte with a high pH value is favorable for CO₂ electrolysis compared to KCl or K₂SO₄ based electrolytes.[73-75] The superior performance of KOH electrolyte is likely due to the favorable anion absorption on the electrode surface and/or the reduced overpotential of the anode. The implementation of KOH electrolyte in a practical electrolyzer could be problematic because KOH reacts strongly with CO₂ and forms carbonate, an inert species that is very difficult to be reduced electrochemically at cathode.

Turning to non-traditional aqueous electrolytes, ionic liquid based electrolytes are proposed as replacements of bicarbonate electrolytes.[59, 76-80] Examples include 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (EMIM-OTf).[59, 76, 80] While ionic liquid based electrolytes exhibited some distinctive properties, such as higher CO₂ solubility and lower overpotentials for CO₂ reduction, they are premature to be considered for practical CO₂ electrolyzers due to the low current density, high cost of ionic liquid comparing with aqueous electrolytes, and poor stability in the presence of water.[69]

Considering all the aspects, an aqueous bicarbonate solution is still the most appreciable electrolyte at current stage for a practical CO₂ electrolyzer system. It is important to note that the role of electrolyte is poorly understood at this moment, while at the same time the significant impact of electrolyte on CO₂ electrolysis is severely underestimated. As for future studies, a

comprehensive understanding of the central role of electrolyte in electrocatalysis would be highly appreciated, especially how the cations and anions in the electrolyte interact with the electrode surface.

While the discussion here is primarily catholyte, the choice of membrane (cation exchange membrane vs. anion exchange membrane) is also critical to the performance of CO₂ electrolyzer. If a bicarbonate catholyte is chosen, a cation exchange membrane is desired as it can minimize the bicarbonate crossover to the anode compartment. The presence of bicarbonate in the anode compartment could lead to the CO₂ gas evolving due to the bicarbonate oxidation. A detailed discussion on the choice of membrane was reported by Delacourt et al.[81]

4.2 Choice of CO₂ reduction product

Since proton-assisted CO₂ reduction can be proceeded along different pathways, a critical question to answer is the choice of CO₂ reduction product. While this article focuses on technical aspects of CO₂ electrolysis, the discussion of which CO₂ reduction product should be pursued heavily depends on the economics. Current prices of major CO₂ reduction products are summarized in Table 2. For comparison, a minimum cost for each individual product is also estimated assuming that the only significant cost is electricity (approximately \$0.07 per kWh in United States). The estimated costs are clearly lower than the realistic costs, while they provide minimum prices to facilitate the discussion. Based on the simple analysis in Table 2, it is unlikely to electrocatalytically convert CO₂ to methane, methanol, ethanol, or ethylene economically at current electricity price. In contrast, carbon monoxide, formic acid, formaldehyde, and propanol may present some opportunities because of their relatively high market values.

Product	# of electrons per product molecule	Market price ^[a]	Estimated cost ^[a]	Best known catalyst
Syngas	2	25-90	376	Au, Ag, Zn
Carbon monoxide	2	600	271	Au (95%), Ag (92%)
Formic acid	2	1200-1600 (90%)	163	Sn (80%)
Formaldehyde	4	3500	501	B-doped diamond (74%)
Methanol	6	350	705	Cu (<5%)
Methane	8	150-250	1880	Cu (55%)
Ethanol	12	700-1000	981	Cu (<5%)
Ethylene	12	950-1200	1611	Cu (<5%)
Propanol	18	1800	1128	Cu (<5%)

Table 2. The estimated costs for major CO₂ reduction products assuming electricity at a price of \$0.07 per kWh, a cell potential of 2V (with minimum overpotentials), no capital cost for cell components, free CO₂ source, and no separation cost. [a] Unit: USD per metric ton; the values are extracted from multiple sources in the internet.

Additionally, the choice of desired CO₂ reduction product should also consider post-electrolysis separation cost and the availability of efficient catalyst. For example, it is energy intensive to separate a liquid product (especially when it is diluted), such as formic acid, formaldehyde, and propanol, from an aqueous electrolyte. The separation cost could increase the total cost substantially and make the whole process uneconomic. Although it might be possible to minimize the separation cost by producing a highly concentrated liquid product, the catalytic reaction likely encounters unforeseen difficulties, such as significant pH change and severe side reactions.

Considering all the constraints, CO is currently the most promising CO₂ reduction product because it is a gas at ambient pressure and easy to separate from aqueous electrolytes and able to be produced selectively using Au and Ag catalysts.[27, 61] More importantly, CO is an important chemical feedstock and widely used in current chemical industry.[82-84] For example, as an important component of syngas CO can be converted to synthetic fuels using well-established Fischer-Tropsch processes.

4.3 Considerations of CO₂ electrolysis process

The overall process design of CO₂ electrolysis depends on the target CO₂ reduction product as well as the method of CO₂ delivery to cathode. The discussion in this section is not going to identify the best strategy for CO₂ electrolysis, but to highlight a few important issues related to current state-of-art. Because CO is the most widely studied product, the discussion focuses on CO as a model product. A typical CO₂ electrolyzer system design with a gas/liquid contactor for CO₂ intake is shown in Figure 25. An ion-conducting membrane separates cathode and anode chambers. On the cathode side, gaseous CO₂ is introduced into the system through a gas/liquid contactor (e.g., a porous sparger), resulting in a CO₂ saturated aqueous electrolyte. Then, the CO₂ saturated catholyte is pumped into the cathode side of the electrochemical flow cell (i.e. CO₂ electrolyzer), where dissolved CO₂ is converted into CO, followed by a product separation process at a gas/liquid separator. The catholyte is pressurized and pumped back into the contactor. A similar process occurs at the anode side except that no contactor is required. This design allows easy separation of CO from the electrolyzer system, while a mild CO current density (typically 10-20 mA/cm²) can be achieved, which is greatly due to the limitation of low CO₂ solubility in the aqueous electrolyte (approximately 0.03 M). Note that CO₂ gas is able to escape from the separator at the cathode side, while the quantity is relative small compared to the amount of products.

Figure 25. A typical CO₂ electrolyzer system design with a gas/liquid contactor for CO₂ intake.

The low CO₂ solubility issue can be partially addressed by feeding additional CO₂ gas into the cell. A strategy proposed by Newman and his co-workers is outlined in Figure 26.[81] The catholyte is first saturated with CO₂ at the gas/liquid contactor and then mixed with additional CO₂ gas before entering the cathode chamber. The CO current density was improved to 30 mA/cm² with a CO FE of 80%, compared to the previous design. At higher potentials, the total current density was increased to approximately 80 mA/cm², while the CO FE was dropped to ~33%. The enhancement of CO current density may be a result of the presence of CO₂ gas bubbles at near electrode surface that created three-phase boundaries for CO₂ electrocatalytic conversion. Further increase of CO₂ flow rate may not be able to improve the CO current density, because the gas bubbles could also block the active sites.

Figure 26. A typical CO₂ electrolyzer system design with both a gas/liquid contactor and an additional CO₂ gas stream for CO₂ intake.

Figure 27. A typical CO₂ electrolyzer system design with CO₂ gas flowing through one side of cathode.

To further improve the CO current density, Kenis et al. reported a microfluidic electrochemical cell design, in which a pure CO₂ gas flows on one side of Ag electrode and a liquid electrolyte flows on the other side (Figure 27).[85] By manipulating the three-phase boundary structure, the CO₂ gas is able to reach the catalyst surface without suffering from the solubility limit in electrolyte, resulting in a significantly higher current density ($\sim 100 \text{ mA/cm}^2$ at 3V).[85] Since CO₂ is not in direct contact with catholyte, a basic electrolyte can be employed in the system. By doing so, the current density can be further improved. While a very high current density for CO₂ reduction was achieved using this design, it is challenging to cost-effectively separate the small portion of CO from more than 90% of unreacted CO₂ due to the “flow-through” design.

Figure 28. A typical pressurized CO₂ electrolyzer system with high pressure CO₂ flowing across cathode.

Another strategy to improve CO₂ solubility in aqueous electrolytes is to increase the cell pressure. Lister et al. developed a pressurized electrochemical cell for CO₂ electrolysis.[86] Instead of

“flow-through”, a high pressure CO₂ gas flows across the catalyst gas diffusion layer (cathode) and reaches the catholyte that is circulating through a separator and a pump (Figure 28). The pressurized CO₂ electrolyzer exhibited a very high current density (~220 mA/cm²) together with a high CO selectivity (~90%) at a pressure of 18.5 atm. The simultaneous achievement of a high current density and a high CO selectivity represents current state-of-art performance for CO₂ electrolysis. Because of the high pressure, the cell components may require additional engineering efforts to improve the robustness.

5. Future directions in CO₂ electrolysis

CO₂ utilization, especially coupling with renewable energy, plays an important role in realizing sustainable energy future.[87, 88] In this article, we reviewed recent development of novel CO₂ reduction electrocatalysts, new understanding of CO₂ reduction mechanism, and design strategies of CO₂ electrolysis. These efforts represent the most important areas to push CO₂ electrolysis technology towards commercialization. In our opinion, the following directions may present new opportunities to break through the CO₂ electrolysis technology.

5.1 New CO₂ reduction electrocatalyst

Hunting for CO₂ reduction catalysts with a high selectivity towards high value chemicals is always a very important direction to pursue. At current stage, only CO and formate can be produced selectively through CO₂ electrolysis using state-of-art electrocatalysts. New catalysts that can produce other high value chemicals from CO₂ in a highly selective way will certainly open new opportunity. Catalysts beyond monometallics, such as bimetallic and non-metallic catalysts, are potential candidates for future investigation. Nanostructuring catalysts is another promising area for potential breakthroughs. Highly nanostructured catalysts not only enable much higher currents, but also they may exhibit unique catalytic properties compared to their bulk counterparts.

5.2 Better understanding of CO₂ reduction mechanism

How CO₂ molecule is reduced on the electrocatalyst surface is still a mystery. It is also not well understood why bicarbonate and carbonate cannot be reduced electrochemically at an appreciable rate. A comprehensive understanding of reaction mechanism of electrochemical CO₂ reduction may provide answers to these critical questions and allow rational design of next generation of CO₂ reduction electrocatalysts as well as novel processes that couple CO₂ capture with CO₂ electrochemical conversion. Efforts in developing new *in operando* spectroscopic tools are highly appreciated as they enable us to probe catalytic reaction occurring at the electrode/electrolyte interface. Other characterization tools, such as time-resolved and surface sensitive techniques, may provide additional insights into the reaction mechanism.

5.3 Engineering CO₂/electrode/electrolyte interface

CO₂ electrochemical reduction is a process involving transfer of multiple electrons and protons. Because of the low solubility of CO₂ in electrolytes, how to deliver CO₂ effectively to the cathode surface becomes the key to achieve a high current density and a high CO₂ reduction selectivity simultaneously in a practical CO₂ electrolyzer. Unfortunately, very limited efforts

have been devoted into engineering CO₂ electrolyzer systems. New strategies to introduce CO₂ to the cell, efficient product separation methods, and membrane/membrane-less designs are all interesting topics for future studies.

To implement CO₂ electrolyzers for practical applications, current price of electricity may be too expensive (approximately \$0.07/kWh). However, there are some niche areas where it is possible to consider the new technology. For example, at specific geographical locations, electricity is produced from geothermal energy at a much lower cost compared to other traditional power generation sources. Therefore, it may be possible to commercialize the CO₂ electrolysis technology in an economical way at these locations. In addition to that, if a carbon tax becomes a reality, CO₂ electrolysis technology will be the critical technology that can reduce CO₂ emission and produce useful chemicals for industry simultaneously. Finally, we hope the discussion presented in this article could stimulate interests in CO₂ electrolysis technology towards real applications.

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Graphical abstract:

Recent progresses on electrochemical CO₂ reduction have been reviewed, with a focus on new development of CO₂ reduction electrocatalysts, mechanistic understanding of CO₂ electro-reduction reaction, and process engineering efforts in CO₂ electrolyzers.