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### Promises of Main Group Metal–Based Nanostructured Materials for Electrochemical CO<sub>2</sub> Reduction to Formate

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Selective CO<sub>2</sub> reduction to formic acid or formate is the most technologically and economically viable approach to realize electrochemical CO<sub>2</sub> valorization. Main group metal-based (Sn, Bi, In, Pb, and Sb) nanostructured materials hold great promise, but are still confronted with several challenges. Here, the current status, challenges, and future opportunities of main group metal-based nanostructured materials for electrochemical CO<sub>2</sub> reduction to formate are reviewed. Firstly, the fundamentals of electrochemical CO<sub>2</sub> reduction are presented, including the technoeconomic viability of different products, possible reaction pathways, standard experimental procedure, and performance figures of merit. This is then followed by detailed discussions about different types of main group metal-based electrocatalyst materials, with an emphasis on underlying material design principles for promoting the reaction activity, selectivity, and stability. Subsequently, recent efforts on flow cells and membrane electrode assembly cells are reviewed so as to promote the current density as well as mechanistic studies using in situ characterization techniques. To conclude a short perspective is offered about the future opportunities and directions of this exciting field.

#### 1. Introduction

Carbon is a versatile element and can be found in a large variety of molecules and compounds. It is an essential ingredient of all living organisms, in the forms of proteins, DNA, and so on. It is the cornerstone of our modern society, in the form of fossil fuels. It also exists in the atmosphere in the form of  $CO_2$ , and in rocks in the form of minerals such as limestone and dolomite. In our planet, carbon continuously moves from one reservoir to another – a process called the carbon cycle.<sup>[1]</sup> Natural carbon cycle is maintained very nearly in balance to keep earth's temperature relatively stable. Unfortunately, increasing human activities and energy consumptions ever since the industrialization has disrupted the natural carbon cycle and led to rising global atmospheric  $CO_2$  concentration at an alarming rate.<sup>[2]</sup>

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combustion reaches the level of gigatons. Correspondingly, the atmospheric CO<sub>2</sub> concentration rises from 320 ppm in 1960 to above 410 ppm in 2019.<sup>[3]</sup> CO<sub>2</sub> accumulation from burning more fossil fuels results in severe environmental issues such as temperature rise and climate change.<sup>[4,5]</sup> In order mitigate or even reverse this trend, it becomes imperative to not only change our energy consumption pattern, but also develop economically viable technologies to capture CO<sub>2</sub> from the atmosphere.<sup>[6–8]</sup> In nature, green plants (and a few other organisms) utilize the abundant energy from the sun to convert water and CO<sub>2</sub> into carbohydrates and O<sub>2</sub> through the process known as photosynthesis. Nevertheless, their photosynthetic efficiency is often less than 1%.<sup>[9]</sup> It would be highly desirable if we could develop artificial approaches to mimic this natural process but at much higher conversion efficiency.<sup>[10–13]</sup>

Existing CO<sub>2</sub> conversion technologies can be generally divided into four different categories: biochemical, thermochemical, photochemical, and electrochemical.<sup>[13-18]</sup> Among them, electrochemical CO2 reduction attracts quickly growing attention recently. This process is driven by energetic electrons at the cathode and transforms CO2 into value-added chemicals such as CO, formic acid (or formate), methane, methanol, ethylene, ethanol, and so on.[19-22] Importantly, electrochemical CO2 reduction can be coupled with photovoltaic or other renewable energy harvesting devices, and enables the storage of intermittent renewable energy in chemical bonds with high volumetric and gravimetric energy density, thus offering a promising solution toward building a sustainable carbonneutral economy (Figure 1).<sup>[20,23–25]</sup> In addition, this technology usually does not require high temperature or high pressure reaction conditions, and is likely to be implemented more quickly on an industrial scale than other competing technologies, such as photocatalytic CO<sub>2</sub> reduction that is also an active ongoing research direction.<sup>[26]</sup>

Electrochemical  $CO_2$  reduction reaction ( $CO_2RR$ ) is confronted with two general challenges. First of all, the relative thermodynamic stability of  $CO_2$  molecules renders their reduction kinetically sluggish.  $CO_2$  is a linear molecule containing two stable C=O double bonds. Its reduction involves a geometry change from the linear molecular geometry to the bent molecular geometry, and hence a large reorganizational energy.<sup>[19]</sup> In the absence of any electrocatalyst, the first electron





**Figure 1.** Schematic illustration of the artificial carbon cycle via electrochemical  $CO_2RR$  powered by renewable energy sources such as wind, solar, and tide. In this way, high concentration of  $CO_2$  released by industrial and human activities can be recycled back and converted to value-added products, effectively closing the carbon cycle.

transfer to form CO<sub>2</sub><sup>--</sup> anion radical occurs at a highly negative potential of -1.90 V (vs standard hydrogen electrode, or SHE), making the reaction energetically prohibitive to take place.<sup>[27]</sup> Second, the multiple reaction pathways of CO<sub>2</sub> reduction limits the reaction selectivity.<sup>[19,28]</sup> CO<sub>2</sub> reduction can proceed via 2, 4, 6, 8, 12, or even more electron-transfer pathways, giving rise to a large spectrum of possible reduction products. In addition, CO<sub>2</sub>RR needs the participation of free protons or proton donators (e.g.,  $HCO_3^{-}$ ) in order to break the C=O double bond. It is thereby not surprising that hydrogen evolution reaction (HER) always exists as the competing side reaction, which, unfortunately, is often kinetically favored over CO<sub>2</sub>RR.<sup>[29]</sup> As a result, we are in urgent need to develop proper electrocatalysts so as to significantly expedite the reaction rate and steer the reaction selectivity toward the target product. Since the pioneering works by Hori et al. in 1980s and 1990s,<sup>[30-33]</sup> great efforts have been devoted to the design and engineering of CO2RR electrocatalysts especially within the past decade.<sup>[13,22,34,35]</sup> There have been many encouraging experimental progresses as well as increasing mechanistic understanding of this complex reaction. However, the above two challenges are not completely solved.

In this progress report, we review the emerging advances in the design and applications of main group metal–based nanostructures for electrochemical  $CO_2$  reduction to formate. Even though there are already a few comprehensive reviews about  $CO_2RR$  in literature, we specifically focus on main group metals here because they represent a relatively underexplored group of materials compared to common transition metals such as Au, Ag, Cu, and so on, and are interestingly unique for the selective production of formate. This progress report starts with fundamentals about  $CO_2RR$  to formate including the technoeconomic viability of the reduction product, possible reaction pathways, experimental procedure and product analysis, and performance figures of merit. We then overview different types of main group metal–based (Sn, Bi, In, Pb, and Sb) electrocatalysts with the emphasis on their structure–property correlation. Subsequently, we discuss recent efforts on flow cells and membrane electrode assembly cells for promoting the current density as well as mechanistic studies using in situ characterization techniques. At last, we summarize existing challenges and present a brief perspective about the future development and opportunity of this exciting field.

## 2. Fundamentals of Electrochemical CO<sub>2</sub> Reduction

#### 2.1. Why Formic Acid (or Formate) as the Reduction Product

Formic acid (or formate) is an important chemical intermediate for many industrial processes, and is widely used in leather, pesticide, medicine, dyestuff, and rubber industries.<sup>[36]</sup> It is a promising liquid hydrogen storage and delivery option, and can release  $H_2$  when needed through its catalytic decomposition.<sup>[37–39]</sup> It can also be used as the chemical fuel for direct formic acid (or formate) fuel cells.<sup>[40–42]</sup> The industrial production of formic acid is conventionally achieved via the carbonylation of methanol and subsequent hydrolysis of the methyl formate. This process is, however, energy





Figure 2. Comparison of the values of different  $CO_2RR$  products in terms of their market prices ( $kg^{-1}$ ) and added values per kWh electrical energy input ( $kWh^{-1}$ ) estimated based on ideal full cells.

intensive, and limited by the slow reaction rate, undesirable by-products, and high cost of investment.<sup>[43]</sup> It is therefore highly appealing to pursue the direct electrochemical  $CO_2$  reduction under mild conditions and with high energy conversion efficiency.

Of important note, the commercial viability of CO<sub>2</sub>RR to different products depends on a series of factors including not only the market demand of the product, but also the material, manufacturing, and separation costs. Although it is intuitively more desirable to control the selectivity toward higher-valued products such as ethylene, ethanol, acetate, n-propanol, or even C4 products,[44-47] recent technoeconomic analysis unambiguously points out that the two-electron electrochemical CO<sub>2</sub>RR to CO or formic acid is the most economically viable, whereas those  $C_2$ – $C_4$  products other than propanol are not even profitable.<sup>[26,48-50]</sup> This is understandable because the electricity cost is the major contributor to the operation cost of CO<sub>2</sub> electrolyzer. CO and formic acid exhibit the highest added value per kWh of electrical energy input, while C2-C4 products have considerably lower added value per kWh of electrical energy input (Figure 2). Moreover, the reaction selectivity dramatically drops when the product molecules become increasingly complex. This is because the coupling to form  $C_2-C_4$  products requires the adsorption of multiple CO<sub>2</sub> molecules on surface and their concerted transformation, and is statistically challenged.<sup>[19,51-53]</sup> Current state-of-the-art electrocatalysts have the maximum selectivity of ≈100% for CO or formate,<sup>[54–58]</sup> but only ≈60% for ethylene,<sup>[59–61]</sup>  $\approx$ 40% for acetate,<sup>[62–64]</sup> and  $\approx$ 15% for *n*-propanol.<sup>[65]</sup> Poor selectivity not only results in ineffective utilization of electrolyzer electricity, but also incurs additional costs for the product separation. As a result, it is not until the further decrease of electricity prices and improvement of electrocatalyst performance that the mass production of  $C_2-C_4$  products from CO2RR would become economically profitable. Selective two-electron CO<sub>2</sub>RR to CO or formate is so far our best

target, and the products can be further upgraded chemically or electrochemically.

#### 2.2. Reaction Mechanism of CO<sub>2</sub>RR

Depending on the working electrocatalysts and actual experimental conditions, CO<sub>2</sub>RR can proceed through different reaction pathways involving the transfer of two, four, six, eight, twelve, or even more electrons to form various products.<sup>[19]</sup> The competition among different reaction pathways gives rise to different product distributions. Over the past few decades, these reaction pathways have been studied both experimentally and theoretically.<sup>[19,66-69]</sup> It is now generally agreed that the ratedetermining step of CO<sub>2</sub>RR is often the first electron transfer to surface-adsorbed \*CO2 (where \* denotes the adsorption site) to form \*CO2<sup>--</sup> intermediate (Figure 3).<sup>[19]</sup> The next step is determined by which atom binds to the electrode surface. If the oxygen atom of \*CO2<sup>-</sup> binds to the electrode surface, the carbon atom would be protonated to form \*OCHO. If the carbon atom of  $^{*}CO_{2}$  binds to the electrode surface instead, the oxygen atom would be protonated to form \*COOH. After the subsequent electron (and proton) transfer, the first pathway eventually leads to the formation of formic acid or formate, while the second pathway leads to the formation of \*CO and eventually CO that releases from the catalyst surface. For some catalyst such as Cu, \*CO on surface can be further reduced to form various hydrocarbons and alcohols, the details of which remain controversial and are not the focus of this review.<sup>[28,66,70]</sup>

The selectivity of CO<sub>2</sub>RR is essentially determined by the relative binding strength of \*OCHO, \*COOH, \*CO, as well as \*H (intermediate to H<sub>2</sub>) at the electrode surface.<sup>[29,69,71]</sup> Since the adsorption of \*OCHO and \*COOH is usually endothermic, the catalyst surface that stabilizes \*OCHO would relatively favor CO<sub>2</sub>RR to formic acid or formate, and the catalyst surface that



Figure 3. Possible reaction pathways for electrochemical CO<sub>2</sub>RR to formate, CO, and other products.

stabilizes \*COOH would relatively favor CO. Based on this consideration, metallic CO<sub>2</sub>RR electrocatalysts can be generally categorized into three different groups.<sup>[32]</sup> Metals in Group I are mostly late transition metals including Au, Ag, Zn, Pd, and so on. They thermodynamically favor the adsorption of \*COOH over \*OCOH, and generally yield CO as the main CO2RR product. Metals in Group II are mostly main group metals including Sn, Pb, Hg, In, Bi, and so on. They thermodynamically favor the adsorption of \*OCOH over \*COOH, and generally yield formate as the main CO2RR product. Cu belongs to Group III for its ability to relatively stabilize both \*COOH and \*CO, and is the only pure metal that can reduce CO<sub>2</sub> beyond two electrons in an appreciable quantity. Of note, the above categorization only applies to CO2RR in aqueous solution. In aprotic solution (such as acetonitrile or ionic liquids) with low proton donor availability, CO becomes the predominant reduction product on main group metals.<sup>[72]</sup> CO<sub>2</sub>RR in aprotic solution is not the focus of our present review because it is less amenable to practical applications.

Figure 4 presents the standard redox potentials (versus SHE) of CO<sub>2</sub>RR to a few common products such as CO, formic acid (or formate),  $CH_4$ , and  $C_2H_4$  as well as HER and oxygen evolution reaction (OER) as a function of solution pH. Since most of these reactions involve proton-coupled electron transfer, their  $E \sim pH$ lines are parallel and have a slope of 59.2 mV pH<sup>-1</sup>. However, CO<sub>2</sub>RR to formic acid (or formate) is a bit more complex. The reduction product is pH-dependent: at pH < 3.75, it exists in the form of formic acid, whereas at pH > 3.75, the product exists in the deprotonated form. Correspondingly, the  $E \sim pH$  line of CO<sub>2</sub>RR to formic acid (or formate) consists of two segments with a slope of 59.2 mV  $pH^{-1}$  at pH < 3.75 and a slope of 29.6 mV  $pH^{-1}$  at pH > 3.75. One implication of this slope change is as follows: while CO2RR to formic acid is the least favored thermodynamically in acids, increasing solution pH causes the product to deprotonate and renders the reaction easier to take place. At  $pH \approx 7$  (the pH of bicarbonate solution), the standard redox potential of CO<sub>2</sub>RR to formate is comparable to that of HER. At pH = 14, the standard redox potential of CO<sub>2</sub>RR to formate is  $\approx$ 230 mV more positive than that of HER, and  $\approx$ 320 mV more positive than that of CO<sub>2</sub>RR to CO. As a result, it is clearly more advantageous to run CO2RR at highly alkaline solution if one targets formate as the reduction product.

#### 2.3. Electrochemical Measurements and Product Analysis

In order to obtain reliable and reproducible results and to allow the cross comparison of experimental data from different

research groups, standardized measurement practices must be rigorously followed. CO<sub>2</sub>RR is typically carried out in twocompartment H-type electrochemical cells using the standard three-electrode system. The working electrode is generally prepared by dispersing the electrocatalyst powder together with the carbon black additive and polymer binder in ethanol under ultrasonication to form a uniform catalyst ink, and then drop casting a calculated amount of the catalyst ink onto a proper current collector such as glassy carbon electrode, glassy carbon plate, or carbon fiber paper. Other common current collectors such as Ni foam, Cu foam, indium tin oxide (ITO), or fluorinedoped tin oxide conducting glass are inappropriate here due to their strong interference with CO<sub>2</sub>RR measurements. The working electrode and the reference electrode are placed in the cathodic compartment, and the counter electrode is placed in the anode compartment. The two compartments are separated by an anion-exchange membrane to prevent the crossover of the reduction product. Typical anion-exchange membranes in use are the Selemion anion exchange membrane from Asahi Glass Company or the Sustainion anion exchange membrane from Dioxide Materials. Aqueous solution of NaHCO3 or KHCO3



**Figure 4.** Standard redox potentials of electrochemical  $CO_2RR$  to different products as well as HER and OER as a function of the solution pH.

is most often selected as the electrolyte. When saturated with CO<sub>2</sub>, the electrolyte can effectively buffer the pH change of the bulk solution and maintain it around neutral. Other buffering or nonbuffering electrolytes are sometimes used but not recommended for standardized measurements. Importantly, it is worth mentioning that CO<sub>2</sub>RR is sensitive to impurities in electrolyte even though it is less an issue for main group metals. Since CO<sub>2</sub>RR usually takes place at highly cathodic potentials, transition metal ions (such as Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and so on) in the electrolyte even at 5 ppm can be electrodeposited onto the working electrode during CO2RR and unexpectedly contaminate the working electrode.<sup>[73]</sup> To remedy this problem, the electrolyte is usually pre-electrolyzed to lower the concentration of transition metal ions or added with, for example, metal chelator ethylenediaminetetraacetic acid to block the deposition of these impurities onto the working electrode.<sup>[74-76]</sup>

During CO<sub>2</sub>RR measurements, high-purity CO<sub>2</sub> gas is continuously bubbled into the electrolyte at the flow rate of 5–20 sccm that is precisely controlled by a digital flow meter. Qualitative and quantitative analysis of CO<sub>2</sub>RR products is typically performed during chronoamperometric (*i*–*t*) measurements at selected potentials. Gaseous products (such as H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and so on) can be periodically sampled from the venting gas and measured by a gas chromatograph (GC) connected online to the H-cell. Liquid products (such as formate, methanol, ethanol, acetate, and so on) accumulated in the catholyte at the end of tests can be measured using proton nuclear magnetic resonance (<sup>1</sup>H NMR). Alternatively, we find that ion chromatography is an effective tool for quantifying the amount of formate in the catholyte.<sup>[56–58,77]</sup> It has a lower detention limit (≈100 ppb) than NMR (1–10 ppm), and is easier to operate.

#### 2.4. Performance Figures of Merit

 $\rm CO_2RR$  electrocatalyst materials are usually assessed for their activity, selectivity, and stability in terms of the following key performance metrics.

#### 2.4.1. Onset Potential

The onset potential is defined as the working potential where the target product is first reliably detected by GC or NMR. For the purpose of consistency, all potential readings are recommended to be reported on the reversible hydrogen electrode (RHE) scale in order to eliminate the pH effect, and compensated for the possible Ohmic loss. We do not recommend the direct determination of the onset potential from the polarization curve like what many people do for HER and OER electrocatalysis. This is because the onset of cathodic current density in the polarization curve does not necessarily reflect the true onset of CO<sub>2</sub>RR. Having a less cathodic onset overpotential indicates that CO2RR can be more easily initiated on the electrocatalyst and thereby is highly desirable. It also translates to less energy consumption when the CO<sub>2</sub>RR electrocatalyst is coupled with an OER electrocatalyst for the full-cell electrolysis. Among all existing formate-producing electrocatalysts, Pd or its alloys are the only known materials to have onset potentials close to the standard reduction potential although they are notorious for their poor stability.<sup>[78]</sup> Main group metals typically have an onset overpotential (that is, the difference between the onset potential and the standard reduction potential) of >300 mV (see **Table 1**).

#### 2.4.2. Faradaic Efficiency

When there are more than one competing reaction processes taking place simultaneously at a given potential, the reaction selectivity becomes a major concern. It is particularly important for CO2RR due to its multiple possible reaction pathways and the strongly competing HER process. Selectivity is often measured by Faradaic efficiency (FE), which is defined as the ratio of charges transferred to the target product over the total charge passed during the reaction. It can be calculated using the follow equation:  $FE = \alpha n F/Q$ , where  $\alpha$  is the number of electrons needed for the formation of one molecule of the target product, n is the amount of the target product, F is the Faraday's constant, and Q is the total charge. Faradaic efficiency reflects how kinetically favorable a particular reaction process is. High Faradaic efficiency is desirable because it may reduce the additional cost for product separation and purification. As we would see from the discussion in Section 3 (Figure 5), main group metals typically have peak formate Faradaic efficiency of 70-100%. How to further promote their selectivity and achieve Faradaic efficiency close to unity over a large potential window (not just one particular potential point) remains to be a challenging task.

#### 2.4.3. Partial Current Density

Partial current density is the effective current density that drives the formation of the target product. It can be derived by multiplying the total current density with the Faradaic efficiency at different potentials. Partial current density is determined by not only the intrinsic activity of electrocatalysts, but also experimental conditions such as the type of current collector, the geometry of electrochemical cell, the electrolyte, and so on. Most previous studies carried out in H-cell report the maximum formate partial current density of <30 mA cm<sup>-2</sup> due to the CO<sub>2</sub> solubility and diffusion limit in the bicarbonate electrolyte. Gas diffusion electrodes can effectively lift this limit and dramatically improve the partial current density. They are now actively pursued for commercial CO<sub>2</sub> electrolyzers.

#### 2.4.4. Stability

The stability of  $CO_2RR$  electrocatalysts measures their capability of retaining the activity and selectivity under prolonged galvanostatic or potentiostatic polarization. Many electrode materials are subjected to the gradual loss and poisoning of active sites or irreversible structural failure under the harsh  $CO_2RR$  condition. At present, the stability studies of most  $CO_2RR$  electrocatalysts in laboratory are carried out for only tens of hours at the most. Successful commercialization of this technology, however, would demand a catalyst lifetime of thousands of hours.<sup>[48,79]</sup> This huge gap needs to be bridged

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Table 1. Performance comparison of different main group metal-based electrocatalysts for CO<sub>2</sub> reduction to formate from recent literature.

Electrocatalysts	Electrolyte	Formate FE <sub>max</sub>	j <sub>HCOO</sub> <sup>-</sup> at FE <sub>max</sub>	Ref.
Nano-SnO <sub>2</sub> /graphene	0.1 м NaHCO <sub>3</sub>	93.6%@-1.8 V versus SCE	9.5 mA cm <sup>-2</sup>	[91]
Sn/SnO <sub>x</sub> thin film	0.5 м NaHCO <sub>3</sub>	40%@-0.7 V versus RHE	1.6 mA cm <sup>-2</sup>	[82]
Ultrasmall SnO <sub>2</sub> NP (<5 nm)	1 м КНСО <sub>3</sub>	64%@-1.21 V versus RHE	92.8 mA cm <sup>-2</sup>	[147]
SnO <sub>2</sub> pNWs	0.1 м NaHCO <sub>3</sub>	80%@-0.8 V versus RHE	4.8 mA cm <sup>-2</sup>	[88]
SnO <sub>2</sub> /CC	0.5 м NaHCO <sub>3</sub>	$87\pm2\%$ @–1.8 V versus Ag/AgCl	45 mA cm <sup>-2</sup>	[84]
Sn dendrite electrode	0.1 м КНСО <sub>3</sub>	71.6%@-1.36 V versus RHE	17.1 mA cm <sup>-2</sup>	[148]
Chain-like mesoporous SnO <sub>2</sub>	0.1 м КНСО <sub>3</sub>	95%@-1.06 V versus RHE	13 mA cm <sup>-2</sup>	[149]
Sn gas diffusion electrode	0.1 м КНСО <sub>3</sub>	64%@-1.2 V versus RHE	NA	[83]
Sn(S)/Au	0.1 м КНСО <sub>3</sub>	93%@-0.75 V versus RHE	51.1 mA cm <sup>-2</sup>	[90]
Sn/CNT-Agls/CC	0.5 м КНСО <sub>3</sub>	82.7%@-0.96 V versus RHE	26.7 mA cm <sup>-2</sup>	[150]
SnO <sub>x</sub> @multiwalled carbon nanotube-COOH	0.5 м КНСО <sub>3</sub>	77%@-1.25 V versus SHE	8.5 mA cm <sup>-2</sup>	[151]
Wire-in-tube SnO <sub>2</sub>	0.1 м КНСО <sub>3</sub>	63%@-0.99 V versus RHE	NA	[152]
Sn-CF1000	0.1 м КНСО <sub>3</sub>	62%@-0.8 V versus RHE	11 mA cm <sup>-2</sup>	[153]
Sn quantum sheets/GO	0.1 м КНСО <sub>3</sub>	89%@-1.8 V versus SCE	18.8 mA cm <sup>-2</sup>	[92]
SnS <sub>2</sub> /rGO	0.5 м NaHCO <sub>3</sub>	84.5%@-1.4 V versus Ag/AgCl	11.7 mA cm <sup>-2</sup>	[89]
Mp-SnO <sub>2</sub> NS	0.5 м NaHCO <sub>3</sub>	83.5%@-0.9 V versus RHE	15 mA cm <sup>-2</sup>	[77]
Electrodeposited Bi dendrites	0.5 м NaHCO <sub>3</sub>	96.4%@-1.8 V versus SCE	14.6 mA cm <sup>-2</sup>	[154]
Bi nanoflake	0.1 м КНСО <sub>3</sub>	≈100%@-0.6 V versus RHE	≈1 mA cm <sup>-2</sup>	[98]
Hierarchical Bi dendrite	0.5 м КНСО <sub>3</sub>	≈89%@-0.74 V versus RHE	2.4 mA cm <sup>-2</sup>	[97]
Bi nanosheets	0.1 м КНСО <sub>3</sub>	86%@-1.1 V versus RHE	16.5 mA cm <sup>-2</sup>	[103]
Ultrathin Bi nanosheets	0.5 м NaHCO <sub>3</sub>	≈100%@-1.0 V versus RHE	12.5 mA cm <sup>-2</sup>	[56]
Few-layer bismuth subcarbonate nanosheet	0.5 м NaHCO <sub>3</sub>	85%@-0.7 V versus RHE	8.5 mA cm <sup>-2</sup>	[155]
Sulfide-derived Bi	0.5 м NaHCO <sub>3</sub>	84%@-0.75 V versus RHE	4.2 mA cm <sup>-2</sup>	[156]
P-orbital localized-Bi	0.5 м КНСО <sub>3</sub>	95%@-1.16 V versus RHE	54.1 mA cm <sup>-2</sup>	[157]
BiO <sub>x</sub> /C	0.5 м NaHCO <sub>3</sub>	92.1%@-1.37 V versus Ag/AgCl	1.35 mA cm <sup>-2</sup>	[105]
Bi–PMo nanosheets	0.5 м NaHCO <sub>3</sub>	93 $\pm$ 2%@-0.86 V versus RHE	30 mA cm <sup>-2</sup>	[158]
Bi <sub>2</sub> O <sub>3</sub> -NGQDs	0.5 м КНСО <sub>3</sub>	98%@-0.87 V versus RHE	16.6 mA cm <sup>-2</sup>	[106]
Мр-Ві	0.5 м NaHCO <sub>3</sub>	≈100%@-0.9 V versus RHE	15 mA cm <sup>-2</sup>	[57]
NTD-Bi	0.5 м КНСО <sub>3</sub>	100%@-0.85 V versus RHE	42 mA cm <sup>-2</sup>	[58]
Hp–In catalyst	0.1 м КНСО <sub>3</sub>	90%@-1.2 V versus RHE	67.5 mA cm <sup>-2</sup>	[108]
In NPs	0.5 м K <sub>2</sub> SO <sub>4</sub>	90%@-1.1 V versus RHE	NA	[159]
Anodized indium	0.5 м K <sub>2</sub> SO <sub>4</sub>	87.2%@-1.7 V versus SCE	NA	[109]
In <sup>0</sup> –In <sub>2</sub> O <sub>3</sub> composite	0.1 м Na <sub>2</sub> SO <sub>4</sub>	≈100%@-1.8 V versus Ag/AgCl	NA	[160]
Sulfur-doped indium	0.5 м КНСО <sub>3</sub>	95%@–0.98 V versus RHE	58.9 mA cm <sup>-2</sup>	[110]
Dendritic indium foams	0.5 м КНСО <sub>3</sub>	86%@-0.86 V versus RHE	5 mA cm <sup>-2</sup>	[107]
Nanolayered Pb	0.1 м КНСО <sub>3</sub>	94.7%@-1.7 V versus Ag/AgCl	NA	[161]
Porous Pb electrode	0.5 м КНСО <sub>3</sub>	96.8%@-1.7 V versus SCE	NA	[112]
Pb granule electrodes	0.2 м K <sub>2</sub> CO <sub>3</sub>	94%@-1.8 V versus SCE	NA	[162]
Oxide-derived Pb	0.5 м NaHCO <sub>3</sub>	≈100%@-0.75 V versus RHE	NA	[111]
Sb nanosheet-graphene	0.5 м NaHCO <sub>3</sub>	84%@-1.06 V versus RHE	NA	[114]

in the near future. An electrocatalyst with satisfactory stability can reduce the maintenance and replacement cost as well as downtime during operation. On the other hand, studying and understanding the material degradation mechanism may inspire possible further improvements, and eventually lead to new generations of electrocatalysts.

#### 2.4.5. Environmental Impact and Cost

In addition to activity, selectivity, and stability, ideal  $CO_2RR$  electrocatalysts should have a low environmental impact and are preferably composed of earth-abundant and low-cost elements. Of the many main group metals first reported by





Figure 5. Selective comparison of formate Faradaic efficiency on main group metal-based electrocatalysts reported in recent literature.

Hori for selective  $CO_2RR$  to formate, Pb, Hg, Cd, and Tl are clearly out of consideration for practical applications because they are highly toxic and environmentally hazardous, while In is too expensive.<sup>[32]</sup> As a result, Sn- and Bi-based materials come to the fore and attract the most research attention at present. Moreover, to fulfil the requirements of low environmental impact and low manufacturing cost, these electrocatalysts would have to be prepared and processed via green and economical methods.

### 3. Main Group Metal–Based Electrocatalysts for Selective CO<sub>2</sub>RR to Formate

In this section, we will review the current development status of different main group metal–based electrocatalysts in detail. Focus will be placed on Sn and Bi owing to their wide popularity in literature. To aid readers in better digesting the large amount of information, we prepare Table 1 and Figure 5 to summarize and compare the performances of different electrocatalysts covered in the following discussion.

#### 3.1. Sn-Based Electrocatalysts

Sn is one of the most widely investigated materials for  $CO_2RR$ . Its first report dates back to the work by Ito et al.<sup>[80]</sup> Early study of Hori et al. suggested that bulk Sn electrode could enable selective  $CO_2RR$  to formate but with relatively large overpotential and low current density.<sup>[32]</sup> Of note, Sn and other main group metals are easily prone to oxidation when exposed to air. Their metallic electrodes are usually covered with oxide layers on surface. Based on the standard redox potential, the surface oxide would be reduced before  $CO_2RR$  can take place.<sup>[81]</sup> Nevertheless, recent study suggests that some oxygen residues can persist even under highly cathodic potentials and may actively participate in  $CO_2RR$ . For example, Chen and Kanan investigated the important role of surface oxide by comparing the CO<sub>2</sub>RR activity of Sn foils that were subjected to different pre-electrolysis treatments (Figure 6a,b).<sup>[82]</sup> They found that compared to the Sn electrode with a freshly exposed metallic surface, the one with a native  $SnO_x$  layer exhibited a lower overall current density but significantly higher formate selectivity. It was believed that the presence of residual surface oxide facilitated the formation of \*CO<sub>2</sub>.- intermediate as the rate determining step, whereas in its absence, HER became the dominant cathodic pathway. Native surface oxide is beneficial to CO<sub>2</sub>RR. However, having a too thick surface oxide layer may cause a negative effect. Zhou and co-workers examined the dependence of formate selectivity on the thickness of surface oxide layer on ≈100 nm Sn nanoparticles (NPs).<sup>[83]</sup> They concluded that nanoparticles with  $\approx$ 3.5 nm native SnO<sub>x</sub> layer exhibited the optimal formate selectivity of 64% at -1.2 V versus Ag/AgCl. Further thickening the oxide layer adversely led to increasing CO and H<sub>2</sub> selectivity.

Given the unique role that the surface oxide layer may play, many research groups employ SnO2 as the starting material or so-called "precatalyst" instead of directly using Sn metal. SnO<sub>2</sub> is then electrochemically reduced to metallic Sn with some residual surface oxide prior to CO<sub>2</sub>RR. This precatalyst approach has several advantages. First, there is a considerably larger library of established synthetic methods for various SnO<sub>2</sub> nanostructures than there is for metallic Sn. By carefully controlling the size and morphology of precatalysts, we are able to indirectly tailor those of the actual working catalysts. Second, the electrochemical reduction of SnO<sub>2</sub> to Sn roughens the catalyst surface and exposes more catalytically active sites. Zhang and co-workers prepared 3D hierarchical mesoporous SnO<sub>2</sub> nanosheets uniformly grown on carbon cloth via a hydrothermal method followed by calcination in air.<sup>[84]</sup> Electrochemical measurements showed that a partial current density of  $\approx$ 45 mA cm<sup>-2</sup> and Faradaic efficiency of ≈87% were achieved for selective  $CO_2RR$  to formate at the overpotential of  $\eta = 0.88$  V.<sup>[84]</sup> The authors believed that the improved performance was due to





**Figure 6.** a) Scanning electron microscope (SEM) image of porous  $SnO_2$  nanosheets on carbon cloth ( $SnO_2/CC$ ). b)  $CO_2RR$  product distribution on  $SnO_2/CC$  at different applied potentials. Reproduced with permission.<sup>[84]</sup> Copyright 2017, Wiley. c) Transmission electron microscope (TEM) image of mesoporous  $SnO_2$  nanosheets (mp-SnO\_2). d) Faradaic efficiency of formate, CO, and H<sub>2</sub> at different potentials on mp-SnO<sub>2</sub> in comparison with the Faradaic efficiency of formate on commercial Sn foil. Reproduced with permission.<sup>[77]</sup> Copyright 2019, The Royal Society of Chemistry. e) TEM images of porous Sn nanowires (Sn-pNWs) with abundant grain boundaries. f) Potential-dependent formate Faradaic efficiency on Sn-pNWs and other Sn electrocatalysts. Reproduced with permission.<sup>[88]</sup> Copyright 2017, Wiley.

the advantageous 3D hierarchical structure, which enlarged the electrochemically accessible surface area, facilitated the charge transfer at the surface, and also promoted the mass transport of reactant and product. Our own research group also prepared mesoporous SnO<sub>2</sub> nanosheets and nanoclusters as the precatalysts, and achieved active and selective CO2RR to formate in 0.5 м NaHCO<sub>3</sub> (Figure 6c,d).<sup>[77,85]</sup> Moreover, electrochemical reduction of SnO<sub>2</sub> to Sn may create abundant structural defects with unusually high activities. Grain boundary is one such type of structural defects. Theoretical computations predict that the broken local spatial symmetry near grain boundaries may effectively stabilize reaction intermediates and thereby promote the reaction activity.<sup>[86,87]</sup> Spurgeon and co-workers prepared porous SnO<sub>2</sub> nanowires as the precatalyst and electrochemically reduced them to metallic Sn nanowires with a high density of grain boundaries (Figure 6e,f).<sup>[88]</sup> The resultant product exhibited an improved activity and selectivity for the formate production, which started at the low overpotential of ≈350 mV and reached steady Faradaic efficiency of ≈80% at -1.0 V versus RHE.

In addition to SnO<sub>2</sub>, the sulfide counterparts (SnS<sub>x</sub>) have are also frequently investigated as the precatalyst. The electrochemical reduction of SnS<sub>x</sub> would give rise to metallic Sn with residual surface sulfide that may similarly facilitate CO<sub>2</sub>RR. For instance, Zhang and co-workers prepared SnS<sub>2</sub> nanosheets supported on reduced graphene oxide (SnS<sub>2</sub>/rGO) via a facile hydrothermal method, and observed that SnS<sub>2</sub> was only partially transformed to metallic Sn under cathodic potentials.<sup>[89]</sup> The thus-derived Sn/SnS<sub>2</sub>/rGO was believed to stabilize the adsorption of \*CO<sub>2</sub><sup>--</sup> intermediate and therefore enhance the CO<sub>2</sub>RR performance. It achieved the maximum formate Faradaic efficiency of ≈85%

and current density of ~14 mA cm<sup>-2</sup> at  $\eta$  = 680 mV in 0.5 M NaHCO<sub>3</sub>. In a parallel study, Sargent and co-workers deposited SnS<sub>x</sub> on Au nanoneedles via atomic layered deposition, then electrochemically reduced it to partially remove the sulfur species and obtained the sulfur-modulated tin (Sn(S)) catalyst for CO<sub>2</sub>RR (**Figure 7**a,b).<sup>[90]</sup> The authors suggested that the presence of remaining sulfur atoms at the surface promoted undercoordinated sites, and favored the selective electrochemical reduction of CO<sub>2</sub> to formate as supported by density functional theory (DFT) calculations. Electrochemical experiments showed that Sn(S)/Au delivered the large geometric current density of 55 mA cm<sup>-2</sup> and formate Faradaic efficiency of 93% at -0.75 V versus RHE in 0.1 m KHCO<sub>3</sub>. It also showed excellent stability with negligible activity loss for more than 40 h.

Integrating electrocatalysts with conductive and high-surfacearea carbonaceous supports such as carbon nanofibers, carbon nanotubes (CNTs), and graphene is an effective approach to further promote their electrocatalytic performances. It not only enhances the overall electric conductivity and facilitates the electron transport to and from the catalyst, but also improves their dispersion and mitigates their possible particle agglomeration during prolonged electrolysis. Moreover, the synergistic coupling between the electrocatalyst and the support may modify the adsorption property of key reaction intermediates, giving rise to an unexpected gain in activity and durability. As a representative of the early works, Meyer and co-workers uniformly decorated graphene nanosheets with  $\approx 5 \text{ nm SnO}_2$ nanoparticles.<sup>[91]</sup> This hybrid electrocatalyst enabled CO<sub>2</sub>RR to formate in 0.1 м NaHCO3 at overpotential as low as ≈340 mV and with the maximum Faradaic efficiency of >93% at -1.8 V





**Figure 7.** a) SEM images and schematics showing the preparation procedure of Sn(S) nanostructured electrodes. b) Potential-dependent Faradaic efficiency and current density for  $CO_2RR$  to formate on Sn(S)/Au and Sn NPs/Au. Reproduced with permission.<sup>[90]</sup> Copyright 2017, Elsevier. c) TEM image of Sn quantum sheets confined in graphene. d) Schematic illustration depicting the advantages of ultrathin Sn quantum sheets confined in graphene for  $CO_2RR$ . e) Formate Faradaic efficiency on graphene confined Sn quantum sheets and other Sn-based control samples at different potentials. Reproduced with permission.<sup>[92]</sup> Copyright 2016, Springer Nature.

versus SHE. Such a great performance was attributed to the synergic effect between reduced Sn nanoparticles and the graphene support, which stabilized the adsorption of  $^{*}CO_{2}^{--}$  intermediate and facilitated its subsequent activation on Sn surface. In a more recent study, Xie and co-workers demonstrated that metallic Sn sheets confined in graphene was a highly promising  $CO_2RR$  electrocatalyst (Figure 7c–e).<sup>[92]</sup> Large current density of  $\approx 21 \text{ mA cm}^{-2}$ , the maximum formate Faradaic efficiency of  $\approx 90\%$ , and impressive stability for >50 h were observed at -1.8 V versus saturated calomel electrode (SCE). It was similarly proposed that the coupling between the graphene support and metallic Sn stabilized the  $^{*}CO_{2}^{--}$  intermediate and therefore accelerated the first electron transfer as the rate determining step.

#### 3.2. Bismuth (Bi)-Based Electrocatalysts

Unlike many of its main group metal neighbors, Bi is wellknown for its unusually low toxicity and environmental benignity. Its cost is also relatively low – comparable to that of Sn and only a small fraction that of In. The  $CO_2RR$  performance of Bi metal was first reported by Komatsu et al. in 1995.<sup>[93]</sup> However, it did not get as much attention as Sn in the early days. Before 2016, studies about Bi for the CO<sub>2</sub>RR application were mostly conducted in ionic liquids or aprotic electrolytes, yielding CO as the major reduction product, as exemplified by the works of Rosenthal and co-workers.<sup>[94,95]</sup> It is not until very recently that the great potential of Bi for selective CO<sub>2</sub>RR to formate in aqueous solution starts to be unveiled and systematically evaluated.<sup>[96]</sup>

Electrodeposition is a common technique to directly deposit metallic Bi nanostructures onto current collectors. By carefully controlling experimental parameters such as the deposition potential and time, it is possible to fine-tune the product size and morphology, and achieve the optimal electrocatalytic performance. Min and co-workers developed hierarchical Bi dendrites by multistep electrodeposition of Bi<sup>3+</sup> precursor in ethylene glycol.<sup>[97]</sup> The product featured high index surfaces with a large amount of coordinately unsaturated sites that were believed to effectively stabilize the \*OCHO intermediate. As a result, it exhibited the maximum formate Faradaic efficiency of  $\approx$ 89% at -0.74 V versus RHE and impressive stability for  $\approx$ 12 h. Moreover, using a novel pulse electrodeposition technique, Lee and co-workers directly grew Bi nanoflakes with abundant edge and corner sites on Cu substrate.<sup>[98]</sup> This electrocatalyst enabled







**Figure 8.** a) Schematic illustration of the topotactic transformation of BiOI nanosheets to metallic Bi nanosheets for  $CO_2RR$ . b) SEM image of reduced Bi nanosheets (BiNS) on carbon fiber paper. c) Potential-dependent Faradaic efficiency of formate, CO, and H<sub>2</sub> on BiNS in comparison with the Faradaic efficiency of formate on commercial Bi nanopowder. Reproduced with permission.<sup>[56]</sup> Copyright 2018, Springer Nature. d) High-angle annular dark field scanning transmission electron microscopy image and e) structural model of Bi<sub>2</sub>O<sub>3</sub> double-walled nanotubes with highly defective outer walls. f) Potential-dependent Faradaic efficiency of formate, CO, and H<sub>2</sub> on metallic Bi nanotubes converted from Bi<sub>2</sub>O<sub>3</sub> double-walled nanotubes. Reproduced with permission.<sup>[58]</sup> Copyright 2019, Springer Nature.

 $\rm CO_2RR$  to formate with the maximum Faradaic efficiency close to 100% at –0.6 V versus RHE and stability for >10 h in 0.1  $\rm _M$  KHCO\_3. However, its reported formate partial current density remained relatively low (<4 mA cm^{-2}) and needed to be further improved.

In addition to electrodeposition, metallic Bi nanosheets or nanoflakes can also be prepared by top-down exfoliation. Bi metal has a layered crystal structure analogous to that of black phosphorus.<sup>[99]</sup> It can be potentially exfoliated - mechanically or chemically - from its bulk crystal to form 2D single- or fewlayered nanosheets. The existence of stable Bi monolayer (or bismuthine) is theoretically predicted. However, experimental preparation of Bi nanosheets or nanoflakes is challenging due to their low melting temperature (i.e., thermal instability) and propensity to oxidation. Liquid phase exfoliation (LPE) is a straightforward method to exfoliate bulk 2D materials.<sup>[100-102]</sup> Ultrasonic waves can interrupt weak interlayer van der Waal interactions and cause the exfoliation to occur at high yields. Recently, Jin and co-workers used LPE to prepare ultrathin 2D Bi nanosheets.<sup>[103]</sup> Compared to the bulk Bi electrode, exfoliated nanosheets presented enhanced formate Faradaic efficiency of 86% and higher current density of 16.5 mA cm<sup>-2</sup>. DFT calculations revealed that the edge sites more effectively stabilized the formation of \*OCHO intermediate and were the preferred active sites.

The precatalyst approach also gains increasing popularity in the preparation of Bi-based  $CO_2RR$  electrocatalysts. Due to difficulties associated with the direct synthesis and engineering of metallic Bi nanostructures, it is more viable to start with precatalysts composed of oxides, oxyhalides, carbonates, or sulfides, and then cathodically convert them to metallic Bi for

CO<sub>2</sub>RR. Following this guiding principle, our group reported the preparation of ultrathin Bi nanosheets from the in situ topotactic transformation of BiOI nanosheets (Figure 8a-c).[56] Interestingly, we found that the 2D geometry and single crystallinity were well-preserved after the cathodic conversion due to the intrinsic structural correlation between BiOI and metallic Bi. Resultant product catalyzed CO<sub>2</sub>RR to formate in 0.5 M NaHCO<sub>3</sub> with excellent selectivity of >90% over a broad potential, large formate partial current density of 24 mA cm<sup>-2</sup> at -1.74 V versus SCE, and impressive stability for at least 10 h. Our study not only highlighted the great potential of Bi for CO<sub>2</sub>RR, but also unveiled the unique structural transformation process from the BiOI precatalyst to the actual working electrode. In a follow-up study, we observed that if Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> nanosheets were instead used, only mesoporous Bi nanosheets were yielded after the cathodic conversion due to the structural mismatch between Bi2O2CO3 and Bi.[57] Sargent and co-workers started with BiOBr as the precatalyst and template, and obtained metallic Bi with a preferential exposure of highly active (1-10) planes after the electrochemical reduction.[104] When assessed in the flow-cell configuration, this electrocatalyst sustained large current density up to 200 mA cm<sup>-2</sup> and >90% formate selectivity in 1 M KHCO<sub>3</sub>. We very recently reported the use of double-walled Bi2O3 nanotubes with fragmented outer surface as the precatalyst (Figure 8d-f).<sup>[58]</sup> Electrochemical reduction transformed the precatalyst to defective Bi nanotubes. Importantly, we found that the presence of structural defects could significantly stabilize the \*OCHO intermediate and thereby dramatically promote the CO<sub>2</sub>RR activity. Large current density of  $\approx$ 288 mA cm<sup>-2</sup> was recorded at -0.61 V versus RHE in 1 м KOH using our home-built flow cell.







**Figure 9.** a) STEM image and schematic representation of  $BiO_x$  nanoparticles supported on Vulcan XC-72R carbon black ( $BiO_x/C$ ). b) Potentialdependent Faradaic efficiency for formate, H<sub>2</sub>, and CO production on  $BiO_x/C$  and commercial  $Bi_2O_3$ . c) Formate partial current density on  $BiO_x/C$  and commercial  $Bi_2O_3$ . Reproduced with permission.<sup>[105]</sup> Copyright 2018, American Chemical Society. d) High resolution transmission electron microscope image of  $Bi_2O_3$  nanosheets hybridized with N-doped graphene quantum dots ( $Bi_2O_3$ –NGQDs). e) Formate Faradaic efficiency and f) formate partial current density on  $Bi_2O_3$ –NGQDs,  $Bi_2O_3$ , and NGQDs at different potentials. Reproduced with permission.<sup>[106]</sup> Copyright 2018, Wiley.

Hybridizing Bi-based nanostructures with conductive carbonaceous supports represents another effective strategy to promote the electrochemical performance. Nam and co-workers successfully synthesized <10 nm BiO<sub>x</sub> nanoparticles uniformly supported on Vulcan XC-72R carbon black by a facile solvothermal method (Figure 9а–с).<sup>[105]</sup> In CO<sub>2</sub>-saturated 0.5 м NaHCO<sub>2</sub>, this hybrid electrocatalyst exhibited average Faradaic efficiency of 93.4% between -1.37 and -1.70 V versus Ag/AgCl and large partial current density up to 18 mA cm<sup>-2</sup> for selective formate production. Large current density and high selectivity were also achieved in 0.5 M NaCl that was used to mimic seawater. Liu and co-workers decorated 2D Bi2O3 nanosheets with N-doped graphene quantum dots (Figure 9d-f).<sup>[106]</sup> The synergistic effect between these two components was believed to enhance the binding of \*OCHO intermediate on surface. Consequently, high formate Faradaic efficiency of >90% was measured within a wide potential range from -0.9 to -1.2 V versus RHE as well as good stability for >14 h.

#### 3.3. Indium (In)-Based Electrocatalysts

Similar to Sn and Bi, In is barely toxic and poses little hazard to the people's health and environment. Unfortunately, it has a relatively high cost (about 10 times that of Sn or Bi) that may become a major concern for its potential industrial implementation. In is among the earliest investigated main group metals for electrochemical  $CO_2RR$  to formate. Hori et al. reported that bulk In electrode could enable selective formate production with the current density of 5 mA cm<sup>-2</sup> and Faradaic efficiency of ~95% achieved at -1.55 V versus SHE in 0.1 M KHCO<sub>3</sub>.<sup>[32]</sup>

Its formate selectivity was noticeably greater than Sn under similar conditions. In order to further promote the current density, strategies are pursued to prepare In nanostructures, one of which is electrodeposition. For example, Hou and co-workers electrodeposited dendritic In foams from Cl<sup>−</sup>containing aqueous solution via templating dynamic hydrogen bubbles.<sup>[107]</sup> Luo et al. prepared 3D hierarchical porous In electrodes by template-free electrodeposition on Cu meshes.<sup>[108]</sup> Electrocatalyst materials in both the reports showed excellent formate selectivity (≈90%) and large current density. Their great performances were afforded by the porous structure which not only enlarged electrochemically accessible surface areas, but also induced high local pH and hence suppressed HER.

Another important aspect similar to Sn and Bi is that In is a highly oxophilic metal and usually covered with a native oxide layer on surface under ambient conditions. Despite its thermodynamic instability, the surface oxide layer may partially remain under the CO<sub>2</sub>RR condition and actively participate in the reaction by enhancing the adsorption of CO<sub>2</sub> and essential reaction intermediates. Bocarsly and co-workers investigated the interaction between CO2 molecules and metallic In during electrochemical CO<sub>2</sub>RR to formate.<sup>[109]</sup> Compared to the In electrode etched to remove its native oxide layer immediately prior to use, an anodized In electrode had significantly improved formate selectivity of >80% and could stabilize the selectivity over a prolonged period of time between -1.5 and -1.8 V versus SCE in CO<sub>2</sub>-saturated 0.5 м K<sub>2</sub>SO<sub>4</sub>. Based on in situ attenuated total reflectance infrared analysis, the authors proposed that the anodization gave rise to redox-active In<sub>2</sub>O<sub>3</sub>, which was subsequently transformed to redox-inactive In(OH)<sub>3</sub>. The latter then reacted with dissolved CO<sub>2</sub> in the electrolyte to



form a surface confined In–CO<sub>3</sub><sup>-</sup> species for CO<sub>2</sub>RR to formate. As a result, it was concluded that the presence of native or anodized oxide layer held the key to stabilize CO<sub>2</sub> adsorption. facilitate its reduction, and suppress competing HER. In addition to oxygen, sulfur residues on surface may also enhance the CO<sub>2</sub>RR performance of metallic In, as demonstrated by the recent work of Wang and co-workers.<sup>[110]</sup> In their study, S-modified In was prepared by the electrochemical reduction of S-doped In2O3 nanoparticles on carbon fibers. The final product enabled selective CO<sub>2</sub>RR to formate with peak Faradaic efficiency of >85% in a broad range of current density (25-100 mA cm<sup>-2</sup>). Using DFT calculations, the authors suggested that the surficial sulfur species accelerated the H<sub>2</sub>O activation and stabilized the adsorption of \*OCHO intermediate, and therefore were responsible for the excellent electrochemical performance observed.

#### 3.4. Lead (Pb)-Based Electrocatalysts

Albeit its good activity and selectivity. Pb is not regarded as an ideal candidate for electrocatalytic CO2RR owing to its high intrinsic toxicity and adverse environmental impact. However, it is still of fundamental interest to study the CO2RR process on Pb for its similarity and difference from other main group metals. There are only a couple of relevant studies in recent literature. Lee and Kanan prepared an oxide-derived nanocrystalline Pb film from the electrochemical reduction of PbO<sub>2</sub> precatalyst.<sup>[111]</sup> It exhibited close to unity formate selectivity between -0.75 and -1.0 V versus RHE in CO<sub>2</sub>-saturated 0.5 M NaHCO<sub>3</sub>, far superior to polycrystalline Pb foil (20-60%) under similar conditions. Electrokinetic analysis indicated that the selectivity difference stemmed from the likely presence of metastable Pb oxide in oxide-derived Pb, which hindered HER but did not compromise CO<sub>2</sub>RR at the catalyst surface. Using electrodeposition, Han and co-workers prepared a honeycomblike porous Pb catalyst on a Cu substrate.<sup>[112]</sup> This advantageous morphology afforded the catalyst with high selectivity up to ≈97% and large current density for CO2RR to formate in 0.5 м КНСО<sub>3</sub>.

#### 3.5. Antimony (Sb)-Based Electrocatalysts

Sb locates next to Sn and Bi in the periodic table, however it is considerably underexplored for  $CO_2RR$  compared to its neighbors. Bulk Sb has low formate selectivity.<sup>[113]</sup> Nanostructural engineering represents an effective strategy to solve this problem and promote the selectivity by exposing a large fraction of catalytically active sites. So far, there are only a few publications about its  $CO_2RR$  application.<sup>[113,114]</sup> Zhang and coworkers prepared 2D few-layered Sb nanosheets from the bulk crystal by cathodic exfoliation.<sup>[114]</sup> When further hybridized with anodically exfoliated graphene nanosheets, the composite electrocatalyst demonstrated peak formate selectivity of 88.5%, partial formate current density up to >8 mA cm<sup>-2</sup>, and impressive stability of >12 h. All these performance metrics were significantly improved over bulk Sb. The enhancement was believed to result from the higher density of active sites upon exfoliation as well as the strong electronic interaction between graphene and Sb.

#### 4. Flow Cells or Membrane Electrode Assembly Cells

The majority of current CO<sub>2</sub>RR researches are conducted in H-type electrochemical cells. While the standard H-cell configuration is beneficial to accurately measuring the intrinsic activity of CO<sub>2</sub>RR electrocatalysts, studying their underlying reaction mechanisms, and revealing their structure-performance correlations, it is not amenable to industrial use. Figure 10a schematically depicts the local environment around the working electrode in an H-cell.<sup>[115]</sup> Only nearby dissolved CO<sub>2</sub> molecules in the electrolyte can diffuse to and get reduced on the working electrode. As a result, the CO<sub>2</sub>RR current density is restricted by the limited solubility (1.45 g  $L^{-1}$  in pure water at 25 °C and 0.1 MPa) and diffusion rate of CO<sub>2</sub> in aqueous electrolytes, especially under large overpotentials where the reaction kinetics becomes relatively fast. This essentially sets an upper limit on the attainable CO<sub>2</sub>RR current density to be less than 100 mA cm<sup>-2</sup>.<sup>[116]</sup> Much smaller current density (<30 mA cm<sup>-2</sup>) is usually measured using the H-cell configuration in reality. On the other hand, industrial scale implement of the CO<sub>2</sub>RR technology would require the current density to be dramatically enhanced from the current level to several hundreds of mA cm<sup>-2</sup> to 1 A cm<sup>-2</sup> without compromising the reaction selectivity and stability.<sup>[8,48,117]</sup> For example, based on the gross-margin model they developed. Kenis and co-workers predicted that the minimum current density required for CO<sub>2</sub>RR to formate was  $\approx 200 \text{ mA cm}^{-2}$  (assuming a catalyst lifetime of 1000 h, electricity cost of \$0.12 kWh<sup>-1</sup>, a cell potential of 2.25 V, and a gross margin of 30%) in order to render this electrochemical process economically viable.<sup>[48]</sup> The huge gap in current density can only be bridged through new designs of electrochemical cells.

Flow cells offer one of the possible solutions. In the flow-cell configuration, electrocatalysts are loaded on the gas-diffusion (GDL) electrode. The GDL is in contact with the catholyte from one side, and is fed with CO<sub>2</sub> gas through the other side. The catholyte is continuously circulated to facilitate the diffusion of reactants and products to and away from catalysts, hence stabilizing the local reaction environment. GDL with a proper surface property can offer abundant solid (catalyst)-liquid (electrolyte)-gas (CO<sub>2</sub>) triple-phase boundaries for CO<sub>2</sub>RR to take place in contrast to the solid-liquid biphasic reaction in standard H-cells. According to the reaction-diffusion model developed by Burdyny and Smith,<sup>[115,118]</sup> the diffusion pathway in flow cells (~50 nm) is predicted to be three orders of magnitude shorter than that in H-cells ( $\approx 50 \,\mu$ m) (Figure 10a,b). It can effectively lift the limitation on the CO<sub>2</sub> solubility and diffusion in aqueous solution, and consequently dramatically promote the current density.

Moreover, flow cells permit the use of concentrated alkaline electrolytes such as 1-10 M KOH in addition to common bicarbonate electrolytes.<sup>[45,119]</sup> This is because in the flow-cell configuration, CO<sub>2</sub> molecules only have to diffuse a short distance to reach the catalyst and get reduced before they react with





**Figure 10.** a) Schematic illustration of species transport in a H-cell where  $CO_2$  is supplied via diffusion from the bulk electrolyte on the microscale. b) Schematic illustration of species transport in a flow cell where  $CO_2$  diffuses from the gas–liquid interface on the nanoscale. Reproduced with permission.<sup>[115]</sup> Copyright 2018, The Royal Society of Chemistry. c) Schematic and d) photography of a flow cell for electrochemical  $CO_2RR$ . e) Polarization curves of NTD-Bi in the flow cell using 0.5  $\times$  KHCO<sub>3</sub> and 1  $\times$  KOH as the electrolyte. f) Long-term amperometric stability and the corresponding selectivity of NTD-Bi in the flow cell. Reproduced with permission.<sup>[58]</sup> Copyright 2019, Springer Nature. g,h) Schematic showing the configuration of a catholyte-free MEA cell for  $CO_2RR$  to formate. i) Amperometric stability and the corresponding formate selectivity of commercial Sn particles in the MEA configuration at 2.2 V. Reproduced with permission.<sup>[126]</sup> Copyright 2018, Wiley.

KOH (with a reaction rate of several seconds) and are converted to carbonate. Three main advantages can be expected when using alkaline electrolytes. First, from the perspective of thermodynamics, rising the electrolyte pH increasingly favors the formate production over other CO2RR pathways and HER as we have learned in Section 2.2, and hence greatly promotes the formate selectivity. Second, KOH has higher ionic conductivity than bicarbonate, which helps diminish the solution Ohmic loss and improve the energy conversion efficiency. Third, using alkaline electrolytes allows us to take advantage of the existing large number of highly active, nonprecious metal-based (for example, Co-, Ni-, and Fe-based) OER electrocatalysts instead of precious  $IrO_x$  (which is arguable the only feasible choice for OER in neutral solution).<sup>[120-122]</sup> It significantly reduces the catalyst cost that accounts for a large fraction of the CO2RR production cost.

Our group very recently demonstrated that using our homebuilt flow cell (Figure 10c,d), much larger current density was attained on a Bi-based  $CO_2RR$  electrocatalyst than using the standard H-cell.<sup>[58]</sup> When tested in 1  $\,$ M KHCO<sub>3</sub>, the flow cell delivered 136 mA cm<sup>-2</sup> at -0.86 V versus RHE as compared to 44 mA cm<sup>-2</sup> delivered by the standard H-cell under the same potential. When tested in 1 m KOH, the reaction onset potential was improved to  $\approx$ -0.3 V versus RHE, and its current density reached 288 mA cm<sup>-2</sup> at -0.61 V versus RHE with the formate selectivity close to unity (Figure 10e,f). Such an outstanding performance already surpassed the minimum requirement for the potential commercialization of the CO<sub>2</sub>RR technique for selective formate production.

Another important cell configuration is membrane electrode assembly (MEA) cells that were initially developed for fuel cells and water electrolyzers, and now become increasingly popular for  $CO_2RR$ .<sup>[123]</sup> In contrast to flow cells, MEA cells do not use liquid electrolyte. They consist of a polymer electrolyte membrane for ion exchange between the cathode and anode (Figure 10g,h). Electrocatalyst layers are either directly coated onto the two sides of the membrane or loaded on the GDL and then pressed to sandwich the membrane. The MEA is further stacked with conductive plates on both sides that have a set of channels machined to allow flow of  $CO_2$ ,  $O_2$ , and water to and from the MEA. The polymer electrolyte membrane is the core component to determine the overall performance of a

MEA cell. Ideal ones should have great ionic conductivity, high mechanical strength, and sufficiently chemical stability to withstand thousands of hours of operation. MEA cells have been proved very successful for electrochemical CO<sub>2</sub>RR to gaseous products such as CO and ethylene.<sup>[119,124]</sup> They are also investigated for formate production but so far only with medium current density.<sup>[125]</sup> Park and co-workers fabricated a MEA cell by using commercial Sn particles and Pt black as the CO<sub>2</sub>RR electrocatalyst and OER electrocatalyst, respectively.<sup>[126]</sup> The cathode was fed with gaseous CO<sub>2</sub> gas saturated with water vapor as the reactant. Full-cell measurements showed that steady current density of ≈38 mA cm<sup>-2</sup> and high formate selectivity of 91.2% were achieved under the applied voltage of 2.2 V for 48 h (Figure 10i).

#### 5. Mechanistic Studies Using In Situ Characterization Techniques

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 $\rm CO_2RR$  is a complicated process. Increasing understanding of its reaction mechanism by studying the structure and surface evolution of electrocatalyst materials as well as the adsorption of key reaction intermediates on surface under real operating conditions would greatly advance the design and development of better  $\rm CO_2RR$  electrocatalysts and systems. Over recent years, several in situ or operando characterization techniques emerge as powerful tools to gain deep insights about  $\rm CO_2RR.^{[127]}$  In this session, three common in situ techniques, namely infrared spectroscopy, Raman spectroscopy, and X-ray absorption spectroscopy would be briefly introduced and discussed, with an emphasis on how these techniques help us better understand the  $\rm CO_2RR$ -to-formate process catalyzed on main group metals.

Infrared (IR) spectroscopy is well-known for its capability to analyze the molecular vibrations of surface-adsorbed species through their interactions with infrared light. However, its direct application to aqueous electrochemical reactions is hindered due to the strong interference from the intense IR signal of water.<sup>[128]</sup> To tackle with this issue, attenuated total reflection infrared spectroscopy (ATR-IR) is developed. ATR-IR is based on total internal reflection resulting in an evanescent wave. For the measurements, electrocatalysts are deposited on the ATR crystal and interfaced with the liquid electrolyte (Figure 11a). IR light travels through the crystal and interacts with the electrocatalysts. Due to the very short effective path length of the evanescent wave at the interface, ATR-IR possesses high surface sensitivity for studying electrochemical processes at the electrolyte-electrocatalyst interface even in the presence of water. In situ ATR-IR has been used to study the catalyst surface chemistry of Sn, In, Pb, and Bi under actual working conditions. For example, Bocarsly and co-workers observed bands located at 1500, 1385, and 1100  $\rm cm^{-1}$  on an electrodeposited Sn/SnO<sub>x</sub> film using in situ ATR-IR at potentials where CO<sub>2</sub>RR to formate took place (Figure 11b).<sup>[129]</sup> The bands were assigned to a surface-bound monodentate tin carbonate species. It was proposed that the formation of this surface-bound tin carbonate was the key step in electrochemical CO2RR to formate because these IR bands were absent on etched Sn that was measured to have a poor electrocatalytic activity (Figure 11c). The same authors later reported a similar observation about In that its oxide/hydroxide persisted during  $CO_2RR$  and actively participated in the reaction.<sup>[130]</sup> By contrast, even though Pb supported a metastable oxide under  $CO_2RR$ , this oxide did not play a direct role in the formate production. As for Bi,  $CO_2$  seemed to be directly reduced on its bare metallic surface.

Raman spectroscopy is based on inelastic light scattering. It is complementary to IR spectroscopy, and can provide the structural fingerprints of surface-adsorbed species in a quick and nondestructive manner. In situ Raman spectroscopy has been used to study the chemical state of catalyst surface during CO<sub>2</sub>RR. Broekmann and co-workers applied potential- and timedependent in situ Raman spectroscopy to monitor the oxidation state change of SnO<sub>2</sub> during CO<sub>2</sub>RR, and observed a strong correlation between the oxidation state and the formate selectivity (Figure 11d-f).<sup>[131]</sup> High Faradaic efficiency was attained at moderately cathodic potentials at which SnO<sub>2</sub> remained on surface as evidenced by its  $E_g$ ,  $A_{1g}$ , and  $B_{2g}$  bands at 482, 623, and 762 cm<sup>-1</sup>, respectively. The formate selectivity was significantly decreased when the surface oxide was reduced to metallic Sn. However, one shortcoming of conventional Raman spectroscopy is the inherently low intensity of Raman scattering, and hence its insufficient surface sensitivity. To this end, surfaceenhanced Raman spectroscopy (SERS) is developed accordingly by depositing electrocatalysts on rough surfaces usually coated with Au or Ag. The Raman signal in this way can be enhanced by several orders of magnitude.<sup>[132]</sup> Very recently, in situ SERS was utilized to track the reaction pathway of oxygen reduction reaction at the Pt surface in alkaline solution.<sup>[133]</sup> The same technique can be potentially extended to CO<sub>2</sub>RR research in the near future.

X-ray adsorption spectroscopy (XAS) has gained rapidly increasing attention in recent catalysis research for its unique capability to probe the fine structures and electronic states of catalyst materials - either crystalline or amorphous. XAS broadly includes both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The former can provide the detailed information about the electronic structure and chemical state of target atoms, while the latter can provide the precise local structural information of target atoms such as coordination number and chemical bond length. XAS in the hard X-ray region can be done under ambient conditions and is suitable for in situ measurements to track the catalyst evolution and surface adsorption during electrochemical reactions.<sup>[134,135]</sup> Our group recently used in situ XAS at the Bi L-edge to study the CO2RR to formate on highly defective Bi2O3 nanotubes (Figure 11g-i).<sup>[58]</sup> Under the working condition, the obvious shift of Bi adsorption edge in XANES from 13.423 to 13.417 keV confirmed the electrochemical reduction of Bi2O3 to metallic Bi (which was named as nanotube-derived Bi or NTD-Bi). The corresponding EXAFS analysis suggested that the coordination number (CN) of Bi-Bi was only 2.6±1.8 for NTD-Bi, markedly smaller than standard Bi metal foil (CN = 6), and thereby evidencing that NTD-Bi was highly defective. Moreover, Bi-O scattering paths were observed in the EXAFS analysis of NTD-Bi, which were assigned to chemisorbed \*OH and \*OCHO by using a modelbased analysis.



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**Figure 11.** a) Schematic illustration showing in situ ATR-IR characterization of Sn/SnO<sub>x</sub> for CO<sub>2</sub>RR to formate. b) In situ ATR-IR spectra of Sn/SnO<sub>x</sub> in the presence of CO<sub>2</sub> at different working potentials. c) Proposed reaction mechanism for CO<sub>2</sub>RR to formate on Sn/SnO<sub>x</sub>. Reproduced with permission.<sup>[129]</sup> Copyright 2015, American Chemical Society. d) Schematic illustration showing the experimental setup for in situ electrochemical Raman measurements. Adapted with permission.<sup>[145]</sup> Copyright 2010, American Chemical Society. e) Raman spectrum of the as-prepared SnO<sub>2</sub>NPs@rGO catalyst. f) In situ Raman measurements of SnO<sub>2</sub>NPs@rGO at different potentials for 1 h. Reproduced with permission.<sup>[131]</sup> Copyright 2015, American Chemical Society. g) Schematic illustration showing the experimental setup for in situ XAS experiments. Reproduced with permission.<sup>[146]</sup> Copyright 2018, Springer Nature. h) Bi L-edge XANES spectra and i) EXAFS as well as the corresponding fitting spectra of Bi<sub>2</sub>O<sub>3</sub> nanotubes at open circuit voltage and the working condition in comparison with Bi or Bi<sub>2</sub>O<sub>3</sub> standards. Reproduced with permission.<sup>[58]</sup> Copyright 2019, Springer Nature.

#### 6. Summary and Outlook

In this progress report, we offer a comprehensive overview of recent advances in main group metal–based electrocatalyst materials for CO<sub>2</sub>RR to formate. Among the various CO<sub>2</sub>RR products, selective two-electron reduction to formate is the most economically viable and has the highest added value per kWh of electrical energy input, as revealed by recent technoeconomic analysis. Main group metals including Sn, Bi, In, Pb, Hg, Cd, Tl, and so on represent a unique group of materials for the selective formate production. This is because they thermodynamically favor the surface adsorption and stabilization of \*OCHO (intermediate to formate) over \*COOH (intermediate to CO) or \*H (intermediate to H<sub>2</sub>). Even though the CO<sub>2</sub>RR properties of these main group metals were first reported more than 30 years, challenges remain at present to further improve their electrocatalytic performances and to better understand their reaction mechanisms.

From the application point of view, Pb, Hg, Cd, and Tl in the list are not suitable candidates because they are highly toxic and environmentally hazardous. Despite its low toxicity, the cost of In is relatively high as driven by the increasing demand for ITO – a transparent conductor for touch screens, flat panel displays, and solar panels. This essentially leaves us with the only choices being Sn or Bi. As we can learn from Figure 5, Bi-based materials hold the greater promise because many of them exhibit high formate selectivity close to unity over a broad potential window. Bi-based materials also markedly outperform other formate-producing CO2RR electrocatalysts including Pd or heteroatom-doped carbon in terms of activity, selectivity, and/ or stability. For example, even though Pd-based materials have small reaction overpotential (≈0 V) and high formate selectivity ( $\approx$ 100%), they suffer from small current density (<5 mA cm<sup>-2</sup>) and poor stability due to CO poisoning.<sup>[78]</sup> Their high costs are also prohibitive toward the large-scale application. On the other

hand, N-doped carbons are appealing for their earth abundance and low costs, but generally have low formate selectivity and large overpotential.<sup>[136,137]</sup> Despite the great promise of Sn or Bi, there is still a large performance gap that we would have to close in order to transform the CO<sub>2</sub>RR-to-formate technology from benchtop science to industrial implementation. In our opinion, future studies can be approached from the following four directions.

First, the development of better electrocatalyst materials remains at the heart of CO<sub>2</sub>RR research. The goal is to increase their active site density and/or promote their site-specific activity. Nanostructural engineering is an effective approach to achieve this goal. When the dimensions of electrocatalyst materials are shrunk from macrosize to nanosize, their surface areas are dramatically enlarged, creating more active sites on surface for electrochemical reactions. Nanostructural engineering may also enable us to selectively expose more active crystal facets, or introduce structural defects such as vacancies and grain boundaries that may afford unexpected electrocatalytic activities. Even though it is challenging to directly prepare nanostructures of main group metals, we are well equipped to prepare various nanostructures of their corresponding oxides, hydroxides, carbonates, or sulfides as precatalysts using well-established colloidal, hydrothermal, or solvothermal chemistry. Moreover, doping main group metals with foreign atoms may tune the surface binding energy of reaction intermediates and improve their CO<sub>2</sub>RR performance. For instance, it was reported that the introduction of a small amount of Cu to Sn and In considerably promoted their formate Faradaic efficiency.<sup>[138-142]</sup> Integrating electrocatalysts with conductive carbonaceous supports is also beneficial since it can enhance the electric conductivity, improve the catalyst dispersion, and modify the adsorption properties of intermediates via the possible catalyst-support synergy. With these efforts, we aim to identify and establish electrocatalyst materials with small onset overpotential (<0.2 V), high formate selectivity close to unity in a broad potential window, current density larger than 200 mA cm<sup>-2</sup> at  $\eta$  = 0.5–0.6 V, and operation stability over 1000 h in the next ten years.

Second, we would have to further our understanding of possible reaction pathways and mechanisms on main group metal-based CO2RR electrocatalysts with the assistance of theoretical computations and in situ spectroscopic characterizations. Although the two-electron pathway for CO<sub>2</sub>RR to formate through the \*COOH intermediate has been widely accepted, the actual reaction pathway and the nature of active sites have not been well understood. What is the rate determining step? What are the most active sites or planes? How would structural defects of electrocatalysts impact the electrocatalytic performance? How would surface ad-species modify the reaction pathway? All these questions remain to be answered. Theoretical computations can simulate the reaction energetics based on the adsorption energy of key reaction intermediates on the catalyst surface. They may unveil the atomic origin of "good" or "bad" CO<sub>2</sub>RR performances, and provide a basis for further catalyst improvements. At present, it is still challenging to accurately simulate the complex reality of catalyst surface, electrolyte, and electric field influence. Future advances in theoretical computations would improve their predictive capability,

and allow us to move away from the current trial-and-error approach to theory-guided rational design of electrocatalysts. On the other hand, in situ spectroscopic characterizations offer detailed information about the structure and surface state of the electrocatalysts as well as the chemical nature and binding configuration of surface-adsorbed intermediates under the actual working conditions. They become an integral part of mechanistic studies. In situ X-ray diffraction, ATR-IR, Raman, and XAS are now available to us with unprecedented capabilities. Further technological development is necessary to meet our increasing demands. For example, adapting  $CO_2RR$  experiments to the vacuum environment would allow us to run in situ XANES in the soft X-ray range and directly probe the surface binding of  $CO_2$  and intermediates during electrocatalysis.

Third, we would have to look beyond the electrocatalyst materials, and optimize the CO<sub>2</sub>RR performance at the cell or system level. Successful commercialization of the CO2RR-to-formate technology would require the current density of  $>200 \text{ mA cm}^{-2}$ , Faradaic efficiency of >95%, and catalyst lifetime of >1000 h in order to minimize capital investment. Such high current density is not possible within standard H-cells due to the limited CO<sub>2</sub> solubility and diffusion in aqueous solution, and can only be achieved using flow cells or MEA cells. However, things become much complicated when it comes to flow cells or MEA cells. Many parameters including cell configuration, GDL, electrolyte, membrane, pressure, and temperature all greatly impact the overall cell performance, which, unfortunately, are not given as much attention as electrocatalyst materials at present.<sup>[79]</sup> For one example, issues such as flooding or drying out of the GDL, and salt precipitate can cause cell failure before electrocatalysts reach their end of lives. Proper water management is therefore of paramount importance to the pursuit of high-performance CO<sub>2</sub>RR electrolyzers. For another example, while it usually does not concern us during the standard three-electrode measurement in H-cells, the proper selection of anodes in flow cells or MEA becomes equally important in determining overall cell performances. Current OER electrocatalysts often suffer from large overpotential (>300 mV) and poor stability particularly in neutral electrolytes. It was recently proposed that replacing the sluggish OER half reaction with less energy intensive alternatives (such as the oxidation of glycerol) could dramatically reduce the system operation cost and carbon footprint.<sup>[143]</sup> In the future, one important task of CO<sub>2</sub>RR research is to better optimize the system design, and assess the electrochemical performance in terms of full-cell figure of merit including cell voltage, cell current density, energy efficiency, and lifetime.<sup>[79,115]</sup> Of course, the existing knowledge about electrolyzers and fuel cells can be readily transplanted to expedite this learning process.

Last but not the least, we would have to develop an effective means for the product separation. Unlike gaseous products such as CO, formic acid or formate from  $CO_2RR$  stays in the catholyte. It would have to be collected from the electrolyte prior to any practical application. Conventionally, the separation of formic acid can be achieved via distillation. This process, however, is highly energy intensive due to the close boiling points of water and formic acid, and is estimated to contribute more than 50% of the system operating cost.<sup>[49]</sup> The development of more cost-effective methods could greatly increase the SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

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profitability of formic acid and is therefore highly desirable. Very recently, Wang and co-workers used solid electrolyte and demonstrated the production of pure HCOOH solutions with concentrations up to 12 M.<sup>[144]</sup> This study opens a new direction for the efficient collection of liquid products from CO<sub>2</sub>RR, and may accelerate the transformation of this technique from laboratory to industry.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

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