Optimizing the Electrochemical Reduction of CO₂ to Formate: A State-of-the-Art Analysis

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ABSTRACT: The electrochemical reduction of carbon dioxide to formate is an appealing carbon utilization method as it can be performed at room temperature and pressure, it only requires two electrons, and it has a high atom efficiency. This reaction has been known and studied for decades, but currently there is no commercial process practiced. This Perspective compares over 500 experimental data points from 65 scientific publications and patents and identifies the gas diffusion electrode as the best technology to scale this reaction. We further discuss the complex layers that make up a gas diffusion electrode and view what has been studied with respect to this reaction. Finally, we identify critical areas where more research can provide crucial understandings to allow this technology to become a commercial process.
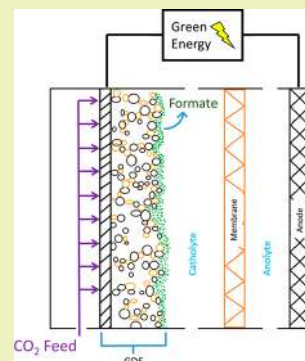
INTRODUCTION

Climate change has been gaining attention over the last several years, and it is generally attributed to the "greenhouse effect": global temperatures increase as a result from a changing atmosphere that retains more heat from the sun.[1] These changes in the atmosphere are caused by various gases also known as greenhouse gases. Carbon dioxide is considered one of the worst greenhouse gases, even though it appears naturally in the atmosphere. This is because its increase in concentration due to human activity accounts for about half of the observed effect of rising global temperatures.[2]

Ways to lower the concentration of CO₂ in the atmosphere include capturing it from the atmosphere or not emitting it by changing process schemes or converting the CO₂ that is generated in existing processes. The conversion of CO₂ comes with several challenges because it is a thermodynamic end state of every organic compound. Thus, it is difficult to economically convert CO₂ to chemicals due to high process costs associated with high temperatures and pressures that are required with conventional catalysis.[3] Electrocatalysis, on the other hand, appears to be more attractive as the reaction takes place at ambient conditions. There are several reduction products that can be formed from CO₂ electrochemically, and recent reviews point to formate/formic acid and carbon monoxide to be the most economically feasible products.[4−7]

One major limitation in the electrocatalytic reduction of CO₂ is the mass transfer of CO₂ to the catalyst surface due to limited solubility of CO₂ in aqueous electrolytes at ambient pressure and temperature (33 mM at 1 atm and 25 °C).[8] The solubility of

CO₂ can be increased by either lowering the temperature or increasing the pressure which has been shown to slightly increase an electrode's performance. Alternatively, gas diffusion electrodes (GDEs) have been shown to perform at high reaction rates and efficiencies even at ambient conditions. Therefore, there is huge potential for their use in electrochemical CO₂ reduction.

GDEs were initially developed and used for fuel cells and then later found use in electrolysis and batteries. These electrochemical devices use GDEs to enhance the mass transfer of the reactants to increase the rate at which they can efficiently operate. A GDE consists of two main layers: the gas diffusion layer and the catalyst layer. These layers should be considered in more detail to understand how a GDE enhances mass transfer. Both layers can strongly influence the electrochemical performance of the GDE. Despite its importance, little attention has been paid to the GDE structure for use in CO₂ reduction until recently: Higgins et al.[9] published a Perspective on CO₂ reduction to fuels on gas diffusion electrodes, and Liu et al.[10] published a Letter which provides guidance to assembling and operating gas diffusion electrodes for CO₂ reduction. This Perspective will provide a deeper and more extensive analysis of

the research that has been performed on methods to achieve higher mass transfer for the reduction of CO_2 to formate/formic acid, with a focus on the design and use of GDEs specifically for this reaction.

■ BACKGROUND

In order to understand and relate experiments and data in the CO_2 to formate electrochemical reduction reaction, the key performance indicators (KPIs) which drive the economics should be understood. Two of the biggest process economic considerations are the capital investment (equipment) and the energy costs required to produce a given amount of product. Capital cost can be estimated by calculation of the number of electrochemical reactors (cells) for a given production rate of a product.

The total cell active area is directly proportional to the number of cells required. Because electrochemical cells begin to be stacked for parallel operation after a maximum size is reached, the number of cells required is an appropriate metric to estimate the capital cost (an adjustment factor may be necessary to adjust for more complex cell costs). Although other equipment costs can have scaling factors less than 1, the total capital cost of a process still increases with an increasing number of cells.[11] The total cell active area required can be calculated using eq 1

$$A_{\text{total}} = \frac{PPR*n*F}{CD*CE*MW*3.6} \qquad (1)$$

where PPR is the product production rate in kg/h, n is the number of electrons transferred for the reaction (dimensionless), F is Faraday's constant in C/mol, CD is the current density in A/m^2, CE is the current efficiency for the desired product (percentage), MW is the molecular weight of the desired product in g/mol, and 3.6 is the conversion factor of $\frac{\text{kg}*\text{s}}{\text{g}*\text{h}}$.

The energy consumption per mass of product can be calculated using eq 2

$$\frac{kW*h}{tonne} = \frac{V_{\text{cell}}*I}{\text{Production rate}} = \frac{V_{\text{cell}}*n*F}{MW*CE*3.6} \qquad (2)$$

where V_{cell} is the full cell potential. Eqs 1 and 2 show that the energy and capital costs of a system decrease when it operates with a high CE, it targets a product that has a high molecular weight, and it uses few electrons in the reaction. However, out of these factors, only the CE can be influenced once a targeted product is selected (i.e., for formate n will be set to 2 and the MW set to 45.02). Additionally, maximizing the operating current density (CD) reduces capital cost, while minimizing the cell potential (V_{cell}) lowers energy costs. Therefore, the current density, current efficiency, and cell potential are the top KPIs for electrochemical reactions. Figure 1 summarizes the KPIs for capital and energy costs for electrochemical cells.

One final consideration is the scalability of the reaction. For example, if the hydrostatic head is not manageable at a larger electrode size for GDEs due to limitations of a gas diffusion layer or a cell design, then the GDE could become flooded resulting in a decrease in performance as the cell size increases. This could severely limit the size of a single cell and thus drastically increase the capital cost for the process. Therefore, generally speaking, to realize an electrochemical technology at a commercial scale, a high current efficiency should be achievable at high current densities and low cell potentials with no dependency on electrode size.
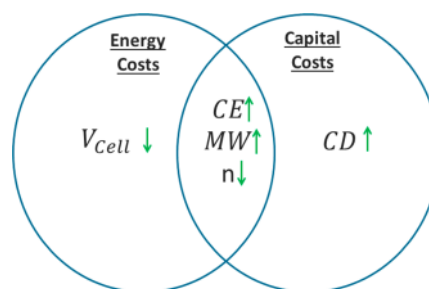

Figure 1. Venn diagram of KPIs for optimizing capital and energy costs of electrochemical cells.[12]

This Perspective covers 554 experimental data points from 65 scientific publications and patents on the performance of the aqueous CO_2 to formate electrochemical reaction. These publications use various catalysts, electrode types, cell types, electrode areas, electrolytes, and separators. All of these varying factors influence the KPIs mentioned above. Unfortunately, whole cell potential data is scarcely reported making insights into reducing energy costs very difficult. However, as displayed in eq 2, a percentage change in CE will have the same impact as the same percentage change in cell potential (i.e., if current efficiency is doubled, then the cell potential can also double without the energy costs increasing). For these reasons, this Perspective focuses on comparing various electrode types/cell configurations based current efficiencies, current densities, and scale.

■ CO₂ TO FORMATE DATA COMPARISON

We encountered four types of electrode/cell configurations in the literature and patents reviewed: 2D electrodes, 3D electrodes, trickle flow, and GDEs.

- The 2D electrode types include wires, rods, flat plates, and single meshes. These electrodes are typically used in H-cell experiments.
- The 3D electrode types include packed areas with granules, beads, shot, meshes, etc.
- Trickle bed flow is distinguished from a 3D electrode by having a mixed feed flow (CO_2 and electrolyte) through the electrode.
- GDEs are porous electrodes that feed CO_2 through the structure directly to the catalyst.

A comparison of the current efficiency toward formate of these electrode configurations as applied current increases is shown in Figure 2. The applied current includes the scale of the reaction (i.e., as cells become larger, more current must be applied to stay in the same current density range). Due to the wide range of operating currents, the x axis is plotted on a log scale.

Different colors represent the four different electrode types, while different current density (CD) ranges are distinguished by different symbols. Over 35 metals were used as a catalyst and reported formate production. However, tin, lead, indium, and copper catalysts make up over 85% of the data in Figure 2. Although the intrinsic activity of catalysts can influence the performances shown in Figure 2, we believe there is sufficient data across the different electrode types to make an assessment of the best electrode type.

Figure 2 shows 2D electrodes rarely get over 90% current efficiency, and the maximum current efficiency achieved by these 2D electrodes appears to decrease as the operating current
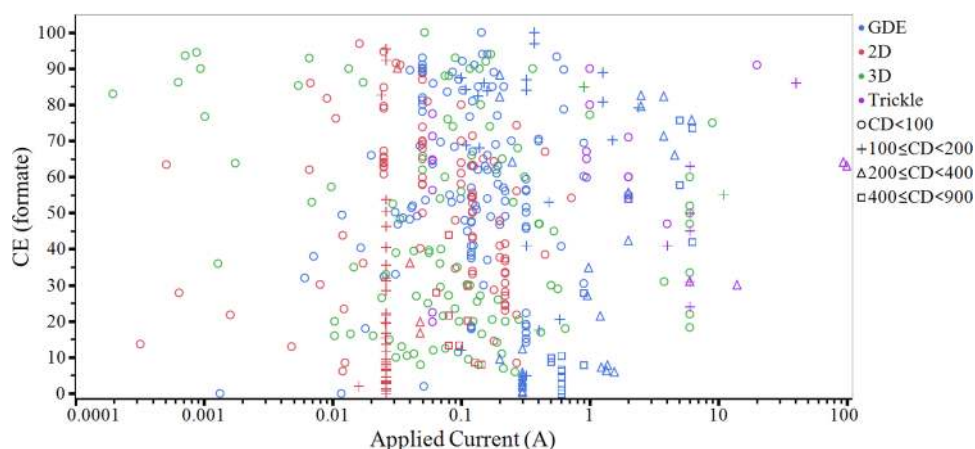
Figure 2. Current efficiency vs applied current. Reported current density in mA/cm^2 (see refs 13, 14, 23−32, 15, 33−42, 16, 43−52, 17, 53−62, 18, 63−72, 19, 73−77, and 20−22).
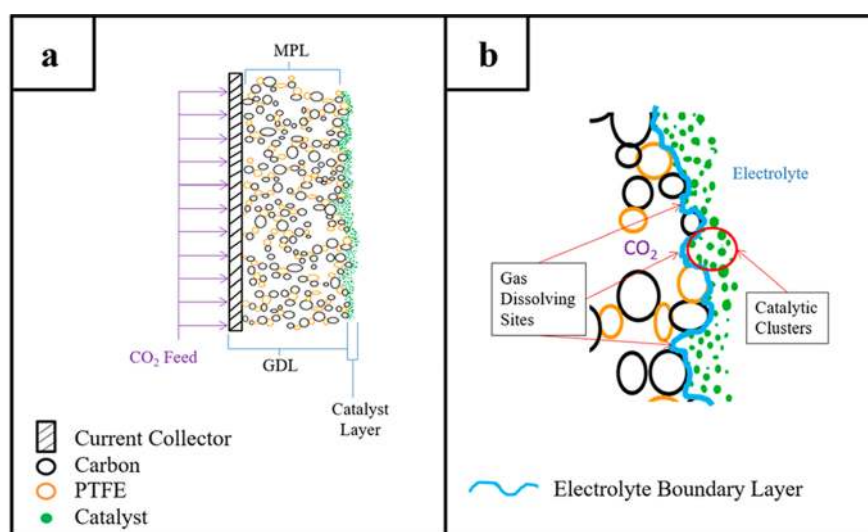

Figure 3. GDE layers (a) and the three-phase boundary (b).

increases. Similarly, 3D electrode reactors appear to drop in current efficiency as the applied current increases. Additionally, both of these electrode types are rarely operated above 100 mA/cm^2. Trickle flow reactors can achieve similar current efficiencies as GDEs; however, the current density is only about one-third of GDEs. The best performance for trickle flow reactors is described in a patent from Oloman et al.[72] where they use a 340 cm^2 trickle flow reactor that operates with Sn granules at current densities ranging from about 59 to 294 mA/cm^2. However, Figure 2 shows that the current efficiency drops to just above 60% at the maximum current density tested.

The 2D, 3D, and trickle electrode types become limited by mass transfer at higher current densities which is why 2D and 3D types are not seen frequently operating over 100 mA/cm^2 and why the current efficiency of the trickle flow electrodes decreases as current densities are increased. The mass transfer of dissolved CO$_2$ in the bulk electrolyte to the surface of the electrode is the limiting factor for these electrode types (i.e., reactant cannot reach the reaction site as fast as the reaction site can convert it). Promoting turbulent flow in these cells (by using flow distributors, a zero gap, flow-through design, or trickle flow) would increase the mass transfer of CO$_2$ to the reaction surface. Although this does not seem to help substantially as Kaczur et

al.[77] (similarly to Oloman et al.[72]) report decreasing current efficiencies with increasing current densities using a zero gap, flow-through design. They report current efficiencies up to 100% at a current density of 56 mA/cm^2 but see the efficiency drop to 54−63% at a current density of about 100 mA/cm^2. GDEs, however, are able to drastically enhance mass transfer which allows them to efficiently operate at current densities higher than 100 mA/cm^2.

Figure 2 shows that GDEs are consistently performing better than 2D and 3D or trickle flow electrode types. Not only are GDEs more efficient throughout the total current range, they are also capable of operating at higher current densities. However, GDEs appear to have a wide range of performance. Larger current densities and different catalysts used can explain some of this variation, but nevertheless, there are two data sets that use similar conditions and achieve different results. Kopljar et al.[65] report a current efficiency of up to 89% using an Sn GDE at a current density of 50 mA/cm^2 and an active area of 12.56 cm^2 using a 0.1 M potassium bicarbonate and potassium hydroxide electrolyte. Comparatively, Castillo et al.[27] report a current efficiency of only 40.8% using an Sn GDE at a current density of 50 mA/cm^2 and an active area of 10 cm^2 using a 0.45 M potassium bicarbonate and 0.5 M potassium chloride electro-

lyte. Although different electrolytes are used, the complexity of GDEs is most likely the main contributor to these stark differences in performance.

Therefore, further analysis of the layers that make up a GDE, the gas diffusion layer (GDL) and the catalyst layer, is required to better understand why GDEs are outperforming other electrodes. These two layers play their own, unique roles in allowing a GDE to achieve better performance. Studies on the catalyst layer for this reaction are discussed in further detail in the remainder of this paper. However, as there are not many studies on gas diffusion layers for this reaction, GDL studies from other fields are considered as well.

THE GAS DIFFUSION ELECTRODE

The GDE consists of a gas diffusion layer (GDL) and a catalyst layer. The GDL consists of a porous conductive material such as carbon felt or a woven carbon structure which also acts as a current collector and can have a microporous layer (MPL) that is typically made from carbon and polytetrafluoroethylene (PTFE). Figure 3a shows these layers of a GDE.

There is common agreement that the GDE functions by maintaining three-phase boundaries with the reacting gas, liquid electrolyte, and catalyst particles.[18,78−81] These three-phase boundaries, shown in Figure 3b, are the reason that gas diffusion electrodes outperform the other electrode types by achieving more favorable mass transfer. All of the other electrodes discussed in the previous section are limited by mass transfer related to the low solubility of CO_2 in water (about 33 mM at room temperature).[8] However, a well synthesized GDE is able to drastically enhance mass transfer by creating a three-phase boundary. Thus, a GDE will not be limited at the same current density as a purely metal electrode.

The Limiting Current of GDEs. Motoo et al.[82] explain the function of the three-phase boundary for fuel cells in four steps:

1. the supply of reactant gas to the gas chamber side of the GDL
2. the diffusion of reactant gas through the GDL to gas dissolving sites
3. the diffusion of dissolved gas from gas dissolving sites to catalytic sites (Figure 3b)
4. the reaction at catalytic sites

They further state that the limiting current of a GDE for fuel cells is determined by one of these four steps and mention that increasing the amount of gas dissolving sites should lead to a better performing electrode. Li et al.[18] have obtained similar results for CO_2 electrochemical reduction as they mention that an increase of the number of three-phase interfaces, or gas dissolving sites, should promote higher reaction rates.

An additional consideration for GDEs in CO_2 reduction to formate is the diffusion of product away from the reaction site. Wang et al.[83] have reported product accumulation in GDEs reacting CO_2 to formate. If the formate does not diffuse away as fast as it is generated, and it is not consumed (e.g., by another chemical in the electrolyte), then there will be local accumulation around the reaction sites. This could then lead to a decrease in performance as well as eventual electrode failure.

Influential Characteristics. The characteristics of the two layers of the GDE will influence the electrochemical performance of the electrode. The GDL's function is to maximize the number of gas diffusion sites that supply reactant gas as well as have a high conductivity to ensure uniform current distribution throughout the structure. The catalyst layer's function is to

convert the dissolved reactant gas by having enough active surface area nearby the gas dissolving sites. Figure 4 lists several characteristics of these two layers that can influence the electrode performance in the form of a fishbone diagram.
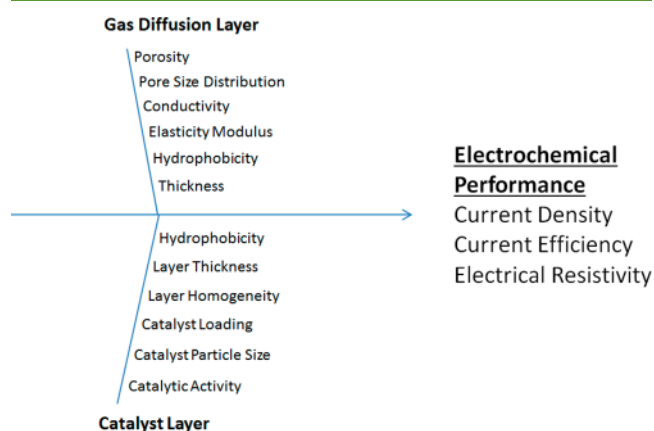

Figure 4. Fishbone diagram of factors influencing the electrochemical performance of GDEs.

The characteristics of each layer should be fully tunable so that optimum GDEs can be identified; however, there is a lack of research reporting on how to tune some of these characteristics. A more detailed analysis of these characteristics for both layers is discussed in the following sections, starting with the GDL.

THE GAS DIFFUSION LAYER

Purpose of the GDL. The GDL has four main roles. It must conduct electrons to the catalyst layer,[82,84] be mechanically stable,[85] supply reactant feed to the catalyst,[78,82] and maintain the three-phase boundary by keeping water at the catalyst layer to prevent flooding.[78,82] The GDE is ineffective if any of these conditions are not met. Furthermore, the ideal GDL should be capable of providing a high number of gas dissolving sites when combined with the catalyst layer.[18,82] Therefore, the characteristics of a GDL will strongly impact the performance of the complete electrode. There are many factors that can influence the characteristics of a GDL. Figure 5 displays these factors.

The materials used in the production, the production method, the measurement system used to quantify a characteristic, and environmental factors (such as humidity, room temperature, etc.) can all influence the reported GDL characteristics. The measurement system is also an important consideration because it can affect which factor is observed to have an effect on the
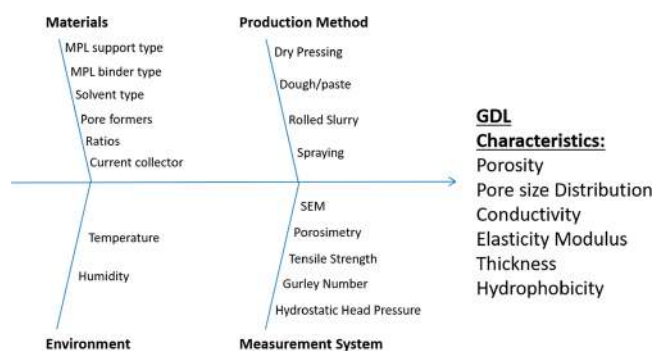

Figure 5. Fishbone diagram of factors in GDL production that can influence GDL characteristics.

characteristic being studied. If there is high measurement error from the way a sample is taken and/or measured, then a certain factor can be deemed as not significant. Whereas, if the measurement system had lower error, the factor may have been deemed significant. Knowing which characteristics of a GDL are most important, and how to quantify them, is not straightforward. Hence, we start by looking at what has been done in GDL research across various fields.

GDL Characteristics and Measurement Systems. The use of GDEs in the field of CO_2 reduction is limited; however, GDLs are used in other electrochemical fields which can still be relevant to CO_2 reduction. A great deal of characterization research has been performed on GDLs for use in polymer electrolyte membrane fuel cells (PEMFC), oxygen electrodes (such as oxygen depolarized cathodes), and GDLs used in alkaline fuel cells. Although these fields are different, and the desired characteristics for the GDLs may differ, the characteristics of interest should still be the same. The various characteristics which have been studied and the methods used for characterization across six fields of GDLs are shown in Table 1 and further discussed next.

Table 1. Common GDL Characterization Methods (See Refs 18, 68, 78−80, and 86−94)

GDL characteristic	method
composition	TGA−DTA
conductivity	contact resistance
electrolyte absorption	weighing
hydrophobicity	wetting
optical/morphological	SEM
	TEM
permeability	diffusion volume
	Darcy's law
	gas perm. coeff
	Gurley densometer
	capillary flow porometer
porosity	SEM
	Hg porosimetry
	KOH porosimetry
	EIS
surface composition	XPS
thickness	calipers
	SEM

Porosity and Pore Size Distribution. Porosity and optical/morphological characterization are performed most for the GDL. Maja et al.[91] and Uchida et al.[94] determined that the pore size distribution in a GDL influences the performance of the electrode for metal air batteries and PEMFCs, respectively. Kong et al.[93] concluded that the pore size distribution is more important than the total porosity in affecting the cell performance of fuel cells.

Various methods are used to measure porosity. Hg porosimetry is most frequently used to characterize the porosity of the GDL. KOH porosimetry, scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS) have also been used to characterize the porosity of structures. SEM seems to be a method prone to large errors if the structures made are not uniform as the number of pores to characterize in a 10 cm^2 structure would be impractical to image with SEM. Furthermore, SEM does not give any information on the pore size distribution or the internal pores in the structure. Hg

porosimetry could also be prone to measurement errors if a structure is not uniform; however, combining various sections of a structure in one sample with this method could reduce this error.[95] Combining a visual microscopy method with Hg porosimetry could confirm the uniformity of a structure and increase confidence in the porosity measurement.

Gas Permeability. The gas permeability of the GDL is the second most studied characteristic between 12 studies found on GDLs, and there is not a common way of measuring this characteristic. Tseng et al.[89] used a capillary flow porometer to measure gas permeability, while Pozio et al.[78] used a Gurley densometer, which has ISO certified methods. Both studies found that gas permeability increased with increasing PTFE concentrations used in GDL synthesis. The other publications that measure permeability each seem to use their own method to estimate the value which causes difficulty in comparing results. Furthermore, the porosity of the GDL should highly influence the permeability of the structure and therefore may be a more important characteristic to use for these structures than gas permeability.

Conductivity, Composition, and Hydrophobicity. The conductivity, hydrophobicity, and composition of the GDL are less studied than the other characteristics. Pozio et al.[78] measured the conductivity of the GDLs by contact resistance and estimated the total composition of commercial GDLs by thermogravimetric analysis−differential thermal analysis (TGA−DTA) measurements. Schulze et al.[79] used X-ray photoelectron spectroscopy (XPS) to measure the surface composition of the GDL and studied the hydrophobicity of the structures by wetting with liquid water and water vapor. Maja et al.[91] measured the absorption of electrolyte in the GDL by weighing the structure before and after operating in a flow cell. They discovered that excessive electrode wettability leads to degradation of the cathode performance. However, this method to determine electrolyte absorption could lead to large variations if used for electrolyte wetted GDEs, and the method of drying the wetted layer is not optimized.

It is surprising that the hydrophobicity of this layer is not more frequently studied. Electrolyte contact angle could be a more useful measurement for hydrophobicity since it is a quantitative rather than qualitative measurement; however, no studies on GDLs were found that use this technique. Furthermore, no studies were found that look into the resistance of this layer to the hydrostatic head. These two factors should play a significant role in preventing flooding and maintaining structural stability as it is scaled up.

GDL Characteristics Outlook. These studies performed on the characterization of GDLs attempt to link the structural characteristics to electrochemical performance, but only one study was found that investigates how production factors influence GDL characteristics. Moussallem et al.[90] studied GDLs for oxygen depolarized cathodes. They found that variations in the temperature between 100 and 160 °C when hot pressing their electrodes led to a more stable performance of their electrode. They also found the sintering temperature had no effect on the performance of the electrodes when between 280 and 380 °C. Finally, they determined that the porosity of their electrode almost linearly decreased with their applied pressure, although this only affected performance when below a certain porosity. This study, however, did not consider the effect of different material types which could also have an influence on the findings. We next consider the materials that are commonly used in GDL production methods before discussing the

Table 2. GDL Synthesis Method Summary (See Refs 15, 18, 19, 65, 68, 78−80, 83, 86, 90, 91, 93, and 96−98)

ref	method type	field of use	additional materials	current collector	carbon type	binder type	solvent type
15	dry pressing approach	CO_2 reduction	graphite	SGL, Sigracet GDL 35BC	acetylene black	PTFE suspension (TF 9207Z, Dyneon)	N/A
18	slurry rolled	CO_2 reduction	Na_2SO_4	foamed nickel	acetylene black	PTFE emulsion	ethanol
19	wet paste	CO_2 reduction	N/A	Ni mesh	Vulcan XC-72	Fluon, GP1, ICI	water
65	dry deposition	CO_2 reduction	N/A	N/A	acetylene black	PTFE suspension (TF 9207Z, Dyneon)	N/A
68	spraying	CO_2 reduction	N/A	Toray Paper, TGPH-90	Vulcan XC-72R	N/A	N/A
78	spraying	PEMFC	Nafion 5% solution	Toray Paper, TGPH-90	Super-P Carbon Black	PTFE suspension (TF 5033, Hoechst)	2-propanol
79	dry coating	PEMFC	N/A	N/A	Vulcan XC-72	PTFE suspension (TF 2053, Hoechst)	N/A
80	dough rolled and hot press	generic	petrol	carbon cloth	SH100 and XC-72R	PTFE suspension	petrol
83	mixed into paste then rolled	CO_2 reduction	N/A	N/A	carbon black	PTFE suspension	ethanol
86	mixed into paste then rolled	oxygen electrode	graphite	stainless steel screen	activated carbon	PTFE dispersion (Polyflon, Daikin)	N/A
90	spraying	oxygen electrode	nonionic surfactant (Triton-X 100)	nickel mesh	N/A	PTFE suspension (TF 5035R, Dyneon)	water
91	single pass wet fabrication	metal air batteries	N/A	N/A	varied	PTFE	alcohol
93	mixed into paste then rolled	PEMFC	LiCO3	carbon cloth	Vulcan XC-72	PTFE solution (60 wt %, Aldrich)	2-propanol
96	dry powder	GDE study	N/A	N/A	acetylene black	PTFE supsension (Fluoroplast 4D)	N/A
97	ink applied to carbon cloth	PEMFC	N/A	hydrophobic carbon cloth	Vulcan XC-72	PTFE solution	2-propanol
98	dry pressing	oxygen electrode	N/A	nickel grid	varied	4D-fluoroplastic (FT-4D)	water

methods that have been used to produce GDLs for the CO_2 to formate reaction.

GDL Materials. There are five common categories of materials used to synthesize a GDL (see Figure 3): support and binder of the MPL, solvent, pore former, and current collector. An overview of the materials used in the GDL production methods found in the literature as well as the production method type and intended field of application can be found in Table 2. In the next paragraphs, the effect of carbon, binder, solvent, pore former, and current collector on the GDL will be discussed.

MPL Support. The only MPL support to date is carbon. Unfortunately, there were no studies on carbon type for GDEs used in CO_2 reduction. However, three studies were found that investigated the carbon used in GDL production for GDLs used in other fields. Maja et al.[91] studied the effect of carbon type on performance of metal air battery gas diffusion electrodes. Acetylene (Shawinigan Black AB50) and two types of oil-furnace carbon (Vulcan XC72R and Black Pearls 3700) were studied. They found that cathode performance decrease is caused by excessive electrode wettability. Additionally, they found that electrodes with oil-furnace blacks were least stable due to the largest wet pore volume in the active layer for their production method. Tomantschger et al.[80] also determined acetylene black to be the material of choice for the diffusion layer of alkaline fuel cells after considering a furnace black (Vulcan XC-72R), acetylene black (Shawinigan SH100), oil flame black (Lampblack), and activated carbon (Black Pearls 2000). Kolyagin et al.[98] determined the best results for GDEs reacting oxygen to hydrogen peroxide composed of a 1:1 mixture of a hydrophobic acetylene black (A473-E) and a semihydrophobic furnace black (P702).

MPL Binder. Three studies were encountered that examined the PTFE content in a generic GDL. Kolyagin et al.[96] found that

an increase in the PTFE content from 8 to 40 wt % results in an increase in the average diameter of hydrophilic pores and a decrease in the surface area of the structure. Additionally the whole carbon black surface is wetted by electrolyte with 8−20 wt % of PTFE. Similarly, Schulze et al.[79] determined that a PTFE concentration of ∼20 wt % marks the transition between hydrophilic and hydrophobic surfaces in their electrode structures. In addition to the permeability studies performed by Tseng et al.[89] and Pozio et al.,[78] Li et al.[18] found CO_2 permeability to be optimal when 30% PTFE is used in the GDL. Furthermore, they found that excess PTFE causes the carbon material to agglomerate too much causing a blockage of pathways for CO_2 transport.

Solvent. Only one source was found that discusses the solvent in the formulation mixture of GDLs. Pozio et al.[78] studied using a water mixture with an alcohol (isopropyl alcohol or ethanol) and found that adding a 1:1 and 1:3 water/alcohol mixture to their 35 wt % PTFE solution resulted in the mixture to turn to a gel. This mixture gelling allowed them to better apply the MPL to the current collector and resulted in a more homogeneous structure seen through surface continuity.

Pore Former. Pore formers have the ability to increase the porosity of the GDL structure which can potentially increase the number of three-phase boundaries and enhance the performance of the overall electrode. However, the use of pore formers in producing GDLs is rare. Consequently, no studies were found that use pore formers in GDLs for CO_2 reduction. Only two studies were found that considered using pore formers in their GDL formulations for PEMFCs. Kong et al.[93] varied amounts of $LiCO_3$ from 0 to 200 wt % relative to the carbon loading in the GDL. Their data suggests using 58 wt % of pore former to create an optimal macropore volume of the GDL which is desirable for PEMFCs. Zhao et al.[99] use several ammonium based salts as pore formers. They found that the addition of NH_4CO_3
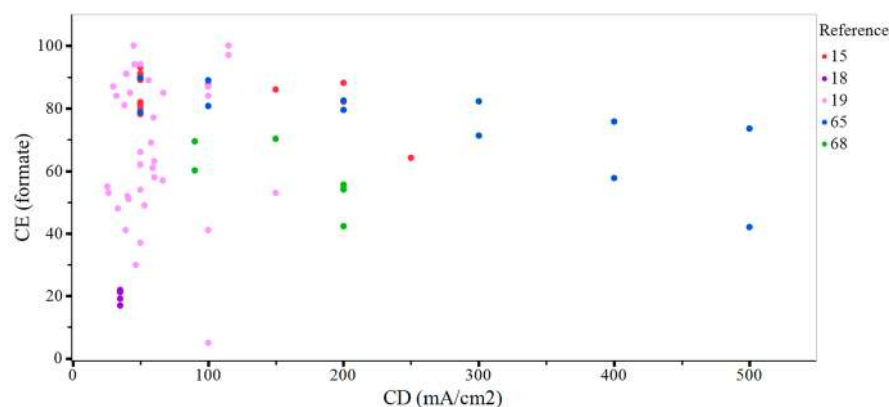
Figure 6. Performance of synthesized GDLs from the literature (see refs 15, 18, 19, 65, and 68).
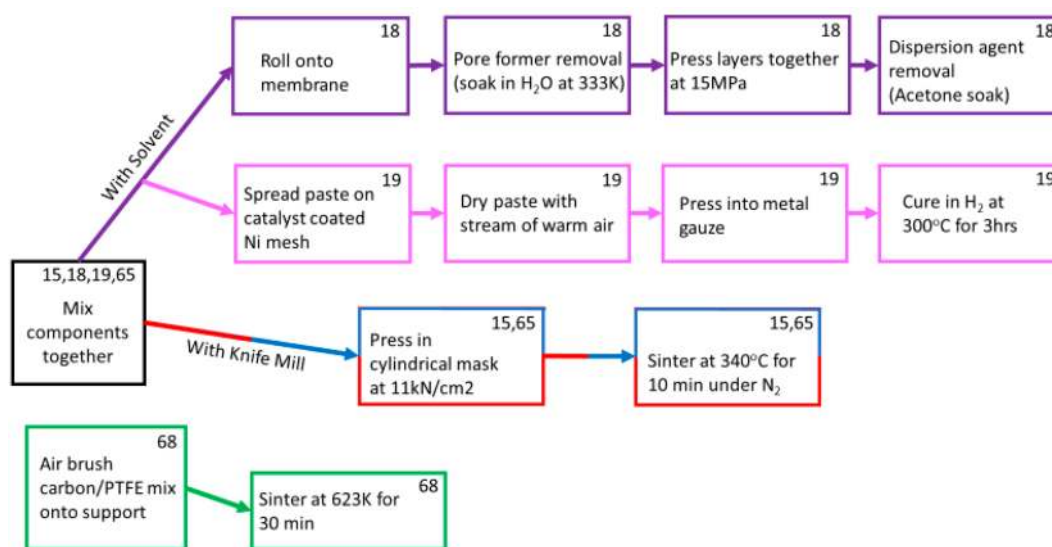

Figure 7. GDL production methods (see refs 15, 18, 19, 65, and 68).

decreased the transport resistance of the structure and reduced the necessary catalyst loading while maintaining the same performance.

Current Collector. No sources were encountered that investigated the effects from varying the current collector on the performance of the GDL. This is most likely because it is not as important as the MPL in the function of the GDE. The current collector must only be conductive and not cause any preferential flow of reactant gas through sections of the structure. Furthermore, there is no way to modify the current collector itself, and in all of the methods reviewed, only one method is used to attach the GDL to the current collector compared to the many methods used to create and structure the GDL.

GDL Materials Outlook. It is very difficult to draw conclusions about materials from combined data because each publication uses a different GDL production method. Furthermore, in most studies, only one material factor is varied, and the results are reported. This linear experimentation methodology neglects any type of interactions of factors that may have an effect on the measured responses. For example, the optimal amount of PTFE can be determined for one carbon type but may be different for another carbon type. Similarly, one carbon type can be determined to be the best for a specific production method; however, another carbon type may be best

for a different method. The variations in production methods are discussed next.

GDL Production Methods in the Literature. The performance of different GDL production methods found for CO_2 reduction to formate reported in five different references are compared in Figure 6, while Figure 7 shows a block diagram of the steps used in the respective GDL production methods.

As seen in Figure 6, Mahmood et al.[19] achieve the highest current efficiency up to current densities near 100 mA/cm^2 while using a wet method to produce GDLs. However, their performance seems to decline at 150 mA/cm^2. Kopljar et al.[15,65] demonstrate the highest current efficiencies at current densities beyond 100 mA/cm^2 using a dry GDL production method.

Of course, there are other factors that could be influencing the reported electrochemical performance. For example, the catalyst layer is different between these studies and will affect the electrochemical performance. However, there is still a great deal of variance observed in data within individual studies and between studies that use the same catalyst.[15,19,65,68] The lack of reproducibility of a GDL production method could be causing a great deal of this variance, yet no studies have been found that investigate reproducibility of a production method. The reproducibility of a method is something that can be advantageous to study as it will be necessary to understand for

the scaling of GDLs. With this in mind, we found two patents on methods to produce a GDL.

Patented GDL Production Methods. Gulla et al.[100] use a wet method to produce a GDL. They use acetylene black (Shawinigan Black), a suspension of PTFE, and a 1:1 isopropyl alcohol (IPA):H_2O as the solvent. The formulation in this method is similar to other wet methods, and the solvent ratio used is in the same optimal range that Pozio et al.[78] found. This method uses calendaring followed by hot pressing to turn the dough mixture into a GDL. In one example given, they first extrude the dough to a desired thickness and then hot press it onto a silver mesh at 17.9 kPa and 120 °C for 30 min, and then they increase the temperature and pressure to 335 °C and 44.8 kPa for 30 min before releasing the pressure and exposing the structure to ambient air for 5 min. The final step is to hot press again at 34.5 kPa at 335 °C for 30 min. This patent mentions advantages of this GDL including its resistance to the hydrostatic head which allows for cheaper cell designs that allow for lower cell potentials. In addition to the hydrostatic head characteristic, this patent characterizes the longitudinal elastic modulus of its structures, and they claim their GDLs have a longitudinal elastic modulus of at least 10,000 MPa.

The method used in this patent is very similar to the method Tomantschger et al.[80] used earlier. Once they make the dough, it is pressed to a carbon cloth backing at 20 kg/cm^2. They heat their structure in three stages starting at 100 °C for ammonium bicarbonate (pore former) decomposition, and then they ramp up to 175 °C for the evaporation of their suspension agent. Finally, they sinter the structure at 320 °C for 20 min.

Another patent was found from Turek et al.[101] who start from a suspension to make GDLs. They make the suspension by mixing a silver catalyst, a PTFE suspension, a nonionic surfactant, and hydroxyethyl methyl cellulose as a thickening agent. They disperse this mixture using a rotor-stator system in pulses to avoid excessive heating of the solution, and then they spray this suspension several times onto nickel foam that is maintained at 100 °C. Once the desired loading is reached, they hot press the structure at 0.14 tonne/cm^2 and 130 °C before ramping to a sintering temperature of 340 °C for 15 min.

GDL Outlook. Patents do not discuss the scientific reasoning behind material choice and the ratios that were used. Additionally, there is a lack of insight into the effect one step may have on the characteristics of the GDL structure. Understanding of the production factors' influence on the characteristics of a GDL is critical for developing GDLs, and more focus should be given to this area in the future. Ideally, a method should be identified and developed to produce tunable GDLs. This would lay the groundwork for future studies to investigate GDL characteristics in more detail.

No studies were found that investigate how the catalyst layer characteristics can interact with the GDL characteristics to affect the electrochemical performance of the GDE. Including GDL characteristics with the optimization of the catalyst layer would be most beneficial as global, rather than local, optimums could be identified. Future research should strive to take this approach to optimize GDEs for this reaction. The catalyst layer is discussed next, in order to better understand the key factors that should be included in studies that combine GDL and catalyst layer characteristics' influence on performance.

■ THE CATALYST LAYER

The catalyst layer consists of the electrocatalyst, usually immobilized on a supporting material that is applied to the

GDL using various methods, with or without the use of a binder. Figure 8 shows factors of the catalyst layer that can influence the electrochemical performance of the GDE.
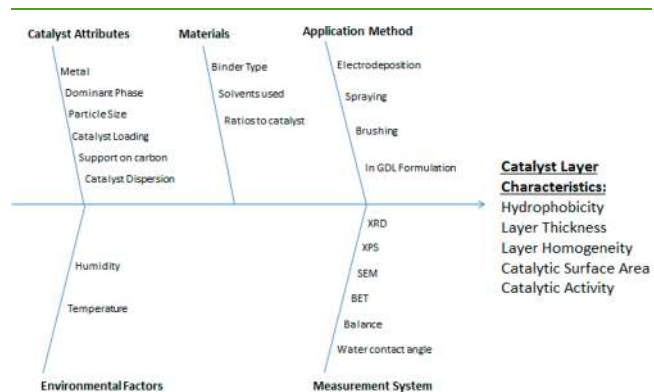

Figure 8. Fishbone diagram of factors influencing the catalyst layer.

The catalyst attributes, the materials used, and the application method can affect the characteristics of the catalyst layer. Similarly to the GDL, the methods used to characterize the catalyst layer, as well as environmental factors, can influence the reported characteristics of this layer. There were 18 papers and 1 patent found that use a GDE for the electrochemical reduction of CO_2 to formate. Only a few of these studies explore the effect of characteristics of the catalyst layer on electrochemical performance. Out of all the factors shown in Figure 8, the effect of catalyst loading and catalyst particle size are the only factors varied within a given study. However, between the studies there are different metal catalysts and binders, different application methods, varying particle sizes, and various catalyst loadings investigated. Therefore, only these five factors will be discussed in more detail.

Catalyst Metal. There were 11 metals used as a catalyst on a GDE from the 19 sources found reporting formate as a CO_2 reduction product. A summary of current efficiencies achieved for these metals is shown in Figure 9.

Indium (In), lead (Pb), and tin (Sn) are the most studied metals on GDEs, and they are seen to achieve the highest CE for this reaction with Pb showing the highest median and maximum CE for formate at 62% and 100%, respectively.[19] For this reason,
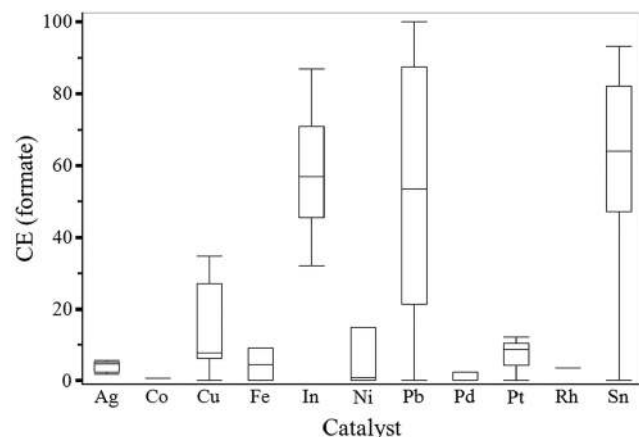

Figure 9. Current efficiency for formate vs catalyst metal (see refs 13−20, 25, 27, 64−69, 75, 102, and 103).
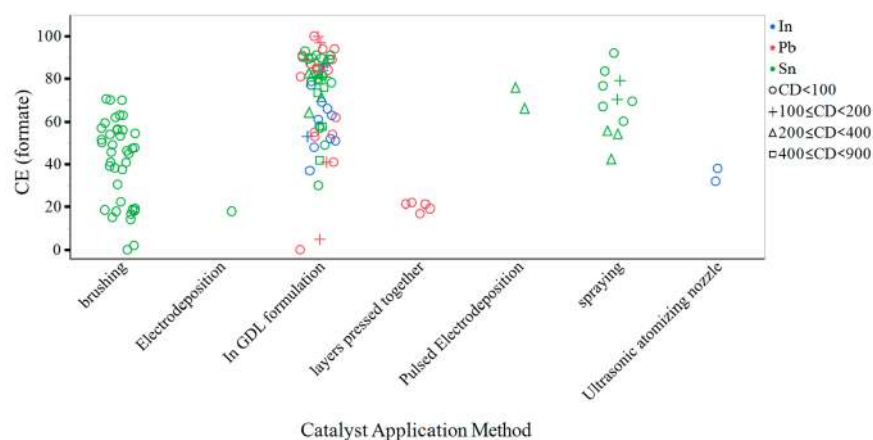
Figure 10. Current efficiency of CO_2 to formate for various catalysts and application methods (see refs 13−15, 18−20, 25, 27, 64, 65, 68, and 75).
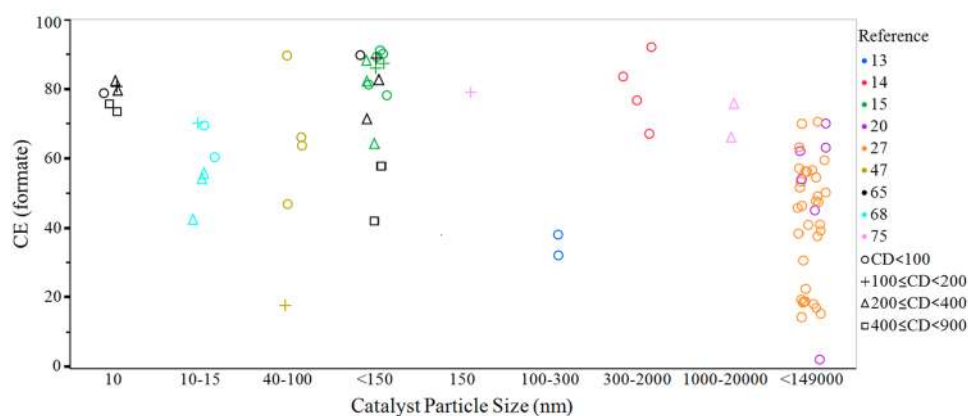

Figure 11. Current efficiency of formate vs catalyst particle size (see refs 13−15, 20, 27, 47, 65, 68, and 75).

we will focus only on discussing the literature that uses these three catalysts in the next sections.

Application Method. Twelve of the 19 sources found use Pb, Sn, or In as a catalyst for CO_2 reduction to formate with a GDE. Seven catalyst application methods have been used across these 12 studies. These catalyst application methods are compared for the three catalysts in Figure 10.

The most frequent catalyst application method used was to include the catalyst in the initial GDL mixture. This could be advantageous by making operation more consistent as performance would be more independent of electrode wettability, but consequently, this method would drastically increase the cost of these electrodes. This is because there would be an additional inactive catalyst in such a structure because it would be dispersed in places other than at the three-phase boundary, and although the common metals used for this reaction may be relatively cheap, the method to produce the catalyst can be expensive when considering the costs of other inputs (e.g., the cost of solvents, reducing agents, energy, and waste disposal). Therefore, this method is not as attractive from a cost perspective to scale up.

Brushing and spraying were the next most frequently used methods in applying a catalyst layer to the GDL. On average, spraying of the catalyst has been shown to result in higher current efficiencies and operated current densities than brushing for the same metal catalyst. Both of these methods involve making a catalyst ink by dispersing catalyst particles in a solvent and either using a paint or air brush to apply the catalyst ink to

the GDL.[14,20,27,68,75] These methods allow for more customization of the catalyst layer than other application methods as the catalyst ink can be easily tuned.

The ultrasonic atomizing nozzle is similar to the spraying application method as a catalyst ink is used and applied as a fine droplet mist which allows this method to achieve a homogeneous distribution of catalyst on the GDL.[13] Electrodeposition involves reducing metallic ions on the GDL surface by applying a potential between the GDL and a counter electrode in a plating solution. This method is limited in the catalytic surface area it can produce compared to the other methods as it typically generates a smooth, uniform layer on the plating substrate. Pulsed electrodeposition uses that same method as electrodeposition except the current is pulsed during the deposition process. This method can lead to a highly dispersed and uniform catalyst nanoparticle layer.[75] These methods tested do not show high current efficiencies (Figure 10); however, there are not nearly as many studies performed on these methods (i.e., the sample size is too small for these methods to draw any conclusions). Pulsed electrodeposition especially seems promising as the only two points for which this method was applied operated at current densities between 200 to 400 mA/cm², while the majority of the points in Figure 10 result from experiments performed at lower current densities.

Catalyst Particle Size. Only eight of the studies found report the catalyst particle size used for Sn and In catalysts. Additionally, of those eight studies, only two vary the catalyst particle size. A summary of studies that report catalyst particle

size and the current efficiency they achieve for In and Sn catalysts is shown in Figure 11. Particle size does not appear to affect the current efficiency toward formate formation below sizes of 20 μm.

Sen et al.[75] compared a pulsed electrodeposition method that produced 1−20 μm Sn particles to a commercially available, 150 nm Sn catalyst. They found the agglomerates were able to achieve 80% current efficiency at a current density of 388 mA/cm^2, while the commercial catalyst achieved about 79% current efficiency at just below 150 mA/cm^2. The loading of catalyst between the electrodes in this study also varies by about a factor of 4 which makes it difficult to draw meaningful conclusions. Kopljar et al.[65] studied <150 nm Sn powder and ∼10 nm SnO$_2$ synthesized particles. They showed that the SnO$_2$ nanoparticles maintained a CE of about 75% as they increased the current density from 50 to 500 mA/cm^2, while the Sn powder showed better performance (∼88% CE) at lower current densities but decayed to below 50% CE at 500 mA/cm^2.

Binder. The binder in the catalyst layer can modify the hydrophobicity of the layer, as well as provide mechanical stability of the catalyst on the GDL. There were two types of binder found in the literature for this reaction: Nafion and PTFE. There were also several studies that did not use any binder in the catalyst layer. A comparison of the CE for the binders used across the 12 studies is shown in Figure 12.
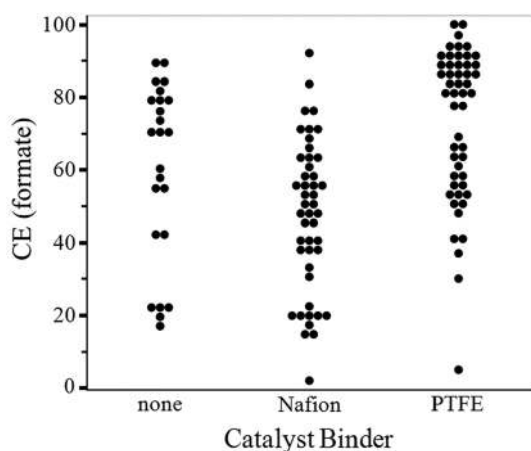

Figure 12. Current efficiency of formate vs catalyst binder (see refs 13−15, 18−20, 27, 65, 68, and 75).
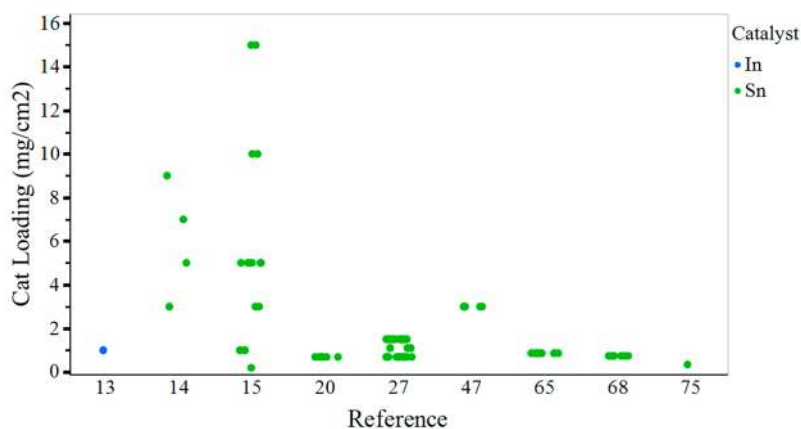
It is difficult to draw conclusions from this data from multiple studies where many factors are different between them. However, the cluster of Nafion data appears to be weighted lower in current efficiency than PTFE or no binder. This may suggest that Nafion could hinder performance when used as a binder for this reaction. This should be a factor to investigate in future studies as a binder may become more important to use when electrode stability for this reaction is studied.

Catalyst Loading. Only four studies varied the catalyst loading of Sn, In, and Pb catalysts.[14,15,19,27] Mahmood et al.[19] was the only study found that varied the loading of a Pb catalyst. A summary of the In and Sn catalyst loadings studied is shown in Figure 13.

Kopljar et al.[15] suggest that the metal loading changes the overpotential for the reaction at a given current density, and a shift in product distribution occurs (i.e., current efficiency of CO increases while the efficiency for formate decreases). Understanding this observation further would be beneficial for developing the CO$_2$ to formate reaction. Furthermore, it would be beneficial to find a catalyst layer that functions through a wide range of operating current densities for a given loading to allow more flexibility in operation at pilot or commercial scale.

Wang et al.[14] studied the effect of catalyst and binder loading. They found the optimal tin loading to be 5 mg/cm^2 with particle sizes between 300 and 2000 nm. They also claim that 50 wt % Nafion is the optimal amount. However, they study Nafion concentrations at one constant catalyst loading and then catalyst loading at a constant Nafion concentration. This method of experimentation does not allow interaction effects between the factors that they study to be estimated. Therefore, there could be a better optimum in their experimental design space.

Mahmood et al.[19] used a Pb catalyst and varied loadings at two levels (50 and 100 mg/cm^2). They do not report the size of their Pb catalyst particles on the GDE, and they do not see a significant change in electrode performance at low pH. However, the electrochemical cell that they use does not seem to allow for uniform current distributions to be achievable on the surface of their electrode. Their cell uses a plastic mesh as a separator, and the anode is perpendicular to the cathode rather than parallel. This could cause a bias in the results when working in electrolytes that are not very conductive.

Castillo et al.[27] performed a three factor, full factorial, design of experiments (DOE) and investigated the Sn catalyst loading,

Figure 13. Catalyst loading studies for indium and tin (see refs 13−15, 20, 27, 47, 65, 68, and 75).

the flow rate of the catholyte standardized by cell area, and the current density. Unfortunately, the current density range studied was much lower than where a limitation should exist for GDEs in this reaction at 12−32 mA/cm^2, whereas current densities up to 500 mA/cm^2 have been reported for Sn GDEs.[65] Nevertheless, they found that the Sn loading in the GDE had the greatest main factor effect on the current efficiency, while the catholyte flow rate had little effect. This study supports the idea that the catalyst layer is more important in overall cell performance than operational parameters such as electrolyte flow rate, pH, temperature, etc. This was the only study that was found which does not use a linear approach at investigating factors which affect cell performance. However, this study only looks at a total of three factors, and only one of them relates to a catalyst layer characteristic.

The other studies that have examined the catalyst layer are performed in a linear approach which neglects any interactions that can exist. For example, the optimum catalyst loading can vary for different catalyst sizes and the amount that is supported on carbon, but these types of interactions have not been considered. As a result, these studies are reporting local maximums in their experimental space rather than global maximums.

OUTLOOK AND RECOMMENDATIONS

In summary, the current density, current efficiency, and cell potential are the main KPIs for a given electrochemical reaction. Virtually all of the studies encountered for the electrochemical reduction of CO$_2$ to formate do not target to optimize the cell potential or report whole cell potential data, so energy costs were not a valid comparison between studies. Future studies should report whole cell and half cell potential data to allow for energy assessments and further insights to be made. Many papers were investigated for this reaction, but not all of them reported enough information to compare the study to the rest. Future studies should report the KPIs discussed in Section 2 at the bare minimum (electrode size, current density, current efficiency, and cell potential).

GDEs are the most promising electrode type to pursue for the development of this reaction. GDEs consistently outperform 2D, 3D, and trickle flow electrode types as they are capable of operating at high efficiencies and higher current densities than these other electrode types. They are able to achieve this high performance by maintaining a three-phase boundary with the reacting gas, liquid electrolyte, and catalyst particles which allows them to overcome mass transfer limitations that all other electrode types encounter at lower reaction rates. However, GDEs are complex, and there is still much more research that should be performed to further optimize GDEs for the commercialization of this reaction.

Overall, there are limited studies that correlate the formulation and production steps of a GDL to the characteristics of the structure. Additionally, there are only a few studies that examine the effect that these structural characteristics have on the electrochemical performance of the electrode. No studies were found that examine the interaction effects of GDL formulation with variations in the production method. Future studies should aim to investigate these areas relating to the GDL in much more detail by using a systematic approach, such as the design of experiments, that can identify factor interactions.

Similarly, the catalyst layer is not well studied for this reaction; there are few publications that study the effects of only one of the characteristics of the catalyst layer (such as loading) on the electrode performance. Only one study was found that uses a design of experiments approach to assess the effects of three factors on the electrode performance. Although only one of the three factors studied was part of the catalyst layer, the study was still useful in showing that the GDE characteristic parameters are more influential than cell operating parameters for this reaction. Furthermore, there is an inconsistency in the amount of data that is reported between the studies. For example, 12 studies were found using tin, indium, or lead on a GDE for the electrochemical reduction of CO$_2$ to formate, but only eight of the 12 studies reported a catalyst particle size. Future studies should aim to be more consistent in the reporting of information such as catalyst particle size, loading, fraction supported, and ratios with a binder.

All of the studies for the GDL and catalyst layer use a linear experimentation methodology which neglects any type of interactions that may have an effect on the measured response. This leads to a large risk of finding a local optimum and missing the global optimum that exists in the experimental parameter space. It would be highly beneficial for a study (or series of studies) to investigate the effect of the interaction between GDL characteristics with catalyst layer characteristics on the electrode's performance. This would allow for the optimum overall structure to be defined (i.e., the most conductive GDL structure that allows for the lowest amount of catalyst loading to achieve a target current density and efficiency). Ultimately this would result in high savings in production costs of the electrode and operating energy costs of the cells.

Finally, the operation of GDEs at larger scale should be studied for longer times because there could be different implications to the scaling and lifetime compared to metal electrodes (e.g., the resistance of the electrode to the hydrostatic head). As GDEs become larger, the pressure at the bottom/inlet of the cell will become greater which could cause flooding in lower sections of the structure. This is especially important because previous research has found that flooding (electrolyte wetting in the GDL) causes a decrease in lifetime and performance of GDEs. Operating at longer times would allow more insights into the failure mechanisms of these structures for this reaction.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Photo provided by Matthew Philips

Matthew Philips received his B.S. in Chemical and Biomolecular Engineering, graduating with Highest Honors, from The Georgia Institute of Technology. After graduating, he worked for R&D companies in the electrochemistry field where he gained knowledge and experience in the design of experiments, test station design and fabrication, electrochemical cell optimization, and process engineering separations. In 2017, he was accepted into ELCOREL, a Marie Curie Innovative Training Network, with a focus on optimizing the electrochemical reduction of CO_2 to formate. He is currently working as a Senior Process Engineer at Avantium, where he is working on a team developing electrocatalytic CO_2 conversion technologies.

Photo provided by Gert-Jan Gruter

Prof. Dr. Gert-Jan Gruter (1963) has a background in Polymer Chemistry (DSM 1993−2000) and has been Professor of Polymer Catalysis at Eindhoven University of Technology. In 2000, he transferred to Avantium where in 2004 he was appointed as Chief Technology Officer (CTO). Gruter initiated the developments for technologies to produce polyester monomers FDCA and MEG from carbohydrates and the subsequent 100% biobased PEF polyester for bottles, fibers, and film. In addition, Gruter is working on the cascading of lignocellulosic biomass to produce 2G glucose and on the electrochemical reduction of CO_2 to formate and CO and downstream formate conversions to polyester monomers such as oxalic acid and glycolic acid and subsequent polymers. Gruter is inventor on more than

100 patent families and (co)author on about 40 scientific papers and book chapters; he was elected "2014 European CTO of the year" and runner-up European inventor of the year in 2017. Gert-Jan is currently part-time Professor of Industrial Sustainable Chemistry at the University of Amsterdam (UvA), where he is working on novel high Tg sustainable materials for reuse, on electrocatalysis and downstream conversions, on plastic biodegradation, on chemical recycling of polyesters, on consumer psychology, and on ocean plastics.

Photo provided by Marc Koper

Marc Koper is Professor of Surface Chemistry and Catalysis at Leiden University, The Netherlands. He received his PhD degree (1994) from Utrecht University (The Netherlands) with a thesis on nonlinear dynamics and oscillations in electrochemistry. He was an EU Marie Curie postdoctoral fellow at the University of Ulm (Germany) and a Fellow of Royal Netherlands Academy of Arts and Sciences (KNAW) at Eindhoven University of Technology, before moving to Leiden University in 2005. His research in Leiden focuses on fundamental aspects of electrocatalysis, theoretical electrochemistry, and electro-chemical surface science, in relation to renewable energy and chemistry. He has received various national and international awards, among which are The Netherlands Catalysis and Chemistry Award (2019) and the Faraday Medal (2017).

Photo provided by Klaas Jan Schouten

Dr. Klaas Jan Schouten is the Program Manager of VOLTA, the electrochemistry technology platform of Avantium. He also leads the Electrocatalysis and Applied Electrochemistry group at the University of Amsterdam as part-time Research Assistant Professor. Klaas Jan obtained his MSc (Cum Laude) and PhD with Prof. Marc Koper at Leiden University. His thesis on electrochemical CO_2 reduction has been awarded with the Dutch Catalysis Society Award 2015 and the European Federation of Catalysis Societies (EFCATS) best PhD Thesis Award 2015.

■ ABBREVIATIONS

GDE, gas diffusion electrode; KPIs, key performance indicators; PPR, product production rate; CE, current efficiency; MW, molecular weight; CD, current density; TPR, total production rate; GDL, gas diffusion layer; MPL, microporous layer; PTFE, polytetrafluoroethylene; PEMFC, polymer electrolyte membrane fuel cells; SEM, scanning electron microscopy; EIS, electrochemical impedance spectroscopy; TGA−DTA, thermogravimetric analysis−differential thermal analysis; XPS, X-ray photoelectron spectroscopy; IPA, isopropyl alcohol; DOE, design of experiments

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