Electrochemical CO₂ reduction - The macroscopic world of electrode design, reactor concepts & economic aspects

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SUMMARY
For the efficient electrochemical conversion of CO₂ into valuable chemical feedstocks, a well-coordinated interaction of all electrolyzer compartments is required. In addition to the catalyst, whose role is described in detail in the part “Electrochemical CO₂ Reduction toward Multicarbon Alcohols - The Microscopic World of Catalysts & Process Conditions” of this divided review, the general cell setups, design and manufacture of the electrodes, membranes used, and process parameters must be optimally matched. The authors’ goal is to provide a comprehensive review of the current literature on how these aspects affect the overall performance of CO₂ electrolysis. To be economically competitive as an overall process, the framework conditions, i.e., CO₂ supply and reaction product treatment must also be considered. If the key indicators for current density, selectivity, cell voltage, and lifetime of a CO₂ electrolyzer mentioned in the techno-economic consideration of this review are met, electrochemical CO₂ reduction can make a valuable contribution to the creation of closed carbon cycles and to a sustainable energy economy.

INTRODUCTION
The electrochemical CO₂ reduction reaction (CO₂RR) powered by electrical energy from renewable sources offers encouraging potential to help counteract a further increase of atmospheric CO₂ concentration and its adverse effects on planet Earth’s climate, ecosystems, and human health. Furthermore, it is providing an alternative to fossil resources as a carbon source. A variety of high-quality reviews on the topic have been published, covering specific catalysts and products, membranes, cell setups etc (Balamurugan et al., 2020; Fan et al., 2020; Hernandez-Aldave and Andreoli, 2020; Kibria et al., 2019; Kumar et al., 2016; Lu and Jiao, 2016; Nitopi et al., 2019; Rabiee et al., 2021; Salvatore et al., 2021; Weekes et al., 2018). However, scientific progress on the topic is rushing over the last years, electrochemical CO₂ reduction is a process of high complexity, and the success of this technology is simultaneously subject to a multitude of factors.

One of those factors is the ambivalent role of water, which, on the one hand, is the source of protons necessary for CO₂RR, and on the other hand, simultaneously a competing substrate for reduction in the hydrogen evolution reaction (HER). Maintaining the right balance and ensuring suitable mass transport of the reactants to and products from the electrode thus plays a key role in the cathodic process of CO₂ electrolysis. In addition, ensuring sufficient quality and concentration of the CO₂ feed before electrolysis as well as the separation of the diverse possible reduction products of CO₂ after the actual electrolysis further influence the economic feasibility of the overall process and thus must be considered. To reduce costs in conjunction with product separation, the selective production of a single and concentrated product is highly desirable. As a measure for selectivity, the faradaic efficiency (FE) is commonly indicated, as it describes the percentage of electrons utilized for the formation of a particular product. Furthermore, any industrial implementation of CO₂RR in the future will require a certain throughput to be economically competitive, which is corresponding to a partial current density of roughly 300 mA cm⁻² reached for a specific product. In addition to the selectivity as one key criterion, an efficient electrolysis process thereby requires operation with low overvoltages to ensure optimal energy efficiency, which is benchmarked by overall cell voltages below 2 V (Jouny et al., 2018; Kibria et al., 2019). The derivation of those key...
performance indicators (KPIs) for an industrially feasible process will be described and discussed in the frame of the techno-economic assessment chapter of this review.

In conclusion, there is no doubt that besides the actual catalyst, the electrode and general reactor design significantly influence the performance of CO₂ electrolysis regarding selectivity, energy efficiency, and profitability. Therefore, the following review focuses on technical aspects of the realization of the CO₂ electrolysis including the description of different electrolyzer-types (H-type and flow cells), membranes, and product separation techniques (Burdyny and Smith, 2019). The development of stable, abundant, and cost-effective catalysts is of no lesser importance to achieve an adequate selectivity and feasible overpotentials in CO₂RR, and quite the contrary requires extensive consideration for itself. Therefore, the first part “Electrochemical CO₂ Reduction toward Multicarbon Alcohols - The Microscopic World of Catalysts & Process Conditions” of this review concentrates on the role of the catalyst in electrochemical CO₂ reduction. Hereby, we aim at painting a preferably comprehensive picture of the overall process and give an overview of the complexity of factors influencing the performance of electrochemical CO₂ reduction.

It should be noted that all current densities given in this work are cathodic. For better comprehension, the authors refer to the absolute values, i.e. when discussing higher current densities, more cathodic values are meant.

OVERVIEW: COMPARTMENTS & REACTOR DESIGNS FOR CO₂ ELECTROLYZERS

The research landscape on electrochemical CO₂ reduction is vast and diverse, and the designs and operation modes of CO₂ electrolyzers described in literature are just the same. The design of the electrochemical cell as well as the chosen compounds are of crucial importance for an efficient CO₂RR performance.

However, the general processes taking place during CO₂ electrolysis are illustrated in Figure 1. CO₂ is supplied to the cathode in dissolved form. There, it is reduced to OH⁻ and, in our example, CO. Cathode and anode compartment are separated by an ion-conductive membrane, through which ion transport closes the electric circuit. In the illustrated case, an anion exchange membrane is used and OH⁻ migrates from the catholyte to the anolyte. At the anode water is oxidized to O₂.

Fundamentally, electrolyzers can be subdivided into so-called H-type and flow cells, whereby in the latter case a distinction can be made between liquid- and solid-phase systems, depending on the physical state of the electrolyte (Kibria et al., 2019). The use cases, benefits, and limitations of those cells will be described.
in the following (chapters 3–5). However, the chapter will start with an overview of the currently used ion-exchange membranes as a component both H-type and flow cells have in common. Thereby, it is distinguished between proton, anion exchange, and bipolar membranes. As the membrane choice will be discussed in the context of all electrolyzer setups, we consider it appropriate to introduce them first.

In chapter 6, the role of CO₂RR product separation is illustrated, as it is an important factor contributing to the profitability of CO₂ electrolysis. The techno-economic assessment is then deepened in chapter 7. In chapter 8, we give an outlook on currently upcoming research topics in the field of electrochemical CO₂ reduction.

ION-EXCHANGE MEMBRANES

Hardly any CO₂ electrolyzer setup gets along without the implementation of ion-exchange membranes (IEM), which are necessary to limit product reoxidation and to allow for an effective separation of reaction environments in both half-cells (Zhang et al., 2020b). At the same time, IEMs must be able to close the electric circuit, i.e. to enable the passage of ions. By significantly contributing to the overall cell voltage, membranes also largely influence the total energy efficiency of the cell (Salvatore and Berlinguette, 2020).

A prominent example of a conductive polymer used to produce IEMs is Nafion (Figure 2A), which can be selectively crossed by cations and is therefore, in the context of electrolysis, categorized as a proton exchange membrane (PEM) (Albo et al., 2019; Han et al., 2020a; Lei et al., 2020; Martić et al., 2019; Song et al., 2020; Zhou et al., 2018).

However, the membranes used primarily for CO₂ electrolysis are anion exchange membranes (AEMs) (Gao et al., 2018; García de Arquer et al., 2020; Hoang et al., 2018; Jeong et al., 2020; Karapinar et al., 2019; Kibria et al., 2018; Kibria et al., 2019; Li et al., 2019; Li et al., 2020; Lv et al., 2018a; Lv et al., 2018b; Ting et al., 2020; Wei et al., 2020; Yang et al., 2020b; Zhuang et al., 2018). A third type of conductive membranes is the bipolar membrane (BPM), which is a combination of a PEM with an AEM.

Proton exchange membranes (PEMs)

Water oxidation, which is the most common anode reaction for CO₂ electrolysis applications, leads to the formation of protons, whose flow to the cathode is enabled by a PEM (Weekes et al., 2018). Compared to AEMs, this electroosmotic flow toward the cathode inhibits product crossover to the anode. However, proton migration from the anolyte leads to a decrease of the pH of the catholyte, creating an environment at the cathode that favors HER over CO₂RR and thus impeding to reach high FEIs for CO₂RR products. For that reason, in most instances, AEMs are employed for CO₂ electrolysis.

Figure 2. Chemical structures of common membrane ionomers

(A) Nafion; (B) Sustainion; (C) Aemion; (D) PiperION (Endrődi et al., 2020; Kutz et al., 2017; Mauritz and Moore, 2004; Thomas et al., 2012).
Still, PEMs find use in three-compartment cells especially designed for the production of anionic liquid products, like formate or acetate. Thereby, anolyte and catholyte are not only separated by a single AEM, but by an additional central flow compartment and a PEM facing the anolyte. The central flow compartment is filled with a porous solid electrolyte to ensure both electrical contacting and product removal (Xia et al., 2019). In this setup, the reoxidation of generated liquid products because of crossover to the anode is prevented. The use of thicker membranes thereby significantly contributes to minimizing the product crossover from the cathode to the anode compartment, as shown by Masel and coworkers. Using the thinnest membrane, Nafion 212 (50.8 μm), the highest crossover of formate from the central flow compartment to the anolyte was observed. However, the use of thicker membranes also leads to increased electrical resistances and thus higher overall cell voltages. The lowest formate migration was obtained for Nafion 324 with a thickness of 150 μm. The authors attributed the lowered formate flux not only to the increased membrane thickness, but also to its structure, as it is a double-layered membrane consisting of two layers with equivalent weights (EW) of 1100 and 1500. Thereby, the equivalent weight describes the dry polymer mass per mole of acid groups. Masel and colleagues observed a markedly low water content in the 1500 EW layer, which, in combination with the decreased number of acid groups, provides unfavorable conditions for formate transport (Yang et al., 2017).

Anion exchange membranes (AEMs)

Contrarily to a PEM, an AEM regulates the flow of anions from the cathode to the anode (Weekes et al., 2018). As the main charge carriers in CO2 electrolysis are carbonate and bicarbonate ions, AEMs provide lower polarization losses and thus higher limiting current densities compared to PEMs (Singh et al., 2015). To date, the most common examples of AEMs are made from Sustainion (Figure 2B). Sustainion membranes are stable toward bases and consist of a polystyrene backbone functionalized with imidazolium groups (Kaczur et al., 2018; Kutz et al., 2017; Liu et al., 2018; Yang et al., 2017). Before use, Sustainion and other AEMs are generally converted from chloride into the hydroxide form by storage in KOH (Kaczur et al., 2018; Liu et al., 2018). Thereby, the duration of this activation step can significantly influence the membranes’ performance and has to be optimized (Ehelebe et al., 2020). Further modification of Sustainion membranes can lead to increased mechanical stability, as shown by Masel and colleagues. Employing a Sustainion membrane modified with divinylbenzene, they were able to operate an electrochemical cell for CO production stably for 3,800 h (158 days) at 200 mA cm−2/C0 Sustainion membrane modified with divinylbenzene, they were able to operate an electrochemical cell for CO production stably for 3,800 h (158 days) at 200 mA cm−2 and thus higher overall cell voltages. The lowest formate migration was obtained for Nafion 324 with a thickness of 150 μm. The authors attributed the lowered formate flux not only to the increased membrane thickness, but also to its structure, as it is a double-layered membrane consisting of two layers with equivalent weights (EW) of 1100 and 1500. Thereby, the equivalent weight describes the dry polymer mass per mole of acid groups. Masel and colleagues observed a markedly low water content in the 1500 EW layer, which, in combination with the decreased number of acid groups, provides unfavorable conditions for formate transport (Yang et al., 2017).

Crossover

Especially when using AEMs, the crossover of CO2 to the anode compartment plays an important role and lowers CO2 utilization, and is therefore associated with the overall efficiency of the cell (Weekes et al., 2018). The basic problem leading to the crossover of CO2 through the AEM is the reaction of CO2 with OH− to carbonate (CO32−) and bicarbonate (HCO3−) in the cathode compartment (Larrazábal et al., 2019; Lin et al., 2019; Liu et al., 2018; Pátrú et al., 2019; Reinisch et al., 2019). Subsequently, OH− in the membrane is exchanged with these carbonate species (Liu et al., 2018; Pátrú et al., 2019). For every two electrons transferred in the electrolysis, crossover of two bicarbonate ions or one carbonate ion as current carriers through the membrane occurs (Pátrú et al., 2019). The predominance of carbonate or bicarbonate in the catholyte depends on various aspects, such as mass transfer within the electrolyte, CO2 availability at the cathode, and the OH− formation rate (Reinisch et al., 2019). In systems with pronounced HER at the cathode, a decrease in the CO2/O2 ratio at the anode becomes visible, presumably because of the crossover of OH− formed in the HER instead of carbonate species (Larrazábal et al., 2019). The anions transported through the AEM are reoxidized to CO2 in the anode chamber according to 2CO32− + O2 + 2 e− → 2 CO2 + 3 O2 (Larrazábal et al., 2019; Pátrú et al., 2019). The preferential oxidation of carbonate toward water was confirmed by the observation that, at high current densities, twice as much CO2 as O2 is formed at the anode (Pátrú et al., 2019). Overall, crossover of CO2 through the membrane is influenced by various factors,
which includes membrane chemistry, electrolyte composition, and mass transfer of CO₂ to the reaction interface (Larrazábal et al., 2019). The overpotential at the cathode has no influence on the transport of CO₂ through the membrane, as the same amount of OH⁻ per reduction equivalent is formed independently from the selectivity of the reaction. CO₂ utilization can be improved by the addition of buffers to the electrolyte, as the buffer anions act as alternative current carriers through the AEM (Lin et al., 2019).

Similarly to CO₂ crossover, also the products of the CO₂RR can migrate through an AEM (Zhang et al., 2020b). Thereby, charged products, such as acetate and formate, migrate more frequently into the anode compartment than uncharged products, e.g., ethanol and propanol, because of their role as current carriers. This so-called electromigration is observed across all current density ranges (Ma et al., 2020a; Zhang et al., 2020b). Thus, crossover of both CO₂ and its reduction products to the anode compartment and their subsequent reoxidation limit the overall efficiency and CO₂ utilization when AEMs are used in CO₂ electrolyzers (Patru et al., 2019).

**Bipolar membranes (BPMs)**

As an alternative to AEMs with the goal to minimize product crossover, bipolar membranes (BPMs) are employed in CO₂ electrolysis. BPMs are produced by the lamination of a PEM and an AEM (Figure 3). Thereby, strong ionic functional groups of the membranes themselves, e.g. sulphonic or carboxylic groups in PEMs or amine or imidazole groups in AEMs, often help to facilitate water dissociation. Alternatively, water dissociation catalysts can be added to the membranes’ interface, like ionic polymers or metal oxides/hydroxides, salts or complexes (Pärnamae et al., 2021).

In BPMs, product crossover is prevented because instead of ion flow from one electrode to the other, water dissociates into OH⁻ and H⁺ in the BPM connection layer and is transported through a PEM in the direction of the cathode and through an AEM to the anode, respectively (Li et al., 2016; Salvatore et al., 2018). Still, crossover of ions through a BPM by both diffusion (at low current densities up to 40 mA cm⁻²) and electromigration take place to a certain extent. Lowest relative ion crossover is observed at high current densities independently from the electrolyte (Blommaert et al., 2020). Research efforts are still needed to increase the durability of BPM and decrease their through-plane resistance. However, the voltage drop caused by water splitting is inevitable and can at best be reduced by means of suitable catalysts (Blommaert et al., 2019).

**Direct comparison of different membrane types in CO₂RR**

Table 1 gives an overview of the advantages and disadvantages of the different membranes for their application in CO₂RR. Along the line of direct comparisons of different membrane types in the context of CO₂RR, Xiang and colleagues compared an AEM (Fumasep AA-3-50; 45–55 μm), a PEM (Nafion 324; 150 μm), and a BPM (Fumasep FBM; 130–160 μm) with a focus on CO₂ utilization of the different systems. AEM and BPM showed stable cell voltages during the measurements, whereas conductivity loss of the
anolyte led to continuously increasing cell voltages when the PEM was used. Circumventing cation deple-
tion in the anolyte by recirculation and mixing of the catholyte and anolyte resulted in a CO₂ utilization ef-
ficiency of 15.1% for the PEM-based system, which is c o m p a r a b l e to t h e v a l u e o b t a i n e d f o r t h eA E M - b a s e d
reactor (14.4%). The by far highest CO₂ utilization efficiency, ranging fr om 58.0–61.4%, was obtained using
the BPM-based reactor ( Lin et al., 2019 ). Conversely, in another comparison of different membranes, Seger
and coworkers found that for the Fumasep FAA-3-PK -75 (AEM), the Nafion 212 (PEM), and the Fumasep
FBM (BPM) membranes, despite their different operating principles, the CO₂ consumption measured in
1MK H CO₃ and at 200 mA cm⁻² was nearly the same. The authors point out that the majority ( R
65%) of
the CO₂ consumption is attributed to carbonate formation in direct proximity of the cathode and that
this process is nearly unaffected by the membrane selection. However, CO₂ utilization was slightly higher
in the BPM-based system: In contrast to the AEM, carbonate does not migrate to the anolyte. Likewise, H +
ions migrating to the catholyte from the BPM led to the rerelease of CO₂, making it again available to the
reaction. The PEM did not offer this benefit, as K + was found to be the main charge carrier. Furthermore,
also the FEs measured did not depend on the type of membrane used, indicating that herein the
membrane selection was not relevant for the observed catalytic selectivity. This observation supports
the hypothesis that the direct environment of the cathode is hardly influenced by the utilized membrane.
However, bulk catholyte pH increased from 8.3 to 9.8 using the PEM, 10.2 using the AEM, and <9 using the
BPM, respectively. Because of anolyte conductivity loss, the PEM-based system was not suitable for long-
term (>3 h) operation. Furthermore, the authors reported that product crossover was similar for charged
and uncharged products but quantitatively negligible in case of the BPM and PEM. For the AEM, crossover
of formate and acetate to the anolyte was found ( Ma et al., 2020b ).

| Membrane type | Advantages                                                                 | Disadvantages                                                                 |
|---------------|---------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| PEM           | - cost-effective because of simple manufacturing processes ( Ramdin et al., 2019 ) | - low pH at the cathode suppresses CO₂RR and favors HER ( Pătru et al., 2019 ) |
|               | - low voltage drop because of thinner membrane ( Ramdin et al., 2019 )      | - higher product crossover than BPM                                            |
|               | - high stability results in increased lifetime ( Ramdin et al., 2019 )      | - expensive purification steps of electrolyte necessary ( Ramdin et al., 2019 ) |
|               | - used in three-compartment cells for the formation of liquid ionic products ( Kúa et al., 2019; Yang et al., 2017 ) | - not always resistant to oxidation reactions ( Yang et al., 2017 )             |
| AEM           | - no delivery of H⁺ to cathode, ensuring a high pH value at the cathode and thus creating favorable conditions for CO₂RR over HER ( Weekes et al., 2018 ) | - CO₂ crossover to anode compartment ( Larrazábal et al., 2019; Lin et al., 2019; Pătru et al., 2019; Reinisch et al., 2019; Weekes et al., 2018 ) |
|               | - more cost-effective than BPM ( Weekes et al., 2018 )                      | - outgassing of CO₂ at anode ( Ma et al., 2020a; Ma et al., 2020b )            |
|               | - stable cell voltages during electrolysis ( Lin et al., 2019 )              | - in part crossover of liquid products (EtOH, n-PrOH) ( Ma et al., 2020a )      |
| Sustainion    | - highly conductive ( Kutz et al., 2017; Liu et al., 2018; Yang et al., 2017 ) | - use of conc. KOH can lead to precipitation of K₂CO₃                           |
|               | - stable against alkaline electrolytes ( Kaczur et al., 2018; Yang et al., 2017 ) | → decrease in current density ( Endrődi et al., 2019 )                           |
| BPM           | - PEM side inhibits CO₂ transport into the anode compartment ( Pătru et al., 2019 ) | - unstable at high EtOH concentrations ( Gabardo et al., 2019 )                 |
|               | - constant pH gradient ( Ramdin et al., 2019; Weekes et al., 2018 )         | - complex and expensive production ( Ramdin et al., 2019 )                      |
|               | - low product crossover/product loss ( Ramdin et al., 2019 )                | - low stability of AEM especially in alkaline medium ( Ramdin et al., 2019 )   |
|               | - acid/base addition for acidification/basification possible ( Ramdin et al., 2019 ) | - short lifetime because of delamination of the ion exchange layers ( Ramdin et al., 2019 ) |
|               | - stable cell voltages during electrolysis ( Lin et al., 2019 )              |                                                                                |
An important property of membranes is their high conductivity, which is necessary to ensure low operation voltages and thus high energy efficiency. In one example using KCl and K\textsubscript{2}SO\textsubscript{4} as electrolytes, examination of a Fumatech Nafion PEM and FAA-3 AEM showed that operation at elevated current densities (>200 mA cm\textsuperscript{-2}) resulted in overvoltages that led to system overload in both cases. As the reason for this overvoltage, the authors stated high membrane resistance caused by insufficient ionic conductivity. Therefore, the necessity to develop either suitable membranes or membrane-free cells is pointed out (Lv et al., 2018\textsuperscript{a}). In the context of the development of such high-performance conductive membranes, Masel and coworkers compared the area-specific resistance of Sustainion 37–50 with other commercially available membranes. With a value of 0.045 U cm\textsuperscript{-2} in 1 M KOH at 60°C, the resistance was more than one order of magnitude lower compared to the resistances of other membranes, such as Nafion N115 (0.52 U cm\textsuperscript{-2}), Fumasep FAPQ-375 (0.83 U cm\textsuperscript{-2}) or PBI (phosphoric acid doped polybenzimidazole, 8.3 U cm\textsuperscript{-2}) (Kaczur et al., 2018). Regarding the influence of the membrane on the ratio of HER and CO\textsubscript{2}RR, a Sustainion PSMIM (polystyrene methyl imidazolium chloride) AEM was compared with various PEMs (Nafion 117, CMI-7000, SPEEK (sulfonated poly(ether ether ketone)), and PBI (polybenzimidazole)) and other AEMs (Neosepta, AMI-7001, PVA (polyvinyl alcohol), and PEI (polyethylenimine)) (Kutz et al., 2017). Therefore, electrochemical tests were performed with moistened CO\textsubscript{2} as water supply, because liquid electrolytes based on KHCO\textsubscript{3} would poison the acidic PEMs and KOH could leach some of the AEMs. Because Ag was used as a cathode catalyst, CO and H\textsubscript{2} were obtained as the only reduction products. The selectivity for the target product CO was lowest for the PEMs, whereby the imidazolium-containing variant PBI performed slightly better (Nafion 117 = CMI-700, 0% < SPEEK; < 10% < PBI, < 20%). Among the AEMs, selectivity grew from PEI (<20%) over AMI-7001 (30%); Neosepta (<40%) and PVA (<60%) to PSMIM (>90%). Therefore, also among the AEMs, the imidazolium-doped variant PSMIM showed enhanced performance. This observation is in agreement with the results of other studies stating imidazolium to be a cocatalyst for CO\textsubscript{2}RR and contributing to HER suppression (Kutz et al., 2017; Rosen et al., 2013; Yang et al., 2017).

In summary, membranes used for electrochemical CO\textsubscript{2} reduction have to provide distinct electric conductivity to minimize the overall cell voltage. AEMs mostly outperform PEMs by ensuring a sufficiently high catholyte pH, which helps favoring CO\textsubscript{2}RR over HER, and maintaining stable cell voltages by avoiding cation depletion in the anolyte. However, a drawback of AEMs is the possible crossover of CO\textsubscript{2} and products to the anolyte. A promising approach to limit general crossover is the use of BPMs; however, BPMs are in turn prone to delamination. Functionalization of membranes with imidazolium can furthermore help to boost selectivity toward CO\textsubscript{2}RR. Because considerable progress has been made in the field of membranes in recent years, further substantial improvements regarding stability, conductivity or cost-effectiveness can be expected in the future.

**H-TYPE CELLS - SETUP, USE CASES & BENEFITS**

H-type cells are liquid-phase electrolyzers that are widespread in fundamental research on the electrochemical CO\textsubscript{2} reduction (Dutta et al., 2020; Gao et al., 2018; Han et al., 2020\textsuperscript{a}; Iijima et al., 2019; Jeong et al., 2020; Jiang et al., 2018\textsuperscript{b}; Lei et al., 2020; Lv et al., 2018\textsuperscript{b}; Shang et al., 2019; Song et al., 2020; Ting et al., 2020; Wei et al., 2020; Zhou et al., 2018). The name is derived from the H-like form (depicted in Figure 4) of the reactor with cathode and anode compartment filled with liquid electrolyte and separated by an ion exchange membrane to prevent the reoxidation of products. CO\textsubscript{2} is supplied to the cathode via...
dissolution in the catholyte, which is why the transport of CO₂ to the catalyst surface takes place exclusively through the electrolyte (Burdyny and Smith, 2019; García de Arquer et al., 2020; Xiang et al., 2019).

H-type cells are widespread particularly for studies that focus on catalyst design and screening, as the setup allows for simple and rapid testing. In terms of electrode preparation, the catalyst is usually deposited on glassy carbon or carbon paper, which is mainly done via electrodeposition, spin coating, dip-coating, or drop-coating (Cook, 1988; Dinh et al., 2018a; Dutta et al., 2020; He et al., 2017; Hou et al., 2020; Lamaison et al., 2020). Also, the use of bulk catalyst material (e.g. polycrystalline Cu) was reported (Ahn et al., 2017; Hori et al., 1986; Kaneco et al., 2002). Furthermore, we recently described the use of bulk pentlandite pellet electrodes for catalyst characterization in H-type cells (Pellumbi et al., 2020; Piontek et al., 2019).

The reaction conditions exert significant influence on the performance of CO₂RR in an H-type cell. Here, the solubility of CO₂ in any electrolyte is directly affected by temperature. Because of higher solubility and thus availability of CO₂, reduced reaction temperatures have been shown to contribute to favoring CO₂RR over HER (Ahn et al., 2017). On the other hand, elevated temperatures enhance the diffusion coefficient of CO₂, contributing to its availability in the opposite way. In addition, the temperature influences the electric conductivity of the electrolyte. It is therefore suspected that, for each individual reaction system, temperature has to be optimized (Löwe et al., 2019). For instance, the necessity of temperature optimization was demonstrated by Palmore and colleagues. They studied the influence of the reaction temperature on electrochemical CO₂ reduction using polycrystalline copper as catalyst and found different temperature optima, depending on the target product. Although the FE for methane increased with decreasing temperatures and peaked at 2°C, the FE for ethylene increased at elevated temperatures, reaching its maximum at 22°C (Ahn et al., 2017). This observation was confirmed in various studies and illustrates how the processes contributing to the selectivity of CO₂RR products are influenced by temperature in different ways (Cook, 1988; Hori et al., 1986; Kim et al., 1986).

Apart from the temperature, also the pressure in an H-type cell influences CO₂ solubility, and thus availability. Applying pressure to an H-type electrolyzer cell increases CO₂ solubility and therefore also the achievable current densities. For example, although CO₂ solubility in water at atmospheric conditions at 25°C is only 0.033 mol L⁻¹, it can be increased to 1.17 mol L⁻¹ by applying a pressure of 60.8 bar. Furthermore, changes in selectivity of the CO₂RR were reported and attributed to facilitated CO desorption at higher CO₂ pressures (Hori and Murata, 1990; Kibria et al., 2019; Kudo et al., 1993; Ramdin et al., 2019). A common observation is a reduction in FEs for HER and methane, assigned to increased coverage of the surface with CO (Hara, 1994; de Jesús-Cardona et al., 2001; Kas et al., 2015).

**Limitations**

The use of H-type cells is limited to a set of specialized applications mainly in the field of catalyst characterization (Burdyny and Smith, 2019). Because the solubility of CO₂ in aqueous electrolytes under atmospheric conditions is as low as 34 mM, electrolysis carried out in H-type cells are prone to reach mass-transport limitations and therefore limited in current density to values well below 100 mA cm⁻² (Fan et al., 2020; Kibria et al., 2019; Malkhandi and Yeo, 2019; Weekes et al., 2018). Furthermore, the delivery of CO₂ in dissolved form impedes the use of basic electrolytes, as a significant proportion of the dissolved CO₂ reacts with OH⁻ to form carbonate (Malkhandi and Yeo, 2019). The consequences are not only a loss of CO₂ but additionally a reduced CO₂RR activity, a lower conductivity of the electrolyte, and a shift of the pH value toward a more acidic milieu (Carroll et al., 1991; Kibria et al., 2019). As the local conditions at and the selectivity of a CO₂RR catalyst are highly dependent on the applied current density and potential, results obtained in an H-type cell are not merely transferable to its performance under industrially relevant conditions. Therefore, testing and optimization of catalysts under realistic conditions at higher current densities demands the use of alternative setups (Burdyny and Smith, 2019; Weekes et al., 2018). To overcome the limitations of the CO₂ solubility in aqueous electrolytes, organic solvents such as acetonitrile or methanol are also commonly used in H-type cells. In case of aprotic solvents, traces of water, however, have to be added to enable any CO₂ reduction. To increase conductivity, conducting salts, e.g. TBAPF₆ (tetrabutylammonium hexafluorophosphate), are used. Obviously, it is problematic to use potential CO₂ reduction products like alcohols as solvents, because precise FEs can no longer be determined. Furthermore, it has to be ensured that CO₂ itself is the substrate for the reduction reaction and the observed products do not originate from undesired side reactions of the solvent. To clarify the origin of a reduction
product, isotope-exchanged solvents or $^{13}\text{CO}_2$ can be used (Oh et al., 2014; Pellumbi et al., 2020; Piontek et al., 2019). Notably, organic electrolytes are suitable for catalysts screening, characterization, and comparison but not for industrial application, as the reachable current densities are insufficient. Furthermore, the prize and the low environmental compatibility of most organic solvents hinder their large-scale use.

**LIQUID-PHASE FLOW CELLS & GAS DIFFUSION ELECTRODES**

In order to achieve an economic operation of any electrolyzer device, a minimum current density of 200 mA cm$^{-2}$ is frequently stated for CO$_2$ reduction products in which two electrons are transferred. In case of multi-electron transfer, as in the formation of multicarbon products, these limits must be correspondingly higher to yield the respective molar amount per area (Burdyny and Smith, 2019). To operate CO$_2$RR under those industrially relevant conditions, different versions of flow cells were developed. Generally in flow cells, the transport of CO$_2$ to the catalyst takes place via the gas phase and is therefore not limited by the solubility of the gas in an electrolyte. Gas and electrolyte streams are continuously cycled, allowing for current densities well above 200 mA cm$^{-2}$ and the potential stacking of electrolyzers in large scale applications (Li et al., 2019; Martić et al., 2019; Weekes et al., 2018). The reactor designs can mainly be categorized into liquid-phase electrolyzers and solid-phase electrolyzers, depending on the physical form of the electrolyte. High-temperature solid-oxide electrochemical cells (SOECs), where a ceramic solid electrolyte is used instead of a conductive polymer, represent a special application and therefore will also be briefly described (Kibria et al., 2019).

**Setup & anode**

Figure 5 provides a schematic illustration of a liquid-phase flow cell architecture. Alternatively, a zero-gap arrangement between anode and IEM can be used to minimize ohmic losses. The zero-gap concept will be further described in the subsequent chapter. The cathodic and the anodic compartments are separated by an IEM to allow for the migration of ions while mitigating the crossover of desired liquid products to the anode side and of anode reaction products to the cathode site (Kibria et al., 2019; Weekes et al., 2018). Besides the membrane, the performance of a liquid-phase flow cell can also be influenced by the fluid dynamics. Therefore, flow fields of different geometries (Figure 6) are applied to direct both the gas and the electrolyte flow at the electrodes and function as electrical contact.
By ensuring a homogeneous current distribution, flow fields prevent the formation of efficiency gradients within the electrodes (Weekes et al., 2018). In the example of PEM fuel cells, it was shown that a large contact area between the gas diffusion electrode (GDE) and the flow field of the bipolar plate is beneficial to enable higher current densities. Furthermore, the current distribution in the GDE was more uniform for shorter-channeled flow fields; therefore, the use of serpentine-type and pin-type flow fields, unlike parallel flow fields, prevented the undesired formation of preferential flow paths, which lead to inhomogeneous reagent distribution. In the case of PEM water electrolyzers, it was found that the geometry of the cathode flow field largely influences the ohmic overpotential, whereas the anode flow field geometry was crucial for water availability (Jeanty et al., 2018; Li et al., 2018; Lin et al., 2020). However, the transferability of these results to CO₂ electrolyzers is limited leading to a knowledge gap about the effects of flow field geometry on CO₂RR.

While CO₂ RR occurs at the cathode, oxygen evolution reaction (OER) is the primarily chosen counter reaction at the anode. The anode reaction also affects the overall energy efficiency of the cell. Hence, publications dealing with the optimization of the OER catalysis have been published (Jiang et al., 2018a; Ma et al., 2014). Also alternative anode reactions, such as the oxidation of chloride to chlorine, have been tested to improve the energy efficiency of the CO₂ reduction cells (Kong et al., 2019; Lister and Dufek, 2013; Verma et al., 2019).

Cathode: gas diffusion electrodes (GDEs)

In contrast to an H-type cell, the CO₂ reduction reaction in a liquid-phase flow cell takes place at a gas diffusion electrode to overcome the issues concerning CO₂ solubility and mass transfer limitations (Albo et al., 2019; Chen et al., 2020b; García de Arquer et al., 2020; Hoang et al., 2018; Karapinar et al., 2019; Kibria et al., 2018; Li et al., 2019; Li et al., 2020; Lv et al., 2018a; Martić et al., 2019; Ren et al., 2019; Xiang et al., 2019; Yang et al., 2020b; Zhuang et al., 2018).

GDEs allow for sufficient supply with CO₂ even at higher current densities because of the reduced diffusion pathway, when CO₂ is provided from the gas phase, compared with diffusion from CO₂ dissolved in aqueous solution (Burdyń and Smith, 2019). The exact phase distribution and the extent of the reaction zone in GDEs is a matter of ongoing debate. Although multiple authors suggest that the reaction is taking place at the three-phase boundary between solid catalyst, liquid electrolyte, and gaseous CO₂ supply, Smith and coworkers conclude that a two-phase reaction between the catalyst and CO₂ dissolved in the electrolyte is more likely (Nesbitt et al., 2020). Either way, the processes taking place in a GDE are far more complex compared to those in a conventional H-type cell. Therefore, CO₂RR at GDEs is prone to relatively small changes in wettability, texture, and morphology, which poses a challenge to reproducibility (Bohra et al., 2020). Furthermore, the complexity of the system makes it hard to predict the optimal composition and structure for a GDE.

Gas diffusion electrodes typically consist of a gas diffusion layer (GDL), which is mostly a dense network of carbon fibers such as carbon paper or carbon cloth or a polytetrafluoroethylene (PTFE) membrane and the catalyst layer (CL). Carbon-based GDLs are furthermore often coated with a microporous layer (MPL), usually consisting of compressed carbon powder or fibers and PTFE (Malkhandi and Yeo, 2019; Weekes et al., 2018). The GDE is installed in the cathode compartment of the flow cell with the catalyst layer facing the electrolyte and the support facing the gas side, where CO₂ is supplied (Figure 7).
The material properties of GDEs are adjustable by the choice of individual components and the process of electrode manufacturing. Apparently, high electrical conductivity is of utmost importance for a GDE to operate with low ohmic overpotential. To modulate mass transport to the catalyst, both porosity and hydrophobicity are particularly relevant. A certain mechanical stability is furthermore helpful for simple incorporation into the cell setup and facilitated upscaling (Weekes et al., 2018).

**GDE fabrication**

A variety of GDE fabrication methods was reported in literature including the deposition of the catalysts on or mixing it with carbon black as well as an additional binder like PTFE followed by hot pressing of the CL on a GDL (Cook, 1990; Junge Puring et al., 2021; Löwe et al., 2019). Alternatively, GDEs can also be obtained by airbrushing/spray coating or drop casting of a catalyst ink onto a GDL (Gregorio et al., 2020; Hara and Saka-ta, 1997; Leonard et al., 2020; Marcos-Madrazo et al., 2019; Martić et al., 2020; Merino-Garcia et al., 2018; Shafaque et al., 2020; Wang et al., 2019; Zhang et al., 2020c). Along this line, Berlinguette and coworkers examined the fabrication of GDEs by spray coating with a focus on a uniform distribution of the ionomer. They found significant deviations from the targeted Nafion contents on the electrode for every tested deposition method, with the most homogeneous results achieved by automated spray coating (Lees et al., 2020). Furthermore, the catalyst ink can also be painted on the GDL (Whipple et al., 2010; Xiang et al., 2019). In cases where a metal catalyst should be applied on a conductive, mostly carbon-based GDL, direct electrodeposition is another possibility for GDE fabrication (Henckel et al., 2021). In addition, atomic layer deposition (ALD) and sputtering of substrates onto GDLs are frequently reported (G. Dinh et al., 2018b; Ren et al., 2019; Tiwari et al., 2018; Wang et al., 2020b). The method of catalyst application strongly influences the catalyst loading and correspondingly the thickness of the CL, which are influential properties of a GDE. If the layer thickness is increased, the diffusional mass transfer resistance simultaneously increases and a modulation of the local CO2 and product concentration takes place. Modulating those concentration ratios exerts a marked influence on the selectivity of the CO2RR.

The local CO2 concentration at the GDE can also be varied directly by applying different CO2 feed flow rates, as reported by Oh and coworkers. They demonstrated that reducing the rate from 40 sccm to five sccm results in a remarkable increase of the selectivity of C2+, products (from FE = 44.9 to 60.3%), and decrease of C1 products, respectively (Tan et al., 2020). However, a higher catalyst loading does not necessarily lead to an improved selectivity of a GDE, as it has more implications than just the modulation of reactant concentrations. For instance, Neyerlin and colleagues observed the influence of CL thickness on the selectivity of a SnO2 GDE toward formate formation and obtained best selectivity at the lowest catalyst loading. They explained this observation with surplus catalyst-ionomer active sites, which favor, contrarily to catalyst-catholyte active sites, HER (Chen et al., 2020c). Besides the catalyst loading, also its structuring and the addition of various additives to the CL influence the properties and performance of a GDE. When examining different configurations of CLs based on Ag and multiwalled carbon nanotubes (MWCNTs), Ke-nis and coworkers found that a mixed layer of MWCNTs and Ag particles yielded the lowest charge-transfer resistance compared to a layered setup and bare Ag particles. Because the availability of the active catalyst sites was improved by the MWCNTs, twice as high current densities were obtained at half the loading for
the mixed and layered versions compared to the GDE without MWCNTs (Ma et al., 2016a). However, addition of a layer of graphene oxide onto the CL of a GDE was shown to provide an effective barrier toward proton mass transport and thus led to markedly favored CO$_2$RR over HER (from 40% FE$_{CO}$ without any coverage to 80% FE$_{CO}$ with 90% coverage) (Le Nguyen et al., 2020). A similar effect was obtained by Perry and coworkers, who applied a hydrophobic layer of 1-octadecanethiol onto a Cu-based GDE. Up to 100 mA cm$^{-2}$, this layer markedly suppressed HER. However, at higher current densities, proton transport to the catalyst was insufficient and the performance was comparable to the untreated electrode (Perry et al., 2021). In general, the limitation of proton supply to the CL of a GDL is a promising approach to enhance FE$s$ for CO$_2$RR. Therefore, besides its role as a binder in thermally treated catalyst layers, PTFE is also used as an additive in spray-coated GDEs to modulate the catalyst’s environment. Because of its hydrophobic properties, PTFE thereby prevents the CL pores from penetration of liquid electrolyte, potentially leading to favoring of CO$_2$RR over HER. Feng and colleagues, for example, were able to increase the partial current density for CO$_2$RR from below 150 mA cm$^{-2}$ to approximately 250 mA cm$^{-2}$ at $-1.0$ V vs. RHE by addition of 50% PTFE to the CL in the form of preferably small particles (30–40 nm). However, at higher PTFE percentages, the proton supply necessary for CO$_2$RR was inhibited, resulting in again decreasing partial current densities (Xing et al., 2021). In addition, promising results regarding the suppression of HER and selectivity modulation for CO$_2$RR were reported using surfactants, such as Triton X-100 (octyl phenol ethoxylate) or CTAC (cetyltrimethylammonium chloride). However, their use is hitherto only described as a surface coating for planar electrodes in an H-type cell or as an additive to the electrolyte in liquid-phase flow cells (Banerjee et al., 2019; Bienen et al., 2020; Zhong et al., 2020). Hence, direct modification of GDEs with surfactants still represents an open research topic.

**GDL materials**

The reason why most GDL$s$s used for CO$_2$RR are based on carbon is, on the one hand, their outstanding conductivity and the uniform current distribution provided by this material (G. Dinh et al., 2018b). On the other hand, carbon materials offer the necessary hydrophobicity for maintaining the separation of gas and liquid compartment and are adaptable to different electrode shapes. Thus, current densities of several hundred mA cm$^{-2}$ are commonly reached with carbon-based GDE$s$s (Hoang et al., 2017; Lv et al., 2018a; Ma et al., 2016b; Martić et al., 2019; Yang et al., 2020b). Commercially available, carbon-based GDL$s$s are composed of a porous carbon tissue, for CO$_2$ electrolysis mostly paper (nonwoven) or cloth (woven), and a hydrophobic microporous layer made of PTFE-bound carbon particles. Often, the carbon tissue itself also contains a certain amount of PTFE for improved hydrophobicity. This PTFE content, as well as the PTFE content of the MPL and the thickness of the tissue, markedly influence the performance of the GDL because of changes in hydrophobicity, resistance, and gas permeability. Kenis and colleagues found an optimum composition with 20 wt % PTFE in the MPL and 10 wt % in a 190 μm thick carbon tissue. A lower PTFE content in the MPL caused detachment of the carbon particles and thus low durability, whereas at higher PTFE contents, both in the MPL and in the tissue itself, the increased electrical resistance caused performance drops. Generally, thinner GDL tissues ensured improved gas diffusion, but tissues thinner than 190 μm did not provide a sufficient barrier between liquid electrolyte and gas compartment and showed extensive flooding (Kim et al., 2016).

Although carbon-based GDL$s$s are used as state-of-the-art technology for CO$_2$ electrolysis, their low mechanical, chemical robustness, and high price limit their upscaling to industrial relevance. Furthermore, the loss of hydrophobicity of carbon-based GDL$s$s during electrolysis, as shown by Sargent and colleagues independently of the catalyst layer, frequently leads to blocking of CO$_2$ diffusion pathways by flooding (B. Dinh et al., 2018a).

A frequently used modification of the GDE setup is the replacement of the carbon-based GDL by a PTFE substrate. An advantage of PTFE for the application as a GDL is its hydrophobicity, which reliably counteracts the penetration of electrolyte through the GDE and thus the flooding of the gas compartment. However, as PTFE is electrically insulating, the functionalities of gas diffusion and current distribution are decoupled in PTFE-based GDE$s$s. Thereby, electrical contacting is realized via the catalyst layer, often leading to a less uniform distribution of electricity across the layer (G. Dinh et al., 2018b). Nevertheless, the successful application of those PTFE-based GDE$s$s, achieving high current densities and selectivities for the target product, was reported in multiple studies. Using their 3D catalyst ionomer bulk heterojunction (CIBH) electrodes, Sargent and coworkers primarily obtained C$_3$ products at current densities of above 1 A cm$^{-2}$, of which a large proportion was C$_2$H$_4$ with an FE of 65–75%. Although the GDL of the
CIBH electrodes was based on PTFE, the CL was composed by Cu and a perfluorosulfonic acid (PFSA) ionomer (Garcı´a de Arquer et al., 2020). As early as 2018, the Sargent group was using PTFE substrates to which firstly a Cu catalyst was applied, followed by layers of carbon nanoparticles and graphite. Afterwards, carbon black was utilized as a current collector via spray coating. Graphite and carbon NPs served to stabilize the catalyst layer. Stabilities of 150 h were achieved, with an FE for ethylene of 70% (B. Dinh et al., 2018a).

Using a bimetallic Ag/Cu catalyst on a PTFE substrate in a flow cell with an AEM and 1 M KOH, they realized an FE of 41% for ethanol at 250 mA cm$^{-2}$ and -0.67 V vs. RHE (Li et al., 2019). To give an overview about the state-of-the-art, Table 2 summarizes the properties of common commercially available GDLs.

**Ionomers**

To enhance the mechanical stability of a GDE and improve its performance in CO$_2$RR by creating a more hydrophilic surface, the electrode can be coated with an ionomer to produce a membrane-coated electrode (MCE). To avoid material loss from their GDE and tune its performance, Casada-Coterillo and colleagues tested different MCE setups for the production of methanol. Although some modifications led to an increase of the resistance of the electrode and had adverse effects on the methanol FE, coating with a mixture of chitosan and PVA with Cu-exchanged zeolite Y as a filler resulted in a marked increase from 40.1% to 68.0% compared to the uncoated variant (Marcos-Madrazo et al., 2019). Alternatively, ionomers can directly be added to and applied with the catalyst ink. Thereby, imidazolium has been shown to form a dense and positively charged layer around Ag-catalysts to repel protons. However, methylimidazolium-based polymers rapidly degrade in alkaline solution. On the example of CO formation it was therefore shown that ionomer-containing GDEs can be operated at higher current densities but with reduced long-term stability compared to ionomer-free electrodes (1,000 h at 200 mA cm$^{-2}$ compared to 4,380 h at 50 mA cm$^{-2}$ before flooding of the electrode) (Kutz et al., 2017). It is required to be aware of the fact that excessive amounts of ionomer can cause the adverse effect of blocking CO$_2$ diffusion to the catalyst. Using polystyrene methyl methylimidazolium chloride (PSMIM) and polystyrene tetramethyl methylimidazolium chloride (PSTMIM) directly mixed into the catalyst ink, Masel and coworkers found that despite maximizing the catalyst surface area, ionomer contents above 8 wt % blocked CO$_2$ diffusion (Kutz et al., 2017; Liu et al., 2018). A variation in the concentration of PSTMIM showed hardly any influence on the onset

| Manufacturer/Series | Type | Hydrophobic treatment | MPL | Thickness [μm] | TP resistance [mΩ cm$^{-2}$] | IP resistance/conductivity | TP air permeability |
|---------------------|------|-----------------------|-----|---------------|-----------------------------|----------------------------|---------------------|
| Freudenberg (B. Dinh et al., 2018a) H series (Yang et al., 2020a) | Carbon paper | Some | Yes | 141–230$^a$ | 5–10 | R = 0.6–1.1 Ω | 0.6–90 s$^b$ |
| Sigracet BC series (Chen et al., 2020c; Kim et al., 2016) | Carbon paper | Yes (5 wt % PTFE) | Yes (23 wt % PTFE) | 235–325 | 7.5–12 | $\sigma = 145$–225 S cm$^{-1}$ | 0.2–1.5 cm$^{3}$ cm$^{-2}$ s$^{-1};$ |
| N/A | 5–15 $\cdot 10^{-12}$ m$^2$ | IP: 1.4–2.7 μm$^2$ | |
| AvCarb (Xing et al., 2021) | Carbon paper | Some (PTFE) | N/A | 184–270 | <14.5 | N/A | 3.5–18 s (100 cm$^{-3}$)$^d$ |
| FuelCellsEtc ELAT (formerly E-TEK) (Chang et al., 2009) | Carbon cloth | Some | Some | 406–490 | 0.17–0.34 (181.4 kg load) | N/A | 2.156 s$^c$ |
| QuinTech (Junge Puring et al., 2021) | Carbon cloth | Some | Some | 360–410 | <5 to <13 | N/A | <10 – < 55$^e$ |
| Toray TGP-H (Aeshala et al., 2012; Albo and Iribien, 2016; Kim et al., 2016) | Carbon paper | N/A | N/A | 110–370 | p = 80 mΩ cm | R = 4.7–5.8 mΩ cm$^{-2}$ | 1,500–2,500 mL mm (cm$^{-2}$ h$^{-1}$ mmAAq$^{-1}$) |
| Sterlitech Aspire (B. Dinh et al., 2018a) | ePTFE | No | No | 76–305 | Insulating | Insulating | 0.07–8.0 ft$^3$ (min$^{-1}$ ft$^{-2}$) @ 125 Pa |

TP: through-plane, IP: in-plane.

$^a$@ 1 MPa.

$^b$according to ISO5636-5.

$^c$according to ISO9237.

$^d$according to Gurley.
potential for CO₂ reduction, but at 1 to 4 wt %, the obtained current density could be doubled (Kutz et al., 2017).

In addition to its amount, also the type of the applied ionomer is crucial for the performance of a GDE regarding reachable current densities and selectivity of the desired product. For instance, the use of the anion exchange polymer Funasep FAA 30 was found to lead to higher current densities (200 mA cm⁻² at 3.3 V cell voltage) in CO production with high selectivity, whereas the cation exchange polymer Nafion XL100 led to significantly lower current densities with lower FE for CO and increased HER (Patru et al., 2019). The use of Sustainion XA7 (PMIM-Cl) in Ag porous carbon GDEs could even lead to three times higher current densities of up to 300 mA cm⁻² for CO formation (Liu et al., 2018). In the case of formate as target product, the comparison of Nafion and a perfluorinated anion exchange (PFAE) polymer showed a low FE <5% for Nafion with simultaneously pronounced HER, while using PFAE, resulted in about an order of magnitude higher FE. In addition, the local pH value at the electrode was raised when using the PFAE ionomer, which results in a suppression of HER (Chen et al., 2020c).

Eventually, also the mode of application of an ionomer can influence its performance. In their CIBH electrodes, Sargent and colleagues controlled the orientation of their PFSA ionomer using a polar solvent for coating of the Cu catalyst in a way that the –SO₃⁻ groups face out toward the metal and the electrolyte. The goal was to create a layered PFSA structure in which ion and water transport are enabled by the hydrophilic –SO₃⁻ domains and the gas transport by hydrophobic –CF₂ domains, respectively. Instead of a partial current density of 64 mA cm⁻² for C₂H₄ at the bare Cu electrode, up to 340 mA cm⁻² were achieved by using the ionomer (García de Arquer et al., 2020).

Variation of the operating parameters

Analogously to the H-type cells, the reaction parameters also influence the performance of CO₂RR in flow cells. To gain insight into the complex mechanistic processes taking place in a GDE, Friedrich and coworkers investigated the influence of current density, temperature, and CO₂ partial pressure on the CO₂RR via electrochemical impedance spectroscopy (EIS). They used a carbon-based GDE with a tin catalyst and identified the charge-transfer reaction step by the respective resistance, which was decreasing with increasing current density or temperature. Furthermore, a decrease of CO₂ partial pressure led to an increase in charge-transfer resistance. The authors analyzed two further processes via EIS taking place at the GDE during CO₂RR: The conversion of CO₂ with OH⁻ to form bicarbonate, and the liquid phase diffusion of CO₂. Thereby, it was found that the resistance attributed to liquid-phase diffusion increases with increasing temperature, with the loss in CO₂ solubility exceeding the enhanced diffusion at higher temperatures. The resistance of bicarbonate formation increases with higher current density, higher temperature, and lower CO₂ partial pressure (Bienen et al., 2020).

When investigating the influence of the temperature on the Sn catalyst-based CO₂RR to formate in a liquid-phase flow cell, Klemm and coworkers identified 50°C as the optimum operating temperature of the system regarding maximized current density and a formate FE of >80%. Higher and lower temperatures led to increased HER at the given current density of 1,000 mA cm⁻². This can be assigned to the oppositional effects of reduced CO₂ solubility and increased diffusion coefficients and reaction kinetics with increased temperature (Löwe et al., 2019). In addition, Lister and colleagues reported a reduction of the cell voltage by 1.57 V at 70 mA cm⁻² while increasing the temperature from room temperature to 70°C when conducting the CO₂RR to syngas with an Ag-based GDE in a liquid-phase electrolyzer (Dufek et al., 2011). Furthermore, in another study, they investigated the influence of both elevated temperature and pressure on the CO₂RR using a Ag GDE at 225 mA cm⁻². Increasing the pressure from atmospheric conditions to 18.7 bar led to a significant reduction of the overall cell voltage from 4.01 V to 3.71 V at 60°C. At 90°C, a cell voltage below 3 V with a CO FE of 82% could be achieved. This decrease in the overvoltage was confirmed by Sinton and coworkers, who utilized an Ag-based GDE cathode at pressures from 1.0 bar to 7.1 bar under alkaline conditions with KOH electrolyte. With 7 M KOH and a pressure of 7.1 bar, the system showed the highest half-cell energy efficiency of 81.5% compared to lower pressures, with a low cathodic overpotential for the reduction of CO₂ to CO of 300 mV at 300 mA cm⁻² as well as an FE of almost 100%. Furthermore, they found that the pressure influenced the selectivity of the reaction, whereby higher pressure led to higher FE for CO and lower pressures favored formate production (Gabardo et al., 2018).

Contrasting observations were made by Schmid and colleagues when comparing the electrolysis of CO₂ to CO at 5 and 25 bar. FEs for CO of >90% at current densities of up to 300 mA cm⁻² were reached independently
from the pressure. At 25 bar, higher cell voltages and thus lower energy efficiency were obtained. The authors concluded that elevated pressure operation offers no benefit for liquid-phase flow cells (Haas et al., 2018).

**Special attempts for liquid-phase flow cells**

Several attempts to adapt liquid-phase flow cells to special applications have been reported. For instance, an approach for the CO$_2$RR to C$_2$H$_5$OH instead of CO$_2$ electrolysis has been shown to be more suitable for reduction to higher alcohols, like ethanol and n-propanol, than CO$_2$, because of the elimination of formate as a side product (Wang et al., 2018b). In this context, Hinrichsen and coworkers compared the reduction of both educt gases on Cu nanoparticles at 300 mA cm$^{-2}$, showing 3-fold higher selectivity for ethanol and n-propanol for CO over CO$_2$. As CO can be produced electrochemically by CO$_2$RR with high FE, the coupling of two electrolyzers in a two-step setup was proposed (Romero Cuellar et al., 2019, 2020). In a cascade setup, CO$_2$ was reduced to CO in an Ag GDE flow cell, unconverted CO$_2$ was subsequently removed from the product gas stream via absorption in NaOH, and the resulting CO gas was fed to the second flow cell. Two-step electrochemical reduction with a current density of 270 mA cm$^{-2}$ for the first electrolyzer and 200 mA cm$^{-2}$ at $-0.82$ V vs. RHE for the second electrolyzer, using Cu nanoparticle based GDEs, could yield an ethanol FE of 18% and an n-propanol FE of 7.5% (Romero Cuellar et al., 2020).

An alternative cell design, the so-called microfluidic flow cell, was established by Kenis and colleagues on similar fuel cell architectures. Hereby, the cathode GDE and anode are not separated by a membrane but just by a channel of up to 1 mm, through which the electrolyte is passed. The laminar electrolyte flow thereby prevents the crossover of molecules (Jayashree et al., 2010; Lu et al., 2017; Monroe et al., 2017; Whipple et al., 2010). Possible advantages of omitting the use of a membrane are reduced capital cost as well as lower ohmic losses affecting the energy efficiency (Esposito, 2017; Kibria et al., 2019; Lu et al., 2017). However, circulation of the electrolyte is not possible when liquid products are formed and upscaling of the electrolyzer design is complex (Kibria et al., 2019).

**Limitations of liquid-phase flow cells & gas diffusion electrodes**

Besides the advantages of liquid-phase flow cell setups equipped with a GDE mentioned at the beginning, a general problem of the use of aqueous electrolytes is the pronounced formation of hydrogen. Because CO$_2$RR takes place at potentials close to HER, both reactions are competing (Garg et al., 2020). Furthermore, the dilution of liquid products in the electrolyte increases the cost for product separation (Gabardo et al., 2019).

Another frequently documented problem when using liquid electrolytes is flooding of GDEs, i.e. penetration of the electrolyte into the electrode structure, which is accompanied by massive performance losses (Larrazábal et al., 2019; Malkhandi and Yeo, 2019). During flooding, the CO$_2$ diffusion paths of the CL are blocked and higher current densities can no longer be obtained (B. Dinh et al., 2018a; Gabardo et al., 2019; Leonard et al., 2020). The decreased availability of CO$_2$ leads to preferential HER in the whole area (Leonard et al., 2020). There are various causes for the phenomenon of electrode flooding, e.g. macroscopic pressure imbalances, the development of surface wettability, and evaporation/condensation effects (Leonard et al., 2020). For carbon-based GDEs, hydrophobicity losses during operation are assumed to be the decisive factor (G. Dinh et al., 2018b; Gabardo et al., 2019). Investigations on the flooding behavior of GDEs with silver showed that GDEs exposed to higher current densities retain less of their original hydrophobicity, i.e. there is a correlation between the current density and the flooding of the GDEs (Leonard et al., 2020). Moreover, the GDEs showed a contrary behavior regarding the amount of CO in the product gas flow and the capacitance of the cathode. Based on the observation that the capacitance increased with a delay of about 15 min after the drop in CO mole fraction in the product gas, it is assumed that the penetration of the electrolyte solution is not the sole cause of the performance loss. According to Rufford and coworkers, crystallography on the back of the flooded GDEs and at the inlet of the cathode flow field indicate a connection between carbonization and flooding. The corresponding hypothesis to this observation is that the electrode failure is caused by the precipitation of carbonates, which is followed by rapid flooding and inhibits further CO$_2$ flow (Garg et al., 2020). When studying the flooding behavior of their GDEs, Brushett and coworkers noted that the collapse of their GDEs always happened after the passage of a certain cumulative charge. They assumed the existence of a material-specific carbonate threshold value, whose attainment inevitably leads to electrode failure (Leonard et al., 2020). Furthermore, the formation of carbonate...
and bicarbonate salts because of the reaction of CO$_2$ with alkaline electrolytes can change the electrolyte pH and conductivity and thus affect the GDE performance (Gabardo et al., 2019; Kibria et al., 2019). Burdyny and coworkers took a closer look into the role of carbon-based GDLs in GDE flooding and found out that in KHCO$_3$, HER activity of the GDL itself can be linked to flooding, making it largely independent from the actual CO$_2$RR. A more active catalyst with decreased onset potentials for CO$_2$RR is assumed to prevent HER at the GDL and the accompanying reduction of capillary pressure initiates flooding (Yang et al., 2020a).

To circumvent flooding, PTFE-based membranes are increasingly used as GDLs. Swiegers and colleagues showed that flooding of a PTFE GDL was just observed at an overpressure of 5.8 bar on the liquid side, which is a magnitude higher than for conventional, carbon-based GDLs (Shafaque et al., 2020). In addition, Sargent and coworkers used PTFE substrates as GDL, with a carbon black layer spray-coated onto the catalyst as current collector (G. Dinh et al., 2018b; Gabardo et al., 2019; Wang et al., 2020b). Thereby, as already mentioned above in this chapter, gas-diffusion functionality and current distribution are decoupled. A drawback of the PTFE-based electrodes is the lack of through-plane conductivity. The insulating PTFE GDL complicates the implementation of such GDEs into electrolyzer stacks. An approach to facilitate carbonate removal at the gas-liquid interface of the GDE and avoid wetting is the integration of application-specific microstructures (Leonard et al., 2020).

In addition to salt precipitation and flooding of the GDE, an additional problem is the potential product crossover through the GDE (Ma et al., 2020b). It has been shown that a considerable amount of alcohols, such as n-PrOH and EtOH, but especially acetaldehyde, evaporate through the GDE. In cases where only the liquid phase is analyzed after electrolysis, the FEs of these products can be significantly underestimated. The formation of bubbles of gaseous products implies another challenge, as the catalyst layer can be damaged or destroyed (Malkhandi and Yeo, 2019).

Overall, liquid-phase electrolyzers represent a promising cell architecture that has been proven to be capable of reducing CO$_2$ to C$_2$+ products at high current densities. However, up to now, there are hardly any studies dealing with the development of gas diffusion electrodes, which are scalable and enabling current densities relevant for industrial scale simultaneously with high FEs (Chen et al., 2020c). Yet, further optimization regarding long-term stability of the GDE and the reduction of the cell voltage is required for industrial implementation. Ohmic losses can occur with poorly conductive liquid electrolytes (Larraza´bal et al., 2019). Membrane electrode assemblies (MEAs), which eliminate the need for a liquid electrolyte, are one approach for improved GDE operation and will be discussed in chapter 5.

**H-type cells & liquid-phase flow cells in direct comparison**

In summary, the use of gas diffusion electrodes within a flow cell has several advantages over the application of H-type cells. A change from the planar cathode geometry of an H-cell to a GDE leads to an overall improvement of the current density in the range of several orders of magnitude because of an increased electrochemically active surface, as well as an improved mass transfer (Weng et al., 2019). It is possible to reduce diffusion limitations, because more CO$_2$ reaches the catalyst surface and products are discharged (Salvatore et al., 2018). As a result, the yield of CO$_2$RR products in flow cells is up to two orders of magnitude higher than in H-type cells (Malkhandi and Yeo, 2019). Furthermore, switching from an H-type to a flow cell can influence the selectivity, as shown in the example of a Cu-ZnO catalyst. Contrarily to the H-type cell, ethanol formation was favored over ethylene formation in the flow system (Ren et al., 2019).

**Table 3** gives an overview of recent developments (2018–2021) in the reduction of CO$_2$ with a focus on the production of multicarbon alcohols, including the cells used and ion exchange membranes. It is difficult to make a direct comparison of the influence of individual parameters on FEs for alcohol production, as each publication shows many differences concerning the process design as well as the operating parameters. However, it becomes visible that the highest current densities are clearly obtained using flow cell architecture. The benchmark for industrially relevant partial current densities and overall cell voltages is at least 300 mA cm$^{-2}$ at a maximum of 2.0 V, which was not demonstrated in an H-type cell yet (Jouny et al., 2018; Kibria et al., 2019). Regarding CO$_2$RR to multicarbon alcohols, selectivity poses a second major challenge. Product yields marked with “C$_2$+” often contain high amounts of C$_2$H$_4$, which is in many cases the reason for the higher FEs obtained. In copper-based electrodes, ethylene is generally formed preferentially to ethanol (Ren et al., 2016). Nevertheless, some publications describe FEs for multicarbon alcohols of 30% and
| FE                      | Current densities [mA cm\(^{-2}\)] | Potential vs RHE [V] | Catalyst                                    | Electrolyte | Membrane            | Ref                          |
|------------------------|-------------------------------------|----------------------|---------------------------------------------|-------------|----------------------|------------------------------|
| **H-type cells**        |                                     |                      |                                             |             |                      |                              |
| 52.3% EtOH             | <15 total                           | −0.3                 | Au@Cu\(_2\)O yolkshell NPs on carbon cloth | 0.1 M KHCO\(_3\) | PEM (Nafion 117)     | (Zhang et al., 2020a)        |
| 80% C\(_2\) products   | 21C\(_2\) products                 | −1.09                | Reconstructed porous Cu                     | 0.1 M KHCO\(_3\) | PEM (Nafion 117)     | (Han et al., 2020b)          |
| 33.7% EtOH             | 8.67 EtOH                           | −1                   | Ag\(_{15}\)Cu\(_{85}\)                     | 0.5 M KHCO\(_3\) | –                    | (Dutta et al., 2020)         |
| 6.9% PrOH              | 1.8 PrOH                            | −0.9                 |                                              |             |                      |                              |
| 64.6% EtOH             | ca. 8 EtOH                          | −1.05                | Cu NPC                                      | 0.2 M KHCO\(_3\) | PEM (Nafion 212)     | (Han et al., 2020a)          |
| 8.7% PrOH              | ca. 1.2 PrOH                        | −1.0                 |                                              |             |                      |                              |
| ≥80% C\(_2\), products| ca. 8C\(_2\), products             | −0.9                 | CuO\(_x\)                                   | 0.1 M CaHCO\(_3\) | AEM (Selemion AMV)    | (Jeong et al., 2020)         |
| ca. 70% C\(_2\), products| 40 to 50C\(_2\), products         | −1.05                | Cu oxide-/hydroxide-derived                 | 0.1 M KHCO\(_3\) | PEM (Nafion 117)     | (Li et al., 2020)            |
| 78% EtOH               | ca. 0.2 EtOH                        | −0.56                | Micropores in N-doped mesoporous carbon     | 0.1 M KHCO\(_3\) | PEM                  | (Song et al., 2020)          |
| 16.4% EtOH             | 4.1 EtOH                            | −1.1                 | Cu-OD + Ag (20 nm)                          | 0.1 M KHCO\(_3\) | AEM (Selemion AMV)    | (Ting et al., 2020)          |
| 14.9% C\(_2\)H\(_4\)  |                                     |                      |                                             |             |                      |                              |
| 80% C\(_2\), products with 40% C\(_2\)H\(_4\), (EtOH, PrOH) | ca. 4 total | −1.2 | Cu NPs + polyaniline | 0.1 M KHCO\(_3\) | AEM (QAPPT) | (Wei et al., 2020) |
| 48% EtOH               | 2.5 total                           | −0.8                 | Cobalt corrole complex on carbon paper      | 0.1 M NaClO\(_4\) | –                    | (Gonglach et al., 2019)      |
| 25% C\(_2\)H\(_4\) 5% EtOH | –                                  | −1.8                 | Cu(OH)\(_2\)/Cu                            | 0.1 M NaHCO\(_3\) | PEM (Nafion) | (Iijima et al., 2019) |
| 21% C\(_2\)H\(_4\) 29% EtOH | 18 total | −1.0 | Cu@Cu\(_2\)O | 0.1 M KHCO\(_3\) | – | (Shang et al., 2019) |
| 69% C\(_2\), products  | 45.5C\(_2\), products               | −1.0                 | CuO\(_x\)                                   | 0.1 M CaHCO\(_3\) +0.1 M CsI | AEM (Selemion AMV) | (Gao et al., 2018) |
| 60% C\(_2\), products (32% C\(_2\)H\(_4\)) | 68 total | −0.96 | Cu-NCs | 0.25 M KHCO\(_3\) | PEM (Nafion 117) | (Jiang et al., 2018b) |
| 79.1–85.2% EtOH        | 0.31 total                          | −0.5 to −0.7         | Ag-graphene-NCF                             | 0.1 M KHCO\(_3\) | AEM                  | (Lv et al., 2018b)           |
| 79% C\(_2\), products (52% C\(_2\)H\(_4\) 27% EtOH) | 10C\(_2\), products | −1.1 | Boron-doped Cu | 0.1 M KHCO\(_3\) | PEM (Nafion 117) | (Zhou et al., 2018) |
| 40.3% C\(_2\)H\(_4\) 16.7% EtOH | 20 to 30 total | −1.3 | CuPb-0.7/C | 0.1 M KHCO\(_3\) | PEM (Nafion 117) | (Wang et al., 2020a) |
| 12.1% n-PrOH 4.4% AcOH |                                     |                      |                                              |             |                      |                              |
| 72% C\(_2\), products (35.9% EtOH) | 8.75 EtOH | −1.25 | Dodecanethiol-modified CuBr | 0.5 M KCl | PEM (Nafion 117) | (Wang et al., 2021) |
| 13.7% n-PrOH           | 1.15 PrOH                           | −0.65                | PdCu alloy foam (Pd\(_{0.8}\)Cu\(_{0.2}\)) | 0.5 M KHCO\(_3\) | PEM (Nafion 117)     | (Rahaman et al., 2020)       |

(Continued on next page)
### Table 3. Continued

| FE | Current densities [mA cm\(^{-2}\)] | Potential vs RHE [V] | Catalyst | Electrolyte | Membrane | Ref |
|---|-------------------|-----------------|-----------|-------------|----------|------|
| 20.2% EtOH | – | –1.1 | OD-Cu\(_{102}\)Zn\(_{10}\) cubes | 0.1 M KHCO\(_3\) | AEM (AHO, AGC Inc.) | (da Silva et al., 2020) |
| 2.1% PrOH | 33.6% C\(_2\)H\(_4\) | <10 total | –1.1 | Multimetallic CuAgHg | 0.1 M KHCO\(_3\) | – | (Kim et al., 2020b) |
| 32% EtOH | 53% EtOH | 30 to 35 total | –1.08 | Defect-site rich Cu | 0.1 M KHCO\(_3\) | – | (Gu et al., 2021) |
| 18% n-PrOH | 52% EtOH | 156 EtOH | –0.68 | Cu + N-C on PTFE substrate | 1 M KOH | AEM | (Wang et al., 2020b) |
| 41% EtOH | 85.5% C\(_2\)H\(_4\) (15% EtOH, 65.2% C\(_2\)H\(_4\)) | 800 total | –0.89 | Fluorine-modified Cu | 1 M KOH | AEM | (Ma et al., 2020c) |
| Flow cells | 36.9% alcohols | 5% PrOH | 28.3% EtOH | 0.6% MeOH | 20 total | –0.67 | Cu + Bivased metal-organic frameworks (MOFs) | 0.5 M KHCO\(_3\) | PEM (Nafion 117) | (Albo et al., 2019) |
| 55% EtOH | 61.7% C\(_2\)H\(_4\) | 42% C\(_2\)H\(_4\) | 14% EtOH | 5% PrOH | 16.2 total | –1.2 | Cu-N-C | 0.1 M CsHCO\(_3\) | AEM (Selemion AMV) | (Karapinar et al., 2019) |
| 41% EtOH | 124 EtOH | 250 total | –0.67 | Ag\(_{0.14}/Cu_{0.86}\) | 1 M KOH | AEM (Fumasep FAA-3-PK-130) | (Li et al., 2019) |
| 67% C\(_2\)H\(_4\) products | 267C\(_2\)H\(_4\) products | 185C\(_2\)H\(_4\) products | –0.61 | Multi-hollow Cu oxide | 2 M KOH | AEM | (Yang et al., 2020b) |
| 52% EtOH | 55% EtOH | 48 total | –0.59 | Cu-CuO\(_3\) | 2.5 M KOH | PEM (Nafion 117) | (Martić et al., 2019) |
| 75.2% C\(_2\)H\(_4\) products | 40% C\(_2\)H\(_4\), EtOH | 10% C\(_2\)H\(_4\) | 25% EtOH | 48.6% C\(_2\)H\(_4\) | 97C\(_2\)H\(_4\) products | –0.68 | ZnO/CuO | 1 M KOH | AEM | (Ren et al., 2019) |
| 40% C\(_2\)H\(_4\), EtOH | 234 total | –1.17 | CuO | 2 M KOH | PEM | (Xiang et al., 2019) |
| 60% C\(_2\)H\(_4\) | 180C\(_2\)H\(_4\) | –0.7 | Cu-Ag | 1 M KOH | AEM (Fumatech FAP-375-PP) | (Hoang et al., 2018) |
| 25% EtOH | 84% C\(_2\)H\(_4\) products (>60% C\(_2\)H\(_4\)) | 336C\(_2\)H\(_4\) products | –0.68 | CuCl-derived Cu | 3 M KOH | AEM | (Kibria et al., 2018) |
| 62% C\(_2\)H\(_4\), EtOH | 411C\(_2\)H\(_4\) products | –0.67 | Cu-NPs | 1 M KOH | AEM (FAA-3 Fumatech) | (Lv et al., 2018a) |
| 32% C\(_2\)H\(_4\), alcohols (25% EtOH, 7% PrOH) | 120C\(_2\)H\(_4\) alcohols | –0.92 | CuS-Cu-V | 1 M KOH | AEM | (Zhuang et al., 2018) |

(Continued on next page)
| FE | Current densities [mA cm\(^{-2}\)] | Potential vs RHE [V] | Catalyst | Electrolyte | Membrane | Ref |
|----|-----------------------------------|----------------------|----------|-------------|----------|-----|
| 29.9% EtOH 1.43% n-PrOH 16.3% AcOH | 400 total | Min. –1.5 | CuPb-0.7/C | 1 M KOH | AEM (Fumasep FAB-PK-130) | (Wang, P. et al., 2020) |
| 64% C\(_2\)\(_2\), products (15% EtOH) | 210 total | –0.7 to –0.75 | P-doped Cu (Cu\(_{0.92}\)P\(_{0.08}\)) | 1 M KOH | PEM (Nafion 115) | (Kong et al., 2021) |
| 52.4% C\(_2\)\(_2\), alcohols | 282.1 total | –0.9 | N-doped graphene quantum dots on Cu-OD Cu-nanorods | 1 M KOH | AEM (Fumasep FAA-3-PK-130) | (Chen et al., 2020a) |
| <30% EtOH | 400 total | – | Ag\(_2\)Cu\(_2\)O\(_3\) | 1 M CsHCO\(_3\) | AEM (Fumasep FAB-PK-130) | (Martić et al., 2020) |
| 40% C\(_2\)H\(_4\) 20% EtOH | – | –0.5 | Cu electrodeposited on carbon paper | 1 M KOH | AEM (Fumatech) | (Hoang et al., 2017) |
| 52% EtOH 15% n-PrOH | 100 total | –0.95 | Defect-site rich Cu | 1 M KOH | AEM | (Gu et al., 2021) |
higher. Best results were obtained with 41% FE$_{\text{EtOH}}$ at 124 mA cm$^{-2}$ for a catalyst consisting of FeTTP[Cl] (TPP = tetraphenylporphyrin) on Cu and sputtered onto a PTFE substrate and with 41% FE$_{\text{EtOH}}$ at 250 mA cm$^{-2}$ for an Ag$_{0.14}$/Cu$_{0.86}$ catalyst (Li et al., 2019, 2020). The other catalysts summarized in Table 3 achieving higher yields generally reached current densities below 20 mA cm$^{-2}$. The Ag-graphene nitrogen-doped carbon foam (NCF) catalyst reached a FE$_{\text{EtOH}}$ of up to 85%, but the current density was less than 1 mA cm$^{-2}$ (Lv et al., 2018b).

With regard to the membranes used, Table 3 shows that AEMs were used more frequently than PEMs, especially in flow cell architecture. The most frequently used electrolytes are KHCO$_3$, C$_3$H$_5$CO$_3$, and KOH. It is required to be aware of the fact that neither the influence of the membranes nor the electrolytes a trend can be derived based on the data given in the table, as completely different catalysts were used.

SOLID-ELECTROLYTE CELLS

In a membrane electrode assembly (MEA), also called zero-gap arrangement, both the cathodic GDE and the anode are in direct contact with the ion exchange membrane, which functions as electrolyte (Gabardo et al., 2019; Larrazabal et al., 2019). The substrates are led to the electrodes from the reverse side, as schematically shown in Figure 8.

The problem of mass transfer limitation of CO$_2$ through the aqueous electrolyte, as it occurs in H-type cells, is commonly eliminated in MEA setups, which guarantee high CO$_2$ concentrations at the catalyst, as well as lower ohmic losses because of the renunciation of the liquid electrolyte between cathode and anode. This omission also prevents the flooding of the GDE as well as CO$_2$ consumption by the electrolyte and contamination that can affect the catalytic performance. In consequence, gas-phase electrolyzers show stable performance regarding cell voltage and product selectivities (Gabardo et al., 2019; Kibria et al., 2019; Lin et al., 2020). A drawback is the possible blocking of the pores of the GDE with liquid products or water at high current densities, impairing the availability of CO$_2$ at the catalyst. For this reason, the removal of liquid products from the GDE is of great importance (Kibria et al., 2019). The migration of liquid products to the anode site and subsequent oxidation could decrease the FEs of those products.

Water management plays a crucial role in the design of MEAs. The water necessary for CO$_2$RR is usually provided via a humidified CO$_2$ stream, which enables effective management of the reactants and the resulting conversion rates (Blommaert et al., 2019; Lee et al., 2015; Wang et al., 2018a). The most common
operation mode of a MEA is with a humidified CO₂ stream to the cathode and a liquid anode substrate. Alternatively, the use of a dry CO₂ stream in combination with a liquid anode substrate was reported, but accompanied by losses in ionic conductivity of the IEM (Shafaque et al., 2020). In addition, the use of humidified gas streams as both cathode and anode substrate resulted in membrane dehydration when the MEA was operated at room temperature. Increasing the temperature to 80 °C led to sufficient hydration of the membrane, but the FE for CO decreased markedly from around 80% at 25 °C to less than 20% at a cell voltage of 2.5 V (Weng et al., 2019). Process parameters like temperature and pressure generally influence the electrochemical performance of solid-phase electrolyzers. An increase in operation temperature of MEA setups was often reported to increase achievable current densities and FE of the target products (Gabardo et al., 2019; Lee et al., 2018; Sebastián et al., 2017). However, it is required to remember the fact that membrane stability and water crossover limit the maximum temperature in a gas-phase electrolyzer (Kibria et al., 2019). Endrödi and coworkers performed electrolysis of moistened CO₂ to CO in a zero-gap MEA stack at pressures up to 10 bar. They pointed out multiple factors that facilitate CO₂ reduction at elevated pressure, i.e., thermodynamically favored CO₂RR because of the higher CO₂ activity and lower relative water amounts, enhanced mass transport to the GDE, and improved mechanical contact with the AEM. A partial current density for CO of 300 mA cm⁻² was achieved with a CO/H₂ ratio >20 at 3 V cell potential. By flushing the cell with deionized water every hour, the performance was maintained for 8 h (Endrödi et al., 2019). However, the detailed influence of the process parameters on the performance of a MEA is not completely understood yet. To enable more directed research on MEA systems, Sinton and coworkers used numerical modeling to assess the influence of potential, CO₂ partial pressure and AEM thickness, porosity, and charge on carbonate and liquid product crossover as well as CO₂ utilization and energy efficiency. The model confirmed experimental observations on the positive influence of high current densities, high temperatures, and decreased partial CO₂ pressure on EtOH selectivity. With this detailed investigation, they proved computer-based research as a powerful tool to gain insight into the processes taking place in a MEA (McCallum et al., 2021).

Notably, catalysts that were incapable of the formation of certain CO₂RR products in the presence of aqueous electrolytes could be reconsidered for the application in a MEA. Perathoner and colleagues showed that Fe, a metal that is not capable of reducing CO₂ to higher alcohols and hydrocarbons under conventional liquid-phase electrolysis conditions, can be active toward the formation of these products under liquid electrolyte-free conditions in a solid-phase electrochemical cell. They assign the different reaction behavior to the higher CO₂ coverage of the catalyst surface (Genovese et al., 2013).

Influence of the membrane type

Compared to liquid-phase electrolyzers, the influence of the membrane is more pronounced in a solid-phase electrolyzer because of the close contact and the omission of the liquid electrolyte, which could for example buffer pH effects. Similar to the other electrolyzer setups, PEMs, AEMs or BPMs can be used (Kibria et al., 2019; Lin et al., 2020). A challenge linked to PEM-based systems is the formation of an acidic environment at the GDE, possibly resulting in increased HER rates at high current densities or prolonged reaction times, making control of the local conditions at the cathode highly important (Dewulf and Bard, 1988; Kibria et al., 2019). Newman and colleagues described the use of an aqueous KHCO₃ pH-buffer layer between catalyst and membrane to prevent the acidification (Delacourt et al., 2008). The proton availability at the cathode is lower in AEM-based MEAs. Different membrane types can thus affect the product distribution (Kibria et al., 2019). A comparison of Nafion PEMs with Fumasep alkaline AEMs in a MEA using a Cu/carbon nanotube (CNT) catalyst showed a preferred CO₂RR in the AEM setup (Wang et al., 2018a). Furthermore, by means of a comparison between PEMs made of Nafion and sulfonated poly(ether ether ketone) and an alkali-doped polyvinyl acetate AEM in a MEA setup, the influence of the membrane choice on the selectivity of CO₂RR was pointed out. Although the PEM utilization rather yielded methanol and formaldehyde, the use of AEMs led to the formation of CO as well as a small amount of formic acid (Aeshala et al., 2012). However, carbonate crossover harshly limits the CO₂ utilization when operating AEM-based systems, resulting in cost-intensive CO₂ recovery steps. To overcome this drawback while still maintaining the necessary alkaline conditions at the cathode, Sinton and coworkers combined a Nafion 117 PEM with a PTFE-based and Cu-based electrode coated with a so-called permeable CO₂ regeneration layer (PCRL) of the anion-exchange polymer Aemion AP1-CNNS-00-X. In this setup, they were able to achieve comparable performance like the AEM-based system (40% FE toward C₂H₄ and 55% FE toward C₂⁺ products, respectively, at 100 mA cm⁻² and 4.2 V cell voltage) with a CO₂ conversion efficiency as high as 85%. Notably, the use of DI water as anode substrate is necessary in
this system, because the migration of other cations than protons would result in carbonate precipitation at the PEM-PCRL interface (O’Brien et al., 2021).

Because of better control of the proton availability, MEA-based CO₂ electrolyzers can be operated at exceptionally high current densities while maintaining high FEs for the target products. For ease of classification, benchmarking examples are given in Table 4. However, changes in selectivity caused by changes in the cathode environment, and in case of liquid anode substrates, water migration from the anode limit the applicable current densities also for MEA-based electrolyzers. At current densities above 200 mA cm⁻², Seger and coworkers observed a selectivity change toward the formation of liquid products and carbonate, which they attributed to the locally enhanced pH value at the cathode. Furthermore, with increasing current densities, also HER became more pronounced, presumably because of flooding of the cathode by migrated anode substrate (Larrazábal et al., 2019).

Overall, MEA-based electrolyzers already show promising results for CO₂RR and constitute an important step in the direction of the industrialization of CO₂ electrolysis. Numerous catalysts for CO₂RR have already been designed and studied in detail on a laboratory scale, but regarding any future implementation in industrial scale electrolyzers, there is a lack of knowledge about their effective integration in MEAs and their operation (Weekes et al., 2018). Furthermore, many studies on MEAs have so far been performed at low current densities, which are not relevant for industrial applications (Gabardo et al., 2019).

### Solid-oxide electrolysis cells (SOECs)

Solid-phase electrolyzers using ceramic electrolytes enable the direct production of syngas out of CO₂ and water at high current densities because of the improved kinetics at elevated temperatures (Liang et al., 2020; Zhang et al., 2017). In this set-up, cathode and anode are separated by a layer of oxide and temperatures of >600°C are required for sufficient conductivity (Song et al., 2019). Common ceramic electrolytes are based on oxidic compounds of ceria, zirconia, and lanthanum gallate. Cathode materials usually deployed are porous metal/ceramic composites (cermets), for example ytrria-stabilized-zirconia with Ni (Bidrawn et al., 2008; Ebbesen and Mogensen, 2009; Inaba, 1996; Ishihara et al., 2006; Yamamoto et al., 1998; Yue and Irvine, 2012; Zhang et al., 2017). The high-temperature solid electrolytes can be classified

| MEA setup   | Product (FE)              | Current Density [mA cm⁻²] | Cell voltage [V] | Ref                  |
|-------------|---------------------------|---------------------------|------------------|----------------------|
| WE: Ag membrane, M: Sustainion AEM, CE: IrOₓ/C | CO (≈80%)                   | 250                        | 3.3               | (Larrazábal et al., 2019) |
| WE: Cu NPs/PTFE, M: Sustainion AEM, CE: IrOₓ/Ti | C₂H₄ (≈80%) C₂H₆ (≈50%)      | 150                        | 4                 | (Gabardo et al., 2019) |
| WE: CuTPI/PTFE, M: Sustainion X37-50 AEM, CE: Ti-IrOₓ mesh | C₂H₄ (66%)                    | ≈ 350                      | ≈ 4.4             | (Ozden et al., 2020) |
| WE: Ag NP/carbon paper, M: PiperION AEM, CE: IrOₓ/Ti | CO                          | 1004 (partial)             | 3.4               | (Endrődi et al., 2020) |
| WE: FeTIP(CI)/Cu/PTFE, M: Sustainion AEM, CE: IrOₓ/Ti mesh | EtOH (41%)                   | ≈ 500                      | 3.7               | (Li et al., 2020) |
| WE: Defect-site-rich Cu/Freudenberg H14C9, M: Sustainion AEM, CE: IrOₓ/Ti mesh | EtOH + n-PrOH (60%)          | 200                        | 3.5               | (Gu et al., 2021) |

CuTPI: copper/tetrahydro-phenanthrolinium/ionomer; M standing for membrane.
into two groups. In the case of oxygen ion ($O^{2-}$) conductors, $O^{2-}$ ions originate from the cathodic reaction of $H_2O$, migrate from the cathode to the anode and are oxidized there. The $CO_2$ molecules are reduced at the anode with activated hydrogen. With proton-conducting oxides, $H_2O$ is oxidized to $O_2$ at the anode and $H^+$ migrates to the cathode, where it reacts with $CO_2$ (Lin et al., 2020; Zhang et al., 2017). Figure 9 shows the scheme of a SOEC setup.

Despite the favorably high current densities they allow, the high temperatures that are required for the operation of SOECs lead to high energy demand and considerable technical complexity. Challenges are the sealing of the cell as well as metal particle oxidation, carbon deposition, and electrolyte degradation because of phase-changes at high temperatures (Liang et al., 2020; Zhang et al., 2017). Although the possible $CO_2$ reduction products of solid-oxide electrolysis itself are rather limited, their subsequent conversion could offer a promising pathway to higher hydrocarbons (Liang et al., 2020). Sargent and coworkers followed this approach and coupled $CO_2$ reduction to $CO$ in a SOEC with subsequent conversion to ethylene in a MEA-based cascade approach. They reached around 48% reduction in energy input compared to a direct $CO_2$ to ethylene route, because the energy-intensive reprocessing of the electrolyte and anode product gas stream caused by carbonate formation were completely avoided. Thereby, 95% FE for $CO$ were reached in the SOEC at a current density of 815 mA cm$^{-2}$ (Ozden et al., 2021).

**PRODUCT SEPARATION**

After conversion, the diverse products of electrochemical $CO_2$ reduction accumulate in rather complex mixtures. The separation of the single compounds from the gas stream and electrolyte requires further process steps to be considered for economic operation.
Gas-phase products

As CO₂ reduction can yield various gas-phase products, they have to be separated from each other and the remaining CO₂ stream for further processing. In Figure 10, different procedures for gas-separation are illustrated.

Greenblatt and colleagues provided a comprehensive overview of possible product separation steps for CO₂ reduction products (Greenblatt et al., 2018). A possible method for gas separation is the pressure swing adsorption (PSA), which is also applied for industrial biogas applications (Bauer et al., 2013; Greenblatt et al., 2018; Ribeiro et al., 2011; Wheeb et al., 2016; Zhu et al., 1991). This method is based on the adsorption of the desired product onto a porous material and its subsequent release under reduced pressure. The energy demand is based on the electricity needed for pressure control (Greenblatt et al., 2018; Wheeb et al., 2016). Spurgeon and coworkers proposed the use of PSA to separate and recover unconverted CO₂ from the gas stream. The technology could also be used for the regeneration of CO₂ and the separation of CO in a two-step electrochemical reduction setup (Spurgeon and Kumar, 2018). Gas product separation via membranes also represents a viable option. Membranes used for this purpose are usually based on polymers which allow for the passage of the desired substances while preventing it for others (Greenblatt et al., 2018). This method promises low energy consumption, but challenges like the plastification of the membranes are still to be overcome (Sanders et al., 2013). Besides membrane separation, Greenblatt and colleagues proposed cryogenic distillation and pressurized liquefaction to separate a hypothetical mixture of CO₂RR gas products. For cryogenic distillation, a mixture of gases with different condensability is liquefied via increased pressure. The different species can then be separated by distillation to their corresponding boiling point. Although the process is energy intensive, it can yield gas products in high purity. The authors described the possible liquefaction of ethylene and CO₂ at elevated pressures of 50 and 70 bar, respectively. However, this process is not suitable to yield products with high purity when separation is done simply by raising the pressure again (Greenblatt et al., 2018).

Liquid-phase products

Alcohols, organic acids or aldehydes represent attractive target products of the electrochemical CO₂ reduction. Distillation is widely used in industry to separate liquid products, based on the control of
temperature and pressure to evaporate the components selectively. The evaporation requires a high energy input, although the heat can partially be recovered (Greenblatt et al., 2018; Halvorsen and Skogestad, 2011; Kiss et al., 2012). However, the required energy is increased with more diluted target products, impeding their separation from the electrolyte stream (Greenblatt et al., 2018; Huang et al., 2008). To effectively increase the concentration of liquid products, the electrolyte can be recycled and passed multiple times through the electrode compartments. However, degradation effects connected to higher concentrations as well as an increased migration of CO_2RR products to the anode compartment have to be taken into account (Jouny et al., 2018; Ma et al., 2017). The situation can furthermore be complicated by difficulties to separate the obtained products (Jouny et al., 2018). The azeotropic behavior of ethanol-water mixtures restricts the product purity obtained via distillation. The obtained purity can be optimized by the addition of another component like benzol or cyclohexane; however, these components have to be separated from the desired product again, resulting in additional process steps and separation costs (Greenblatt et al., 2018). Furthermore, the use of vacuum distillation reduces the required energy (Beebe et al., 1942; Greenblatt et al., 2018). The combined use of membrane technology and distillation, the so-called pervaporation, is another possibility to yield pure liquid products like ethanol. The desired product has to permeate the membrane selectively, where it is evaporated under reduced pressure and subsequently collected with a condenser (Al-Asheh et al., 2004; Greenblatt et al., 2018; Sanders et al., 2013). Some liquid products can also be extracted via liquid-liquid extraction. For example, the addition of solvents such as n-pentanol or higher alcohols allows for the preferential dissolution of n-propanol in the organic phase which is not miscible with the aqueous phase and thus can be separated (Greenblatt et al., 2018; Stoicescu et al., 2011). Because of their similar boiling points, the separation of formic acid from water requires alternative methods. BASF SE described a liquid-liquid extraction process for formic acid from aqueous solutions with amides as potential extractants and subsequent distillation. In addition, the separation of formic acid, ethanol, and propanol can be facilitated by the addition of salts before extraction (Card and Farrell, 1982; Greenblatt et al., 2018; Li et al., 2000; Singh and Bell, 2016). Sing and Bell postulated the use of a concentrated Cs_2CO_3 electrolyte, leading to a phase separation of produced ethanol into microemulsion, which is subsequently collected in a liquid-liquid extractor, while the Cs_2CO_3 solution is recycled (Singh and Bell, 2016). For the use of additional solvents or salts, efficient regeneration of those additives is important to limit the cost of the separation steps (Greenblatt et al., 2018).

Altogether, the capture of CO_2 as well as the separation of the desired products has a significant influence on the successful realization of industrial CO_2 reduction. Optimization and efficient integration of those process steps can improve the overall efficiency and thus economic feasibility. With further technical improvement, the direct air capture (DAC) of CO_2 could prospectively become an attractive CO_2 source, facilitating the reduction of atmospheric CO_2. As the separation of different products requires complex process steps, catalyst designs achieving high FE are of great importance. Furthermore, process optimization in direction of product streams that are less diluted with CO_2 would be desirable.

TECHNO-ECONOMIC ASSESSMENT

Although the electrochemical reduction of CO_2 is a promising technology for both energy storage and carbon supply applications, the overall process has to be economically feasible for a successful industrial implementation. Techno-economic assessments have been issued to determine desired products as well as target parameters that the system has to meet. Thereby, every process step, ranging from CO_2 capture, the actual electrolysis, to product separation, has to be considered.

Carbon capture from point sources

For the electrochemical conversion of CO_2 into valuable products, CO_2 is required in high purity and must therefore be captured e. g. from the feedstock gas stream of a point source or directly from the atmosphere. The costs of capturing CO_2 from power plants and chemical process exhausts using amine-based chemical absorption, which is mainly used for the CO_2 capture from industrial flue gases, are currently at around 70 $ \text{t}^{-1}. The amine-based solvent selectively absorbs CO_2 via the formation of water-soluble salts (Zhang et al., 2020d). Via process optimization, a price of 40 $ \text{t}^{-1} could be reached, according to the techno economic analysis by Jiao, Sargent, and their coworkers (Jouny et al., 2018; Kibria et al., 2019; Raksajati et al., 2013, 2018). Common amine-based solvents are ethanolamine or Mitsubishi’s commercial KS-1 solvent. After CO_2 absorption, the solvent is regenerated with water vapor. Via condensation of water, CO_2 is then purified and further processed (Moiooli et al., 2019; Rochelle, 2009). The drawback of the process is the high energy demand of the desorption process, as well as corrosiveness and amine loss during operation.
(Ho et al., 2009; Hüser et al., 2017; Rochelle, 2009). Therefore, Ho and colleagues calculated that the price of 70 $ t⁻¹ could be reduced to 55 $ t⁻¹ with the integration of waste heat into other processes (Ho et al., 2009). It is of particular importance that the solvents have the highest possible tolerance to SOₓ and NOₓ impurities, because solvent regeneration is a major contributor to operating costs. Furthermore, the solvents should exhibit low heats of reaction and evaporation rates, and be inexpensive to achieve deposition costs of about 37 $ t⁻¹ (Raksajati et al., 2018). The use of KS-1 could lower the CO₂ price only up to 46 $ t⁻¹, which, however, is lower than for ethanolamine because of a lower regeneration energy demand. Besides ethanolamine and KS-1, other amine-based and amino acid-based solvents have been proposed (Chowdhury et al., 2013; Dubois and Thomas, 2012; Hüser et al., 2017; Moioli et al., 2019).

Alternatively to KS-1 and ethanolamine, it is possible to use weak alkali salts. Their application is characterized by lower regeneration costs, because less regeneration energy is required, and less degradation occurs. Using these solutions as an example, Ho and coworkers calculated a possible CO₂ price of 30 $ t⁻¹ for K₂CO₃. However, it is problematic that weak alkali salt solutions react less rapidly with CO₂ than those containing amines. An increase in reaction rate can be achieved by adding additives such as boric acid or piperazine (Cullinane and Rochelle, 2004; Ho et al., 2009).

As other technologies to realize carbon capture at industrial facilities, oxy-combustion and calcium looping have been described (Vatopoulos and Tzimas, 2012; Yin and Yan, 2016). When pure oxygen instead of air is used for combustion, CO₂ in high concentration is obtained for further utilization (Yin and Yan, 2016). The calcium looping process is based on the reversible reaction of CO₂ with calcium oxide to calcium carbonate at temperatures between 600°C and 700°C, followed by the release of CO₂ at temperatures above 900°C (Martínez et al., 2011; Vatopoulos and Tzimas, 2012).

**Direct air capture**

Capturing CO₂ from point sources, such as waste gas streams, can reduce greenhouse gas emissions, whereas direct air capture (DAC) is a negative emission technology as it directly removes CO₂ from the atmosphere. However, it has not been commercially realized yet and is challenging because of the low atmospheric concentrations of CO₂. Assuming a CO₂ capture capacity requirement of 0.98 Mt a⁻¹, a techno-economic assessment issued in 2018 estimated a levelized cost of 94–232 $ t⁻¹ CO₂ (Keith et al., 2018). Potentially, DAC can involve capture using amine-functionalized solids, porous materials such as zeolites or MOFs, and the use of liquid alkaline sorbents (Kumar et al., 2015; Sanz-Pérez et al., 2016). When CO₂ is adsorbed to solid sorbents, a lower regeneration temperature of 80°C–100°C is required to release it, and the remaining air can therefore be removed via a pressure drop by evacuation to some extent and/or insertion of steam (Fasihi et al., 2019; Kulkarni and Sholl, 2012; Sinha et al., 2017). A classification by Fasihi and colleagues divides the potential technologies into capture via aqueous solutions and regeneration at high temperatures (HT DAC), temperature swing adsorption (TSA) on solid sorbents and at low temperatures (LT DAC), and moisture swing adsorption (MSA) (Fasihi et al., 2019). For an LT DAC system case study, powered by a photovoltaic-wind-battery system in Morocco, the potential cost was calculated at 105 € t⁻¹ and 60 € t⁻¹ in 2030, depending on the possibility to use free waste heat from other facilities. A further reduction of the costs to 54 and 38 € t⁻¹ in 2050 was proposed, based on reduced capital expenditures (CAPEX) with larger-scale implementation. The authors judge the LT DAC process as more promising, because of the possible use of excess waste heat (Fasihi et al., 2019). An example for the first attempts to implement DAC is the company Carbon Engineering with an LT DAC pilot plant with a capacity of 1 t d⁻¹ (Keith et al., 2018). This plant absorbs CO₂ with KOH in an air-liquid contractor and uses a CaO-calcium cycle for regeneration. The Swiss-based company Climeworks developed an LT DAC process based on PSA on amine-modified porous granulates which reversibly bind CO₂. The system is regenerated via pressure reduction and heating to 100°C (Climeworks, 2020; Christoph Gebald, Nicolas Repond, Jan Andre Wurzbacher). The company Global Thermostat is working on an LT DAC process based on amino-polymer sorbents, allowing for low cycle times of 30 min and regeneration at 85–94°C (Fasihi et al., 2019; Exxonmo-bil, 2019).

**Alternatives**

In order to avoid the complex and expensive CO₂ separation processes, there are approaches to operate CO₂RR directly with industrial flue gases without previous CO₂ capture. The challenges here are low CO₂ concentrations, which lower the activity, and the contamination with other components. Oxygen can reduce the catalyst selectivity via the occurring ORR and substances like SOₓ and NOₓ act as catalyst.
poisons (Verma et al., 2019; Xu et al., 2020). Kenis and coworkers investigated the effect of CO₂ concentration in the stream on the reduction to CO with a Ag catalyst. At 3.0 V cell potential, a diluted stream with 10% CO₂ could still achieve a CO FE of over 80%. Switching from 100% to 10% CO₂, the decrease in partial current density was below 45%. Lower voltages led to significantly reduced FEs (Kim et al., 2015). By using an ionomer layer containing hydrophilic nanopores which was bound with TiO₂ nanoparticles, Sinton and colleagues could yield a C₂ FE of 68% at 260 mA cm⁻² from a simulated flue gas stream comprising 15% CO₂ and 4% O₂. The ionomer was successful in reducing O₂ transport, and a pressure of up to 15 bar was applied to suppress the HER and increase the CO₂ reduction activity (Xu et al., 2020). Oh and coworkers showed that the CO FE remains over 90% with an Au₂₅ nanocluster catalyst reducing a 10% CO₂ stream. They also demonstrated a 15.9% solar-to-CO conversion efficiency in an electrolyzer coupled to a Ga₀.₅In₀.₅P/GaAs photovoltaic cell (Kim et al., 2020a).

Product separation

Not only carbon capture plays an important role in the techno-economic evaluation of the whole route of electrochemical CO₂ reduction, but also the evaluation of the possible products. Because the CO₂ reduction reaction can theoretically yield a variety of C₁ to C₃ chemicals, different target products are conceivable. To identify economically attractive products, the price, often normalized to the stored energy, and the market size is used (Jouny et al., 2018; Kibria et al., 2019). Table 5 provides an overview of the market prices of possible target products (Jouny et al., 2018). Based on these values, the authors selected methanol, ethylene, ethanol, and n-propanol as potential target products. However, among these products, methanol failed to yield a positive net present value (NPV) in the economic cost analysis (Jouny et al., 2018). For the analysis, the market value of pure CO as well as syngas, which is commonly used as an industrial feedstock mixture, was considered. Formic acid achieves the highest normalized market price, but shows low market volume, so its importance as a target product is limited. The market size for propanol is also small, but more efficient and consequently cheaper production could increase demand according to Jiao and coworkers (Jouny et al., 2018). Because of their high market size with a moderate normalized market price at the same time, Sargent and colleagues selected ethanol and ethylene as promising target products. Based on normalized prices, CO and formic acid would be the most attractive products, but would have a limited market (Kibria et al., 2019). However, the possibility of converting CO and formic acid to more valuable products also makes it an attractive target product.

In addition to the market price, selectivities and process parameters also play a crucial role in the conversion of CO₂ to value-added products. According to Masel and colleagues, the Faraday efficiency for multi-carbon products should be at least 60% with a current density of at least 200 mA cm⁻² (Masel et al., 2021). Furthermore, the use of KOH should be avoided, because it reacts with CO₂ to form carbonate and furthermore causes the oxidation of copper catalysts when no reductive potential is applied. Potassium salts containing halides should also not be present in the electrolyte, as this would lead to the formation of gas products such as Cl₂ or Br₂ at the anode (Masel et al., 2021).

In addition, the processes required for product separation affect the overall costs of CO₂ electrolysis. Although the separation processes have similar capital cost, liquid product separation has higher operational costs (Kibria et al., 2019). The estimated operational cost for the separation used by Sargent and colleagues is $300 per ton of product (Kibria et al., 2019).
coworkers were 10 $ t^{-1}$ for gas products via pressure swing adsorption, based on industrial biogas separation, and 60 $ t^{-1}$ for liquid product separation via distillation with a minimum input of 10 wt % liquid product. Possible further process steps for gas products, like compression for transport, were not considered (Dahmus and Gutowski, 2007; Greenblatt et al., 2018; Jouny et al., 2018; Kibria et al., 2019).

Capital & operating costs of the electrolyzer

Apart from the target product, the capital and operating costs of the utilized electrolyzer system, as well as additional process steps, contribute to the economic viability of the overall technology. Based on similar costs for PEM water electrolyzers, the electrolyzer cost was estimated at 5,000–15,000 $ m^{-2}$ by Sargent and colleagues, whereas Jiao and coworkers estimated 920 $ m^{-2}$ for the optimistic case of their model (Jouny et al., 2018; Kibria et al., 2019). The operational cost of the electrolyzer is largely dependent on electricity costs, more so for products that require a higher number of reduction steps. The required electricity can be reduced by achieving higher energy efficiencies of the system (Kibria et al., 2019). For the calculation of their techno-economic models, the estimated electricity cost used by Sargent and coworkers was two cents KWh$^{-1}$, based on estimates of the US Department of Energy for 2030 (Solar Energy Technologies office, 2020; Kibria et al., 2019). Jiao and colleagues assume costs of three cents KWh$^{-1}$ based on estimations for 2030 for the optimistic case (Haegel et al., 2017; Jouny et al., 2018).

To ensure profitable production cost for a desired product, the multicomponent system consisting of an electrochemical cell and catalyst must meet certain performance targets and should be considered one entity.

(1) The reaction rate, in terms of the electrochemical reduction, is defined via the current density. Required target values for current density and FE are related to the capital cost, because lower values require a larger electrolyzer size to reach the target rate of production. In the techno-economic model of Sargent and colleagues, a reduction of the current density from 300 mA cm$^{-2}$ to 100 mA cm$^{-2}$ would raise the price by more than 500 $ t^{-1}$ of ethanol (Kibria et al., 2019). Overall, industrial CO$_2$ reduction processes should aim at current densities of at least 300 mA cm$^{-2}$ (Jouny et al., 2018; Kibria et al., 2019).

(2) Another important parameter is the cell voltage, which determines the energy efficiency of the electrolyzer. Thus, a reduced cell voltage lowers the power requirement. This is especially relevant for products, which need a high number of reduction steps. Sargent and coworkers showed that with a cell voltage of 1.8 V, several products would become economically feasible with 90% FE (Kibria et al., 2019). Jiao and colleagues chose a cell voltage of 2 V for the optimistic case in their techno-economic model (Jouny et al., 2018).

(3) Furthermore, the system lifetime is a factor for the overall economic viability. Sargent and colleagues proposed a lifetime of 80,000 h as desirable, based on values reached by industrial water electrolyzers (Kibria et al., 2019). Jiao and coworkers assumed a 20-year lifetime with 350 days per year operating time (Jouny et al., 2018). Perez-Ramirez and colleagues postulated a much lower lifetime of at least 5,000 h as requirement (Martin et al., 2015). Spurgeon and coworkers assumed a system lifetime of 20 years with costs for replacement of the major components after 7 and 14 years (Spurgeon and Kumar, 2018).

Table 6 shows the proposed key performance indicators that could yield a positive net present value in the techno-economic studies of Sargent, Jiao, and their coworkers.

| Table 6. Electrolyzer KPI targets | (Jouny et al., 2018) | (Kibria et al., 2019) |
|----------------------------------|----------------------|----------------------|
| Faradaic efficiency [%]          | 90                   | 80–90                |
| Current density [mA cm$^{-2}$]   | 300                  | >300                 |
| Cell voltage [V]                 | 2                    | <1.8                 |
| Lifetime [h]                     | 168,000              | >80,000              |

In their techno-economic evaluation of low-temperature electrochemical reduction of CO$_2$ to CO, Masel and colleagues identified the lack of alternatives for iridium as anode catalyst and the necessity of lowering

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**Table 6. Electrolyzer KPI targets**

| KPI                         | (Jouny et al., 2018) | (Kibria et al., 2019) |
|-----------------------------|----------------------|----------------------|
| Faradaic efficiency [%]     | 90                   | 80–90                |
| Current density [mA cm$^{-2}$] | 300                  | >300                 |
| Cell voltage [V]            | 2                    | <1.8                 |
| Lifetime [h]                | 168,000              | >80,000              |
the cell voltage while avoiding the use of wearing materials (e.g. KOH or additives) as key factors that impede application on an industrial scale. For the production of formic acid, there is a lack of sufficiently selective and stable catalysts, while C₂ products cannot be obtained yet with adequate current densities or FEs without the use of KOH or halides as electrolytes (Masel et al., 2021).

**Tandem processes**

Although the normalized market price of CO is lower compared to other CO₂RR products, reduction of CO₂ to CO with in-line processing to further value-added products may be a profitable pathway (Haas et al., 2018; Krause et al., 2020; Schmidt et al., 2018). High-temperature co-electrolysis of CO₂ and water to syngas in SOECs is nowadays comparably close to reaching industrially relevant and profitable performance. In a direct comparison of an alkaline liquid-phase flow cell, a neutral MEA, and a tandem CO₂-CO₂-ethylene process, Sargent and colleagues concluded that the one-step processes suffer from low energy efficiency and CO₂ losses because of crossover and carbonate formation, markedly contributing to the system costs. However, avoiding carbonate formation by utilizing the two-step tandem process leads to possible profitability at viable system parameters. Provided that the first step, the electrolysis of CO₂ to CO in a SOEC, reaches an energy efficiency of 80%, and in the second step ethylene can be obtained with an energy efficiency of 40%, a price of 1,000 $ t⁻¹ could be achieved at electricity costs of 0.02 $ kWh⁻¹. Already in 2010, Fu and coworkers modeled the combination of CO₂/H₂O co-electrolysis in a SOEC, followed by Fischer-Tropsch process to liquid fuels. They pointed out the beneficial carbon balance as a benefit in comparison to gas-to-liquid and coal-to-liquid processes, but stated the importance of low-cost renewable electricity and concentrated CO₂ feed for the profitability (Fu et al., 2010). As additional factors, Bao and coworkers identified extended lifetimes (>50,000 h), lower overpotentials, and a suitable successive conversion of the produced syngas as crucial parameters for market maturity (Song et al., 2019). The necessity of enhanced lifetimes was confirmed by Desideri and colleagues when examining CO₂/water co-electrolysis with subsequent conversion to methanol. Furthermore, they found that the stack costs still have to be reduced and that the supply of excess renewable energy to the system must be stable to maintain reasonable payback times. Benefits of the technology, however, are its high energy and carbon-conversion efficiencies of 72 and 93.6%, respectively, and good heat integration properties between high-temperature electrolysis and methanol production (Zhang and Desideri, 2020). As energy efficiencies of >80% are already reached in commercially available SOECs, CO-to-ethylene electrolyzers with energy efficiencies of 30% are already reported, and ethylene is nowadays traded for 800–1,200 $ t⁻¹, the economic perspectives of the tandem process are encouraging (Sisler et al., 2021).

**OUTLOOK & TRENDS**

CO₂ electrolysis is an emerging technology, which will most likely contribute to both energy storage and base chemicals supply in the future. Particularly the production of syngas via high-temperature co-electrolysis of CO₂ and water is already possible at industrial scale and close to being economically competitive. Nevertheless, there are still challenges that have to be solved to allow for full industrial implementation. A majority of research data concerning CO₂ electrolysis refers to purified CO₂ feedstocks. However, the production of high-purity CO₂ is cost-intensive and it should be kept in mind to develop catalyst and reactor systems that are able to work with either impure or diluted CO₂ streams. In addition to that, there is still a general lack of sufficiently robust and selective electrocatalysts for CO₂ reduction to individual products. Product separation is another complex and costly procedure, which is why it is desirable to obtain highly concentrated single products. In case of CO and formic acid, this criterion can already be met at a large scale, but the production of C₂ products has to be improved in this regard. Furthermore, most of the catalysts employed in research are either based on precious metals or require complex manufacturing procedures, which make them cost-intensive and insufficiently abundant for industrial implementation. It has to stay in mind that there is also an urgent need for alternative anode catalysts under acidic conditions as the state-of-the-art material iridium does not meet those criteria. Gas-diffusion electrodes became the predominant electrode design because of overcoming the mass-transport limitation of CO₂. Although significant advances were made in recent years, some unsolved issues remain. Research efforts mostly focus on carbon-based and PTFE-based GDLs. Although carbon-based GDLs are not suitable for upscaling because of their high costs and insufficient mechanical stability, PTFE membranes cannot deliver through-plane electrical conductivity and are therefore not suitable for stacking. Current research is already focusing on alternative materials, which combine electric conductivity with sufficient gas permeability and hydrophobicity to create highly functional GDLs. Furthermore, the long-term water management at the CL presents a challenge. In many cases, flooding causes significant performance losses over time, leading to
favored HER, and consequently, clogging because of carbonate formation. To improve water management, zero-gap PEM cells were developed, where water is no longer supplied via liquid electrolytes but a humidified CO₂ feed instead. Another advantage of the renunciation of liquid electrolytes is the elimination of wear materials. Alternatively, the electrolysis of supercritical CO₂ might also be an attractive way to overcome CO₂ mass transport limitations as well as challenges of water management and product separation. Furthermore, CO₂ itself serves as a solvent in this technology. Certainly, the technical requirements for this technology are increased and efforts must be made to avoid product reoxidation. Another way to enhance CO₂ availability is the application of differential pressure on the gas side, which allows operation at higher current densities compared to atmospheric conditions. Challenges for the application of this technique are increasing mechanical stress on the membrane and enhanced CO₂ crossover. However, the success of CO₂ electrolysis in most cases depends on conductive membranes and ionomers. Those highly specialized materials are to date hardly available on a sufficient scale, at moderate costs and consistent quality. Furthermore, a balance between mechanical robustness and sufficiently low resistance is still to be found to lower overall cell voltage. Future research efforts should therefore also focus on the development of highly conductive polymers with a scalable synthesis. It is noticeable that because of environmental concerns, fluorine-free ionomers should be developed. In conclusion, products of CO₂ electrolysis are, apart from CO, not yet economically competitive. It is indeed important to gain mechanistic insights into the complex CO₂RR by fine-tuning sophisticated catalysts and ionomers. However, to enable the economic future of these processes, the focus of research must eventually shift to large-scale applicable and affordable materials. Therefore, close and interdisciplinary collaboration between academia and industry is necessary to ensure technological progress in the general field of electrolysis (Siegmund et al., 2021). Time will tell if science overcomes this challenge and which potential products of CO₂RR will prospectively be produced via electrochemical methods.

Limitations of the study
Because of the tremendous research progress and accordingly high number of publications on the topic, this review does not include every single study on the technical aspects of electrochemical CO₂ reduction. However, no specific author was excluded intentionally. With the division of the manuscript into two parts, we try to cover as many aspects of the topic as possible. The focus of the catalytic considerations thereby lies on the production of multibar carbon alcohols though. Other products of electrochemical CO₂RR require different catalysts and reaction conditions than the ones presented.

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DECLARATION OF INTERESTS
The authors declare no competing interests.

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