

## REVIEW

# Does electrifying organic synthesis pay off? The energy efficiency of electro-organic conversions

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## ABSTRACT

*The electrification of organic syntheses is a vividly growing research field and has attracted tremendous attention by the chemical industry. This review highlights aspects of electrosynthesis that are rarely addressed in other articles on the topic: the energy consumption and energy efficiency of technically relevant electro-organic syntheses.*

*Four examples on different scales are outlined.*

Electro-organic synthesis has experienced a renaissance within the past years. This review addresses the energy efficiency or energy demand of electrochemically driven transformations as it is a key parameter taken into account by, for example, decision makers in industry. The influential factors are illustrated that determine the energy efficiency and discussed what it takes for an electrochemical process to be classified as “energy efficient.” Typical advantages of electrosynthetic approaches are summarized and characteristic aspects regarding the efficiency of electro-organic processes, such as electric energy consumption, are defined. Technically well-implemented examples are described to illustrate the possible benefits of electrochemical approaches. Further, promising research examples are highlighted and show that the conversion of fine chemicals is rather attractive than the electrochemical generation of synthetic fuels.

**Keywords:** electrochemical synthesis; efficiency; sustainability

## DISCUSSION POINTS

- What are the most important figures of merit in the evaluation of electrochemical processes and how do they contribute to the energy consumption of electrosynthesis?
- Electrosynthetic approaches toward organic commodities and fine chemicals are illustrated. What are the main drivers for their energy consumption and why are electro-synthesized commodities from CO<sub>2</sub> to date economically less attractive than fine chemicals?

## Introduction

The first attempts of organic electrosynthesis date back over 170 years. However, electrochemical approaches had been underestimated for a long time and have experienced a renaissance within the past few years.<sup>1,2</sup> Many contemporary societal issues and also in chemistry deal with renewable energy, the avoidance of greenhouse gases and waste, as well as the replacement of fossil resources. Since electrochemistry may offer greener chemical routes, scientists have focused on electro-organic synthesis and conversions to support a sustainable ecological footprint.<sup>1,3,4</sup>

In the 21st century, electrochemistry and its application will play an important role in the industry, for example, within the Baizer or Lysmeral processes and also in the commercial world.<sup>5,6</sup> Electrochemistry offers numerous advantages, such as working under mild conditions, avoiding aggressive and hazardous reagents, and working with alternative feedstock. It is possible to improve the selectivity of existing reactions and to initiate novel chemical transformations.<sup>2,7,8</sup>

The generation of synthetic fuels has attracted much attention during recent years. Using electric current, CO<sub>2</sub> and water are reduced into energy carriers such as methanol or methane. In a scenario wherein electricity is generated by regenerative resources, power-to-fuel technologies may support the implementation of closed artificial carbon cycles.

However, the electrosynthesis of platform chemicals like alcohols, ethylene and methane from CO<sub>2</sub> is mostly achieved by using copper-based catalysts, which on the one hand is capable of generating C-C bonds, but on the other hand produces a variety of hydrocarbons at the same time. The gaseous and liquid fractions obtained represent multicomponent mixtures, which require costly purification. The electrolytes are mostly of aqueous nature, providing rather small concentrations of alcohols and formate, which makes the product separation even more cost-intensive. As these products are required in large quantities, the according capital costs for the downstream processing as well as its running costs are enormous. At the same time, platform chemicals are sold at a rather low price, narrowing down the profit margin.

In contrast, fine chemicals are produced at lower scale and with a significantly higher revenue per kilogram. Electrosynthetic approaches may offer two main benefits in the production of fine chemicals. As the reaction is driven by electrical current, strong and hazardous oxidizing or reducing agents like LiAlH<sub>4</sub> can be omitted, which saves on costs for reagents and safety precautions. Noteworthy, the electron is one of the cheapest and most versatile redox agents. Furthermore, electrosynthesis may help facilitate the downstream processing since reagent waste is avoided. For example, in the Baizer process, an annual amount of 300,000 tons adiponitrile are produced. The product adiponitrile forms due to lower miscibility an organic layer, which is easily separated from the aqueous electrolyte. The translation of the concept from a divided cell to an undivided cell could improve cost factors as investment, maintenance, and energy. The converted mass yields over 90%, and the separation of the biphasic phase of adiponitrile and acetonitrile is cost efficient.<sup>9</sup>

As illustrated in Fig. 1, electrochemical approaches may offer products in different sections, such as synthetic fuels, commodities, fine chemicals, and specialties. An important aspect to address, especially for decision makers in industry, is whether an electrochemical alternative is superior to the existing process in terms of costs. Energetic considerations are of particular interest in process development. Therefore, it is necessary to answer the question whether it is energy efficient to use electricity as a driving force for chemical reactions. Here, we survey whether electrifying organic syntheses pays off and under

which circumstances it is superior over traditional chemical routes.

## Energetic evaluation of electrochemical conversions

The evaluation of an electrochemical process involves multiple aspects, whereas the energy requirements are mainly governed by the applied cell voltage  $U_{\text{cell}}$  [which depends on the applied current ( $i$ ), the Ohmic resistance ( $R_{\text{cell}}$ ) of the electrolysis cell, and on the difference of the anodic and the cathodic redox potentials ( $E_{\text{anode/cathode}}$ )].

$$U_{\text{cell}} \text{ (V)} = E_{\text{anode}} - E_{\text{cathode}} + iR_{\text{cell}}$$

While the redox potentials and the current depend on the electrochemical reaction and its optimization, the cell resistance depends on multiple factors including the cell design (e.g., interelectrode gap), the electrolyte and its conductivity, and the usage of a separator (membrane) between catholyte and anolyte. Noteworthy, when conducting an electrochemical conversion at constant potential, all energy-consuming contributions (separator, Ohmic resistance, and overpotential) are set to zero, but are still there and require in the end most of the energy applied. The cell resistance  $R_{\text{cell}}$  has high impact onto the overall cell voltage. This is, in particular, the case for divided cells wherein the applied cell voltage easily reaches 5 V or more. All contributions to the Ohmic cell resistance having a direct impact onto applied cell voltage and the electric current have to be taken into account for optimization of the energy efficiency (Fig. 2).

The operating cell voltage  $U_{\text{cell}}$  (in some literature also written as  $E$ ) should not be mixed up with the redox potential  $E$  as in the above equation. The redox potential does not take into account the Ohmic resistance of the cell. Noteworthy, when operating an electrolysis cell at higher productivity, the contributions like the overpotential, increase due to kinetics.

The electric energy consumption (EEC) is given by the following equation:

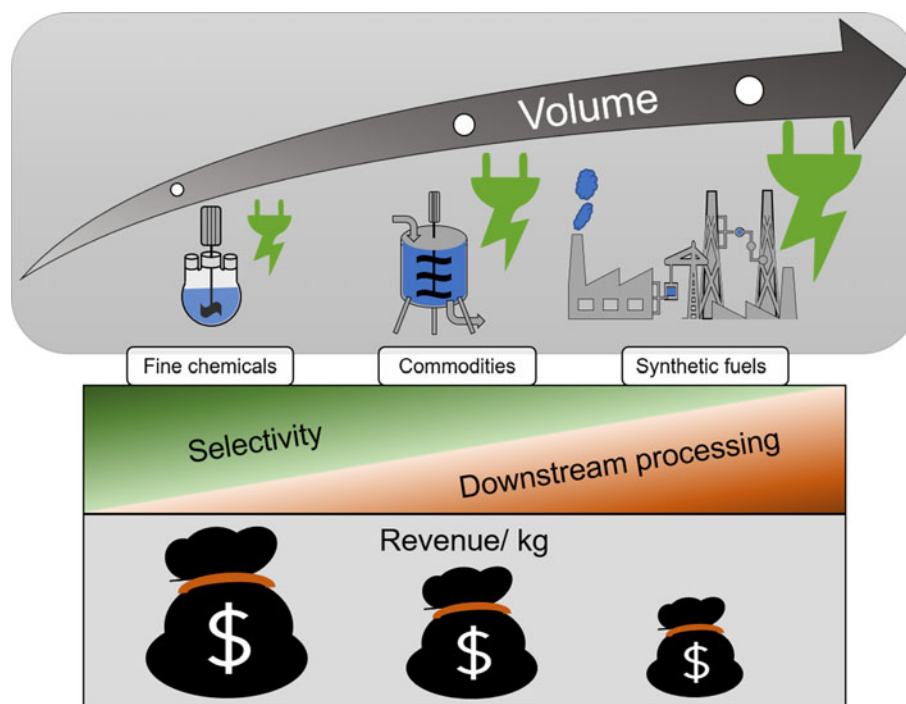
$$\text{EEC (kWh/kg)} = \frac{z * F * U_{\text{cell}}}{\text{CE} * M}$$

Where  $z$  is the number of electrons transferred per molecule,  $F$  is the Faraday constant,  $U_{\text{cell}}$  is the cell voltage,  $M$  is the molar mass, and CE is the current efficiency.

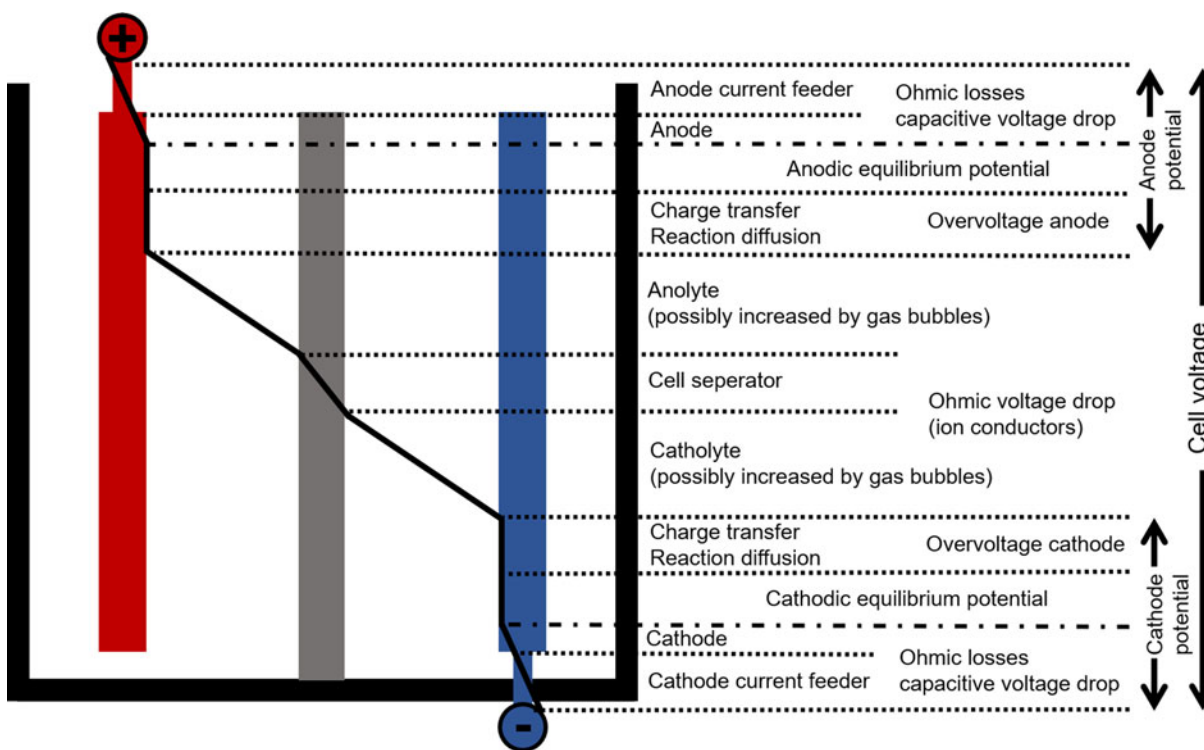
CE sets a target approaching 100% in order to maximize the performance. The current efficiency is calculated by the following equation:

$$\text{CE (\%)} = \frac{Q_{\text{theoret.}}}{Q_{\text{pract.}}} * \frac{n_{\text{product}}}{n_{\text{substrate}}} * 100\% = \frac{Q_i}{Q_{\text{total}}} * 100\%$$

The expression  $Q_i/Q_{\text{total}}$  is also known as the Faradaic efficiency (FE) that is used for the generation of a specific compound ( $Q_i$ ) divided by the total charge ( $Q_{\text{total}}$ ) that is applied during the reaction. In other words, it describes how much of



**Figure 1.** Characteristics of the different electro-organic products by volume of production, electricity, influence of crucial process aspects as selectivity and downstream processing, and revenue expected.



**Figure 2.** Individual contributions to the applied cell voltage and their locations in the electrochemical reactor.

the total charge is effectively used to produce the desired product. Therefore, it is a measure of the selectivity of the process. Reaching FEs (or CEs) close to 100% is challenging, especially for reductions in aqueous media, where the reaction of interest competes with the hydrogen evolution reaction. In general, the production of side products will always diminish the current efficiency.

As illustrated by the above equations, EEC depends on the efficiency of the conversion (CE) as well as the characteristics of the electrolyzer and the electrolyte, which influence the value of  $U_{\text{cell}}$ . Moreover, a reaction that involves the transfer of fewer electrons per mole of substrate will, of course, lead to smaller EECs as  $z$  contributes linearly to the EEC. In addition to the electric energy that is necessary to drive the electrochemical reaction, further energy might be required for heating, mechanical stirring, operating pumps, and downstream processing. The energetic efficiency (EE) characterizes the efficiency of converting electric potential into a desired product. It combines the Faradaic efficiency (FE) with the applied overpotential ( $\eta$ ), which is the deviation of the electrode potential ( $E$ ) from the equilibrium redox potential ( $E^\circ$ ).

$$\text{EE (\%)} = \frac{E^\circ}{E^\circ + \eta} \text{FE} = \frac{E^\circ}{E} \text{FE}$$

The overpotential may arise from the limiting rate of electron transfer (*electron transfer overpotential* - mainly at low current densities), from slow transport of reactants to the electrode surface (*diffusion overpotential*), and from the inability of the reaction itself to keep pace (*reaction overpotential*).<sup>10</sup> Obviously, when the overpotential is negligible small, the EE only depends on the efficiency of the electrochemical reaction, that is, the Faradaic efficiency. This consideration is providing only half of the information and becomes less valid when a high current density is applied. The system boundary for EE calculation does not include the applied cell voltage; therefore, an alternative definition of the energetic efficiency (EE') can be established as a more meaningful figure of merit:

$$\begin{aligned} \text{EE' (\%)} &= \frac{Q_i * (E_a^\circ - E_c^\circ)}{Q_{\text{total}} * (E_a^\circ + \eta_a - E_c^\circ + |\eta_c| + iR_{\text{cell}})} \\ &= \text{FE} * \frac{U^\circ}{U^\circ + \eta_a + |\eta_c| + iR_{\text{cell}}} \end{aligned}$$

where  $U^\circ$  is the equilibrium cell voltage. From the above equation, it can be concluded that EE' is maximized when the entire charge is used for the desired reaction (FE = 100%), when anodic and cathodic overpotentials as well as the cell resistance are small. However, an upscaled reactor cannot possess a negligible cell resistance, making the resistance of the cell one of the key aspects in optimizing the energy efficiency.

Furthermore, the applied current needs to be considered when maximizing the energy efficiency. It may influence the Faradaic efficiency as the selectivity is dependent on the applied current density. Furthermore, a faster electron transfer leads to

higher overpotentials and finally the numeric value for the current  $i$  determines the product  $iR_{\text{cell}}$ .<sup>11</sup>

## Conversion of CO<sub>2</sub> to synthetic fuels and commodity chemicals

The electrochemical production of commodity chemicals from CO<sub>2</sub> has become an emerging research field during the past decades. Via electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R), numerous products with large market sizes are potentially accessible (Fig. 3). The conversion of atmospheric or waste stream CO<sub>2</sub> to CO and hydrocarbons such as ethylene, formate, and ethanol is an attractive technique helping to close an artificial carbon cycle. Moreover, the usage of renewable energy leads to a second benefit: the conversion of electric to chemical energy enabling the storage of energy in the form of chemicals. In recent years, research of electrocatalysts and electrochemical cell design has led to significant improvements in selectivity and efficiency of the according reactions.

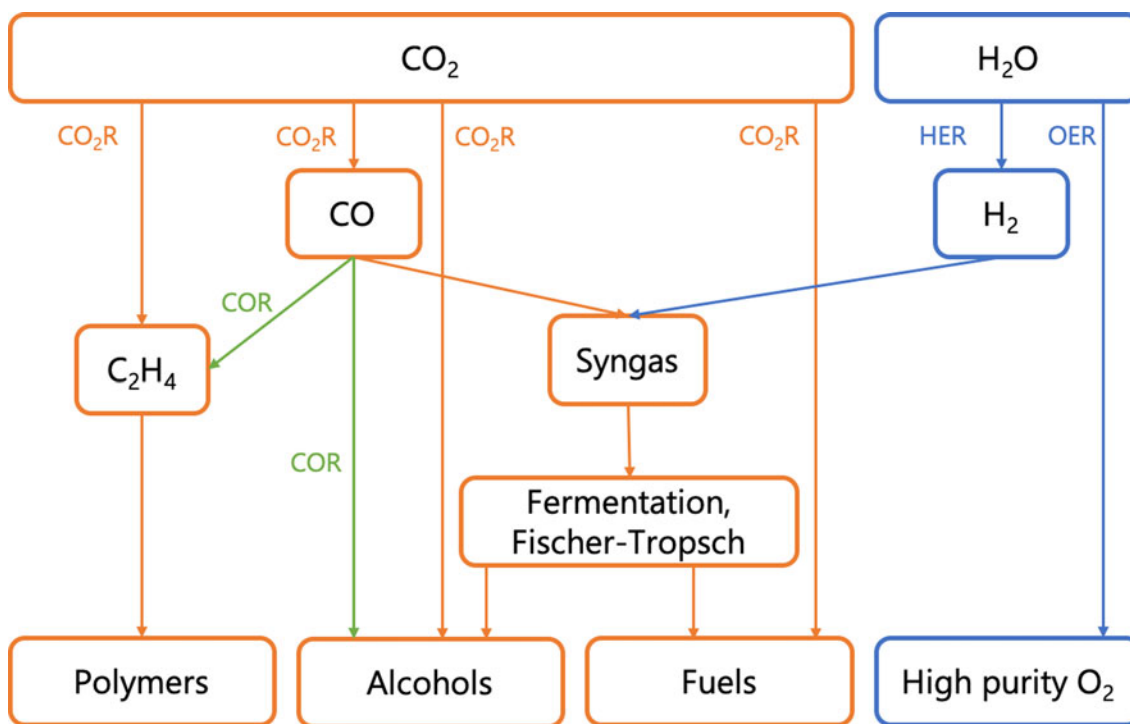
Research on the production of commodity chemicals from CO<sub>2</sub> mainly focuses on CO, formate, ethylene, and ethanol since they are accessible at relatively high Faradaic efficiencies.<sup>12,13</sup> While Ag and Sn catalysts are mainly used to reduce CO<sub>2</sub> to CO and formate, respectively, copper-based electrodes are applied for the production of chemicals with multiple C-atoms like ethanol and ethylene.<sup>14</sup>

Noteworthy, carbon electrodes are for the CO<sub>2</sub> reduction of limited interest due to their interface performance. Most carbon-based electrodes suffer from low electrocatalytic activity toward CO<sub>2</sub> reduction.<sup>15</sup> As electrochemical CO<sub>2</sub> reduction is mainly carried out in aqueous solutions, hydrogen is formed in a parasitic reaction. To overcome the poor solubility of CO<sub>2</sub> in aqueous media and to minimize the hydrogen evolution reaction at high current densities (>100 mA/cm<sup>2</sup>), gas diffusion electrodes are applied.<sup>16</sup>

Nevertheless, main challenges remain increasing the Faradaic efficiency of the desired products at high current densities. At the same time, the cell resistance needs to be minimized to keep the cell voltage as low as possible. However, only CO has been generated from CO<sub>2</sub> under stable conditions, at relevant current densities, and high Faradaic efficiency. Other products are obtained at significantly lower FEs, which contribute to the high energy consumption of the according products (Fig. 4). Even at low cell voltages, the EEC is substantial. For example, assuming an electric energy price of 0.1 €/kWh<sup>17</sup> and an operating voltage of 3 V, the electricity for 1 kg ethanol would cost approx. 7.5€, excluding the workup of the sophisticated electrolysis mixture.

A number of reviews have been dedicated to investigate whether the electrocatalytic production of commodity chemicals from CO<sub>2</sub> can compete with traditional, mainly fossil fuel-derived alternatives in terms of production cost.<sup>12,13,18,19</sup>

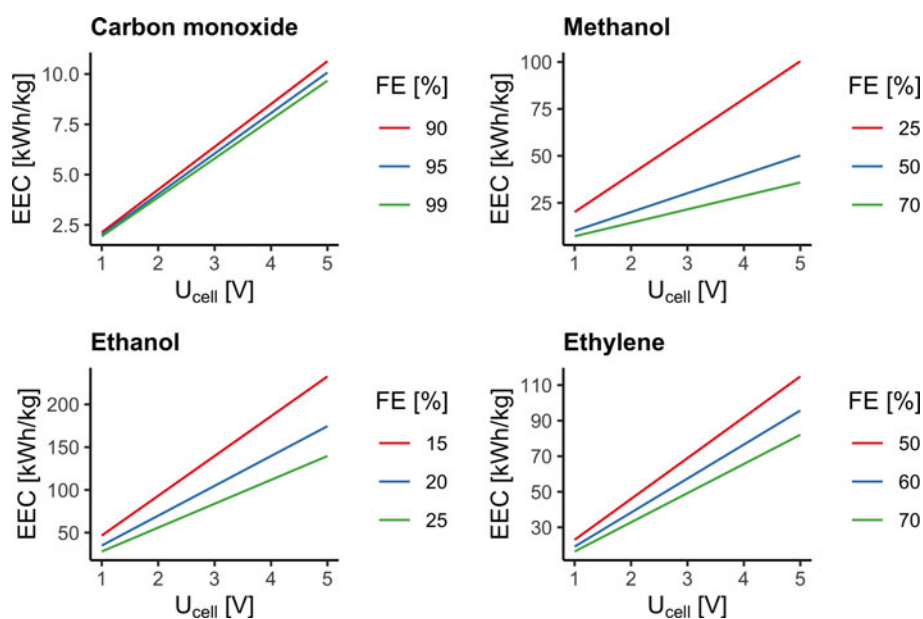
De Luna et al. address multiple challenges that have to be overcome in order to replace petrochemical processes. Inhibiting factors are limited energy conversion efficiencies of



**Figure 3.** Possible CO<sub>2</sub>R pathways to commodity products. COR: CO reduction; HER: hydrogen evolution reaction; OER: oxygen evolution reaction.

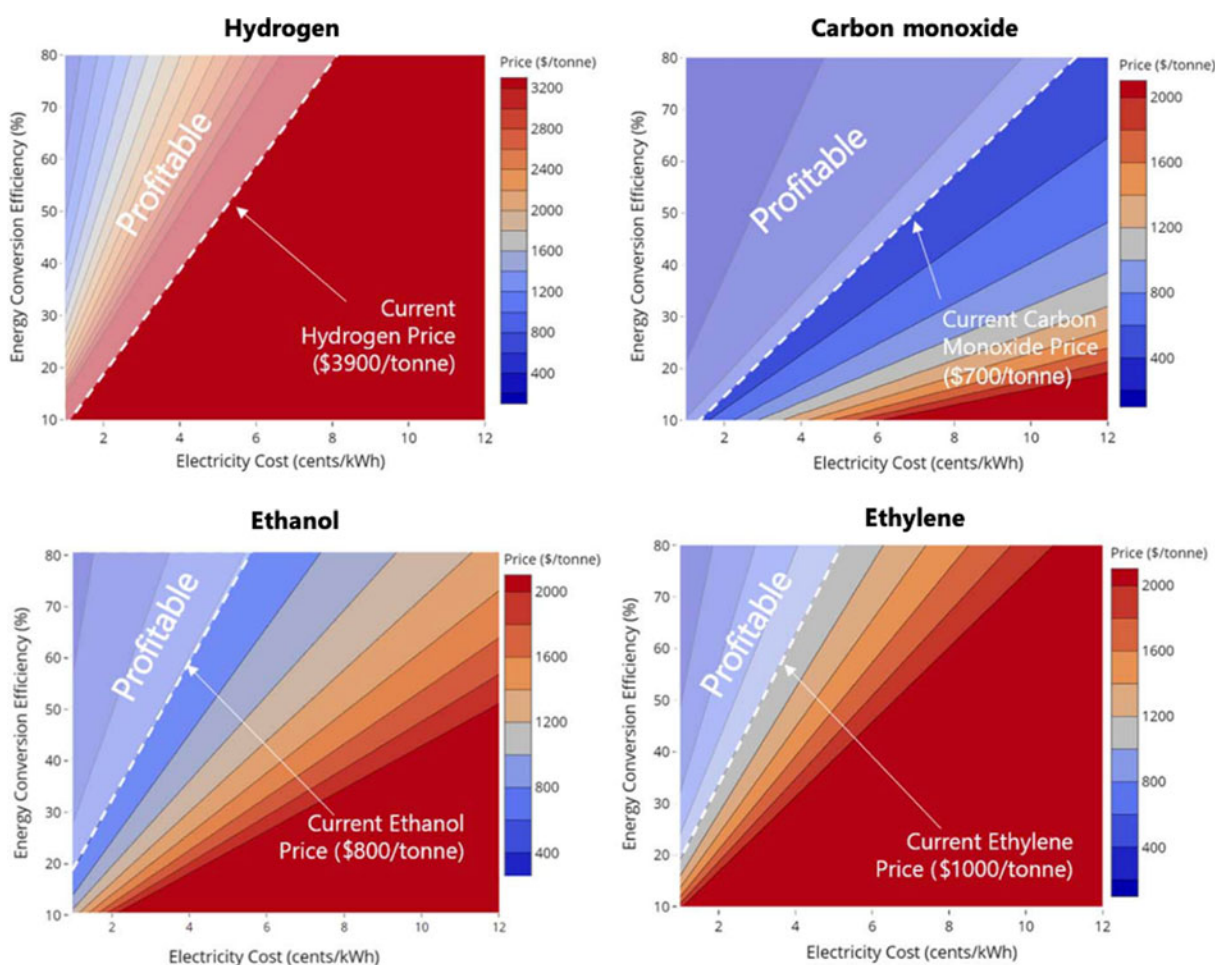
electrolyzers as well as the operating stability of these systems. Another key role plays the availability of low-cost renewable energy. The authors specify 4 cents/kWh as the maximum

electricity cost for a scenario where electrochemical approaches are competitive. Other challenges are costs for CO<sub>2</sub> capture and transportation. Especially, the large manufacturing scale and



**Figure 4.** EEC of CO<sub>2</sub> electroreduction products at different cell voltages and Faradaic efficiencies. The FE values are based on the current literature, only FE values at current densities >100 mA/cm<sup>2</sup> were considered, except for methanol which has not been produced at comparable current densities yet.





**Figure 5.** Production costs of electrosynthesized products. The graphs show techno-economic analyses of hydrogen, carbon monoxide, ethanol, and ethylene costs as a function of electrolyzer energy conversion efficiency (=energy efficiency EE defined in this review without the FE term) and electricity costs. The authors assume a pure CO<sub>2</sub> price of \$30/t, Faradaic efficiency of 90%, current density of 500 mA/cm<sup>2</sup>, electrolyzer costs of \$300/kW, and plant lifetime of 30 years. The area above the white dashed line in lighter color indicates profitable production costs based on average global prices. From [13]. Reprinted with permission from AAAS.

the saturation and complexity of the market for commodity chemicals such as ethylene are major barriers for the new technology.<sup>13</sup> From all CO<sub>2</sub> reduction products, CO appears to have the highest chance for an industrial implementation (Fig. 5).

In the scenario calculated by De Luna et al., the electricity cost must not exceed approx. 5 cents/kWh, even at high energy conversion efficiencies as high as 80% for ethanol and ethylene to be economic. Also, the values for Faradaic efficiencies of 90% and current densities of 500 mA/cm<sup>2</sup> are rather optimistic, making the profitable region for ethylene and ethanol even more difficult to reach. The high current densities will lead to a substantial hydrogen evolution, which lowers the FEs for CO<sub>2</sub> reduction products. Therefore, FEs of 90% for ethanol and ethylene can be considered a best-case scenario. CO<sub>2</sub> reduction to CO is already feasible at high Faradaic efficiencies (>90%) using Ag catalysts as there is no C-C bond formation

involved, which can potentially lead to side products. Also, high current densities above 200 mA/cm<sup>2</sup> have already been demonstrated.<sup>20</sup> In contrast, CO<sub>2</sub>R to methanol suffers from low efficiencies and has mainly been reported at current densities below 50 mA/cm<sup>2</sup>.<sup>21,22</sup> Hybrid processes, which combine thermocatalytic and electrocatalytic transformations to methanol, might be more promising until FEs and current densities for CO<sub>2</sub>R to methanol are significantly increased, at least two orders of magnitude higher than current laboratory results (currently less than 50% FE and currents below 50 mA/cm<sup>2</sup>).<sup>23</sup>

Among the accessible products from CO<sub>2</sub>R, CO and formic acid come along with the highest revenue per mole of electrons.<sup>12</sup> However, most CO<sub>2</sub>R reactions are carried out in basic media with formic acid being present as formate. The follow-up step to generate the protonated form might consume equal amounts of acid, making the process

uneconomical. Other challenges addressed by Chen et al. are the high capital costs (approx. \$300/kW<sup>13</sup>) and the associated risks that come with the large production scale of commodity chemicals. Furthermore, pure CO<sub>2</sub> is a bulk chemical itself and providing CO<sub>2</sub> in adequate quality represents a substantial hurdle.<sup>12</sup>

The electrochemical production of commodity chemicals like CO, formate, ethanol, and ethylene from CO<sub>2</sub> needs to meet several requirements in order to be a sensible and competitive technique, including the following aspects:

1. The electricity used has to originate from a carbon-neutral source. Burning fossil fuels in order to generate electricity with the goal of reducing CO<sub>2</sub> electrochemically is not useful.
2. High Faradaic efficiencies at low overpotentials and high current densities are necessary, combined with a low applied cell voltage.
3. CO<sub>2</sub> needs to be converted at high manufacturing scales, both to benefit from the economy of scale and to be able to enter the market of commodity chemicals.
4. Price for renewable electricity must not exceed a threshold (relative to prices for fossil fuels) in order to make CO<sub>2</sub>R economical. For example, De Luna et al. specify \$0.04/kWh as threshold.<sup>13</sup>
5. CO<sub>2</sub> reduction plants have to be flexible in terms of electricity supply. To make the best use of intermittent energy sources, the CO<sub>2</sub> electrolyzers should allow running at higher capacities when a surplus of energy is available (which leads to lower energy prices).

Products of higher complexity than ethanol, ethylene, CO, and formate may not have to compete directly with the fluctuating and highly complex fossil fuel market. In those cases, the implementation of electrochemical approaches can be beneficial compared with traditional chemical routes, as we will show for the Baizer and Lysmeral processes.

## Industrially implemented processes

In comparison to traditional chemical processes, electrochemistry offers many advantages as the easy accessibility of appropriate reagents and the controlled reaction. For industrial processes, advantages as the avoidance of reagent waste, the adjustable reaction speed, and power are important aspects. One emerging view is the possibility of using renewable energy as a driving force for a specific and selective conversion. Furthermore, electrochemistry is inherently safe and reduces

the use of rare elements and metals. The performance of speed up the catalytic cycles is given by using electricity and avoiding of runaway reactions is possible.

Numerous companies have tried to exploit these advantages. To limit the size of the electrolysis cells, the current densities are kept in a range of 10–30 mA/cm<sup>2</sup>.<sup>24</sup> Following the conversion, a work-up strategy as the separation of the products from unreacted reactants and electrolytes should be developed. The supporting electrolyte is an important factor, because it should be compatible with wastewater and explosive precipitates (e.g., from perchlorates) need to be avoided.

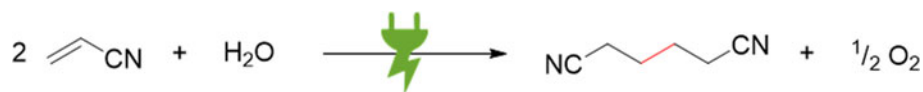
The following section describes two brilliant electro-organic methods, which could be considered as landmarks.

### Baizer process

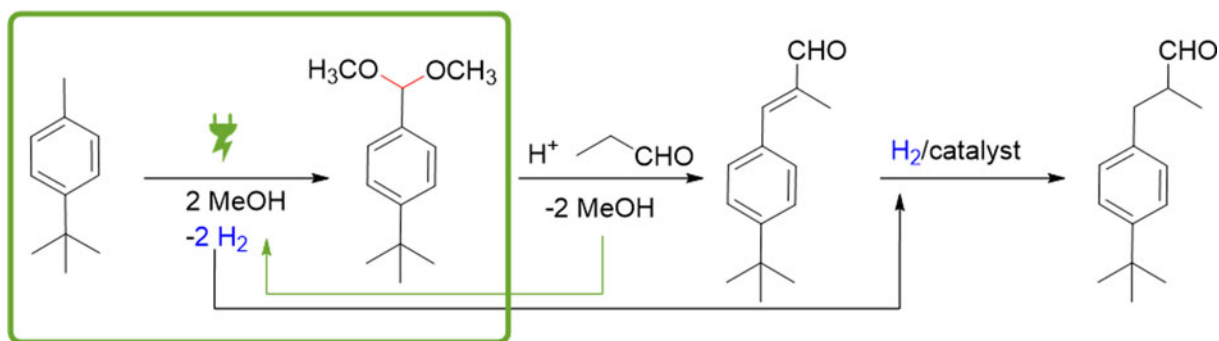
The Baizer process is one of the biggest and most important industrial electro-organic synthesis methods with a market size within the past two decades of 300,000 tons/year.<sup>25</sup> In 1960, the electro-organic chemist Manuel M. Baizer was working at the company Monsanto's Technical Center in Florida, because of this the process is also called Monsanto process. In the early 1970s, the Baizer process was a milestone in electrochemistry. After reduction of acrylonitrile, the product is adiponitrile, which represents a central intermediate to manufacture polyamides but also polyurethanes (Scheme 1).<sup>24</sup>

To produce adiponitrile, a cathodic electro-hydrodimerization of acrylonitrile is required. The break-through of this process was in an undivided work cell by using quarternary ammonium salts such as tetraethylammonium *p*-toluenesulfonates as supporting electrolytes which led to mass yields of 90%. Before that, a divided cell with an aqueous catholyte mixture of acetonitrile and adiponitrile in tetraethyl ammonium sulfate and an anolyte of diluted sulfuric acid was used.<sup>9</sup> Because of their high overpotential, cadmium or lead electrodes were used, and the anode had an alloy of silver.<sup>24</sup> The cadmium cathodes were partially replaced by copper-lead alloys or stainless steel because of the significant environmental issues. The current densities were high with 4.5 kA/m<sup>2</sup>.

The problem of the prior process was that, because of high current densities, the cathodes were not stable and caused high maintenance costs. The undivided cell, in comparison with a divided cell, provided a better performance and the cost of electric energy for the conversion was lower. With such cells, the energy consumption was reduced. The cell voltage decreased from 11.65 to 3.83 V, and the specific energy consumption was reduced from 6.61 to 2.43 kWh/kg which is an improvement in electric efficiency of approx. 40%.<sup>25</sup> The



**Scheme 1.** Used technical electrochemical process called Baizer process: electro-conversion of acrylonitrile in industrial processes.



**Scheme 2.** Anodic dimethoxylation reaction within the Lysmeral process.

current efficiency is above 90%. Significant in the process is the use of water as the hydrogen source. Molecular oxygen and propanitrile are the byproducts. The production of oxygen is one safety problem because of the possibility to corrode metals and react with other chemicals. Additionally, oxygen needs a departure in the used cell to avoid a pressure increase. Nevertheless, the separation of the resulting biphasic electrolyte-adiponitrile mixture facilitates the downstream processing. The crude adiponitrile is purified by distillation, whereas the electrolyte fraction is enriched with water and acrylonitrile prior returning to electrolysis.<sup>9</sup>

Baizer extended the hydrodimerization to a variety of activated olefins.<sup>26</sup> The initial scientific discovery happened almost 20 years prior Baizer implemented the process and demonstrates the power of chemical engineering and process development to translate such research onto an industrial scale.<sup>6,27</sup>

### Lysmeral process

The company BASF is using electro-organic synthesis on an industrial scale. One of their most important electric conversions is to afford protected benzaldehydes. The technically most relevant intermediate reacts with propanal and via subsequent hydrogenation to Lysmeral. The electrochemical synthesis of this benzaldehyde equivalent is conducted in several 10,000 tons/year. For the production of the protected benzaldehyde, 4-*tert*-butyltoluene is dimethoxylated at a graphite anode (Scheme 2).

Lysmeral is a fragrance and smells like lily of the valleys.<sup>28</sup> Methanol is used as solvent and reagent. One important point is the recovery of methanol by condensation reaction with propanal within the subsequent step. The hydrogen formed by the electrolysis could be partially used in the hydrogenation reaction. Another product of such anodic dimethoxylation is anisaldehyde. It is used as intermediate for drug synthesis or as fragrance to cover unpleasant odors, for example, in sanitary applications. For the anodic dimethoxylation, BASF designed a bipolar packed electrode stack, which is called capillary gap cell. Versatile electrode materials such as graphite, platinum, and mixed-oxide electrodes can be used, whereas graphite

represents the working horse. The reaction temperature is 50 °C, the current density is 4.2 A/dm<sup>2</sup>, and yields up to 78% for the acetal are reached. The process shows a high selectivity with 91%. The theoretical required charge is 4 F, and the applied charge is 4.5 F. The current efficiency is up to 70%.<sup>29</sup> With a voltage of 4 V, the calculation of the EEC resulted in 2.94 kWh/kg. Assuming an electric energy price of 0.1 €/kWh,<sup>17</sup> the electricity for 1 kg Lysmeral would cost approx. 0.29 €, excluding the workup. Meanwhile, the cell design is used in a number of technical processes, for example, in water treatment.<sup>30</sup>

In consideration of the two aspects: selectivity and downstream cost, companies such as Monsanto with Baizer and BASF with Lysmeral were able to implement important industrial electrochemical processes with high performance.

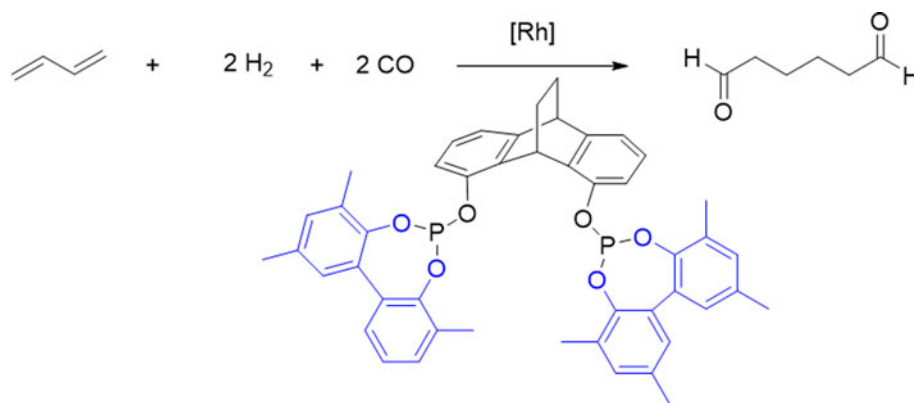
### Current state of art

Meanwhile, electro-organic synthesis is successfully explored at a laboratory scale. With new approaches, it is possible to achieve the C-C-bond formation in excellent yields and exclusive selectivity.<sup>31,32</sup>

Here, some innovative syntheses of symmetric and mixed biphenols and phenol-(hetero) arenes using dehydrogenative cross-coupling strategies will be introduced. Cross-coupling products and nonsymmetric biaryls represent valuable products in organic synthesis. Biaryls are utilized in the synthesis of natural products, catalysis, and material science.<sup>33</sup> An important application of biphenols is their usage as ligand components in transition metal catalysis.<sup>34,35</sup> 3,3',5,5'-Tetramethyl-2,2'-biphenol is one of these useful building blocks but challenging in its synthesis. This biphenol is used, for example, as a ligand precursor for copper<sup>34</sup> or rhodium<sup>36</sup> in catalytic asymmetric addition of an alkyl radicals to a double bond. One of the most important applications is the oxo synthesis for the production of oxo chemicals (Scheme 3). Technically, such biphenols have their main application area in hydroformylation producing about 10.4 million tons/year of oxo chemicals.<sup>37,38</sup>

The classical synthesis of this biphenol needs stoichiometric or even more oxidizing agent. With the conventional method, a





**Scheme 3.** Twofold hydroformylation of 1,3-butadiene.

large amount of reagent waste is generated, and the selectivity and yields might be low. Another synthetic approach uses transition metal catalysts as  $\text{VO}(\text{acac})_2$ , methyltrioxorhenium, or  $\text{RuCl}_3$ .<sup>39–41</sup> However, with the transition metal method, the yields are also often low. Additionally, the used catalysts are mostly expensive and toxic. The conventional chemical route can neither be considered ecological nor economical.

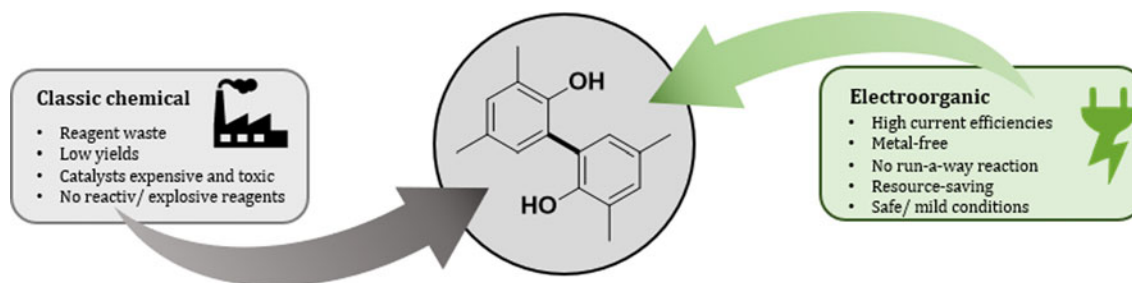
Regarding the current global challenges as climate change and resource scarcity, the interest in renewable technologies for chemical industry increases. With electro-organic synthesis, some of these issues can be successfully tackled. Electrochemistry uses only electrons as clean reagent for oxidation or reduction

processes. Avoiding amounts of catalysts and oxidizing or reducing agents are significant for sustainability strategies (Fig. 6).

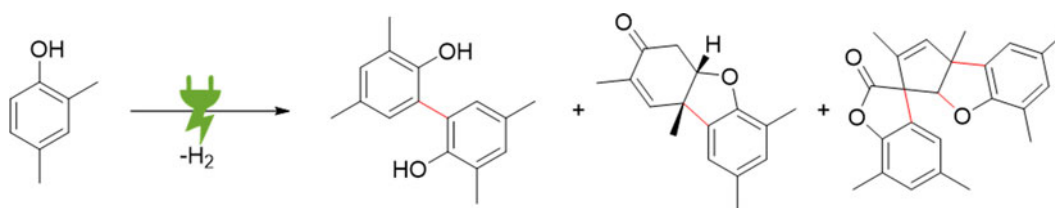
The following will show the electrochemical development for a synthetic strategy to produce 3,3',5,5'-tetramethyl-2,2'-biphenol. In the conventional synthetic approaches, overoxidation and the formation of different polycyclic derivatives, for example the Pummerer ketone, are unavoidable (Scheme 4).<sup>42–45</sup>

To prevent other byproducts and overoxidation, a two-step synthesis via tetraphenoxy borates is used (Scheme 5).<sup>46</sup>

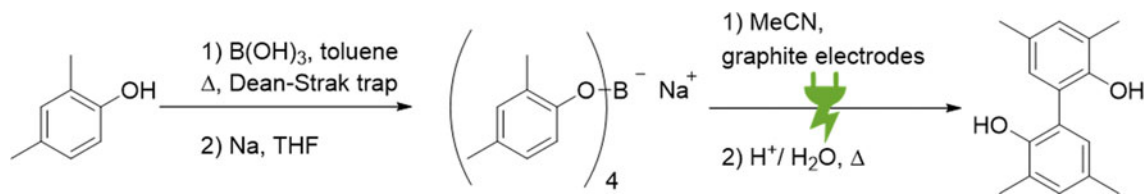
The borates are used as templated substrates for oxidative cyclization as well as a supporting electrolyte.<sup>42,47</sup> Yields up to 85% are achieved even in a multi-kilogram scale.<sup>48</sup> However, this



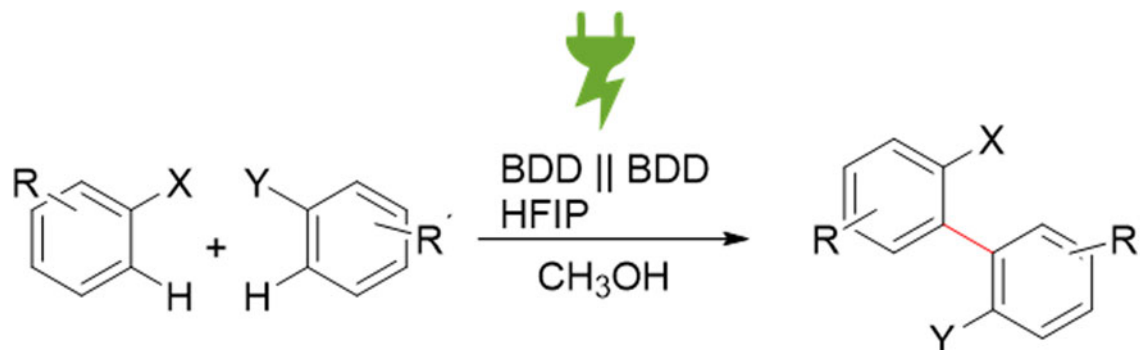
**Figure 6.** Advantages of electrochemical methods in comparison to conventional organic chemistry.



**Scheme 4.** Synthetic strategy to 3,3',5,5'-tetramethyl-2,2'-biphenol and polycyclic derivatives.



**Scheme 5.** Two-step synthesis via boron-tethered phenolates for anodic phenol-coupling.



**Scheme 6.** Phenol/aniline-arene cross-coupling. X = OH, NHR; Y = H, OH, NHR, OTIPS.<sup>33</sup>

electrosynthesis generates borate containing wastewater which is problematic within the EU. In addition, the process is a multi-step protocol. In order to reduce the multi-step protocol, the first direct way for the anodic cross-coupling of phenols without using leaving functionalities, protecting groups, or reagents was introduced in an undivided cell with a boron-doped diamond (BDD) anode and nickel as a cathode.<sup>49</sup> Either hexafluoroisopropanol (HFIP) or HFIP/methanol is used as an electrolyte with methyl triethylammonium methylsulfate as a supporting electrolyte. By using HFIP-based electrolytes, a high selectivity is achieved.<sup>50</sup> Working with BDD electrodes in combination with

HFIP as a solvent showed a high performance and robustness.<sup>51</sup> In protic media, the electrochemical window is extended with HFIP at BDD electrodes to 5 V. HFIP has a stabilizing effect on anodically generated radicals, so the decomposition of reactants is avoided.<sup>51</sup> Additionally, the recovery and direct reuse of this solvent is almost completely achieved.<sup>31,52</sup> BDD has unique properties such as a high chemical stability and high hydrogen overpotential in aqueous solutions. Due to its properties, BDD opens a wide field of new synthetic strategies.<sup>53,54</sup>

The method was improved by using HFIP with 5 vol.% pyridine as an electrolyte and electrolysis was conducted with a

**Table 1.** Products obtained by electrochemical CO<sub>2</sub> reduction and associated energy consumption.

Reaction	Faradaic efficiency <sup>a</sup> (%)	EEC (kWh/kg) <sup>b</sup>	Electricity costs <sup>d</sup> (€/kg)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	90–99 <sup>20</sup>	5	0.5
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH}_{(\text{aq})} + \text{H}_2\text{O}$	<sup>c</sup> 25–70 <sup>21,22</sup>	20	2.0
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH}_{(\text{aq})} + 3\text{H}_2\text{O}$	15–25 <sup>59,60</sup>	75	7.5
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4_{(\text{g})} + 4\text{H}_2\text{O}$	50–70 <sup>61,62</sup>	50	5.0

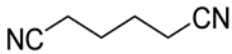
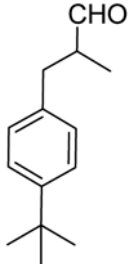
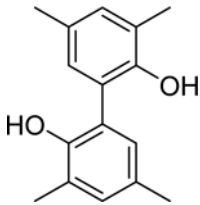
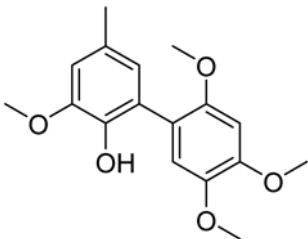
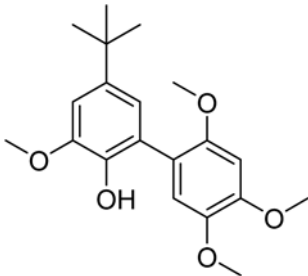
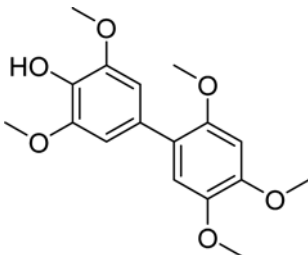
<sup>a</sup>Data regarded as reasonable based on the literature. Only current densities >100 mA/cm<sup>2</sup> were considered.

<sup>b</sup>Hypothetical cell operating voltage = 3 V, highest FE of range assumed.

<sup>c</sup>Current densities higher than 50 mA/cm<sup>2</sup> have not been reported.

<sup>d</sup>Assumed electricity price = 0.1 €/kWh.

**Table 2.** Energy consumption in the electrosynthesis of chemicals.

Process	Products	Current efficiency (%)	EEC (kWh/kg) <sup>a</sup>	Electricity costs <sup>b</sup> (€/kg)
Baizer		90	2.43	0.24
Lysmeral		70	2.94	0.29
Anodic homo-coupling		71 <sup>58</sup>	0.93 <sup>b</sup>	0.09
Anodic cross-coupling		69 <sup>57</sup>	0.77 <sup>b</sup>	0.08
Anodic cross-coupling		60 <sup>57</sup>	0.77 <sup>b</sup>	0.08
Anodic cross-coupling		62 <sup>57</sup>	0.81 <sup>b</sup>	0.08

<sup>a</sup>Operating at average terminal cell voltage = 3 V.

<sup>b</sup>Assumed electricity price = 0.1 €/kWh.

current density of 60 mA/cm<sup>2</sup>. By using pyridine as a base, salt-based additional supporting electrolytes are avoided. This is a big advantage over previous works because an expensive supporting electrolyte recovering is prevented. The flow process is very efficient, has satisfactory yields up to 59%, and is suitable for technical processes.<sup>7,55,56</sup> The lower yield is beneficial for the sake of recovery and reuse of starting materials. Particularly, the presented reaction could be used industrially since important key steps have already been developed. Especially, the application of a flow cell is superior to conventional batch reactions. In the flow cell, the electrode surface to volume ratio can be improved by the narrow gap design. Because of this setup, the electrolysis time is reduced, the temperature control is possible, and the cell voltage can be lowered. Due to the small electrode distance, no conducting salt is necessary.<sup>56</sup> By the flow rate, the contact time of the reactant with the electrode surface can be controlled and overoxidation is avoided. These advantages offer about 40% more electric efficiency.

Other anodic carbon-carbon bond formations, for example, with aniline-arenes are also possible. Over 70 derivatives are known with yields up to 92%. For high selectivity, a bipolar electrode arrangement is used.<sup>33,57,58</sup> Only the outer electrodes are connected, and the electrodes in between are polarized by the electric field. The electrode surface is drastically enhanced by this approach. Furthermore, using bipolar cells has the advantage that the number of electrodes can be varied and used flexible in different cells (Scheme 6).

## Conclusions

Electro-organic synthesis has experienced a renaissance during the past years, as it offers conversions under mild conditions, replaces chemical oxidizing and reducing agents, and opens up novel synthesis routes and strategies. From an industrial point of view, the energy efficiency or energy demand plays a key role. The electrochemical production of synthetic fuels and commodities from CO<sub>2</sub> is mainly challenged by high capital costs, the price of electric energy, and the enormous size of the petroleum-based market. Furthermore, it takes comparatively high amounts of charge to produce C<sub>2+</sub> products from CO<sub>2</sub>. For example, in order to generate one mole of ethanol from CO<sub>2</sub>, 12 electrons are needed, which is substantially higher compared to fine chemical synthesis, where usually less than 5 electrons are transferred per product molecule which exhibit substantially larger molecular weight. The amount of charge contributes to the high EEC (Table 1).

Other than platform chemicals and synthetic fuels, electrochemically synthesized fine chemicals do not have to compete with the feedstock of crude oil itself. They are higher priced and at the same time produced more selectively and at lower scales, which lead to smaller capital costs.

In comparison to the CO<sub>2</sub> conversion, the discussed industrial processes show significantly lower EECs per kg product (Table 2). Since, on the laboratory scale, multi-purpose cells

were employed and not as on a technical process the energy optimized and tailor-made electrolyzer, the energy efficiency on a laboratory scale is usually significantly lower.

In cases where large amounts of chemical oxidizing and reducing agents can be avoided, an electrochemical approach is highly favorable. The downstream processing is often neglected but is crucial for a later translation into technical use, as outlined with the formation of borate containing wastewater. The application of stabilizing agents like HFIP opens up new synthesis strategies, reaching increased selectivity and in turn higher energy efficiency as well.

The chemical route from CO<sub>2</sub>-based commodities to fine chemicals still provides a gap, as building complex molecules from CO<sub>2</sub> is challenging. A more efficient approach might be fermentation. The electrochemical generation of aromatic structures from CO<sub>2</sub> cannot be achieved directly; however, aromatic compounds would be accessible by reforming of CO<sub>2</sub>-based hydrocarbons.

We conclude that electro-organic synthesis is more likely to pay off when fine chemicals rather than commodities are produced. Capital costs, energy prices, and downstream processing are driving factors. The margin becomes more favorable when the costs for electrolyzers and downstream processing are low, and the product can be sold for a high price, which is the case for fine chemicals.

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