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From CO₂ to formic acid fuel cells

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KEYWORDS

CO₂, Formic acid, Fuel Cell, DFAFC, stack

ABSTRACT

Formic acid is a liquid, safe and energy-dense carrier for fuel cells. Above all, it can be sustainably produced from the electroreduction of CO₂. The formic acid market is currently saturated and it would require alternative applications to justify additional production capacity. Fuel cell technologies offer a chance to expand it while creating an opportunity for sustainability in the energy sector. Formic acid-based fuel cells represent a promising energy supply system in terms of high theoretical open-circuit voltage (1.48 V). Compared to common fuel cells running on H₂ (e.g., proton-exchange membrane fuel cells), formic acid has a lower storage cost and is safer. This review focuses on the sustainable production of formic acid from CO₂ and on the detailed analysis

of commercial examples of formic acid-based fuel cells, in particular direct formic acid fuel cell stacks. Designs described in the literature are mostly at the laboratory scale, still, with 301 W as the maximum power output achieved. These case studies are fundamental for the scale-up, however, additional efforts are required to solve crossover and increase performance.

1. Introduction

CO₂ accounts for over 80% of the global anthropogenic greenhouse gas (GHG) emissions that contribute to climate change ¹. Fossil fuel combustion is the largest contributor to the CO₂ released into the atmosphere. For instance, fossil fuel combustion represents over 75% of the total CO₂ emissions in the United States ². Transportation is the largest contributor to CO₂ emissions, with an estimated 15% share globally ³, with peaks over 30% for some countries, such as the United States. ² After transportation, electric power, industrial and residential sectors are the ones with most CO₂ emissions ².

A downstream CO₂ capture/conversion technology (CO₂ sink) would reduce the GHG concentration in the atmosphere. To sink CO₂ resulting from fossil fuel combustion, the first stage is CO₂ capture ^{4,5} and then either its storage ⁴ or conversion to fuels and chemicals ⁶⁻⁸. A more or less appropriate approach to decrease CO₂ emissions depends on the sector and follow technological trends ⁹. For instance, in the transportation sector, electrification ¹⁰ through plug-in hybrid electric vehicles (PHEVs) and plug-in electric vehicles (PEVs) equipped with efficient Li-ion batteries ^{11,12} seems the most viable short-term option. In the electric power sector, renewable energy feeding smart electricity grids in distributed energy generation (DEG) systems have the potential to replace traditional electricity power plants and decrease CO₂ emissions ¹³. For the

industrial sector, process intensification (PI) technologies promise to decrease energy requirements from 20 to 80 % ¹⁴, with a corresponding reduction in GHG emissions ^{9,15}.

Global sales of electric vehicles (EVs) expanded from less than 10,000 units in 2010 to 2.2 million in 2019 ^{16,17}. Breakthroughs in electrochemical energy storage technologies contributed to its rapid development over the last decade ¹⁶. EVs have a huge potential market. Tesla and Nissan are established EV global players ¹⁸, while BMW ¹⁹ and Volvo ²⁰ have committed to invest in electric cars and fuel-cell research. EVs are an environmental-friendly alternative to fossil fuel powered vehicles (especially when the electricity comes from a renewable source). Although EVs powered by Li-ion batteries dominate the market, issues concerning their energy storage capacity, safety and cost encouraged a shift towards alternative technologies such as fuel cells (FC) ¹⁶. A FC requires a continuous source of fuel (chemical energy) and oxygen (or air) to sustain the redox reactions. FC technology prevents environmental pollution and provides environmentally friendly energy ²¹. Furthermore, it offers practical benefits over batteries with high energy density and requires only 5 to 10 minutes for a full recharge ^{22,23}. FA is a candidate fuel for FC applications that may in turn be produced from CO₂, thus also contributing decreasing greenhouse gases in the atmosphere.

Electrochemical reduction can convert carbon feedstock into liquid fuels such as formic acid (FA) and alcohols. The CO₂ to FA transformation occurs in the presence of post-transition metal catalysts such as Sn, Pb, and Bi ^{24,25}, but it occurs on Cu as well ²⁶. While there are various methods of storage and conversion to fuels and chemicals from CO₂, this review focuses on FA from CO₂ as a green feedstock for FC ⁶⁻⁸. Despite the rise of electricity-driven technologies and the production of FA from green feedstock, the FA market is still limited and the demand is currently

saturated, unless new technologies requiring it reach commercial maturity. FA fuel cells (FAFC) will likely be one of these technologies. FA is a small molecule that does not require storage at high pressure and it feeds directly the FC, without the need for a catalytic reforming unit²⁷. Since FA represents a form of carbon-based energy from CO₂ and H₂, it is an ideal feedstock for FCs to produce electricity and reduce environmental impact. Specifically, direct FA fuel cells (DFAFC) are attractive for small portable FC applications and promising for automotive batteries by vehicle electrification^{28–30}. DFAFC have the potential for a carbon neutral cycle where CO₂ is first captured and then transformed into FA through an electrolyzer (Figure 1). Afterwards, FA is used in the FC to generate electricity and power vehicles, reemitting the previously captured CO₂. The carbon neutrality of this cycle clearly depends on leveraging renewable sources to produce electricity (e.g., photovoltaic, wind, hydro-electricity, etc.).

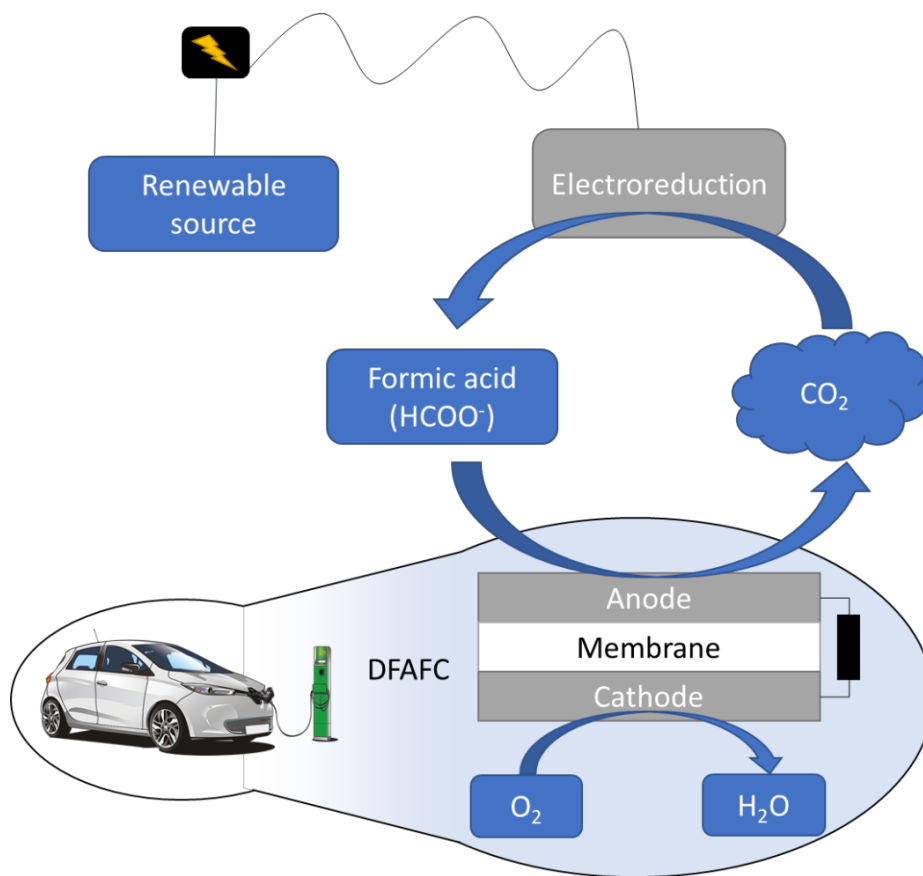


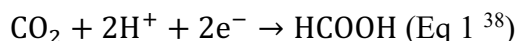
Figure 1 Simplified life cycle of CO₂ through an electroreduction unit and a DFAFC.

In 2009, Yu and Pickup reviewed the state of the art on DFAFC, focusing on anodic catalysts, and fuel crossover through Nafion® membranes ³⁰. They point out that micro-FCs have a greater commercial potential than conventional batteries as they deliver more energy per volume and weight ³⁰. In another review, Rees and Compton cover DFAFC with an emphasis on anode and cathode materials, and fuel crossover relative to membranes, where fuel crossover causes the fuel to move from the anode to the cathode ³¹. They concluded that the available catalysts either had high performance and short longevity or vice versa, with one of the main aspects deactivating them being acid corrosion and poisoning by CO and by-products ³¹. Since 2011, new literature data on DFAFC and innovative technologies have become available. Soloveichik reviewed liquid direct FC, including alcohols, FA and other fuels ³². In 2017, Fukuzumi's evaluated the photocatalytic production of different solar fuels (methanol, formaldehyde, and FAs), and the theory and chemistry behind their application in FC ³³. All the reviews cited above, agree on the potential of DFAFC as portable electronics in a not too far future, mainly due to their limited fuel crossover, and high-power densities at low temperature.

In this review, we examine the potential of FA production from CO₂, targeting the progress in the field of DFAFC since Rees and Compton's 2011 review. This review presents the trending choices for anode and cathode materials, and the scale-up efforts of DFCAFC in the form of electrolytic stacks, which the literature has not yet covered. We also present the major issues limiting the spread of this technology and the impact on FA market, as well as the options in terms of FCs technology.

2. CO₂ electroreduction to formic acid

FA is typically produced by the reaction between methanol and CO in the presence of a strong base, followed by methyl formate hydrolysis ³⁴, hydrolysis of formamide, and acidolysis of formate salts ³⁵. The production of FA from renewable sources, either from biomass ³⁶ or from CO₂ brings environmental benefits while reducing our dependence on fossil fuels ³⁷.



In CO₂ electroreduction, cell conditions are neutral to alkaline in most cases, and formate (HCOO⁻) is thus produced. Lowering the pH then generates FA. Several papers refer to FA, while they actually produce formate. The conversion of formate to FA is unrelated to electrochemical performance. For simplicity, we will refer to “FAFCs” herein.

Most literature data on the CO₂ electroreduction refer to H-cells (simplest devices for quick electrochemical tests, so called for the typical H-shape). However, from an industrial standpoint, there is a growing interest in flow cells mostly because of increased mass transfer ³⁹. Several H-type and flow cells from literature report Faradaic efficiencies of more than 80 % for large current densities (Table 1).

Table 1 Examples of recent CO₂ electroreduction.

Catalyst	Electrolyte	Potential (V vs RHE)	Faradaic efficiency toward FA (%)	Current density (mA/cm ²)	Reference
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Nanotube derived - Bi	0.5 KHCO ₃	M	-0.61 V	100	288	40
nBuLi-Bi	Porous solid electrolyte		-0.77 V	97	450	41
Ultrathin nanosheets	Bi 0.5 NaHCO ₃	M	-1.5 V	95	11	25
Sulfur-doped indium	0.5 KHCO ₃	M	-0.98 V	93	~60	42
Chain-like mesoporous SnO ₂	0.1 KHCO ₃	M	-1.06 V	95	13.6	43
Sn nanoparticles (commercial)	Catholyte-free and 1 M KOH anolyte		-0.2 V	93.3	51.7	44
Bi-PMo nanosheets	0.5 NaHCO ₃	M	-0.86 V	93	30	45
Electrodeposited Bi dendrites	0.5 KHCO ₃	M	-1.0 V	92	38.1	46
Boron-doped Sn	1 M KOH		-0.72 V	91	65	47
Bi/C nanoparticles	1 M KOH		-	89.2	45	48
Sn-based	0.1 – 1 M KHCO ₃		-	90	~30	38
Carbon supported SnO ₂	0.4 M K ₂ SO ₄		-	90	500	49
2D-Bi	Deionized water (solid electrolyte)		-0.79 V	90	30	50
Sn/SnO _x	0.1 KHCO ₃	M	-1.2 V	89.6	11.2	51
Sn plate	0.1 Na ₂ SO ₄	M	-1.35 V vs SCE	82.5	-	52

Sn plate	0.125 – 0.5 M K ₂ SO ₄	-	80	~30	⁵³
Tin (Sn) oxide - C	Deionized water only	-	80	200	⁵⁴

Previous relevant works are presented by Han et al. ⁵⁵

H-cells are an appropriate set-up to screen and compare catalysts. However, there are several issues preventing the scalability of the system, i.e. poor solubility of CO₂ in water and aqueous electrolytes, as well as limited diffusivity towards the electrode. Between 2007 and 2017, more than 1,000 research articles report catalysts analyzed on H-cells; however, only 21 articles report on flow cells for CO₂ reduction ⁵⁶. Commercially-viable systems to convert CO₂ to FA require current densities of at least 200 mA/cm² stable over time ⁵⁶ and higher for more compact electrodes, driving the overall electrolyzer cost down, whereas Faradaic efficiency, which can reach 90%, are less of a limiting factor for commercial applications. Like water electrolyzers, industrial CO₂ electrolyzer systems consist of stacked flow cells. Some literature examples report lab-scale cell designs that allow a systematic scale up, i.e. membrane-based and microfluidic flow cells ⁵⁶. Both of these cells attain current densities beyond 200 mA/cm² at the laboratory scale. This threshold is suitable for commercial applications, however, when scaling fuel cells up, it is uncertain that current density will scale linearly, and achieving higher density at the lab scale is required to accelerate their market adoption. Strategies to further improve the current density consist of (1) modifying the electroreduction cell geometry and/or reactor design (i.e. electrodes configuration) in continuous or discontinuous configurations for liquid electrolytes to flow between the electrodes, increase both energy and current efficiency ⁵⁷, and (2) increase CO₂ solubility with non-aqueous electrolytes ⁵⁸. In the first case, the cathode electrode can be placed at the interface between the electrolyte and the gaseous CO₂ for enhanced mass transfer ⁵⁹. As such,

pressure equilibration between the liquid electrolyte and the gaseous CO₂ need to be ensured to prevent products crossflow through the porous electrode.

The reactor design is a critical step that must be considered in concomitance with new catalyst development to meet high current and energy efficiencies⁵⁷. Zero-gap assembly of gas diffusion electrodes maximizes energy efficiency but inhibits CO₂ reduction, while introducing a thin liquid buffer layer between the cathode and the membrane to achieve high current efficiencies⁵⁷. Another recent comparison was presented by Diaz-Sainz et al., where gas diffusion electrodes and catalyst coated membrane electrodes are compared for Sn and Bi-based materials⁴⁸. In terms of material choice, Bi-based configurations outperform the Sn-based ones, while in terms of electrodes design gas diffusion electrodes present lower performance in terms of formate concentration and energy consumption⁴⁸. Several techno-economic analyses on the electroreduction of CO₂ to FA show that the process is economically viable despite the large consumption of electricity⁶⁰. Agarwal et al. propose a scenario under which CO₂ flow cells could be economically viable. This scenario includes an electricity consumption of 5.2 MWh/ton of generated FA with an electricity cost of 0.07 US\$/kWh. It also comprises the condition of CO₂ provided at no cost and FA being the feedstock for high value applications, such as H₂ storage or chemical feedstock.⁶⁰ Although electrochemical reduction of CO₂ to FA is both technically and economically feasible, technical challenges remain an obstacle to commercialization, namely the needs of high overpotential, cathode stability as well as the integration of high steam consumption in final separation and CO₂ capture at ambient temperature and pressure⁶¹. Finding new applications and markets for FA will incentivize the development of CO₂ electrolyzers and make FAFCs pertinent for CO₂ electroreduction.

3. Formic acid market

In the 2014-2019 period, the worldwide production of FA fluctuated between 750,000 – 800,000 tons^{34,62}. The total trade value of FA in 2018 was \$430 million⁶³. The predominant markets for FA demand are Asia and Europe (48% and 36% share, respectively)⁶⁴. FA sold at a concentration of 85% is the global industry standard, but special applications require a concentration of 99%⁶⁴. The historic use of FA for leather hide tanning has decreased over the past 20 years due to the leather industry shrinking. Pharmaceutical production, food industry, textiles, drilling fluids, and airport runway deicers, natural rubber, chemicals, and animal feed account for the remaining consumption⁶⁴.

IHS Markit reported that the market of FA is amply supplied⁶⁴. Silage preservation/animal feed additives and leather and tanning account for nearly 49% of world consumption⁶⁴. As a result, these applications define demand-driven growth. Consumption in silage preservation and animal feed additives have benefitted from the continuously improving living standards (particularly in Asia) and the increasing meat consumption⁶⁴. The lower labor and capital costs, as well as the rapidly growing market will allow China to increase FA capacity; China will remain the single-largest producer and exporter of FA⁶⁴.

FA's price also affects its application in fuel cells (Figure 2). Between 2011 and 2013, FA reached its highest price (over \$1100). Afterwards, the Chinese market crash of 2014 affected the FA market price until 2017. Between 2017 and 2019, the price of FA increased at around \$ 700. However, the COVID-19 outbreak has almost halved the price. A recent FA market forecast predicts a revised compounded annual growth rate of 3.3%, accounting for US\$ 363.4 million⁶⁵⁻⁶⁷.

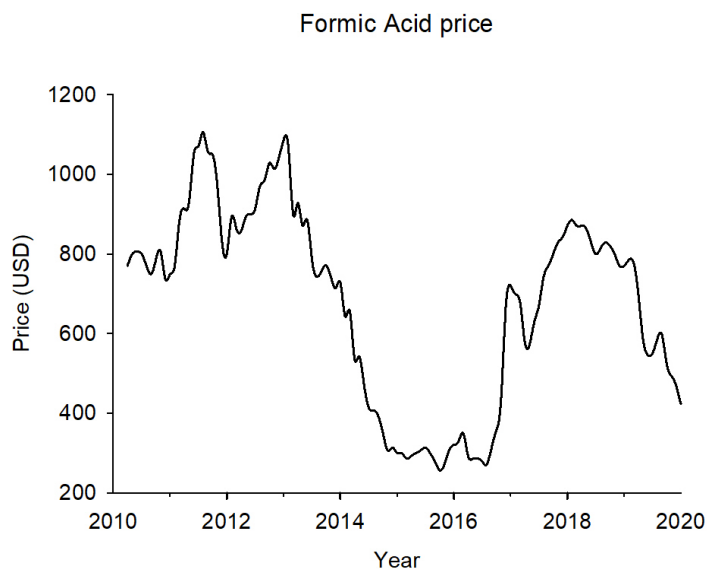


Figure 2 China's market price of FA (94%) from April 2010 to April 2020 ⁶⁸.

4. Formic acid fuel cells (FAFC)

4.1 Fuel cells

A fuel cell is a device that generates electricity from chemical energy. The electrolyte determines the operating temperature and fuel type ⁶⁹. Depending on the electrolyte type, there are solid oxide fuel cells (SOFC), molten carbonate fuel cells (MCFC), alkali fuel cells (AFC), phosphoric acid fuel cell (PAFC) and proton exchange membrane fuel cell (PEMFC). SOFC uses a hard, ceramic material (oxides of calcium, zirconium, etc.) as the electrolyte. In SOFC temperatures reach 800 – 1000 °C, leading to a voluminous fuel cell unit and an increased risk of cracking ⁷⁰. In an MCFC, salts (Na or Mg) facilitate the movement of carbonate ions ⁷¹. Despite advantages such as variable fuel options, resistance to impurities, the high temperatures required limit SOFC and MCFC when portability is one of the characteristics desired ⁷².

AFC have historical relevance, being the primary electrical source in the Apollo space program. AFC operates on pure compressed H₂ and O₂ with expensive Pt electrode catalysts ⁷³. AFC technology leverages a wide range of electrocatalysts, such as Ni, Ag, metal oxides, and noble metals ⁷⁴. Their operating temperature ranges from 150 to 200 °C and cell output ranges from 300 W to 5 kW with an energy efficiency of 70 % ⁷⁵. AFC is sensitive to CO₂, requiring thorough purification of H₂ from CO₂ ⁷⁵. Concentrated KOH or NaOH serves as the electrolyte, presenting a chemical hazard risk in case of leakage ⁷⁵.

Phosphoric acid is an ion-conducting electrolyte that forces electrons to travel from the anode to the cathode through an external electrical circuit. The working temperature for PAFC is between 150 to 200 °C, and cell output can be up to 200 kW with an efficiency between 40 % to 80 % ⁷⁶. Drawbacks of PAFC's include its reliance on hydrocarbons, the high cost of Pt catalysts and rather low power density ⁷⁷.

PEMFCs are considered competitive candidates to substitute batteries for EVs ³⁰. A proton-conductive polymer membrane (typically Nafion[®]) separates the anode and cathode. The operating temperature is about 40 – 100 °C and the cell output ranges from 50 kW to 250 kW with an efficiency of 40 – 50 % ⁷⁸. Commercial PEMFC utilize H₂ But the need of pressurizing it up to 700 bar for storage and transport translates into the need of particular infrastructure to ensure safe storage and refilling by vehicle users. H₂ cost is estimated at an average of 2.6-5.1 US\$ per kg ^{79,80} (comparing to FA of ~0.7 US\$ per kg in 2017-2019, Figure 2). Since FCEV are 2.5 times more fuel-efficient than gasoline, a gallon of the latter needs to be 2.5 times less expensive than a kilogram of H₂ to keep the same cost per mile ⁸¹.

Compared to H₂-fed fuel cells, direct liquid fuel cells (DLFCs) are easier to handle, store and transport ⁸². Alcohols ²¹, such as methanol ⁸³, ethanol ⁸⁴ and ethylene glycol ⁸⁵, are the most common liquid fuels. Methanol has excellent energy density (~4900 Wh/L), but is toxic and it has a high rate of fuel crossover at high concentration ⁸⁶. The oxidation of ethanol is slow since it involves a 6-electron reaction ⁸⁷. Ethylene glycol as a fuel and hydrogen peroxide as an oxidant in alkaline fuel cells may help overcome the issue of carbonate formation when CO₂ in the air reacts with OH⁻ to form CO₃²⁻ ⁸⁸.

FA is a promising fuel for DLFC over alcohols, because of lower fuel crossover, higher theoretical cell potential and power densities, as well as faster oxidation kinetics when compared to alternative options ³⁰. This work focuses on FA FCs, where electrochemical reduction of CO₂ produces the feed.

We provide a comparison of cost, energy density, operating temperature, energy density and pressure storage of some fuels. We selected these fuels as they can be produced from renewable sources (FA and alcohols through CO₂ reduction; H₂ through electrolysis with renewable electricity; gasoline from biomass or gas to liquid processes starting either from CO₂ or biomass) When compared to H₂ and methanol, which are commonly used in fuel cells, FA requires milder operating conditions, has a higher energy density than H₂ and is inherently safer than methanol Gasoline is unrivaled as a fuel considering the energy density. However, producing gasoline from either biomass or CO₂, involves multi-step, high temperature processes, whereby carbon losses and emissions are more likely than in electricity-driven technologies ^{89,90}(Table 2).

Table 2 Comparison of fuels price, energy density, operating temperature and storage pressure.

Fuel		Price (retail)	Energy density	Operating Temperature	Storage Pressure
Fuel Cells	FA	0.7 US\$ / kg ⁶⁸	2.1 kWh dm ⁻³ ⁹¹	20-60°C (DFAFC) ⁸⁷	-
	H ₂	2.6-5.1- US\$ / kg ^{92,93}	0.53 kWh dm ⁻³ ⁹⁴⁻⁹⁶	150-200°C (AFC) ⁷⁵	700 bar ⁸¹
	Methanol	0.2-0.4 US\$ / kg (China) ^{79,80}	4.4-4.9 kWh dm ⁻³ ^{3 96,97}	30-90°C (DMFC) ⁹⁸	-
Gasoline		0.6-2.3 US\$ / gallon ⁹⁹	13 kWh dm ⁻³ ¹⁰⁰	-	-

4.2 Direct formic acid fuel cell

DFAFC are a technology characterized by relatively easy power system integration, low toxicity, and stability compared to other fuel cell types ¹⁰¹. FA crossover flux through Nafion[®] membrane is low because the repulsive force between formate anions and ion clusters enhances the compatibility with membranes. Moreover, they are characterized by a theoretical electromotive force of 1.48 V (1.18 V for methanol) and an energy density of 2.11 kWh dm⁻³ (4.4 kWh dm⁻³ for methanol) ^{96,97}. As a reference, H₂ fuel cells (FCs) have an electromotive force and energy density of 1.23 V and 0.53 kWh dm⁻³ ⁹⁴⁻⁹⁶.

4.2.1 Reaction mechanism of DFAFC

DFAFCs operate on the same principle as other FCs. They generate electric energy from FA oxidation and O₂ reduction. In the electrochemical device, FA and O₂ (or air) are fed to the anode and the cathode, respectively. An electrolyte membrane allows the protons to flow ⁹⁷ (Figure 3).

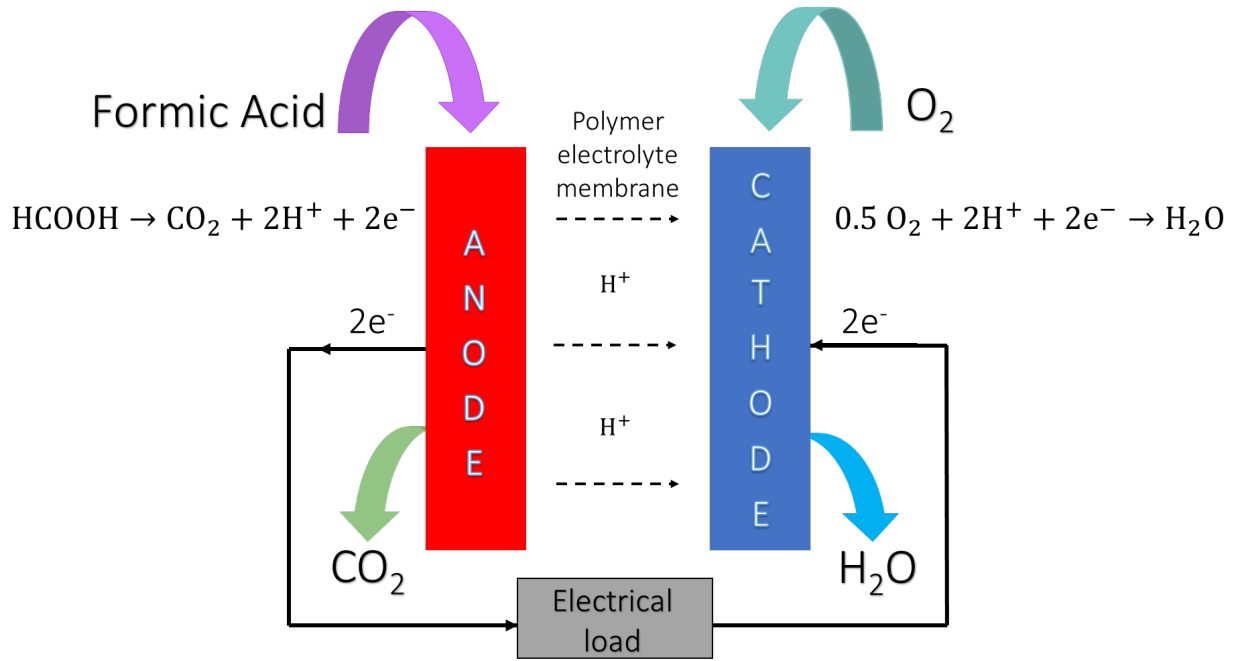
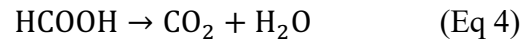
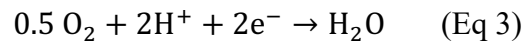
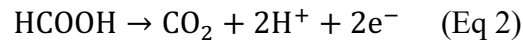
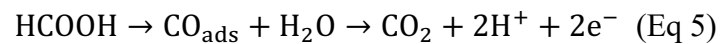


Figure 3 Direct formic acid fuel cell (DFAFC) scheme.

The direct anode, cathode and the overall reaction of DFAFC are as following ³⁰:



The indirect anode reaction:



At the anode, the direct FA oxidation proceeds via decomposition (Eq 2) ²¹. In the ideal direct pathway, $\text{HCOOH} \rightarrow \text{*HCOO}$ (formate) or *COOH (carboxyl) then completely transforms into H_2 and CO_2 ¹⁰³. In the indirect dehydration of FA (Eq 5), $\text{HCOOH} \rightarrow \text{*COOH} \rightarrow \text{*CO} \rightarrow \text{CO}_2$, the undesired CO could poison the catalysts by interacting with the active sites, thus increasing the required overpotential for oxidation ²¹. Experiments ^{104–108} and theoretical studies ^{103,109–111} attempted to suggest the reaction mechanism. The pathway of FA oxidation depends on the nature of the catalyst, like the pH at the anode/electrolyte interface ¹⁰³. For example, the electrooxidation current of $\text{HCOOH}/\text{HCOO}^-$ on a Pt catalyst exhibited a maximum oxidation current at a pH of 3.75 over a pH range of 0–12, close to the pKa of FA ¹⁰⁷.

4.2.2 Anode catalysts

Anode catalysts with high reactivity and durability are essential for DFAFC ^{112–116}. Platinum (Pt) and palladium (Pd) based catalysts are two prominent anode options for DFAFC ^{103,117}.

Weber et al. first introduced Pt as an electrode in 1996 ¹¹⁸. They demonstrated that Pt/Ru catalyst is more active than Pt-black in FA oxidation. Pt electrode surfaces influenced the reaction path: on the steps and terraces of Pt nanoparticles, the FA oxidation proceeds via the direct pathway; differently, on plain Pt nanoparticles it occurs via the indirect pathway ^{119,120}. Voltammetry studies showed that Pt (111) suffers of poisoning ^{120–123}. There are however difficulties to mass-produce Pt nanoparticles with controlled shape ¹¹⁹.

As an alternative, Pd catalysts present better CO tolerance and higher power density than Pt-based catalysts ^{124,125}. Pd also catalyzes FA to CO_2 primarily via the direct pathway ^{103,117}. However, the agglomeration of Pd particles and the accumulation of CO on Pd surfaces promote the design and

synthesis of nanoparticle catalysts with large superficial areas with 3D porous or hollow structures^{126–128}; and the introduction of a more oxyphilic metal, such as Ni¹²⁹, Co¹³⁰, Cu¹³¹, and P¹³², to form OH*, which oxidizes CO* to CO₂¹⁰².

DFAFC performance improves when Pt or Pd form alloys with metals such as Pb, Sn, Au, Bi, As, and Sb^{133–139} or their surface is modified^{140–142}, such as by irreversibly adsorbing a second metal¹¹⁹.

Carbon nanotubes or expanded graphite layers as supporting material reduces the loading of noble metal and improves the electrical conductivity and stability of Pt or Pd catalysts¹⁴³. Other supporting materials include titania¹⁴⁴, zirconia¹⁴⁵, V, Mo, W and Au¹²³, and tungsten carbide^{91,146}.

4.2.3 DFAFC stack designs

PEMFC stack design principles

The heart of a fuel-cell system is the membrane electrode assembly (MEA, includes the proton exchange membrane, and the anode and cathode catalyst layers and gas diffusion layers (GDLs) on each side of the membrane)¹⁴⁷. A single cell resembles a sandwich with a MEA, sealed with gaskets to prevent gas leakage, between two separators or bipolar plates. The potential of a single FC decreases during the operation as a function of current density¹⁴⁸. Individual cells are stacked to achieve the voltage, current or electric power for industrial generators or automobiles¹¹⁹. Increasing the number and the area of the MEAs raises the voltage and the output of the stack¹¹⁹. A commercial H₂ FC stack, acting as a tiny electric power station, consists of hundreds of single

cells, like slices in a loaf of bread ¹⁴⁹. Other components include current collector and end plates. The whole stack is tightly held in place by tie-rods, bolts, shrouds or other arrangements ¹⁴⁸.

A typical PEMFC works as follows: air and fuel (H_2 source) are fed to the bipolar plates and flow into the channels of the plates; H_2 diffuses through the GDL, contacts the anode catalyst layer and is then split into protons H^+ and electrons e^- . Electrons pass through the GDLs, the bipolar plates, the current collectors and arrive at the cathode via an external circuit. O_2 reduces to water as a by-product with the protons H^+ passing through the membrane ¹⁵⁰. The MEA acts as a barrier for electrons, creating a flow of direct electrical current in the external circuit ¹⁵⁰.

Other than bipolar configurations, ideal for large fuel cells, there are also side-by-side configurations such as zig-zag or flip-flop connections that increase the fuel concentration at the anode by order of magnitudes compared to other arrangements ¹⁴⁸.

The main key features for the design of a stack include:

- Uniform distribution of the reactants to each cell by an external or internal parallel manifold: the flow pattern can be "U" shaped (inlet and outlet are at the same side but in opposite direction) or "Z" shaped (inlet and outlet are at different side). Alternatively, a parallel-serial manifold has the depleted gas flow from the first "Z" shaped segment to the next cell ¹⁴⁸. The latter operates at higher stoichiometry ¹⁵¹.
- Uniform distribution of reactants inside each cell by selecting the shape of the flow field (square, rectangular, etc.); flow field orientation (top to bottom, bottom to top, side to side, etc., considering water condensation); channel configuration (straight, criss-cross,

single/multi-channel serpentine, mesh, porous, etc.); channel shape, dimensions and sizing¹⁴⁸.

- Cooling system with coolant (between or at the edge of the cells), phase change material, or reactant air itself¹⁴⁸.
- Proper clamping force to prevent leakage (depending on the gasket material and design) and diminish contact resistance (1.5 - 2.0 MPa)¹⁵².

DFAFC stack examples

A FC stack includes repetitive, simple geometry cells¹⁴⁸. Despite most research focuses on the choice of anode catalysts, a FC's performance does not depend only on the anode's and cathode's catalyst, but also on the membrane, gas diffusion layers, hardware, stack design, etc.¹¹⁹. The selection of key parameters and operating conditions affects the whole stack performance, which is crucial for industrial applications. Examples of practical devices for DFAFC stacks are not abundant in the literature, but each stack has a distinct design and has been tested under optimal operation conditions, providing insights for further study (Table 3).

Table 3 Catalysts and performances of DFAFC stacks reported in literature.

Number of stacks	Air breathing type	Anode catalyst	Cathode catalyst	Maximum power density (mW cm ⁻²)	Power output (W)	Reference
15 MEAs	Active	Pt-Ru (Johnson Matthey)	Pt black (Johnson Matthey)	60	30	153
2 MEAs	Passive			44.5	0.4	87,154

4 MEAs		40 wt.% Pt/C (Johnson Matthey)	40 wt.% Pt/C (Johnson Matthey)	56.6	0.9	
10 MEAs	Passive	60wt% Pt/C + 60wt% Pd/C (Pt- Pd/C)	60 wt.% Pt/C	130	32	155
35 MEAs	Passive	40% Bi- modified Pt/C	Pt Black	191	301	119

DFAFCs classify into 1) active DFAFCs, where the liquid fuel is fed to the anode through a pump and compressed air to the cathode; 2) active air breathing DFAFCs, where the cathode is exposed to ambient air; 3) passive air breathing DFAFCs ¹⁵⁶, whereby there are no pumps and/or compressors metering fuels and/air to the cell, which makes them compact and portable.

Miesse et al. ¹⁵³ were the first to report an active DFAFC stack in 2006, which is capable of 30 W at 60 mW/cm² to power a laptop computer over 150 mins. The MEAs were separated by bipolar plates (Figure 4, Table 3). The packed stack includes a fuel tank, tubing, a miniature liquid fuel pump and an air compressor, and a power conditioning control board (PCB). It is a hybrid system, as there is a small battery to drive those components during start-up. They were able to operate at 50 % by weight of FA. Together with the work Zhu et al. ¹⁵⁷, who adopt FA concentrations between 1M and 12M, the data from Miesse et al. are the ones gathered at the highest FA concentration in the literature, which is key for industrial applications. Indeed mass-transfer limitations and crossover ^{158,159} seem to occur consistently at concentrations < 3M and > 6M, respectively. In the work by Miesse et al., the flow field orientation also affected the stack performance: feeding FA

from the bottom to the top of the stack avoided CO₂ accumulation. Poor distribution of FA in the cells resulted in an earlier onset and downward trend of the polarization curve, which translates into decreased performance. Dynamic response reflects the stack response to the demand change of the electronic devices, and also determines the need for supplementary equipment ¹⁵³. The transient response showed that this 15 MEA stack reacted to a step change in current and power with no power lag. This stable long-term performance is key for commercial feasibility. Miesse et al. conducted a three-month continuous operation on a single cell MEA. Steady state was reached after several hundred hours of operation (degradation <15%). Furthermore, applying a high anodic potential to the catalyst re-establish the anode activity once lost ¹²⁴. Based on this study, Miesse et al. suggested a cell or stack cycling to recover decreased performance. A circulating fuel loop, a sensible pH meter, or an electrochemical sensor is recommended to monitor the continuous decline of FA concentration inside the tank during operation.

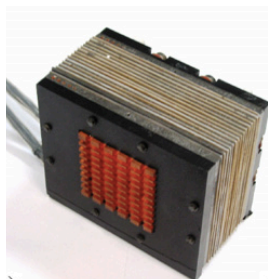
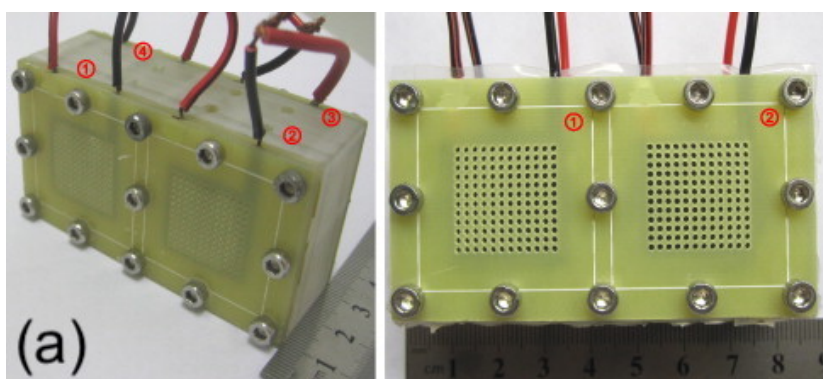


Figure 4 Stack with 15 MEAs in series, 88mm×70mm. Air and FA was fed to each MEA in parallel through internal manifolds. The graphite-composite bipolar plates (1.5 mm pitch) had square-grooved, parallel, serpentine flow fields. Reproduced with permission from ¹⁵³.

Passive FCs are lighter and smaller compared to active ones with auxiliary equipment (e.g., liquid fuel pumps and air fans). Hong et al. designed a passive air-breathing two-cell stack ¹⁵⁴ and four-

cell stack ⁸⁷ DFAFC. The two-“face-to-face”-cell stacks shared one fuel reservoir. The design of two-cell and four-cell stacks was similar (four-cell stack as an example: Figure 5a). FA has high electrical conductivity properties, and water electrolysis can readily occur when over three cells share one fuel reservoir ^{154,160}. In the four-cell stack, Hong et al designed a fuel reservoir with four independent cavities for individual cells (Figures 5b). This design avoids water hydrolysis between electrodes ⁸⁷. The four-cell stack was assembled with gold coated printed circuit boards as end plates and current collectors (Figure 5c). The MEA were prepared by direct catalyst spraying ¹⁶¹. The performance of each cell is uniform according to the overlapping curve of the open-circuit voltage. The optimal concentration of FA in this work was 5M. The transient response of each cell under a step change in current had a relatively stable voltage. The stack and each single cell showed similar “fast-slow-fast” degradation pattern, thanks to the symmetrical stack design; ~20 % of the stack voltage dropped during the 10 h long term performance test due to the deactivation of the catalysts and of the MEA. The authors specifically mention the limited fuel supply and its consumption in the reservoir as a matter to investigate further.



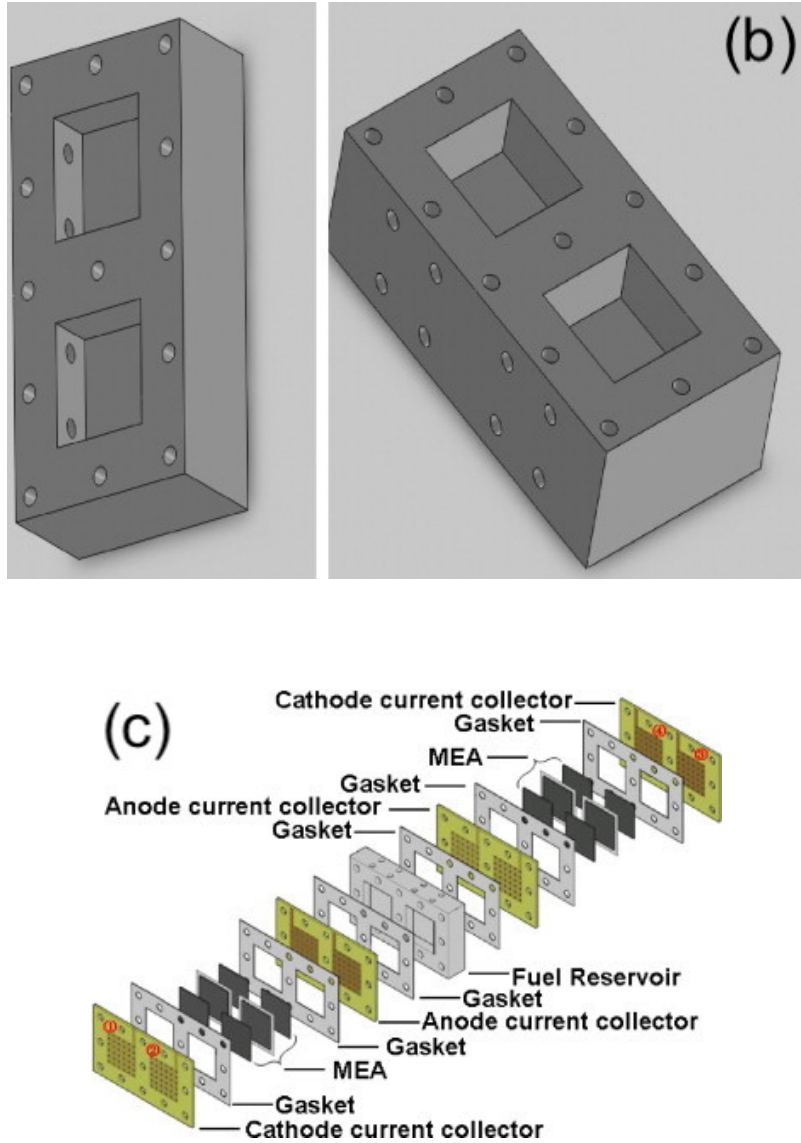


Figure 5 (a) Passive air-breathing DFAFC four-cell stack: 7.5cm×3.0cm×4.0cm. The anode of one cell is connected to the cathode of next cell. Two external wires are for the performance testing of each cell. (b) Left and right views of fuel reservoir (by AutoCAD): four cavities store the fuel and support individual cell. (c) Detail breakdown sketch of the four-cell stack ⁸⁷.

Cai et al ¹⁵⁵ designed and fabricated a medium-scale 10-cell (5 cm × 5 cm) DFAFC stack (Figure 6). The anode catalyst was 60 wt% Pt/C + Pd/C catalyst synthesized in laboratory, mixed by

ultrasound and sprayed on the wet-proof carbon papers. The MEA was formed by two electrodes with a Nafion© 117 membrane via hot pressing. The bipolar plates are graphite with serpentine channels on both sides. Under optimal operation conditions (10 mol L^{-1} FA solution and $2.0 \text{ L min}^{-1} \text{ O}_2$), the power output of this stack reached 32 W, suitable for most portable electrical devices. The stack can stably operate for 50 h with 1.5 L fuel and up to 240 h (with refueling) with no decline of performance. Furthermore, by washing the anode catalyst significantly increased the maximum power output 60 % higher than the unused stack.

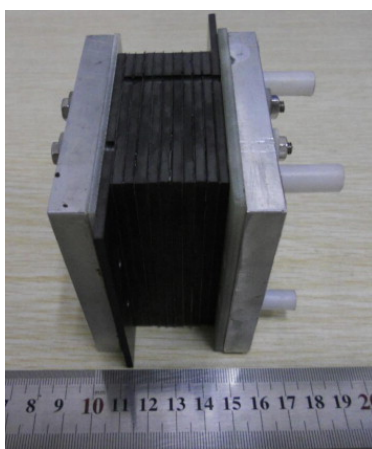


Figure 6 The DFAFC 10-cell stack with bipolar graphite plates ¹⁵⁵

Most stacks employ commercial catalysts. Choi et al. ¹¹⁹ prepared an irreversibly adsorbed Bi on Pt/C catalyst to prevent the Pt catalyst from CO poisoning and applied it in the stack. Adding Bi formed Pt ensembles which favored the direct oxidation of FA and thus decreased CO production. A high loading of Bi covers the dehydrogenation Pt sites; hence, a coverage of 0.25 was a good compromise. The O_2 reduction reaction rate was lower compared to commercial Pt/C catalysts. Yet, the FA oxidation activity of the Bi-Pt/C catalyst was 13 times higher than Pt/C at 0.58 V. The authors applied this catalyst to a DFAFC stack of 35 membrane electrode assemblies (MEAs). MEAs fabrication followed a catalyst-coated membrane method. A manual air-brush system (GP2,

Japan) directly sprayed the anode and cathode layers on both sides of the membrane (NR212). Figure 7 displays the fabricated DFAFC stack with Bi-Pt/C catalyst. 35 MEAs are stacked, each with a geometric area of 50 cm² and the maximum power is 301 W. The cell that performs the worst determines the overall performance, and usually is the main cause of performance degradation of the stack ⁸⁷. In this case, most cells have similar single cell performance. Three cells close to the anode have relatively poor performance, probably because of insufficient air or liquid fuel supply ¹⁶².

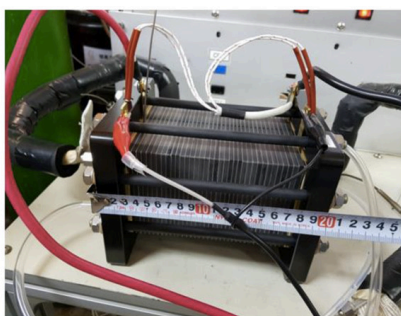


Figure 7 300 W DFAFC stack includes MEAs, GDL, gaskets and bipolar plates (15.6cm×11.6cm×9.8cm) ¹¹⁹

4.2.4 Status, challenges and opportunities

DFAFCs stacks are still limited to the laboratory scale, with typical power outputs from below the unit to ~30 W, with an outlier of ~301 W (Table 3). Most catalysts under investigation in the literature are commercial catalysts, except the one from Choi et al. ¹¹⁹ who tested Bi-modified catalysts. Stack geometries and experimental conditions are similar with FA concentrations ranging from 2 M to 12 M and temperatures between 20°C and 60°C, with the exception of Hong et al. who developed their four-cavity geometry ⁸⁷. Data indicate that FA concentrations at 5-6 M lead to higher power densities with optimal temperatures at 60°C. The superior performance from

Choi et al. advocates for the development of new efficient catalysts ¹¹⁹. More data on DFAFC stacks will help identify optimal working conditions, including FA concentration and flow rate, air flow rate, and cell temperature. Up to now, there are no commercial DFAFC devices. Comparatively, Horizon Fuel Cell Group ¹⁶³ built a liquid-cooled H₂ FC that has been implemented in around 10 buses and trucks, with a power output ranging from 60 to 150 kW. They plan to produce the world's highest power PEMFC with 300 kW stacks by 2020 ¹⁶⁴.

Challenges for commercial DFAFCs that remain to tackle include the crossover of FA through Nafion© membranes (fuel permeates the membrane from anode to cathode, a common issue for PEMFC). Kim et al. reviewed the characterization techniques (stand-alone membranes and MEA configurations) of FC membrane ¹⁶⁵. The chemical structure and operation conditions of PEMs greatly affect the ion exchange capacity, water uptake, ion conductivity, gas/liquid permeability and chemical/physical stability ¹⁶⁵. Although FA has a low crossover through Nafion©, it still affects the performance of DFAFCs ¹²³. Increasing FA concentration and operating temperature raises the risk of crossover ¹⁶⁶. The choices and preparation of the gas diffusion layer, catalysts and MEA also cause the crossover problem. Hence further studies are needed to improve the performance of DFAFCs.

4.3 Pre-commercial indirect formic acid fuel cells

There are examples in the literature of indirect FAFCs where FA plays the role of H₂ source. An indirect FAFC is a fuel cell whereby the feed is FA, but the fuel is H₂ being stored in it. It combines the advantage of having FA as a liquid feed, which is easy to transport and store vs. H₂. Indeed this latter must be stored and transported under pressure, besides carrying higher safety concerns. Team FAST, a student-run project at the Technical University of Eindhoven in the Netherlands,

designed the world's first electric-powered bus based on Hydrozine (99% of FA and 1% of an undisclosed performance enhancing agent) ¹⁶⁷. Hydrozine is sustainably produced from the electrochemical reduction of CO₂ by VoltaChem ¹⁶⁸. The system transforms the Hydrozine into CO₂ and H₂, which is then sent to a FC to produce electricity in a closed carbon-loop ¹⁶⁹. In 2014, Pico, a device driven by Hydrozine, was developed for the first time ¹⁶⁹. In 2015, Team FAST created a scale model, Junior, which works on Hydrozine and has a maximum speed of 70 km/h. In early 2016, Team FAST built their current system, REM, with an output of 25 kW thought to power electric buses ¹⁶⁷. REM is still a prototype and the FC suffers from issues such as temperature control and unstable electrical power ¹⁷⁰.

Being FA a very efficient H₂ carrier (1 L FA carrying 590 L H₂), it makes H₂ easier to store and transport in a liquid form to feed into a conventional H₂FC ¹⁷¹. In 2018 GRT group ¹⁷², a company focused on energy transition with energy-storage development solutions, and the Laurency group from EPFL ¹⁷³ developed the world's first integrated FA-H₂ FC device. The device consists of two main parts, a H₂ reformer (HYFORM) to extract H₂ from FA and a proton-exchange membrane fuel cell (PEMFC). FA is produced from biomass or through the hydrogenation of CO₂ and is stored at room temperature in a tank. The HYFORM uses a Ru-based catalyst to transform FA into H₂. H₂ then passes through the FC to produce electricity. Excess CO₂ can be recycled to produce FA. The HYFORM-PEMFC has a capacity of 7000 kWh per year with an electrical efficiency up to 45%, and its theoretical power is 800 W. This design claims a 100% closed CO₂ loop and absence of particles and nitrogen oxides ¹⁷⁴.

5. Conclusion

This manuscript reviews the latest advances in formic acid fuel cells (FAFCs) where CO₂ represents the suggested feedstock for FA. The market for FA is currently saturated but the increasing demand for electricity-driven devices brings interest in the development of FA fuelled FCs for a sustainable energy supply solution.

Literature examples with Faradaic efficiency of above 80% are many, whereby increasing current density beyond 200 mA/cm² is the main challenge for commercial applications for CO₂ to FA. However, the increasingly performing cells reported in the literature are encouraging the transition towards industrial scale cells for CO₂ electroreduction to FA.

The DFAFC stacks examples presented in this manuscript represent important milestones for the future development of prototypes, scale-up and commercialization. Stack examples have a number of membrane electrode assemblies (MEA) ranging from 2 to 35, with consequent power outputs ranging from 0.4 to 301 W. Commercial FAFCs face challenges to directly apply FA as a fuel, and future works need to tackle direct formic acid fuel cells (DFAFC) issues such as the crossover (fuel crossover causes the fuel to move from the anode to the cathode) deriving from high FA concentrations that are necessary in commercial FC.

Another application for FA relies on extracting H₂ from it in a reforming step and use this latter in a conventional H₂ FC (or indirect FA fuel cell). Indeed, FA is a very efficient H₂ carrier (1 L FA carrying 590 L H₂), which makes H₂ easier to store and transport in a liquid form to feed into a FC. Renewable carbon feedstock such as CO₂ or biomass is once again the recommended raw material to produce FA.

Further developments are looking at testing novel materials as catalysts and surveying new FC stacks designs to improve the power output of DFAFCs and overcome the performance of available commercial catalysts.

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Author Contributions

ZM lead the bibliographic research and drafted the manuscript. EP, UL and DCB performed the bibliographic research and drafted the manuscript. DCB also supervised the post-doctoral fellows involved and secured funding. JRT drafted the manuscript and supervised the post-doctoral fellows involved. All authors approved the final version of the manuscript.

Notes

The author Dr. U. Legrand is the CTO of Electro Carbon Inc., a company aiming to commercialize CO₂ to formic acid electrolyzers and thus have financial interest in the present research. This conflict of interest did not influence the conclusions presented in the article.

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