

Sustainable energy: a review of formic acid electrochemical fuel cells

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Abstract Of the many candidate fuels for low-temperature fuel cells, one of the most promising is formic acid. Although it has been investigated as such for nearly 50 years, rapid advances in recent times have begun to release the potential for formic acid fuel cells as high-performance, portable fuel cells with some products about to reach the market. In this review, we briefly summarise the recent advances in formic acid fuel cells.

Keywords Fuel cells · Formic acid · Oxidation · Electrochemistry

Introduction

The pace of research and development of fuel cell technology has increased sharply over the last 20 years, partly driven by the desire to improve urban air quality and reduce CO₂ emissions. Fuel cells also promise increased fuel flexibility and diversity at a time when many nations are becoming net energy importers and an industrial sector for sustainable economic development in the twenty-first century.

Commercial demand for fuel cells has been estimated to have a total global market value of £13bn [1]. Applications include low power output for mobile products (e.g. battery replacements, vehicular propulsion and auxiliary power units) and high power output for stationary use (e.g. residential heating and power and electricity generation for distribution). Of these applications, the largest commercial

potential is for portable battery replacements with a market value of ca. £6bn.

Current fuel cell designs can be classified into high- and low-temperature cells. The former include molten carbonate and solid oxide fuel cells and typically operate at 400–800 °C, whilst the low-temperature cells such as proton-exchange membrane (PEMFC) and direct methanol fuel cells can operate at 60–100 °C. It is the PEMFCs, including methanol and formic acid fuel cells, that probably offer most promise for viable commercial products, with operating temperatures of 50–80 °C and a typical efficiency of 40–60%.

Although these fuels are carbon-containing and so generate CO₂ upon oxidation, the overall energy generation process is carbon-neutral provided the fuelstock is produced from sustainable sources. Due to the progress made in the sequestration of carbon dioxide from exhaust mixtures (www.netl.doe.gov/technologies/carbon_seq/core_rd/co2capture.html) [2–5], the process can in principle be rendered CO₂-negative if sequestered CO₂ is converted into the starting fuelstock. Whilst there are several candidate fuels that are effectively hydrogen storage compounds containing no carbon, such as ammonia and hydrazine, these have the potential drawback of possible toxicity, and so these products are typically some way from reaching the commercial marketplace, although progress is being made regarding the safe storage and release of these chemicals within the fuel cell system [6–8]. In this mini-review, we survey the recent progress made in the field of direct formic acid fuel cells (DFAFCs).

Direct formic acid fuel cells

Formic acid has emerged as a highly promising candidate for a commercially viable fuel cell feedstock owing to its

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favourable oxidation kinetics enabling low operating temperatures, high theoretical cell potential and relatively mild fuel crossover problems [9–11]. As illustration, Tekion Inc and BASF are in joint development of a commercial DFAFC for portable electronic products that uses an optimised formic acid fuel by the tradename Formira® (<http://www.tekion.com>; http://www.basf.de/en/intermed/products/formic_acid/tekion). The Formira Power Pack® is a micro-fuel cell/battery hybrid where the fuel cell recharges the battery for extended operation. The fuel cells are refuelled by swapping a cartridge of the formic acid fuel. It is claimed that it has a power range of up to 50 W and an energy range of up to 100 Wh (http://www.basf.de/en/intermed/products/formic_acid/tekion; Fig. 1).

As with many other fuel cells, the DFAFC first received attention in the 1960s. Since then, work has focussed on the development of electrocatalysts for the formic acid oxidation and understanding the kinetics and mechanism, particularly on single crystals [12, 13]. Considerable research effort has been made into modifying noble metal surfaces in order to reduce the amount of CO poisoning, from which Pt especially is vulnerable, and also maintain resistance to acid-attack for metals such as Pd [10, 11].

The DFAFC is based on the two-electron anodic oxidation of formic acid to produce carbon dioxide and water and a theoretical cell voltage of +1.48 V [14].

Anode reaction : $1/2 \text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/2 \text{HCOOH} \quad E^0 = -0.25 \text{ V}$

Cathode reaction : $1/4 \text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/2 \text{H}_2\text{O} \quad E^0 = +1.23 \text{ V}$

Overall cell reaction : $1/2 \text{HCOOH} + 1/4 \text{O}_2 \rightarrow 1/2 \text{CO}_2 + 1/2 \text{H}_2\text{O} \quad E^0 = +1.48 \text{ V}$

The oxidation mechanism at a metal surface is generally accepted as proceeding via two reaction paths [11, 15–17], either direct oxidation (Eq. 1) or via weakly adsorbed

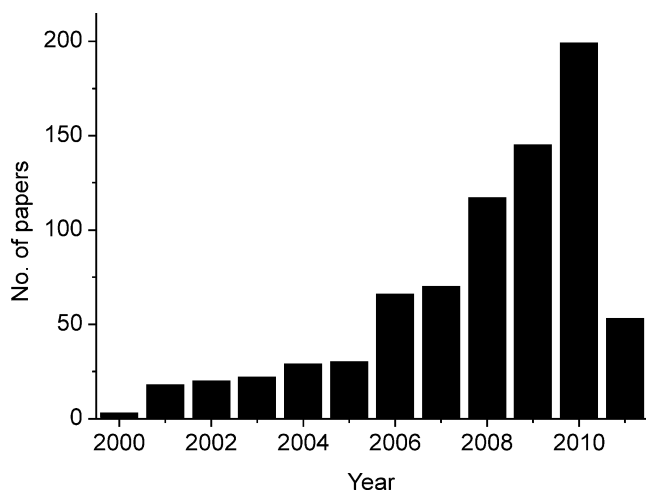


Fig. 1 Publications on formic acid fuel cells since the year 2000. Data obtained from ISI Web of Science up to and including March 2011

intermediates (Eq. 2). Behm et al. have suggested a third pathway, similar to Eq. 2, involving a bridge-bonded formate intermediate, which is subsequently oxidised to CO_2 [18, 19].

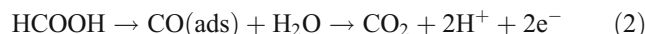
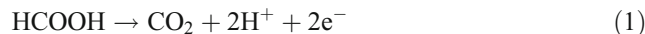


Figure 2 illustrates the direct and indirect mechanistic pathways identified to date.

Anode catalyst materials

Of the many anode materials reported in the literature, Pt and Pd have been the most studied due to their general catalytic activities. Their interactions with formic acid have become well understood, with Pd tending to break only O–H bonds across the entire potential window and Pt discriminating between cleavage of the O–H bond at high overpotentials and C–O and/or C–H bonds at low overpotential [21]. Hence, the electrooxidation on Pd proceeds via initial dehydration—mechanism 2—and on Pt varies between mechanistic pathways according to overpotential. However, despite being

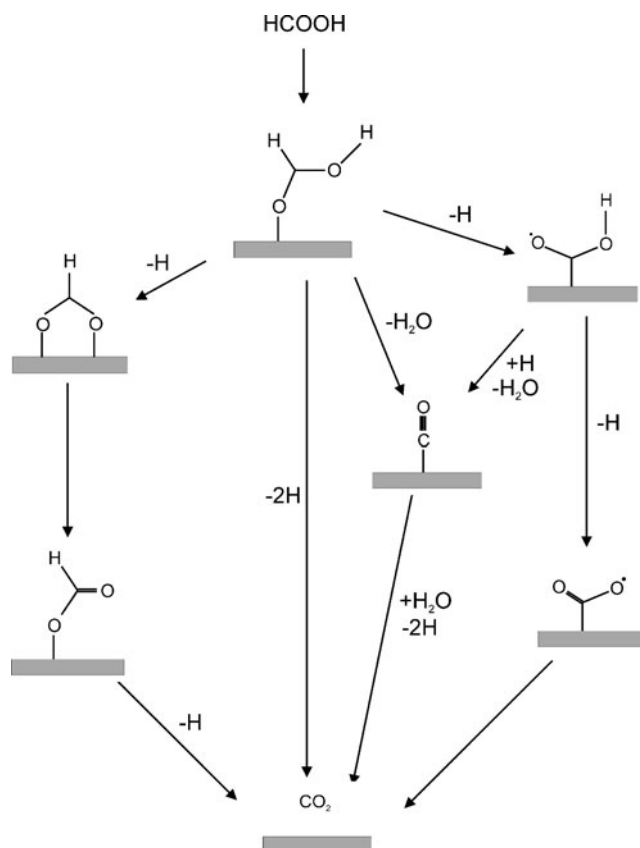


Fig. 2 Formic acid electrooxidation pathways showing direct and indirect routes. Adapted from [20]

excellent catalysts for C–O and C–H bond cleavage, both have weaknesses: Pt is rapidly poisoned by CO, and Pd is susceptible to acid dissolution [10, 11].

The best (short-time) catalyst performance on a ‘per weight of metals’ basis has been obtained from pure Pd, from experiments carried out by the Masel et al. [22–26] in ultrapure formic acid. Pure Pd outperformed Pt-based catalysts even at low temperatures. Although it is resistant to CO adsorption, there was evidence that unidentified intermediates caused a reduction in performance along with the recognised susceptibility to acid dissolution [27–30].

Since the formic acid oxidation is understood to exhibit an ensemble effect [31, 32] with regard to surface composition of the catalyst, the strategy adopted by most researchers has been to use a Pd or Pt nanoparticle (NP) base catalyst and decorate or alloy with other metals to improve longevity or resistance to poisoning, etc. Examples of this include Pd decorated PtNPs, Au and Ir deposition onto Pt NPs and the Pt deposition onto AuNPs. In all three cases, the catalyst performance was lowered (*vide infra*).

However, the use of Ru alloyed with Pt has been reported as potentially one of the best electrocatalysts for the oxidation of organic fuelstocks such as methanol [10] and has been excellently reviewed by Petrii [33]. This is ascribed to the adsorption of OH species onto Ru, which then promote the oxidation of CO to CO₂ [34–36]. However, the Pt–Ru alloy, although effective for formic acid and more active than Pt black, does not reach the performance levels of pure Pd or Pt catalysts, presumably because of the different oxidation pathways available [35, 36]. Waszczuk and co-workers [37] decorated Pt NPs by depositing either Pd or Ru, finding that Pd decorated Pt yielded the greatest catalytic activity. This was followed by Rice et al. [35], who compared Pt/Ru and Pt/Pd with Pt black and found that the respective current densities at 0.5 V were 35, 46, and 22 mA cm⁻². Waszczuk et al. later showed that there was no so-called synergistic effect of combining Pt and Pd and that any enhancement in activity was due to increased resistance to poisoning [37].

The above reported use of Au [10, 22, 26, 31, 36, 38, 39] and Ir [40, 41] as a co-alloy of Pt arises from the ‘third-body effect’, where the Au (or Ir) occupies or blocks adsorption sites on the base Pt catalysts that would otherwise be occupied by poisoning CO and other inhibiting species. Once again though, the catalytic performance does not match the pure Pt or Pd surfaces. However, Choi et al. found that Pt–Au did have a higher activity than Pt–Ru over a significant length of time [36], with current densities of ca. 30 and 80 mA cm⁻², respectively (measured at 0.5 V). Decoration with early transition metals (Cr, Fe, Mo, Nb, V) has been studied, but it has been found that these tend to dissociate in the potential window of operation [38, 42–45].

Recently, post-transition metals (Sb, Sn, Pb, Bi) have received attention due to their propensity for underpotential deposition. They typically show durability in the presence of acids and tend not to suffer from strong adsorption of CO, as well as offering a significant cost reduction over the platinum group metals [46–55]. Intermetallic phases of a range of combinations have been investigated, with PtBi, PtBi₂, PtPb and PtIn identified as the best candidates [56]. PtPb alloys are found to have greater stability than Pt over more than 1,000 s [57], and the PtPb nanoparticles catalysts have been shown to be stable for over 9 h, outperforming Pt, PtRu and Pd [58]. The enhanced activity of PtPb has been explained by means of an electronic interaction between the metals [16].

So far, the most promising appears to be PtNPs decorated with Bi (PtBi), using PtNPs in the size range 20–70 nm, deposited onto commercially sourced carbon paper (Vulcan®). This combination has been found to be tolerant of high levels of CO with no lowering of catalyst performance, has good acid resistance and a wide potential range [49–51, 59–61]. Whilst PtBi still does not perform as well as pure Pd, it does outperform Pd black [49]. There are reports that catalyst performance is below that expected theoretically for PtBi due to surface oxidation of the Bi adatoms suppressing proton conductivity in the catalyst layer [60], and further investigations are no doubt required to fully understand the optimisation of the PtBi system.

One fruitful strategy in advancing research into the use of noble metal catalysts for commercially attractive fuel cells has been the use of high-surface area carbon materials (carbon black, nanotubes etc.) as catalyst support; Lovic et al. showed in 2005 that the formic acid oxidation kinetics were indistinguishable between Pt/C (of size 2–6 nm) and pure Pt [62]. The carbon offers a chemically stable, low cost support with high conductivity. As a result, many papers have investigated the Pd/C and Pd-alloy/C systems as catalysts [22, 23, 63–66]. In the case of Pd, the NPs are formed by chemical reduction *in situ* of PdCl₂ with a variety of reducing agents such as NaBH₄. Ha et al. [23] have found that using this methodology, it is relatively easy to synthesise finely dispersed Pd NPs on commercial carbon black support (e.g. Vulcan®) with well-defined metal loadings, in his case of 20 and 40 wt.%. These catalysts gave maximum power densities of 145 and 172 mW cm⁻², respectively (at 303 K in 5 M formic acid), which represented a higher power density per unit mass of Pd than normal Pd-black [23]. Further improvement on the power density per unit mass of this system was found by adding Au to the Pd/C [22].

Zhang et al. have reported that the use of boric acid and ammonium fluoride in the Pd NP synthesis promotes the formation of finely dispersed 3.2 nm PdNPs, which shows an enhanced catalytic behaviour accordingly [64]. The

same group have also reported a Pd-P/C catalyst with the phosphorous introduced in synthesis via the precursor NaH_2PO_2 [65], which shows improved activity and stability of the catalyst.

In terms of other support materials, Qi et al. [41] have proposed a Ti support for nanoporous Pt–Ir which exhibit a significantly higher catalytic activity than pure Pt, and Larsen et al. have investigated sub-monolayer coverages of Pd on Au, W, Mo and V foil supports, with the latter appearing to be the most stable over the duration of a 3,000-s oxidation experiment [38] (Table 1).

Fuel crossover and membrane issues

Fuel crossover is a phenomenon where the fuel fed to the anode compartment diffuses through the separating membrane to the cathode compartment. This leads to a loss of fuel, the development of a mixed potential and competition at the cathode catalyst. Since most cathode catalysts are Pt-based due to its catalytic activity towards oxygen reduction, formic acid crossover also results in poisoning of the cathode catalyst as it decomposes into CO [67, 68]. In addition to the reduction in efficiency and cell performance, crossover can cause flooding of the cathode [68].

Although fuel crossover is substantially lower for formic acid than for, for example, methanol when using PEMs such as Nafion[®], it can still be significant. The crossover rate for formic acid is between two and ten times lower than methanol depending on the study [34, 69–72], and this has been ascribed to coulombic repulsions between formate anions and the polysulfonate groups in the PEM [10, 11].

According to Rhee et al., the crossover flux at the routinely used formic acid concentration of 5 M varies from 123 to 406 $\text{nmol cm}^{-2} \text{s}^{-1}$ for Nafion[®] 117 and 112 membranes, respectively [73], the variation being due to membrane thickness (180 and 50 μm). It was also found in general that the crossover flux increases with formic acid concentration and temperature [69, 73].

The hydrophilicity of formic acid can also potentially dehydrate the PEM, especially at high acid concentrations. This in turn leads to a decrease in proton conductivity and a concomitant increase in cell resistance. Jaime Ferrer et al. [74] have shown that there is an optimum composition of formic acid–water mixtures with a maximum dissociation of the acid [73], which indicates that a concentration of ca. 6 M formic acid is desired [74]. Since the crossover of formic acid cannot completely be eliminated, recent studies have turned towards reducing its deleterious effect, for example, by attempting to design cathode catalysts that will

Table 1 Selected literature data on performance of DFAFCs

Fuel details	Anode	Cathode	PEM	Output	Ref
5 M HCOOH/0.1 M H_2SO_4	Pd black (Alfa Aesar/Aldrich)	Pt black (Johnson Matthey)	Nafion 112	OCV 0.85 V 350–450 mA cm^{-2} @ 0.5 V	[21]
5 M HCOOH/0.1 M H_2SO_4	Pd (3–30 nm) on C (Vulcan XC72)	Pt black (Johnson Matthey)	Nafion 112	OCV 0.85 V 250 mA cm^{-2} @ 0.5 V	[21]
5 M HCOOH/0.1 M H_2SO_4	PdAu (3–30 nm) on C (Vulcan XC72)	Pt black (Johnson Matthey)	Nafion 112	OCV 0.85 V 250 mA cm^{-2} @ 0.5 V	[21]
3 M HCOOH/0.1 M H_2SO_4	Pd black (Alfa Aesar/Aldrich)	Pt black (Johnson Matthey)	Nafion 112	OCV 0.85 V 550 mA cm^{-2} @ 0.5 V	[25]
2–13 M HCOOH	Pt black	Pt black (Johnson Matthey)	Nafion 115	OCV 0.65–0.75 V 20 mA cm^{-2} @ 0.5 V	[34]
6 M HCOOH	PtAu	Pt black (Johnson Matthey)	Nafion 115	OCV 0.60 V 80 mA cm^{-2} @ 0.5 V	[34]
6 M HCOOH	PtRu	Pt black (Johnson Matthey)	Nafion 115	OCV 0.75 V 30 mA cm^{-2} @ 0.5 V	[34]
5 M HCOOH	PtPd (Pt black with sub-monolayer Pd)	Pt black	Nafion 117	OCV 0.91 V 62 mA cm^{-2} @ 0.5 V	[36]
5 M HCOOH	PtRu (Pt black with sub-monolayer Ru)	Pt black	Nafion 117	OCV 0.59 V 38 mA cm^{-2} @ 0.5 V	[36]
5 M HCOOH	Pt black	Pt black	Nafion 117	OCV 0.71 V 33 mA cm^{-2} @ 0.5 V	[36]
0.5 M HCOOH/0.5 M H_2SO_4	Pt	Pt wire	–	22 mA cm^{-2} @ 0.5 V	[39]
0.5 M HCOOH/0.5 M H_2SO_4	PtIr (44:56%) on Ti foil	Pt wire	–	76 mA cm^{-2} @ 0.5 V	[39]
0.125 M HCOOH/0.1 M HClO_4	PtBi	Not stated	–	Peak current density 3.8 mA cm^{-2}	[54]
0.125 M HCOOH/0.1 M H_2SO_4	PtBi	Not stated	–	Peak current density 2.4 mA cm^{-2}	[54]
0.25 M HCOOH/0.1 M H_2SO_4	PtPb	Not stated	–	Peak current density 8.2 mA cm^{-2}	[54]

be tolerant to formic acid decomposition products, most notably CO [75, 76].

Conclusions

The development of DFAFCs has made significant improvements in the understanding of the processes occurring within the fuel cell, to the extent that commercial products are on the verge of reaching the market. From the initial focus on Pd and Pt catalysts, a wide range of bimetallic, alloyed and modified metals have been investigated, using an expanding list of supports. Formic acid and formates have even been demonstrated to be viable fuels in microbial fuel cells [77, 78]. However, a critical appraisal of progress would also conclude that the catalysts so far developed either have high performance and short longevity or vice versa, and the challenge remains to develop a class of catalysts with the composition and morphology to combine the output of, say, pure Pd, whilst being resistant to acid corrosion and poisoning by CO and side products, etc. Some candidate materials for this fuel cell ‘holy grail’ have been put forward, and further investigations should yield significant improvements in this regard. In addition, the carrier materials for the catalysts have been paid little attention, with carbon cloth/paper the norm. Recent advances in the development and improved understanding of the surface chemistry of new carbon materials from nanotubes [79–86] to graphenes [87–91] have already begun to be applied as catalyst supports and must surely have a significant future impact in catalyst performance.

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