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► **To cite this version:**

Katerina Bretosh, Mathieu Beaucamp, Florine Toulotte, Jinyi Yuan, Philippe Hapiot, et al.. Mediated formic acid flow fuel cell (MFAFFC) based on biomimetic electrolytes. *Journal of flow chemistry*, 2023, 10.1007/s41981-022-00245-x . hal-03969077

HAL Id: hal-03969077

<https://hal.science/hal-03969077v1>

Submitted on 15 Feb 2023

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Mediated formic acid flow fuel cell (MFAFFC) based on biomimetic electrolytes

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Abstract

Water soluble biomimetic models of Riboflavin (B2 vitamin) and Folic acid (B8 vitamin) demonstrated to be good oxidant of formic acid at various pH. Their usage as anolyte mediators in a flow fuel cell to convert formic acid (or formate) into electricity is validated with measured power densities up to 16 mW.cm⁻². These preliminary optimum conditions demonstrated a volumetric energy density of 0.68 Wh.L⁻¹ when operating at 5 mA.cm⁻² and neutral pH. These new conditions inspired from redox flow batteries processes permit to remove noble metals at both sides of the formate flow fuel cell.

Keywords: biomimetic, direct formate flow fuel cell, non-noble metals, folic acid, alloxazine.

Introduction

Over the past decades, new technologies based on flow electrolytic cells have opened the way of liquid phase fuels for energy conversion (formic acid/formate ^{[1],[2]}, ethanol ^[3], methanol ^[4], ...). Recently, the rapid development of redox flow batteries devices permits today to envisage new technologies and approaches in order to limit the usage of rare earth metals at electrodes ^[5]. Even if these new approaches still need some more research studies before becoming competitive with already mature hydrogen fuel cells technologies, they are already emerging as alternatives to reduce the security limitations encountered with hydrogen storage. Additionally, the search for low-cost devices have reinforced such developments.

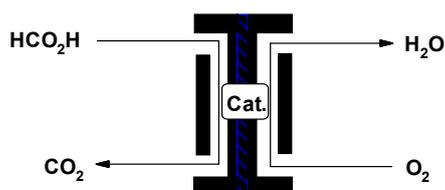
In the large set of possible liquid fuels, formic acid (FA) appears of high interest for its high volumetric energy density, its open circuit voltage (OCV, 1.40 V) ^[6], its high theoretical energy efficiency ^[7], and its better safety compared to the traditional hydrogen. If the volumetric energy density of FA is significantly lower than methanol, higher concentrations of FA can be used because of the lower crossover through the polymer electrolyte membrane ^[8]. As other advantages, FA is relatively safe with low flammability under ambient conditions.

If all these technologies are particularly promising and efficient, they require large quantities of rare earth metals such as platinum, iridium or palladium as electrocatalysts, to permit the direct conversion at the electrodes of all these fuels into protons and electrons. If those metals would have been more abundant at lower prices, it is probable that such technologies would have already been the definite alternative to oil world consumption since those fuels can easily be regenerated from biomass or CO₂ recycling ^[9]. For this reason, the quest for other electrocatalytic systems is also a nowadays challenge.

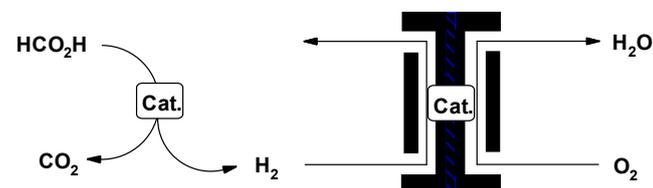
In this study, we focused in evaluating some aqueous bioorganic molecules and their derivatives (Figure 1, X) as FA oxidant, in order to build a spontaneous mediated formic acid flow fuel cell process (MFAFFC) by transporting

its two protons and two electrons (Figure 1, XH_2) to the anode. Such new system has never been described in literature and modifies the way of converting formic acid to electricity compared to classical indirect formic acid fuel cells or direct formic acid fuel cells. In this system, redox properties (kinetic and thermodynamic) will be governed by a low cost and abundant organic electrolyte. One major advantage of aqueous organic electrolytes is their high redox activity at low cost carbon electrodes. In the present study, we propose to introduce a new liquid phase electrochemical cell process deriving from redox flow batteries in order to remove rare earth metals from both anode and cathode for formic acid conversion into electricity. A rapid survey of literature indicates that in the human body, three B vitamins are implicated in the formic acid metabolism based on redox pathways for methylation reaction (Riboflavin – B2 Vit., Folic Acid – B8 Vit, Cobalamin B12 Vit.)^{[10][11]}. At this stage, we hypothesized the ability of these molecules (X) to oxidize formic acid into CO_2 and being reduced in the form of XH_2 similar to the reduced forms suggested in most of electroanalysis articles^{[12][13]}. This reduction pathway being the active pathway at the carbon anode of a flow fuel cell as recently observed for redox flow batteries for Riboflavin^[14]. We limit the list of possible candidates to Riboflavin and Folic Acid for their low cost in the preview of eventual larger scale evaluation. In a previous study, we have demonstrated that Riboflavin can be degraded when acting as a photochemical fuel^[15] leading us to focus our effort on its natural degradation side product the Lumichrome to produce biomimetic models. In this context, since Lumichrome is not water soluble, we envisaged, according to a procedure already described in literature by Janáky and Rajeshwar^[16], to add ammonium chains on the two acidic nitrogens of alloxazine skeleton in order to increase their water solubility and as a consequence their overall fuel cell capacity.

1 - Direct Formic Acid Fuel Cell:



2 - Indirect Formic Acid Fuel Cell (= Hydrogen Fuel Cell):



3 - This study: Mediated Formic Acid Flow Fuel Cell:

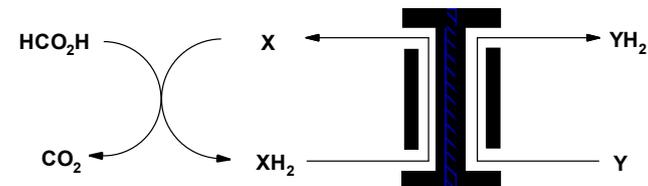


Figure 1. Schematic representations of Direct and Indirect Formic Acid Fuel Cells main approaches vs our Mediated Formic Acid Flow Fuel Cell (MFAFFC) approach

Materials and methods

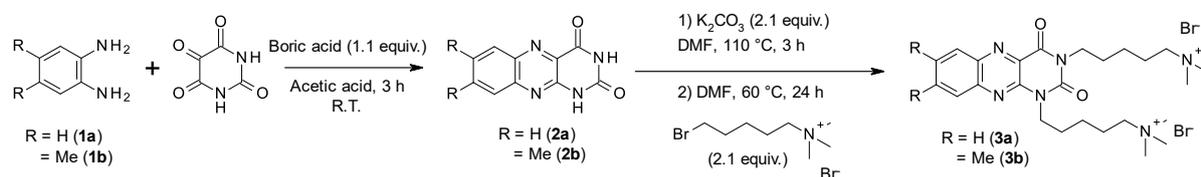
General information

All reagents were purchased from commercial suppliers (Strem Chemicals Inc., Sigma-Aldrich or Alfa Aesar) and were used without further purification. DMF (Fisher Scientific, Illkirch, France) was stored with active molecular sieves (3 Å) for 24 hours before usage. Water used was MilliQ grade. Thin-layer chromatography (TLC) were performed on Silica gel 60 F254 plates (Merck, Fontenay-sous-Bois, France) and visualized under UV (254 nm) or by staining with potassium permanganate or phosphomolybdic acid. NMR spectra were recorded on a Bruker (Wissembourg, France) AVANCE 300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C . Gas emission measurements were performed with Dräger X-am[®] 5000 gas detector for H_2 , CO_2 , CO .

General procedure for the synthesis of electrolytes **3a** and **3b**:

Step 1: To a solution of O-phenylene diamine **1a** or 4,5-dimethyl-1,2-phenylene diamine **1b** (1 equiv. 10 mmol) in acetic acid (400 mL) under inert atmosphere, Alloxane (1 equiv.) and boric acid (1,1 equiv.) are added. The solution is maintained at room temperature for 3 h. The resulting precipitate is filtered and washed with acetic acid, diethyl ether and water to yield benzo[g]ptéridine-2,4(1H,3H)-dione (**2a**) (97%) and 7,8-diméthylbenzo[g]ptéridine-2,4(1H,3H)-dione (**2b**) (96%).

Step 2: In a 25 mL flask, benzo[g]ptéridine **2a** or **2b** (1 equiv., 8.3 mmol) is dissolved in DMF (15 mL) and K_2CO_3 (2.1 equiv. 17 mmol) is added. The solution is heated under inert atmosphere at 110 °C for 3 h. The resulting precipitate is filtered and washed with DMF. Next, the precipitate is added to a solution of (2-bromoalkyl)trimethylammonium bromide (2.1 equiv., 17 mmol) in DMF (15 mL) in a 25 mL flask. The resulting solution is maintained à 60 °C for 24h under inert atmosphere. The dark yellow precipitate is filtered and washed with diethyl ether and acetone to yield the 5,5'-(2,4-dioxobenzo[g]ptéridine-1,3(2H,4H)-diyl)bis(N,N,N-triméthylpentan-1-ammonium) bromide (**3a**) (80%) or 2,2'-(7,8-diméthyl-2,4-dioxobenzo[g]ptéridine-1,3(2H,4H)-diyl)bis(N,N,N-triméthylethanammonium) bromide (**3b**) (71%).



Scheme 1. Electrolytes **3a** and **3b** synthetic pathways

General procedure for electrochemical characterization of species **3a**, **3b** and folic acid (**5**).

To a 20 mL water-jacketed reactor (T = 298 K), 10 mL of the analytical solution is added containing: (i) the electroactive species (**3a,b** and **5**) (1 mM) and (ii) the supporting electrolyte (100 mM). Depending on the pH values, supporting electrolyte are Na_2SO_4 (pH range = 1-4), AcONa (pH range = 3-6), NaH_2PO_4 (pH range = 5-9) and Na_2HPO_4 (pH range = 7-13), final pH values are obtained with little additions of 1 M sodium hydroxide or sulfuric acid solutions. A 3-electrodes system is used (Working Electrode (WE) = 1 mm glassy carbon, Auxiliary

Electrode (AE) = Pt wire, Reference Electrode (RE) = AgCl/Ag) to perform Differential Pulse Voltammetry (DPV) with Metrohm PGSTAT 128N potentiostat/galvanostat. Peak potentials E_p were directly considered for evaluating the formal redox potential E° . The reference (RE) potential is regularly checked using ferricyanide/ferrocyanide couple ^[17]. During DPVs, voltage step was 1 mV and pulse amplitude 10 mV.

Description of the experimental set-up for the mediated formic acid flow fuel cell (MFAFFC) with oxygen gas catholyte – Setup A: The flow fuel cell is composed of a commercially available TDM[®] fuel cell (<http://www.fuelcellstore.com/>) in which the original membrane electrode assembly (MEA) has been replaced by a custom 4 layers MEA composed of [Carbon cloth (Anode) / Nafion[®] 117 / Carbon gas diffusion layer / Pt-C 0.5 mg.cm⁻² (60%) (Cathode)] (<http://fuelcellsetc.com/>) (see figure 2). This custom MEA is clamped into two PTFE gaskets, two graphite monopolar plates (serpentine design at the anode/straight channels design at the cathode), two collecting plates and two plastic plates on which are connected 1/16" tubings for the inlet and the outlet. At the anode, the degassed electrolyte solution circulates after addition of formic acid (50 μ L) to a solution of ammonium alloxazine **3b** (0.1 M, 3 mL). At the cathode, oxygen gas circulates and was introduced into the straight channels by 1/16" tubing connected to a manifold, itself connected to an oxygen gas cylinder. The active surface (3.9 cm²) has been calculated as the anode serpentine/carbon cloth connection surface. The total internal volume of the fuel cell at the anode is 390 μ L (depth of flow field = 1 mm). All electrochemical measurements were performed using a potentiostat/galvanostat (Metrohm Autolab[®], PGSTAT128N, Villebon Courtaboeuf, France).

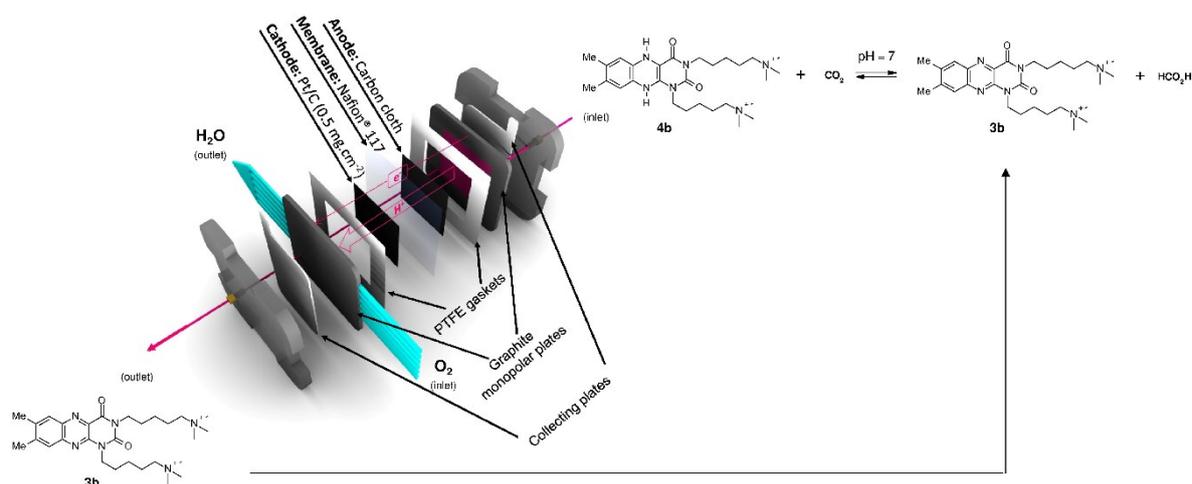


Figure 2. Schematic representation of the experimental MFAFFC **setup A** based on TDM[®] fuel cell.

Description of the experimental set-up for the mediated formic acid flow fuel cell (MFAFFC) with liquid $K_3[Fe^{(III)}CN_6]$ catholyte - Setup B: The flow fuel cell is composed of a commercially available C-Flow[®] Lab 1x1 with a zero-gap flow cell configuration (Fig 3). Electrodes of 1 cm² geometric surface area were comprised of a stack of porous carbon felt and graphite at the anode and the cathode. A sheet of Nafion 117 membrane was pretreated in 1 M solution KOH or NaOH (boiling 8 h with stirring), served as the ion-selective membrane. The rest of the space between the plates were flow distributor frames and

gaskets. The electrolytes were fed (anolyte: 5 mL; catholyte: 15 mL) into the cell through FEP tubing, at a flow rate of 10 ml/min controlled by ISMATEC Reglo Analog MS-2/12 peristaltic pumps. All electrochemical measurements were performed using a Potentiostat Galvanostat OrigaFlex OGF500.

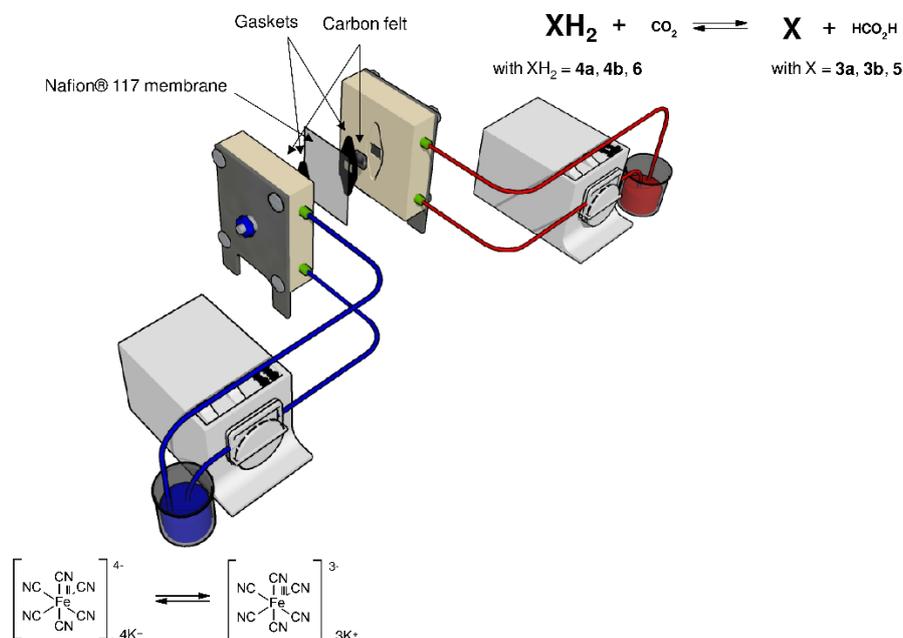


Figure 3. Schematic representation of the experimental MFAFFC **setup B** based on C-Flow® Lab 1x1 cell.

Results and discussion

In a prior step, the objective was to synthesize two water soluble derivatives of alloxazine skeleton **3a** and **3b** as biomimetic models of Riboflavin and to evaluate their properties as formic acid oxidant. Lumichrome and most of its alloxazine derivatives are not water soluble. In order to improve their solubility (up to 0.1M), we introduced on the molecules two arms composed of a C5 carbon chain and prolonged with a trimethyl ammonium function. The C5 carbon chain demonstrated to present a higher stability versus basic conditions and drastically reduces Hoffman elimination with shorter carbon chains, also the usage of bromide counterion is privileged for similar reasons ^{[18][19]}.

As an important observation, the reaction between formic acid and isoalloxazines results in a strong gas production. The characterization of the gas composition evidences the formation of carbon dioxide as a single emitted gas and no hydrogen, nor carbon monoxide production were detected showing a unique redox pathway. Simultaneously, NMR spectroscopy shows a complete reduction of **3a** ring in the presence of formic acid (Fig. 5). Similar gas production was observed with **3b** and folic acid (**5**). All reactions appear spontaneous and we can reasonably confirm for these three molecules the formation of a reduced form incorporating the 2 hydrogens from formic acid at acidic/neutral pH. In basic medium, ¹H NMR study was rendered difficult due to partial deprotonation and important shifting of every signals.

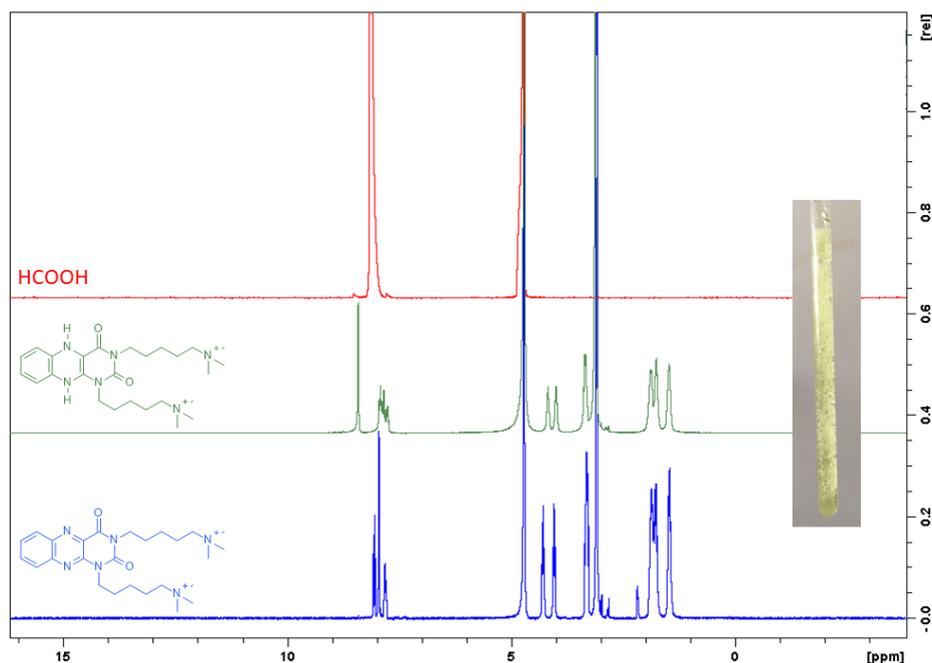
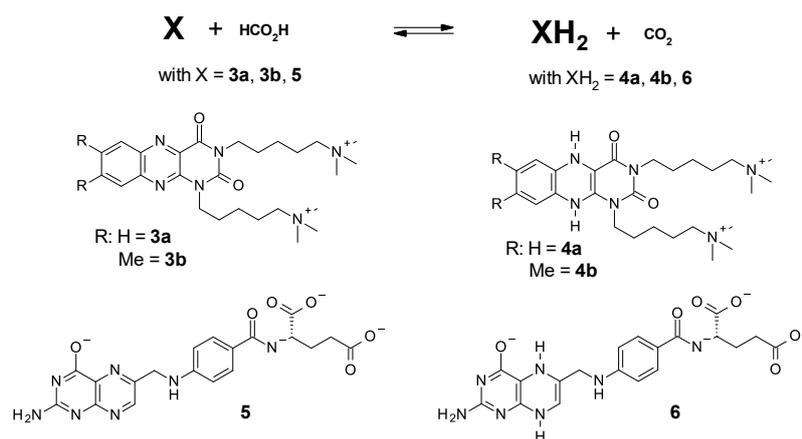


Figure 4. ^1H NMR characterization of (red) formic acid; (green) reduced isoalloxazine **4a** at pH = 7 in the presence of 1 equiv. of formic acid; (blue) **3a**; (right insert) view of the strong CO_2 gas production in the NMR tube.

According to these observations, we can propose a general reaction scheme for the reduction of **3a,b** into **4a,b** and folic acid (**5**) into its reduced form **6** (scheme 2).



Scheme 2. Reduction of X (**3a,b** and **5**) into XH_2 (**4a,b** and **6**) in the presence of formic acid.

Electrochemical properties of **3a** and **3b** have been investigated at various pH using DPV, in order to identify formal potentials E^0 . This method is often more precise than cyclic voltammetry^[20]. The peak potential E_p is related to the half-wave potential $E_{1/2}$ and pulse amplitude ΔE , and $E_{1/2}$ is assimilated to the formal redox potential when diffusion and activity coefficients (D and γ , respectively) of the oxidized and reduced species are close (Eq. 1 and 2).

$$E_{1/2} = E_p + \frac{\Delta E}{2} \quad 1$$

$$E^{10} = E_{1/2} + \frac{RT}{nF} \ln \frac{\sqrt{D_{Ox}} \gamma_{Red}}{\sqrt{D_{Red}} \gamma_{Ox}} \quad 2$$

By comparison with previously reported formic acid Pourbaix diagram ^{[21][22]}, the E-pH diagrams for **3a** and **3b** show that both molecules are good oxidant for formic acid at every pH (Figure 5). Unfortunately, folic acid reduction on glassy carbon was too slow that DPV is no longer suitable for a redox potential estimation. Cyclic voltammetry is then performed on folic acid (**5**) at pH = 14 and shows a slow reversible equilibration. At this pH, folic acid appears to be good oxidant for formic acid too.

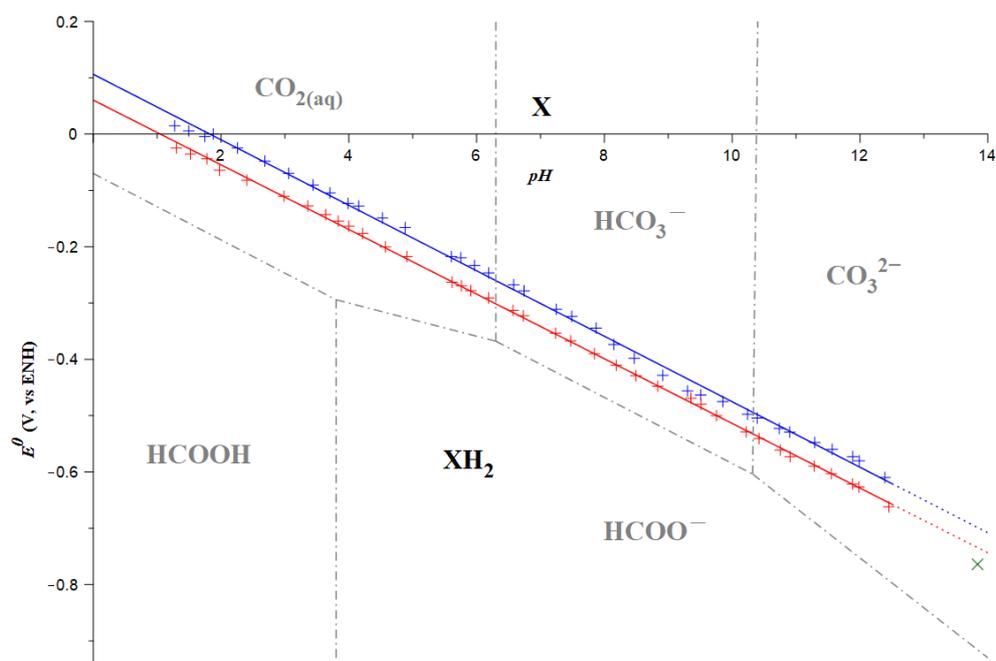


Figure 5. E-pH diagrams for **3a** (red) and **3b** (blue) and **5** (green) superimposed with formic acid Pourbaix diagram (grey) taken from literature ^{[21][22]}.

In order to quantify the potential efficiency of these electroactive bioorganic molecules to effectively convert formic acid into electricity, we build two different flow fuel cells dedicated to gas or liquid catholytes to use oxygen gas as the catholyte. We modified a commercially available hydrogen fuel cell (TDM[®] fuel cell) in order to introduce a nitrogen degassed buffered (pH = 7) aqueous mixture of **3b** at 0.1 M (0.5 mmol) concentration mixed with formic acid (5 equivalents, 2.5 mmol) at the anode. For this purpose, we replaced the graphite hydrogen flow field by one usually dedicated to methanol fuel cells and we designed a membrane electrode assembly composed of (i) carbon paper at the anode, (ii) Nafion[®] 117 as the membrane and carbon gas diffusion layer on which platinum catalyst (0.5 mg.cm⁻²) is deposited on surface to play the role of the cathode for oxygen gas conversion (see setup A, Fig. 2). After pre-activation of the MEA in boiling water for 8 hours, and after the end of CO₂ bubbling, the resulting anolyte preparation is pumped at 10 mL.min⁻¹ in the flow fuel cell without any leakage observed and oxygen gas is introduced at the cathode. The voltammetry characterization of the cell was

then realized by applying a progressive current discharge and by monitoring the voltage. Such approach is conventional and permits to evaluate the maximum power density delivered by the system (for an example of such curve see figure 6). Despite a low open current voltage at 0.44 V which could be explained by a very high resistance and/or high activation losses (i.e. low overall kinetics) of our system, the results validated the ability to produce electricity by this innovative method (Table 1, entry 1). However, the power density was low with a maximum value at 0.69 mW.cm⁻². The limited characteristics of this system could probably be ascribed to the cathode and the usage of gas phase. To check that explanation, we used a liquid catholyte for comparison instead of the oxygen cathode. In that particular case our system is very similar to a redox flow battery (RFB) process, for which the charge step is replaced by a spontaneous chemical reduction by formic acid of the anolyte. In order to evaluate this approach, we introduced two porous carbon felt electrodes (1 cm²) in the electrode's volumes of a commercially available C-Flow[®] Lab 1×1 cell (see setup B, Fig. 3). In this system the same anolyte preparation than for setup A (5 mL) was used but oxygen gas was replaced by a benchmark catholyte aqueous solution used in RFB for its high redox stability composed of K₃[Fe^(III)CN₆] (0.4 M) and K₄[Fe^(III)CN₆] (0.04 M) (11 mL) at pH = 12, playing the role of oxidant in this redox mechanism. In this process, the negative terminal remains the capacity-limiting and irreversible side. In the same way than for RFB processes, the volume of each electrolyte reservoir can be modulated to increase the fuel cell capacity, but for simplicity the two reservoirs volumes were kept identical for the all set of experiments. Our first test demonstrated much encouraging results than those obtained with setup A, with a great increase of the open current voltage to 0.715 V and a maximum power density of 3 mW.cm⁻² (entry 2), demonstrating our initial assumption that aqueous electrolyte would present lower resistance. In this first experiment the Nafion[®] 117 membrane was pre-activated as previously by boiling the membrane for 8 hours in water and we next tried to pre-activate the Nafion[®] 117 membrane by boiling in NaOH (0.1 M) solution as described earlier in literature for an analog RFB process ^[23]. This pre-activation method is preferable (entry 3) and we kept it for the next experiments.

In order to improve the aqueous solubility of **3b** we investigated the addition of small quantities of sodium dodecyl sulfate (SDS) as a surfactant. Increasing the concentration of **3b** is supposed to increase the capacity of the anolyte side. SDS clearly demonstrated a great effect on **3b** solubility in water (up to 0.46 M with 10% SDS) but to our surprise the performances of the fuel cell dropped (entry 4). Cyclic voltammetry with **3b** (1 mM) and progressive increased concentration of SDS (see SI) show a drop of the maximum current density. This can be explained by the formation micelles associated to our anolyte increasing the overall solubility but limiting the diffusion of the molecules at the anode. Finally, best results were obtained by replacing liquid formic acid by potassium formate (3 equivalents), its basic form which is the main specie at pH = 7 (entry 6). Indeed, under such conditions, both OCV and power densities were influenced to a maximum of 16 mW.cm⁻². This obtained result is particularly interesting since today's, formate can be produced with excellent faradic yields by carbon dioxide electro-reduction and any further optimization of this system would permit to recycle easily the produced CO₂ into a fuel ^[24]. To our knowledge no such fuel cell process based on potassium formate at pH = 7 exists. Increasing the pH is also a strategy since the redox potential of **3b** should decrease and the resulting OCV should be higher. By working at pH = 7 instead of pH = 12, we effectively observed a lower OCV value with probably lesser losses since the power density dropped drastically to 3.2 mW.cm⁻² (entry 8). Also, it is observed a slight increase of OCV

when using potassium formate instead of formic acid, this could be justified by a higher pH after addition of potassium formate than for formic acid addition, resulting in lower redox potentials for **3b**. Study of **3a** under similar conditions always gave lower OCVs and power densities (entries 5 and 7). This highlights the interest of methyl substituents on the alloxazine ring as observed in riboflavin and their electroactive role. Indeed, the natural presence of methyl substituents on 7- and 8- positions of the Riboflavin's isoalloxazine ring has been the subject of numerous discussions in literature and they are implicated in the isoalloxazine ring electron transfer by stabilizing/destabilizing each one of the redox states and consequently result in an optimized mid-point redox potential [25]. Here we can reasonably produce similar conclusions considering the important differences between **3a** and **3b**.

Remarkably, folic acid that can be only used at pH = 14 for reversibility reasons, is also a good candidate for potassium formate conversion into electricity since measured OCVs and power densities are from the best observed so far during this study (entry 9). Another interest for the use of this molecule for formate conversion into electricity is its very low price and its high international production scale level.

Entry	Anolyte mediator (Conc.)	Formate Source (Nb. Equiv.)	Catholyte ^[e]	Setup	pH	OCV (V)	Power density (mW.cm ⁻²)
1	3b (0.1 M)	HCO ₂ H (5 equiv.)	O ₂	A ^[a]	7	0.44	0.69
2	3b (0.1 M)	HCO ₂ H (5 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[c]	7	0.715	3
3	3b (0.1 M)	HCO ₂ H (5 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	7	0.73	3.24
4	3b (0.46 M) ^[d]	HCO ₂ H (5 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	7	0.45	0.14
5	3a (0.1 M)	HCO ₂ K (3 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	7	0.69	0.63
6	3b (0.1 M)	HCO ₂ K (3 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	7	0.88	16.02
7	3a (0.1 M)	HCO ₂ K (3 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	12	0.85	1.10
8	3b (0.1 M)	HCO ₂ K (3 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	12	1.15	3.20
9	5 (0.5 M)	HCO ₂ K (5 equiv.)	K ₃ [Fe ^(III) CN ₆]	B ^[b]	14	1.28	8.96

Table 1. Results with MFFAFC.

[a] Anolyte mediator and formic acid were mixed in N₂ degassed buffered aqueous solution. The flow fuel cell operating at 10 mL.min⁻¹ for the anolyte and with O₂ gas as the catholyte. [b] Anolyte mediator and potassium formate were mixed in N₂ degassed buffered aqueous solution. The flow fuel cell operating with degassed K₃[Fe^(III)CN₆] solution as the catholyte. Both anolyte and catholyte were pumped at 10 mL.min⁻¹. Nafion® 117 membrane was pre-activated 8 h in boiling NaOH (1 M) solution. [c] Nafion® 117 membrane was pre-activated 8h in boiling deionized water instead of NaOH (1 M). [d] Sodium dodecyl sulfate (10 %) was added. [e] The catholyte for setup B was composed of a mixture of K₃[Fe^(III)CN₆] (0.3 M) + K₄[Fe^(III)CN₆] (0.03 M).

Optimal conditions in hand, we wanted to evaluate a full discharge of the system by chronopotentiometry. We applied a 5 mA discharge current to the system based on the conditions **3b** in the presence of potassium formate at pH = 7 operated for 86.7 minutes (Fig. 6 – right panel). This means that 210 mg of potassium formate produces 0.3 mW using this system which corresponds to a 0.68 Wh.L⁻¹ energy density at pH = 7.

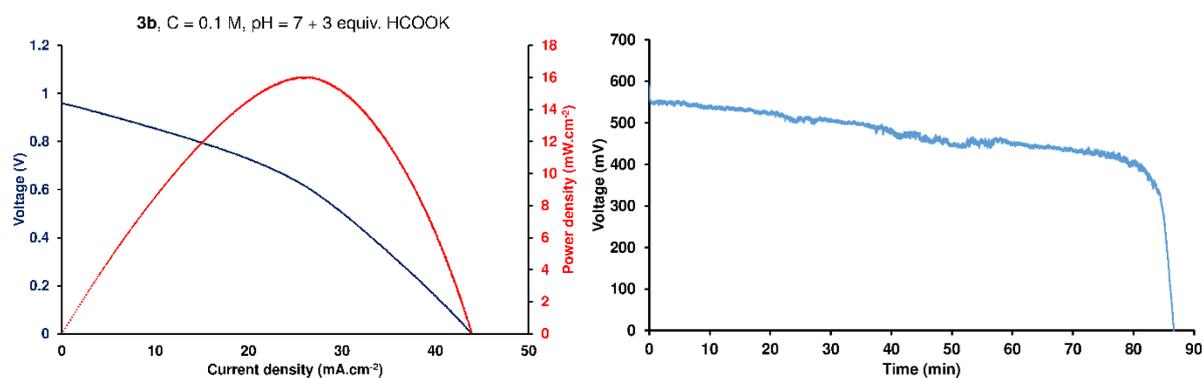


Figure 6. (left) Polarization curve of **3b** at pH = 7 using setup B at $10 \text{ mL}\cdot\text{min}^{-1}$ in the presence of 3 equivalents of potassium formate. (right) Chronopotentiometry curve at 5 mA discharge current for **3b** at pH = 7 using setup B at $10 \text{ mL}\cdot\text{min}^{-1}$ in the presence of 3 equivalent of potassium formate.

Conclusion

In summary, we synthesized two derivatives of B2 vitamin presenting much higher water solubility and simplified chemical structures and we evaluated their use in fuel cells in comparison with folic acid (B8 vitamin) as formic acid oxidants under different pH conditions. All of them demonstrated to be spontaneous formic acid oxidants and this particular reactivity was confirmed by their redox properties. Indeed, all three molecules show to be able to efficiently convert formic acid (or formate) into electricity (up to $16 \text{ mW}\cdot\text{cm}^{-2}$) using two different fuel cells operating in liquid phase. Such process has never been described earlier and introduce a new approach for removing noble metals at the electrodes by using biomimetic mediators in the electrolyte system.

At the present stage, the optimization as only focused on a limited range of aqueous conditions and only carbon materials have been evaluated as electrodes, but we can envisage some progress in the future in order to improve their performances by changing the set-up of the fuel cell. Nevertheless, our preliminary results clearly demonstrate that methyl substituents on alloxazine ring are a key parameter for obtaining an efficient redox process. Compared to a recent reported study^[26] in which authors replaced Pd metal by $\text{CoFe}(\text{CN})_6$ complex at the formate fuel cell anode, combined with Ce^{4+} as the terminal electron acceptor at a carbon felt cathode to remove noble metals, their maximum power density was lower than the ones obtained in the present study with only $8.6 \text{ mW}\cdot\text{cm}^{-2}$. Also considering the performances of redox flow batteries, we can envisage some progress in the future of a mediated formic acid (or formate) fuel cell in order to remove noble metals from electrodes and considering the very low price of folic acid, some more work should be performed. Further work for a better understanding of these redox mechanisms is also of high importance since most of proposed biological mechanisms involve enzymes and NADH coenzymes in the oxidation process of formic acid into carbon dioxide. Here spontaneous reaction is observed and structural similarities between these three evaluated mediators strongly suggest an important role of common pyrazine ring to (i) recognize (acid base reaction) and (ii) transform formic acid into carbon dioxide (redox reaction). The repercussion of these chemical systems in chemistry will probably be more important than expected considering the observed reactivity.

Acknowledgements

The authors gratefully acknowledge the Region Hauts de France and ISITE Lille for the financial support (START AIRR, H₂-Switch project).

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