Review

Direct liquid-feed fuel cells: Thermodynamic and environmental concerns

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Abstract

The present paper briefly reviews the different direct liquid-feed fuel cells that have been regarded through the open literature. It especially focuses on thermodynamic-energetic data and toxicological–ecological hazards of the chemicals used as liquid fuels. The analysis of those two databases shows that borohydride, ethanol and 2-propanol would be the most adequate liquid fuels for the polymer electrolyte membrane fuel cell-type systems, even if they are inferior to hydrogen. All the fuels and also all the by-products stem from their decomposition are more or less harmful towards health and environment. More particularly, hydrazine should be avoided because it and its by-product are very dangerous. It is to note that the present paper does not intend to review and to compare the performances of those fuel cells because of great differences in the efforts devoted to each of them.
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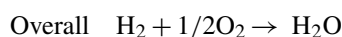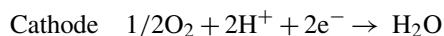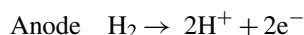
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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is regarded as being a very promising low-temperature power generation device thanks to it excellent performances when fed with hydrogen (cell voltage of 1.23 V):

Anode $H_2 \rightarrow 2H^+ + 2e^-$

Cathode $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall $H_2 + 1/2O_2 \rightarrow H_2O$

However, the production, storage and distribution of hydrogen are still strong limitations for its development [1]. Alternative hydrogen carrier fuels are investigated. In a "fuels

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Table 1
Liquid fuels for DLFCs (the second column gives the abbreviation used in the text for each fuel; it replaces then L of DLFC; the fourth column gives the densities at 20 °C).

(Sodium)borohydride	B	$(Na^+)\,BH_4{}^-$ (aq)	$1.07\ g\ ml^{-1a}$
Dimethoxymethane	DM	$(CH_3O)_2CH_2$ (l)	$0.86\ g\ ml^{-1}$
Dimethyl ether	DE	$(CH_3)_2O$ (g)	$0.002\ g\ ml^{-1b}$
Ethanol	E	C_2H_5OH (l)	$0.79\ g\ ml^{-1}$
Ethylene glycol	EG	$C_2H_6O_2$ (l)	$1.11\ g\ ml^{-1}$
Formic acid	FA	HCOOH (l)	$1.22\ g\ ml^{-1}$
Hydrazine	H	N_2H_4 (l)	$1.00\ g\ ml^{-1}$
Methanol	M	CH_3OH (l)	$0.79\ g\ ml^{-1}$
1-Methoxy-2-propanol	MP	$CH_3OCH(OH)CH_3$ (l)	$0.92\ g\ ml^{-1}$
1-Propanol	P1	$CH_3CH_2CH_3OH$ (l)	$0.81\ g\ ml^{-1}$
2-Propanol	P2	$CH_3CH(OH)CH_3$ (l)	$0.79\ g\ ml^{-1}$
Tetramethyl orthocarbonate	TO	$(CH_3O)_4C$ (l)	$1.02\ g\ ml^{-1}$
Trimethoxymethane	TM	$(CH_3O)_3CH$ (l)	$0.89\ g\ ml^{-1}$
Trioxane	T	$C_3H_6O_3$ (s)	$1.17\ g\ ml^{-1c}$

[a] $NaBH_4$ (s) with a solubility of 550 g in 1 l of water at 25 °C.
[b] $(CH_3)_2O$ (g) with a solubility of 3280 g in 1 l of water at 25 °C.
[c] Density at 65 °C; $C_3H_6O_3$ (s) with a solubility of 211 g in 1 l of water at 25 °C.

race", many liquid fuels (Table 1) and then many direct liquid-feed fuel cells (DLFC) have been proposed. The most common and studied fuel is methanol, which use as energy carrier represents an important challenge for PEMFC since the system is simpler without a reformer. Methanol has several advantages with respect to hydrogen. It is a cheap liquid fuel, easily handled, transported and stored, and it has a high theoretical energy density [2].

In recent decades, the fuel cells have attracted more and more attention due to high-energy demands, fossil fuel depletion and environmental pollution. On that last point, hydrogen is seen as the cleanest fuel because the fuel cell fed with it solely produces water, even if it is true that its production by reforming, oxidation or water gas shift, produces carbon dioxide, a greenhouse gas [1]. However, all the liquid fuels regarded as alternative to hydrogen are chemicals that are more or less harmful towards health and environment. It is also the case for the reaction products. The following question is then asked: what can be the toxicological and ecological impacts of those substances?

The present paper reviews the direct liquid-feed fuel cells (DLFCs) regarded through the literature (Table 1 for the liquid fuels). For each fuel cell, it proposes a discussion about the fundamentals, the fuels and the by-products. Finally, the relevance of each system is tackled. It is to note that the present paper is not a review devoted to the DLFCs performances. It rather focuses on the overall interest of those fuel cells.

Table 2
Reactions of DLFCs

DBFC	Anode	$BH_4{}^- + 8OH^- \rightarrow 8BO_2{}^- + H_2O + 8e^-$	Overall	$BH_4{}^- + 2O_2 \rightarrow BO_2{}^- + 2H_2O$
	Cathode	$2O_2 + 4H_2O + 8e^- \rightarrow 8OH^-$		
DDMFC	Anode	$(CH_3O)_2CH_2 + 4H_2O \rightarrow 3CO_2 + 16H^+ + 16e^-$	Overall	$(CH_3O)_2CH_2 + 4O_2 \rightarrow 3CO_2 + 4H_2O$
	Cathode	$4O_2 + 16H^+ + 16e^- \rightarrow 8H_2O$		
DDEFC	Anode	$(CH_3)_2O + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$	Overall	$(CH_3)_2O + 3O_2 \rightarrow 2CO_2 + 3H_2O$
	Cathode	$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$		
DEFC	Anode	$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$	Overall	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
	Cathode	$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$		
DEGFC	Anode	$C_2H_6O_2 + 2H_2O \rightarrow 2CO_2 + 10H^+ + 10e^-$	Overall	$C_2H_6O_2 + 5/2O_2 \rightarrow 2CO_2 + 3H_2O$
	Cathode	$5/2O_2 + 10H^+ + 10e^- \rightarrow 5H_2O$		
DFAFC	Anode	$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$	Overall	$HCOOH + 1/2O_2 \rightarrow CO_2 + H_2O$
	Cathode	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$		
DHFC	Anode	$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^-$	Overall	$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$
	Cathode	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$		
DMFC	Anode	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	Overall	$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$
	Cathode	$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$		
DMPFC	Anode	$CH_3OCH(OH)CH_3 + 4H_2O \rightarrow 3CO_2 + 16H^+ + 16e^-$	Overall	$CH_3OCH(OH)CH_3 + 4O_2 \rightarrow 3CO_2 + 4H_2O$
	Cathode	$4O_2 + 16H^+ + 16e^- \rightarrow 8H_2O$		
DP1FC	Anode	$CH_3CH_2CH_3OH + 5H_2O \rightarrow 3CO_2 + 18H^+ + 18e^-$	Overall	$CH_3CH_2CH_3OH + 9/2O_2 \rightarrow 3CO_2 + 4H_2O$
	Cathode	$9/2O_2 + 18H^+ + 18e^- \rightarrow 9H_2O$		
DP2FC	Anode	$CH_3CH(OH)CH_3 + 5H_2O \rightarrow 3CO_2 + 18H^+ + 18e^-$	Overall	$CH_3CH(OH)CH_3 + 9/2O_2 \rightarrow 3CO_2 + 4H_2O$
	Cathode	$9/2O_2 + 18H^+ + 18e^- \rightarrow 9H_2O$		
DTOFC	Anode	$(CH_3O)_4C + 6H_2O \rightarrow 5CO_2 + 24H^+ + 24e^-$	Overall	$(CH_3O)_4C + 6O_2 \rightarrow 5CO_2 + 6H_2O$
	Cathode	$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$		
DTMFC	Anode	$(CH_3O)_3CH + 5H_2O \rightarrow 4CO_2 + 20H^+ + 20e^-$	Overall	$(CH_3O)_3CH + 5O_2 \rightarrow 4CO_2 + 5H_2O$
	Cathode	$5O_2 + 20H^+ + 20e^- \rightarrow 10H_2O$		
DTFC	Anode	$C_3H_6O_3 + 3H_2O \rightarrow 3CO_2 + 12H^+ + 12e^-$	Overall	$C_3H_6O_3 + 3O_2 \rightarrow 3CO_2 + 3H_2O$
	Cathode	$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$		

2. Fundamentals

2.1. Reactions

Table 2 summarizes the anode, cathode and overall reactions for each DLFC. The liquid fuels are given in Table 1. For all DLFCs, the cathode is fed with oxygen.

As all the liquid fuels, except hydrazine and borohydride, are composed with carbon, hydrogen and oxygen, the "ideal" reaction products are CO_2 and water (Table 2). Even if CO_2 is a greenhouse gas, the "ideal" products are environmentally acceptable. Regarding hydrazine, the ideal products are N_2 and water. The borohydride ion oxidation leads to the formation of the metaborate ion, BO_2^-, which is slightly harmful (will be discussed in Section 3).

Another observation from Table 2 is related to the number of electrons involved in the DLFCs during the fuel oxidation and then the oxygen reduction. The number of electrons involved is linked to the molecular weight and the atomic composition of the fuel. The more hydrogen and carbon atoms the molecule has, the higher the number of electrons involved is. Hence, trimethoxymethane (4C, 10H) oxidises producing 24 electrons, while formic acid (1C, 2H) gives two electrons. For borohydride, the number of electrons involved is eight because H^- oxidise into H^+ by liberating two electrons per H^-. For hydrazine, each hydrogen atom produces one electron.

Those numbers of electrons are important because they condition, with other parameters, the theoretical energetic capacities of the fuel cells.

2.2. Thermodynamics

Table 3 shows the thermodynamic comparison of the DLFCs. The theoretical energy conversion efficiency of all the DLFCs exceed 90%, what is larger than that of the PEMFC fed with H_2 (83%).

The theoretical specific energy E_{sp} is proportional to both the number of electrons n involved (in oxidation and reduction reactions) and the overall cell voltage (electromotive force) E^0, and is inversely proportional to the fuel molecular weight M_w:

$$\frac{nE^0}{M_w}$$

Hence, this ratio means that a compound is all the energetic since it is a light molecule that involves many electrons (high n/M_w ratio) and it displays a high cell voltage. Even if some data defaults (Table 3), one may consider that the cell voltages of the fuel cells for which no data are given are of about 1.2. If so, one can remark that the best fuel cell is the DBFC in term of theoretical specific energy E_{sp}. This technology is followed by DP1FC, DP2FC, DDEFC, DEFC and DMPFC. Except DFAFC, the other fuel cells are relatively close. The DFAFC displays the lowest E_{sp} that represents 17.5% of the best one (i.e. that of DBFC).

The pure compound capacity, which is independent of E^0, is completely proportional to the ratio n/M_w. The highest C values are displayed by DP1FC, DP2FC, DEFC, DDEFC and DBFC. This ranking confirms the previous one even if there is not an exact parallel.

It is interesting to compare the data given in Table 3 to that of the H_2/O_2 PEMFC. This latter presents the following theoretical features: M_w of 2.01 g mol^{-1}, n of 2, n/M_w of 0.995, E^0 of 1.23 V, E_{sp} of 32 802 Wh kg^{-1}, C of 26668 Ah kg^{-1} and η of 0.83. The ratio n/M_w shows that H_2 is really the best fuel and that if there were not the H_2 production, storage and distribution issues, the liquid fuels would be uninteresting from an energetic point of view.

Table 3
Thermodynamic features of DLFCs at 25 °C and 1 atm (M_w: fuel molecular weight; n: number of electrons involved; E^0: cell voltage; E_{sp}: theoretical specific energy; C: pure compound capacity; η: theoretical energy conversion efficiency)

DLFC	Fuel/Oxidant	M_w (g mol^{-1})	n	n/M_w (e^- mol g^{-1})	E° (V)	E_{sp} (Wh kg^{-1})	C (Ah kg^{-1})	η (%)
DBFC	BH_4^-/O_2	37.74	8	0.212	1.64	9 295	5 668	91
DDMFC	$(CH_3)_2CH_2/O_2$	76.10	16	0.210	1.23	6 931	5 635	98
DDEFC	$(CH_3)_2O/O_2$	46.07	12	0.260	1.20	8 377	6 981	95
DEFC	C_2H_5OH/O_2	46.07	12	0.260	1.15	8 028	6 981	97
DEGFC	$C_2H_6O_2/O_2$	62.07	10	0.161	1.22	5 268	4 318	99
DFAFC	$HCOOH/O_2$	46.03	2	0.043	1.40	1 630	1165	106
DHFC	N_2H_4/O_2	32.05	4	0.125	1.62	5 419	3 345	100
DMFC	CH_3OH/O_2	32.04	6	0.187	1.21	6 073	5 019	97
DMPFC [a]	$CH_3OCH(OH)CH_3/O_2$	76.10	16	0.210	α	α.5635	5 635	-
DP1FC	$CH_3CH_2CH_3OH/O_2$	60.10	18	0.300	1.13	9 070	8 027	97
DP2FC	$CH_3CH(OH)CH_3/O_2$	60.10	18	0.300	1.12	8 990	8 027	97
DTOFC [a]	$(CH_3O)_4C/O_2$	136.15	24	0.176	β	β.4725	4 725	-
DTMFC [a]	$(CH_3O)_3CH/O_2$	106.12	20	0.189	γ	γ.5051	5 051	-
DTFC [a]	$C_3H_6O_3/O_2$	90.08	12	0.133	δ	δ.3570	3 570	-

[a] No thermodynamic data available from sources to author's knowledge.

3. Concrete features

3.1. Environmental concerns of the fuels

The fuel cells are considered as being environmentally friendly. However, the chemicals used as liquid fuels are not completely safe and the fuel cells are not emission-free. For example, the carbon-containing fuels "ideally" produce CO_2, which is a greenhouse gas (Table 2). Otherwise, methanol and the other alcohols produce hazardous by-products (will be discussed below).

All the chemicals, taken as liquid fuels, are produced in more or less important amounts in accordance with the needs, and that is why the production processes are well established, the main issue being, generally, the production cost. To illustrate those words, the production ways of some fuels can be suggested. The most studied liquid fuel, i.e. methanol, is predominantly produced by steam reforming of natural gas and, although both coal and biomass (e.g. wood) can be used, today's economics favour natural gas [3]. The second most studied liquid fuel, i.e. ethanol, is produced by hydration of acetylene or, biologically, by fermenting sugar-rich raw materials from agriculture. It can be produced from cellulose-based biomass, such as trees and grasses, as well [4]. It is obvious that the transformations of raw materials from agriculture and cellulose-based biomass are safer processes. Besides the ethanol production, acetylene is also used to catalytically produce ethylene glycol via ethylene oxide [4]. As a last example, one can suggest that methanol is used as raw material for the production of dimethyl ether, dimethoxymethane and formic acid [4].

Table 4 summarises the known main hazards of the liquid fuels. It is to note that all the information provided in Table 4 are especially stem from "material safety data sheet" documents available on the websites of the chemicals suppliers [5,6].

A first glance to Table 4 shows that all the chemicals used as liquid fuels are hazardous. Nevertheless, one can distinguish some differences. Hydrazine should be avoided because it has nearly all the drawbacks: carcinogenic, very hazardous towards health and environment, and unstable. It is not a fuel that can be proposed to customers for their daily use. All the chemicals are polluting and flammable. They are irritant or even toxic. Dimethyl ether distinguishes itself because its "single" drawback is its extreme flammability. Borohydride is one of the most hazardous chemical and its use, even in solution, should be avoided. It is to remark that the borohydride-based solution is in fact an aqueous alkaline solution, which is highly concentrated in sodium hydroxide with pH > 13 [7]. Sodium hydroxide is corrosive, irritant, slightly polluting and non-flammable.

In fact, the choice of the "ideal" liquid fuel is quite difficult on the basis of their hazardous features (Table 4) because they are all harmful. That choice should be a compromise between the hazardous effects and the performances of the corresponding fuel cells. However, from Table 4, one can assert that hydrazine should really be avoided.

As a conclusion to this section, one can add that ethanol is presently viewed by many scientists as the "perfect" fuel for the portable fuel cells because ethanol is easily produced, is one of the less harmful chemical and is sufficiently energetic.

3.2. Brief survey about DLFCs

The main expectation for a DLFC is that the "ideal" anodic oxidation takes place on the anode electrocatalyst without the occurrence of side reaction(s) (Table 2). Unfortunately, it is never the case whatever the liquid fuel. On the basis of this statement,

Table 4
Hazards of the liquid fuels from Refs. [5,6].

	Health Effects	Environmental Hazards	Fire Hazard	Others
(Sodium) Borohydride	Toxic, Causes severe burns	Polluting	Highly Flammable	Corrosive, Liberates toxic and highly flammable gas
Dimethoxymethane	Irritant	Slightly polluting	Highly Flammable	-
Dimethyl ether	-	-	Extremely Flammable	-
Ethanol	Irritant	Slightly polluting	Highly Flammable	-
Ethylene glycol	Irritant, Harmful if swallowed	Slightly polluting	Flammable	Corrosive
Formic acid	Irritant, Harmful, Causes severe burns	Slightly polluting	Flammable	Corrosive
Hydrazine	Irritant, Harmful, Toxic, Causes severe burns, Sensitizing	Very Toxic to aquatic organisms, Dangerous for the environment	Highly Flammable	Carcinogenic, Unstable
Methanol	Toxic	Slightly polluting	Highly Flammable	-
1-Methoxy-2-propanol	Irritant	-	Flammable	-
1-Propanol	Irritant	Toxic, Slightly polluting	Highly Flammable	Carcinogenic
2-Propanol	Irritant	Slightly polluting	Highly Flammable	-
Tetramethyl orthocarbonate	Irritant	-	Flammable	Sensitive to humidity
Trimethoxymethane	Irritant	Slightly polluting	Highly Flammable	-
Trioxane	Irritant, Toxic for reproduction	Slightly polluting	Highly Flammable	-

the following lines briefly review some experimental features for the different DLFCs, particularly emphasizing on the side reactions and the by-products formed.

For the DMFC, the "ideal" anodic reaction is not completely reached as methanol is mainly decomposed into CO; furthermore, its principle by-products are formaldehyde and formic acid [2,8,9]. Some of these species, adsorbed on the catalyst surface, are not readily oxidizable and remain strongly adsorbed, preventing fresh methanol from adsorbing and undergoing further reaction. The methanol oxidation requires active multiple sites: the ones for adsorbing methanol and the others for donating OH species that are necessary for the oxidation and desorption of the adsorbed intermediates [8]. Platinum is the most active metal for the dissociative adsorption of methanol but it is readily poisoned by CO. Therefore, new electrocatalysts, i.e. Pt-based bimetallic alloys, are developed and there is a consensus about the fact that Pt–Ru is the best material for the methanol total oxidation. Power densities of 40–120 mW cm^{-2} at a cell potential of 0.4 V were reported for single cells operating at 60–90 °C [2,8–11].

With ethanol, the main challenge is the cleavage of the C–C bond, what makes difficult its oxidation into $2CO_2$. Song et al. [12,13] worked on the DEFC because they thought that, in the long run, the combination of ethanol (a renewable resource) and fuel cell (a promising and attractive technology) would have brought benefits of not only lowering emission and increasing the air quality from the environmental point of view but also increasing energy security and creating economic opportunities from the social point of view. They observed that the best anode catalyst for the DEFC was the bimetallic Pt-Sn, what was also observed by Lamy et al. [2]. However, even with that catalyst, ethanol did not "ideally" oxidize and the final products were mainly acetaldehyde and acetic acid [2,12,14].

Lamy et al. [2] proposed a short survey about DMFC, DEFC and DP2FC. The authors asserted that those alcohols had a very good energy density that were close to that of hydrocarbons and gasoline (i.e. 10–11 kWh kg^{-1}), so that they appeared as reasonable alternative energy carriers for the electric vehicle. This study confirmed the observations relative to both DMFC and DEFC that are given above and added that the oxidation of higher alcohols always produced some amounts of adsorbed CO. DP1FC and DP2FC were investigated more in details by Wang et al. [15]. They evaluated ethanol, 1-propanol and 2-propanol as alternative fuels for DMFC by using Pt–Ru and Pt-black catalysts. The main products of ethanol were acetaldehyde and CO_2. For the 1-propanol, propanal and CO_2 were mainly produced. In contrast, the main by-products of 2-propanol oxidation were 2-propanone and negligible amounts of CO_2. Wang et al. [15] concluded their investigation by the following remark: "both 1-propanol and 2-propanol are not suitable fuels because of their low electrochemical activity, but ethanol is the most promising candidate for an alternative fuel for DMFCs".

Regarding ethylene glycol, Peled et al. [16] showed that their DEGFC was 33% more powerful than their DMFC. They concluded that this put the DEGFC in direct competition with DMFC and as ethylene glycol was well known in automotive industry and as its distribution infrastructure already existed,

this liquid fuel was a promising candidate for practical electric vehicles. de Lima et al. [17] analysed the oxidation products and proved that CO_2, glycolic acid and oxalic acid were formed.

Rice et al. [18] studied DFAFCs constructed with Pt-based bimetallic catalysts and showed that the best catalyst was Pt–Pd. The addition of Pd enhanced the rate of formic acid oxidation via a direct reaction mechanism [19]. Formic acid oxidised according to two paths. According to the first path, the dehydrogenation path (or direct path), formic acid was directly dehydrogenated into CO_2. According to the second path, the dehydration path (or CO path), formic acid was dehydrated into CO, which poisoned the electrode or was further oxidized to produce CO_2. The main by-product in DFAFC is CO [20]. Muller et al. [21] criticised the use of formic acid as liquid fuel because of its low energy density (Table 3) and its corrosive and toxic nature (Table 4).

Dimethyl ether is less toxic than methanol and in principle available in large quantities. The vapour pressure of dimethyl ether is between those of propane and butane, what means that a technology for storing and handling the fuel is already available.

Müller et al. [21] demonstrated a DDEFC yielding comparable power density and higher total efficiency than a DMFC. They proposed a mechanism where dimethyl ether was oxidised into methanol that was then oxidised over Pt–Ru (as in DMFC). Wang et al. [22] observed the formation of CO, H_2, CH_4, H_2CO, CO_2 and H_2O.

Dimethoxymethane, trimethoxymethane and trioxane are derivatives of natural gas. One of their advantages is that they have no C–C bond. Their oxidation led to the formation of methanol and ultimately carbon dioxide [23,24]. Pt–Ru and Pt–Sn were efficient catalysts. Dimethoxymethane underwent more facile oxidation than trimethoxymethane, while trioxane oxidised at significant rates only above 55 °C. Crossover occurred with those three fuels but at a lesser degree than that occurring with methanol [23]. It is to note that dimethoxymethane and trimethoxymethane are not currently available in large commercial quantities and are, therefore, very expensive.

Yamada et al. [25] are the first scientists to run a DHFC using a Nafion$^®$ membrane. Hydrazine showed better performances than methanol in the direct fuel cell. The cell using hydrazine gave voltages twice as high as those of the cell using methanol. The catalytic decomposition reaction of hydrazine proceeded further than the oxidation reaction on the anode side. Two routes of decomposition occurred: the first producing N_2 and $2H_2$; and the second producing from $3N_2H_4$, $1N_2$ and $4NH_3$. The latter decreased the fuel utilization and seemed to cause the lowering of the cell voltage. Moreover, the DHFC suffered from hydrazine and ammonia crossover through the membrane.

Different from the previous fuels, the borohydride fuel is an alkaline aqueous solution of sodium borohydride, which is completely carbon-free. Against DMFC, DEFC and DFAFC, this is a non-negligible advantageous because no CO-like species will poison the electrocatalyst. The ideal eight-electron oxidation is not effective because hydrolysis of borohydride occurs in some extent with production of BO_2^- and H_2 [26]. Finding an anode catalyst inactive towards the borohydride hydrolysis is one of

the main objectives. The most promising catalysts are the Au-based ones because they catalyze the borohydride oxidation by involving 7–8 electrons per molecule [27].

To briefly summarise the present section, one can assert that the main problem with the carbon-containing fuels is the formation of CO that poisons the anode catalyst. Besides, another problem for the two-carbon-containing fuels, like e.g. ethanol, is the difficulty, for the catalyst, to cleave the C–C bond, what is at the origin of the formation of by-products like acetic acid and acetaldehyde. With hydrazine and borohydride as fuels, the "ideal" direct oxidation does not completely take place and by-products such as ammonia and hydrogen, respectively, are produced. It is to note that for the DBFC, the $BO_2{}^-$ ions are formed whatever the reactions at the anode side may be (i.e. oxidation or hydrolysis). Hence, it will be interesting to shortly review the environmental concerns of the by-products that are discussed in the present section.

3.3. Environmental concerns of the by-products

The purpose of the present section is to give information about the environmental concerns relative to the by-products listed in the previous section. It is true that the investigations about the DLFCs focus on avoiding the formation of those undesired by-products and then their hazardous properties would become a minor issue. Nevertheless, it is likely that a failing fuel cell system could produce such chemicals and it is important to keep in mind such information.

Table 5 proposes the hazards of the by-products of the DLFCs. Except three substances, namely ammonia (stem from hydrazine), acetaldehyde (stem from ethanol) and formaldehyde (stem from methanol), the by-products are no more harmful and no more flammable than the liquid fuels of Table 4.

Hydrazine as fuel should be avoided and even renounced since both reactant and by-product are very dangerous towards health and environment (Tables 4 and 5).

As methanol is the fuel for which the investigations are the most developed, few words concerning its by-products are required (Table 5). One of its by-products is formaldehyde. It is one of the common indoor air pollutants. Irritating at low concentrations, it is potentially lethal at large exposures. Formaldehyde is classified as a probable human carcinogen [4,5]. Formaldehyde and formic acid can cause blindness by destruction of the optic nerve. Any exposure to formic acid can cause severe chemical burns and eye exposure can result in permanent eye damage [4,5].

It is to remark that the liquid fuels are often aqueous acidic solutions of the chemicals. The main acid used is H_2SO_4, which is known to be corrosive, non-flammable and slightly polluting. It is an issue that should be taken into account in the environmental concerns as well.

As a conclusion, one can emphasize that recycling processes and facilities must be created and developed to salvage the emissions of the by-products.

4. Short discussion about the relevance of each DLFC

The efforts devoted to the DLFCs are variable from one fuel to the other: e.g. huge amount of studies about both DMFC and DEFC, increasing number of works devoted to DBFC and only few papers about e.g. DTFC and DTOFC. In the opinion of the author, it is not relevant to compare the DLFCs performances that have been published through the open literature. Indeed, the differences in the efforts devoted to the development of each technology are too different to get a realistic comparison. Hence, the relevance of those DLFC technologies will be briefly discussed on the basis of the theoretical data, which are the objectives to reach, and of the environmental concerns of the liquid fuels. Moreover, as a secondary criterion, it will be taken into consideration the by-products hazardous properties.

For the present discussion, Table 6 is proposed as a discussion support. This table classifies the DLFCs by giving notes (see

Table 5
Hazards of the by-products of the DLFCs from Refs. [5,6]

By-products		Health Effects	Environmental Hazards	Fire Hazard	Others
Ammonia	in DHFC	Irritant, Harmful, Toxic, Causes severe burns	Very toxic to aquatic organisms, Dangerous for the environment	Non-Flammable	Corrosive
Acetaldehyde	in DEFC	Highly Irritant, Toxic, Harmful	Marine Pollutant	Extremely Flammable	Unstable, Carcinogenic
Acetic acid	in DEFC	Irritant, Harmful, Causes severe burns	Slightly polluting	Flammable	Corrosive
Formic acid	in DMFC	Irritant, Harmful, Causes severe burns	Slightly polluting	Flammable	Corrosive
Formaldehyde	in DMFC, DDEFC	Highly Irritant, Toxic, Sensitizing, Harmful	Toxic	Flammable	Severely corrosive, Carcinogenic
Glycolic acid	in DEGFC	Harmful, Causes burns	Slightly polluting	Flammable	Corrosive
Methanol	in DDEFC, DDMFC, DTMFC, DTFC	Toxic	Toxic, Slightly polluting	Highly Flammable	-
Oxalic acid	in DEGFC	Harmful	Slightly polluting	Flammable	Corrosive
Propanal	in DP1FC	Irritant	Slightly polluting	Highly Flammable	-
Propanone	in DP2FC	Irritant	Slightly polluting	Highly Flammable	-
Metaborate	in DBFC	Irritant	Slightly polluting	-	-

Table 6
DLFCs relevance: "the lower the total is, the more relevant the DLFC is" (notes for energy—0: more than 10,000 Wh kg^{-1}, 1: from 8000 to 10,000 Wh kg^{-1}, 2: from 5000 to 8000 Wh kg^{-1}, 3: below 5000 Wh kg^{-1}, 4: below 1000 Wh kg^{-1}; notes for hazards—0: no effect, 1: low effect, 2: moderate effect, 3: high effect, 4: extreme effect)

DLFC	Fuel/oxidant	Note for theoretical specific energy	Note for the fuels hazards	Note for the by-products hazards	Total of the notes[a]
DBFC	BH_4^-/O_2	1	3	1	4.5
DDMFC	$(CH_3O)_2CH_2/O_2$	2	2	3	5.5
DDEFC	$(CH_3)_2O/O_2$	1	3	3	5.5
DEFC	C_2H_5OH/O_2	1	2	4	5.0
DEGFC	$C_2H_6O_2/O_2$	2	3	3	6.5
DFAFC	$HCOOH/O_2$	3	3	–	6.0
DHFC	N_2H_4/O_2	2	4	4	8.0
DMFC	CH_3OH/O_2	2	3	3	6.5
DMPFC	$CH_3OCH(OH)CH_3/O_2$	2	2	3	5.5
DP1FC	$CH_3CH_2CH_3OH/O_2$	1	4	2	6.0
DP2FC	$CH_3CH(OH)CH_3/O_2$	1	2	2	4.0
DTOFC	$(CH_3O)_4C/O_2$	2	2	3	5.5
DTMFC	$(CH_3O)_3CH/O_2$	2	2	3	5.5
DTFC	$C_3H_6O_3/O_2$	2	3	3	6.5

[a] Total = (note for theoretical specific energy) + (note for the fuels hazards) + 1/2(note for the by-products hazards).

Table 6 caption). This table takes into consideration the theoretical energy data, more especially the theoretical specific energy, the liquid fuels environmental concerns and the by-products environmental concerns. It is to remark that the availability of the fuel is not regarded because it is very likely that the production of a chemical will quickly adapt to the market.

From Table 6, the worst fuel is hydrazine because it is highly dangerous towards both health and environment. In fact, it can be proposed two categories for Table 6: the liquid fuels having a total above 5, and the ones for which the total is equal or below 5. From that classification, DBFC, DEFC and DP2FC would be the most adequate fuel in a compromise between the energetic data and the environmental concerns. The other DLFCs, except DHFC, would be relatively similar and might be regarded as alternative options to the DBFC, DEFC and DP2FC.

DEFC is likely the fuel cell for which the utilization perspectives are the greatest [15]. DBFC is a technology for which the investigations continuously increase and the research groups involved in that fuel cell support its high potential as a power generation system for mobile and portable applications. Its potential would be superior to that of the DMFC [7].

"Ideally" oxidised, the carbon-containing liquid fuels produce CO_2 and water. CO_2 is a greenhouse gas and men are working to the reduction of its emission. It is interesting to compare the productions of CO_2 from hydrocarbons and those from DLFCs. Let *n*-heptane be a hydrocarbon with a theoretical specific energy of about 10,000 Wh kg^{-1}. Given methanol and ethanol liquid fuels for the DMFC and the DEFC, respectively, with theoretical specific energies of about 6000 and 8000 Wh kg^{-1}, respectively. By a simple calculation, one can remark that the "ideal" CO_2 production from the DMFC and the DEFC will be about 30% and 20% lower than that from *n*-heptane "ideal" combustion. By "ideal", it is meant 100% efficient. Hence, even if these fuel cells produce CO_2, the amounts produced are reduced and that contributes to the efforts for reducing the greenhouse gas emissions.

To conclude the present section, one can compare the H_2 features to those proposed in Tables 3–5. Even if only two electrons are produced from the H_2 oxidation, thanks to its very low molecular weight, its theoretical specific energy is of about 33,000 Wh kg^{-1}, what is more than three times higher than the best DLFC, i.e. DBFC. H_2 is extremely flammable in presence of oxygen: it is likely its single drawback in terms of hazardous effects. Its oxidation leads to the production of water. However, as underlined in introduction, it has non-negligible disadvantages relative to its production, storage and distribution. Hence, if one obscures these last drawbacks, there is no doubt about the fact that the ideal fuel for the PEMFC is H_2. According to the classification provided in Table 6, H_2 has a total of 2 $(0 + 2 + 0)$.

5. Conclusion

The present paper reviews the theoretical energy properties and the environmental concerns of liquid chemicals used as hydrogen carrier fuels for the PEMFC-type system.

Except formic acid, all the fuels display acceptable theoretical energy properties. On the basis of such data, the DP1FC, DP2FC, DEFC, DDEFC and DBFC are the most promising systems. However, there are all below the PEMFC fed with hydrogen, which is able to show energetic capacities more than three times superior to that of the DBFC.

There is an important question about the utilization of such liquid fuels: what are the hazards of these chemicals towards both health and environment? In fact, all of them are more or less hazardous. Besides the liquid fuels, the by-products, stem from side reaction(s) in competition with the "ideal" oxidation, are also more or less hazardous. Hydrazine distinguishes itself because it and the by-products stem from its decomposition are very dangerous and harmful. The analysis of the toxicological and ecological data draws a negative picture for the chemicals used as liquid fuels.

The relevance of each DLFC is suggested and it appears, as it is commonly admitted by the scientists working on the DLFCs, that the DEFC is one of the most relevant PEMFC-type systems. However, if one obscures the storage issue of H_2, there is no doubt about the fact that the "ideal" fuel for the PEMFC is H_2.

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