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Review

Novel materials for fuel cells operating on liquid fuels

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Abstract: Towards commercialization of fuel cell products in the coming years, the fuel cell systems are being redefined by means of lowering costs of basic elements, such as electrolytes and membranes, electrode and catalyst materials, as well as of increasing power density and long-term stability. Among different kinds of fuel cells, low-temperature polymer electrolyte membrane fuel cells (PEMFCs) are of major importance, but their problems related to hydrogen storage and distribution are forcing the development of liquid fuels such as methanol, ethanol, sodium borohydride and ammonia. In respect to hydrogen, methanol is cheaper, easier to handle, transport and store, and has a high theoretical energy density. The second most studied liquid fuel is ethanol, but it is necessary to note that the highest theoretically energy conversion efficiency should be reached in a cell operating on sodium borohydride alkaline solution. It is clear that proper solutions need to be developed, by using novel catalysts, namely nanostructured single phase and composite materials, oxidant enrichment technologies and catalytic activity increasing. In this paper these main directions will be considered.

Keywords: low-temperature fuel cells; liquid fuels; electrocatalysts; energy; materials

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1. Basics of Fuel Cell Materials

During the last three decades, four long-term markets and energy solutions in which fuel cell systems may play an important role were identified [1,2,3]: lowest cost energy to end users, combined heat and power or high-value premium power solutions, peak-shaving technologies, and load-management and grid-power support for varying supply. Accordingly, in the direction of the commercialization of fuel cell products in the near future, the fuel cell system is being redefined by means of a strong focus on lowering costs of basic elements, electrolytes and membranes, electrode and catalyst materials, as well as on increasing power density and long-term stability [3].

A fuel cell is an energy conversion device operating on the principle of a galvanic electrochemical cell, whereas the fuel at the anode (negative electrode) and oxidant at the cathode (positive electrode) are converted by an electrochemical reaction into electrical energy [1]. The key feature of fuel cells is that they convert chemical energy directly to electrical energy isothermally, according to the following equation:

$$\Delta G = -nFE = \Delta H - T\Delta S \tag{1}$$

in which G is the Gibbs energy, n is the number of changed electrons, F is the Faraday's constant and E is the cell potential. At the limit of reversibility, the Gibbs energy released by the system can be converted to electrical energy with 100% efficiency. The thermodynamic efficiency of a fuel cell is defined by the ratio of the maximum obtainable electrical energy, ΔG, to the enthalpy, ΔH, of the reaction:

$$\eta_{th} = \eta_f = \Delta G/\Delta H = 1 - T\ \Delta S/\Delta H \tag{2}$$

If the thermal cell potential is defined as $E_H = -\Delta H/nF$, then

$$\eta_f = E/E_H \tag{3}$$

and generally, for $\Delta S < 0$, i.e. $|\Delta G| < |\Delta H|$, then $E < E_H$. As example, for the methanol fuel cell reaction $CH_3OH + 3/2O_2 = CO_2 + 2H_2O$, $\eta_f = 0.97$ for liquid methanol fuel. Once the cell is under load, the efficiency will fall. Including the internal resistive loss in the electrolyte as an ohmic overpotential, $\eta_R = iR$, and taking into account the charge transfer and diffusion overpotentials at the two cell electrodes, η, and the load efficiency, η_l, the electric efficiency, η_e, is defined with respect to the actual cell potential, $E_{i,}$ at current i as:

$$\eta_l = \eta_e = -nFE_i/(-nFE_{th}) = nF(E^0 - |\eta(i)|)/(-nFE_{th}) = (\Delta G + nF\Sigma\ |\eta(i)|)/\Delta H \tag{4}$$

For the alkaline fuel cell, for example, technically interesting current densities can be obtained at cell potential of ca. 0.9 V, giving a load efficiency of 0.9/1.48 = 0.61. The fuel utilization, U_f, is the mass of fuel reacted in cell with respect to the mass of input fuel (commonly up to 90%). The real efficiency, η_r, is then given by the product of the fuel efficiency, electric efficiency, and fuel utilization, as follows

$$\eta_r = \eta_{th}\,\eta_l\,U_f = \eta_f\,\eta_e\,U_f \tag{5}$$

The net heat balance per unit time of a cell can be written:

$$W = -(iT\Delta S/nF) + i\Sigma\ |(i)| + i^2R = i(E^0{}_H - E^0) + i\Sigma\ |\eta(i)| + i^2R \tag{6}$$

where the internal cell resistance is included. W is given in watts, and has great importance in industrial engineering design. The efficiency of a fuel cell may be compared to the theoretical efficiency of a heat engine, such as an internal combustion engine (ICE). Typically, the theoretical efficiency for an ICE is ca. 0.5, but in city driving, for example, this can drop to as low as 0.1. The advantage of a fuel cell is thus its ability to convert chemical to electrical energy with high efficiency, particularly under part load.

The possibility to oxidize fuel isothermally and at high efficiency in fuel cells is indeed very attractive. However, there are still several aspects that will be determinant for their success or failure [1,2,3]. One of the most important is the R&D ability to understand and overcome issues related with the three main components of the system: the use of noble metals for both the anode and the cathode, and the lack of a good cation-exchange membrane with a performance comparable to Nafion. Furthermore, lowering the cost considerably is fundamental. Moreover, it has been ignored the fact that wide use of fuel cells would certainly increase the price of Pt. In this way, different non precious metal catalysts have been investigated in order to reduce the cost. Among them, transition metal nitrogen and carbon species (M–N–C) have received particular interest as ORR catalyst for the polymer electrolyte fuel cell cathode [4,5,6].

There are four primary sub-systems in a fuel cell system [1]: (1) cell: anode, electrolyte, cathode and supporting structures; this is the heart of the cell also known as Membrane Electrode Assembly, MEA; (2) Stack: cell, interconnector, gas/liquid flow structure, fuel/air sealing, contact layers, gas/fluid manifolds, flow configurations, top end plates, current collectors and pressure spring plates; (3) balance of plant (BOP): supports all system operating modes such as cold start, cool-down to ambient, power-up from stand-by, cool-down to stand-by, load following and emergency shut-down; (4) external BOP: provides connections to the exterior. It is then clear that materials R&D is critical in the development of fuel cells. The following sections deal with the materials used in the components (i.e., electrodes, membrane electrolytes, interconnects, current collectors, etc.) of a fuel cell, whose properties and challenges require adequate consideration to lead fuel cells into commercialization.

The operating temperature regime [low temperature (LT) < 300 °C; intermediate temperature (IT) < 600 °C; high temperature (HT) > 600 °C] determines material choices, fuels used in the fuel cells and fuel processing options. Therefore, it can be used to classify the fuel cells, as shown in Table 1.

A single fuel cell is a low potential (< 1 V) high current (10–500 A) device, and when its potential is not high enough to operate as a useful generator it is necessary to use a fuel cell stack consisting of a number of single cells connected in series and packaged as a unit. For certain applications there are also stacks of cells connected in parallel. Basically, a simple repeat fuel cell unit consists in a MEA, the interconnector, a gas/liquid flow structure and fuel/air sealing (Figure 1) [1]. The cell stack is terminated by the manifold plate, top end plates and stack thermal insulation. The MEA can be dispersed in support structures that can also act as gas/liquid diffusion layers. Additional catalytic functions can be added as well as contact layers (Figure 2). To increase cell performance, it is essential to substitute expensive materials with cheaper ones and simplify fabrication processes. Moreover, membranes for fuel cells are required to have high ionic conductivity, high electronic resistance, low fuel and oxidant crossover, low cost, high mechanical durability, high chemical durability, and compatibility with other cell and stack components.

Table 1. Common fuel cell types and characteristics.

	Alkaline AFC	Polymer SPFC	Methanol DMFC	Phosphoric Acid PAFC	Low Temperature SOFC (LT)	Molten Carbonate MCFC	Solid Oxide SOFC
Operating temperature (°C)	LT 60–90 HT (pressurized) >100	LT < 80 HT 90–120	50–100	150–220	400– 600	650	800–1000
Transfer species/electrolyte	OH^- 30% KOH	LT: H^+, Nafion type HT: H^+, Phosphoric acid	H^+, Nafion type	H^+, Phosphoric acid (concentrated)	O^{2-}, GDC/SDC, LGSM, H^+, cerates, zirconates	CO_3^{2-}, Li, K, Na carbonates in $LiAlO_2$ matrix	O^{2-}, 3Y5Z, 8YSZ, LSGM
Anode materials	Pt, Ni, PTFE-bonded carbon with noble metal loading	Pt, thin noble metal layers that may be dispersed on C.	Pt, Pt–Ru, others	Pt, graphite felt with low noble-metal loading	Ni-cermet, Pt alloys, carbon composites, others	Ni, others	Ni-cermet, others
Cathode materials	Pt or Ag, spinel or perovskite catalysts	Pt, graphitized C, polymer materials	Pt, others	Pt dispersed on C black in PTFC structure	La–Sr–Fe–GDC composites, others	Li-doped NiO, $LiFeO_2$, $LiCoO_2$, others	Perovskites, doped $LaMnO_3$ W/Sc-doped ZnO_2
Additional construction materials	Polymer materials	Polymeric materials	Metallic, Polymer materials	Polymeric materials	Metals, oxide dispersions	Ceramic, steel	Ceramics, high alloy steels
Main additional components	Water evaporator	Water evaporator	Water evaporator, CO_2 separation ion exchanger	Water separation, heat exchanger, reformer	Water evaporator, heat exchanger, reformer	Water evaporator, heat exchanger, reformer, combined cycle possibility for heat usage	Water evaporator, heat exchanger, reformer, possibility of using combined cycle systems to exploit high - grade waste heat
Oxidant, primary fuel and cost/kWh	Pure O_2, pure H_2, ca. 1€/kWh	O_2 or air, pure H_2, ca. 1€/kWh	O_2 or air, methanol, ca. 0.8€/kWh	Oxygen or air, H_2, methane, natural gas, W/reformer, ca. 0.1€/kWh	O_2 or air, H_2, methane, natural gas, ca. 0.08€/kWh	O_2 or air, H_2, methane, natural gas, W/reformer, ca. 0.1€/kWh	O_2 or air, H_2, methane, natural gas, W/H_2 reformer, ca. 0.1€/kWh
Anodes reactions	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$; $H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$; $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$; $CO + O^{2-} \rightarrow CO_2 + 2e^-$
Cathodes reactions	$1/2\,O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$1/2\,O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$3/2\,O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$1/2\,O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$O_2 + 4e^- \rightarrow 2O^{2-}$	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$	$O_2 + 4e^- \rightarrow 2O^{2-}$

Power densities	LT < 200 mW/cm^2 HT > 500 mW/cm^2	> 500 mW/cm^2	< 100 mW/cm^2	150–175 mW/cm^2	100–150 mW/cm^2	100–150 mW/cm^2	Small cells up to 1 W/cm^2
Status (power level)	Small commercial available units, up to ca. 100 kW	Small commercial available, up to 100 kW	Small units available, up to 5–750 W, cell stacks up to 100kW operated	Commercialization mainly for smaller units (2000 kW), prototypes up to 400 kW constructed	Small units available, up to 270 kW; prototypes up to 10 MW constructed	Prototypes up to 10 MW in construction; MCFCs may cover 15 GW in 2022	Small units available, up to 500 kW; prototypes up to 100 MW constructed
Current costs	2000–3000€/kW	3000–6000€/kW	10.000€/kW	2500€/kW	8000€/kW	2000€/kW	10.000€/kW
Uses	Mainly military and space uses	Military uses, particularly in submarines operation; space flight	Portable power generation, light traction	Local residential power supplies, small distributed power supplies (< 11 MW)	Off-grid distributed power generation applications	Power station, load-levelling, CHP	Stationary power systems transportation, CHP
Fuel conversion efficiency	Up to 55%	55%	50%	Cell alone: 60% W/reformer: 40%	Cell alone: 60% W/reformer: 55%	Cell alone: 55–65% W/reformer: up to 55%	Cell alone: 55–65% W/reformer: 55%
Problems	Price	Price	Slow kinetics of methanol oxidation, methanol crossover, cell design	Reliability, lifetime, price, maintenance costs.	Electrode activity, ohmic resistance of electrolyte	Stability of electrodes/electrolyte, costs must be reduced to 500–1000€/kW	Reliability, product cost, sealants, interconnects, cell design
Countries where development is taking place	USA, Canada, Germany	USA, Canada, Germany	USA, Japan, Germany, UK, France	USA, Japan	USA, Japan, Germany, UK	USA, Japan, Holland	USA, Japan, Germany, UK
Remarks	Mature technology, feed gases without CO, CO_2	CO content of fuel < 100 ppm	Membranes, diffusion layers, design require consideration	CO content of fuel gas < 1%	Many problems need to be overcome	Internal reforming increases and use of coal decreases efficiency	Many problems need to be overcome

GDC/SDC denotes gadolinia – or samaria–doped ceria; LSGM denotes lanthanum–strontium–magnesium–gallate.

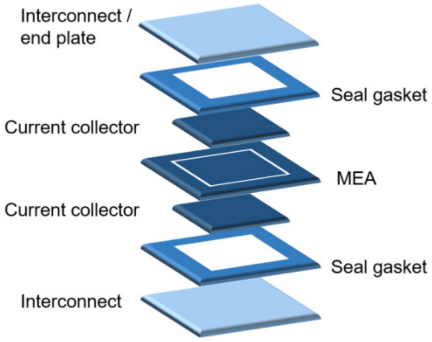

Figure 1. Schematic of fuel cell repeat unit.

MEAs are generally prepared by coating the catalyst onto the membrane to form a three layer catalyst-coated membrane. Carbon-supported platinum nanoparticles (Pt/C) catalysts are common catalysts, usually made into a slurry or ink (using alcohol, water, glycerol, etc.) with a binder (generally a Nafion solution) in a consistency suitable for the coating method employed [2]. Platinum alloys are also being considered due to better long-term stability [7].

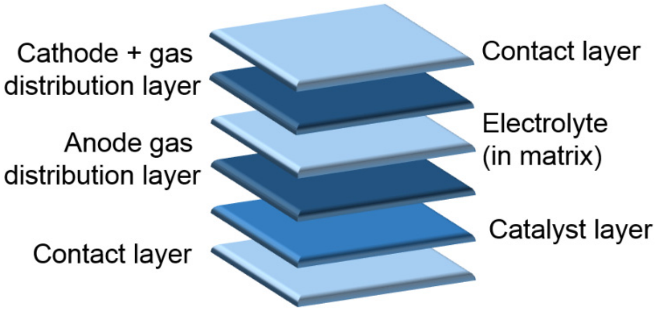

Figure 2. Schematic of cell structure.

The majority of fuel cells are stacked with bipolar interconnectors in order to ensure the lowest contact resistance losses. Interconnectors are multifunctional and thus pose significant challenges to materials selection, in terms of stability/corrosion resistance/cost.

Apart from the MEA and its issues, critical parameters for cell stack performance are the need to prevent high resistive conductors, avoid thermal losses and large temperature gradients. Moreover, the BOP for uniform gas flow, start-up and shut-down, control and power conditioning, which makes up almost three-quarters of the fuel cells system cost, with heat exchangers, reformer, rotating equipment and electrical system, also requires great consideration. Figure 3 shows a generic fuel cell system block diagram.

Additionally to cost issues, reliability and lifetime are still significant hurdles for the commercialization of fuel cell technology. Different applications demand demonstration of life of 1 to 10 years, and therefore manufacturers need to develop new products in record times, which requires accelerated testing and lifetime prediction models [3,8].

Only through building of competitive manufacturing, operation and disposal chains, will successful commercialization of fuel cell products be possible [9]. The disposal issue requires full attention and shortage of materials used in fuel cells has been predicted [10]. This issue of supply chain development and recycling can be more successfully solved in the case of fuel cells operating on liquid fuels, as it will be discussed in the following sections.

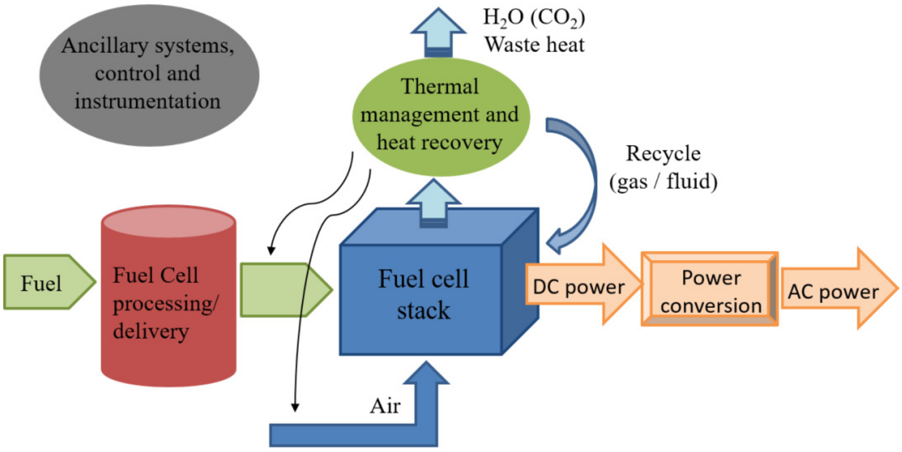

Figure 3. Schematic of a generic fuel cell power plant (adapted from [1]).

2. Direct Liquid-Feed Fuel Cells

Significant progress has been made in the area of nanostructured catalysts and composite membranes, which allowed to improve the catalytic activity of the electrode materials used in the liquid fuel cells and to bring these cells closer to commercial viability. These cells may use several types of fuel, which are summarized in Table 2.

Table 2. Types of liquid fuels for PEMFC application and corresponding fuel cell parameters (adapted from [1]).

Type of fuel	Chemical formula of the fuel	Number of electrons involved in reaction of fuel oxidation	Theoretical open circuit voltage (V)	Theoretical energy conversion efficiency (%)
Methanol	CH_3OH	6	1.21	97
Ethanol	C_2H_5OH	12	1.15	97
Dimethyl ether	$(CH_3)_2O$	12	1.2	95
Formic acid	HCOOH	2	1.4	-
1-Propanol	$CH_3(CH_2)_2OH$	18	1.13	97
2-Propanol	$CH_3CHOHCH_3$	18	1.12	97
Ethylene glycol	$C_2H_6O_2$	10	1.22	99
Trioxane	$C_3H_6O_3$	12	-	-
Dimethoxy methane	$(CH_3O)_2CH_2$	16	1.23	98
Hydrazine	N_2H_4	4	1.62	100
Sodium borohydride	$NaBH_4$	8	1.64	91

The most studied liquid-feed fuel is methanol, which is cheap, easy to handle, transport and store, and has a high theoretical energy density in respect to hydrogen. It is used in DMFCs and also for synthesis of other liquid fuels. The second most studied liquid fuel is ethanol. This fuel can be obtained from agriculture, forestry and urban residues and is attracting increasing interest. Ethanol is a hydrogen-rich liquid, thus, by its reforming, hydrogen can be produced with potentially attractive application. It has a high specific energy of 8.01 kWh kg^{-1} compared to methanol, 6.1 kWh kg^{-1}, and also comparable to that of gasoline [11]. Ethanol is also less toxic than methanol, and remains the easier fuel to work with for widespread use by consumers. However, the kinetics of the ethanol oxidation reaction (EOR) involves multi step mechanisms, which present a major issue for the development of direct ethanol fuel cells (DEFCs). Therefore, higher performance catalysts are needed to overcome this bottleneck. Di-, tri-, tetra-methoxymethane, hydrazine, ammonia and borohydride can be also considered as potential fuels.

The easy use of hydrazine, which produces N_2 and H^+, as an alternative to hydrogen has been proposed because it can produce over 200 mW cm^{-2} more than a similar hydrogen cell without requiring Pt catalysts. By storing the liquid N_2H_4 in a tank full of a double-bonded carbon-oxygen carbonyl, a safe solid called hydrazone is formed. Then, the tank is flushed with warm water and the liquid hydrazine hydrate is released. Hydrazine breaks down in the cell to form N_2 and H_2 which bonds with oxygen, releasing water [12]. Ammonia and borohydride theoretically produce nitrogen and water, and metaborate ion, BO_2^- and water, respectively.

Wojcik et al. [13] proposed a direct ammonia fuel cell which uses a solid proton conducting electrolyte. The anode (fuel side) reactions can be written as:

$$2NH_3 + \text{heat} \rightarrow 3H_2 + N_2 \tag{9}$$

$$3H_2 \rightarrow 6H^+ + 6e^- \tag{10}$$

The cathode (air side) reactions can be written as:

$$3O_2 + 6e^- \rightarrow 3O^{2-} \tag{11}$$

$$6H^+ + 3O^{2-} \rightarrow 3H_2O + \text{heat} \tag{12}$$

Therefore the overall reaction is:

$$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \tag{13}$$

Clearly, the products of the fuel cell are nitrogen, water, electric power and heat. These fuel cells are practically ready for production and, because they are fueled by readily available ammonia, hydrogen electric vehicles could be shortly implemented.

It seems appropriate at this point to note that the proton exchange membrane fuel cell has a theoretical energy conversion efficiency of 50–70%, which is lower than those presented in Table 2 for the cells utilizing higher molecular weight fuels. Therefore, under the point of view of fuel cell efficiency at moderate temperatures, it is better to operate in sodium borohydride.

3. Materials for Methanol Fuel Cells

One of the key components of a DMFC is a membrane that separates the water-methanol mixture on the anode side of the cell from the air on the cathode side. Permeable to protons but impermeable to electrons, this membrane is usually coated with a platinum containing catalyst. Attention has been given to the minimization of the amount of platinum required and to the optimization of the contact between the catalyst and the plates of the cell, which is usually ensured by the use of graphite paper.

At around 110 °C, a reaction occurs that produces electrical energy. The water-methanol mixture is broken down into carbon dioxide plus protons and electrons. While protons migrate through the proton exchange membrane to the cathode side of the cell and gather there to generate a positive charge, a corresponding negative charge is created on the anode side. An electric current flows through the system as soon as the two poles are connected. The electrons and protons on the cathode side then combine with oxygen and form water. Some of this water is then used to feed the system while the rest is emitted as water vapor.

Unlike other systems being developed, there is no need for the intermediate stage of a reformer to extract hydrogen from the fuel. At present, methanol is mainly produced from natural gas but, in the long term, methanol could be produced on an industrial scale from renewable resources such as biomass and waste wood or even from the exhaust gases produced by industry. In fact, fuel cell vehicles powered by biomass methanol emit only as much CO_2 into the environment as was originally absorbed by the plants used to produce the methanol. Indeed, methanol is seen as a fuel of the future, because harmful emissions are negligible and CO_2 emissions are one third lower than for internal combustion engines. However, before we see a DMFC vehicle in extended service, a strong focus on making the technology cheaper, more compact and more efficient is needed. Apart from the automobile sector, the DMFCs are also finding many applications in other transportation sectors, and as portable power sources. Their full development requires significant enhancement of electrocatalytic activity for the 6-electron transfer electrooxidation of methanol.

3.1. Anode catalysts for methanol oxidation

Electrocatalysts for the electrooxidation of methanol in fuel cells are generally based on Pt alloys supported on carbon black or high surface area unsupported catalysts. The electrocatalytic activity of Pt is known to be promoted by the presence of a second metal, such as Ru or Sn, acting either as an ad-atom or a bimetal. The most studied catalysts for methanol electro-oxidation are Pt–Ru alloys. These materials generally have high activity attributed to the ability of the Ru in the alloys to form active oxygen species (OH^-) at low electrode potentials and to hinder poisoning from carbon monoxide on the Pt sites. The Pt sites in these alloys also contribute to the methanol dehydrogenation step [14,15]. A comparison of the in situ stripping behavior of adsorbed methanolic residues for three Pt–Ru/C catalysts at various temperatures [16] showed that above 90 °C, the stripping area of the methanolic residues decreased and the peak shifted towards lower potentials on account of the decrease of the activation energy for CO removal.

The development of decorated catalysts [17] and of highly dispersed electrocatalyst phases in conjunction with high metal loadings on carbon support has been among the main goals of the last twenty years research activity in the field of DMFCs [17,18,19]. It was found that carbon nanotubes (CNTs) used as supports can enhance the catalytic activity of Pt–Ru alloys. Moreover, one the goals in DMFC research has been the preparation/optimization of highly dispersed Pt–Ru electrocatalysts with high metal loadings on carbonaceous supports such as fullerene and carbon nanotube-based electrodes [16,17,20,21]. However, the long-term stability of the PtRu/C catalyst is still a concern, particularly in acid-based systems, due to ruthenium dissolution from the anode and its migration to cathode, which decreases the kinetics of both the MOR and ORR at the anode and cathode, respectively. Strategies to address this issue have been the development of Pt–Ru-based ternary catalysts, by the addition of Mo, Sn, Os, or W, as well as the modification of the carbon support [21].

One interesting aspect is that, due to the enhanced methanol oxidation reaction rate at high pH, alkaline DMFCs can employ non-precious transition metals, for example, Ni [22], which are characterized by low intrinsic activity. The Ni-based catalysts can operate suitably in combination with a liquid electrolyte containing a concentrated base such as 5 M KOH or NaOH. Pt-based electrocatalysts, including the conventional Pt/C catalyst, platinized Ti electrodes and Pt–Ru alloys [22], have been operating jointly with anion exchange membranes. Platinized mesh anodes, in which mass transport resistance is reduced due to the open area of the mesh, have shown higher catalytic activity than conventional Pt/C electrodes [22]. Platinized mesh anodes [23], gradient porous media [24], Ru/C, Pd/C and Pd_xRu/C (x = 1,3,5) binary Pd-based electrocatalysts [25], Pt modified tungsten carbide (WC) materials [26], nickel nanocatalysts supported on sulfonated polyaniline [27], and novel anode structures with uneven catalyst loadings [28] were found to be great potential candidates for decreasing Pt usage whilst achieving high catalyst utilization and exhibiting satisfactory reactivity.

3.2. Cathode catalysts for DMFCs

For the catalytic oxygen reduction reaction (ORR) to occur, molecular oxygen is first absorbed laterally on adjacent metal ions on the surface of the metal oxide. The O–O bond is lengthened and weakened by the metal–oxygen interaction. The dissociative adsorption of O_2 happens simultaneously with proton addition and an increase in the valence of the metal. In alkaline media, the kinetics of the ORR is more favorable, being easier to replace Pt by other less expensive catalysts, namely Ag and MnO_2, which have shown suitable methanol tolerance and catalytic activity for oxygen reduction [22]. Along the last 30 years, metal chalcogenides [29], phthalocyanines and porphyrins [30] based cathodes, which show catalytic activities close to those of Pt in the presence of methanol poisoning, are among the developments in methanol tolerant oxygen reduction catalysts. Other available non-noble metal oxides for DMFCs cathodes are, for example, tungsten oxides and Co-oxides with a perovskite structure [31]. It was also found that the intrinsic electrocatalytic activity of Pt alloys (Pt–Cr, Pt–Ni, Pt–Co, Pt–Cu, Pt–Fe) is often higher than that of the base metal [32,33], which is related to the nearest neighboring distance of Pt–Pt atoms on the surface of the fcc crystals. This increased activity has also been associated to the increased Pt d-band vacancy (electronic factor) and its relative effect on the OH chemisorption from the electrolyte [34].

Furthermore, iron or cobalt organic macrocycles from the families of phenylporphyrins, phthalocyanines and azoannulenes have also been tested as ORR electrocatalysts in fuel cells [30,35]. Several other materials were studied and showed high activity as electrocatalysts for ORR in these fuel cells. Bimetallic Pt–M/C (M = Fe, Cu, Co) cathodes characterized by a high concentration of metallic phase on carbon black and a particle size smaller than 3 nm showed a high degree of alloying, along with a decrease of the lattice parameter [36]. The formic acid method was recently used by Zignani et al. [37] to deposit well-dispersed Pt_xNi_y nanoparticles (x:y = 3:2) on the surface of a carbon black support. A heat treatment then led to a partial modification of the crystalline structure from the face centered cubic, typical of Pt, to a tetragonal structure of Pt–Ni alloy and an acid leaching treatment partially removed unalloyed surface nickel atoms, leading to an enrichment of Pt concentration (x:y = 2:1). The authors reported that their Pt–Ni/C catalysts showed a good tolerance to methanol and an increase in electroactivity compared to a commercial Pt/C catalyst [37]. High methanol oxidation reaction tolerance of Au–Pt–Pd/C NPs is ascribed to the synergistic effect resulting from its thin structure and bimetallic Pt–Pd composition [38]. In fact, structural analysis of a core-shell structured Au–Pt–Pd/C nanoparticles prepared by a successive reduction process revealed uniformly distributed fine particles on carbon particles and selectively deposited Pt and bimetallic Pt-Pd structures on the Au surface. In H_2SO_4, the ORR activity decreased as the amount of Pd increased; in the H_2SO_4 solution with methanol, the ORR activity increased as the amount of Pd increased due to its enhanced tolerance for methanol oxidation [38]. NP–Pd–Cr alloys with uniform ligament dimensions and controllable bimetallic ratio, were prepared by a simple dealloying method [39]. The NP–Pd–Cr alloy with unique structural stability, is comprised of a nanoscaled interconnected network skeleton and hollow channels extending in all three dimensions. It was demonstrated that the weakened Pd–O bend and high ORR performance depend on the downshifted d-band center of Pd due to the alloying of Pd with Cr. Yang and Nakashima [40] developed an high durability electrocatalyst based on poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole]-wrapped multi-walled CNTs, on which Pt nanoparticles were deposited, and then coated with poly(vinylphosphonic acid) (PVPA). The polymer coated electrocatalyst showed an ORR activity compared to that of the commercial Pt/carbon black (Pt/CB) and methanol tolerance to the electrolyte due to a 50% decreased methanol adsorption on the Pt after coating with the PVPA. Moreover, by adding 2 M methanol to the electrolyte, it was possible to highly reduce the peroxide generation as compared to that of the non-PVA coated electrocatalyst and conventional Pt/CB. Further Pd–Pt cathodes were prepared by Choi et al. [41], having high activity for the ORR and low activity for the methanol oxidation reaction; in this research, carbon-supported Pd–Pt bimetallic NPs electrocatalysts with 60 wt.% metal content were prepared by sodium borohydride reduction of metal chlorides.

A new ultrafine np–Pt_3Cu alloy, prepared by mechanical alloying and subsequent two-step chemical dealloying, modified the electronic structure of Pt with the shift of Pt-d band center with Cu [42]. This decreased CO poisoning and enhanced methanol oxidation and ORR activities, thus demonstrating better performance as electrodes in acidic medium for DMFCs than the commercial Pt/C. Pt nanorod assemblies prepared from platinum carbonyl complexes and assembled on top of a Pt/C catalyst layer with significant catalyst loading reduction up to 50% were reported by Pu et al. [43], and led to improved cell performance due to increased catalyst utilization and charge-transfer in the double layer cathode. The use of trimetallic catalysts (e.g. Pt–M–Ru/C with M = Co or Fe) was also reported recently [44], showing high performance for ORR in the presence of methanol, even after being subjected to potential cycling for 2000 times. Recently, Sebastian et al. [5] reported on PGM (platinum metal group)-free catalysts based on Fe–N–C with high performance for DMFC at a low MEA cost. A maximum power density of 50 mW/cm^{-2} at high methanol concentration (10 M) was achieved. Moreover, a 100 h experiment at high temperature showed a similar current-time behavior compared to common MEAs on Pt cathodes [5].

It should be pointed out that non-platinum catalysts research have made a great progress in recent years. However, the activity and stability of non-platinum catalysts still need further improvement to meet the requirements of commercial application. Besides, the synergistic effect between Pt-based catalyst and the catalyst supports also needs consideration [45].

3.3. DMFC membranes

Electrolyte membranes for DMFC applications are usually proton exchange membranes, which consist in polymers that contain free H^+ ions, and that can only serve for transferring H^+ within the electrolyte membrane from anode to cathode, or vice-versa. It is possible to use membranes operating at high temperatures, with low methanol crossover (MCO) ($< 10^{-6}$ mol min^{-1} cm^{-1}) or low methanol diffusion coefficient in the membrane ($< 5–6 \times 10^{-6}$ cm^2 s^{-1} at T = 25 °C), high ionic conductivity (> 80 mS cm^{-1}), high chemical and mechanical durability, especially at T > 80 °C (for increased CO tolerance), low ruthenium crossover (in the case that the anode catalyst contains Ru), and low cost [20,46].

DuPont Nafion membranes, Dow Chemical XUS membranes, 3P energy membranes, fluorinated, zirconium hydrogen phosphate modified Nafion, silica and molybdophosphoric acid modified Nafion, Nafion-polyfurfuryl alcohol nanocomposite membranes, Nafion polypyrrole based membranes, Pall Ion clad membranes, polyvinylidene fluoride + SiO_2 (or SiO_2 gel) + acid membranes, silanes/silica modified sulfonated poly(ether ketone), polybenzimidazole based membranes, acid-base or acid-base composite membranes (direct modification of a polymer backbone), poly(arylene ether sulfone) based membranes, composite membranes of sPEEK (or sPSU) with P4VP (or PBI), asymmetric acrylic membranes, polyvinylidene fluoride or low density polyethylene + styrene membranes, sulfonated poly(aryletherketone) membranes, polyfuel polycarbon membranes, Ballard membranes and fluorocarbon membranes of Hoku Scientific Inc., are examples of polymer electrolyte membranes as described by Neburchilov et al. [46], which are already impacting the fuel cell market. The authors compared the main hydrocarbon membranes to Nafion for DMFC applications and concluded that some suitable hydrocarbon membranes are sPTES, sPEEK + PBI blend, and sPPZ. sPPZ has low MCO (0.7×10^7 cm^2 s^{-1}) and high chemical stability, PBI has high thermal stability (160–200 °C), and sPTES has high conductivity (> 100 mS cm^{-1} at 85 °C and relative humidity of 85 %) compared to 80–112 mS cm^{-1} for Nafion). The PBI membranes have the best thermal stability along with high power density (250 mW cm^{-2} on air at 110–130 °C).

Different formulations of PBI have also led to membranes with excellent performances for DMFCs. For example, proton-conducting polymer electrolytes based on new porous films of PBI doped with phosphoric acid led to mechanically stable membranes with ionic conductivity as high as 5×10^{-2} S cm^{-1} [47]. A porogen, which is a space-filing material that resists polymerization, is dispersed in films formed after the polymerization, and can be leached from the polymeric film after formation is used to prepare the porous PBI films. Comparing the methanol permeability in phosphoric acid-doped membranes based in poly[2,2-(m-phenylene)-5,5-bibenzimidazole] (PBI) and poly [2,5-benzylimidazole] (ABPBI) with commercial Nafion 117 membrane, it was observed that methanol crossover in ABPBI was higher than in PBI, but one order of magnitude lower than in Nafion 117 in the temperature range of 20–90 °C. The ratio of proton conductivity and methanol crossover coefficient for the ABPBI membrane was much higher as compared to Nafion and PBI membranes. A technique to increase the efficiency of polymer electrolyte membrane fuel cells (PEMFCs) was developed by using triazole to increase conductivity and reduce moisture dependence in polymer membranes [48]. More specifically, by using triazole-containing PEMs, they were able to increase PEMFC operating temperatures to above 120 °C, eliminating the need for a water management system and dramatically simplifying the cooling. Several research teams worldwide are currently looking into better polymers to significantly increase the overall efficiency of the DMFC.

4. Materials for Ethanol Fuel Cells

Ethanol can be produced from a wide range of feedstock, from sugar-cane, wheat or corn to waste from agro-industries or forestry residue. This makes ethanol interesting as a fuel from both the economical and the environmental perspectives. Direct ethanol fuel cell systems are therefore promising devices, but the complete oxidation reaction of ethanol requires 12 electrons per molecule, which makes this a sluggish process. However, the ethanol oxidation may proceed only to acetaldehyde or acetic acid involving only 2 or 4 electrons, respectively [49]. There are several types of fuel cells that may use ethanol. In order to improve the kinetics and efficiency of DEFCs, the synthesis and characterization of materials, including membranes and catalysts, as well as mechanistic studies of the ORR and the EOR, have been the main focus of research [49,50]. Most of these materials are carbon-based materials mainly synthesized for energy conversion storage systems [51]. It was shown that Pt–Pd/C bimetallic cathode materials have higher tolerance to ethanol than the traditional Pt/C catalyst [52]. As anode materials, the use of Pt and binary Pt–Ru and Pt–Sn and ternary Pt–Re–Sn based catalysts have been reported for the electro-oxidation of ethanol in DEFCs [53,54]. For instance, meso-porous carbons, hollow graphitic nanoparticles, CNTs, carbon nano-coils, carbon nanofibers (CNFs), graphene nano-sheets, and functionalized graphene nano-sheets have been investigated as potential catalysts supports with excellent electrical, physical and thermal properties [55–60]. However, other alternative supports in DEFCs have also been studied due to their high surface area, stability and low resistance, such as conducting polymers incorporating metallic particles into porous polymeric matrix [49,61]. Metal oxides such as CeO_2 or NiO have also been shown enhanced catalytic performance for electrooxidation of ethanol [62].

It was also observed that the immobilization of metal nanoparticles, MNPs, onto CNFs, improved their catalytic activity [57,63]. Besides, 3D–NPs behaved very well as electrodes in biofuel cells, BFCs [64]. For the synthesis of CNFs, electrospinning is an appropriate technique that from the 1930s onwards has found its way on countless applications [65,66], which has even started being industrialized [67]. Starting from polymeric fibers obtained directly by electrospinning, the heat treatment transforms the polymeric chains in carbon chains with enriched fiber mat [68], having very low mean diameter [69,70] and long enough to form a free-standing paper or mat of fibers [71,72]. Currently, some developments on the electrospinning technique and synthesis of CNFs have been reported with enhancing electrochemical response for diverse low-temperature fuel cells [66].

Plasma deposition techniques are also used for the preparation of novel electrocatalysts, namely supported bimetallic catalysts [73,74]. Such techniques allow changing the nanostructure (clusters, thin films, alloys, multilayers, etc.) [75,76], and optimizing the composition of the catalysts only by varying deposition parameters. These explain the large use in the industry and in research of these techniques for the fabrication of fuel cell catalytic layers [77,78,79].

The membrane is also a very important component in DEFCs. Nafion is one of the most widely used membranes in polymer electrolyte membrane for DEFCs [80]. Several approaches have been suggested in order to optimize $DEFC_S$ which includes Nafion membrane modification, using alternative polymer or composite membranes, membrane/electrode interface modifications or better membrane electrode assembly processes.

Many other procedures, membranes and catalysts have been developed for DEFCs [49,61,81–86]. It should be noted that many of the materials reported in the previous section are also being studied for ethanol cells (e.g. Pt–Sn/C, Pt–Ru/C and Pt–Ox/C as anodes; Pt/C, Ru/C cathodes; and hydrocarbon membranes). Moreover, the attention of the interested reader is called for two books recently edited, that provide a lot of useful information on materials for anode and cathode catalysts, as well as on polymer electrolyte membranes for DEFCs [87,88].

5. Materials for Borohydride Fuel Cells

Direct borohydride fuel cells (DBFCs) are of great interest especially for portable applications due to the capability of borohydride anion BH_4^- to deliver up to 8 electrons per molecule at very low potentials of –1.24 V vs. SHE [89]. Sodium borohydride, $NaBH_4$, first proposed as anodic fuel in 1962, has the benefits of high storage density and long-term stability in alkaline solution [90,91]. An oxygen, air or hydrogen peroxide electrode in combination with a sodium borohydride electrode, and a cation exchange membrane, CEM, is depicted in Figure 4. The theoretical energy density for the $NaBH_4$ / H_2O_2 system is 17 kWh kg^{-1}, followed by the $NaBH_4/O_2$ cell with 9.3 kWh kg^{-1}. The theoretical energy density of a $NaBH_4$ / H_2O_2 cell is at least five-fold that of a H_2 /O_2 fuel cell, two-fold that of an ethanol/O_2 cell and three-fold that of a methanol/O_2 cell. In other words, the problems arising from the use of alcohol in direct alcohol fuel cells (DABFCs) can be overcome by using other hydrogen carrier materials such as various borohydride compounds as fuel. Despite much effort regarding anode catalyst developments, the promising advantages of the fuel cannot by fully utilized so far. On the one hand, this originates from the fact that the electrode potential is a theoretic thermodynamic concept which cannot be reached in practice. On the other hand, the complete oxidation of BH_4^- to BO_2^- ($E^0 = -1.24$ V vs. SHE) undergoes complex reactions steps depending on the anode material and the electrode potential [1,91–97].

In general, catalysts can be divided into hydrolyzing and non-hydrolyzing materials. Catalysts that show high adsorption tendency of hydrogen such as Pd or Pt belong to the first group [33,63]. The main side reaction, namely the borohydride hydrolysis reaction [90], is catalyzed by this kind of materials, which powers the coulombic efficiency and can lead to mechanical stress inside the electrode. There is not much information in the literature about the exact reactions, their kinetics and rate determining steps in order to be able to produce high performance borohydride fuel cells.

The electrode and electrolyte materials used in other electrochemical devices such as batteries [97], electrochemical supercapacitors [98], electrochemical sensors [99], etc., can also be considered for application in DBFCs. Moreover, since DBFCs are most attractive in portable applications, more research efforts need to be carried out toward making DBFCs miniaturized and lightweight. Among all these important aspects, it is clear that cathode and anode materials, as well as electrolyte membrane separators for the MEAs of the DBFCs, continue to be key aspects for developing an economically viable DBFC.

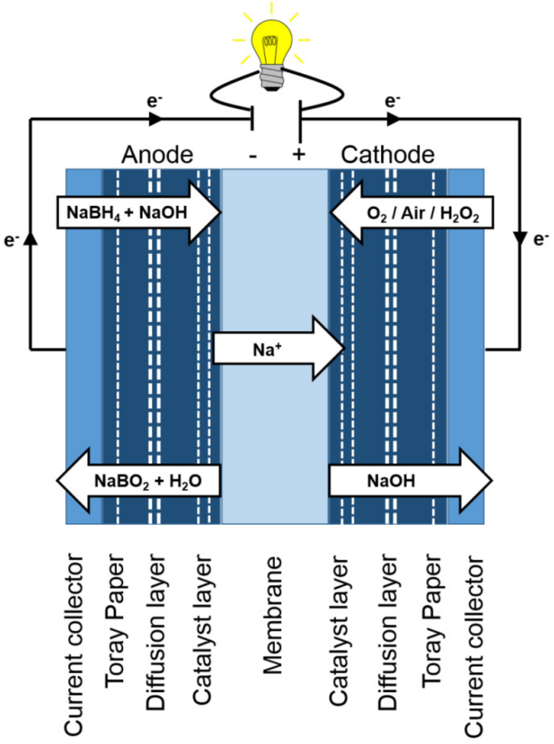

Figure 4. Schematic diagram of a DBFC employing oxygen, air or hydrogen peroxide as oxidant.

5.1. Anode catalysts for borohydride oxidation

Pt and its alloys, Au, Ag, Ni, Zn, Pd, Os, Cu, AB_5^- and AB_2^--type hydrogen storage alloys, as well as three-dimensional materials were studied as anode catalysts by Çelikan [100], Chatenet [101] and many others. Amendola et al. [102] reported that 6.9 electrons can be utilized on gold electrode. Gyenge et al. [103]; studied a bimetallic Pt–Au catalyst that combined the favorable kinetics on Pt with the higher coulombic efficiency for borohydride oxidation on Au. The experiments showed that the peak current was higher on Pt–Au compared to pure Pt; the number of transferred electrons was 8 on the Pt–Au alloy. The authors also tested Pt–Ir and Pt–Ni alloys, which gave in both cases a power density of 53 mW cm^{-2} at 75 °C. Additionally, Pt–Ir and Pt–Ni showed the highest cell potentials at any given current densities, e.g., at 100 mA cm^{-2} and 333 K the cell potential was 0.53 V vs. MMO (mercury / mercury oxide) with an anode catalyst loading of 5 mg cm^{-2}. Chatenet et al. [104] claimed that the amount of hydrogen released at an Au electrode is not negligible and they proposed two pathways for borohydride oxidation at low (E < 0.3–0.5 V vs. RHE) and high potential values (E > 0.3–0.5 V vs. RHE). The authors suggested that, at low overpotentials, the hydrolysis of BH_4^- proceeds in one chemical step producing BH_3OH^-; then the oxidation of these species on Au can involve 3 or 6 electrons, leading to BO_2^-. At high overpotentials, the direct oxidation of BH_4^- occurs involving 2 electrons, followed by the oxidation of the BH_3OH^-, which involves again 3 or 6 electrons; thus the oxidation releases between 5 and 6 electrons in total. J. Ma et al. [105] investigated Ni composite anodes, such as Pt–Ni/C and Pd–Ni/C (the ratio of Pt–Ni or Pd–Ni was 25:1). A BH_4^-/ O_2 fuel cell consisting of 1 mg cm^{-2} Pt/C cathode separated from the anode by a Nafion membrane was assembled with this cell they reached a value of 204 mW cm^{-2} with the Pt/C cathode and a value of 273 mW cm^{-2} when using Pt-Ni/C under similar conditions. A higher power density, up to 665 mW cm^{-2} (at 60 °C and with 1 mg cm^{-2} Pt–Ni loading and a 1 mg cm^{-2} Pd/C cathode) was achieved in a $NaBH_4$ / H_2O_2 system. Pd_xCu_y/C alloys, in particular, $Pd_{50}Cu_{50}$/C, were also reported to be effective anode catalysts with a maximum power density of ca. 98 mW cm^{-2} at a current density of 223 mA cm^{-2} at 60 °C [106]. Zinc could also be a suitable anode catalyst for the DBFC since, in theory, it is a relatively poor electrocatalyst for hydrogen adsorption and reduction, it is a low cost material and it is suitable for energy storage [107]. Santos and Sequeira [107] measured the electrode potential of Zn / $NaBH_4$, NaOH, which was –1.57 V vs. SCE, more negative than that obtained with other metals, offering the possibility of achieving a higher cell potential. The Zn/$NaBH_4$, NaOH//HCl, H_2O_2/Pt cell potential obtained by Santos and Sequeira was 2.14 V [107], which is appreciably lower than the theoretical value (3 V) for BH_4^-/H_2O_2 system. The cell discharge curves led to good results, particularly for short time operation. At high cell currents [107], short time anode limitations were also observed. Miley et al. [108] used an MEA with a Pd/C anode and an Au/C anode, and constructed a 500 W cell-stack of 15 $NaBH_4$/H_2O_2 fuel cells, resulting in a power density of 231 mW cm^{-2}. Zhi-Fang et al. [109] reported a DBFC with a Cu anode and a Pt cathode, at 25 °C, that maintained a stable cell potential of ~ 0.6 V at 20 mA cm^{-2} for 50 h. Current density and power density as high as 235 mA cm^{-2} and 46.14 mW cm^{-2}, respectively, were obtained with nickel-rare earth electrodes [110]; platinum-rare earth intermetallic alloys [111], namely Pt–Dy alloys [112], were also studied as anode electrocatalysts for borohydride electrooxidation leading to reasonable results.

AB_5 and AB_2-type hydrogen storage alloys have also been recognized as suitable anode catalysts for DBFC [113,114], with the capacity to absorb and release significant amounts of hydrogen gas. For AB_5 alloys, A is designated as an hydride forming metal, usually a rare earth metal (e.g., La, Ce, Nd, Pr, Y or a mixture/mischmetal) and B is a non-hydride forming element, such as Ni, which can be doped with other metals (e.g., Co, Sn or Al) to increase the stability or to balance hydrogen pressure and temperature required to charge/discharge hydrogen [114]. In the AB_2 alloys, A represents a large group of alloys containing Ti, Zn or Hf, and B is a transition metal (e.g., Mn, Ni, Cr or V). AB_5-type alloys [115], are reported to have higher power densities which can be attributed to their increased capacities at high discharge rates [116].

Electrodes such as reticulated vitreous carbon (RVC), reticulated nickel (RN) or a silver sponges have been investigated [117]. Their high surface area and porosity allow the achievement of high rates of conversion per unit volume [118]. The use of silver sponge electrodes prepared from the calcination of a polymer matrix and silver nitrate mixtures was examined by Ponce de León et al., [119] showing activity towards the oxidation of borohydride ions at positive potentials. Demirci reported on the main issues met by the MEAs of DBFCs and summarized the number of electrons generated during electrooxidation of BH_4^- for a large number of anode materials [120].

5.2. Cathode catalysts for oxidant reduction

Platinum is a good cathode catalyst for DBFCs due to its high electrical conductivity, and good chemical stability [121]. Cheng et al. [121], as well as Sequeira et al. [122], studied the electrocatalytic activity of various cathode catalysts, and observed that Pt/C demonstrated the highest catalytic activity towards the O_2 /H_2O_2 reductions and the best stability as compared to Pd/C, Ag/C and Ni/C cathodes. The great concern of Pt/C is the high cost. Potential low cost materials are manganese oxide-based electrocatalysts, which display good selectivity for ORR and poor activity towards sodium borohydride electrooxidation and hydrolysis, thus minimizing BH^{4-} crossover and cathode degradation [123,124]. Ma et al. [125] and Santos et al. [126] prepared carbon-supported $LaNiO_3$ and La_2NiO_4, respectively, perovskite catalysts and employed them as cathode catalysts for DBFC. A DBFC with $LaNiO_3$/C-catalyzed cathode and hydrogen storage alloy-catalyzed anode and no membrane separator exhibited a peak power density of 127 mW cm^{-2} at 65 °C under atmospheric pressure and good performance stability for 500 h. Thus, the probability of developing mixed-reactant DBFCs that employ perovskites and no cost-effective membrane separators is increased. Another alternative cost effective cathode material is Prussian Blue (PB) [127,128] that led to good results in direct borohydride hydrogen peroxide fuel cells. Employing PB/C anchored with cetyltrimethyl ammonium bromide as cathode catalyst, Selvarani et al. [128] achieved a peak power density of 68 mW cm^{-2} at 30 °C.

Coulombic efficiencies of DBFCs using carbon-supported and unsupported platinum anodes (the non-carbon with much less Pt loading) have been found to be 62.3 and 68.1%, respectively [129]. Activated carbon cloth with a surface area of 2000 m^2 g^{-1} was chosen by Gu et al. [130] as the supporting material for noble metals. As the results were not as good as expected, it was shown that there is an optimal activation level for supporting materials [112,131].

Research interests continue focused on developing novel cathodic catalysts for DBFCs, related with high oxygen or hydrogen peroxide reduction activity. In particular, RuO_2 has high electronic and proton conductivity and high chemical and thermodynamic stability under electrochemical environments, being widely studied as supercapacitor materials, water oxidation catalysts, and diffusion layer materials in fuel cells, and as ORR catalyst in acid and alkaline solutions. It is considered that oxides, as opposed to pure metals, may be less sensitive to poisoning by fuel, such as alcohol or borohydride. Therefore, Yang et al. [132] studied recently RuO_2 as an ORR catalyst in DBFCs. Au electron transfer number of ~ 3.7 was observed as well as a 200 h support stability; peak power densities of the order of 425 mW cm^{-2} at 60 °C was achieved.

5.3. Membrane materials

Membranes can be evaluated in terms of many properties, such as conductivity, composition, thickness, mechanical strength, equilibrium water content (EWC), and ion exchange capacity (IEC) values. For DBFC applications, it is necessary to balance the membrane water content, since membrane hydration is essential to maintain proton conductivity whereas excess water leads to flooding [133]. It is also important to note that an increase in temperature increases membrane conductivity and therefore enhances power density [134]. However, a temperature increase should be moderate because dryness/poor water balance originates higher resistance and poor cell behavior [133,134].

Cation-exchange membranes, CEMs, can be employed in DBFC and would reduce alkali concentration in the anolyte, causing instability and inefficient use of the borohydride. Besides, cathode membrane deactivation and restriction flow of oxygen/air to the cathode also creates a problem which becomes more severe with time of operation [135]. Nafion-961 contains carboxylate (10 µm thick) polymer layer which offers resistance to flow of NaOH from anode to cathode, thereby improving cathode polarization behavior of DBFC [136]. Therefore, by using Nafion-961 instead of Nafion-117, it is possible to reduce alkali crossover from anode to cathode in the DBFC.

Choudhury et al. [137] have reported a DBFC/H_2O_2 cell with PVA hydrogel membrane and compared it with a similar DBFC with Nafion-117. The nominally better cell performance of the Nafion-117 based DBFC could be due to the higher ionic conductivity of Nafion-117 (10^{-1} S cm^{-1}) than PVA hydrogel membrane (10^{-2} S cm^{-1}) [137]. Other DBFC arrangements using KOH-doped polyvinyl alcohol (0.08 S cm^{-1}) or polymer fiber membranes were reported by Huang et al. [138] and Yang et. al. [139] achieving power densities of ca. 184 and 663 $mWcm^{-2}$, respectively.

Finally, it should be pointed out that operating a DBFC without a membrane, by using cathodes that are inactive towards electrooxidation and chemical hydrolysis of BH_4^-, would simplify the engineering aspects. These electrodes include manganese oxide [123], iron tetramethoxy phenyl porphyrin [140], iron phthalocyanine [141], cobalt phthalocyanine [142], among others. Using a MnO_2 cathode material, Feng et al. [143] demonstrated that a DBFC without membrane may reach a cell potential of 0.6 V and current densities between 1 and 5 mA cm^{-2}, using a dispersed gold catalyzed anode (7.4–8 electrons interchanged), a solution containing 1 M KBH_4 in 6 M KOH and a MnO_2 catalyzed air cathode. Even superior performance was achieved by Verma et al. [144] who used a Pt–Ni anode and a flowing alkaline electrolyte and obtained a power density of 19 mW cm^{-2} at a current density of 39 mA cm^{-2} using 1 M $NaBH_4$ in 3 M KOH.

6. Conclusions

DMFCs, DEFCs and DBFCs, are electrochemical cells operating on methanol, ethanol and borohydride liquid fuels, respectively, which are promising cost-effective power systems for many energy applications. This paper discusses prominent features of these cells, and reviews recent developments in their research including their strengths, weaknesses and practical applications. In particular, novel anode, cathode and membrane materials, which potentially increase their performance and durability are analyzed, while some related issues needing further investigation are pointed out.

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

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