

Review

Direct borohydride fuel cells

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Abstract

The recent, rapid progress in the development of direct borohydride fuel cells is reviewed. Electrochemical reactions are considered together with the importance of operating parameters on cell performance. The advances in technology necessary for a widespread testing and more application of borohydride fuel cells are highlighted. A comparison of borohydride and methanol fuel cells shows that both systems exhibit similar cell voltages, current and power densities despite that methanol cells operate at higher temperatures. The results are encouraging although more research is necessary, particularly in the synthesis of new electrocatalysts for borohydride oxidation.

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1. Introduction

Few now doubt that fuel cells have an important role to play in the future of mankind, for the generation of electric power, for transportation and as replacement for batteries in portable electronics. The most highly developed systems are based on hydrogen as the fuel but there remain serious question marks relating to safety and efficiency during storage and supply of this light and inflammable gas. This has led to a search for alternative fuels; key requirements are that the fuel should be readily available, safe and easily transported, rapidly oxidised at a neg-

ative potential, available to the fuel cell anode in a concentrated form and give a large energy and power output/unit weight (and unit volume) of the fuel. Methanol has been widely supported as the fuel of choice. Another solution is sodium borohydride, which is available as a solid or as a 30% solution in concentrated, aqueous sodium hydroxide.

In 2003, two very extensive reviews of the science and technology of fuel cells [1,2] were published. However, the discussion of direct borohydride fuel cells was brief. This is, perhaps, not surprising since there is little literature on the development of direct borohydride fuel cells prior to 2000. Recent progress has been rapid and it is timely to review the progress in the design of direct borohydride fuel cells and to consider the steps that need to be taken in order to develop a viable technology. The direct borohydride fuel cell employs an air (or oxygen) breathing cathode

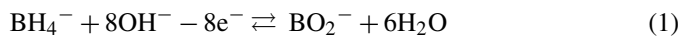
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and since these are well characterised, commercially available components very little will be said about them. Recently, hydrogen peroxide has also been considered as an alternative to air (oxidant), but this is only applicable to anaerobic situations, such as power sources for underwater vehicles. Hence, this oxidant will be only considered briefly. This paper considers the consequences of using cationic or anionic membranes to separate anodic and cathodic compartments in the direct borohydride fuel cell. Some reported membraneless fuel cells are also considered. Indirect borohydride fuel cells, in which borohydride serves as a hydrogen source which then feeds a PEM fuel cell, are briefly mentioned.

2. Electrode cell and chemical reactions

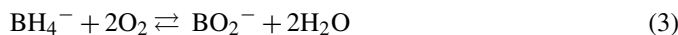
The formal potential for the reaction



in strongly aqueous alkaline media has been calculated as -1.24 V versus SHE [3–5]. Hence, if this reaction is paired with oxygen reduction



the fuel cell would have a cell reaction



with an equilibrium voltage ≈ 1.6 V. This compares very favourably with both H_2/O_2 and $\text{CH}_3\text{OH}/\text{O}_2$ fuel cells that have equilibrium voltages ≈ 1.24 V and ≈ 1.21 V, respectively. Likewise, the energy density of 9.3 kWh kg^{-1} of solid sodium borohydride is attractive compared to the 6.2 kWh kg^{-1} of pure methanol. Of course, the energy densities are lower if based on

aqueous solutions, but sodium borohydride is highly soluble in concentrated sodium hydroxide (up to 30%). Fig. 1a shows the cell voltage and power density of a methanol fuel cell operated at 110°C [6] and Fig. 1b shows a borohydride fuel cell operated at 85°C [7]. Despite the 25°C difference in temperature, the performance of both fuel cells is similar; the cell voltage for both systems shows that the open circuit potential falls below the theoretical value and that the borohydride fuel cell voltage is higher than that of the methanol fuel cell. As the current density increases, the borohydride cell voltage decays more rapidly than the methanol cell voltage and both systems approach similar values at a current density of approximately 400 mA cm^{-2} . The power density is also higher for the borohydride system at similar current densities; at the highest point of power density in each system, the methanol fuel cell shows higher current densities.

The only products of the cell chemistry indicated in reaction (3) are water and borate ion. Borate is both environmentally acceptable and potentially convertible back to borohydride [8–11]. Sodium borohydride itself can be shipped as a white solid or as 30% aqueous solution and both can be handled in air. Sodium borohydride neither ignites in contact with moisture nor is it sensitive to shock. The applications of sodium borohydride are expanding rapidly, for example, as a reducing agent in the manufacture of low tonnage organic compounds, as a source of pure hydrogen, in the pulp and paper industry and in waste treatment. The increase in demand for sodium borohydride should introduce improved production technology and lower its cost.

A borohydride fuel cell can only be operated in strongly alkaline media because borohydride is rapidly hydrolysed in acid and at a significant rate in neutral solution [4]:

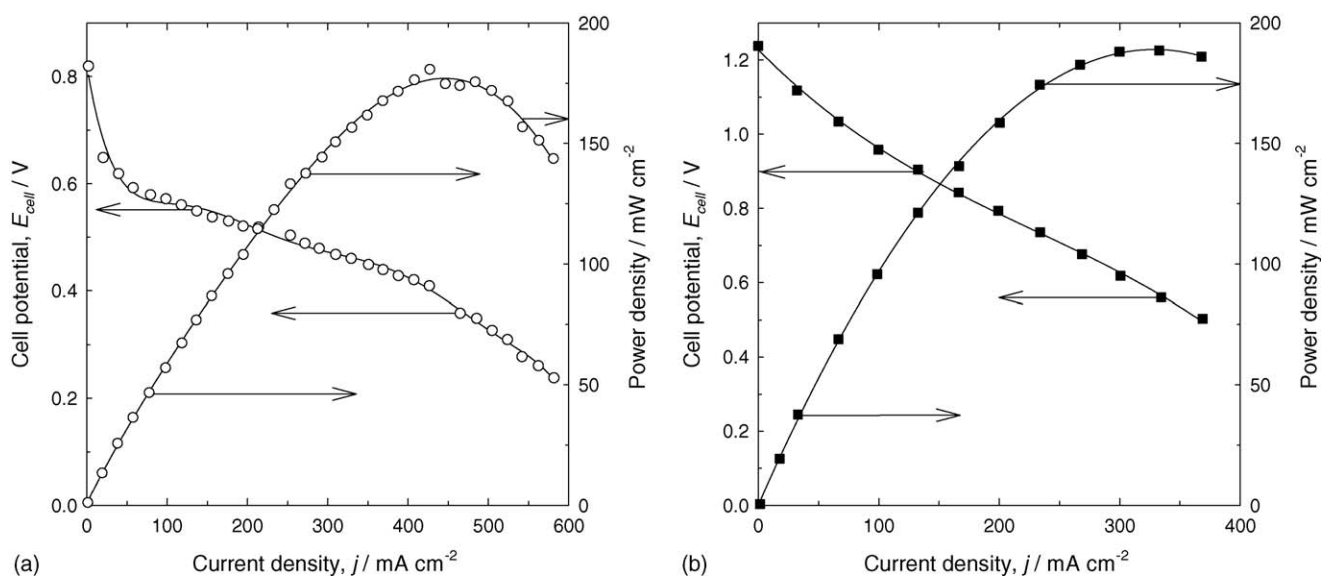
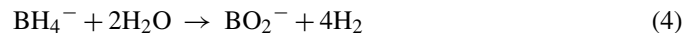


Fig. 1. (a) Cell voltage and power density vs. current density for methanol (○) from a single cell in a 150 W fuel cell stack with $1 \text{ mol dm}^{-3} \text{ CH}_3\text{OH}$. Anode: 85% Pt/Ru in Vulcan XC carbon; cathode: air feed 85% Pt on Vulcan, temperature 110°C [6]. (b) Cell voltage and power density vs. current density for borohydride (■) single fuel cell at 85°C . Anode: $\text{AB}_2 (\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Mn}_{0.6}\text{V}_{0.2}\text{Co}_{0.1}\text{Ni}_{1.1})$ alloy feed with 10 wt% NaBH_4 in 20 wt% NaOH at a flow rate of 0.2 L min^{-1} ; cathode: Pt/C feed with humidified O_2 at 0.2 L min^{-1} at 1 atm and Nafion NE-424 membrane as electrolyte [7].

In practice, and in the absence of impurities or a catalyst, borohydride ion is stable in strongly alkaline solutions (i.e., $>6 \text{ mol dm}^{-3}$ hydroxide).

The hydrolysis reaction, even in strongly alkaline media, is, however, catalysed by many metals and their compounds. An early study identified cobalt chloride as an effective catalyst in neutral media [12]. More recent work has targeted catalysts for the efficient conversion of alkaline borohydride solutions (that are stable and can be stored) to hydrogen gas at close to ambient temperatures. A number of catalysts have been identified including dispersed Ru metal on ion exchange beads [13,14], dispersed Pt on an oxide [15–17] or carbon supports [18] and high area nickel materials [19,20]. Hydrogen generators based on these catalysts are now commercially available and are components of ‘indirect borohydride fuel cells’ as well as sources of pure hydrogen. In ‘indirect borohydride fuel cells’ [21], the concentrated borohydride solution in aqueous alkali is converted to hydrogen gas in a catalytic generator and the hydrogen gas is then fed to a PEM or other hydrogen-fuelled cell. Such systems have been described for applications as varied as automobile traction [22] and micro-fabricated fuel cells to power electronics circuits [23,24].

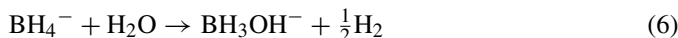
It will be apparent that the hydrolysis reaction is a problem in ‘direct’ borohydride fuel cells. Not only does it restrict the selection of electrolyte media to pure, strongly alkaline solutions, it also interferes in the selection of anode electrocatalyst. Materials that are obvious candidates for the electrocatalyst for the oxidation of borohydride are also catalysts for the chemical hydrolysis of the fuel. Hence, it is to be expected that the hydrolysis reaction (4) and the electrode reaction (1) will occur in parallel at the anode surface and that the rates of both reactions will increase with the use of high area forms of anode material. The relative rates will be a function of anode material as well as potential, temperature and other conditions. Indeed, the situation is, in fact, more complex. The formal potential for the $8e^-$ oxidation of borohydride via reaction (1) is $>300 \text{ mV}$ negative to the formal potential for hydrogen evolution in the same conditions:



At the formal potential for reaction (1), the reduction of water to hydrogen is thermodynamically favourable. Thermodynamics therefore predicts that less than $8e^-$ will be involved in the anodic oxidation of borohydride. Experimentally, it is certain that hydrogen is evolved during the anodic oxidation of borohydride at most anode materials and that $n < 8$. Whether this is due to hydrolysis at the anode surface, in parallel to oxidation, or complication in the electrode reaction alone leading to the transfer of less than $8e^-$, is a matter of speculation.

Another experimental observation is that the open circuit potential of borohydride fuel cells never approaches the predicted value and much of the shortfall is associated with the anode reaction. It is likely that the anode takes up a mixed potential determined by both $\text{BH}_4^-/\text{BO}_2^-$ and $\text{H}_2\text{O}/\text{H}_2$ couples. The presence of partially hydrolysed species could also influence the open circuit potential of a borohydride fuel cell. Polarograms

for solutions of borohydride at pH around 9 showed two oxidation waves [25,26]. The main wave was attributed to the simple oxidation of borohydride ion, but a much smaller wave was observed at more negative potentials. This was thought to arise from the oxidation of species such as BH_3OH^- which are formed by partial hydrolysis of the borohydride ion during the reaction:



Since it appears that BH_3OH^- is more readily oxidised than BH_4^- such species in solution would have the effect of increasing the open circuit potential, this is not an important mechanism in determining the open circuit potential.

3. Fuel cell configurations

Most borohydride fuel cells have a membrane separating the two electrodes. Fuel cells with both cation and anion permeable membranes have been tested. Either choice has consequences with both advantages and disadvantages. Fig. 2 shows sketches of the cell with each type of membrane drawn for a cell with sodium electrolytes. It is assumed that the electrode reaction (1) is occurring without the competing hydrolysis of borohydride, and the figure is drawn to emphasise the chemical changes during energy generation, even with idealised chemistry.

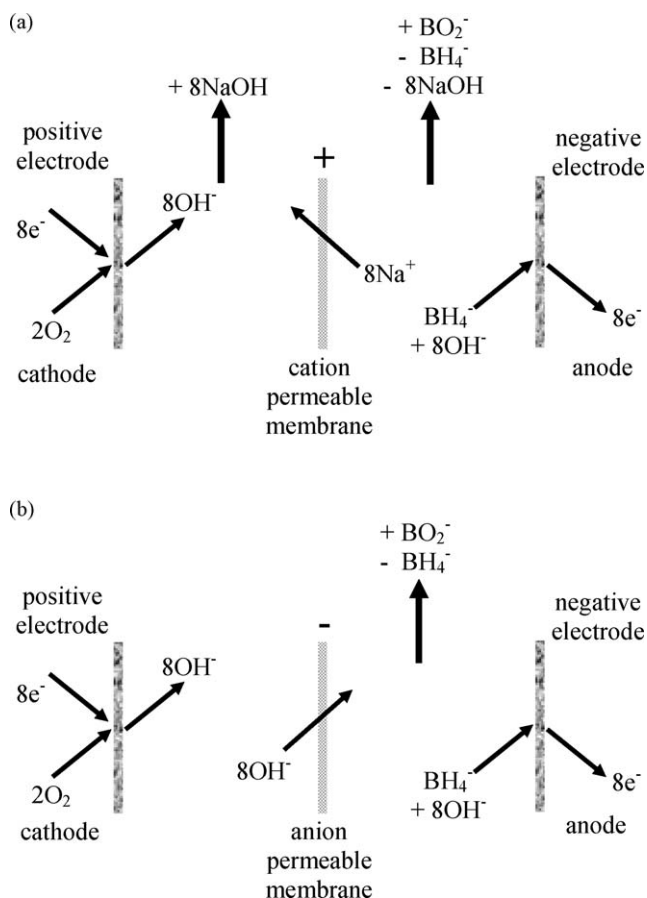


Fig. 2. Borohydride fuel cells with: (a) a cation permeable membrane and (b) an anion permeable membrane, drawn to emphasise the chemical balance.

The advantage of cation permeable membranes is that they are readily available and, particularly the perfluorinated membranes, extremely stable [27] even in contact with strong alkali and a powerful reducing agent. The most common choice of membranes is one of the Nafion® 1100 EW series manufactured by Dupont. Operation with a cation permeable membrane, however, inevitably leads to a chemical imbalance. The oxidation of 1 mol of borohydride is accompanied by the transfer of 8 mols of sodium ions across the membrane with a consequent build up of sodium hydroxide in the catholyte and loss of sodium hydroxide from the anolyte. Clearly, for extended operation of the fuel cell, there must be a procedure for returning the sodium hydroxide from catholyte to anolyte. This is difficult to achieve. Moreover, the drop in alkali concentration in the borohydride anolyte as the fuel cell operates will lead to a decrease in stability of the borohydride and less efficient use of the fuel.

With an anion permeable membrane, the borohydride fuel cell chemistry is in balance except for the conversion of the fuel to borate. Unfortunately, most anion permeable membranes are unstable in alkali [27]. The perfluorinated anion membrane Tosoh®, is no longer manufactured because of the very high production cost. Currently there are probably no commercially available anion permeable membranes which are sufficiently stable in strong alkali. There has been substantial R&D targeted towards improving the stability of membrane polymers to alkali but, at the present time, there are no anion membranes on the market stable to hydroxide concentrations above $\approx 5\%$. Use of such a low hydroxide concentration leads to increased loss of borohydride by hydrolysis. Borohydride transport from anolyte to catholyte is another concern with all membranes. There is a very high borohydride concentration gradient across the membrane and borohydride transport is particularly likely with the anion membrane with the cell on open circuit. Fig. 3 shows a comparison of the performance of both a cationic Nafion

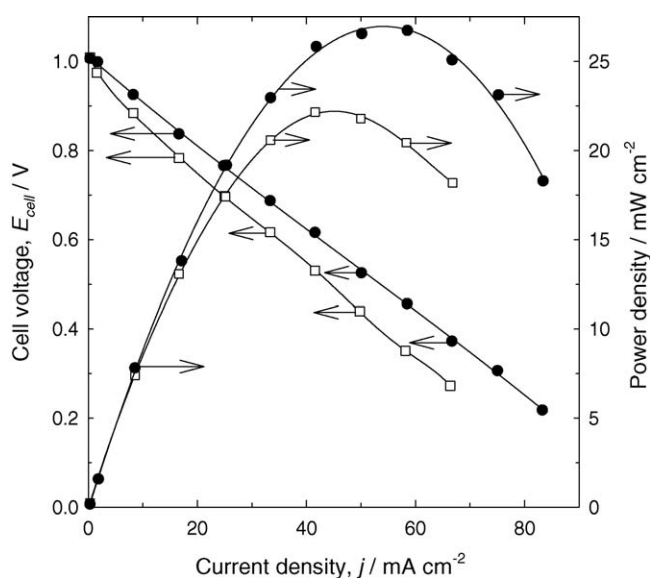


Fig. 3. Cell voltage and power density vs. current density for a borohydride fuel cell using a cationic (●) Nafion 115 and an anionic (□) Asahikasei A-501SB membranes at 25 °C. Ni + PTFE powders pressed on Ni foam as anode and air cathode made of Pt or Ag supported on carbon black [28].

N115 and an anionic Asahikasei A-501SB membrane on a borohydride membrane–electrode assembly (PEM) fuel cell, both membranes having an approximate thickness of 130 μm [28]. The membranes were immersed in 6 mol dm⁻³ NaOH before cell assembling. The anode in this cell was nickel and PTFE powders pressed on nickel foam and the cathode was platinum or silver supported on carbon black. With both membranes, the open circuit potential was similar, but as the current density increased, the cationic membrane showed a higher cell voltage and power density than the anionic membrane at the same current densities. The authors suggest that with the anionic membrane the cathodic side becomes deficient in water, leading to increased Ohmic and interfacial resistances between the cathode and the membrane, thereby leading to a reduction in power density [28].

The influence of current density on the transport of borohydride is important. The migration of ions through the membrane is driven by a potential field created by the electrodes. In a fuel cell (and battery), consideration of the field must include the substantial potential drop created by the spontaneous electron transfer reactions at the two surfaces, which determine the direction of field to drive anions towards the anode and cations towards the cathode. In a cell with an anion membrane, the potential field opposes migration of borohydride ion into the catholyte and during fuel cell operation, the transport rate should always be low and decrease further with increasing current density. Under open circuit conditions the forces leading to transport of borohydride ion through an anion permeable membrane may be strong. Charge balance within both electrolytes is essential, and one mechanism for borohydride transport involves hydroxide moving in the opposite direction. This will be particularly favourable if the hydroxide ion concentration is higher in the catholyte than the anolyte. The crossover of borohydride ion from a 30 wt% NaBH₄ in 6 mol dm⁻³ NaOH solution to a 30 wt% NaOH one, across different membranes, was investigated by Lakeman et al. [29]. The crossover measurements were taken from a four-electrode cell with gold gauzes as cathode and anode, and the polarization of the electrodes was between -1300 mV and -300 mV versus a saturated mercurous sulphate (SMSS) reference electrode over 1 h of intermittent scans. The highest crossover value was 4.6×10^{-6} mol cm⁻² s⁻¹ for a membrane identified as 3541P (prepared by Cranfield University) and the lowest value 0.4×10^{-6} mol cm⁻² s⁻¹ was observed for Nafion 117. When comparing the thickness and the conductivity of the different membranes the authors have noted that the thickness of the membrane is important in retarding migration of borohydride ions.

The ideal situation in electrochemical technology is to operate cells without a membrane (or any other separator). Membranes tend to be expensive, the selectivity of ion transport is never 100% [27] and a membrane significantly complicates cell design. Although the transport of other ions is generally minor, it usually causes substantial complications to cell operation. Membranes are, however, commonly essential in fuel cells to avoid reactant/product interactions at both anode and cathode, either because of explosion hazards or unacceptable losses of fuel. Since borohydride does not react with oxygen in homogeneous solution, an undivided borohydride fuel cell is possible, provided

the oxygen cathode catalyst does not catalyse either the reaction of borohydride with oxygen or the hydrolysis of borohydride. It would also be balanced with respect to hydroxide (the cell chemistry is effectively that shown in Fig. 1b). Indeed, an undivided borohydride fuel cell has been described [30]. The cathode catalyst employed was MnO_2 ; and the presence of 1 mol dm^{-3} KBH_4 in the 6 mol dm^{-3} KOH electrolyte was shown to have no adverse influence on the voltammetry of oxygen. When the air breathing, MnO_2 catalysed cathode was combined with a dispersed gold catalysed anode, a satisfactory fuel cell was achieved. The cell voltage was $\sim 0.6 \text{ V}$ although with a current density of only $1\text{--}5 \text{ mA cm}^{-2}$ and discharge curves showed a good utilisation of the borohydride fuel equivalent to $n = 7.4$ at 1 mA cm^{-2} , cf. $n = 8$ for the complete oxidation of borohydride according to reaction (1). These are low current densities for a fuel cell, but the cathode catalyst appeared to be capable of sustaining higher current densities. This has been confirmed by other workers [31], who also demonstrated that at the MnO_2 catalysed cathode in alkaline solution, oxygen underwent the full $4e^-$ reduction. The effect of the concentration of NaOH on the cell voltage of a 2 mol dm^{-3} NaBH_4 fuel cell with no membrane, $\text{MnO}_2/\text{C}/\text{Ni}$ cathode and Pt black on a Ni mesh anode, shows that the highest cell voltage was obtained for 1 mol dm^{-3} and 5 mol dm^{-3} NaOH at 0.8 V , with a current density of around 35 mA cm^{-2} [32]. A similar system with no membrane, called the compact mixed-reactants (CMR) fuel cell, where an alkaline solution of NaBH_4 saturated with air flows through a porous anode and cathode electrodes has been proposed by the Generics Group Ltd., to increase benefits in cost, size, power density and reliability of fuel cells [33–35].

4. Electrode materials for the oxidation of borohydride

Early studies of the electrochemical oxidation of borohydride were carried out on mercury electrodes, but this liquid metal has little possibility of application in practical fuel cells. Furthermore, this literature has been thoroughly reviewed elsewhere [4,36].

The interest in defining solid electrocatalysts for the oxidation of borohydride for fuel cell applications dates back to the late 1950s. It was recognised early on that strong sodium or potassium hydroxide were the only reasonable electrolytes to ensure the stability of borohydride in the bulk electrolyte. Moreover, achieving a high n -value (n is defined as the number of electrons released per borohydride ion consumed in the fuel cell) was recognised as important in order to maximise the energy output from the fuel and minimise safety issues from hydrogen gas formation. An n -value of 8 indicates that all the borohydride is undergoing complete oxidation via reaction (1). A lower value occurs when only partial anodic oxidation is occurring or the anode catalyst is promoting hydrolysis of the borohydride.

Early papers reported the oxidation of borohydride in strong alkali at nickel [37], platinum [38,39], palladium [39] and gold [40] electrodes. While it was possible to achieve open circuit potentials that confirmed interest in borohydride as a fuel and acceptable current densities (say 0.1 A cm^{-2}), the n -values were disappointingly low (4 at Ni and <4 at Pt). Jasinski [39] also

examined nickel boride as the catalyst and concluded that this material was significantly better than all the metals. A Japanese group [41] re-examined Pt and Pd in high surface area forms on Ni and C substrates and observed that Pt gave a more negative open circuit potential. They deposited Pt on a sintered porous Ni plate and found that borohydride underwent a $6e^-$ oxidation at current densities in the range $50\text{--}200 \text{ mA cm}^{-2}$. Okinsaka [40] investigated the oxidation of borohydride at gold electrodes in low concentrations of borohydride in 0.2 mol dm^{-3} KOH because of an interest in electroless plating baths. The work is interesting because it provides clear evidence for a change in the boron speciation with time with a new oxidation wave at more negative potentials increasing in importance with time. Fig. 4 shows the performance of different electrode materials in a borohydride fuel cell with respect to cell voltage (Fig. 4a) and power density (Fig. 4b). The electrodes are: (a) an air cathode (Johnson Matthey) and anode made of highly dispersed gold/platinum particles supported on high surface area carbon silk [47], (b) Ni + PTFE powders pressed on a Ni foam as anode and air cathode made of Pt or Ag supported on carbon black [28], (c) cathode and anode inks prepared using unsupported Pt black and Nafion [50] and (d) manganese dioxide cathode and standard Pt/Ni anode (Electro-Chem-Technic, UK) with no membrane [31]. The cell voltage and power density of a Ni electrode shows higher performance than Au/Pt, Pt inks and MnO_2 electrodes. These experiments cannot be closely compared as the operation conditions and membranes are different.

Bard and co-workers [42,43] have reported a more detailed electroanalytical investigation of borohydride at gold electrodes. Using ultra-microelectrodes, they concluded that borohydride ion experienced a complete $8e^-$ oxidation, and that the reaction became mass transport controlled at high overpotentials. They also showed that the application of fast scan cyclic voltammetry allowed the identification of metastable intermediates. Gyenge [44] also applied modern electroanalytical methods to the study of borohydride ion oxidation at gold and platinum. The results are complex, particularly at Pt where a low n -value was again found. The use of an adsorbing additive, such as thiourea to inhibit hydrogen evolution, also showed a positive effect on the performance. While these studies are interesting, it is difficult to assess their impact on fuel cell technology since the oxidation waves/peaks reported occur at a potential significantly positive to the open circuit potentials in fuel cell conditions. Liu et al. [45] revisited nickel as a possible anode material. They confirmed that a rather negative open circuit voltage was obtained and that high current densities, several hundred milliamperes per square centimetre, could be obtained at acceptable overpotentials, especially at elevated temperature. The n -value was, however, also confirmed to be 4 indicating that, with a nickel anode, the fuel cell could, at best, be expected to deliver approximately half the theoretical energy value.

The application of hydrogen storage alloys as anodes in borohydride fuel cells has also been explored [7,46,47]. Here, it is envisaged that the role of the borohydride ion is to replenish the hydrogen within the lattice of the alloys and that the hydrogen filled alloy then acts as the anode in the fuel

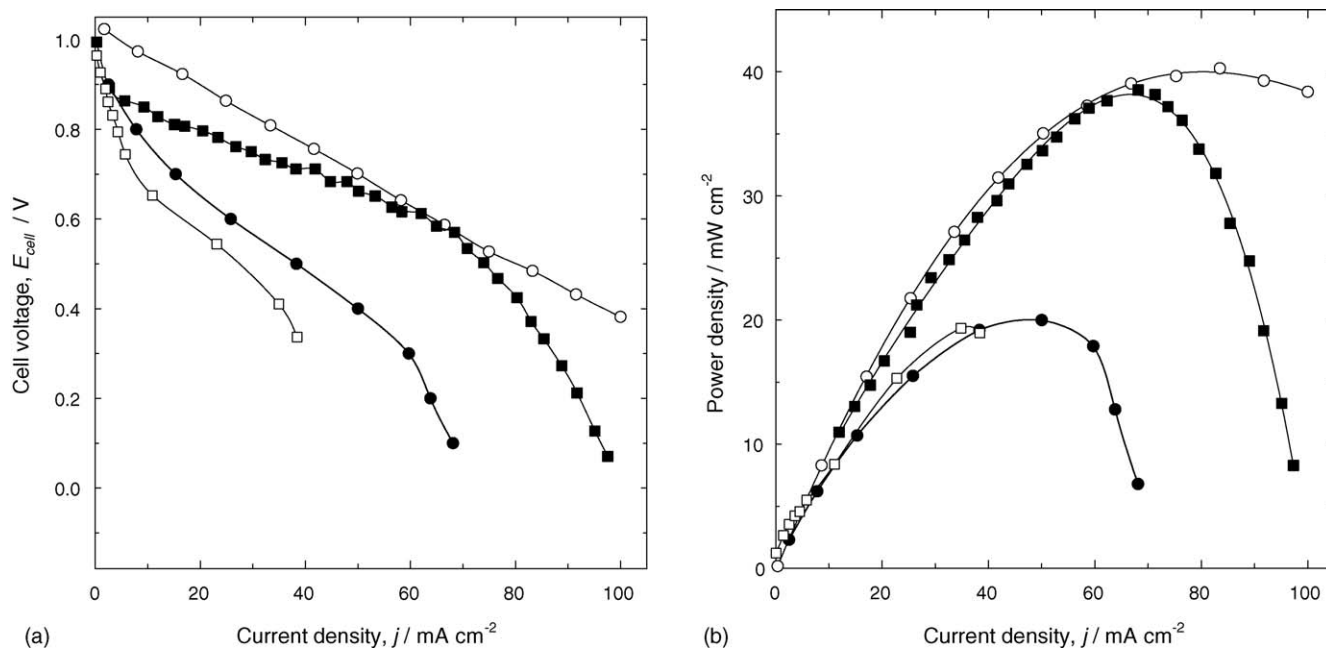


Fig. 4. (a) Cell potential vs. current density and (b) power density vs. current density for different anodes in a borohydride fuel cell: (●) commercial air cathode (Johnson Matthey) and anode made of highly dispersed gold/platinum particles supported on high surface area carbon silk separated by 2259-60 Pall anion membrane with 5% NaBH₄ in 25% NaOH [47], (○) Ni + PTFE powders pressed on a Ni foam as anode and air cathode made of Pt or Ag supported on carbon black separated by a NRE211 Nafion membrane, 5% NaBH₄ in 6 mol dm⁻³ NaOH [28], (■) cathode and anode inks prepared using unsupported Pt black and Nafion, 0.5 mol dm⁻³ NaBH₄ in 6 mol dm⁻³ NaOH [50] and (□) manganese dioxide cathode and standard Pt/Ni anode (Electro-Chem-Technic, UK) with 1 mol dm⁻³ NaBH₄ in 3 mol dm⁻³ KOH with no membrane [31]. All experiment reported at room temperature.

cell chemistry. The alloys examined include ZrCr_{0.8}Ni_{1.2} [46], Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1} [7] and LmNi_{4.78}Mn_{0.22}, where Lm is a lanthanum rich mischmetal [47]. As with nickel, the conclusion is that high current densities can be achieved at an acceptable potential (e.g., 300 mA cm⁻² at -0.7 V versus SHE) but the efficiency for releasing the energy from borohydride does not exceed 50% (i.e., $n = 4$). Wang et al. [47] also show that the efficiency in fuel use increases with increasing current density confirming that the performance of borohydride fuel cells will be a complex function of the operating conditions. A US patent application [48] has suggested that the two steps in the mechanism envisaged in the oxidation of borohydride at the hydrogen storage alloys could be mimicked by a two component catalyst, one component to convert the borohydride to hydrogen and a second for the efficient oxidation of hydrogen. It is claimed that such two component catalysts could be operated without off-gassing of hydrogen from the fuel cell.

Amendola et al. [49] have described studies of borohydride oxidation at high area electrodes, where the catalyst was gold or gold (97 wt%)/platinum (3 wt%) alloy. They were able to achieve n -values of ≈ 7 with moderate current densities at room temperatures, and current densities above 0.1 A cm⁻² at 343 K. A Korean Group [50] has employed high area Pt electrodes but largely report their results in terms of fuel cell performance (see below). They have discussed the influence of fabrication on the electrode performance, including factors such as catalyst loading and Nafion[®] content, but could only achieve current densities in the range of 10–60 mA cm⁻², with an n -value of only 5–5.5 so that fuel efficiency is only moderate.

Suda and co-workers [51] provided a comparison of six materials in terms of n -value and current density versus potential characteristics. They employed high area forms of electrodes to demonstrate that, in terms of fuel efficiency, both Pd/C and Pt/C were significantly better than nickel. All three electrodes allowed current densities up to 0.8 A cm⁻², but Ni was better than both Pt/C and Pd/C in terms of the anode potential. Table 1 provides a summary and comparison of anode materials for borohydride oxidation. At present, the optimum choice of anode catalyst is either gold or nickel-based material. Nickel gives the most negative potential for borohydride oxidation but a very low n -value while gold required a higher overpotential but gives a better fuel efficiency. Clearly further work on electrocatalytic materials for BH₄⁻ oxidation is essential.

Finally, some general comments on mechanism are important. While it should be stressed that the detailed mechanism of borohydride oxidation remains total speculation, it would appear that there are two general types of mechanism. In the first, the initial step is electron transfer



followed by rapid decomposition of the radical, and further electron transfer. In the second, the initial step is pre-disassociation at surface sites, e.g.:



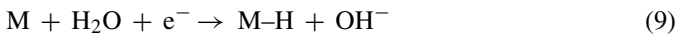
followed by electron transfer, further surface reaction and, hydrogen atom combination to yield hydrogen gas as a

Table 1
Summary of the performance of electrode materials for the oxidation of borohydride

Anode material	<i>n</i> -Value	Open circuit potential vs. SHE (V)	Comment	References
Ni	4, 4, 4	−1.03	>0.2 A cm ^{−2} at −0.70 V	[37,45,51]
Raney Ni		−1.03	≈0.6 A cm ^{−2} at −0.6 V	[59]
Cu	N.G.	−1.02	N.G.	[51]
Au	8, 7	−0.99	>0.1 A cm ^{−2} possible	[42,49,51]
Pt	2–4	≈−1.0	≈0.7 A cm ^{−2} at −0.6 V	[38,50]
Dispersed Pd on Ni	6	−1.00, −0.91	0.1 A cm ^{−2} at −0.92 V	[39,41,51]
Dispersed Pt on Ni	5, 6	−0.91	<0.1 A cm ^{−2}	[50,51]
Dispersed Au on Ni	N.G.	−0.99	N.G.	[51]
Ni ₂ B	N.G.	−1.07	0.1 A cm ^{−2} at −0.99 V	[39]
H ₂ storage alloys	4	−1.15	0.3 A cm ^{−2} at −0.7 V	[44,47]

N.G. = not given.

competing reaction. Certainly, surfaces able to support pre-dissociation are commonly good catalysts and the presence of adsorbed hydrogen atoms is always likely to lead to hydrogen gas evolution. Gold is not able to support appreciable coverage of adsorbed hydrogen, and mechanisms of the first type might be expected to predominate, but substantial overpotentials for electron transfer are common. Nickel, platinum and palladium favour adsorbed hydrogen and are candidates for the second type of mechanism. It was noted above that the formal potential for borohydride oxidation by reaction (1) is significantly negative to the formal potential for the H₂O/H₂ couple under the same conditions. The reaction:



is likely to occur at the open circuit potential for borohydride oxidation. The consequence is that a mixed potential is likely at

all materials that are effective catalysts for hydrogen evolution. Also, the occurrence of reaction (9) leading to hydrogen evolution fully or partly from water makes measurement of the H₂ evolution rates an unreliable way to estimate *n*-values for borohydride oxidation. The approach to the determination of *n*-value will lead to low *n*-values.

5. The influence of electrolyte parameters

There is general agreement that the fuel cell could be operated with Na⁺ or K⁺ electrolytes and that it is likely to be advantageous to operate with a MOH concentration in the range 10–40 wt% and a MBH₄ concentration in the range 10–30 wt%. The sodium compounds are likely to be cheaper and have a lower molar mass, but the potassium solutions have a higher conductivity and may give better membrane performance. It is known

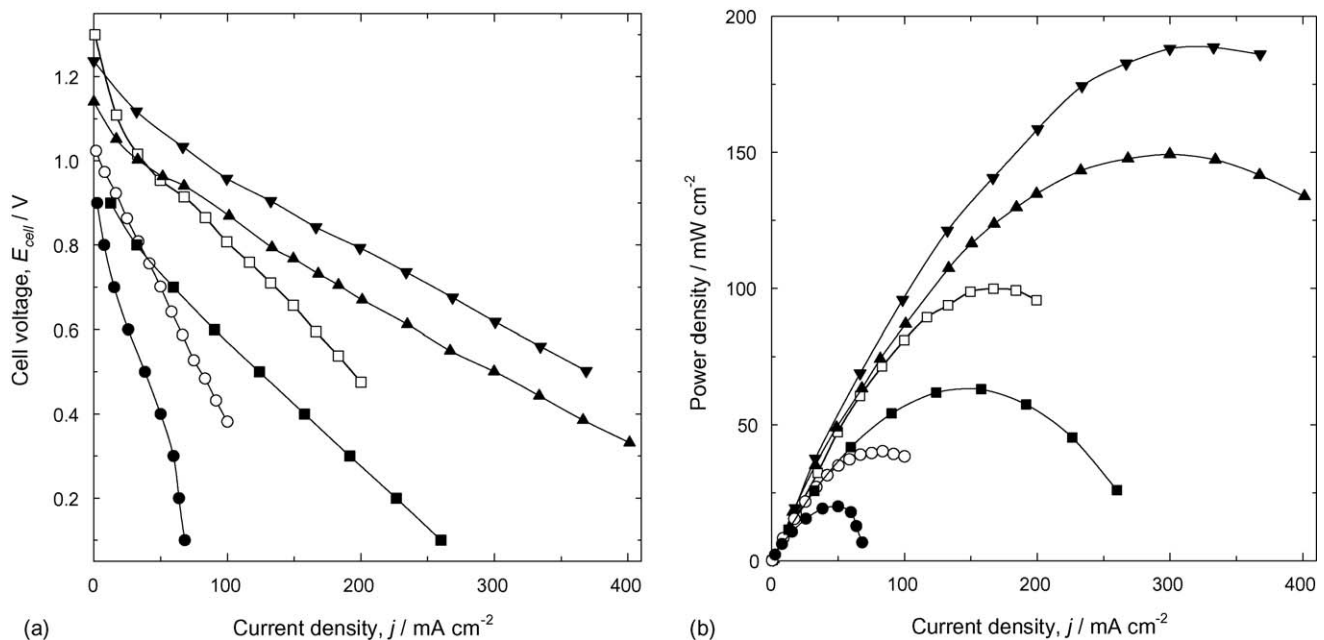


Fig. 5. (a) Cell voltage vs. current density and (b) power density vs. current density of a borohydride fuel cell at different temperatures. (●) Room temperature and (■) 70 °C borohydride–air cell with an air cathode and anode made of highly dispersed Au/Pt particles on carbon silk separated by 2259-60 Pall RAI anion membrane [49], (○) 25 °C with Ni + PTFE powders pressed on a Ni foam as anode and air cathode made of Pt or Ag supported on carbon black, separated by a NRE211 Nafion membrane [28] and (□) 50 °C, (▲) 70 °C and (▼) 85 °C with AB₂ (Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}) anode, feed with 10 wt% NaBH₄ in 20 wt% NaOH at a flow rate of 0.2 L min^{−1}. Cathode: Pt/C feed with humidified O₂ at 0.2 L min^{−1} at 1 atm and Nafion membrane as electrolyte [7].

[27] that cation permeable membranes in contact with potassium solutions are significantly less hydrated than when contacted by sodium electrolytes, and this can improve their resistance to unwanted ion transport (i.e., membranes in their K^+ form are more selective).

Two papers provide some useful information on the physical properties of possible borohydride fuel cell electrolytes [45,52]. Specific gravity, viscosity and melting point are reported as a function of both borohydride and hydroxide ion concentrations. In addition, the variation of the open circuit potential, polarisation curves, transport rates of borohydride through the membrane and n -values with these parameters, is also reported. Above a critical concentration of borohydride ($\approx 5\%$), the open circuit potential and polarisation curve at a Zr–Ni alloy are not sensitive to the borohydride concentration.

One advantage of borohydride fuel cells is their capability to provide energy near room temperature. In comparison, methanol fuel cells perform poorly at room temperature and most performance data is reported to temperatures in the range 343–373 K. As a result, much of the data for borohydride fuel cells is reported at a temperature ≈ 298 K, although there is evidence that performance improves at elevated temperatures. Fig. 5 shows a comparison of borohydride fuel cell performance at different temperatures from literature sources in terms of voltage and power versus current density. The systems considered are: (a) room temperature and 70°C for a borohydride–air fuel cell with an air cathode and anode made of highly dispersed Au/Pt particles on carbon silk [49], (b) a borohydride fuel cell at 25°C with Ni + PTFE powders pressed on a Ni foam as anode and air cathode made of Pt or Ag supported on carbon black [28] and (c) a borohydride fuel cell at 50°C , 70°C and 85°C with AB₂ anode ($\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Mn}_{0.6}\text{V}_{0.2}\text{Co}_{0.1}\text{Ni}_{1.1}$) and a Pt/C cathode [7]. As expected, the highest cell voltage and power density are observed at the highest temperature reported of 85°C . The curves show two different results reported for the cell operating at 70°C with different electrode materials. Highly dispersed Au/Pt on carbon silk shows lower voltage and power density than a cell operating with an AB₂ alloy anode.

6. Borohydride fuel cell performance

Table 2 reports some typical performance data for direct borohydride fuel cells. Diverse catalysts and separators have been used and several of the fuel cells have been fabricated in the form of MEAs (single component, membrane–electrode assemblies). In interpreting this table, it must be stressed that the different groups have chosen to operate the fuel cells under quite different conditions and, frequently not all the conditions are reported, which makes comparisons very difficult. In addition, the timescale for the data collection is never disclosed; hence, it is not known whether the values quoted are ‘instantaneous’ values with fresh components and solutions or whether the performance is maintained over an extended period. It is not clear that there has been any consideration of borate removal from the anolyte during continuous operation, or that the hydroxide balance in fuel cells with cation membranes has been addressed.

Table 2
Some typical performance data for borohydride fuel cells at a current density of approximately 50 mA cm^{-2}

Cell components		Conditions			Fuel cell performance				References		
Anode catalyst	Cathode	Membrane	$[\text{OH}^-]$ (mol dm^{-3})	$[\text{BH}_4^-]$ (mol dm^{-3})	T (K)	Open circuit voltage (V)	Typical current density (A cm^{-2})	Cell voltage at 0.1 A cm^{-2}	Specific energy density (Wh kg^{-1})	Maximum power output (W cm^{-2})	
Ni ₃ B alloy	Ag on Ni	Asbestos	6.2	0.4	298	0.92	0.01–0.06	0.73	N.G.	–N.G.	[39]
97%Au + 3%Pt particles on carbon cloth	Pt/C	Anion Pall RAI No. 2259-60	6	5	343	0.95	0.01–0.3	0.6	184	0.06	[49]
ZrCr _{0.8} Ni _{1.2}	Pt/C	N.G.	6	0.05	N.G.	N.G.	0.12	0.7	420	0.09	[46]
Zr _{0.9} Ti _{0.1} Mn _{0.6} V _{0.2} Co _{0.1} Ni _{1.1}	Pt/C	Cation Nafion NE-424.	5	2.5	358	1.26	0.02–0.3	0.95	–N.G.	0.18	[7]
Pt/C	Pt/C	Cation, 5% Nafion binder solution	6	0.5	298	1.05	0.01–0.1	0.7	2800	0.04	[50]
Au	MnO ₂	Undivided	6	1	298	0.6	1–5	N.G.	N.G.	N.G.	[30]
Pt/Ni	MnO ₂ /C/C	Undivided	1–5	2	–	0.8	35	N.G.	N.G.	0.019	[32]

N.G.: not given.

It is clear that, while their performance falls well short of the theoretical expectation, the performance of the direct borohydride fuel cell also compares well with methanol/air (see Fig. 1a and b) and H_2/O_2 fuel cells. Even at room temperatures, cell voltages of ≈ 700 mV can be obtained at a discharge rate of 0.1 A cm^{-2} and as shown in Fig. 5a, considerable improvements in the current density can be achieved by increasing the temperature to 323–363 K [39,49]. It is also clear that the cells perform reasonably at rather low borohydride concentrations, and this allows the fuel to be added periodically as solid sodium or potassium borohydride [46,49]. It also minimises borohydride transport into the catholyte.

Raman et al. [53] have demonstrated a borohydride fuel cell using hydrogen peroxide as the oxidant. They used an acid catholyte and a dispersed Pt on C cathode, an AB_5 metal hydrogen storage alloy (as [47]) as the anode and a pre-treated Nafion 117 membrane sandwiched between anode and cathode. The cell voltages were as high as 1.6 V at 0.1 A cm^{-2} at a temperature of 343 K and 1.2 V at room temperature. Consequently, substantially improved power densities are obtained, 0.12 W cm^{-2} and 0.35 W cm^{-2} at 308 K and 343 K, respectively. These data confirm earlier indications (e.g., Fig. 8 of reference [52]) that much of the overpotential losses in the fuel cell occur at the oxygen cathode. The formal potential of the reduction of hydrogen peroxide in acidic media is 1.77 V versus SHE:



The increased pH gradient across the membrane when using peroxide (rather than oxygen) as the cathode reactant also contributes to a higher cell voltage. If a borohydride fuel cell oper-

ates with acidic hydrogen peroxide as an oxidant, the theoretical equilibrium potential is ≈ 3 V, whereas with hydrogen peroxide in alkaline media the equilibrium potential would be around 2 V. Fig. 6 shows the performance of two borohydride fuel cells at 70°C , one operating with an oxygen cathode [7] and one with acidic hydrogen peroxide solution as catholyte [54], and both cells with 10 wt% NaBH_4 in 20 wt% NaOH as anolyte. These curves show that although the hydrogen peroxide fuel cell achieves higher cell voltage and power density; the cell potential is far from the theoretical value, perhaps indicating that there is a high rate of peroxide decomposition. Overall, the performance of the fuel cell with hydrogen peroxide is higher than the oxygen cathode borohydride fuel cell.

7. Commercial ventures

Despite the promising results with borohydride fuel cells in the laboratory, there has been a surprising lack of commercial activity in North America and Europe. In North America, the emphasis has been on the development of indirect borohydride fuel cells, and programmes led by Millennium Cell Inc. and its partners have developed units with a hydrogen generator and PEM fuel cell at different scales [55].

In Japan, Merit Ltd. (Materials and Energy Research Institute Tokyo) is targeting the development of direct borohydride fuel cells for applications ranging from microelectronics to automobile traction [56]. They are near market launch with a 20 W cell based on a nickel anode designed to power notebook PCs, and have also announced the successful testing of a 400 W unit. In the UK, QinetiQ Ltd. have also developed a direct borohydride micro-fuel cell around a gold catalysed anode for niche applications [57,58]. Medis, of Israel, are commercialising a direct borohydride fuel cell and are initially targeting niche markets such as military applications and other portable electronic markets [59].

8. Future developments

Considering the relatively small number of person years of R&D invested in direct borohydride fuel cells compared to methanol and hydrogen fuel cells, the performance of borohydride fuel cells must be considered promising. There are real opportunities for improvements and we would highlight the need for the following components:

- Improved oxygen cathodes to deliver performance in strong alkali comparable to that routinely obtained in acid media. Tolerance to borohydride without catalysis of the borohydride would be advantageous.
- Anode catalysts with a low overpotential and delivering the full electrical energy from borohydride.
- Anion permeable membranes stable to strong alkali.

Studies of long-term operation must be carried out. For the goal of continuous operation of direct borohydride fuel cells, a number of issues relating to mass balance need to be resolved. In particular, a way to remove the product of the oxidation of

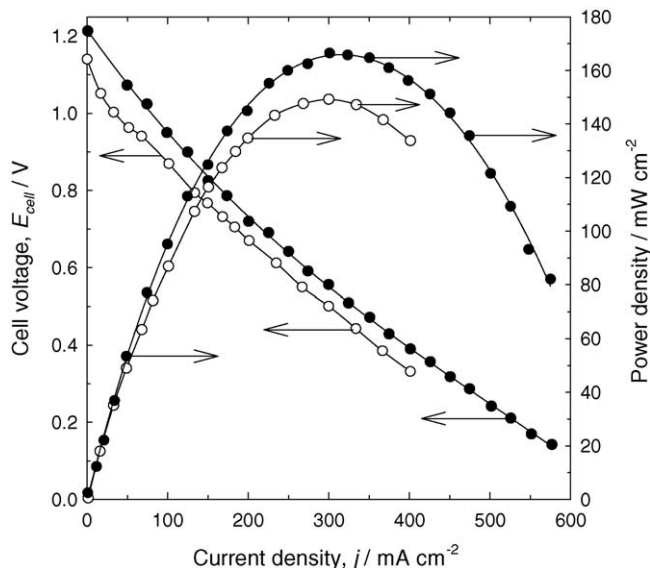


Fig. 6. Comparison of two borohydride fuel cells operating at 70°C with different oxidants: (○) O_2 cathode, 2 mg cm^{-2} Pt on carbon Vulcan XC-72 feed with humidified O_2 at 0.2 L min^{-1} and 0.2 g of AB_2 ($\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Mn}_{0.6}\text{V}_{0.2}\text{Co}_{0.1}\text{Ni}_{1.1}$) alloy/ cm^2 as anode with 10 wt% NaBH_4 in 20 wt% NaOH , and flow rate of 0.2 L min^{-1} [7]. (●) 8.9 mol dm^{-3} H_2O_2 in contact with a cathode made of 60 wt% Pt/C (1 mg cm^{-2} of Pt) and a AB_5 anode made of $\text{MmNi}_{3.55}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.75}$ (5 mg cm^{-2}) in contact with 10% aqueous NaBH_4 in 20 wt% NaOH [52].

borohydride, borate, from the anolyte needs to be defined. Also, while membranes that minimise unwanted transport processes would also be welcome, a strategy to return NaOH (or KOH) from the catholyte to anolyte shall be devised if cation permeable membranes are to be used.

This review has focused on fuel cells involving direct oxidation of borohydride ion, this process being inherently more efficient than indirect oxidation. Alternative strategies using borohydride ion and other hydrogen producing energy carriers are considered elsewhere [1,17,18,60–62].

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