A short review on direct borohydride fuel cells

Vankayala Kiran AND Sampath Srinivasan

Abstract | Direct borohydride fuel cells (DBFC) use aqueous alkaline sodium borohydride ($NaBH_4$) as anode fuel to generate electric power with either oxygen or hydrogen peroxide as oxidant. The DBFCs are projected to be very handy for portable power appliances such as laptops and mobile phones in addition to their use in extreme conditions such as underwater and portable military applications. This short review discusses the progress in DBFC research based on electrode materials and membranes.

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012
sampath@ipc.iisc.ernet.in

Keywords: Borohydride, fuel cells, Anode, Cathode, Membrane, Oxygen, Hydrogen Peroxide

Introduction

Fuel cells are electrochemical devices that convert chemical energy into electrical energy based on redox reactions occurring at electrode-electrolyte interfaces. The performance of fuel cells is better than conventional heat engines as the former is not controlled by carnot cycle limitations. Additionally, fuel cells are environmental friendly and do not result in emission of pollutants or green house gases. Hence, fuel cell research and development has grown in line with worldwide demand for energy. Recently, considerable efforts have been directed to the development of polymer membrane electrolyte fuel cells (PEMFCs) which is one of the promising alternates for portable as well as stationary applications [1–4]. Under this category, H_2-O_2 PEMFCs have been well-studied over the past few decades. However, the use of H_2 as an anode fuel involves several issues including safety, storage, supply etc. Apart from these aspects, it is also mandatory to scrub carbon monoxide (that will poison the electrode surface) that may be present along with H_2. These problems have led to search for alternate fuels to be used in fuel cells. Methanol has been widely reported in direct methanol fuel cells (DMFC). Sluggish kinetics of methanol oxidation, low open circuit potential and cross-over issues limit the use of methanol for further development [5–6]. Hydrogen containing fuels such as sodium borohydride ($NaBH_4$), ammonia borane are projected to be good alternates. The advantages of using $NaBH_4$ over other fuels are as follows. The theoretical open circuit voltage (OCV) for DBFC (1.64 V) is higher than that of the DMFC (1.21 V) and of the H_2-O_2 PEMFC (1.23 V). The direct oxidation of borohydride generates eight electrons per molecule as against two and six for hydrogen and methanol, respectively. DBFC possess 50% higher specific energy than the DMFC [7] [Table 1].

The cell that utilizes $NaBH_4$ directly as a fuel to generate electricity is referred to as DBFC whereas the one that use $NaBH_4$ indirectly is named indirect borohydride fuel cells (IBFC). In IBFC, electric power is generated by the use of hydrogen as anode fuel that is released from $NaBH_4$. The schematic diagram of the DBFC is shown in figure 1.

Direct borohydride fuel cell (DBFC) is in existence since early 1960s' [8,9] and the progress in its development has been very slow until late 1990s. Indig and Synder [9] demonstrated that electricity is produced via anodic oxidation and cathodic reduction reactions as given below, [Eq (1) and Eq (2)] to yield overall reaction [Eq (3)];

Anode (negative electrode) reaction

$$NaBH_4 + 8OH^- \longrightarrow NaBO_2 + 6H_2O + 8e^- \qquad E^0 = -1.24 \text{ V vs SHE} \quad (1)$$

Table 1: Thermodynamics and energy characteristics of DBFC and DMFC.

Characteristics	DBFC	DMFC
Theoretical open circuit volatge (V)	1.64 V	1.21 V
No. of electrons	8	6
Specific energy (Wh kg^{-1})	9295	6073
Specific Capacity (Ah kg^{-1})	5668	5019

Cathode (positive electrode) reaction

$$2O_2 + 4H_2O + 8e^- \longrightarrow 8OH^- \qquad E^0 = 0.40 \text{ V vs SHE} \tag{2}$$

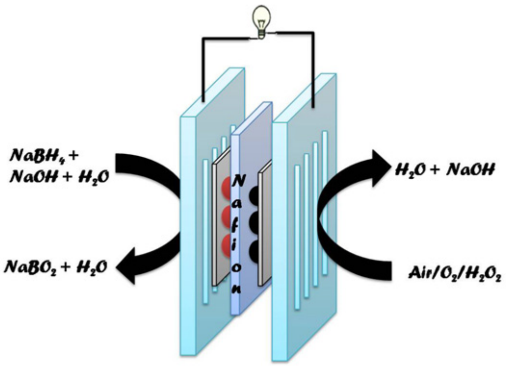
Over all reaction

$$NaBH_4 + 2O_2 \longrightarrow NaBO_2 + 2H_2O \qquad E^0 = 1.64 \text{ V vs SHE} \tag{3}$$

The recent resurgence of research on DBFCs is credited to Amendola et al. who reported [10] the performance of borohydride—air fuel cell with an anion exchange membrane (AEM) electrolyte that exhibit a maximum power density of 60 mW/cm^2 at 70°C. It has been shown that the utilization of the fuel is very efficient and about seven out of a theoretically maximum eight electrons is used in the fuel cell reaction. The use of alkaline medium opens up the possibility of the use of non-noble metals as negative electrodes to oxidize $NaBH_4$. It should be noted that the product of the reaction, borate (BO_2^-) is non-toxic and can in principle be regenerated back to BH_4^-, a very tough task though [11].

The first review reported by Lakeman [12] et al. stresses the promising future of the DBFCs and the issues to be solved. Subsequently, Wee [13,14,15] reviewed the progress in DBFCs where the performances of two borohydride - based fuel cells, DBFC and IBFC are compared. The main issues that dogs the commercialization of borohydride based fuel cells include the loss of borohydride by chemical hydrolysis, borohydride crossover and the cost. This short review presents recent developments in DBFCs and some of the potential solutions that could be used to take DBFC technology towards commercialization.

Figure 1: Schematic diagram of DBFC.



Reactions occurring at the electrodes

Anode reactions

One mole of $NaBH_4$ generates 8 mol of electrons as given by the electrochemical oxidation according to reaction [Eq 1.]. However, in practical systems, it is predicted that the number of electrons actually utilized per BH_4^- is less than eight. It is reported that the number of electrons generated is 6.9 for Au [10], 6 for Pd [16] and 4 for Ni catalysts [17]. The decrease in the number of generated electrons leads to a decrease in the energy density to 7.6 Whg^{-1} for six electrons and 5.8 Whg^{-1} for four electrons [13]. Hence, the electrocatalyst plays a significant role in the performance of DBFCs. Further, H_2 is reported to be evolved from the anode side under both open circuit conditions as well as during operation of the cell. The generation of H_2 a process that decreases the over-all cell efficiency, can be from hydrolysis reaction [Eq (4)] and also from an electrochemical step [9] as shown in Eq (5):

$$NaBH_4(aq) + 2H_2O \longrightarrow NaBO_2(aq) + 4H_2 + \text{Heat (217 kJ)} \tag{4}$$

$$NaBH_4(aq) + 4OH^- \longrightarrow NaBO_2(aq) + 2H_2 + 2H_2O + 4e^- \tag{5}$$

Thus, the side reactions hinder the effective use of the BH_4^- since, for every molecule of hydrogen formed, two electrons are no longer available to provide electrical energy. It is one of the main disadvantages of DBFC. The anode reaction may be written as,

$$BH_4^- + xOH^- \longrightarrow BO_2^- + (x-2)H_2O + (4-1/2x)H_2 + xe^- \tag{6}$$

where x is the actual no. of electrons that are generated during the direct oxidation of BH_4^-

The detailed mechanism of the BH_4^- oxidation is not yet well understood. However, a plausible mechanism has been reported on Pt electrodes

[18,19]. Gyenge [20] has reported that BH_4^- oxidation occurs by the generation of hydrogen which is further oxidized at potentials between −0.7 and −0.9 V, and direct oxidation of BH_4^- occurs in the potential range from −0.15 to −0.05 V vs. Ag/AgCl. Jamard et al. [21] have reported similar findings with Pt electrodes. Mirkin et al. [22] have studied the electrochemical oxidation of BH_4^- on Au electrode using fast scan voltammetry and concluded that the rate determining step involves electrochemical-chemical-electrochemical (ECE) pathway with unstable intermediates. The kinetics of borohydride electro-oxidation on rotating gold disk electrode has been studied by Cheng and Scott [23] who reported that at 0.45 V, the number of electrons transferred in borohydride oxidation is around 8. Thus the mechanism of oxidation of BH_4^- is still not quite clear. In general, there are two types of mechanisms that are proposed on any electrode material [6]. The first one involves electron transfer as given below and subsequent steps

$$BH_4^- - e^- \longrightarrow BH_4^{\cdot} \tag{7}$$

involve decomposition of radicals and further electron transfer.

In the second mechanism, the first step involves pre-dissociation of brohydride at certain surface sites, for example,

$$2M + BH_4^- \longrightarrow M-H + M-BH_3^- \tag{8}$$

followed by electron transfer and further surface reactions. The presence of adsorbed hydrogen is likely to lead to hydrogen gas evolution. Gold for example, cannot accommodate significant amount of adsorbed hydrogen and hence the mechanism involves predominantly the first type and over potentials for direct oxidation of borohydride are high. Nickel, platinum and palladium, on the other hand, favour adsorption of hydrogen and are candidates for the second type of mechanism.

Cathode reactions

The cathode reaction may involve either oxygen or acidic hydrogen peroxide as oxidant.

Oxygen as oxidant

Oxygen can undergo electrochemical reduction at the cathode surface in two ways.

In direct pathway, it gets reduced directly to water involving four electrons.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad E^0 = 0.40 \text{ V vs SHE} \tag{2}$$

In an indirect pathway, oxygen forms hydrogen peroxide as an intermediate which subsequently gets reduced to water.

Hydrogen peroxide as oxidant

The theoretical open-circuit voltage of DBFC is 1.64 V with oxygen as the oxidant, and between 1.64 and 3.02 V with hydrogen peroxide as the oxidant depending upon the pH of the catholyte [24,25]. Since OCV is high in case of H_2O_2, it is expected to yield high power densities and efficiencies.

$$2H_2O_2 + 4e^- + 4H^+ \longrightarrow 4H_2O \qquad E^0 = 1.78 \text{ V vs SHE} \tag{9}$$

Electrode materials

Anode catalysts

Several noble and non-noble metals have been studied as anode materials for BH_4^- oxidation. Noble metals (Pd, Pt, Au), transition metals (Ni, Cu), AB_5 and AB_2-type hydrogen storage alloys have been reported as anode catalyst materials in DBFCs. Suda [26] reported that DBFCs do not require noble metal catalysts that are conventionally used in PEMFCs for the reaction, H_2 to H^+. Table 2 lists different catalysts that have been are reported for borohydride oxidation.

The catalyst for DBFC should be efficient for borohydride oxidation at low over-potentials and should also be inactive towards the borohydride hydrolysis. Chatenet et al. [27] studied borohydride oxidation on Au and Ag catalysts on bulk as well as on nanosized materials dispersed over carbon and showed that gold performs better than silver. Their findings also revealed that nanodispersed materials are better catalysts than their bulk counterparts. Gyenge et al. [28–30] proposed colloidal Os and Os-based alloys (Os–Sn, Os–Mn and Os–V), colloidal Au and Au-based alloys (Au–Pt, Au–Pd) and colloidal Pt and Pt-based alloys (Pt–Ni, Pt–Ir) for borohydride oxidation and concluded that Pt-Ir and Pt–Ni show high activity among the investigated Pt-alloys. Also, alloying of Pt with Au (Pt–Au) has been shown to generate almost 8 electrons, the maximum expected theoretically. This enables high faradaic efficiencies. Towards this direction, our group has been working on nanostructured catalytic materials that are efficient for borohydride oxidation. We have recently studied Rh, Ir and bimetallic Rh-Ir alloy nanoparticles and showed improved activity in the case of Rh-Ir based fuel cell [figure 2].

Hydrogen storage alloys are promising materials as anode catalyst for DBFCs. Wang et al. [31,32] have explored the use of AB_5-type $LaNi_{4.5}Al_{0.5}$ and Si-modified $LmNi_{4.78}Mn_{0.22}$ alloys and noticed promising catalytic activities in both oxidation and hydrolysis of the fuel. Wang and Xia [33] have reported that the hydrogen storage capacity of such alloys is limited. But details regarding comparison of the performance of DBFCs using AB_5-type alloys and Pt-based catalysts are still unavailable in the literature.

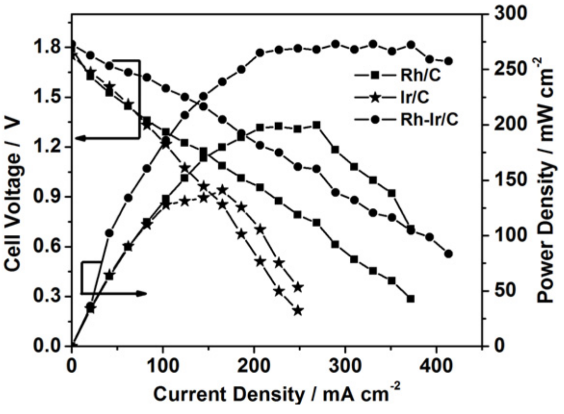
Table 2: Cell performance data for different anode catalysts.

Anode	Cathode	Membrane	Oxidant	Temperature (^{0}C)	Power Density (mW/cm^2)	Ref.
Ni/C	Pt/C	Nafion-117	O_2	85	40.5	[34]
Pd/C	Pt/C	Nafion-117	O_2	85	89.6	[34]
Pt/C	Pt/C	Nafion-117	O_2	85	59.3	[34]
Pt/C	Ni mesh	Morgane –ADP	Air	RT	200	[21]
Ni + Pd/C + Zr–Ni alloy	Co-PPY-C	Nafion-117	Air	RT	65	[42]
Pt-NI	Ni mesh	Morgane –ADP	Air	RT	115	[21]
Pt-Ru	Ni mesh	Morgane –ADP	Air	60	149.33	[21]
Ag/C	Pt/C	Nafion-117	O_2	85	43.6	[34]
Au/C	Pd/C	Nafion-117	O_2	85	65.6	[34]
Au/C	Ag/C	Nafion-117	O_2	85	32.8	[34]
Au/C	Ni/C	Nafion-117	O_2	85	35.4	[34]
Au/C	FeTMPP	Nafion-117	O_2	85	65.3	[35]
97% Au+3% Pt	NA	AEM	Air	60	70	[10]
Pd	Au	Nafion	Acidified H_2O_2	60	680	[46]
Au	Pt/C	Nafion-117	Acidified H_2O_2	20	63.5	[45]
$MmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$	Prussian Blue	Nafion117	Acidified H_2O_2	30	68	[48]
$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$	CoPc	None	Air	RT	90	[36]
$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$	FePc	None	Air	RT	92	[37]
$MmNi_{3.35}Co_{0.75}Mn_{0.4}Al_{0.3}$	MnO_2/C	None	O_2	25	70	[33]
$MmNi_{4.5}Al_{0.5}$	Pt/C	Nafion-117	H_2O_2	70	130	[24]
$MmNi_{3.2}Al_{0.2}Mn_{0.6}Co_{1.0}$	Pt/C	Nafion-117	H_2O_2	70	100	[24]

Cathode catalysts

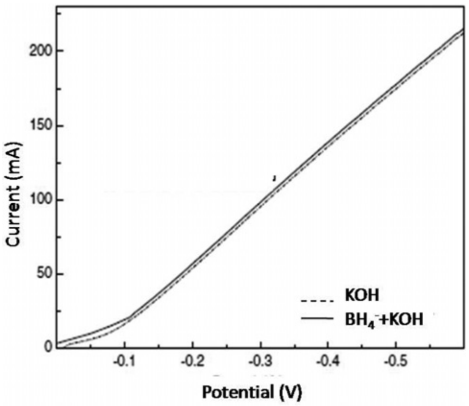
Due to its high electrical conductivity, good chemical stability and high electroactivity for oxygen reduction reaction (ORR), Pt has been extensively studied as the preferred cathode material in PEMFCs [34]. Cheng et al. [34,35] have reported high activity for Pt/C over Ag/C, Pd/C, Ni/C catalysts. Commercialization of fuel cells demands that the amount of platinum used is minimum. Also, cross-over of BH_4^- may result in getting oxidized at the cathode resulting in mixed potentials that will detoriate the performance of the cathode and in turn the fuel cell. Hence, there are considerable efforts in search of non-Pt catalysts for ORR. In this direction, different phthalocyanines (Pc) have been used as cathode materials in DBFCs that show good borohydride tolerance [36,37] [figure 3]. The DBFCs employing CoPc or FePc as cathodes and hydrogen storage alloy as anode possessed a peak power density as high as 92 mWcm^2 and also revealed very good short-term durability over a period of 50 hours under ambient conditions [figure 4].

Figure 2: Polarization data for DBFC with Rh/C, Ir/C and Rh-Ir/C as anode and Pt/C as cathode. Anode loading is 0.5 mg/cm^2 and cathode loading is 2 mg/cm^2.



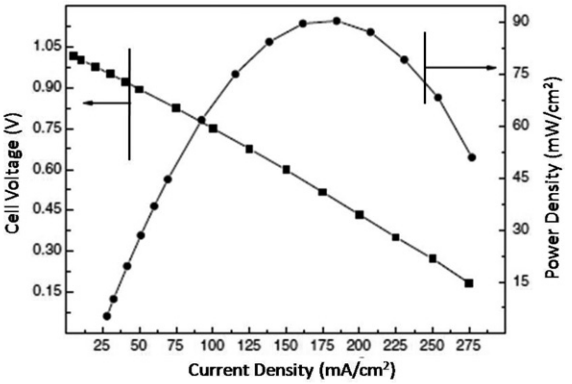
The ORR has been studied on non-precious materials such as iron tetramethoxyphenyl porphyrin (FeTMPP), silver and nickel as cathode electro-catalysts [35]. Among them, FeTMPP has shown the best borohydride tolerance and superior performance. Comparable performance to Pt cathode has been achieved with FeTMPP and silver cathodes. Similarly, manganese oxide (MnO_2)

Figure 3: Polarization curves for CoPc-catalyzed air cathode in 6M KOH electrolyte with and without addition of 1M KBH_4. Scan rate used is 5 mV s^{-1}. Adapted from ref. [36].



is also explored as a cathode material. MnO_2 exhibits considerable electrochemical activity for ORR and revealed good borohydride tolerance as well. It is worth mentioning that MnO_2 is inactive towards borohydride oxidation as well as hydrolysis. A DBFC based on MnO_2cathode and hydrogen storage alloy anode achieved a peak powder density of 70 $mWcm^2$ at a load current density of 180 mA cm^2 operating at a temperature of 25°C [38]. Verma et al. [39,40] have shown that MnO_2 is a good catalyst for oxygen reduction using voltammetric techniques. Feng et al. [41] have utilized MnO_2 as a cathode and assembled a simple DBFC-air cell that led to DBFC without a special ion exchange membrane or a noble metal catalyst [41]. Other example includes, metallo-organic compound, cobalt polypyrrole carbon (Co-PPY-C), employed as a cathode catalyst in the DBFC showing a comparable ORR activity to Pt/C. Improved stability has also been shown with Co-PPY-C cathode over Ag/C and Pt/C catalyst [42].

Figure 4: Electrochemical performance of DBFC based on CoPc cathode and hydrogen storage alloy anode. Adapted from ref. [36].



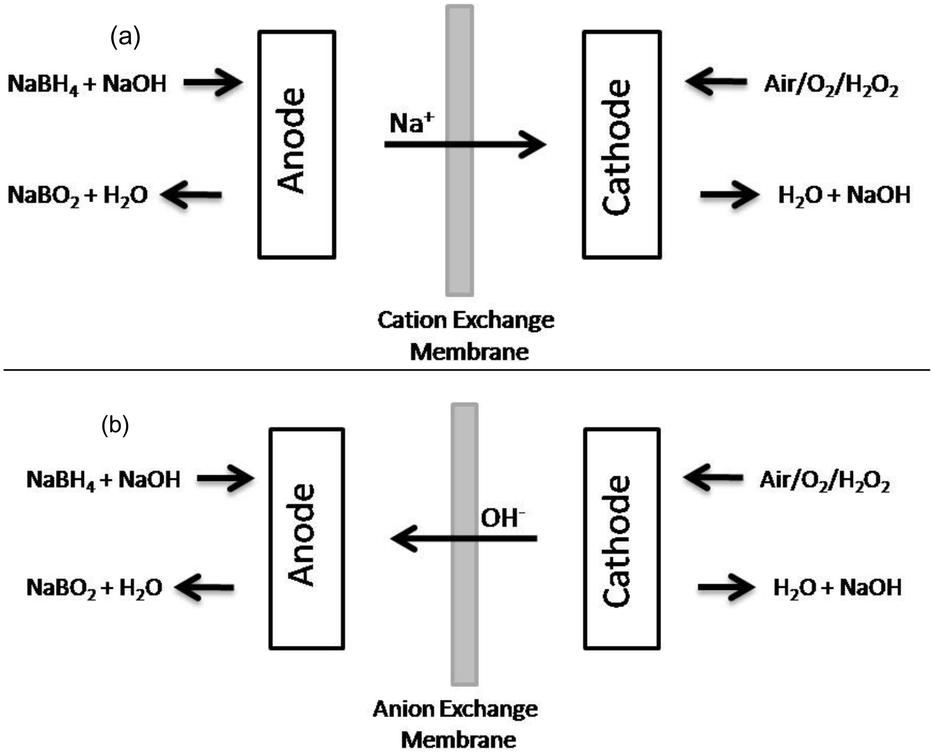
As mentioned earlier, H_2O_2 can yield high power densities and efficiencies. Additionally, use of H_2O_2 in the catholyte enables one to employ DBFCs in anaerobic atmosphere and also for sub-mersible applications. Several groups [24,25,43–45] have reported DBFCs with H_2O_2 as the catholyte. Gu et al. [46] used Pourbaix diagrams as tools to find appropriate candidates for peroxide reduction and concluded that gold is an effective cathode catalyst. Gold effectively reduces H_2O_2 yielding high power density, diminishing H_2O_2 decomposition and resisting corrosion. In their attempt to develop non-platinum and cost-effective cathode catalysts for the electro-reduction of hydrogen peroxide, Raman et al. [47] studied carbon supported iron tetramethoxy phenyl porphyrin (FeTMPP/C) and carbon supported lead sulphate ($PbSO_4$/C) electrodes for peroxide reduction and employed in DBFCs. Selvarani et al. [48] used prussian blue (PB) as cost effective cathode material and obtained a peak power density of 68 $mWcm^2$ at 30°C in a direct borohydride/hydrogen peroxide fuel cell.

Membrane

In PEMFCs, membrane is a solid polymer that acts as separator between anode and cathode. Good membrane should possess high ionic conductivity; high thermal stability and should prevent the migration of anolyte from anode to cathode. In DBFCs, balance of water content is necessary to maintain proton conductivity as excess water leads to flooding [34]. Membranes can be anionic or cationic. The following schematics portray the working principle of the DBFC with anionic (AEM) and cationic (CEM) membranes (figure 5).

The use of CEM over AEM has two distinct advantages: (i) prevention of borohydride anion cross-over and (ii) good chemical and mechanical stability in strongly alkaline environment and in presence of strong reducing agent. The most common choice of membranes is one of the Nafion®1100 EW series manufactured by Dupont, USA. It has beenreported that the cell performance depends on the thickness of the membrane. However, the use of CEM has some disadvantages as well. DBFCs used in conjunction with CEM, reduce the alkali concentration in the anolyte causing instability and inefficient use of the fuel, borohydride. The accumulation of alkali in the cathode compartment as well as ORR results in the formation of carbonates in presence of CO_2 in air. This in turn, deactivates the cathode as

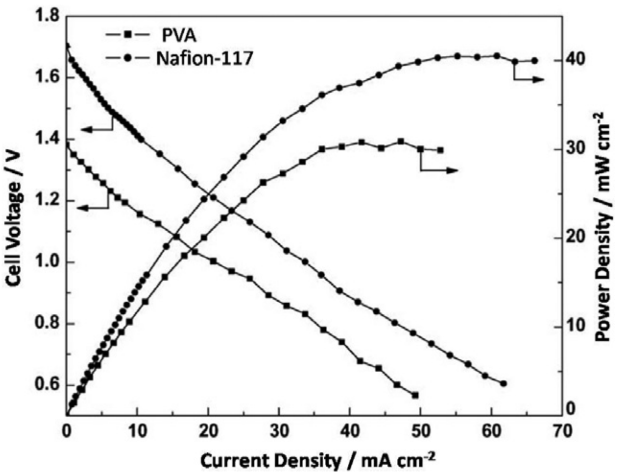
Figure 5: Borohydride fuel cells with: (a) a cation permeable membrane and (b) an anion permeable membrane, drawn to emphasise the chemical balance.



well as the membrane and blocks the free passage of oxygen/air to the cathode [12]. To reduce the alkali cross-over, Raman et al. [49] have used Nafion-961, a teflon-fiber reinforced composite membrane with sulfonate (100 μm thick) and carboxylate (10 μm thick) polymer layers. The flow of NaOH is prevented by the carboxylate layer of Nafion-961 and thus it actually helps in improving the cathode polarization behaviour in DBFC-hydrogen peroxide based cell. Lakeman et al. [50] reported a comparative study of twelve cation exchange membranes prepared by radiation grafting and two Nafion®membranes. The resistance of the synthesized membranes are found to be comparable with commercial membranes. Several radiation grafted ion membranes (styrene grafted polyethylene-tetrafluoroethylene, acrylic acid grafted polytetrafluoroethylene, and acrylic acid grafted low density polyethylene membranes) are developed by Cheng et al. [51]. They have reported that the performance of the styrene grafted polyethylene-tetrafluoroethylene membrane is better than the other membranes including Nafion-117. The improved performance has been attributed to the high ion-exchange capacity and high conductivity of the membrane. Yang et al. have reported a peak power density of 45 mW/cm^2 under ambient conditions using poly (vinyl alcohol)/hydroxyapatite (Ca_{10} $(PO_4)_6(OH)_2$) (PVA/HAP) composite polymer membrane [52]. A DBFC-H_2O_2 fuel cell with poly(vinylalcohol) (PVA) hydrogel as membrane is reported by Choudhury et al. [53] and its performance has been shown to be similar to Nafion-117 membrane electrolyte. Peak power densities of ~ 30–40mW/cm^2 have been reported for the DBFC with PVA based membrane [figure 6]. The observed cell performance of Nafion-117 based DBFC is attributed to the higher ionic conductivity of Nafion-117 than that of PVA hydrogel membrane.

Finally, it is worth mentioning the possibility of constructing a DBFC without a membrane [12]. This “new type of DBFC” does not need any expensive ion exchange membrane. In this direction, Wang and Xia [38] used alkaline electrolyte, i.e. a $NaBH_4$ in aqueous NaOH to demonstrate this concept and further studies are required to understand and optimize the fuel cell.

Figure 6: Cell performance data for DBFCs employing AB$_5$-type alloy of composition $MmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ as anode, gold-plated stainless steel mesh as cathode and (i) polyvinyl alcohol hydrogel; (ii) Nafion1-117 membranes as electrolytes. Adapted from ref. [53].



Conclusions

DBFCs with different anode, cathode catalysts and membrane electrolytes have been discussed in this short review. It is mandatory to develop the anode materials that will oxidize BH_4^- at low overpotentials without hydrolysis. Cathode materials with good kinetics should be developed towards ORR. By optimizing parameters such as anolyte concentration, loading of catalyst, fuel and oxidant flow rates, membrane, it is possible to improve the performance of DBFCs. Three main issues need to be addressed, (1) borohydride hydrolysis, (2) borohydride cross-over and (3) borohydride cost before this technology is commercialized.

Acknowledgement

V. Kiran acknowledges CSIR, New Delhi, for financial assistance.

Received 18 November 2009; revised 19 December 2009.

References

1. R. Dillon, S. Srinivasan, A. S. Arico, and V. Antonucci, *J. Power Sources*, 127 (2004) 112
2. C. K. Dyer, *J. Power Sources,* 106 (2002) 31.
3. Z. P. Li, B. H. Liu, K. Arai, and S. Suda, *J. Alloy Compd.*, 404 (2005) 648
4. T. Schultz, S. Zhou, and K. Sundmacher, *Chem. Eng. Technol.* , 24 (2001) 1223.
5. A K Shukla et al *J. Electroanal chem.,* 119, (2003) 391
6. A K Shukla et al *J. Electroanal chem.,* 181, (2004) 563
7. U. B. Demirci, *J. Power Sources*, 172 (2007) 676
8. M. E. Indig and R. N. Synder, *J. Electrochem. Soc.,* 109 (1962) 1104
9. R. Jasinski, *Electrochem. Technol.* , 3 (1965) 40.
10. S. C. Amendola, P. Onnerud, M. T. Kelly, P. J. Petillo, S. L. Sharp-Goldman, and M. Binder, *J. Power Sources,* 84, (1999), 130
11. E. Fakioglu, Y. Yurum, and T. N. Veziroglu, *Int, J. Hydrogen Energy,* 29, (2004), 1371.
12. C. Ponce-de-Leon, F. C. Walsh, D. Pletcher, D. J. Browning, and J. B. Lakeman, *J. Power Sources,* 155 (2006) 172.
13. J. H. Wee, *J. Power Sources,* 155 (2006) 329
14. J. H. Wee, *J. Power Sources*, 160 (2006) 514
15. J. H. Wee, *J. Power Sources,* 161 (2006) 1.
16. B. H. Liu, Z. P. Li, and S. Suda, *Electrochim. Acta.,* 49 (2004) 3097.
17. B. H. Liu, Z. P. Li, and S. Suda, *J. Electrochem. Soc.,* 150 (2003) A398.
18. J. H. Morris, H. J. Gysing, and D. Reed, *Chem Rev,* 85, 1985, 51.
19. J. P. Elder, and A. Hickling, *Trans Faraday Soc.,* 58, 1962, 1852.
20. E. L. Gyenge, *Electrochim. Acta,* 49 (2004), 965
21. R. Jamard, A. Latour, J. Salomon, P. Capron, and A. M. Beaumont, *J Power Sources,* 176 (2008),287.
22. M. V. Mirkin, H. Yang, and A. J. Bard, *J Electrochem Soc,* 139, (1992), 2212.
23. H. Cheng and K. Scott, *Electrochim Acta,* 51, (2006), 3429.
24. N. A. Choudhury, R. K. Raman, S. Sampath, and A. K. Shukla, *J. Power Sources,* 143, (2005), 1.
25. R. K. Raman, N. A. Choudhury, and A. K. Shukla, *Electrochem Solid-State Lett.,* 7, (2004), A488.
26. S. Suda, *Encyclopaedia of Materials: Science and Technology*, Elsevier Ltd., 2006, pp. 1.
27. M. Chatenet, F. Micoud, I. Roche, and E. Chainet, *Electrochim. Acta*, 51 (2006) 5459.
28. M. H. Atwan, D. O. Northwood, and E. L. Gyenge, *Int. J. Hydrogen Energy,* 30 (2005) 1323
29. M. H. Atwan, C. L. B. Macdonald, D. O. Northwood, and E. L. Gyenge, *J. Power Sources*, 158 (2006) 36.
30. E. Gyenge, M. H. Atwan, and D. O. Northwood, *J. Electrochem. Soc.* , 153 (2006) A150.
31. L. Wang, C. Ma, X. Mao, J. Sheng, F. Bai, and F. Tang, *Electrochem. Commun.* , 7 (2005) 1477.
32. L. Wang, C. Ma, and X. Mao, *J. Alloys Compd.,* 397 (2005) 313.
33. Y. G. Wang and Y. Y. Xia, *Electrochem. Commun.,* 8 (2006) 1775.
34. H. Cheng and K. Scott, K. Lovell, *Fuel Cells,* 6, (2006)6, 367.
35. H. Cheng and K. Scott, *J Electroanal Chem.,* 596, (2006), 117.
36. J. Ma, Y. Liu, P. Zhang, and J. Wang, *Electrochem Commun.,* 10, (2008),100.
37. J. Ma, J. Wang, and Y. Liu, *J Power Sources,* 172, (2007), 220.
38. Y. G Wang,Y. Y. Xia, *Electrochem Commun.,* 8, (2006), 1775.
39. A. Verma, A. K. Jha, and S. Basu, *J. Power Sources*, 141 (2005) 30.
40. A. Verma and S. Basu, *J. Power Sources,* 145 (2005) 282.
41. R. X. Feng, H. Dong, Y. D. Wang, X. P. Ai, Y. L. Cao, and H. X. Yang, *Electrochem. Commun.* 7 (2005) 449.
42. H. Y. Qin, Z. X. Liu, W. X. Yin,J. K. Zhu, and Z. P. Li, *J Power Sources,* 185, (2008), 909.
43. G. H. Miley, N. Luo, J. Mather, R. Burton, G. Hawkins, L. Gu, E. Byrd, R. Gimlin, P. J. Shrestha, G. Benavides, J. Latstrom, and D. Corroll, *J. Power Sources,* 165, (2007), 509
44. C. A. Sequeria, T. C. Pardal, D. M. Santos, J. A. Condeco, M. W. Franco, and M. C. Gonacalves, *ECS Trans.,* 3, (2007), 19
45. C. Ponce de Leon, F. C. Walsh, A. Rose, J. B. Lakeman, D. J. Browning, and R. W. Reeve, *J. Power Sources*, 164, (2007), 441.

46. L. Gu, N. Luo, and G. H. Miley, *J Power Sources,* 173, (2007), 77.
47. R. K. Raman and A. K. Shukla, *J. Appl. Electrochem*., 35, (2005), 1157.
48. G. Selvarani, S. K. Prashant, A. K. Sahu, P. Sridhar, S. Pitchumani, and A. K. Shukla, *J. Power Sources*, 178, (2008), 86.
49. R. K. Raman, A. K. Shukla*, Fuel Cells*, 7, (2007), 225.
50. J. B. Lakeman, A. Rose, K. D. Pointon, D. J. Browning, K. V. Lovell, S. C. Waring, and J. A. Horsfall, *J. Power Sources*, 162 (2006) 765.
51. H. Cheng, K. Scott, K. V. Lovell, J. A. Horsfall, and S. C. Waring, *J. Membr. Sci.,* 288 (2007) 168.
52. C. C. Yang, Yingjeng J. Li, S. J. Chiu, K. T. Lee, W. C. Chien, and C. A. Huang*, J. Power Sources,* 184 (2008) 95.
53. N. A. Choudhury, S. K. Prashant, S. Pitchumani, P. Sridhar, and A. K. Shukla, *J Chem Sci, In Press.*

Kiran completed his post graduation from Andhra University, Visakhapatnam with physical chemistry as specialization. Currently, he is working under the supervision of Prof S Sampath in the area of development of novel electrode materials for fuel cell applications.

Sampath is currently a faculty in the Department of Inroganic and Physical Chemistryof the IISc. His research interests are in the areas of surfaces and interfaces with emphasis on applications in sensors andenergy systems.