

Short communication

Study of fuel efficiency in a direct borohydride fuel cell

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Abstract

In this study, direct borohydride fuel cells (DBFCs) potentialities are evaluated. These emerging systems make it possible to reach maximum powers of about 200 mW cm^{-2} at room temperature and ambient air (natural convection) with high concentrated borohydride solutions. On the other hand, a part of borohydride hydrolyses during cell operating which leads to hydrogen formation and fuel loss: the practical capacity represents about only 18% of the theoretical one. In order to improve fuel efficiency, thiourea is tested as an inhibitor of the catalytic hydrolysis associated with BH_4^- electro-oxidation on Pt. The practical capacity is drastically improved: it represents about 64% of the theoretical one. Against, electrochemical performances (I – E curves) are affected by the presence of thiourea.

Last, both playing with platinum anodic mass loading and the nature of catalyst, a good compromise has been found in terms of both specific capacity and power.

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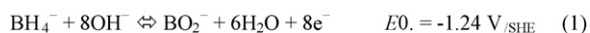
Keywords: Direct borohydride alkaline fuel cell; Borohydride oxidation; Borohydride hydrolysis; Thiourea; Pt–Ni; Anion-exchange membrane

1. Introduction

Currently, ‘low-temperature’ fuel cells developments are mainly focused on two technologies: DMFC (direct methanol fuel cell) and PEMFC (proton exchange membrane fuel cell supplied with hydrogen). The very fast oxidation kinetic of hydrogen makes it unassailable: the DMFC cannot compete with the PEMFC technology in terms of power density [1]. However, the advantage of the DMFC is the undoubted easiness of storage and management of its liquid fuel. Even if improvements have been realized to reduce the permeability of the membrane to methanol and to make cathodic catalysts insensitive with methanol, the cross over of methanol from the anodic compartment to the cathodic one leads to an irremediable downfall of the DMFC performances.

In this environment, other liquid fuel cells are emerging such as direct borohydride fuel cells (DBFCs). Indeed, from a thermodynamical point of view, the electromotive force of a DBFC

working with borohydride as the fuel is higher (1.64 V) than the one of the PEMFC (1.23 V). It is the same way for the theoretical yield (0.91 for the DBFC working with borohydride against 0.83 for the PEMFC). Lastly, if the oxidation of borohydride ions is straight, which means that there is no hydrogen intermediate formation (Eq. (1)), 1 mol of borohydride releases 8 mol of electrons. Then it should make it possible to reach 9300 Wh kg^{-1} of NaBH_4 .



In practice, Amendola et al. [2,3] were one of the first team to announce in 1999 the fabrication of a DBFC. Its fuel core was composed of an anionic hydroxide ion-exchange membrane and a Au–Pt bimetallic anodic catalyst. The authors succeeded in reaching 20 mW cm^{-2} at room temperature and about 60 mW cm^{-2} at 70°C . More recently, Liu et al. [4,5] carried out several efficient DBFC tests: one with non-noble metallic catalysts (nickel on the anodic side, silver on the

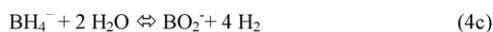
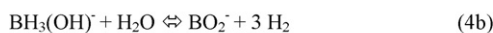
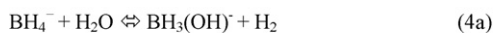
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cathodic one) which get at 35 mW cm^{-2} at room temperature and an other one which reached 290 mW cm^{-2} at 60°C with humidified air (palladium and Zr–Ni alloy on the anodic side, platinum on the cathodic side).

Obviously, despite its good reported results, DBFC still needs some specific efforts of development and especially ones concerning fuel management: a part of borohydride hydrolyses during cell operating which leads to hydrogen formation and fuel loss (Eq. 4c).



This reaction involves the decrease of faradic capacity of borohydride solutions. In addition, the accumulation of H_2 in the anodic side generates some safety and packaging problems for industrial applications. For these reasons, most of the published DBFC studies focused on the anodic side of the fuel cell: some mention the use of H_2 production inhibitors (use of thiourea [6,7] which is known to block hydrogen adsorption on several metals such as Pd and Pt, use of Si [8] which allowed the authors to decrease hydrogen losses and to enhance the use of NaBH_4 from 20 to 95%) while others quote the use of selective anodic catalysts (Au [3,6], $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Mn}_{0.6}\text{V}_{0.2}\text{Co}_{0.1}\text{Ni}_{1.1}$ [9] and Ni [4]).

In this work, we present our contribution to the development of DBFC. In particular, we tried to evaluate the ability of thiourea to be a good inhibitor of hydrogen production as it seems to be very discussed in different works [6,10,11,12].

2. Experimental details

The core part of the DBFC consists basically of two electrodes (anode and cathode) separated by a anion-exchange membrane supplied by Solvay (Morgane[®] ADP).

The anode Pt catalyst is prepared by mixing 80 wt.% Pt/C (E-TEK 80% Pt on Vulcan XC72) and Pt black (E-TEK) with ethanol–water (1:1) and a 60 wt.% PTFE dispersion in H_2O (Aldrich). The resultant ink is then pulverized on a $3 \text{ cm} \times 3 \text{ cm}$ carbon cloth. The anodic mass load of Pt is about 1.3 mg cm^{-2} or 0.3 mg cm^{-2} depending on the experiments.

The anode Pt–Ni catalyst is prepared by mixing Pt–Ni/C (E-TEK 20% Ni–Pt (1:1) on Vulcan XC72), PTFE dispersion (60 wt.% in H_2O , Aldrich) and ethanol–water (1:1). The resultant ink is then pulverized on a $3 \text{ cm} \times 3 \text{ cm}$ carbon cloth. The anodic mass load of Pt–Ni is about 0.8 mg cm^{-2} .

The cathode used is a O’CAT[®] air cathode from Evionyx made of a no-platinum active layer on a Ni mesh. There is no preliminary hot-pressing process to prepare the membrane-electrodes-assembly (MEA) contrary to PEMFC. Electrodes are just pressed together to have a mechanical contact during the cell assembling. The test cell is presented in Fig. 1.

Liquid fuel of DBFC is a borohydride alkaline aqueous solution ($\text{NaBH}_4 = 2 \text{ M}$ and $\text{NaOH} = 1 \text{ M}$) with or without 10^{-4} M

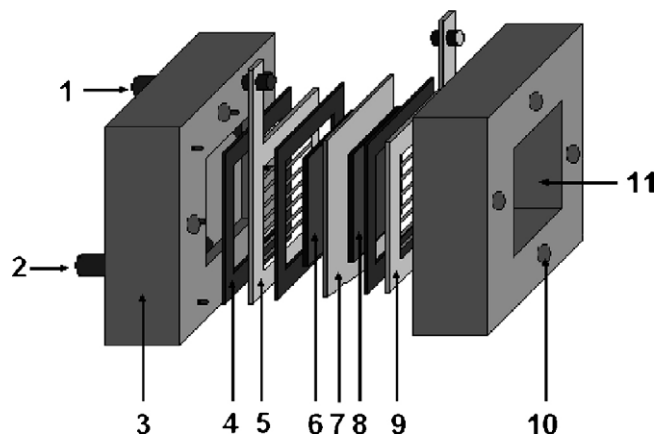


Fig. 1. Schematic drawing of the test cell. (1) Exit of fuel, (2) entrance of fuel, (3) clips, (4) joints, (5) current collector, (6) anode, (7) anion exchange membrane, (8) cathode, (9) current collector, (10) screws and (11) air brought by natural convection.

thiourea (Fluka). A peristaltic pump (Cole Parmer Masterflex[®] C/L) is used to make the liquid fuel circulate in closed circuit; static ambient air is used on the cathodic side.

Electrochemical tests of DBFC are performed at room temperature using an electrochemical-regulation 8-channel system (Solartron 1470 electrochemical interface). The measurement set is controlled by a PC equipped with Corrware[®] software. I – E curves are obtained by setting a slope in current of 2 mA s^{-1} from the initial open circuit voltage (OCV) to 0 V. Hydrogen evolution in the anodic side is recorded with a flow meter (Brooks[®]) during all the experiments. Chronopotentiometric curves are also plotted at room temperature, at a constant current of 1 A ($\sim 111 \text{ mA cm}^{-2}$). Chronoamperometric curve is also plotted at room temperature, at a constant potential of 0.6 V.

Voltametric measurements have been achieved on three-electrode cells using a potentiostat (Votalab PST050) controlled by a PC equipped with Voltmaster[®] software. The studied solution is made of 10^{-2} M NaBH_4 and 1 M NaOH . Thiourea is then added in different concentrations (10^{-4} or 10^{-3} M). The working electrode is a platinum disk electrode (DE), the auxiliary one is carbon-made and the reference electrode is a mercury/mercury sulfate reference electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4$). The equivalent sweep rate used in this work is 25 mV s^{-1} at room temperature. The voltage is first driven from the initial OCV (located between -1500 and -1200 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) to -250 mV versus $\text{Hg}/\text{Hg}_2\text{SO}_4$. Then the cell is cycled between -1400 and -250 mV versus $\text{Hg}/\text{Hg}_2\text{SO}_4$.

3. Results and discussion

3.1. Voltametric study

Fig. 2 exhibits the voltametric second cycles at 25 mV s^{-1} from -1500 to -250 mV (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) and at 100 mV s^{-1} from -1500 to 0 mV on a platinum disk electrode (DE) for 10^{-1} M NaBH_4 and 1 M NaOH medium. Fig. 3 exhibits the voltametric second cycle from -1450 to -250 mV at 25 mV s^{-1} on a platinum disk electrode (DE) for different concentrations

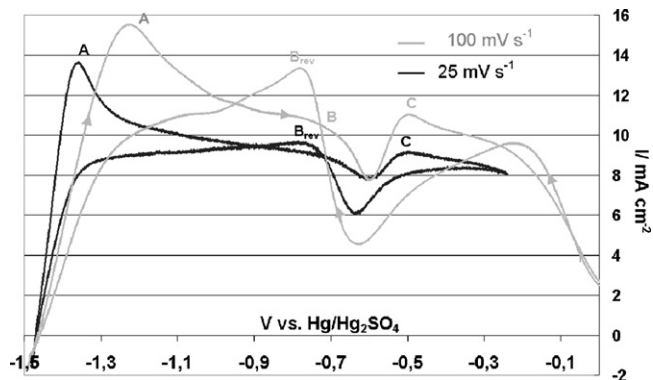


Fig. 2. Cyclic voltammogram (second scan) of 0.1 M NaBH₄ in 1 M NaOH on Pt disk electrode (5 mm diameter). Scan rates = 25 and 100 mV s⁻¹, rpm = 0, room temperature.

of thiourea in 10⁻¹ M NaBH₄ and 1 M NaOH medium. Open circuit potential of Pt DE have also been measured in the different solutions: -1500 mV is OCP for 10⁻¹ M NaBH₄ and 1 M NaOH, -1353 and -1218 mV are OCP in presence of 10⁻⁴ and 10⁻³ M thiourea, respectively. In the three cases, OCP is very far from the theoretical BH₄⁻/BO₂⁻ equilibrium potential of -1890 mV versus Hg/Hg₂SO₄. It could be explained by the fact that borohydride ions hydrolyse very fast as soon as they meet a platinum catalytic particle in the anodic side and release to H₂. The induced OCP of the anode is a mixed potential approximate to the H⁺/H₂ potential in 1 M NaOH medium (~-1490 mV). In the presence of thiourea, the mixed open circuit potential of the anode shifts to values greater than the H⁺/H₂ potential: it could be attributed to the adsorption of thiourea on platinum.

Voltamperograms of Fig. 2 are in good agreement with those of Gyenge in similar conditions [6]: at 25 mV s⁻¹, a first peak (A) is detected around -1350 mV, a second one (B) at about -700 mV (which is easier to distinguish on the voltamperogram plotted at 100 mV s⁻¹) and a third oxidation peak (C) is observed at -500 mV. As discussed in Ref. [6], the first peak could be attributed to H₂ oxidation, H₂ coming from the catalytic hydrolysis of BH₄⁻; the second one could be ascribed to the oxidation of BH₃OH⁻ principally (Eq. (4a)). The third peak might be associated with the BH₄⁻ direct electro-oxidation in

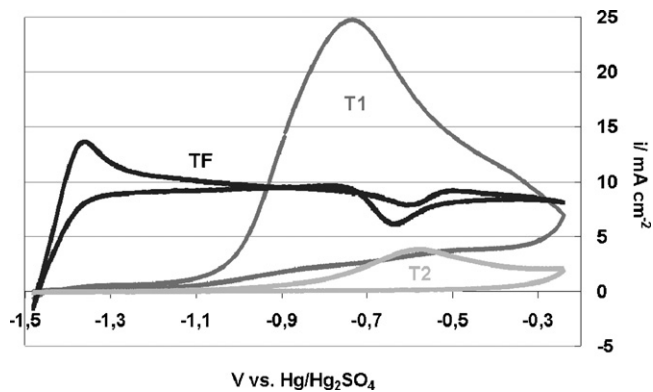


Fig. 3. Cyclic voltammogram (second scan) of 0.1 M NaBH₄ in 1 M NaOH on Pt disk electrode (5 mm diameter). Scan rate = 25 mV s⁻¹, rpm = 0, room temperature. (TF) thiourea-free, (T1) thiourea = 10⁻⁴ M and (T2) thiourea = 10⁻³ M.

alkaline medium. On the return scan, in the potential region of -250 to -600 mV, BH₄⁻ is still directly oxidised and a new peak (B_{rev}) appears at -750 mV, which could be assigned to the oxidation of BH₃OH⁻ [6]. Voltametric cycles are very different when thiourea is added to the alkaline solution of borohydride (Fig. 3). Indeed, only one peak of potential is observed: it is positioned in the -750; -550 mV potential range. Peaks relative to both H₂ and BH₃OH⁻ electro-oxidation have disappeared as it was expected allowing for the fact that thiourea is supposed to inhibit BH₄⁻ hydrolysis. Peak relative to the direct oxidation of BH₄⁻ decreases with the concentration of thiourea. Indeed, as thiourea strongly adsorbs on Pt, some platinum sites are not accessible for oxidation any more.

This voltametric preliminary study on Pt DE shows that thiourea inhibits BH₄⁻ hydrolysis and consequently H₂ oxidation. Thiourea does not allow to reach OCP approximate to the theoretical BH₄⁻/BO₂⁻ equilibrium potential. DBFC voltage efficiency will not be improved by this additive. Moreover, as BH₄⁻ direct oxidation current peak tends to decrease with the concentration of thiourea, 10⁻⁴ M thiourea is the only concentration we choose to test in the next study. With a lower hydrogen loss, DBFC specific capacity should be improved and specific energy maybe too. This is what we checked in the experiments described in the following section.

3.2. DBFC operating tests with Pt anodic catalyst

Fig. 4 shows two typical polarization curves of a DBFC supplied with a borohydride alkaline thiourea-free solution and with a borohydride alkaline solution containing 10⁻⁴ M thiourea, respectively. H₂ evolution in the anodic side is also measured all over the electrochemical tests and reported in Fig. 4. For thiourea-free DBFC, initial open circuit voltage (OCV) is located around 850–900 mV, far from the theoretical electromotive force (1640 mV) due to the anodic mixed potential (Section 3.1). Maximum power peak of 200 mW cm⁻² has been obtained at about 400 mA cm⁻² (Fig. 5) and H₂ loss is over 60 SCCM all over the polarization curve.

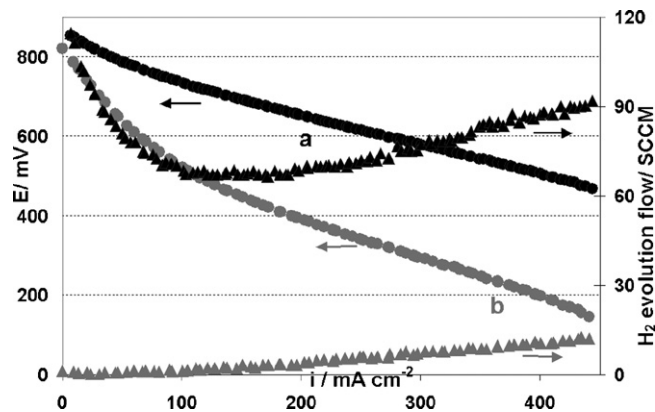


Fig. 4. Polarization curve of a DBFC supplied with (a) 2 M NaBH₄ and 1 M NaOH, or (b) 2 M NaBH₄, 1 M NaOH and 10⁻⁴ M thiourea. Scan rate = 2 mV s⁻¹, room temperature. H₂ evolution flow is also reported on the graph (a) ▲ and (b) ▲. Anodic Pt mass loading = 1.3 mg cm⁻².

After thiourea addition, OCV is lightly smaller than in the last case: thiourea which is supposed to block hydrogen adsorption on platinum does not allow to reach greater values than 900 mV at open circuit which corroborates observations made in the voltametric study (Section 3.1). The 10^{-4} M thiourea effect is double. On the first hand, H_2 emissions are really falling down: they do not go beyond 10 SCCM all over the polarization curve. On the other hand, the power peak is unfortunately divided by two with a maximum power of 90 mW cm^{-2} at about 300 mA cm^{-2} (Fig. 5). The oxidation mechanism does not follow only one pathway on platinum catalyst. There are at least two scenarios: the borohydride oxidation is direct (1) and indirect ((4c) and (6)), one way being preponderant on the other one depending on functioning current and voltage.



Even with thiourea weak concentration (10^{-4} M), most of available sites for borohydride hydrolysis are blocked, making only the direct oxidation of borohydride possible. This direct oxidation does not allow to reach power values as great as the ones generated in the case of indirect oxidation. Moreover, thiourea which blocks free sites available for BH_4^- hydrolysis also prevents direct oxidation on these sites. Thiourea acts as a poison and the “active area” decreases in size. That is what Demirci [10] seems to suggest by explaining that sulfur species involve the formation of strong Pt–S bonds and are believed to be at the origin of the catalytic deactivation of free sites and the premature ageing of the active layer.

Fig. 6 shows the 1 A-chronopotentiometric curve carried out on a thiourea-free DBFC supplied with 200 ml of 2 M $NaBH_4$ and 1 M NaOH. Theoretically, with such a fuel solution, it is possible to collect 85 Ah considering a 8-electron oxidation process. The measured capacity is 15 Ah (Fig. 6), which is approximately 18% of the theoretical value of the fuel. This very poor coulombic efficiency is first attributed to H_2 loss by borohydride catalytic hydrolysis: the equivalent capacity of 50 Ah has been lost by H_2 evolution (value calculated with H_2 flow from Fig. 6). Second, the solution is not fully used: some BH_4^- ions are neither hydrolysed nor oxidised and some others cross over the anionic membrane from the anodic side to the cathodic one.

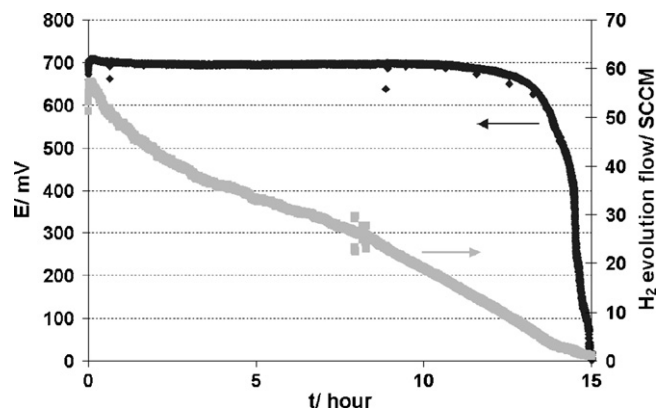


Fig. 6. Chronopotentiometric curve of a DBFC supplied with 2 M $NaBH_4$ and 1 M NaOH. $I=1$ A, room temperature. Anodic Pt mass loading = 1.3 mg cm^{-2} . H_2 evolution flow vs. time is also reported on the graph.

Fig. 7 shows the 1 A-chronopotentiometric curve carried out on a DBFC supplied with 200 ml of 2 M $NaBH_4$, 1 M NaOH and 10^{-4} M thiourea. Theoretically, with such a fuel solution, the capacity of such a solution remains the same than the one of an equivalent thiourea-free solution (85 Ah namely). The measured capacity is 55 Ah, which is approximately 64% of the theoretical value of the fuel. The coulombic efficiency of the DBFC is drastically improved by thiourea. Hydrogen loss has been estimated to 3.3 equiv. Ah only, which is much lower than the first case. Nevertheless, the fuel solution is not either fully used and the average power at 1 A is about 25 mW cm^{-2} only, which is three times lower than what is obtained without thiourea in the same conditions. The additive quickly leads to a fall down in DBFC power. There is probably an accelerate ageing of the fuel cell core and/or a poisoning of catalysts, which is detrimental for long-term operations.

Fig. 8 shows the 1 A-chronopotentiometric curve carried out on a DBFC supplied with 200 ml of 2 M $NaBH_4$, 1 M NaOH, thiourea-free. The platinum anodic mass loading of Fig. 8 is about four times smaller than the one of Figs. 6 and 7. The measured capacity is 55 Ah, which is the same value than the one achieved with thiourea (Fig. 7). Moreover, the average power obtained during the 1 A-chronopotentiometric test is around

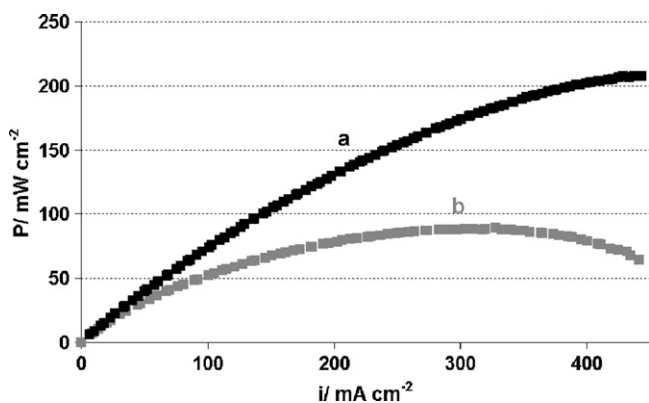


Fig. 5. Specific power vs. current density of a DBFC supplied with (a) 2 M $NaBH_4$ and 1 M NaOH, or (b) 2 M $NaBH_4$, 1 M NaOH and 10^{-4} M thiourea. Scan rate = 2 mA s^{-1} , room temperature. Anodic Pt mass loading = 1.3 mg cm^{-2} .

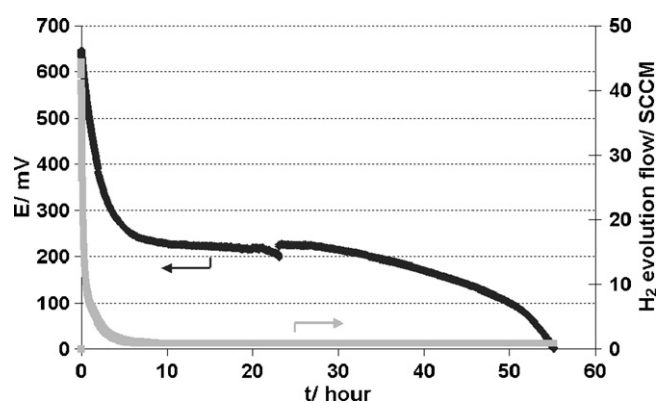


Fig. 7. Chronopotentiometric curve of a DBFC supplied with 10^{-4} M thiourea, 2 M $NaBH_4$ and 1 M NaOH. $I=1$ A, room temperature. Anodic Pt mass loading = 1.3 mg cm^{-2} . H_2 evolution flow vs. time is also reported on the graph.

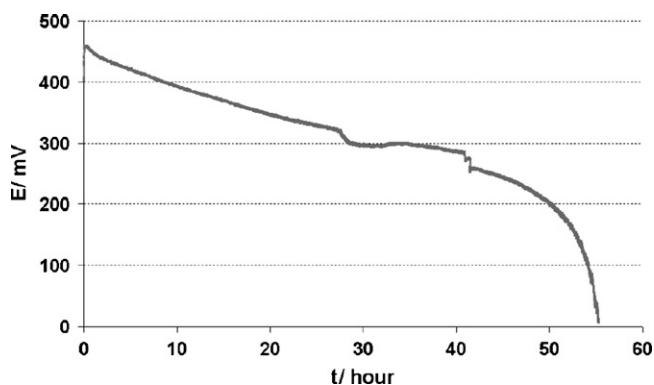


Fig. 8. Chronopotentiometric curve of a DBFC supplied with 2 M NaBH₄ and 1 M NaOH. $I=1$ A, room temperature. Anodic Pt mass loading = 0.365 mg cm^{-2} .

35 mW cm^{-2} , which is better than the feature get with thiourea and regarding the polarization curve (Fig. 9), maximum power peak of 70 mW cm^{-2} has been obtained at about 200 mA cm^{-2} , which is very worthy allowing for the low Pt mass loading.

3.3. Preliminary DBFC operating tests with Pt–Ni anodic catalyst

DBFCs running with thiourea additive showed disappointing results. As an alternative, only playing with platinum anodic mass loading allowed us to find a low-cost compromise between electrical performances and hydrogen loss.

In order to still improve both autonomy and power performances with low platinum mass loading, Pt-based bimetallic alloys have been investigated. First, a comparative study of their catalytic activity with reference to BH₄[−] hydrolysis has been achieved (Fig. 10). In the decreasing order, the class list of catalysts is the following: Pt–Ni < Pt < Pt–Co, Pt–Ru, Pt–Cr. Pt–Ni could be a likely candidate for a further use in DBFC anodic side. That is what we checked by plotting the galvanodynamic curve of a DBFC whose anode is composed of Pt–Ni 0.8 mg cm^{-2} (Fig. 11). Maximum power peak of 115 mW cm^{-2} has been obtained at about 300 mA cm^{-2} , which is a rather good value for

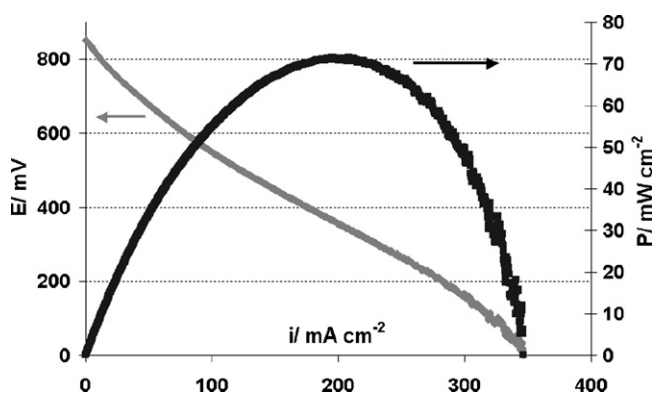


Fig. 9. Polarization curve of a DBFC supplied with 2 M NaBH₄ and 1 M NaOH. Scan rate = 2 mA s^{-1} , room temperature. Anodic Pt mass loading = 0.365 mg cm^{-2} .

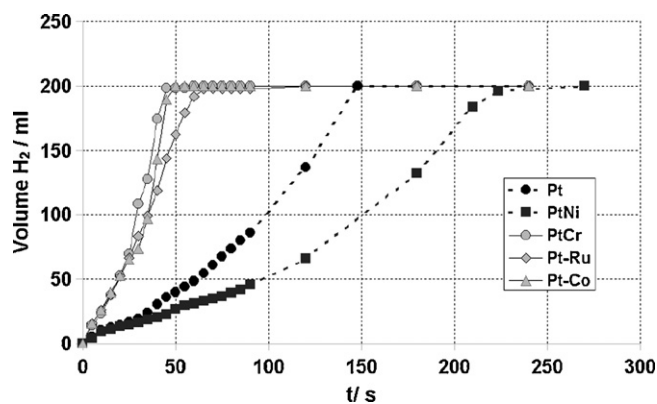


Fig. 10. H₂ evolution vs. time of 2 M NaBH₄ and 1 M NaOH solution (1 ml) reacting with 10 mg of catalyst. E-TEK catalysts: 20 wt.% Pt/C Vulcan XC72, 20 wt.% Pt–Ni (1:1)/C Vulcan XC72, 20 wt.% Pt–Cr (3:1)/C Vulcan XC72, 20 wt.% Pt–Co (1:1)/C Vulcan XC72 and 58 wt.% Pt–Ru (1:1)/C Vulcan XC72.

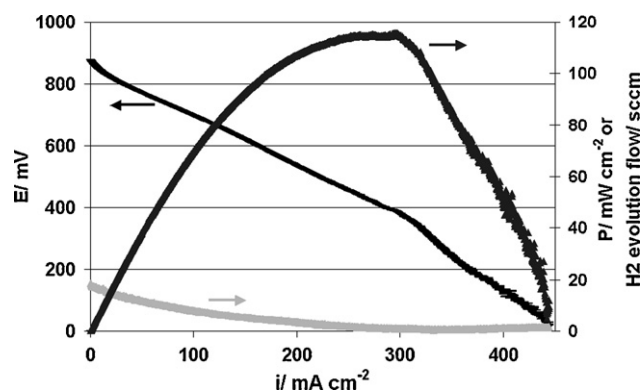


Fig. 11. Potential and specific power vs. current density of a DBFC supplied with 2 M NaBH₄ and 1 M NaOH. Scan rate = 2 mA s^{-1} , room temperature. Anodic Pt–Ni mass loading = 0.8 mg cm^{-2} . H₂ evolution flow vs. time is also reported in the graph.

Pt–Ni catalyst compared to literature [13,14]. Moreover, H₂ loss does not go beyond 10 SCCM all over the polarization curve.

Fig. 12 shows the 0.6 V-chronoamperometric curve carried out on a DBFC with Pt–Ni as the catalyst in the anodic side which is supplied with 200 ml of 2 M NaBH₄ and 1 M NaOH. The measured capacity is 59 Ah which is approximately 69%

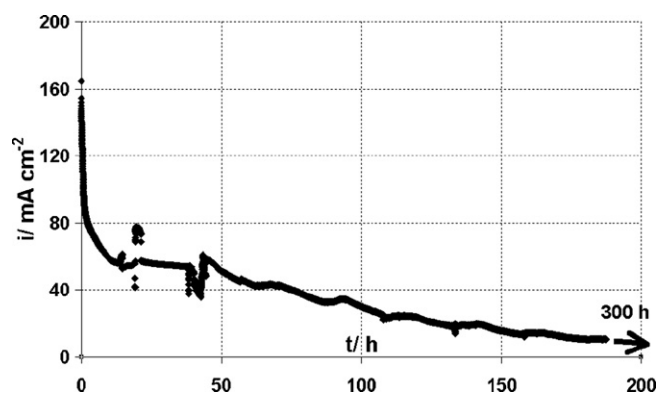


Fig. 12. Chronoamperometric curve of a DBFC supplied with 2 M NaBH₄ and 1 M NaOH (200 ml). $E=0.6$ V, room temperature. Anodic Pt–Ni mass loading = 0.8 mg cm^{-2} .

of the theoretical value of the fuel. In these conditions, the coulombic efficiency of the DBFC is even better than the one obtained with thiourea but the average power during the 0.6 V-chronoamperometric test is quite low and still needs improvements.

4. Conclusion

The DBFC presents great power performances: indeed, the electrochemical study of a DBFC supplied with an alkaline solution of 2 M NaBH₄ and 1 M NaOH shows that it is possible to reach 200 mW cm⁻² at room temperature and ambient air. On the other hand, the autonomy of such a system is quite poor: NaBH₄ hydrolysis is catalysed by platinum, that leads to huge hydrogen loss. At 1 A only 18% of the fuel is effectively used in the DBFC while 58% is lost by hydrogen production. 24% of the fuel is not used at all: some BH₄⁻ ions are neither hydrolysed nor oxidised and some others cross over the anionic membrane from the anodic side to the cathodic one.

So DBFC is a high-power system with low efficiency: how could it be a powerful one with high efficiency?

One of the proposed solution is the use of thiourea as an inhibitor of borohydride hydrolysis. Better coulombic efficiency is actually obtained in the same test condition (64% of the fuel is effectively used). Against, the DBFC voltage at 1 A is far smaller than the one obtained when the fuel is thiourea-free. It means that thiourea presents a dual influence: a good one concerning the stability of the fuel when in contact with the anodic catalyst and a detrimental one concerning the achieved power in the tested concentration. In other words, thiourea helps to increase the coulombic efficiency of the DBFC system by poisoning the active sites of hydrogen adsorption, which leads in return to drastically decrease specific power of the fuel cell.

By only reducing with a 4-factor the platinum anodic mass loading, the DBFC supplied with an alkaline thiourea-free solution of 2 M NaBH₄, 1 M NaOH is able to reach 70 mW cm⁻² at room temperature and ambient air in galvanodynamic conditions while coulombic efficiency at 1 A represents 64% of the theoretical one, i.e. as much as the case where thiourea is added to fuel. Moreover, the DBFC voltage at 1 A is higher than the one get with thiourea.

Consequently, it seems to be more attractive to reduce platinum anodic mass loading than to add thiourea in fuel

solution—say nothing of the cost, which will be obviously much more attractive too. Indeed, by only playing with the anodic mass loading it is possible to both improve fuel efficiency and keep good power performances.

The solution to get a powerful DBFC system with high efficiency is maybe not to stop borohydride hydrolysis but preferably to run it down just enough to reach the accurate balance between the quantity of H₂ released by hydrolysis and the one which the DBFC anode is able to oxidise simultaneously at a given functioning point. For this purpose, Pt–Ni is currently studied as the anodic catalyst instead of Pt and preliminary results are very promising. Other incoming DBFC studies will focus on this bimetallic alloy and also on the optimisation of the anodic active layer in order to improve both autonomy and power performances.

Acknowledgements

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