



Direct borohydride/peroxide fuel cells using Prussian Blue cathodes

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ABSTRACT

Direct borohydride fuel cells (DBFCs) are receiving much attention during the last decade. Many researchers are now focused on DBFCs operating on sodium borohydride (NaBH₄) as the fuel and hydrogen peroxide (H₂O₂) as the oxidant. In the present work, direct NaBH₄/H₂O₂ fuel cells consisting of platinum (Pt) anodes, a Prussian Blue (PB)-coated Pt or a Pt cathode, and a Nafion N117 membrane as the separator, are assembled. The effect of different operational conditions, namely the fuel (NaBH₄ + NaOH) and oxidant (H₂O₂ + HCl) compositions, as well as the operation temperature, on the performance of these DBFCs is investigated. The obtained results are evaluated and the most suitable conditions for the operation of these NaBH₄/H₂O₂ systems are proposed. The use of the PB-coated electrode can lead to up to a 50% increase in the peak power density, as compared to the cell using a single Pt cathode. At 65 °C, the DBFC using the PB-modified electrode attained over 200 mW cm⁻², at a cell voltage of 0.8 V.

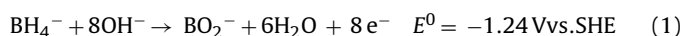
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1. Introduction

Sodium borohydride (NaBH₄) is gaining increasing interest for its possible applications in energy systems [1]. It may be used either as a hydrogen source [2,3] for conventional proton exchange membrane fuel cells (PEMFCs) or as an energy carrier for direct borohydride fuel cells (DBFCs) [4–9].

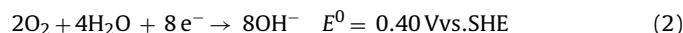
PEMFCs pose several constraints concerning the hydrogen storage and distribution. Direct liquid-fed fuel cells have the general advantage over PEMFCs of using a liquid fuel, which is easier to handle, transport, and store. The direct methanol fuel cell (DMFC) has been widely studied but shows some problems with the methanol toxicity and the CO poisoning of the platinum (Pt) electrocatalyst. Therefore, the DBFC is drawing a lot of attention because of its new features: the solid state NaBH₄ is chemically stable and can be stored and distributed easily; the oxidation product, sodium metaborate (NaBO₂) is non-toxic and may be recycled back to NaBH₄ [10]; and there are no gaseous pollutants exhausted from the fuel cell reactions. Moreover, the DBFC presents higher energy density than the DMFC [11,12].

In a regular DBFC, borohydride (BH₄⁻) is oxidised in strong alkaline media (pH > 12) to metaborate (BO₂⁻) and water, generating 8 electrons according to Eq. (1) [13,14].

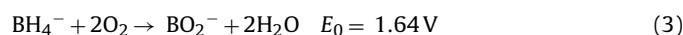


However, although a number of exchanged electrons, *n*, of about 7–8 electrons have been found experimentally for gold (Au) electrodes [15], this value is much lower for most electrode materials used for BH₄⁻ oxidation. Platinum (Pt), palladium (Pd), or nickel (Ni) are known to be able to oxidise BH₄⁻ at lower overpotentials [16], but have the drawback of being simultaneously catalysts for the BH₄⁻ hydrolysis. For this reason, typical *n* values ranging from 2 to 4 have been reported for Pt electrocatalysts [17], 4 to 6 for Pd [15], and 4 for Ni [15].

With the BH₄⁻ oxidation at the anode, humidified oxygen or air is electrochemically reduced at the interface between the cathode catalyst and the aqueous electrolyte, being the eight electrons consumed according to Eq. (2).



Coupling of Eqs. (1) and (2) leads to the overall cell reaction (Eq. (3)).



The DBFC theoretical cell voltage of 1.64 V is about 0.4 V higher than that of the ordinary PEMFC. It is also very high when compared to the methanol, formic acid and hydrazine systems, with theoretical cell voltages of 1.19, 1.45, and 1.56 V, respectively.

However, recent advances in the research on these borohydride energy devices show several opportunities for direct sodium borohydride/hydrogen peroxide (NaBH₄/H₂O₂) fuel cells [18–22]. The fact that both fuel and oxidant solutions are liquids, simplifies their handling, storage, and controllable feeding to a fuel cell, making this direct borohydride/peroxide fuel cell (DBPFC) a preferential power

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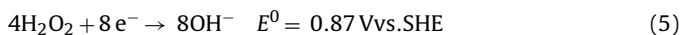
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source for space and underwater applications, where oxygen is not readily available [21].

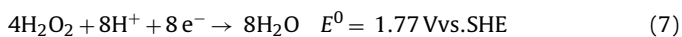
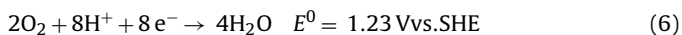
In the DBPFC, the BH_4^- anodic oxidation proceeds through Eq. (1). On the other hand, H_2O_2 is decomposed into oxygen and water at the catalyst/electrode interface according to Eq. (4), with the produced oxygen being subsequently reduced through Eq. (2).



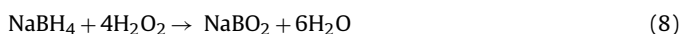
Alternatively, H_2O_2 may also be directly electrochemically reduced according to Eq. (5).



When the pH of the H_2O_2 catholyte solution is low ($\text{pH} < 1$), two reactions may take place: decomposition of H_2O_2 to O_2 (Eq. (4)) followed by O_2 reduction to water (Eq. (6)); or the direct H_2O_2 electroreduction described by Eq. (7).



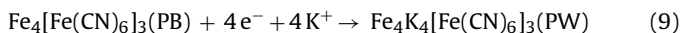
So, the net cell reaction in such DBPFC system is given by Eq. (8).



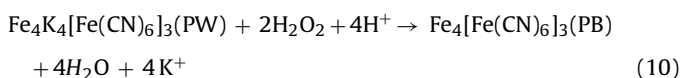
The theoretical cell voltages for this DBPFC are 2.11 and 3.01 V when considering the cathode reactions described by Eqs. (5) and (7), respectively. Even though substantially higher cell voltage values are expected for the DBPFCs assuming oxidant reduction at low pH (Eqs. (6) and (7)), the realisation of cells operating at this extreme pH gradient is not very practical, which in some way justifies the fact that open circuit voltages (OCVs) higher than about 2.0 V are hardly ever observed. Accordingly, appropriate anode and cathode materials should promote the reactions shown in Eqs. (1) and (7), respectively, avoiding the BH_4^- hydrolysis and the H_2O_2 decomposition to oxygen (Eq. (4)).

Pt, which is the most commonly used electrocatalyst for O_2 reduction, has been shown to be active for H_2O_2 reduction as well [23,24]. But besides the problem of its high price, Pt catalysts also promote the undesirable H_2O_2 chemical decomposition (Eq. (4)), while other electrode materials not (e.g., Au, Hg) [25], although the kinetics of the H_2O_2 reduction reaction on Pt are faster and occur at lower overpotentials. It is expected that modifications on Pt electrodes may minimise the problem of H_2O_2 chemical decomposition and simultaneously decrease the electrocatalyst excessive cost.

Prussian Blue (PB), also known as iron(III) hexacyanoferrate, finds many electrochemical applications in electrochromism, ion selective electrodes, charge storage devices, and electrocatalysis, but there are only a few papers on the use of PB as an electron transfer mediator of the H_2O_2 reduction reaction [26–34]. When PB is submitted to negative overpotentials, it converts to its reduced form, known as Prussian White (PW), according to Eq. (9) [26].



Itaya et al. have shown that PW presents a catalytic effect both towards the reduction of O_2 and H_2O_2 [35]. In acid medium, the mechanism for the H_2O_2 reduction on the reduced PB film (i.e., PW), is generally given by Eq. (10) [26].



The catalytic effect of PB owes to its zeolitic nature, with a cubic unit cell of 10.2 Å and channel diameter of about 3.2 Å, which enables the diffusion of O_2 and H_2O_2 molecules through the crystal lattice. For this reason, PB is described as a three-dimensional catalyst. In fact, molecules with molecular weights higher than H_2O_2

cannot diffuse through the PB lattice, making it an electrochemically selective catalyst [34]. Karyakin et al. reported the catalytic activity of PB for H_2O_2 reduction to be about 100 times higher than that for O_2 [29]. Furthermore, preparation of PB is simple and cost effective, and PB films show high stability in acidic media.

Selvarani et al. recently reported that PB can act as a mediated electron-transfer cathode catalyst in direct $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cells [34]. They obtained good indications on the use of PB on these DBPFC systems, but it seems clear that systematic studies are still required. For this reason, the present paper analyses the use of Pt and PB-modified Pt electrodes as cathodes in DBPFCs. To further investigate the efficiency of the PB catalyst, a laboratory direct $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell consisting of a Pt anode, a PB-coated Pt cathode, and a Nafion N117 ion-exchange membrane as the separator, was assembled and tested. The influence of different operational conditions, namely the fuel ($\text{NaBH}_4 + \text{NaOH}$) and oxidant ($\text{H}_2\text{O}_2 + \text{HCl}$) concentrations, and the cell's temperature, on the behaviour of this DBPFC was investigated. Moreover, the catalytic efficiency of the PB/Pt cathode was evaluated by providing a direct comparison of the performance of DBPFCs using this electrocatalyst and using solely the single Pt cathode. Hopefully, the PB/Pt electrode would improve the H_2O_2 reduction process in the DBPFC and lead to considerable developments on the cell performance.

2. Experimental

A simple two-compartment acrylic cell was assembled employing standard platinum (Pt) foil commercial electrodes (Metrohm 6.0305.100) of 1 cm² geometric surface area, for both anode and cathode electrodes of the fuel cell. Each compartment of the cell contained 70 ml of the corresponding aqueous electrolyte. On the left side, the anolyte was composed of an alkaline mixture of $\text{NaBH}_4 + \text{NaOH}$, and on the right side, the catholyte contained $\text{H}_2\text{O}_2 + \text{HCl}$. NaBH_4 (Panreac, 96 wt.%), NaOH (AnalaR NORMAPUR, 99 wt.%), H_2O_2 (MERCK, 35 wt.%) and HCl (Carlo Erba, 37 wt.%) were used as received and all solutions were prepared with deionised (Elix 3 Millipore) water. To prevent H_2O_2 decomposition and possible loss of BH_4^- by hydrolysis during storage, the test solutions were prepared immediately before the measurements. A Nafion N117 membrane, from DuPont (Wilmington, DE), was used to separate the anodic and cathodic compartments of the single direct $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell. The membrane active area was ca. 30 cm².

Cell measurements were conducted using a PAR 273A EG&G computer controlled potentiostat (Princeton Applied Research, Inc.) with the associated PowerSUITE software package. Saturated calomel electrode (SCE) references (Metrohm 6.0701.100) were used to measure the anode and cathode overpotentials associated with the cell discharge. For each analysed factor, the performance of the fuel cell was evaluated by recording the cell polarisation and obtaining the corresponding power density curves.

The tested experimental conditions involved changing the DBPFC's fuel ($\text{NaBH}_4 + \text{NaOH}$) and oxidant ($\text{H}_2\text{O}_2 + \text{HCl}$) compositions and also the cell's operation temperature. Cells assembled with Pt–Pt electrodes, and with Pt–PB/Pt electrodes were studied.

The PB/Pt electrode was obtained by depositing a thin film of Prussian Blue (PB) on the Pt surface, under galvanostatic conditions, at a constant current of 40 $\mu\text{A cm}^{-2}$, during 3 min. The PB electrodeposition solution was prepared by mixing 25 ml of 0.02 M $\text{HCl} + 0.02 \text{ M FeCl}_3 \cdot 6\text{H}_2\text{O}$ (AnalaR NORMAPUR, 99.2 wt.%) solution with 25 ml of 0.02 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ (MERCK, 99 wt.%), at constant stirring. Fig. 1 shows SEM micrographs of the Pt electrode and of the PB/Pt electrode, at two different magnifications. The images show that the PB coating is not homogeneous, and that there is formation of small aggregates on the electrode surface (Fig. 1c and d).

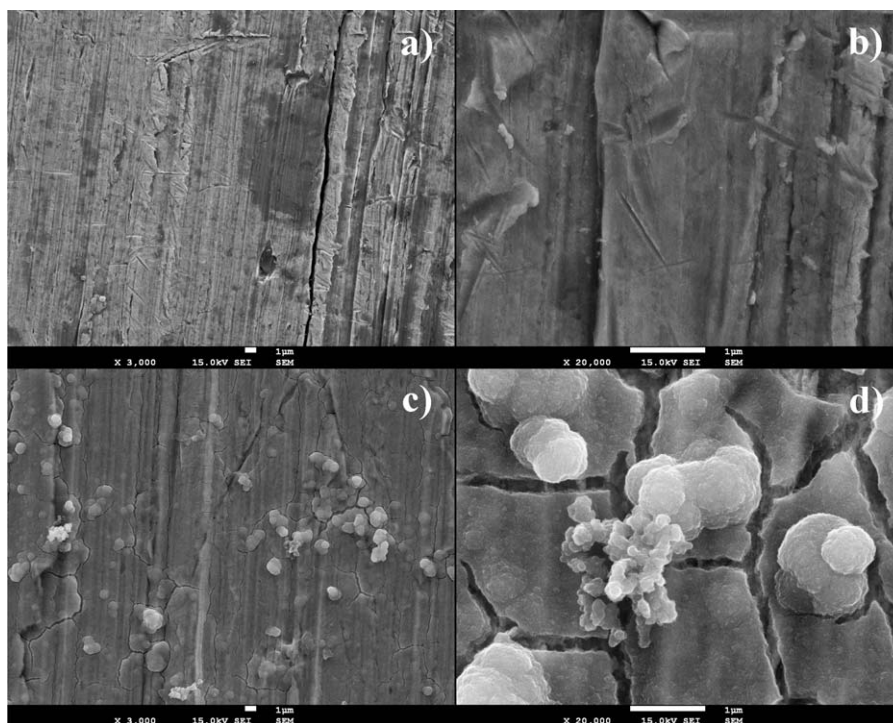


Fig. 1. SEM micrographs of a Pt electrode at (a) 3000× and (b) 20,000× magnification and of a PB/Pt electrode at (c) 3000× and (d) 20,000× magnification. Bar size = 1 μm.

For all the DBPFCs, both with and without the PB-coated Pt cathode, several relevant parameters (e.g., maximum cell voltage, maximum power density, short-circuit current density) were obtained, for the different experimental conditions tested.

3. Results and discussion

Two different approaches have been pursued: the first step consisted in characterising the main cell parameters by changing several operational parameters, namely the electrolytes' compositions and temperature, and to observe their influence on the polarisation behaviour of the cell; the second step was intended to further improve the cell performance by replacing the single Pt cathode by a PB-coated Pt cathode.

3.1. Analysis of the cell operational parameters

Several operational parameters have been changed and the effect of those changes on the fuel cell performance has been evaluated by obtaining cell polarisation curves and the corresponding power density curves for each different tested experimental condition. The assembled laboratory $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell is very simple and practical as illustrated in Fig. 2.

The success of the electrochemical processes (Eqs. (1) and (7)) occurring in the DBPFC can depend critically on the selection of the proper electrode materials and membrane separator [36]. Studies reported in the open literature [34] and others resulting from own experience in DBPFCs [8,19,36] suggested the use of Pt and Pt–PB/Pt electrodes and Nafion N117 membranes, as described in the present paper. But, as already discussed, heterogeneous side reactions, electrolyte compositions, operational temperatures, etc., can alter the real effectiveness of the general electrode reactions given by Eqs. (1) and (7), as well as the best performance of the Nafion membrane. In other words, side reactions can affect the desired oxidation and reduction processes, decreasing the expected cell voltage of 3.01 V for a lower value. Moreover, considering that in the tested lab cells (Fig. 2) the Nafion N117 membrane separates two compartments

containing solutions with very different pHs, the fixed charged sites in the membrane promote a local separation of ionic charge, which sets up a potential across the membrane. For a membrane with 100% ion selectivity in 1:1 electrolytes, this membrane potential, which is due to the Donnan equilibrium, can be estimated by the Nernst equation (Eq. (11)),

$$E_M = \frac{RT}{F} \ln \left(\frac{C_1}{C_2} \right) \quad (11)$$

where E_M is the membrane potential (V), and C_1 and C_2 are the electrolyte concentrations (strictly activities) of transported ion on either side of membrane (kmol m^{-3}). Membrane potentials can be significant (e.g., 0.83 V for a membrane between 1.0 M NaOH and 1.0 M HCl at 25 °C) and should be accounted for in the voltage balance in membrane cells. In summary, the realisation of DBPFCs operating at the present extreme pH gradient is not very practical,

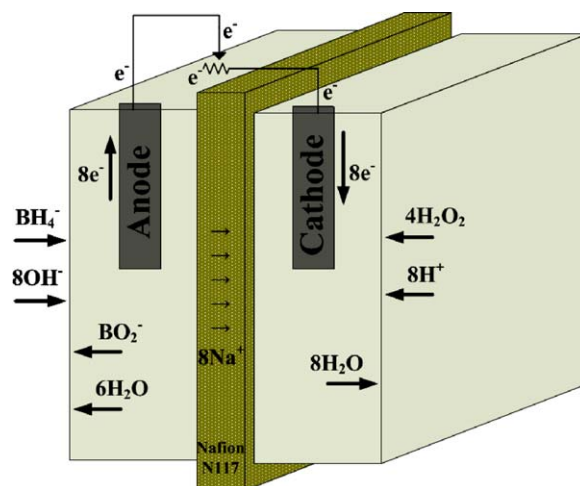


Fig. 2. Schematic drawing illustrating the electrochemical processes occurring in a DBPFC.

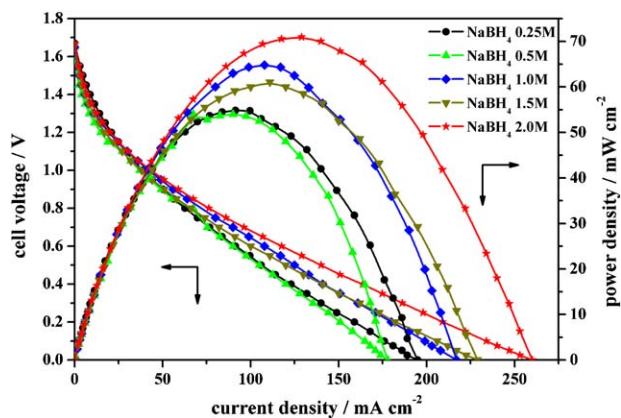


Fig. 3. Effect of NaBH_4 concentration on the current and power density of the DBPFC at 25 °C. Fuel: $x \text{ NaBH}_4 + 1.0 \text{ M NaOH}$. Oxidant: $2.5 \text{ M H}_2\text{O}_2 + 0.7 \text{ M HCl}$.

which may justify the fact that the measured OCVs were always close to 2.0 V and not 3.0 V, as desired.

Despite the high pH gradient, with a pH close to 14 in the anodic compartment and a pH lower than 1 in the cathodic compartment, the membrane does not show any instability problems, even after extensive use [36]. As shown in Fig. 2, the sodium ion (Na^+) is the major charge carrier by migration in the DBPFC, but the migration of H^+ should also be considered. To a minor extent, a limited migration of Cl^- , OH^- , BH_4^- and BO_2^- into the anolyte compartment may also take place. In addition to ion conductivity, diffusion of HCl , H_2O_2 , NaOH , and NaBH_4 occurs to a certain extent, caused by the concentration gradient between the anode and cathode compartments, leading to diffusional crossover of certain species (e.g., NaBH_4 , H_2O_2) [36].

3.1.1. Effect of fuel composition

The effect of the used NaBH_4 amount on the performance of the assembled laboratory DBPFC has been observed by varying the NaBH_4 concentration between 0.25 M and 2.0 M (Fig. 3). The arrows next to the cell polarisation and power density curves in Fig. 3 indicate the corresponding X and Y axes.

When the NaBH_4 concentration changes, the cell OCV keeps practically constant (1.65–1.67 V), the short-circuit current density acquires values in the 178–240 mA cm^{-2} range, and the peak power density is as high as 71 mW cm^{-2} , at 0.55 V and 129 mA cm^{-2} , for 2.0 M NaBH_4 . From a cost-effective perspective, the 1.0 M NaBH_4 concentration seems the best composition for the fuel, this value being fixed for the remaining experiments.

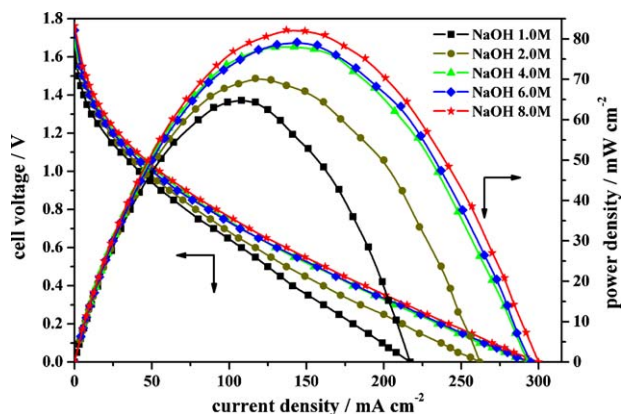


Fig. 4. Effect of NaOH concentration on the current and power density of the DBPFC at 25 °C. Fuel: $1.0 \text{ NaBH}_4 + x \text{ M NaOH}$. Oxidant: $2.5 \text{ M H}_2\text{O}_2 + 0.7 \text{ M HCl}$.

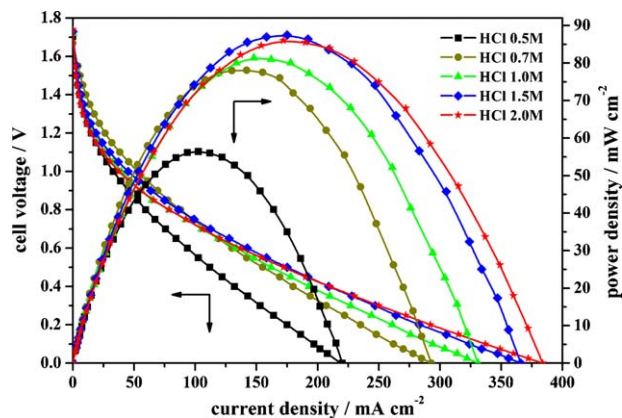


Fig. 5. Effect of HCl concentration on the current and power density of the DBPFC at 25 °C. Fuel: $1.0 \text{ M NaBH}_4 + 4.0 \text{ M NaOH}$. Oxidant: $2.5 \text{ M H}_2\text{O}_2 + x \text{ HCl}$.

Next, the NaOH concentration in the fuel has been varied between 1.0 M and 8.0 M (Fig. 4).

It is clear from Fig. 4 that increasing the NaOH amount in the fuel from 1.0 M to 4.0 M causes a significant increase in the peak power density, this increase being more moderate for NaOH concentrations from 4.0 M to 8.0 M. For the tested NaOH concentrations, the OCV is not as constant with the NaOH amount, as it is with the NaBH_4 concentration change. In fact, OCV values in the range 1.65–1.76 V were measured. For the short-circuit current densities, the values varied between 217 and 300 mA cm^{-2} . The maximum peak power density was 82 mW cm^{-2} , at 0.60 V and 137 mA cm^{-2} , at 8.0 M NaOH . Using NaOH concentrations higher than 4.0 M do not substantially improve the polarisation behaviour of the cell. Therefore, the NaOH concentration in the anolyte solution has been fixed as 4.0 M for the remaining experiments.

3.1.2. Effect of oxidant composition

The oxidant ($\text{H}_2\text{O}_2 + \text{HCl}$) compositions for this DBPFC have also been tuned. The HCl concentration was varied between 0.5 M and 2.0 M. The highest short-circuit current density (384 mA cm^{-2}) was obtained at 2.0 M HCl . Fig. 5 shows that the peak power density values for the lab fuel cell increase up to a HCl concentration of 1.5 M. Further increasing the HCl concentration shows no improvement in the cell performance. Therefore the value of 1.5 M has been fixed for the HCl concentration in the oxidant solution.

The effect of the H_2O_2 composition in the oxidant solution has also been analysed. The tested H_2O_2 concentrations ranged from 1.25 M to 6.0 M (Fig. 6). For this H_2O_2 concentrations range, the OCV is practically constant, and the short circuit current density

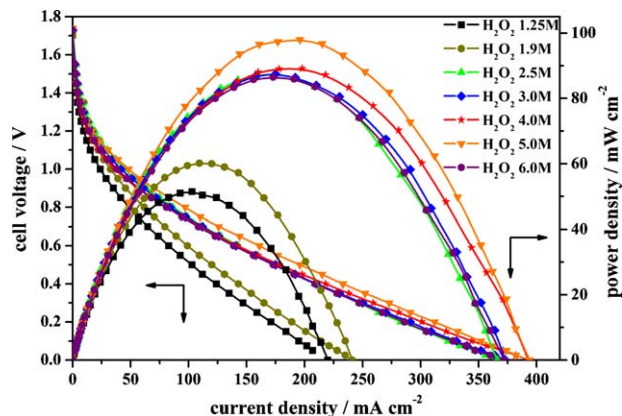
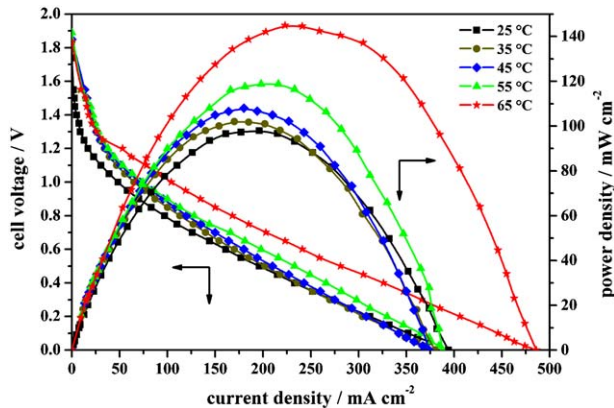


Fig. 6. Effect of H_2O_2 concentration on the current and power density of the DBPFC at 25 °C. Fuel: $1.0 \text{ NaBH}_4 + 4.0 \text{ M NaOH}$. Oxidant: $x \text{ M H}_2\text{O}_2 + 1.5 \text{ M HCl}$.

Table 1Effect of the electrolyte composition on the Pt | NaBH₄, NaOH || HCl, H₂O₂ | Pt cell at 25 °C.

	NaBH ₄ 1.0 M	NaOH 4.0 M	HCl 1.5 M	H ₂ O ₂ 5.0 M
Open circuit voltage (V)	1.65	1.67	1.73	1.74
Short-circuit current density (mA cm ⁻²)	217	293	366	394
Peak power density (mW cm ⁻²)	65	78	88	98
Cell voltage at peak power density (V)	0.60	0.55	0.50	0.50
Current density at peak power density (mA cm ⁻²)	108	142	175	196

**Fig. 7.** Effect of temperature on the current and power density of a DBPFC. Fuel: 1.0 M NaBH₄ + 4.0 M NaOH. Oxidant: 5.0 M H₂O₂ + 1.5 M HCl.

considerably varies from 220 mA cm⁻² (1.25 M H₂O₂) to 394 mA cm⁻² (5.0 M H₂O₂). The cell performance is largely improved by increasing the H₂O₂ concentration from 1.9 M to 2.5 M. A maximum peak power density of 98 mW cm⁻² was observed at an H₂O₂ concentration of 5.0 M.

Table 1 provides relevant data on the effect of the electrolyte compositions on the studied Pt cells at 25 °C. It should be noted that the values obtained in each column consider previously adjusted concentrations for the species indicated in the preceding columns. In other words, for the last column of Table 1, which shows the cell parameters obtained at 5.0 M H₂O₂, it implies that those measurements were done with 1.0 M NaBH₄, 4.0 M NaOH, and 1.5 M HCl.

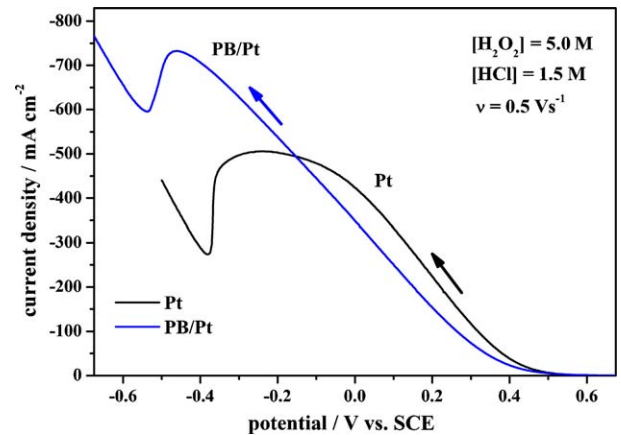
3.1.3. Effect of operation temperature

The effect of the cell's operation temperature on the current density and power density curves of the laboratory DBPFC has been analysed (Fig. 7). The temperature was varied from 25 °C to 65 °C.

There is an apparent continuous improvement of the fuel cell performance with the temperature increase (Table 2). However, for temperatures above ca. 60 °C a clear instability was observed in the cell solutions (i.e., gas evolution on both electrodes), leading

Table 2Effect of temperature on the Pt | NaBH₄, NaOH || HCl, H₂O₂ | Pt cell.

	Temperature (°C)				
	25	35	45	55	65
Open circuit voltage (V)	1.74	1.84	1.85	1.89	1.84
Short-circuit current density (mA cm ⁻²)	394	380	374	388	486
Peak power density (mW cm ⁻²)	98	102	108	118	145
Cell voltage at peak power density (V)	0.50	0.60	0.60	0.60	0.65
Current density at peak power density (mA cm ⁻²)	196	170	180	198	223

**Fig. 8.** Typical LSV measurements in 5.0 M H₂O₂ + 1.5 M HCl solution, at 25 °C. Pt and PB/Pt working electrode; Pt counterelectrode; SCE reference; Scan rate = 0.5 V s⁻¹.

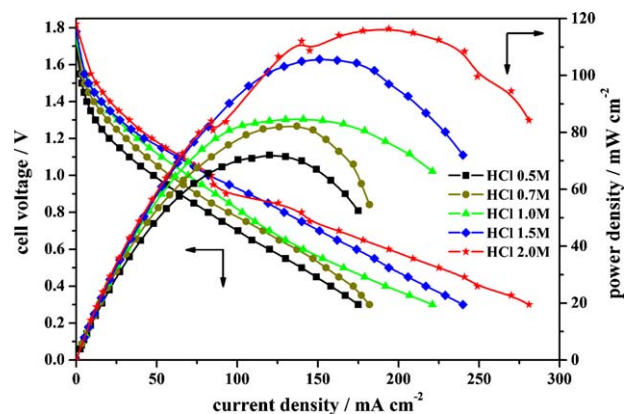
to faster fuel and oxidant degradation. To avoid such problems, an operation temperature around 55 °C is recommended.

3.2. Prussian Blue cathode

According to previously reported literature data [34], it is possible to enhance the H₂O₂ electrochemical reduction reaction using Prussian Blue (PB) as a mediator for the electron transfer process. Therefore, preliminary linear scan voltammetry (LSV) measurements, at several different potential scan rates, ν , ranging from 5×10^{-3} V s⁻¹ to 5 V s⁻¹, have been used to evaluate and compare the H₂O₂ electroreduction in the Pt and in the PB/Pt electrode surfaces. Typical LSV plots are shown in Fig. 8. The corresponding plots of i_p vs. $\nu^{1/2}$ and E_p vs. $\ln \nu$ allowed an approximate determination of the number of exchanged electrons, n , which was higher for the PB/Pt electrode. Approximate n values of about 1.4 and 1.9 were obtained for Pt and PB/Pt, respectively, at 25 °C, corresponding to an increase of ca. 30% in the n value. Based on these findings, a NaBH₄/H₂O₂ fuel cell containing a PB/Pt cathode was assembled and evaluated.

3.2.1. Effect of oxidant composition

The operational parameters that had been tuned for the DBPFC containing two single Pt electrodes could change when replacing the Pt metal cathode by the newly prepared PB/Pt cathode electrocatalyst. Therefore, to study the effect of the HCl concentration present in the oxidant composition, the former has been varied

**Fig. 9.** Effect of HCl concentration on the current and power density of a DBPFC using a PB/Pt cathode at 25 °C. Fuel: 1.0 M NaBH₄ + 4.0 M NaOH. Oxidant: 2.5 M H₂O₂ + x M HCl.

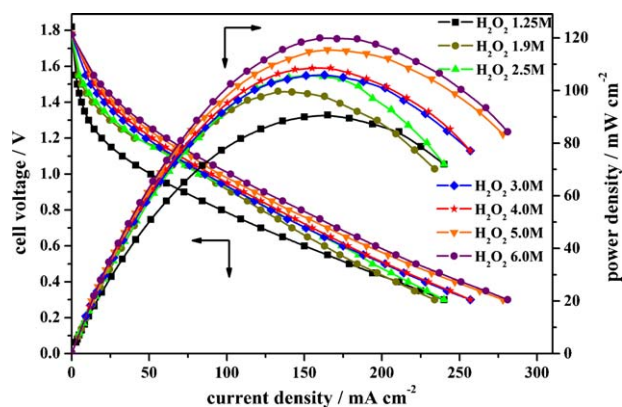


Fig. 10. Effect of H_2O_2 concentration on the current and power density of a DBPFC using a PB/Pt cathode at 25 °C. Fuel: 1.0M NaBH_4 + 4.0M NaOH. Oxidant: x M H_2O_2 + 1.5 M HCl.

between 0.5 M and 2.0 M and the changes in the cell performance have been observed (Fig. 9).

In this experiment (Fig. 9), and to be able to relate directly the improvements obtained with the PB/Pt cathode in comparison to the single Pt cathode, the same experimental conditions used in Fig. 4 have been maintained. It was observed that the OCV increases with the HCl concentration, from 1.70 V to 1.82 V. A gradual increase of the power density curve is also observed with the HCl concentration increase. A maximum cell voltage (0.70 V) is attained at the peak power density for 1.5 M HCl and, therefore, a value of 1.5 M HCl seems the most appropriate for the oxidant composition.

It should be noted that short-circuit currents were not measured for the DBPFCs using the PB/Pt cathode. To obtain these cell polarisation curves, cell voltages have been limited to values above 0.3 V to avoid too high currents and, therefore, preventing any possible degradation of the PB coating. In fact, it was experimentally observed that after running a number of chronoamperometric measurements at higher temperatures ($T \geq 55$ °C) and at currents near the short-circuit value (i.e., at $\Delta V \approx 0$), there was a slight fading of the blue colour of the PB coating, indicating a small dissolution of the PB film at these conditions ($j > \sim 600$ mA cm^{-2}). For this reason applied cell voltages were limited to values in the range ~ 1.8 –0.3 V.

Then, the H_2O_2 concentration has been varied between 1.25 M and 6.0 M (Fig. 10). There is a gradual increase of the cell performance with the increase in the H_2O_2 concentration. The value of 5.0 M H_2O_2 has been selected as the best oxidant concentration for the operation of the laboratory DBPFC, although there is a minor improvement when using 6.0 M H_2O_2 , but with the drawback of not being so cost-effective.

3.2.2. Effect of operation temperature

The effect of the cell's operation temperature on the current density and power density curves of the $\text{NaBH}_4/\text{H}_2\text{O}_2$ laboratory cell using a PB/Pt cathode has also been analysed. The operation temperature has been varied between 25 °C and 65 °C. Again, there is an increase in the cell performance with the temperature (Fig. 11). The most notorious improvements occur when the temperature is increased from 25 °C to 35 °C, and then for temperatures higher than 45 °C.

A maximum peak power density of 206 mW cm^{-2} , at a cell voltage of 0.80 V and a current density of 257 mA cm^{-2} , was obtained at 65 °C. However, the polarisation curves at this temperature show several oscillations due to the higher instability of the fuel and oxidant solutions. This leads to hydrogen and oxygen evolution in the anodic and cathodic cell compartments, respectively. The formed gas bubbles partially cover the electrodes' surfaces, for short times, causing small difficulties in the cell current measurements

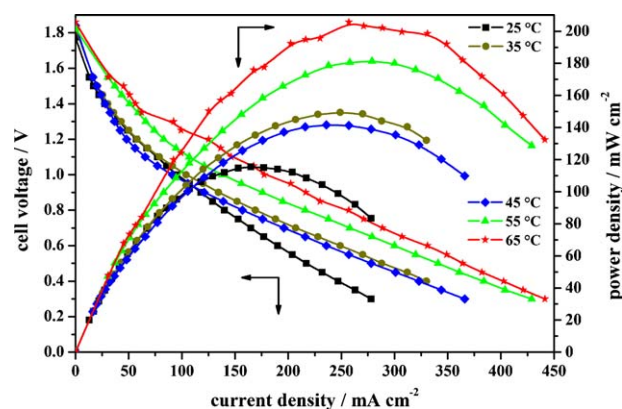


Fig. 11. Effect of the operation temperature on the current and power density of a DBPFC using a PB/Pt cathode. Fuel: 1.0M NaBH_4 + 4.0M NaOH. Oxidant: 5.0 M H_2O_2 + 1.5 M HCl.

Table 3

Effect of temperature on the Pt | NaBH_4 , NaOH || HCl, H_2O_2 | PB, Pt cell.

	Temperature (°C)				
	25	35	45	55	65
Open circuit voltage (V)	1.79	1.83	1.84	1.83	1.86
Peak power density (mW cm^{-2})	116	145	142	181	206
Cell voltage at peak power density (V)	0.70	0.70	0.60	0.65	0.80
Current density at peak power density (mA cm^{-2})	165	207	236	279	257

(Fig. 11). Therefore, for this particular DBPFC with PB/Pt cathode, it is strongly recommended to use operation temperatures not higher than 55 °C. A peak power density value of about 180 mW cm^{-2} has been obtained for the cell operating at 55 °C, which corresponds to a 53% increase as compared to the same cell using a single Pt cathode (Table 3). It is expected that further improvements in the design of this DBPFC (e.g., cell configuration, MEA preparation procedures) will lead to an additional increase in the fuel cell's power density.

4. Conclusions

A direct $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell using two Pt electrodes and a Nafion N117 membrane as the separator was assembled. The influence of different operational conditions, namely the fuel (NaBH_4 + NaOH) and oxidant (H_2O_2 + HCl) concentrations and the cell temperature, on the performance of this DBPFC, was investigated. Experimental results showed that the best compositions for the operation of our laboratory DBPFC should consist of an anolyte containing 1.0 M NaBH_4 + 4.0 M NaOH and a catholyte containing 5.0 M H_2O_2 + 1.5 M HCl.

PB had been recently reported as a mediated electron-transfer cathode catalyst in such direct $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cells and, therefore, a PB film was coated in a Pt electrode. The catalytic efficiency of this PB/Pt cathode was evaluated by making a direct comparison of the performance of DBPFCs using this electrocatalyst and using solely the single Pt cathode. From the obtained results it was clear that the PB coating promotes the H_2O_2 electroreduction, therefore improving the cell performance. A cell temperature around 55 °C is advisable for the operation of this DBPFC, with peak power densities of 180 mW cm^{-2} being attained.

Studies are in progress to determine the number of electrons effectively transferred during cell operation. Carbon-supported PB/Pt nanoparticles are being prepared to improve the activity of

the cathode electrode. New electrocatalysts are being envisaged since they are giving promising results in other DBPFCs.

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