



Sodium borohydride as an additive to enhance the performance of direct ethanol fuel cells

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ABSTRACT

The effect of adding small quantities (0.1–1 wt.%) of sodium borohydride (NaBH₄) to the anolyte solution of direct ethanol fuel cells (DEFCs) with membrane-electrode assemblies constituted by nanosized Pd/C anode, Fe–Co cathode and anion-exchange membrane (Tokuyama A006) was investigated by means of various techniques. These include cyclic voltammetry, *in situ* FTIR spectroelectrochemistry, a study of the performance of monoplanar fuel cells and an analysis of the ethanol oxidation products. A comparison with fuel cells fed with aqueous solutions of ethanol proved unambiguously the existence of a promoting effect of NaBH₄ on the ethanol oxidation. Indeed, the potentiodynamic curves of the ethanol–NaBH₄ mixtures showed higher power and current densities, accompanied by a remarkable increase in the fuel consumption at comparable working time of the cell. A ¹³C and ¹¹B {¹H}NMR analysis of the cell exhausts and an *in situ* FTIR spectroelectrochemical study showed that ethanol is converted selectively to acetate while the oxidation product of NaBH₄ is sodium metaborate (NaBO₂). The enhancement of the overall cell performance has been explained in terms of the ability of NaBH₄ to reduce the PdO layer on the catalyst surface.

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1. Introduction

Much attention has been recently devoted to the design and development of efficient direct ethanol fuel cells (DEFCs), largely due to the renewable nature of ethanol, its well-established distribution infrastructure and much lower toxicity as compared to methanol or ethylene glycol [1]. The large majority of electrocatalysts at both anodes and cathodes of DEFCs running with cation-exchange membranes, hence in acidic media, contain platinum-based materials [2–4]. Besides the cost of these materials, the diffusion of the current DEFC technology is hampered by the inability of platinum and its alloys to bring about efficiently and selectively the oxidation of ethanol in either complete or selective way as well as its propensity to be poisoned by CO [2,4]. Nanostructured palladium is emerging as an alternative to platinum for manufacturing anodes for DEFCs operating in alkaline media where the utilization of non-noble metal electrocatalysts at the cathode is a well-established achievement [5–7]. Unlike platinum, palladium promotes the selective oxidation of ethanol to acetate, provided the

pH of the anolyte is kept higher than 13 [1,8,9]. This selectivity is a positive characteristic in the perspective of using direct alcohol fuel cells (DAFCs) as reactors for the simultaneous production of energy and chemicals [1,10,11], but it is drawback in terms of exploitation of the specific energy of the fuel. Other drawbacks of the current Pd-based technology are provided by the price of palladium, which is not remarkably lower than that of platinum, and by the fact that all known catalysts show a significant decay in the power output approximately when a 50% conversion of ethanol into acetate is achieved [10,11]. Such polarization losses do not originate from an irreversible catalyst poisoning, yet their true origin is still uncertain. Several hypotheses have been forwarded: these include the difficult desorption of the acetate group from the catalyst surface, a competitive adsorption of ethanol, acetate and hydroxyl ions on the catalytically active sites [1,10,11] as well as catalyst passivation due to the formation of a palladium oxide layer as the ethanol oxidation in alkaline media occurs in a range of potentials where PdO is formed [12,13]. The last hypothesis has been recently substantiated by a CV study of ethanol oxidation on a Pd disk electrode [12]. In the same paper, it was reported that the dissociative adsorption/dehydrogenation of ethanol on Pd to give Pd–(COCH₃)_{ads} is a fast process, while the rate-determining step is the coupling of the adsorbed acyl with the adsorbed hydroxyl, Pd–OH_{ads} (Eq. (1)). Accordingly, the formation of Pd–OH_{ads} at low potential is crucial

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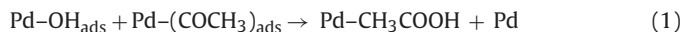
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Table 1

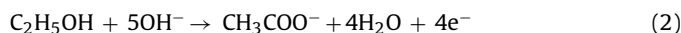
The analytes studies in this work. In all cases was employed a 2 M KOH solution.

Analyte	NaBH ₄ (wt.%)	EtOH (wt.%)
1	–	–
2	–	10
3	0.1	–
4	0.2	–
5	0.5	–
6	1.0	–
8	0.1	10
9	0.2	10
10	0.5	10
11	1.0	10

for an effective ethanol electrooxidation in alkaline media.



In an attempt of gaining insight into the mechanism through which Pd-based electrocatalysts lose activity with time during the selective conversion of ethanol into acetate (Eq. (2)), we decided to explore the use of additives that might interact with the catalyst surface so as to reduce/inhibit the formation of an extensive PdO coverage. Our first choice was sodium borohydride (NaBH₄) as it is a relatively cheap and nontoxic reducing agent that can be indefinitely stored in the solid state and for months in alkaline water solutions. It is also a well known fuel for direct fuel cells [14]. Our strategy was to add different amounts of NaBH₄ to aqueous ethanol solutions either in half cells or in the anode compartment of passive DEFCs and look at eventual variations of the electrochemical performance, fuel consumption and oxidation selectivity. The data obtained have been compared to those available in the literature for half cells and DEFCs operating in alkaline media with Pd-based anode electrocatalysts [1,10,11]. In addition to this study, the effect of NaBH₄ addition on ethanol oxidation has been investigated by *in situ* FTIR spectroelectrochemistry using a polycrystalline Pd electrode. The beneficial effect of adding NaBH₄, even in amounts as low as 0.1 wt.%, has been unequivocally demonstrated in terms of both ethanol conversion, almost doubled, catalyst durability and power output.



2. Experimental

2.1. Fuel cell testing

Ten different analytes were prepared, all of them containing a 2 M KOH concentration, yet with different amounts of NaBH₄, ranging from 0.1 to 1 wt.% (Table 1). The ethanol concentration was fixed at 10 wt.% in order to compare the results obtained with those previously reported for analogous DEFCs [1,10,11,13].

The Pd/C electrocatalyst was prepared by a previously reported electroless procedure [13]. The sample used in this work contains 5 wt.% Pd (ICP-OES analysis). Vulcan XC-72 (C) was purchased from Cabot. The membrane-electrode assembly (MEA) and the passive cell hardware used in this work have been described in detail elsewhere [1,11]. The anion-exchange membrane (A006) was provided by Tokuyama Soda, while the Fe-Co/C cathode electrocatalysts (1.13 wt.% Fe and 1.71 wt.% Co) were synthesized in our laboratory (C = Ketjen Black).

The anode was realized depositing the appropriate amount of the catalytic ink onto a 5.13 cm² nickel foam plate. The catalytic ink was prepared introducing the catalyst (100 mg) into a high-density polyethylene container with 100 mg of deionized water and 100 mg of 5 wt.% PTFE (60 wt.% dispersion in water by Sigma-Aldrich). The Pd loading was determined weighting the deposited ink. The membrane was conditioned in a saturated KOH solution for 1 min under

nitrogen and dried before assembling the MEA. The volume of the anode compartment was 25 mL and the actual fuel solution was 10 mL. The fuel solutions were prepared as follows: NaBH₄ (98.5% Aldrich) 0.1, 0.2, 0.5 and 1 wt.%, respectively, in 2 M KOH and 10 wt.% EtOH.

The polarization and power density curves were recorded with an ARBIN BT-20005A-4 channels instrument. The polarization curves (5 mV s⁻¹) were obtained after conditioning the cells for 1 h at the OCV. In order to avoid any contamination by atmospheric CO₂, the potentiostatic experiments were conducted inside a dry-box keeping where the anode compartment was kept under a nitrogen stream, while the cathode was exposed to an oxygen flow. The curves were recorded at 0.2 V for 17 h, after 1 h conditioning.

2.2. Quantitative and qualitative analysis of the cell exhausts

The anode exhausts were analyzed by ¹³C{¹H} and ¹¹B{¹H} NMR spectroscopy using a Bruker Avance DRX-400 instrument. The calibration curves for the quantitative analysis were obtained using pure samples of ethanol and potassium acetate in the appropriate range of concentrations, using 1,4-dioxane as internal reference. Ionic chromatography (IC) was also used to identify the oxidation products (Metrohm 761 Compact instrument equipped with a Metrosep Organic Acids column).

2.3. Half cell testing

A portion of Pd/C (about 45 mg) was introduced into a 5 mL high-density polyethylene container together with water (1.01 g), KOH (99.99%, 65 mg, Sigma-Aldrich), absolute ethanol (99.8%, 0.50 g, Fluka), and 5 wt.% Nafion ion-exchange resin (0.37 g, Sigma-Aldrich) in alcohols and water solution. The resulting suspension was sonicated for 90 min using a FALC bath. Each suspension was freshly prepared just before carrying out the experiment scheduled. The metal loading on each electrode was determined by weighting the amount of the deposited ink onto the glassy carbon electrode. Cyclic voltammetry (CV) experiments were conducted on a Princeton 2273A potentiostat/galvanostat, using a three-electrode arrangement with a saturated Ag/AgCl reference electrode and a platinum wire as counter electrode. The potential scale of the CV curves was expressed according to the RHE.

2.4. Electrochemical and spectroelectrochemical studies using a polycrystalline palladium foil

All 2 M KOH solutions were prepared using deionized water (18.3 MΩ cm⁻¹). To these solutions were added different amounts of NaBH₄ (0.01–0.1 wt.%) with or without ethanol (10 wt.%). The electrochemical activity of the Pd electrode was studied by CV in a three-electrode cell. The working electrode was a palladium disk 6 mm in diameter. A platinum foil and an Hg/HgO electrode were used as the counter and reference electrode, respectively. High-purity nitrogen was used to remove oxygen from all solutions. Before each experiment, the palladium electrode was polished with alumina powder, followed by an ultrasonic rinsing in acetone, ethanol and deionized water orderly. The potential was varied between –1.0 and 0.6 V vs. the Hg/HgO electrode at a scan rate of 50 mV s⁻¹. All the experiments were performed at a temperature of 25 ± 2 °C.

The FTIR spectroelectrochemical measurements were performed on a 263A potentiostat/galvanostat (EG&G-PARC, USA), connected to a FTIR spectrometer (Nicolet 5700 with DTGS detector, Thermo Electron Corporation, USA). Details of the *in situ* FTIR experiments have been provided elsewhere [9,15,16]. The wave numbers were varied between 4000 and 1000 cm⁻¹ with a resolution of 4 cm⁻¹. Every infrared spectrum recorded was based on 128

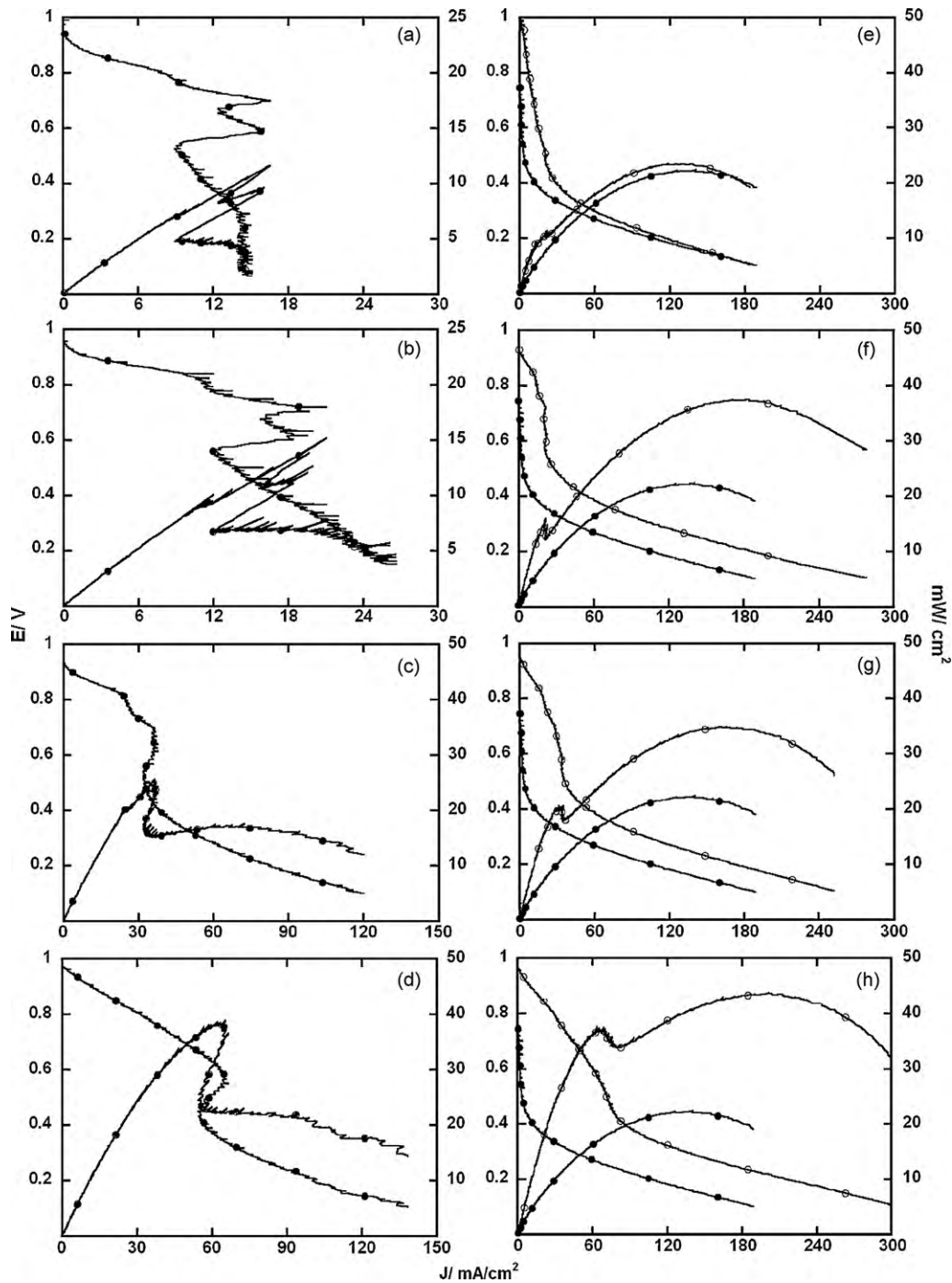


Fig. 1. Polarization and power density curves provided by the direct fuel cells fuelled with the following analytes: (●) NaBH₄ (0.1 wt.%) (a); (●) NaBH₄ (0.2 wt.%) (b); (●) NaBH₄ (0.5 wt.%) (c); (●) NaBH₄ (1 wt.%) (d); (○) ethanol (10 wt.%) + NaBH₄ (0.1 wt.%) and (●) ethanol (10 wt.%) (e); (○) ethanol (10 wt.%) + NaBH₄ (0.2 wt.%) and (●) ethanol (10 wt.%) (f); (○) ethanol (10 wt.%) + NaBH₄ (0.5 wt.%) and (●) ethanol (10 wt.%) (g); (○) ethanol (10 wt.%) + NaBH₄ (1 wt.%) and (●) ethanol (10 wt.%) (h).

individual scans. The equilibrium at each potential was achieved in 5 s before the collection of the sample spectra (R_s). Each final spectrum was reported using Eq. (3). Accordingly, the negative bands represent the species produced and the positive bands the species consumed.

$$\frac{\Delta R}{R} = \frac{R_s - R_{ref}}{R_{ref}} \quad (3)$$

All the potentials in the figures were quoted with respect to the reversible hydrogen electrode (RHE).

3. Results and discussion

3.1. Performance of direct borohydride (DBFC) and ethanol (DAFC) fuel cells

Fig. 1 shows the potentiodynamic and power density curves recorded on passive monoplanar direct fuel cells [11]. The potentiodynamic curves on either NaBH₄ or 2 M KOH solutions with no added ethanol were performed as a blank. The results obtained show that (i) the power density of the direct borohydride fuel cell (DBFC) increases by increasing the NaBH₄ concentration (Fig. 1a and d); (ii) at the low NaBH₄ concentrations investigated, both the

potentiodynamic and power density curves of the DBFCs exhibit irregular features.

Depending on the anolyte, one (Fig. 1c and d) or two (Fig. 1a and b) peaks appear in the high potential region. We attribute these peaks to the oxidation of the absorbed and adsorbed hydrogen [17,18], which forms on the nanostructured palladium surface upon interaction with the NaBH_4 solution (*vide infra*). For the anolytes with 0.1 and 0.2 wt.% NaBH_4 (Fig. 1a and b), the current densities at 0.2 V were 14 and 24 mA cm^{-2} , respectively, while at the same potential the anolyte containing only 10 wt.% ethanol gave 107 mA cm^{-2} (Fig. 1e). The addition of NaBH_4 to the 10 wt.% EtOH/2 M KOH makes the Pd/C electrode more efficient for the oxidation of ethanol: indeed, just by adding 0.1 wt.% NaBH_4 (Fig. 1e), the current density increased to 124 mA cm^{-2} , which is slightly higher than the sum of the current densities recorded for the single anolytes (121 mA cm^{-2}). A more remarkable effect was obtained by adding 0.2 wt.% NaBH_4 (Fig. 1f). In this case, in fact, the current density at 0.2 V was 188 mA cm^{-2} , a value much higher than the sum of the current densities provided by the solutions of the single fuels (131 mA cm^{-2}).

From a perusal of the curves shown in Fig. 1e–g, one may readily realize that NaBH_4 , in concentrations lower than 0.5 wt.%, promotes the oxidation of ethanol on the palladium electrocatalyst. At concentrations higher than 0.5 wt.%, the oxidation of NaBH_4 prevails over that of ethanol so that NaBH_4 behaves as a fuel rather than an additive. Indeed, in this case the current density at 0.2 V was 170 mA cm^{-2} (Fig. 1g), while the sum of the contributions of ethanol and NaBH_4 alone is 190 mA cm^{-2} . The observed decrease in power output suggests that the sluggish ethanol oxidation subtracts active

Table 2

EtOH to AcO^- conversions for 17 h at 0.2 V potentiostatic experiments.

NaBH_4 (wt.%)	Conversion ratio AcO^-/EtOH
0	1:1
0.1	1.7:1
0.2	3.5:1
0.5	3.6:1
1	3.6:1

sites to NaBH_4 oxidation, which is also confirmed by other experiments (*vide infra*).

The enhanced ability of Pd/C to oxidize ethanol in the presence of tiny amounts of NaBH_4 added to the anolyte, has been unequivocally proved by the quantitative analysis of the cell exhausts obtained by potentiostatic experiments at 0.2 V for 17 h. A $^{13}\text{C}\{^1\text{H}\}$ NMR analysis of the fuel exhausts of a DEFC with no NaBH_4 showed the selective 50% conversion of ethanol into of acetate (Table 2), while the conversion efficiency increased to 80% upon addition of 0.2 wt.% NaBH_4 . An $^{11}\text{B}\{^1\text{H}\}$ NMR analysis of the same cell exhausts showed the selective oxidation of BH_4^- to metaborate (BO_2^-). For further additions of NaBH_4 , neither the ethanol conversion nor the selectivity showed substantial changes (Table 2).

3.2. Cyclic voltammetry studies on the nanostructured electrocatalyst Pd/C of 2 M KOH solutions containing ethanol, NaBH_4 or ethanol– NaBH_4

In an attempt of rationalizing the results of the mixed EtOH– NaBH_4 cells, CV experiments were performed on solu-

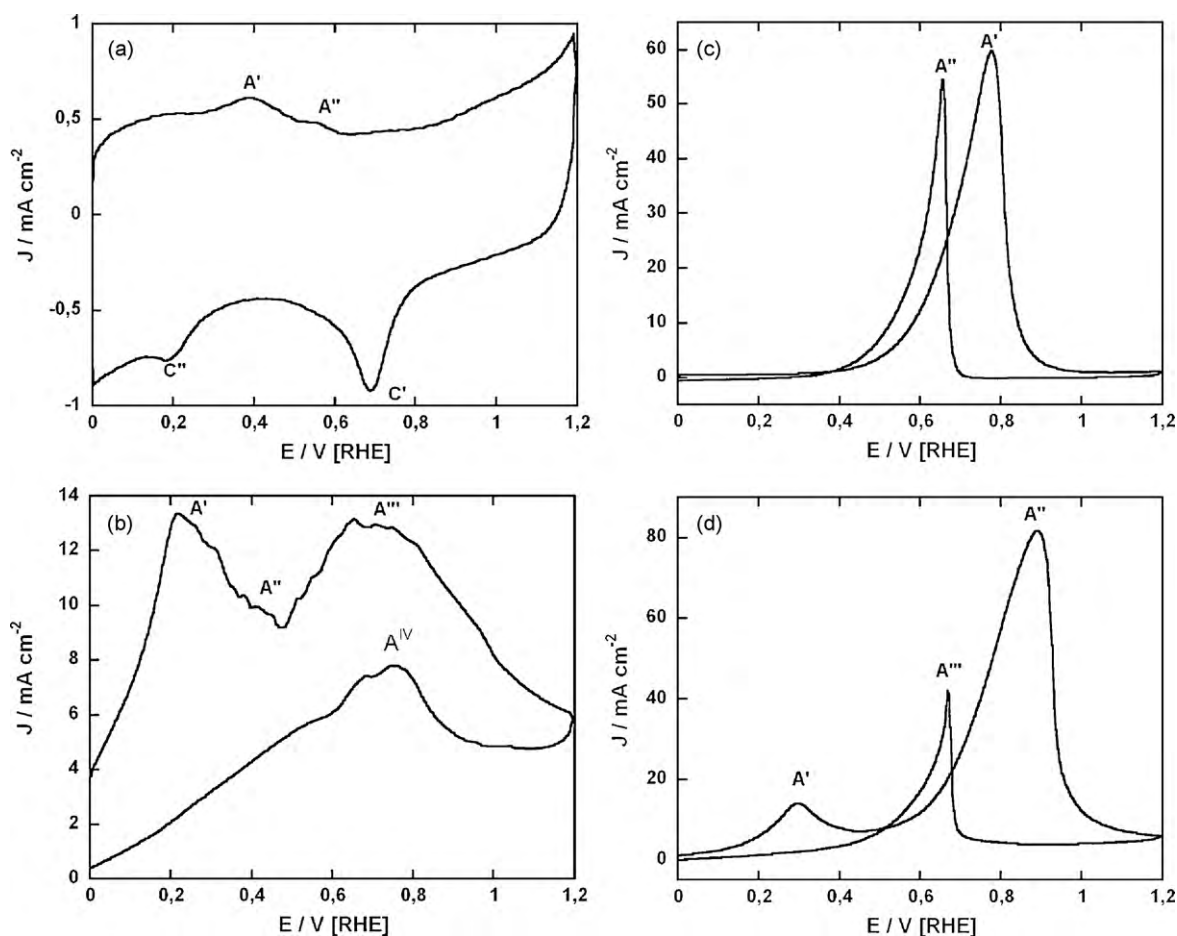


Fig. 2. Cyclic voltammograms of Pd/C in the presence of: (a) 2 M KOH, (b) 2 M KOH + NaBH_4 (0.1 wt.%), (c) 2 M KOH + EtOH (10 wt.%) and (d) 2 M KOH + NaBH_4 (0.1 wt.%) + EtOH (10 wt.%).

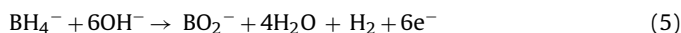
tions containing (a) 2 M KOH, (b) 2 M KOH + 0.1 wt.% NaBH₄, (c) 2 M KOH + 10 wt.% EtOH and (d) 2 M KOH + 0.1 wt.% NaBH₄ + 10 wt.% EtOH. A brief description of each experiment is given below.

Experiment (a) 2 M KOH (Fig. 2a): The CV interpretation of this experiment is straightforward as this system has been widely investigated in the past [17,18]. Starting from the negative potential side, one may notice the appearance of a very broad anodic region, due to the oxidation of the adsorbed and absorbed hydrogen, the current density of which is apparently limited by the amount of hydrogen dissolved into palladium. The peak A'' (0.53 V), assigned to the formation of palladium (I) hydroxide species (PdOH), partially overlaps with the hydrogen oxidation peak (A' 0.39 V) [12], while the formation of PdO starts at potential values higher than 0.6 V. The formation of an oxide coverage on the catalyst surface is accompanied by a gentle increase of the current. The well defined cathodic peak C' at 0.69 V in the reverse scan can be straightforwardly assigned to the reduction of PdO [13,17], while the cathodic peak C'' at 0.18 V is attributed to the hydrogen uptake [19].

Experiment (b) 2 M KOH + 0.1 wt.% NaBH₄ (Fig. 2b): A very intense peak A' at 0.22 V, followed by a shoulder A'' at 0.41 V, features this system. According to the literature [18], peak A' can be attributed to the oxidation of the adsorbed hydrogen, while peak A'' is consistent with the oxidation of adsorbed hydrogen. The hydrogen source is NaBH₄ as it can be hydrolyzed by Pd (Eq. (4)) [20].



Increasing the potential to 0.69 V results in the appearance of peak A''', which can be safely assigned to the direct oxidation of the BH₄⁻ anion (Eq. (5)) [20–22]. A mix of palladium oxidation and mass transport most likely controls the current density. At the end of the direct scan (1.2 V) the current is still anodic, indicating that the oxidation of NaBH₄ continues also when the Pd surface is largely covered by PdO.



Experiment (c) 2 M KOH + 10 wt.% EtOH (Fig. 2c): This system is dominated by ethanol oxidation that culminates with peak A' at 0.78 V whose magnitude is controlled by the progressive coverage of the electrode surface with PdO [12,13]. In fact, at potentials higher than 1 V, the anodic current is comparable to that observed

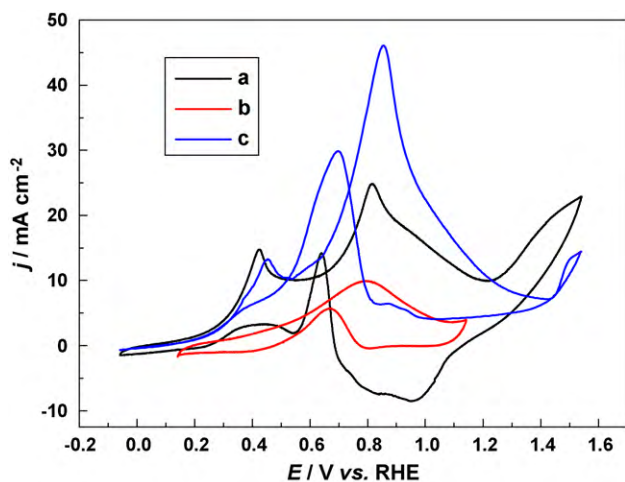


Fig. 3. Cyclic voltammograms at a scan rate of 50 mV s⁻¹ over a Pd electrode. (a) 0.1 wt.% NaBH₄ + 2 M KOH; (b) 10 wt.% ethanol + 2 M KOH and (c) 0.1 wt.% NaBH₄ + 10 wt.% ethanol + 2 M KOH.

for the 2 M KOH solution alone (Fig. 2a), indicating that only a negligible fraction of the catalyst sites remains active for ethanol oxidation. The reverse scan shows a further anodic peak A'' occurring at 0.65 V due to the oxidation of fresh ethanol on the catalyst surface freed from palladium oxide [12,13].

Experiment (d) 2 M KOH + 0.1 wt.% NaBH₄ + 10 wt.% EtOH (Fig. 2d): The peak due to hydrogen oxidation (A') is observed at 0.30 V, while the onset of a broad and intense peak (A''), resulting from the convolution of the voltammetric waves due to the oxidation of both NaBH₄ and ethanol, occurs at 0.4 V. A maximum intensity peak is observed at 0.89 V and, as previously noticed (Fig. 2c), the current density is controlled by the Pd oxidation to PdO. It worth mentioning that the ethanol oxidation peak, with no added NaBH₄, exhibits its highest current density at 0.78 V (Fig. 2c). Accordingly, one may conclude that the addition of NaBH₄, even at concentrations as low as 0.1 wt.%, allows for an efficient oxidation of ethanol at more positive potentials (Fig. 2d) than those observed when no NaBH₄ is present in the anolyte. It is also worth noticing that the peak current density is higher (82 mA cm⁻²) than the sum of the peak current densities (72 mA cm⁻²) supplied by the cells containing the anolytes 2 M KOH + 0.1 wt.% NaBH₄ and 2 M KOH + 0.1 wt.% NaBH₄ + 10 wt.% EtOH. These results are in agreement with the potentiodynamic curves. Notably, the current density continues to be anodic even at the end of the forward scan at 1.2 V, which suggests that the surface is still catalytically active for the oxidation of the ethanol–NaBH₄ mixture.

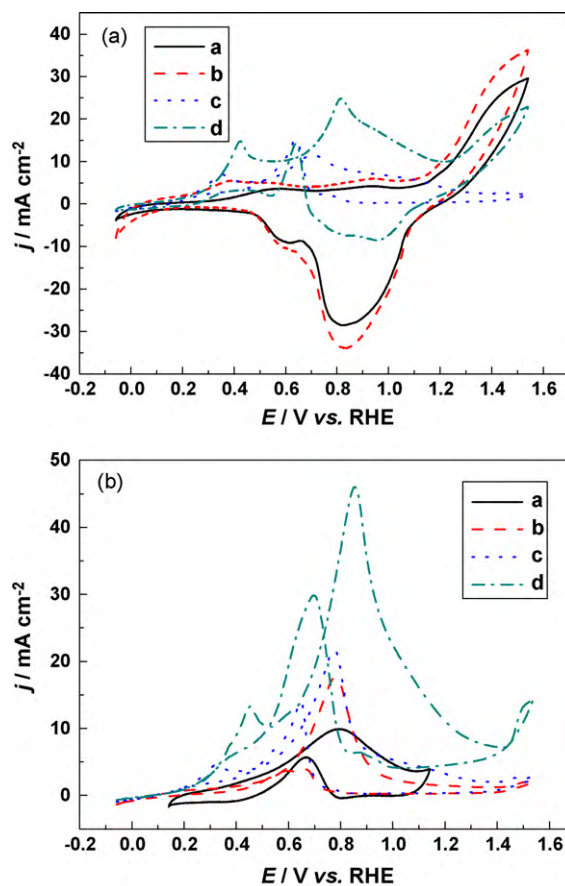


Fig. 4. (a) Cyclic voltammograms recorded on a plain Pd electrode at a scan rate of 50 mV s⁻¹ for 2 M KOH solutions with different NaBH₄ concentrations (wt.%): (a) 0; (b) 0.01 (c) 0.05 and (d) 0.1. (b) Cyclic voltammograms at a scan rate of 50 mV s⁻¹ recorded on a plain Pd electrode for 2 M KOH solutions containing 10 wt.% ethanol and NaBH₄ in different weight ratios: (a) 0; (b) 0.01; (c) 0.05 and (d) 0.1.

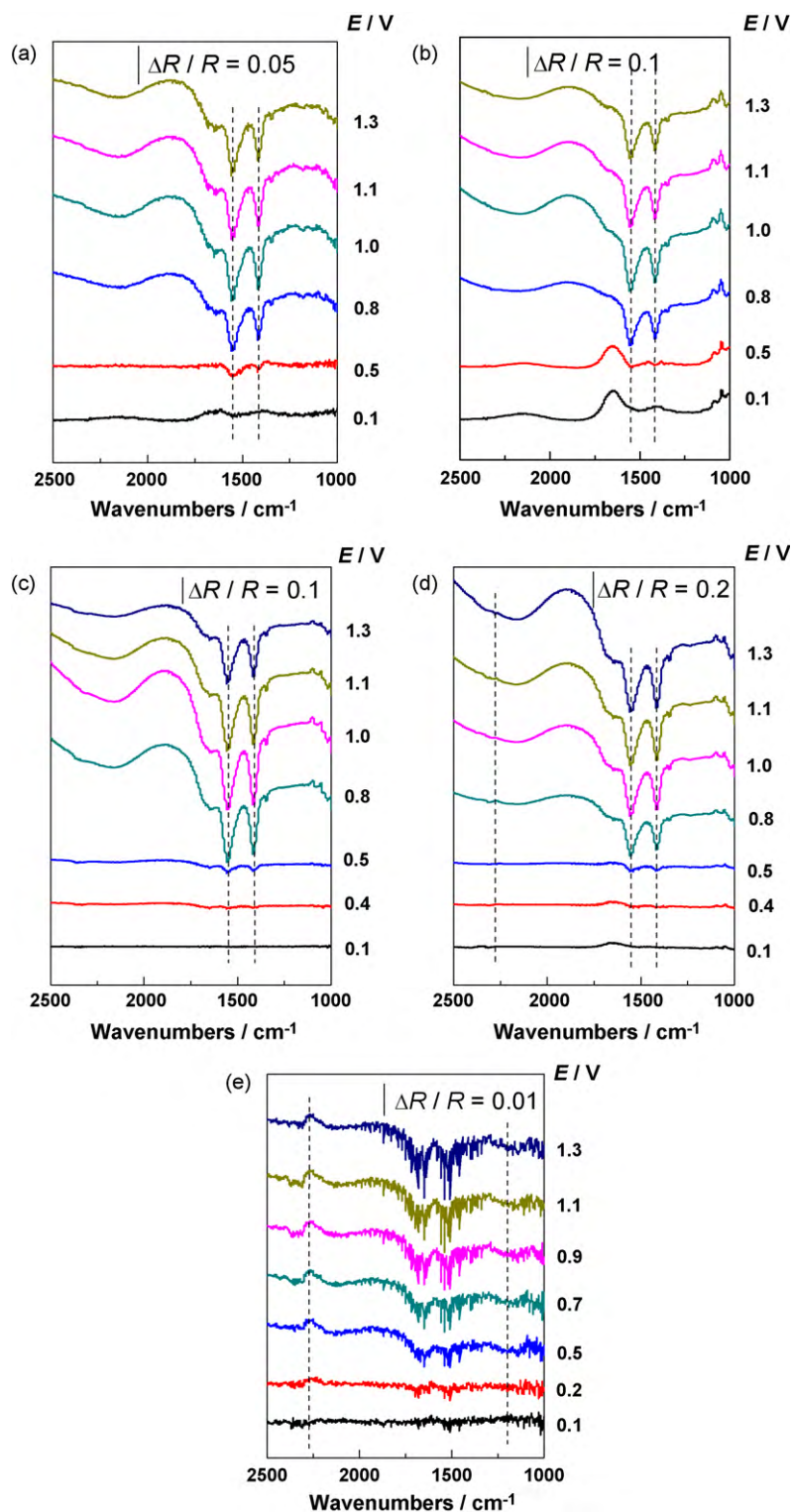


Fig. 5. *In situ* FTIR spectra obtained under potential step polarization in (a) 10 wt.% ethanol + 2 M KOH; (b) 0.01 wt.% NaBH₄ + 10 wt.% ethanol + 2 M KOH; (c) 0.05 wt.% NaBH₄ + 10 wt.% ethanol + 2 M KOH; (d) 0.1 wt.% NaBH₄ + 10 wt.% ethanol + 2 M KOH; (e) 0.1 wt.% NaBH₄ + 2 M KOH. $E_r = 0$ V, scan numbers: 128.

3.3. Electrochemical and spectroelectrochemical studies on a polycrystalline palladium disk electrode

3.3.1. Cyclic voltammetry studies of 2 M KOH solutions containing ethanol, NaBH₄ or ethanol–NaBH₄ mixtures

The CV curves recorded on a plain Pd electrode for 2 M KOH solutions containing 0.1 wt% NaBH₄, 10 wt.% ethanol and 0.1 wt% NaBH₄ + 10 wt.% ethanol are shown in Fig. 3, while Fig. 4 illustrates

the curves of 2 M KOH solutions containing NaBH₄ concentrations spanning from 0.01 to 0.1 wt%.

As one may readily realize from a perusal of Fig. 3a, NaBH₄ is irreversibly oxidized at 0.42, 0.81 and 0.64 V on the Pd electrode, while the oxidation of ethanol exhibits a peak at 0.79 V in the positive scan and at 0.67 V in the reverse scan (Fig. 3b), which is a typical feature of ethanol electrooxidation on Pd in alkaline media [10]. The concomitant presence of NaBH₄ and ethanol as in the solution leading

to the CV shown in Fig. 3c causes a positive shift of the three peaks of NaBH_4 electrooxidation due to the influence of ethanol. Actually, the peak of ethanol electrooxidation is not clearly visible due to overlapping with the NaBH_4 peaks, yet its presence is inferred from the extensive broadening of the peak at 0.70 V as well as the current intensity enhancement as compared to the curve shown in Fig. 1a. A comparison of the two peaks around 0.43 V, due to NaBH_4 oxidation, shows that the addition of ethanol solution decreases the extent of NaBH_4 oxidation, likely due to competitive adsorption of the two substrates on the catalytically active sites.

In the potential range from -0.06 to 1.54 V, shown in detail in Fig. 4, one may observe that the highest current density values for NaBH_4 oxidation are obtained for a concentration of 0.1 wt.%. The effect of adding ethanol (10 wt.%) to the different NaBH_4 solutions is illustrated in Fig. 5. From a comparison of the curves reported in Figs. 4 and 5, one may also realize that the CV profile of the NaBH_4 oxidation changes upon addition of ethanol. In particular, the intensity of the peaks around 0.43 V decreases for the three electrolyte solutions upon addition of ethanol. As shown in Fig. 5b, only two peaks, at 0.78 and 0.67 V, are present, which indicates that NaBH_4 is not electrooxidized in these conditions. Furthermore, the two peak values are significantly higher than the corresponding peaks in Fig. 3a, i.e. with no NaBH_4 in solution. It is also worth noticing that all the peaks in Fig. 4a are positively shifted as the NaBH_4 concentration increases, while the reverse occurs for the peaks reported in Fig. 4b.

3.3.2. In situ FTIR spectroscopy studies

Selected *in situ* FTIR spectra for the adsorption and oxidation of ethanol and NaBH_4 over Pd, in the region between 1000 and 2500 cm^{-1} , are shown in Fig. 5. In accord with previous studies in 2 M KOH solutions, only the characteristic bands of the acetate ion (1558 and 1415 cm^{-1}) were observed. Indeed, the oxidation of ethanol on Pd electrodes in alkaline media gives acetate as the largely major product when the OH^- concentration is higher than 0.5 M [9]. Notably, the intensity of the acetate band increases by increasing the weight ratio of NaBH_4 to ethanol (Fig. 6a–d), which again confirms that NaBH_4 promotes the electrooxidation of ethanol. The band at 2270 cm^{-1} due to the B–H bond stretch (its positive direction indicates a consumption of NaBH_4) was exclusively observed in the experiment with the highest NaBH_4 concentration (0.1 wt.%, Fig. 5d). No trace of CO is observed, either free or Pd-bonded, which is a typical feature of ethanol oxidation on Pd-based electrocatalysts in alkaline media by virtue of its high chemoselectivity [1,9].

The FTIR spectra recorded for a 0.1 wt.% NaBH_4 solution in 2 M KOH are shown in Fig. 5e. Irrespective of the applied potential, all spectra share two bands: the first, around 2270 cm^{-1} is assigned to the B–H stretch, the second, around 1200 cm^{-1} , might result from the combination of two B–O deformation modes, of the metaborate anion [23] (see above the ^{11}B NMR analysis of the cell exhausts). From a comparison of Fig. 5d and e, one may readily realize that (i) the intensity of the band at 2270 cm^{-1} is higher in the former figure than in the latter and (ii) the band at 1200 cm^{-1} is present only in Fig. 5e. This evidence confirms that ethanol inhibits the electrooxidation of NaBH_4 , likely due to competitive adsorption at the catalytically active sites. Once more, this result is in nice accord with the CV studies on either nanostructured or plain Pd electrodes.

Fig. 6 reports the plots of the IR intensity of selected acetate and BH_4^- bands vs. the applied potential, respectively. In particular, Fig. 6a shows the potential dependence of the integrated intensity of the 1550 cm^{-1} band of the acetate ion in the thin layer when different amounts of NaBH_4 are added to a 10 wt.% ethanol solution in 2 M KOH. Data obtained for a 10 wt.% ethanol solution in 2 M KOH are also reported. One may notice that the onset of acetate formation shifts to negative potential values by increasing the con-

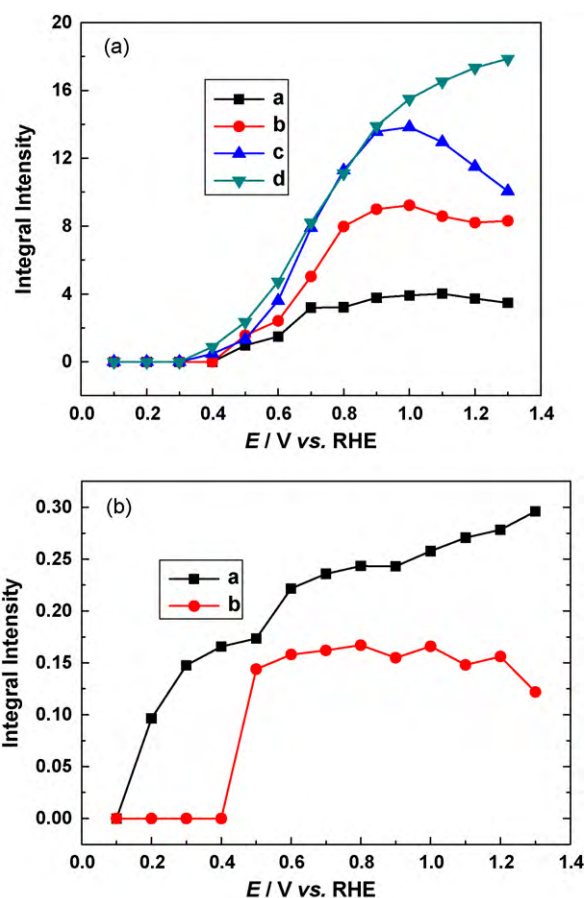


Fig. 6. (a) Plot of the IR intensities of the acetate band at 1550 cm^{-1} as a function of the polarization potential. (a) 10 wt.% ethanol + 2 M KOH; (b) 0.01 wt.% NaBH_4 + 10 wt.% ethanol + 2 M KOH; (c) 0.05 wt.% NaBH_4 + 10 wt.% ethanol + 2 M KOH; (d) 0.1 wt.% NaBH_4 + 10 wt.% ethanol + 2 M KOH. (b) Plot of the IR intensity of the NaBH_4 band at 2270 cm^{-1} as a function of the polarization potential. (a) 0.1 wt.% NaBH_4 + 2 M KOH and (b) 0.1 wt.% NaBH_4 + 10 wt.% ethanol + 2 M KOH.

centration of NaBH_4 (0.5 V in Fig. 6a (traces a and b) and 0.4 V in Fig. 6a (traces c and d)). At the same time, the intensity of the acetate band increases significantly with the NaBH_4 concentration. Moreover, the acetate band intensity increases gradually moving from 0.4 V to about 0.9 V, while it decreases steadily in the potential range between 0.9 and 1.3 V (Fig. 6a (traces a and c)). Fig. 6a(d) shows that appreciable formation of acetate commences at 0.4 V and its concentration in the thin layer increases up to 1.3 V.

A plot of the IR intensity of the NaBH_4 band at 2270 cm^{-1} as a function of the polarization potential is shown in Fig. 6b for 2 M KOH analytes containing 0.1 wt.% NaBH_4 with or without 10 wt.% ethanol. As already shown in Fig. 5, the B–H stretching band, due to the consumed NaBH_4 , becomes visible at potential values > 0.2 V for the analyte comprising 0.1 wt.% NaBH_4 in 2 M KOH, while it appears at ca. 0.5 V for the analyte comprising 0.1 wt.% NaBH_4 and 10 wt.% ethanol in 2 M KOH. The integrated intensities of the B–H band increases steadily with the polarization potential in the absence of ethanol (Fig. 6b(a)), while they do not appreciably vary between 0.5 and 1.3 V with ethanol (Fig. 6b(b)). It is also apparent that that all the B–H band intensities of Fig. 6b(a) are higher than those in Fig. 6b(b).

4. Conclusions

In this paper we have investigated the effect of adding small amounts of NaBH_4 into the anode compartment of DEFCs equipped

with a nanostructured Pd/C anode electrocatalyst and fuelled with 10 wt.% ethanol in 2 M KOH. We have found that the addition of 0.2 wt.% NaBH₄ gives a current density of 180 mA cm⁻² at 0.2 V. Such a value is much higher than the sum of the current densities (117 mA cm⁻²) supplied by similar DEFCs fuelled with 0.2 wt.% NaBH₄ + 2 M KOH and with 10 wt.% ethanol + 2 M KOH. On the basis of this finding, it is apparent that NaBH₄ promotes the ethanol oxidation on palladium-based electrocatalysts. Unequivocal evidence supporting the ability of NaBH₄ to favor the oxidation of ethanol on Pd has been provided by the amount of ethanol converted into acetate: in the absence of NaBH₄, the acetate to ethanol conversion (17 h at 0.2 V) is 50% in fact, while it increases up to 80% just by adding 0.2 wt.% NaBH₄.

Consistent with the DEFCs performance, CV studies with similar Pd/C electrodes have shown that the potential of the current intensity peak due to the concomitant oxidation of ethanol and NaBH₄ (Fig. 2d, 0.92 V) is higher than that of the anolyte comprising only ethanol (Fig. 2c, 0.83 V). Moreover, the current density remains anodic even at the end of the forward scan at (1.2 V), which proves that the surface is still catalytically active for both ethanol and NaBH₄ oxidation. Such a result can be accounted for by admitting that NaBH₄ increases the number of catalytically active Pd sites by reducing PdO to Pd.

The ethanol and NaBH₄ oxidation in 2 M KOH solution was also investigated on a polycrystalline Pd disk electrode by CV and *in situ* FTIR spectroelectrochemistry. CV showed that the oxidation peaks shift positively by increasing the NaBH₄ concentration, whereas the peaks shift negatively by adding ethanol. Both CV and *in situ* FTIR spectroelectrochemistry suggest that ethanol compete with NaBH₄ for adsorption on the catalytically active Pd sites. In actuality, ethanol seems to prevail for adsorption so as to disfavor the electrooxidation of NaBH₄ at the low concentrations investigated.

Incorporation of all the results reported in the present study leads us to conclude that the addition of tiny amounts of NaBH₄ (0.1–0.2 wt.%) in the anode compartment of DEFCs with Pd-based anodes enhances both the power densities and the cell lifetime. Besides, the ethanol conversion to acetate is almost doubled, thus

boosting the interest in DAFCs as reactors for the simultaneous conversion of renewable alcohols into energy and chemicals [1,10,11,24,25]. To this purpose, the effect of adding NaBH₄ to the solutions of other alcohols such as glycerol and ethylene glycol in DAFCs is presently investigated in our laboratory.

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