



## Electrocatalytic performance of Pt–Dy alloys for direct borohydride fuel cells



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### H I G H L I G H T S

- Effect of temperature and concentration on  $\text{BH}_4^-$  oxidation at prepared Pt–Dy alloys.
- Pt–Dy alloy with lower Pt content shows higher activity for  $\text{BH}_4^-$  oxidation.
- Pt–Dy alloys show higher Coulombic efficiency than Pt at higher temperatures.
- Lab fuel cell with Pt–Dy anode reaches higher power density than one with Pt anode.

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### A B S T R A C T

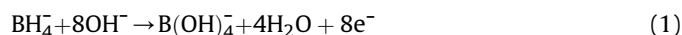
The electrochemical oxidation of sodium borohydride ( $\text{NaBH}_4$ ) is systematically studied on platinum–dysprosium (Pt–Dy) alloys in alkaline media with respect to application in direct borohydride fuel cells (DBFCs). Using several different techniques, namely cyclic voltammetry, chronoamperometry and chronopotentiometry, reaction parameters are evaluated for  $\text{NaBH}_4$  electrooxidation in 2 M NaOH supporting electrolyte. The values obtained for the number of electrons exchanged are comparable for the two alloys and close to 2.5. Dependence of Pt–Dy alloys activity for  $\text{NaBH}_4$  oxidation on the electrolyte composition and temperature is also investigated. Test fuel cell is assembled using Pt–Dy alloy as anode, reaching peak power density of  $298 \text{ mW cm}^{-2}$  at current density of  $595 \text{ mA cm}^{-2}$  and cell potential of 0.5 V at 25 °C. Pt–Dy alloys exhibit comparable behavior with pure Pt electrode at room temperature, while at higher temperature they exhibit improved Coulombic efficiency, with the advantage of significantly lower price.

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## 1. Introduction

Sodium borohydride ( $\text{NaBH}_4$ ) was first synthesized at Chicago University during the 1940s' search for volatile compounds to be used for military purposes [1–3]. Today it is widely employed as a reducing agent in numerous organic and inorganic reactions [4,5]. Its potential application as hydrogen ( $\text{H}_2$ )/energy carrier for energy systems, namely for  $\text{H}_2$  production and storage or for fuel cells (FCs), was also early recognized, although further research in this area started only with the energy crisis emerging in the 1990s [6].  $\text{NaBH}_4$  is characterized by high theoretical hydrogen density (10.8 wt.%) with ease of  $\text{H}_2$  release, as well as low cost and safe handling [7,8].

Direct borohydride fuel cells (DBFCs) with  $\text{NaBH}_4$  as fuel and oxygen ( $\text{O}_2$ ) as oxidant [9–12] were first assembled in the early 1960s [13,14], and nowadays are finding use in mobile and transport applications [15]. Recently, DBFCs using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as the oxidant, known as direct borohydride peroxide fuel cells (DBPFCs), have also been proposed [16–18], mainly for space, underwater, and specific terrestrial applications where  $\text{O}_2$  is not available [16]. The DBFC anode has a high theoretical specific capacity of  $5.67 \text{ Ah g}^{-1}$  (based on  $\text{NaBH}_4$ ), provided that borohydride ( $\text{BH}_4^-$ ) is fully oxidized (Eq. (1)).



The complete eight-electron oxidation process has a standard electrode potential of  $-1.24 \text{ V vs. SHE}$ , i.e., ca. 0.4 V more negative than in the case of  $\text{H}_2$  or methanol ( $\text{CH}_3\text{OH}$ ) oxidation. Consequently,

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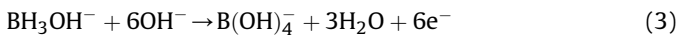
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DBFCs and DBPFCs have equilibrium cell voltage as high as 1.64 V and 3.01 V, respectively, and theoretical specific energy (based on NaBH<sub>4</sub>) of 9.25 Wh g<sup>-1</sup> and 17 Wh g<sup>-1</sup>, respectively [15,19]. These theoretical cell voltage values are significantly higher than that of FCs using H<sub>2</sub> (1.24 V) or CH<sub>3</sub>OH (1.19 V) as fuels [20]. Moreover, the theoretical specific energy for the DBPFC is ca. 5 times higher than that of H<sub>2</sub>/O<sub>2</sub> system, 3 times higher than in the case of CH<sub>3</sub>OH fuel cell (6.09 Wh g<sup>-1</sup>) and 2 times higher than that obtained for ethanol (C<sub>2</sub>H<sub>5</sub>OH) fuel cell (8.01 Wh g<sup>-1</sup>) [15,20].

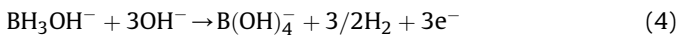
However, at solutions of pH < 12, as well as in the presence of some electrode materials, BH<sub>4</sub><sup>-</sup> hydrolysis proceeds in parallel with its oxidation [21], generating hydroxyborohydride ion (BH<sub>3</sub>OH<sup>-</sup>) and H<sub>2</sub> (Eq. (2)) [22–27] and consequently reducing Coulombic efficiency.



The generated BH<sub>3</sub>OH<sup>-</sup> can be fully oxidized according to Eq. (3) with release of 6 electrons and no H<sub>2</sub> gas.



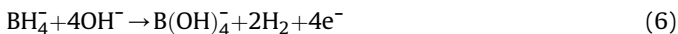
with a peak appearing at a potential ca. 0.5 V more negative than that of direct BH<sub>4</sub><sup>-</sup> oxidation (Eq. (1)) [28–30]. Alternatively, the BH<sub>3</sub>OH<sup>-</sup> ion can also undergo stepwise oxidation [31] with only 3 electrons being released along with H<sub>2</sub> gas (Eq. (4)).



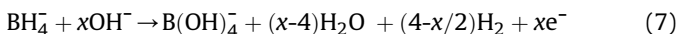
Part of the evolved gas that remains at the electrode surface can be oxidized via Eq. (5).



Thereafter, the indirect BH<sub>4</sub><sup>-</sup> oxidation can be presented with Eq. (6) corresponding to the sum of Eqs. (2), (4) and (5):



This mechanism is characteristic for metals such as platinum (Pt) [32], palladium (Pd) [33] and nickel (Ni) [34]. In general, both BH<sub>4</sub><sup>-</sup> oxidation and the competing BH<sub>4</sub><sup>-</sup> hydrolysis reaction proceed in parallel [19,35–37], so the overall borohydride oxidation reaction (BOR) can be given as Eq. (7) [5]:



where *x* is the Coulombic number, i.e., the actual number of exchanged electrons, which depends on the anode material [38,39]. Therefore, the anode material is a key factor for achieving complete direct oxidation of BH<sub>4</sub><sup>-</sup> and consequently for high efficiency of DBFCs. Two other important features affecting BOR are electrolyte solution composition (ratio of BH<sub>4</sub><sup>-</sup> and OH<sup>-</sup> concentrations) and its temperature [18,40–42]. To enhance complete BH<sub>4</sub><sup>-</sup> oxidation and DBFCs efficiency it is necessary to understand reaction mechanism and clarify effects of the mentioned factors.

Among various anode materials studied for DBFCs, gold (Au) stands out for its high activity for BH<sub>4</sub><sup>-</sup> oxidation and, at the same time, inactivity for BH<sub>4</sub><sup>-</sup> hydrolysis, yielding 8 electrons exchanged during the reaction [42–45]. However, BH<sub>4</sub><sup>-</sup> oxidation at Au proceeds at very low rate. On the other hand, this reaction is ca. 10 times faster at Pt electrodes [15]. Still, the fact that Pt promotes BH<sub>4</sub><sup>-</sup> hydrolysis, results in lower Coulombic efficiency. Platinum-Rare Earth (Pt-RE) alloys have been reported to exhibit better electrocatalytic activity for H<sub>2</sub> evolution reaction [46], [47,48] as well as for methanol [49] and ethanol [50–52] oxidation in comparison with pure Pt. Higher activity of Pt-RE electrodes may be due to the improved three-dimensional hydridic factors of composite

catalysts [53,54]. Based on theoretical considerations [55–57], Pt-RE/BH<sub>4</sub><sup>-</sup> interfaces can be considered to be systems of interest for application in DBFCs and PEMFCs, depending on the nature and composition of the alloying RE element. Also, it is known that alloys show higher electroactivity due to the synergistic effect of their constituents. Therefore, equiatomic-composition Pt-RE alloys, with RE being holmium (Ho), samarium (Sm) and cerium (Ce), have been recently investigated for their activity for BH<sub>4</sub><sup>-</sup> oxidation [58].

Herein, alloys of Pt and dysprosium (Dy) were studied as anode materials for DBFCs. For this preliminary study, alloys of two different compositions were explored. In order to investigate the mechanism of BH<sub>4</sub><sup>-</sup> oxidation at these alloy electrodes, reaction parameters including number of electrons exchanged (*n*), were evaluated from cyclic voltammetry (CV), chronopotentiometry (CP) and chronoamperometry (CA) data. Dependence of the alloys activity for BOR on the BH<sub>4</sub><sup>-</sup> concentration, as well as on the electrolyte temperature, was also explored.

It is expected that present results can lead to an advance in DBFCs technology, having in mind that an important aspect for a new technology to be broadly accepted and employed is its cost. From the economic point of view, Pt–Dy alloys offer further benefits as Dy current price (630 \$ kg<sup>-1</sup>) is considerably lower than Pt price (46,620 \$ kg<sup>-1</sup>) resulting in significantly lower cost of Pt–Dy alloy electrodes than that of pure Pt electrodes [59]. This may considerably lower the price of DBFCs employing these anodes, having in mind that the cost of equiatomic Pt–Dy electrodes would be about half of that of pure Pt.

Finally, it should be mentioned that the name “Rare Earths” could be misleading as, for instance, the most abundant RE element, Ce, is approximately equally abundant in the earth's crust as other elements used for everyday applications, such as copper (Cu), and is more abundant than boron (B, a major constituent of Pyrex), lead (Pb, for automobile batteries) or tin (Sn, for cans). Even the rarest of the REs, thulium (Tm) is more abundant than cadmium (Cd, a battery component), and certainly than Au and Pt. Although many of the RE elements are more abundant than common metals such as Pb or Cd, one of the main problems concerning RE elements is their separation in the individual elements. In fact they are extracted in minerals all together, that is, all the light REs, from lanthanum (La) to Sm are extracted from minerals such as monazite, and the heavy REs, starting from gadolinium (Gd) are extracted from minerals such as xenotime. Their separation is difficult since they have the same chemical properties. Generally, only separation based on their physical properties can be used, for instance the ion-exchange method. For these reasons the prices of RE elements are higher than, for instance, that of Pb.

## 2. Experimental

### 2.1. Preparation and characterization of the Pt–Dy alloys

Pt–Dy alloys with 50 at.% Dy (Pt<sub>0.5</sub>Dy<sub>0.5</sub>) and 60 at.% Dy (Pt<sub>0.4</sub>Dy<sub>0.6</sub>) nominal compositions used herein were prepared as described elsewhere [47,48], using arc melting in an inert atmosphere, starting from stoichiometric amounts of the two elements (Pt, 99.99 wt.%, Johnson Matthey & Co. Ltd., London, UK and Dy, 99.9 wt.%, Koch Chemical Ltd., Hertford, UK). The two samples were remelted several times to ensure their uniformity. Smooth alloy surfaces suitable for the microscopic examinations were obtained after polishing with SiC papers and diamond pastes with particle size decreasing from 6 to 1 μm. Microstructure observation and qualitative/quantitative analyses were performed by a scanning electron microscope (SEM) EVO 40 (Carl Zeiss SMT Ltd, Cambridge, England) provided with a Pentafet Link energy dispersive X-ray spectroscopy (EDX) system controlled by the Inca Energy package

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