Investigations of the Process Involved in the Borohydride Oxidation on La-Ni-Based Hydrogen Storage Alloys

Waldemir J. Paschoalino[a]; Stephen J. Thompson[b], Andrea E. Russell[b] and Edson A. Ticianelli [a]

This work provides insights into the processes involved in the borohydride oxidation reaction (BOR) in alkaline media on metal hydride alloys formed by LaNi[4,7]Sn[0.2]Cu[0.1] and LaNi[4,7]Al[0.22] with and without deposited Pt, Pd and Au. Results confirmed the occurrence of hydrolysis of borohydride ions when the materials are exposed to BH₄⁻ and a continuous hydriding of the alloys during BH₄⁻ oxidation measurements at low current densities; the activity for the direct BOR is low in both bare metal hydride alloys, but the rate of the BH₄⁻ hydrolysis and the hydrogen storage capacity are higher, while the rate of H diffusion is slower in the bare LaNi[4,7]Al[0.22]. Addition of Pt and Pd on both alloys resulted in an increase of the BH₄⁻ hydrolysis, but the H₂ formed is rapidly oxidized at the Pt modified catalysts. In the case of Au modification a small increase of the BH₄⁻ hydrolysis is observed, as compared to the bare alloys. The presence of Au and Pd also lead to a reduction of the rates of alloy hydriding/de-hydriding.

1. Introduction

High-energy density portable electricity generators are becoming of increasing importance. Direct borohydride fuel cells (DBFC) constitute an attractive class of renewable and sustainable energy sources that may help to meet these needs. However, there are some difficulties to be overcome to achieve full commercial implementation of such cells, including the need to improve the efficiency of the catalysts for the borohydride oxidation reaction (BOR) taking place in the DBFC anode. In alkaline media the BOR, can be promoted, liberating a maximum of 8 electrons and this main reaction is given in equation 1, below [1-3]:

\[
\text{BH}_4^- + 8 \text{OH}^- \rightarrow \text{BO}_2^- + 6 \text{H}_2\text{O} + 8 \text{e}^- \quad (E^0 = -1.24 \text{ V vs. ENH}), \quad (1)
\]

However, there are several parallel reactions that compete with the main reaction, diminishing the fuel utilization efficiency. These parallel reactions are the hydrolysis (equations 2 and 3) and the partial oxidation (equation 4) of the borohydride ions [1-4]:

\[
\begin{align*}
\text{BH}_4^- + \text{H}_2\text{O} & \rightarrow \text{BH}_2\text{OH}^- + 2 \text{H}_2\text{O} \quad & (2) \\
\text{BH}_4^- + 2 \text{H}_2\text{O}^- & \rightarrow \text{BO}_2^- + 8 \text{H}_2\text{O} \quad & (3) \\
\text{BH}_4^- + 4 \text{OH}^- & \rightarrow \text{BO}_2^- + 2 \text{H}_2\text{O} + 4 \text{H}_2\text{O} + 4 \text{e}^- \\
& \rightarrow \text{BO}_2^- + 2 \text{H}_2\text{O} + 2 \text{H}_2 + 4 \text{e}^- \quad (4)
\end{align*}
\]

Reaction (2) is predominant at low borohydride concentrations and reaction (3) at high concentrations. In the course of the BOR, the negative effect of hydrolysis may be reduced by the oxidation of the produced hydrogen in the working electrode:

\[
\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^- \quad (5)
\]

The borohydride oxidation reaction has been studied at a variety of materials, with the aim to prepare more efficient catalysts, and by employing a number of techniques, so to understand the reaction mechanisms. Hydrogen storage alloys formed by LaNi[4,7]Sn[0.2]Cu[0.1] and with and without deposited Pt, LaNi[4,7]Al[0.22], and LaNi[4,7]Mn[0.22] have been previously investigated as electrocatalysts [5]. Evidence was found that wet exposure to sodium borohydride lead to the hydriding of the metal alloys, which were then capable of partially oxidizing the borohydride ions at same time during which the hydrogen produced by hydrolysis or partial oxidation of BH₄⁻ (reactions (2) - (3)) was being stored in the hydride form, that is,

\[
\text{M}_{\text{H}^{\text{ads}}} \rightarrow \text{M}_{\text{H}^{\text{ads}}}. \quad (6)
\]

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[5]
As seen in previous work [5], the presence of platinum on the surface of 
LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> alloys provides a higher activity for the BOR, but at the same time the hydrolysis is more evident [5] when the electrode is at the open circuit potential. In spite of this, no hydrogen evolves from the electrode during anodic potential scans as any H<sub>2</sub> present is rapidly oxidized at the Pt sites.

The BOR has been extensively studied at Pt, Pd and Au catalyst surfaces [1-4,6-9]. It has been found that Pd catalysts generally present similar behaviour as for Pt but with smaller involvement of the borohydride hydrolysis, whilst for gold the occurrence of hydrolysis in very small although not negligible.

This work provides further insights into the processes involved in the borohydride oxidation reaction in alkaline media on metal hydride alloys, by investigating the reaction pathways of the BOR using on line mass spectrometry. Several metal hydride alloys were considered, including LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> and LaNi<sub>4.7</sub>Al<sub>0.22</sub> at different electrode configurations, with and without deposition of platinum, palladium and gold. These alloys were chosen because of their reported high catalytic activity for the borohydride oxidation reaction, either directly or eventually involving a previous process of alloy hydriding [5,10]. The alloy with aluminium presents higher hydrogen storage capacity [10] compared to LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub>, but the hydrolysis pathways are higher more important than for LaNi<sub>4.7</sub>Al<sub>0.22</sub> [5]. The deposition of the noble metals was made as an attempt to either modulate the participation of the borohydride hydrolysis or to contribute to the oxidation of the gaseous hydrogen evolved.

2. Results and Discussion

2.1. Physical and compositional characterization

The results obtained by EDS analyses confirmed, within the experimental errors, the alloy compositions given here by the metal alloy formulas. However, the noble metals (Pt, Pd and Au) could not be detected since there was a superposition of the EDS peaks with those of the other elements, which were present at much higher contents. Figure 1 shows the diffractograms obtained for the alloys with different compositions, with copper and tin or with aluminium. The results clearly show the formation of the metal hydride alloy of interest, as confirmed by the hexagonal CaCu<sub>5</sub>-type features, characteristic of this type of material [11], and confirm the absence of segregated phases. However, also in these cases it was not possible to identify any characteristic fcc peak of Pt, Pd or Au, evidencing, as expected, the presence low amounts of these materials in the structure of the alloys particles. Figure 2 shows the TEM images for the LaNi<sub>4.7</sub>Al<sub>0.22</sub> – Pd (Figure 2a) and LaNi<sub>4.7</sub>Al<sub>0.22</sub> – Au (Figure 2b). It is possible to observe, for both compositions, the formation of a number of individual crystallites, present as planes of atoms with varying spatial orientations. Such features are characteristic of these types of metal alloys.

ICP-AES (Medac) was used to determine the noble metal loading of each of the modified catalysts and the results are presented in Table 1. These data indicate that the depositions resulted in a very low loading of the noble metals, in the range of 0.1 to 0.3 wt.%. Since the total loading of the materials in the TPC layer in the working electrodes are of the order of 1.5 mg and the geometric area is 0.196 cm<sup>2</sup>, these results indicate a loading of 9 to 25 µg cm<sup>2</sup> of the noble metal in the catalyst layer.

Cyclic voltammograms were obtained using TPC electrodes in 1.0 mol L<sup>-1</sup> KOH solutions for the LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> with and without the noble metals and the results are shown in Figure 3.

![Figure 1](image1.png)

**Figure 1.** XRD features for the metal hydride alloys with and without deposited Pt, Pd and Au. Dashed, dotted and line dotted lines are placed to localize the diffraction peaks of Pt, Au and Pd, respectively.

![Figure 2](image2.png)

**Figure 2.** TEM of a LaNi<sub>4.7</sub>Al<sub>0.22</sub> – Pd (a) and LaNi<sub>4.7</sub>Al<sub>0.22</sub> – Au (b) alloy particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Composition (wt. %)</th>
</tr>
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<tbody>
<tr>
<td>LaNi&lt;sub&gt;4.7&lt;/sub&gt;Sn&lt;sub&gt;0.2&lt;/sub&gt;Cu&lt;sub&gt;0.1&lt;/sub&gt; – Pt</td>
<td>Pt</td>
<td>0.14</td>
</tr>
<tr>
<td>LaNi&lt;sub&gt;4.7&lt;/sub&gt;Sn&lt;sub&gt;0.2&lt;/sub&gt;Cu&lt;sub&gt;0.1&lt;/sub&gt; – Pd</td>
<td>Pd</td>
<td>0.34</td>
</tr>
<tr>
<td>LaNi&lt;sub&gt;4.7&lt;/sub&gt;Sn&lt;sub&gt;0.2&lt;/sub&gt;Cu&lt;sub&gt;0.1&lt;/sub&gt; – Au</td>
<td>Au</td>
<td>0.12</td>
</tr>
<tr>
<td>LaNi&lt;sub&gt;4.7&lt;/sub&gt;Al&lt;sub&gt;0.22&lt;/sub&gt; – Pt</td>
<td>Pt</td>
<td>0.16</td>
</tr>
<tr>
<td>LaNi&lt;sub&gt;4.7&lt;/sub&gt;Al&lt;sub&gt;0.22&lt;/sub&gt; – Pd</td>
<td>Pd</td>
<td>0.30</td>
</tr>
<tr>
<td>LaNi&lt;sub&gt;4.7&lt;/sub&gt;Al&lt;sub&gt;0.22&lt;/sub&gt; – Au</td>
<td>Au</td>
<td>0.33</td>
</tr>
</tbody>
</table>
It is observed that there is an increase of the currents in the more negative potential regions of the cyclic voltammograms for the Pt-coated electrode, demonstrating an improvement of the electrocatalytic activity for the production/oxidation of adsorbed hydrogen, thus confirming the presence of Pt at the surface of the alloy particles [12]. Similar results were obtained when Pd was deposited in the alloy.

In contrast, for the gold containing particles there is no change of the hydrogen oxidation/reduction currents, consistent with the inactivity of the gold metal in this potential region. In summary, these results clearly evidence the presence of noble metals at the surface of the alloy particles, although no quantitative information regarding the surface area of the noble metal present could be obtained, given the broad features of the voltammograms and the need to limit the upper potential limit to -0.4 V (explained further, below), and therefore no correlations could be made with the quantitative data presented in Table 1.

2.2. Borohydride oxidation reaction

The polarization results of TPC rotating electrodes for LaNi$_4$Sn$_2$Cu$_{1.1}$ and LaNi$_4$Al$_{0.22}$ with and without Pt, Pd or Au, when BH$_4^-$ ions were present in the solution, are shown in Figure 4. In these experiments the upper potential limit did not exceeded -0.4 V to avoid severe electrochemical oxidation of the metal hydride alloys. Particularly in the absence of Pt, Pd or Au for both group of alloys, the peak oxidation currents appearing in this range of potential do not evidence mass transport phenomena related to the presence of BH$_4^-$ in the solution, so that the currents in Fig. 4 are not dependent on the rotation rate. This behavior has been attributed to the occurrence of the hydride oxidation reaction, for which the hydride formation is promoted by the hydrolisis of the borohydride ions [5]. In the presence of the noble metals, the direct oxidation of the borohydride ions is also evidenced by the increase of the currents at the more positive electrode potentials and their increase with the rotation rate, as illustrated in Fig. 4 with the results for LaNi$_4$Sn$_2$Cu$_{1.1}$ with Pt and LaNi$_4$Al$_{0.22}$ with Pd. Results also indicate that the magnitude of the hydride oxidation currents is strongly dependent on the metal hydride composition; this may be a consequence of the extension of the occurrence of the hydrolisis reaction of BH$_4^-$ producing hydrogen or, more probably, of the rate of the hydriding process, leading to a smaller accumulation of hydrogen atoms inside the alloy structure after the deposition of the noble metal.

Figure 4 shows results of DEMS for the detection of H$_2$ for the electrodes at the open circuit potential (OCP), after the BH$_4^-$ ions are added to the solution at t = 100-200 s. These results show that in all cases there is a release of H$_2$ as soon as the BH$_4^-$ ions are introduced in the solution. However, for the bare LaNi$_4$Sn$_2$Cu$_{1.1}$ alloy and for that containing Au the evolution of H$_2$ is much less significant. It should be also noted that at the other extreme, for the LaNi$_4$Al$_{0.22}$ alloys, the DEMS signals for H$_2$ are much higher than for the LaNi$_4$Sn$_2$Cu$_{1.1}$-based materials. As all of these experiments were conducted at the OCP, these results evidence very clearly the occurrence of the hydrolisis of the BH$_4^-$ ions, but in the case of the bare and Au coated LaNi$_4$Sn$_2$Cu$_{1.1}$ materials the extent of this reaction is much smaller. For the LaNi$_4$Al$_{0.22}$ alloy, as H$_2$ is released at the bare alloy it is difficult to separate the specific effects of the noble metals on the release of H$_2$.

The effects of the electrode potential are evidenced by the results in Figure 6. The top pictures (labeled a) show the oxidation currents of the BOR, while in the bottom ones (labeled b) are the lines representing the ionization currents measured by the MS detector, corresponding to the m/z mass = 2. For LaNi$_4$Sn$_2$Cu$_{1.1}$ (Fig. 6A) it is observed that there is some hydrogen evolution during the course of the BOR, but only at higher electrode potentials where some currents related to the oxidation process of BH$_4^-$ are evidenced. This indicates the occurrence of a partial oxidation of borohydride ions (reaction 4), as already proposed for bulk nickel-based catalysts [13]. For LaNi$_4$Sn$_2$Cu$_{1.1}$ with Pt or Au, the evolution of H$_2$ stops as soon as lower potential limit is applied. Moreover, even when the electrode potential is scanned to less negative values, the hydrogen evolution remains inactive. The causes of these effects might be different for both alloys: in the case of the gold-coated alloy it must be related to the small rate of the hydrolisis of BH$_4^-$, while for the Pt-containing material it is probably related to the facile oxidation of H$_2$ catalyzed by Pt. These currents are not observed in the corresponding voltammogram because of insufficient sensitivity.
Figure 5. Mass spectrometry responses for H₂ detection for LaNi₄.7Sn₀.2Cu₀.1 and LaNi₄.78Al₀.22 without and with Pt, Pd and Au, in the presence of borohydride 10⁻² M. Electrodes at the open-circuit potential.

Figure 6. Online differential electrochemical mass spectrometry (DEMS) measurements for LaNi₄.7Sn₀.2Cu₀.1 with and without Pt, Pd and Au in the presence of borohydride 10⁻² M: (a) voltammetric responses, (b) spectrometric responses for H₂ detection.
When Pd is present, the DEMS results show a decrease in \( \text{H}_2 \) production with increasing electrode potential in the forward scan, while in the backward scan the hydrogen evolution remains inactive. These results suggest that there is some hydride accumulation inside the alloy before the beginning of the potential scan, which is then slowly but completely released along the forward scan. Here the rate of \( \text{H}_2 \) oxidation must be smaller than when Pt is present.

The results for the group of alloys based on LaNi\(_{4.78}\)Al\(_{0.22}\) are shown in Figure 7. Here, a much greater release of \( \text{H}_2 \) is observed at the most negative potentials is observed for the alloy with and without Pt, evidencing a larger amount of BH\(_4^-\) hydrolysis. However in the course of the potential scan the hydrogen evolution diminishes rapidly indicating the BH\(_4^-\) hydrolysis stops and also that the BH\(_4^-\) partial oxidation reaction is not important. In the case of the Pt containing alloy, \( \text{H}_2 \) oxidation may also decrease the amount of \( \text{H}_2 \) detected by the DEMS measurements.

The corresponding results for LaNi\(_{4.78}\)Al\(_{0.22}\) with Pd or Au present are similar to those of LaNi\(_{4.78}\)Sn\(_{0.2}\)Cu\(_{0.1}\) with Pd. That is, a decrease hydrogen evolution in the course of the potential scan is observed. However, here the suppression of the \( \text{H}_2 \) signal seems to be not total and this may be due to the larger rate of the BH\(_4^-\) hydrolysis.

Figure 8 shows galvanostatic discharge curves for LaNi\(_{4.78}\)Sn\(_{0.2}\)Cu\(_{0.1}\) without and with Pt, Pd and Au for TPC electrodes electrochemically charged (Fig. 8a) and previously exposed to 10\(^{-2}\) M BH\(_4^-\) for 2 h, for electrolytes in the absence of dissolved BH\(_4^-\) (Fig 8b). Results for the LaNi\(_{4.78}\)Al\(_{0.22}\) alloys previously exposed to 10\(^{-2}\) M BH\(_4^-\) for 2 h are shown in Figure 9. The time scales for the galvanostatic discharge curves reported were converted into discharge capacity (mA h g\(^{-1}\)) by multiplying by the time (h) for the discharge current (mA) and dividing by the alloy mass (g).

The discharge profiles in Fig. 8a for LaNi\(_{4.78}\)Sn\(_{0.2}\)Cu\(_{0.1}\) based TPC electrodes show very similar characteristics to those reported for standard negative metal hydride electrodes of Nickel-metal hydride batteries, with some degradation of the maximum discharge capacity of the alloys observed after the incorporation of noble metals [5,11]. Interestingly, results for the alloys in Fig. 8b present essentially the same profiles as in Fig. 8a, confirming that all the materials are hydrided either electrochemically or by exposition to BH\(_4^-\) solutions. The lower maximum discharge capacities for the LaNi\(_{4.78}\)Al\(_{0.22}\) based materials (Fig. 9), especially for the noble metal modified materials, is a consequence of the smaller alloy hydriding, as evidenced in Fig. 4b. This phenomenon can be attributed to the low diffusion rate of the H atoms inside the alloy. These results are consistent with the larger amount of \( \text{H}_2 \) released during the charging of the alloys, as observed in Fig. 6 for the LaNi\(_{4.78}\)Al\(_{0.22}\)-based materials, implying that the rates of the BH\(_4^-\) hydrolysis and \( \text{H}_2 \) release are greater than the rate of the hydrogen uptake by the alloy.
4.7. the rates of the alloy hydriding/dehydrolysis were obtained using a JEOL JEM 2100 electron microscope with X-ray diffraction (XRD) conducted using a Rigaku RU200B X-ray diffractometer with Cu Kα radiation source. Normal (TEM) images (JEOL JEM 2100) of the alloy particles were obtained to characterize the alloy micro- and nano-structures. Elemental analyses were made for identifying the amount of Pt, Pd and Au in each sample. Elemental analysis (MEDAC LTD) were performed to confirm the noble metal loading in the materials.

3. Conclusion

The present investigation shows that state of hydriding of LaNi4.7Sn0.2Cu0.1 and LaNi4.7Sn0.2Al0.2 is important in defining the kinetics and outcome of the BOR at these materials. The extent of hydride formation has been shown to depend on the rate of the BH4− hydrosis, the hydrogen storage capacity of the alloy, and kinetics of H atom diffusion inside the alloy. The activity for the direct BOR is low in both bare metal hydride alloys, but the rate of the BH4− hydrosis and the hydrogen storage capacity are higher, while the rate of H diffusion is slower in the bare LaNi4.7Sn0.2Al0.22.

Results have shown that both the bare and all the noble metal modified alloys can be hydried either electrochemically or by exposure to BH4− solutions, although for the LaNi4.7Sn0.2Al0.22-based materials the extent of this phenomenon is smaller. A continuous hydriding of all LaNi4.7Sn0.2Cu0.1-based and the bare LaNi4.7Sn0.2Al0.22 alloys are observed in the chronoamperometric BH4− oxidation measurements at low current densities. Addition of Pt on both alloys resulted in an increase of the BH4− hydrosis, but the BH4− formed is rapidly oxidized, confirming the initial predictions for this noble metal. In addition, the rates of the alloy hydriding/dehydriding were not significantly affected by the presence of Pt, but this was not the case for Pd and Au, for which there was a drastic reduction of the rate of these processes. In the case of gold some increase of the BH4− hydrosis is observed, although its presence does not change significantly the performances of the bare alloys. All these phenomena point to the bare LaNi4.7Sn0.2Cu0.1 as a more adequate alloy system for applications in DBFC/MH batteries.

Experimental Section

The LaNi4.7Sn0.2Cu0.1 and LaNi4.7Sn0.2Al0.22 base alloys were prepared from high-purity metals by the arc melting technique under an inert gas atmosphere [11]. After that, the samples were grided, and then a portion of these materials were separated and had the particle surfaces partially covered by a Pt, Pd or Au layers using galvanic displacement. This process involved the immersion of the metal hydride alloy in a 1.0 M of KOH solution containing 10−2 M of borohydride for two hours. After that, these materials were immersed in KOH 0.5 M solution containing 10−2 M of Pt or Pd or Au for more two hours.

Chemical and physical analyses of these materials were performed by energy dispersive spectroscopy (EDS) conducted using a scanning electron microscope (EDX LINK, Isis System Series with detector of SiLi pentafet, ATW II (Atmosphere Thin Window) with resolution 133 eV until 5.9 keV linked to electronic microscope ZEISS LEO 440) and X-ray diffraction (XRD) conducted using a Rigaku RU200B X-ray diffractometer with Cu Kα radiation source. Normal (TEM) images (JEOL JEM 2100) of the alloy particles were obtained to characterize the alloy micro- and nano-structures. Elemental analyses were made for identifying the amount of Pt, Pd and Au in each sample. Elemental analysis (MEDAC LTD) were performed to confirm the noble metal loading in the materials.

The working electrode was a thin porous coating (TPC) structure deposited on rotating glassy carbon disc substrate. The TPC layer was prepared using 300 mg of the alloy in 0.5 mL of Nafton 0.05 wt.%; 15 µL of this suspension was deposited on the rotating glassy carbon disc, which was then allowed to dry under ambient conditions [5].
The TPC working electrode was evaluated in a single compartment cell with a high surface area platinum screen counter electrode and an Hg/HgO/KOH 1.0 M reference electrode. The experiments were conducted in 1.0 mol L$^{-1}$ KOH, in the absence or in the presence of sodium borohydride $10^{-2}$ or $10^{-1}$ mol L$^{-1}$ as a reactant. Results were collected using cyclic voltammetry, galvanostatic chronopotentiometric discharge measurements, and online differential electrochemical mass spectrometry (DEMS). For the DEMS measurements, the setup consisted of a Pfeiffer Vacuum QMA 200 quadrupole mass spectrometer with two differential pumping chambers [14]. The mass spectrometry (MS) measurements were conducted in 1 M KOH + $10^{-2}$ M NaBH$_4$ solution and the $m/z = 2$ signal (the H$_2$ signature) was measured as a function of the electrode potential.

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Continuously chemically rechargeable metal hydride electrodes: insights for the understanding of the borohydride oxidation reaction in alkaline media are provided for metal hydride alloys formed by LaNi$_{4.7}$Sn$_{0.2}$Cu$_{0.1}$ and LaNi$_{4.78}$Al$_{0.22}$ chemically modified by platinum, palladium, and gold deposits. Occurrence of hydrolysis of borohydride ions when the materials are exposed to BH$_4^-$ and the continuous hydriding of the alloys are confirmed when the materials are exposed to BH$_4^-$.

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