

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

An investigation of the borohydride oxidation reaction on La–Ni-based hydrogen storage alloys

Waldemir J. Paschoalino, Edson A. Ticianelli*

Instituto de Química de São Carlos, Universidade de São Paulo, Avenida Trabalhador Sãocarlense, 400 Parque Arnold Schmidt, CP 780, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 16 February 2013

Received in revised form

4 April 2013

Accepted 5 April 2013

Available online 6 May 2013

Keywords:

La–Ni-based alloy

Borohydride oxidation reaction

Hydrogen oxidation reaction

Metal hydride alloy

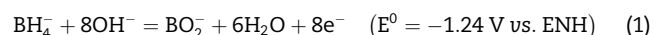
ABSTRACT

In this study, $\text{LaNi}_{4.7}\text{Sn}_{0.2}\text{Cu}_{0.1}$ metal hydride alloys, with and without surface deposits of Pt, are investigated as electrocatalysts for the borohydride oxidation reaction (BOR) in alkaline media. Results obtained for $\text{LaNi}_{4.78}\text{Al}_{0.22}$ and $\text{LaNi}_{4.78}\text{Mn}_{0.22}$ are used for comparison. It is observed that wet exposition to hydrogen or sodium borohydride lead to some hydriding of the metal hydride alloy particles, particularly that with a coating of Pt. In the presence of borohydride ions, the hydrided charged alloys present more negative potentials for the (boro)hydride oxidation process, and these enhancements are significantly larger for the Pt-coated material. In the potential range of interest, the results demonstrate considerable activity for the BOR, but just for the alloy with Pt. In the presence of borohydride ions in the solution there is a continuous hydriding the alloy during the discharge of the metal hydride electrode. Differential electrochemical mass spectrometry (DEMS) measurements showed that there is formation of H_2 , either by hydrolysis or by partial oxidation of the borohydride ions, but in the absence of Pt the hydrolysis process is quite slow.

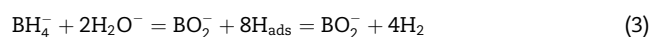
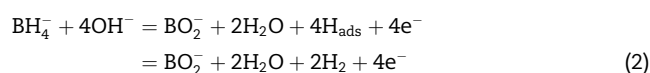
Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Direct borohydride fuel cells (DBFC) are high-energy density portable electricity generators, which work by converting the chemical energy stored in borohydride ions (BH_4^-) into electrical energy. However, there are some challenges to be overcome to make this system viable, one of them being the development of more efficient catalysts for the promotion of the borohydride oxidation reaction (BOR) taking place in the fuel cell anode. The main reaction expressing complete borohydride oxidation is given by [1]



but many other parallel or successive steps may occur depending on the reaction catalyst, the main ones involving the partial oxidation and the hydrolysis of BH_4^- [1]:



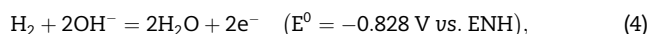
Several kinds of bulk materials have been investigated as electrocatalysts for the BOR, and these include Pt, Au, Pd, Ni, and Cu, among others [1,2]. Particularly interesting catalysts often considered are those formed by metal hydride alloys,

* Corresponding author. Tel.: +55 16 33739945; fax: +55 16 3373 9952.

E-mail address: edsont@iqsc.usp.br (E.A. Ticianelli).

typically used in the negative electrode of Ni-metal hydride batteries [3]. A special feature pointed out regarding these materials is the possibility of the alloy hydriding, either chemically or electrochemically, after exposition to BH_4^- as suggested by reactions (2) and (3). A direct borohydride fuel cell using an MnO_2 -catalyzed cathode and an $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ hydrogen storage alloy anode was assembled [4]. High fuel cell performance was obtained, with the results indicating a maximum power density near 70 mW/cm^2 at a current density of 180 mA/cm^2 at 25°C .

A series of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ - [5–7] and Mm-based [8–11] (Mm = misch metal, an alloy of rare earth elements) metal hydride alloys have been already investigated as anode catalysts for DBFC. In the case of $\text{LaNi}_{4.5}\text{Al}_{0.5}$, results [5] indicated that H_2 evolution was unavoidable during the BOR because of the occurrence of reactions (2) and/or (3). This creates a mixed potential at the anode due to the occurrence of the hydrogen/hydride oxidation reaction



which lowers the open-circuit potential of the anode. The addition of an Au layer on the surface of the $\text{LaNi}_{4.5}\text{Al}_{0.5}$ particles [6] improved fuel utilization and the catalytic activity for the BOR. Increasing the temperature [7] led to positive effects for the open-circuit potential, the discharge potential, and the power density, but it increased the occurrence of the hydrolysis reaction, decreasing fuel utilization.

In the case of the Mm-based alloys, results for an $\text{MmNi}_{4.78}\text{Mn}_{0.22}$ material [8] in 4 wt.% KBH_4 and in 30 wt.% KOH aqueous solutions indicated high catalytic activity for both the BOR and the hydrogen evolution reaction, in which case the reaction rate increases with the increase of the current density, evidencing the occurrence of reaction (2). Studies employing the same experimental conditions with the same alloy modified by Si [9] have shown that modification by Si decreases the electrochemical catalytic activity at the same time that the H_2 generation rate also decreases in the discharge process. At a small current density this leads to an increase in fuel utilization from 21.37% for the parent alloy to 95.27% for the modified alloy.

When $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ is used as the anode catalyst for the BOR in 6.0 M KOH or NaOH solutions [10], results proved that the hydrogen storage material can absorb hydrogen during immersion in a 0.9 M potassium borohydride solution. In the course of the BOR, the hydrogen generated is partially oxidized in the electrode, particularly at low borohydride concentrations. However at higher concentrations, the importance of the direct BOR increases. Increasing the alloy surface area (by decreasing the particle size) and the temperature improves the polarization behavior of the alloy electrode, but hydrogen evolution also increases, reducing fuel utilization. Activation of an $\text{MmNi}_{4.03}\text{Co}_{0.42}\text{Mn}_{0.31}\text{Al}_{0.24}$ alloy through immersion in a 6.0 M NaOH/0.1 M NaBH_4 solution [11] led to a great increase in catalytic activity in the beginning of the BO experiment, and this was attributed to the electrooxidation of the hydride inserted into the alloy during activation. After some time, the current stabilized because of the occurrence of direct oxidation of the borohydride ions.

These investigations have indicated that there is quite a good perspective for these materials to be introduced in the

anode of a direct borohydride fuel cell. The main limitations are the loss of fuel utilization introduced by the occurrence of reactions (3) and (4), the consequent release of H_2 gas, and the mixed electrode potential created as a consequence of these phenomena. The stability of these electrode systems is an issue yet to be addressed. In this study, $\text{LaNi}_{4.7}\text{Sn}_{0.2}\text{Cu}_{0.1}$ alloys, with and without surface deposits of Pt, were investigated as electrocatalysts of the BOR in alkaline media in conventional and thin-layer electrodes. Results obtained for $\text{LaNi}_{4.78}\text{Al}_{0.22}$ and $\text{LaNi}_{4.78}\text{Mn}_{0.22}$ were used for comparisons. The processes of the alloys hydriding by wet expositions to hydrogen and to borohydride ions are specifically treated with the aim of understanding the behavior of the materials on different media at different electrode configurations. The use of an alloy containing Sn and the incorporation of Pt, respectively, aim at improving alloy stability [12] and the electrocatalysis of the hydrogen oxidation reaction so as to minimize the release of gas due to the hydrolysis of BH_4^- .

2. Experimental section

The $\text{LaNi}_{4.7}\text{Sn}_{0.2}\text{Cu}_{0.1}$, $\text{LaNi}_{4.78}\text{Al}_{0.22}$, and $\text{LaNi}_{4.78}\text{Mn}_{0.22}$ alloys were prepared by melting mixtures of high-purity metals in an arc furnace with an ultradry argon atmosphere [12]. After grinding, a fraction of the $\text{LaNi}_{4.7}\text{Sn}_{0.2}\text{Cu}_{0.1}$ material had the particle surfaces partially covered by a Pt layer using galvanic displacement [13]. Briefly, the process involved the immersion of the metal hydride alloy in a solution of KOH 0.5 M containing 10^{-2} M of Pt for 2 h. 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) coupled to a ZEISS LEO 440 microscope and X-ray diffraction (XRD) conducted using a Rigaku RU200B X-ray diffractometer with Cu K_α radiation source. Normal (TEM) and high resolution transmission electron microscopy (HRTEM) images (JEOL JEM 2100F) of the alloy particles were obtained so to characterize the alloy micro- and nano-structures.

Working electrodes were prepared in two different configurations: (1) A rotating glassy carbon disc with a thin porous coating structure was prepared using an aqueous suspension containing 300 mg of the alloy and 0.5 mL of Nafion 0.05 wt.%. Next, 15 μL of this suspension was placed on a glassy carbon disc of a rotating electrode embedded on a Teflon holder. The coated layer was allowed to dry under ambient conditions. (2) A conventional flag-type structure was prepared by using a mixture of 50 mg of the AB₅-type hydrogen alloy powders ($\leq 50 \mu\text{m}$) and 50 mg of the carbon Vulcan XC72R with 35 wt.% polytetrafluoroethylene; this mixture was smeared onto a $2 \text{ cm} \times 2 \text{ cm}$ nickel screen to which a nickel wire was welded as current collector [12]. These two electrodes will be designated here as TPC and FLAG, respectively. The TPC electrode was used primarily to explore its rotating feature to characterize if the electrode reaction involves species in solution (dissolved hydrogen, borohydride) or inside the metal hydride alloy electrode (hydride).

A single compartment cell was employed when using the TPC electrode, while a two-compartment cell was used for the electrochemistry measurements involving the FLAG

Download English Version:

<https://daneshyari.com/en/article/7723043>

Download Persian Version:

<https://daneshyari.com/article/7723043>

[Daneshyari.com](https://daneshyari.com)