



# Corrosion degradation of powder composite hydride electrodes in conditions of long-lasting cycling



Henryk Bala\*, Martyna Dymek

Department of Chemistry, Czestochowa University of Technology, 42-200 Czestochowa, Poland

## HIGHLIGHTS

- Hydride material capacity fade with cycling obeys first order reaction decay law.
- Encapsulation of La(Ni,Co)<sub>5</sub> particles with Ni–P improves the electrode stability.
- Ni–P coatings improve the hydride material charge/discharge kinetics.

## ARTICLE INFO

### Article history:

Received 26 June 2015

Received in revised form

4 October 2015

Accepted 13 October 2015

Available online 23 October 2015

### Keywords:

Intermetallic compounds

Coatings

Electrochemical properties

Corrosion

## ABSTRACT

The LaNi<sub>4.5</sub>Co<sub>0.5</sub> hydrogen storage material degradation process in 6 M KOH solution fulfills first-order chemical reaction kinetic law. After ca 10 first cycles, up to  $N = 45$  cycle, the logarithm of discharge capacity linearly decreases with cycle number. The slope of  $\log Q_{\text{disch}} = f(N)$  straight lines is a measure of degradation rate constant ( $k_{\text{degr}}$ ). Corrosion rate of the tested material is directly proportional to  $k_{\text{degr}}$ . The LaNi<sub>4.5</sub>Co<sub>0.5</sub> powder encapsulation with electroless Ni–P is prone to evident increase of the hydride electrode corrosion resistance. Additionally, encapsulation improves the charge/discharge kinetics: the exchange currents of H<sub>2</sub>O/H<sub>2</sub> system are 20% greater for the chemically treated powder.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

One of the most serious disadvantages of LaNi<sub>5</sub>-based hydrogen storage materials is their poor corrosion resistance in aqueous solutions, including strong alkaline environments, typical for NiMH batteries. The enormous sensitivity of these alloys to corrosion is caused by presence in their composition of ca 32 mass% of lanthanum – highly electrochemically active element, the standard potential of which is  $E_{\text{La}^{3+}/\text{La}}^0 = -2.52 \text{ V}$  [1,2]. There exists plenty of publications dealing with kinetics of deterioration of the lanthanum- and other rare-earth containing alloys in alkaline media. In a series of recent papers of our team [3–8] we describe our attempts to corrosion problems of hydrogen storage materials, with special attention focused on electrochemical charge/discharge characteristics. It is well known that hydrogen storage material parameters undergo continuous deterioration with electrode

cycling, so the capacity fade vs. long-lasting cycling should act as a convenient measure of actual material stability. The capacity fade was being observed as a function of large amount of charge/discharge cycles (up to  $N = 100$ –500 cycles) by many authors (e.g. in Refs [9–14]). Unfortunately, because of rather low reproducibility of these results as well as uncertainty of real active material surface, there is hard to define the electrode material corrosion rate on the basis of these investigations. First of all, however, the theoretical appearance of mathematic relationship of the electrode capacity ( $Q_N$ ) vs cycling (cycle number,  $N$ ) is not obvious and not settled. In particular, in most of papers one can find mainly linear- and exponential types of  $Q = f(N)$  dependences.

According to Durairajan et al. [15,16], electrode cycling releases degradation of hydride alloy (LaNi<sub>4.27</sub>Sn<sub>0.24</sub>) particles which manifests itself by further powder material pulverization and the mean particle size linearly or exponentially decreases with cycle number (up to ca  $N = 60$  cycles). In first approximation, the  $Q_N = f(N)$  relationship was linear in the cited papers, with a slope of 1–2 mA h g<sup>-1</sup> per cycle, depending of initial particle size. The authors found [15,16] that particle encapsulation with cobalt was

\* Corresponding author.

E-mail address: [hbala@wip.pcz.pl](mailto:hbala@wip.pcz.pl) (H. Bala).

prone to strong decrease of the capacity fade – the encapsulation markedly inhibited the degradation phenomenon.

Souza and Ticianelli [17] found linear- or exponential type capacity fade with cycling (60–120 cycles) for a series of LaNi<sub>5</sub>-based alloys doped with 5 at% of Sn, Al, Mn or Pd and for the linear  $Q = f(N)$  segments the  $dQ/dN$  slope was 0.7–1.8 mA h g<sup>-1</sup> per cycle.

The linear capacity fade with fairly low slope ( $dQ/dN$ , ca 0.1–0.3 mA h g<sup>-1</sup> per cycle), has been found (up to 170 cycles) by Notten and Hokkelling [18] for La(Ni,Co)<sub>5</sub> double phase alloys doped with 1.7 at% of Si.

Nearly linear  $Q = f(N)$  relationship has been found by Ferey et al. [19] for (La,Mg)<sub>5</sub>Ni<sub>19</sub> electrode. After first 2–4 cycles, the capacity fade became practically linear (up to  $N = 280$  cycles) with a  $dQ/dN$  slope of ca 0.8 mA h g<sup>-1</sup> per cycle.

Linear capacity fade has also been observed by Ye et al. [12] for a series of mischmetal (Mm) based alloys with different Ni content, of MmNi<sub>x</sub>(Co,Mn,Al)<sub>1.5</sub> stoichiometry. The authors observed rectilinearity of  $Q = f(N)$  dependence up to 500 cycles with exceptionally low  $dQ/dN$  decay rate, equal to 0.08–0.16 mA h g<sup>-1</sup> per cycle.

Reilly et al. [13] presented similar capacity fade curves for analogous type of materials and in most of cases they found rectilinear relationships of capacity versus cycle number (up to  $N = 400$  cycles). It must be mentioned however, that for alloys without Co-additions the dependence was exponential with high decay rate. Also Adzic et al. [11] registered linear  $Q = f(N)$  plots and assumed the  $dQ/d(\text{cycle})$  derivative to be a measure of corrosion rate (expressed in mol%/cycle). The authors determined the  $dQ/d(\text{cycle})$  derivative to be mostly between 0.1 and 0.5 mA h/(g cycle) for a series of (La,Ce)M<sub>5</sub> type alloys.

Looking critically at the assumption that the theoretical  $Q = f(N)$  dependence is linear, one should take into account that for the most common capacity loss [of the order of 1 mA h g<sup>-1</sup> cycle<sup>-1</sup>], the virtual capacity of the best hydrogen storage alloys should be reduced to zero after roughly 300 cycles.

Among the authors who observed exponential capacity fade with cycling one should mention Willems [9] and Belgacem et al. [20]. In his pioneering work [9], Willems showed that  $Q$  decreased with cycle number exponentially (up to  $N = 300$ –350) both for LaNi<sub>5</sub> (charge/discharge rate:  $-1.25C/+1.25C$ ) and LaNi<sub>4</sub>Cu ( $-2C/+2C$ )<sup>1</sup> alloys and a general mathematical fit for this dependence (the symbols are changed here so that they were consistent with further considerations) was as follows:

$$Q_N = Q_0 \exp\left(-\frac{N}{N^*}\right) \quad (1)$$

where  $Q_0$  denotes a theoretical storage capacity at given temperature (for LaNi<sub>5</sub> at 25 °C it equals 371 mA h/g [9]),  $N$  is a cycle number and  $N^*$  – a constant that reflects the decay rate (the author regards it as a stability constant).

Similar, evident exponential relationship is presented by Belgacem et al. [20] for LaY<sub>2</sub>Ni<sub>9</sub> electrode (it has been obtained at  $-0.1C/+0.1C$  rate and up to ca 100 cycle; for later cycles however, the  $Q_N$  becomes nearly constant). Of course, the strictly exponential (similarly as the linear) plots do not occur at some of initial cycles because the material is not fully activated, especially at high charge/discharge rates [9].

It should be noted that exponential type of discharge capacity fade is common not only for hydride batteries. It also occurs for

many other batteries with aqueous electrolytes [21], including lithium-ion batteries [22], particularly at high discharge rates (2C, 3C etc.) [23].

The porous, powder composite electrodes of LaNi<sub>5</sub> type undergo corrosion degradation in aqueous alkaline solutions principally as result of cycling and this process is very much complex and of complicated nature [3,4,10]. It includes oxidation of metallic constituents [4,5,11,24], active surface development (mainly due to crystal lattice expansion/contraction) [6] and mechanical degradation of the hydride alloy material [13,25]. Additionally, due to limited chemical stability in strong alkaline solutions, the applied modifying additions (binders and conducting powders) also undergo corrosion in strong alkaline solution in the course of long-lasting cycling which cause mechanical deterioration of the composite electrode structure, particle crumbling etc. [26]. Another words, after ca 100 cycles (or even earlier) the electrode degradation rate starts to depend on chosen powder consolidation method.

Certain alloying elements (e.g. Co or Fe) enhance hydride material cycle life possibly owing to reduction of lattice expansion/contraction occurring during the hydrogen absorption/desorption [13,25]. However, such elements as Co, Fe or Mn decrease electrochemical discharge rate because they modify the oxide passive layer and are slowing the hydrogen diffusivity through it [25,27].

As it results from thermodynamic considerations [2,3], at potentials corresponding practical battery use (i.e.  $-1.3$  to  $-0.6$  V vs HgO/Hg), at ambient temperatures and in strong alkaline solutions lanthanum forms very stable oxide/hydroxide deposit (equilibrium potential of La(OH)<sub>3</sub>/LaH<sub>2</sub> couple at pH = 14 is  $-1.73$  V (i.e.  $-1.83$  V vs HgO/Hg) [2,10]) whereas nickel forms oxide/hydroxide phases, most probably of NiO·H<sub>2</sub>O formula. The Ni(II) hydroxide slightly dissolves in concentrated KOH solution to produce HNiO<sub>2</sub><sup>-</sup> ions (the theoretical equilibrium activity of these ions is at pH = 14 on the order of 10<sup>-4</sup>) [1,2].

Calculations and observations show that NiO·H<sub>2</sub>O reduces to Ni at  $E < -0.81$  V (vs HgO/Hg) in 6 M KOH [3–5]. Accordingly, one may expect oxidation of Ni during electrode discharging and oxide/hydroxide phase reduction during electrode charging. These expectations have been confirmed for LaNi<sub>5</sub> powder composite electrode by thorough analysis of charge/discharge plots at some initial cycles ( $N = 1$ –10) [3–5]. As a consequence, during LaNi<sub>5</sub>-type electrode cycling, nickel undergoes “reversible corrosion”: Ni oxidizes in anodic route of given cycle but the oxidized phase, being in contact with the active alloy particle, easily reduce in cathodic route. Thus, the nickel (II) oxides/hydroxides do not accumulate in the electrode material as a result of corrosion unless they lost electrical contact with the metallic substrate. Contrary to nickel, lanthanum oxidizes spontaneously (both during charging and discharging) with a comparatively slow rate (to produce La(OH)<sub>3</sub>) and this process runs irreversibly. As a result, lanthanum hydroxide accumulates in the electrode as its corrosion product. The consequences of La oxidation on capacity are negligible for some initial cycles. They appear visible after long-lasting cycling and their resulting reflection is just the capacity fade.

The role of increasing formation of La(OH)<sub>3</sub> during prolonged cycling has been also discussed in many other papers [6,9,18]. Permanent oxidation of lanthanum during electrode performance and surface passive layers enrichment with La(OH)<sub>3</sub> deteriorates not only capacity but also hydrogen transport and catalytic properties of the electrode material. As a consequence, the atomic hydrogen transport across the particles is slowed down and decrease of H<sub>2</sub>O/H<sub>2</sub> exchange current density appears with cycling. The impenetrable passive layers on metal hydride particles strongly inhibit the vital electrode processes. Although passivation favors corrosion protection of numerous metallic substrates [28,29], in case of metal storage alloys the presence of La(OH)<sub>3</sub>-rich passive

<sup>1</sup> For rechargeable batteries the anode discharge with 1C rate conventionally equals to theoretical capacity of the anode material divided by 1 h. For example, in case of LaNi<sub>5</sub> type intermetallics, the hydride capacity of fully hydrogenated material (LaNi<sub>5</sub>H<sub>6</sub>) is 372 mA h g<sup>-1</sup>, thus 1C = 372 mA g<sup>-1</sup>, 0.5C = 186 mA g<sup>-1</sup>, etc.

Download English Version:

<https://daneshyari.com/en/article/1521003>

Download Persian Version:

<https://daneshyari.com/article/1521003>

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