Study of metal hydride electrodes for Ni-MH batteries by acoustic emission

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Abstract

The study of the pulverization of metal hydride (MH) electrodes is essential for optimizing their performance in Ni-MH batteries. In this context, in-situ monitoring of the pulverization of MgNi and LaNi₅-based alloys have been studied during their charge by coupling acoustic emission and electrochemical measurements. In both alloys, two populations of acoustic signals were detected during their charge: (i) a P1 population related to the MH particle cracking and characterized by short rise time (<30 µs) and duration (<100 µs), high amplitude (up to 70 dB), energy (up to 100 eu) and peak frequency (250-350 kHz) and (ii) a P2 population due to the formation of H₂ bubbles and characterized by long rise time (up to 200 µs) and duration (up to 250 µs), low amplitude (<40 dB), energy (<20 eu) and peak frequency (80-150 kHz). By comparing the P1 activity on both materials as a function of the charge input, it was shown that the pulverization phenomenon becomes significant from a much lower charge input for the LaNi₅-based electrode (50 mAh g⁻¹) than for the MgNi electrode (350 mAh g⁻¹), which correspond to an absorbed H-content of 0.19 and 1.30 wt.%, respectively.

Introduction

The nickel-metal hydride (Ni-MH) battery is one of the most attractive power sources for various applications, including hybrid electric vehicles (HEVs), thanks to their good overall performance, safety and environmental friendliness [1]. However, the Ni-MH battery is now being supplanted by the Li-ion battery due to its higher energy density. Therefore, in order to compete with the Li-ion battery and target the emerging EV and HEV market, initiatives must be taken to increase the energy density of the Ni-MH battery, especially through the development of new metal hydride (MH) electrodes.

Presently, LaNi₅-based alloys are mostly used as MH electrodes in commercial Ni-MH batteries. They are multicomponent systems with a composition such as (Mm)(Ni-Co-Mn-Al)₅ where Mm is a mixture of rare earths (La, Ce, Nd, Pr). The various substituents for La and Ni stabilize the electrode during charge/discharge cycling by reducing the alloy expansion and/or forming protective surface films [2]. However, such materials have a rather low gravimetric capacity (ca. 300 mAh g⁻¹) and remain expensive. Recently, promising results have been obtained with MgNi-based compounds prepared by mechanical alloying. These materials typically have a maximum capacity of 400-500 mAh/g but they display a very low cycle life, which nullifies their commercial use. However, a significant increase of their cycle life (capacity decay as low as 0.2 % per cycle) was recently obtained by combining an optimal composition (Mg₀.₉Ti₀.₁NiAl₀.₀5), an adequate morphology (particle size >150 µm) and an appropriate control of the charge input [3].

In Ni-MH batteries, the volume expansion of the metal hydride (MH) during the hydrogen absorption reaction (charge) causes its fracture in smaller particles. In the case of LaNi₅-based electrodes, this pulverization leads to their activation by breaking the native surface oxide layer and by increasing the effective surface area of the electrode [4] but it also decreases their cycle life due to the increase of the alloy corrosion rate [5]. In the case of MgNi-based electrodes, this
pulverization phenomenon during the charge/discharge cycles intensifies the irreversible oxidation of the active material by the KOH electrolyte (i.e., formation of Mg(OH)$_2$), which greatly decreases the electrode cycle life [3,6,7].

Therefore, the study of the MH electrode pulverization is fundamental in order to optimize their performance in Ni-MH batteries. In this context, we have recently demonstrated that acoustic emission (AE) techniques coupled to electrochemical measurements can be successfully applied for the in-situ monitoring of the particle cracking of LaNi$_5$ and MgNi based materials upon cycling [8]. In the present paper, the AE signals upon cycling are analyzed in more detail in order to determinate the critical charge input inducing the pulverization of the LaNi$_5$ and MgNi based electrodes.

**Experimental**

An amorphous MgNi alloy obtained by high energy ball milling [6] and a commercial LaNi$_5$-based alloy (MmNi$_{5.68}$Co$_{0.78}$Mn$_{0.36}$Al$_{0.28}$) from Japan Metals and Chemicals Co. were studied. They were mixed with 0.2 g of pure copper and cold pressed on 2 g of pure copper powder into a stainless steel dye of 1.6 cm diameter with a load of 6 tons cm$^{-2}$ for 10 min in order to form a working electrode.

The experimental set-up coupling AE and electrochemical measurements is shown in Fig. 1. The reference electrode and the counter electrode were respectively an Hg/HgO electrode and a nickel wire. The three-electrode cell was monitored by a Voltalab PGZ 301 potentiostat and Voltmaster 4 software. The working electrode was charged at -100 mA g$^{-1}$ for 3 h for LaNi$_5$-based alloy and 5 h for MgNi, and discharged at 20 mA g$^{-1}$ until -0.6 V vs. Hg/HgO. All the experiments were carried out at room temperature in a 6 mol L$^{-1}$ KOH solution.

The AE signals were recorded by a wide band sensor EPA micro 80 (frequency range 175-1000 KHz) and transmitted via an EPA USB Node acquisition card to the computer. For all the experiments, the gain $G$ and the threshold $S$ were fixed at 40dB and 30dB, respectively. The recorded acoustic signals were treated and the waveforms were obtained with AE Win software (EPA). From the acoustic signals, characteristic parameters of the recorded signal were obtained, such as its amplitude $A$, its duration $D$, its rise time $R$, and its energy $E$. Rise time corresponds to the duration between the passing of the first threshold and the maximum signal amplitude. The energy is the integral of the squared amplitude over time of the signal duration and is expressed in term of energy units (eu). One eu means $10^{-14}$V$^2$s, corresponding to $10^{-18}$J at a reference resistor of 10 kOhm. In addition, the fast Fourier transform (FFT) based spectral analysis of the AE signal enables the determination of the peak and barycentric frequencies.
Results and discussions

During the charge of the MH electrode, two populations of acoustic signals can be detected: the first one (labelled $P1$) is attributed to the cracking of the MH particles occurring during the hydrogen absorption reaction (HAR), and the second one (labelled $P2$) is due to the release of $H_2$ bubbles associated with the hydrogen evolution reaction (HER) [8]. No acoustic activity is detected during the discharge step. Fig. 2A shows the typical waveforms and associated power spectra of recorded $P1$ and $P2$ type signals on a MgNi electrode (first charge). The repartition of these two AE populations as a function of their rise time and energy is shown in Fig. 2B. Their respective characteristics are reported in Table 1. $P1$-type signals related to the MH pulverization exhibit short rise time and duration (<30 µs and <100 µs, respectively), high amplitude and energy (up to 70 dB and 100 eu, respectively) and a high peak frequency (250-350 kHz). $P2$-type signals related to the formation of $H_2$ bubbles are characterized by longer rise time and duration (up to 200 µs and 250 µs, respectively), lower amplitude and energy (<40 dB and <20 eu, respectively) and a lower peak frequency (80-150 kHz). Similar results were obtained on the LaNi$_5$-based electrode (not shown).

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<th>Table 1 – Main characteristics of recorded P1 and P2 type AE signals</th>
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Fig. 2 – (A) Typical waveforms and associated power spectra of recorded $P1$ and $P2$ type AE signals on a MgNi electrode (first charge); (B) repartition of the $P1$ and $P2$ populations as a function of their rise time and energy.
The evolution of the electrode potential and the acoustic activity (number of events) of the \textit{P1} and \textit{P2} type AE signals as a function of the charge input are shown in Fig. 3A and 3B for LaNi\textsubscript{5}-based and MgNi electrodes (first charge), respectively.

On the LaNi\textsubscript{5}-based electrode (Fig. 3A), a rapid decrease of the electrode potential (from \textit{ca.} -0.8 to -1.1 V \textit{vs.} Hg/HgO) is observed up to a charge input of \textasciitilde20 mAh g\textsuperscript{-1}. This is only observed during the first charge cycle and it is mainly attributed to the reduction of the native copper oxide layer present on the Cu powder added in the working electrode. No acoustic activity is observed during this period. Then, the electrode potential slowly decreases from \textit{ca.} -1.1 to -1.15 V \textit{vs.} Hg/HgO up to a charge input of \textasciitilde240 mAh g\textsuperscript{-1}. This slow potential evolution is associated with the hydrogen absorption reaction (HAR), leading to the formation of the \textit{β} hydride phase. Additionally, an abrupt increase of the \textit{P1} acoustic activity is observed from a charge input of 70 mAh g\textsuperscript{-1} and becomes much less important for a charge input \(\geq 110\) mAh g\textsuperscript{-1}. Thus, after

\begin{itemize}
  \item \textbf{Figure 3} - Evolution of the electrode potential and the acoustic activity (number of events) of the \textit{P1} and \textit{P2} type AE signals as a function of the charge input on (A) LaNi\textsubscript{5}-based and (B) MgNi electrodes (first charge).
\end{itemize}
subtraction of the initial charge input spent for CuO\textsubscript{x} reduction (20 mAh g\textsuperscript{-1}), the critical hydrogen charge input value inducing a significant cracking of the LaNi\textsubscript{5}-based particles is estimated at 50 mAh g\textsuperscript{-1}. Assuming that the totality of this charge is consumed for the HAR, this corresponds to an amount of hydrogen absorbed into the alloy of 0.19 wt.%. On the basis of typical hydrogen pressure-composition isotherms of LaNi\textsubscript{5}-based alloys [9], this H-content value is close to the minimum hydrogen concentration inducing the conversion of the α solid solution to the β hydride phase. In other words, this tends to demonstrate that the mechanical stress inducing the cracking of the LaNi\textsubscript{5}-based alloy is concentrated at the α-to-β phase transition region. This is in accordance with the study of Notten et al. who demonstrated from in situ XRD investigations on LaNi\textsubscript{5}-based alloys that the discrete α-to-β lattice expansion rather than the total lattice expansion is responsible for the particle cracking [9]. Finally, as seen in Fig. 3A, for a charge input ≥ 240 mAh g\textsuperscript{-1}, the electrode is almost fully charged and then, the potential stabilizes around -1.16 vs. Hg/HgO due to the hydrogen evolution reaction (HER). As a result, an important increase of the \textit{P2} acoustic activity related to the formation of H\textsubscript{2} bubbles is observed.

On MgNi (Fig. 3B), the electrode potential displays a similar evolution to that observed previously on LaNi\textsubscript{5}-based electrode, that is a rapid decrease in the first stage of the charge due to CuO\textsubscript{x} reduction, followed by a slow decrease (from \textit{ca}. -0.97 to -1.06 V vs. Hg/HgO) related to the HAR and then a stabilization associated with the HER when the electrode charge is completed (\textit{i.e.}, for a charge input ≥ 400 mAh g\textsuperscript{-1}). In contrast, the evolution of the \textit{P1} activity with the charge input notably differs from that observed on the LaNi\textsubscript{5}-based electrode. Indeed, a small increase of the \textit{P1} activity is observed around 70 mAh g\textsuperscript{-1} followed by an abrupt and large rise at about 370 mAh g\textsuperscript{-1}. Thus, after subtraction of the initial charge input of 20 mAh g\textsuperscript{-1} spent for CuO\textsubscript{x} reduction, the critical H-charge input value inducing a significant cracking of the MgNi particles is estimated at 350 mAh g\textsuperscript{-1}. This corresponds to an amount of hydrogen absorbed into the alloy of 1.30 wt.% (assuming that the totality of the 350 mAh g\textsuperscript{-1} is consumed for the HAR). This value is much higher than that estimated for the LaNi\textsubscript{5}-based material (\textit{i.e.}, 0.19 wt.%). It may be related to the absence of abrupt α-to-β phase transition in this material due its amorphous structure. Consequently, the mechanical stress related to volume expansion upon hydrogen absorption in amorphous MgNi is expected to be lower and more progressive than for crystalline LaNi\textsubscript{5} alloy. The volume change induced by hydrogen charging/discharging may also be easier to relax with the ball-milled MgNi particles due to their porous morphology [7]. As a result, the MgNi particles are able to maintain a good mechanical stability up to a H-content as high as 1.29 wt.%. On the other hand, as seen in Fig. 3A and 3B, the total number of \textit{P1} events at the end of the charge step is equivalent for the MgNi and LaNi\textsubscript{5}-based alloys (~ 5700 events), which indicates that the intensity of the pulverization phenomenon is equivalent on the MgNi and LaNi\textsubscript{5}-based electrodes. Further experiments are planned to complete this study. For instance, the influence of the particle size (not controlled in the present study), charge rate and cycle number on the \textit{P1} activity will be studied in detail.

**Conclusion**

In this study, the various acoustic emissive phenomena occurring during the electrochemical hydriding of MgNi and LaNi\textsubscript{5}-based alloys were detected and characterized from AE temporal and energetic parameters associated with recorded wave forms. Their analysis made it possible to discriminate the signals generated by the decrepitation of the MH particles and to formulate the acoustic signature related to this type of damage. The correlation between the AE activity related to the MH decrepitation and the electrode charge input permitted to estimate the critical H-content from which significant decrepitation occurs and can thus be regarded as a reference mark in the electrode lifetime estimation.
Acknowledgments

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References