On the Use of the Acoustic Emission Technique for In-situ Monitoring of the Pulverization of Battery Electrodes

Aurélien ETIEMBLE 1,2, Hassane IDRISSI 2, Lionel ROUÉ 1

1 INRS-Énergie, Matériaux et Télécommunications, 1650, bd. Lionel Boulet, Varennes, Québec, J3X1S2 Canada. Tel.: +1 514 228 6985; fax: +1 450 929 8102; e-mail: etiemble@emt.inrs.ca, roue@emt.inrs.ca
2 INSA-Lyon MATEIS CNRS UMR5510, F-69621 Villeurbanne, France Tel.: +33 4 72 43 89 20; fax: +33 4 72 73 87 15; e-mail: hassane.idrissi@insa-lyon.fr

Abstract

Acoustic emission coupled with electrochemical measurements has been successfully applied for the in-situ monitoring of the cracking upon cycling of metal hydride electrodes for Ni-MH batteries and Si-based electrode for Li-ion batteries. This method offers the possibility to characterize the electrode disintegration process depending on the electrode composition and cycling conditions and then, it would become a powerful tool in the evaluation/optimization of new electrode materials for different types of batteries.

Keywords: particle cracking, metal hydride, silicon, Ni-MH battery, Li-ion battery

1. Introduction

In various batteries, the electrode cracking due to the volume variation of the active materials with cycling has a negative effect on the battery durability by accelerating the electrode corrosion by the electrolyte and/or by inducing a loss of electronic connectivity. For instance, for LaNi5-based alloys used as metal hydride materials in commercial Ni-MH batteries, the pulverization phenomenon induces the breaking of the native surface oxide layer and increases the effective surface area of the electrode. This favors the hydriding reaction but it also decreases the MH cycle life by increasing the alloy corrosion rate [1,2]. For Mg-based alloys, which present higher hydrogen storage capacities than the conventional LaNi5-based alloys, the pulverization process intensifies the irreversible oxidation of the active material by the KOH electrolyte. For instance, amorphous MgNi and crystalline MgTi-10% w Pd alloys obtained by high-energy ball milling have a maximum discharge capacity close to 500 mAh/g, but retain less than 50 % and 70 % of it after only 10 cycles, respectively [3,4]. For Li-ion batteries, silicon-based anode appears as an attractive candidate to replaced carbon based anode, thanks to a ten-times higher capacity (3572 mAh/g) and safer behavior than that of graphite electrodes [5]. However, the cracking of the silicon-based anodes due to the important volume variation of the Si particles (up to ~300 %) with lithiation has a negative effect on their cycle life by inducing a loss of electronic connectivity within the composite electrode to be additionally unfavourable to the formation of a stable solid electrolyte interface (SEI) resulting in severe electrolyte degradation at the surface of the Si particles. To date, the study of the electrode cracking in batteries is generally limited to a post mortem examination of the electrode by microscopy. This does not allow a detailed analysis of the cracking process, which can significantly vary depending on the electrode composition and processing, and the charge/discharge conditions. However, we have recently shown that the acoustic emission (AE) technique is a relevant tool for in situ monitoring of the cracking of MgNi and LaNi5-based electrodes for Ni-MH batteries [6,7]. We have demonstrated that MgNi and LaNi5-based alloys present different pulverization mechanisms. It was also shown that the cracking of MgNi increases with the particle size and the charge rate [7]. An new experimental set-up constituted of an electrochemical cell connected to a compression load cell and an acoustic emission equipment was also used to characterize the force and the cracking of LaNi5-based and MgNi electrodes generated by their volume expansion and/or contraction during their cycling [8].
In the present paper, acoustic emission coupled with electrochemical measurements is performed on different metal-hydride electrodes for Ni-MH batteries and on a Si-based anode for Li-ion batteries. It will be shown that this methodology is very effective for determining the main process responsible of their degradation.

2. Experimental

2.1 Metal hydride electrode

A commercial LaNi$_5$-based alloy (MmNi$_{3.68}$Co$_{0.78}$Mn$_{0.36}$Al$_{0.28}$) powder from Japan Metals & Chemicals Co, MgNi and MgTi-10%w Pd alloy powders obtained by high energy ball milling [3,4] were studied as active materials. Here, Mm is a mixture of rare earth elements (La, Ce,...). 0.2 g of active material was manually mixed with 0.2 g of copper powder. The mixture was then cold pressed on 2 g of copper powder at 6 tons cm$^{-2}$ for 10 minutes in a stainless steel die to form a pellet (16 mm in diameter, ~2 mm in thickness), which is used as working electrode.

The experimental set-up coupling AE and electrochemical measurements has been described elsewhere [6]. 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 galvanostat/potentiostat. The working electrode was charged at -100 mA/g for 3 h for the LaNi$_5$-based alloy and 5 h for MgNi and MgTi-10%w Pd. It was discharged at 20 mA/g until reaching -0.6 V vs. Hg/HgO for the LaNi$_5$-based and MgNi alloys and -0.5 V vs. Hg/HgO for MgTi. All the experiments were carried out at room temperature in a 6 mol/L KOH solution. Before the first charge, the potential of the working electrode was maintained at -0.85 V vs. Hg/HgO for a few minutes to reduce the native oxide layer present on the Cu and active material powders.

The AE signals were recorded during cycling by a wideband sensor EPA micro 80 (frequency range 100-1000 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 40 dB and 27 dB, respectively. The recorded acoustic signals were treated and the waveforms were obtained with AEWin and Noesis software (EPA). The AE signals are separated into two classes. The first one, labelled P1, is attributed to cracking of MH particles and the second one, labelled P2, is due to the release of H$_2$ bubbles [6,7]. The temporal and energetic characteristics of the P1 and P2 classes were described in detail in ref. [6].

2.2 Silicon electrode

Pure Si (99.999%, 20 mesh) ball-milled for 20 h with a ball-to-powder ratio of 5:1 using a SPEX 8000 mixer was used as active material, Super P carbon black (CB) as the conductive agent and carboxymethyl cellulose (CMC) as the binder. A mixture of 200 mg of active material + CB + CMC in a weight ratio of 80:12:8 with 0.5mL of citric acid + KOH buffer solution at pH 3 was mixed at 500 rpm for 1 h using a Fritsch Pulverisette 7 mixer. The slurry was tape cast onto a 25 μm thick copper foil and dried for 12 h at room temperature and then 2 h at 100°C in vacuum. Structural and morphological characteristics of the Si powder and electrochemical behaviour of the Si/CB/CMC anode were described in detail in ref. [9].

Two-electrode Swagelok cells were used for the cycling tests performed at room temperature using a VMP3 potentiostat/galvanostat. The cells were assembled in a glove box under argon atmosphere and comprised (i) a 1cm$^2$ disc of composite working electrode containing 0.7 mg ±10% of active material, (ii) a Whatman GF/D borosilicate glass-fiber sheet saturated with the electrolyte (1M LiPF$_6$ dissolved in 1:1 dimethyl carbonate/ethylene carbonate and (iii) a 1 cm$^2$ Li metal disc as the negative and reference electrode. Cycling tests were performed in gal-
vanostatic mode between 1 and 0.005 V versus Li+/Li at a current density of 400 mA/g. AE set-up was identical to that used in Sec. 2.1.

3. Results and discussions

3.1 Metal hydride electrodes for Ni-MH batteries

3.1.1 Electrochemical behaviour

The evolution of the discharge capacity with cycling for LaNi$_{5}$-based, MgNi and MgTi-10%$_{w}$Pd electrodes is shown in Fig. 1. In the case of the LaNi$_{5}$-based electrode, a slight increase of the discharge capacity is observed during the two first cycles. This increase can be attributed to the particle cracking due their volume expansion with hydriding, leading to their activation by breaking the native surface oxide layer and by increasing the effective surface area of the electrode [1]. For the MgNi electrode, the discharge capacity decreases strongly with cycling. This is related to the irreversible oxidation of the active material by the KOH electrolyte (i.e., formation of Mg(OH)$_{2}$), which is intensified by the creation of new surfaces with the particle cracking [3]. For the MgTi-10%$_{w}$Pd electrode, the discharge capacity increases during the two first cycles. This activation is associated with the phase transition from a bcc+hcp initial structure to an fcc phase induced by the hydriding reaction [4]. After the third cycle, the discharge capacity decreases with cycling due to the irreversible oxidation of the active material by the KOH electrolyte as observed for the MgNi electrode.

![Figure 1 - Evolution of the discharge capacity with cycling for LaNi$_{5}$-based, MgNi and MgTi 10%$_{w}$ Pd electrodes](image)

3.1.2. Acoustic Emission Measurements

The evolution of the P1-type normalized acoustic activity (related to the particle cracking) and P2-type normalized acoustic activity (related to the formation of H$_{2}$ bubbles) during the first charge on LaNi$_{5}$-based, MgNi and MgTi-10%$_{w}$Pd electrodes are shown in Figs. 2a and 2b, respectively. Note that no significant acoustic activity was observed during the discharge step (not shown).
Figure 2 - Evolution of the P1-type (a) and P2-type (b) normalized acoustic activities as a function of the charge input on LaNi$_5$-based, MgNi and MgTi-10% Pd electrodes

For the LaNi$_5$-based electrode, an abrupt increase of the P1-type acoustic activity is observed from ~5 to 25 mAh/g (Fig. 2a). Almost no additional P1 events are observed during the rest of the charge period, except at the end of the charge (i.e., from ~260 mAh/g) where a small increase in P1 activity is again observed. This indicates that the mechanical stress inducing the cracking of the LaNi$_5$-based alloy is concentrated at the beginning of the charge, i.e. in the α-to-β phase transition region. This is in accordance with in situ generated stress measurements [8] and in situ XRD investigations [1] on LaNi$_5$-based alloys showing that the volume expansion does not increase linearly with the H-content in the alloy but occurs abruptly when the α-to-β phase transition is initiated.

For the MgNi electrode, the evolution of the P1 activity with the charge input differs notably from that observed for the LaNi$_5$-based electrode. Indeed, a small increase of the P1 activity is observed from ~25 to 100 mAh/g. Then, no P1 activity is detected before reaching a charge input of ~365 mAh g$^{-1}$ where an abrupt and large rise of the P1 activity is observed. At the
same time, an important increase of the P2 acoustic activity related to the release of H\textsubscript{2} bubbles through the hydrogen evolution reaction (HER) is detected as shown in Fig. 2b. These observations demonstrate that the MgNi-particle cracking is mainly induced by the HER rather than by the α-β lattice expansion in contrast to that was previously observed for the LaNi\textsubscript{5}-based electrode. It can be explained by the fact that the MgNi alloy produced by ball milling has an amorphous structure, which results in the absence of abrupt volume expansion during the hydrogen absorption reaction (HAR) [8]. On the other hand, ball-milled MgNi powder is constituted of porous agglomerates made up of many particles cold-welded together. These agglomerates are likely to be broken down by the mechanical stress induced by the accumulation of H\textsubscript{2} bubbles into the agglomerate pores during the HER.

For the MgTi-10\%\textsubscript{w} Pd electrode, no P1 activity is detected before reaching a charge input of ~300 mAh/g where an abrupt and large rise of the P1 activity is observed (Fig. 2a). At the same time, an important increase of the P2 acoustic activity related to the release of H\textsubscript{2} bubbles is detected (Fig. 2b). These observations suggest that the MgTi-10\%\textsubscript{w} Pd electrode pulverization is mainly induced by the mechanical action of the H\textsubscript{2} bubbles as observed for the MgNi electrode. This is not surprising since both materials are elaborated by ball milling and present the same porous agglomerate morphology (not shown).

The evolution of the P1 acoustic activity with cycling on LaNi\textsubscript{5}-based, MgNi and MgTi-10\%\textsubscript{w} Pd electrodes is shown in Fig. 3. On the three electrodes, the P1 activity is maximum during the first charge. This clearly indicates that the pulverization of the LaNi\textsubscript{5}-based, MgNi and MgTi-10\%\textsubscript{w} Pd electrodes mainly occurs during the first charge. Note that the P1 activity is lower for the MgTi-10\%\textsubscript{w} Pd electrode, which may indicate that this alloy is less sensitive to cracking. In addition, the fact that its P1 activity is maximum at the first cycle despite its low H-storage capacity (60 mAh/g, see Fig. 1) tends to confirm that its pulverization is mainly related to HER and not to the HAR.

\includegraphics{figure3}

**Figure 3 - Evolution of the P1 acoustic activity with cycling for LaNi\textsubscript{5}-based, MgNi and MgTi-10\%\textsubscript{w} Pd electrodes**

### 3.2 Silicon electrode for Li-ion batteries

#### 3.2.1. Evolution of the acoustic activity during the first charge (lithiation)

The evolution of the electrode potential and the acoustic activity as a function of the charge capacity during the first lithiation of the silicon electrode are shown in Fig. 4.
During the first lithiation, the electrode potential first decreases quickly to reach a sloping plateau between ~0.15 and ~0.05 V. During this stage, the crystalline Si reacts with lithium to form amorphous SiLi₄ [10]. At the end of the charge (i.e., below ~0.05 V), the crystalline Li₁₅Si₄ phase is formed [10]. Regarding the acoustic activity, a small increase is observed at the beginning of the charge and may be related to surface reactions such as the reduction of the native Si oxides and/or the formation of the solid electrolyte interface (SEI). Then, from a charge capacity of ~600 mAh/g to ~2700 mAh/g, the acoustic activity increases almost linearly and could be associated with the Si particle cracking induced by their volume expansion with lithiation. At the end of the discharge (i.e., at ~0.05 V), an abrupt increase of the acoustic activity is observed, which can be correlated to the formation of the crystalline Li₁₅Si₄ phase [10].

3.2.2. Evolution of the acoustic activity during the first discharge (delithiation)
The evolution of the electrode potential and the acoustic activity as a function of the discharge capacity during the first delithiation of the silicon anode is shown in Fig. 5. An abrupt increase of the acoustic activity attributed to the particle cracking is observed when the electrode potential reaches 0.4 V, corresponding to a discharge capacity of 1100 mAh/g. At this potential, the phase change from crystalline Li₁₅Si₄ to amorphous silicon occurs [10]. This tends to confirm that the electrode degradation is mainly induced by the abrupt volume variation related to the formation and disappearance of the Li₁₅Si₄ phase.

3.2.3. Evolution of the acoustic activity and charge capacity with cycling
The evolution of the acoustic activity with cycling is shown in Fig. 6a. The acoustic activity is maximum during the first charge (lithiation) and discharge (delithiation). Then, the acoustic activity decreases rapidly with cycling to reach less than 50 events per cycle after the third cycle. Similar evolution with cycling is observed for the electrode charge capacity as shown in Fig. 6b. This clearly indicates that the degradation of the silicon electrode mainly occurs during the first three cycles and greatly affects the electrode cycle life. After the third cycle, it is assumed that Si particles have reached a critical size, which limits further particle cracking.
Additional AE study about the influence of the initial Si particle size on their cracking sensitivity will be performed to confirm this issue.

![Graph](image)

**Figure 5 - Evolution of the electrode potential and the acoustic activity as a function of the discharge capacity during the first delithiation of the silicon anode.**

![Graph](image)

**Figure 6 - Evolution with cycling of the acoustic activity (a) and charge capacity (b) of the Si electrode.**

### 3.2.4. Characterization of the AE classes

From the analysis of the AE signals performed using Noesis software, the peak frequency appears as the most discriminating AE parameter. The peak frequency histogram of the AE signals detected during the first 10 cycles on the Si electrode is shown in Fig. 7. Three classes of AE signals can be distinguished. The first one, labelled $P_A$, exhibits peak frequencies between 80 and 250 kHz with a maximum number of events at ~150 kHz. The second one, labelled $P_B$, is characterized by peak frequencies between 250 and 400 kHz with a maximum number of events at ~330 kHz. These $P_B$-type signals also exhibit short duration and high energy. This is characteristic of AE signals related to cracking phenomenon, as observed on metal hydride electrodes [6] and during aluminium exfoliation corrosion [11] or hydrogen embrittlement process [12]. The third AE class, labelled $P_C$, exhibits high peak frequencies, between 500 and 950 kHz. Further investigation using different electrode materials, electrolytes, particle mor-
phology, etc. are planned in order to identify the main sources of these three AE classes and to evaluate their respective influence of the electrode cycle life.

![Figure 7 - Peak frequency histogram of the AE signals detected during the ten first cycles of the silicon electrode.](image)

4. Conclusion

The study confirms that acoustic emission techniques coupled to electrochemical measurements is an effective *in situ* method for studying the pulverization of electrodes for Ni-MH and Li-ion batteries. With metal hydride electrodes for Ni-MH batteries, it was demonstrated that the process inducing the pulverization of MgNi and MgTi-10%Pd produced by ball milling differs notably from that of LaNi$_5$-based material. The pulverization of the latter occurs at the beginning of the charge step and can be related to the abrupt volume change in the $\alpha$-to-$\beta$ phase transition zone whereas for MgNi and MgTi-10%Pd, it is mainly due to the mechanical action of the $\text{H}_2$ bubbles produced at the end of the charge step. On silicon electrode for Li-ion batteries, the AE measurements tend to indicate that the electrode degradation is mainly due to the abrupt volume variation related to the formation (in charging) and disappearance (in discharging) of the crystalline Li$_{15}$Si$_4$ phase.

References