Short communication

Inner pressure characterization of a sealed nickel-metal hydride cell

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ABSTRACT

This paper studies the electrochemical behaviour of the pressure inside a sealed Ni-MH cell due to gases evolved under different charge/discharge currents and states of charge (SOC). The work is focused to determine the best procedure to get fast charge and long cycle life without detrimental effects on the battery and possible hazards affecting the safety of the user. The device was studied under a wide range of charge current (0.1–5 C), establishing that optimum conditions to minimize the inner pressure during uninterrupted use are obtained if either charge rates up to 0.5 C or higher rates not surpassing 90% of the nominal capacity are employed. Charge times corresponding to the range between 80% and 130% of the nominal capacity were also tested, analyzing the effect of overcharges on inner pressure, discharge capacity, efficiency and integrity of the cell. It was verified that charging the cell up to 130% at 2 C rate reaches an inner pressure 5 times higher than that obtained at 0.5 C. High rate discharge was also characterized at uninterrupted use of the cell, demonstrating the importance of the cut-off discharge criterion at high rates, to avoid the inner gases accumulation due to incomplete discharge of electrodes and overcharge in a following electrochemical cycle.

1. Introduction

The active development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) has been accompanied by advances in new batteries that require high technology for energy storage [1]. The energy density requirements for HEV are relatively low; however, specific power and power density requirements are very high. In addition, the modality of fast charge and working in a wide range of temperature (0–60 °C) are requirements technically necessary for HEV application [2,3].

The nickel-metal hydride (Ni-MH) battery is very competitive to be used as power source for HEV because it has high specific energy, high-power capability, inherent safety, design flexibility and it is environmental friendly [4–10]. In commercial Ni-MH batteries, the relative amounts of electrochemically active materials employed in the fabrication of the positive and the negative electrodes are usually so determined that the charge–discharge capacity of the battery is "positive-electrode limiting" [10,11].

Due to the electrochemistry of Ni-MH batteries, fast charge is a technologic challenge because it may lead to a remarkable increase in pressure inside a sealed cell. Overcharging Ni-MH batteries also causes the internal gas pressure to increase. This pressure increase is due to hydrogen evolution at the surface of the negative electrode and oxygen evolution at the surface of the positive electrode [12], as shown in the following equations for negative and positive electrodes respectively:

$$4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- \tag{1}$$

$$4OH^- \rightarrow 2H_2O + O_2\uparrow + 4e^- \tag{2}$$

Nevertheless, in positive-electrode limiting batteries, the negative electrode has a sufficient reserve charge and thus hydrogen evolution on the electrode may not be a major issue. In addition, the oxygen generated on the positive electrode at the end of the charging process and during overcharging [13] can move through the separator and be transformed to water on the surface of the negative electrode by the following recombination reaction:

$$4MH + O_2 \rightarrow 4M + 2H_2O \tag{3}$$

This reaction avoids the inner pressure build up. However, it may increase if the electrodes are seriously deteriorated and the recombination process (as suggested in Eq. (3)) does not work properly [11,14,15]. For this process, the oxygen generated at the positive electrode diffuses principally through the empty spaces in the separator toward the negative plate [16]. Since the oxygen diffusion in the electrolyte is slow and its solubility low, the hydrogen and oxygen recombination process is very closely related to the amount of electrolyte [2,17]. The overall diffusion coefficient of oxygen will vary according to factors such as the separator saturation level and

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tortuosity, showing optimal oxygen transport at electrolyte saturation level of the separator between 20% and 30% [16]. When the electrode assembly is over wetted, the recombination process is slow, an indication that the electrolyte is a barrier for the oxidation reaction [17]. However, if the electrolyte inside Ni-MH cells is excessively reduced, the internal resistance will rise and the charge efficiencies are lowered, leading to performance deterioration of Ni-MH cells. Hu et al. [2] showed that after opening a sealed Ni-MH cell, subjected to many cycles at elevated temperatures and long-term overcharges, and putting it into an electrolyte container, a significant reduction of the charge voltage and an increase of discharge voltage were observed, indicating that the electrolyte inside the Ni-MH cells had been at least partly consumed.

In the last few years, many efforts have been made on the research of the inner pressure of Ni-MH batteries [13,18,19]. Yang and Liaw [18,19] have characterized a Ni-MH module with a nominal capacity (C_n) of 85 Ah under certain fast charge conditions and found that internal pressure of the cell is the most critical parameter to be controlled for fast charge processes under safe operation. Shi et al. [14] confirmed the hydrogen gas evolution from an MH electrode during overcharges in a laboratory-made cylindrical 8 Ah Ni-MH battery, and proposed a temperature-dependent pressure model to investigate the kinetics of hydrogen evolution during fast charge. Cha et al. [3] studied the behaviour of a sealed Ni-MH system regarding its ability to consume gaseous products generated during the overcharge stage. They found that the internal pressure of sealed Ni-MH cells can be kept under control if the current rate is not too high, and if there is sufficient excess charging capacity in the negative electrode. Zhang et al. [11] found that the pulse charging technique is an effective approach to reduce the internal pressure of the battery and to extend the battery cycle life.

The aim of this work is to characterize the inner pressure produced by gas evolution in a laboratory-made sealed Ni-MH cell. For this purpose, electrochemical charge and discharge of the cell were monitored under different current rates and states of charge, looking for optimum conditions of use considering performance, efficiency and safety.

2. Experimental procedure

LmNi$_4$Co$_{0.31}$Mn$_{0.31}$Al$_{0.42}$ (Lm = lanthanum rich mischmetal, 84 wt% La, 8 wt% Ce, balance other elements) intermetallic alloy was used as the active material of the negative electrodes. It was obtained using an induction furnace, by melting the constitutive elements inside a boron nitride crucible, under an inert atmosphere (Ar). In order to ensure the alloy homogeneity, the sample was re-melted twice during the fabrication. For the negative electrode preparation, 100 mg of active alloy were freshly crushed and sieved between a 44 and 74 μm mesh; the resultant particles were then mixed with an equal amount of teflonized black carbon (Vulcan XC-72 + 33 wt% PTFE), as mechanical and conductive supports. This mixture was pressed to 300 MPa within a cylindrical matrix. The electrode obtained was a disk-shaped, of 11 mm diameter and 1 mm thickness. The capacity of the negative electrode, calculated from the specific alloy capacity previously determined (314 mAh g^{-1} [20]) and the alloy mass, was 31 mAh approximately.

The positive electrode used in measurements was provided by INIFTA (La Plata, Argentina). It is a commercial Ni(OH)$_2$ electrode for aerospace use, with a capacity of 20 mAh, since the specific capacity of the positive electrode is 143 mAh g^{-1} [21], and the mass of the sample was tailored to 140 mg. Thus, the capacity of the negative electrode was 55% in excess over the positive electrode, confirming a "positive-electrode limiting" cell working condition. The final dimensions of the parallelepiped electrode were 8 mm × 8 mm × 0.74 mm.
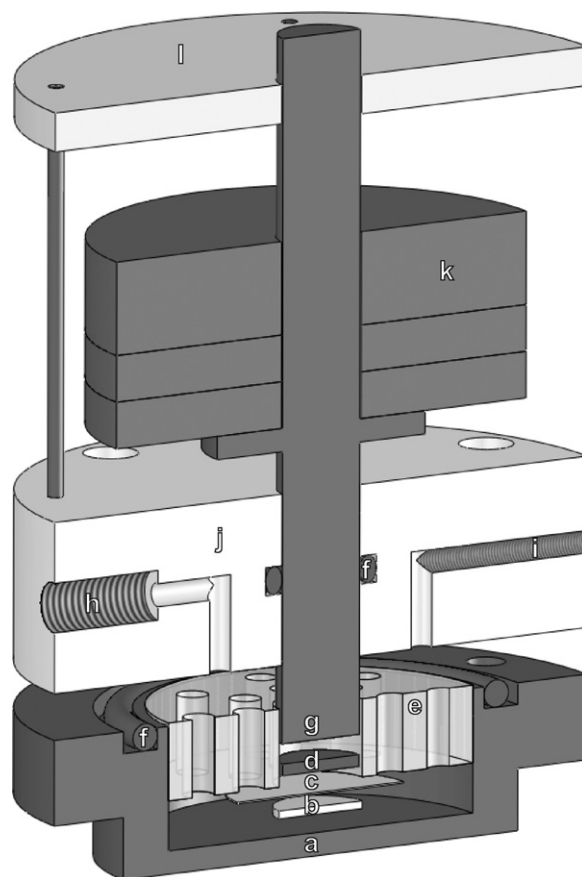

Fig. 1. Cross-section of cell used: (a) metallic base; (b) positive electrode; (c) separator; (d) negative electrode; (e) nylon piece for electrodes centring; (f) O-ring; (g) metallic piston; (h) duct for pressure transducer; (i) duct for purge; (j) nylon top; (k) masses for electrode compaction; (l) guide for piston.

The separator of the cell was a piece of woven roving glass-based material (RT200) provided by the Saint-Gobain Vetrotex Company, composed of E glass type, with a thickness of 150 μm and 204 g m^{-2} specific weight. The dimensions of the separators were adjusted to ensure insulation of the electrodes in the assembly.

Fig. 1 shows a cross-section of the cell used for electrochemical measurements [22]. It mainly consists of a metallic structure containing a moulding for the battery elements, i.e., electrodes, separator, electrolyte. The top of the system is composed by a cap and a metallic piston. Two O-rings seal the battery compartment and two ducts are placed for installing a pressure transducer and a screw for inner pressure purge. The electric path to the electrodes goes through the metallic base for the positive electrode and through the metallic piston for the negative electrode.

For electrochemical characterization, the electrodes and the separator assembled inside the cell were flooded with a concentrated solution of KOH 8 M as electrolyte, avoiding deterioration of cell performance by electrolyte consumption, but also working with a saturation level of the separator of nearly 100%. The electrochemical charge–discharge measurements on all experiments were performed at 23 °C, with an own laboratory developed galvanostat.

Table 1 shows some parameters of electrodes and electrolyte used in this work and compare them with those used by other researchers. It shows that the thickness of the positive electrode and separator of our setup configuration are similar to those used by other researchers in Ni-MH batteries. However, the negative electrode thickness is greater than the one used by other authors. This is due to the fabrication process because electrodes used in commercial developments are generally prepared by pressing solely