# Self-discharge characteristics of a metal hydride electrode for Ni-MH rechargeable batteries

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## Abstract

The factors that affect the self-discharge characteristics of a metal hydride (MH) anode are investigated, which include the state of charge (SOC), temperature, storage time and microencapsulation of the alloy with a thin copper (Cu) layer. It is found that the self-discharge rate of the MH electrode decreases with decreasing temperature and storage time. Microencapsulation of the alloy with a thin Cu layer is found to greatly decrease the self-discharge rate. Also, it is found that the self-discharge rate of the Ni-MH cells is not correlated with SOC. It is believed that the main mechanism for the self-discharge of the Ni-MH cells is related to the hydrogen release from the MH anode.
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## 1. Introduction

Nickel-metal hydride (Ni-MH) rechargeable batteries have been attracting considerable attention because they offer several advantages over conventional lead–acid and nickel–cadmium batteries [1,2], e.g., high-energy density, no concentration change of the electrolyte, the capability of overcharging and overdischarging, and the absence of poisonous heavy metals. However, the self-discharge rate is relatively higher than that of the Ni–Cd batteries [3], which should be certainly disadvantageous for practical applications. The self-dischargeability is an important property for the unloaded condition of the batteries and self-discharge rate must be as low as possible for practical applications.

Several researchers have investigated the self-discharge mechanism of Ni-MH batteries. It has proposed that self-discharge of Ni-MH batteries [4–7] is caused by (1) the reaction of the residual hydrogen in the cell with the positive electrode; (2) the slow decomposition of both electrodes; and (3) the shuttle effect of impurity ions (such as nitrates) from the separator or sintered positive electrode. It has also been proposed that the main mechanism for the self-discharge of Ni-MH batteries is attributed to the desorption of hydrogen from the MH anodes [4].

In this work, the self-discharge behavior of a MH alloy is investigated, which includes the effect of state of charge (SOC), temperature, storage time and microencapsulation of alloy powder with copper (Cu). The self-discharge mechanism of the MH alloy is discussed in the view of hydrogen desorption or release from the MH electrodes. The purpose of the present research is to get a guideline for the improvement of the self-dischargeability.

## 2. Experimental details

The $LaNi_{4.7}Al_{0.3}$ alloy was obtained from Ergenics (Hy-stor 207). It was first mechanically pulverized to a particle size of around 40–60 μm and then was electroless-coated

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with Cu to 9.0%. The Cu plating is done by immersing the alloy powder in an aqueous acid bath containing only $CuSO_4$ ($0.16\,g\,ml^{-1}$) and $H_2SO_4$ (pH=4–5). The coating is easy to apply without the need for any pretreatment of air-exposed alloys. The negative electrode with the 9% Cu-coated powders was made by mixing the alloy power (the weight of the alloy powder with Cu-coating was 70.00 mg and the un-coated $LaNi_{4.7}Al_{0.3}$ alloy was 63.70 mg) with nickel powder (63.70 mg). Thus the weight ratio of active material to nickel powder is 1:1. A polytetrafluoroethylene (PTFE) dispersion (4 wt%) was added to the mixture as a binder. The mixture was filled into a porous nickel foam plate with a diameter of 1.0 cm, and was then pressed at a pressure of 500 MPa for 2 min into a sheet of 0.5 mm thickness.

A sintered glass apparatus with three compartments was used for the electrochemical charge/discharge experiments. The negative electrode was placed in the central compartment and two nickel positive electrodes ($Ni(OH)_2/NiOOH$) were placed on either side. The hydride electrode and counter electrode were separated by a porous frit. The experimental apparatus was set in a water bath at controlled ($\pm0.5$ K) temperatures ranging from 298 to 308 K. The charge/discharge and polarization tests were conducted using a Solartron 1285 Potentiostat with Corrware software. The emphasis of these charge/discharge tests of the cells was on the electrochemical stability of the negative electrode. Thus, the capacity of the positive electrode was designed to be sufficiently higher than that of the negative MH electrode to avoid cathode limitation. The electrolyte was a 6 M KOH aqueous solution. A Hg/HgO/6 M KOH electrode was used as a reference electrode. A Luggin capillary tube, which connected to the reference electrode and working electrode, was placed close to the working electrode in order to minimize the ohmic drop across the electrolyte solution.

After an activation treatment, which involved 8 charge/discharge cycles, the MH electrode was charged at a constant current ($100\,mA\,g^{-1}$) until the hydrogen concentration reached its saturated value and discharged at a constant current density ($100\,mA\,g^{-1}$) to a cutoff potential of $-0.6$ V versus Hg/HgO after 5 min resting time.

## 3. Results and discussion

### 3.1. Determination of self-discharge rate

The rate at which a battery loses its power in an open circuit condition is called the self-discharge rate. The self-discharge rate is usually calculated from the lost discharge capacity after 2 days storage of fully charged MH electrodes to maximum discharge capacity after the activation by repeated charge–discharge cycling

$$\text{Self-discharge rate (\%)} = \frac{C_{max} - C_{ret}}{C_{max}} \times 100\%, \qquad (1)$$



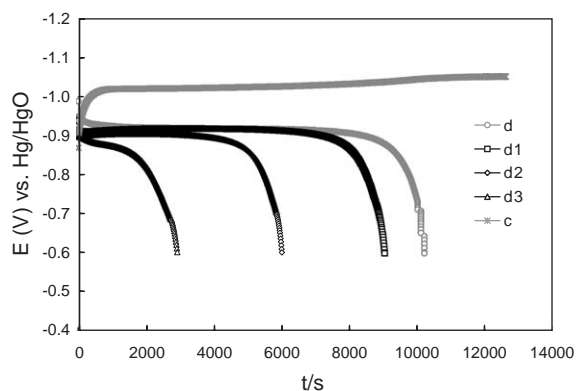Fig. 1. Charge and discharge curves of Cu-coated $LaNi_{4.7}Al_{0.3}$ alloy electrodes at different states of charge (SOC) at 25 °C (charge: 100 mA/g for 3.5 h, discharge: 100 mA/g to $-0.6$ V). (c) charge 100 mA/g for 3.5 h, (d) charge, then completely discharge, (d1) charge for 3.5 h (SOC = 100%), store for 2 days, and then completely discharge, (d2) charge for 3.5 h, discharge 3400.3 s (SOC = 66.7%), store for 2 days, and then completely discharge, (d3) charge for 3.5 h, discharge 6800.7 s (SOC = 33.3%), store for 2 days, and then completely discharge.
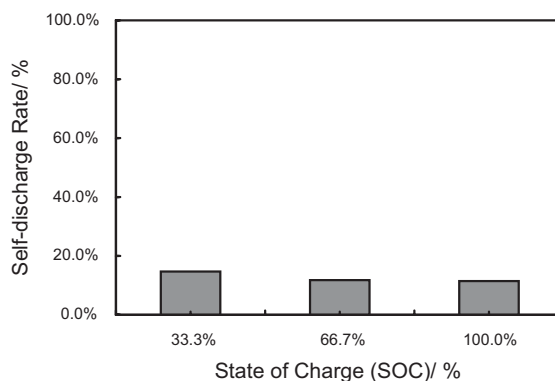


Fig. 2. Variation of self-discharge rate with state of charge (SOC) for the Cu-coated $LaNi_{4.7}Al_{0.3}$ alloy electrode at 25 °C.

where $C_{max}$ is the maximum discharge capacity at a discharge current density of $100\,mA\,g^{-1}$ and $C_{ret}$ the retained capacity at a discharge current density of $100\,mA\,g^{-1}$, respectively. In order to compare the effect of other storage time (such as 1 month) on the self-discharge behavior, the self-discharge rate is calculated from the capacity loss after that storage time.

### 3.2. Effect of state of charge (initial hydrogen concentration)

Fig. 1 shows the discharge curves of Cu-coated alloy at different SOC (i.e., initial hydrogen concentration in the MH electrode). Fig. 2 shows the effect of SOC on the self-