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# ELECTROCHEMICAL AND IN SITU NEUTRON DIFFRACTION INVESTIGATIONS OF La-Ni-Al-H ALLOYS

by

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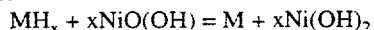
## Introduction

The nickel/metal hydride (Ni/MH) battery is a strong contender to replace the nickel/cadmium battery because of its superior performance, low impedance, and absence of toxic cadmium. However, the present Ni/MH battery is limited by hydrogen management problems associated with charge/discharge operation and self-discharge of the battery and by long-term capacity loss due to corrosion of the MH electrode. Rare earth metal-based alloys such as  $\text{LaNi}_5$ , preferably with the partial substitution of lanthanum or nickel by a small amount of other metal elements, seem to be promising MH materials to improve the stability and capacity of the MH electrodes. However, the role of alloying components is not yet clearly understood. Therefore, a combination of electrochemical and neutron diffraction techniques has been designed to investigate metal hydrides. This combination of the surface and bulk investigation techniques provides a unique tool to study the properties of the alloy electrodes *in situ* with respect to composition, atomic structure, and phase change [1-3].

In this work, several Al-substituted  $\text{LaNi}_5$  alloys were investigated with respect to their specific capacity (measured by mAh/La and symbolized by  $x$  in  $\text{LaNi}_{5-y}\text{Al}_y\text{H}_x$ ), impedance, and cycling stability. In addition to the extensive electrochemical investigations, *in situ* neutron diffraction measurements were performed to characterize the electrochemically induced phase transformation and structure change during charge and discharge of the metal hydride electrodes.

## Experimental

The following simple cell reaction permits simple cell construction.



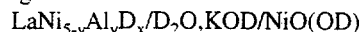
The electrochemical testing was carried out in a three-electrode cell consisting of a commercial  $\text{NiO}(\text{OH})$  positive electrode, a  $\text{Hg}/\text{HgO}$  reference electrode with electrolyte bridge and Luggin capillary, a metal-hydride electrode, and 15% KOH electrolyte. Teflon mesh separator was used between the working and counter electrodes. The alloy powder (Rhône-Poulenc, -400 mesh size) was mixed with 5% carbon (Shawinigan Black) conducting additive and 10% DuPont Teflon 30 suspension and pressed onto an expanded nickel mesh to form 1-mm-thick electrodes.

To investigate the electrochemical performance of the metal hydride electrode, plane-parallel or jelly-roll electrode combinations were used to ensure uniform current density.

The following alloys in this study were investigated:  $\text{LaNi}_5$ ,  $\text{LaNi}_{4.8}\text{Al}_{0.12}$ , and  $\text{LaNi}_{4.4}\text{Al}_{0.6}$ . The electrochemical properties of the metal hydride electrodes, such as capacity, cell voltage, electrode potential,  $\text{ASi}_{30}$ , and cycle-life, were

investigated at room temperature and ambient (1 atm) pressure by interrupted galvanostatic cycling.

A different cell design was used for the *in situ* neutron diffraction measurements because the neutron diffraction measurements are adversely affected by the presence of protons. For these *in situ* experiments, a fully deuterated cell was designed:



To obtain a deuterated  $\text{NiO}(\text{OD})$  electrode, two identical pieces of  $\text{NiO}(\text{OH})$  electrodes removed from  $\text{Ni}/\text{Cd}$  cells were cycled in 15% KOD/ $\text{D}_2\text{O}$  solution for 16-20 cycles. The electrolyte was exchanged every 4 cycles and analyzed by FTIR to determine the H/D ratio in the solution, which indicated the remaining proton content of the  $\text{NiO}(\text{OD})$  electrode. A  $\text{NiO}(\text{OD})$  electrode with an H/D ratio of less than 0.02 was accepted for the neutron diffraction measurements. The cell used in the *in situ* neutron diffraction measurements was constructed in a quartz tube (Fig. 1). The neutron diffraction patterns were recorded simultaneously with the electrochemical data. Neutron diffraction data from these operating cells comprise scattering from four components: the  $\text{LaNi}_{5-y}\text{Al}_y\text{D}_x$  electrode, the Ni mesh support, the electrolyte and the quartz tube. With modern multi-phase analysis techniques, scattering from the electrolyte and quartz tube can be modelled as background, leaving only the crystalline Ni and  $\text{LaNi}_{5-y}\text{Al}_y\text{D}_x$  phases to consider. Rietveld profile refinements provide precise data corresponding to phase identification, deuterium siting, and phase composition as a function of charge/discharge state.

## Results and Discussion

The discharge capacity indicates the change in the value of  $x$  in the formula of metal hydride. Figure 2 shows plots of open-circuit cell voltage versus  $x$  for alloys of three different Al content. The open-circuit cell voltage was measured at the end of 150-second-long current interruptions. In Fig. 2, the data are shown for the fourth charge/discharge cycle. There are distinct differences in the capacities of the MH electrodes.  $\text{LaNi}_5\text{H}_x$  exhibited low specific capacity, while the Al-substituted alloys have dramatically increased cell capacity up to more than 10 times higher than that of the pure  $\text{LaNi}_5$  parent alloy. It is evident from Fig. 2 that higher Al content of the alloy produces higher specific capacity. The low specific capacity of the  $\text{LaNi}_5$  electrode at ambient pressure is mainly due to its inherent nature, which would require a high hydrogen pressure to achieve a higher  $x$  value [4]. The effect of higher Al concentrations on the cell performance improvement can be partly explained by the lowered hydrogen equilibrium pressure requirement of the Al-containing alloys [5]. This behavior can be assessed from the structure analysis of the neutron diffraction investigation.

Subtle crystallographic differences between electrodes containing Al and those without may provide insight into the mechanism. The presence of Al does influence the disposition of deuterium in the  $\text{LaNi}_{5-y}\text{Al}_y\text{D}_x$  phases. Aluminum preferentially substitutes into one of three available crystallographic sites. When no aluminum is present, the maximum amount of deuterium that enters the alloys ( $x < 0.5$ ) is limited to inclusion in the alpha phase. When deuterium is placed into an alloy containing aluminum, the amount of deuterium in the alpha phase remains constant, while the extra deuterium enters the beta phase. Results correlate with electrochemical measurements of  $x$ .

The stability of the selected hydride alloys was studied by electrochemical cycling. Figure 3 shows plots of specific capacity (as  $x$  value) of the three investigated alloy compositions versus the cycle number for cycles 1-20. The  $\text{LaNi}_5$  electrode has low, but very stable, capacity. The  $\text{LaNi}_{4.4}\text{Al}_{0.6}$  alloy electrode has the highest capacity ( $x \leq 4.4$ ) with a relatively small drop. The alloy with a low concentration of Al,  $\text{LaNi}_{4.87}\text{Al}_{0.12}$ , however, has a rather poor stability indicated by a large capacity decay. One possible reason for this behavior is the selective dissolution of aluminum. Analysis of the electrolyte solutions from the cells indicated the presence of dissolved aluminum. Electrolytes from cells made with the  $\text{LaNi}_{4.87}\text{Al}_{0.12}$  alloy contained 5 ppm Al after 12 cycles, 14 ppm after 29 cycles. Lanthanum was not detectable in these electrolytes. The higher concentration of Al in the  $\text{LaNi}_{4.4}\text{Al}_{0.6}$  alloy, however, can compensate for the corrosion loss of Al for a longer time than in the case of the  $\text{LaNi}_{4.87}\text{Al}_{0.12}$  alloy. Thus, electrodes with higher Al content have longer cycle life. These experiments show that the Al-alloying component is very important to produce a high specific capacity, but, also increases the sensitivity to corrosion. Surface modification of the alloy particles or introduction of other corrosion-suppressing alloying elements are necessary to achieve longer cycle life.

To explain the variation in electrochemical performance among the Al-containing alloys, the *in situ* neutron diffraction data were analyzed to gain insight on relationships between structural and electrochemical phenomena of these alloys. Preliminary results show correlations between electrochemical measurements and neutron diffraction refinements for endmember states.

#### Acknowledgment

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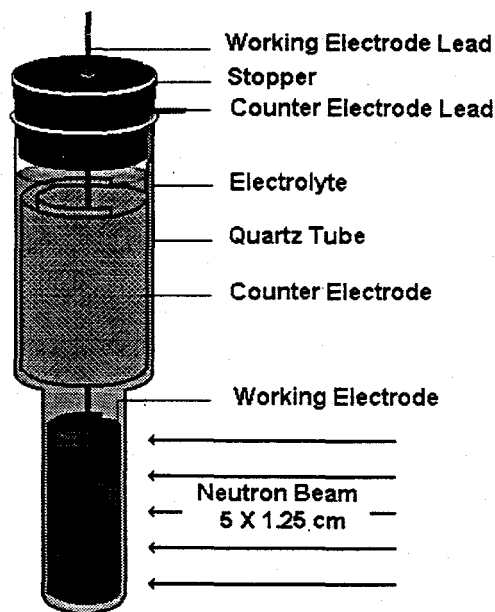


Fig. 1 Schematic diagram of the electrochemical cell for *in situ* neutron diffraction measurements.

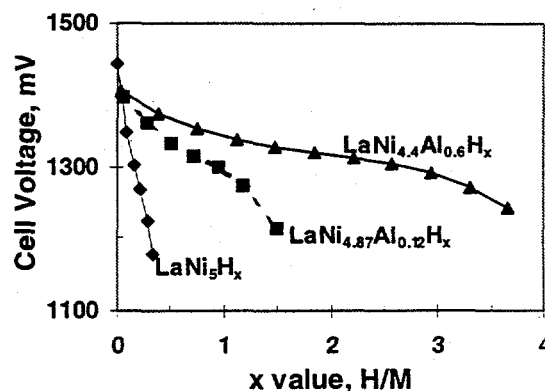


Fig. 2 Open-circuit voltage for  $\text{MH}_x/\text{NiO}(\text{OH})$  cells as function of discharge capacity.

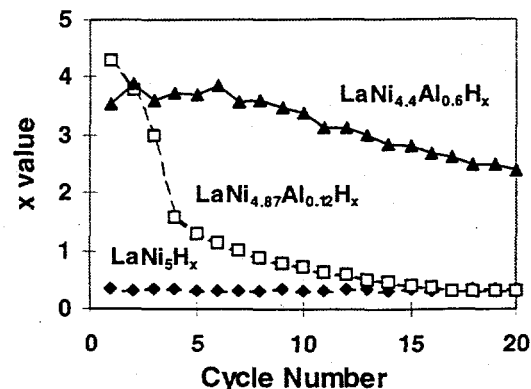


Fig. 3 Cycling behavior of the La-Ni-Al-H alloys for three aluminum composition.