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Relationship between composition, volume expansion and cyclic stability of AB_5-type metalhydride electrodes

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Abstract

Metal hydride alloys as electrode material for battery application contain up to 15 at.% cobalt. Alloys without cobalt show a much shorter cycle life compared to cobalt containing alloys. The mechanism of how cobalt influences the cycle life is still not well understood. The aim of this work is to investigate the influence of cobalt on the properties of the electrode. A series of alloys with different cobalt content and several other substituents for nickel (Fe, Cu,...) were prepared in two different ways. A set of samples was conventionally melted. A second set of samples was prepared by gas atomization. The volume expansion upon hydriding was analyzed by means of X-ray diffraction. Electrochemical measurements, e.g., discharge capacity as a function of cycle number, were performed. The volume expansion upon hydriding decreases with increasing cobalt content of the alloy. Cobalt substitution for nickel improves the cycle life of an electrode, especially at elevated temperatures (40°C). However, alloys where cobalt is partially substituted by iron show an even better cyclic stability and rate capability.

Keywords: Metal hydrides; Electrode; Volume expansion; AB_5

1. Introduction

Cobalt is the most expensive element used today in the metalhydride alloys for battery applications. It is well known that cobalt in the alloy has a positive effect on the cycle life of metalhydride electrodes. However, the mechanism of the improvement of the cycle life through cobalt is still not clearly understood. The effect of substituting elements in the $LaNi_{5-x}M_x$ (M=Ni, Mn, Cu, Cr, Al and Co) on the cycle life and the mechanical properties of the alloys was investigated by Sakai et al. [1]. The cycle life was improved for alloys with a small volume expansion upon hydriding, a low reversible capacity and a low Vickers hardness. The volume expansion upon hydriding and the Vickers hardness of the alloy have a pronounced influence on the rate of pulverization and the final grain size. The influence of the discharged capacity on the cycle life was studied by Boonstra et al. [2] and it was concluded, that corrosion is related to the discharge capacity used per cycle. Notten et al. [3] concluded, that the lattice expansion between the α-phase hydride and the β-phase hydride rather than the total lattice expansion upon hydriding was responsible for the mechanical stability of the powders.

In order to substitute cobalt with other elements without sacrificing the cycling stability, the influence of cobalt on the material's properties was investigated.

2. Experimental

The alloy samples $LmNi_{4.3-x}Al_{0.4}Mn_{0.3}Co_x$ (Lm: lanthanum rich mischmetal: 51% La, 33% Ce, 12% Nd, 4% Pr) and $LmNi_{3.8}Al_{0.4}Mn_{0.3}Co_{0.3}Fe_{0.2}$ were conventionally melted and gas atomized as well. Gas atomized alloys were produced by spraying the molten alloy in an inert gas chamber usually using argon atmosphere. The resulting powder consists of spherical particles with an average grain size of approximately 100 μm. X-ray diffraction was performed with copper radiation (Cu K_α λ=1.5406 Å). Channel width was set to 2Θ=0.05° and the angular

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resolution was found to be $2\Theta=0.2°$ (FWHM: full width at half maximum). The count time was set to 5 s per channel resulting in a maximum count rate of approximately 10 000 counts for the main peak in the spectrum (1.0% error in the count rate). The samples were analyzed in the unhydrided and in the partly hydrided state. The lattice constants were calculated for the unhydrided alloys, α-phase hydrides and β-phase hydrides.

For the electrochemical measurements approximately 25 mg of the alloy powder was mixed with 75 mg copper powder (Merck p.a. <63 μm) under the open atmosphere and cold pressed (500 MPa) to a pellet ($d=7$ mm). The pellets were fixed with a cylindrical Teflon-clip on a nickel holder. The electrodes were charged and discharged electrochemically in a 6 *M* KOH electrolyte in a cell open to the atmosphere. A nickel plate was used as counter electrode and potentials were referred to a mercury/mercury oxide electrode. The discharge cut-off potential was −0.6 V with respect to the Hg/HgO/OH$^-$ reference electrode. The electrodes were tested in a half-cell with constant charge and discharge current (5 mA, i.e., 200 mA g^{-1}). The cycle life experiments were carried out at a temperature of 40°C.

3. Results and discussion

The conventionally melted alloy $LmNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ (Fig. 1) has a reversible electrochemical capacity of 337 mAh g^{-1} at 20°C (326 mAh g^{-1} at 40°C) and a very good cycle stability, 0.05% at 20°C (0.2% at 40°C) loss of capacity per cycle. Furthermore this alloy shows a good rate capability, the 1C discharge capacity, i.e., the maximum discharge capacity which can be retrieved in one hour, is 325 mAh g^{-1} at 20°C (326 mAh g^{-1} at 40°C). The cycle stability was calculated from a fit of our previously published model for the cycle life curve [4]. The alloy where cobalt is partially substituted with iron $LmNi_{3.8}Al_{0.4}Mn_{0.3}Co_{0.3}Fe_{0.2}$ has a reversible electrochemical capacity of 320 mAh g^{-1} at 40°C and a cycle stability of 0.15% (loss of capacity per cycle at 40°C). Furthermore this alloy shows a good rate capability, the 1C discharge capacity is 295 mAh g^{-1} at 40°C. The reversible capacities were measured in a special deep discharge cycle at low current and represent the maximum reversible electrochemical capacity of the alloy. This value is usually different from the maximum capacity measured in the cycle life curve (Fig. 1) due to kinetics, rate of activation and corrosion.

The volume expansion between the metal and the β-phase hydride (total) and the volume expansion between the saturated α-phase and the β-phase hydride (discrete) was determined from X-ray diffraction (Fig. 2). The investigated samples show a volume expansion upon hydriding between 7% and 16%. The volume expansion is up to 6% larger for the conventionally melted samples compared to the gas atomized samples of the same composition. The lowest discrete volume expansion upon hydriding was found for the $LmNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ gas atomized sample which was only 7.1%. Increasing cobalt contents lowers the volume expansion upon hydriding of $LaNi_5$−type alloys in agreement with the results obtained by Willems [5]. The partial substitution of cobalt with iron has no distinct effect on the volume expansion.

The cyclic stability is expressed in terms of λ_{ox}, i.e., the loss of discharge capacity per cycle (Fig. 3). This number is a constant for a few hundred cycles. λ_{ox} decreases with increasing cobalt content in the alloy except for concentrations below 5 at.%. The best cyclic stability was found for the gas atomized $LmNi_{3.8}Al_{0.4}Mn_{0.3}Co_{0.3}Fe_{0.2}$ sample with only 0.1% loss of capacity per cycle at 40°C.

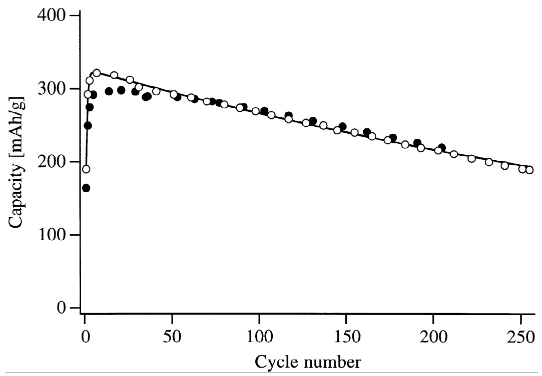

Fig. 1. Cycle life curve (○) and fit of the cycle life model (-) for $LmNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ and for $LmNi_{3.8}Al_{0.4}Mn_{0.3}Co_{0.3}Fe_{0.2}$ (●). Charge and discharge current were 200 mA g^{-1}, cut off potential was −0.6 V vs. Hg/HgO and cell temperature was 40°C.

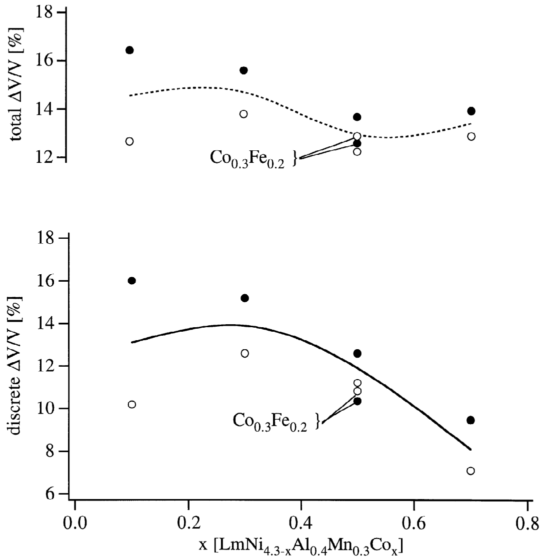

Fig. 2. Volume expansion upon hydriding between the metal and the β-phase (hydride phase) on top and between the α-phase (solid solution) and the β-phase on bottom, for the conventionally melted alloys (●) and the gas atomized alloys (○).

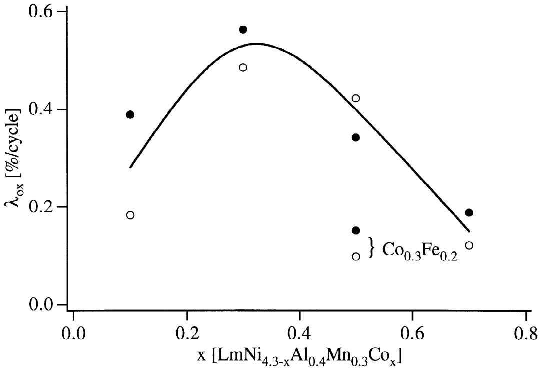

Fig. 3. Oxidation constant (λ_{ox}), i.e., loss of capacity per cycle, for the conventionally melted alloys (●) and the gas atomized alloys (○). Charge and discharge current were 200 mA g^{-1}, cut off potential was −0.6 V vs. Hg/HgO and cell temperature was 40°C.

In contrast to the non-iron containing alloys the conventionally melted iron containing alloys show a slightly smaller volume expansion than the gas atomized alloys. Furthermore the iron containing alloys exhibit an excellent cyclic stability which cannot be explained only with their small volume expansion. There may be other very important factors contributing to the cycle stability e.g. hardness of the alloy, final grain size distribution, and the formation of protecting surface oxide layers.

4. Conclusion

In this work we have shown a possibility of partly replacing cobalt with iron in the $LmNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ alloy system without sacrificing some of their electrochemical properties, such as capacity and rate capability.

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