IN SITU GRAZING INCIDENCE X-RAY INVESTIGATIONS ON THE ANODIC BEHAVIOUR OF METAL HYDRIDE ELECTRODES

Selma Hansal,, W.E.G. Hansal, R.Krendelsberger, J.O.Besenhard, G.Fafilek, H.Kronberger, G. E. Nauer*
ECHEM Center of Competence in Applied Electrochemistry
Viktor Kaplan Straße 2, 2700 Wiener Neustadt
Austria

Introduction

For an efficient usage of metal hydride alloys in alkaline Ni-MeH batteries , properties like decrepitation behaviour or corrosion stability must be improved. Especially the long term behaviour of alloys of the $LaNi_5$ type with complex compositions is influenced by the corrosion properties during the discharge process and by changes in the lattice parameters during cycling.

Besides *ex situ* investigations and characterisation of powdered samples using an image plate Guinier camera with a high resolution, *in situ* X-ray investigations on $LaNi_5$ type electrode material were performed in 6 M KOH for the determination of corrosion products on the electrode surfaces and for the characterisation of the changes of the lattice parameters during cycling of the electrodes.

Experimental

The samples (working electrodes) were arc melted (some compositions are shown in Table 1), cutted in slabs, embedded in the electrochemical cell, grinded and polished. As counter electrodes pure Ni sheets also embedded in the cell were used. A Hg/HgO/6 M KOH reference electrode was connected to the cell via a salt bridge and acts also as a reservoir for the electrolyte. Details are given in [1].
The treatment of the electrodes was done in the galvanostatic mode, the measurements were done potentiostatically at potentials generated during the galvanostatic treatments.

The grazing incidence experiments were performed on two different diffraction equipments. One is a special designed arrangement with a Cu X-ray tube and a monochromator in combination with an image plate camera covering 100° in the 2 theta range vertically mounted, allowing a horizontal position of the electrochemical cell. A variable tube holder allows the variation of the angle of incidence in the range between 0.1° and 18° (Fa.Huber, D). The second one is a classical vertically mounted theta-theta diffractometer equipped in the primary beam path with a Goebel mirror and on the detection side with a very fast and sensitive registration system also based on the image plate technique. The detection system covers a range of 120° in 2-theta with a resolution of 0.02° and allows the registration of a complete *in situ* diffractogram within a time range of 30 seconds (Fa.Stoe, Darmstadt, D). Using this equipment, X-ray diffractometry in the grazing incidence mode can be performed during a classical electrochemical experiment with an appropriate high time resolution. Since the intensity of the primary beam is focussed on an area of less than 2 mm^2 , the intensity of the reflected beam is high enough to generate diffractograms on a appropriate time scale.

Results and Discussion

The *in situ* grazing incidence diffractograms exhibit at higher angles of incidence all characteristic reflections of the $CaCu_5$ type crystal structure. Lowering the angle of incidence down to values < 2° additional reflections appear which can be attributed mainly to oxides and hydroxides on the surface. The compound $La(OH)_3$ is the main product generated during the anodic treatment of the electrode material, which was also proved

by external reflection absorption FT infrared spectroscopy [2]. The amount on the surface depends mainly on the concentration of La in the “mischmetal” and on the time of the anodic polarization treatment. Cycling the metal hydride material results in an enrichment of the $La(OH)_3$.surface concentration.

Alloying elements like Ge or Cu lead to a significant enhancement of the corrosion reaction and therefore to a further enrichment of $La(OH)_3$ in the surface region. These elements cause also a significant decrease in capacity at higher cycle numbers.

At an angle of incidence of 1° texture effects change the shape of the diffractograms. The intensity of some lower indexed reflections is significantly enhanced and the overall counting rate is reduced.

We will present some recent results on the alloys investigated and discuss the compositional changes measured by varying the angle of incidence causing a different penetration and therefore information depth.

Table 1: Composition of some alloys investigated

1	$Mm_{20\%La}Ni_{3.96}\,Mn_{0.4}\,Al_{0.1}\,Co_{0.6}$
2	$Mm_{40\%La}Ni_{3.96}\,Mn_{0.4}\,Al_{0.1}\,Co_{0.6}$
3	$Mm_{60\%La}Ni_{3.96}\,Mn_{0.4}\,Al_{0.1}\,Co_{0.6}$
4	$Mm_{80\%La}Ni_{3.96}\,Mn_{0.4}\,Al_{0.1}\,Co_{0.6}$
5	$Mm_{40\%La}Ni_{3.96}\,Mn_{0.2}\,Al_{0.1}\,Co_{0.6}\,Ge_{0.2}$
6	$Mm_{40\%La}Ni_{3.96}\,Mn_{0.2}\,Al_{0.1}\,Co_{0.6}\,Cu_{0.2}$

Acknowledgement

This work was supported by the K*plus* program of the Austrian government.

Literature

[1] Nauer, G.E.; “*Mat.Sci.Forum*” 228-231 (1996) 387
[2] Hansal, S., Hansal W., Köberl, A., Nauer, G.E.; “Electrochimica Acta”, submitted.