

ELUCIDATION OF REASONS FOR PERFORMANCE FADING OF ALPHA NICKEL HYDROXIDE

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Abstract: Commercial alkaline accumulators with positive electrode based on nickel hydroxide generally comprise beta modification of the active material at present due to its excellent stabilization of performance during electrochemical cycling. The paper relates to research focused on utilization of alpha nickel hydroxide in alkaline batteries and verifying of ways how make it stable in strong alkaline electrolyte. Referred-to work is aimed at clarifying of reasons for its transformation tendency with the aim of finding proper inhibition method.

Keywords: alkaline accumulators, nickel hydroxide electrode, cathodic active material, crystallographic modifications of nickel hydroxide

1. INTRODUCTION

Alpha nickel hydroxide attains superior performance compared to commonly produced beta hydroxides in consequence its transition ability to nickel in tetravalent state (although partially) in stabilized forms and thereby gain higher capacity from the same nickel content.

Alpha nickel hydroxide is rather more complicated intercalate compound comprising of variable stages of hydration. Compound with idealized composition and simplified formula $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (specific weight is about $2,5 \text{ g}\cdot\text{cm}^{-3}$) is quite unstable in alkaline medium and easily transforms to $\beta\text{-Ni}(\text{OH})_2$. Therefore, it is necessary to find solution of structure stabilization. Gamma phase formed by charging of alpha nickel hydroxide represents a mixture of trivalent and tetravalent nickel as hydrated oxides where contained tetravalent nickel is stabilized by corresponding amount of intercalated anions (including OH^- anions from the electrolyte) to ensure charge equilibrium. For that reason, electrochemical reactivity of alpha nickel hydroxide should overcome that of $\beta\text{-Ni}(\text{OH})_2$.

The unquestionable advantage of the „ α/γ “ systems is that material can be electrochemically cycled without having perceptible volumetric changes. The outstanding feature is the effectual overcharging tolerance as well. It is caused by very close lattice constants for both of the redox couple components. Despite all of the advantages which are potentially offered by using of alpha nickel hydroxide in alkaline accumulators there is a fundamental problem if is this system able to provide such parameters in the long term conditions. There is obvious inclination that there is a crystal-phase transformation toward more stable and thermodynamically preferable beta form in general alpha phase definition according to Bode's diagram.

2. EXPERIMENTAL

2.1. MEASUREMENT OF DISCHARGE CAPACITY BY GALVANOSTATIC TESTS

The active material and construction of electrodes

The electrochemical behavior of the substituted alpha nickel hydroxides was studied in Ni-Cd cells with 6M KOH electrolyte. There were used pressed electrodes in pocket version for the investiga-

tions on all of nickel hydroxide samples. The electrodes were constituted of an activated mixture of nickel hydroxide and graphite which gives improved electronic conductivity. The active material using β_{bc} -Ni(OH)₂ has served as a comparative mass/reference sample in carried out tests.

Measuring conditions

All measurements were performed using non-commercial equipment of Bochemie Inc. The cycling process at the 0,17 C rate is typically used in our laboratory for testing of the type of accumulator mass. It consists in continuous, galvanostatically led charging and discharging of the cell with short relaxation between the various steps. Four "forming" cycles of these electrodes are performed at the same rate (0,17 C) at the very beginning of the cycling, including strong overcharging of the cell in the first cycle (20 h successfully). The overcharging corresponds to 200% of the theoretical capacity for common accumulator mass based on beta nickel hydroxide.

2.2. EQCM/CV MEASUREMENT

Reverzibility evaluation of redox reactions in cycled material

2.3. XRD STRUCTURE ANALYSIS

Evaluation of lattice parameters

3. RESULTS AND DISCUSSION

3.1. ELECTROCHEMICAL MEASUREMENTS OF DISCHARGE CAPACITY

Al-substituted alpha nickel hydroxide

Maximal discharge capacity provided by active materials based on Ni-Al LDH is apparent in cycle life records for our prepared and evaluated types of alpha nickel hydroxide. However, having been attained during formation period the discharge capacity began to drop rapidly.

Mn-substituted alpha nickel hydroxide

On the other hand, discharge capacity of active materials based on Ni-Mn LDH in dependence on cycle numbers fast faded immediately after cycling process had been started. The performance loss was early stopped and kept steady values (corresponding to the beta hydroxide) in relatively long time.

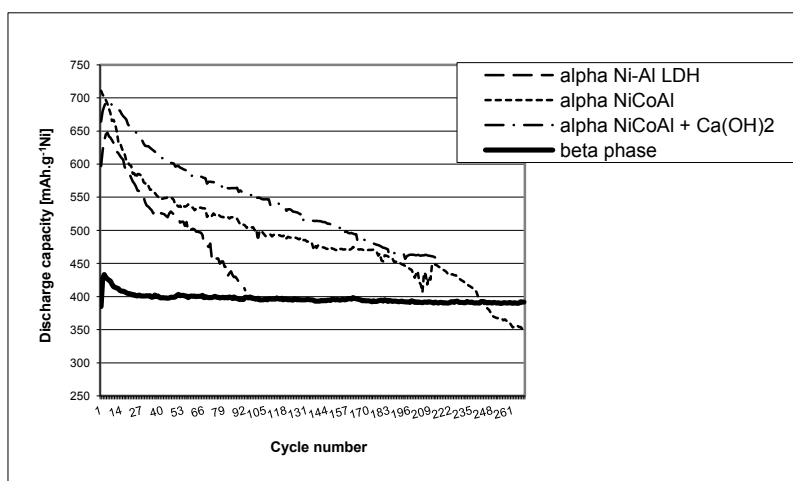


Fig. 1: Performance of Al-doped alpha nickel hydroxide related to nickel content

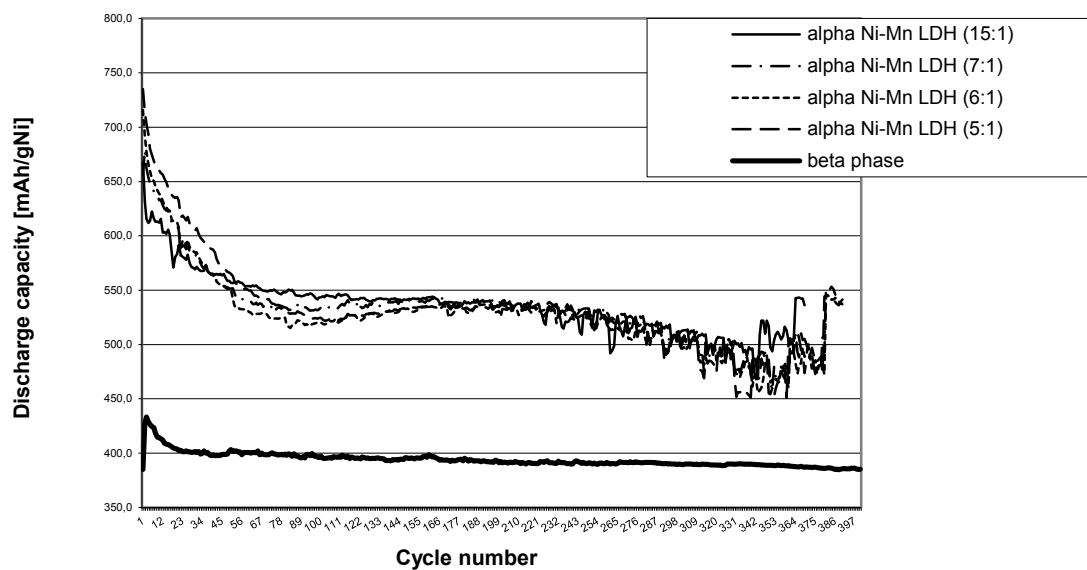


Fig. 2: Performance of Mn-doped alpha nickel hydroxide related to nickel content

3.2. EQCM MEASUREMENT

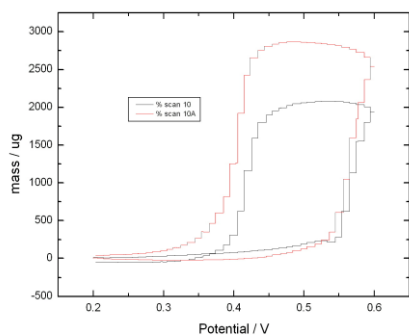


Fig. 3: Massogram for scan 10

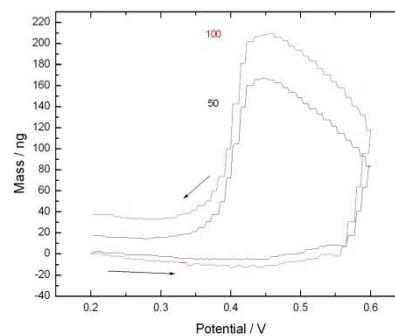


Fig. 4: Massogram for scans 50 and 100

Very good reversibility of the electrode processes including cycled Al-substituted alpha nickel hydroxide is observed from the beginning. However, the material participation in redox reactions occurring in cycled cell drastically decreases with increasing cycles. The residual participating indicates that best part of Al-substituted alpha nickel hydroxide (about 90%) remains inactive.

3.3. RD STRUCTURE ANALYSIS

Velicka 8. Ni(OH)₂ srazeni c:42 12.01.05. - File: 50102VELRAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 90.000 ° - Step: 0.020 ° - Step time: 2.4 s - Temp.: 25 °C (Room) - Time Started: 3 s - 2-Theta: 5.000 ° - T 38-0715 (N) - Nickel Hydroxide Hydrate - alpha-Ni(OH)₂·0.75H₂O - Y: 41.36 % - d x by: 1. - WL: 1.5406 - Hexagonal (Rh) - a 3.08000 - b 3.08000 - c 23.41000 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primit

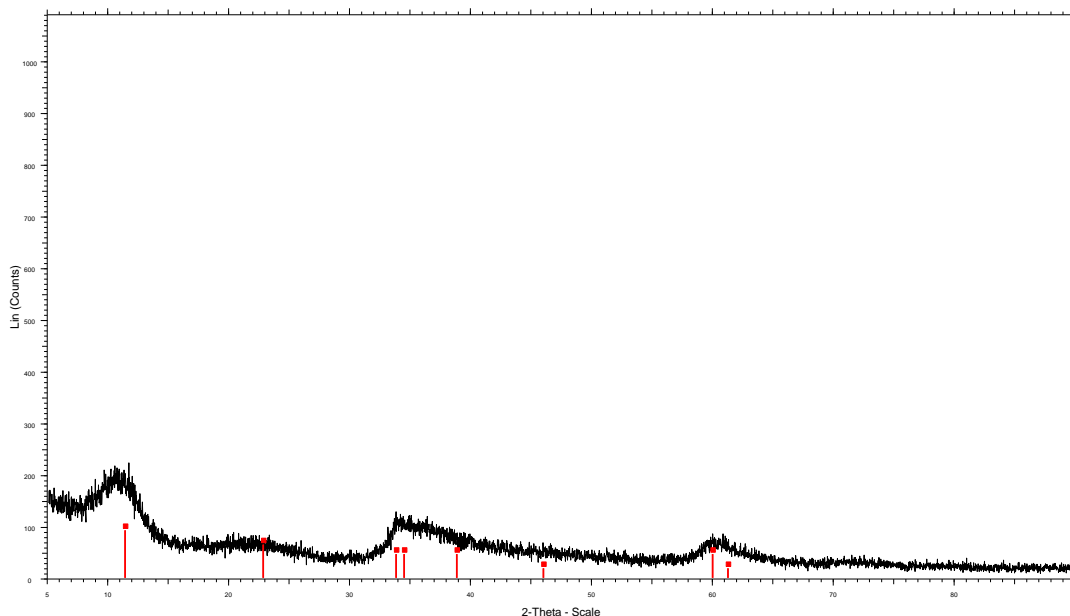


Fig. 5: Uncycled active material based on Al-doped alpha nickel hydroxide

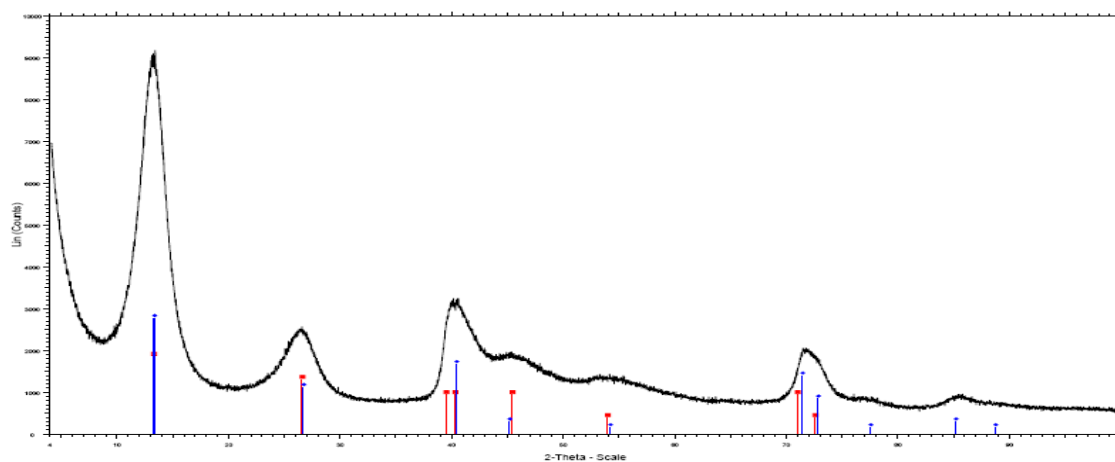


Fig. 6: Active material based on Al-doped alpha nickel hydroxide after finished cycling

3.4. DISCLOSED REASONS OF PERFORMANCE FALLING

Ni-Al LDH

Passivation of higher-valent nickel fast occurs without being transformed to the beta phase. Material becomes isolated in charged state and thereby can not be completely discharged. The effect accelerates in several initial cycles. I have not elucidated exact mechanism of the passivation yet and our work on solving that continues.

Ni-Mn LDH

Phase separation – beta nickel hydroxide is formed from initial alpha structure. The transformation is also considerably sped. The active material becomes better reversible and behaves as common beta phase.

4. CONCLUSION

All prepared samples of nickel hydroxide have been proved to be alpha modification in this work. Electrochemical tests of the samples have been made. Despite most of the papers regarding the alpha nickel hydroxide we haven't obtained any results like the published ones. I have disclosed causes, why the capacity of the measured samples faded, but I haven't found yet, how to prevent from this phenomenon.

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