

THE EFFECT OF COBALT, MANGANESE AND ALUMINIUM SIMULTANEOUS ADDITION INTO NICKEL HYDROXIDE LATTICE ON ITS ELECTROCHEMICAL BEHAVIOR

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Abstract: This report discusses partial results of research project of the company Bochemie Inc. and Institute of Electrotechnology, Technical University of Brno focused on utilization of alpha nickel hydroxide in alkaline batteries and verifying of ways how to make it stable in a strong alkaline electrolyte. Based on our former experience with an individual-element's doping, simultaneous incorporation of the selected elements into brucite type lattice of nickel hydroxide appears to be suitable solution for fulfilment of the purpose.

Keywords: alkaline accumulators, cathodic active material, crystallographic modifications of nickel hydroxide, transformation tendency of alpha to beta phase, inhibition methods of irreversible phase changes, doped LDH crystal lattice.

1. INTRODUCTION

Nickel hydroxide is used as an electrochemically active component of accumulator masses for positive electrode of Ni-Cd, Ni-MH and Ni-Zn alkaline accumulators.

From morphological point of view there are two basic versions of nickel hydroxide known as crystallographic modifications, alpha phase and beta phase. Alpha nickel hydroxide attains a superior performance compared to commonly produced beta hydroxides in consequence of its transition ability to nickel in tetravalent state (although partially) in stabilized forms and thereby they gain higher capacity from the same nickel content.

Alpha nickel hydroxide is rather more complicated intercalate compound comprising of variable stages of hydration. A wide group of layered double hydroxides (LDH) with partially substituted nickelous ions by suitable trivalent stabilizing cations (most often Al^{3+}) is considered to be alpha nickel hydroxide. A replacement of nickelous ions Ni^{2+} by trivalent metal cations Me^{3+} imparts excess of positive charge to primarily electroneutral layers is mentioned. The positive charge excess is directly proportional to range of cation substitution and it is compensated by the charge of hydrated anions being placed in an intersheet region. There is an electrostatic attraction (coulombic forces) between alternating hydroxide sheets $[\text{Ni}_{1-x}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+}$ and interlayer space of hydrated anions $[\text{A}^{n-}_{x/n}\cdot y\text{H}_2\text{O}]^{x-}$. Better intersheet region's permeability improves mobility of ions there, especially H^+ protons. Consequently, over one-electron exchange can be expected since the number of exchanged electrons during the charge/discharge process is equivalent to the number of H^+ protons which are removed from hydroxide sheets or inserted into them, respectively. The overall electrochemical reaction can be understood as proton deintercalation and intercalation reactions. 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 $\beta\text{-Ni}(\text{OH})_2$.

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. Therefore, it is necessary to find the solution of structure stabilization.

2. EXPERIMENTAL

2.1. MATERIAL SYNTHESIS

All LDHs samples were prepared with coprecipitation technique. An aqueous solution of Ni, Co, Al, Mn and Ca salts with chosen molar ratio was added with a given flow rate into vessel containing certain volume of distilled water. The reaction pH of 10 was kept at the constant value by controlled flow rate of simultaneously added alkaline solution. The coprecipitation was carried out under vigorous stirring at 30°C. The product was filtered off, washed thoroughly with distilled water and dried overnight at 60°C.

2.2. ELECTROCHEMICAL TESTS OF POSITIVE ELECTRODES BASED ON Ni(OH)₂

Measuring conditions

The electrochemical studies of the prepared alpha nickel hydroxide samples was accomplished in Ni-Cd cells with 6M KOH as an electrolyte. There was used a pocket construction of electrodes for the investigations on all of nickel hydroxide samples. The electrodes were constituted of pressed activated mixture of nickel hydroxide and graphite which gives an improved electronic conductivity. The active material based on β_{bc} -Ni(OH)₂ has been used as a reference sample in carried out tests.

Galvanostatic measurement of discharge capacity

The cycling process at the 0.17 C rate is typically used in our laboratory for testing of the commercial positive accumulator mass of Bochemie Inc., named NICOL G. The test consists of the continuous, galvanostatically led charging and discharging of measured cell with a short relaxation between the various steps. The procedure involves four "forming" cycles 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. All measurements were performed using non-commercial equipment of Bochemie Inc.

Reversibility of redox reactions taking place in cycled materials based on variously doped alpha nickel hydroxide and amount of participated active mass were investigated by cyclic voltametry (CV) method combined with an electrochemical quartz crystal microbalance (EQCM) study, i.e. registration of mass changes during potential scans.

3. RESULTS AND DISCUSSION

3.1. ELECTROCHEMICAL MEASUREMENTS OF DISCHARGE CAPACITY

A treatment of chemical composition were carried out for purposes of optimizing product formula ensuring excellent electrochemical parameters and their durability in cycling process. Set of several samples with variously modified molar ratios of doping elements to nickel was prepared. All these propositions were based on our former experience with an individual-element's doping and consequent conclusions:

Al-substituted alpha nickel hydroxide potentially offers superior performance characteristics with high placed voltage plateau in discharge curves. Very good reversibility of the electrode processes

including cycled Al-substituted alpha nickel hydroxide is observed from the beginning. However, a drastic weakness of the material participation in redox reactions of cycled half-cell NHE with on-going cycles has been proved in our experiments. Having provided maximal value during formation period the discharge capacity began to drop rapidly. Such behaviour originates from fast insulation of higher-valent nickel in charged state without any ability to be completely discharged. The major part of material (about 90%) remains inactive. The effect accelerates in several initial cycles. No transformation to the beta phase was observed.

On the other hand, the phase transformation has occurred and beta phase was gradually formed from initial alpha structure in case of Mn-doped alpha nickel hydroxide. The transformation is also considerably accelerated. The active material becomes better reversible and behaves as a common beta phase. The performance loss was early stopped and kept steady values corresponding to the beta hydroxide in relatively long time.

Cobalt introduced into lattice of nickel hydroxide generally improves reversibility of redox reactions on cycled nickelhydroxide electrode (NHE) and charge acceptance of the active material via lowered anodic oxidation potential and increased oxygen over-voltage η_{O_2} on charged NHE at the same time.

Based on these experiences, simultaneous incorporation of the selected elements into brucite type lattice of nickel hydroxide appeared to be appropriate solution for fulfilment of our purposes, i.e. an excellent steady performance. Such hydrotalcite-like compound was prepared through optimizing process toward the most favourable composition with regard to required electrochemical properties.

A slow down effect for rapidly dropping performance through co-doping by chosen mixture of divalent and trivalent metal cations in proper molar ratios really occurs on initial charge/discharge galvanostatically realized cycles, as shown in Fig.1. However, the performance decline systematically continues without being stopped at medium and latter stage of cycling. All galvanostatic measurements were accomplished at current regime of full discharge cycles, i.e. until the cell voltage equal to 1.00 V was reached. Abrupt enhancing of discharge capacity of „alpha NiCoMnAl + Ca(OH)₂ powder“ sample after 130th cycle in Fig. 1 corresponds to accomplished electrolyte exchange.

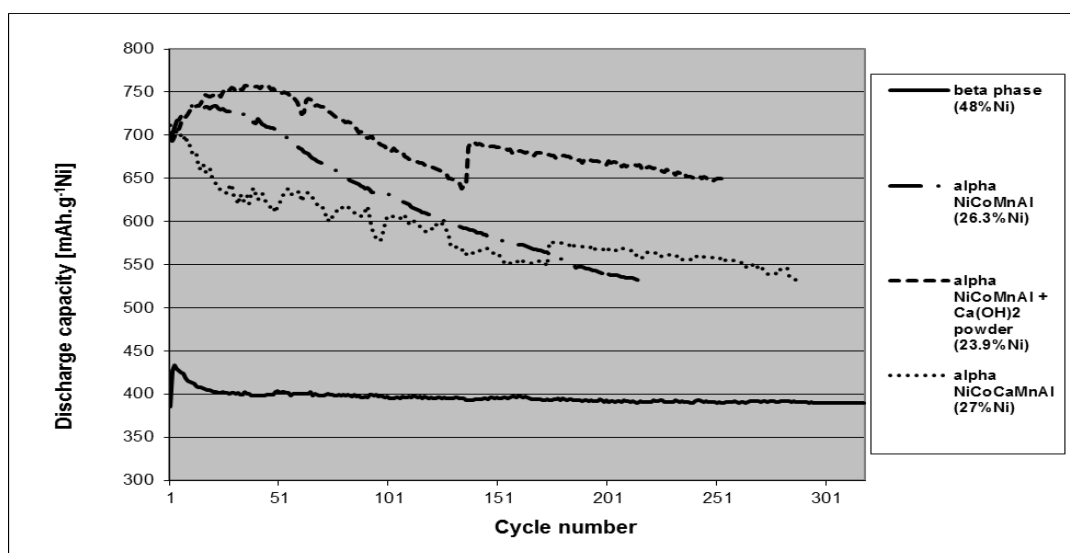


Figure 1 The performance of multidoped alpha nickel hydroxide related to nickel content.

3.2. CV MEASUREMENTS OF OXYGEN EVOLUTION

Cobalt and calcium addition should ensure an increasing of the difference between oxygen evolution potential E_{O_2} and anodic oxidation potential E_a of nickelhydroxide electrode (NHE) by enhancing of an oxygen overvoltage η_{O_2} on charged NHE with better charge acceptance and thereby lower E_a and consequently an improvement of the charge efficiency. Although E_{O_2} was really elevated after Ca incorporation, the distance between E_{O_2} and E_a positions on potential axe was maintained almost unchanged due to unfavourable raising of E_a . The position of anodic peak shifts to more positive values, from initial 0.33 V, during cycling. Fig.2 gives a nice overview of the gradual shifting.

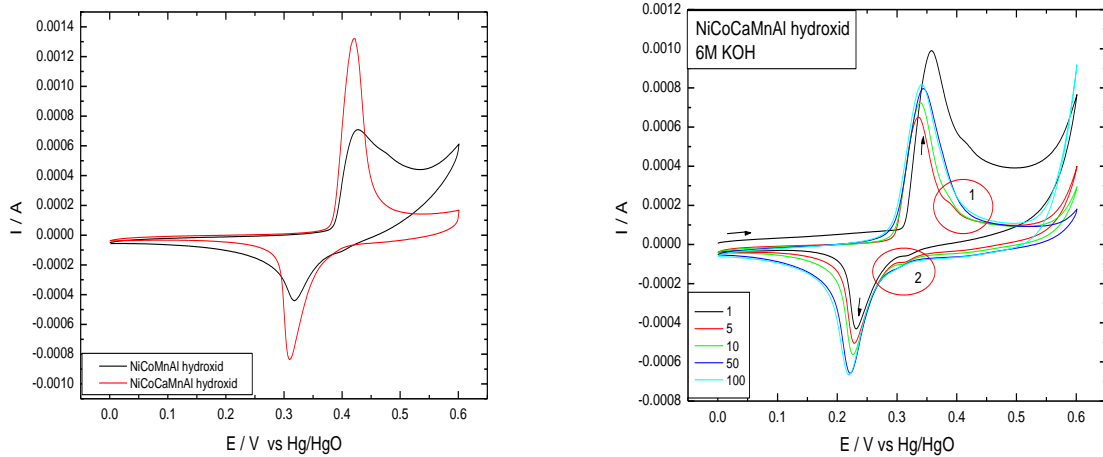
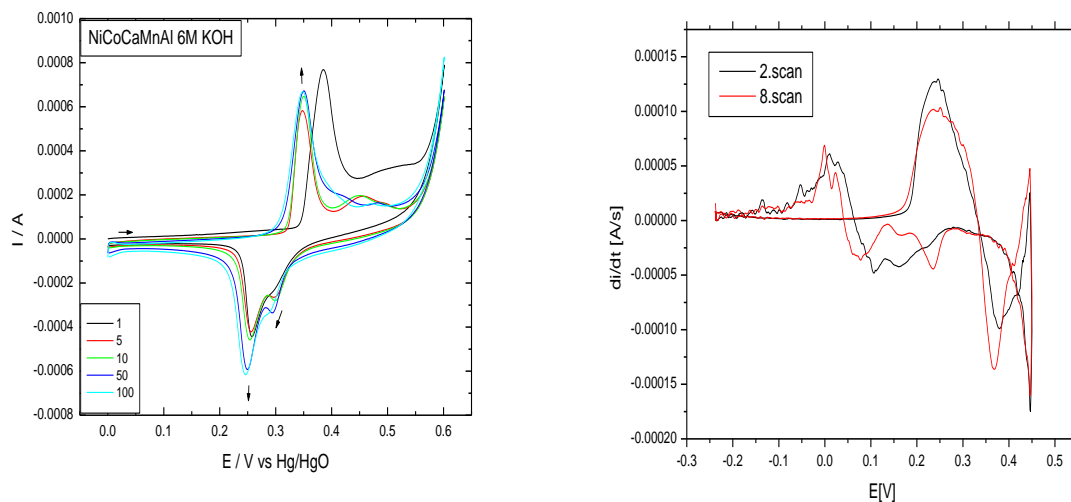


Figure 2: An influence of Ca and Co addition on oxygen evolution at NHE during charging.

3.3. EQCM/CV REVERSIBILITY STUDY



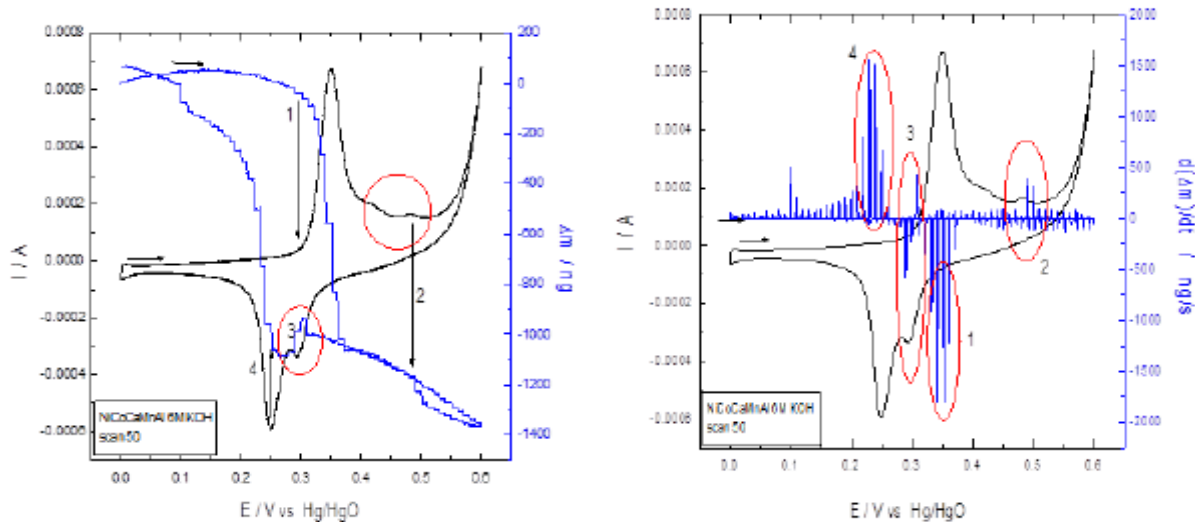


Figure 3: EQCM/CV reversibility study for multidoped alpha nickel hydroxide.

It can be seen that cycled active material based on multidoped alpha nickel hydroxide tends to a phase separation. The active mass is subjected to certain structural changes in the consequence of recrystallization involving dissolution, nucleation and growth processes. The mechanism is supposed to proceed via local dissolution of the particles at their surface followed by a partial segregation and reprecipitation of the new phases with different contents of dopant elements unlike original structure as prepared.

When such a phase separation is being run, some portion of beta nickel hydroxide is formed from initial alpha structure while the significant part of structure remains as predominant alpha phase. Fig. 3 shows this transformation to beta phase which is depicted by regions 2 and 3 in voltammogram and derivatogram $d(\Delta m)/dt$ of EQCM record; regions 1 and 4 correspond to initial alpha phase. (*Recrystallization toward well-crystallized beta phase revealing weak activity). The separation tendency is more obvious from derivation of CV and EQCM records, respectively.

4. CONCLUSION

The contributions of individual doping elements in multidoped alpha nickel hydroxide are put together creating some synergy effect which gives maximal values of the performance parameters during initial and moderate stage of cycling. Nevertheless, the disintegration onto separately cycled components with strongly weak participation occurs in latter period of cycling due to decay of the original structure. The overall discharge capacity (in a summary) of all resultant products is insufficient compared to level of as-prepared sample.

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