EVALUATION OF DISCHARGING DEPTH AND OVER-CHARGE INFLUENCE IN RELATION TO ELECTROCHE-MICAL PROPERTIES OF ALPHA NICKEL HYDROXIDE

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ABSTRACT

The paper refers to a part of research work accomplished in R&D Department of company Bochemie Inc. which has been aimed to utilization of alpha nickel hydroxide in alkaline batteries including exploration of possibilities to attain its stability in strong alkali medium of the electrolyte. We have focused effort to elucidate reasons for its transformation tendency and to find way of their suppression. Based on previous obtained empirical evidence, introduction of appropriate variations in depth of discharge seems to be potentially proper solving for us, which led us to verify that.

1. INFLUENCE OF DISCHARGING DEPTH AND OVERCHARGING ON PERFORMANCE OF ALPHA NICKEL HYDROXIDE

1.1. SHALLOW DISCHARGE OF Al-DOPED ALPHA NICKEL HYDROXIDE

Discharge curves of Al-doped alpha nickel hydroxide are characterized by higher situated potentials in comparison with common beta phase and further by sharp breaks of progression when discharge is being finished i.e. abrupt potential falling in region of voltage for NiCd cell at 1,1 V. This featured property determines negligible charge retention and useless capacity below mentioned level of the cell voltage. Withal, major portion of charge corresponding to main working part of curve should be delivered in region of higher voltage greater than about 30 up to 50 mV compared with beta phase of nickel hydroxide. Such behavior theoretically appears to be very advantageous and that´s why we have decided to shallow discharge of these materials.

1.2. DEEP DISCHARGE OF Mn-DOPED ALPHA HYDROXIDE

After being discharged to 1V Mn-doped alpha hydroxides retain still significant portion of capacity below this voltage level. The capacity retention results from lower discharge potentials of Mn-doped alpha hydroxides which has been observed in the discharge curves and that´s why it is necessary to consider those discharging processes as insufficient and prematurely terminated. The share of discharge capacity with the discharge voltage lower than 1 V is relatively high which indicates certain weakness of useful capacity. The retained capacity is delivered only after discharge was adjusted to cut off voltage equal to 0,8V. Described behavior well corresponds to content of manganese – this effect becomes more apparent with increasing amount of manganese in alpha nickel hydroxide.

1.3. VERIFY OF THE TOLERANCE AGAINST IRREVERSIBLE STRUCTURAL CHANGES DURING OVERCHARGING OF ALPHA NICKEL HYDROXIDE

Regularly arranged crystal lattice of alpha phase does not obviously become damaged when it is being overcharged. The only evolution of oxygen on positive and hydrogen on negative electrodes takes place. Following generation of gas microbubles causes rise of pressure inside both electrodes and cell with consequent elutriation of accumulator mass from carrier/current collector and structural degradation of pressed electrode and thereby enhancement of internal resistance. Gradual transition part of alpha phase to beta phase also proceeds with increasing cycle number and overcharging of this manner created beta modification to gamma phase leads to volumetric changes of active material joined by swelling and mechanical stress which can induce conductivity loss. Meanwhile formation of electrode for about first 5 cycles involving gradual stabilizing and hydration of structure together with irreversible transition of secondary cobalt to conductive part of surface is running a moderate slow overcharging of accumulator mass appears to be favourable for complete utilization of its entire volume. Further overcharging doesn´ t yield any benefit to working of electrode.

2. EXPERIMENTAL

2.1. THE ELECTROCHEMICAL TESTS OF POSITIVE ELECTRODES BASED ON $Ni(OH)_2$

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 investigations 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. Results and discussion

Testing of shallow discharge for Al-doped alpha nickel hydroxide

We have focused to verify the fact of assumed beneficial influence of such discharge regime on cyclic stability for Al-doped alpha nickel hydroxide. Levels of 1,15 V, 1,1V and 1V (common value) were chosen as final discharge voltage. A slow down effect for rapidly dropping performance through higher final discharging voltage really occurs on first charge/discharge cycles. However, the performance decline systematically continues, unless it is being stopped. Experimental results in the case of the highest final discharge voltage seems to be little bit unusual with regard to least steady continuance discharge capacity with increasing number of cycles. On the contrary performance falling accelerates (between 3rd and 4th cycle and between 6th and 7th cycle) in comparison to common discharge to 1V. Lower delivered charge corresponds with it. Comparison of discharge to 1V and 1,1 V can be evaluated more clearly. Discharge capacity declension of initial 10 cycles really slows down and moreover the capacity falls from higher achieved values. However, rates (sharpness) of the performance declension for both discharge ways equilibrate after achievement of 10th cycle. It is surprising, that delivered capacity for final voltage of 1,1 V in comparison with 1 V. This discrepancy could be better explained by different insulating range of active material in charge state in particular cases. This insulation occurs very fast in case of Al-doped alpha nickel hydroxide after the beginning of electrochemical cycling.

It can be concluded that shallow discharge has not proved ability to restrain the active material from being insulated or transformed.

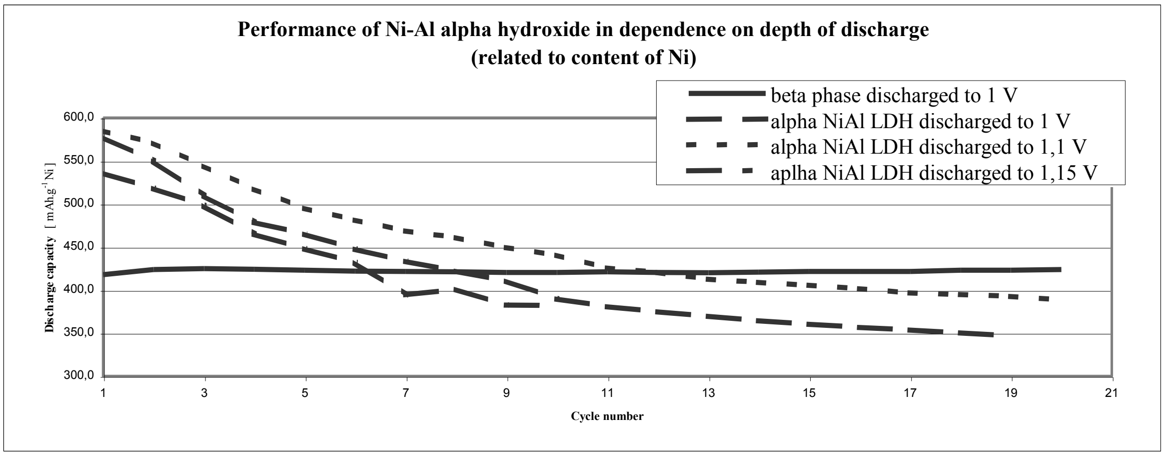

Fig.1 Different depth of discharge for Ni-Al alpha nickel hydroxide

Testing of deep discharge for Mn-doped alpha nickel hydroxide

Range of capacity retention was experimentally investigated by galvanostatic measuring of samples with molar ratio Ni:Mn = 9 synthesized by continually led precipitation in a flow reaction vessel for two different flowing-through period 1 hour and 3 hours. In order to more precious expression long-term deep discharging were discontinued and further accomplished till cut off voltage equal to 1V for several more cycles. Degree of charge retention for sample NiMn (9:1)/3h in 228th cycle means 21,3 % of discharge capacity delivered by deeper discharging to final cell voltage equal to 0,8 V in previous cycle and in case of sample NiMn (9:1)/1h loss of capacity represents 19,9 % in 229th cycle.

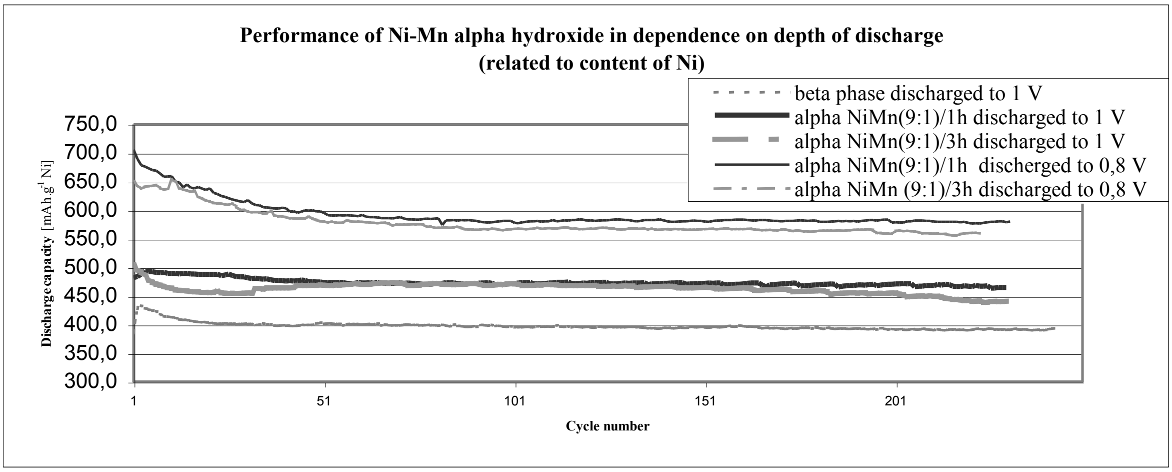

Fig.2 Different depth of discharge for Ni-Mn alpha nickel hydroxide

Overcharging of Al-doped alpha nickel hydroxide

Influence of overcharging on properties deterioration has not been confirmed yet. Two series of measurements have been accomplished – the first with vigorous overcharging in excess of 1,7 V and the second with charging of the same accumulator mass by commonly used algorithm till the cell voltage equal to 1,47V. Almost identical capacity continuance and rate of phase transformation (from alpha toward beta modification) has been exhibited for both methods and any deviations have not been found. Slightly higher capacity can be delivered from the sample of overcharged active material in comparison with the sample that was charged to standard voltage. However such enhancing of discharge capacity occurs to be the detriment of considerable energy losses at charging (decreasing of charge efficiency) and possibility of construction´ s damage during short period if the active material is regularly overcharged.

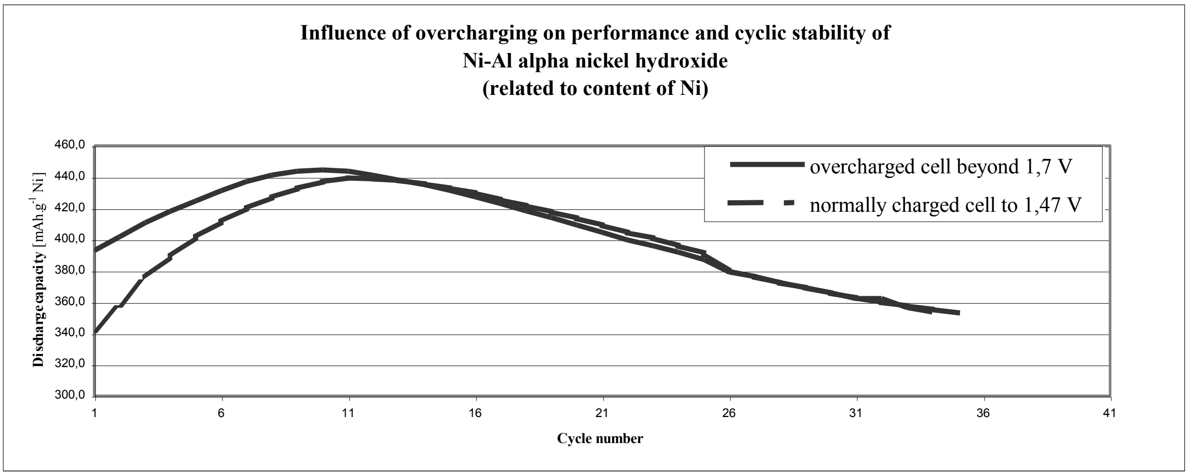

Fig.3 Overcharging tests for Ni-Al alpha nickel hydroxide

3. CONCLUSION

We have evaluated influence of deep discharging on electrochemical behavior of alpha nickel hydroxide with aluminium or manganese as doping agents. Our measurements were carried out to check slowing downs in performance declension through shallow discharge regimes. With the shalower discharge ,we haven´t found out any significant effect on improvement in electrochemical properties such as performance and efficiency characteristics by shallower discharge which means that there is any capability to attain prolonged cyclic life of accumulator masses based on Al-doped alpha nickel hydroxide by adjusted operating conditions in this manner.

On the other hand, deeper discharge has clearly proved, that for Mn-substituted alpha nickel hydroxide is necessary to gain retained portion of capacity.

The tolerance of alpha nickel hydroxide toward irreversible structural changes in conditions of intensive overcharging has been studied. There hasn´t been found out any difference between electrochemical behavior of charged alpha nickel hydroxide to standard voltage and intensive overcharged state, which means that overcharging does not reduce cyclic life of positive accumulator masses based on alpha nickel hydroxide.

ACKNOWLEDGEMENT

This article was supported by the Ministry of Education, Youth and Sports, Czech Republic (project MSMT 0021630516).

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