

ALUMINIUM AND MANGANESE SUBSTITUED NICKEL HYDROXIDE

Jiří Vrbický

Doctoral Degree Programme (1), FEEC BUT
E-mail: xvrbic00@stud.feec.vutbr.cz

Supervised by: Jiří Vondrák

E-mail: Vondrakj@iic.cas.cz

ABSTRACT

This article deals with nickel hydroxide modification measurements with added various admixtures as aluminium and manganese. The possibility of alpha modification stabilization are described.

1. INTRODUCTION

Nickel hydroxide is the basic material for positive electrode of alkaline accumulators as Ni-Cd, Ni-MH and Ni-Fe. The three modification of nickel hydroxide is known, alpha, beta and gama. Alpha nickel hydroxide is stable in normal conditions, but in alkaline electrolytes is unstable and turns into β - Ni(OH)₂. The β - Ni(OH)₂ has half capacity than beginning alpha electrode, and when β - Ni(OH)₂ is overcharged to γ - NiOOH, the volume expansion is increasing so it occurs many construction and durability problems, it also solves the electrode made of α - Ni(OH)₂. If stable form of α - Ni(OH)₂ could be available, the positive electrode will be half weighty by the same capacity, it means the total weight of accumulator could get to 80% of standard accumulator. Possibility to prepare α - Ni(OH)₂ more stable in strong alkaline media is to add some other tri- or more-valent metals metals such as Al, Fe, Mn, Co and maybe others.

2. EXPERIMENTAL

2.1 MATERIALS AND METHODS

The samples of aluminium (NiAl) and manganese (NiMn) substituted nickel hydroxide were pressed into nickel mesh without any cement or other aditives. The surface of electrode were about 1cm² and density of material 0,035g. Electrodes was measured by cyclic voltammetry, 3 electrode method, in 6 M KOH, counterelectrode was platinum plate and reference electrode was SCE. Scan rate was 0,5mV/s, potential window 0-0,45V (vs. SCE).

2.2 RESULTS AND DISCUSSION

NiAl was measured for 100 scans. During measurement took effect the degradation of structure (Fig.1). After ten scans was the structure hlaf degraded, and after 20 scans was

degradation complete. The discharging (reduction) peak decreases, so the electrochemical effectivity was very less, only about 30%. The charging (oxidation) peak has the same volume through whole measurement. Probably some irreversible processes occurred. The colour of electrode material turned from light green into dark brown, it signifies the charged trivalent nickel was not completely discharged. The material was in electrolyte hydrated for several hours, but during the cyclic voltammetry occurred the degradation, accordingly the aluminium substituted nickel hydroxide is stable in alkaline media if it is not cycled.

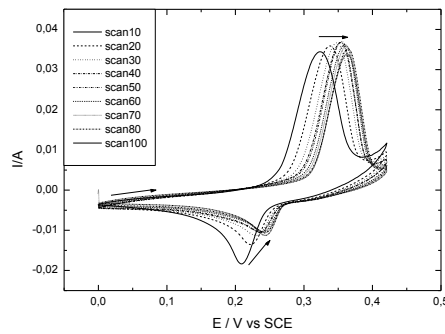


Fig. 1: Voltammograms NiAl

NiMn was measured for 15 scans, for better observation of the progression of degradation the hydrotalcite structure. Measurement begins immediately after inserting the electrode into electrolyte. The discharging peak shows only one and during cycling decreases, it means the similar processes like in NiAl structure. The charging peak was divided into two parts. The first lower peak, signifies the presence of α -Ni(OH)₂, the second higher peak signifies the presence of β -Ni(OH)₂. During 10 scans (Fig.2) the alpha peak lowered and the beta peak increased. After 10 scans could be observed only beta modification. The comparison of voltammograms NiMn hydroxide electrode measured after the insertion into electrolyte and electrode measured after 7 days (Fig.3) in electrolyte before measuring, The long time hydrated electrode shows no alpha peak, so the NiMn hydroxide decreases in alkaline media even without cycling.

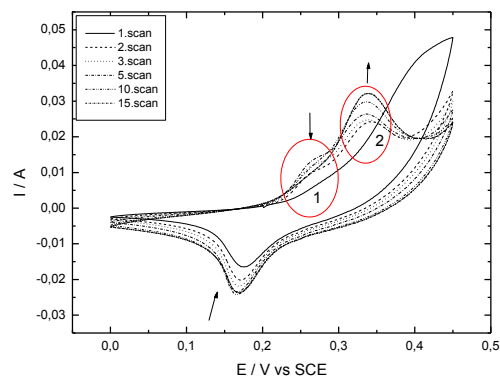


Fig.2: NiMn without hydration

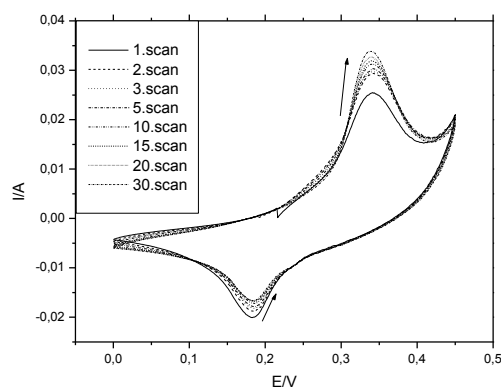


Fig.2: NiMn after 7day hydratation

3. CONCLUSION

Aluminium substituted alpha nickel hydroxide is stable in alkaline media, but degrades during charging and discharging. Manganese substituted nickel hydroxide is unstable in alkaline media and degrades faster than NiAl. The irreversible reactions occur for both samples and the colour turns into dark brown, the trivalent nickel rests in electrodes and can't be completely discharged. The alpha modification in stable form is very interesting to increase the capacity of alkaline accumulators. Adding some combination of admixtures is possible to prepare more stable modification, which offers higher capacity and less alkaline cell weight. Also less concentrated electrolyte offers higher durability of nickel hydroxide.

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REFERENCES

- [1] Rand, D.A.J., Woods, R., Dell, R.M.: Batteries for electric vehicles – Tauton, Somerset, England, Research studies press, 1998
- [2] Falk, S.U., Salkind, A.J.: *Alkaline storage Batteries* - New York, The electrochemical society INC., 1969
- [3] Wang, C.Y., Zhong, S., Konstantinov, K., Walter, G., Liu, H.K.: *Structural Study of Al-substituted nickel hydroxide*, University of Wollongong, Australia, 2002
- [4] Guerlou-Demourgues L., Denage C., Delmas C.: New manganese-substituted nickel hydroxides Part 1. Crystal chemistry and physical characterization, Université Bordeaux I, France, 1994