NICKEL HYDROXIDE ELECTODE STUDIED BY EQCM

Petr Špičák
Doctoral Degree Programme (2), FEEC BUT
E-mail: xspica03@stud.feec.vutbr.cz

Vít Svoboda
Doctoral Degree Programme (2), FEEC BUT
E-mail: xsvobo39@stud.feec.vutbr.cz

Supervised by: Jiří Kazelle
E-mail: kazelle@feec.vutbr.cz

ABSTRACT

Nickel hydroxide has been used as an active material for nickel positive electrodes in Ni-based rechargeable batteries such as Ni/Cd, Ni/Zn, Ni/MH. The Electrochemical Quartz Crystal Microbalance (EQCM) is used to study the proton intercalation performance $Ni(OH)_2$ layers. Using EQCM much information can be obtained, as both the electrochemical response and accompanying mass changes can be measured simultaneously. EQCM was extensively used to investigate the effect of the conditions on the formation of Ni(OH)2.

1. INTRODUCTION

Ni(OH)2 is widely used as a cathode material in NiCd and NiMH batteries. The electrochemical charge transfer reaction, as represented by Eq. (1), is very simple, but the real mechanism is very complex.

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \qquad (1)$$

Bode et al.'s proposal of the diagram shown in Fig. 1. This diagram describes that $Ni(OH)_2$ and the oxidized compound NiOOH can both exist in two different structures. The typical beta phase is conventional material for batteries, alpha phase has better electrochemical aktivity (two electron exchange theoretically), but it is unstable in the strong alcalic medium (6M KOH) and transform into beta.

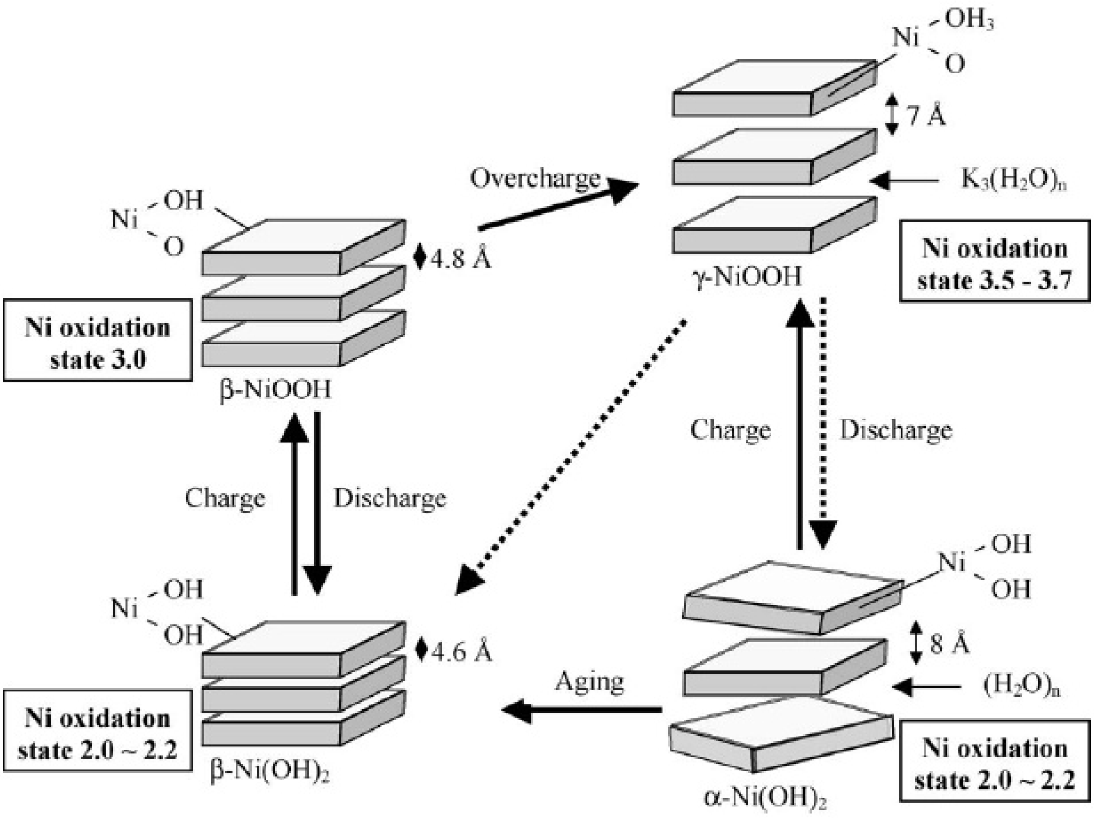

Fig. 1: Bode's diagram of $Ni(OH)_2$

The operation of the quartz crystal microbalance (QCM) is based on the converse piezoelectric effect in which an electric field applied across a piezoelectric material (quartz crystal) induces a mechanical strain in that material. The QCM consists of a thin quartz crystal, which has thin metal film electrodes on its both sides. The electrodes are used to induce the oscillation in the quartz crystal.

In the electrochemical application (EQCM), one electrode of the crystal serves also as the working electrode in the electrochemical cell. For thin rigid deposits, the change in the resonant frequency of the oscillating crystal (Δf) is proportional to the change in mass (Δm) per unit area (A) of the deposit on the working electrode as described by the Sauerbrey equation:

$$\Delta f = -\frac{2 * \Delta m * f_0^2}{A * (\mu\rho)^{1/2}} \quad (2)$$

where, f_0 is the fundamental frequency of the crystal and μ is the shear modulus ($2.947*10^{11}$ $g*cm^{-1}*s^{-2}$) and ρ is the density of quartz (2.648 $g*cm^{-3}$).

The EQCM can differentiate both phases, during charging (oxidation) beta phase decrease mass, on the other hand alpha increase.

2. EXPERIMENTAL

The nominal resonance frequency of the EQCM was 5 MHz (QCM200 SRS Inc.).

The supporting electrolyte was 6M KOH in destiled water. Working electrode was quartz resonator with deposited active matherial on the surface, counter electrode platinum wire and referent electrode was Hg/HgO.

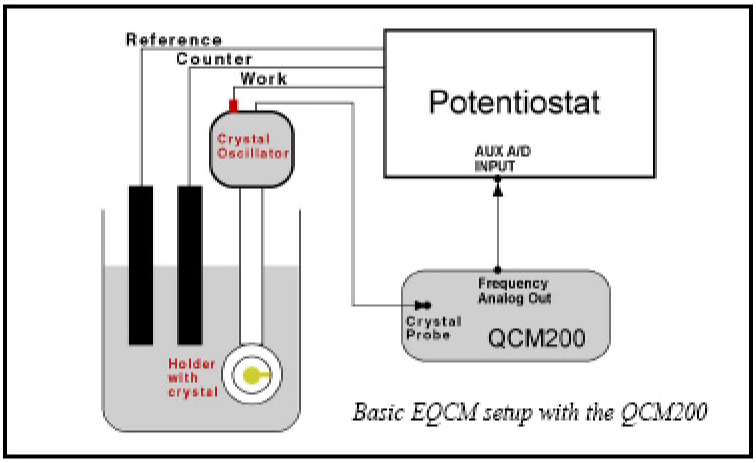

Fig. 2: EQCM and potentiostat, connection diagram

3. RESULTS AND DISCUSSION

Differences between β and α nickel hydroxides meassured by quartz resonator are in mass changes during charging (oxidation) and discharging (reduction). The typical material (β phase) decrement mass during charging and increment during discharging. It is due to expulsion and picking up of H^+ cations from structure to electrolyte. On the contrary the α form (electrochemicaly more active, poor stability in strong alkaline medium, transforming into β) increment mass during charging and decrement during discharging. It is probably caused by picking up and expulsion of the cations from electrolyte (K^+ with molecules of water).

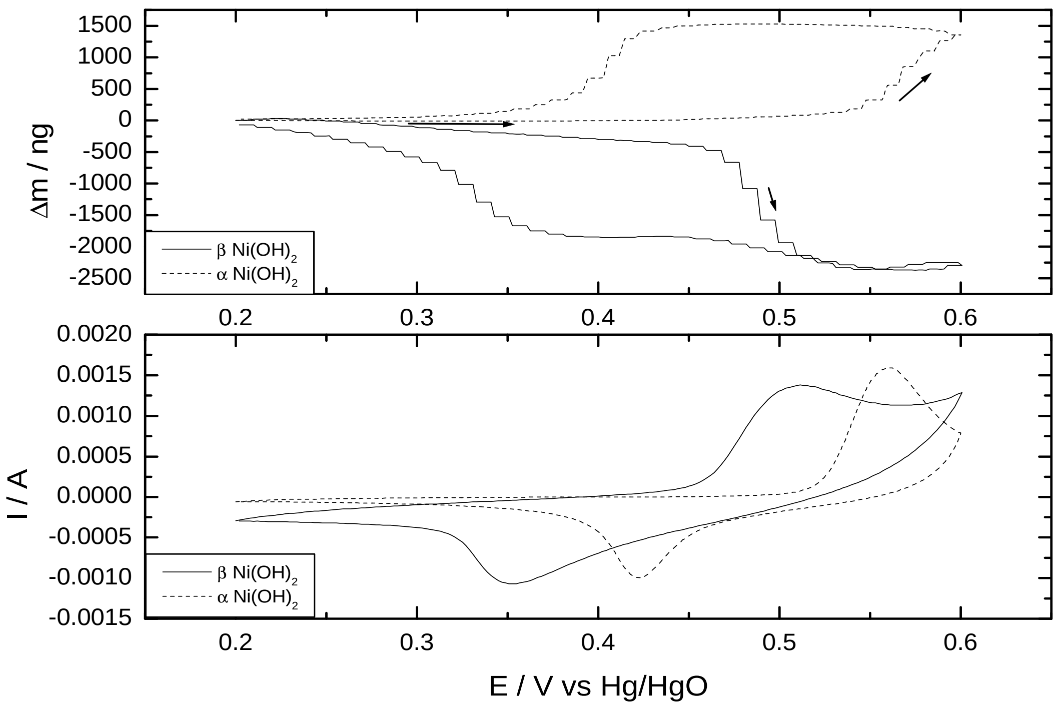

Fig. 3: CV and massograms of β and α nickel hydroxides

4. CONCLUSION

Electrochemicaly more active α phase of nickel hydroxide increasing mass in anodic scan (charging) and decreasind mass in cathodic scan (discharging). The typical β phase have opposite behaviour, there is only H^+ exchange in comparison with α hydroxide (H^+ and cation from electrolyte exchange). Quartz microbalnace is very reliable method for resolution of this two kinds, can be used for study of transformation process.

REFERENCES

1. R. Roto, A. Yamagishi, G. Villemure: Journal of Electroanalytical Chemistry 572 (2004) 101–108
2. M. Wehrens-Dijksma: Electrochimica Acta 51 (2006) 3609–3621
3. T. Ohligschlager, G. Schwitzgebel: Phys. Chem. Chem. Phys., 2001, 3, 5290-5296

ACKNOWLEDGMENTS

Grant Agency of Czech Republic (grant NO. MSM0021630516)

Bochemie, s.r.o.