

EFFECT OF SUBSTITUTED ZINC ON THE ELECTROCHEMICAL BEHAVIOUR OF NICKEL HYDROXIDE

L. Guerlou-Demourgues^a, C. Tessier^b, A. Demourgues^a,
G. Nabias^c, P. Bernard^b and C. Delmas^a

^a Institut de Chimie de la Matière Condensée de Bordeaux
ICMCB-CNRS

and Ecole Nationale Supérieure de Chimie et Physique de
Bordeaux,

Université Bordeaux I

87, Av. du Dr. A. Schweitzer, 33608 PESSAC Cedex (France)

^b SAFT, Direction de la recherche, 111 Bd. Alfred Daney,
33074 Bordeaux Cedex (France).

^c Ecole Nationale Supérieure de Chimie de Montpellier,
8, rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

Nickel hydroxide is widely used as positive electrode material in Ni//Cd, Ni//MH and Ni//H₂ batteries. The electrochemical cycling is commonly performed between the β (II)-Ni(OH)₂ and β (III)-NiOOH phases, the structure of which consists of packed NiO₂ brucite type slabs, between which protons can be reversibly intercalated and deintercalated. Long term overcharge or floating leads to the formation of the γ oxyhydroxide, with an expanded interslab space, by intercalation of water molecules and K⁺ ions. The repeated shift, cycle after cycle, from the unhydrated phases to the hydrated ones (and vice versa), entails mechanical strains and irreversible damages to the electrode. Among the numerous elements, commonly substituted by the battery manufacturers in order to improve the electrochemical behaviour, zinc is intensively studied, especially because it tends to prevent the formation of the γ phase upon overcharge in concentrated electrolyte [1-3]. The present work aimed at clarifying the role of zinc in the stabilization mechanism of the unhydrated β (III)- β (II) system, which remained unclear. For this purpose, attempted correlation was performed between the structure of the zinc substituted nickel hydroxides and the electrochemical properties [4].

While hydrated α type phases, with interslab distances close to 8 Å, are obtained from 20 up to 50 (mole)% zinc, the β (II) structure is retained up to 10% zinc. Investigation of the local structure by EXAFS has allowed to locate zinc cations in tetrahedral interslab sites in the α phases and in slab octahedral sites in the β (II) phases.

Ageing tests in KOH electrolytic medium as well as chemical redox cycling tests were carried out separately in order to decouple the various processes involved in the electrochemical cycling; significant zinc part passes into solution. As suggested by the morphology of the particles investigated by SEM (Fig. 1), ageing phenomena take place via the solution while redox processes are performed in the solid state. During the redox cycling, the zinc loss is therefore necessarily performed via a migration from the slab to the interslab space, entailing the formation of octahedral vacancies within the slabs. From a structural point of view, in the material that is obtained after ageing of a pristine β phase in the battery electrolyte, zinc ions are rather located in interslab tetrahedral sites, as shown by EXAFS measurements. Such zinc surrounding is confirmed, on the basis of structural considerations, by the absence of deformation stacking faults within the structure, suggested by analysis of the X-ray diffraction patterns.

The presence of tetrahedral interslab zinc as well as of octahedral slab vacancies allows largely to address the electrochemical properties. On one hand, interslab zinc

acts as a pillar within the structure and prevents therefore the expansion of the interslab space, which would lead to the hydrated system. The capacity must therefore be improved during a long term cycling. On the other hand, the protons (in tetrahedral sites) that are in the zinc neighbouring are electrostatically destabilised: they must be therefore easily deintercalated at the first charge and cannot be reintercalated at the subsequent discharges, which entails the presence of Ni³⁺ in the material at the discharged state and improves its conductivity. Moreover, the existence of vacancies within the slabs must permit the nickel oxidation up to the 4+ state, without any shift to the hydrated system. As shown in Fig. 2, the number of electron exchanged per nickel atom in zinc substituted nickel hydroxides, tested as positive electrode materials in experimental Ni/Cd cells with a galvanostatic mode, seems to increase with the substituted zinc amount. Such capacity increase may be related to the above mentioned latter phenomena.

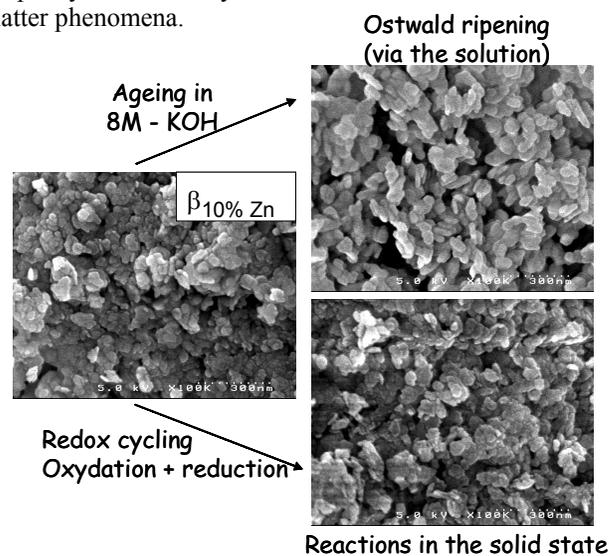


Fig. 1 – Evolution of the SEM micrographs of a β phase after ageing and redox cycling

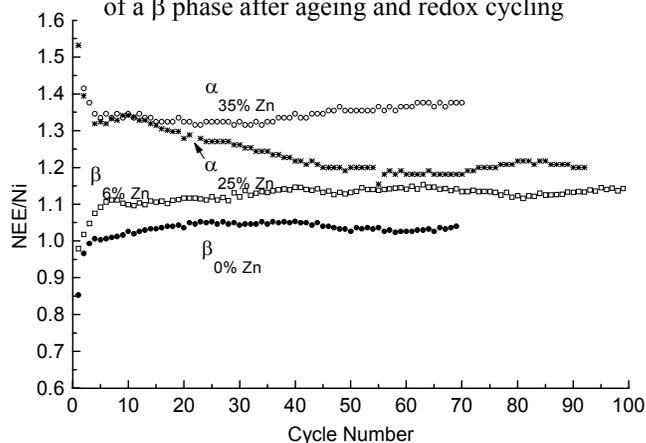


Fig. 2 – Evolution of the capacity vs cycle number for nickel hydroxide type phases with various substituted zinc amounts

References

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