

Ozonation: a new route to prepare nickel and cobalt oxyhydroxides.

Syntheses optimization and reaction mechanism study

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Despite the great concurrence of the Li-ion technology, alkaline batteries such as Ni//Cd or Ni//MH are still widely used. Numerous studies have been devoted to the nickel oxyhydroxide electrode (NOE) in order to enhance its performances and get a deeper insight in some remaining issues dealing with problems of chargeability, occasional appearance of a "second plateau", or self-discharge...[1] Many efforts have been made over the years to tackle these problems from a crystal chemical point of view [2]. In parallel, numerous studies have been aimed at improving the capacity of the NOE that involves different phases [3]: α II-Ni(OH)₂ and β II-Ni(OH)₂ in the reduced state and β III-NiOOH and γ III-NiOOH in the oxidized state.

Obviously the γ III-NiOOH phase could present great interest in term of capacity, if we succeed in obtaining a very high nickel oxide state.

The main chemical route to prepare the oxidized NOE phases consists in the oxidation in an aqueous solution of the reduced hydroxides by means of NaClO. With such a method, compounds in which the oxidation state of Ni can be as high as 3.6 are obtained. Another approach to prepare the γ -phase consists, as reported by Megahed et al., of an ozonation of the reduced NOE phase in presence of KOH. It was claimed that the obtained γ -phases had a higher nickel oxidation state compared to the ones prepared from solution. Thus, we revisited the oxidation mechanisms of the β -II phase using ozone as oxidizing agent.

We will detail the reaction of α II-Ni(OH)₂ and β II-Ni(OH)₂ with ozone. The reaction products at different oxidation stages have been investigated by X-ray Diffraction (see Figure 1), TEM, TGA and FTP-IR. The texture/structure of the obtained powders were found to strongly depend upon the use of either dry or moist ozone. Nevertheless, whatever the various synthesis conditions tried in neither case did we succeed in preparing phases with higher oxidation states than those obtained with NaClO. In contrast, we noted a drastic difference in the oxidation reacting path depending whether we were using ozone or NaClO. Using ozone, the oxidation steps are easier to control, enabling the preparation of pure β III-NiOOH starting from β II-Ni(OH)₂ or of a new structural type of β III-NiOOH phase starting from α II-Ni(OH)₂.

These interesting results and the similarity between cobalt and nickel hydroxides led us to apply the same ozone treatment to cobalt hydroxide as will be reported. Interestingly, we noted that the ozonation of β II-Co(OH)₂ rapidly led to pure β III-CoOOH (see Figure 2), a material whose presence is known to be critical for the efficient electrochemical use of NOE electrodes.

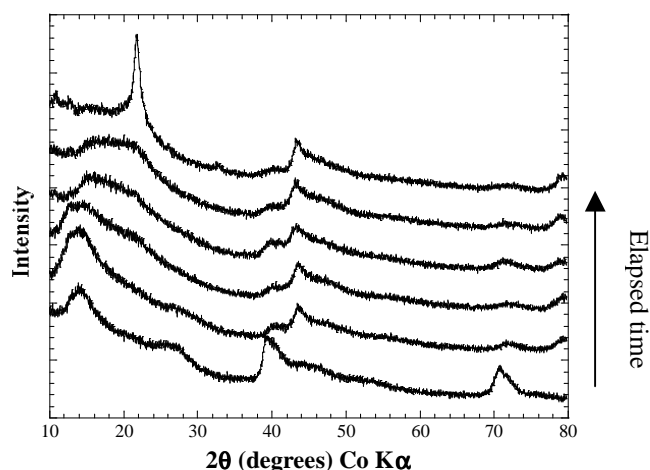


Figure 1: X-Ray Diffraction of samples taken off during α II-Ni(OH)₂ ozonation

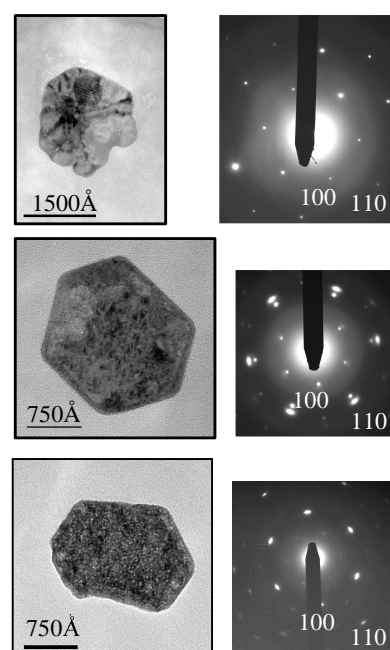


Figure 2: TEM and SAED observations of samples taken off during β II-Co(OH)₂ ozonation: (a) initial β II-Co(OH)₂, (b) mixture of β II-Co(OH)₂ and β III-CoOOH; (c) pure β III-CoOOH

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