

In search of new cobalt conductive additives for the positive electrode of high power Ni-MH cells

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In modern Ni-MH batteries, the positive electrode is composed of a nickel foam, in which the spherical particles of nickel hydroxide, the electrochemical active matter, are trapped; the isolating character of nickel hydroxide requires to add a conductive additive, which is usually based on cobalt. Industrial process consists of incorporating CoO or Co(OH)₂ within the electrode, where it is transformed during the first charge, in usual conditions, into the conductive H_xCoO₂ cobalt oxyhydroxide [1]. This conductive phase is unfortunately unstable during deep discharge or long-term floating in the alkaline electrolyte, where it tends to be reduced into Co(OH)₂, which passes into solution, thus resulting in damaging the conductive network. Such behavior can lead, in specific conditions, to more than 10% capacity lost, which is not acceptable for battery manufacturers. The research of new stable cobalt compounds is therefore a critical aim, especially to promote the Ni-MH batteries for high power applications. The present communication deals with the study of two different new conductive additive families : Co₃O₄ type spinels, and lamellar oxides and oxyhydroxides deriving from metallic Na_{0,6}CoO₂.

Contrarily to ideal spinel Co₃O₄, the original spinel phases that were synthesized in the lab exhibit high electronic conductivity (10⁻¹ to 10⁻² S.cm⁻¹ at RT), linked with the presence of lithium, proton and cobalt vacancies within the structure, as well as to tetravalent cobalt in the octahedral subnetwork. Moderate thermal treatment was shown to entail significant increase of conductivity (3 orders of magnitude), which is due to an increase of the Co⁴⁺/Co³⁺ ratio in the octahedral network, coupled with a cationic redistribution. Such phases can be prepared as more or less agglomerated nanoparticles, or directly chemically coated on the surface of electroactive nickel hydroxide. The resulting electrode materials appear to lead to interesting performances.

The promising behavior of a metallic Na_{0,6}CoO₂ sodium cobaltite has also to be noticed, especially in extreme deep discharge conditions, which represent an important challenge for battery manufacturers. This material is indeed converted, during the cycling, into cobalt oxyhydroxide, then in an intermediate phase, which exhibits a slow reduction kinetics, due to its original interstratified structure. The integrity of the conductive network is therefore maintained, even at very low potential. The nanostructure of sodium cobaltite was shown to have an effect on the electrochemical performances through the interactions with nickel hydroxide particles.

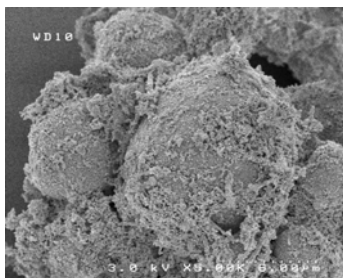


Figure 1: SEM image of spherical nickel hydroxide particles coated with conductive spinel - type Co₃O₄.

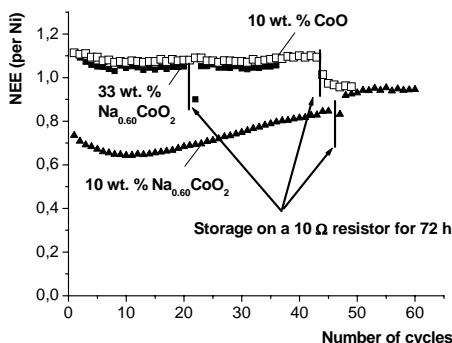


Figure 2: Variation of capacity vs cycle number for nickel hydroxide in the presence of our Na_{0,6}CoO₂ conductive additive, in comparison with CoO reference additive. Performances after low potential storage (short-circuit test) are maintained or improved with Na_{0,6}CoO₂ and lowered with reference CoO.