

Synthesis and structural characterization of a new spinel type cobalt oxide, a potential conductive additive for positive electrode of nickel metal hydride batteries

Frédéric Tronel^{a,b}, Liliane Guerlou-Demourgues^a, Lionel Goubault^b, Patrick Bernard^b and Claude 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. Dr. A. Schweitzer
33608 Pessac Cedex, France

^b SAFT, direction de la recherche
111-113, Boulevard Alfred Daney
33074 Bordeaux Cedex, France

In the field of nickel metal hydride batteries, the problem of the conductive additive within the nickel hydroxide based positive electrode concentrates today a significant part of the research topics. The chemical requirements for an efficient additive are a good conductivity and a good stability upon electrochemical cycling. Since the work of Oshitani et al [1], cobalt oxide is commonly added to nickel hydroxide; during the first charge it transforms in the H_xCoO_2 conducting phase [2]. But this material presents a major drawback: at low potential it transforms slowly in $Co(OH)_2$, which dissolves in the electrolyte and migrates within the battery [3]. Preliminary experiments have shown that a material, which seems to be close to the Co_3O_4 spinel phase, may be formed in the electrodes in specific conditions. But whereas the ideal Co_3O_4 phase shows an insulating behaviour ($\sigma_{RT} = 10^{-6} S.cm^{-1}$), the obtained material has a conductivity at least 4 order of magnitude greater.

In order to understand the structure and the properties of this material, we synthesised different cobalt based materials: CoO , pasted on a nickel foam, was hydrolysed in pure and mixed alkaline electrolytes; then it was used as positive electrode material of a cell which was charged at $90^\circ C$ in the same medium. The resulting cobalt material was recovered and characterised. Electrolytes were pure KOH , $LiOH$, $NaOH$ or a ternary mixture. As shown in Fig. 1, all the obtained materials consist of a " Co_3O_4 " spinel type phase with impurities like $CoOOH$ and $LiCoO_2$. But, as emphasised in Fig. 2, whereas the sample obtained in KOH is really a poor conductor, those obtained in $LiOH$ or in ternary electrolyte exhibit a 4 order of magnitude greater conductivity, making them potentially interesting as conductive additives.

Coupled SEM and X-ray diffraction studies of the electrodes, recovered after increasing charging time, have shown that, during hydrolysis, CoO is transformed into $Co(OH)_2$. This material, which was initially present within the pores of the nickel foam, is transformed into " Co_3O_4 " that is deposited on the surface of the foam. These observations suggest a dissolution-electrodeposition mechanism allowed by the significant solubility of $Co(OH)_2$ in concentrated alkaline medium at $90^\circ C$.

Structural, thermal and chemical characterisations of the obtained materials were performed. Rietveld refinements of the XRD patterns confirm the spinel structure but with a significant amount of cobalt vacancies. For example, the " $Co_{2.51}O_4$ " formula, corresponding to the following cationic distribution

$[(Co_{0.71}\square_{0.29})_{Tetra.}(Co_{1.8}\square_{0.2})_{Octa.}O_4]$ is obtained in the case of the phase prepared in ternary electrolyte. Coupled thermo-gravimetric analysis and mass spectroscopy (TGA/MS) experiments show a significant water loss between 200° and $500^\circ C$, suggesting the presence of structural water. The measured chemical composition was close to " $H_{0.73}Li_{0.18}Co_{2.35}O_4$ " in the case of the sample obtained in ternary electrolyte.

These formulae allow us to propose an explanation for the improved conductivity. The charge deficiency induced by the cobalt vacancies and by the substitution of an element with a lower oxidation state for cobalt can be partly compensated by oxidation of Co^{3+} to Co^{4+} in octahedral sites of the spinel structure. Possible electronic exchange in the sub-network of octahedral sites, improving conductivity, can be envisaged.

As a conclusion, at $90^\circ C$ in concentrated alkaline media, phases other than H_xCoO_2 , also exhibiting a good electronic conductivity, can be formed during the first charge. Moreover, an original low temperature synthesis process for Co_3O_4 type phases was proposed, leading us to obtain new materials with improved properties.

Acknowledgements

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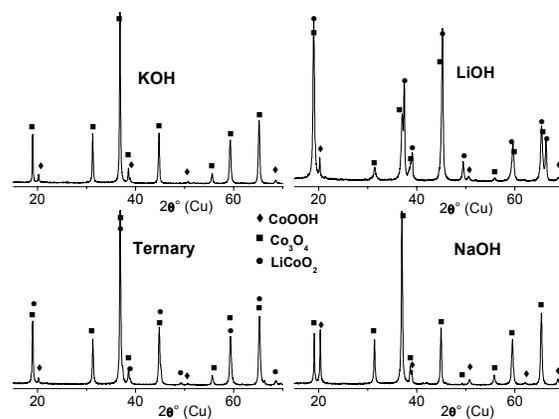


Fig. 1 Comparison of the X-ray powder diffraction patterns of the materials obtained in different alkaline electrolytes.

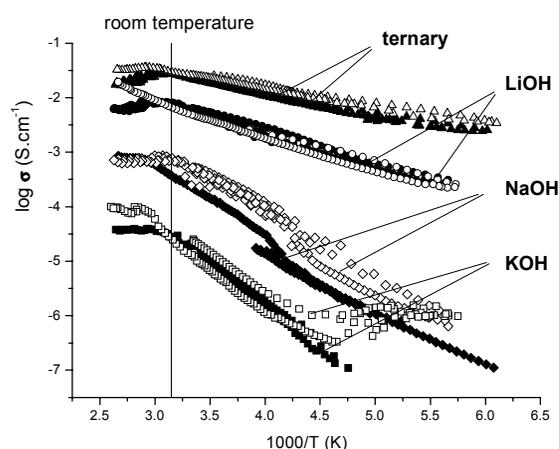


Fig. 2 Variation of the conductivity logarithm vs reciprocal temperature for two samples of the materials obtained in each alkaline electrolyte.