Effect of deep discharge on the electrochemical behavior of cobalt oxides and oxyhydroxides used as conductive additives in Ni-MH cells

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ARTICLE INFO

ABSTRACT

When used as conductive additive at the positive electrode of Ni-MH batteries, the $Na_{0.6}CoO_2$ phase is converted, during the first charge, by oxidation, in a γ-hydrated cobalt oxyhydroxide, which exhibits promising performances. The behavior of these phases was studied in specific deep discharge or low potential storage conditions, through electrochemical short-circuit experiments. The evolution of the electrodes during the cycling was followed by X-ray diffraction and SEM analysis. These novel additives appear to be more efficient in these extreme conditions than the CoO or $Co(OH)_2$ additives, commonly used in industrial devices.

1. Introduction

In Ni-MH batteries, the current technology of pasted positive electrodes needs to use conductive additives, since the electrochemical active material, $Ni(OH)_2$, exhibits a poor electronic conductivity [1,2]. CoO cobalt oxide or $Co(OH)_2$ cobalt oxyhydroxide, which are usual additives, are transformed, during the first charge, into a conductive H_xCoO_2 type phase [3,4]. This one is unstable at low voltages; it is indeed reduced into $Co(OH)_2$, which is soluble in the electrolyte, leading to a degradation of the conductive network and a capacity loss of the battery [5–7]. That is the reason why research works are now devoted to new additives, to prevent the instability of the conductive network. The addition of bismuth to the cobalt phases [8] or the use of a conductive $H_xLi_yCo_{3-\delta}O_4$ spinel type phase, formed in situ under specific conditions [9–11], are solutions proposed in literature.

In this context, the effect of the $Na_{0.6}CoO_2$ phase, as conducting additive to $Ni(OH)_2$, has been investigated in our lab. This layered oxide is a promising conductive additive, thanks to its metallic electronic conductivity and its good stability in the potential range of Ni-MH batteries. Preliminary works of Tronel et al. have shown, in our lab, a good efficiency of the additive, even at low potential [12].

This study was motivated by the registration, by Japanese battery manufacturers, of several patents, which underlined the beneficial effect of sodium on the stabilisation of the cobalt conductive subnetwork [13–15]. Tronel et al. have shown that the $Na_{0.6}CoO_2$ phase is transformed, after few cycles within the electrode, into a γ-type hydrated cobalt oxyhydroxide [16]. This latter phase, formed in situ, is a promising candidate because it exhibits a slow reduction kinetics in concentrated alkaline electrolyte [17].

The usual method, employed to test "resistance" of the battery with regard to a deep discharge or a long storage in discharged state, consists in keeping the cell, at the end of a discharge, in short-circuit on a resistor during several days. The present paper aims at comparing, in these conditions, the behaviors and the evolutions of the $Na_{0.6}CoO_2$ phase and deriving γ-type cobalt oxyhydroxides with those of the usual $Co(OH)_2$ additive, which is known to entail a loss of efficiency of the conductive network in such conditions.

2. Experimental

2.1. Synthesis of the conductive additives

The $Na_{0.6}CoO_2$ phase is synthesized by solid-state reaction from Co_3O_4 and Na_2O (12 wt.% excess) oxides in a tubular furnace, at 550 °C, during 15 h, under oxygen flux [18]. The Co_3O_4 precursor is obtained by decomposition of $CoCO_3$, during 12 h, at 440 °C, under flowing O_2.

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Three different processes are used to prepare γ-cobalt oxyhydroxide phases (denoted as γ-Co in the following) from $Na_{0.6}CoO_2$. The first method consists of an oxidizing hydrolysis, which is performed by introducing 1 g of $Na_{0.6}CoO_2$ in 200 mL of a 4 M KOH–0.8 M NaClO solution [4]. After a 15-h stirring, the material is recovered by centrifugation, rinsed in deionised water and dried 15 h at 60 °C. The second technique used consists of an electrochemical oxidation of the $Na_{0.6}CoO_2$ phase. 3 g of $Na_{0.6}CoO_2$ is trapped, by mechanical pressure, between two pieces of nickel foam. The so-constituted electrode is "sandwiched" between two cadmium electrodes. The cell is immersed into an 8 M KOH electrolyte. After a 20-h soaking, the cell is charged for 5 h at the C/20 rate. (The theoretical capacity "C" of the battery is calculated on the basis of one electron exchanged per cobalt atom.) Then, the positive electrode is removed, rinsed in deionised water and dried for 15 h at 60 °C. The two pieces of nickel foam of the electrode are simply unsticked one of each other, to recover the cobalt material. Finally, the third method that is used to obtain a γ-Co phase consists in ageing the $Na_{0.6}CoO_2$ phase, during one month, in 8 M KOH electrolyte. Such treatment leads to spontaneous transformation of $Na_{0.6}CoO_2$ into a mixture of a majority γ-Co type phase and of a β(III) type phase, as described in a previous paper [17].

2.2. Preparation of the cells

Electrodes for electrochemical experiments are prepared by mixing 2/3 of $Ni(OH)_2$ active material (OMG E148309-1 nickel hydroxide, containing small amounts of syncrystallized cobalt and zinc) and 1/3 of studied conductive material (weight fraction). 1 wt.% "powdered" PTFE is then added as a binder. 200 mg of the mixture is pasted on a nickel foam (1 cm × 4 cm), which play both the roles of electrode support and current collector. The so-constituted positive electrode is pressed at 1 t cm^{-2}, wrapped into a non-woven tissue and then positioned between two polyvinyl chloride plates. Two sintered cadmium hydroxide electrodes are placed on both sides of the positive electrode. Their capacity is strongly exceeding that of the positive electrode, so as not to play a limiting role with regard to the cycling of the battery. The cadmium electrode plays also the role of reference electrode, so that all potential values are given in this paper versus $Cd(OH)_2/Cd$ potential. The cell is immersed in an 8 M KOH electrolyte solution.

2.3. Characterization

A galvanostatic cycling is started about 18 h after the addition of the electrolyte. The first cycle consists of a charge, for 20 h, at the C/10 rate, followed by a discharge, down to 0.9 V, at the C/5 rate (the theoretical capacity "C" of the battery is calculated on the basis of one electron exchanged per nickel atom.) Then, the cycling process consists in alternating 6-h charges and discharges down to 0.9 V, at the C/5 rate. In the middle of the cycling, a low potential storage test is carried out by performing a short-circuit of the cell on a 10 Ω resistance, during 3 days. The classical cycling at the C/5 rate is afterwards started again (up to 60 cycles).

X-ray diffraction (XRD) data are collected with a PANalytical X'pert Pro diffractometer, using the Kα Co radiation. The diffraction patterns are recorded in the [5–110°] (2θ) angular range, using a 0.0167° (2θ) step, with an active length of 2.122° in the detector and a constant counting time of 100 s per step. XRD characterizations of the electrode materials are systematically performed in the discharged state. Let us note that, when XRD analysis is performed directly on the electrode, no special care is taken in terms of sample preparation; the rules of isodensity and random disorientation of crystallites are therefore not systematically matched. Consequently, XRD patterns give qualitative but not quantitative information: the relative intensity of the diffraction

lines, corresponding to two phases in a sample, cannot be directly compared.

Scanning electron micrographs are collected with a Hitachi S-4500 field emission microscope, with an accelerating voltage of 3.0 kV, in secondary electrons mode.

Temperature-dependent electronic conductivity measurements are carried out with the four-probe technique [19], using a direct current. Because of the low-temperature synthesis, the studied material could not be sintered. For this reason, pellets (8 mm of diameter and approximately 1.2 mm in thickness) are only obtained by compacting 200 mg of powder, at 8 t cm^{-2}, under vacuum.

Inductively coupled plasma (ICP) spectrometry, performed at SAFT laboratory, in Bordeaux (France), was used for Na, K, and Co titrations. The oxidation state of cobalt was determined in the laboratory by the iodometric titration method [11].

3. Electrochemical performances of the cobalt conductive additives

3.1. Conductive additives studied

In the present paper, five cobalt phases are studied as conductive additive at the positive electrode of Ni-MH battery: $Na_{0.6}CoO_2$, the three derivative γ-Co phases, obtained in different synthesis conditions (as described in Section 2.1), and $Co(OH)_2$, which, commonly used in industrial devices, plays the role of reference additive. Table 1 summarises the chemical compositions and the average oxidation degree of cobalt in these synthesized four materials. Comparison of the chemical compositions of the three γ-Co derivatives materials with the composition of the $Na_{0.6}CoO_2$ precursor phase shows the exchange of a majority part of the sodium ions by potassium ions, which occurs simultaneously with insertion of water molecules [17].

As these materials are intended to be used as conductive additives, their electronic conductivity was examined. The curves are presented in Fig. 1, while conductivity and activation energy values at room temperature are reported in Table 1.

The $Na_{0.6}CoO_2$ and the γ-Co phases, obtained by chemical or electrochemical oxidation, exhibit high conductivity with a metallic behavior, whereas the material obtained by ageing presents a lower conductivity. Let us remember that, as mentioned in Section 2.1, this latter phase is biphasic, containing a γ-Co type and a β(III)-
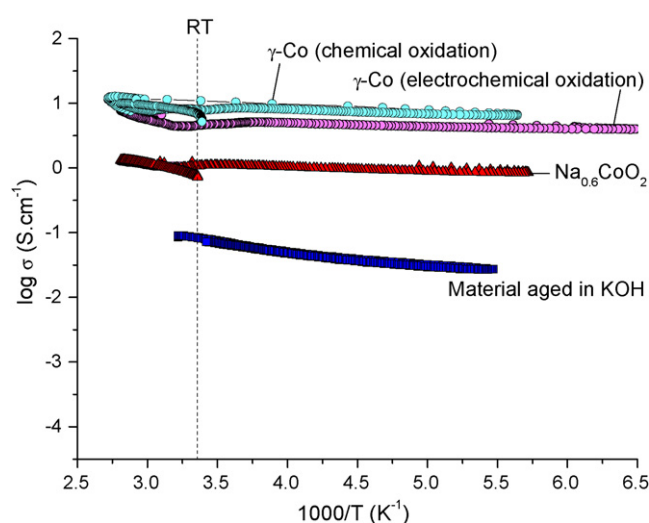

Fig. 1. Variation of the logarithm of electrical conductivity versus reciprocal temperature for the $Na_{0.6}CoO_2$ phase and the derived γ-Co phases, obtained by ageing in KOH, electrochemical oxidation or chemical oxidation from $Na_{0.6}CoO_2$.