

Study of the electro-oxidation of CoO and Co(OH)₂ at 90 °C in alkaline medium

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Abstract

Cobalt is usually post-added as CoO or Co(OH)₂ to nickel hydroxide at the positive electrode (nickel oxide electrode) of alkaline batteries, to form a conductive network. In the present work, we focus on the transformation of CoO and Co(OH)₂ phases when oxidized at 90 °C. The Co₃O₄ phase is the majority product of such a reaction, with CoOOH as a secondary product. It is shown that the Co₃O₄ phase results from the reaction of the CoOOH phase, formed by electrochemical oxidation of Co(OH)₂, with Co²⁺ species in the electrolyte, which is made possible by temperature. This process requires a global migration of the cobalt phases towards the current collector.

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1. Introduction

Cobalt addition plays a key role to improve the performances of the nickel hydroxide electrode, the positive electrode of Ni-MH cell. Cobalt is usually added in two different ways to β-nickel hydroxide, the active material that stores energy: it can either be co-precipitated with nickel hydroxide, to form a mixed nickel–cobalt hydroxide, or post-added by mixing cobalt monoxide or cobalt hydroxide to nickel hydroxide. In co-precipitation, adding cobalt improves the conductivity of the active material [1,2] and reduces charge and discharge potential, compared to pure nickel hydroxide [3,4]. The conductivity increase as well as the decrease of the oxidation potential of the active material in charge, leads to an increased chargeability of the electrode and thus a higher capacity of the battery. Co-precipitation of cobalt in β-nickel hydroxide also tends to prevent the formation of the γ-type hydrated nickel oxyhydroxide phase during overcharge, and therefore the associated

swelling of the electrode [5]. The life duration of the electrode is thus improved. In the case of post-added cobalt, the positive effect is linked to the high porosity of the nickel foam, used for non-sintered high-capacity electrodes, which plays both roles of substrate and current collector. Nickel hydroxide is filling the pores of the substrate. However, the low conductivity of the active material leads to isolating parts, which are located in the middle of the pores, and thus far away from the current collector. The result is a low active material utilization rate. When cobalt is added, either in the form of Co(OH)₂ or CoO, a conductive sub-network is formed within the pores, linking electronically the whole active material to the current collector, and thus allowing an active material utilization rate as high as 100% [6,7]. Such a role requires three main properties of the cobalt derivative: it is able to spread over the electrode, to form a wide conductive sub-network from localized addition; it forms a conductive phase after oxidation; the so-formed phase is stable in usual cycling conditions.

Though most of the work has been focused on the global performance of nickel hydroxide electrode, some studies have dealt with the mechanism of post-added cobalt effects. It has been shown that, whatever the cobalt phase added, it is oxidized into conductive CoOOH during the first charge [6]. Actually,

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further work has demonstrated that the conductive phase was a non-stoichiometric H_xCoO_2 phase [8]. In the following the stoichiometric phase $HCoO_2$, which is a bad conductor, will be denoted as $CoOOH$. Two mechanisms were reported for the oxidation of $Co(OH)_2$ into $CoOOH$, depending on the charge rate [9]. At high charging rate, the oxidation proceeds via a solid-state reaction and the formed phase is the conductive H_xCoO_2 phase. At low charging rate, the $CoOOH$ phase can also be formed by a dissolution–reprecipitation process. When CoO is used as an additive, it is hydrolyzed into $Co(OH)_2$. This step, occurring through dissolution–reprecipitation via the electrolyte, allows to better distribute the cobalt within the electrode and thus obtain a better effect of cobalt than with $Co(OH)_2$, for the same amount of cobalt added [6]. However, post-adding cobalt to the electrode exhibits some drawbacks. During storage at low potential, for example when a discharge cell is left in short circuit, cobalt is reduced and migrates to the surface of the current collector [10]. Such a phenomenon was already observed for co-precipitated cobalt [11]. The formation, in peculiar cycling conditions, of insulating phases like $CoOOH$ [12,13] or Co_3O_4 [10,14], was also underlined, the latter phase being favored by higher temperature. Those studies pointed out the role of dissolved cobalt, as a blue cobalt complex formed in highly concentrated alkaline medium. These species were sometimes described as $HCoO_2^-$ [11,15]. More recent studies, based on visible spectroscopy, identified $Co(OH)_4^{2-}$ complexes [10,16] and a nucleation-growth mechanism in solution was proposed for the formation of Co_3O_4 . A solution has been proposed to overcome the capacity loss by processing the first charge of the electrode, when the cobalt conductive network is formed, at $90^\circ C$, which allows to maintain the performances of the electrode after a discharge or a storage at low potential [17]. These conditions tend to favor the formation of a Co_3O_4 -type phase. Though the ideal Co_3O_4 phase is known as insulating, we could obtain Co_3O_4 -type conductive phases ($10^{-1} S cm^{-1}$) by electro-oxidation of cobalt at $90^\circ C$ in different electrolytes [18]. The conductive phases were shown to be spinel-type cobalt derivatives, with the formula “ $H_xLi_yCo_{3-z}O_4$ ”, exhibiting cobalt vacancies, lithium, hydrogen and tetravalent cobalt in their structure. Such conductive phases were formed in $LiOH$ electrolytes, but also in the ternary electrolyte (KOH , $LiOH$, $NaOH$) used in commercial cells, which is mainly constituted by KOH (approximately 8 M). Hence, to consider a less complicated chemical system though not too far from the commercial cells, the electrochemical oxidation of cobalt was studied in 8 M KOH . It was thus shown that in optimized conditions (CoO as starting phase and $C/100$ charge rate) a pure Co_3O_4 -type phase was formed, with low conductivity but a structure close to the conductive phases. It is thus possible to investigate the formation mechanism of these phases in 8 M KOH .

In the present work, the behavior of cobalt derivatives during the charge at $90^\circ C$ in KOH 8 M is investigated. We focus on the mechanism leading to the Co_3O_4 -type phase by studying the structural and morphological evolution of two different cobalt-starting phases: CoO and $Co(OH)_2$. The solubility of cobalt derivatives within the electrolyte and its evolution during electrochemical oxidation is also studied, to link the presence

of $Co(OH)_4^{2-}$ species in the electrolyte to the formation of either Co_3O_4 or $CoOOH$. Finally, various KOH concentrations and charge rates were tested in order to confirm the proposed mechanism.

2. Experimental

All the materials were obtained by electro-oxidation of a cobalt-based electrode. The electrodes are made from a viscous paste consisting of CoO or $Co(OH)_2$, mixed with distilled water, that was introduced into porous nickel foam, dried 2 h at $85^\circ C$ and pressed at $1 t cm^{-2}$. No mechanical binder such as PTFE was used, considering that only one charge is performed and that the material has to be recovered from the electrodes afterwards. The electrode was then set between two over-capacitive cadmium electrodes, playing both roles of counter electrode and reference electrode, with a polyamide separator avoiding short circuit. The electrolyte was 8 M KOH , but for additional experiments other concentrations between 1 M and 15 M were used. In the so-constituted Co – Cd cells, the cobalt-based electrode was the positive pole and the cadmium-based one the negative electrode. This convention will be used in the whole work, so that cell “charge” corresponds to cobalt oxidation. In the case of CoO as starting electrode material, the cells were kept 4 days at room temperature, after introducing electrolyte, to complete CoO hydrolysis into $Co(OH)_2$ before oxidation. They were then heated at $90^\circ C$ and charged at a $C/100$ rate, except for final experiments where various rates were used. Electrochemical oxidations were performed in a galvanostatic mode, with a homemade cycling apparatus and software. The recorded potentials are given vs. $Cd(OH)_2/Cd$ electrochemical couple. Charge rates are given as C/n , meaning that one electron is exchanged per nickel or cobalt atom in n hours. After charge, electrodes were left 24 h in distilled water, with periodic change of the rinsing solution, in order to remove all trace of electrolyte. They were then dried one night at $60^\circ C$ and milled to complete an efficient recovery of the cobalt material. Separation of nickel, coming from the nickel foam, was performed by sieving on a sieve with $80 \mu m$ holes.

The X-ray diffraction (XRD) patterns were collected using either an INEL CPS 120 curve position sensitive detector with a cobalt anode or a Siemens D5000 diffractometer ($Cu K\alpha$). In the first case 1-h long acquisitions were performed; in the latter case, the data were recorded with a scan step of $0.02^\circ (2\theta)$ for 10 s.

Scanning electron microscopy (SEM) was performed upon pieces of electrode (approx. $2 mm \times 2 mm$) with a field effect gun Hitachi S4500 microscope. A 2-nm layer of platinum was previously sputtered on the samples to evacuate charges.

Cobalt in alkaline solution was titrated either by EDTA titration or by atomic absorption spectrometry at 242.5 nm using a PerkinElmer 2280 apparatus. Atomic absorption was preferred in the case of electrolyte testing during oxidation because the volume of available solution was low. In order to investigate the nature of cobalt in the electrolyte, UV–vis spectra were collected on a Varian Cary 5E apparatus in the 300–1200 nm wavelength range.

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