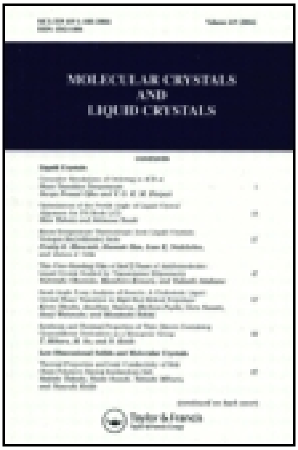

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Competition between the Two Reduction Reactions of the γ(III) Phase in the Ni-Based Batteries

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COMPETITION BETWEEN THE TWO REDUCTION REACTIONS OF THE γ(III) PHASE IN THE Ni-BASED BATTERIES

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ABSTRACT: We show that the γ(III)/β(II) phase transition is at the origin of the second plateau at 0.8V in the Ni-based batteries by means of transmission electron microscopy (TEM) and X-ray diffraction (XRD) studies and intermittent galvanostatic measurements (GITT). This study shows that the equilibrium voltage of this transition is 1.25V vs Cd-$Cd(OH)_2$, thus implying an overvoltage of 400 mV. Direct evidence for a textural memory effect trough the γ(III)/β(II) phase transition is given by TEM studies. The reoxidation of the β(II) phase to γ(III) phase occurs without going trough the β(III) phase.

INTRODUCTION

Rechargeable alkaline Ni-based cells, such as Ni/H_2, Ni/Cd or Ni/MH are widely used in today's space, and portable applications. The usual voltage profile for these batteries consists of a plateau at 1.2 V related to the β(III)/β(II) phase transition. However, these Ni-based cells are occasionally known to exhibit a residual capacity at voltages lower than 1 V,[1] and capacity transfers from the 1.2 V plateau to a 0.8 V or a 0.5 V plateau are often observed. This capacity transfer results in a loss of useful energy for users. This phenomenon, usually reported as "residual capacity" or "second plateau" has been frequently adressed, [2-8] but its origine still remains controversal.

Recently, Sac-Epee et al. clearly demonstrated that, out of its appearance mainly due to preparation modes and electrochemical cycling conditions, the second plateau capacity is directly related to the charged state of the positive electrode prior to its discharge, i.e. to the presence of the γ(III) phase in the oxidized state.[9] This phase appears as an impurity resulting from local overcharge in the positive electrode.

In this paper, we present the γ(III) phase reduction mechanism giving rise to the second plateau by means of X-ray diffraction and transmission electron microscopy studies. Intermittent galvanostatic measurements were performed to determine the equilibrium potential γ(III)/β(II) phase transition.

EXPERIMENTAL

1/ Different samples

The morphology and phase composition of the samples used in this study were determined by means of transmission electron microscopy (TEM) and X-ray diffraction (XRD). The diffraction patterns have been collected using a Philips diffractometer PW1710 with a Cu(kα1) radiation. TEM studies were carried out using a Philips CM12.

The starting material used in this study, is synthezised in two steps described as follows. The first step consists in synthesizing an α(II) phase by adding nickel nitrate solution to ammonia solution. Then the α(II) phase is placed in hydrothermal conditions around 125°C to the β(II) material, denoted **B2** in the following of this paper. In these conditions, sample B2 consists of large hexagonal platelets (200Å*1000Å).

Oxidized nickel oxyhydroxides containing various quantities of β(III) and γ(III) are chemically prepared. Such a chemical oxidation is carried out by reacting sample B2 with NaClO. Depending on the ageing temperature, the relative volume of NaClO (15% chlore active) and the presence of KOH or not, we are able to obtain a set of samples with different average oxidation states for nickel with different compositions. The total amount of nickel in the samples was determined by complexometric EDTA titration, whereas its oxidation state was determined by iodometry. The resulting oxidized phases consist of mosaïc platelets with the same overall dimension as their β(II) precursor sample.

2/ Electrochemical measurements

All electrochemical measurements were carried out using a Mac-Pile system (Biologic S.A., Claix, France) that operates both in potentiostatic and galvanostatic modes. A three-electrode cells with either a Hg-HgO or a Cd-$Cd(OH)_2$ reference electrode and a Pt or Ni thread as counter electrode.

The positive electrode is made by first mixing the active material (usually 100 mg) and micro-bread meso-carbon (MCMB 25-28) in a 1 to 5 weight ratio, and pressing the mixture with a disk of sintered glass and a separator on a nickel or platinum disk ($2cm^2$) as current collector. Impregnation of the active material with electrolyte is made by outgasing under vacuum several times down to the limit vapor pressure of the electrolyte. Galvanostatic measurement were performed with either continuous or intermittent application of the current (GITT), in order to determine the equilibrium potentials from observation of the time dependences of the potential during open circuit sequences.

RESULTS AND DISCUSSION

1/ Study of the reduction of the γ(III) phase by XRD and TEM studies

All oxidized samples are reduced in a three electrode cell with C/20 rates, and the first discharge curve show the appearance of the second plateau (figure 1). The relative capacity on the second plateau was found to continuously increase, from a relative capacity of 34, 50, 71 to 81%, together with the increase of the γ(III) amount as shown in figure 2a as determined by XRD. There is a direct correlation between these two parameters: a straight line going through zero is expected but not observed. This is consistent with the fact that XRD is not an accurate quantitative analysis method for samples which present preferential crystal orientations. Figure 2b describes the relationship between the relative capacity on the second plateau and the oxidation degree of the oxidized samples, i.e. the amount of the γ(III) phase present in the samples.There is no second plateau for an oxidation degree of 2.8 (pure β(III) phase) and only one second plateau for an oxidation degree of 3.65 (pure γ(III) phase). The relationship between the second plateau and the γ(III) phase is thus clearly demonstrated.

In addition, practically pure γ(III) sample (oxidation degree=3.53) after being electrochemically reduced (-0.3 V vs Hg/HgO) has been characterized by TEM and XRD. The resulting phase, denoted here after βexγ, corresponds to a β(II) phase as can be seen from both the XRD pattern and the selected area electron diffraction pattern (SAED) (figure 3b). Note that the reflections on the SAED corresponding to β(II) phase are broad arcs implying a mosaic texture. The results confirm that the γ(III) phase reduction on the second plateau is a direct solid state phase transformation without formation of α(II). Indeed, if the reduced β(II) phase could appear from the reduction of γ(III) via the formation of α(II), the β(II) particles would be monolithic and never mosaic because it is well-known that the β(II) phase forms from the α(II) phase by dissolution-recrystallization process. Thus, the origin of the second plateau is now unambiguous and it is due to the direct reduction of the γ(III) phase into β(II).

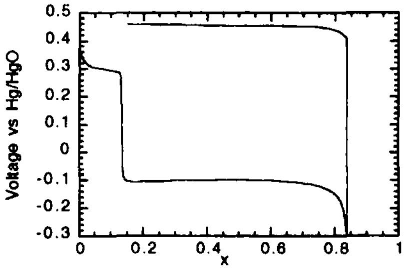

Figure 1: First discharge/charge of a chemically oxidized sample (oxidation degree of nickel =3.53)

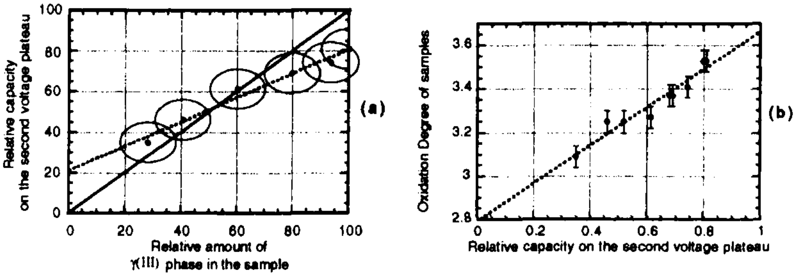

Figure 2: Correlation between the relative capacity on the second plateau and (a) the relative amount of γ-phase as deduced by XRD patterns (full line: theorical line, dashed line: experimental line), (b) the average oxidation degree of the active material, which reflects the amount of γ-phase in the sample.

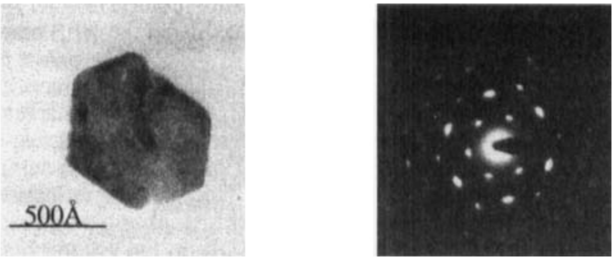

Figure 3: TEM micrograph of a βexγ particle lying on the (001) plane after discharge at C/20 rate in the three electrode cell and the corresponding SAED pattern.

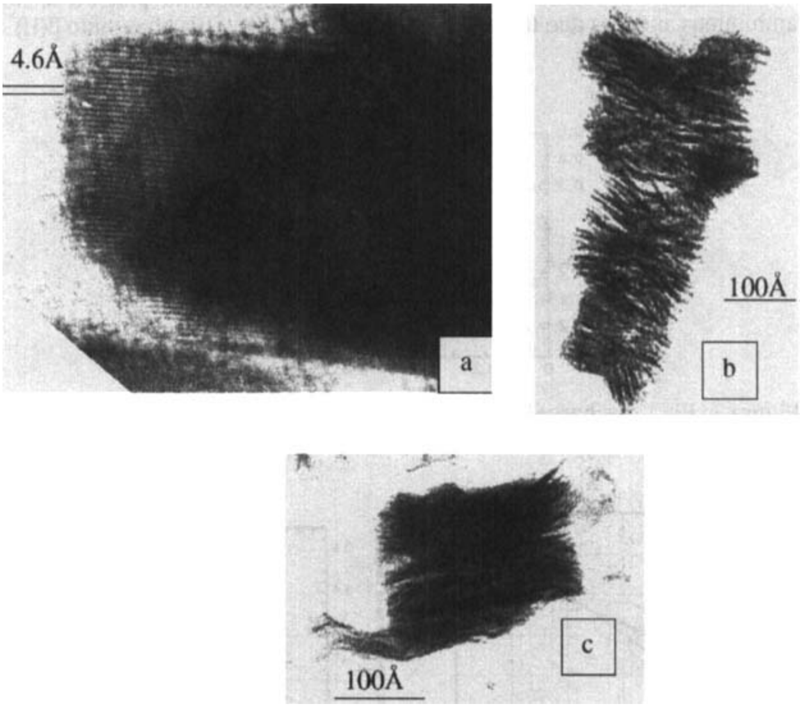

Figure 4: TEM Micrograph of particles lying along the c axis: (a) B2; (b) γ(III); (c) βexγ.

However, while the layers in B2 particles are perfectly stacked along the c-axis, the reduced βexγ phase particles lying along the c axis exhibit partial exfoliation as seen for the γ(III) phase (figure 4). The only difference between βexγ and γ is the interlamellar distance measured on the TEM images: 4.7 Å against 7.1 Å. Thus, it seems that there is a textural memory in the βexγ phase. In order to investigate the role of this feature, the βexγ phase is reoxidized in a three electrode cell configuration at a C/20 rate to 0.36 V vs Hg/HgO (figure 1). At this point, the sample is removed and studied by XRD (figure 5). The XRD pattern shows a mixture of β(II) and γ(III) phases, so it seems that the βexγ phase is oxidized to γ(III) phase without β(III) as intermediary. It can thus be concluded that there is a textural memory in the βexγ phase. In these conditions, one can understand that the relative capacity on the second plateau upon cycling is constant.[10]

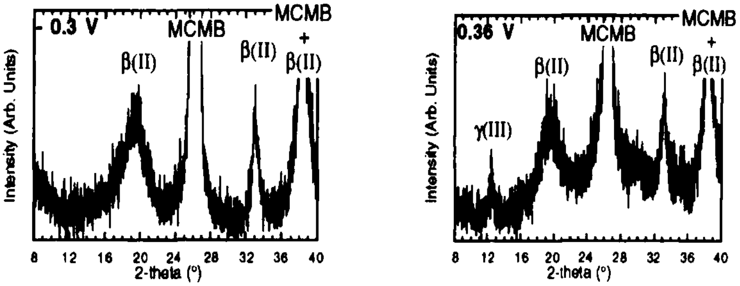

Figure 5: XRD patterns of samples removed at -0.3 V and 0.36 V vs Hg/HgO during cycling at C/20 rate from an almost pure γ(III) phase as starting material.

2/ Study of the second plateau potential level by using GITT measurements

The striking figure (figure 1) is that when turning to charge, the potential almost instantaneously raises above 1.35 V, which would mean that a very large hysteresis is involved in the second plateau phenomena.

A three electrode cell loaded with a chemically oxidized nickel hydroxide (initial mixture of β(III) and γ(III) phases) was cycled in continuous galvanostatic regime during charge but in GITT mode during discharge down to 0.4 V. Periodic interruptions of the current were performed for time durations in the range of hours, values which appeared necessary for reaching open circuit potential values variations by less than a few mV per hour, which is a good approach of the equilibrium potentials.

The charge (figure 6) was continuous for 15h at 2 mA (C/15 rate), while the GITT regime upon discharge usually was 1mA for 0.5h, corresponding to a nominal C/30 regime for the current value (and thus to 1/60 discharge increments), followed by 2h in open circuit. Note that the current-on sequence was changed twice to 0.5 mA for 1h, in order to probe the change in the second plateau level with regime, and that when reaching the end of the second plateau discharge we had to increase the open circuit duration to 6h to get potential values close to equilibrium. One clearly sees that for this NOE, which presents a O.8V second plateau with 30% relative capacity, the open circuit equilibrium potentials during this second plateau are close to 1.25 V, that is the same value as at the end of the usual 1.2 V discharge level. This means that an overvoltage of 400 mV is necessary for the phase transition to occur.

In other words, this means that the activation energy for the γ(III)/β(II) phase transition is high. At first, it is not surprising since such transformation involves the gliding of the NiO_2 layers of one third parameter together with the removal of bulk water molecules and potassium from the interlamellar space, both of these events are costly in energy. Now the remaining question is how to explain the 0.4 V overvoltage on discharge and the absence of second plateau on charge. Experiments are in progress to throw light on this issue.

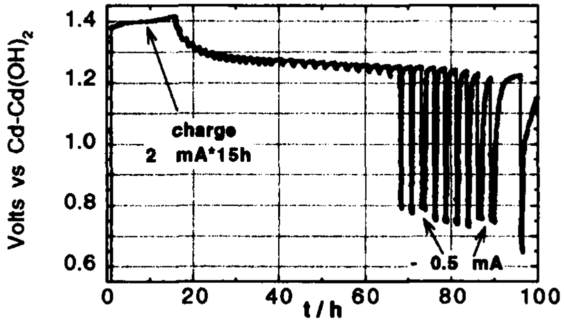

Figure 6: GITT measurements on discharge of an oxidized sample with an oxidation degree of 3.27 (1 mA * 0.5 h steps on discharge)

CONCLUSION

This study confirms that the second plateau at 0.8 V in the Ni/Cd batteries originates from the direct reduction of γ(III) phase to β(II) phase while the equilibrium potential is 1.25 V vs $Cd\text{-}Cd(OH)_2$. We have shown that the reduced βexγ phase keeps a textural memory of the γ(III) precursor, which induces the recovery of γ(III) phase at 1.36 V vs $Cd\text{-}Cd(OH)_2$ upon oxidation. Direct evidences are given to prove the existence of the γ(III)/β(II) transition. Such a phase transition has never been encountered previously in the literature. Having defined the origine of the second plateau, the next challenge is to find a way to eliminate it.

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