

A semi theoretical approach of the second plateau appearing during the discharge of aged nickel oxyhydroxide electrodes

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Abstract

A semi theoretical explanation of the appearance of a second plateau during the discharge of overcharged nickel oxyhydroxide electrodes (NOHE) is proposed, based on transmission line models of the charge–discharge processes of the active matter. The model takes into account the double electronic and protonic conduction involved in nickel II α and β or nickel III β and γ phases: electrons and protons reach the transformation front inside the matter through the less resistive paths. The secondary plateau may occur when a resistive layer of β (II) isolates the transformation front from the nickel electron sink. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Secondary batteries are more and more widely used in consumer, military and space areas. Among them alkaline batteries using a positive Nickel OxyHydroxide Electrode (NOHE) are recognised for their reliability, i.e., Ni/Cd, Ni/MH and Ni/H₂ batteries. Nevertheless, when ageing and more specifically if frequently overcharged an inefficient discharge behaviour may occur in the form of a secondary plateau located at 0.8 V versus the cadmium electrode at the expense of the normal one at 1.25 V. This Second Discharge Plateau (SDP) has been evidenced many years ago [1] but is still the object of conflicting debates.

In 1960 Falk [2] suggested the reduction of oxygenated species formed at the NOHE during its overcharge: in fact such an hypothesis does not readily account for the related loss of capacity observed on the first plateau itself.

In 1965 Tuomi [3] proposed the intervention of the γ phase. The occurrence of this phase during over oxidation

processes was clearly identified by Bode et al. [4] in their well-known cycle, which involves the β (II) and β (III) phases (i.e., Ni(OH)₂ and NiOOH) in the “normal” charge–discharge processes at high pH, and the α/γ phases at lower pH or after overcharge, according to:



In the α (II) and γ (III) phases, unlike in the β phases, water and alkali ions are intercalated between the nickel hydroxide layers. Moreover the nickel oxidation state in the γ phase is known to exceed 3, due to Ni⁴⁺ defects (3.3 to 3.7 according to [5]). It will nevertheless be called γ (III) in the following.

In 1980 Barnard et al. [6], using XRD, chemical analysis and linear sweep voltammetry, demonstrated that the γ phase can be discharged as efficiently as the β (III) one and therefore is not the main cause of the SDP. They considered this phenomenon as a kinetics one, originating from a high ohmic resistance due to thoroughly reduced Ni(OH)₂, acting as an insulating barrier between the active material and the electron collector (such an isolating barrier was

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firstly presumed by Tichenor in 1952 [7]). More explicitly the $\beta(\text{II})$ and $\beta(\text{III})$ phases are non-stoichiometric considering their H content and consequently the nickel oxidation state, which is usually admitted to vary from 2 to 2.25 for the $\beta(\text{II})$ phase and from 2.7 to 2.8 for the $\beta(\text{III})$ phase. These black non-stoichiometric phases behave like semi-conductors with a pretty good electronic conductivity while the stoichiometric ones are more typically insulators, like the green $\text{Ni}(\text{OH})_2$. These conductive phases are obtained during the formation process [3]. The loss of electrical contact between the active matter and the nickel electron sink has also been claimed to explain the SDP. In 1982 Klapste et al. [8] showed that some additives like cobalt or manganese hydroxides, which enhance the conductivity of NOHE, prevent the apparition of the SDP in agreement with Barnard's views.

Nevertheless, in 1994 Suresh and Subrahmanyam [9] demonstrated again the influence of overcharging on the SDP.

Very recently (1998) an attractive new interpretation has been proposed by Sac-Epée et al. [10] involving the direct reduction of the γ phase into the $\beta(\text{II})$ one competing with the more usual $\gamma(\text{III})/\alpha(\text{II})$ transformation. Using a Galvanostatic Intermittent Titration Technique (GITT) for cycling the NOHE they assumed that the $\gamma(\text{III})/\beta(\text{II})$ transformation would need a high over potential (400 mV) for its initiation along three phases lines (current collector, active matter and electrolyte), taking into account that intercalated water and alkali ions are rejected during this reaction. Difficulties arise nevertheless with this interpretation: why such an energy expensive transformation should

occur while the usual $\gamma/\alpha(\text{II})$ one needs only a low over potential (about 50 mV)? It is also known that the α phase is not stable in presence of the usual highly basic electrolyte media and transforms itself into the $\beta(\text{II})$ form, making difficult to prove experimentally by ex-situ observations the authors assertion. It is also difficult to verify by XRD the absence of $\beta(\text{III})$ in the charged electrode, as this compound is badly organised and diffracts less intensively than the γ phase. A third difficulty is how to explain by this theory the observed enhancing of the SDP with the hydrogen pressure in Ni/H_2 batteries [11]: how the over oxidised γ phase should be favoured by a reduction agent? In the contrary this phenomenon can more comprehensively originate from the growth of the isolating barrier claimed by Barnard et al. [6].

2. Discussion

Departing from a Transmission Line (TL) model developed for the electrochemical impedance spectroscopy behaviour of the NOHE [12] we propose here an alternative explanation. Taking into account the mixed electronic–protonic conduction of the NOHE and its large mass-related “faradaic” capacitance, the TL was viewed as a significant representation of the active matter behaviour, principally in its one-phase domains. The electronic conduction paths were seen as physically located around the Ni–Ni bonds and the protonic conduction paths themselves located between the layers. These two planar conductive paths were viewed as linked by distributed capacitors

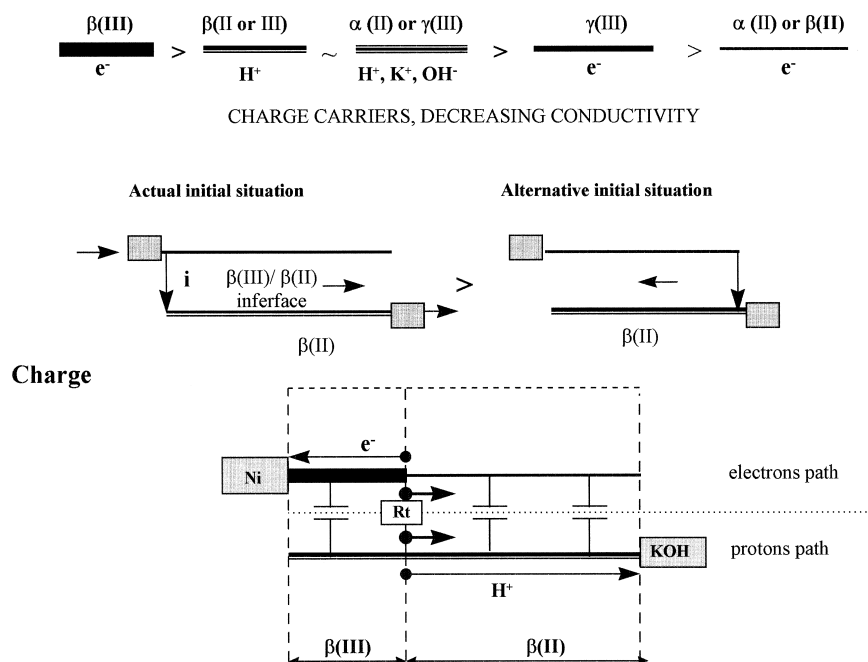


Fig. 1. Transmission line model of the nickel oxyhydroxide electrode explaining the movement of the inter-phase front during its **charge**, considering the assumed classification of electronic and ionic conductivity.

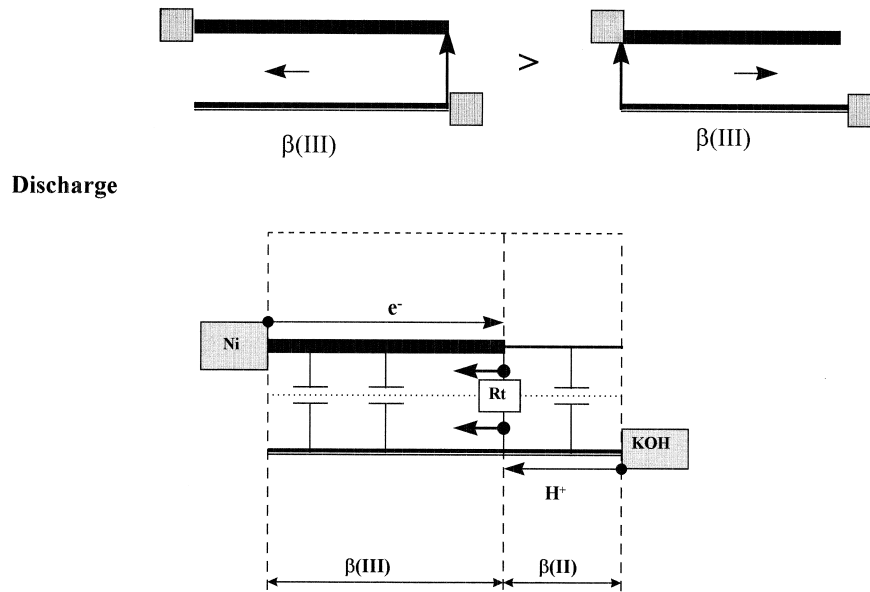


Fig. 2. Transmission line model of the nickel oxyhydroxide electrode explaining the movement of the inter-phase front during its **discharge**.

resulting from the blocking behaviour of their internal “interfaces”, in the same way as in ordinary Helmholtz double layers. This view may appear rather new for this kind of materials but was extrapolated from the well established model of graphite bisulphates [13]. In this TL model only the β phases were considered in order to represent the normal charge–discharge processes of the NOHE. A main difficulty was to fit such a simple model with the actual behaviour of commercially available electrodes, i.e., including their complex active material geometry together with the nickel substrate texture. Even if quite

reproducible mass-related capacitance values were obtained, only imprecise mean values were attainable for the electronic and protonic resistance, linked to the spatial geometry.

The two-phases behaviour (i.e., for a nickel oxidation state varying between 2.25 and 2.7) was described by the combination of two TL with the addition at their junction of a “faradaic” transfer resistance. The movement of the transformation front was supposed to obey in this case a “least resistive paths” law, i.e., electrons and protons arrive always from their sinks to the front *through the*

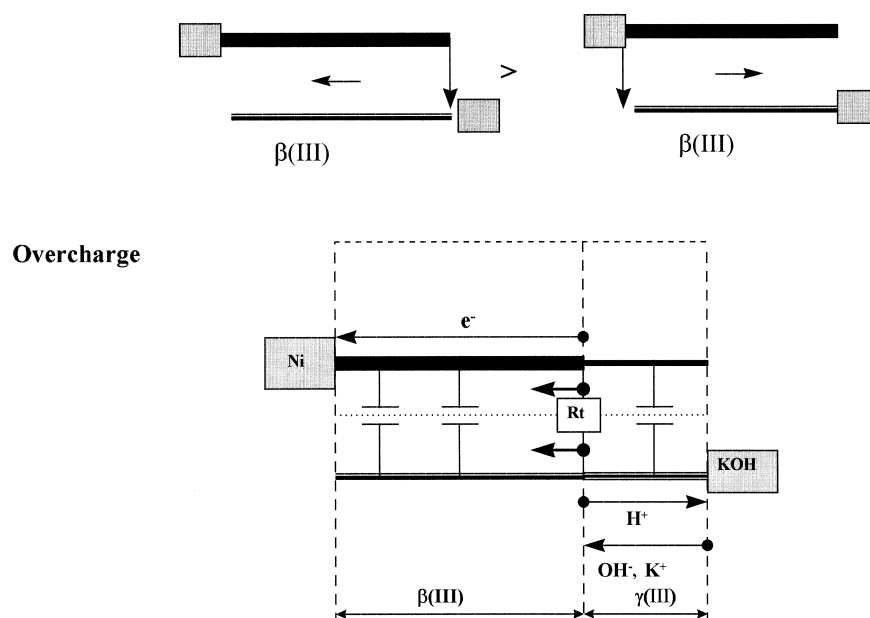


Fig. 3. Transmission line model of the nickel oxyhydroxide electrode explaining the movement of the inter-phase front during its **overcharge**.

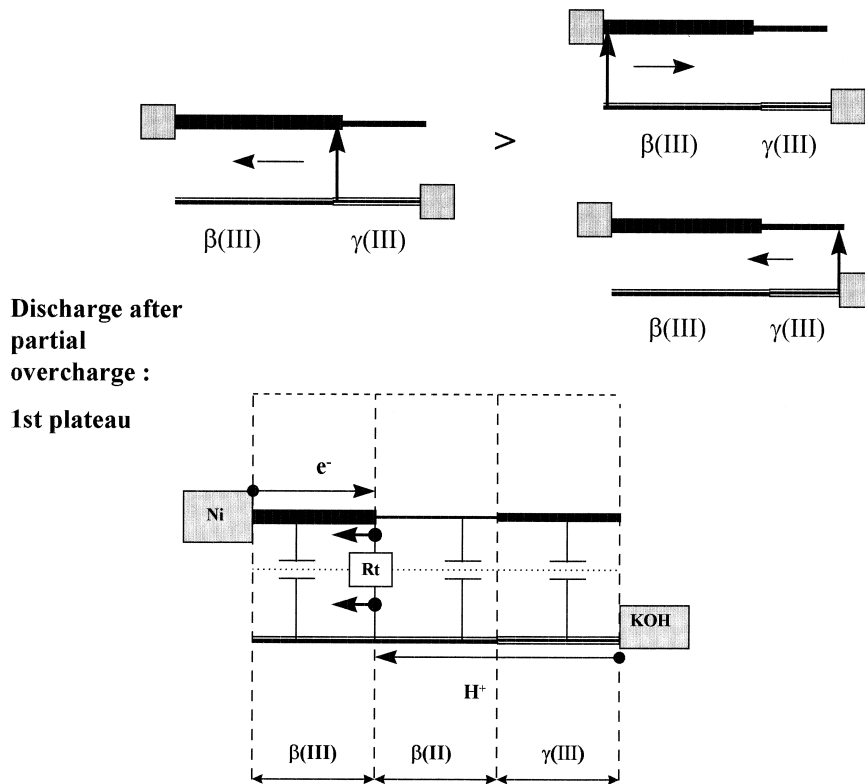


Fig. 4. Transmission line model of the nickel oxyhydroxide electrode explaining the movement of the inter-phase front during its **discharge** after partial overcharge (**1st plateau**).

most conductive ways. Preliminary fitted resistance values suggested that this front moved from the electrolyte towards the nickel substrate both during the charge and the

discharge which indeed was contradictory with previous observations [3,6,13]. We have undertaken new measurements and fittings which do not confirm these preliminary

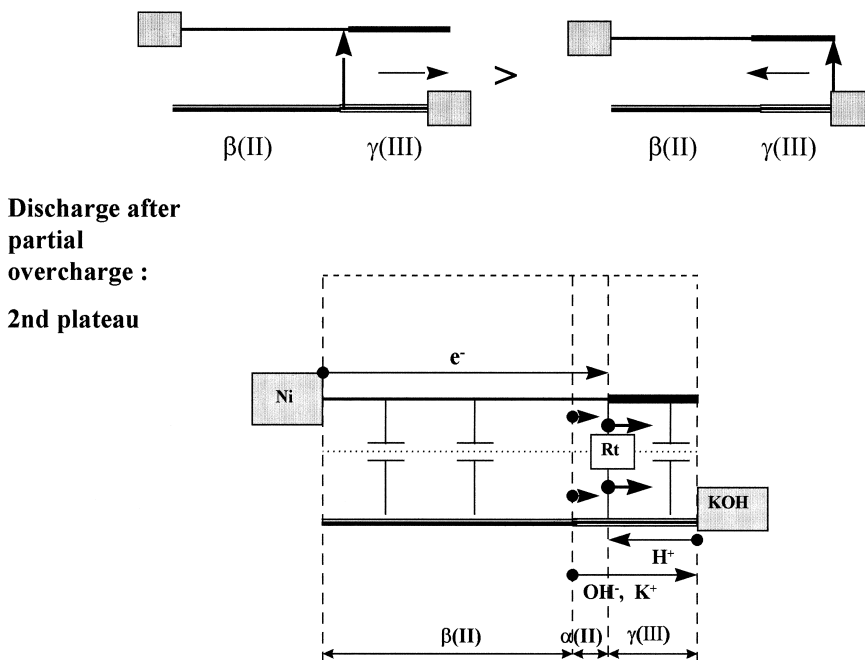


Fig. 5. Transmission line model of the nickel oxyhydroxide electrode explaining the movement of the inter-phase front during its **discharge** after partial overcharge (**2nd plateau**).

data. We propose now the following order for the electronic ρ_e and ionic ρ_i resistivity of the active species, near the two-phases domains:

$$\rho_e[\beta(\text{II}) \text{ or } \alpha] > \rho_e[\gamma(\text{III})] > \rho_i[\beta(\text{II}), \beta(\text{III}), \alpha(\text{II}) \text{ or } \gamma(\text{III})] > \rho_e[\beta(\text{III})]$$

Hence applying the least resistive paths law may explain the SDP appearance as the result of the γ phase formation during overcharge. Let us consider the charge/discharge and then the charge/overcharge/discharge processes of the NOHE (Fig. 1).

In a discharged $\beta(\text{II})$ electrode the charge front should start from the nickel substrate towards the electrolyte as the electronic resistance of $\beta(\text{III})$ is lower than the $\beta(\text{II})$ ones (Fig. 1: the total $e^- + H^+$ path is less resistive for the “actual” situation than for the “alternative” one). When all the material has been transformed into the $\beta(\text{III})$ phase the discharge will start from the electrolyte side, for the same reasons: the current paths remain the same while the current directions are reversed (Fig. 2). In the case of overcharge of the $\beta(\text{III})$ phase with formation of $\gamma(\text{III})$ phase the transformation front starts from the electrolyte side, considering that the electronic resistance of $\beta(\text{III})$ is still lower than the γ one (Fig. 3). H_2O molecules together with K^+ and OH^- ions may enter the interlayer spaces of the γ phase. A more complex situation arises for the discharge following a partial overcharge: its front may start at the $\gamma/\beta(\text{III})$ interface, affecting the $\beta(\text{III})$ phase and going towards the nickel side without reduction of the γ phase (Fig. 4). This process should correspond to the first shortened plateau located at about 1.25 V. At its end the remaining $\gamma(\text{III})$ species are then isolated from the nickel substrate by a resistive barrier of $\beta(\text{II})$. The γ phase reduction may then start at the $\gamma(\text{III})/\beta(\text{II})$ interface and

progress in the electrolyte direction, whatever it occurs directly into $\beta(\text{II})$ or via the $\alpha(\text{II})$ phase (Fig. 5). Then an ohmic drop in the resistive $\beta(\text{II})$ layer explains the SDP occurrence at a lowered potential.

In many practical cases some overcharged γ species may remain at the periphery of the electrode without no further participation to the charge–discharge processes, so explaining the lost of capacity of the NOHE. This model explains also that in some cases a deep discharge along the second plateau may cure the battery by regeneration of the β phases. This qualitative explanation of the DSP agrees in some parts with the Barnard’s views of an isolating barrier [5,6], without neglecting the role played by the γ phase as highlighted recently [10].

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