

# Electrical properties of nickel hydroxide for alkaline cell systems

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## Abstract

The electrical behaviour of nickel hydroxide/oxyhydroxide electrodes for advanced alkaline cell systems is investigated as a function of oxidation degree which usually changes during practical operation of these systems. The d.c. electrical conductivity, relative dielectric constant and loss factor as a function of oxidation degree, temperature and frequency (a.c. properties) are investigated and discussed. Moreover, the effect of water absorption on the electrical conductivity is investigated. An insulating behaviour and ionic mechanism of conduction is pointed out for the uncycled and reduced electrodes, while the oxidized electrode behaves essentially as a semiconductor. Water absorption causes a strong increase in the electrical conductivity of the uncycled and reduced electrodes. Cycling enhances the dielectric losses of the active material.

## Introduction

The  $(\text{Ni}(\text{OH})_2/\text{NiOOH})$  electrodes have been subjected to numerous investigations, as they can operate with high efficiency for a long life as positive electrodes in alkaline cell systems with various negative electrodes, such as cadmium, iron, zinc and hydrogen [1]. Much work has been devoted to the analysis of the charge and discharge mechanism and a variety of physical techniques, such as infrared (IR) spectroscopy [2–4], thermal analyses (differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)) [4, 5], X-ray diffraction (XRD) [5, 6], scanning electron microscopy [4, 7–9], and Raman spectroscopy [10] have been used to study the structure and microstructure of electrochemically impregnated nickel hydroxide electrodes before and after charge/discharge cycling. No investigations, however, have been performed on intrinsic electrical behaviour of active materials based on nickel hydroxide.

In this paper, the direct current (d.c.) and alternating current (a.c.) electrical behaviour of uncycled and cycled pure nickel hydroxide electrodes has been investigated and discussed, in order to find correlations with the structural changes caused by charge/discharge cycling. Moreover, the influence of water absorption on the electrical behaviour of nickel hydroxide electrodes has been studied.

## Experimental

### *Electrode materials*

Pure nickel hydroxide electrodes were obtained by electrochemical deposition of  $\text{Ni}(\text{OH})_2$  on different plane supports, such as thin strips of nickel metal or sintered nickel plates, from a concentrated nitrate solution at 80 °C [4, 7]. Active-material thickness from 120 to 200  $\mu\text{m}$  was obtained. The electrodes were then subjected to cathodic polarization in hot NaOH to eliminate the nitrate residue. Materials in the charged and discharged state were then obtained by cycling the electrodes for at least twenty times in a 6 N KOH solution, with a charging and discharging rate of 1 C (C being the nominal Ah capacity removed in 1 h). After cycling, the electrodes were thoroughly washed in water and dried (although this treatment could slightly discharge the oxidized samples).

### *Electrical measurements*

D.c. electrical conductivity measurements were made by the voltmeter–ammeter method according to ASTM Standard D 257 with three-terminal cells and instrumentation described in ref. 11. D.c. charging currents were measured as a function of time and temperature (temperature range 25–150 °C) under a constant electrical field of 10 kV  $\text{cm}^{-1}$ ; d.c. conductivity was then calculated as a function of reciprocal absolute temperature. D.c. discharging currents were also measured as a function of time by shorting the electrodes, to detect possible dielectric relaxation effects in the ultra-low frequency range ( $<10^{-2}$  Hz) by the Hamon method and its improvements [12–16].

A.c. properties (relative dielectric constant and loss factor) were measured over wide frequency ( $10^{-2}$ – $10^6$  Hz) and temperature (25–150 °C) ranges, according to ASTM Standard D 150, using three-terminal cells and instrumentations elsewhere described in ref. 11.

Before both d.c. and a.c. measurements, specimens were gold coated by vacuum deposition, to obtain the suitable three-terminal electrode configuration and avoid the introduction of stray impedances [11]. All measurements were performed in a dynamic vacuum for the highest to the lowest temperature, to minimize the effects of accidental adsorption of gases or vapours on the sample surfaces.

D.c. measurements on moist specimens were also made, in order to point out the effect of water absorption on the conductivity of the active material; specimens were conditioned in saturated air at room temperature for different times, and measured in the same cells in a tight atmosphere of inert gas at 25 °C.

## Results

### *Pure nickel hydroxide electrode*

The electrical conductivity at 1, 10 and 120 min after the application of the step voltage for the pure uncycled nickel hydroxide electrode is plotted in Fig. 1 as a function of reciprocal absolute temperature. A small transition, which decreases with increasing time of voltage application and separates two regions with different slope, i.e., with different apparent activation energy of the conduction process, can be observed at about 110 °C. Furthermore, remarkable transient phenomena are present which decrease as temperature increases and tend to disappear in the high-temperature range. The conductivity values, ranging from less than  $10^{-13}$  S/cm at 150 °C to  $10^{-17}$  S/cm at 25 °C and 120 min after voltage application, point out an insulating

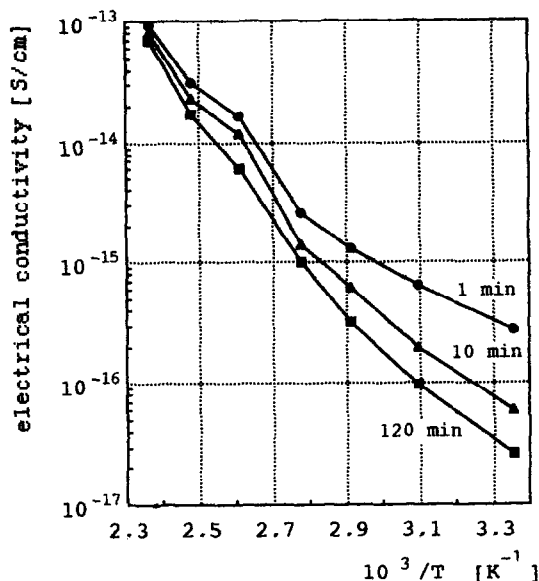


Fig. 1. Electrical conductivity (at 1, 10 and 120 min after voltage application) vs. reciprocal absolute temperature for the pure uncycled electrode.

behaviour of the material. Isochronal charging currents (not reported for the sake of brevity) exhibit the same temperature behaviour. Moreover, a systematic decrease in charging currents after repeated measurements at the highest temperature (150 °C) was observed.

The isochronal discharging currents are reported in Fig. 2 as a function of temperature. A linear trend and nearly constant transient phenomena in the whole temperature range can be observed. Moreover, the transition formerly detected at 110 °C in Fig. 1 is practically absent. Fourier transform of the d.c. discharging currents did not reveal any other polarization process.

The dielectric loss factor, plotted versus frequency in Fig. 3 over the same temperature range 25–150 °C, exhibits a weak relaxation peak at about  $10^4$ – $10^5$  Hz and increases with decreasing frequency and increasing temperature. Dielectric constant (Fig. 4) also shows a strong increase with decreasing frequency and increasing temperature.

Measurements made on the active material alone or deposited on different kinds of support (sintered nickel plates and thin strips of nickel metal) provided practically the same results: therefore, effects of the support on the electrical behaviour of nickel hydroxide can be ruled out.

#### *Cycled nickel hydroxide electrode*

Some nickel hydroxide electrodes were subjected to a deep electrochemical oxidation by overcharging up to 20% which changed the original gray-green colour of the active material into a black colour with bright, metallic luster. After oxidation, some samples were subjected to a reduction process after which the active material remained black losing, however, its brightness.

In Fig. 5, the electrical conductivity at 10 min after voltage application for the oxidized and reduced electrodes is plotted as a function of reciprocal absolute temperature

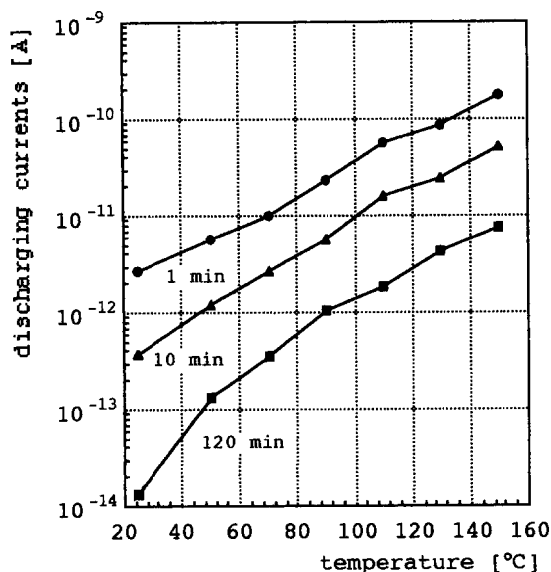


Fig. 2. Isochronal discharging currents (at 1, 10 and 120 min after voltage removal) vs. temperature for the pure uncycled electrode.

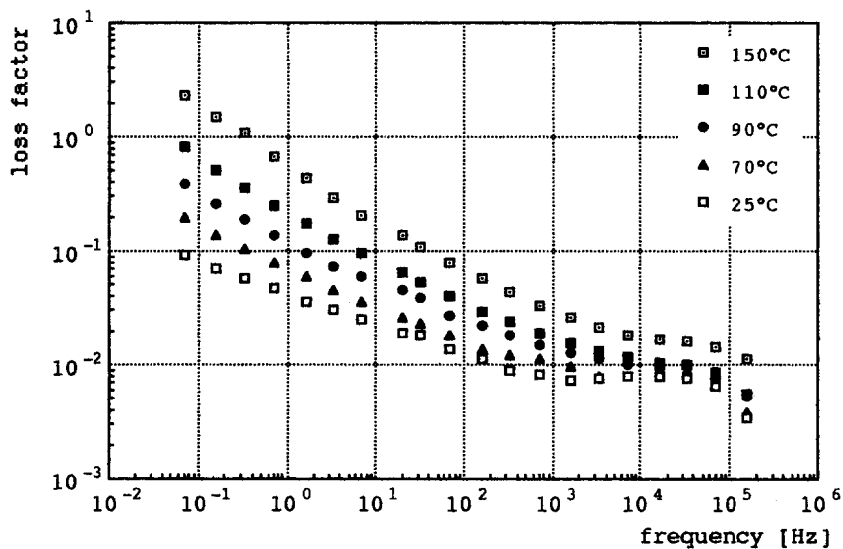


Fig. 3. Dielectric loss factor vs. frequency for the pure uncycled electrode.

in comparison with that of the uncycled nickel hydroxide electrode. Oxidized and reduced electrodes conductivity did not exhibit changes with time of electrification, i.e., transient phenomena are absent for these electrodes.

The electrical conductivity of the oxidized electrode exhibits only a slight, linear dependence on temperature: the slope (and thus the average apparent activation energy

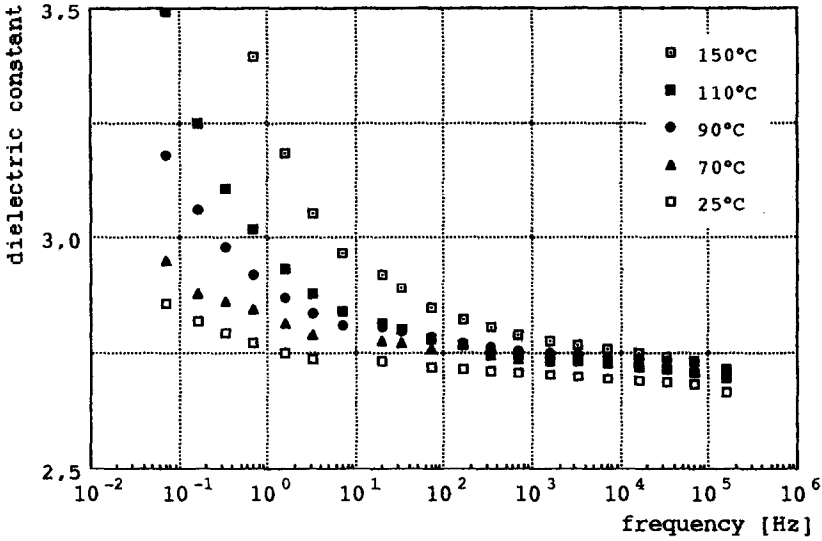


Fig. 4. Dielectric constant vs. frequency for the pure uncycled electrode.

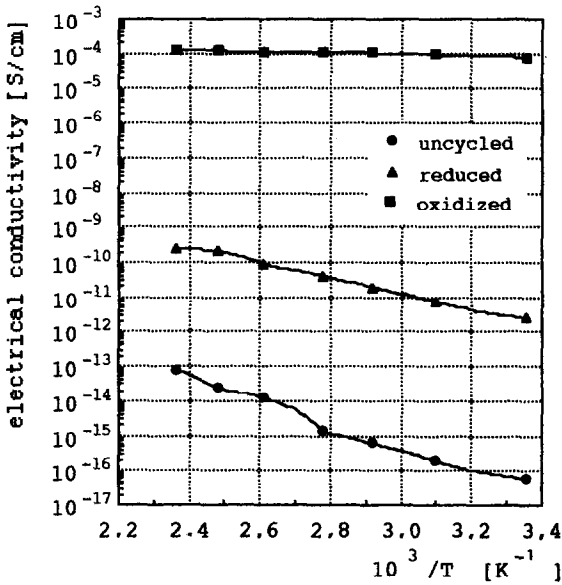


Fig. 5. Electrical conductivity (at 1 min after voltage application) vs. reciprocal absolute temperature for the uncycled, oxidized and reduced electrodes.

of the conduction process) is much lower than that of the uncycled electrode, and conductivity ranges from  $10^{-4}$  S/cm (at 150 °C) to  $10^{-5}$  S/cm (at 25 °C), thus pointing out a semiconducting behaviour of the active material.

The electrical conductivity of the reduced electrode also exhibits an essentially linear temperature dependence with an intermediate slope between those of the

uncycled and oxidized electrodes, and conductivity values ranging from  $10^{-10}$  S/cm (at 150 °C) to  $10^{-12}$  S/cm (at 25 °C): this points out an insulating behaviour with a conductivity about four orders of magnitude higher than that of the corresponding uncycled material at all the investigated temperatures.

The results of a.c. measurements, performed on the oxidized and reduced electrodes, point out a strong decrease in the loss factor and dielectric constant with respect to the uncycled material in the whole temperature and frequency range investigated, as can be observed in Fig. 6 to 9. Values pertaining to reduced electrodes are again intermediate between those of the uncycled and oxidized electrodes.

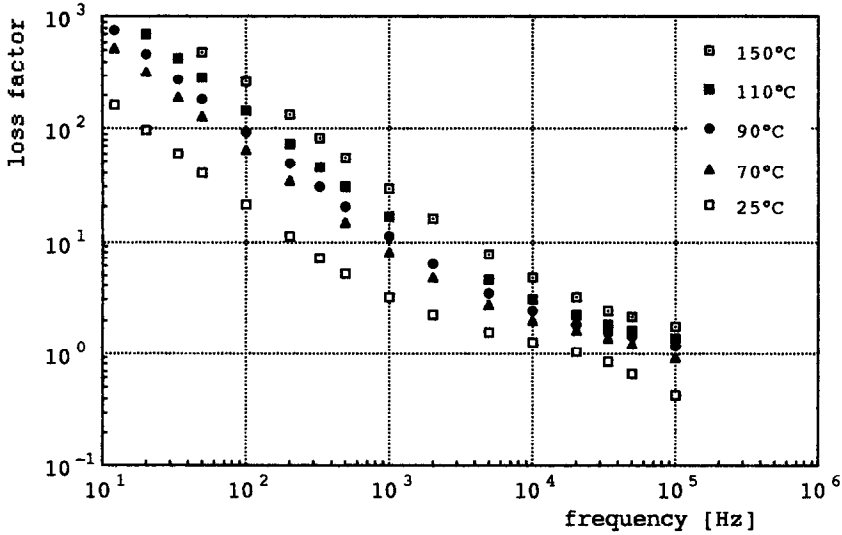


Fig. 6. Dielectric loss factor vs. frequency for the oxidized electrode.

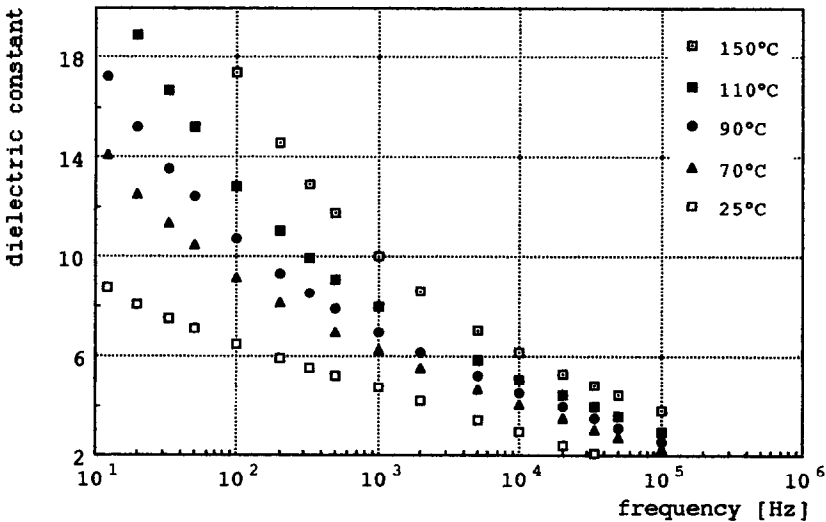


Fig. 7. Dielectric constant vs. frequency for the oxidized electrode.

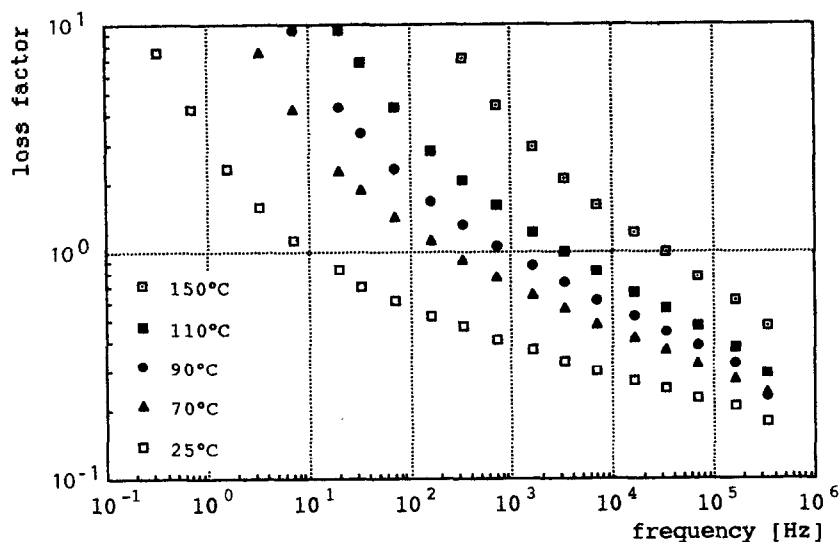


Fig. 8. Dielectric loss factor vs. frequency for the reduced electrode.

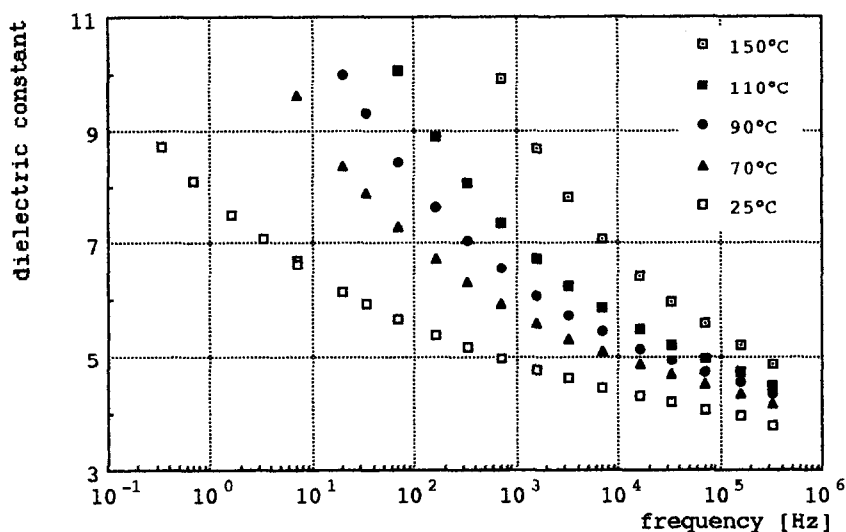


Fig. 9. Dielectric constant vs. frequency for the reduced electrode.

#### *Effect of water absorption*

The electrical conductivity of the uncycled and reduced electrodes, measured in air at 25 °C and 1 min after voltage application, is reported in Fig. 10 as a function of absorbed water content. As can be seen, water absorption causes a very strong conductivity increase for both the electrodes; on the contrary, only a slight effect was detected for the oxidized material.

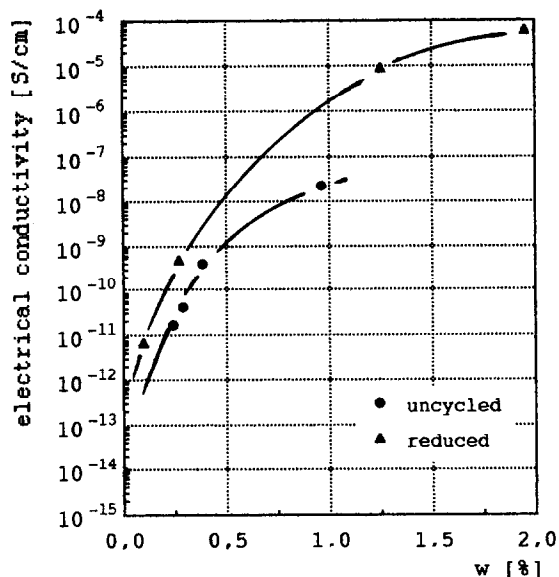


Fig. 10. Electrical conductivity (at 1 min after voltage application) vs. absorbed water content for the uncycled, oxidized and reduced electrodes.

## Discussion

It is commonly accepted that the basic oxidation/reduction process involves the oxidation of divalent nickel  $\text{Ni}^{2+}$  to trivalent nickel  $\text{Ni}^{3+}$  and can be described by the overall reversible reaction [4]:



Both  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  exist in two well-known structural modifications, which are called  $\alpha$  and  $\beta$  for the former and  $\beta$  and  $\gamma$  for the latter species and may undergo chemical interconversion [17]. However, higher oxidation states can be involved in the electrochemical behaviour of the nickel oxide/hydroxide electrodes [6, 10, 18]. It has been observed by some workers that in hot sodium hydroxide the  $\alpha$ -variety transforms into the  $\beta$ -variety.

However the as-prepared uncycled electrode material subject of this study is  $\alpha$ - $\text{Ni}(\text{OH})_2$ , as revealed by IR spectroscopy [4]. The results of the electrical measurements, previously reported, point out an insulating behaviour of this material. Moreover, the presence of transient phenomena in the d.c. electrical conductivity curves versus reciprocal absolute temperature, their decrease as temperature increases (so that they practically disappear in the high-temperature range), the systematic decrease of charging currents after successive measurements at 150 °C (probably due to sweeping away of charge carriers), the strong conductivity increase even for a low content of absorbed water, the sharp increase in the dielectric constant, and loss factor with increasing temperature and decreasing frequency provide evidence for ionic conduction [16, 19, 20]. Protonic contribution to the conduction process is undoubtedly active also in the actual service conditions of these cell systems. On the other hand, ionic and molecular impurities (mainly water, nitrates and carbonates) are unavoidably present in the lattice of the active material due to its layered structure [4]. Moreover, the weak transition



observed in the conductivity curves of Fig. 1 at about 110 °C could be ascribed to the presence of interlayer bonded water in the  $\alpha$ -phase, i.e., water molecules trapped in the crystal lattice by weak coordinate-covalent bonds to the nickel ions, as revealed by IR spectroscopy, DSC, TGA and XRD studies [2–5]. It must be observed that, even if dehydration starts at 90 °C, most of this structural water is removed only above 170 °C [5]. As to a.c. results, the weak relaxation process detected in the high-frequency region must be related to local molecular motions to be recognized by further investigations.

The charged electrode, which is characterized by the crystalline structure of the  $\beta$ -phase [4], behaves as a semiconducting material at all the investigated temperatures. The absence of transient phenomena in the conductivity curves and the low activation energy of the conduction process can be related to an electronic mechanism of conduction via electrons supplied by delocalized  $\pi$  bonds [18, 21]; therefore, the  $\beta$ -phase of the oxidized electrode can be essentially considered a n-type semiconductor [6, 22]. However, some ionic contribution to conduction cannot be excluded: indeed, protons can be provided by dissociation of the hydrogen bonds existing in the charged structure, thus explaining the observed sharp rise of dielectric constant and loss factor with increasing temperature and decreasing frequency.

The reduced electrode behaves as an insulating material, like the uncycled electrode, but it exhibits much higher conductivity, dielectric constant and loss factor values at all the investigated temperatures. These differences can arise from structural changes caused by the reduction process: even if the basic crystal symmetry is the same as of the uncycled  $\text{Ni}(\text{OH})_2$  [2, 4], the active material in the discharged state may be characterized by a highly defect, disordered structure [2, 6] which enhances solid-state diffusion processes and, hence, ionic conduction processes. There is also likely to be an electronic contribution since the average nickel oxidation state in the reduced electrode lies in the range 2.2–2.3. Furthermore, complete discharge may be hindered by the formation of a layer of nickel hydroxide between the charged active material and the substrate surface [6, 18, 22].

The observed strong variation of the d.c. and a.c. electrical properties of the active material with the oxidation degree may remarkably affect its electrochemical behaviour. Hence, inefficiencies, such as low discharge capacity and failure on discharge at high rates observed in these alkaline cell systems [6, 18, 21, 22], could be explained through the electrical properties changes during practical operation of such systems.

Closest correlations between practical behaviour of  $(\text{Ni}(\text{OH})_2/\text{NiOOH})$  electrodes in advanced alkaline cell systems and electrical properties changes during cell operation will be acquired from tests on prototype or pilot cells.

## Conclusions

1. An insulating behaviour is exhibited by the uncycled nickel hydroxide electrode material. An ionic mechanism of conduction, based on protons as charge carriers, can be postulated.

2. The reduced electrode still behaves as an insulating material, but exhibits d.c. conductivity and dielectric losses much higher than those of the uncycled electrode. This electrical behaviour can be ascribed to the usually highly defect and disordered structure of the reduced material, which enhances solid-state diffusion and ionic conduction processes together with an electronic contribution.

3. The oxidized electrode behaves as a semiconductor and electrons supply the observed high conduction.

4. The observed strong dependence of the electrical properties of the active material on the oxidation degree may remarkably affect its electrochemical behaviour. Further correlations should be made with the actual state of the electrode material in the various steps of practical operation of prototype or pilot alkaline cell systems.

### Acknowledgement

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