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Electrochemical properties of mechanically activated nickel hydroxynitrate

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The activation of a non-stoichiometric nickel hydroxynitrate subjected to grinding is studied through its electrochemical behaviour when it is used as an active material for the positive electrode of a nickel–cadium cell. The textural modifications of the milled material are measured from BET specific surface area and X-ray diffraction line broadening analysis. A sudden change of the initial capacity is observed when grinding times increase. This change is associated with a critical thickness of diffracting domains (~ 6 nm) for which the capacity of activated hydroxynitrate goes from a low to a high initial value.

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1. Introduction

In general, mechanical treatment of a solid increases its reactivity. The detailed effects on solid-state reactions as well as on physical properties have frequently been described. The influence of grinding on the microstructural properties of some bivalent metal hydroxides with a CdI_2-type structure has been reported [1, 2]. No similar studies have been made concerning the structurally related hydroxysalts. Nickel hydroxynitrates present a lamellar crystalline structure when proceeding from nickel hydroxide by the substitution of some hydroxyl ions by nitrate groups or water molecules [3]. This paper presents the effect of mechanical treatment on the electrochemical properties of a non-stoichiometric nickel hydroxynitrate $Ni(OH)_{1.45}(NO_3)_{0.55}$. This material, prepared by a solid-state process, belongs to Type I of the structural classification of bivalent metal hydroxynitrate [3], having an interlayer spacing of 0.69 nm, which is greater than the 0.46 nm value found in the hydroxide. In order to measure the mechanical activation of this solid, and by analogy with the remarkable cycling durability of nickel hydroxide electrodes in alkaline cells, the nickel hydroxynitrate has been used as active material for the positive electrode of a nickel–cadmium cell.

2. Experimental details

2.1. Material preparation

The non-stoichiometric hydroxynitrate $Ni(OH)_{1.45}(NO_3)_{0.55}$ was prepared by solid-state thermal decomposition in air, at 200° C, of the nickel nitrate dihydrate [4, 5]. The finely powdered material obtained in this way has planar defects and the fluctuations in the interlayer spacing are negligible [6, 7]. This material was subjected to grinding for different periods up to 3 h in a planetary mill equipped with jars of tungsten carbide (capacity 150 cm^3) containing three balls of the same material 20 mm in diameter and two balls 30 mm in diameter. The specific surface area of the sample was calculated from adsorption measurements by the BET method.

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2.2. X-ray diffraction analysis.

A Fourier analysis of the broadened 0 0 *l* reflections of the powder pattern was performed. The lines 0 0 1 and 0 0 2 were carefully scanned in steps of 0.02° (2θ) over a wide angular range. Data were obtained by using a powder-diffraction system (Compagnie Générale de Radiologie) equipped with an incident-beam curved-crystal quartz monochromator ($\lambda K\alpha_1 =$ 0.15405 nm). Experimental details have been published elsewhere [8].

The data were corrected for polarization and the Lorentz factor; the background obtained by a least-squares procedure was subtracted. To correct the broadened profile $h(s)$ for the contribution from the instrumental function $g(s)$, deconvolution of $h(s)$ was carried out by the LWL method [9] to give the intrinsic profile $f(s)$. The reflections 1 0 0 and 2 0 0 of highly oriented well-crystallized zinc hydroxynitrate ($d_{100} =$ 0.692 nm) were used to obtain the standard $g(s)$ profile [10]. The Fourier coefficients were obtained from the inverse transform of $f(s)$. In spite of a reduction in the height of the receiving slit in order to minimize asymmetry occurring at low diffraction angles, the 0 0 1 line has a small asymmetry after deconvolution. Thus to avoid errors due to the determination of the centroids of the f profile, comparison of the 0 0 1 and 0 0 2 Fourier transforms was carried out by employing the modulus of the Fourier coefficient $|F(n)| = [A^2(n) + B^2(n)]^{1/2}$ as this is independant of the choice of origin [11]. For the 0 0 2 line it was noted that $A_n \gg B_n$. The Fourier coefficients are normally expressed as a function of a distance L in the direction of the normal to the diffracting planes. Further details about the procedures used and the interpretation in terms of apparent sizes and microstrains are given in recent papers [7, 12]. When $f(s)$ is due entirely to size effects, the distribution of lengths of columns of unit cells can be ascertained. This was carried out from the 0 0 2 diffraction lines by the method proposed by Le Bail and Louër [13].

2.3. Electrochemical analysis.

The general reaction scheme of oxido-reduction of nickel hydroxide has been proposed by Bode *et al.* [14]. Reactions take place in one step characterized by electronic and protonic transfers between active species, and have been studied previously [15]. Oxidation leads to Ni(III) or Ni(IV) according to the initial phases and experimental conditions. In Bode's scheme, nickel hydroxynitrate could substitute the α-Ni(OH)$_2$ phase, allowing electrochemical analysis to be a means of controlling the activity and phase transformations. The latter were studied by cyclic voltammetry with a linear potential sweep, and the activity of phases was followed by capacity measurements on thick electrodes: the oxido-reduction of Ni(II) should correspond to an exchange of at least one faraday mol^{-1} of nickel. Lower capacities are characteristic of unreacted phases.

Cycling voltammograms were performed by using flat thin layers of a mixture of nickel hydroxynitrate and nickel powder, deposited on a porous electronic conductor. The electrochemical cell has already been described [16]. The electrolyte was 2.5 or 8 N KOH; the scan rate was low enough (0.3 mV sec^{-1}) to ensure a total oxido-reduction of the active material during cycling. Plastic-bonded electrodes (0.5 mm thick) containing a mixture of hydroxynitrate and graphite were used to obtain capacity measurements.

3. Results and discussion

The textural modifications of nickel hydroxynitrate subjected to grinding were evident from BET specific surface area measurements and X-ray diffraction line broadening analysis. The latter measures crystallite sizes in the sense of coherent diffraction domains.

The variation of specific surface area with grinding time is given in Fig. 1. The specific surface area reaches a maximum at about 45 min of continuous grinding, and thereafter begins to diminish. The value after 3 h of grinding is smaller than for the initial material. To explain this kind of curve two processes proceeding simultaneously have been suggested by Gregg [17]: a size reduction and a reaggregation. The former predominates before the maximum has been reached, and after this the latter is dominant. In the present study reaggregation is probably favoured by the small size and the anisotropic morphology of the crystallites, due to the layer structure of the hydroxynitrate.

The Fourier transforms of 0 0 1 and 0 0 2 lines were calculated for the initial material and samples ground for 30 min, 1 h and 3 h (Fig. 2). In the four cases a superposition of these

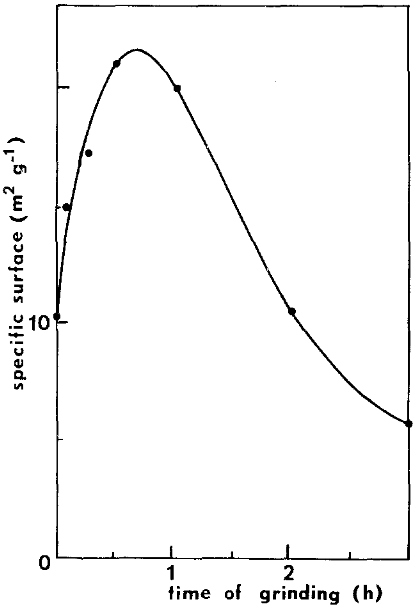

Figure 1 Plot of specific surface against grinding time.

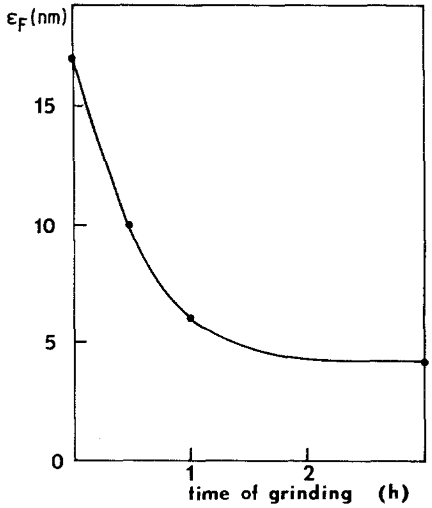

Figure 3 Crystallite sizes for milled nickel hydroxynitrate.

functions is observed. As microstrain effects are dependent on the order of the reflection, it can be concluded that the initial sample and the material subjected to grinding are not affected by reticular distortions, at least in the range of grinding times considered and in a direction perpendicular to the layers. On the other hand, the mean apparent size ε_F, which is inversely proportional to the initial slope of the Fourier transforms, is changed with continuous grinding (Fig. 3). A rapid decrease of the size of the diffracting domains in the direction [0 0 1] up to ~45 min and thereafter a smaller reduction is observed. The negligible microstrains and the reduction in thickness of the crystallites can be explained by the strong anisotropy of the chemical bonds in the material which favour a cleavage of the crystallites. Furthermore, because the microdistortions are negligible, size-distribution functions can be deduced from the 0 0 2 line. The resulting area-weighted distributions of size $P(L)$ are given in Fig. 4. The effect of grinding is to shift the mean and to reduce the range of dispersion of the size distributions.

The general electrochemical behaviour of

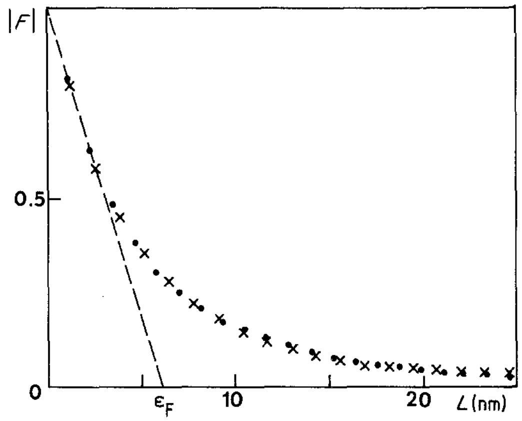

Figure 2 Discrete Fourier transforms for 0 0 1 and 0 0 2 line profiles of hydroxynitrate ground for 1 h.

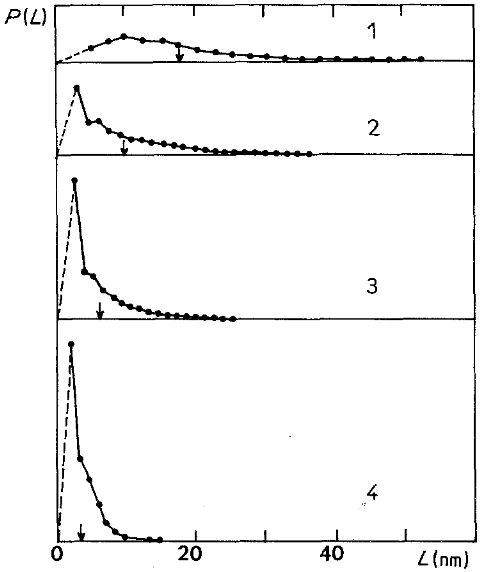

Figure 4 Crystallite-size distributions for milled nickel hydroxynitrate. Times of grinding: (1) 0 h, (2) 30 min, (3) 1 h and (4) 3 h.

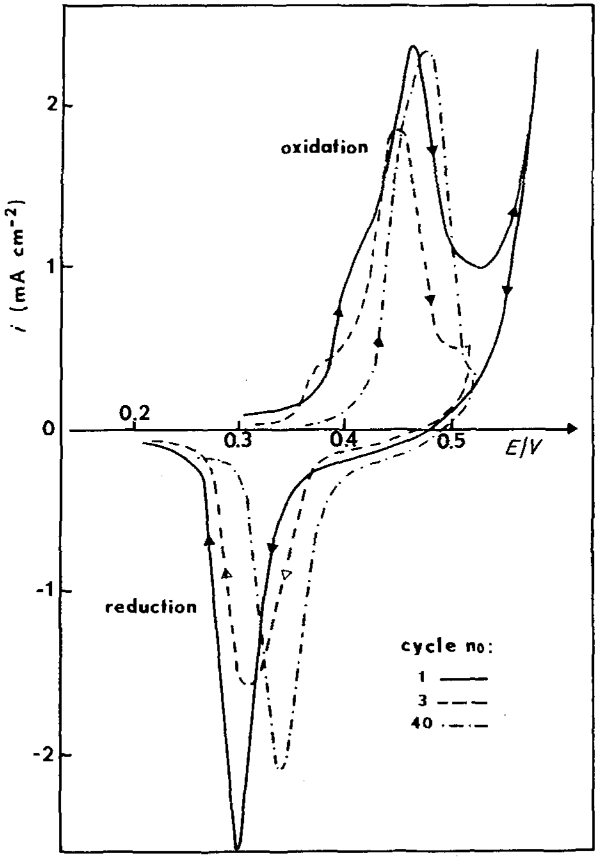

Figure 5 Current/potential curve of a nickel hydroxynitrate ground for 1 h, cycling in 8 N KOH. Peaks of Cycle 1 are characteristic of hydroxynitrate; at cycle 40 the transformation to $Ni(OH)_2$ is complete, and peaks of the β-$Ni(OH)_2 \rightleftarrows \beta$-$NiOOH$ system are only present.

nickel hydroxynitrate is depicted in Fig. 5. Cyclic voltammograms show one oxidation and reduction process related to the active product and oxygen evolution at higher potentials. During continuous cycling there is a slow shift of the peaks, which points to the phase transformation of hydroxynitrate to β-$Ni(OH)_2$. The crystallographic description of this transformation has previously been reported [7]. The final oxido-reduction process, characterized by well-defined peaks at 0.488 V and 0.330 V against Hg/HgO reference electrode, can be ascribed to the β-$Ni(OH)_2 \rightleftarrows \beta$-$NiOOH$ reaction [15].

The effect of grinding on the capacity of nickel hydroxynitrate electrodes is clearly seen in Figs. 6 and 7. Fig. 6 shows the first oxidation scan of the cyclic voltammograms. Three oxidation processes can be seen in the curves: at 0.4 V against Hg/HgO the oxidation of the α-$Ni(OH)_2$ remaining on oxidized nickel powder takes place. Beyond 0.5 V oxygen evolution begins. These two processes are common to the three curves. On the contrary, there is a two-fold and very sensitive effect of grinding on the oxidation of hydroxynitrate:

(a) After grinding oxidation is easier, as indicated by the shift of the oxidation peak. Without any grinding (Curve 1) oxidation takes place at high potential, and the peak related to the oxidation of Ni(II) is beyond oxygen evolution. The oxidation peak is shifted to a more cathodic potential when grinding time is increased (Curves 2 and 3).

(b) The capacity, defined by the surface area under the oxidation peak, increases with grinding. This increase is seen better in Fig. 7 which shows the cycling capability of thick electrodes. Indeed there is a spectacular modification of the initial capacity. For the non-ground material it is well below the exchange rate of one faraday mol^{-1}. There is one steep increase between 30 min and 1 h of grinding.

The results can be explained by the existence of a "critical value" of the activation which leads to a high initial capacity. This critical value can be compared with the characteristics of the curves given in Figs. 1 and 2, where changes in

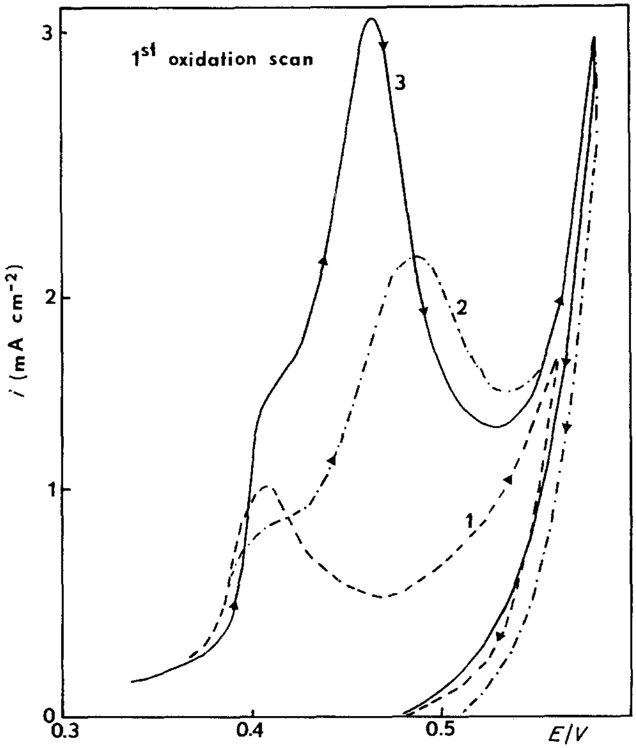

Figure 6 Activation of nickel hydroxynitrate: effect of grinding on oxidation capacity, pointed out on current/potential curves (against Hg/HgO). Curve 1: no activation; Curve 2: 30 min grinding; Curve 3: 1 h grinding (Cycling in 8 N KOH; scan rate 0.3 mV sec^{-1}).

textural properties appeared after about 45 min of grinding. In the case of the specific surface area, related to the surface of the grains, the decreases due to reaggregation processes do not favour an improvement of the kinetics of redox transfer. On the other hand, the regular variation of the size of the diffracting domains is in good agreement with electrochemical results. Consequently the concept of diffracting domains appears as a significant element in the modification of reactivity induced by mechanical treatment. From Fig. 3, the critical value (which corresponds to the transition from a low to a high initial capacity) is about 6 nm. This value is the mean thickness if a plate-like crystallite habit is assumed. The measure of size in a direction perpendicular to the normal to the layers will be useful. A difficulty is encountered because of the broadening of $hk0$ diffraction lines as a consequence of turbostratic disorders; so a meaningful measurement of the "diameter" of the crystallites is not possible by X-ray diffraction. An examination with the help of electron microscopy is also affected by the reaggregation process of the grains.

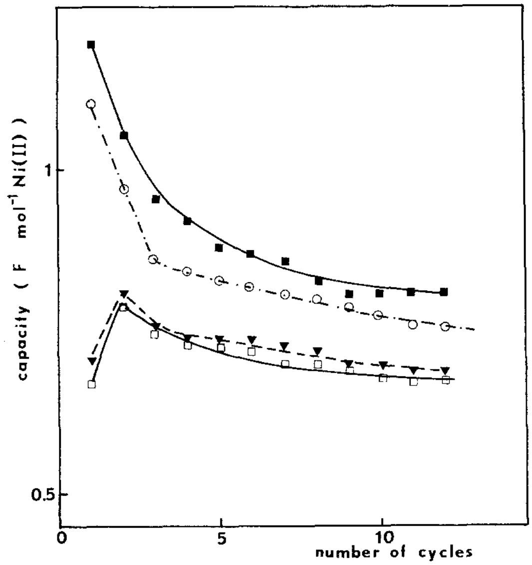

Figure 7 Effect of grinding on the capacity delivered by nickel hydroxynitrate electrodes. Time of grinding (□) zero; (▼) 30 min; (○) 1 h; (■) 3 h. Electrodes are plastic-bonded and 0.5 mm thick.

Finally, the influence of the grinding of nickel hydroxynitrate has been clearly demonstrated by the study of the specific redox reaction at the positive electrode of a nickel–cadmium accumulator. The existence of a critical value of the crystallite size resulting in an improvement of the electrochemical activity should be noted.

Acknowledgements

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References

1. S. J. GREEG and J. P. SAENZ, *J. Appl. Chem.* **16** (1966) 300.
2. A. NONAT and J. C. MUTIN, *Mater. Chem.* **7** (1982) 479.
3. M. LOUËR, D. LOUËR and D. GRANDJEAN, *Acta Crystallogr.* **B29** (1973) 1696.
4. D. WEIGEL, B. IMELIK and P. LAFFITTE, *Bull. Soc. Chim. Fr.* **2** (1962) 345.
5. P. GALLEZOT and M. PRETTRE, *ibid.* **2** (1969) 407.
6. D. LOUËR, *J. Solid State Chem.* **13** (1975) 319.
7. A. LE BAIL and D. LOUËR, *Rev. Chimie Min.* **17** (1982) 522.
8. D. LOUËR, J. P. AUFFREDIC, J. I. LANGFORD, D. CIOSMAK and J. C. NIEPCE, *J. Appl. Cryst.* **16** (1983) 183.
9. D. LOUËR, D. WEIGEL and R. LOUBOUTIN, *Acta Crystallogr.* **A25** (1969) 335.
10. M. LOUËR, D. LOUËR and D. WEIDEL, *Compt. Rend. Acad. Sci. (Paris)* **270** (1970) 881.
11. R. DELHEZ, Th. H. DE KEIJSER and E. J. MITTEMEIJER, *Fres. Z. Anal. Chem.* **312** (1982) 1.
12. D. LOUËR, R. COUPE and A. LE BAIL, *J. Appl. Cryst.* **17** (1984) 131.
13. A. LE BAIL and D. LOUËR, *ibid.* **11** (1978) 50.
14. H. BODE, K. DEHMELT and J. WITTE, *Electrochim. Acta* **11** (1966) 1079.
15. P. OLIVA, J. LEONARDI, J. F. LAURENT, C. DELMAS, J. J. BRACONNIER, M. FIGLARZ, F. FIEVET and A. DE GUIBERT, *J. Power Sources* **8** (1982) 229.
16. J. MARIE, doctoral thesis, Paris (1974).
17. S. J. GREEG, *Chem. and Ind.* (1968) 611.

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