Synthesis, XRD characterization and electrochemical performance of overlithiated LiNiO$_2$

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Abstract

The synthesis and XRD characterization of overlithiated LiNiO$_2$ samples is briefly described. The effect of the extraction of the residual LiOH from the samples after their synthesis is studied. The extraction in water even at a low liquid/solid ratio leads to a considerable chemical delithiation accompanied by the loss of oxygen from the crystal lattice of LiNiO$_2$. It is supposed that oxygen vacancies are formed in part of the NiO$_6$ octahedra. The defective octahedra cannot release electrons whereby the number of Li$^+$ which can be deintercalated during the electrochemical delithiation of the cathodes prepared with chemically delithiated LiNiO$_2$ samples are reduced. Although the fast XRD characterization here employed shows negligible change in the criterial parameters, the cycling test reveals a considerable decrease in the charge capacity and consequently in the next discharge capacity. The change in the crystal structure of the water extracted samples is more clearly observed in the VA-grams showing a considerable shift of the first R$_1$/M peaks in anodic direction and a strong reduction in the areas of the R$_2$/R$_3$ peaks. Ethanol as a nonaqueous solvent was found to extract the residual LiOH without causing any chemical delithiation of the LiNiO$_2$ samples, thus, preserving their good electrochemical characteristics. The effect of storage of the LiNiO$_2$ powdered samples in the ambient atmosphere was investigated. The results revealed that the ethanol extracted samples are more resistant to chemical delithiation by the water vapours in the air than those containing residual LiOH. A beneficial effect on the cycling characteristics of LiNiO$_2$ cathodes containing 10% of the newly developed UFC (ultra-fine carbon) conductive material is established. The cycling by potentiostatic charging to 4.20 V with initial limited current of 60 mA/g was found to contribute substantially to the discharge capacity and cycling stability of the LiNiO$_2$ cathodes, yielding more than 170 mA h/g after 50 cycles between 3.00 and 4.20 V. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The good cycling characteristics of LiNiO$_2$ make it very attractive as cathode material for Li-ion cells. Despite this, it has not achieved the wide commercial application of the more costly LiCoO$_2$. One disadvantage of the LiNiO$_2$ cathode material, which has been frequently pointed out and which has retarded its popularity is the unsatisfactory reproducibility in the preparation of high stoichiometry products. This is especially true for the industrial synthesis method carried out in air atmosphere. One recent breakthrough in this respect is the remarkable achievement of the SAFT group [1] which has developed a

successful 100 A h Li-ion battery with LiNiO$_2$ cathode. One of the reason for this situation is perhaps that the only reliable method for the assessment of the stoichiometry of LiNiO$_2$ presently employed is the Rietveld profile refinement analysis. This method consumes rather long operational time of the expensive XRD apparatus which renders difficult the characterization of a large number of samples necessary for the optimization of the synthesis conditions.

This obstacle was to a large extent overcome by the use of a faster, reliable and sensitive XRD method developed in this laboratory [2,3]. With the aid of this method an optimization of the synthesis in air was achieved readily permitting preparation of overlithiated samples Li$_x$Ni$_{2-x}$O$_2$ with $x > 1.00$ [1]. The reproducibility of the synthesis method was proved by the synthesis of a series of over 60 samples with x in the range between 1.007 and 1.014. The cathodes prepared with these samples exhibited very good cycling characteristics.

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It is well recognized, however, that even the best synthesized $LiNiO_2$ samples, cannot yield good electrochemical characteristics unless adequate methods for the cathode preparation are employed. In the case of $LiNiO_2$, the first step in this respect is the extraction of the excess of LiOH, added in the starting reaction mixture to ensure the complete lithiation of the nickel oxide and the good cation ordering in the $LiNiO_2$ layered structure. Dahn et al. [4] were the first to establish that a 10 to 25% stoichiometric excess of LiOH is indispensable for the synthesis of well lithiated $LiNiO_2$. The unreacted LiOH should be extracted from the raw (as synthesized) product not only because it is an inert component but mainly because the free LiOH evolves gases during cycling, this leading to pressure build-up in the cell.

Besides this, there are several other not less important steps in the cathode fabrication such as: choice of the conductive binder and solvent materials, method of mixing of the cathode ingredients, type of the cathode mixture applied (powder, paste, slurry), ways for its application on the current collector and type of the mechanical and thermal treatments.

The principal aim of this paper is to study the processes occurring during the extraction of the residual LiOH, more specifically the chemical delithiation of $LiNiO_2$ and its effect on the XRD characteristics and electrochemical behaviour.

Another purpose was to explore alternative cathode formulations based on the recently developed by Kozawa et al. [5] ultra-fine carbon suspensions (UFC) in organic solvents, known to improve the performance of the $LiMn_2O_4$ spinel cathodes [6].

2. Experimental

2.1. Synthesis

An optimization program was carried out in this laboratory which resulted in the development of a laboratory method for the synthesis of overlithiated $Li_xNi_{2-x}O_2$ with $x > 1.00$. As described earlier [2,3], NiO powder with a large surface area was mixed with a stoichiometric excess of $LiOH \cdot H_2O$. The NiO was prepared by a slow thermolysis of basic nickel carbonate. The reaction mixture with 10% stoichiometric excess of LiOH was heated in alumina crucible under a constant flow of dry air first at 480°C so that the molten LiOH could coat uniformly the fine NiO grains. The synthesis itself was performed under a flow of dry air at 660 to 730°C. The product was ground in a glass mortar and dry sieved in 120 mesh screens.

2.2. XRD characterization

A fast and reliable XRD method [3] was applied in this study consuming only 8–10 min apparatus time based on

four criterial XRD parameters: (i) the integrated intensity ratio $R = \{I(102) + I(006)\}/I(101)$ introduced by Dahn et al. [7] and recently used by other authors: Reimers et al. [8], Hirano et al. [9] and Li et al. [10]; (ii) the Bragg angle of the (110) plane, reflecting the a lattice parameter; (iii) the c—the lattice parameter estimated from the Bragg angles of the (110) and (108) planes as shown in Ref. [3]; and (iv) the Bragg angle separation between the (108) and (110) peaks, $\Delta\Theta$ [2]. The XRD measurements were carried out on a Philips APD15 diffractometer provided with a modern computer system. The data were recorded at 0.025° step size with 2 s counting time, collected in the computer and printed after processing. The overlapping peaks were separated and fitted to Gaussian or pseudo-Voigt functions with a correlation coefficient better than 0.998.

Based on literature data [8–10], a linear relationship between R and x was plotted in the narrow $0.995 \leq x \leq 1.014$ range from which the values of x in $Li_xNi_{2-x}O_2$, denoted as x_R, were determined. An empirical linear dependence was established between the x_R values and the measured Bragg angles $2\Theta(110)$ in the same x range. The regression equation based on 17 experimental points (Fig. 1)

$$x_\Theta = -13.2322 + 0.1975\{2\Theta(110)\}$$

has a correlation coefficient of 0.9842 and a standard deviation of $0.001 x$.

2.3. Electrochemical testing

The coin cells for the cycling tests were assembled with commercial cell parts of the 2032 size. They housed the cathode, the Li anode and an Al disc spacer to provide reliable electronic contact of the electrodes with the cap and can. The electrodes were separated by several sheets of Whatman glass filter paper soaked in most cases with 1 M $LiClO_4$ solution in EC + PC (1:1 vol.) as electrolyte with less than 20 ppm H_2O. Most of the cells were cycled galvanostatically at 25 mA/g or ca. 0.4–0.5 mA/cm^2
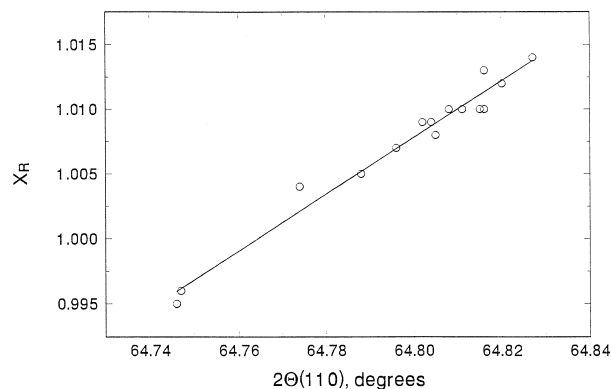

Fig. 1. Dependence of the Bragg angle $2\Theta(110)$ on the value of x_R determined from the experimental data of the ratio R.

between 2.6 and 4.25 V. Some of the cells were cycled by potentiostatic charging to 4.20 V with a limited c.d. of 60 mA/g or ca. 1.02 mA/cm^2 to a minimum c.d. of 55 μA/cm^2 and then discharged galvanostatically to 3.00 V at 40 mA/g. Unless otherwise indicated, the cathodes were prepared by pressing a mixture of the $LiNiO_2$ powder with 20 wt.% of teflonized acetylene black (TAB) on Al foil discs, 15 mm in diameter. The loading was ca. 20 mg/cm^2.

Voltammetric cycling was carried out potentiodynamically at a low scan rate of 27 mV/h between 3.40 and 4.30 V.

## 3. Results and discussion

3.1. Extraction of the residual LiOH

A series of extractions were carried out with one and the same sample to determine the volume of water necessary to remove the excess of LiOH introduced in the starting mixture as well as to assess the evolution of the XRD criterial parameters of the extracted samples. For this purpose, a 3-g sample of the $LiNiO_2$ synthesized with 10% excess of LiOH was stirred for 30 min in 10 ml of distilled water. After sedimentation the extract was filtered in a 25-ml measuring flask and analyzed for Li by AAS. The solid was washed with 5 ml of ethanol to remove the residual water as to avoid an additional high temperature delithiation during the subsequent drying of the $LiNiO_2$ sample at 60–70°C and then at 100°C. The dried samples were subjected to XRD measurement and used for the preparation of cathodes. The same extracting procedure was repeated three more times with the same sample and the results are presented in Table 1.

The data in Table 1 exhibit a small difference 3 mg/g between the LiOH content in the reaction mixture and that in the first extract. This led us to the erroneous conclusion that all the extracted LiOH represents the excess of LiOH added before the synthesis, i.e., that practically there were no losses due to evaporation of LiOH. This supposition was supported by the very low LiOH content in the next

extracts, which was attributed to the chemical delithiation of the phase. Besides, the changes in the criterial XRD parameters R, c and $\Delta\Theta$ after the first extraction were insignificant to suppose a considerable deintercalation of Li. The drastic decrease in the charge capacity in the first cycle of 30–35 mA h/g of cathodes prepared with $LiNiO_2$ after a single extraction however, revealed a considerable degree of Li extraction, corresponding to $\Delta x = 0.11$–0.13. This is somewhat larger than the value of $\Delta x = 0.08$ calculated from the LiOH content found in the first extract. This result lends a strong evidence that the LiOH in the first extract originates basically from the chemical delithiation of the $LiNiO_2$ phase. In contrast to the electrochemical delithiation where the deintercalated Li is intercalated to a discharge capacity of 180–190 mA h/g in the case of the chemically delithiated the discharge capacity is ca. 150 mA h/g, i.e., a loss of 30–40 mA h/g. It is noteworthy that this considerable degradation of the hydrolyzed $LiNiO_2$ after a single extraction is accompanied by only very small changes in the criterial XRD parameters (Table 1). This indicates that the above parameters, which are successfully used to assess the stoichiometry of the as synthesized $LiNiO_2$ samples, cannot be applied for the chemically delithiated ones.

Dahn et al. [4] have assumed that the chemical delithiation of $LiNiO_2$ during its extraction in limited water volume (3.3 ml/g) proceeds by cation exchange of Li^+ with H^+. In view of the considerable alkalinity of the extract such an exchange seems very improbable.

The delithiation of $LiNiO_2$ during its extraction in water proceeds in a strong alkaline medium (ca. 0.3 N LiOH) where the solubility of oxygen is low. The respective Pourbaix diagram shows that under these conditions the potential of the $O_2 + 2H_2O/4OH^-$ couple is much lower than that of the Ni^{4+}/Ni^{3+} couple, so that the oxidation of Ni^{3+} is not feasible. This means that the delithiation of $LiNiO_2$ should proceed without electron exchange. On the other hand, it is well known that γ-NiOOH, the positive in alkaline cells undergoes selfdischarge in the presence of water through in a purely chemical reaction by evolution of oxygen. Since γ-NiOOH is isostructural with $LiNiO_2$, it can be expected that the chemical delithiation of the latter could proceed by a similar reaction:

$$LiNiO_2 + y/2H_2O \rightarrow Li_{1-y}NiO_{2-y/2} + yLiOH \qquad (1)$$
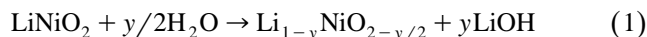
It is evident from Eq. (1) that the loss of positive charges from the crystal lattice of $LiNiO_2$ during the deintercalation of Li^+ is compensated by an equivalent evolution of oxygen. Thus, part of the NiO_6 octahedra will become defective with one oxygen vacancy and consequently with two positive charges. The observed capacity loss of the chemically delithiated $LiNiO_2$ (Table 1) suggests that the defective octahedra can release no more electrons during the electrochemical charging in the non-

Table 1
Stepwise extraction of a $LiNiO_2$ sample in water at a ratio 10 ml H_2O/3 g $LiNiO_2$

Extract	LiOH [mg/g]	c [Å]	$\Delta\Theta$ [°2Θ]	R	$q_{c,1}$	$q_{d,1}$	Δx
no	23[a]	14.184	0.310	0.287	215	181	–
1	20	14.188	0.315	0.395	180	150	0.08
2	5.2	14.190	0.357	0.401	–	–	0.02
3	4.3	14.201	0.358	0.411	–	–	0.02
4	3.5	14.206	0.360	0.413	–	–	0.01

Note: [a]calculated excess of LiOH/g of $LiNiO_2$ introduced before the synthesis. The LiOH contents are with respect to the mass of the unextracted sample.

Table 2
Extraction of 1 g $LiNiO_2$ sample with 98% ethanol

Ethanol [ml/g]	Extracted LiOH [mg/g]	c [Å]	$\Delta\Theta$ [°2Θ]	R	$q_{c,1}$ [mA h/g]	$q_{d,1}$ [mA h/g]	Δx
0	–	14.185	0.312	0.386	210	185	0
10	3.20	14.189	0.306	0.390	215	191	0.013
20	3.98	14.190	0.307	0.389	–	–	0.016
30	4.20	14.190	0.305	0.395	–	–	0.017

aqueous solution. Besides, in the absence of water they also cannot fill up the oxygen vacancies. The decrease in the number of extractable electrons in the chemically delithiated $LiNiO_2$ precludes the deintercalation of an equivalent number of Li^+ ions, causing an irreversible loss of capacity.

The strong negative effect of the water extraction on the structural and electrochemical characteristics of $LiNiO_2$ incited the search of an alternative solvent. Being almost a nonaqueous liquid and capable of dissolving a considerable amount of LiOH ethanol was explored for the purpose. The solubility of LiOH in ethanol with water contents of 0.02 to 4% determined experimentally is not less than 4.3 mg/ml. Table 2 presents the results of the extraction of three 1 g samples of $LiNiO_2$ with increasing volumes of ethanol (98%).

Having in mind that the smallest volume of 10 ml ethanol used can dissolve 43 mg LiOH, the amount of LiOH found in the extracts compared to that in water is surprisingly low (Table 2). The three-fold increase in the ethanol volume increases the LiOH content in the extract by only 31%. It can be supposed that the lower extraction in the smaller volumes is due to kinetic hindrances. Nevertheless, if it is assumed that all the LiOH found in the 30 ml of ethanol is due to chemical delithiation of $LiNiO_2$, the estimated value of Δx is only 0.017. This value of course is an overestimation since some if not most of the LiOH found in the extracts is unreacted LiOH. This supposition is corroborated by the insignificant changes not only in the XRD criterial parameters but mainly by the cycling performance of the cathodes prepared with ethanol extracted $LiNiO_2$ samples (Table 2) which are slightly improved not only with respect to the initial capacities but also in their cycling stability. On the other hand, even if it is assumed, that all the LiOH extracted in 30 ml/g ethanol originates only from the chemical deintercalation of $LiNiO_2$, i.e., that all of the excess of LiOH has evaporated during the synthesis, the calculation based on the extracted 4.2 mg LiOH/g $LiNiO_2$ corresponds to a deintercalation degree of only Δx 0.017, which is ca. 5 times lower than that by the extraction in water. This value is of course an overestimation since it is hardly possible that all the 10% excess of LiOH have evaporated during the synthesis, so that the value of Δx is actually lower. This is confirmed by the insignificant changes in the XRD parameters and especially by the most sensitive of them $\Delta\Theta$.

The insignificant values of Δx after the extraction in ethanol at a ratio 10 ml/g and the good electrochemical performance of the cathodes prepared with the extracted $LiNiO_2$ samples were the reasons to prepare all our cathodes with such samples.

It is noteworthy that the maximum extracted LiOH 4.2 mg/g by 30 ml EtOH/gl corresponds to 4200 ppm LiOH in the extracted sample, while using 10 ml/g we extract only 1000 ppm this leaving 3200 ppm in the sample. This value is lower than that recommended by Dahn et al. [4] as the maximum 'most preferable content of 5000 ppm'.

3.2. Storage

The considerable negative effect of the chemical delithiation of $LiNiO_2$ in water on its electrochemical performance suggested that a similar deterioration could take place by exposing the compound to the water vapours in the ambient atmosphere. From a practical point of view, it was essential to study the rate of this process in order to know how to avoid it during the handling of the compound. For this purpose, three $LiNiO_2$ powdered samples were stored for 75 h in the ambient atmosphere of the laboratory at room temperature (23 ± 3°C). The moisture content of the air was not monitored and it is only roughly defined as high or low depending on the outside atmosphere temperature. The delithiation process was followed by XRD measurements of the c lattice parameter and the
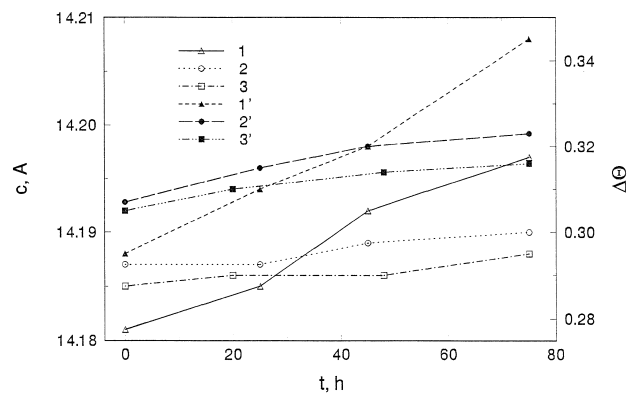

Fig. 2. Effect of storage time in the ambient room atmosphere on the values of c and $\Delta\Theta$: open symbols, c; filled, $\Delta\Theta$. (1, 1′) Not extracted sample in moist air; (2, 2′) extracted sample in moist air; (3, 3′) not extracted sample in dry air.

Bragg angle separation between the centers of the (108) and (110) peaks, $\Delta\Theta$.

Fig. 2 presents the results from this experiments. Plots 1 and 1′ show the increase of c and $\Delta\Theta$ of a unextracted $LiNiO_2$ sample stored in a higher moisture atmosphere in the summer, $23 \pm 4°C$. The relative increase in c is 0.10% while that of $\Delta\Theta$ is 17%. Plots 2 and 2′ are for a sample extracted with ethanol stored also in a high moisture atmosphere. In this case, the value of c and $\Delta\Theta$ increased only by 0.02% and 5.2%, respectively. The much slower hydrolysis of the sample not containing any free LiOH was unexpected, since it was more reasonable to suppose that the chemical delithiation reaction (Eq. (1)) will be retarded in the presence of excess of LiOH. The results actually found can be explained basically with the irreversibility of the chemical delithiation reaction and the higher hygroscopicity of the samples containing free LiOH. Plots 3 and 3′ pertain to a unextracted sample but stored in winter time $(-6 \pm 5°C)$, i.e., at a much lower content of water vapours in the air. As a result, the relative increases of c and $\Delta\Theta$ are lower than those of sample 1 (0.02% and 4.3%, respectively).

The larger relative increase of $\Delta\Theta$ than that of c during storage makes the former the more reliable parameter in controlling the degree of chemical delithiation of the $LiNiO_2$ samples.

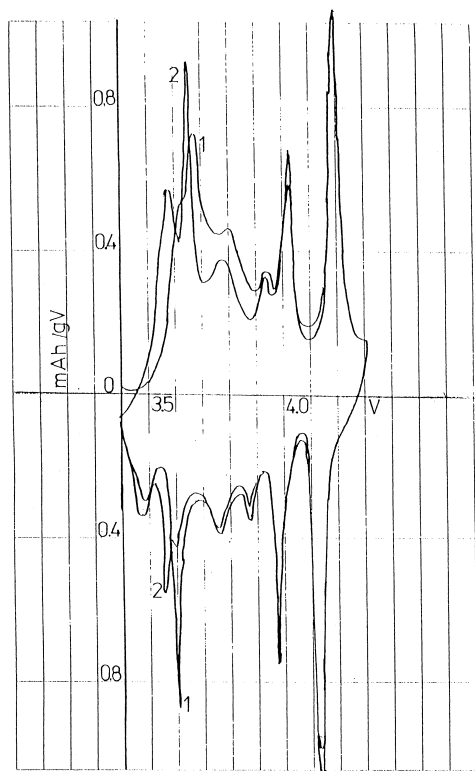On the other hand, our long experience has proved that when kept in the dry box (≤ 20 ppm H_2O) the XRD
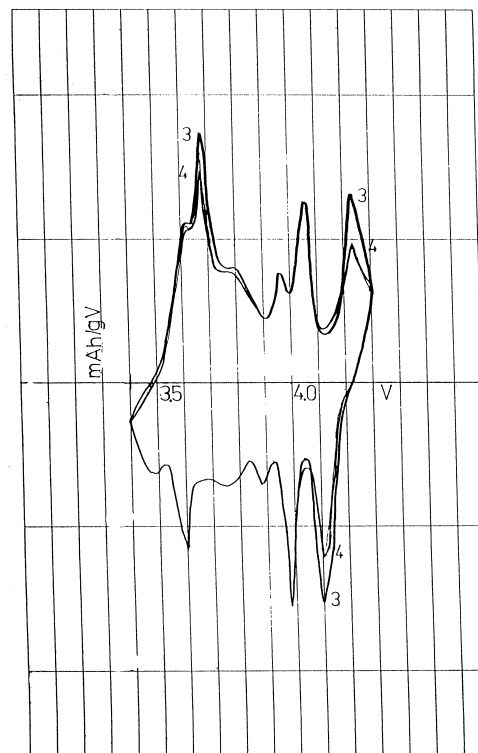

Fig. 4. VA-grams of the third and fourth cycles of the same cathode as in Fig. 3.

parameters as well as the electrochemical characteristics of both unextracted and extracted in ethanol $LiNiO_2$ samples are preserved for period of 5–6 months.

3.3. Cyclic voltammetry

Fig. 3 presents the VA-grams of the first two cycles of a cathode prepared with an overlithiated $Li_xNi_{2-x}O_2$ sample with $x = 1.014$, from which the free LiOH was extracted in ethanol as described above. The positions and profiles of all major and minor peaks are in good agreement with those recently reported in the literature [11,12]. With the exception of the first peak in the first charging, reflecting the R_1/M phase transition,[1] all other peaks maintain their positions and profiles. The position of the R_1/M peak in the first cycle is by ca. 10 mV more anodic than that of the second. In the second and in all the next cycles (1 to 4), the position of this peak remains invariable at 3.68 ± 0.02 V. The small unidentified peak at 3.57 V appearing in the second charging is a characteristic feature of the overlithiated $LiNiO_2$ cathodes but it gradually disappears in the next two to four cycles. Between the first and second charging, the areas of the R_1/M and the next two small peaks are reduced. This reduction corresponds ap-

Fig. 3. VA-grams of the first and second cycles of an overlithiated $LiNiO_2$ cathode with $x = 1.014$.

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[1] Here and in the following text, we employ the phase notations introduced by Ohzuku et al. [13].

proximately to a capacity decrease of ca. 25 mA h/g, which is always observed in the first cycle under galvanostatic conditions (Table 2). On the other hand, all other peaks in both half-cycles (anodic and cathodic) retain almost completely their areas in the first two cycles. This implies that the capacity loss during the first cycle characteristic for the $LiNiO_2$ cathode material is associated with the structural changes in the range of the R_1/M peaks between 3.40 and 4.02 V occurring after the first charging.

Excluding a small reduction the areas of all peaks are preserved in the second, third and fourth cycles of the VA-grams (Figs. 3 and 4). The reproducibility of the R_2/R_3 peaks at 4.20 V in both branches during all four cycles recorded is quite impressive. It was pointed out by Ohzuku et al. [13] that at slow charging at potentials just above 4.20 V there occurs a strong contraction of the *c* lattice parameter by 0.9 Å. This contraction according to Ref. [13] is the cause for a poor reversibility of the R_2/R_3 peak. We are inclined to believe that the reversibility of the R_2/R_3 peak observed in Fig. 3 is related to the low cation mixing in the overlithiated sample.

In support to this assumption are the VA-grams in Fig. 5 of the first two cycles of a 'underlithiated' $LiNiO_2$ sample with $x = 0.998$, from which the residual LiOH was extracted in ethanol. The VA-grams are characterized by the strong anodic shift of ca. 100 mV of the first R_1/M peak in anodic direction, and by broader peaks. The most
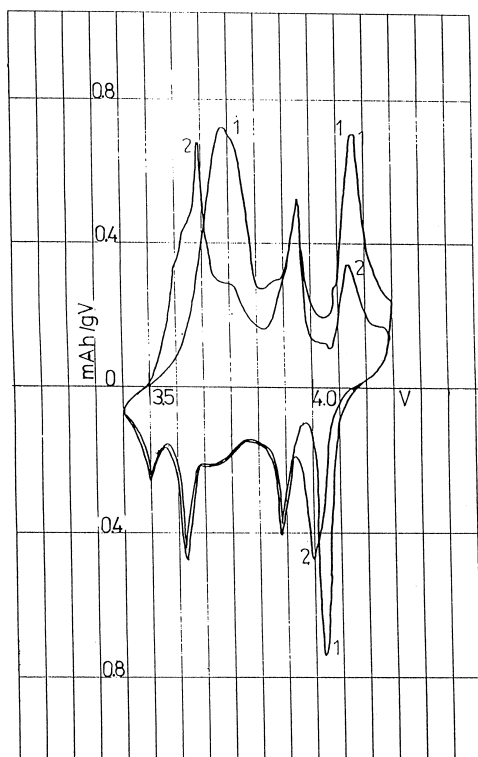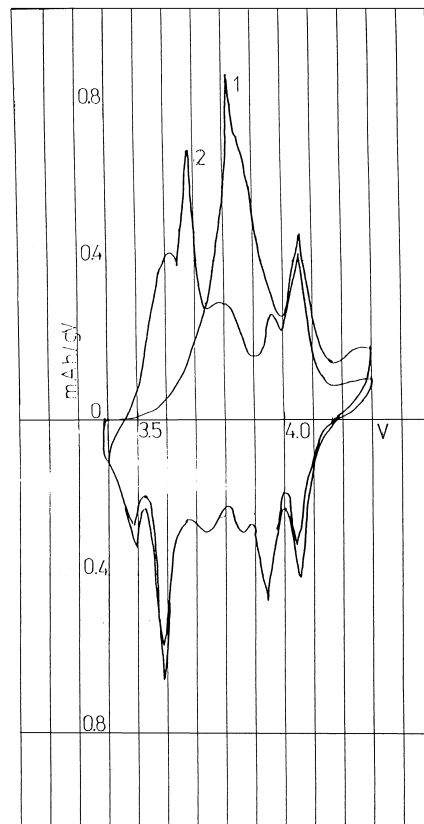

Fig. 6. VA-grams of the first and second cycles of a $LiNiO_2$ cathode extracted in water at a ratio 3.3 ml/g.

significant difference between the VA-grams in Figs. 3 and 5 lies in the lower, broader and decreasing peaks of the R_2/R_3 phase transition. The poor reversibility of this peak is most probably caused by the increased cation disorder in the low stoichiometry sample.

The VA-grams of an overlithiated $LiNiO_2$ sample extracted once in 3.3 ml water/g are illustrated in Fig. 6. One can see the strong shift of the R_1/M peak by 130 mV in anodic direction. The peak is larger and it has overlapped completely the two smaller M peaks. The strong reduction in the areas and the broadening of the R_2/R_3 peaks is quite remarkable. Following the first charge, all characteristic peaks in the first discharge and in the following cycles reappear with positions very close to those of the normal samples but their area (capacity) is considerably reduced in agreement with the data for the galvanostatic cycling of a chemically delithiated sample in Table 1. The decrease in the capacity in the first charge of the sample in Fig. 6 is obviously due to the loss of Li^+ during the chemical delithiation. This reduction, however, cannot be recovered by the electrochemical intercalation in the next cycles because of the changes of the crystal structure due to the loss of oxygen. The strong reduction of the R_2/R_3 peaks which almost disappear in the fourth cycle (not shown here) is probably also related to the oxygen loss.

Fig. 5. VA-grams of the first and second cycles of a $LiNiO_2$ cathode with $x = 0.998$.

The present results illustrate clearly the potentialities of the volumetric measurements in the assessment of structural alterations in $LiNiO_2$ almost not detectable by the XRD parameters employed in this study.

3.4. Cycling tests

The positive effect of the stoichiometry on the cycling characteristics of the $LiNiO_2$ cathodes was reported in a previous paper [3]. The increase in the value of x from 0.995 to 1.014 brought about an average rise in the discharge capacity by ca. 13% at the fifth cycle and improved the cycling stability. Our previous tests were carried out with cathode mixture containing 20% TAB containing ca. 35% Teflon. The cycling was performed galvanostatically at 25 mA/g (ca. 0.4 mA/cm^2) between 2.60 and 4.25 V. In the present paper, we explore the effect of the conductive UFC material developed by Kozawa et al. [5]. It represents a 7–9% colloid solution in N-methylpyrolidon of fine carbon particles with polyvinilpyrolidone (PVP) as a binder in a weight ratio C:PVP = 10:2, denoted as UFC No. 4.

Fig. 7 presents the cycling behaviour of two cathodes prepared with $Li_xNi_{2-x}O_2$ ($x = 1.009$), with different formulations of the cathode mixture. Cathode 'a' is with 20% TAB, while cathode 'b' contains 10% TAB and 10% UFC No. 4 (as dry substance). The cathodes were cycled galvanostatically at 25 mA/g between 2.60 and 3.00 V. The beneficial effect of the UFC material is expressed by an average increase of the discharge capacity of ca. 6% in the first 30 cycles and ca. 13% in the next 50, this implying a considerable improvement in the cycling stability.

The charging of Li-ion cells under potentiostatic conditions with a limited initial current was recently introduced by some of the leading producing companies (Sony, Toshiba). They offer for sale the battery packs together with the charging unit, which provides the potentiostatic
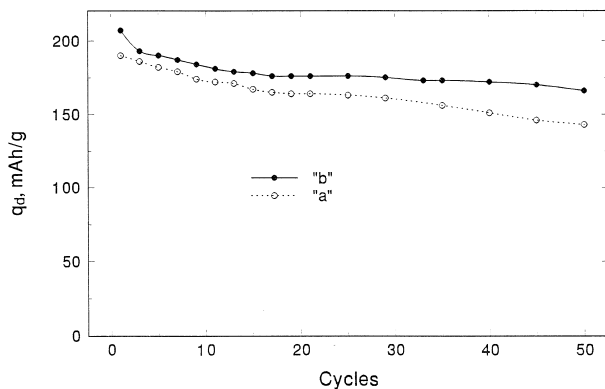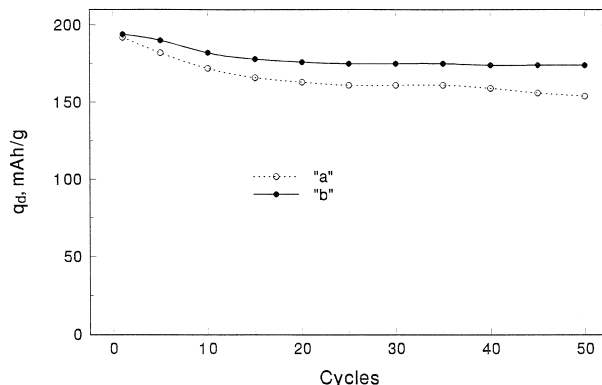

Fig. 8. Cycling performance of one and the same cathode as that of 'b' in Fig. 7 (with UFC): (a) galvanostatic charging; (b) potentiostatic charging.

charging mode. This policy was adopted mainly to avoid the overcharging of the cells and thus to protect them from hazardous situations. The potentiostatic charging possesses two additional advantages. It provides a faster and more complete charging of the cathode, and as a consequence a larger capacity in the next galvanostatic discharge. This in turn makes it possible to reduce the maximum charging voltage, whereby the rate of the electrolyte oxidation and the structural changes of the cathode material are diminished.

The favorable effect of the potentiostatic charging is in agreement with the data in the VA-grams in Figs. 3 and 4 exhibiting the reversibility of the R_2/R_3 peak at 4.20 V of the overlithiated $LiNiO_2$ cathode, corresponding to the rhombohedral two phase transition from the R_2 to the NiO_2 phase, which according to Ohzuku et al. [13] is of the $R3m$ space group in which the N sites are occupied by Ni^{4+} ions and the L sites are ideally vacant. It was shown by the same authors that at slow charging rate at potentials above 4.20 V corresponding to $x \leq 0.20$ a strong contraction of the c-axis is observed, implying a poor reversibility in the range above 4.20 V. On the other hand, the capacity associated with the R_3 phase cannot be neglected. So, by

Fig. 7. Cycling performance of two cathodes prepared with one and the same $LiNiO_2$ sample with $x = 1.009$ with different cathode mixtures: (a) 20% TAB, (b) 10% TAB and 10% UFC No. 4, both cycled galvanostatically (see text).
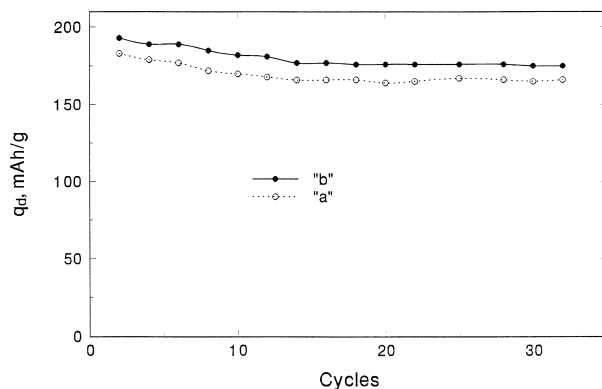

Fig. 9. Cycling performance of two cathodes with different formulations as those in Fig. 7 both cycled by potentiostatic charging: (a) 20% TAB; (b) 10% TAB and 10% UFC No. 4.
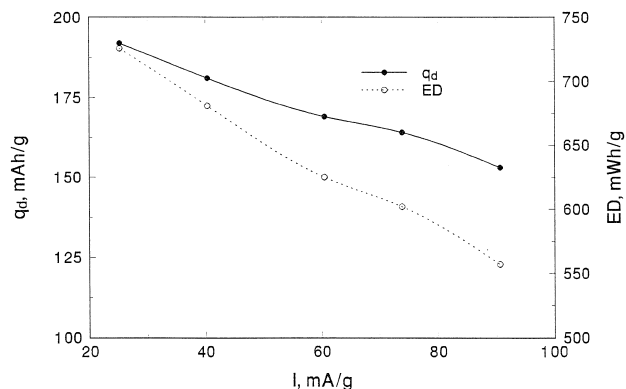
Fig. 10. Effect on the discharge capacity and energy density with respect to the mass of the active material of the discharge rate expressed in mA/g of a LiNiO$_2$ cathode with 10% TAB and 10% UFC No. 4 charged potentiostatically to 4.20 V at 60 mA/g and discharged galvanostatically after 10 cycles at a discharge current of 40 mA/g.

the slow charging at 4.20 V, we can gain both in capacity and in cycling stability.

These advantages are illustrated in Fig. 8 presenting the cycling performance of one and the same cathode mixture as that of cathode 'b' in Fig. 7 (i.e., with UFC No. 4 additive). Plot 'a' is obtained by galvanostatic cycling between 2.60 and 4.25 V at 25 mA/g charging current and 40 mA/g discharging current. The results for plot 'b' are obtained under potentiostatic charging at initial charging current of 60 mA/g. Upon reaching the maximum charging voltage of 4.20 V the current decreases exponentially to ca. 3 mA/g, where the galvanostatic discharge at 40 mA/g is switched on. The discharge is interrupted at 3.00 V when the next cycle begins. The comparison between the two plots in Fig. 8 reveals that in spite of the higher initial charging current and the lower maximum charging voltage, as compared to that for plot 'a', the discharge capacity of the cathode is increased by ca. 20 mA h/g or by ca. 13% due to the potentiostatic mode of charging.

Fig. 9 juxtaposes the cycling behaviour of two cathodes with different formulations as those in Fig. 7, both charged under potentiostatic conditions as in Fig. 8. In this case, the improvement due to the use of the UFC material is not

so strongly expressed as that obtained under the galvanostatic cycling shown in Fig. 7.

Fig. 10 presents the effect of the discharge rate expressed in mA/g on the discharge capacity and energy density of a LiNiO$_2$ cathode prepared with UFC No. 4 as above, charged potentiostatically at 60 mA/g to 4.20 V and discharged galvanostatically at different currents to 3.00 V after a preliminary cycling for 10 cycles at a discharge current of 40 mA/g. It can be seen that by the two-fold increase of the discharge rate from 30 to 60 mA/g the discharge capacity drops by only 10%, and the energy density by 11%. It is worth noting that the discharge current of the Li-ion cells with LiCoO$_2$ cathodes and carbon anodes for the five leading Japanese producers at the usual discharge rate lies between 18 and 26 mA/g [14].

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