

Available online at www.sciencedirect.com



JOURNAL OF SOLID STATE CHEMISTRY

Journal of Solid State Chemistry 180 (2007) 1816-1825

www.elsevier.com/locate/jssc

# Effect of the high pressure on the structure and intercalation properties of lithium–nickel–manganese oxides

M. Yoncheva<sup>a</sup>, R. Stoyanova<sup>a</sup>, E. Zhecheva<sup>a,\*</sup>, R. Alcántara<sup>b</sup>, G. Ortiz<sup>b</sup>, J.L. Tirado<sup>b</sup>

<sup>a</sup>Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria <sup>b</sup>Laboratorio de Química Inorgánica, Facultad de Ciencias, Universidad de Córdoba, 14071 Córdoba, Spain

Received 21 December 2006; received in revised form 19 March 2007; accepted 23 March 2007 Available online 6 April 2007

#### Abstract

Lithium–nickel–manganese oxides  $(\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2, x = 0 \text{ and } 0.2)$ , having different cationic distributions and an oxidation state of Ni varying from 2+ to 3+, were formed under a high-pressure (3 GPa). The structure and cationic distribution in these oxides were examined by powder X-ray diffraction, infrared (IR) and electron paramagnetic resonance (EPR) in X-band (9.23 GHz) and at higher frequencies (95 and 285 GHz). Under a high pressure, a solid-state reaction between NiMnO<sub>3</sub> and Li<sub>2</sub>O yields LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> with a disordered rock-salt type structure. The paramagnetic ions stabilized in this oxide are mainly Ni<sup>2+</sup> and Mn<sup>4+</sup> together with Mn<sup>3+</sup> (about 10%). The replacement of Li<sub>2</sub>O by Li<sub>2</sub>O<sub>2</sub> permits increasing the oxidation state of Ni ions in lithium–nickel–manganese oxides. The higher oxidation state of Ni ions favours the stabilization of the layered modification, where the Ni-to-Mn ratio is preserved: Li(Li<sub>0.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>)O<sub>2</sub>. The paramagnetic ions stabilized in the layered oxide are mainly Ni<sup>3+</sup> and Mn<sup>4+</sup> ions. The disordered and ordered phases display different intercalation properties in respect of lithium. The changes in local Ni,Mn-environment during the electrochemical reaction are discussed on the basis of EPR and IR spectroscopy. © 2007 Published by Elsevier Inc.

Keywords: High-pressure synthesis; Intercalation compounds; Cathode materials for lithium-ion batteries; Electron paramagnetic resonance

## 1. Introduction

Lithium–nickel–manganese oxides,  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ , have been considered as alternative to up-to-day used LiCoO<sub>2</sub> electrodes for lithium-ion batteries since they deliver a higher reversible capacity at room and elevated temperatures [1,2]. The crystal structure of  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ is composed by consecutive arrangement of lithium and transition metal ions in the close-packed oxygen arrays leading to the formation of discrete lithium and transition metal layers [3,4]. The oxidation states of the nickel and manganese ions are (+2) and (+4), respectively, the Ni<sup>2+</sup> ions being electrochemically active [7–11]. Contrary to the ideal layered structure, some structural peculiarities can be outlined for  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ . First, there is partial mixing of Li and Ni between the layers leading to the following cation distribution:  $[\text{Li}_{1-\delta}\text{Ni}_{\delta}][\text{Li}_{\delta}\text{Ni}_{1/2-\delta} \text{Mn}_{1/2}]\text{O}_2$  with

E-mail address: zhecheva@svr.igic.bas.bg (E. Zhecheva).

 $\delta \approx 0.10$  [3,6]. Secondly, the Li<sup>+</sup> and Mn<sup>4+</sup> ions in the layers display a tendency to ordering [12–17]. In order to stabilize the layered structure, Dahn et al. have proposed overlithiated oxides of the type  $\text{Li}[\text{Ni}_x\text{Li}_{(1-2x/3)}]$  $Mn_{(2-x)/3}O_2$ , which can be considered as solid solutions between layered LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> and monoclinic Li<sub>2</sub>MnO<sub>3</sub> (expressed in the layered notation as  $Li[Li_{1/3}Mn_{2/3}]O_2$ ) [18]. Based on analysis of the magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectra and lattice imaging by transmission electron microscope (TEM), Thackeray et al. have suggested that "Li[Ni<sub>x</sub>Li<sub>(1-2x/3)</sub>]  $Mn_{(2-x)/3}$ ]O<sub>2</sub>"-oxides represent a complex domain structure of integration of monoclinic into layered oxides, Li<sub>2</sub>MnO<sub>3</sub>\*LiNi/MnO<sub>2</sub> [19]. The electrochemical performance of these electrode materials is strongly sensitive towards the synthesis procedure [20,21], which is shown to affect the cationic distribution in oxides [22].

High-pressure synthesis has been used for the preparation of new structural modifications of lithium transition metal oxides [23–28]. For example, high-pressure synthesis

<sup>\*</sup>Corresponding author. Fax: +35928705024.

<sup>0022-4596/</sup>\$ - see front matter O 2007 Published by Elsevier Inc. doi:10.1016/j.jssc.2007.03.025

allows stabilization of a new form of LiMPO<sub>4</sub> (M = Fe and Ni), where the main crystal difference comes from the oxygen arrangement [23]. Substitution of Ga for Ni and Co in layered LiNi/CoO<sub>2</sub> can be realized under a high-pressure only [24-26]. In addition, the high-pressure in an oxygenrich atmosphere allows controlling the oxidation state of transition metal ions. For example, novel compositions, Li[Li<sub>x</sub>Ni<sub>1-x</sub>]O<sub>2</sub>, with 0 < x < 1/3 and a layered structure have been prepared under high pressure in an oxygen-rich atmosphere [27,28]. A new structural feature of these compositions as compared to the well-known Li[Ni]O<sub>2</sub> is the development of mixed  $[Li_xNi_{1-x}]O_2$ -layers in addition to nearly pure Li-layers. Charge compensation is achieved by the appearance of Ni<sup>4+</sup> ions. The compounds prepared under high-pressure display different electrochemical properties as compared to the oxides prepared under atmospheric pressure [23–28].

The aim of this work was to study the effect of high pressure on the structure and electrochemical properties of lithium-nickel-manganese oxides. Keeping the Ni-Mn ratio equal to 1, two compositions were obtained under a high pressure:  $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$  with x = 0 and 0.2. To affect the oxidation state of the nickel ions, highpressure synthesis in an oxygen-rich atmosphere was performed for the latter composition. The crystal structure of the oxides was determined by powder X-ray diffraction (XRD) analysis. The local cationic distribution was analysed by electron paramagnetic resonance (EPR) spectroscopy. This method had been shown to give valuable information on the cationic distribution in  $LiNi_{1/2}Mn_{1/2}O_2$  obtained under atmospheric pressure [17]. The electrochemical extraction and insertion from/ into  $LiNi_{1/2}Mn_{1/2}O_2$  obtained under a high pressure were tested with constant current experiments. The changes in local metal environment during Li extraction/insertion were monitored by EPR and infrared (IR) spectroscopy.

## 2. Experimental

 $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$  oxides with x = 0 and 0.2 were prepared by solid-state reaction using NiMnO<sub>3</sub> as a precursor. The initial NiMnO<sub>3</sub> oxide with an ilmenite type structure was obtained by thermal decomposition of Ni,Mn co-precipitated carbonates at 450 °C for 5 h.

High-pressure synthesis was performed at 700 °C and 3 GPa using a 1/2 in end-loaded piston-cylindrical apparatus at the Bayerisches Geoinstitut. The details of the high-pressure synthesis are given elsewhere [24–28]. For the preparation of  $\text{Li}_{1+x}(\text{Ni}_{1/2}\text{Mn}_{1/2})_{1-x}\text{O}_2$  oxide with x = 0, Li<sub>2</sub>O was used and the reaction mixture was sealed in a Pt-capsule. For the preparation of  $\text{Li}_{1.2}\text{Ni}_{0.4}$  Mn<sub>0.4</sub>O<sub>2</sub>, Li<sub>2</sub>O<sub>2</sub> was used instead of Li<sub>2</sub>O and the reaction mixture was sealed in an Au-capsule. Thermal decomposition of Li<sub>2</sub>O<sub>2</sub> under the experimental conditions ensured an oxygen-rich atmosphere, which was necessary for the stabilization of the nickel ions in higher

oxidation states in Li<sub>1.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub>. To compensate for the lithium volatility at the relatively high synthesis temperature (700 °C), a 5% Li<sub>2</sub>O or Li<sub>2</sub>O<sub>2</sub> excess to the stoichiometric amount was used. For the sake of comparison, the same reaction mixture was used for the preparation of lithium–nickel–manganese oxides under atmospheric pressure.

X-ray phase analysis was carried out on a Philips X'Pert powder diffractometer with Co $K\alpha$ -radiation, reflection mode, using Si as an internal standard. The scan range  $15 \leq 2\Theta \leq 120$  in a step increment of  $0.02^{\circ}$  was utilized. The Fullprof computer program was used for the calculation [29]. The diffractometer point zero, Lorentzian/Gaussian fraction of the pseudo-Voigt peak function, scale factor, lattice constants (*a* and *c*), oxygen parameter (*z*), thermal factors for 3*a*, 3*b* and 6*c* positions, halfwidth parameters, preferred orientation were refined. To gain stability during the refinement, the Ni/Mn-ratio was imposed by the chemical composition of the oxides. Subsequently, the cationic occupancy factors were refined taking into account that the total occupancies of the 3*a* and 3*b* sites were equal to unity.

EPR measurements at 9.23 GHz (X-band) were carried out in an ERS 220/Q spectrometer within the temperature range 85–410 K. The high-frequency EPR spectra were recorded on a single-pass transmission EPR spectrometer built in the High-Magnetic Filed Laboratory, Grenoble, France. The frequencies were changed from 95 to 285 GHz using Gunn diodes and their multipliers. The detection of absorption was performed with a bolometer. The recording temperatures were varied between 5 and 100 K using a variable temperature insert (Oxford Instruments).

The electrochemical oxidation/reduction of LiNi1/2Mn1/2O2 was carried out using two-electrode Swagelok<sup>TM</sup> cells of the type Li|LiPF<sub>6</sub>(EC:DEC)| LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>. The positive electrode, having about  $4 \,\mathrm{mg}\,\mathrm{cm}^{-2}$  of active material supported onto an aluminium foil (Goodfellow), was prepared as a 9mm diameter disk by drying at 120 °C into vacuum, then pressing a mixture of 80% of the active oxide, 5% of PVDF binder, and 15% of carbon (50% weight mixture of graphite and carbon black) previously dispersed in 1-methyl-2-pyrrolidone. Lithium electrodes consisted of a clean 9mm diameter lithium metal disk. The commercial (Merck LP40) electrolyte solution was 1 M LiPF<sub>6</sub> in a 1:1 w/w mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) that was supported by Whatman<sup>TM</sup> porous glasspaper discs as separators. The electrochemical reactions were carried out using a multichannel MacPile II system in potentiostatic mode at 10 mV/0.1 h of scan rate. The cells were mounted in a dry box under Ar atmosphere. To obtain the ex-situ EPR spectra of the electrochemically oxidized (charge process) LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O, the electrochemical process was interrupted at selected charge levels and then, after a relaxation period, the electrochemical cells were dismounted in an Ar-containing dry-box and the electrodes were recuperated.



Fig. 1. XRD patterns of ordered  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.4}\text{Mn}_{0.4}]\text{O}_2$  and disordered  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$  obtained at 3 GPa. The difference between the observed and calculated profiles is plotted. Bragg reflections for disordered and ordered oxides, as well as the Si standard, are indicated.

# 3. Results

## 3.1. High-pressure synthesis of disordered $LiNi_{0.5}Mn_{0.5}O_2$

Under a high pressure, the solid-state reaction between NiMnO<sub>3</sub> and Li<sub>2</sub>O yields LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> with a disordered rock-salt type structure (Fig. 1). However, the low-intensity peak at 21° demonstrates that some degree of cationic order still remains with this composition. The unit cell dimensions of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained under a high pressure are given in Table 1. From the Rietveld analysis of the XRD patterns, the following cation distribution can be extracted: [Li<sub>0.63</sub>Ni<sub>0.37</sub>][Li<sub>0.37</sub>Ni<sub>0.13</sub>Mn<sub>0.5</sub>]O<sub>2</sub> (Table 1). When the solid-state reaction between NiMnO<sub>3</sub> and Li<sub>2</sub>O proceeds under atmospheric pressure, LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> with a layered structure is obtained. The corresponding cation distribution is as follow:  $[Li_{0.91}Ni_{0.09}][Li_{0.09}Ni_{0.41}Mn_{0.5}]O_2$ (Table 1). It is noticeable that no more than 15% of cationic mixing has been reported for LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained under atmospheric pressure [2-6]. The results obtained show that the high pressure favours the cationic disorder in the framework of the close oxygen packing. As a comparison, this picture bears a resemblance to the formation of solid solutions between cubic NiO and layered LiNiO<sub>2</sub> oxides,  $Li_xNi_{2-x}O_2$  [30–33]. With a low Li content (x < 0.62), a disordered rock-salt structure is formed, while for  $0.62 \le x \le 1$  lithium and nickel ions show a tendency to order in (111) cubic planes, culminating at Li/Ni = 1 in discrete layers of Li and Ni [30,31]. While the cationic order in the "NiO-LiNiO<sub>2</sub>" system is driven by the changes in the Li-Ni and the corresponding Ni<sup>2+</sup>-Ni<sup>3+</sup> ratios, the high pressure gives rise to cationic mixing between the layers in  $LiNi_{0.5}Mn_{0.5}O_2$  without changing the Li-Ni/Mn ratio.

Table 1

Structural parameters determined from XRD pattern Rietveld refinement for disordered  $LiN_{i_0.5}Mn_{0.5}O_2$  and ordered  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$ , obtained under high-pressure

Samples	a (Å)	c (Å)	Ζ	δ
Li[Li <sub>0.2</sub> Ni <sub>0.4</sub> Mn <sub>0.4</sub> ]O <sub>2</sub> -ordered	2.8830	14.2536	0.2577	0.087
$Li[Li_0 Ni_0 Mn_0 G]O_2-AP$	2.8577	14.2584	0.2582	0.046
LiNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> -disordered	2.9256	14.3285	0.2524	0.375
LiNi <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub> -AP	2.8844	14.3000	0.2580	0.099
$ \begin{array}{l} LiNi_{0.5}Mn_{0.5}O_2 \text{-} disordered \\ LiNi_{0.5}Mn_{0.5}O_2 \text{-} AP \end{array} \end{array} \\$	2.9256 2.8844	14.3285 14.3000	0.2524 0.2580	0.3 0.0

For the sake of comparison, structural parameters for  $LiNi_{0.5}Mn_{0.5}O_2$  and  $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$  obtained at atmospheric pressure are also given (AP).

Both compositions are characterized by different electrochemical properties. For layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained at atmospheric pressure, a reversible Li extraction/ insertion was shown to take place between 3.5 and 4.5 V [2–6]. Contrary to layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, the disordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained under high pressures displays irreversible Li extraction. Fig. 2 shows the mass-normalized intensity vs. voltage curves of disordered LiNi<sub>0.5</sub>  $Mn_{0.5}O_2$  electrodes in lithium test cells. The first charge/ discharge process was carried out in the voltage limit of 5.1-2.5 V. Two intense peaks, at 4.1 and 4.8 V, in the charge curve were well resolved, while no peaks appeared in the discharge curve. During the second charge up to 5.1 V, the peak at 4.1 V was not recovered and the peak at 4.8 V lost in intensity. Based on the oxidation/reduction processes of manganese ions in lithium transition metal oxides with spinel and layered structures [34], one can assign the oxidation peak at 4.1 V to the  $\text{Mm}^{3+}/$ Mn<sup>4+</sup> ionic couple. The capacity corresponding to this peak is 30 mAh/g. This means that about 10% of the



Fig. 2. Potentiostatic curves corresponding to three charge/discharge cycles of disordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> in lithium cells.

manganese ions in the oxide prepared under a high pressure appear in the oxidation state (+3). The oxidation peak at 4.8 V bears a resemblance to that observed for overlithiated layered  $Li[Li_{(1-2x)/3}Ni_xMn_{(2-x)/3}]O_2$  oxides with x < 0.5. The origin of this peak has been associated with the irreversible loss of oxygen from layered oxides, leading to the formation of an oxygen deficient layered oxide  $[Li_{(1-2x)/3}Ni_xMn_{(2-x)/3}]O_{1.5+x}$  [3]. Keeping the upper voltage limit at 5.1 V, the low voltage limit is reduced to 1.5 V. In this case, a reduction peak at about 2.25 V is developed. In the discharge curve, the reduction peak at 2.25 V can be associated with the reduction of the residual Ni<sup>3+</sup> ions to Ni<sup>2+</sup> ions [35,36]. The same peak has been detected in the discharge curve of layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and has been assigned to the reduction of residual Ni<sup>3+</sup> in the Li-site to  $Ni^{2+}$  ions [35,36].

To determine the cationic distribution and changes in the metal environment during the electrochemical reaction in the oxides, EPR spectroscopy was undertaken. Recently we showed that irrespective of Ni<sup>2+</sup> and Mn<sup>4+</sup> being EPR active, an EPR response from Mn<sup>4+</sup> ions only was detected [17]. Fig. 3 compares the EPR spectra of both ordered and disordered compositions. In the X-band, the EPR spectrum of ordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> consists of one single Lorentzian, while one asymmetrical signal is detected at a frequency higher than 95 and 285 GHz. The effective g-factor is insensitive towards the frequency used. Based on the systematic EPR studies of LiNi<sub>0.5-x</sub>Mg<sub>x</sub>Mn<sub>0.5</sub>O<sub>2</sub> systems [17], the EPR signal observed on ordered  $LiNi_{0.5}Mn_{0.5}O_2$  can be assigned to  $Mn^{4+}$  ions. Contrary to ordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, the EPR spectrum of disordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> displays two overlapping signals (Fig. 3). In the X-band, the broader signal has an effective g-factor close to that of  $Mn^{4+}$  in ordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained at atmospheric pressure (g = 1.96 at 103 K). Moreover, the effective g-factor increases strongly with the registration temperature, this dependence being nearly the same for both compositions (Fig. 4). This indicates clearly that the broader signal detected for disordered  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  is also due to  $\text{Mn}^{4+}$  ions. However, there is a difference in the EPR line width: 360 mT for the disordered oxide and 105 mT for the ordered oxide (Fig. 3). With increasing registration frequency, a line broadening and an increase in the effective *g*-factor are observed (Figs. 4 and 5). These EPR features are consistent with the appearance of impurity  $\text{Mn}^{3+}$  ions in close proximity of  $\text{Mn}^{4+}$  ions.

The narrow signal detected in the EPR spectrum of disordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> is characterized by a *g*-factor of 1.985 (at 103 K), which is also typical of  $Mn^{4+}$  ions. At 103 K, the *g*-factor is retained by increasing the registration frequency from 9.2 to 95 GHz (Fig. 5). At a higher frequency (285 GHz), the narrow symmetrical signal becomes an asymmetrical one:  $g_1 = 2.000$  and  $g_2 = 1.964$ (Fig. 3, 285 GHz, T = 60 K). It is worth mentioning that the mean value of the *q*-factor for the asymmetrical signal is 1.976, which is close to 1.985 as determined at lower frequencies. This allows one to assign the narrow signal to Mn<sup>4+</sup> ions also. Contrary to the broader signal, these Mn<sup>4+</sup> ions are mostly surrounded by diamagnetic Li<sup>+</sup> ions and allied paramagnetic Mn4+ ions. In addition, the temperature dependence of the *q*-factor observed in the X-band (Fig. 4) gives an indication that at least one  $Ni^{2+}$ ion is also included in the first coordination sphere of  $Mn^{4+}$ . The registration of the two EPR signals reveals inhomogeneous cationic distribution at a short-scale range in disordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>. This is consistent with a small degree of cationic order in these oxides detected by XRD.

Fig. 6 gives the EPR spectra of electrodes obtained after 1 cycle between 5.1 and 2.5 V, followed by 8 cycles between 5.1 and 1.5 V and stopped at 1.5 V. After the electrochemical reaction, the low-temperature EPR spectrum (103 K) of the electrode also displays two overlapping signals as in the case of the pristine composition, while only one broader signal is visible at a higher temperature



Fig. 3. EPR spectra at 9.23, 95 and 285 GHz of disordered  $LiNi_{0.5}Mn_{0.5}O_2$  oxides obtained under high pressure and layered  $LiNi_{0.5}Mn_{0.5}O_2$  obtained at atmospheric pressure.



Fig. 4. The temperature dependence of the *g*-factor and the line width for disordered Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. Open symbols connected with dotted lines correspond to disordered Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> obtained after 1 cycle between 5.1 and 2.5 V, following then 8 cycles between 5.1 and 1.5 V, and stopped at 1.5 V. Si<sub>1</sub> and Si<sub>2</sub> denote the broader and the narrow signals detected at disordered Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. For the sake of comparison, the dependence of the *g*-factor and the line width for Mn<sup>4+</sup> ions in layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> obtained at atmospheric pressure is also given.



Fig. 5. The effective g-factor and the EPR line width for ordered  $Li[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$  and disordered  $Li[Ni_{0.5}Mn_{0.5}]O_2$  as a function of the frequency used. Si<sub>1</sub> and Si<sub>2</sub> denote the broader and the narrow signals detected at disordered  $Li[Ni_{0.5}Mn_{0.5}]O_2$ .

(273 K). The EPR parameters of both the narrower and the broader signals (in terms of the effective *g*-factor and EPR line width) are changed after the electrochemical reaction (Fig. 4). By way of comparison, when the layered  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  oxide cycles between 5.0 and 2.5 V, the EPR response from  $\text{Mn}^{4+}$  is close to that of the pristine composition, which agrees with the excellent structural stability of the layered composition [35,36]. With disordered oxides, the EPR line width for both signals



Fig. 6. EPR spectra at X-band of disordered  $Li[Ni_{0.5}Mn_{0.5}]O_2$ , obtained after 10 cycles of lithium extraction/insertion between 5.0 and 2.5 V, and ordered  $Li[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$ , obtained after 1 cycle between 5.1 and 2.5 V, following then 8 cycles between 5.1 and 1.5 V.



Fig. 7. IR spectra of pristine disordered Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> and disordered Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> obtained after 1 cycle between 5.1 and 2.5 V, following then 8 cycles between 5.1 and 1.5 V, and stopped at 1.5 V. The asterisk corresponds to the characteristic IR modes of organic groups of the electrolyte.

decreases. The effective g-factor of the broader signal (Si 1) also decreases, but its dependence on the registration temperature remains. This can be associated with an irreversible consumption of  $Mn^{3+}$  during the first charge process at 4.1 V, as observed in the first charge curve (Fig. 2). The narrow signal (Si 2) displays an increase in g-factor, indicating that paramagnetic neighbours (such as Ni<sup>2+</sup> or Mn<sup>4+</sup>) of Mn<sup>4+</sup> ions undergo irreversible changes.

The irreversible electrochemical processes with disordered  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  were followed on their IR spectra. Fig. 7 compares the IR spectrum of the pristine composition with that of the electrode obtained after 1 cycle between 5.1 and 2.5 V, followed by 8 cycles between 5.1 and 1.5 V and then stopped at 1.5 V. The IR spectra are given in the range of  $400-950 \text{ cm}^{-1}$ , where the lattice vibrations of the transition metal ions appear [37–39]. The IR spectrum of the pristine composition displays one broad band at  $520 \text{ cm}^{-1}$ , which is in accordance with the statistical cationic distribution in the framework of the close cubic packing [37–39]. After the electrochemical reaction, the IR spectrum of the electrode consists of two intense peaks at 475 and 545 cm<sup>-1</sup>. The splitting of the IR spectra can be related to the irreversible structural changes appearing at 4.8 V.

# 3.2. High pressure synthesis of layered $Li_{1,2}Ni_{0,4}Mn_{0,4}O_2$

Keeping Ni and Mn in equal amounts, a mixture of NiO and  $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$  is obtained when NiMnO<sub>3</sub> reacts with  $Li_2O_2$  in air. On the contrary, a  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  oxide with a layered structure is formed under a high pressure in an oxygen reach atmosphere (Fig. 1). Evidently, thermal decomposition of  $Li_2O_2$  ensures an oxygen-rich atmosphere inside the Au capsule, as a result of which the Ni<sup>2+</sup> ions are oxidized. The appearance of Ni ions in higher oxidation states contributes to the stabilization of the layered modification. The same has been observed with cationic order in the "NiO–LiNiO<sub>2</sub>" system.

The unit cell dimensions are given in Table 1. The cationic distribution, determined from the XRD peak analysis, corresponds to  $[\text{LiNi}_{0.087}][\text{Li}_{0.287}\text{Ni}_{0.313}\text{Mn}_{0.4}]\text{O}_2$ . For the sake of comparison, the same Table gives the unit cell dimensions and the cationic distribution of  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  obtained at atmospheric pressure. As one can see, the cationic disorder is more significant for the oxide prepared under a high pressure.

Another feature of the XRD pattern of the  $Li_{1.2}Ni_{0.4}$ Mn<sub>0.4</sub>O<sub>2</sub> oxide is the appearance of low-intensity peaks around 23°. Super-lattice reflections have been detected for the complex "Li<sub>2</sub>MnO<sub>3</sub>\*LiNi/MnO<sub>2</sub>" system. The XRD patterns have been interpreted by the formation of



Fig. 8. Potentiostatic curves corresponding to two charge/discharge cycles of ordered LiNi0.5Mn0.5O2 in lithium cells.

"Li<sub>2</sub>MnO<sub>3</sub>–LiNi/MnO<sub>2</sub>" solid solutions, where long-range Li ordering on the  $3^{1/2}a \times 3^{1/2}$  a super-structure appears together with a uniform mixing of Ni and Mn on the transition-metal sites [18]. On the other hand, based on NMR and TEM analysis, formation of local Li<sub>2</sub>MnO<sub>3</sub>-rich regions has been suggested [19].

As described above, disordered HP-LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> showed a poor electrochemical response in lithium batteries, which is an expected behaviour for a non-layered rock-salt structure. A better electrode performance in lithium test cells was obtained for Li<sub>1,2</sub>Ni<sub>0,4</sub>Mn<sub>0,4</sub>O<sub>2</sub>. Potentiostatic experiments at 10 mV/0.1 h were carried out in the 2.5-5.0 V range (Fig. 8). The first charge yielded a capacity of  $275 \,\mathrm{mA}\,\mathrm{hg}^{-1}$ , which was not recovered on successive cycling. Reversible discharge capacities were close to  $135 \text{ mA h g}^{-1}$  during the first few cycles. The mass-normalized intensity vs. voltage curves of the same electrode during the first three charge/ discharge cycles are shown in Fig. 8b. In this plot, no peaks are visible at ca. 3V, this being indicative of the absence of Mn<sup>3+</sup> ions in the layered oxide. Assuming that nickel is initially in the 3+ oxidation state in Li<sub>1.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub>, the Ni<sup>4+</sup>/Ni<sup>3+</sup> pair should allow a maximum theoretical capacity of  $125 \text{ mA h g}^{-1}$  for this oxide. Thus, the presence of an irreversible signal at ca. 4.7 V and its corresponding  $275 \text{ mA h g}^{-1}$ , during the first charge, can be ascribed to simultaneous extraction of lithium and oxygen leading to a solid with a stoichiometry closer to  $Li_xMO_2$  [3,40]. The maximum theoretical capacity value corresponding to the oxidation of  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  to "Ni<sub>0.4</sub> $Mn_{0.4}O_{1.6}$ " is 375 mA h g<sup>-1</sup>. It means that there is still some capacity not used during the oxidation of the inorganic oxide and thus the final product could be Li<sub>0.56</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>1.88</sub>. However, as this effect is completely irreversible and unrecovered in the second and successive charge branches, one cannot discard that the electrolyte decomposition contributes to the first charge capacity.



Fig. 9. EPR spectra at 9.23 and 285 GHz for ordered  $Li(Li_{0.2}Ni_{0.4} Mn_{0.4})O_2$  obtained under high-pressure.

On cycling, the main broadened signal is located between 3.6 and 4.2 V in the charge process, and between 3.4 and 4.0 V in the discharge process. According to previous studies, these signals could be ascribed mainly to the Ni<sup>4+</sup>/Ni<sup>2+</sup> redox couples in the transition metal slab. Now the total theoretical reversible capacity would be 250 mA h g<sup>-1</sup>. However, the observed values,  $135 \text{ mA h g}^{-1}$ , are well below this estimate. Moreover, since the peak is broadened and complex and shows increasing broadening on cycling, the participation of other redox couples, such as those involving Ni<sup>3+</sup> and Mn<sup>4+</sup> ions and transition metal ions in the lithium slab cannot be discarded [40,41].

The EPR spectra of the pristine and the cycled compositions give further information on the changes in the local environments of the Mn ions during lithium extraction and insertion. The EPR spectrum of pristine  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  consists of one signal with a Lorentzian line shape (Fig. 9). At 103 K, the *g*-factor is 1.995 and becomes slightly higher at a higher registration temperature (g = 2.015 at 413 K, Fig. 10). These values are spread out into the limits typical of Mn<sup>4+</sup> ions in oxide matrices. The high-frequency EPR spectrum of  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  at 103 K also displays only one signal with a Lorentzian line



Fig. 10. The temperature dependence of the *g*-factor and the line width for ordered Li(Li<sub>0.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>)O<sub>2</sub>. Open symbols connected with dotted lines correspond to ordered Li(Li<sub>0.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>)O<sub>2</sub> obtained after 10 cycles between 5.0 and 2.5 V, and stopped at 2.5 V. For the sake of comparison, the dependence of the *g*-factor and the line width for Mn<sup>4+</sup> ions in layered Li(Li<sub>0.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>)O<sub>2</sub> obtained at atmospheric pressure is also given.

shape (Fig. 9). This means that no  $Li_2MnO_3$ -rich regions appear in  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  obtained under a highpressure. The *g*-factor remains the same in the frequency range 9.2–285 GHz (Fig. 5). This indicates that the signal originates from  $Mn^{4+}$  ions. No signals due to  $Ni^{2+}$  or  $Ni^{3+}$  ions are observed.

To rationalize the oxidation state of the Ni ions in the layered high-pressure oxide, Fig. 10 gives the EPR parameters (determined at 9.2 GHz) for Li[Li<sub>0.2</sub>Ni<sub>0.2</sub> Mn<sub>0.4</sub>]O<sub>2</sub> obtained at atmospheric pressure and containing Ni<sup>2+</sup> and Mn<sup>4+</sup> ions. As one can see, the line width is larger for Li<sub>1.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub>, while the values of the g-factors are close for both oxides. This result can be related with the different oxidation states of nickel ions in  $Li_{1,2}Ni_{0,4}Mn_{0,4}O_2$  and  $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ . Recently we demonstrated that the Ni<sup>3+</sup> ions had a stronger broadening effect on the EPR line width of Mn<sup>4+</sup> as compared to that of the Ni<sup>2+</sup> ions [36]. Thus, comparison of the EPR line widths of Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> and Li<sub>1.2</sub>Ni<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub> allows assigning the charge distribution in  $Li_{1,2}Ni_{0,4}$  $Mn_{0,4}O_2$  to  $Ni^{3+}$  and  $Mn^{4+}$  rather than to  $Ni^{2+}$  and  $Mn^{4+}$ . However, the contribution of same amount of Ni<sup>2+</sup> ions to the charge distribution cannot be rejected.

Fig. 6 shows the EPR spectrum of the  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  electrode after 10 cycles between 5.0 and 2.5 V and then stopped at 2.5 V. Contrary to the pristine composition, the EPR spectrum of cycled  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  consists of a

single Lorentzian line superimposed on a low-magnetic field absorption, while at low registration temperatures (103 K) the Lorentzian dominates the EPR spectrum (Fig. 6). In comparison with the pristine composition, the *g*-factor of the single Lorentzian line decreases slightly, while the line width undergoes a strong change. This means that the  $Mn^{4+}$  environment in respect of the Ni-to-Mn ratio has changed after cycling. In addition, the line width decreases on cycling and tends to the line width determined with Li[Li<sub>0.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>]O<sub>2</sub> obtained at atmospheric pressure (Fig. 10). This indicates that the Ni-to-Mn ratio around Mn<sup>4+</sup> ions decreases after lithium extraction and reinsertion.

The observed low-magnetic field absorption is related to magnetically correlated spin systems rather than to isolated paramagnetic ions. Searching for the origin of this EPR absorption, it is worth mentioning that a low-magnetic field absorption due to  $180^{\circ}$  coupled  $Ni^{2+}-Ni^{3+}$  spin systems is detected for non-stoichiometric  $Li_{1-x}Ni_{1+x}O_2$ with  $x \approx 1/3$  [42]. Comparison also allows assigning the low-magnetic field absorption detected for cycled  $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$  to magnetically correlated  $Ni^{2+}-Ni^{3+}$ spin systems.

Thus, we can suggest that during the electrochemical reaction of  $\text{Li}_{1.2}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{O}_2$ , Ni ions from the pristine  $\text{Mn}^{4+}$  environment are released, leading to phase separation into:  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.4}\text{Mn}_{0.4}]\text{O}_2 \rightarrow a \text{Li}_y\text{Ni}_{0.4-y}\text{Mn}_{0.4}\text{O}_{1.88} + y/(1+x)$  " $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}$ "+ $b\text{Li}_2\text{O}$ , where 0 < y < 0.2 and  $x \approx 1/3$ . The proposed phase separation reaction can be associated with the irreversible peak at 4.8 V in the first charge curve of  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.4}\text{Mn}_{0.4}]\text{O}_2$ . Further on, the reversible Li insertion and extraction proceed together with reduction and oxidation of  $\text{Ni}^{2+/3+}-\text{Ni}^{4+}$ .

Fig. 11 compares the IR spectra of the pristine oxide and the electrode composition obtained after 11 cycles between



Fig. 11. IR spectra of pristine ordered Li[ $Ni_{0.5}Mn_{0.5}$ ]O<sub>2</sub> and ordered Li[ $Ni_{0.5}Mn_{0.5}$ ]O<sub>2</sub> obtained after 10 cycles between 5.0 and 2.5 V and stopped at 2.5 V. The asterisk corresponds to the characteristic IR modes of organic groups of the electrolyte.

5.0 and 2.5 V (the cell is stopped at 2.5 V). The IR spectrum of the pristine composition contains a broad band split into several components: 468, 520 and  $615 \text{ cm}^{-1}$ . According to the IR study of lithium transition metal oxides [37–39], this feature is associated with a cationic order in the close cubic packing. After the electrochemical reaction, the broad band still appears with slight changes in the positions of the IR components. This is consistent with the proposed mechanism of the electrochemical reaction including the preservation of the layered matrix during lithium extraction and insertion.

## 4. Conclusions

High-pressure synthesis allows obtaining Lithiumnickel-manganese oxides having different oxidation states of Ni ions and cationic distributions. A solid-state reaction between NiMnO<sub>3</sub> and Li<sub>2</sub>O yields, at 3 GPa, a LiNi<sub>0.5</sub>  $Mn_{0.5}O_2$  phase characterized by a disordered rock-salt type structure. However, some cationic ordering is still preserved. The paramagnetic ions stabilized in this oxide are mainly  $Ni^{2+}$  and  $Mn^{4+}$  together with  $Mn^{3+}$  (about 10%). After the first charge to 5.1 V, disordered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> delivers  $115 \text{ mA h g}^{-1}$ , corresponding to 42% of extracted lithium. This process takes place concomitantly with oxidation of  $Mn^{3+}$  to  $Mn^{4+}$  ions and irreversible phase transformation. The reverse process of Li insertion does not proceed up to 2.5 V. Between 2.0 and 2.5 V, some residual nickel ions (mainly in the Li environment) are reduced.

The oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup> in lithium–nickel– manganese oxides has been performed using Li<sub>2</sub>O<sub>2</sub> instead of Li<sub>2</sub>O as an initial reagent for the high-pressure synthesis. The higher oxidation state of Ni favours the stabilization of the layered modification, as a result of which Li(Li<sub>0.2</sub> Ni<sub>0.4</sub>Mn<sub>0.4</sub>)O<sub>2</sub> oxides are formed. Contrary to the disordered oxides, the layered modification displays reversible lithium extraction/insertion. The electrochemical reaction is due to oxidation of nickel ions and phase separation into Li<sub>y</sub>Ni<sub>0.4-y</sub>Mn<sub>0.4</sub>O<sub>1.88</sub> (0<y<0.2) and Li<sub>1-x</sub>Ni<sub>1+x2</sub> ( $x \approx 1/3$ ). Further on, the reversible Li insertion and extraction is associated with the Ni<sup>2+/3+</sup>/Ni<sup>4+</sup> ionic couple within the layered Li<sub>y</sub>Ni<sub>0.4-x</sub>Mn<sub>0.4</sub>O<sub>1.88</sub> phase.

## Acknowledgments

The authors thank the National Science Fund of Bulgaria (Contract no. Ch1304/2003) for financial support. M.Y. and G.O. are grateful to EC for a grant within the Centre of Competence MISSION (SSA, EC-INCO-CT-2005-016414). R.S. and M.Y. are grateful to the EC for a grant of a EU "Research Infrastructures: Transnational Access" Programme (contract no. 505320 (RITA)–High Pressure) for performing high-pressure synthesis experiments at the Bayrisches Geoinstitute. The high-frequency EPR measurements carried out at High Magnetic Field Laboratory in Grenoble, France, were supported by the European Commission within the 6th framework programme "Transnational Access—Specific Support Action" (Contract no. RITA-CT-2003-505474)—"Access to research in very high magnetic field". The authors are very grateful to Dr. T. Boffa-Ballaran and Dr. C. McCammon, from Bayerisches Geoinstitut, and Dr. A.-L. Barra, from High Magnetic Field Laboratory in Grenoble, for their help.

#### References

- M.E. Spahr, P. Novák, B. Schnyder, O. Haas, R. Nesper, J. Electrochem. Soc. 145 (1998) 1113.
- [2] M.S. Whittingham, Chem. Rev. 104 (2004) 4271.
- [3] Z. Lu, L.Y. Beaulieu, R.A. Donaberger, C.L. Thomas, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A778.
- [4] K. Ariyoshi, S. Yamamoto, T. Ohzuku, J. Power Sources 119–121 (2003) 959.
- [5] T. Ohzuku, Y. Makimura, Chem. Lett. (2001) 744.
- [6] Z. Lu, D.D. MacNeil, J.R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A191.
- [7] J. Reed, G. Ceder, Electrochem. Solid-State Lett. 5 (2002) A145.
- [8] M. Saiful Islam, R. Andrew Davis, J.D. Gale, Chem. Mater. 15 (2003) 4280.
- [9] Y. Arachi, H. Kobayashi, S. Emura, Y. Nakata, M. Tanaka, T. Asai, Chem. Lett. 32 (2003) 60.
- [10] W.-S. Yoon, C.P. Grey, M. Balasubramanian, X.-Q. Yang, J. McBreen, Chem. Mater. 15 (2003) 3161.
- [11] C.S. Johnson, J.S. Kim, A.J. Kropf, A.J. Kahaian, J.T. Vaughey, L.M. Fransson, K. Edström, M.M. Thackeray, Chem. Mater. 15 (2003) 2313.
- [12] W.-S. Yoon, S. Iannopollo, C.P. Grey, D. Carlier, J. Gorman, J. Reed, G. Ceder, Electrochem. Solid-State Lett. 7 (2004) A167.
- [13] J. Bréger, N. Dupré, P. Chupas, P.L. Lee, T. Proffen, J. Parise, C.P. Grey, J. Am. Chem. Soc. 127 (2005) 7529.
- [14] Y.S. Meng, G. Ceder, C.P. Grey, W.-S. Yoon, Y. Shao-Horn, Electrochem. Solid-State Lett. 7 (2004) A155.
- [15] Van der Ven, G. Ceder, Electrochem. Commun. 6 (2004) 1045.
- [16] J. Bréger, M. Jiang, N. Dupré, Y. Meng, Y. Shao-Horn, G. Ceder, C.P. Grey, J. Solid State Chem. 178 (2005) 2575.
- [17] R. Stoyanova, E. Zhecheva, S. Vassilev, J. Solid State Chem. 179 (2006) 378.
- [18] Z. Lu, Z. Chen, J.R. Dahn, Chem. Mater. 15 (2003) 3214.
- [19] J.-S. Kim, C.S. Johnson, J.T. Vaughey, M.M. Thackeray, S.A. Hackney, W. Yoon, C.P. Grey, Chem. Mater. 16 (2004) 1996.
- [20] O.A. Schlyakhtin, S.H. Choi, T.S. Yoon, Y.J. Oh, J. Power Sources 141 (2005) 121.
- [21] D.A.R. Barkhouse, J.R. Dahn, J. Electrochem. Soc. 152 (2005) A746.
- [22] E. Zhecheva, R. Stoyanova, R. Alcántara, P. Lavela, J.L. Tirado, Pure Appl. Chem. 74 (2000) 1885.
- [23] O. García-Moreno, M. Alavarez-Vega, F. García-Alvarado, J. García-Jaca, J.M. Gallardo-Amores, M.L. Sanjuán, U. Amador, Chem. Mater. 13 (2001) 1570.
- [24] R. Stoyanova, E. Zhecheva, G. Bromiley, T. Boffa Ballaran, R. Alcántara, J.I. Corredor, J.L. Tirado, J. Mater. Chem. 12 (2002) 2501.
- [25] E. Zhecheva, R. Stoyanova, R. Alcántara, J.L. Tirado, J. Phys. Chem. B 107 (2003) 4290.
- [26] R. Stoyanova, E. Zhecheva, R. Alcántara, J.L. Tirado, G. Bromiley, F. Bromiley, T. Boffa Ballaran, J. Mater. Chem. 14 (2004) 3663.
- [27] R. Stoyanova, E. Zhecheva, R. Alcántara, J.L. Tirado, G. Bromiley, F. Bromiley, T. Boffa Ballaran, Solid State Ionics 161 (2003) 197.
- [28] E. Shinova, E. Zhecheva, R. Stoyanova, G. Bromiley, J. Solid State Chem. 178 (2005) 1661.
- [29] J. Rodríguez-Carvajal, in Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, 1990, p. 127.

- [30] J.B. Goodenough, D.C. Wickham, W.J. Croft, J. Phys. Chem. Solids 5 (1958) 107.
- [31] W. Li, J.N. Reimers, J.R. Dahn, Phys. Rev. B 46 (1992) 3236.
- [32] H. Wulf, M. Mohan Rao, F. Scholz, Chem. Mater. 15 (2003) 988.
- [33] C. Delmas, M. Menetrier, L. Croguennec, I. Saadoune, A. Rougier, C. Poillerie, G. Prado, M. Grüne, L. Fournes, Electrochim. Acta 145 (1999) 243.
- [34] R. Alcántara, M. Jaraba, P. Lavela, J.L. Tirado, Electrochim. Acta 47 (2002) 182.
- [35] C.S. Johnson, A.J. Kahaian, J.S. Kim, A.J. Kropf, J.T. Vaughey, M.M. Thackeray, Electrochem. Commun. 4 (2002) 492.
- [36] R. Stoyanova, E. Zhecheva, R. Alcántara, J.L. Tirado, J. Mater. Chem. 16 (2006) 359.
- [37] C.M. Julien, M. Massot, C. Poinsignon, Spectrochim. Acta A 60 (2004) 689.
- [38] P. Tarte, J. Preudhomme, Spectrochim. Acta A 26 (1970) 747.
- [39] R. Moore, W. White, J. Am. Ceramic Soc. 53 (1970) 679.
- [40] Z. Lu, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A815.
- [41] J.H. Kim, C.S. Yoon, Y.K. Sun, J. Electrochem. Soc. 150 (2003) A538.
- [42] R. Stoyanova, E. Zhecheva, C. Friebel, Solid State Ionics 73 (1994) 1.