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Enhanced electrochemical properties of $LiNi_{1/2}Mn_{3/2}O_4$ by acid treatment

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New data on the improvement of the electrochemical properties of high-voltage $LiNi_{1/2}Mn_{3/2}O_4$ electrodes by controlling particle size distribution are provided. Acid treatment is used as an effective experimental tool to modify the particle size distribution without changing the Ni,Mn distribution on the octahedral spinel sites. The mechanism of the acid action depends on whether nano- or submictometric spinel particles are treated. We found that acid treatment of $LiNi_{1/2}Mn_{3/2}O_4$ with submicronmetric particles has a strong impact on its capacity and cycling stability.

Keywords: Lithium nickel manganese spinels, Cation distribution, Lithium intercalation, Lithium ion batteries, Acid treatment

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INTRODUCTION

Lithium nickel manganese spinel, $LiNi_{1/2}Mn_{3/2}O_4$, is nowadays considered as a promising cathode material for a new generation lithium-ion batteries. The most remarkable property of $LiNi_{1/2}Mn_{3/2}O_4$ is its capability to intercalate lithium reversibly at a high voltage (around 4.7 V) delivering a high specific energy [1]. The electrochemical reaction is concomitant with a reversible oxidation of Ni^{2+} to Ni^{4+} ions, while the role of Mn^{4+} is to stabilize the spinel structure. The electrochemical performance of $LiNi_{1/2}Mn_{3/2}O_4$ has been shown to depend critically on its structure and morphology [2-4]. There are two spinel cubic modifications that can be differentiated on the basis of the way of Ni/Mn distribution in octahedral spinel sites [5-7]: disordered spinel with a *Fd-3m* space group and 1:3 ordered spinel with $P4_332$ space group. Recently we have demonstrated that the Ni/Mn distribution has an impact on the lithium intercalation properties of $LiNi_{1/2}Mn_{3/2}O_4$, while the particle size distribution affects their rate capability and interactions with electrolytes [8].

In this contribution we extend our studies on the relations between particle size distribution and electrochemistry of both structural modification of $LiNi_{1/2}Mn_{3/2}O_4$. For the preparation of disordered and ordered spinels, we applied an acetate-oxalate precursor method, which is based on the interaction of metal acetates with oxalic acid at room temperature. The modification of the particle size distribution is carried out by acid treatment. The probable Li^+-H^+ exchange reaction is studied by thermogravimetric and differential thermal analysis (TG and DTA). Powder XRD, IR spectroscopy and TEM analysis are employed for the structural and morphological characterization of the spinel compositions. The electrochemical performance of pristine and acid treated $LiNi_{1/2}Mn_{3/2}O_4$ is evaluated in model lithium cells using a galvanostatic mode.

EXPERIMENTAL

Pristine $LiNi_{1/2}Mn_{3/2}O_4$ spinels are prepared by the acetate-oxalate precursor method. The details are given elsewhere [8]. Spinel compositions were annealed at 400, 600 and 800 °C for 10 h. Acid treatment of the spinels was achieved by processing of 1.5 g of $LiNi_{1/2}Mn_{3/2}O_4$ at room temperature with 100 ml 0.1 M HNO_3 for 4 hours. The solid residues were then dried at 40 °C under vacuum. Further on, the pristine spinels will be denoted as LNM-400, LNM-600, LNM-800 (where 400, 600 and 800 correspond to the annealing temperature), while acid treated counterparts with A-LNM-400, A-LNM-600 and A-LNM-800, respectively.

The X-ray structural analysis was made by Bruker Advance D8 powder diffractometer with CuKα-radiation. The scan range was $15\leq 2\theta \leq 120$ with a step increment of 0.02°. The IR spectra were recorded on a Fourier transform Nicolet Avatar-320 instrument using KBr pellets (resolution < 2 cm^{-1}). The thermal analysis of the acid treated

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compositions is carried out by a combined LABSYS™ Evo DTA/TG system of the SETARAM Company, France. The samples are investigated at a heating rate of 10 °C/min in O_2 flow (20 ml/min). The TEM investigations were performed on a TEM JEOL 2100 instrument at an accelerating voltage of 200 kV. The electrochemical charge-discharge of $LiNi_{1/2}Mn_{3/2}O_4$ was carried out by using a two-electrode cells of the type $Li|LiPF_6$ (EC:DMC)$|LiNi_{1/2}Mn_{3/2}O_4$. The positive electrode, supported onto an aluminium foil, was a mixture containing 80% of the active composition $LiNi_{1/2}Mn_{3/2}O_4$, 7.5% KS 6L graphite (TIMCAL), 7.5% Super C65 (TIMCAL) and 5% polyvinylidene fluoride (PVDF). The electrolyte was an 1M $LiPF_6$ solution in ethylene carbonate and dimethyl carbonate (1:1 by volume) with less than 20 ppm of water. The electrochemical reactions were carried out using an eight-channel Arbin BT 2000 system in galvanostatic mode. The cell is cycled between 4.95 and 3.5 V at C/20, C/10, C/5 and C/1 rates.

RESULTS AND DISCUSSION

In accordance with our previous studies [8], the acetate-oxalate precursor method yields at 400 °C the disordered modification of $LiNi_{1/2}Mn_{3/2}O_4$, while between 600 and 800 °C an ordered modification is stabilized.

Acid treatment of spinels takes place with preservation of the spinel structure. For $LiNi_{1/2}Mn_{3/2}O_4$ obtained at 800 °C the lattice parameters remain the same, while for the low-temperature spinels they are slightly lower: 8.1851, 8.1700 and 8.1580 Å for LNM-400, LNM-600, LNM-800 respectively and 8.1665, 8.1587 and 8.1562 Å for the acid treated LNM-400, A-LNM-600 and A-LNM-800.

In order to distinguish clearly between the two cubic modifications of $LiNi_{1/2}Mn_{3/2}O_4$ with *Fd*-3*m* and *P4₃32* space groups, the IR spectroscopy is applied (Fig. 1). The IR spectrum of the low-temperature modification consists of two typical spinel modes at 500 and 610 cm^{-1}, while the high-temperature modification display a splitting of the IR spectra into several components, indicating the reduction of the symmetry due to the Ni^{2+}/Mn^{4+} ordering. It is noticeable that the IR spectra display the same features for the pristine and acid treated spinels. The changes in the IR profile demonstrate clearly that LNM-400 and A-LNM-400 adopt a disordered spinel structure, while the 1:3 ordered spinel structure is stabilized for LNM- 600 and LNM-800 and acid treated A-LNM-600 A-LNM-800. Thus, IR spectroscopy reveals that the Ni^{2+}/Mn^{4+} cationic distribution is preserved after acid treatment.

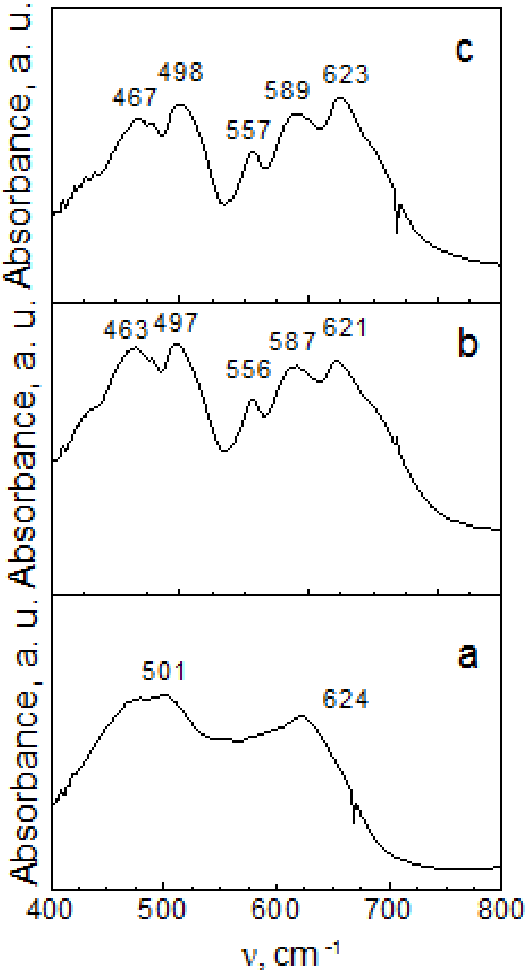

Fig. 1. XRD patterns of pristine $LiNi_{1/2}Mn_{3/2}O_4$ annealed at 400 °C and 800 °C: LNM-400 (a), LNM-800 (b) and acid treated spinel oxides A-LNM-400 (a') and A-LNM-800 (b'). The asterisks denote the most intensive diffraction peaks due to the impurities of NiO phase.

The next question is related with a possible exchange of Li^+ with protons from the acidic solution. This reaction usually proceeds during acid treatment of lithium transition metal oxides [9]. To check for possible H^+/Li^+ exchange reactions, TG experiments were undertaken. TG analysis shows that the acid treated spinels release H_2O after heating up to 250 °C, the H_2O amount being 1.50, 0.47 and 0.12 wt.% for A-LNM 400, A-LNM-600 and A-LNM-800, respectively. Comparison shows that the H^+/Li^+ exchange reaction proceeds easily for the disordered spinels. It is noticeable that LNM-800 is most stable against acid treatment.

An important parameter that changes after acid treatment is the particle size distribution (Fig. 2).

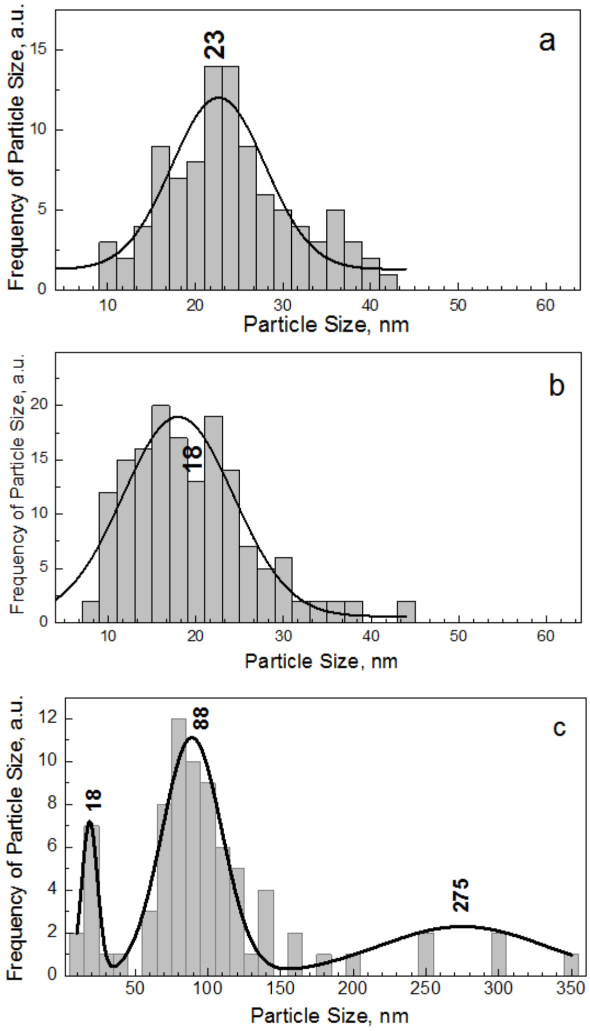

Fig. 2. Particle size distribution of acid treated $LiNi_{1/2}Mn_{3/2}O_4$ A-LNM-400 (a), A-LNM-600 (b), A-LNM-800 (c).

The low-temperature disordered modification consists of well-crystallized particles with nanometric dimensions and a close particle size distribution: more than 50% of the particles are between 10 and 20 nm for LNM-400 (Fig. 2). Acid treatment of LNM-400 leads to a broadening of the particle size distribution due to preferential dissolution of the smallest particles (Figs. 2). For the pristine spinels obtained at 600 and 800 °C, the ordered modification is obtained in the form of nanometric and submicronmetric particles: at 600 °C, the particles are distributed predominantly between 15 and 30 nm, while at 800 °C there is a particle growth, resulting in formation of thick particles with dimensions of 150 - 300 nm. The acid treatment of nano- and submicronmetric ordered spinels proceeds in a different way: the particle size distribution becomes broader for A-LNM-600, while a three-modal particle size distribution curve with maxima at 18, 88 and 275 nm is obtained for A-LNM-600 (Fig. 2).

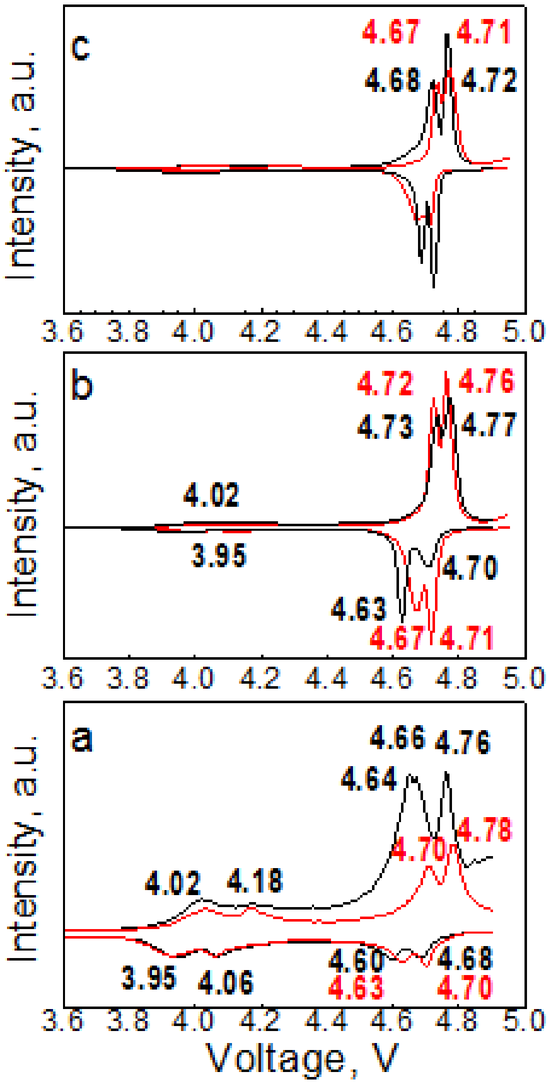

Fig. 3. First derivative of the capacity –voltage curves (right) of LNM-400, LNM-600, LNM-800 (red lines) and the acid treated counterparts A-LNM-400, A-LNM-600 and A-LNM-800 (black lines). Figures *a, b, c* are related to the annealing temperature: 400, 600, 800 °C respectively.

Figure 3 compares the first charge-discharge curves for pristine and acid treated spinels. The figure gives the capacity-voltage curves as first derivatives. All curves show intensive peaks of oxidation and reduction in the high voltage region of 4.7 V due to Ni^{2+}/Ni^{4+} couples. In addition, low-intensive peaks in the 4.0 -V region, which originate from the Mn^{3+}/Mn^{4+} couple, are also distinguished. Both oxidation and reduction peaks are split, this splitting being dependent on the Ni,Mn cationic distribution. In the 4.7 V-region, the peak splitting decreases when going from disordered to ordered composition: 80 mV versus 40 mV, respectively. In the 4.0 V region, the peak splitting seems to increase for the spinels having an ordered Ni/Mn distribution: from 140 mV to 210 mV, respectively. It is of importance that both reactions at 4.0 and 4.7 V are reversible. The insensitivity of the peak positions on the particle size distribution indicates that Ni,Mn cation distribution is the main factor controlling the electrochemical reaction. This result is in a good agreement with the data established by several research groups [2]. The new finding is the preservation of the charge-discharge profile of the spinels after acid treatment (Fig. 3). This is an another proof that acid treatment does not attack the Ni,Mn distribution on the spinel sites. The acid treatment of the spinels has a significant impact on the capacity and its stability during cycling (Fig. 4).

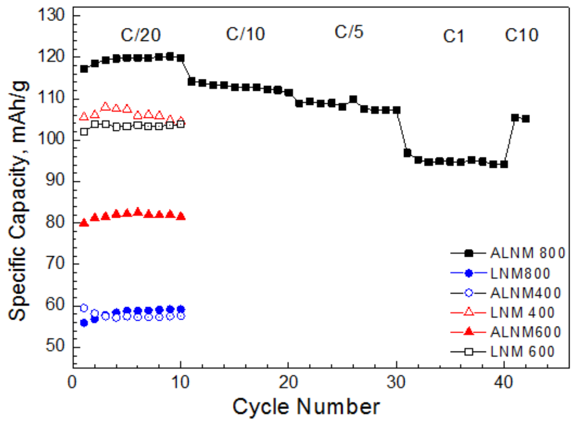

Fig. 4. Cycling stability curves at different rates for LNM-400, LNM-600, LNM-800 and the acid treated spinels A-LNM-400, A-LNM-600 and A-LNM-800.

The first charge capacity increases for both disordered and ordered spinels, while the first discharge capacity displays a complex dependence: there is a decrease in the discharge capacity for nanometric A-LNM-400 and A-LNM-600 spinels, while A-LNM-800 spinel that encompass both nano- and submicronmetric particles is characterized with an increased discharge capacity (Fig. 4). As a result, the first irreversible capacity is significant for A-LNM-400 and A-LNM-600, while the irreversibility is limited for A-LNM-800.

The next cycles reduce the irreversibility and the columbic efficiency reaches of 98-99%. A characteristic feature of all acid treated spinels is their good cycling stability during cycling (Fig. 4). The best electrochemical performance is observed for the acid treated spinel having ordered type structure and three modal particle distributions. This spinel provides also good rate capability: by increasing the rate from C/20 to C/1, discharge capacity decreases only from 120 mAh g^{-1} to 95 mAh g^{-1}.

CONCLUSION

Acid treatment is an effective way to modify the particle size distribution of $LiNi_{0.5}Mn_{1.5}O_4$ spinels without changing the Ni,Mn distribution over the octahedral spinel sites. When nanometric $LiNi_{0.5}Mn_{1.5}O_4$ spinels with ordered and disordered structure are treated with acid, the particle size distributions are broadened. The submicronmetric particles are broken during acid treatment, as a result of which the particle size distribution becomes complex comprising both nano- and submicronmetric particles. The mechanism of acid treatment is associated with partial spinel dissolution. The side reaction of exchange of Li^+ with H^+ proceeds more easily for the disordered spinel modification, while the ordered modification is most stable.

After acid treatment, both disordered and ordered spinels display good cycling stability. The best electrochemical performance in terms of capacity, cycling stability and rate capability is achieved for the ordered spinel $LiNi_{0.5}Mn_{1.5}O_4$ having a combination of nano- and submicronmetric particles.

In general, an enhancement of the electrochemical performance of high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ can be achieved by acid treatment of the spinel with submicronmetric particles. This approach can be applied to other Mn^{4+}-containing lithium transition metal oxides in order to improve their electrochemical performance.

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ПОДОБРЯВАНЕ НА ЕЛЕКТРОХИМИЧНИТЕ ХАРАКТЕРИСТИКИ НА $LINI_{1/2}MN_{3/2}O_4$ ЧРЕЗ ТРЕТИРАНЕ С КИСЕЛИНА

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(Резюме)

Все по-широката употреба на литиево-йонни батерии налага разработването на батерии с по-висока плътност на енергията и на мощността, които да са безопасни за околната среда, с висока плътност на енергията и ниска цена. $LiNi_{1/2}Mn_{3/2}O_4$ шпинелен оксид е от технологичен и изследователски интерес като електроден материал за литиево-йонни батерии, тъй като литий се интеркалира обратимо при висок потенциал (4.7 V), което способства за висока плътност на енергията (658 Wh/kg), стабилен е и има добри електрохимични характеристики. Разпределението на никеловите и мангановите йони в октаедричните позиции оказва влияние върху свойствата на литиево-никелово-мангановия шпинел. В тази статия са показани ефектите от третиране на $LiNi_{1/2}Mn_{3/2}O_4$ с киселина чрез прилагането на дифракционни и спектроскопски методи. Третирането на подреден субмикроразмерен шпинелен оксид с киселина модифицира разпределението на частиците по размер без да настъпва промяна в разпределението на катионите в октаедричните шпинелни позиции. Синергичният ефект между нано- и микроразмерни частици оказва влияние върху стабилността на капацитета на $LiNi_{1/2}Mn_{3/2}O_4$ шпинел при многократно циклиране.