

Investigation of structural and interfacial characteristics of electrode materials for lithium batteries

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Abstract

In the present paper the electrochemical behavior, as cathodes, of the inverse spinels of general formula $\text{LiCo}_y\text{Ni}_{(1-y)}\text{VO}_4$ has been studied in comparison with other mixed oxides, in which V is substituted by Sb (LiCoSbO_4) and Ni and Co by Mn (LiMnVO_4). The experimental findings showed that the oxides $\text{LiCo}_y\text{Ni}_{(1-y)}\text{VO}_4$ are promising cathode materials. The other samples did not show good results: their structures proved to be irreversibly modified in some way by Li-ion deintercalation. This problem, seemingly, cannot be overcome by changing synthesis parameters. The preliminary series of tests, whose results are here reported, served as a first insight in the relations that tie method of preparation, morphology, crystallochemical and intercalation–deintercalation properties together. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: X-ray diffraction; Li-ions intercalation; Spinel mixed oxides; Li-ion cell

1. Introduction

Secondary electrochemical lithium devices are a promising response to the present demand of power sources for electronic portable devices. The development of future generations of rechargeable Li-ion batteries depends critically on the advances in the field of cathode materials [1].

In general, there are two important families of Li-ion cathode materials (layered as LiMO_2 with $M = \text{Co}, \text{Ni}$, and spinel compounds as, LiMn_2O_4) that notoriously operate around 4 V versus lithium. In order to achieve a higher voltage, we have investigated materials that belong to a third class of intercalation compounds. They are mixed vanadium oxides with general formula LiMVO_4 , where M ions are Ni^{2+} and/or Co^{2+} . These compounds have an inverse spinel structure, where the Li^+ , Ni^{2+} and Co^{2+} ions reside in octahedral sites, while V^{5+} ions occupy tetrahedrally coordinated sites [2].

In this paper, we have studied the electrochemical behavior of the compounds of general formula $\text{LiCo}_y\text{Ni}_{(1-y)}\text{VO}_4$ and extended the researches to other oxides, in which V is substituted by Sb (LiCoSbO_4) and Ni and Co by Mn (LiMnVO_4).

The preparation methods were chosen so to get a morphology suitable to the electrochemical processes, i.e. to say homogeneous size grains tied together in groups with an irregular surface to assure a large area and a tight connection with graphite. X-ray powder diffraction (XRPD) measurements have been carried out both on the as-prepared and on the cycled samples. The aim was to control the purity and the structure of the synthesized compounds and to observe the modifications induced by the electrochemical processes in view of establishing the relation between the crystallochemical situation (the description, obtained by crystallographic data, of the chemical constitution of the material under study, i.e. to say its composition, the kind of interaction among the atoms and their oxidation state), and cycling performance.

2. Experimental

2.1. Preparation of the samples

$\text{LiCo}_y\text{Ni}_{(1-y)}\text{VO}_4$ samples with $y = 0.2, 0.5$ and 0.8 were prepared by a wet chemistry route. The precursors, i.e. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{LiOH} \cdot \text{H}_2\text{O}$ and NH_4VO_3 (all reagent grade chemicals) were dissolved in water and the mixing of solutions resulted in a brownish suspension. After

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prolonged stirring for assuring homogeneity, the solvent was evaporated, the precipitate collected, ground and calcinated at 120°C for 12 h. The powders were further reacted in air by rapidly heating at a certain temperature of 400, 500 and finally at 600°C, always grinding in order to reduce grains dimensions.

LiMnVO₄ was synthesized by separately dissolving every precursor ((CH₃COO)₂Mn·4H₂O, LiOH·H₂O, NH₄VO₃) in water and then adding the obtained solutions together. The solution was stirred and heated to 80°C in order to evaporate the water. The compound was annealed at 500°C in an argon flow for 24 h.

The sample with formula LiCoSbO₄ was obtained by a solid state preparation from Sb₂O₃, Co(NO₃), ascorbic acid and LiOH which were mixed and annealed at 700°C for 12 h and 800°C for 36 h.

The chemical composition of all annealed compounds was determined by plasma atomic emission (ICP) analysis, which confirmed the expected stoichiometries.

2.2. Experimental techniques

The electrodes for the electrochemical characterization were prepared by spraying on an Al foil, a slurry of the given compound (90%), acetylene black (5%) and poly(vinylchloride) (PVC) binder (5%). Punched out disks were dried and weighed before their use in the testing cells. These were of the button-type with lithium metal as both the counter and the reference electrode. Between the electrodes a fiberglass separator, soaked by the electrolyte, was interposed. The electrolyte consisted in a 1 M solution of LiPF₆ dissolved in a propylene carbonate (PC)–ethylene carbonate (EC)–dimethyl carbonate (DMC) 1:1:2 mixture.

The electrochemical tests consisted in a cyclic voltammetry carried out at potentials up to 4.6 V/Li–Li²⁺ at a scanning rate of 0.1 mV/s. An AMEL 568 function generator was used to carry out the cyclic voltammetry measurements. Charge–discharge cycles at constant current were also performed and the electrodes submitted to X-ray analysis at various stages of the tests.

The structure and the phase purity of the synthesized compounds before and after the electrochemical tests were investigated by the XRPD technique. The morphology of the samples was observed using a scanning electron microscope (SEM).

3. Results and discussion

XRPD data obtained from the LiCo_yNi_(1–y)VO₄ samples confirmed that the inverse spinel phase is not formed below an annealing temperature of 300°C; the pure phase is formed only at temperatures ≥400°C. At higher temperatures there is no structure modification, as also shown by TG/DTA data reported in a previous work [2]; the diffraction peaks, however, become more narrow indicating an increase in

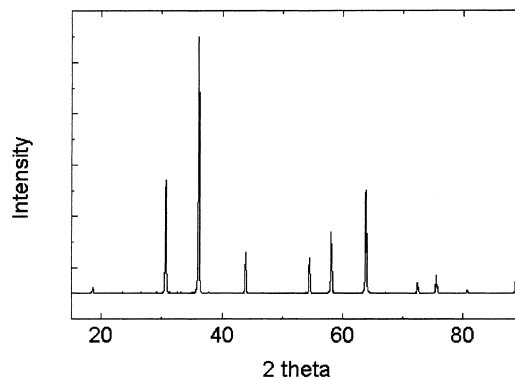


Fig. 1. X-ray diffraction patterns for LiCo_{0.5}Ni_{0.5}VO₄ samples annealed at 500°C.

crystallinity. Fig. 1 shows, as an example, the XRPD patterns for the sample with formula LiCo_{0.5}Ni_{0.5}VO₄ annealed at 500°C. The compound shows a cubic structure (*Fd3m*) and can be interpreted by means of the JCPDS Card nos. 38-1395 and 38-1996. The lattice parameter *a*₀ has been refined and is equal to 8.248 Å; this value is intermediate between the lattice parameter of LiCoVO₄ (8.276 Å) and LiNiVO₄ (8.215 Å) as reported in the literature [3].

In the temperature range considered, from 300 to 600°C, the lattice parameter does not change markedly (Fig. 2): there is just a very small contraction, probably due to a better packaging of the atoms. This same diagram shows that for different compositions of the sample (from *y* = 0.2 to *y* = 0.8), only slight variations of the lattice parameter take place.

As reported elsewhere [2], analysis of the X-ray data showed that a minor part (~15%) of Co²⁺ and Ni²⁺ and the related quantity of V⁵⁺ occupy tetrahedral sites; Li⁺ and the remaining Co²⁺, Ni²⁺ and V⁵⁺ occupy octahedral sites (~85%). Following the notation proposed by Goodenough, we can write the comprehensive formula: Me_{0.15}V_{0.85}[Li–Me_{0.85}V_{0.15}]O₄ where Me = 0.5Co + 0.5Ni (in the case of our sample, LiCo_{0.5}Ni_{0.5}VO₄) where the cations in square brackets occupy octahedral sites and those unbracketed

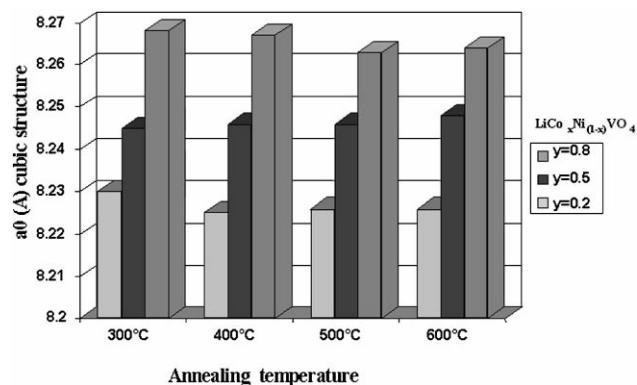


Fig. 2. Diagram of the LiCo_xNi_(1–x)VO₄ lattice parameter vs. the annealing temperature.

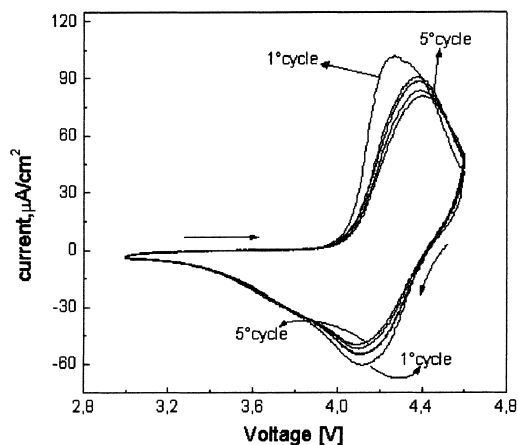


Fig. 3. Cyclic voltammogram of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$; range: 3–4.6 V vs. Li; scan rate: 0.1 mV/s.

occupy tetrahedral sites of the oxygen array [4]. The temperature variation (in the range 300–600°C) does not significantly influence the occupation of the octahedral and tetrahedral sites.

Similarly to the results of the X-ray data showing minor differences, the electrochemical behavior of the $\text{LiCo}_y\text{Ni}_{1-y}\text{VO}_4$ mixed oxides with $y = 0.2, 0.5$ and 0.8 has been, at least for these initial tests, quite homogeneous. Fig. 3 shows, as an example, the voltammogram of the sample with same cobalt/nickel relative quantities, which seems to show the best performances. It is shown that the insertion–deinsertion process occurs reversibly in the 4.1–4.4 V range. The present results show, for this and the mixed oxides with $y = 0.2$ and 0.8 , a modest result in the discharge capacity (a medium value of 50 mAh/g referred to a theoretical capacity of ~ 140 mAh/g) but a good performance in cycle life provided the range of charge voltage is limited to 4.6 V to prevent electrolyte decomposition.

It is possible to notice, in particular, a small loss in capacity after the first cycle. This is probably due to an irreversible activation process which involves a structural modification; but this does not to exclude the possibility of partial decomposition of the electrolyte.

The reported results have been confirmed by the XRPD analysis on cobalt/nickel vanadates on samples submitted at constant current cycling ($50 \mu\text{A}/\text{cm}^2$) where they gave a constant specific capacity of about 50 mAh/g. The $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$ lattice parameter values (Table 1) and the X-ray patterns showed very similar results at the various stages of the tests putting in evidence that the structure of the electrode is maintained throughout cycling. SEM observation of the electrode after cycling showed no change of the sample morphology with respect to the pristine material.

As the electrochemical results for the vanadates were very encouraging, we decided to substitute vanadium ions with a metal ion having the same oxidation states and similar chemical properties. Nevertheless, the cycling capability of LiCoSbO_4 was very poor as shown by the voltammogram

Table 1

Lattice parameters of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$ (500°C annealing temperature) at different stages of constant current density ($0.05 \text{ mA}/\text{cm}^2$) cycling

a_0 (Å)	Description (cycling rate $50 \mu\text{A}/\text{cm}^2$)
8.248	Pristine electrode
8.250	After deintercalation of 0.2 equivalents
8.251	After deintercalation of 0.4 equivalents
8.248	After an entire cycle of charge–discharge
8.250	After two charge–discharge cycles
8.249	After prolonged cycling

reported in Fig. 4. Only deintercalation of Li-ions, which practically ceases after the third cycle, can be observed. The structure itself or the modifications induced on it by the initial charging, seem to make Li-ions intercalation impossible.

The reason for such different electrochemical behavior can be attributed to the crystallographic structure of the Sb-containing sample which is markedly different from that of the vanadates as the XRPD diffractogram (Fig. 5) puts in evidence. The cubic cell of LiCoVO_4 is distorted and the structure becomes orthorhombic (space group Imma) as reported in JCPDS Card no. 25-0477. In this structure, cobalt ions occupy octahedral sites, while lithium ions the tetrahedral ones. (The lattice parameters have been refined and are equal to $a_0 = 6.03$, $b_0 = 18.11$, $c_0 = 8.54$).

The morphology of the sample also plays an important role in determining the poor electrochemical performance of the Sb-containing sample. The LiCoSbO_4 phase is formed at 700°C already but the pure phase is obtained by repeated annealing at 800°C and in fact the modification of the diffractograms becomes more and more negligible with the number of the annealings at 800°C. As it can be

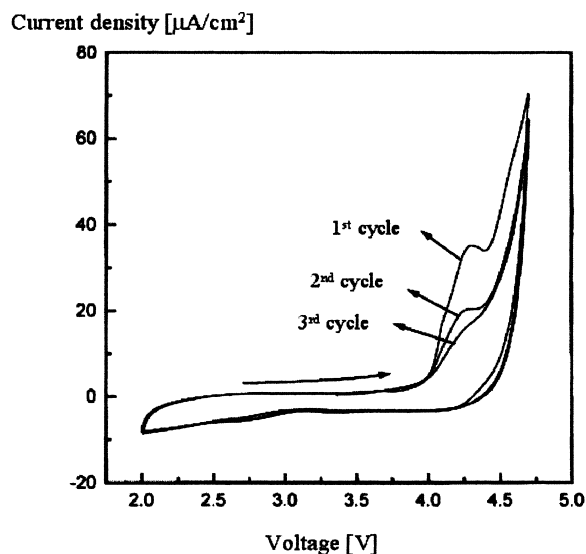


Fig. 4. Voltammogram of LiCoSbO_4 ; range: 2–4.7 V vs. Li electrode; scan rate: 0.1 mV/s.

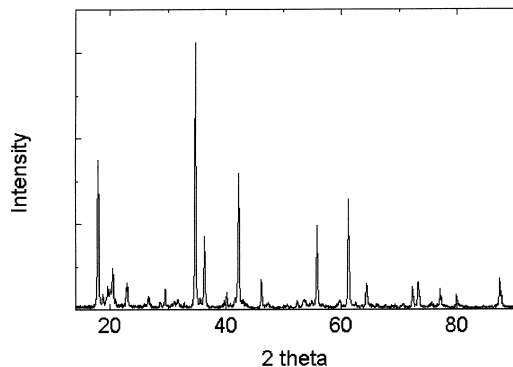
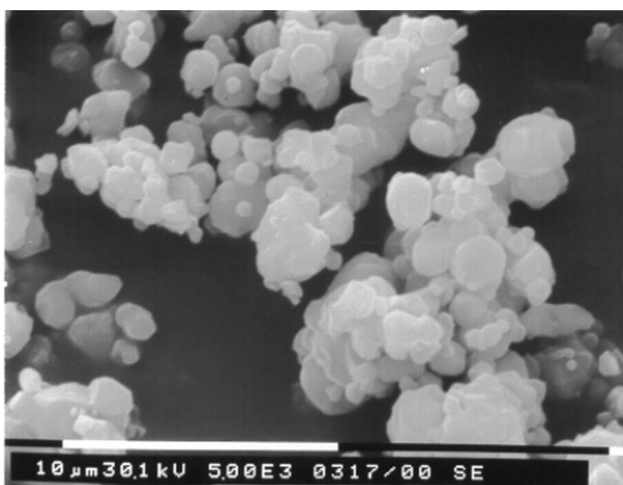
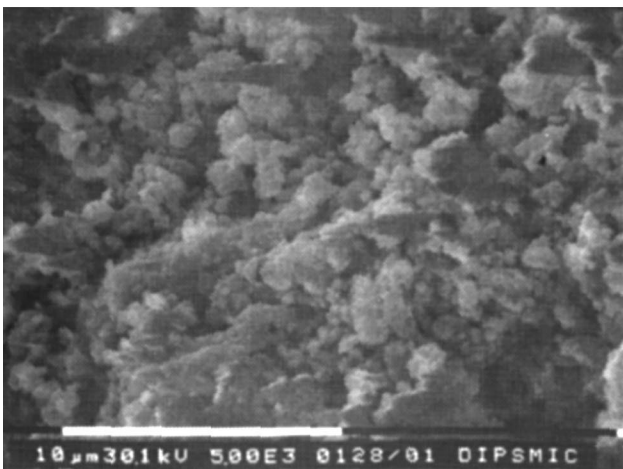


Fig. 5. X-ray diffraction patterns for LiCoSbO_4 samples after fifth annealing at 800°C .

expected, repeated annealing at high temperature induces important modifications on the powder morphology. In Fig. 6, the SEM micrographs of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$ (Fig. 6a) and LiCoSbO_4 (Fig. 6b) are compared. The V containing



(a)



(b)

Fig. 6. SEM microphotographs of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$ annealed at 500°C (section a) and LiCoSbO_4 annealed at 800°C (section b).

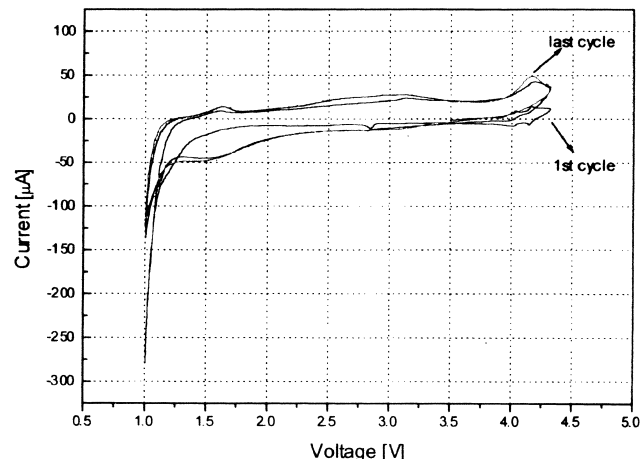


Fig. 7. Cyclic voltammogram of LiMnVO_4 ; range: 3–4.6 V vs. Li; scan rate: 0.1 mV/s.

sample, annealed at 500°C , shows little particles having few micrometers size. LiCoSbO_4 presents, in general, grains similar in dimension but condensed together as if they were synthesized. The crystallites of $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$ give rise to high surface area clusters grouped together but with spaces between them. This morphology assures good electric contact with acetylene black and allows for the passage of the electrolyte. At higher annealing temperatures, as it is for LiCoSbO_4 , the particles agglomerate compactly together and the surface area and the porosity are greatly reduced.

Finally, the substitution of Co and Ni with Mn gave rise to the LiMnVO_4 species. Unfortunately, its X-ray pattern at the chosen annealing temperature bears an orthorhombic symmetry which is inconsistent with the spinel-type structure. Padhi et al. [4] referred that only at synthesis of high pressure (~ 55 kbar) one can get a spinel-type structure. As expected, the electrochemical results are not satisfying: though LiMnVO_4 voltammetry, Fig. 7, shows a certain degree of cycling capacity, after the first cycle the structure seems to enhance deinsertion and lower insertion. The voltammetry, carried out to an extended range of low potential values, shows also the presence of other processes due to Mn changing its oxidation state.

4. Conclusions

On the basis of the present initial experimental results, we have found that only some of the samples considered ($\text{LiCo}_y\text{Ni}_{(1-y)}\text{VO}_4$ with $y = 0.2, 0.5$ and 0.8) proved to be promising as cathode materials. LiCoSbO_4 and LiMnVO_4 showed some Li-ions deinsertion features but no possibility of reinsertion.

It has been found that there is a strict correlation between crystallochemical properties and insertion–deinsertion behavior. A complete crystallochemical analysis of the material includes other experimental techniques beyond

X-ray diffraction (XRD), like solid state NMR. While XRD data forward information about the long range crystalline ordering, the NMR technique is very sensitive to the local structural environment.

Our findings suggest also that a direct connection exists between performance of the electrode and morphology of the sample. Investigations are continuing on this aspect that would assign a great importance to the choice of the method of preparation.

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