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Correlation between structural and electrochemical properties of Li metal vanadates

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Abstract

LiCo_yNi_{1-y}VO₄ compounds ($y = 0, 0.2, 0.5, 0.8, 1$) have been prepared for lithium-ion cell cathode applications by different chemical routes. The polycrystalline materials were characterized by X-ray powder diffraction (XRPD) and by solid state ⁷Li and ⁵¹V nuclear magnetic resonance (NMR) analysis. The results show an increase of the lattice parameter with increasing Co content and a varying distribution of Co, Ni, and V in the crystallographic sites. Moreover, both XRPD and NMR data reveal different degrees of crystallinity depending on the preparation method. The first electrochemical tests show that the distribution of ions in the various crystallographic sites and the crystallinity degree are correlated to the electrochemical performances. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mixed oxides; X-ray powder diffraction; Solid state ⁷Li; ⁵¹V nuclear magnetic resonance (NMR); Cathodes; Lithium-ion batteries

1. Introduction

The importance of lithium-ion power sources in portable electronics applications [1] has stimulated research on new types of lithium insertion electrode materials. Considerable efforts are presently devoted to the evaluation of high voltage, lithium-rich materials which can be employed as cathodes in Li-ion cells. The main candidates are the layered LiMO₂ (M = Co, Ni) [2,3] and the spinel structures of the type LiMn₂O₄ [4].

A current trend of research is directed towards the study of positive materials with even higher voltage, i.e. approaching 5 V versus Li. Towards this end, we have investigated the family of the mixed Li transition metal vanadates like those already taken into account by Fey and coworkers [5,6]. Concurrent aim of our investigations was the organization of the data coming from the different experimental techniques, today at disposal, in a structured ensemble.

When the metal ion is Ni²⁺ or Co²⁺, the corresponding LiCo_yNi_{1-y}VO₄ compounds adopt an inverse spinel struc-

ture, where Li⁺ ions reside in octahedral sites, Ni²⁺ and Co²⁺ ions and V⁵⁺ ions can be distributed both in octahedrally and tetrahedrally coordinated sites [7,8]. This structure should allow easy removal of lithium at potentials of the order of 4.2–4.8 V versus Li, depending upon the Ni/Co ratio.

As it is well known, different preparation routes lead to powders with different electrochemical efficiency. In order to investigate this aspect, we have prepared, by two different methods, some LiCo_yNi_{1-y}VO₄ ($y = 0, 0.2, 0.5, 0.8, 1$) compounds. These powders have been extensively characterized by XRPD and NMR analyses. The first results, here reported, allowed us to give a preliminary correlation between the different electrochemical behaviors and the structural properties of the studied samples.

The XRPD technique, while an indispensable tool in the structural characterization of battery cathode materials, provides information only by averaging over hundreds of lattice sites. Thus, it is relatively insensitive to the local structural variations that occur when one kind of transition metal ion is sequentially substituted for another (although it does give the average change in lattice parameter according to Vegard's Law^(R)). However, because NMR is particularly sensitive to short-range interactions, it yields information on

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short-range spatial correlations, especially when the ions being substituted into the lattice are paramagnetic.

2. Experimental

A series of the $\text{LiCo}_y\text{Ni}_{1-y}\text{VO}_4$ family, namely LiCoVO_4 , $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{VO}_4$, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$, $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{VO}_4$, and LiNiVO_4 have been considered in this work. These compounds have been synthesized starting from reagent grade chemicals (Aldrich chemicals) by two different preparation methods: a wet chemistry and a solid state route.

The wet chemistry preparation procedure has been described elsewhere [7]. In the solid state route, the precursors were LiCo_3 , CoO , NiO , and V_2O_5 . These precursors were finely ground in a ball mill before the annealing at 530°C . The samples were annealed for about 200–230 h, and during this time the powders were grounded every 24 h to reduce grain dimensions.

The structure of the compounds was probed by XRPD (Philips PW Diffractometer with graphite monochromator) and their morphology by SEM. The measured integrated intensities were used for the refinement of the unit cell dimensions, the atomic coordinates, the site occupancies, and the isotopic thermal factor related to a crystallographic model developed by XRD123, a publically available software (internet address: <http://www.polito.it/Ulisse/Corsi/TLC/F0620/materiali>).

About 500 mg of sample was packed into 5 mm OD pyrex tubes for the NMR measurements, which were conducted with a Chemagnetics CMX300 Spectrometer, operating at ^7Li and ^{51}V resonance frequencies of 116.8 and 79.2 MHz, respectively. Both single pulse and quadrupole echo excitation sequences were employed, the latter exclusively for ^{51}V . A typical $B/2$ pulse width was 2.5 μs . The pulse separation in the quadrupole echo sequence was about 150 μs . For ^7Li , typically 1200 spectral acquisitions were required, and 64,000 for ^{51}V . Chemical shift references were aqueous solutions of LiCl and VOCl_3 .

The electrochemical tests consisted of cyclic voltammeteries (CV) at a sweep rate of 0.1 mV/s. The electrodes, the electrolyte, and the complete test cell used have been described elsewhere [7]. The measurements were carried out using an AMEL 2051 potentiostat coupled with an AMEL 568 function generator.

Table 1
Diffractometric data for $\text{LiCo}_y\text{Ni}_{1-y}\text{VO}_4$ samples

Sample	Lattice parameter a_0 (\AA)	Preparation method
LiCoVO_4	8.278	Solid state
$\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{VO}_4$	8.261	Wet chemistry
$\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$	8.248	Wet chemistry
$\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$	8.249	Solid state
$\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{VO}_4$	8.225	Wet chemistry
LiNiVO_4	8.213	Solid state

3. Results and discussion

The analysis of the XRPD data confirms that all prepared samples have a spinel structure. As expected, the solid state route leads to an observable increase in the crystallinity degree (crystallites size) of the samples compared to the wet chemical preparation. The diffraction peaks become narrower during the annealing treatment, revealing a progressive increase in crystallite size. Table 1 summarizes the diffractometric data for all prepared samples. The values reported show that the lattice parameter increases linearly with Co content within the limits of the unsubstituted nickel (LiNiVO_4 , 8.213 \AA) and cobalt (LiCoVO_4 , 8.278 \AA) compounds. Moreover, the results of the analysis suggest that the occupation of the octahedral and tetrahedral sites is dependent on the composition of the sample and the preparation method. In the LiCoVO_4 sample, all Li and Co ions occupy octahedral positions, and V ions are all located in tetrahedral sites. When the Ni content is increased, Co/Ni and V ions are distributed in both octahedral and tetrahedral sites as reported in Table 2.

These findings are quite interesting, since they are opposite to what has been reported for the pure spinels where Co^{2+} appears to have a tendency (of the order of 13 kJ/mol, difference between the octahedral and tetrahedral coordination lattice energies) to assume a tetrahedral coordination, and Ni^{2+} even a stronger tendency (of the order of 50 kJ/mol, difference between the tetrahedral and octahedral coordination lattice energies) to assume an octahedral coordination [9].

One could suppose that the inversion found in the mixed $\text{LiCo}_y\text{Ni}_{1-y}\text{VO}_4$ compounds is to be ascribed to the influence of vanadium. To confirm this assumption, NMR analysis of all powders has been performed.

Table 2
Co, Ni, V occupation sites (atoms per unit cell)

Sample	Co/Ni		V		Preparation method
	Octahedral	Tetrahedral	Octahedral	Tetrahedral	
LiCoVO_4	8	0	0	8	Solid state
$\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{VO}_4$	7	1	1	7	Wet chemistry
$\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$	6.8	1.2	1.2	6.8	Wet chemistry
$\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$	5	3	3	5	Solid state
$\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{VO}_4$	6	2	2	6	Wet chemistry
LiNiVO_4	5	3	3	5	Solid state

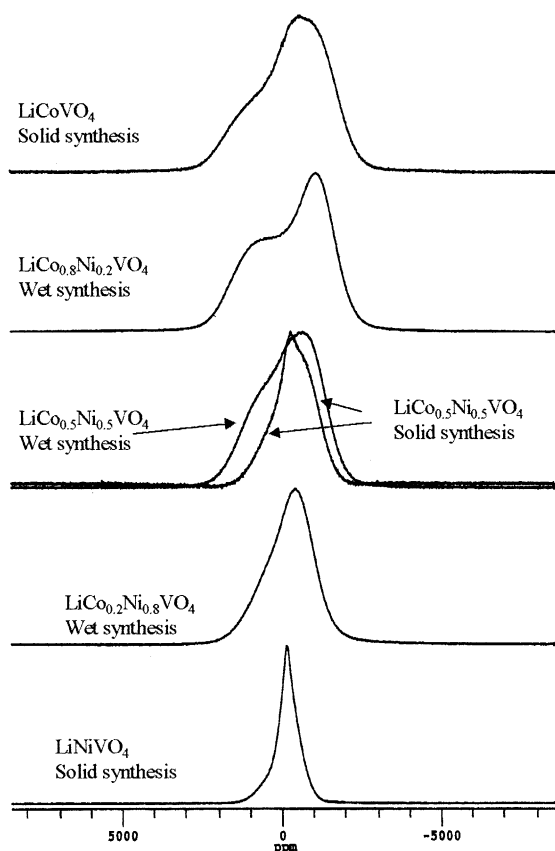


Fig. 1. ^7Li NMR signal at room temperature.

Lithium-7 NMR spectra of all samples are displayed in Fig. 1. The spectrum of LiNiVO_4 (bottom) is a relatively narrow line with no evidence of quadrupole satellite transitions, consistent with Li in an octahedral environment. Substitution of Co^{2+} for Ni^{2+} broadens the ^7Li resonance line significantly due to the strong magnetic dipolar interaction with spins localized on the Co site. In the single sample composition, for which both preparation mechanisms were employed ($\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{VO}_4$), the ^7Li NMR line shapes are substantially different, reflecting a different spatial distribution of paramagnetic Co^{2+} ions with respect to the Li^+ ions. The line width of the solid synthesis (SS) sample is narrower than that of the wet synthesis (WS) material, and the peak positions of the two lines differ, with the SS peak appearing between the main peak and observable shoulder of the WS sample. This is consistent with a statistically random distribution of Li–Co spatial correlations in SS as opposed to a non-random distribution in WS.

A similar effect is present in the ^{51}V spectra displayed in Fig. 2. The LiNiVO_4 spectrum (bottom) is characterized by a relatively narrow central transition and a single set of resolved first order quadrupole transitions. The narrow central transition is expected from the diamagnetic nature of the unsubstituted compound. Although, all vanadium ions are presumed to reside in tetrahedral sites, all of the other spectra show two inequivalent V environments. As in the

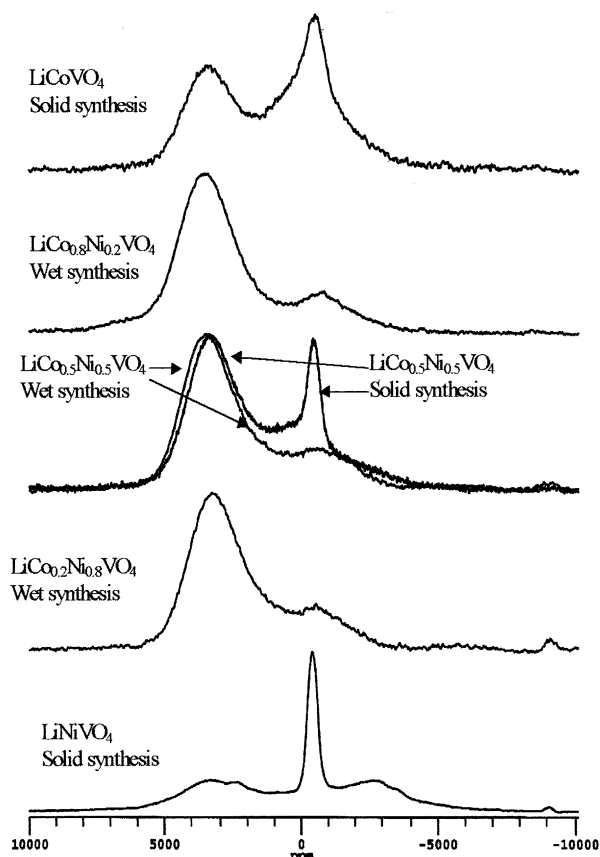


Fig. 2. ^{51}V NMR signal at room temperature.

case of the ^7Li results, this reflects the different magnetic environments of ^{51}V nuclei as a function of Co^{2+} substitution. However, further details are required to explain the presence of two V sites in the “pure” Co compound (top) as well as in the “pure” Ni compound (bottom), the latter of which also exhibits a small but broad feature to the left of one of the quadrupole satellites. These matters will be deferred to a later publication in which the entire composition range of the samples prepared by both synthetic methods will be addressed. In addition, ^{51}V NMR is usually characterized by strong quadrupole interactions, often second order. In the presence of other broadening mechanisms, such as high-spin densities from Co^{2+} substitution, the spectral line shapes can often only be properly interpreted when the NMR measurements are performed at a second frequency (the second-order quadrupole interaction is frequency dependent).

The middle spectra in Fig. 2 again highlight the difference between the SS and WS materials at the same composition, implying a random V–Co spatial distribution in the former versus a non-random one in the latter.

The first electrochemical data for WS materials, f.i. $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{VO}_4$ in Fig. 3a, show that the electrochemical lithium insertion–deinsertion process of the $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{VO}_4$ electrode occurs reversibly in the 4.3–4.4 V versus Li range. As typically observed for the majority of the

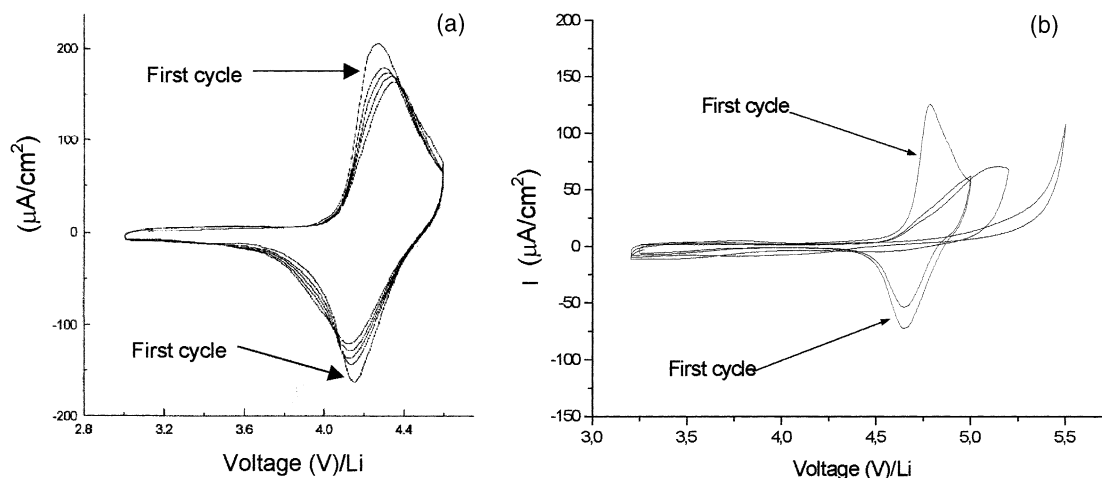


Fig. 3. Cyclic voltammetry of the $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{VO}_4$ electrode (wet preparation) (section a) and of the LiNiVO_4 electrode (solid state preparation) (section b) in a 1 M LiPF_6 in PC–EC–DMC (1:1:2) electrolyte cell. Li counter and reference electrode; scan rate: 0.1 mV/s; room temperature.

lithium insertion compounds, there is a decay in capacity passing from the first to the subsequent cycles. This is due to irreversible activation processes which probably involve structural rearrangements, although decomposition of the electrolyte to form a protective layer on the electrode surface cannot be ruled out for high-voltage cathodes [10,11]. The LiNiVO_4 SS sample (Fig. 3b) shows considerably lower electrochemical performance, as the reversibility of this electrode is not observable. The abrupt disappearance of the current peaks at the second cycle suggests that decomposition of the electrolyte is probably involved.

The CV response of SS samples indicates that they perform worse than WS ones. Low capacity values have been observed also for WS samples that had been calcined at temperatures higher than 600°C [12]. As in both cases, the materials consist of larger size crystallites, it is well evident that the higher crystallinity of the powders is not producing the desired electrochemical performance. An important assumption here, justified by the first experiments, is that the vast difference observed in Li insertion–deinsertion capacity is attributable mostly to the differences between WS and SS samples than to the compositional difference (partial Co substitution with Ni in the material). We will address this issue fully in a future paper, including results for the entire composition range prepared by both methods.

It can be concluded that the structural characterization of the powders is fundamental in the study of new materials for Li-ion batteries application. In this case, two important points have been put in evidence: the transition metal ions are distributed differently between the octahedral and

tetrahedral crystallographic sites, depending on the sample preparation method; the increase in the degree of crystallinity of the samples does not lead to an improvement of the performance.

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