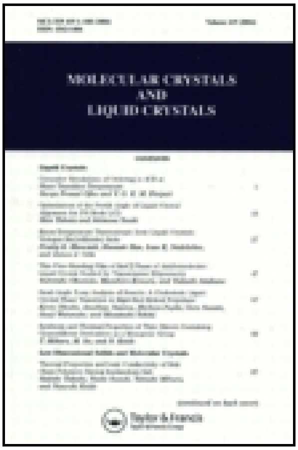

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Lithium Insertion Study in Vanadium Oxide Bronze by NMR and X Ray Diffraction

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LITHIUM INSERTION STUDY IN VANADIUM OXIDE BRONZE BY NMR AND X RAY DIFFRACTION

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Abstract The insertion of lithium in vanadium pentoxide at high temperature is followed both by Xray diffraction and ^{7}Li NMR studies. A correlation between the lithium sites found by structure determination and the isotropic chemical shifts is established and a mechanism of the lithium insertion proposed. Calculations of the valence of the vanadium atoms and the simulation of NMR spectra allows to localise the V^{4+} in the highest lithium rate phases.

INTRODUCTION

The structures and the electronic properties of the vanadium oxide bronzes lead to use these compounds as positive electrode in lithium batteries.[1-5] It appears rapidly that structure transformations occur during the electrochemical cycles which lowers the performances [6,7]. Recently, NMR studies have been performed in order to determine the dynamics of the lithium migration in the host,[8,9] but the interpretation of the NMR observations with respect to the structural knowledge is not well established. In order to calibrate the NMR response, a study of the high temperatures phases is undertaken both by precise X ray structure determination and ^{7}Li NMR.

EXPERIMENTAL SECTION

The rate of lithium to be inserted is chosen according to the phase diagram determined from former studies [10-12]. Samples of x=0.02, x=0.30, x=0.48 and x=1.00 are made according to the process already developed [13] and following the reaction :

$$V_2O_5 + x/2\ Li_2C_2O_4 \rightarrow Li_xV_2O_5 + x\ CO_2$$

The compounds obtained are analysed by comparison of their X ray diffraction (XRD) patterns with the ones of the known phases.[10-12] Details of the structure determinations are given elsewhere.[14]

^{7}Li NMR measurements are carried out on a Bruker MSL-300 (B_0=7.1T, $\omega_0/2\pi$=116.598MHz) using both static and MAS (spinning frequencies from 0.4 to 15 kHz) techniques at room temperature. The isotropic chemical shifts reported in the following study are relative to an external sample of 1.0M LiCl solution in methanol.

RESULTS

x=0.02

The XRD pattern reveals with the α phase a small amount of the β phase. Figure 1a displays three peaks in the ^{7}Li NMR MAS spectrum at δ=-2ppm, -16ppm and -28ppm with an intensity partition of 5%, 23% and 72% respectively.

Comparison with α phase made using the low temperature process [16] allows to assign the two lowest chemical shifts to the α phase, the highest one pertains to the β phase. Because few lithium atoms are inserted in α phase, only one site, Li1, was found by structure determination, the second site, Li2, being postulated.[10] (figure 2).

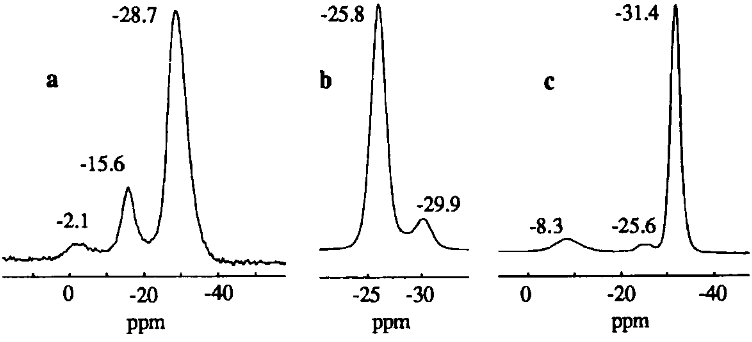

FIGURE 1 . Chemical shift of ^{7}Li NMR MAS spectra of : a - α + β phases, b - β phase, c - β' + γ phases

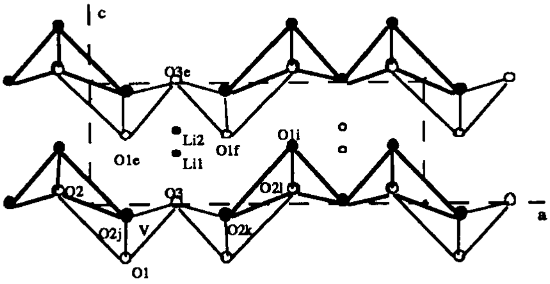

FIGURE 2 . Projection onto the [0 1 0] plane of the α-$Li_xV_2O_5$ structure.

x=0.30:

The β-$Li_{0.30}V_2O_5$ phase is obtained pure and a precise structure determination is undertaken in order to localise the lithium atoms. The cell dimensions and the V_2O_5 skeleton agree with the known ones [11](figure 3).

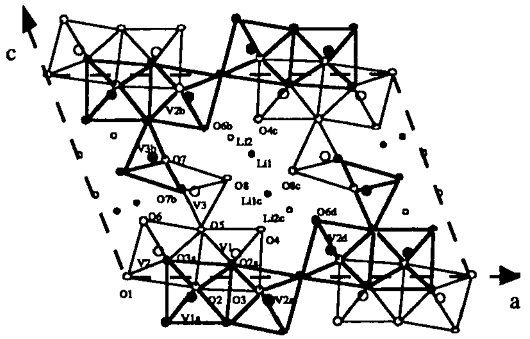

FIGURE 3 . Projection of the β-$Li_xV_2O_5$ structure onto the [0 1 0] plane

In addition to the classical site, Li1, of the β phase, a small amount of lithium is found in the site Li2, the distribution of the lithium atoms being 82% in site Li1 and 18% in site Li2. The ^7Li NMR spectrum shows two peaks, δ=-26ppm and -30ppm, with an intensity allotment of 89% and 11% respectively (figure 1b).

x=0.48:

The value x=0.48 corresponding to the upper end of the lithium insertion range in the β'phase, a small amount of the γ phase is revealed by powder XRD. A quantitative analysis is done by Rietveld technique using the known structures of each phase [12] as starting point. The lithium rates in each phase (β' and γ) are determined too. The structure of the β'phase being similar to the one of the β phase, the same numbering as in figure 2 is used.

The ^{7}Li NMR spectrum of this sample reveals three peaks, δ=-8ppm, -26ppm and -31ppm with an intensity distribution of 13%, 4%, 83% respectively (figure 1c). Comparison with the spectrum of the γ-$Li_xV_2O_5$ leads to attribute the first peak (δ=-8ppm) to the γ phase. Both other peaks showing similar chemical shifts than those of the β phase, a test using Rietveld analysis is done in order to verify that there is no more β phase in the sample. So lithium in Li1 site is added in the β' structure. The obtained quantitative results show that the sample is constituted of 13% γ-$Li_{0.88}V_2O_5$ and 87% of β'-$Li_{0.45}V_2O_5$ with a distribution of the lithium on both sites of Li1 5% and Li2 95%.

x=1.00:

The obtained compound is made of pure γ phase with cell parameters (a= 9.711(9)Å, b=3.619(9)Å, c= 10.722(9)Å) in agreement with the ones determined by Galy, Darriet, Hagenmuller.[12] A projection of the structure onto the [0 1 0] plane is given figure 4.

The ^{7}Li NMR spectrum presents one peak with δ = -8ppm.

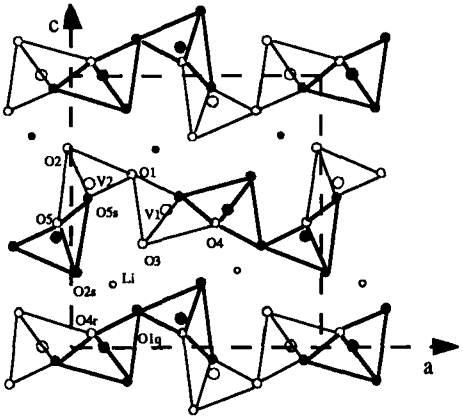

FIGURE 4 . Projection onto the [0 1 0] plane of the γ-$Li_xV_2O_5$ structure

DISCUSSION

In every phases, the V_2O_5 network was already determined [10-11] and the main difficulty occurs with the localisation of the lithium atoms. Every isotropic chemical shift corresponding to a unique electronic surrounding of the probe atom, it appears in many cases that the NMR study imposes and adds new lithium sites. Once these new sites are determined by the XRD study, their occupancies can be compared with the intensities of the NMR peaks which are proportional to the number of lithium in a site. The comparisons lead to attribute a chemical shift to a lithium site and the results are given in table I.

TABLE I Attribution of a chemical shift to a lithium site

phase	site	Coordination number	occupancy (%) (X ray)	intensity(%) (NMR)	δ (ppm)
α-$Li_{0.02}V_2O_5$	Li1	6 (TP)	100	23*	-16
	Li2	8 (BTP)	0	5*	-2
β-$Li_{0.30}V_2O_5$	Li1	7 (MTP)	82	89	-26
	Li2	4 (T)	18	11	-30
$\beta'Li_{0.45}V_2O_5$	Li1	7 (MTP)	4*	4*	-26
	Li2	4 (T)	75*	83*	-31
γ-LiV_2O_5	Li1	6 (O)	100	100	-8

* These values coming from mixtures, the remainder represents the missing component. TP: trigonal prism, BTP: bicapped trigonal prism, MTP: monocapped trigonal prism, T: tetrahedron, O: octahedron

Looking at the β and β' phases, an insertion mechanism of the lithium can be proposed : At the beginning, the lithium occupies the Li1 site, then before the saturation of this site (x=0.33) some lithium goes into the Li2 site. After the phase transition, the lithium atoms are always inserted in Li2 site and, while one lithium is added in Li2 site, one lithium leaves the Li1 site and goes in Li2 site.

The results reveal that the ^7Li chemical shifts are not correlated with the oxygen surrounding of the lithium atoms. Indeed the NMR spectra are influenced by interactions from both quadrupole couplings and the paramagnetic shift due to the dipole interactions of the Li nuclear moment with the paramagnetic ion moments. The paramagnetic ions being the V^{4+} ions, their localization in the structure becomes of great importance. A rough evaluation of this localization can be obtained from valence calculations[16] (table II). Partitions of the V^{4+} ions in the vanadium sites of the β, β' and γ $Li_xV_2O_5$ phases are tested for NMR MAS spectra simulations.[17] The sets which give the best fit between the calculated and the experimental spectra are also presented in table II. The good correlation between both results strengthens the allotment of the V^{4+} proposed.

TABLE II Partition of the V^{4+} in the vanadium sites

phase	β-$Li_xV_2O_5$			β'-$Li_xV_2O_5$			γ-$Li_xV_2O_5$	
vanadium site	V1	V2	V3	V1	V2	V3	V1	V2
valence*	4.9	4.8	5.0	5.1	4.7	5.5	4.3	5.0
NMR partition (%)	30	40	30	50	50	0	100	0

* valence = $\Sigma \exp[(r_0-r_{ij})/B]$, $r_0=1.783$, $B=0.37$, r_{ij} = vanadium-oxygen distances

CONCLUSIONS

The high temperature phases of lithium insertion in vanadium pentoxide followed by structure determination and ^{7}Li NMR studies are examined. A mechanism of the lithium insertion in the β and β' phases is proposed. Every chemical shift is attributed to a lithium site and the simulation of the NMR spectra associated with the calculation of the vanadium valence allows to localise the V^{4+} in the β, β' and γ phases. These results can act as a good basis set to the study of the low temperature $Li_xV_2O_5$ phases and further more of the V_2O_5 electrodes used in the lithium batteries.

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