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Local structure and lithium mobility in intercalated $Li_3Al_xTi_{2-x}$ $(PO_4)_3$ NASICON type materials: A combined Neutron diffraction and NMR study.

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ABSTRACT

Structural features of intercalated $Li_3Al_xTi_{2-x}(PO_4)_3$ compounds, with x= 0 and 0.2, have been deduced by Rietveld analysis of neutron diffraction (ND) patterns recorded between 100 and 500K. The Li insertion decreases the symmetry from R-3c to R-3 in analyzed compounds. In pristine $Li_{1+x}Al_xTi_{2-x}$ $(PO_4)_3$ samples, Li occupies mainly six-fold M_1 sites at ternary axes; but in lithiated $Li_3Al_xTi_{2-x}(PO_4)_3$ samples, Li is located near M_2 positions at M_3/M_3' four-fold coordinated sites. In both cases, Li arrangement minimizes electrostatic Li-Li repulsions. The insertion of lithium produced the reduction of Ti^{4+} to Ti^{3+} that shifts ^7Li, ^{27}Al and ^{31}P MAS-NMR resonances towards more positive chemical shifts, improving the resolution of differet sites. The detection of twelve components in ^7Li MAS-NMR spectra recorded at room temperature, suggests the location of Li^+ ions at three-oxygen faces that define M_2 cavities. From ^7Li MAS-NMR spectra, sites occupancy and mobility of lithium were investigated in the temperature range 100-500 K. The correlation between structural information, deduced by neutron diffraction, and lithium mobility, deduced by NMR spectroscopy, provides new insights on structural factors that affect lithium mobility in materials with NASICON structure.

Keywords: Li insertion, Li mobility, NMR spectroscopy, Neutron Diffraction, Fourier map differences, NASICON, LATP, Li batteries.

Introduction

Extensive investigations have been addressed to the exploitation of new energy sources, such as solar, wind, tidal, and geothermal energy[1]. Lithium ion batteries (LIBs) have been the most efficient energy storage devices since their commercialization, with high open-circuit voltage, large discharge capacity, long cycle life and environmental friendliness characteristics. LIBs have been widely applied to portable electronic devices and will be extensively used in electric, hybrid vehicles and smart grids[2-4]. The development of new generation lithium ion batteries requires a specialized research and industry attention for developing high performance electrode/electrolyte materials. Lithium metal phosphates, with higher energy and power densities, are between active materials, those capable to answer safety concerns surrounding oxides chemistry used as solid electrolytes[5]. Among phosphates, stability and good electrochemical performances have been reported for NASICON type materials, proposed as electrode and/or electrolyte for secondary lithium batteries[6-8].

The NASICON framework is built up by $M_2(PO_4)_3$ units, in which two MO_6 octahedrons share oxygen vertices with three PO_4 tetrahedra[9,10]. Tetrahedra and octahedra of contiguous $M_2(PO_4)_3$ units are bounded to form the three-dimensional network. The usual symmetry of $LiM_2(PO_4)_3$ compounds is rhombohedral R-3c, although in some cases a triclinic distortion (space group C-1) was found[11-15]. In rhombohedral phases, Li ions are usually surrounded by six oxygen atoms at M_1 sites[11, 12]; but in triclinic ones, Li ions are coordinated to four oxygen atoms and located between M_1 and M_2 positions[13-15]. The ionic conductivity of $LiM_2(PO_4)_3$ series can be enhanced when tetravalent (M^{4+}) are partially substituted by trivalent (R^{3+}) cations such as Al^{3+}, Ga^{3+}, Sc^{3+}, In^{3+}, etc.[16-24]. In the rhombohedral $Li_{1+x}R_xM_{2-x}(PO_4)_3$ compounds, a maximum conductivity between 10^{-2}-10^{-3} Scm^{-1} was reported at room temperature in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ [LATP] and $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ [LAGP] series[16, 21-24].

In lithium intercalated $Li_3Ti_2(PO_4)_3$ samples, diffraction patterns were indexed with the rombohedral R-3 space group and Li ions were placed near M_2 sites, at fourfold coordinated M_3 and M_3' sites[25-27]. In a recent neutron diffraction (ND) study of Al-doped $Li_{1+x}Ti_{2-x}Al_x (PO_4)_3$ compounds[28], it was deduced that beside M_1 sites, Li ions partially occupy M_3/M_3' sites, indicating that these sites are favored when the amount of Li increases above 1 per structural formula. The occupation of M_3/M_3' sites should reduce the electrostatic repulsion between Li ions.

In the present work, structural features of lithium intercalated $Li_3Ti_{2-x} Al_x(PO_4)_3$ samples, with x= 0 and 0.2, have been investigated by Rietveld analysis of neutron diffraction patterns. In this work, special attention has been paid to the location and mobility of Li in the 100-500 K temperature range. For that, Fourier map differences have been calculated from neutron diffraction patterns. A detailed [6]Li,

^{7}Li, ^{27}Al and ^{31}P MAS-NMR study of lithium intercalated samples provides complementary information about structural factors that affect cation distribution and lithium mobility in NASICON compounds.

Experimental section

Pristine $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ samples, with x= 0 and 0.2, were prepared by heating stoichiometric mixtures of Li_2CO_3, $(NH_4)_2HPO_4$, Al_2O_3 and TiO_2 in the interval 573-1373 K, following the procedure described previously[24,29,30]. Lithium intercalated $Li_3Ti_{2-x}Al_x(PO_4)$ samples were prepared by chemical lithium insertion; for that, n-butyl-lithium was added under stirring to pristine $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ samples dispersed in hexane[31]. The product was washed with dry hexane and finally dried under vacuum.

X-Ray diffraction (XRD) patterns of lithium intercalated samples were recorded with Cu-K$_\alpha$ radiation (λ=1.5405981 Å) in a PW 1050/25 Phillips apparatus to identify crystalline phases. Unit cell parameters of $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples were determined with the Fullprof program (LeBail procedure)[32]. In order to increase the sensitivity to oxygen and lithium positions, high-resolution neutron diffraction (ND) patterns were collected in the high-resolution powder SPODI diffractometer of the FRM-II reactor (Garching, Munich, Germany). In this analysis, a wavelength of 1.548 Å was selected from a Ge monochromator. Cylindrical vanadium cans of 8 mm diameter were filled with 2g of powder sample and mounted in a high-temperature vacuum furnace equipped with Nb heating elements. ND patterns were collected for 4h over the 5-160 2θº range with a step size of 0.05º in the temperature range 100-500K.

In this work, structural features of intercalated $Li_3Ti_{2-x}Al_x(PO_4)$ samples have been investigated with the Rietveld method[33]. For that, a pseudo-Voigt function was chosen to reproduce the line-shape of diffraction peaks[32]. Neutron scattering lengths used for Li, Ti^{3+}, Al, P and O atoms were -1.90, -3.30, 3.45, 5.13 and 5.80 fm[34]. Negative lengths factors of Li atoms improves the contrast of light O and Li elements, making possible Fourier map differences addressed to localize Li atoms. The Rietveld analysis performed on ND patterns afforded relevant information about Li site occupancies and atom thermal factors at increasing temperatures.

^{31}P, ^{27}Al and ^{7}Li (^{6}Li) NMR spectra were recorded at room temperature in a MSL-400 Bruker spectrometer (9.4 Tesla). The frequencies used for ^{7}Li (^{6}Li), ^{31}P and ^{27}Al were 155.50 (58.88), 161.97 and 100.4 and MHz, respectively. ^{7}Li (^{6}Li) and ^{31}P NMR signals were obtained after $\pi/2$ (3 and 4 μs) and ^{27}Al NMR signal after $\pi/8$ (1 μs) single pulse irradiations in 4 mm probes. To avoid saturation effects, the recycling time was fixed at 10s in quatitative analyses. During spectra recording, samples were spun at 2 kHz (7Li and 6Li signals) and 4 kHz (31P and 27Al signals) around an axis inclined 54º74'

with respect to the external magnetic field (MAS technique). The magic-angle setup was performed with the KBr sample.

The number of scans was in the range of 100-800. ^{7}Li, ^{27}Al and ^{31}P NMR chemical shifts were referred to 1M LiCl, 1M AlCl3 and 85% H3PO4 aqueous solutions. The fitting of NMR spectra was performed with the Bruker WINFIT software package[35]. This program allows the position, linewidth and intensity of components to be determined with a non-linear least-square iterative method. The quadrupole C_Q and η parameters had to be deduced with a trial and error procedure. To study paramagnetic interactions, the dependence of line positions with temperature was analyzed. ^{7}Li MAS-NMR spinning side-bands profiles, recorded at low spinning rates, were used to determine quadrupole interactions (Li sites symmetry). For that, the Winfit software was used to simulate first-order quadrupole interactions. The comparison between experimental and calculated profiles allowed the estimation of C_Q and η parameters.

Results

ND diffraction

Figure 1 illustrates the variation of ND patterns of the $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ sample with temperature. In this sample, the structural analysis was performed in the 5-500K interval; but, in the case of the non-doped $Li_3Ti_2(PO_4)_3$ sample, the analysis at 500K could not be done because of sample decomposition under vacuum. The structural analysis of two samples was performed with the Rietveld technique. This analysis confirmed that both compounds display the R-3 symmetry reported previously[26]. In the case of Al doped sample, additional small peaks attributed to the presence of a minor amount of aluminum phosphate were detected.

Unit cell parameters of $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples, with x= 0 and 0.2, were determined with the LeBail technique (Fullprof program). In Al doped sample, *a* and *c* parameters decrease as a consequence of the lower Al radius.The temperature dependence of unit cell parameters is given in Figure 2, where it is observed that *a* parameter increases, but *c* decreases in a non-linear way with temperature. Mean expansion coefficients deduced for two axes are near 1.3 10^{-4} and -1.7 10^{-4} ÅK^{-1} in both samples.

The crystal structure was refined with the Rietveld method, using as starting model that proposed by Delmas et al. for $Li_3Ti_2(PO_4)_3$ (S.G. R-3)(see Table I)[26]. In this analysis, overall histogram, scale factors, background coefficients, unit-cell parameters, zero-shift error and pseudo-Voigt peaks[36] corrected for asymmetry[37] were first refined. Then, positions, sites occupancy and thermal factors of atoms

were determined. The structural refinement of two samples becomes unstable and some refinements displayed negative thermal factors. In order to avoid this problem, B_{Li} and B_{Ti} thermal factors of two (18f and 6c) sites were constrained to be the same[38]. Information deduced for Li inserted $Li_3Ti_{2-x}Al_x(PO_4)_3$ materials is given as supplementary material in Tables SM 1 and 2. In these tables, agreement factors obtained in structural refinements are included.

In general, P tetrahedra remain almost unaffected (P-O distances = 1.53 Å), but Ti octahedra expand (Ti,Al-O increasing from 1.93 to 2.04 Å) as a consequence of the reduction of Ti^{4+} to Ti^{3+} produced during lithium insertion[39] (see Table II). The occupation of two octahedral sites was similar, displaying a lower Al content than nominal values (Table SM 2). In order to analyze the Li site occupation, Fourier map differences were illustrated in z/c= 0.047 plane (M_3 sites) at 5K, using the structural R-3 model without lithium, and in z/c= 0.33 plane (M_1 sites) at 500K, in samples with lithium (Figure 3). The insertion of Li increases electrostatic repulsions between Li1-Li3 sites ($d_{Li-Li} \sim$ 3.3 Å) in lithiated samples, destabilizing the occupation of M_1 sites. The location of Li at M_3 or M_3' sites improved considerably agreement factors in refinements performed between 100 and 500K. The analysis performed at 500K showed that occupation of M_3/M_3' decreases appreciably, favoring the partial occupation of structural sites located near M_1 sites. In analyzed samples, mean Li-O distances at M_3 are smaller than at M_3' sites (2.04 and 2.16 Å), justifying the lower occupation of M3' sites.

The analysis of thermal factors is illustrated in Figures 4 and 5. In the case of P tetrahedra, B_P factors increase with structural disorder in Al-doped samples; however, octahedral $B_{Ti,Al}$ factors decreased with Al content. The variation of B_P and $B_{Ti,Al}$ is not linear with temperature, increasing considerably above 300 K.

The temperature dependence of B_O factors shows that, in all cases, the trend is similar increasing in the order O2<O1<O4<O3. In general, B_O factors of Al-doped samples are higher than those of the Ti pure member. In the case of lithium, B_{Li} factors are almost constant below 200K, but increases considerably above 300 K. This dependence is bigger than that detected in other atoms supporting the existence of Li mobility. The variation of B_{Li} does not depend significantly on the Al content (see bottom of Figure 5).

NMR spectroscopy

In lithiated samples Ti^{4+} is reduced to Ti^{3+}, increasing paramagnetic interactions. The life time of electron states is very short with respect to the time scale probed by NMR (10^{-8} s); from this fact, the electron magnetic moments is averaged according to the expression[40]

$$\mu_e = g.\mu_B< S_z >= g^2. \mu_B^2.S(S+1).B_0/3.k.T$$

Where g is the electron g-factor, μ_B is the magneton de Bohr, S the electron spin, and T the temperature. Paramagnetic interactions are formed by an isotropic term (Fermi contact) and an anisotropic one (dipolar interaction) [(40)]. The first type causes changes on the position and the second one an important broadening of components.

^{31}P (I=1/2) MAS-NMR spectra of $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples are shown in Figure 6. In two compounds, spectra are formed by two components centered near 9.6 and -26 ppm that correspond to phosphorous in lithiated and pristine phases. Important shifts detected in lithiated samples must be ascribed to paramagnetic (isotropic term) interactions created by lithium insertion. The quantitative analysis of ^{31}P NMR spectra shows that only a small amount (3-9%) of titanium remains as Ti^{4+} in lithiated samples, in agreement with magnetic susceptibility measurements[31]. Heating of the sample did not produce appreciable changes in ^{31}P NMR spectra.

^{27}Al (I= 5/2) MAS-NMR spectra of the Al-doped sample are formed by five nuclear transitions, modulated by equally spaced spinning side bands. The central part of spectra (Figure 7) is formed by a complex broad component at $\delta\approx40$ ppm that mainly corresponds to aluminum in octahedral coordination (AlO_6). This component was shifted from $\delta\approx-15$ ppm to 40 ppm by paramagnetic interactions[31]. The heating of the sample at 400 K produced important changes in ^{27}Al NMR spectra, favoring the detection of two octahedral Al components at 27 and 34 ppm. The resolution of these components, ascribed to two octahedral sites of R-3 compounds, was possible by decreasing paramagnetic interactions. The narrow line detected at 41 ppm corresponds to tetrahedral Al of the secondary non-paramagnetic $AlPO_4$ phase, whose position does not change with temperature.

^7Li (I= 3/2) MAS-NMR spectra of lithiated samples are formed by three nuclear transitions modulated by spinning side bands. The analysis of spinning side-bands patterns indicates that symmetry of occupied sites decreases from axial ($C_Q \sim 25$ kHz and $\eta = 0$) in pristine to a lower symmetric one ($C_Q \sim 80$ kHz and $\eta = 0.6$) in intercalated samples. The centre band of $LiTi_2(PO_4)_3$ is formed by twelve narrow lines between +80 and 0 ppm, denoted with increasing numbers, each arising from the central transition of a different lithium environment (Figure 8). The peak 0 refers to the Li environment without Ti^{3+} cations. Similar observations were obtained in the ^6Li MAS-NMR spectrum of this sample, where a better resolution of components was achieved (see inset).

Below 330 K, the heating of the sample decreases the isotropic shift of ^{7}Li MAS-NMR compo-nents, The paramagnetic shift of components is given by $\Delta\omega/\omega_0= -A_c.< Sz >/\omega_0.h$, where the term A_c/h depends on the electron density at Li ions[40]. Taken into account that components display similar intensi-ty in ^{6}Li and ^{7}Li NMR spectra, relative intensity of components were deduced from ^{6}Li MAS-NMR spectra, where spinning side bands patterns are simplified. Above 350 K, Li motion produced the pro-gressive elimination of spinning sidebands and the collapse of central NMR components. In the case of Al-doped samples, ^{7}Li MAS-NMR spectra are formed by a broad line at about +20 (lithiated) and a nar-row one at 0 ppm (pristine sample), indicating that Li mobility has produced the collapse of NMR com-ponents at room temperature.

Discussion

Structural analysis

The insertion of lithium in $Li_3Ti_{2-x}Al_x(PO_4)_3$ (x= 0 and 0.2) produces reduction of Ti^{4+} to Ti^{3+}, increasing the size of octahedra and expanding the unit cell in an anisotropic way. In lithiated samples, the a-axis decreases from 8.50 to 8.35 Å, but the c-axis increases from 20.73 to 22.75 Å with respect to the pristine sample[28]. These changes are a consequence of different Ti^{4+} (0.74 Å) and Ti^{3+} (0.78 Å) cati-on sizes[39]. In lithiated samples, differences on octahedral cation sizes, Ti^{3+} (0.78 Å) and Al^{3+} (0.53 Å), reduces the *a* axis from 8.38 to 8.36 Å and the *c* axis from 22.87 to 22.75 Å with incorporation of Al in the $Li_3Ti_2(PO_4)_3$ sample.

The reduction of Ti produces small distortions that reduce the symmetry of lithiated samples from R-3c to R-3. As a consequence of the symmetry decrement, the number of Li, Ti,Al and O sites are doubled with respect to pristine samples. However, NMR and ND Rietveld analyses do not show any preference of Al^{3+} cations for a particular octahedron. The increment of the Li content enhanced Li-Li repulsions (distance M1-M3 ~ 3.7 Å), favoring the occupation of M_3/M_3' at the expense of M_1 sites in lithiated samples. In these samples, the occupation of M3 or M3' sites maintains Li-Li distances near 6.2 Å.

The temperature dependence of *a* and *c* axes is completely different in pristine and Li intercalat-ed materials. In the pristine $Li_{1.2}Ti_{1.8}Al_{0.2}(PO_4)_3$ sample, the sample heating increases the *c* axis but af-fects moderately the *a* axis[28]. In the lithiated $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ sample, *a* increases from 8.35 to 8.40 Å, but *c* decreases from 22.80 to 22.73 Å. To explain these differences, it can be assumed that Li occu-pation of M_1 sites produces the thermal expansion of the *c* axis, but that of M_3/M_3' sites favors the ex-

pansion of the *a* axis. On these bases, dimensions of two axes (c/a ratio) could be used to analyze Li occupation of M_1 and M_2 sites.

In general, B_P factors increase but $B_{Ti,Al}$ decreases with Al content, indicating that disorder and cation size affect this parameter in different way. In the case of oxygen thermal factors, B_{O3} is higher than B_{O4}, suggesting that coordination of Li3' (O1, O2, O3, O3) is less stable than that of Li3 (O1, O2, O4, O4). This could explain the lower occupancy and higher mobility of lithium at Li3' sites.

Lithium location

Changes produced in lithium sites were investigated by ^{7}Li MAS-NMR spectroscopy. In lithiated samples, the quadrupole C_Q constant increases from 25 to 80 KHz and asymmetry parameter η from 0 to 0.6 with respect to pristine samples[28]. These changes agree with structural information deduced by Rietveld analysis. In pristine samples, Li ions occupy regular six-fold M1 (*6b* sites) coordinated sites at ternary axes, but in lithiated samples, Li ions occupy two distorted four-fold coordinated M_3/M_3' sites (18f sites) out of axes.

^{7}Li MAS-NMR spectra of Li intercalated samples display lithium components that are shifted with respect to those of pristine samples, because of paramagnetic interactions with Ti^{3+} cations[40]. In lithiated samples, the isotropic paramagnetic term has allowed a better resolution of sites occupied by lithium. In $Li_3Ti_2(PO_4)_3$, twelve components were detected in ^{7}Li MAS-NMR spectra recorded at 300 K. Taken into account structural refinements deduced from ND patterns at 5K, only two Li components, ascribed to fourfold M_3 and M_3' sites, should have been detected. In order to explain NMR results, it must be assumed that Li ions are shifted from fourfold to lower coordinated sites (Figure 9).

The structural analysis of M_2 cavities shows that eight oxygen atoms are located at shorter distances than 3.1 Å. If it is assumed that Li ions are disposed near three-oxygen faces that define M2 cavities, the number of possible positions increases to twelve, what is near to that detected in $Li_3Ti_2(PO_4)_3$ by ^{7}Li MAS-NMR spectroscopy. Differences detected in diffraction and spectroscopic techniques must be ascribed to differences on spatial resolution. In NMR spectroscopy, the resolution of twelve components was based on the increment of the residence time and differences on paramagnetic interactions at different structural sites. In neutron diffraction, lithium density detected at M3 and M3' must correspond to spatial averages of positions occupied by Li ions around each site. In these sites, the coordination of Li ions would not be stable and Li mobility should be favored. This explains the collapse of Li components detected near 350 K (see top of Figure 8). Taken into account that ^{7}Li MAS-NMR spectra of $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ are only formed by two components, ascribed to Li ions in lithiated and pristine sam-

ples, it must be concluded that structural disorder associated with Ti for Al substitution favors Li mobility, impeding at room temperature the detection of twelve NMR components.

In order to explain differences observed in ND and NMR results, structural analyses were performed at increasing temperatures. For that, location of lithium was investigated by Fourier map differences at 100, 300 and 500 K using structural models where Li ions were not included. This analysis showed that occupation of M3/M3' decrease with temperature, remaining the occupation of these sites higher than that of M1 sites (Figure 3). In agreement with NMR results, other sites near M3 and M3' sites were also detected. However, the existence of several small peaks makes the occupation of these sites difficult to be analyzed by Rietvel analysis. To investigate alternative sites, DFT calculations oriented to investigate Li coordination are necessary.

Lithium mobility

In the present work, the temperature dependence of chemical shifts of components affords additional information about Li mobility. Below 330K, the NMR shift of detected components must be ascribed to the variation of the isotropic term of paramagnetic interactions. Above 330K, all components collapse indicating that exchange motions between neighboring sites are more effective than paramagnetic interactions to modify Li NMR spectra (Figure 8). Slow exchanges produce the broadening of the main component; however when the exchange rate increases, the NMR line becomes narrowed. As a result of the Li motion, dipolar and quadrupolar interactions are cancelled, producing the elimination of spinning side bands and the spectral narrowing of the central component. The position of this band is the weighted averaged position of different components.

The analysis of the temperature dependence of oxygen thermal factors (BO2 < BO1< BO4 < BO3) suggest that Li mobility in Li3' (O1, O2, O3, O3) is higher than that in Li3 (O1, O2, O4, O4) sites; however, exchange processes impede its confirmation. In $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ sample, Li mobility is higher than in non-doped one, suggesting that exchange processes are already operative at room temperature (Figure 8). In the Li inserted Al-doped sample, B_{Li} factors measured below 330K are slightly higher than those determined in non doped samples.

The temperature dependence of B_{Li} parameters affords information about local lithium motions. In analyzed compounds, B_{Li} remains constant at low temperatures but increases considerably above 300K. The increment of B_{Li} was detected at lower temperatures, 150K, in non-lithiated samples, indicating that the insertion of lithium increases correlation effects on the Li motion, making mobility of lithium more difficult. In agreement with this fact, the decrease observed in the linewidth of ^{7}Li NMR spectra is produced at higher temperatures in lithiated samples than in pristine samples[24] (bottom of Figure

10). On the other hand, local exchanges of lithium between structural sites are more effective in Al-doped than in non-doped samples, indicating that substitution of Ti by Al improves Li mobility (top of Figure 10).

Conclusions

The lithium insertion into $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ (x= 0 and 0.2) materials produce the anisotropic expansion of the unit cell parameters decreasing the symmetry from R-3c to R-3. Fourier map differences performed on ND patterns proved that Li ions occupy M3/M3' sites inside M2 cavities. The Li arrangement at M3 sites minimize electrostatic repulsions between M1 and M3 sites. The analysis of ^7Li MAS-NMR spectra, however, showed the existence of twelve Li sites that have been ascribed to the occupation of three-oxygen faces that surround M2 cavities. Differences detected in both techniques have been ascribed to different spatial resolution achieved in diffraction and spectroscopic methods.

Lithium mobility was estimated by analyzing the evolution of Li NMR spectra with temperature. Local motion of lithium produces first the collapse of detected components and then the progressive narrowing of the Li signal. The mobility of lithium was improved in Al doped samples. Similar conclusions were deduced from the analysis of Li and O thermal factors. Local structural information deduced by ND and NMR techniques is of special relevance for the optimization of transport properties in NASICON materials.

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Figure captions

Figure 1. Rietveld analysis of ND patterns of the lithiated $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ sample recorded at 5 and 500K. In this plot, Bragg positions, calculated and observed profiles are depicted.

Figure 2. Temperature dependence of unit cell *a* and *c* parameters of $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples.

Figure 3. Fourier map differences calculated at $z/c= 0.047$ (top) and $z/c= 0.33$ (bottom) sections from ND patterns of the $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ sample recorded at 5K (left part) and 500K (right part).

Figure 4. Temperature dependence of B_P and B_{Ti} parameters in $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples.

Figure 5. Temperature dependence of B_O and B_{Li} parameters in $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples.

Figure 6. ^{31}P MAS-NMR spectra of $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples, recorded at 300K. Spectra recorded at 410 K are similar.

Figure 7. ^{27}Al MAS-NMR spectra of the $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ sample recorded at 300 and 400 K. The spectrum of the non-lithiated sample is included as reference.

Figure 8. Temperature dependence of ^7Li MAS-NMR spectra of $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples for indicated compositions. ^6Li MAS-NMR spectra recorded at 300K are given as insets.

Figure 9. Schematic representation of conduction pathways (top) and M2 cavities, where M3 and M3' sites are indicated (bottom).

Figure 10. Temperature dependence of chemical shifts (δ) of components and linewidth ($\upsilon_{1/2}$) of ^7Li NMR spectra of lithiated samples. Data of pristine $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$, $x= 0$ and and 0.2 samples, are included as reference.

Table I. Structural model used for refinement of intercalated $Li_3Ti_{2-x}Al_x(PO_4)_3$ samples.

Atom	Wickoff position	x/a	y/b	z/c	Occ
Li3	18f	0.030	0.319	0.045	0.72
Li3'	18f	0.055	0.373	0.117	0.34
Ti1	6c	0	0	0.145	1
Ti2	6c	0	0	0.348	1
P	18f	0.291	y/b ~0	0.250	1
O1	18f	0.167	0.216	0.089	1
O2	18f	0.136	0.229	0.398	1
O3	18f	0.197	0.992	0.193	1
O4	18f	0.911	0.145	0.299	1

Table II. Structural parameters deduced from ND patterns of lithiated $Li_3Ti_{2-x}Al_x (PO_4)_3$ samples. Distances P-O, Ti,Al-O and Li-O distances are given in Angstroms.

Sample/T		4K	100K	200K	300K	400K	500K
Li3-O	x=0	-	2.035	2.034	2.035	2.055	-
	x=0.2	2.030	2.032	2.036	2.041	2.056	2.073
Li3'-O	x=0	-	2.165	2.164	2.180	2.192	-
	x=0.2	2.161	2.160	2.161	2.165	2.170	2.182
(Ti, Al)1-O	x=0	-	2.039	2.040	2.045	2.042	-
	x=0.2	2.022	2.021	2.024	2.025	2.023	2.027
(Ti, Al)2-O	x=0	-	2.041	2.041	2.037	2.043	-
	x=0.2	2.030	2.032	2.031	2.032	2.032	2.033
P-O	x=0	-	1.535	1.535	1.534	1.530	-
	x=0.2	1.531	1.531	1.530	1.530	1.531	1.529