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On the influence of the cation vacancy on lithium conductivity of $Li_{1+x}R_xTi_{2-x}(PO_4)_3$ Nasicon type materials

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ABSTRACT

Structural features responsible for outstanding Li conductivity of $Li_{1+x}R_xTi_{2-x}(PO_4)_3$ (LRTP) Nasicon samples ($0 \le x \le 0.6$ and R = Al, Sc, In) prepared by the ceramic route have been analyzed by XRD, ND, MAS-NMR and impedance spectroscopy. The structural analysis showed that all samples display the rhombohedral (S.G. R-3c) symmetry. The structural site occupancy has been investigated by ^{7}Li, $^{27}Al/^{45}Sc$ and ^{31}P MAS-NMR spectroscopy. The Fourier map differences deduced from high-resolution ND patterns of LAlTP samples revealed that Li ions occupy Li1 sites and to a lower extent Li3/Li3′ sites inside Li2 cavities. The location of Li at 3 sites minimizes electrostatic Li (Li1–Li3) repulsions, enhancing local mobility in LRTP samples. A maximum of conductivity was detected for $0.2 \le x \le 0.4$, when a significant amount of vacant Li1 sites was created at the intersection of conduction pathways. The increment of vacant Li1 sites explains the existence of two Li motion regimes detected by ^{7}Li NMR and impedance spectroscopy. In the low temperature regime, activation energy and migration entropy of Li have been related by the Meyer–Neldel relationship. In the high-temperature regime, further investigation is required to assess the role of vacancy in lithium conductivity.

1. Introduction

Lithium batteries (LIBs) remain the most promising electrical energy storage systems for many emerging technologies, from portable electronics to electric vehicles (EVs), hybrid vehicles (HEVs) and smart grids [1], by offering significantly improved performances, energy efficiency, and reliability, permitting a drastic reduction of fuel consumption and emissions.

Among active materials for all-solid-state lithium ion batteries (ASS-LIBs), the solid electrolyte is one of the most important key components that could improve electric performances and security. These electrolytes must meet a series of requirements before they can be used, including high conductivity, large number of vacancies and charge carriers, wide potential window and low electronic conductivity [2]. Recently, lithium transition metal phosphates have found application in the field of electrochemical energy storage, especially those with Nasicon [3] structure, because of their good electrochemical performances and capability to answer safety concerns surrounding oxide chemistry.

In the past decades, extensive investigations have been carried out on Nasicon-type lithium ion conductors with formula of $LiM_2(PO_4)_3$, M = Ge, Ti, Sn, Zr, Hf [4–11]. Among them, $LiTi_2(PO_4)_3$ (LTP) based materials present the best channel size for Li ion migration (Fig. 1a). When titanium is partially substituted by trivalent R cations (R = Al, Ga, In, Fe, Sc, etc.) lithium conductivity increases in a significant way [12–19]. This increment has been ascribed to the creation of vacant Li1 sites at the intersection of conduction pathways. Among analyzed $Li_{1+x}Ti_{2-x}R_x(PO_4)_3$ series [12,14,16–18,20], the best conductivity was reported for $x \approx 0.3$ in LAlTP samples, where Ti^{4+} is partially substituted by Al^{3+} ($\sigma_{300K} > 10^{-3}$ S cm^{-1}).

In the present work, electric characteristics of LTP samples doped with trivalent Al^{3+}, Sc^{3+} or In^{3+} cations will be analyzed, investigating the enhancement of Li conductivity in the $Li_{1.3+x}Al_{0.3}R_xTi_{1.7}(PO_4)_3$ series. In this study, structural features deduced by ^{7}Li, $^{27}Al/^{45}Sc$ and ^{31}P MAS-NMR spectroscopy will be compared with those deduced by diffraction techniques. Finally, Li mobility deduced by impedance spectroscopy (IS) will be compared with that deduced by NMR results of different analyzed series.

2. Experimental

$Li_{1+x}R_xTi_{2-x}(PO_4)$ samples (denoted hereafter LRTP), with R = Al, Sc, In, were prepared by heating stoichiometric mixtures of Li_2CO_3, $(NH_4)_2HPO_4$, R_2O_3 and TiO_2 at increasing temperatures in the 573–1373 K interval, following the procedure described previously [14,16,17]. The composition of prepared samples covers x values between 0 and 0.3 in binary series and x values between 0 and 0.6 in ternary samples (Al = 0.3/structural formula), see Table 1.

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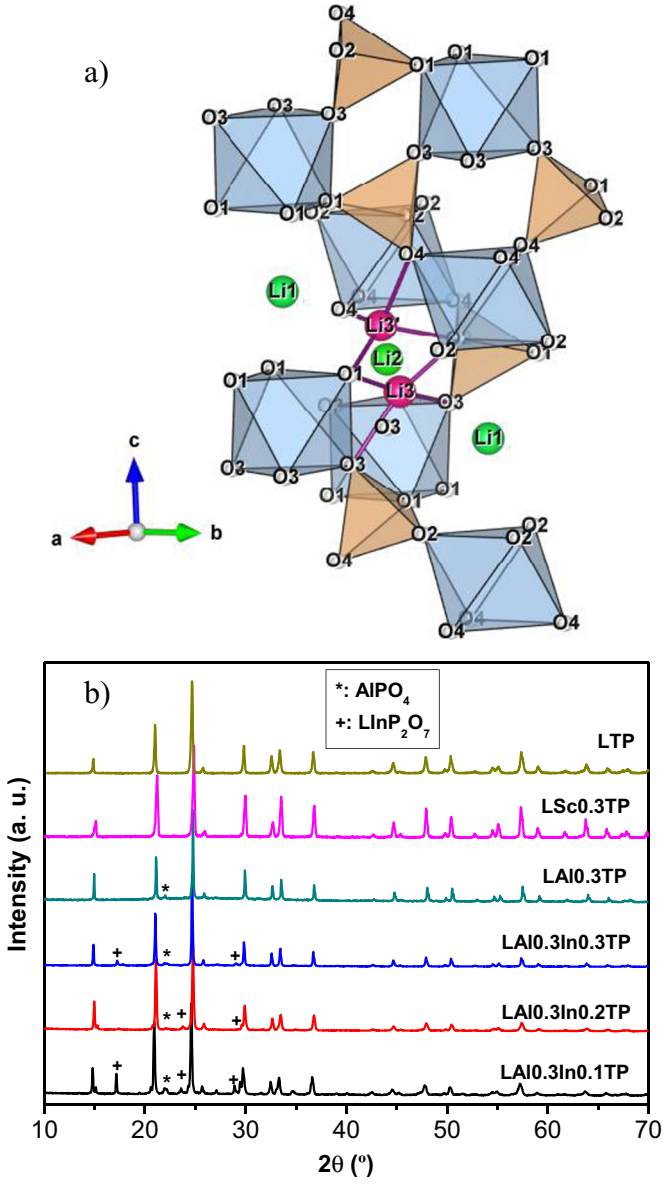

Fig. 1. a) Nasicon structure of LAlTP sample displaying different lithium sites and b) XRD patterns of analyzed samples recorded at room temperature.

X-ray diffraction (XRD) patterns were recorded with the Cu-K_α radiation ($\lambda_{K\alpha} = 1.5418$ Å) in a PW 1050/25 Phillips apparatus. Unit cell parameters of samples were determined with the FullProf program (Le Bail technique) [21]. In order to increase the sensitivity to oxygen and lithium positions, neutron diffraction (ND) patterns of LAlTP samples, collected in the high-resolution powder SPODI diffractometer of the FRM-II reactor (Garching, Munich, Germany), were analyzed [19]. In this analysis, a wavelength of 1.548 Å was selected from the Ge monochromator. For Rietveld analysis, ND patterns collected for 4 h over the 5–160 2θ° range with a step size of 0.05° in the temperature range of 100–500 K were analyzed [19].

^{7}Li, ^{27}Al, ^{31}P, and ^{45}Sc NMR spectra were recorded at room temperature in a MSL-400 Bruker spectrometer (9.4 T). The frequencies used for ^{7}Li (^{6}Li), ^{27}Al, ^{45}Sc and ^{31}P and signals were 155.50 (58.88), 100.4, 97.2 and 161.97 MHz, respectively. ^{7}Li (^{6}Li) and ^{31}P NMR signals were obtained after π/2 (3 and 4 μs) and ^{27}Al/^{45}Sc NMR signals after π/8 (1 μs) single pulse irradiations, with a recycling time of 10 s. During spectrum recording, sample was spun at 2 kHz (^{7}Li and ^{6}Li signals) and 4 kHz (^{31}P and ^{27}Al/^{45}Sc signals) around an axis inclined at 54°44′ with respect to the external magnetic field (MAS technique). The number of scans was in the range of 100–800. ^{7}Li, ^{27}Al, ^{45}Sc and ^{31}P NMR chemical shifts were referred to 1 M LiCl, 1 M $AlCl_3$, 1 M $Sc(NO_3)_3$ and 85% H_3PO_4 aqueous solutions. The fitting of NMR spectra was performed with the Bruker WINFIT software package [22]. 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.

Impedance measurements, recorded between 100 and 500 K in the wide frequency range (20 Hz to 3 GHz), were performed on cylindrical pellets of 6 mm diameter and approximately 1 mm thickness. Pellets were first compacted by cold pressing at 0.5 MPa, and then sintered at 1273 K for 12 h. For electric measurements, gold electrodes were deposited by sputtering on two faces of pellets. The sample was placed in a JANIS VPF 750 cryostat, allowing 4L-configuration measurements. For low frequency measurements (20 Hz–2 MHz), an automatically controlled Agilent Precision LCR E4980-A Analyzer was used. High frequency measurements (1 MHz–3 GHz) were carried out using an automatically controlled Agilent E4991-A RF Impedance/Material Analyzer.

Table 1
Al contents incorporated in Nasicon samples, as deduced from the quantitative analysis of ^{27}Al and ^{31}P NMR spectra of LRTP series.

Binary systems			Ternary systems			
LAl_xTP			$LAl_{0.3}In_xTP$			
x	Al(^{27}Al)	Ti(^{31}P)	x	Al(^{27}Al)	In(^{31}P)	Ti(^{31}P)
0.0	–	2.0	0.0	–	–	2.0
0.2	0.17	1.83	0.1	0.24	0.08	1.68
0.3	0.27	1.73	0.2	0.28	0.21	1.51
$LSc_{0.3}TP$			0.3	0.27	0.26	1.48
0.3	0.29	1.71				

3. Results

3.1. Structural analyses

XRD patterns of analyzed samples (Fig. 1b) annealed at 950 °C were matched with those reported for the Nasicon R-3c $LiTi_2(PO_4)_3$ sample (JCPDS 35-0754) [23]. For x > 0.3, small reflections associated with aluminum phosphate were detected in LAlTP samples. As the R content increases, hexagonal a and c parameters change according to octahedral compositions (see Table 1). In LAlTP samples, diffraction peaks shift towards lower angles as a consequence of smaller Al^{3+} radius (0.53 Å); but they shift towards higher angles in LScTP/LInTP, because of bigger radii of Sc^{3+}/In^{3+} (0.74/0.80 Å) compared to Ti^{4+} ions (0.60 Å) [24]. In the $LAl_{0.3}In_xTP$ system, a small amount of pyrophosphate secondary phase was also detected; similar results were also found for Sc doped samples [25].

To illustrate Li site occupation, ND patterns were analyzed with the Rietveld technique in LAlTP samples displaying the highest conductivity [16,19]. The amount of Al incorporated into the Nasicon's framework was lower than nominal ones. In the case of $Li_{1.2}Al_{0.2}Ti_{1.8}(PO_4)_3$ the amount of Al was 0.17, but in the case of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ the amount of Al was 0.27, indicating that the amount of segregated $AlPO_4$ increases with Al concentration (see Table 1) [16,19]. In order to investigate Li sites, Fourier map differences between observed data calculated from structural models without Li and with Li occupying Li1 sites were calculated. In both cases, negative peaks for lithium at Li1 (0, 0, 0) and Li3 (0.06, 0.34, 0.08) positions were detected (Fig. 2). In this study, it was showed that Li occupation of Li1 sites decreases with the amount of Al/Li incorporated. The inclusion of Li at these two sites improved considerably structural refinements [19].

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