Experimental Report

Proposal: **5-24-541** **Council:** 4/2014

Title: Lithium diffusion in NASICON-type structures

This proposal is a new proposal

Researh Area: Materials

Main proposer: **MONCHAK Mykhailo**

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Samples: Li1+xTi(Zr)2-xAlx(PO4)3

Instrument	Req. Days	All. Days	From	To
D2B	0	4	28/11/2014	02/12/2014

Abstract:

The search for stable and incombustible inorganic solid electrolytes with high lithium ion conductivity is currently one of primary issues in battery research aiming at higher energy densities. The lithium based NASICON-type compounds with general formula LiM2(PO4)3 and M=Ge, Ti, Sn, Hf, Zr etc. were
considered as promising candidates for their applications as solid lithium-ion conducting electrolytes. Their characterization is an important task of further material development, revealing the underlying Li-ion conduction mechanisms and identifying the most relevant transport limitations. The direct determination of diffusion pathways by bulk property measurements of polycrystalline samples is not possible, since it requires the accurate knowledge of crystal structure. The weaknesses of X-ray diffraction for accurate lithium determination make neutron powder diffraction indispensable. The proposed set of high-temperature neutron powder diffraction data on Al-doped LiZr(Ti)2(PO4)3 NASICON-type compounds from D20 in its high – resolution mode will provide the experimental background for a systematic development of solid electrolytes with enhanced Li-ion conductivity.

Lithium diffusion in NASICON-type structures (proposal 5-24-541)

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Lithium-ion batteries are important for a wide range of applications – from small devices being used every day, like phones or laptops, to electric vehicles. Battery performance crucially depends on the materials used, so the development of new materials is an important issue. The search for new electrode materials with increased energy/power density, better stability, higher voltage, etc. is one of the major challenges for Li-ion energy storage technology. Liquid electrolyte (typically a solution of ethylene carbonate (EC), dimethyl carbonate (DMC) and the Li salt, lithium hexafluorophosphate ($LiPF_6$) [1]) commonly used in commercial batteries, is yet another bottleneck of Li-ion technology due to its flammability and limited stability. One of the recent trends in Li-ion batteries investigation is a search for solid lithium electrolyte which can substitute organic solvents and, thus, simplify the cell design, improve safety and durability. Inorganic ceramic is one of possible materials for such purpose [2]. Among a few promising candidates for solid-state lithium electrolytes the complex lithium phosphates with NASICON-type structure (a class of 3D framework compounds) and general formula $LiM_2(PO_4)_3$ and M=Ge, Ti, Sn, Hf, Zr etc. attract considerable interest. The introduction of different dopant elements often increases ionic conductivity of the compounds. For example, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with x=0.3 (LATP) possesses the ionic conductivity ~10^{-3} S/cm, about three orders higher than undoped $LiTi_2(PO_4)_3$ [3,4].

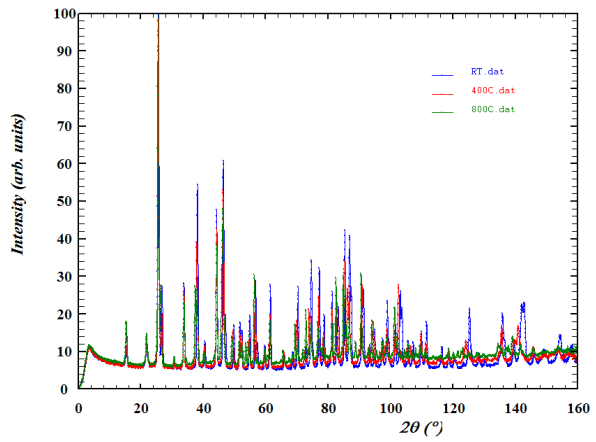

Fig.1 Diffraction patterns of the sample P423-900 ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) at RT, 400 and 800 ºC.

To study the role of dopant element on the Li-ion conduction mechanism compounds $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ and $LiE_xM_{2-x}(PO_4)_3$ (where E = Si, Al, Ge or Ti and M = Ti or Zr) were chosen. Neutron diffraction patterns of 7 samples (**P423-900** ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$), **P422-1300** ($LiSi_{0.3}Ti_{1.7}(PO_4)_3$), **P700-900** ($LiGe_{0.3}Ti_{1.7}(PO_4)_3$), **P800-1200**, **P800-900** ($LiTi_{0.3}Zr_{1.7}(PO_4)_3$), **P801-900** ($Li_{1.3}Al_{0.3}Zr_{1.7}(PO_4)_3$), **P418-900** ($Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$)) were collected at D2B diffractometer. Samples P423-900, P422-1300, P700-900 and P800-1200 were measured at high temperatures: first one in the range RT-1000 ºC, three other - at RT-800 ºC. P801-900, P800-900 and P418-900 were measured only at room temperature.

Rietveld refinement of the patterns was performed using Fullprof software package. The peak profile shape was described using pseudo-Voigt function. The background of the diffraction patterns was fitted using a linear interpolation between selected data points in non-overlapping regions. The scale factor, lattice parameters, fractional coordinates of atoms and their isotropic displacement parameters, zero angular shift, profile shape parameters and half width (Caglioti) parameters were allowed to vary during fitting.

In spite of the data analysis, which is in progress the lithium diffusion is intended to be studied by the combination of structural analysis, maximum entropy method and anharmonic refinement techniques (similar to an approach applied by us earlier and reported in [5]). Due to the low scattering power of aluminum the obtained experiments will be supplemented by undergoing

lithium and aluminum MAS NMR and high-temperature X-ray powder diffraction studies. Obtained results will reveal the role of aluminum in the conduction process and form a base for further systematic optimization of NASICON-type compounds for applications in all-solid-state batteries.

Table 1. Structural parameters of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (the sample P 423-900).

a = 8.5031(2) Å, c= 21.0241(6) Å					
Atom	Wyckoff	x	y	z	Biso, Å^2
Li1	6b	0	0	0	12.1 (9)
Li1	36f	0.07	0.034	0.07	12.1 (9)
Ti1	12c	0	0	0.1428(3)	0.94(9)
Al1	12c	0	0	0.1428(3)	0.94(9)
P1	18e	0.2885(3)	0	0.25	1.51(4)
O1	36f	0.1802(2)	0.9884(2)	0.19067(6)	2.43(3)
O2	36f	0.1910(2)	0.1645(2)	0.08308(7)	1.76(3)
U	V	W	Asym1	Asym2	
0.127(4)	-0.248(7)	0.238(3)	0.057(6)	-0.009(2)	
Phase fractions, % w/w	$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ Sp. gr. $R\bar{3}c$		$AlPO_4$ Sp. gr. C 2221		
	98.7(7)		1.3(2)		
Fit residuals	Rp	Rwp	χ^2		
	3.56	4.60	3.22		

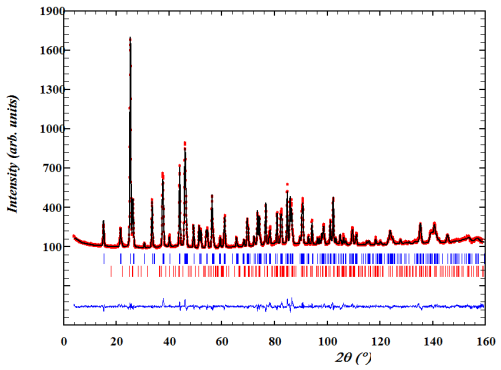

Fig. 2. Refinement of diffraction pattern of the sample P423-900 at 400 ºC

References

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[3] H. Aono, E. Sugimoto, Y. Sadaoka et al., J. Electrochem. Soc. 136 (2) (1989) 590.
[4] Y. Kobayashi, T. Takeuchi, M. Tabuchi et al., J. Power Sources 81–82 (1999) 853.
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