Solid-State NMR Studies on Li^+ Ion Dynamics and Structure of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$

C. Vinod Chandran,[1] Sylke Pristat,[2] Elena Witt,[1] Frank Tietz,[2] Paul Heitjans[1]

[1]Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Callinstr. 3 - 3a, 30167 Hannover, Germany
[2]Forschungszentrum Jülich GmbH, Jülich, Wilhelm-Johnen-Straße 52425 Jülich, Germany

Corresponding author: Paul Heitjans, E-Mail: heitjans@pci.uni-hannover.de

Solid-state nuclear magnetic resonance (NMR) studies of Li^+ ion dynamics based on spin-lattice relaxation (SLR) experiments on lithium aluminum titanium phosphates (LATP) are reported. The samples were synthesized by conventional solid-state reaction using stoichiometric amounts of Li_2CO_3, TiO_2, $(NH_4)H_2PO_4$ and Al_2O_3 at high pressure and heated in a Pt crucible up to 1000 °C for 12 hours [1-4]. LATP with different lithium contents is studied with ^{7}Li SLR measurements (in the laboratory frame (T_1) and rotating frame ($T_{1\rho}$)) as well as multinuclear magic-angle spinning (MAS) NMR experiments. The solid-state SLR experiments were done with a Bruker 600 AV-III spectrometer at a ^{7}Li Larmor frequency of 233 MHz over a wide range of temperature. The high-temperature range was achieved using LASER-heating in a 7mm MAS probe at 3 kHz spinning. ^{7}Li, ^{27}Al and ^{31}P MAS NMR measurements were done using a 4mm MAS probe at 7-11 kHz spinning frequencies.

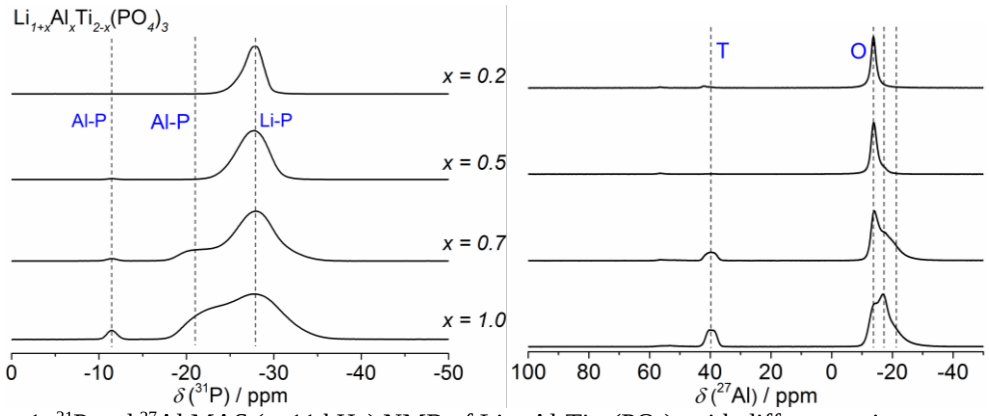

Fig. 1: ^{31}P and ^{27}Al MAS (at 11 kHz) NMR of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with different cation contents.

From the diffusion induced ^{7}Li NMR SLR rates Li jump rates and activation energies were deduced and the LATPs were found to be fairly fast ion conductors. The different compositions provided signature NMR signals for different cation stoichiometries (Fig. 1). From the various NMR methods, a detailed characterization of LATPs is obtained, with information on local ion dynamics and many structural aspects.

References

[1] B. Key, D. J. Schroeder, B. J. Ingram, J. T. Vaughey, *Chem. Mater.* **24** (2012) 287-293.
[2] S. Duluard, A. Paillassa, L. Puech, P. Vinatier, V. Turq, P. Rozier, P. Lenormand, P. L. Taberna, P. Simon, F. Ansart, *J. Eur. Ceram. Soc.* **33** (2013) 1145-1153.
[3] H. Morimoto, H. Awano, J. Terashima, Y. Shindo, S. Nakanishi, N. Ito, K. Ishikawa, S. Tobishima, *J. Pow. Sources* **240** (2013) 636-643.
[4] E. Dashjav, R. Hermann, F. Tietz, *poster presentation, this conference*.