NASICON MATERIALS – A LONG NEGLECTED CLASS OF SOLID ELECTROLYTES

Frank Tietz, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Germany
f.tietz@fz-juelich.de
Qianli Ma, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1) ; Jülich Aachen Research Alliance, JARA-Energy ; Helmholtz-Institute Münster, c/o Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
Marie Guin, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1) ; Jülich Aachen Research Alliance, JARA-Energy ; Helmholtz-Institute Münster, c/o Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
S. Naqash, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1) ; Jülich Aachen Research Alliance, JARA-Energy ; Helmholtz-Institute Münster, c/o Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
O. Guillon, Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1) ; Jülich Aachen Research Alliance, JARA-Energy ; Helmholtz-Institute Münster, c/o Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Key Words: solid electrolyte, NASICON, ionic conductivity

The so-called NASICON materials $AT_2P_3O_{12}$ (A = alkaline metal, T = tetravalent transition metal) are known since the 1970s [1] and are derived from the first "Na^+ super-ionic conductor", $Na_3Zr_2Si_2PO_{12}$, of this group of materials. The aims of current investigations are on the one hand the better understanding of the ionic conduction and on the other hand the search for new materials with very high ionic conductivity.

For this purpose, new and simple synthesis methods have been developed, which deliver very homogeneous powders with reduced temperatures for the preparation of ceramics. In this way a lithium ion conductor with the composition $Li_{1.5}Al_{0.5}Ti_{1.5}P_3O_{12}$ was manufactured. After sintering to highly dense ceramics a total conductivity of 0.7 mS/cm was achieved at room temperature [2] and therefore this material belongs to the best known solid oxidic Li^+ ion conductors. NMR and impedance spectroscopy investigations [3-5] have shown that the bulk conductivity amounts to 3-5 mS/cm and that the grain boundaries determine the quality of the material.

In the case of Na^+ ion conductors, the prototype $Na_3Zr_2Si_2PO_{12}$ was newly synthesized and gave a previously not achieved conductivity of 1 mS/cm [6]. The modification of the composition by substitution with scandium delivered conductivities of 0.8 mS/cm ($Na_{3.4}Sc_2Si_{0.4}P_{2.6}O_{12}$) [7] and 4 mS/cm ($Na_{3.4}Zr_{1.6}Sc_{0.4}Si_2PO_{12}$) [8]. The latter composition possesses one of the highest known Na^+ ion conductivities of oxide ceramics and reaches the conductivity of liquid electrolytes. The mentioned compositions confirm the empirical criteria which are necessary for achieving high ionic conductivities in NASICON materials [9].

References:

[1] H. Y. P. Hong, Mater. Res. Bull. 11 (1976) 173-182; H. Y. P. Hong, J. B. Goodenough, J. A. Kafalas, Mater. Res. Bull. 11 (1976) 203-220
[2] Q. Ma, Q. Xu, C.-L. Tsai, F. Tietz, O. Guillon, J. Am. Ceram. Soc., (2016), in press
[3] V. Epp, Q. Ma, F. Tietz, M. Wilkening, Phys. Chem. Chem. Phys., 17 (2015) 32115-32121
[4] S. Breuer, D. Prutsch, V. Epp, Q. Ma, F. Preishuber-Pflügl, F. Tietz, M. Wilkening, J. Mater. Chem. A, 3 (2015) 21343-21350
[5] D. Rettenwander, A. Welzl, S. Pristat, F. Tietz, S. Taibl, G. J. Redhammer, J. Fleig, J. Chem. Mater. A, 4 (2016) 1506-1513
[6] S. Naqash, Q. Ma, Tietz, O. Guillon, in preparation
[7] M. Guin, F. Tietz, O. Guillon, in preparation
[8] Q. Ma, M. Guin, S. Naqash, C.-L. Tsai, F. Tietz, O. Guillon, in preparation
[9] M. Guin, F. Tietz, J. Power Sources, 273 (2015) 1056-1064