Mg^{2+} doping effect on ionic conductivity of Li_1,15Zr_1,85Y_0,15(PO_4)_3 Nasicon-type solid electrolyte for all-solid-state lithium ions batteries

Adriana Castillo, Saïd Yagoubi, Olivier Rapaud, Nicolas Pradeilles, Thibault Charpentier, Eddy Foy, Hicham Khodja

Mg^{2+} doping effect on ionic conductivity of $Li_{1,15}Zr_{1,85}Y_{0,15}(PO_4)_3$ Nasicon-type solid electrolyte for all-solid-state lithium ions batteries

Adriana Castillo[1], Saïd Yagoubi[1], Olivier Rapaud[2], Nicolas Pradeilles[2], Thibault Charpentier[1], Eddy Foy[1], Hicham Khodja[1]

[1] NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif sur Yvette Cedex, France

[2] IRCER, UMR CNRS 7315, 12 rue Atlantis, 87068 Limoges Cedex, France

Solid electrolytes with Nasicon structure are already envisioned as promising Li^+ conductive materials for all-solid-state batteries with good chemical stability in ambient atmosphere and wide electrochemical stability window [1] [2] . Li^+ ionic conductivity of ~10^{-4} S/cm at room temperature was achieved for $Li_{1,15}Zr_{1,85}Y_{0,15}(PO_4)_3$ due to stabilization of better conductive rhombohedral phase (alpha) toward orthorhombic phase (beta) by Y^{3+} doping of Zr sites in the structure [2], [3]. Here we examine the impact of Mg doping and evaluate the potential Li^+/Mg^{2+} conductivity in these structures for hybrid « Li^+/Mg^{2+} » all-solid-state batteries, already demonstrated in conventional batteries with liquid electrolyte [4].

Several Mg^{2+} doped Nasicon samples were synthetized by modified Pechini route, and the gels were heated from 350°C to 1200°C under air with intermediate grindings. XRD was used to follow the synthesis and identify the formed phases depending on the doping level. ^6Li and ^{31}P MAS NMR will be used to evaluate the ions sites occupancy on the different samples. Ionic conductivity measurements were done by Electrochemical Impedance Spectroscopy on gold sputtered samples sintered by Spark Plasma Sintering method with high relative density (>95%).

We found that Mg^{2+} doping hinders the alpha phase formation, but at the same time both Li^+ and Mg^{2+} are suspected to contribute to the conductivity in this solid electrolyte material. Further analysis will be held to study the Li^+ and Mg^{2+} diffusions in these materials using post-mortem ion beam analysis on half-cells with Mg metal or Li metal anodes.

[1] N. K. Anuar, S. B. R. S. Adnan, and N. S. Mohamed, "Characterization of Mg0.5Zr2(PO4)3for potential use as electrolyte in solid state magnesium batteries," *Ceram. Int.*, vol. 40, no. 8 PART B, pp. 13719–13727, 2014.

[2] H. Xu, S. Wang, H. Wilson, F. Zhao, and A. Manthiram, "Y-Doped NASICON-type LiZr2(PO4)3Solid Electrolytes for Lithium-Metal Batteries," *Chem. Mater.*, vol. 29, no. 17, pp. 7206–7212, 2017.

[3] Y. Li, M. Liu, K. Liu, and C. A. Wang, "High Li+conduction in NASICON-type Li1+xYxZr2-x(PO4)3at room temperature," *J. Power Sources*, vol. 240, pp. 50–53, 2013.

[4] Y. Cheng *et al.*, "Rechargeable Mg-Li hybrid batteries: Status and challenges," *J. Mater. Res.*, vol. 31, no. 20, pp. 3125–3141, 2016.

Presenting author:

Adriana Castillo, Email: adriana.castillo@cea.fr

2015- 2018: PhD candidate at NIMBE/ IRAMIS in CEA Saclay, Gif-sur-Yvette, France.
Development and study of solid electrolyte materials for all-solid-state batteries.

2011-2015: Master and bachelor, Grenoble Institute of technology, Grenoble, France.