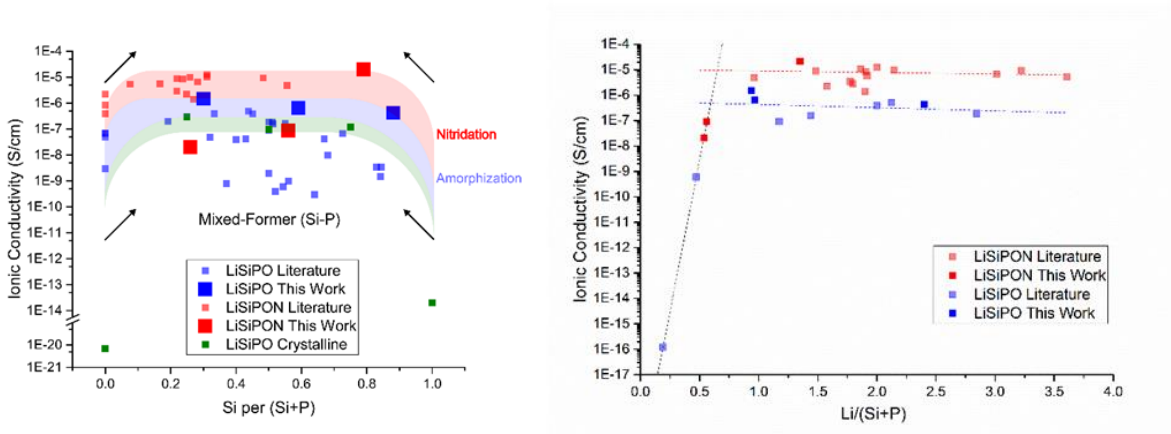
Promises and challenges in the preparation of highly conductive thin film electrolytes for all-solid-state Li batteries: LiSiPO(N) glasses as a case study

Theodosios Famprikis [a,b], Brigitte Pecquenard [b], Frédéric Le Cras [a]
[a] *Univ. Grenoble Alpes, CEA, LETI, F-38000 Grenoble, France*
[b] *CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France*

E-mail: frederic.lecras@cea.fr

Current all-solid-state thin film lithium batteries available on the market are using glassy lithium phosphorus oxynitride (LiPON) as the electrolyte. This ionic conducting material has been considered so far an optimal trade-off in terms of ionic conductivity (10^{-6} S·cm^{-1} at 25°C), chemical reactivity, compatibility with the Li metal anode, and processability for microbattery applications [1]. Recent evolutions towards Li-ion systems and insisting demands for less resistive cells have motivated renewed studies about more conductive (~10^{-5} S·cm^{-1}), but *a priori* less electrochemically stable materials such as LiSiPO(N) glasses [2-3]. This work reports for the first time the preparation of such materials by radio-frequency magnetron sputtering of single-phase crystalline $Li_{3+x}Si_xP_{1-x}O_4$ targets (γ-Li_3PO_4 - Li_4SiO_4 system [4-5]). Resulting amorphous thin film electrolytes exhibit an enhanced conductivity close to the value of LiPON, due to the presence of both phosphate and silicate building units (mixed-former effect). Reactive sputtering under N_2 leads to oxynitride (LiSiPON) thin films with a maximum Li^+ conductivity of 2.1·10^{-5} S·cm^{-1} (E_a=0.42 eV), about one order of magnitude higher than LiPON. The present results are considered in the framework of available literature in order to determine the influence of Si:P and Li:(Si+P) compositional ratios on the ionic conductivity. Parallel to these considerations, the use of highly Li^+ conductive $Li_{3+x}Si_xP_{1-x}O_4$ targets has revealed significant accumulation of Li_3P and Li_2O on their surface under the form of thick dark rings, during the sputtering process. The potential origins of this particular phenomenon, its influence on film composition are discussed. Finally, possible variations of the present sputter deposition process to get a better monitoring and stability are proposed.



(a) Li^+ conductivity of $Li_{3+x}Si_xP_{1-x}O_4$ crystalline target materials and related amorphous thin films obtained by sputtering. (b) Ionic conductivity with increasing Li:(Si+P) ratio to display composition/percolation threshold.

References:
[1] J. B. Bates, Solid State Ionics 53-56 (1992) 647–654.
[2] J. B. Bates, N. J. Dudney, B. C. Sales, J. D. Robertson, R. A. Zuhr, G. R. Gruzalski, C. F. Luck, MRS Proc. 210 (1990) 569.
[3] S.-J. Lee, J.-H. Bae, H.-W. Lee, H.-K. Baik, S.-M. Lee, J. Power Sources 123 (2003) 61–64.
[4] R. A. Huggins, Electrochim. Acta 22 (1977) 773–781.
[5] Y. Deng, C. Eames, J. N. Chotard, F. Lalère, V. Seznec, S. Emge, O. Pecher, C. P. Grey, C. Masquelier, M. S. Islam, J. Am. Chem. Soc. 137 (2015) 9136–9145.