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Ilyass Ghandari, Nicolas Gauthier, Sylvain Poulet, Mikhael Bechelany,
Messaoud Bedjaoui

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ALD for advanced lithionic devices: Hybrid ultrathin Solid-State Electrolytes.

Ilyass GHANDARI¹, Nicolas GAUTHIER¹, Sylvain POULET¹, Mikhael BECHELANY², Messaoud BEDJAOU¹

¹ CEA Leti, 38000 Grenoble, France

² IEM UMR 5635, CNRS, 34090, Montpellier, France

ilyass.ghandari@cea.fr

Innovative micro-supercapacitors (MSCs) such as LiPON based MSCs are emerging to address the technological challenges faced at higher frequencies (>kHz), especially energy harvesting and storage, which requires efficient materials coupled with improved microfabrication techniques to unlock the full potential of such devices. In this way, conformal and self-limiting surface reactions enabled by Atomic Layer Deposition (ALD) give great advantages to form and optimize Lithium based thin films compatible with complex geometries. Here in, a multidisciplinary approach was conducted to develop the thermal ALD process, characterize the physico-chemical properties and evaluate the electrical performances of nano-hybrid Solid State Electrolytes (SSE).

The thermal ALD process for ultrathin LiPON films (<25nm) is realized using Li-Bis(trimethylsilyl)amide (LiHMDS) and Diethylphosphoramidate (DEPA) precursors in a deposition temperature range 300–350°C. To further optimize LiPON's electrochemical performances, Trimethyl Aluminium (TMA) and H₂O were pulsed to incorporate Al₂O₃ in SSE films. Ellipsometry was used to calibrate the growth rate of LiPON-based films. The microstructure was analyzed by X-Ray Diffraction (XRD) to highlight the amorphous nature of the thin films, indicating that the Al₂O₃ incorporation preserves favorable amorphous structure, which is a key characteristic for achieving excellent electrochemical performances [1]. The XPS spectra show typical core peaks (Li_{1s}, P_{2p}, O_{1s}, N_{1s}, Al_{2p}) corresponding to different LiPON based samples. The analysis reveals that Al₂O₃ insertion seems to impact the nitrogen environment. From N1s spectra (Fig.1), the peaks present two main components located at 397 eV and 399 eV, attributed respectively to a divalent nitrogen state (N_d) and a trivalent nitrogen state (N_t) [1], whose proportion evolves as a function of Al₂O₃ incorporation. Thus, the concentration of divalent nitrogen becomes predominant over trivalent nitrogen, inducing an increase in the N_d/N_t fraction when more Al₂O₃ is introduced. This variation has frequently been reported as a major factor in improving Li-ion mobility [1]. The Electrochemical Impedance Spectroscopy (Fig.2) addresses the changes in Li-ion conductivity of the LiPON films upon addition of Al₂O₃ concentration.

This work provides a solid ALD approach with promising potential to optimize the electrical performances (ie Li⁺ mobility, areal capacitance etc) in ultrathin SSE, shedding light on the application of such hybrid microstructures in several Lithionic devices such as micro-supercapacitors, micro-batteries and transistors.

[1] ACS Appl.Mater.Interfaces2016,8,11,7060–7069

Supporting Information

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ilyass.ghandari@cea.fr

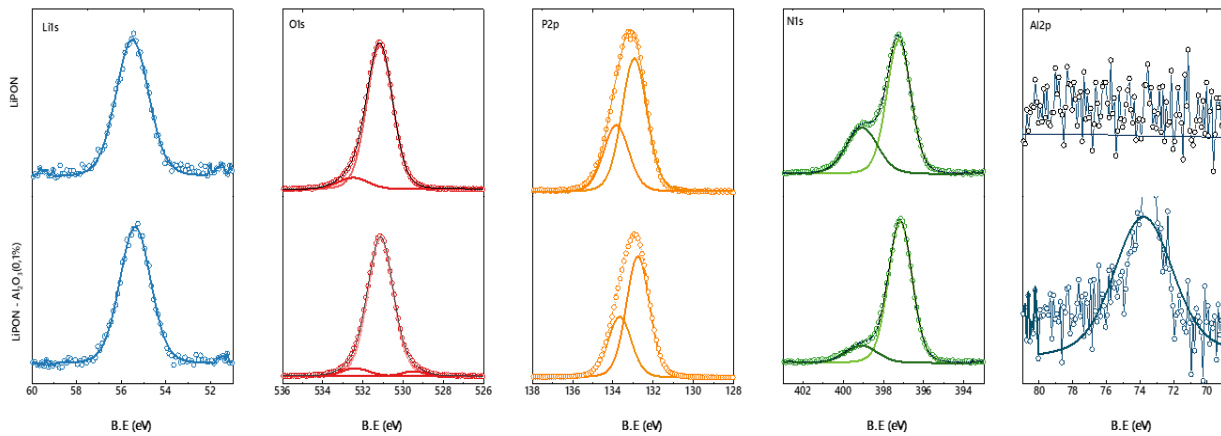


Fig 1 : Typical core peaks (Li1s, P2p, O1s and N1s) corresponding to two different LiPON samples : LiPON (reference) and LiPON Al₂O₃ (0,1%)

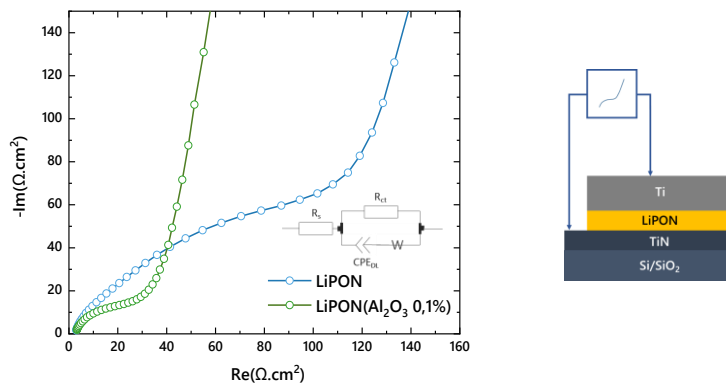


Fig 2: Nyquist plots of electrochemical impedance spectroscopy (EIS) of two samples tested: LiPON (reference) and LiPON Al₂O₃(0,1%), for a frequency range of 1Hz - 1MHz, in a MIM structure Ti/LiPON/TiN.