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► **To cite this version:**

Ilyass Ghandari, Nicolas Gauthier, Sylvain Poulet, Mikhael Bechelany, Messaoud Bedjaoui. ALD for advanced lithionic devices: Hybrid ultrathin Solid-State Electrolytes. AVS ALD/ALE 2024, AVS, Aug 2024, HELSINKI, Finland. cea-04679132

**HAL Id: cea-04679132**

**<https://cea.hal.science/cea-04679132v1>**

Submitted on 27 Aug 2024

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

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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 H<sub>2</sub>O were pulsed to incorporate Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> incorporation preserves favorable amorphous structure, which is a key characteristic for achieving excellent electrochemical performances [1]. The XPS spectra show typical core peaks (Li<sub>1s</sub>, P<sub>2p</sub>, O<sub>1s</sub>, N<sub>1s</sub>, Al<sub>2p</sub>) corresponding to different LiPON based samples. The analysis reveals that Al<sub>2</sub>O<sub>3</sub> 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<sub>d</sub>) and a trivalent nitrogen state (N<sub>t</sub>) [1], whose proportion evolves as a function of Al<sub>2</sub>O<sub>3</sub> incorporation. Thus, the concentration of divalent nitrogen becomes predominant over trivalent nitrogen, inducing an increase in the N<sub>d</sub>/N<sub>t</sub> fraction when more Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> concentration.

This work provides a solid ALD approach with promising potential to optimize the electrical performances (ie Li<sup>+</sup> 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

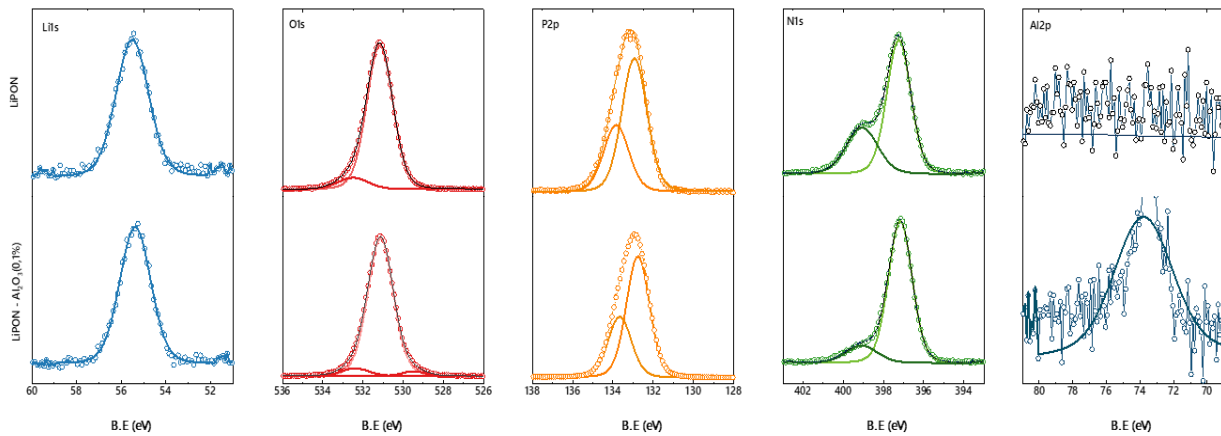
## Supporting Information

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

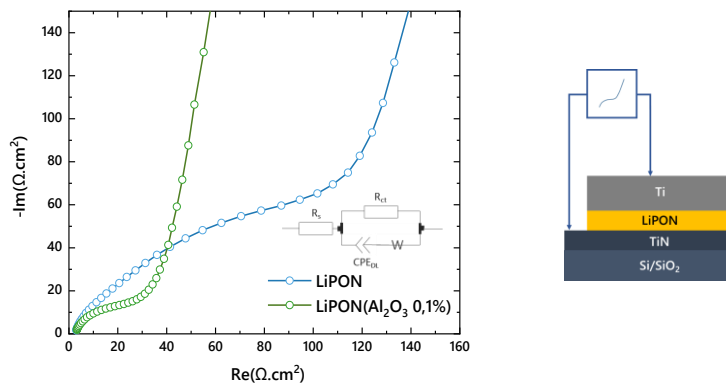
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**Fig 1 :** Typical core peaks (Li1s, P2p, O1s and N1s) corresponding to two different LiPON samples : LiPON (reference) and LiPON Al<sub>2</sub>O<sub>3</sub>(0,1%)



**Fig 2:** Nyquist plots of electrochemical impedance spectroscopy (EIS) of two samples tested: LiPON (reference) and LiPON Al<sub>2</sub>O<sub>3</sub>(0,1%), for a frequency range of 1Hz - 1MHz, in a MIM structure Ti/LiPON/TiN.