

# Atomic Layer deposition of thin films materials for 3D solid state Li-ion microbattery

Manon Létiche<sup>1,2</sup>, Jeremy Freixas<sup>1,3,4</sup>, Etienne Eustache<sup>1,3,4</sup>, Arnaud Demortière<sup>4,5</sup>, Pascal Roussel<sup>2</sup>, Thierry Brousse<sup>3,4</sup> and Christophe Lethien<sup>1,4</sup>

<sup>1</sup>*Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), CNRS UMR 8520 – Université de Lille Sciences et Technologies, 59652 Villeneuve d'Ascq cedex, France*

<sup>2</sup>*Unité de Catalyse et de Chimie du Solide (UCCS), CNRS UMR 8181 – Université Lille 1 Sciences et Technologies, 59655 Villeneuve d'Ascq Cedex, France*

<sup>3</sup>*Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502 – Université de Nantes, 2 rue de la Houssinière BP32229, 44322 Nantes cedex 3, France*

<sup>4</sup>*Réseau sur le Stockage Electrochimique de l'Energie, CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France*

<sup>5</sup>*Laboratoire de Réactivité et de Chimie des Solides (LRCS), CNRS UMR 7314 – Université de Picardie Jules Verne, 100 Rue St Leu, 80000 Amiens, France*

Nowadays, millimeter scale power sources are key devices for providing autonomy to smart, connected and miniaturized sensors. Planar solid state microbatteries do not exhibit a sufficient surface energy density. 3D microbatteries<sup>1–3</sup> appear therefore to be a good solution to improve the material mass loading while keeping small the footprint area. Nevertheless, the main technological barrier deals with the conformal deposition of unlithiated and lithiated thin films on 3D structures and Atomic Layer Deposition (ALD) technology seems to be a powerful technique to coat complex substrate. Silicon simple and double microtubes technology has been proposed as an original, robust and highly efficient 3D scaffold to significantly improve the geometrical surface of miniaturized 3D microbattery. Four functional layers composing the 3D lithium ion microbattery stacking has been successfully deposited. In depth X-Ray nanotomography and Transmission electron microscope analyses are performed to check the interfaces between each layer. For the first time, 3D anatase TiO<sub>2</sub> negative electrode is coated with a lithium phosphate thin film proposed as the 3D solid electrolyte. Li<sub>3</sub>PO<sub>4</sub> low temperature form (from 10 up to 60 nm thick) exhibits a notably high ionic conductivity ( $\approx 6.2 \times 10^{-7} \text{ S.cm}^{-1}$ ) for a solid electrolyte grown by ALD and an electrochemical stability window close to 4.2V. The specific area resistance has been found to be the lowest reported so far ( $\approx 3.8 \Omega.\text{cm}^2$ ). The deposited Li<sub>3</sub>PO<sub>4</sub> is a pinhole free and step-conformal layer (100 %) on original, high aspect ratio (> 50:1) and highly robust 3D silicon scaffolds. The surface capacity of TiO<sub>2</sub> thin film electrodes, coated with the Li<sub>3</sub>PO<sub>4</sub> solid electrolyte and evaluated as a part of a 3D all solid state Li-ion microbattery fabricated at the wafer level, is significantly increased by the proposed topology (high AEF – thick 3D layer), from 3.5  $\mu\text{Ah/cm}^2$  for a planar layer up to 0.37  $\text{mAh/cm}^2$  for a 3D thin film (105 times higher).

1 J. W. Long, B. Dunn, D. R. Rolison and H. S. White, *Chem. Rev.*, 2004, **104**, 4463–4492.

2 J. F. M. Oudenhoven, L. Baggetto and P. H. L. Notten, *Adv. Energy Mater.*, 2011, **1**, 10–33.

3 E. Eustache, P. Tilmant, L. Morgenroth, P. Roussel, G. Patriarche, D. Troadec, N. Rolland, T.

Brousse and C. Lethien, *Adv. Energy Mater.*, 2014, **4**, 1–11.