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

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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 microbatteries¹–³ 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 TiO₂ negative electrode is coated with a lithium phosphate thin film proposed as the 3D solid electrolyte. Li₃PO₄ low temperature form (from 10 up to 60 nm thick) exhibits a notably high ionic conductivity (# 6.2 x 10⁻⁷ 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 (# 3.8 Ω.cm²). The deposited Li₃PO₄ 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 TiO₂ thin film electrodes, coated with the Li₃PO₄ 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 µAh/cm² for a planar layer up to 0.37 mAh/cm² for a 3D thin film (105 times higher).

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