

# Layer-by-layer spray deposition of structured cathodes for improved rate performance in lithium-ion electrodes

Jack Evans<sup>a</sup>, Chuan Huang<sup>b</sup>, Mauro Pasta<sup>c</sup>, Patrick Grant<sup>d</sup>  
<sup>a,b,c,d</sup> *University of Oxford, Department of Materials, Parks Rd, Oxford OX1 3PH*

E-mail: [jack.evans@materials.ox.ac.uk](mailto:jack.evans@materials.ox.ac.uk)

In order to achieve high rate capability lithium-ion batteries (LIBs), it is common to reduce particle size and electrode thickness, or to increase electrode porosity. However, these approaches also reduce volumetric energy density of full cells and packs [1]. As an alternative, it has been postulated that electrodes with through-thickness spatial variation in *local* porosity and/or particle size can also improve rate performance of LIBs while minimising the energy density penalty [2,3]. Unfortunately, these ideas are difficult to explore experimentally because manufacturing approaches for these types of electrodes have not been widely developed [1]. In this research, through-thickness spatial variations of particle size and porosity have been achieved in LiFePO<sub>4</sub> cathodes at a practical scale (13 mg cm<sup>-2</sup>) using a novel layer-by-layer (LbL) spray deposition technique. LbL spray deposition of aqueous cathodes showed inherent improvements in structural and chemical stability during and after processing when compared to aqueous slurry casting, such that electrode cracking was eliminated and aluminium current collector corrosion was not observed. Electrodes consisting of small (<100 nm) and large (0.5 - 1 μm) LiFePO<sub>4</sub> primary particles were spray deposited to generate both layered and mixed particle electrodes. Distinct layers were confirmed by cross-section electron microscopy and energy storage performance investigated using electrochemical impedance spectroscopy and galvanostatic cycling. The layered electrodes showed greater capacity retention (54% vs 37% at 5C) at high C-rates versus the randomly mixed and inversely layered electrodes composed of the same materials at the same thickness of 85 μm. These improvements are shown to arise from increased Li-ion mobility within the electrode and more uniform ion concentrations through the electrode thickness.

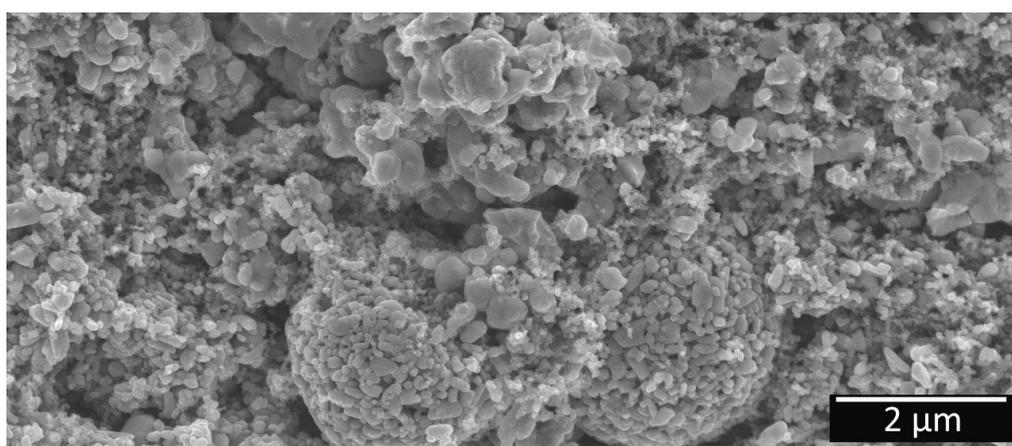


Figure 1: A cross-section of a layered electrode showing the boundary between large (top layer) and small (bottom layer) LiFePO<sub>4</sub> primary particles within the electrode.

## References:

- [1] A. Vlad, N. Singh, C. Galande, P.M. Ajayan, *Adv. Energy Mater.* 5 (2015) 1402115
- [2] S. Golmon, K. Maute, M.L. Dunn, *Int. J. Numer. Meth. Eng.* 92 (2012) 475–494.
- [3] Y. Qi, T. Jang, V. Ramadesigan, D.T. Schwartz, V.R. Subramanian, *J. Electrochem. Soc.* 164 (2017) A3196–A3207.