

Thin layers of Cu_2O on three-dimensional copper current collectors for Li-ion microbatteries

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Three-dimensional (3D) electrodes play a key role in improving the performances of electrochemical devices and have attracted great attention for applications in Li-ion batteries. In particular, 3D nanostructured current collectors represent the base for the development of novel rechargeable Li-ion microbatteries in the prospect of achieving autonomous operation of advanced microelectronic and microelectromechanical systems (MEMS). Powering these miniaturized devices by built-in batteries requires increasingly higher levels of energy and power densities per footprint area, which cannot be supplied by conventional planar electrodes [1, 2].

3D electrodes based on large area nanostructured current collectors coated with thin films of active materials represent a valid approach to simultaneously sustain high energy and power densities. 3D current collectors relying on high aspect ratio metal structures are particularly interesting, because they enable an enhancement of the surface area and the incorporation of both active materials and suitable electrolytes in contained volumes. They also increase the overall conductivity and mechanical stability of the electrode, since the thin active layers are directly connected to the underlying metal substrate. In this way it is possible to sensibly boost the overall capacity per footprint area without spoiling the favorable charge transfer properties offered by thin films (e.g., reduced path lengths for Li^+ and e^- charge carriers). However, the uniform deposition of thin layers on high aspect ratio structures is not always easy and often requires dedicated techniques, especially when narrow spaces are available within the 3D architecture.

Electrodeposition has proved a straightforward and cost-effective methodology for the fabrication of the required components for 3D Li-ion microbatteries [3] (i.e. current collectors, active materials and polymer electrolytes). Nevertheless, the assembly of a full 3D microbattery remains challenging, especially if convenient coverage and adhesion of the stacked functional layers has to be preserved in the various deposition stages.

Here template-assisted electrodeposition of Cu nanorods [4] with high aspect ratio is presented as a direct route to not only deposit a large area 3D current collector with high conductivity, but also to envelope in situ the Cu structures with a thin active layer of Cu_2O . The spontaneous formation of Cu_2O [5] at the end of the electrodeposition process provides a negative electrode layer rooted onto the Cu substrate without any further deposition step. The conversion of the cuprous oxide deposits into Li_2O and Cu nanoparticles [6] upon reaction with Li^+ ions offers a direct means to access the advantageous properties of the 3D substrate and its extended contact at the Cu/ Cu_2O interface. The overall interfacial area of the active material is further enhanced during the conversion mechanism, which generates boundaries [7, 8] between the Cu and Li_2O phases, thus yielding a highly divided nanocomposite. The capacity per

footprint area of the resulting electrodes grows upon progressive cycling even at moderate rates, due to the creation of new interfaces upon repeated conversion and de-conversion, giving rise to an electrochemical milling of the material [9]. It will be shown that the large reactive area deriving from the combination of the 3D Cu substrate and such grinding mechanism is very effective in increasing electrical double layer charging effects. Accordingly, an electrode system that bridges the electrochemical behaviour of Li-ion batteries and supercapacitors can be obtained.

Strategies to eventually improve such coated structures will be presented as well.

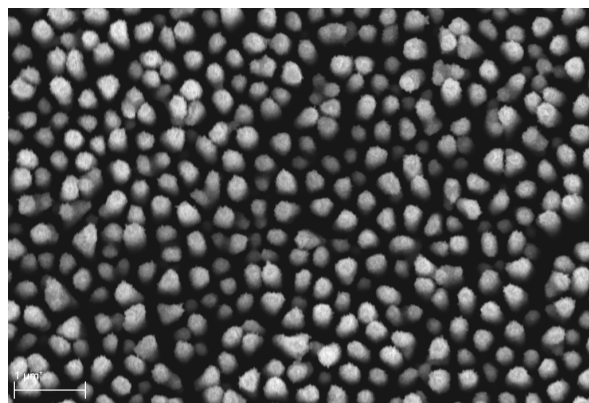


Figure 1: SEM top view of Cu_2O -coated Cu nanorods with high aspect ratio directly fabricated via template-assisted electrodeposition.

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References

- [1] J.W. Long, B. Dunn, D.R. Rolison, H.S. White, *Chem. Rev.* 104 (2004) 4463.
- [2] M. Roberts, P. Johns, J. Owen, D. Brandell, K. Edström, G. El Enany, C. Guery, D. Golodnitsky, M. Lacey, C. Lecoer, H. Mazor, E. Peled, E. Perre, M.M. Shaijumon, P. Simon, P-L. Taberna, *J. Mat. Chem.* 21 (2011) 9876.
- [3] K. Edström, D. Brandell, T. Gustafsson, L. Nyholm, *Electroch. Soc. Interface* 20 (2011) 41.
- [4] P. L. Taberna, S. Mitra, P. Poizot, P. Simon, J. M. Tarascon, *Nature Mater.* 5 (2006) 567.
- [5] J. Eskhult, M. Herranen, L. Nyholm, *J. Electroan. Chem.* 594 (2006) 35.
- [6] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, *Nature* 407 (2000) 496.
- [7] J. Maier, *Nature Mater.* 4 (2005) 805.
- [8] J. Maier, *J. Pow. Sources* 174 (2007) 569.
- [9] S. Grugeon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizot, J. M. Tarascon, *J. Electrochem. Soc.* 148 (2001) A285.