Electrodeposition as a Tool for 3D Microbattery Fabrication

by Kristina Edström, Daniel Brandell, Torbjörn Gustafsson, and Leif Nyholm

It is not difficult to explain the increasing worldwide interest in battery development. The current changes in the global energy outlook, including the shift to a higher fraction of solar and wind power, as well as the declining use of fossil fuels in vehicles, call for new autonomous energy storage solutions. The downscaling of microelectronic systems to produce small devices such as medical implants, micro sensors, self powered integrated circuits or microelectromechanical systems (MEMS), requires rechargeable batteries with better energy and power densities per footprint area than can be achieved with the thin film 2D batteries existing today.

Today's rechargeable lithium-ion batteries—with the best performance when it comes to energy density and with a reasonably good power efficiency—are dominating the market for consumer electronics. There is, however, a need for rechargeable storage devices that combine small volume with high energy and power densities. Typically, there is a demand for batteries on the 1-10 mm^3 volume scale, including all components and associated packaging. Moreover, miniaturized devices usually need the energy storage functions to be physically located on a small area—on a chip—making the energy and power density per footprint area a key factor for these batteries. The energy demand for these products is generally in the order of 1 $J/(mm^2$ day), which conventional battery technologies fail to supply by an order of magnitude or more. Given the wide range of electrode chemistries available for lithium-ion batteries, these batteries are well-suited to be shaped into different complex 3D high-capacity architectures.

This article focuses on the use of electrodeposition as a tool for manufacturing complex 3D battery architectures.

Why 3D Microbatteries?

The most promising way to obtain a high storage capacity (high energy density) and a high power capability on a limited surface area is to integrate the battery components—current collectors, electrodes and electrolyte—in a 3-dimensional arrangement, thus generating a 3D-micro-battery (3D-MB; Fig. 1).[1-3] Due to the large surface area of the electrodes, high capacities per footprint area can then be obtained. By careful design of the battery to obtain short transport distances between the electrodes, and thin layers of the electrode materials on the current collectors, high power capabilities also can be realized. Furthermore, as these batteries would require the same amount of packaging and substrate material as their thin-film counterparts, the volumetric energy density likewise can be increased.

The 3D-MB approaches proposed so far can be divided into four general categories (1.) interdigitated-, (2.) trench-, (3.) concentric-, and (4.) sponge-type structures, (see Fig. 1), which differ significantly with respect to architecture, materials, and synthesis techniques. There are also additional microbattery designs, based on the use of micro-channels plates[4] or microstructured $Li_{0.35}La_{0.55}TiO_3$ templates.[5]

The 3D-MB approaches also differ widely with respect to dimensionality, and most of the devices can be classified as either micro- or nano-architectures. The micro-architectures are generally fabricated using lithographic techniques, and although they do not provide a very high energy or power
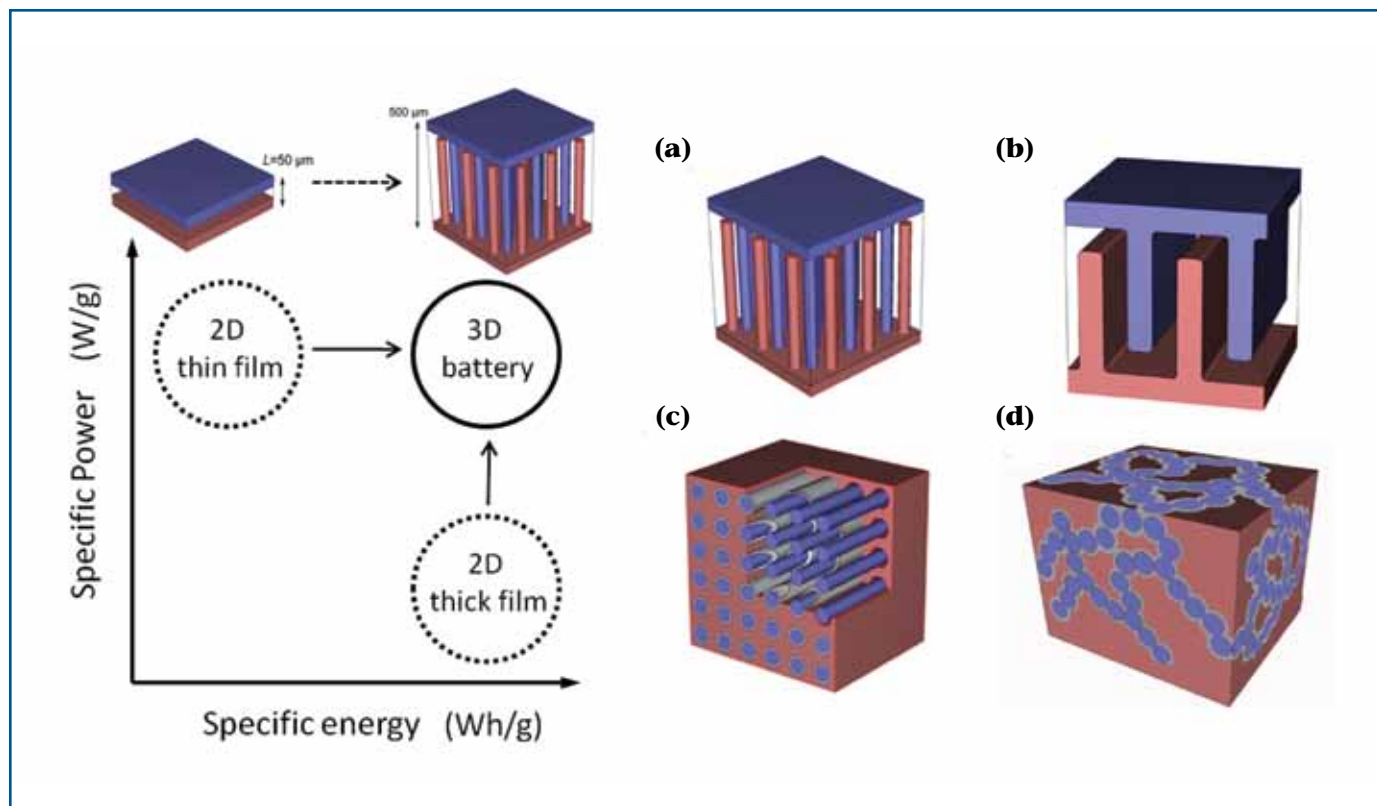
FIG. 1. *3D microbattery designs: (a) interdigitated pillars, (b) trenches, (c) concentric, and (d) aperiodic. All the architectures imply high surface area for lithium-ion storage and short pathways for lithium-ion transport. This means that both high specific energy and high specific power can be obtained.*

density per footprint area, they comprise the strategies that most easily can be realized. The nano-architectures, on the other hand, are hampered by difficulties with the materials deposition techniques, but provide a much larger surface area gain compared to 2D designs.

Why Electrodeposition?

The realization of a 3D-MB requires manufacturing of three-dimensional current collectors coated with thin layers of active electrode materials and electrolyte. As these requirements can be fulfilled employing electrodeposition, this technique has emerged as a particularly promising tool for low-cost manufacturing of 3D-MB devices. Electrodeposition is a method that can be used to coat and modify conducting surfaces with complicated geometries at low temperatures. The latter feature is particularly important since high-temperature processing is undesirable in the manufacturing of 3D-MBs. With electrodeposition, the morphologies of the electrode materials can also be closely controlled and new types of batteries can be built by adopting a layer by layer deposition strategy. The technique is especially suitable for the realization of nano-scale architectures for which other approaches such as sputtering or chemical vapor deposition (CVD) generally have problems in regard with the attainment of conformal coatings.

As depicted in Fig. 1, several 3D-MB concepts have been proposed so far. Most of these are, however, only conceptual, and almost all published reports have up to now focused only on the development of half-cell devices; *i.e.*, on only one of the electrodes.

The manufacturing of nanostructured current collectors by electrodeposition of arrays of nanorods, has been studied[6-9] as a starting point for building interdigitated structures. In Li-ion batteries, copper is commonly used as the current collector material for the negative electrode as the potential of this electrode is close to 0 V versus Li/Li$^+$ and there is no significant reaction between lithium and copper. For the positive electrode, aluminum is instead generally used as it is one of the few metals that does not corrode at potentials close to +4.5 V vs. Li/Li$^+$.

Electrodeposition has been used for the deposition of 3D arrays of copper nanorods on a copper foil substrate employing a nanoporous anodic alumina membrane (AAO) template open on both sides, that was subsequently etched away.[6] During the deposition, the AAO membrane is normally placed under pressure between two Cu foils (serving as the substrate and the counter electrode) separated by a porous cellulose separator (soaked with Cu^{2+} containing electrolyte) in a two-electrode set-up (see Fig. 2). The deposition of copper, which can be carried out in aqueous solutions, is generally done employing pulsed potentiostatic or galvanostatic techniques to circumvent problems with limited mass transport rates of copper ions within the pores of the AAO. Purely diffusion controlled deposition conditions should be avoided as this may yield dendritic or powdery copper deposits.[6]

The corresponding electrodeposition of an array of Al nanorods (see Fig. 2) has also been demonstrated.[7,8] This deposition process is, however, less straightforward than that for copper since the deposition of aluminum needs to be carried out in non-aqueous media. Ionic liquids have therefore been used.[7,8] In this instance, it has been shown that the attainment of a large number of nuclei at the start of the electrodeposition process is important for the realization of a homogeneous coverage of nanorods of equal height.
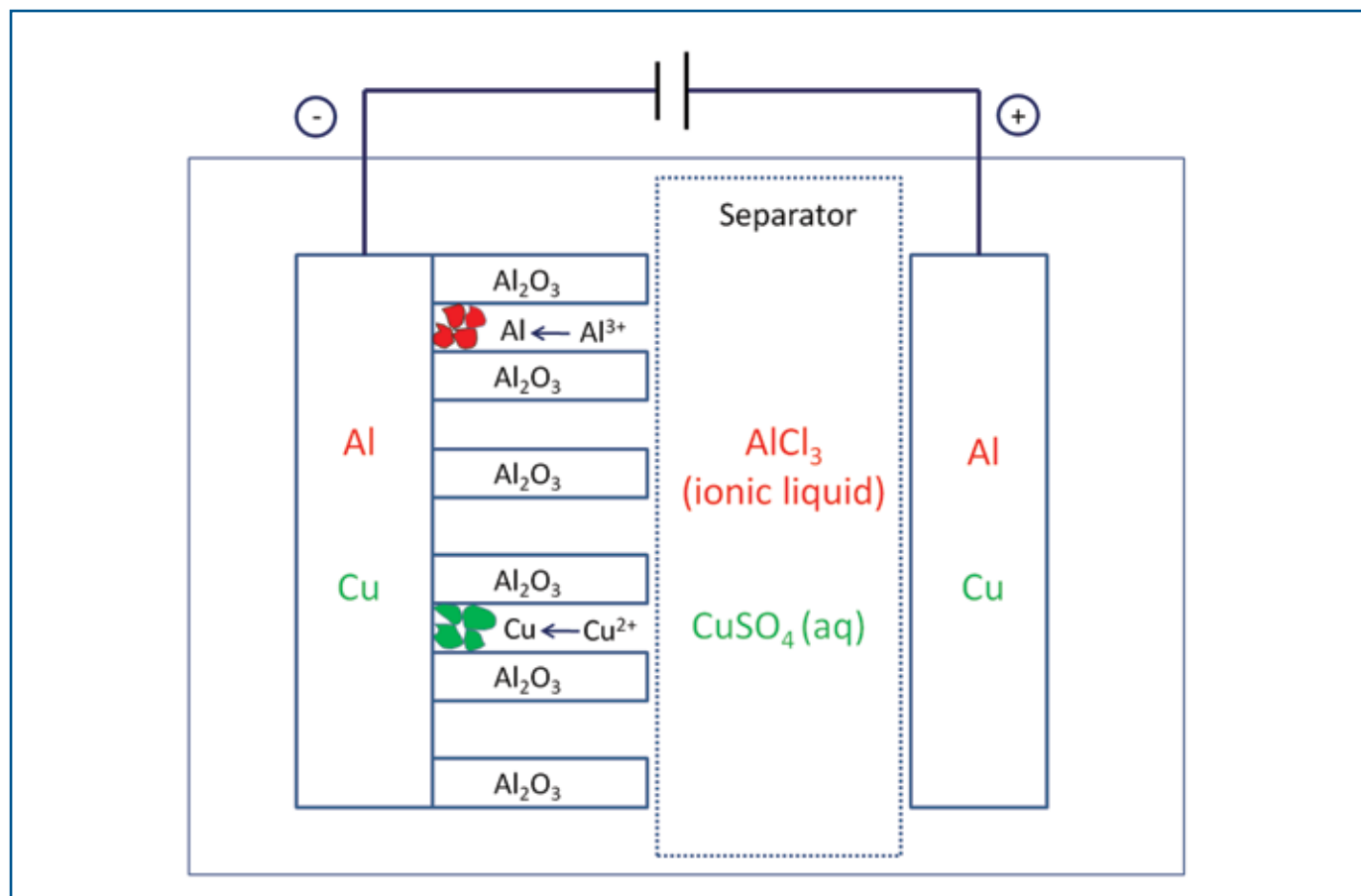

Fig. 2. *Deposition of 3D arrays of aluminum nanorods on an aluminum foil substrate employing a nanoporous anodic alumina membrane (AAO) template that subsequently was etched away. In a similar way deposition of 3D arrays of copper nanorods on a copper foil substrate was carried out. The AAO membrane is normally placed under pressure between two Al or Cu foils (serving as the substrate and the counter electrode, respectively) separated by a porous cellulose separator (soaked with Al^{3+} or Cu^{2+} containing electrolyte) in a two-electrode set-up.*

Electrochemical structuring of aluminum substrates without the use of nanoporous alumina membranes has likewise been carried out.[9] This approach involves reduction of aluminum from an electrolyte consisting of 1-ethyl-3-methylimidazolium bis-trifluoromethanesulfonylimide (EMIm-TFSI) and $AlCl_3$. Specifically, it was shown that different aluminum morphologies can be obtained depending on the deposition conditions, e.g. the type of ionic liquid and current densities used. While the template assisted deposition approach provides nanorods, the direct synthesis route generally yields less well-ordered rods with larger dimensions.

Using Electrodeposition for the Synthesis of Negative Electrode Materials on 3D Current Collectors

One approach (depicted in Fig. 3) has been to directly use the copper nanorod current collector made on a planar copper surface as a platform for the synthesis of the negative electrode material.[10,11] A suitable material in this respect is antimony (Sb), as it is known to alloy with lithium; this process however would result in a large volume expansion, which limits cycling and battery lifetime. One way to circumvent and reduce such volume expansion is to form intermetallic compounds where one metal is inactive with respect to lithium alloying while the other metal is active. Cu_2Sb is one example[11,12] of such a negative electrode material. The Sb electrodeposition strategy adopted in this case included careful control of the local pH at the electrode to prevent formation of Sb_2O_3.[10,11] After deposition, the sample was heat-treated for 12 hours at 300°C to ensure the formation of Cu_2Sb-nanorods with a core of Cu. The sample was found to exhibit excellent capacity retention with a capacity about ten times higher than for a 2D sample treated in the same way.[10]

Tin can also be electrodeposited on different complex architectures.[13,14] In this case, the deposition requires either an acidic electrolyte,[14,15] or a solution with a high pH containing a complexing agent such as oxalate,[13] to give deposits of pure tin. To coat complex architectures, the use of pulsed deposition has proved successful.[14] By tuning the duration of the off periods between the current pulses, control of the concentration gradient along the nanopillars can be achieved to obtain conformal coatings of thicknesses between 20 and 50 nm.

Electrodeposited intermetallics have also been tested on copper nanorods[15] and on electrodeposited sintered copper foam substrates, respectively.[16,17] NiSn has been directly deposited as an
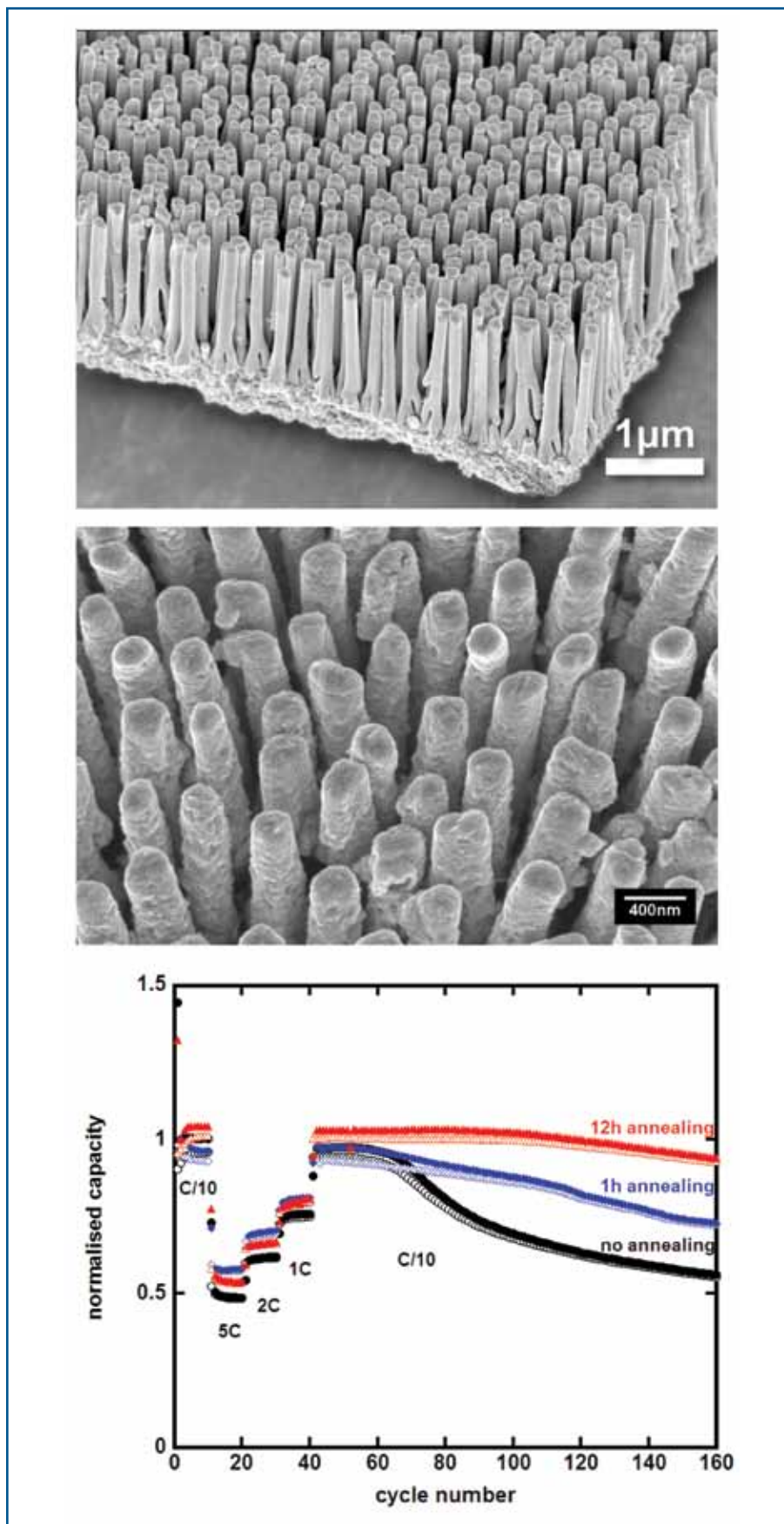
(continued on next page)

FIG. 3. *Top: electrodeposited Cu nanorods (From Ref. 6, reprinted with permission from Elsevier). Middle: electrodeposited Cu_2Sb nanorods. Bottom: cycling results for Cu_2Sb samples heat-treated at 300°C. (From Ref. 10, reprinted with permission from the Materials Research Society)*

amorphous layer completely covering the copper rods,[16] while Cu_6Sn_5 can be electrodeposited using a tin-rich electrolyte containing both copper and tin chloride by employing the fact that the reduction of copper takes place at more positive potential than the Sn deposition. Alloy deposition can then be achieved using a square wave deposition potential program.[17]

Another metal that can alloy with lithium and that can be deposited on copper nanorods is bismuth.[18] Highly conformal layers could be obtained, in this case when tuning the pH of the deposition bath to 3.

An electrode material that exploits conversion instead of intercalation reactions is Fe_3O_4 (+1.6 V vs., Li/Li^+).[6] This oxide has been electrodeposited onto Cu-nanorods[6] using an alkaline aqueous solution generating polycrystalline but inhomogeneous deposits. The half-cells showed promising capacity retention when the electrode was deposited for 150 s, while the capacity retention deteriorated for electrodes made using longer deposition times due to the coalescence of Fe_3O_4 particles.

New results based on other hierarchical structures than copper nanorods are also appearing. One recent example deals with the electrodeposition of porous cobalt oxides on polystyrene sphere templates to obtain a 3D anode material.[19]

The Positive Electrode of a 3D Battery

There are so far very few examples of electrodeposited materials suitable for use as the positive electrode in a 3D-MB. This research area can, however, be expected to grow rapidly during the next few years as a consequence of the demand generated by the promising results obtained for the negative 3D electrodes. In general, the electrodeposition of positive electrode materials is more demanding than that of the negative electrode materials since it typically involves deposition of oxides, phosphates, or sulfides rather than pure metals. One important example involves the electrodeposition of molybdenum sulfide on nickel-coated silicon and glass substrates for a 3D microbattery with a concentric structure.[4,20,21] An electrolyte consisting of an aqueous solution of Na_2S and Na_2MoO_4, with a pH adjusted to 7.5-8.0 using KH_2PO_4, was used for the deposition. The molybdate anion undergoes sulfidation in four steps and a thin-film molybdenum-sulfide layer was obtained during the reduction of the thiomolybdate anions by use of a constant cathodic potential/current.[20] It was found that thicknesses larger than 500 nm were difficult to achieve due to the formation of cracks.[20,21]

In a similar way CuS has been electrodeposited by tuning the pH between 6 and 9 and using an electrolyte comprising 1,2-propanediol propylene glycol, ethylenediaminetetraacetic acid–disodium–copper $CuNa_2EDTA$, and elemental sulfur. Ammonium chloride NH_4Cl and ammonia were added to obtain a buffer solution of high ionic strength and a polymer additive was also used to decrease the internal stresses within the deposit. In this case, semi-three-dimensional concentric microbatteries (3DCMBs) were made on perforated silicon substrates. The latter devices showed a stable electrochemical behavior and a superior peak-power capability of 50 mW/cm² compared to that of a similar 2D model.[22]

Another example involves electrodeposition of dodecylbenzenesulphonate doped polypyrrole (PPYDBS), by electrochemical polymerization of pyrrole in a sodium dodecylbenzenesulfonate aqueous solution.[23] Recently, a challenging work involving the coating of a nanostructured reticulated vitreous carbon (RVC) foam with MnO_2 cathode material has been described,[24] in which a capacity increase per footprint area of ~250 times was found. Conformal coating films were obtained at elevated temperatures by galvanostatic deposition from acidic aqueous solutions containing 0.3 M $MnSO_4·H_2O$. MnO_2-based aerogels have also previously been investigated for microbatteries by other groups.[25-27]

In the manufacturing of positive electrodes for 3D-MB, other deposition methods such as ALD[28] of TiO_2 and spray coating with $LiCoO_2$ precursors followed by annealing at 650º C[29] have also been employed on electrodeposited alumina nanorods. (See Fig. 4 for an example of TiO_2 conformally coated on aluminum nanorods.)

The Electrolyte: A Challenge

Traditionally, a liquid electrolyte including a lithium salt (most commonly $LiPF_6$) and organic solvents is used in Li-ion batteries, either with a separator or as a component in a polymer gel. However, it is difficult to obtain conformal coatings of either the separator or the inert polymer gel component onto complex substrates, both at the nano- and micro-scale. Thermally activated PMMA[30] or polycondensated PVDF[10] based hybrid polymer electrolytes have, for example, been used in 3D-MBs, but would not provide conformal coating layers on the electrodes using current strategies. When miniaturizing the battery, new methods are therefore required.

Another drawback with liquid electrolytes is that these are prone to leakage and harmful side-reactions with the electrode materials. The problem of finding a suitable, solid-state electrolyte is therefore crucial in many of the currently studied 3D-MB approaches. Some attempts have been made with sputtering of LiPON glass electrolytes,[31] but this constitutes an expensive technique and generates brittle materials with poor contacts to the electrodes. The use of 3D-structured crystalline electrolytes such as $Li_{0.35}La_{0.55}TiO_3$ suffers from similar problems.[5] Solid polymer electrolytes (SPEs) seem to be more attractive candidates due to their low cost, safety, and possibility to be cast in thin layers, although they need to be cast pinhole-free. As has been shown recently,[32] this requirement can be fulfilled through the use of short-chain oligomeric surfactants which are capable of self-assembling onto the electrode surfaces. SPEs based on polyetheramine (PEA), which self-assembles onto $LiFePO_4$ electrodes with a thickness of ~2 µm can be blended with oligomeric poly(propylene glycol) diacrylate, (PPGDA), which in turn can be cross-linked *in situ* by UV, providing sufficient mechanical stability to the SPE.

Electrodeposition techniques can also be used for the synthesis of SPE or hybrid (gel) electrolytes using an electropolymerization approach. The technique has the advantage that the oligomer after polymerization becomes electronically insulating, thereby limiting subsequent depositions and generating homogeneous and conformal coatings; *i.e.*, the process is self-limiting. This can give rise to very thin polymer layers on complex electrode structures; <25 nm has been reported for a poly(phenylene oxide) separator film onto MnO_2 aerogels.[25] Despite its thinness, the material worked as electrolyte when soaked with a $LiClO_4$ solution. Another hybrid electrolyte deposited by electropolymerization and investigated for 3D-MBs is polyacrylonitrile (PAN) gelled with 1 M $LiPF_6$ in propylene carbonate.[33] The PAN film was generated by cathodic electropolymerization of acrylonitrile in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte, and could be deposited directly onto glassy carbon, nickel foam, and MnO_2 substrates. The subsequently constructed cells comprised a Hg electrode and displayed stable cycling data, indicating that the electrolyte might be useful for various 3D-MB systems.

How Much Better is 3D Compared to 2D?

Calculations show that an area gain factor of 30 is a realistic design goal for a 3D micro battery. A typical benchmark for a "footprint" battery capacity is 300 µAh/mm² delivering an energy density of 900 µWh/mm² for a stack-thickness of 500-1000 µm. So far these estimations are based on what is achievable in "half-cell studies" (lithium metal *vs.* the 3D structured anode- or cathode materials).

The conformally deposited $LiCoO_2$ positive electrode (on Ni/Al nanorods)[29] showed a capacity of ~ 100 µAh cm⁻², while results for template-free deposition of $LiFePO_4$ onto an Al

substrate in an ionic liquid medium[9] indicated that 80% of the theoretical capacity could be utilized at a 5C rate (discharge/charge time 20 min.). The conformal layer of TiO_2 deposited with ALD on Al nanorods[28] indicated that an area-gain of >10 could be obtained during cycling. Excellent capacity retention has also been observed for electrophoretically deposited SnO_2/Cu nanorod negative electrodes, with a final constant capacity of 25 µAh cm^{-2}.[14] The homogeneously electrodeposited Cu_2Sb onto Cu nanorods[10] exhibited at least ten times higher capacity than the corresponding 2D system.

Aperiodic sponge-type cells with a MnO_2 cathode[24] and concentric and interlaced perforated-silicon cells with CuS[22] or MoS_2[20,21] cathodes have also demonstrated increased battery capacities per footprint area, in good agreement with the area gain when moving from 2D to 3D. Capacities ranging from 1.0 to 2.5 mAh cm^{-2} with little degradation during more than 100 cycles have been obtained.[20-22]

These results clearly show that the Li-ion battery capacities can be increased by a factor of 10-30 per footprint area by adopting the 3D-MB concept.

Future Outlook

Electrodeposition has been shown to be a promising method for the manufacturing of 3D current collectors and the coating of these with active electrode material as well as electrolytes. Within the next few years more work on the electrodeposition of cathode materials onto 3D current collectors and electrodeposition of electrolytes can be anticipated, as well as the demonstration of complete 3D-MB devices. Throughout this process, more emphasis needs to be placed on the development of a fundamental understanding of the different electrodeposition processes, as such an understanding will be essential for the development and optimization of 3D-MBs. ■

About the Authors

Daniel Brandell is an associate professor within the Ångström Advanced Battery Centre at Uppsala University, Sweden, where his research is centered on computational and experimental chemistry of polymer electrolytes for batteries, fuel cells and other applications, with a particular focus on the 3D-microbatteries. He received a PhD in chemistry from Uppsala University in 2005, and has since then been on post-doctoral visits to Tartu University, Estonia, and Virginia Tech, USA. He may be reached at Daniel.Brandell@mkem.uu.se.

Kristina Edström is a professor of chemistry at the Department of Materials Chemistry at Uppsala University, Sweden. She is the leader of the largest Li-ion battery group (the Ångström Advanced Battery Cenre) in Sweden. Her research is focused on new materials for anodes and cathode in Li-ion and the development of new *in situ* characterization tools for studying processes occurring during battery cycling. She is also involved in the development of new lithium based battery concepts such as Li-air and 3D microbatteries. Uppsala University is coordinating the FP7 EU program SUPERLION that is focused on 3D microbatteries. She may be reached at Kristina.Edstrom@mkem.uu.se.

Torbjörn Gustafsson is an associate professor of inorganic chemistry within the Ångström Advanced Battery Centre at Uppsala University, Sweden. His research covers a broad aspect of Li-ion battery research, ranging from materials synthesis to whole-cell characterization. His interest in 3D-microbatteries is focused on electrode preparation and conformal electrolyte deposition. He may be reached at Torbjorn.Gustafsson@mkem.uu.se.
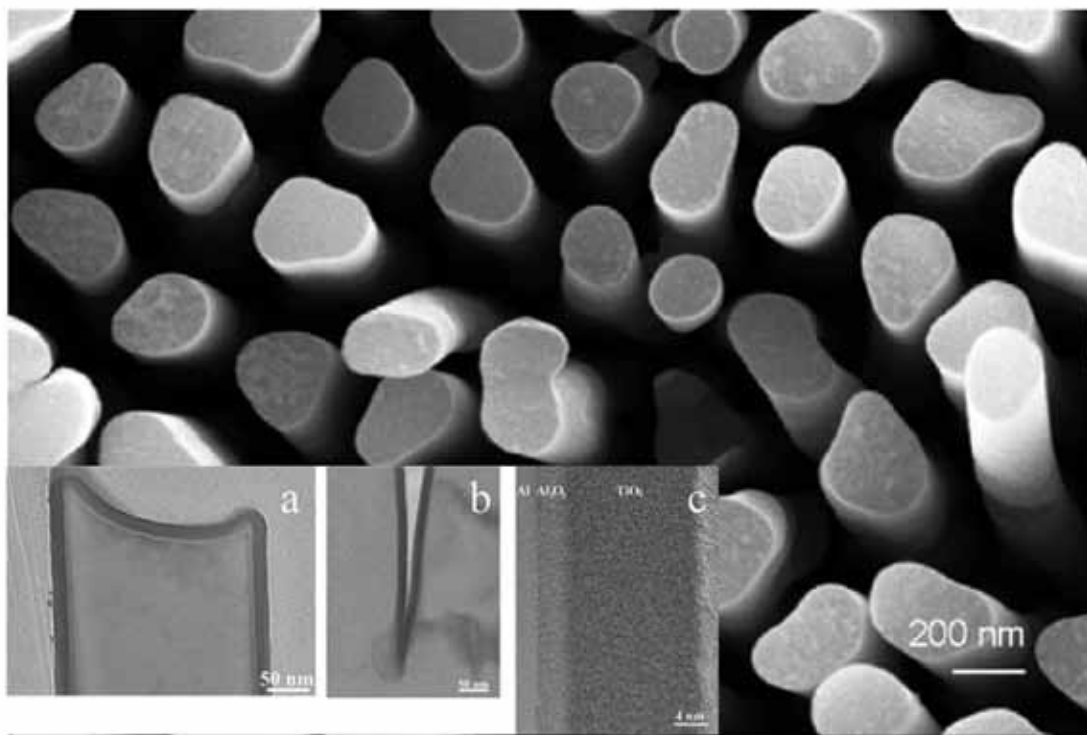
Fig. 4. *SEM micrograph of aluminum nanorods deposited using −5mA pulses for 0.2s and rest periods of 2s for 7000 cycles with an initial 50ms nucleation potential step to −0.9V vs. Al/Al^{3+}.[8] Inset: TEM micrographs of ALD deposited TiO_2 on aluminum nanorods displaying a full coverage of the rods.[28] (The insets are reprinted with permission of the American Chemical Society)*

Edström, *et al.*
(continued from previous page)

Leif Nyholm is a professor of analytical chemistry at the Department of Materials Chemistry at Uppsala University, Sweden. His research is focused on electrochemistry and electrochemical techniques and mainly involves work on the electrodeposition of nanostructured materials for Li-ion batteries, paper-based charge storage devices, electrochemistry coupled to electrospray mass spectrometry, and electrochemical lab-on-a-chip devices. He may be reached at Leif.Nyholm@mkem.uu.se.

References

1. J. W. Long, B. Dunn, D. R. Rolison, and H. S. White, *Chem. Rev.*, **104**, 4463 (2004).
2. J. F. M. Oudenhoven, L. Baggetto, and P. H. L. Notten, *Adv. Energy Mater.*, **1**, 10 (2011).
3. D. R. Rolison, J. W. long, J. C. Lytle, A. E. Fischer, C. P. Rhodes, T. M. McEvoy, M. E. Bourg, and A. M. Lubers, *Chem. Soc. Rev.*, **38**, 226 (2009).
4. M. Nathan, D. Golodnitsky, V. Yufit, E. Strauss, T. Ripenbein, I. Shechtman, S. Menkin, and E. Peled, *Mater. Res. Soc. Proc.*, **835**, 367 (2005).
5. M. Kotobuki, Y. Suzuki, H. Munakata, K. Kanamura, Y. Sato, K. Yamamoto, and T. Yoshida, *J. Electrochem. Soc.*, **157**, A493 (2010).
6. P. L. Taberna, S. Mitra, P. Poizot, P. Simon, and J.-M. Tarascon, *Nature Mater.*, **5**, 567 (2006).
7. E. Perre, L. Nyholm, T. Gustafsson, P. L. Taberna, P. Simon, and K. Edström, *Electrochem. Comm.*, **10**, 1467 (2008).
8. G. Oltean, L. Nyholm, and K. Edström, *Electrochim. Acta*, **56**, 3203 (2011).
9. C. Lecoeur, J.-M. Tarascon, and C. Guery, *Electrochem. Solid-State Lett.*, **14**, A6 (2011).
10. E. Perre, P.-L. Taberna, D. Mazouzi, P. Poizot, T. Gustafsson, K. Edström, and P. Simon, *J. Mater. Res.*, **25**, 1485 (2010).
11. H. Bryngelsson, J. Eskhult, L. Nyholm, and K. Edström, *Electrochim. Acta,* **53**, 7226 (2008).
12. L. M. L. Fransson, J. T. Vaughey, R. Benedek, K. Edström, J. O. Thomas, and M. M. Thackeray, *Electrochem. Commun.*, **3**, 317 (2001).
13. C. Arbizzani, S. Beninati, M. Lazzari, and M. Mastragostino, *J. Power Sources,* **141**, 1495 (2005).
14. L. Bazina, S. Mitra, P. L. Taberna, P. Poizot, M. Gressie, M. J. Menu, A. Barnabé, P. Simon, and J.-M. Tarascon, *J. Power Sources*, **188**, 578 (2009).
15. J. Hassoun, S. Panero, P. Simon, P. L. Taberna, and B. Scrosati, *Adv. Mater.*, **19**, 1632 (2007).
16. H. C. Shin, J. Dong, and M. L. Liu, *Adv. Mater.*, **15**, 1610 (2003).
17. L. Trahey, J. T. Vaughey, H. H. Kung, and M. M. Thackeray, *J. Electrochem. Soc.,* **156**, A385 (2009).
18. A. Finke, P. Poizot, C. Guery, L. Dupont, P. L. Taberna, P. Simon, J.-M. Tarascon, *Electrochem. Solid-State Lett.*, **11**, E5 (2008).
19. X. H. Xia, J. P. Tu, J. Y. Xiang, X. H. Huang, X. L. Wang, and X. B. Zhao, *J. Power Sources,* **195**, 2014 (2010).
20. D. Golodnitsky, M. Nathan, V. Yufit, E. Strauss, K. Freedman, L. Burstein, A. Gladkich, and E. Peled, *Solid State Ionics,* **177**, 2811 (2006).
21. D. Golodnitsky, V. Yufit, M. Nathan, I. Shechtman, T. Ripenbein, E.Strauss, S. Menkin, and E. Peled, *J. Power Sources,* **153**, 281 (2006).
22. H. Mazor, D. Golodnitsky, L. Burstein, and E. Peled, *Electrochem. Solid-State Lett.,* **12**, A232 (2009).
23. H. S. Min, B. Y. Park, L. Taherabadi, C. Wang, Y. Yeh, R. Zaouk, M. J. Madou, and B. Dunn, *J. Power Sources,* **178**, 795 (2008).
24. P. Johns, M. Roberts, and J. Owen., *J. Mater. Chem.*, DOI: 10.1039/c0jm04357e.
25. C. P. Rhodes, J. W. Long, M. S. Doescher, B. M. Dening, and D. R. Rolison, *J. Non-Cryst. Solids*, **350**, 73 (2004).
26. A. E. Fischer, K. A. Pettigrew, D. R. Rolison, R. M. Stroud, and J. W. Long, *Nano. Lett.*, **7**, 281 (2007).
27. A. E. Fischer, M. P. Saunders, K. A. Pettigrew, D. R. Rolison, and J. W. Long, *J. Electrochem. Soc.*, **155**, A246 (2008).
28. S. K. Cheah, E. Perre, M. Rooth, M. Fondell, A. Hårsta, L. Nyholm, M. Boman, T. Gustafsson, J. Lu, P. Simon, and K. Edström, *Nano Lett.*, **9**, 3230 (2009).
29. M. M. Shaijumon, E. Perre, B. Daffos, P. L. Taberna, J.-M. Tarascon, and P. Simon, *Adv. Mater.,* **22**, 4978 (2010).
30. K. Dokko, J. Sugaya, H. Nakano, T. Yasukawa, T. Matsue, and K. Kanamura, *Electrochem. Comm.*, **9**, 857 (2007).
31. F. Xu, N. Dudney, G. M. Veith, Y. Kim, C. Erdonmez, W. Lai, and Y. M. Chiang., *J. Mater. Res.*, **25**, 1507 (2010).
32. S. Tan, S. Walus, J. Hilborn, T. Gustafsson, and D. Brandell, *Electrochem. Comm.*, **12**, 1498 (2010).
33. G. El-Enany, M. J. Lacey, P. A. Johns, and J. R. Owen, *Electrochem. Comm.*, **11**, 2320 (2009).