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Scaling Methods for High Rate TiO_2 Nanotube Anodes for Short Time-Scale PV Buffering

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With the ever greater penetrations of solar photovoltaics (PV) globally, questions are increasingly being raised about problems associated with short time scale intermittency. In particular, with higher levels of PV penetration at a local grid level, weather effects causing short time scale intermittency can potentially have a destabilising effect on the local electricity grid. As a result there has been an increasing interest in using energy storage to limit ramp rates of PV systems [1]. This, however, presents several constraints on the energy storage system; *viz* long cycle life, high rate capability, and high energy density. While Li-Ion batteries are adequately placed to meet these demands, and concerted research efforts are focused on increasing their rate capability, they aren't a perfect solution. A reliance on bulk lithium diffusion for example limits long term cycle life, and tends to inhibit fast rate charge/discharge. Lithium ion capacitors however are far more suited to the requisite lifespan and rate capabilities [2]. This subset of energy storage sits midway between electrochemical capacitors and lithium ion batteries, aiming to bridge the gap between them. These energy storage systems typically rely on fast faradic reactions (like short diffusion length lithium intercalation) and double layer storage.

One such LiC anode is of particular interest: amorphous titanium dioxide nanotube arrays, grown anodically into the surface of a titanium mesh substrate (a-TNTA@Ti Mesh). In this electrode system, the lithium intercalating material (with a shallow diffusion length determined by nanotube wall thickness) inherently has high surface area, and open electrolyte diffusion. This system is show in Figure 1, where the TNTA active material is grown into the surface of the Ti mesh current collector. The net result is a material with fast lithium intercalation kinetics and complementary double layer storage. The major drawback of this electrode system is that it has insufficient energy density for use in any fast frequency PV buffering, as a result of the inherently low tapped density of the mesh substrate.

The transition, however, from promising research materials to a function, 3-dimensional electrode system is not trivial. Results to this effect are shown in Figure 2, where the scaling consists simply of folding the material back on itself in such a way that a similar projected area has double or triple the active material/current collector. From this it can be seen that at lower charge/discharge rates, as expected, there is an increase in the capacity over an equivalent projected area. However, at faster charge/discharge rates, the 3D electrodes retain less capacity (both relatively and absolutely) than the analogous, single-layer research material. There is, then, a need to investigate scaling methods for increased energy density that preserve rate capabilities. Hence, future work seeks to investigate alternative scaling methods for a-TNTA@Ti Mesh Li-Ion Capacitors with the aim of retaining a higher rate capability, while also moving toward a meaningful energy density required for fast frequency buffering in PV system.

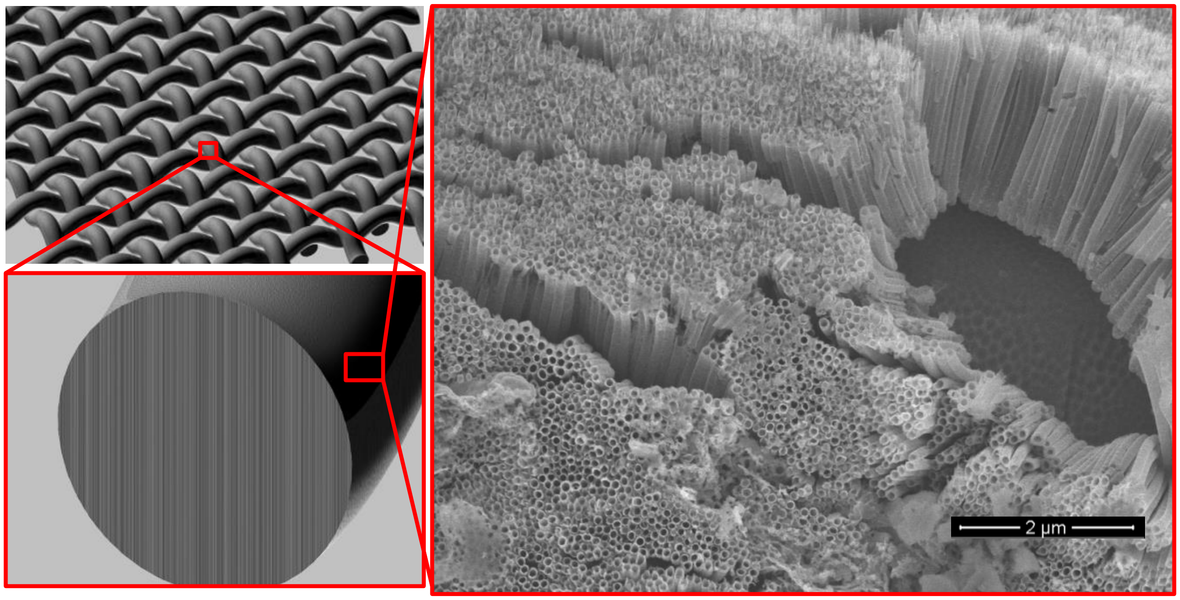

Figure 1. Electrode structure of anodically grown, amorphous TiO2 nanotube arrays hierarchically grown on a titanium mesh substrate, for use as a Lithium Ion Capacitor anode

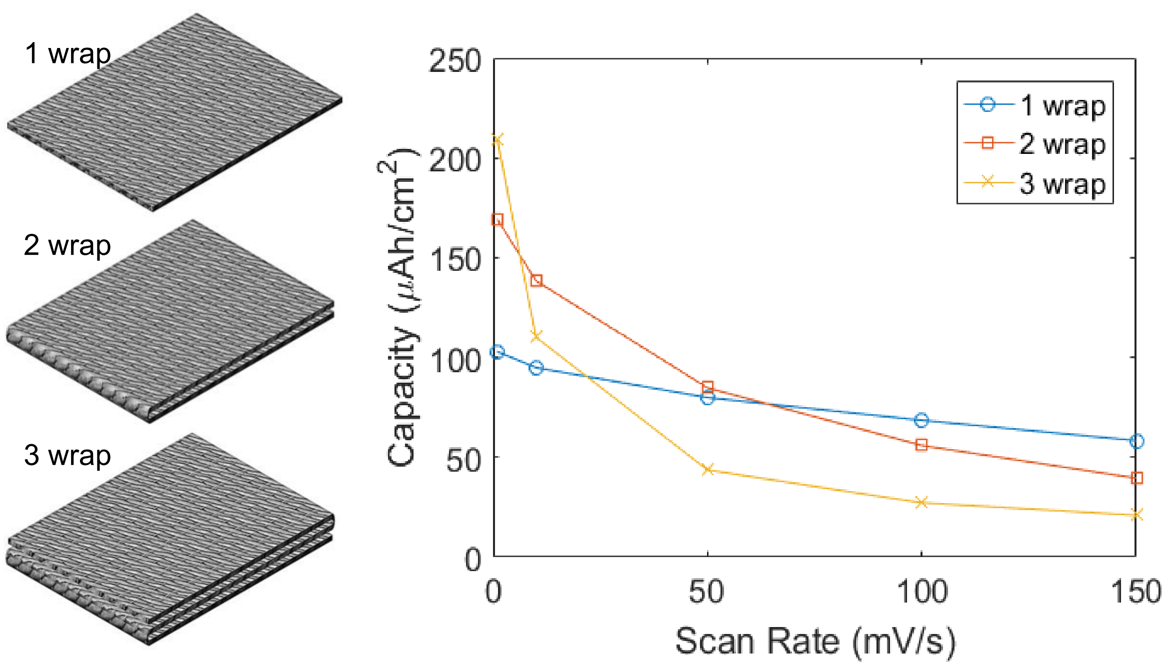

Figure 2. Capacity retention (as indicated by cyclic voltammetry) at higher scan rates for an unoptimized scaling method, showing poorer retention for the stacked, 3d electrode ("3 wrap") than for the analogous single layer, research style ("1 wrap") electrode

References

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