

**SILICON BASED NANO-ARCHITECTURES  
FOR  
HIGH POWER LITHIUM-ION BATTERY ANODES**

By

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## ABSTRACT

Lithium-ion batteries have now become an inseparable part of modern day society as the power source for several portable electronics like cell phones, digital cameras and laptops. Their high energy density compared with other electrochemical battery systems has been their most attractive feature. This has led to a great interest in developing lithium-ion batteries for hybrid and all-electric vehicles. Eventually such vehicles will help drastically reduce the carbon footprint making the environment cleaner and healthier.

In spite of their high energy density, Li-ion batteries are known to have poor power densities. This forms a major limitation in their deployment as a power source on vehicles. Electric vehicles need power sources that can provide both high energy and power densities. This requires the development of anode, cathode and electrolyte materials that would transform the capabilities of existing Li-ion batteries. Among anode materials silicon has received great attention because of its very large theoretical capacity of  $\sim 4200$  mAh/g based on the alloy  $\text{Li}_{22}\text{Si}_5$ . It should be noted that storage of charge in the anode occurs through the alloying of Li with the host anode material. However, the large specific capacity of silicon also results in a  $\sim 400\%$  volume expansion which could lead to pulverization and delamination reducing the cycle life of the electrode. These failure processes are exacerbated at high rates making it extremely difficult to use silicon for high-power Li-ion battery anodes. The major research thrust supporting this Ph.D. thesis involved exploring silicon based nano-architectures that would provide high energy and power densities over a long cycle life. The key technique used to design different nano-architectures was DC Magnetron sputtering with oblique angle deposition.

The main development of this research was a functionally strain graded Carbon-Aluminum-Silicon nanoscoop architecture for high-power Li-ion battery anodes. This consisted of Carbon nanorods with an intermediate Aluminum layer finally

capped by a nanoscoop of Silicon. The strain gradation arises from the fact that each of these materials has differential volumetric expansions due to different extents of Li uptake. Such a strain gradation from Carbon towards Silicon would provide for a less abrupt transition across the material interfaces thereby reducing interfacial mismatch and improving the tolerance to delamination at very high rates. This nano-architecture provided average capacities of  $\sim 412$  mAh/g with a power output of  $\sim 100$  kW/kg<sub>electrode</sub> continuously over 100 cycles. Even when the power output was as high as  $\sim 250$  kW/kg<sub>electrode</sub>, the average capacity over 100 cycles is still  $\sim 90$  mAh/g.

Furthermore, scanning electron microscopy and X-ray photoelectron spectroscopy investigations revealed that the functionally strain graded nanostructures were being partially lithiated in the bulk even at high rates. The fact that charge storage was not merely a surface phenomenon supported the high energy densities obtained at high charge/discharge rates.

In an attempt to improve the mass loading density of Silicon based nano-architectures, a nano-compliant layer (NCL) supported thin film architecture was also explored. This consisted of an array of oblique nanorods (the nano-compliant layer) sandwiched between the substrate and the thin film. The NCL layer was used to improve the stress tolerance of the thin film thereby allowing the use of bulk thin films as opposed to nanostructures. This would directly improve the mass loading density. Silicon films with Carbon NCLs and Carbon films with Silicon NCLs were both deposited and tested. It was found that Li<sup>+</sup> diffusivity is higher in carbon than in silicon by at least two orders of magnitude. This was calculated from cyclic voltammetry tests using the Randles-Sevcik equation. This difference in Li<sup>+</sup> diffusivity within the two materials was found to be the C-rate limiting factor for a given nano-architecture design.