Laser Pyrolysis Derived Silicon-Carbon Core-Shell Nanomaterials for Lithium Ion Battery Anodes

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Attachment : Resume

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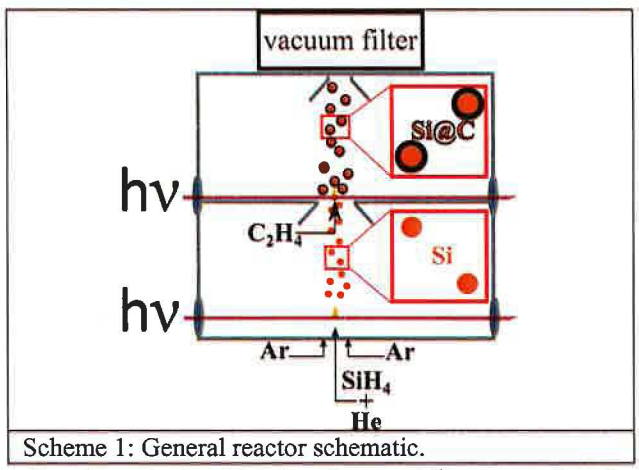
Current LiB technology relies on graphitic carbon as the anode material, with a theoretical capacity of 372 mAh/g. In order to increase the energy density of LiBs, anode materials with a greater capacity for lithium storage are under intense investigation. Materials which form alloys with lithium such as antimony, germanium, silicon, and tin, all have theoretical capacities which far surpass graphite. However silicon, as the most naturally abundant element and possessing a theoretical capacity of 3579 mAh/g in the $Li_{15}Si_4$ alloy, is the most promising for global adoption in next generation LiBs.

There are issues which require resolution before silicon can be implemented. Large volumetric changes associated with the lithiation-delithiathion process (~300%) result in material pulverization and loss of electrical contact[1]. Also unstable solid-electrolyte-interphase (SEI) formation during cycling results in the consumption of lithium during operation and capacity fade[2]. Previous studies have conclusively shown that the former issue may be mitigated by utilizing nano-scale silicon materials, with particles under 150 nm in diameter remaining intact during the swelling and contraction associated with cycling[3]. It has also been demonstrated that encapsulation of silicon nanomaterials in carbon shells shows promise in stabilizing the SEI. Highly rational silicon-carbon architectures have been developed to accomplish this, such as the carbon clamped hollow silicon nanosphere, "yolk in shell", and pomegranate geometries[4] which achieve high capacity and robust performance over hundreds of cycles. Guided by these achievements, we seek to develop a scalable process to synthesize silicon nanoparticle in carbon shell nanostructures which may enable robust battery anodes with enhanced energy storage capacity.



Scheme 1: General reactor schematic.

Specifically we are utilizing laser mediated pyrolysis which has the capability to produce kg/h of high purity nanoparticles within a narrow size distribution. This technique has already been used to produce various ceramic, oxide, and metallic particles[5], and implemented for industrial scale silicon nanoparticle production. In this work, a novel two stage gas flow reactor, which synthesizes silicon nanoparticles in the first stage and adds a nanometric carbon shell in the second stage, is being developed and is pictured in Scheme 1[6]In summary, silane diluted with helium is introduced into the first stage, contained by an argon sheath. The silane molecues absorb photons from the 10.6 μm IR laser and decompose to form silicon nanoparticles. A carbon precursor, ethylene, is then added to the particle flow. A second pass of the laser decomposes the ethylene, depositing a carbon shell. The particles are collected on an external vacuum filter. The technique avoids any manipulation of the pure silicon powders prior to carbon coating, mitigating oxidation and particle degradation, as well as worker exposure to nanopowders.

The current reactor design can operate continuously for over three hours and in the bench scale, synthesize over 10 g/h of core-shell material. Furthermore control of particle size and coating thickness can be achieved by varying the precursor flow rates and dilution in the reactor. As shown in Figure 1, we have developed process parameters to yield a range of particle sizes, from ~10-100 nm diameters, with shell thicknesses varying between ~3 - ~15 nm.

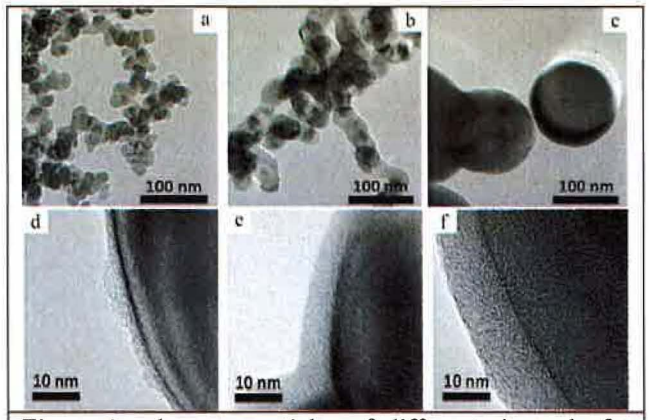


Figure 1. a,b,c: nanparticles of different sizes. d,e,f : shells of varying thickness.

Cycling capacity of current crystalline silicon core-carbon shell materials reaches ~2500 mAh/g at C/10 and retains over 70% capacity at a 2C rate over 500 cycles[7]. As amorphous silicon has been demonstrated to have improved fracture behavior, lithiation kinetics, and first cycle performance[8,9], methods to produce amorphous silicon particles and their performance will be discussed. In order to achieve higher rate capabilities, this study is also focused on developing procedures to supply dopant atoms to the carbon shell via ammonia addition at the second stage and improve shell conductivity. Initial results indicate improved cycling performance, with a capacity of ~3000 mAh/g achieved after 10 cycles at C/5, as shown in Figure 2. Optimization of the carbon doping is on-going and our most recent results will be discussed.

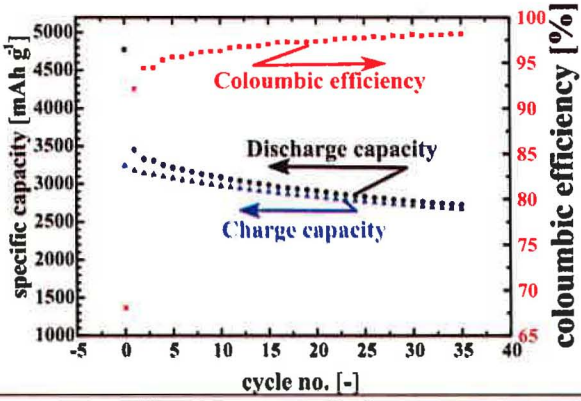


Figure 2: Specific charge and discharge capacity and coulombic efficiency of silicon nanoparticles coated with nitrogen doped carbon, at a C/5 rate.

Physico-chemical analysis results and development of methods to increase the lifetime of these materials during application, such as by mixing with graphite and encasing in pyrolized polymers to reduce solid electrolyte interphase formation[10], will also be presented. Currently we observe an increase in first cycle coulombic efficiency of ~20% and an increase of ~4% for subsequent cycles, as shown in Figure 3, when using a PVC polymer precursor, mechanically mixed with the core-shell nanoparticles prior to pyrolysis in Ar. Other dispersion techniques such as spray drying and electrospinning are to be compared, and the performance dependence on polymer choice elucidated.

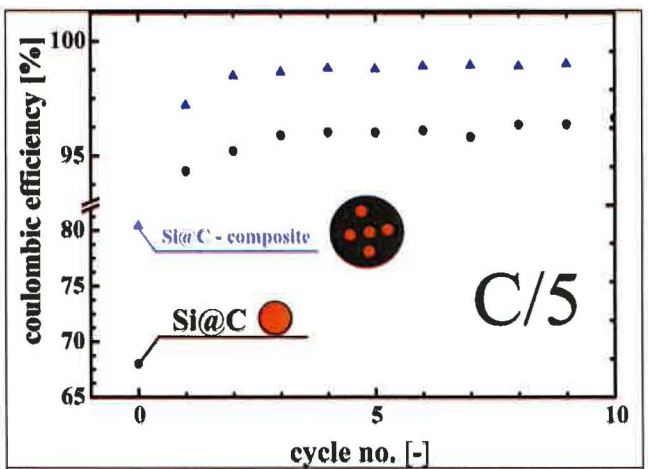


Figure 3: Coulombic efficiency comparison between silicon particles in a carbon shell (Si@C) and Si@C encapsulated in a graphite-PVC derived composite, at a C/5 cycling rate.

References

1. Obrovac, M. N. & Chevrier, V. L. Alloy negative electrodes for Li-ion batteries. *Chemical Reviews* (2014). doi:10.1021/cr500207g

2. Liu, N. *et al.* A yolk-shell design for stabilized and scalable Li-ion battery alloy anodes. *Nano Lett.* (2012). doi:10.1021/nl3014814

3. Liu, X. H. *et al.* Size-Dependent Fracture of Silicon Nanoparticles During Lithiation. **6,** (1522).

4. Wu, H. & Cui, Y. Designing nanostructured Si anodes for high energy lithium ion batteries. *Nano Today* **7,** 414–429 (2012).

5. Nathalie Herlin-Boime, Martine Mayne-L'Hermite, C. R. in *Encyclopedia of Nanoscience and Nanotechnology* 301–326 (2004).

6. N. Herlin-Boime, F. Boisman, J. P. A. Dispotif pour la synthesis de nanoparticules de type couer-coquille par pyrolyse laser et procede associe. Patent Pending: n°FR1661759 (2016).

7. Sourice, J. *et al.* One-Step Synthesis of Si@C Nanoparticles by Laser Pyrolysis: High- Capacity Anode Material for Lithium-Ion Batteries. doi:10.1021/am5089742

8. Mcdowell, M. T. *et al.* In Situ TEM of Two-Phase Lithiation of Amorphous Silicon Nanospheres. doi:10.1021/nl3044508

9. Beaulieu, L. Y., Hatchard, T. D., Bonakdarpour, A., Fleischauer, M. D. & Dahn, J. R. Reaction of Li with Alloy Thin Films Studied by In Situ AFM. (2003). doi:10.1149/1.1613668

10. Luo, F. *et al.* Review—Nano-Silicon/Carbon Composite Anode Materials Towards Practical Application for Next Generation Li-Ion Batteries. *J. Electrochem. Soc.* **162,** 2509–2528 (2015).