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Plasma-produced silicon particles enable highly stable lithium-ion battery anodes

L. Mangolini[1], B.Wagner[2] and P.Ghildiyal[3]

[1] *Department of Mechanical Engineering, University of California Riverside, Riverside CA USA*
[2] *Materials Science and Engineering Program, University of California Riverside, Riverside CA USA*
[3] *SiLi-ion Inc., CA USA*

Abstract: Despite being heralded as the next high-capacity lithium-ion anode material, silicon remains barely utilized by the battery industry. This is mainly due to the poor stability of the material, which typically shows a high rate of capacity loss. Here we show that exceptionally stable lithium-ion anodes can be realized by utilizing plasma-produced silicon nanoparticles. Ultra-fine particles, with size well below 10 nm, have been produced using trichlorosilane as a precursor. Extensive material and battery characterization suggest that the improved capacity retention is largely due to the narrow particle size distribution, which is uniquely accessible by this class of plasma-based processes.

Keywords: silicon anode, coulombic efficiency, capacity retention.

1. Introduction

Silicon is widely considered as the best candidate anode material for next-generation lithium-ion batteries. Its specific capacity largely exceeds that of the current anode material, graphite, both on a gravimetric and a volumetric basis.[1] Substituting graphite with silicon would enable a maximum theoretical capacity gain of roughly 25% at the cell level, i.e. when incorporating the silicon anode with real-life components (cathode, separator, current collectors, and packaging). While promising, silicon-dominant anodes have yet to be broadly utilized. The main issue with this material is its low cycling stability. While graphite retains its capacity over thousands of charge-discharge cycles, silicon shows much faster degradation. Moreover, this behavior is not rooted in a single cause, but it is due to a multitude of failure mechanisms. Lithium does not intercalate in silicon, but rather it forms a silicide resulting in large volume change (roughly 400% upon lithiation).[2] This results in mechanical failure, pulverization, and loss of electrical contact. The use of nanoscale silicon has been accepted by the community as one viable approach to avoid pulverization of the active material.[3] Still, this introduces additional challenges. While the single particle may not fracture, the use of small particles inevitably increases the number of particle-to-particle contact, requiring the need for specialized binders and conductive additives. Finally, a solid electrolyte interphase (SEI) layer is well-know to develop on the surface of the active material. For the case of graphite, this is highly stable due to the negligible volume change. For the case of silicon, the large volume change upon lithiation degrades the SEI, which then partially reforms every cycle leading to the irreversible loss of lithium.[4]

Because of these reasons, the design of a silicon-based anode that achieves sufficient stability for real-life applications has proved to be a major challenge. This has attracted the attention of several research groups. Many different approaches have been proposed to solve the many issues, ranging from the use of nanowires,[5] to careful engineering of void spaces around silicon particles.[6]

Our approach focuses on the engineering of small silicon particles, with the goal of stabilizing the SEI formation and achieving high charge-discharge stability. We specifically design the material so that it is compatible with water-based slurries for application in roll-to-roll coating of the anode onto the copper foil. This is by far the most widespread approach towards anode manufacturing, with

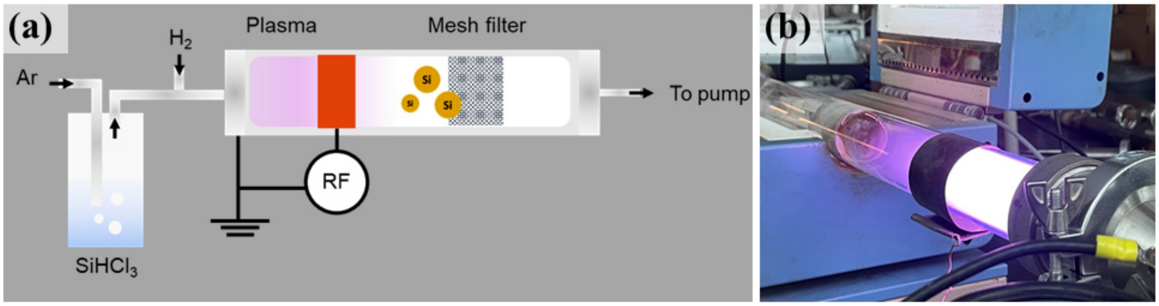

Figure 1. (a) Schematic of the precursor delivery system and of the reactor. (b) Photograph of the plasma reactor in operation.

the industry having already invested significant capital in this manufacturing strategy.

We have found that the use of ultra-fine silicon particles is needed to enable a highly stable anode. We utilize a flow-through low-temperature plasma to produce ultra-fine (<10 nm) particles. Anodes realized with these nanoparticles show excellent charge-discharge stability, with Coulombic efficiency approaching 99.9%. This contribution highlights the importance of a plasma-based manufacturing approach in enabling next-generation energy storage technologies.

2. Experimental Details

The silicon particles are produced in-house using the low-temperature plasma technique pioneered by the Kortshagen group,[7] with the key difference that trichlorosilane ($SiHCl_3$) is used as precursor for this study. As shown by Yasar-Inceoglu,[8] chlorosilanes are viable precursors for the production of silicon nanoparticles under the condition that hydrogen is added to the gas mixture to drive the particle nucleation. A schematic of the reactor is shown in Figure 1a. Trichlorosilane is delivered to the gas phase using a custom-built bubbler. The mixture of trichlorosilane, argon, and hydrogen is fed to a tubular quartz reactor with a 100 mm diameter. The reactor pressure is typically in the 1-5 Torr range. A radio-frequency (RF) electrode is used to sustain the plasma, with a typical power of 100W. The precursor is fed continuously to the reactor volume, and particles are continuously nucleated, grown, and collected downstream of the plasma on a stainless steel metal cloth. A photograph of the reactor is shown in Figure 1b. The tubular quartz reactor is placed inside a tube furnace so that the filter cloth is within the heated zone. Immediately after synthesis, the reactor is evacuated and refilled with acetylene to a pressure of ~1 bar. Thermal CVD at a temperature of roughly 600°C is used to grow a carbon shell around the silicon particles. After the CVD step, the reactor is again evacuated, and argon is flown. At this stage, the furnace temperature is raised to 800°C to induce graphitization of the carbon shell. This approach has been demonstrated to enhance the quality of the carbon shell, improving its electrical conductivity and the performance of the resulting anode.[9] Moreover, this approach allows protecting the silicon nanoparticles from oxidation since they are never exposed to air before the CVD coating step. This is crucially important for battery applications since lithium is irreversibly consumed to reduce any silicon oxide during the first lithiation cycle.

After production, the particles are added to deionized water via high-shear mixing, and the electrode binders are added to the slurry. The typical binder composition is 7.5% of carbomethoxycellulose (CMC) and 7.5% of polyacrylic acid (PAA). These binders have been selected because they have been shown to cross-link upon curing in vacuum, greatly enhancing the structural stability of the anode. The slurry is coated onto copper foils, vacuum annealed, and then transferred to a glove box for battery assembly. Anodes are tested against lithium foil as counter-electrode in coin-cell format. For the results reported here, the batteries have been tested in the 0-1.5 V window at a charge-discharge rate of C/10.

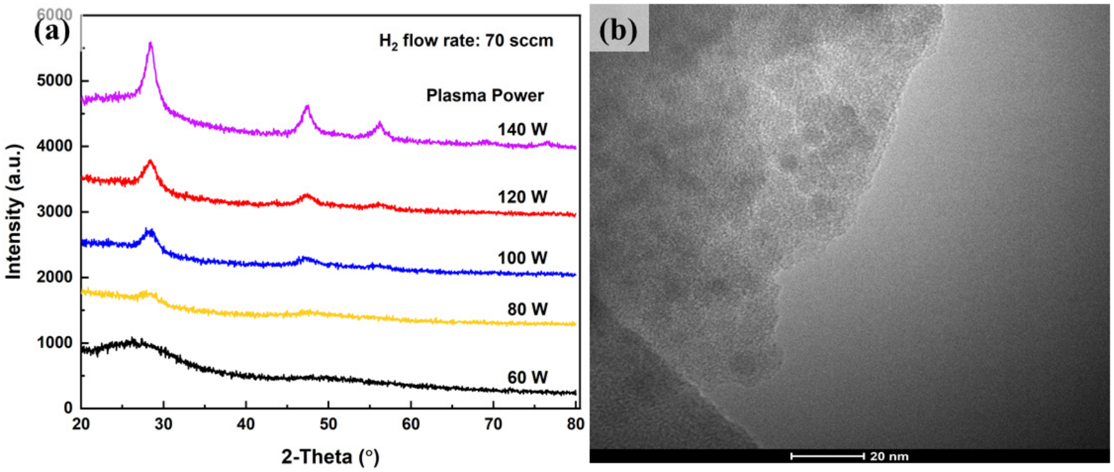

Figure 2. (a) X-ray diffraction patterns as a function of plasma input power. (b) TEM micrographs of the produced particles.

3. Results

Figure 2a shows a typical XRD diffraction pattern for the nanoparticles produced from trichlorosilane. Particles are crystalline with a size of ~4 nm based on Scherrer analysis. Figure 2b shows a TEM micrograph of the same particles, confirming the small particle size. The particles are encased in a carbon shell, which is the product of the thermal CVD process. In Figure 3a we show the variation in discharge capacity over cycle number for the plasma-produced nanoparticles. We measure a capacity of roughly 600 mAh/gram based on the whole weight of the anode (silicon-carbon composite and binders). The capacity is highly stable, with no detectable loss in capacity over 100

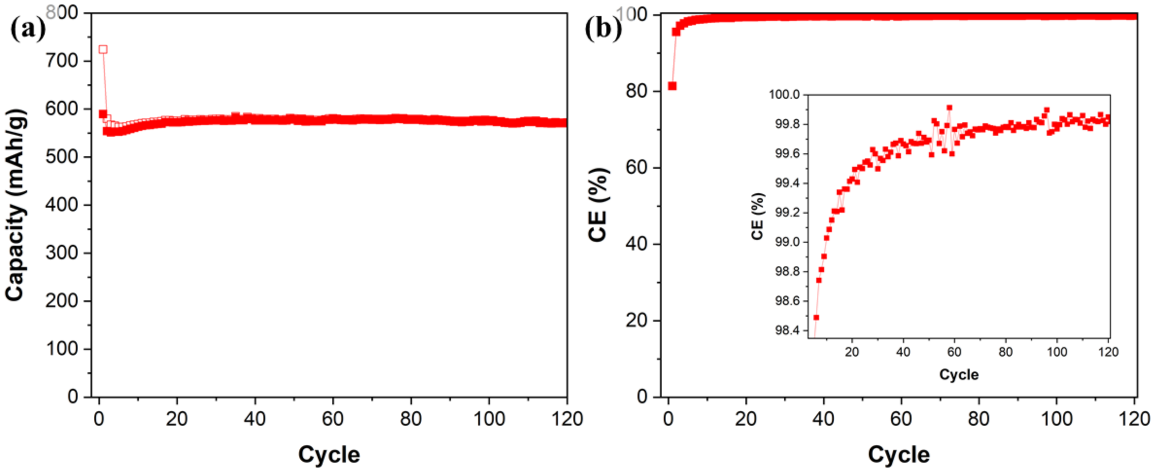

Figure 3. (a) Charge and discharge capacities for plasma-produced silicon nanoparticles. (b) Coulombic efficiency as a function of cycle number. In the inset we show the same curve in a 98.4%-100% range.

deep charge-discharge cycles. Most importantly, we observe a coulombic efficiency that approaches 99.9% after 100 cycles. Coulombic efficiency is a predictor of anode stability in a full-cell format. In half-cell, the lithium foil counter-electrode is effectively a large reservoir of lithium ions; therefore half-cells can be highly stable even if the coulombic efficiency is low. In a full-cell, i.e. when operating with a real-life cathode such as a lithium-iron phosphate (LFP) or lithium-nickel-manganese-cobalt oxide (NMC), any irreversibly lost ion cannot be replenished, leading to rapid capacity decay. We stress that a coulombic efficiency of 99.9% largely exceeds that obtained using commercially available silicon nanoparticles processed and assembled using the same protocol.

This promising performance is a consequence of the very small size distribution of plasma-produced particles. As shown by Schwan and coworkers,[10] commercially available particles always have a small fraction of particles with size larger than 150 nm. These particles are expected to fracture during cycling. While only a small fraction of large particles may exist, their volume and mass fraction is significant. Plasma-produced particles are not only small but also have a very narrow size distribution. This synthesis approach ensures that all particles are sufficiently small to operate in a stable manner.

4. Conclusions

Low-temperature plasmas are well-known to enable the scalable synthesis of very small particles. Here, we take advantage of this property to realize highly stable anodes for lithium-ion batteries. Nanoparticles nucleated from trichlorosilane have been produced, characterized, and incorporated into anodes, which have then been tested in coin cells against a lithium counter electrode. The resulting anodes are among the most stable ever reported for a silicon-dominant structure. These results confirm the importance of plasma-based processes to meet the need for improved energy storage solutions.

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