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Customizing Silicon Particle Size and Shape Through Ball Milling for High Performance Battery Anode Materials

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Fritsch Ball Mills have enabled Ionobell to rapid prototype through a variety of Silicon particle geometries to produce the next generation of high-capacity silicon-based lithium-ion batteries.

Our Materials Research Laboratory (San Jose, CA) develops processes to convert low-cost abundant silicon waste byproduct to high performance pure silicon anode materials for lithium-ion batteries. This requires that we tune the materials size, shape, and porosity to optimize our battery capacity and stability performance depending on the application.

To develop our silicon-based anode material, Ionobell receives a variety of silicon powder waste byproduct of varying compositions, size, and shapes, which needs to be converted to pure silicon, then modified to uniform size distribution, shape, and porosity. This requires laboratory equipment with precise and repeatable parameter controls that can be tuned for specific powder characteristics. Through vigorous experimental testing we have developed robust processes to achieve tunable particle characteristics by ball mill process. Our high-performance Si-based anode material is achieved by creating a highly porous, high surface area and uniform particle, resulting in high capacity and long cycle life.

Through collaboration with Fritsch and their commercially available Planetary Mill PULVERISETTE 5 *Premium Line* from Fritsch shown in Figure 1 and Planetary Mill PULVERISETTE 7 *Premium Line* from Fritsch, we have been pushing the capabilities of their systems to uncharted territories. Through the control of the rotational speed, media material/size, jar material/size, and process timing, we have been able to develop unique recipes to tailor the particle geometries to provide a high capacity, stable long cycle life Si-based anode for lithium-ion batteries. 3-20 mm ZrO_2 media balls were used along with a ZrO_2 lined stainless steel mill jar, with a material to ball ratio of 4:75 and 1:30. Si powder was sealed in the grinding jar under Argon atmosphere using both gassing lids and standard air-tight seals, while the milling was carried out at room temperature under different conditions. One of the conditions employed was a 1 hour mill time at 900 rpm and the second condition was carried out for 3 hours at 500 rpm with and without breaks every hour.

Figure 1: Planetary Mill PULVERISETTE 5 *Premium Line* from Fritsch

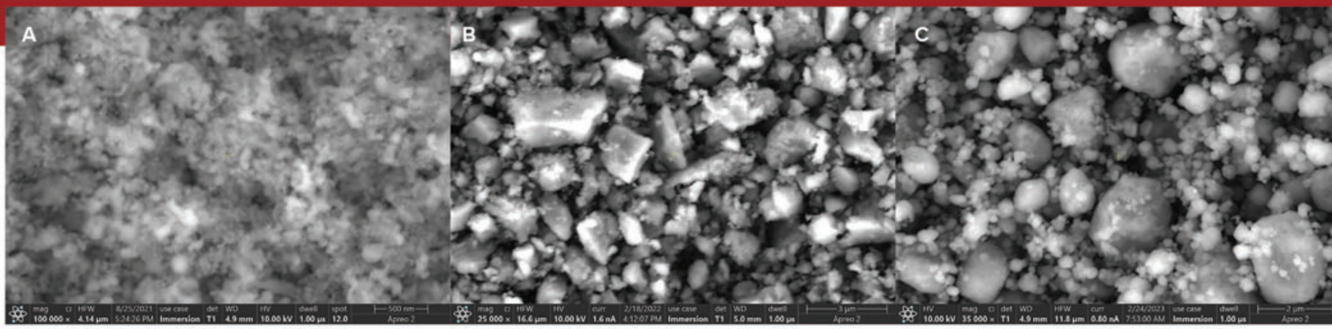

Figure 2: A) Our 10-100 nm sized Si nanoparticles before ball milling. B) Straight edge micron sized particles fabricated at 900 rpm for 1 hour. C) Oval micron sized particles fabricated at 500 rpm over 3 hrs.

Traditionally, ball milling is used to decrease particle size, however we have been able to utilize the cold-welding phenomenon with ball milling to increase the size of our Si powder particulates. Originally, the Si primary particles are between 10-100 nm in diameter as shown in figure 2a. If we apply the 900 rpm mill for 1 hour we are able to create micron-sized particles with sharp jagged straight edges as shown in figure 2b. However, if a lower rpm (500 rpm) is applied and the total mill time is increased to 3 hours with breaks, we are able to further utilize the cold-welding effect to not only increase the particle size but also alter the shape. Figure 2c demonstrates the fabrication of a large micron sized oval particle formed using the cold-welding effect. Thus, with careful manipulation of the rpm, total milling time and break durations we can control the particle shape, size, and porosity. This control is due to the total energy input over time. The lower rpm (500 rpm) results in a low energy input, while the high rpm (900 rpm) generates much higher energy. The higher rpm phenomenon results in fracturing of the large Si particles giving a straight edge morphology.

The anode surface area is also a very critical parameter for lithium-ion anode materials to optimize capacity and stability in the battery. Although a high specific surface area is good in theory to maximize the capacitance of the battery a low specific surface area is needed to minimize the total volume of the solid electrolyte interface (SEI) layer which consumes lithium; thus a balance needs to be achieved to optimize the anode materials shape and porosity.

Control of the porosity and surface area of the particles was also achieved using milling and are demonstrated through Brunauer-Emmet-Teller (BET) measurements shown in figure 3. The specific surface area of the unprocessed Si powder was measured to be ~194.6 m^2g^{-1} (black squares) After milling treatments at 500 rpm with breaks gives Oval (green triangles, BET = 10.2 m^2g^{-1}) particles, while without breaks shows straight edge (blue diamonds, BET = 10.5 m^2g^{-1}). Finally, at 900 rpm sharp straight edge (red circles) were produced with specific surface areas of 10.8 m^2g^{-1}.

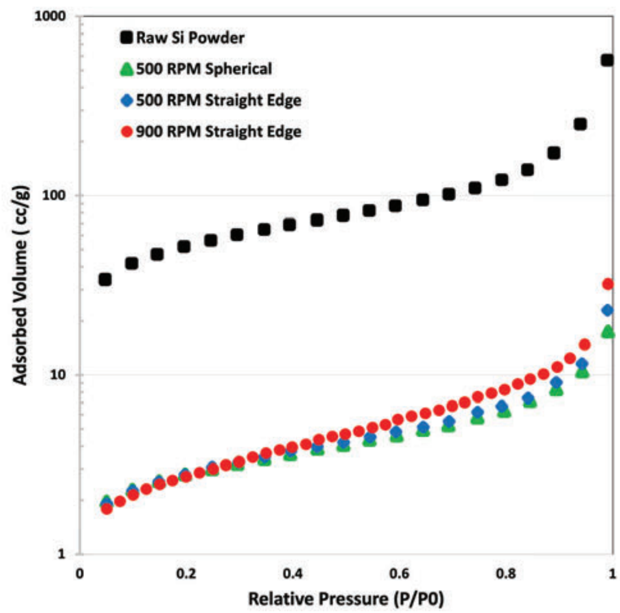

Figure 3: BET specific surface area results for unprocessed Si powder (black square), 500 rpm spherical particles, 500 rpm processed straight edge particles (blue diamonds) and 900 rpm process straight edge particles (red circles).

Ball milling is demonstrated in the competence to modify Si anode materials in particle size and morphology and BET specific surface area. Lower rotational speed give rise to spherification, which is better for rate capability. We were also able to further decrease the BET surface area, which improve the first cycle Coulombic efficiency and cycle life of the Si-based anode cell.

About the Authors

Robert Ionescu is the Chief Technology Officer at Ionobell, and oversees all the technical scientific and engineering developments at Ionobell. Isaac Ruiz is a Staff scientist and manages the material development, processes and Characterization. Chueh Liu is the Lead Test engineer and oversees all electrical testing. Matthew Garrity is our Lead Materials Process Engineer.