High Energy Density and Specific Energy Silicon Anode-Based Batteries

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Abstract: Amprius' unique, patent-protected, silicon nanowire technology addresses swelling by enabling anodes to expand and contract internally, in a very robust mechanical structure. As a result, Amprius has achieved 1000 Wh/L and 400Wh/kg levels of energy density and specific energy, respectively, in lithium-ion cells with a cycle life in the hundreds of cycles. Manufacturing capacity and products are currently available for mission critical applications in aerospace and military.

Keywords: silicon anode; lithium-ion; batteries; energy density; specific energy; power; aerospace; wearable batteries; drones.

Introduction

Current state-of-the-art lithium-ion cells with graphite anodes have specific energies of up to 250 Wh/kg. There is very limited room for improvement because the active materials are utilized at capacities close to their theoretical limits and the packaging has been substantially optimized. Hence, new materials are required to increase performance.

There is an abundance of research on active materials that can increase either the capacity (mAh/g) or the voltage (V vs. Li/Li+) of the cathode side of the cell, but these increases are rather small, around 10-20% at the component level, and about 5% at the cell level. On the anode side, there are active materials such as Si, Ge, Sn, Al and combinations of these that can offer capacities up to an order of magnitude larger than carbon. Silicon offers the most significant increase. But, despite many years of research, none of these materials, in any structure or composition, has been developed to meet the requirements of a commercial product. The key metric in the search for better materials is not only the specific energy capability, but also the cycle life and rate capability of the active material. Amprius is the first to report a stable anode made of 100% pure silicon that can cycle in a full cell for hundreds of cycles and retain more than 80% of initial capacity, at a rate and capacity loading compatible with commercial application requirements. Amprius' technology thus provides a significant step forward in lithium-ion battery development. The anode-based performance improvement is independent of the cathode material. Any increase in cathode capacity will be enhanced in a silicon battery due to the higher percentage of cathode in the cell.



Figure 1. Silicon materials have a theoretical capacity ten times higher than that of graphite anodes

For example, when paired with commercially available cathodes (e.g., LCO and NCM type materials with a cycling capacity of 150-200mAh/g), Amprius' silicon nanowire anode-based cells have demonstrated 300-400Wh/kg - an increase of 30-50% in specific energy over state-of-the-art lithium-ion cells. Amprius' volumetric energy improvements are similarly impressive compared to carbon cells because the anode is the most voluminous component of the cell. See Figure 2. Amprius' anode takes up less space and weighs less than state-of-the-art anodes, giving the cell higher energy for a lower volume/mass (or, allowing for more run time with the same volume/mass). Amprius' silicon anode cells currently reach over 1000 Wh/L and can potentially achieve over 1200 Wh/L, depending on cell design, capacity and other cell components.





Technical Description

Structure and Properties: The silicon nanowire structure, shown in Figure 3, includes a metallically conductive nanowire core, metallurgically connected to the current collector. This robust connection is essential in creating and maintaining a stable electrical connection and mechanical structure at the electrode level. Each silicon wire is directly connected and does not need to rely on particle-to-particle contacts for conductivity. Since this connection is very

robust compared to connections between particles created by electrode calendaring and binders, the silicon material remains in electrical contact, i.e. electrochemically active, over the entire cycle life of the cell. The fast loss of electrical connectivity and changes in mechanical structure that plague the majority of other silicon technologies are virtually non-existent in the rooted silicon nanowire anodes. Moreover, this significant stability is achieved in a structure that is virtually 100% silicon, without any binder or conductive additive to dilute its active material content.



Figure 3. Amprius' growth rooted silicon nanowire structure

The silicon nanowire has a tapered shape, with a much lower thickness toward the root, where it connects to the current collector. This shape is essential in reducing the mechanical stress at the interface during lithiation/ delithiation cycles. When silicon films or particles are coated on foils as thin as those used currently in lithium ion cells, e.g. 6-12 μ m in thickness, upon lithiation the foils are stretched and that leads to wrinkles, ripples and foil ripping. In the case of silicon nanowire electrodes, the minimum contact surface between the root of the silicon wire and foil eliminates mechanical stress in the foil during cell cycling.

A second feature of Amprius' silicon nanowire material is its nanostructure. The internal porosity and amorphous structure accommodate and dissipate some of the mechanical stress induced in the material during lithiation/delithiation processes. Since these processes start from the silicon/electrolyte interface, they occur mostly radially, and the stress and material swell are of the same geometry. The silicon nanowire structure can accommodate a large amount of lithium without significant radial swell. Even at full lithiation, the axial swell, which is responsible for the cell swelling, is less than 30%.

The nanowire material structure also enables a relatively high 94% first coulombic efficiency in half cells and 90% coulombic efficiency in full cells with LCO cathode. These values are competitive with graphite materials and reduce or eliminate the need for prelithiation steps that compensate for the first cycle loss in the cell fabrication. A typical first cycle at a 0.05C rate of a silicon nanowire electrode is shown in Figure 4.



Figure 4. Silicon nanowire voltage profile in half cell, lithiated to 10mV vs. Li/Li+ electrode and delithiated to 0.9V at a 0.05C rate

Energy Density and Specific Energy: The main advantage of using silicon materials in lithium ion cells reaches the highest level with silicon nanowire technology. Since silicon is the material with the highest capacity for lithium storage, a 100% silicon anode would bring the most performance advantage to lithium ion cells. The reduction in anode thickness frees more space in the cells for the rest of the cell components, including the other active material, the cathode. As a result, cell energy can be increased in the same cell volume, or the size of the cell can be reduced while keeping the energy at the same level. Both options are a result of a significant increase in energy density. The reduction in anode volume of 2-2.5 times compared to graphite results in an increase in energy density of 30-60%, depending on the cathode material and type, loading and other cell component specifications. The cell specific energy increases as well but by a slightly smaller percentage (see Figure 5).



Figure 5. With the same cathode and separator components, the silicon nanowire anode technology significantly increases energy density and specific energy (solid circles are demonstrated products)

Cycle Life: The silicon nanowire anodes can cycle for hundreds of cycles in full cells due to limited swell at the material and cell level, and stable material and electrode structure. The stability of the material and partial utilization of the theoretical capacity of silicon also limit lithium consumption for SEI repair and, thus, extend the cycle life to numbers approaching those of graphite cells. In cells with LCO cathode, the cycle life depends on the cathode loading and charging voltage, which are adjusted based on the target energy density and specific energy. Moreover, the rate of lithium consumption and SEI growth are strongly affected by the cycling rate. The increase in volume and lithium consumption can be mitigated by improved electrolyte formulations. However, during anode delithiation (cell discharge), higher discharge rates lead to increased tensile stress in the outer regions of the silicon material and eventual crack formation at the surface. Crack formation is more damaging to cycle life because it increases significantly the surface area of the silicon, which leads to accelerated lithium loss and impedance increase. The nanowire structure with a porosity gradient in its structure reduces these effects, but the SEI growth is still faster than on graphite materials. Figure 6 presents cycle life curves for cells with capacities of 2.6-3.1Ah in the same form factor as a function of their energy density. The increased energy density was achieved in this case by changing the cathode loading and maximum operating voltage.



Figure 6. The cycle life of Si/LCO cells ranges from 200 to 500 cycles, and depends on cathode loading and maximum cell voltage

Rate and Power: The nanowire structure has higher surface area than typical lithium ion material structures in graphite electrodes. This advantage can be exploited in silicon nanowire cells by matching the nanowire anodes with a cathode designed for a target rate capability. For example, in cells designed mostly for high energy applications (smartphones, tablets, day-night cycling etc.), the acceptable continuous discharge rate is limited to 1C rate (see Figure 7A). However, in cells designed for power and high rate continuous discharge (drones, power tools), the continuous discharge rate can be as high as 10C (see Figure





Figure 7. A – Discharge curves at different rates after charging at C/5 rate for a high energy density cell; B-Discharge curves at different rates after charging at 1C rate for a high-power density cell

The high energy density and specific energy performance of the silicon nanowire cells, coupled with its superior power performance, result in a relatively flat and wide range Ragone plot, as shown in Figure 8. This property is very appealing to a wide range of applications in aerospace and telecommunications, which can take advantage of high specific energy and energy density cells while still requiring high power for limited amount of time. The power/energy ratio is controlled by the cathode specifications because the cathode is the limiting rate component.



Figure 8. Energy vs. Power density curves (Ragone plot) of Si/LCO cells are controlled mostly by cathode structure, which is the limiting rate component.

Safety: Silicon nanowire cells developed in the last few years were successfully tested in multiple abuse and safety evaluation conditions, including electrical, mechanical and thermal factors. For example, 2.2Ah pouch cells with silicon nanowire anode and LCO cathode were certified to pass the tests required for air cargo shipping, according to UN 38.3 specifications. These tests include Altitude Simulation (low pressure test), Thermal Shock Test (-40°C to 72°C), Vibration, Mechanical Shock and External Short Circuit, done sequentially on the same cells, as well as Crush and Forced Discharge tests, done separately. The same type of cells also passed the suite of tests included in the UL 1642 specification. Separately, silicon nanowire cells passed other abuse and safety test, including nail penetration and overcharge to by 150% charge capacity. These results suggest that there is little argument to support the assumption that silicon materials are inherently less safe than graphite anodes.

Products: Amprius has already developed and demonstrated the performance of its patented silicon nanowire anode structure in prototype cells of different form factors, with cathodes that include LCO, NCM and NCA materials, and with capacities up to 45 Ah. Amprius has also begun commercializing its cells for high-end and mission critical applications. Some of the form factors developed are shown in Figure 9.





In an Army (NSRDEC) conformal battery project, Amprius developed a 2.2 Ah cell. Amprius' cell exceeded the project's energy goal (301 Wh/kg) by 8%. Independent, third party testing houses (UL) tested and validated Amprius' cell (in the form factor developed for the project) for both performance and safety (UL 1642 and other tests, including nail penetration). Amprius' cell received the UN 38.3 certification for air transportation. The cell was designed for a 150 Wh CWB that reduced the weight of the Army's current battery pack by 40%.

Amprius developed a 5.8Ah cell under a contract with NASA Glenn Research Center, which verified that the performance (specific energy and cycle life) of Amprius' cells exceeded the project's targets; Amprius achieved >340Wh/kg and more than 200 cycles at both at 0°C and 30°C.

With USABC (Ford, GM, Fiat Chrysler and DOE) support, Amprius developed a 45 Ah cell in a standard form factor for electric vehicle applications. Cells with NCM cathodes achieved 340Wh/kg and were tested by Idaho National Laboratory and Sandia National Laboratory for performance and safety. Amprius' smaller Silicon-NCM cells passed over 500 cycles of driving cycle stress tests.

Commercial entities from the aerospace industry tested Amprius cells designed for very high specific energies (>350 Wh/kg). Amprius' cells achieved 400 Wh/kg in a 3.8Ah cell form factor and are currently powering advanced aircraft.

Summary and Conclusions

Silicon is recognized as one of the most promising materials for next generation lithium-ion battery anode to replace the conventional carbon-based anode due to its high theoretical capacity, similar discharge potential and reliable operation safety. However, in most silicon material structures and compositions, the critical drawback of huge volume expansion upon lithiation causes series of adverse consequences, leading to very poor cyclic stability.

The rooted silicon nanowire structure developed by Amprius has largely mitigated the drawbacks that afflict other silicon materials and has led to the development of lithium-ion pouch cells with energy and power performance significantly above those of commercial state of the art graphite anode cells, in most cases by 30-50% improvement. Moreover, the cycle life of these cells is closing in on graphite cell performance, already meeting the requirements of a variety of markets. Some of the silicon nanowire cell products have been already qualified for applications, including safety and abuse tolerance validation. In general, the development of first silicon nanowire products has shown that the safety and abuse tolerance of silicon nanowire cells can be as good or better than that of similar graphite cells. It is expected that, in parallel with an increase in manufacturing capability and capacity, the application scope of silicon nanowire cells will expand from premium and mission critical markets to consumer and commercial application in the next few years.

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