Silicon-Nanowire Anode Battery Assessment and Comparison to Li-Ion

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Abstract

Silicon is considered a viable substitute for graphitic carbon as an electrode in lithium-ion batteries. It has a theoretical capacity ten times that of graphite however there are issues regarding extreme volume change during cycling leading to reduced cycle and calendar life. Amprius Technologies has developed a novel silicon nanowire architecture that attempts to mitigate this problem. This study sought to assess the silicon nanowire battery capability under a variety of test conditions.

Keywords

Lithium-ion battery; silicon anode; rechargeable battery

Introduction

Over the last 15 years, lithium ion (Li-ion) batteries have become the established leader in energy and power densities for electronic devices. The BB-2590, with an energy density of 186 Wh/kg (278 Wh/L) and composed of 18650-type cells, is the military's standard rechargeable Li-ion battery. Developed in the 1980's, Li-ion is nearing its theoretical limits in energy. Today's cells already have twice the gravimetric energy density (~250 Wh/Kg) of the first commercial versions sold by Sony in 1991 and they cost ten times less.[1] Only modest improvements are expected in future years. Therefore, new electrode materials and novel power source device architectures will be necessary if the military chooses to use advanced electronics and weapon systems that require ever increasing power and energy.

One approach to obtain energy densities that are beyond present Li-ion battery capabilities is to replace the layered graphitic anode with silicon (Si). While the specific capacity of graphite (372 mAh/g) is higher than present cathodes materials, it has a relatively low density of 2.25 g/cm^3 that limits capacity to 837 mAh/cm^3. Si however, exhibits one of the highest theoretical specific and volumetric capacities (4,200 mAh/g and 9,782 mAh/cm^3) of the various anode materials investigated. In addition, it has a low electrode potential (~0.3 V versus the Li/Li$^+$ electrode). Anodes using Si allow the battery to be designed using a thinner, lighter electrode than the present graphite electrode. As a consequence, both battery gravimetric and volumetric energy densities are increased.

Experimental

Prototype cells utilizing Si nanowires as anodes were obtained from Amprius Technologies. The high-energy cells referred to as CL-0009 were designed for high altitude drones, targeting the highest energy density for a cycle life of at least 100 cycles. The cells were of laminate aluminum foil pouch cell construction and used a lithium cobalt oxide cathode and a proprietary electrolyte consisting of $LiPF_6$, ethylene carbonate and ethyl methyl carbonate. The supplier's specifications noted a cell voltage range of 2.75 V to 4.39 V, a nominal voltage of 3.60 V and a nominal capacity of 3.7 ampere hour (Ah). The dimensions of the cells were approximately 57 mm high, 49 mm wide and 4.75 mm thick. The weight was approximately 33.4 g.

Lithium-ion cells were obtained from Samsung for comparison purposes. The cells (INR18650-35E) are of 18650 configuration, a nominal capacity of 3500 mAh and a nominal voltage of 3.6 V. The cells consist of a graphite anode and a lithiated nickel manganese cobalt oxide cathode. The voltage range is 4.2 V to 2.65 V and they are capable of a continuous 8 A discharge rate.[2] The diameter of the cell is 18.75 mm and the length is 65.25 mm. The cell typically weighs 47.63 g.

A MACCOR 4000 Battery Cycler was used for galvanostatic cycling tests. Unless noted, cells were evaluated using a constant-current/constant-voltage (CC-CV) protocol. In this procedure, the cell is charged at a current to a pre-determined voltage followed by holding the cell at that voltage until the current declines below a specified current or for 1 hour. A Tenney Environmental Chamber was used to control cell temperature during testing. Cells were allowed to equilibrate at temperature for at least 4 hours.

Results

A comparison of cell specific energy density of the silicon pouch-cell design and the 18650 cylindrical-cell design is shown in Figure 1. Both Amprius and Samsung cells were cycled to the voltage endpoints (2.75 V to 4.39 V, 2.65 V to 4.2 V respectively) recommended by the manufacturer at the 5-hour (C/5) charge/discharge rate and 25^{o}C. The silicon pouch-cell delivered approximately 120 cycles with a specific energy density at mid-point averaging 51% higher than the 18650 cell. Cells showed evidence of gassing during these experiments suggesting decomposition of the electrolyte. Discussions with Amprius later revealed that lowering the upper voltage cutoff to 4.25 V would minimize gassing and extend cycle life although at the expense of specific energy.

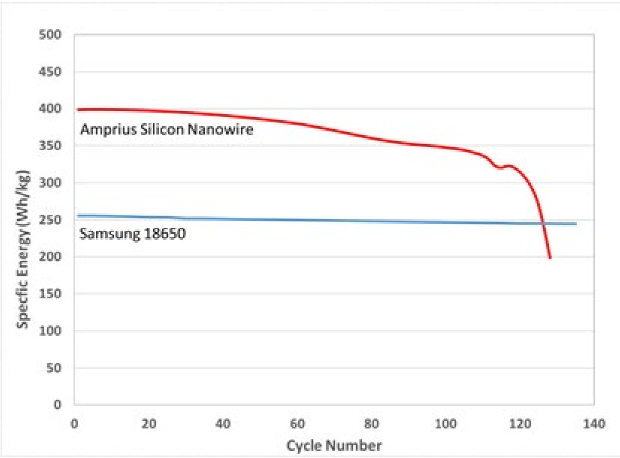

Figure 1. Gravimetric energy density comparisons of an Amprius pouch cell and a Samsung 18650 cell. Both cells were charged and discharged at 25 ºC and the C/5 rate**.**

Battery investigators evaluating new technologies often charge and discharge cells at the same temperature to minimize the time to conduct experiments. Although informative, the data does not necessarily represent real-world scenarios when batteries are used in the field at sub-ambient temperatures. Most military users recognize that batteries charge more efficiently near 20ºC and consequently avoid charging at or below 0ºC. To gain a better assessment of the silicon nanowire cell under more realistic military conditions, one group of cells was cycled using the more typical method (0ºC for both charge and discharge) and another group cycled using the following test procedure: (1) equilibrate cell at 0ºC for 8 hours, (2) discharged at 0ºC (C/5 rate) to 2.75 V, (3) equilibrate cell at 25ºC hours for 8 hours, (4) charge at 25ºC (C/5 rate) to 4.39 V, then (5) trickle charge at 4.39 V until either the current falls to 0.075A or 1 hour has passed. Cells charged at 25ºC delivered over 30% more cycles than cells charged at 0ºC (Figure 15). A subset of the study was to investigate the effect of cell compression on electrochemical performance. Figure 2 shows the applying 30 psi pressure to the cell may be beneficial especially when cycling at low temperatures. We speculate that applying pressure forces the active electrode materials to be in intimate contact with each other and with the current collector and therefore extends cycle life.

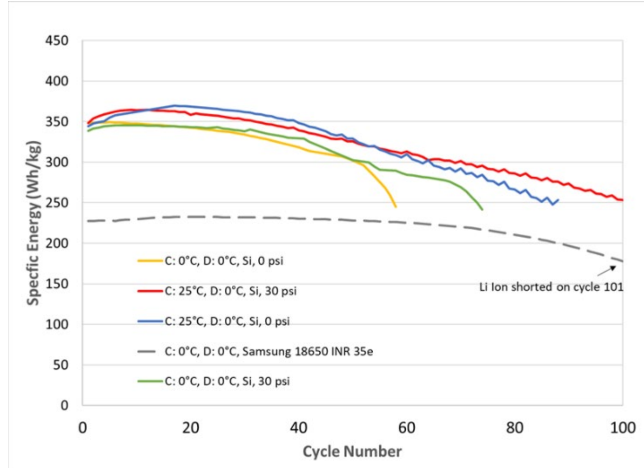

Figure 2. Effect of charging temperature and compression on specific energy density and cycle life of Amprius cells discharged at 0ºC. Dash line denotes performance of Li-ion 18650 (3.5 Ah Samsung INR) cell cycled at 0ºC and C/5 rate.

Summary

Silicon nanowire prototype cells (3.7 Ah) were evaluated to determine their potential value for Navy and Marine Corps applications. Cells were cycled under the supplier's recommended "high-energy" test procedures. The silicon anode cells displayed approximately 40% greater specific energy than the graphite-anode (18650) cells (100th cycle). Despite this promising feature however, the Amprius prototype cells charged to 4.39 V displayed limited cycle life. To realize the full potential of this technology, the upper limit of the charging voltage should be reevaluated and/or improved electrolytes and protective anode coatings should be considered.

Acknowledgements

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References

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