Studies on ALE 4Ah Li-ion 18650 Cylindrical Cells with zero volts stability at Extremely Cold Temperature -57°C

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Abstract

A high energy and high-power ALE 4Ah Li-ion 18650 cylindrical cell has been studied extensively for space exploration and military applications. The cell showed not only a high specific energy ~330 Wh/kg and high power ~700 W/kg, but also strong stability at zero volts. No loss in the power and capacity was observed after repeatedly discharged to zero volts at C/5 and then held at zero volt at 20 ohms for 7 days. Further, there is no change in the cell self-discharge test for ALE 4Ah 18650 cells with zero voltage design. The self-discharge during rest is negligible after 5 times of zero-volt exposure (ZVE) at 20 ohm resistance discharging for 7 days (total 35 days). For a comparison, the commercial 3.5 Ah 18650 cell showed a significant self-discharge after 4 times of ZVE for 7 days (total 28 days). The cell also showed good cycle life and demonstrated about 500 cycles at 80% DOD and >6000 cycles (about two years and cycle life testing is still ongoing) at 20% DOD with <2% energy loss. Further, the cell performed well at extremely low temperatures. No capacity loss was observed after -65°C storage for 3 hours. The cell can deliver >3Ah capacity at -40°C and C/5 rate, and 1.8Ah at -57°C and C/16 rate, respectively, which is the best among all commercial 18650 cells. The results will be discussed according to the military and NASA applications.

Keywords

Li-ion Batteries; 18650 Cylindrical Cells; Si electrode; Zero-volt Exposure; Zero-volt Stability; Zero-volt tolerance; ZVE; ZVT; High energy; High power; Extremely Cold Temperature; NASA; Low Earth Orbit; LEO; Satellite

Introduction

Cylindrical cells have been well developed and one of the top Li-ion batteries (LIB) products for commercial markets and military applications owing to wide voltage window, high energy, and good cycle life. 18650 cylindrical cells have been reported and produced by renowned manufacturers, including LG, Samsung, and Panasonic, etc. A strategy that has gained popularity since 2010 is the addition of Si into graphite electrodes, forming an anode material combination, to increase the nominal cell capacities from 2.2Ah to 3.5Ah. The reported maximum specific energy is ~250Wh/kg, less than pouch cells/prismatic cells with similar chemistry. On the one hand, the demand of high energy density LIB is increasing in military applications where minimal loss of cell capacity is required when LIBs are subject to different abusive conditions.

Specifically, the performance of cylindrical cells at low temperature is severely degraded due to low conductivity of electrolyte, especially at the simulated temperature of space environment, thus limiting their practical applications in aerospace for satellites.

American Lithium Energy Corporation (ALE) has developed a high energy and high-power 4Ah Si Li-ion cell using negative electrodes by Si chemistry and exclusive zero-volt tolerance (ZVT). The theoretical capacity of pure Si anode is ~4000mAh/g, which is nearly 10 times the capacity of traditional graphite anodes. However, the volume expansion is also high, up to ~300%, thus resulting in electrode delamination and poor cycle life. ALE has combined high Si (>50%) and graphite electrodes to get high capacity and also address the expansion issue with exclusive slurry formulation and electrode fabrication.

The corrosion of negative current collector, i.e., Cu foil is the main challenge when the cell is discharged below 1V. ZVT is a patented ALE technology, the central strategy is to add a sacrificial electrode into negative electrode and can protect Cu foil when the voltage is discharged close to 0V or negative voltage. The benefits of ALE patented ZVT are multiple points: (1) sacrificial materials are low cost and not moisture sensitive or air sensitive, (2) not participate in the normal electrochemical reaction, (3) improvement of cycle life owing to the protection as early as cell wetting before formation, (4) wide application for any cell using Cu foil as current conductor, (5) improvement of cell shelf life and cell safety, (6) low temperature performance cooperated with electrolyte additive.

ALE is currently focusing on the production line of 18650 cylindrical cells. ALE has gained 10 million funding support from California State.

4Ah Si Li-ion Cell Rate and Cycle Life

As shown in Figure 1, the 4Ah Si Li-ion cell discharge rates were tested at 0.2C, 0.5C, 1C, and 2C, respectively. The voltage window is 4.4V-2V. The discharge capacity at 1C is 4.2Ah, very close to 2C. The rate capability is excellent and can fit the high-power cell requirement. Therefore, the 4Ah Si Li-ion cell has a high specific energy ~330Wh/kg, and a high-power ~700W/kg.

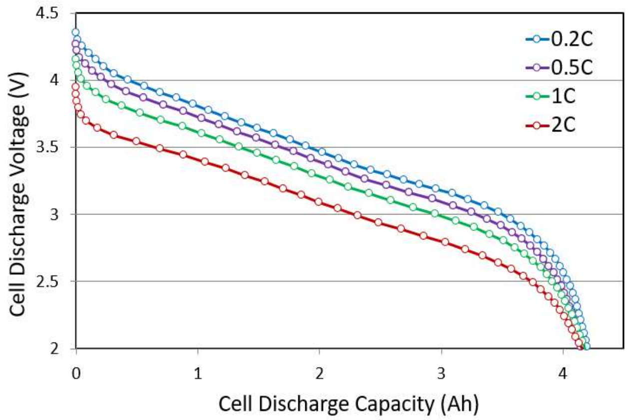

Figure 1. 4Ah Si Li-ion Cell capacity-voltage profiles at different rates

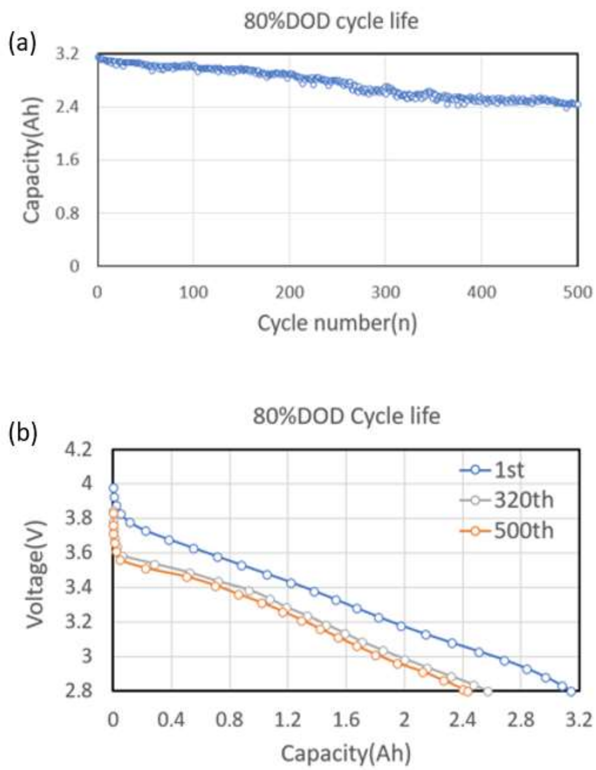

Figure 2. 4Ah Si Li-ion Cell 80%DOD Cycle life (a)Capacity vs cycle number (b) Voltage-capacity profiles at different cycle numbers

The cycle life of 4Ah Si Cell has been tested in 80% DOD and 20% DOD, respectively, per different requirements. Figure 2(a) shows the discharge capacity-cycle number profile of 80%DOD. Figure 2(b) shows the voltage-capacity profile of 80%DOD. The capacity after the 1st cycle is ~3.2Ah, 80% of 4Ah, after the 320th cycle is 2.57Ah, and after the 500th cycle is 2.4Ah. The capacity retention is 80% after 320 cycles, 75% after 500 cycles.

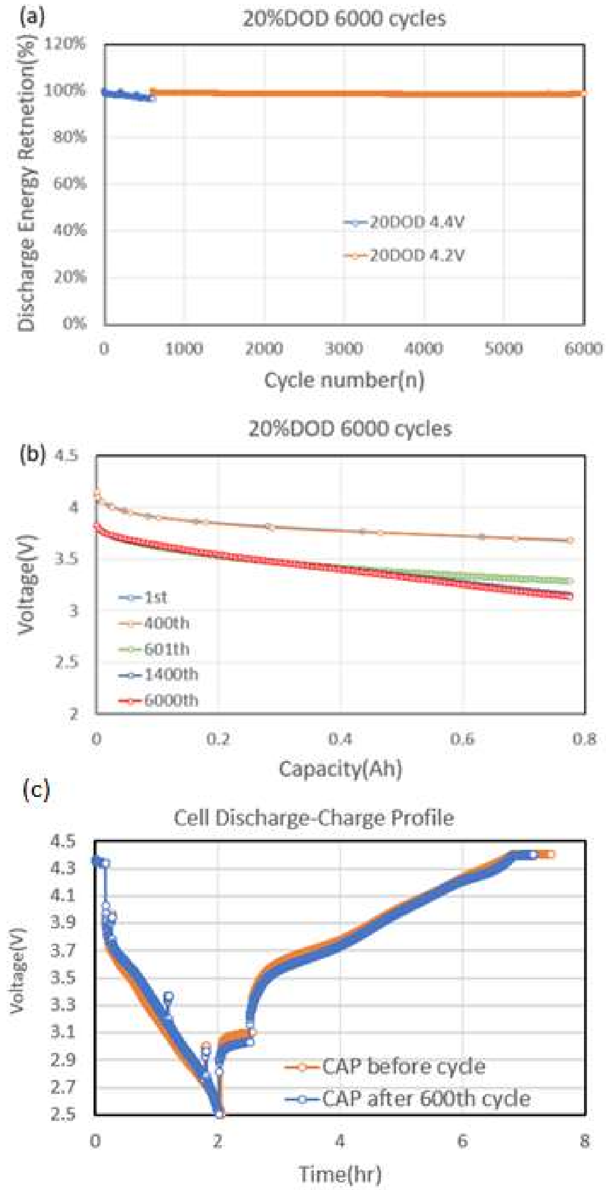

Figure 3. ALE 4Ah Si Li-ion Cell 20%DOD cycle life (a) discharge energy retention vs cycle number (b) Voltage-Capacity profiles at different cycle numbers (c) discharge-charge profile before cycle and after cycles.

Table 1 Capacity and DCR analysis before cycle and after 600 cycles

Parameter	Before Cycle	After 600 cycles	Δ(%)
Ch. Capacity (Ah)	3.692	3.584	-2.92
Dis. Capacity (Ah)	3.684	3.599	-2.30
Ch. Energy (Ah)	14.67	14.06	-4.15
Dis. Energy (Ah)	11.62	11.60	-0.17
C.E. (%)	99.77	100.40	0.63
E.E. (%)	79.18	82.49	4.18

Figure 3 summarizes 20%DOD of 4Ah Si cell. The 1-600 cycles (blue line) were operated at 4.4V, and 601-6000 cycles (orange line) were at 4.2V, respectively. The observed discharge energy loss is 3.3% in this case after 600 cycles is attributed to polarization accumulation, decrease in state of charge (SOC), and cell degradation (Figure 3a). The voltage-capacity between 1st and 400th is identical, indicating no degradation at 4.4V. The voltage-capacity between the 1400th and the 6000th is almost identical, indicating little degradation at 4.1V(Figure 3b). To further verify the real cell degradation, the discharge energy between the 1st cycle and the 600th cycle has been compared with the same procedure (Figure 3c). The real discharge energy loss is 0.17% (Table 1). The total discharge energy loss is ~1.5% after 6000 cycles (~5400 cycles at 4.1V). The projected 20%DOD cycle life is 70000 cycles at 4.1V with ~20% energy loss, which is very promising to fulfill the LEO satellite mission task (25000 cycles, 20%DOD, 5 years shelf life) and close to the requirement of LEO satellite mission task (75000 cycles, 20%DOD, 15 years shelf life).

Zero-Volts Stability

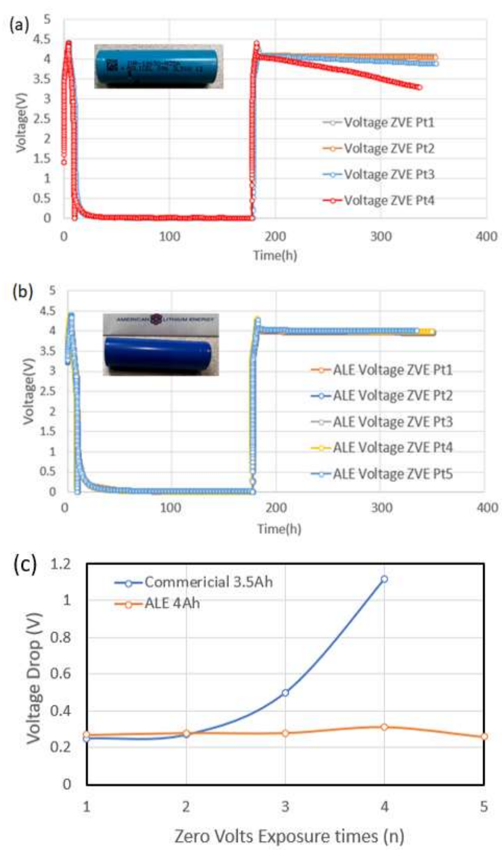

Figure 4. (a) Commercial Graphite 3.5Ah Cell ZVE 20ohm 7days and Rest 7days for 4 times (b) ALE 4Ah Nano Si Li-ion Cell ZVE 20ohm 7days and Rest 7days for 5 times (c) Self-discharge analysis based on voltage drop

Table 2 Self-discharge of commercial 3.5Ah cells and ALE 4Ah Cells after ZVE 20ohm 7days

ZVE	Voltage (V)			
Cell	Commercial 3.5Ah		ALE 4Ah	
Step 8	Before Rest	After Rest	Before Rest	After Rest
1st ZVE	4.28	4.03	4.22	3.95
2nd ZVE	4.34	4.07	4.25	3.97
3rd ZVE	4.40	3.90	4.27	3.99
4th ZVE	4.40	3.28	4.30	3.99
5th ZVE	-	-	4.26	4.00

Zero-volts stability is an important feature of ALE 4Ah Si Li-ion Cell. The self-discharge of the cells have been tested according to the following procedure: (1) CC-CV to 4.4V at C/5, cut off current C/20; (2) Rest 10 minutes; (3) CC DC to 2.5V at C/5; (4) Rest 30 minutes; (5) CC DC to 0V at C/5; (6) Discharge with 20ohm at 0V for 7 days; (7) CC 5hrs at C/5; (8) Rest 7days; (9) Measure OCV at step 7 and step 8.

Figure 4 and Table 2 summarize the zero-volts stability studies after ZVE at 20ohm 7days for up to 5 times. The self-discharge analysis was evaluated based on OCV before rest and after 7 days rest (Step 8). The voltage drops in the first two ZVEs for 3.5Ah is ~ 0.25V, however, the value fast increased larger than 1V after the 4th ZVE. In contrast, the voltage drop for 4Ah Si cell is very stable, ~ 0.26V after the 5th ZVE. This indicates that ALE 4Ah Si cell has excellent zero volts stability. The detailed capacity and DCR studies have been reported in our previous reports.

Cell Abuse Test

Safety is an indispensable feature for all commercial and military cell applications. ALE 4Ah Si Li-ion Cell have subjected to abusive testing including crust, impact, and hotbox per the UN 38.3 requirements.

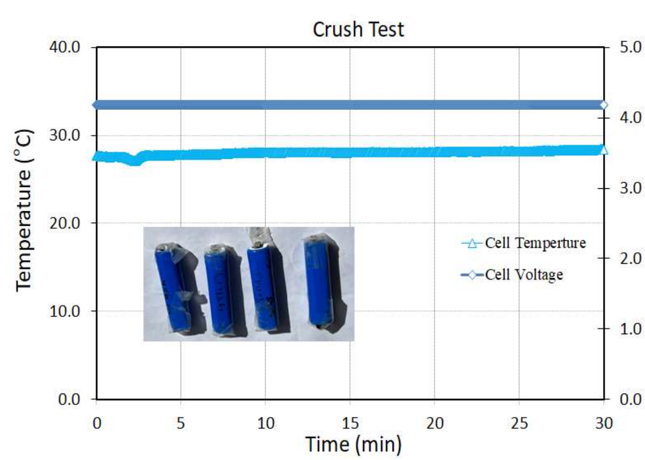

Figure 5. ALE 4Ah Si Li-ion cell crush test at 100% SoC

Figure 5 shows a typical crush test profile at 4.2V under pressure >2500 Psi. The crushed cells are distorted with a flat shape. The initial voltage was 4.2V and doesn't drop after 30 minutes, and the temperature did not significantly change from its initial reading of 28°C during the test. The was repeated several times and has proven reliable.

Figure 6 shows a representative hot box test. The fully charged cell was placed in a temperature-program controlled chamber. The initial temperature was 20°C ramped to 130°C and kept at temperature for 60 minutes, and finally cooling down 60 °C. No leaks, fire, or explosions were observed for all cells subjected to test.

Figure 7 shows a typical impact test at 50% SOC. The voltage was stable during the test at ~3.6V, and temperature was ~25°C. All cells passed the above abuse tests, without fire, explosion, or leakage observed.

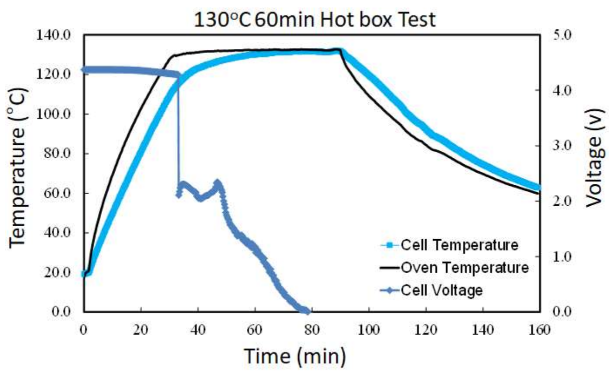

Figure 6. ALE 4Ah Si Li-ion cell hot box test at 100%SOC

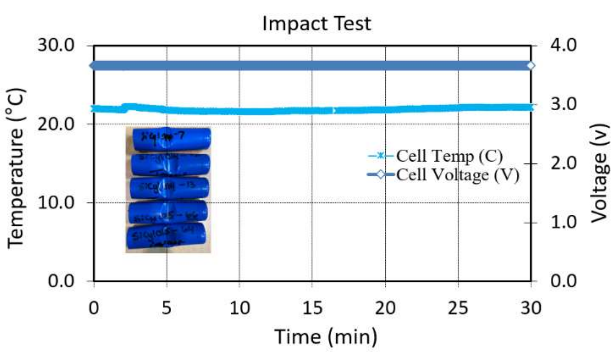

Figure 7. ALE 4Ah Si Li-ion cell impact test at 50% SOC

Low Temperature Performance

The performance of ALE 4Ah Si cells have been tested at various sub-zero temperatures. Figure 8 shows the voltage-capacity profiles at RT, -32°C, -40°C, -51°C, and -57°C. The corresponding capacity is 4.20Ah at C/5, 3.13Ah at C/4, 3.05Ah at C/5, 2.20Ah at C/4, and 1.8Ah at C/16, respectively. Figure 9 shows the cell capacities before and after -65°C storage for 3 hours. No capacity loss was observed for the extremely cold temperature treatment. This is the best result among the current 18650 commercial cells.

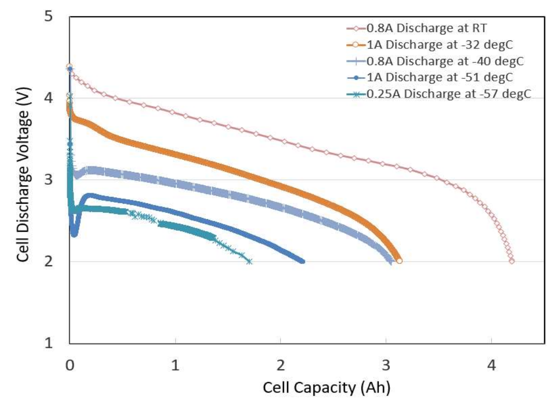

Figure 8. ALE 4Ah Si Li-ion cell capacities at low temperatures down to -57°C

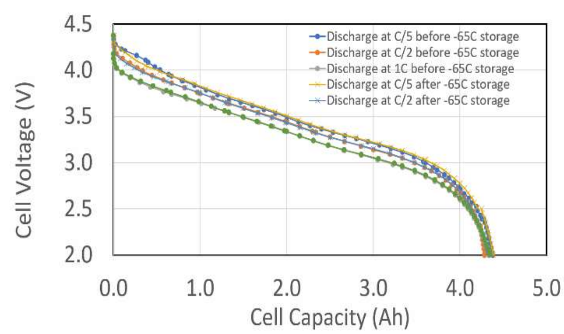

Figure 9. ALE 4Ah Si Li-ion cell capacities before and after -65°C storage for 3 hours.

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