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Low Temperature Cycling Performance of the SONY 18650 Hard Carbon Mandrel Cell

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Nomenclature

Ah = ampere hour
V = volts
A = amps
EoCV = end of charge voltage
°C = degrees Celsius
C = capacity
SEI = Solid Electrolyte Interphase (SEI)
HCM = 18650 hard carbon mandrel cell

EnerSys/ABSL Space Products (ABSL) has extensively used Sony Corporation's 18650 hard carbon cells in the manufacturing of its space flight battery systems. Occasionally there is a need for a space battery that is capable of operating at low temperature which is below the cell manufacturer's stated operating temperature range. Low temperature cycling of the 18650 hard carbon cells has been shown to generate lithium plating within the cells resulting in potential internal shorting conditions. The generation of lithium plating is an understood phenomenon however the specific conditions under which the plating occurs has not been characterized in detail[2]. In this paper ABSL will provide an overview of the performance of the Sony 18650 hard carbon mandrel cell under various low temperature charging regimes. The goal of the low temperature charging of the 18650 cell was to determine the low temperature operating conditions in which lithium plating would occur, thereby establishing a lower temperature bound for use.

I. Background

One of the major limiting factors for low temperature charging of lithium-ion (Li-ion) cells is the rate of lithium diffusion in the anode. When the charge is applied, the concentration of Li at the anode surface can reach a point where the potential at the electrode surface falls below that required for lithium deposition. Lithium is then plated on the anode surface. This deposited lithium may result in dendrite formation on the anode which may become free within the cell and cause a shorting path within the cell. Additionally, the plated lithium will react with the electrolyte resulting in increased thickening of the Solid Electrolyte Interphase (SEI) layer resulting in increased internal resistance and limiting capacity or cycle life.

The occurrence of lithium plating can be seen during a discharge cycle following the low temperature charging cycle. Lithium plating causes a spiking or increased voltage bump during the initial phase of the discharge cycle as shown in Figure 1.

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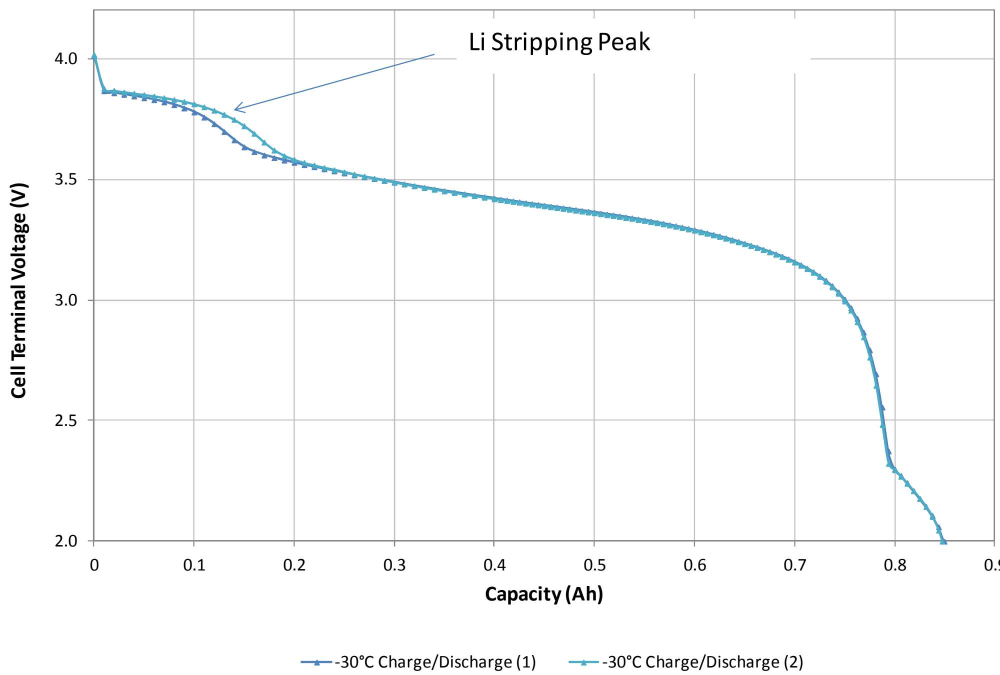

Figure 1. Spiking due to lithium plating

To determine the performance characteristics of the Sony 18650 hard carbon mandrel (HCM)cell during low temperature operations, cells were subjected to various charge rates at environmental temperatures of +20°C, 0°C, -10°C, -20°C, and -30°C. The +20°C condition was used as a baseline comparison condition as it is known no lithium plating occurs at that temperature. The cell's nominal capacity was measured at +20°C for the baseline.

II. Performance Testing

The charge tests were carried out using the procedure described below; for each step, the data that can be obtained is described[1].

1. **Capacity Measurement at 20°C.** This gives the nominal capacity, and a discharge curve without Li plating.

2. **C/10 Charge at 20°C**. Li plating does not occur at this rate and temperature for the HCM cell. Sets the cell up for the first low temperature discharge.

3. **Discharge at test temperature**. The discharge curve at test temperature after the ambient charge is used as reference to determine whether any Li stripping peaks can be seen on later low temperature charges. It also gives an indication of the resistance increase compared to ambient conditions, which will cause a decrease in the available cell capacity.

4. **Charge/discharge at test temperature and chosen rate**. The cells are then charged at the chosen capacity, and then discharged at the nominal C/10 rate at the test temperature. Comparison with the discharge (Step 3 above) gives indication of increased voltage peaks indicative of Li plating. The capacity during the discharge is relatively affected, as the cells were taper charged to C/50. The charge/discharge cycle was carried out twice to ensure repeatability.

Table 1 shows that rates that were tested. The same cells were used for all rates at a single temperature. Testing started at a rate where Li plating was not thought to occur, and continued until (i) plating was observed, (ii) the maximum charge rate for the cell was reached (C-rate), or (iii) to the point where the cell maximum voltage was hit when charge started. Thus, the initial charge rate for -30°C is lower than for 0°C, and testing at -20°C stopped at C/2 as the voltage immediately reached 4.2V.

Table 1. Test Parameters

Temp °C	Charge Rates					
0	C/10	C/7	C/5	C/2	C	
-10	C/10	C/7	C/5	C/2	C	
-20	C/15	C/10	C/7	C/5	C/3	C/2
-30	C/15	C/10	C/7	C/5*		
* test in progress						

III. Test Results

<u>0°C Testing:</u> Two fully charged Sony 18650 hard carbon cells were placed in a thermal chamber and brought to a steady state temperature of 20°C. The capacity measurement and 20°C pre-charge were performed prior to the thermal chamber temperature being reduced to 0°C. Following equilibration, the cells were subjected to the charge rates shown in Table 1.

As an example, the results from the C/7 charge are shown in Fig. 2. The red curve shows the discharge during the capacity measurement; this involved a C/10 charge (no taper) to 4.1 V, followed by a C/10 discharge. An end of charge voltage (EoCV) of 4.1 V was used for comparison with on-going low temperature tests on cells with graphite anodes, which can be more sensitive to EoCV. This +20°C charge/discharge curve can be compared to the green discharge curve which represents charge at +20°C and discharge at 0°C. The higher cell resistance at 0°C is shown by the lower voltage during discharge. After ~0.6 Ah have been transferred, the voltages of both curves are approximately equal; this is due to slightly different states of charge at the beginning of the discharge. The cell pre-charge and subsequent charges at low temperature involved tapering the cell to C/50 to ensure almost 100% SoC prior to discharge. As per the standard ABSL regime, the capacity measurement did not involve a taper charge.

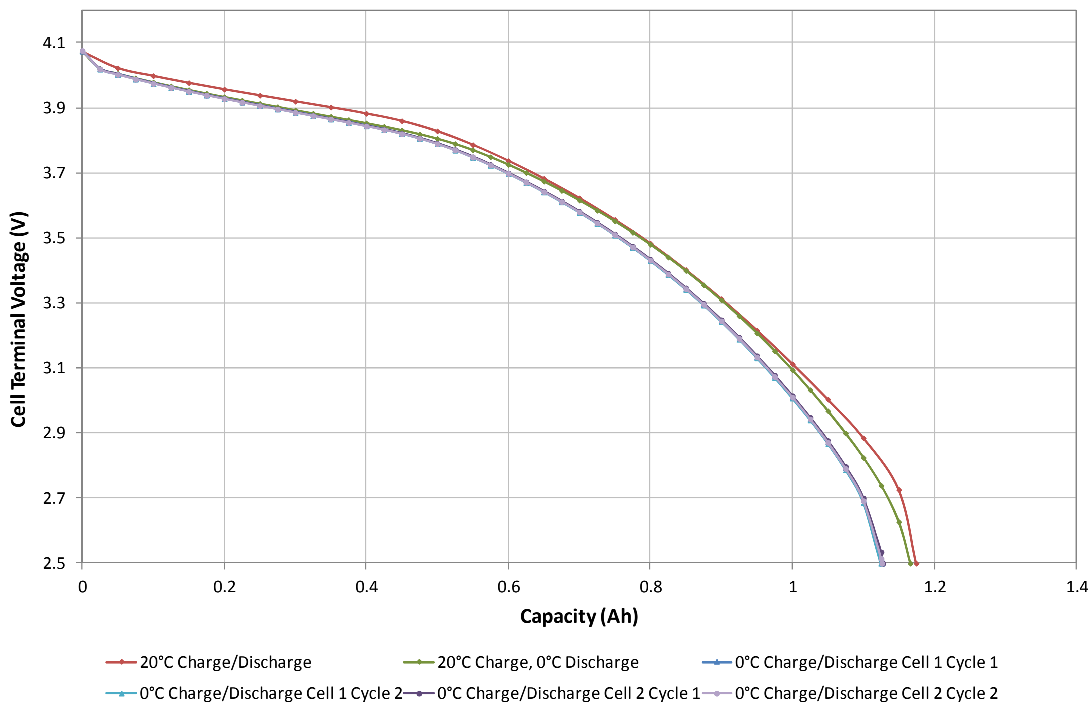

Figure 2. 0°C C/7 Charge Rate Results

The discharge curves after the C/7 taper charge at 0°C follow the green baseline 0°C discharge curve until ~0.5 Ah. After this point the curves deviate due to differences in available capacity. When cells are charged at low temperature, the higher resistance means that the final SoC is lower than would be the case at +20°C. Therefore, there is less available capacity for discharge; this effect is relatively small at 0°C with a difference of 42 mAh. The consistency of the cell performance between the two runs and the two cells used should be noted. This confirms the uniformity of this cell type.

Figure 3 shows the discharge curves for the remaining rates tested at 0°C. No Li stripping peaks were observed in the discharge curves following charges up to rates of 1C (1.5 A).

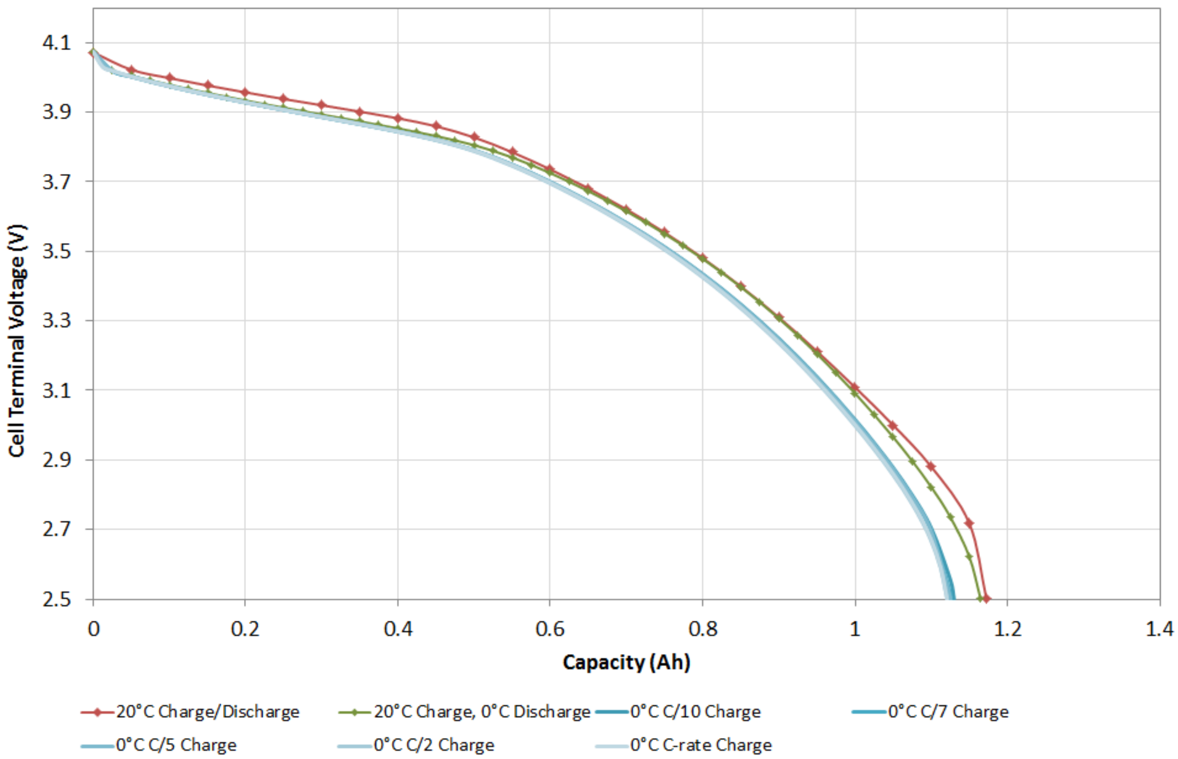

Figure 3. 0°C Charge Test Results

The charge curves for the tests show the challenge of charging at low temperature (fig. 4). Due to the increasing resistance, the cell voltages during the charge reach the maximum cell voltage quickly, especially at high rate. For example during a C/5 charge the cell started tapering when 0.9 Ah had been transferred into the cell after having been charged for 160 minutes. When the same cell was charged at C-rate, taper charging started after only 0.38 Ah had been transferred, 15 minutes into the charge. As the current is reducing when in taper charge, this can limit the energy that can be transferred into the cell in a set time.

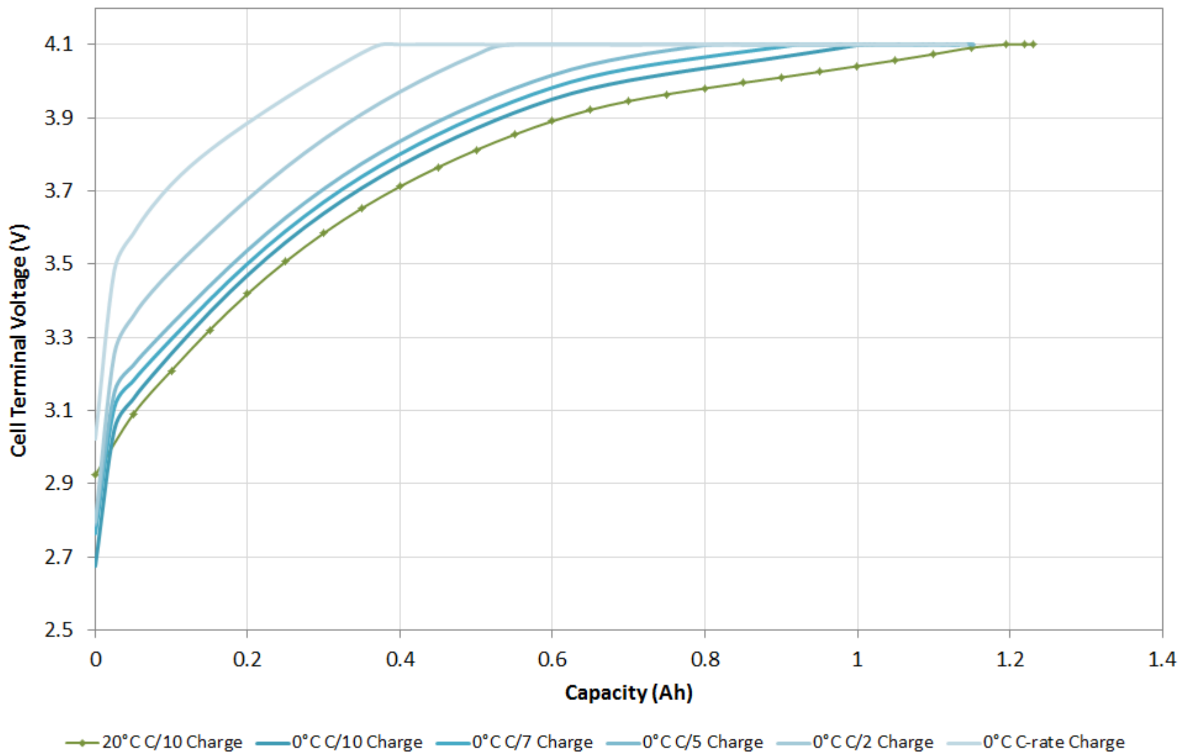

Figure 4. 0°C Charge Curves

-10°C Testing: Two fully charged Sony 18650 hard carbon cells were placed in a thermal chamber and brought to a steady state temperature of 20°C. The capacity measurement and 20°C pre-charge were performed prior to the thermal chamber temperature being reduced to -10°C. Following equilibration, the cells were subjected to the charge rates shown in Table 1.

All the cells charged and discharged at -10°C and various current rates show no indication of lithium plating as the capacity and voltage profiles are consistent with that of the 20°C charge/discharge profile as shown in Fig. 5. For these tests, the EoCV was changed to 4.2 V, to reflect the usual operation of this cell type. An error on the pre-charge meant that the cells were only charged to 4.1 V in this stage. However, there is sufficient data to verify that Li plating has not occurred during these tests.

The tests at -10°C show a more pronounced voltage drop during the low temperature discharges compared to the 0°C data. This reflects the increasing cell resistance, due to increasing electrolyte viscosity. The data below also seem to suggest that the C-rate charge increased the cell resistance significantly, which would indicate some damage. However, the data actually show a difference in EoC current limit, and therefore the SoC at the beginning of the discharge. The limit was reduced from C/50 to C/20 for the C-rate test due to the time required for the full taper becoming unrealistic for any application. The charge curves for each rate are shown in Fig. 6.

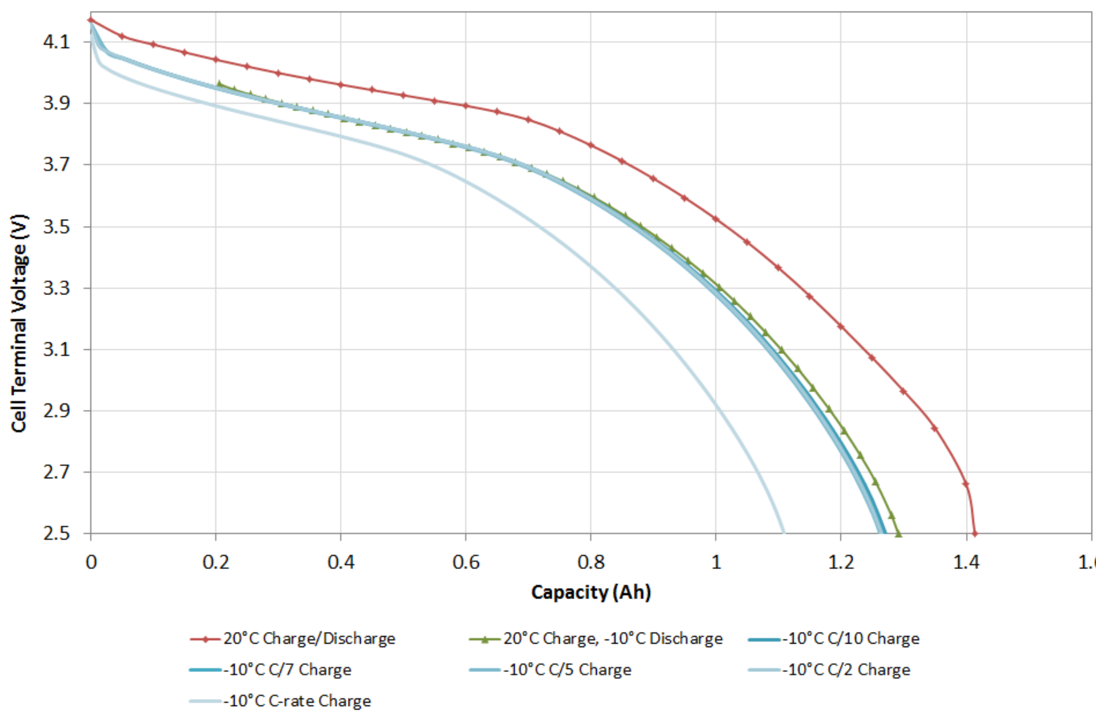

Figure 5. -10°C Test Results

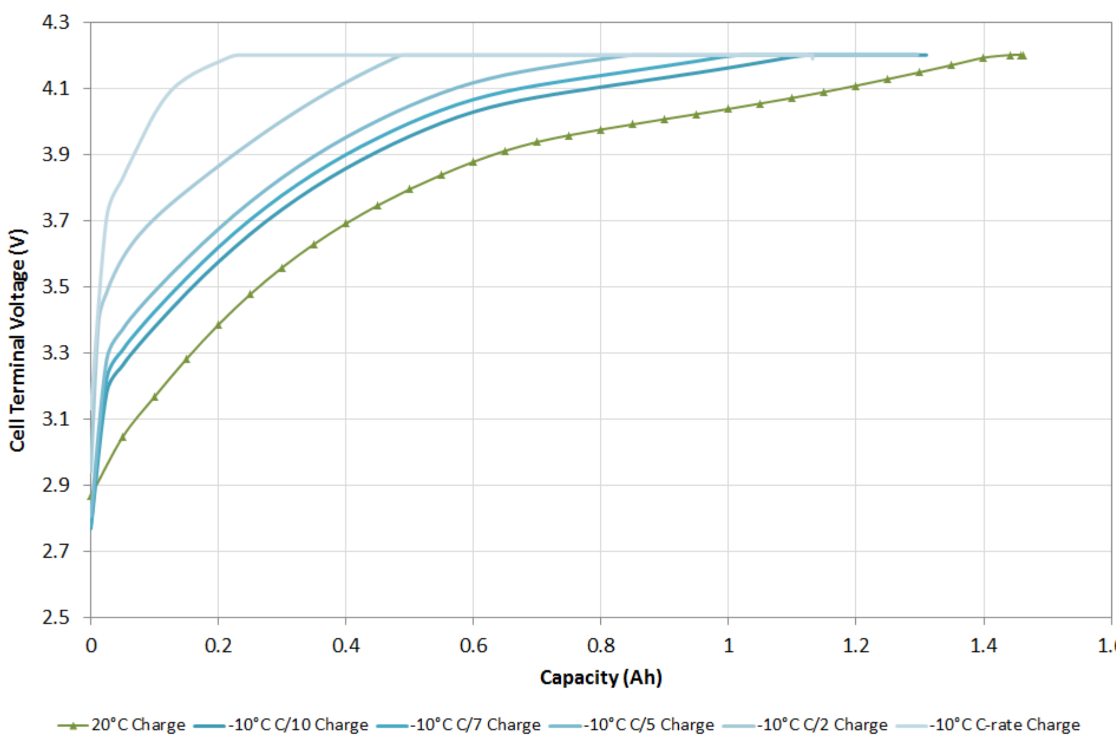

Figure 6. -10°C Charge Curves

-20°C Testing: Two fully charged Sony 18650 hard carbon cells were placed in a thermal chamber and brought to a steady state temperature of 20°C. The capacity measurement and 20°C pre-charge were performed prior to the thermal chamber temperature being reduced to -20°C. Following equilibration, the cells were subjected to the charge rates shown in Table 1.

All the cells charged and discharged at -20°C and various current rates shows no indication of lithium plating as the capacity and voltage profiles are consistent with that of the 20°C charge/discharge profile as shown in Fig. 7. As for the -10°C testing, the pre-charge was only run to 4.1 V. However, there is sufficient data to determine Li-stripping peaks in the discharge curves.

The resistance of the cell can be seen to be increasing; the voltage drop between the +20°C and -20°C curves is approximately 250 mV. This increasing resistance decreases the available cell capacity. At -20°C, the cell can discharge 80% of its room temperature capacity. The discharge capacity plot shown later in Fig. 10 demonstrates the capacity drop due to increasing cell resistance.

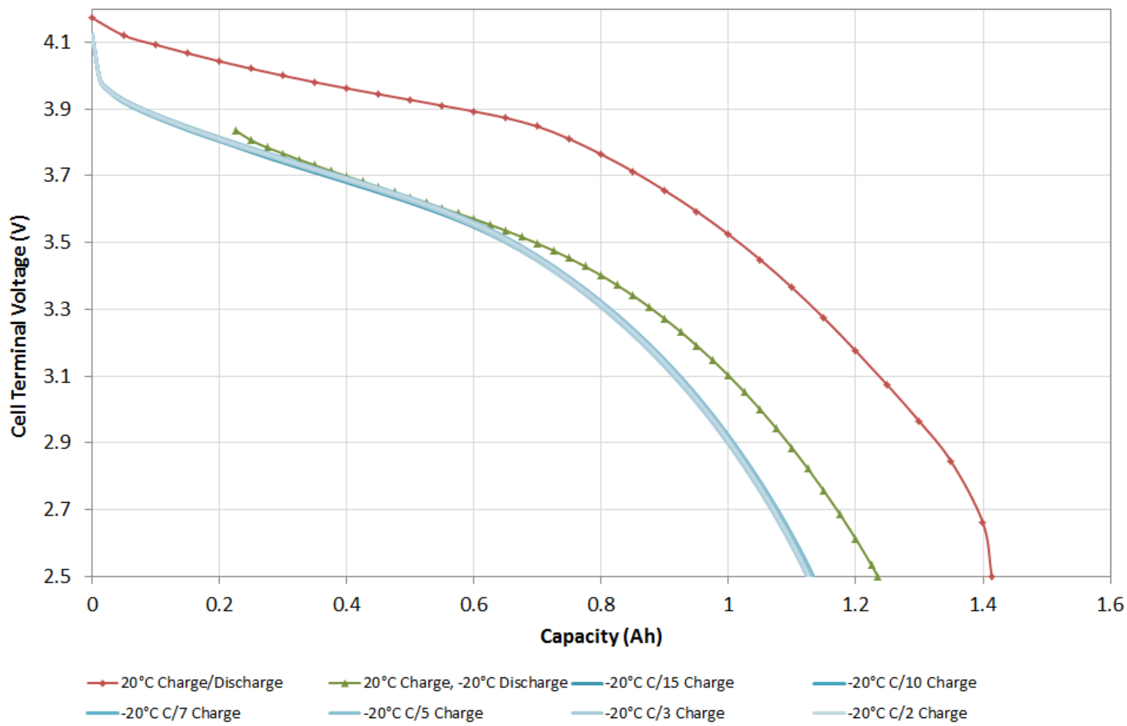

Figure 7. -20°C Test Results

The charge curves are presented in Fig. 8. Although the cells are taper charged to C/20, the capacity that can be transferred is considerable less than at room temperature. At a moderate rate of C/7, only 0.55 Ah can be transferred at constant current; this represents less than 40% of the total cell capacity.

The possibility that Li will be plated onto the anode surface increases with increasing rate and decreasing temperature. This is due to the large voltage drop across the cell and therefore electrode. The charge curves illustrate the effect of the voltage drop well. The -20°C C/2 charge causes an increase of 0.8 V as soon as the current is applied, whereas a C/15 charge shows an increase of 0.4 V.

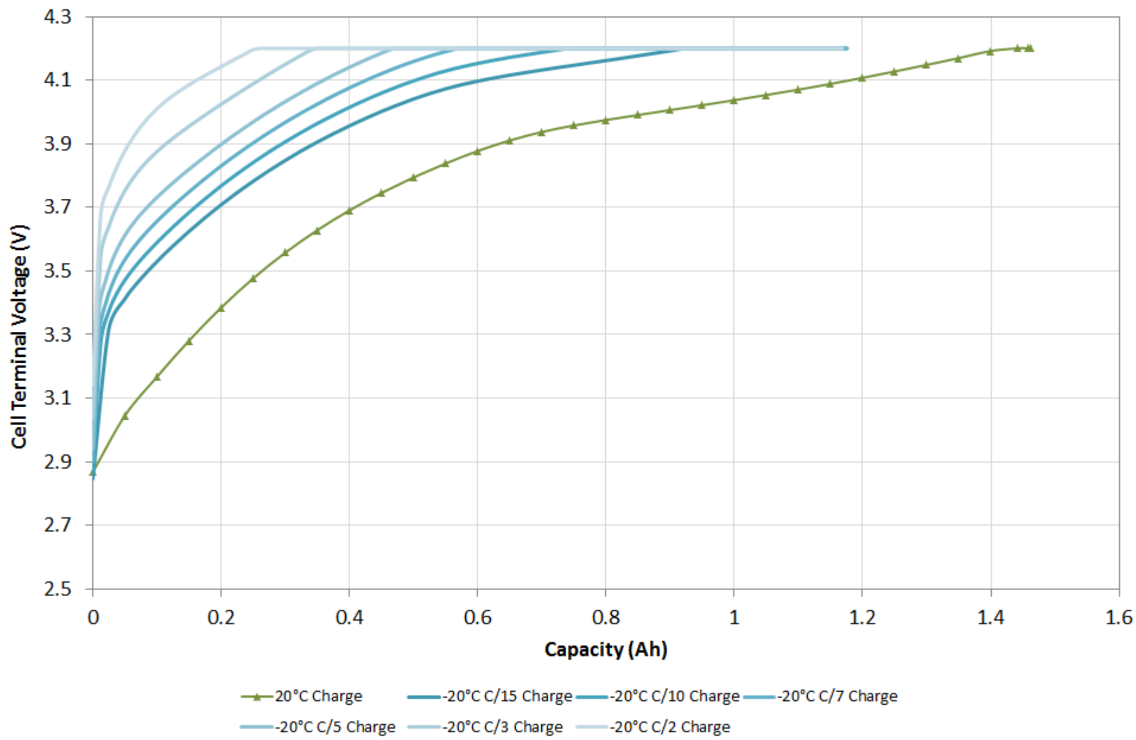

Figure 8. -20°C Charge Curves

<u>-30°C Testing:</u> Two fully charged Sony 18650 hard carbon cells were placed in a thermal chamber and brought to a steady state temperature of +20°C. The capacity measurement and 20°C pre-charge were performed prior to the thermal chamber temperature being reduced to -30°C. Following equilibration, the cells were subjected to the charge rates shown in Table 1.

Again all the cells charged and discharged at -30°C and C/10 charge/discharge rate show no indication of lithium plating as the capacity and voltage profiles are consistent with that of the 20°C charge/discharge profile as shown in Fig. 9. In this case the voltage of the cells during the discharge following the -30°C charge are slightly higher than the discharge following the charge at +20°C. It is thought this effect is due to a small temperature variation in the chamber, rather than being an indication of Li-plating.

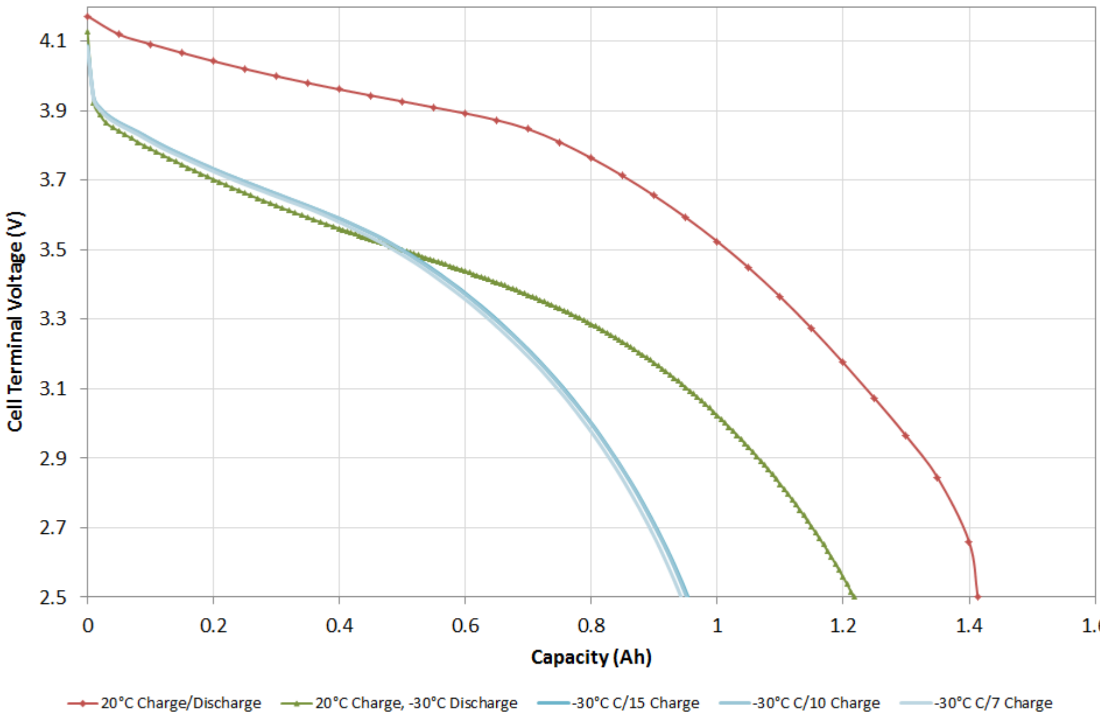

Figure 9. -30°C Test Results

The available cell capacity has reduced further to less than 1 Ah at -30°C. This gives an energy density of ~ 80Wh/kg at this extreme temperature. A summary of the available capacity of cells charged to near 100% SoC is shown in Fig. 10. Data for 0°C testing is not shown, as the cells were only charged to 4.1 V, rather than 4.2 V.

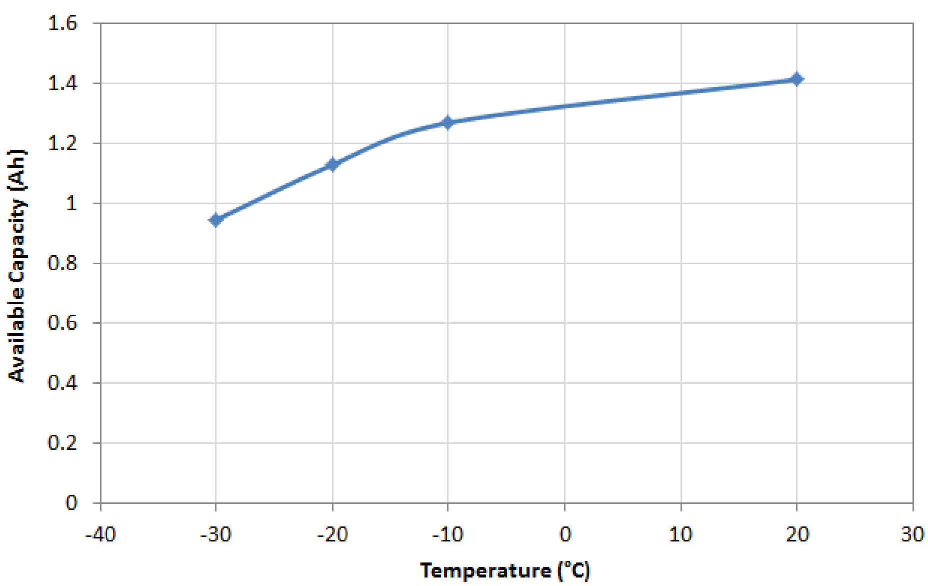

Figure 10. Effect of Temperature on Capacity

The charge curves for testing at -30°C are shown in Fig. 11. As for the other temperatures, the time spent in constant current charge decreases as the current is increased. The effect of the temperature and rate on the capacity transferred during the constant current charge section is summarized in Fig. 12. In this case the 0°C data are shown, but it should be recalled that these data show the capacity to 4.1 V, so will be lower compared to the other data.

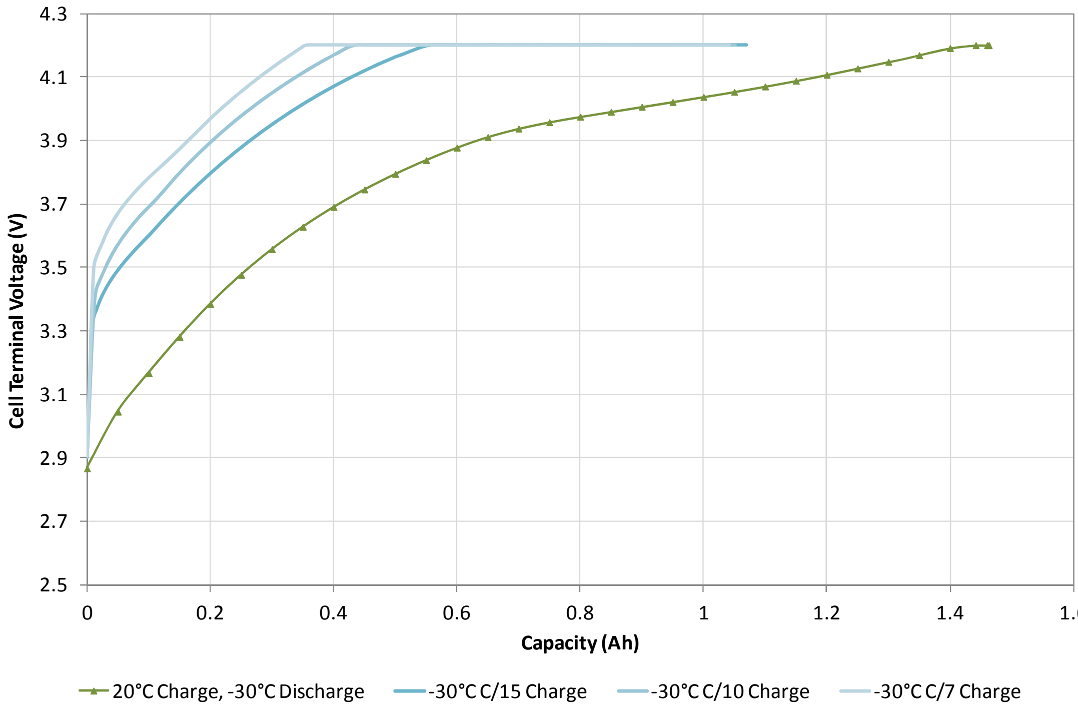

Figure 11. -30°C Charge Curves

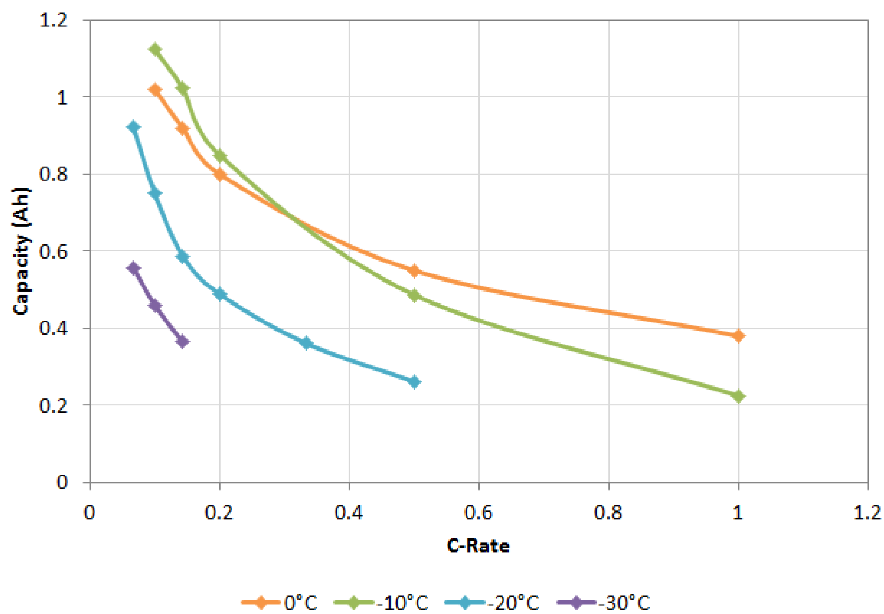

Figure 12. Capacity Transferred during Constant Current Charge

IV. Conclusions

Based upon the available test data generated by EnerSys /ABSL, the hard carbon mandrel cell appears to be a robust cell under low temperature charging environments. There were no indications of lithium plating occurring at the various charge rates thus far at temperatures down to -30°C. It is therefore concluded the Sony 18650 hard carbon mandrel cell is capable of being used in a low temperature space application. However, other performance considerations must be understood regarding low temperature charging in general. The internal resistance of the cell increases as the operating temperature is decreased due to the lower conductivities of the electrolyte and electrodes at low temperatures. This increase in internal resistance leads to extended charge times due to the fact that only a small portion of the charge energy is going into the cell. The increase internal resistance also decreases the capacity of the cell as the maximum voltage for the cell is reached at a low SoC.

References

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[2]Low Temperature Battery Program, 2010 BDEV-ABSL-0167/10 Vol 2 Technical, Nick Simmons, ABSL Space Products, Culham, Oxfordshire, United Kingdom.