

AT WHAT POINT DOES COLD CHARGING DAMAGE LITHIUM ION CELLS?

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Winter is here and I belong to two forums where people wondered about the point at which lithium ion batteries can no longer be safely charged when it is cold. I put together the informal paper which follows since most people would not know where to look or that such data exists. The direct answer is that only the battery manufacturer will have meaningful data.

This paper shows test results from Boeing 787 cells after investigating a series of thermal runaways. The 787 cells are cobalt based (LiCoO₂) which is more reactive than the majority of cells which are iron based (LiFePo₄). The test curves from the 787 data were similar in general form to those of LiFePo₄ data that I am familiar with but the LiFePo₄ data were proprietary and the 787 data is in the public domain.¹ The plots shown below are from an Underwriters Laboratories report developed for the investigation, the numbering of Figures in this paper are the Figure numbers used in the report, and the captions shown in red are also from the report.²

COLD DISCHARGE:

It is worth discussing discharge first because discharging is generally believed not to be a problem. The ions are being released from the negative electrode surface layer (anodic SEI), rather than being driven into it and a decrease in efficiency is created largely from the characteristics of the electrolyte shown in this chart. (See Figure 104)

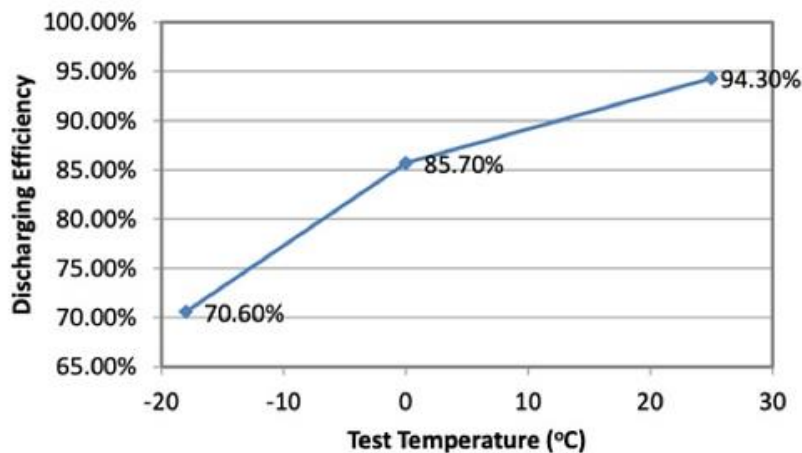


Figure 104 Relation between Test Temperature and Discharging Efficiency in 1st run of APU start [redacted] on Cell 7 of Battery 459

The reason to show this is that some people warm lithium ion cells by applying a high discharge, but this can also cause damage. If using a high C discharge to warm the cells, it is suggested to do so in short cycles and pause at least a few minutes before pressing a starter button or other

¹ https://www.nts.gov/investigations/...sic_Report.pdf

² The NTSB worked with Underwriters Laboratories to examine the 787 battery, worked out with Yuasa and Boeing what needed to be redacted (blacked out text in 1st chart), and everything shown is in the public domain.

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high load to let the heat distribute through the cell. Not waiting results in uneven cell heating which concentrates the discharge in a smaller area close to the current collectors. (See Figure 97)

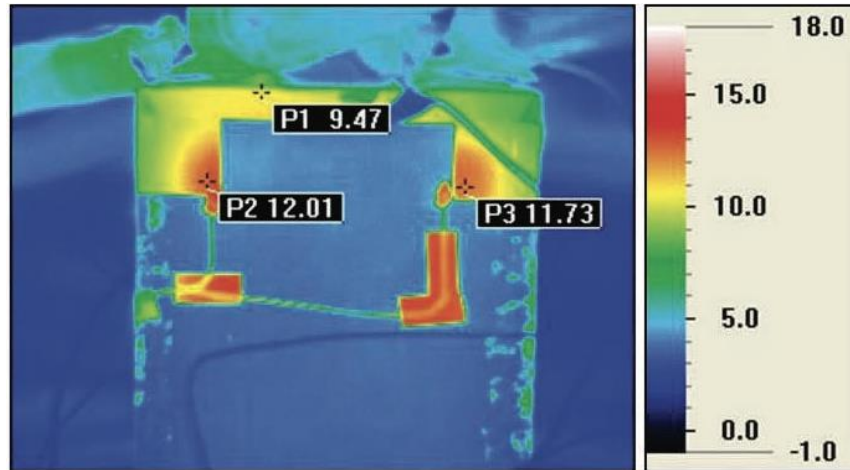


Figure 97 IR Thermal Imaging of Cell 3 from Battery 459 during APU start at 0 °C
Note that a rectangular piece of tape behind the label “P2 12.01” is obscuring the thermal colors in the middle of the cell.

Localized high temperatures in tests of 787 cells melted portions of the separator film between the anode and cathode which degraded the cell very quickly.

THE BASIS OF TEMPERATURE CHANGES:

The lithium ions move through a petroleum-based electrolyte and the conductivity and viscosity of the electrolytes change in relation to temperature. Tests were able to show that as the electrolyte approached the freezing point of water (0°C) the properties of the electrolyte became harder for the ions to move through. (See Figure 81)

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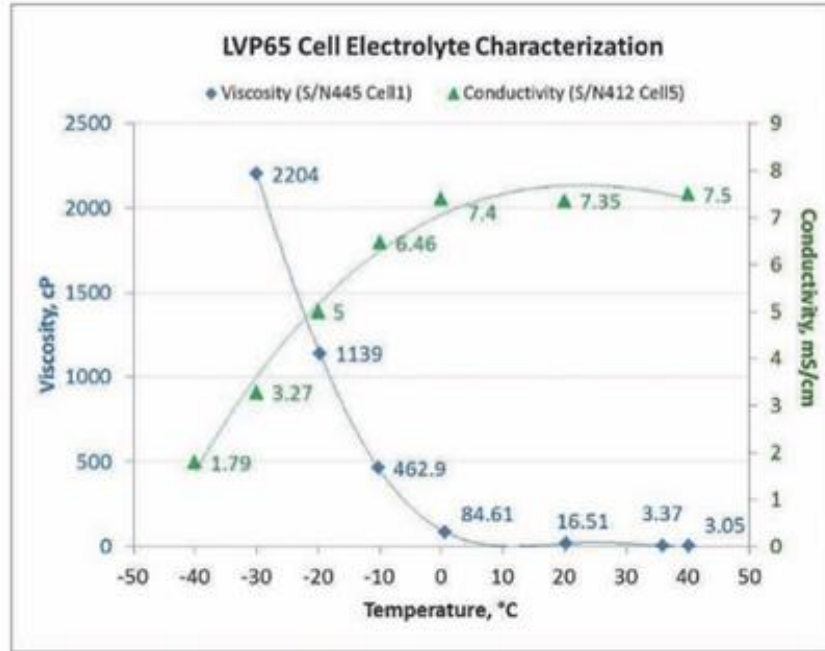


Figure 81 Electrolyte Viscosity and Electrical Conductivity as a function of Temperature

Most commercial LiFePo₄ cells contain thinner electrolytes and have additives which will move these curves slightly to the left. But only the engineers at the manufacturer will know what the specific curves are or how they relate to charge rates and this is generally proprietary information.

CHARGE RATE VERSUS TEMPERATURE:

When the charge rate at any temperature is too high, the lithium ions are not able to work their way into the SEI layer in a process called intercalation and may collect on the surface of the anode as dendrites. (Report Fig. 1)



Figure 1 Photo of Dendrites in Windings of Cell 5 (100% SOC) from Battery 412 (gold color shows a high charged region and the brown shows a lower charged region)

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These ion deposits of lithium cannot go back into solution on discharge and once the deposits are created the cell rapidly begins to degrade both in capability and life. In other words, the degradation is the point at which the charge rate exceeds temperature-dependent rate of intercalation and a high enough charge rate can cause this at any temperature, including well above freezing.

Enough of these lithium dendrite deposits in a cobalt-based cell can lead to thermal runaway with sufficient charge rate. The iron-based LiFePo₄ doesn't have the reactance of the cobalt so while the fire risk is greatly reduced, the deposits will still very rapidly lead to the end of usefulness for very expensive battery cells. (High enough rate or voltage can still lead to runaway in LiFePo₄.)

The following chart is called an EIS curve³ and it is difficult to truly understand without an engineering degree. (See Figure 78) The EIS test passes high frequencies between the cathode & anode to characterize how well the ions intercalate into the SEI. The electrolyte properties curve previously discussed showed a rapid change to properties near and below freezing. (Figure 81) The EIS chart more directly conveys the onset of dendrite formation.

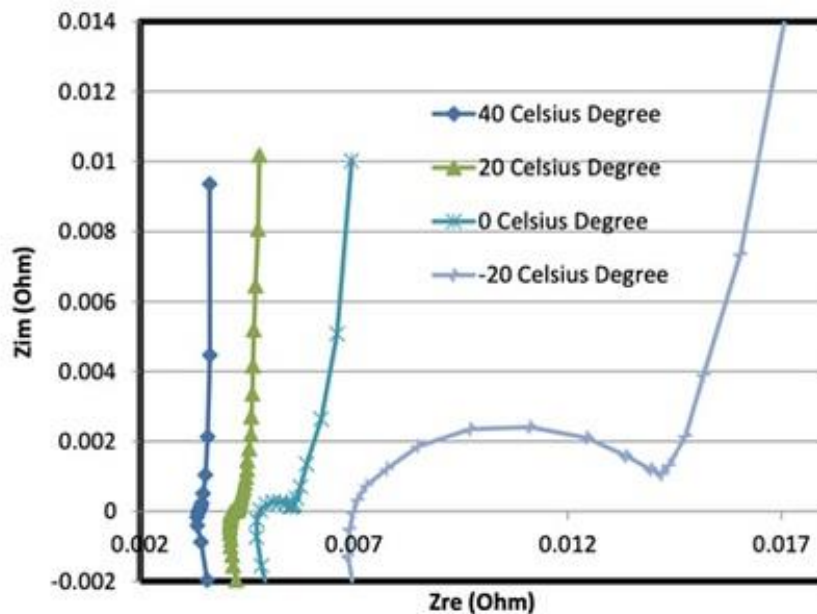


Figure 78 EIS measurements of Cell 2 from Battery 412 under 40, 20, 0, and -20°C

The summary about reading this chart is that you do not want to see the charge rate create the C-shaped curve exhibited by the right two plots. The testing at UL used a fixed charge rate. If the charge rate had been reduced, then the ions would have been able to intercalate into the SEI layer and so the C-shape would not develop until colder temperatures were experienced. The degradation began with only a few cycles during the cold temperature charge testing. (See Figure 93)

³ electrochemical impedance spectroscopy

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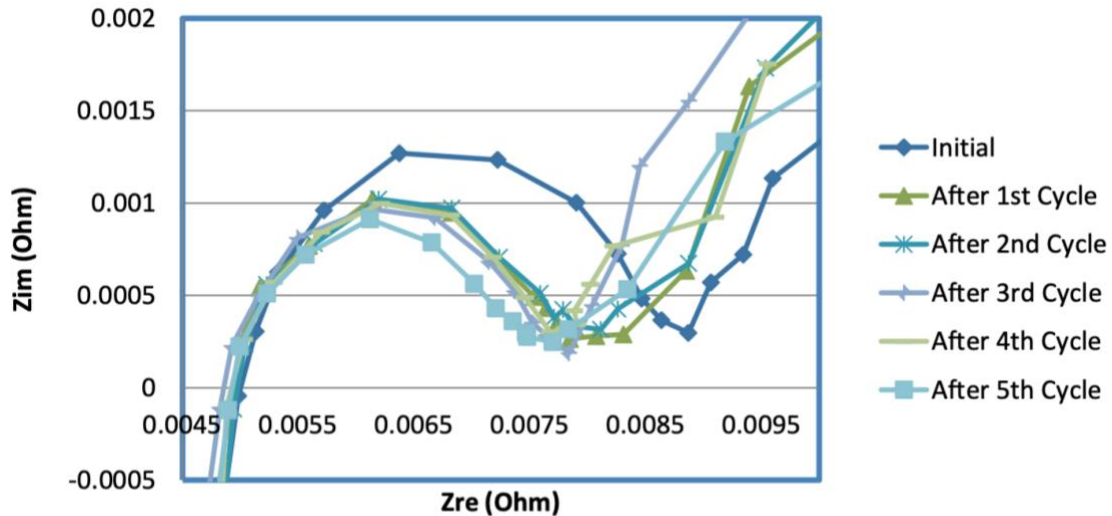


Figure 93 EIS Profiles before and after Pulse Charge test under -18°C (Cell 3 of Battery 412)

The benefit to the EIS plot (Fig 78) is that it points out how close the bottoms of the left three curves are, how rapidly the curve changes near freezing (second and third curves), then there is a big step to the -20°C (-4°F) curve. The data is similar for LiFePo4 cells which basically means that somewhere in that tight spot between the 2nd and 3rd curves is a fine line at which the charge rate will develop dendrites that can damage the battery. The EIS chart nicely shows the point at which the cell is damaged is more like a cliff and is not a straight line relationship.

If the charge rate could be very slowly increased, at some point the rate of lithium deposition would rapidly increase. The point is that the loss of usable life of the cell will approximately match this sudden loss. This balance between charge rate and temperature is going to be very specific and unique to each manufacturer's chemistry but the manufacturers can't go too far when below freezing because there's only so much they can do with the additives.

Without laboratory test results the manufacturer recommendations are all we have to go by for safe and longest cell life.