10 Year Discharge Experiment of Electrochem CSC DD Cells
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December 20, 2018

Summary

Discharge testing conducted at Electrochem from 1992 to 2002 demonstrated that it is possible to discharge the CSC DD cells at very low rates continuously over a period of almost ten years without dramatic loss of capacity. Furthermore, it was possible from those same test results to estimate, and validate, a rate of self-discharge of less than 2% per year over for our CSC DD cells.

Introduction

Electrochem CSC DD cells (3B0036) are optimized for applications that operate within a range of temperatures from -20°C to +93°C. The cells can deliver very high rate discharge, up to 4 amps, or they can also be used at much lower discharge rates where the cells might operate over a period of years (i.e. <4 mA). An example of a longer-term uses could include environmental or oceanographic sensors that are deployed on multi-year missions. In devices of this sort, the batteries are typically exposed to temperatures in a moderate range; usually from 0°C to +40°C.

All batteries undergo processes that degrade their performance over time, chief among them being self-discharge, the direct consumption of the active materials in the absence of any current flow. In many applications self-discharge can be ignored, but in cases where the battery operates over several years, self-discharge can consume a noticeable portion of the cell capacity that would otherwise be available in the case of higher rate discharge. Thus, it is useful to characterize how a cell performs when it is discharged at very low rates, to allow a better understanding of how much energy the cell will ultimately be able to deliver over the course of a multi-year discharge.

Discharge reactions in CSC cells

When discharged under a constant current or constant power load, lithium-sulfuryl chloride cells put out a very flat voltage that only decreases very near the end-of-life, when the active materials have been consumed. In some cases, two distinct voltage plateaus are observed. These correspond to two different discharge reactions that can occur in lithium-sulfuryl chloride cells:

1) $2Li + SO_2Cl_2 \rightarrow 2LiCl + SO_2$
2) $2Li + 2SO_2 \rightarrow Li_2S_2O_4$

The bulk of the discharge involves the main reaction, Equation 1, where the cells give closed-circuit voltages in a flat plateau at 3.0-3.8 V when the cells are discharged at mid-range temperatures (0-90°C) under light to moderate loads. One of the discharge products of the first reaction is sulfur dioxide. This discharge product can itself be discharged in the second reaction, shown in Equation 2, giving a second lower voltage plateau at 2.5-2.9 V. The second plateau is usually only observed in low rate discharge. Under some conditions, it can correspond to several amp-hours of capacity that might not otherwise be obtained in higher rate discharge.

Both of these voltage plateaus are visible in the curves shown in Figures 1 and 2, where fresh cells were discharged under a constant load of 100 mA at room temperature (RT, 23°C), or at 0°C.

Figure 1. 100 mA at RT.

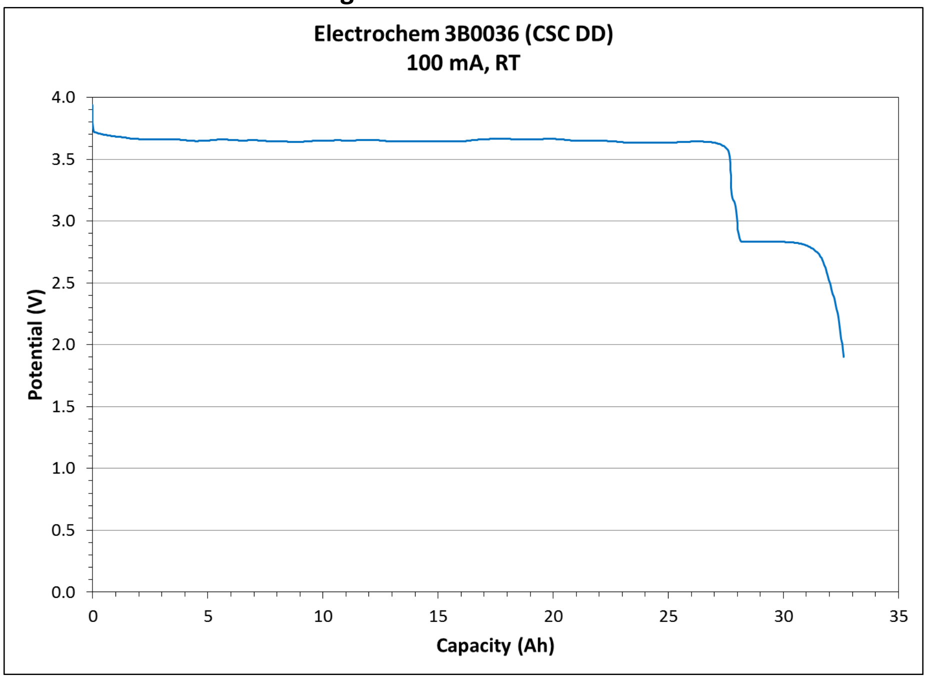
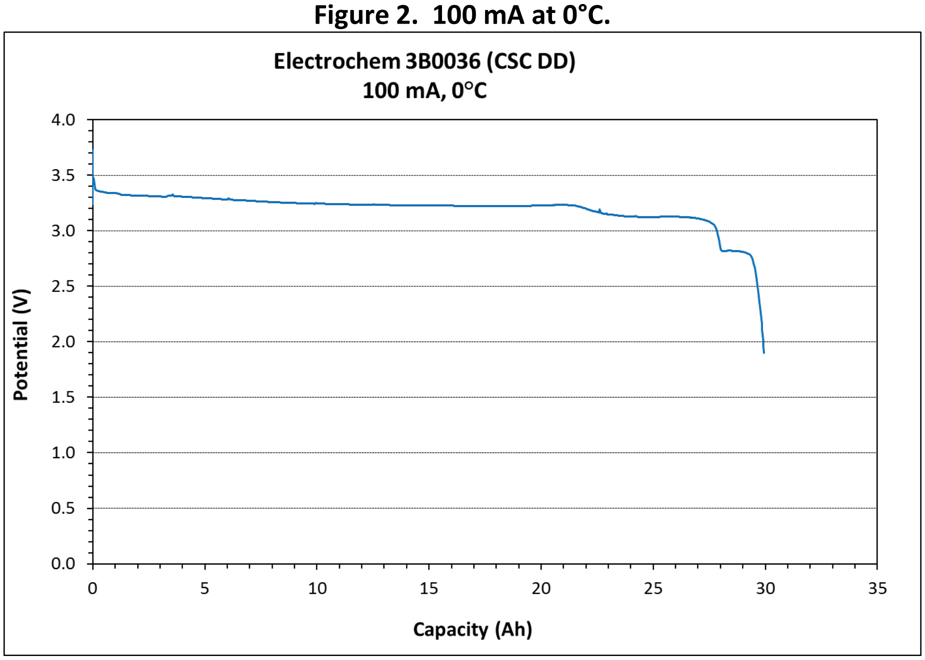


Figure 2. 100 mA at 0°C.



Tests on very low rate discharge

Tests on discharge at very low rates were conducted at Electrochem over the course of ten years, from 1992 to 2002. In these tests, cells were connected to resistors with values of 1.0, 3.74, 7.5, and 10.7 kΩ. The cells were kept in storage at room temperature or approximately 0°C. The voltages were measured by hand every month throughout the cell life. Representative discharge curves are shown in Figures 3 through 10 at the end of this report.

Although a very few test cells did fail prematurely, the great majority of the cells remained at above 3.7 V for about 24-25 Ah, and dropped to 2.9 V for several Ah near the end-of-life. Overall the cells were very consistent in delivering approximately 28 Ah to a cut-off of 2.0 V.

To calculate the rate of self-discharge that occurred during the nearly ten years of discharge, it would be necessary to have a clearly defined maximum capacity for the cells in the absence of any self-discharge. It is possible to obtain as much as 32 Ah at RT under ideal conditions (see Figure 1). Based on this value we can calculate an overall self-discharge rate of between 1 and 2% per year in this multi-year discharge. That value is consistent with the value reported on our marketing data-sheets for this cell type (<3% per year). In this and other work we have found that the self-discharge rate is highest during the first year, but decreases during more prolonged discharge or storage.

Acknowledgment

The work that is summarized in this report was performed by David Spillman and other members of the Electrochem Research and Development team.

Figure 3. RT, 1.0 kΩ.

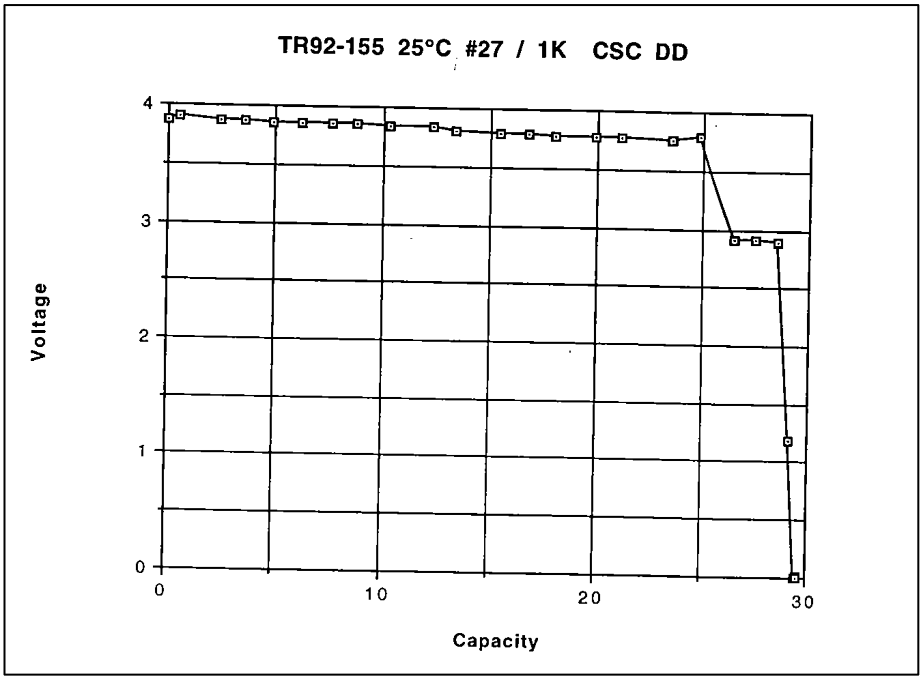


Figure 4. 0°C, 1.0 kΩ.

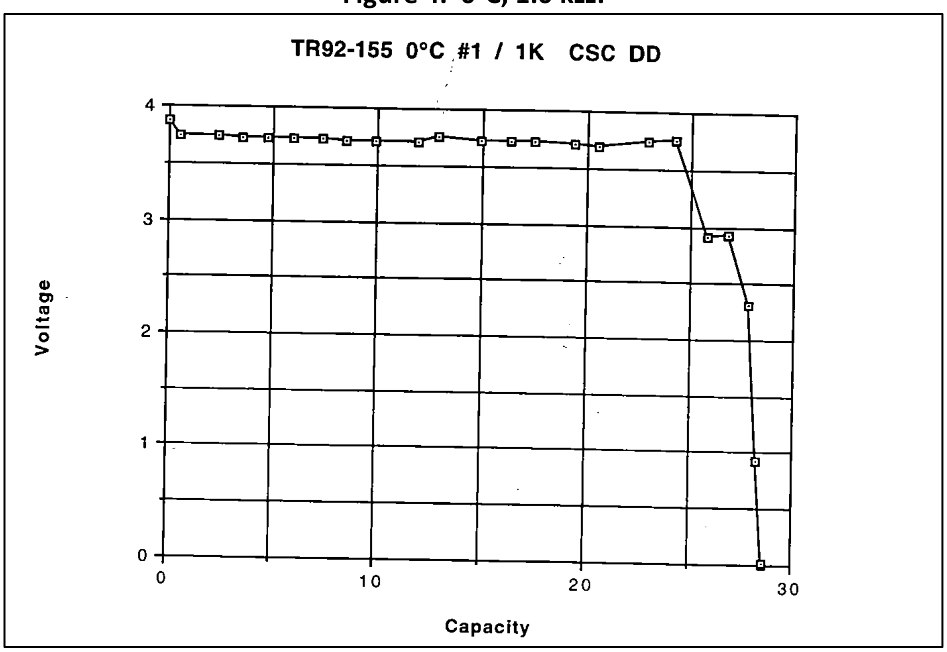


Figure 5. RT, 3.74 kΩ.

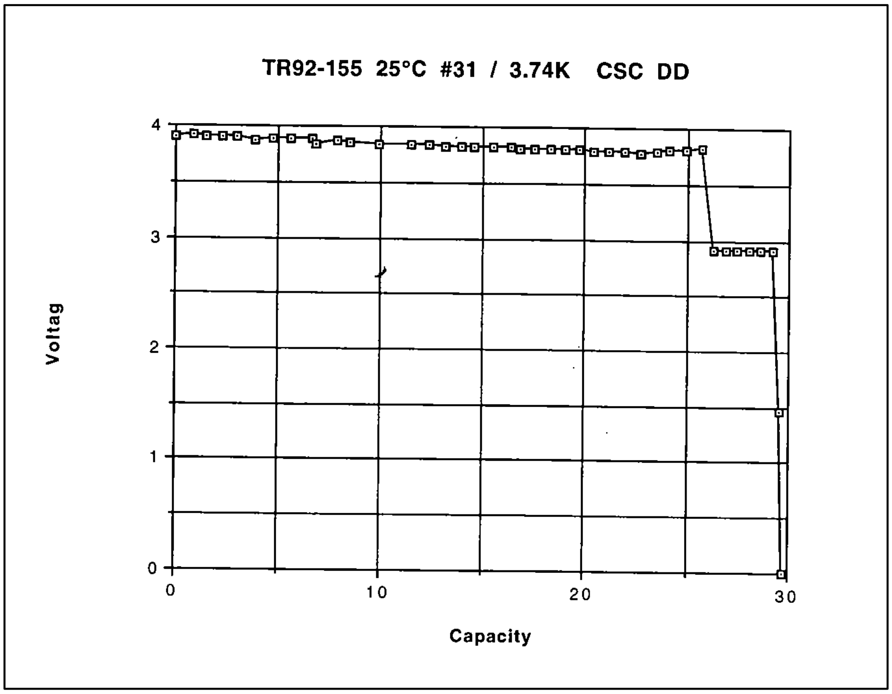


Figure 6. 0°C, 3.74 kΩ.

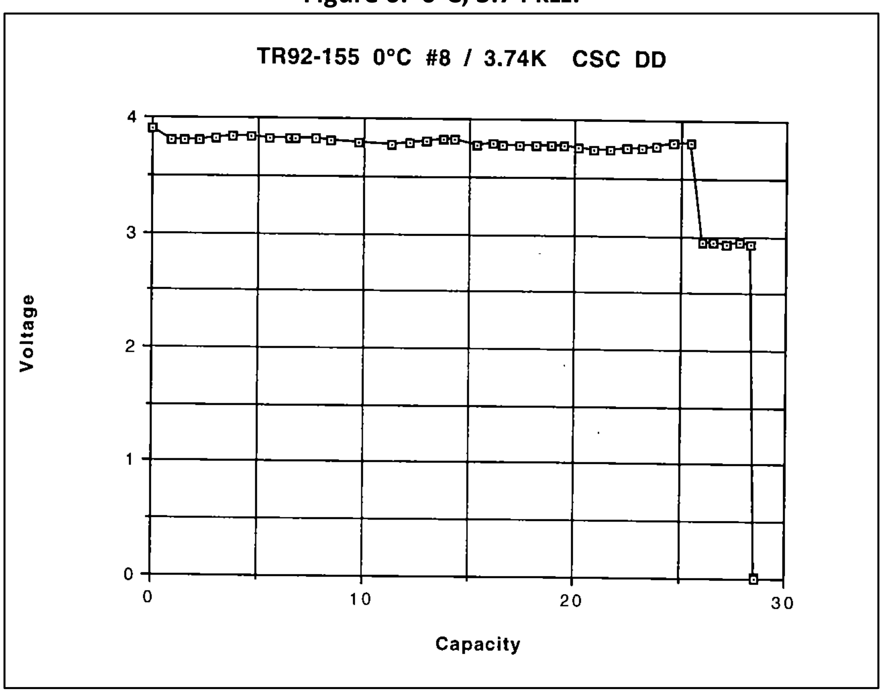


Figure 7. RT, 7.5 kΩ.

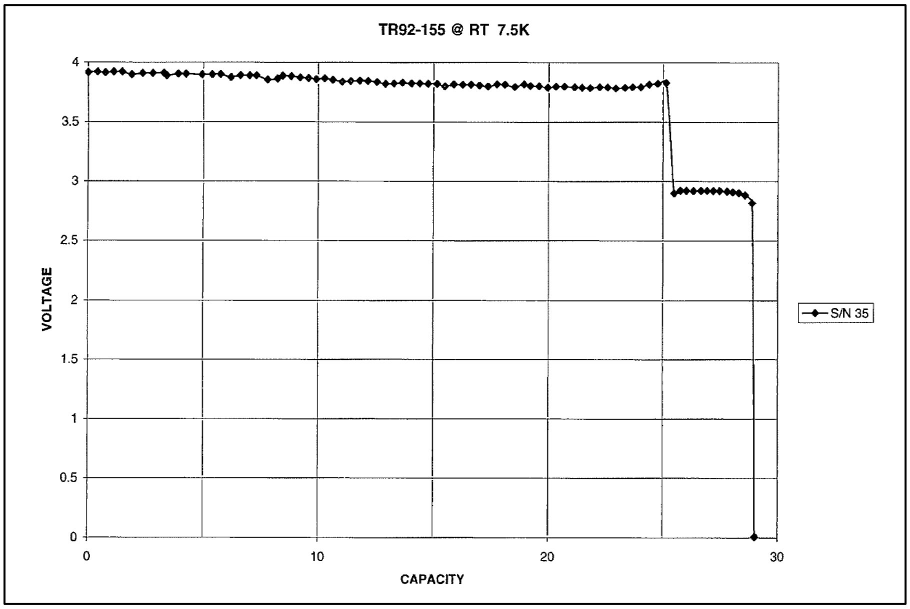


Figure 8. 0°, 7.5 kΩ.

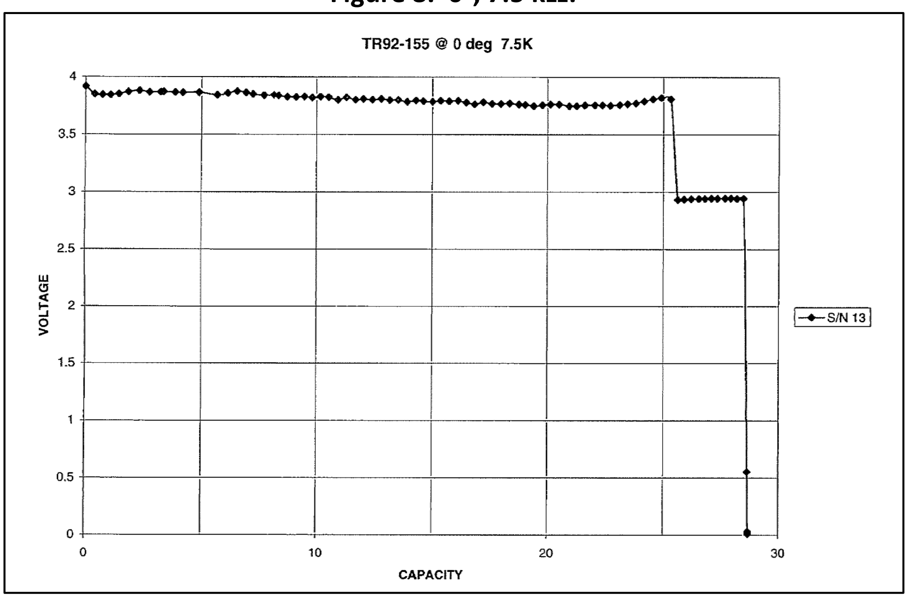


Figure 9. RT, 10.7 kΩ.

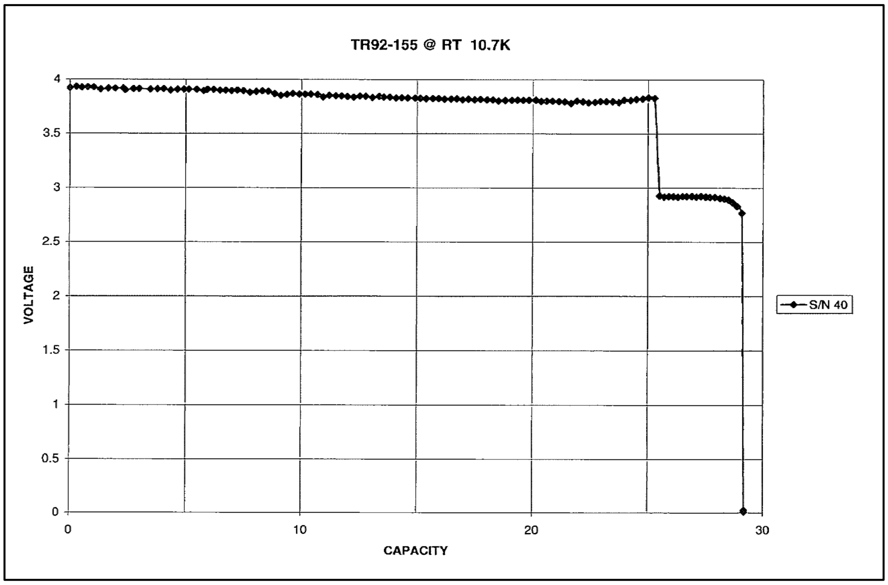


Figure 10. 0°, 10.7 kΩ.