Effects of Low Temperature Discharge on Performance of Lithium Oxyhalide Primary Cells

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Abstract: *Lithium oxyhalide primary batteries can function at temperatures well below 0°C, though with reduced running voltage and rate capability. In this talk we show discharge results comparing the capabilities of the different oxyhalide chemistries in the temperature range from 0°C down to -40°C, with a focus on identifying detrimental effects of low temperature discharge. We include results from mixed temperature testing in which the cells are first discharged at very low temperature and then at a higher temperature; the results help establish whether starting the battery discharge in cold conditions will harm the subsequent performance of the batteries.*

Keywords: lithium primary battery; thionyl chloride; sulfuryl chloride; low temperature.

Introduction

General effects of temperature on cell discharge: Chemical reaction rates decrease at low temperatures, and both the oxidation-reduction reactions and charge transfer processes that occur during battery discharge occur more slowly. As a consequence, the closed-circuit voltages when a load is applied are lower, and this in turn results in lower capacity being obtained to a given cut-off voltage. All batteries show diminished performance under low temperature conditions. Indeed, many familiar battery chemistries cannot operate at all below about 0°C. Only a few battery types can deliver usable performance in the cold environments that can occur, for example, in the winter, at high altitudes, or in the Arctic.

Lithium oxyhalide primary cells: In lithium oxyhalide primary batteries, the anode is lithium metal, while the active cathode material is an oxidizing liquid that also serves as the electrolyte.[1,2,3] During discharge, the liquid cathode undergoes reduction at the surface of a porous carbon structure, and solid reduction products are deposited on the surface of the carbon. The electrolytes, thionyl chloride and sulfuryl chloride, remain liquid to very low temperatures (sulfuryl chloride freezes at -54°C, while thionyl chloride freezes at -105°C), and in principle the cells can operate down to those low temperatures. However, because of the limited chemical kinetics under those conditions, the solid discharge products can end up poorly distributed in the carbon, with solids that deposit on the outer surface of the carbon blocking access to pores that are deeper in the carbon structure. As a result, the discharge efficiency can end up much lower than it would be at higher temperatures. This phenomenon is referred to as “cathode freeze-over.” It is irreversible, so excessive blockage that occurs at low temperature will continue to limit the cell performance even if the operating temperature is later increased. The possible harmful effects of low temperature discharge can be a particular concern in situations where cells have been stored in a cold environment and have then been placed into use while they are still cold.

The present work compares the capabilities of three lithium oxyhalide systems: thionyl chloride (“QTC”); “BCX,” a thionyl chloride-based system with a bromine-chlorine additive; and sulfuryl chloride (“CSC”). Cells containing these electrolytes were discharged at various temperatures from room temperature (RT, 23°C) down to -40°C, under both constant current and constant power loads, and also under a pulsed discharge condition. Because the voltage profile of the three electrolyte types is different, the capacity that is obtained can vary considerably, because it depends strongly on the voltage cut-off. We also include results for tests in which the discharge was started at -40°C, but the temperature was then increased after several hours. These results provide a basis for assessing what effect the initial low temperature discharge had on subsequent performance.

Experimental

All of the discharge results described here were obtained using DD-sized (33.5 mm diameter, 111.5 mm length) cells from standard Electrochem production lots. The low temperature tests were conducted in Tenney environmental chambers, with temperatures controlled within ±0.5°C. The room temperature tests were carried out in a room that is maintained at 23±2°C. Cells in the low temperature tests were allowed to stand at the test temperature for at least four hours before any discharge load was applied. The discharge control and data-collection were conducted using battery testing equipment from Maccor.

Five cells of each of the three cell types were tested under each test condition. In the graphs shown here, only one discharge curve for each cell type is shown. In every case the curve that was closest to the average of the five cells tested is shown.

Low Temperature Discharge

Constant Current Discharge: Constant current is the discharge condition most typically shown on manufacturers' datasheets. The lithium oxyhalide chemistries generally give a very flat voltage profile under constant current discharge. In the case of BCX, the bromine-chlorine additive gives a higher voltage plateau at the beginning of the discharge, followed by a lower voltage plateau that continues through the remainder of the discharge.

Figures 1-4 show discharge at 500 mA for each cell type at RT, 0°C, -20°C, and -40°C. Although the relative performance of the three cell types is different at the different temperatures, BCX clearly gives the best performance at -40°C. Note that in the case of constant current discharge, the run-time is directly proportional to the capacity that is delivered.

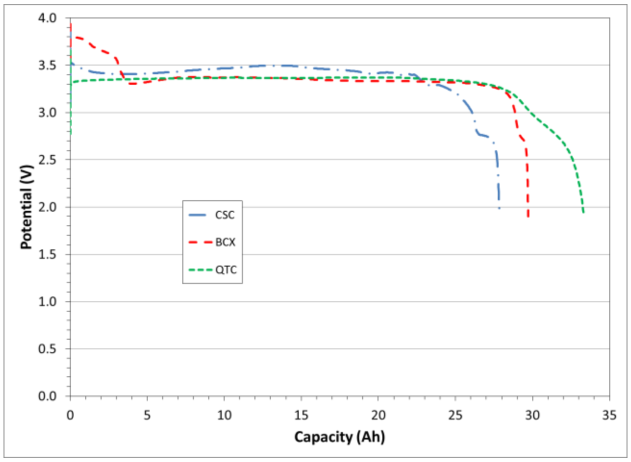

Figure 1. DD cells, 500 mA, 23°C.

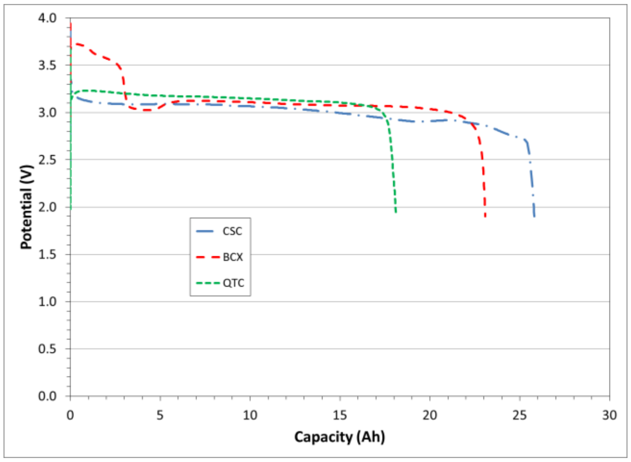

Figure 2. DD cells, 500 mA, 0°C.

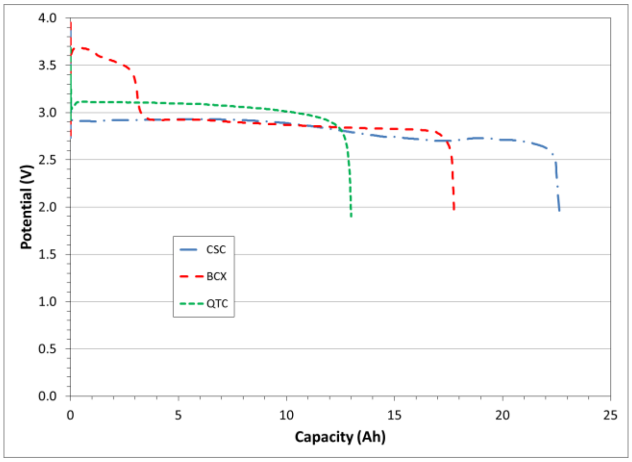

Figure 3. DD cells, 500 mA, -20°C.

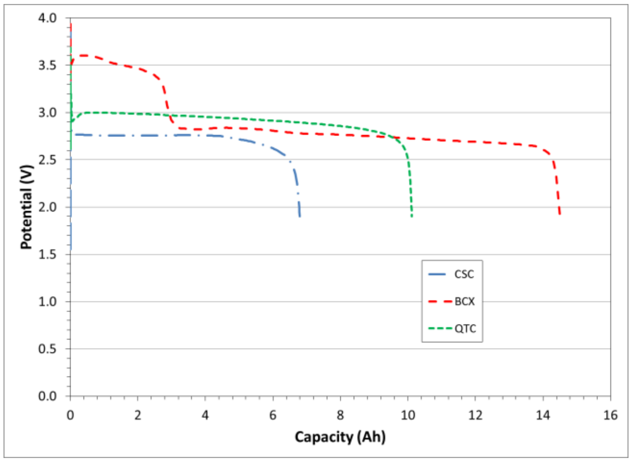

Figure 4. DD cells, 500 mA, -40°C.

Constant Power Discharge: Discharge under a constant power load is different from constant current discharge in that the amount of current drawn from the cell changes as the voltage changes. Because the voltage profile of the oxyhalide cells is flat, however, the two types of discharge condition generally give very similar behavior. In the case of BCX, the initial high voltage plateau in discharge curve provides an advantage to that chemistry because less current is required to maintain the constant power, and a cell with the same capacity can thus deliver a longer run-time.

Figures 5-8 show discharge for the three cell types under a constant power load of 3.6 W. This corresponds to a current level of slightly more than 1 A that increases as the discharge proceeds.

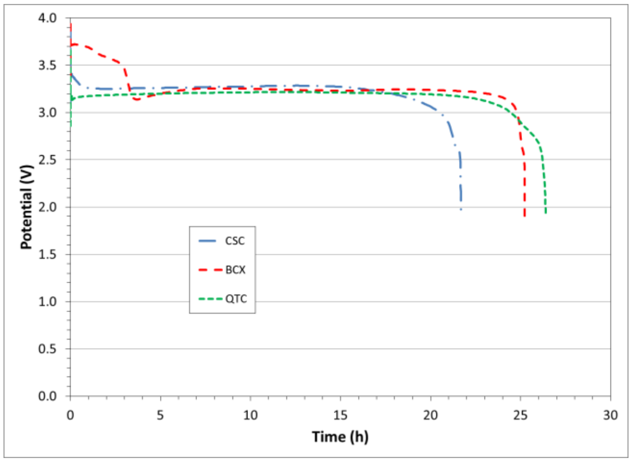

Figure 5. DD cells, 3.6 W, 23°C.

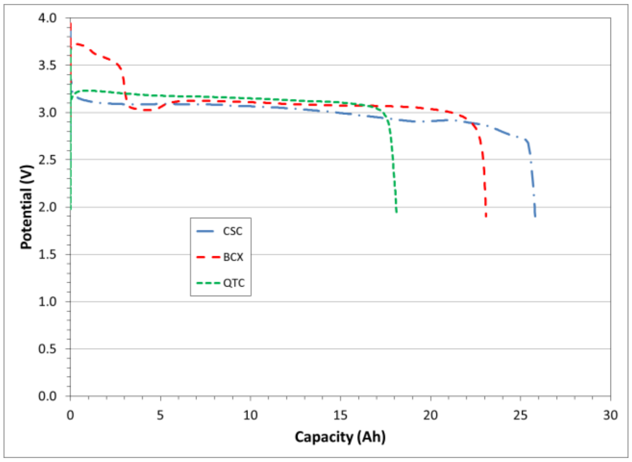

Figure 6. DD cells, 3.6 W, 0°C.

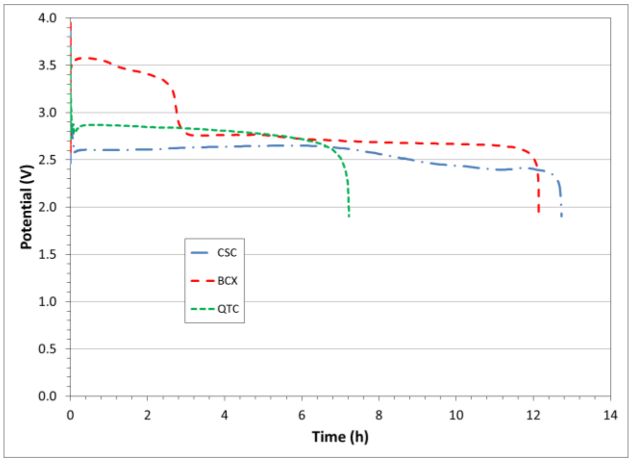

Figure 7. DD cells, 3.6 W, -20°C.

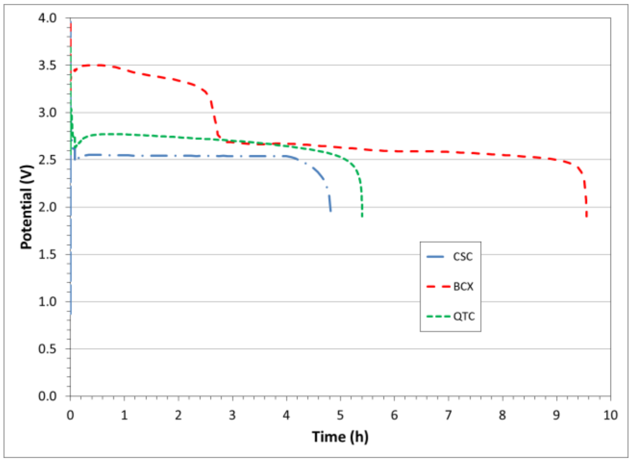

Figure 8. DD cells, 3.6 W, -40°C.

Figure 9 shows discharge of BCX cells at 0°C under a constant power load of 3.6 W and a constant current load of 1.25 A. The voltage profiles and the run-times obtained under these two conditions were nearly identical.

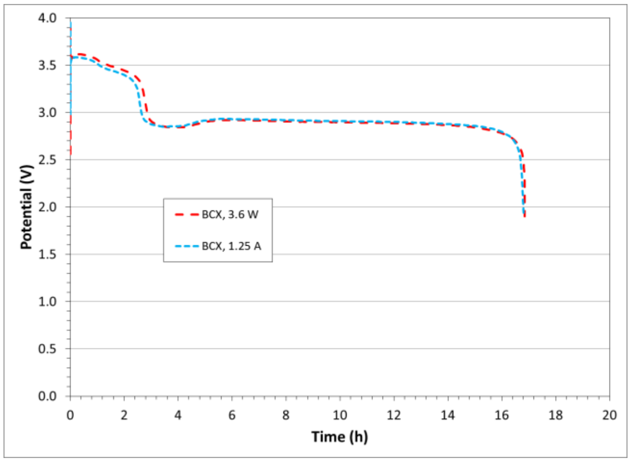

Figure 9. BCX DD cells, 3.6 W vs. 1.25 A at 0°C.

Pulsed Discharge: Under pulsed discharge conditions, the amount of capacity that can be obtained from the cell is determined by when the voltage drops below the voltage cut-off of the device during the heaviest pulse. Because the voltages are lower overall at cold temperatures, modest differences in the voltage drop that occurs during the pulsing can lead to dramatic differences in when the device cut-off is reached.

Figure 10 shows an example of pulsed discharge at 0°C. If the voltage cut-off is taken as 2.0 V, the CSC cell gives the longest run-time, but in the case of a 2.5 V cut-off it is the BCX cell that give the best performance.

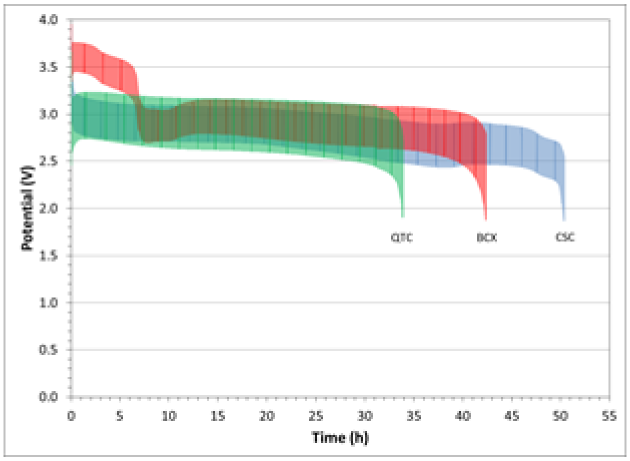

Figure 10. DD cells, pulsed discharge, 0°C.

Mixed Temperature Discharge

Figures 11 and 12 show discharge results for tests in which the cell was discharged under a 3.6 W load for several hours at -40°C, and the temperature was then ramped up to 0°C or RT over the course of two hours, after which the discharge was allowed to proceed until the cells dropped below a final cut-off of 2.0 V. These conditions are intended to simulate a scenario in which cells that have been stored in a cold environment are installed in a tool and the tool is powered up so that its operation can be assessed before the tool is deployed into a warmer environment. Such scenarios are common, for example, in the case of pipeline inspection in northern regions.

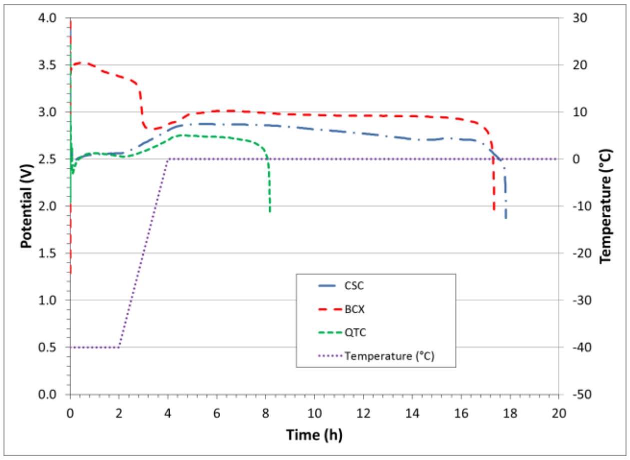

Figure 11. DD cells, 3.6 W: 2 h at -40°C, 2 h ramp to 0°C, discharge to end-of-life at 0°C.

In the first test, the cells were run at -40°C for two hours before the temperature was increased. The voltages of the cells increased with the temperature, and the final capacities obtained were close to 100% of the expected higher temperature capacity.

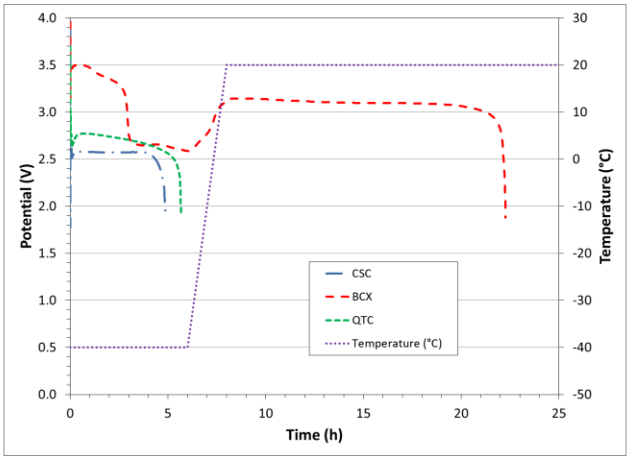

Figure 12. DD cells, 3.6 W: 6 h at -40°C, 2 h ramp to 23°C, discharge to end-of-life at 23°C.

In the second test, the cells were allowed to run for six hours at -40°C before the temperature was increased. During that six hours, the QTC and CSC cells dropped below 2.0 V, and did not restart. The BCX cells, however, remained at usable voltages throughout, and delivered their full higher temperature capacity with no apparent harm from the low temperature discharge.

Conclusions

Both the running voltage and the capacity will decrease when a battery is run at low temperatures. Lithium oxyhalide cells can operate at extremely low temperatures, but the performance available from the cell is very sensitive to the cut-off voltage of the device. Excessive discharge at very low temperature can lead in some cases to reduced capacity due to cathode freeze-over.

Acknowledgements

The authors wish to thank Jim Stawitzky for tabulating information from customers about typical cell usage under low temperature field conditions.

References

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