Characterizing end of life cells characteristics with different formation protocols

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Abstract

End of life behaviour in Lithium-ion (Li-ion) batteries often takes long periods of time to characterize, mostly from aging the cells under study. With accelerated cycle life testing, which rapidly ages cells by continuously cycling them, end of life can be achieved in cells quickly. 40 total pouch cells fabricated at the University of Michigan Battery Lab were originally made to investigate the impact of fast formation protocols on battery lifetime via accelerated cycle life testing. Of those 40 cells, 7 of them were characterized using tests/metrics such as HPPC (Hybrid Pulse Power Characterization), constant discharge capacity (at 1C and C/20), self discharge rate etc. These end of life metrics were compared with the same metrics measured when the cell was new to understand the impact of cell aging. Furthermore, as some cells (2 of the 7 under study) underwent fast formation, the impact of formation protocols on aged cells characteristics were also investigated. Cathodic degradation was observed in most cells, while cell relaxation also obscured much of the self-discharge data.

1 Introduction

The 7 cells under study are are subset of 40 NMC/graphite pouch cells made at the University of Michigan Battery Lab, originally used to study impacts of new fast formation protocols, which aims to cut down on time spent on formation, a significant fraction of the overall battery production time. All of the cells had been cycle tested as part of the aforementioned study, and hence are at their "end of life". Out of the 7 total cells, 3 underwent fast formation, which allows for investigation on effects of formation protocols on end of life characteristics.

End of life NMH/graphite cells have been studied by Jalkanen et al. Their study looked at effects of discharge/charge temperature, and observed cell aging manifesting as "capacity fade and resistance increase", which was exacerbated by high temperatures. After disassembling their cells, lithium plating and SEI-layer growth were found and theorized to be the main mechanisms of aging [1]. The current cells in interest also vary in cycling temperature, in addition to the fast formation protocols - these cells were subjected to a series of diagnostic tests which include: HPPC, constant discharge capacity (at 1C and C/20), self discharge rate, EIS (electrochemical impedance spectroscopy). Characteristics observed in these diagnostic tests were then be compared with the same metrics before aging to quantify the effects of aging. The following report details experimental procedures and results gleaned from aforementioned diagnostic tests.

2 Experimental

The 7 cells chosen from the 40 total cells fabricated were all subject to a final discharge to 3V after the accelerated cycle life testing. The 1C discharge capacity at the end of cycling was divided by the initial rated capacity of 2.37 Ah to get the state of health (SOH) before post-mortem analysis. After allowing the cells to relax (across a time interval of nearly a year), the OCV (open circuit voltage) of each cell was measured before the diagnostic tests were ran, displayed below in Table 1. Of the cells studied, one of the cells (ID: 7) had an OCV of less than 3V, which can possibly be explained by micro shorting, causing the battery to continuously discharge and age.

Cell ID	OCV	Formation type	Cycling temp.	Capacity (Ah)	SOHz
4	2.14	baseline	HT	0.29	12.3%
5	3.47	baseline	HT	0.18	7.6%
13	3.54	baseline	RT	0.86	36.3%
14	3.53	baseline	RT	0.88	37.1%
21	3.54	fast	RT	1.22	51.4%
22	3.55	fast	RT	0.41	17.3%
34	3.23	fast	HT	1.13	47.7%

Table 1: Table of end-of-life cells analysed. Each cell (of the initial 40 cells made) has an ID for identification, while OCV was measured before analysis. The final 1C discharge capacity at the end of cycling and the corresponding SOH is also shown. Different cells studied have gone through different processes like formation types (baseline formation/fast formation) and cycling temperature (room temperature (RT)/high temperature (HT)).

3 Results

Pertaining to the voltage monitoring tests, the preceding tests should also be taken into account when interpreting the data. The previous test ran was HPPC characterization, with around 19 days in between. An HPPC test implies a discharge to minimum voltage, or 0% SOC, at which self-discharge should theoretically not be observed. This aligned with the data in general - 4 out of 7 cells exhibited an increase in measured voltage in the ranges of 1-10 mV throughout the testing period (which elapsed 2 weeks), which can be attributed to cell relaxation. 2 out of 7 cells exhibited a slight decrease in measured voltage in the ranges of 1-4 mV, which could because the HPPC test did not truly discharge it to 0% SOC. 1 anomalous cell showed an increase in voltage of 0.24 V, which seems too large of a magnitude to be attributed to cell relaxation, considering the time elapsed between the HPPC test and the voltage monitoring test.

The HPPC characterization showed results consistent with Jalkanen et al, where high temperature cycling lead to higher overall resistance at all SOCs. However, fast formation does not show a significant effect in cell resistances in comparison to cycling temperature. All cells exhibited higher cell resistance at higher SOC's, which could be an indicator of cathodic degradation. This degradation could have arose during two time periods, either during accelerated cycling or during storage time, the latter of which elapsed around 8-9 months.

During capacity diagnostic tests, several cells tripped the temperature limit of the testing hardware, causing the test sequence to end early. Among these cells were cells ID 21 and 5, which have the opposite testing conditions - regular temperature cycling vs high temperature cycling (respectively), fast formation vs regular formation (respectively).

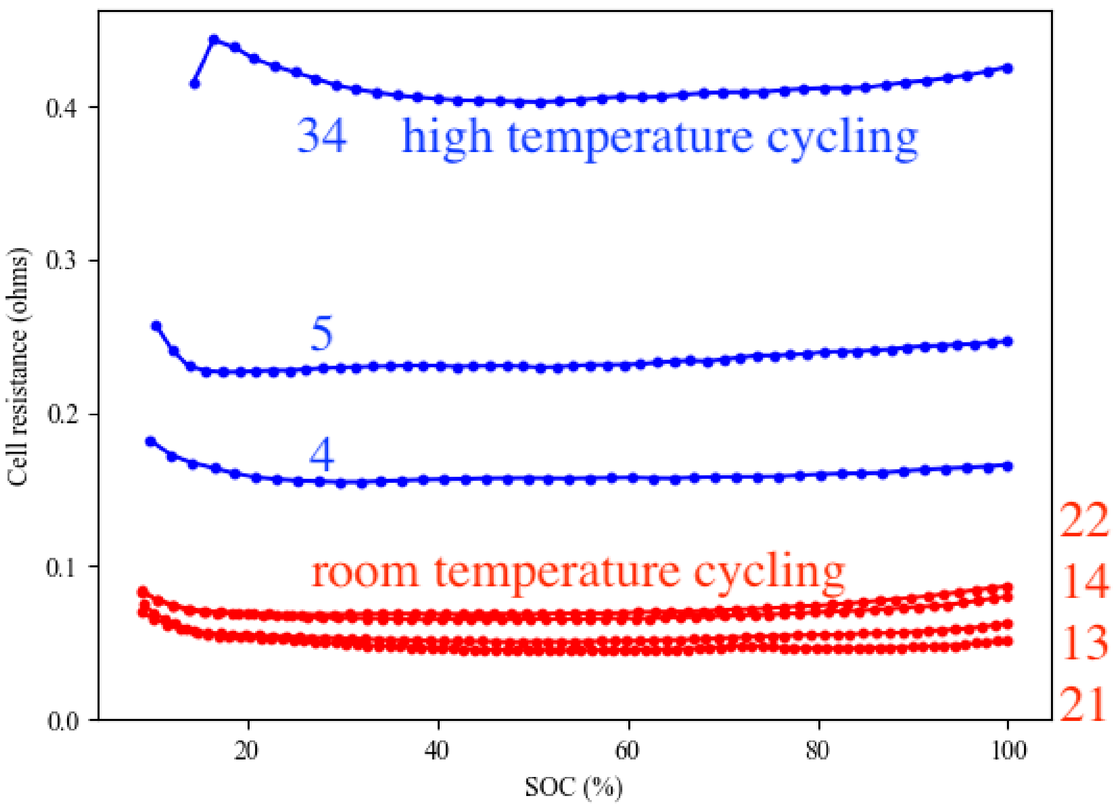

Figure 1: Resistance vs SOC. Data was collected from HPPC tests. The cells are colour coded by their cycling temperature.

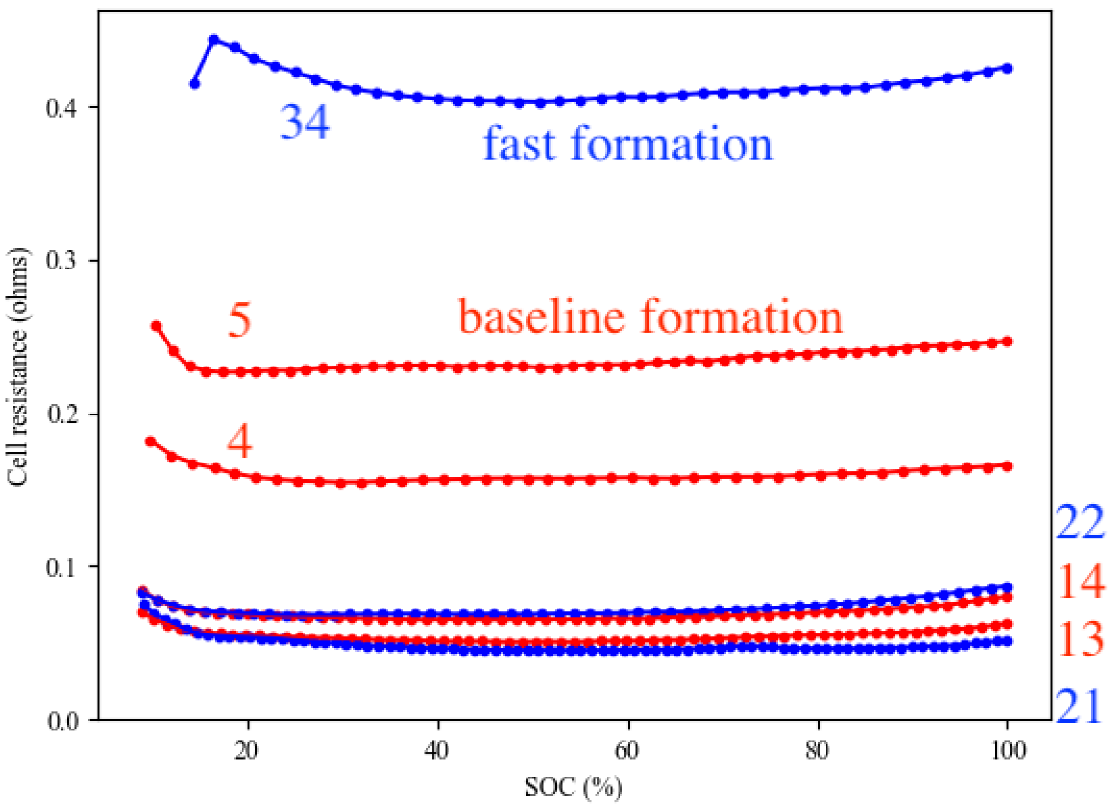

Figure 2: Resistance vs SOC. Data was collected from HPPC tests. The cells are colour coded by their formation protocol.

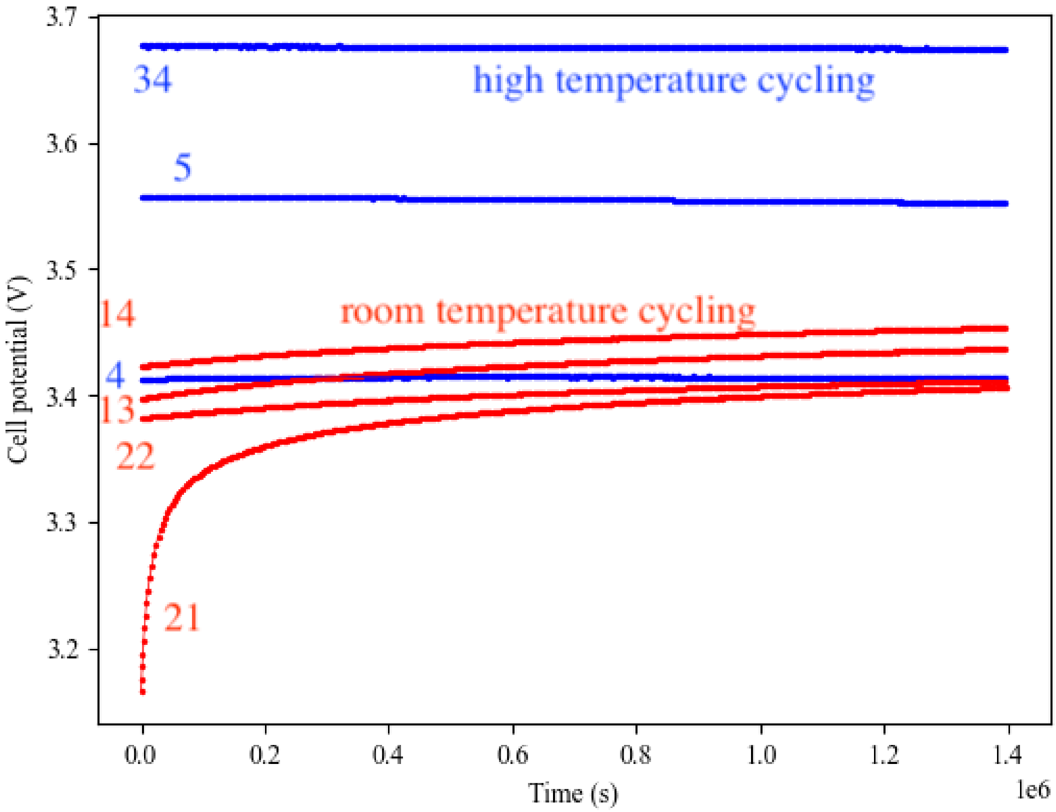

Figure 3: Self discharge rate measured from voltage monitoring test, high temperature cycling vs room temperature cycling.

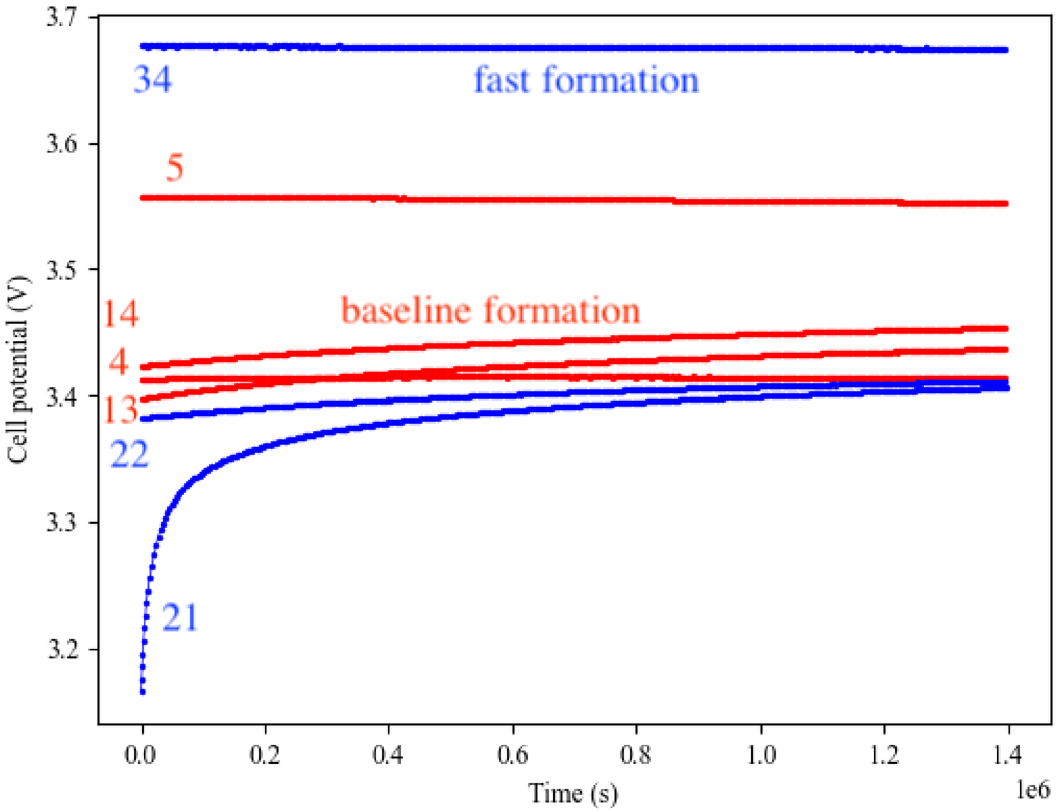

Figure 4: Self discharge rate measured from voltage monitoring test, fast formation vs baseline formation.

4 Discussion

5 Conclusions

References

[1] K. Jalkanen, J. Karppinen, L. Skogström, T. Laurila, M. Nisula, and K. Vuorilehto, "Cycle aging of commercial nmc/graphite pouch cells at different temperatures," *Applied Energy*, vol. 154, pp. 160–172, 2015.

A Appendix

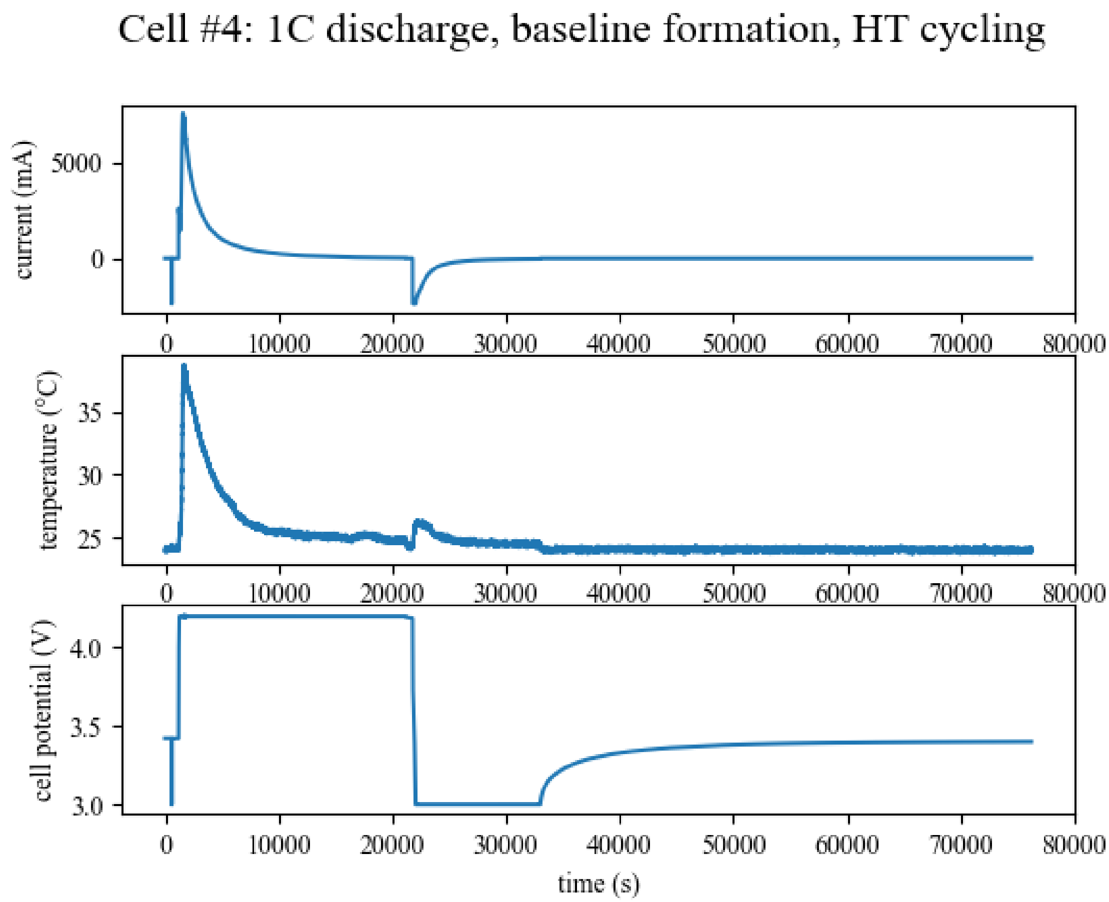

Figure 5: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.

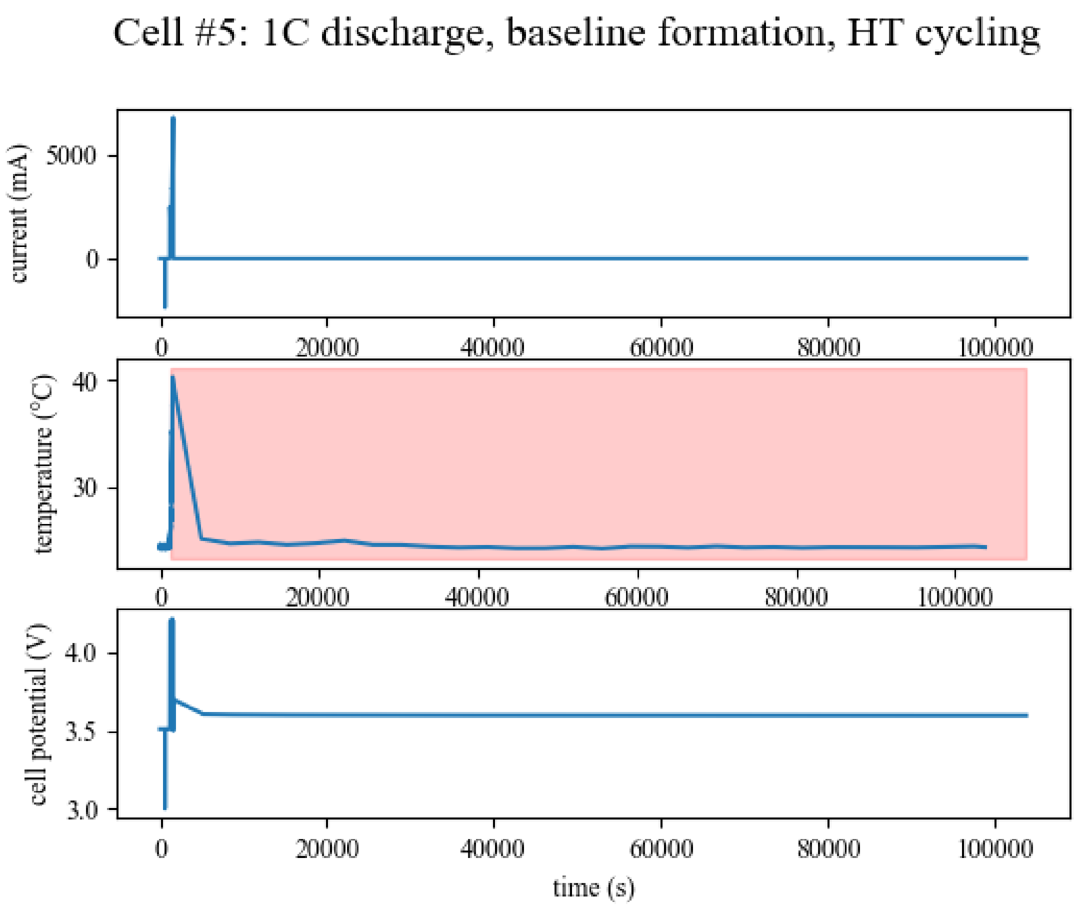

Figure 6: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.

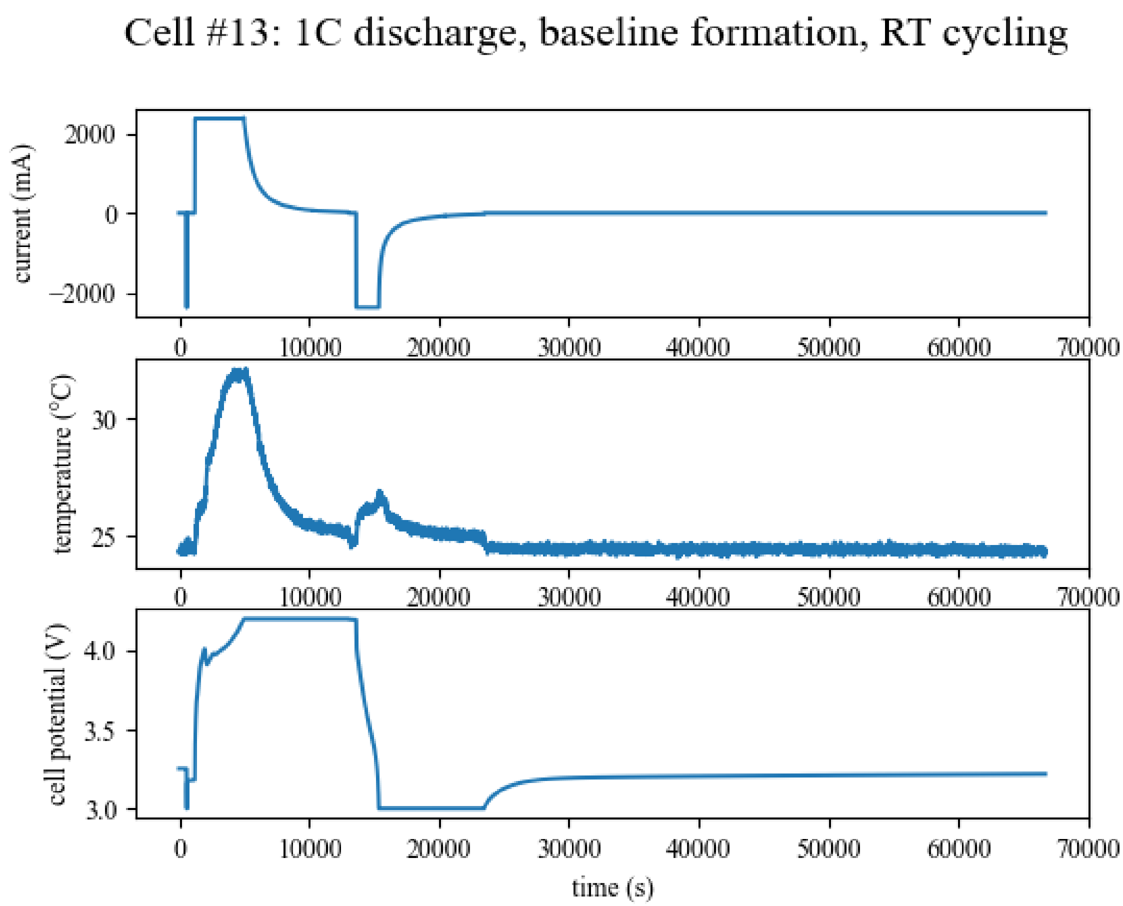

Figure 7: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.

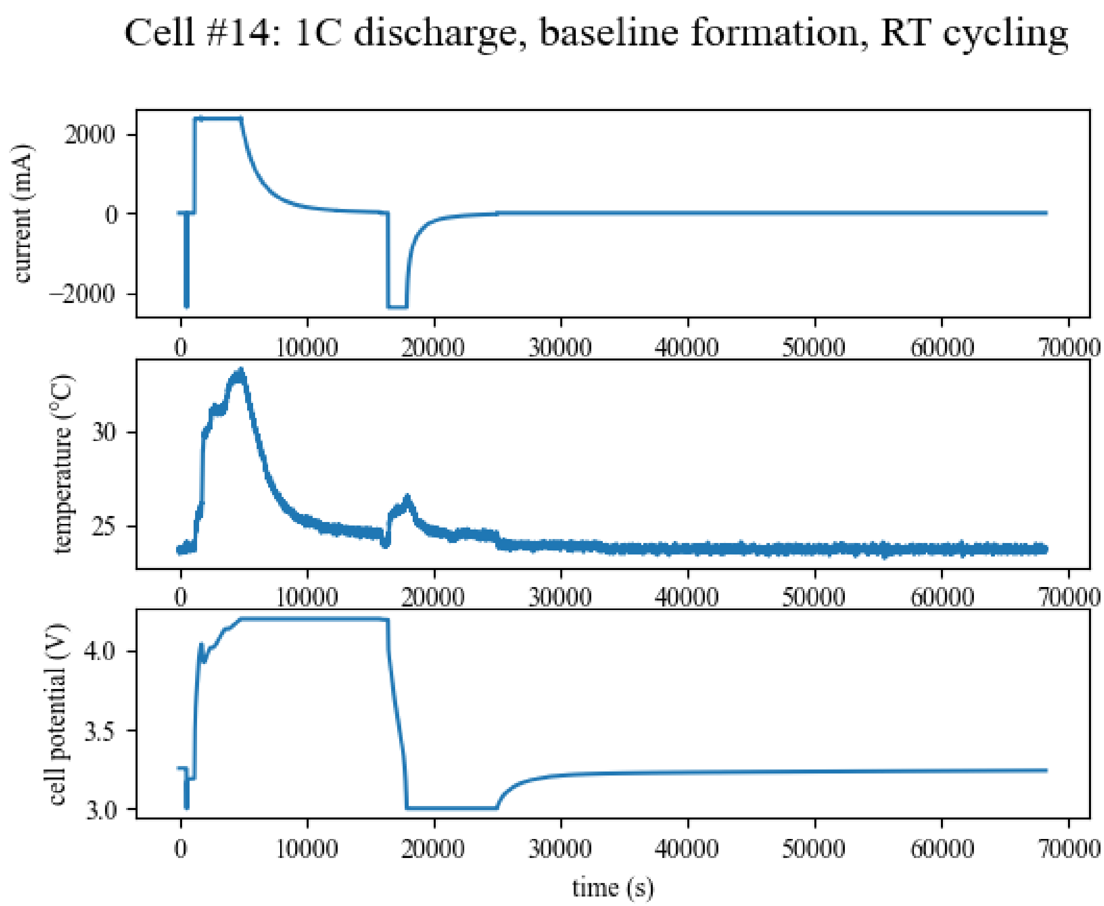

Figure 8: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.

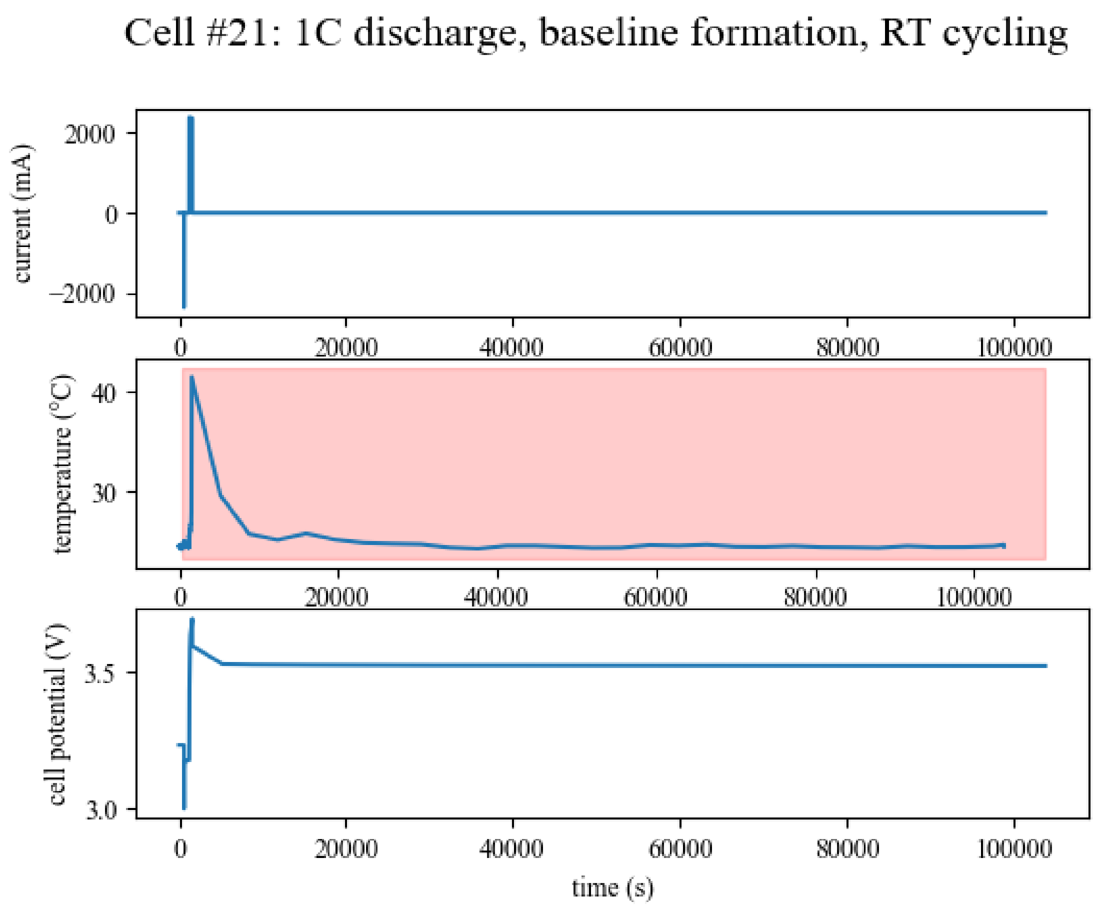

Figure 9: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.

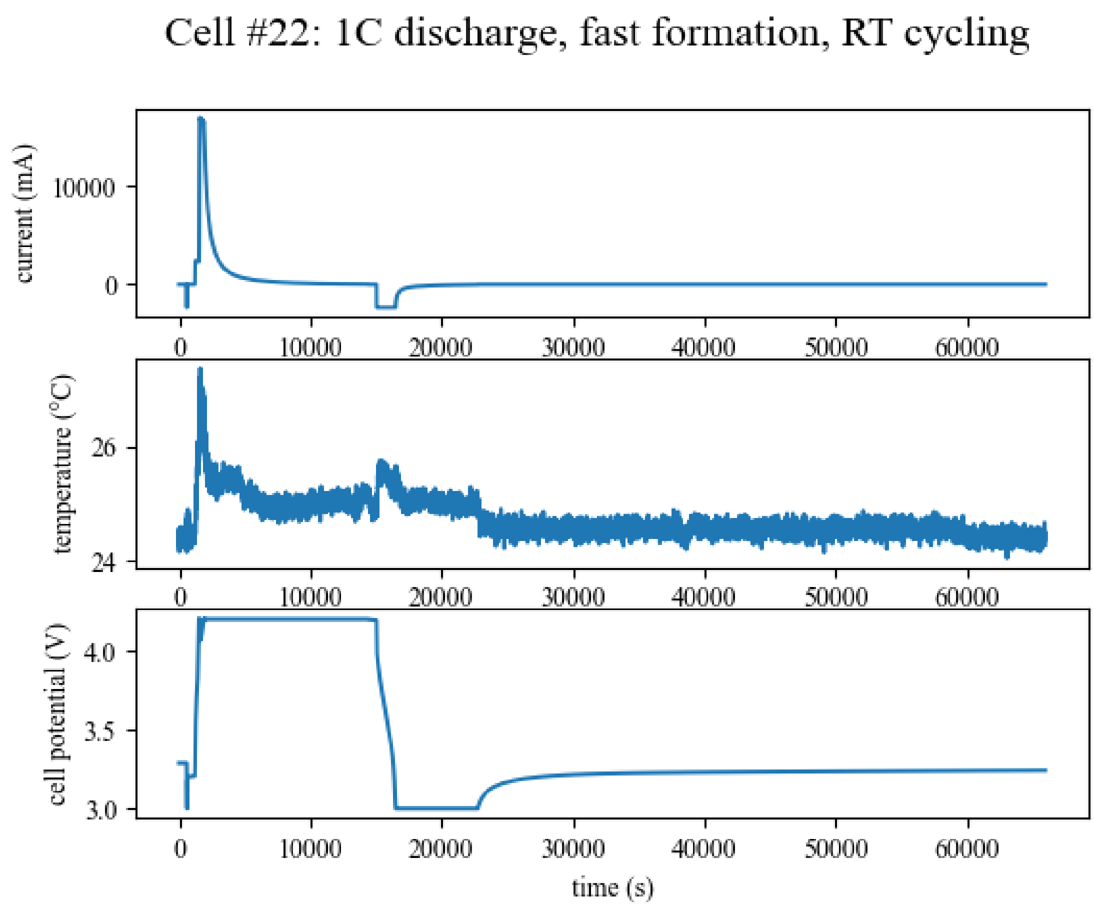

Figure 10: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.

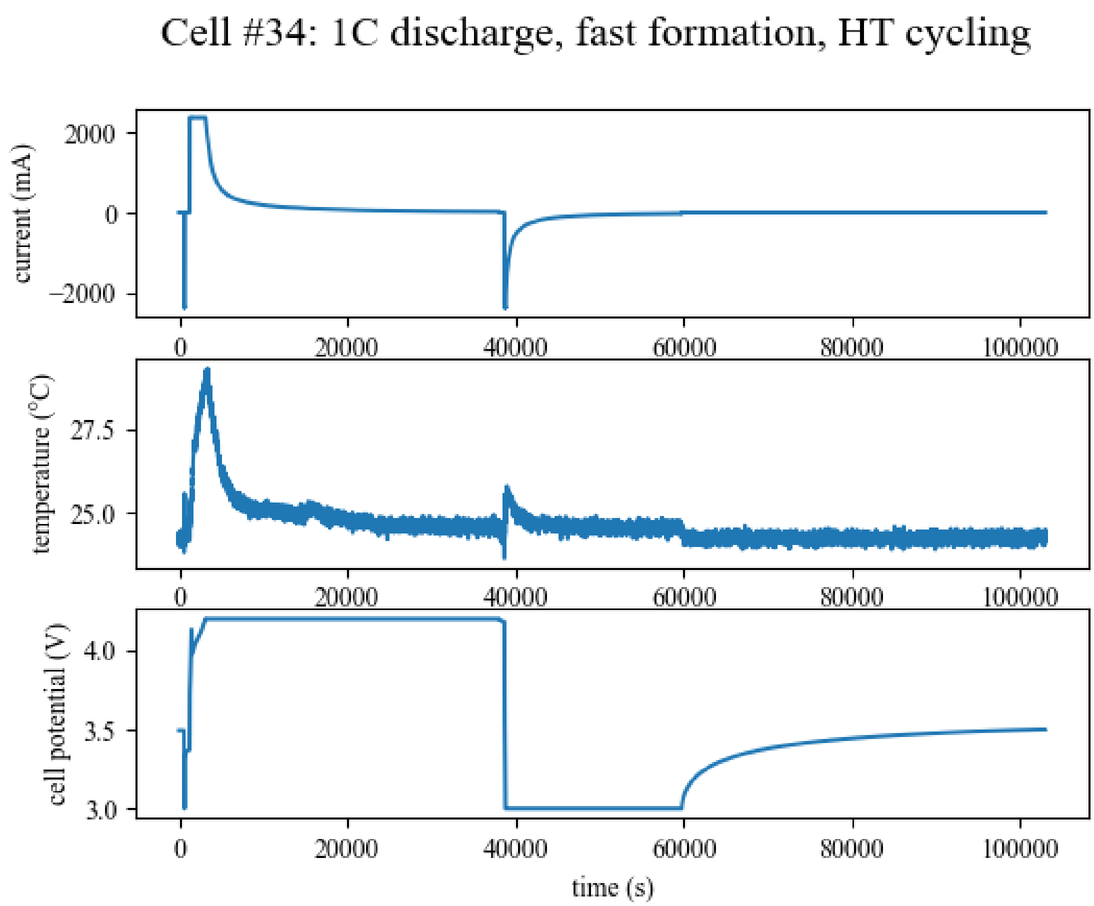

Figure 11: Plot of current, voltage, and temperature of a standard 1C discharge on the aged cell. Temperature plots shaded red mean that the 40°C safety switch had been tripped, and the resulting test sequences were not ran as a result.