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Electric Vehicle Transportation Center

Battery Cycling and Calendar Aging: Year One Testing Results

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I. Abstract

This report is meant to provide an update on the ongoing battery testing performed by the Hawaii Natural Energy Institute to evaluate Electric Vehicle (EV) battery durability and reliability under electric utility grid operations. Commercial EV battery cells have been under test for over a year in order to assess the impact of vehicle to grid and grid to vehicle applications on cell degradation.

II. Introduction

In our first report [1], a test plan based on the application of design of experiments techniques for both the cycling and the calendar aging study was proposed. With this plan, the impact of vehicle to grid (V2G) and grid to vehicle (G2V) strategies as well as the impact of charging habits on lithium-ion (Li-ion) cells can be assessed. In our second report, the results of the initial conditioning and characterization test (ICCT) [2] were presented. A progress report was completed in early 2016, focused on preliminary results from the aging study and cell emulation. This progress report provides an update after a full year of testing.

Since the testing first started in April 2015, 52 cells have been tested continuously (24/7) in order to assess the impact of V2G and G2V scenarios on battery degradation. The 36 cells undergoing cycle aging have performed the equivalent of 1.5 years of driving and the 16 cells undergoing calendar aging have been aged for more than a year. Although the analysis of the results is not completed, this report will showcase some emerging trends.

The testing is currently on hold due to an unrelated laboratory incident at HNEI in early March 2016. All HNEI laboratories were closed and experiments were put on hold until an independent investigation is completed and a thorough safety inspection of each lab is conducted. This delay in the testing will limit the number of cycles to be performed for the cycling experiment. The calendar aging experiment will be affected to a lesser extent, since the cells were left at temperature. The testing is expected to resume this summer.

III. Cycle aging experiment

As described in [1, 2], the aging schedules last 11 hours. The schedules are repeated 24/7 for 6 weeks before a reference performance test is performed in order to check on the cell degradation. During those 6 weeks, the schedules are repeated 90 times. Each aging schedule accounts for 1 equivalent day, so the cycling tests conducted over each 6 week timeframe represent 90 “days” or 3 months. Figure 1 presents the observed capacity retention for an equivalent of a year and a half of driving. Over these more than 500 equivalent days (or 16.5 months) simulated by the testing experiment, the cells lost between 5 and 9% of their capacity.

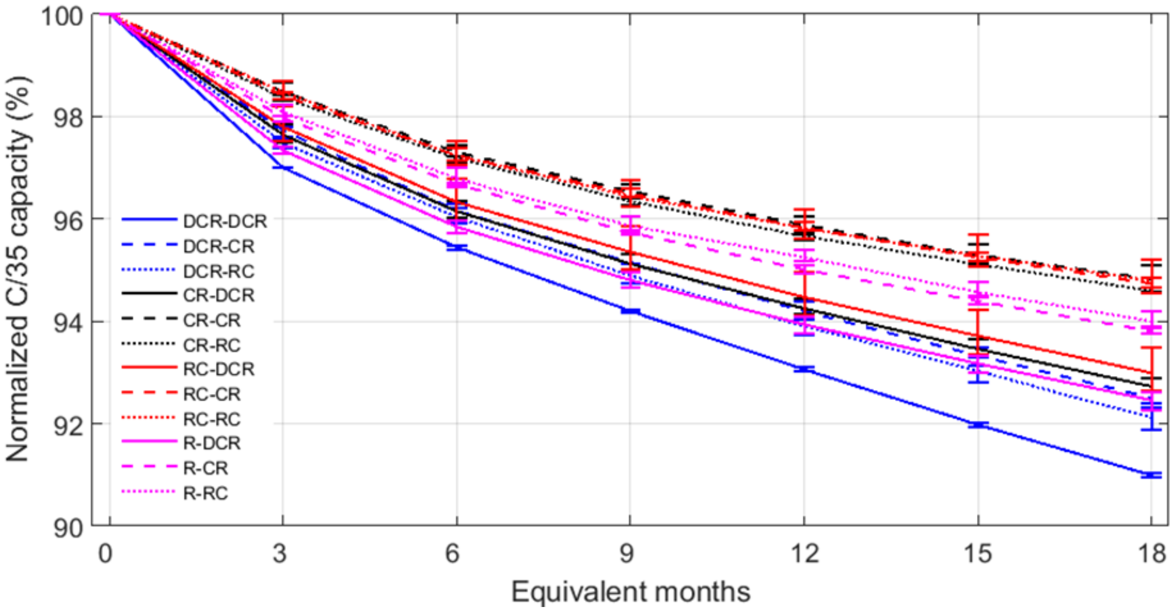

Figure 1: Capacity retention under cycle-aging experiment

Figure 2 presents the capacity loss after 18 months equivalent as a function of the testing schedule. As can be seen, there is a clear impact of the V2G implementation which always induces more capacity loss (DCR schedules). Each occurrence of the DCR schedule induces about 50% more capacity loss on the cells (6%, as compared with 4% loss) There is therefore a clear impact of the V2G schedule. The impact of the G2V strategies is really limited and the RC and CR schedules are inducing similar capacity loss. Interestingly, the schedules with only 1 charge per day (R-*) are degrading the cells faster than the schedules with 2 charges per day. This might be induced by the shallower DOD and will be investigated further in the next few months.

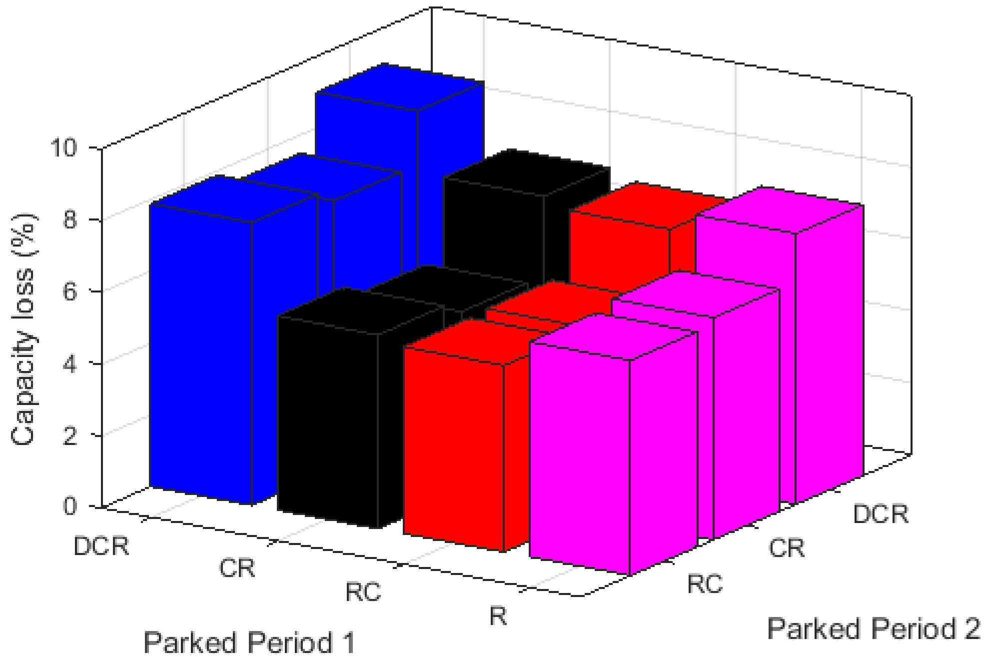

Figure 2: Capacity loss after 18 months as a function of the schedule.

IV. Calendar aging experiment

Figure 3 presents the capacity retention associated with the first 36 weeks of calendar aging. The temperature and SOC combinations are described in detail in [1]. Depending on the conditions, the cells lost between 1 and 10% of their capacity. Figure 4 showcases the relationship between capacity loss, temperature and SOC after 36 weeks. The colored surface on Figure 4 represents the modeled quadratic relationship between the parameters. Temperature and SOC are definitive aggravating factors in terms of calendar aging, both increasing the aging of the cells. Room temperature loss is between 2 and 3% after 36 weeks (9 months).

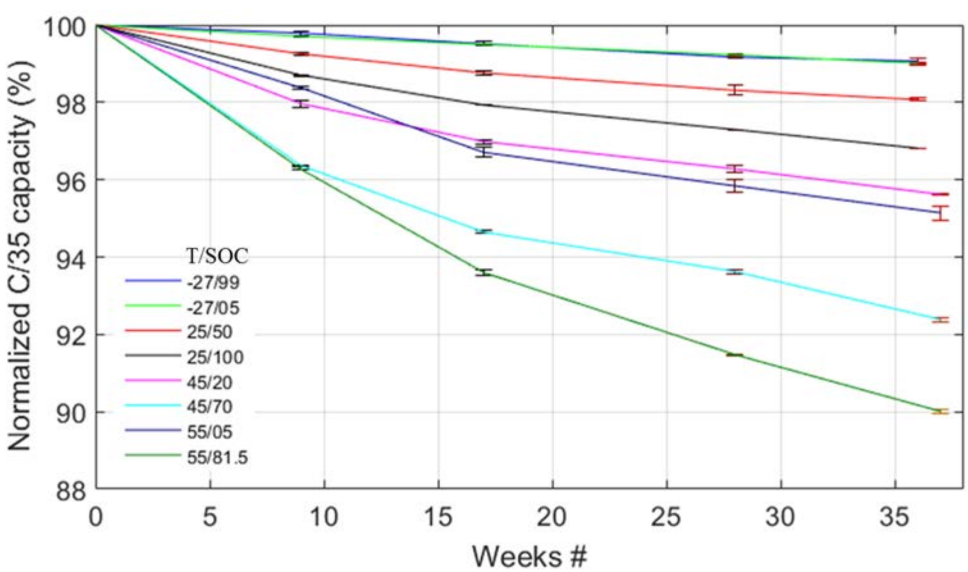

Figure 3: Capacity retention under calendar aging experiment.

Combining these results with results from the cycling experiment, we can estimate that if we were to have 24h schedules with a combination of cycling and calendar aging, the cells would have lost an additional 2-3% to the cycling loss (15 months with 13/24h of the day resting = 8 months calendar aging at 25°C), therefore between 7% (no V2G) to12% (V2G twice a day), after one year and a half of driving.

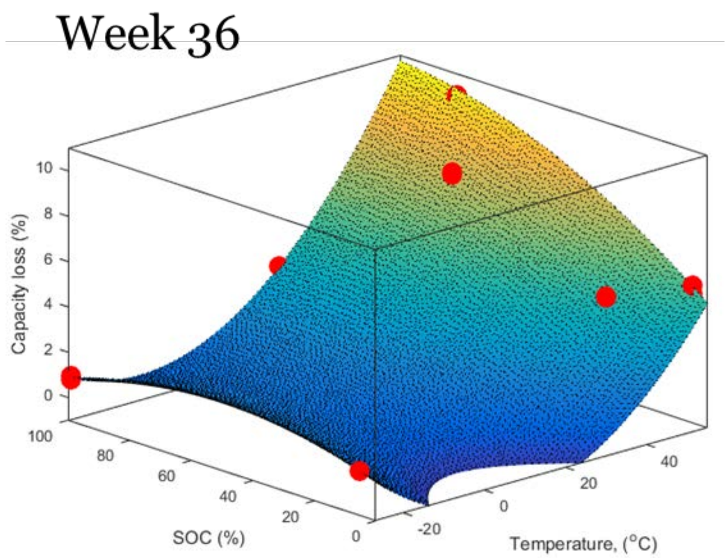

Figure 4: Calendar aging capacity loss vs. temperature and SOC at 36 weeks.

Capacity loss is influenced by both temperature and SOC and for the 4 instances at which we had reference tests. The data can be fitted with a quadratic model:

$Q_{loss} = a + b\,T + c\,SOC + d.T.SOC + eT^2 + fSOC^2$ ($R^2 = 0.99$)

This quadratic model works well for temperature above room temperature (RT) but not for temperatures below RT. However, the majority of the losses are above room temperature. Since all reference tests results could be fitted using the same quadratic model, Figure 5, the evolution of parameters *a* to *f* in function of time can be studied (inset on Figure 5). Their evolution seems to vary linearly with the square root of time. This allows us to introduce another model that could account not only for the impact of temperature and SOC but also time:

$Q_{loss} = W^{0.5} (a + b\,T + c\,SOC + d.T.SOC + eT^2 + fSOC^2)$ ($R^2 = 0.99$)

The R^2 of the model, 0.99, is very close to 1, so this simple model is therefore effective in estimating the capacity loss as a function of time, temperature and SOC. Once the testing resumes, some cells with additional conditions will be launched to validate the model further.

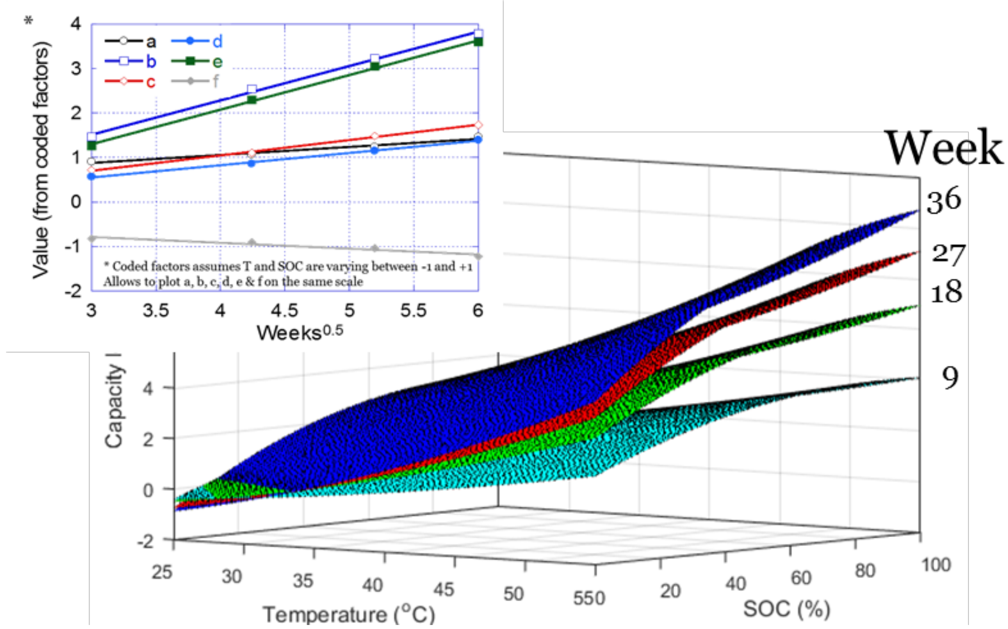

Figure 5: Calendar aging capacity loss vs. temperature and SOC at different times.

V. Path dependence of the degradation

From Figure 1 and Figure 3 it is undeniable that the different cycling conditions affect how much capacity is lost. This raises an essential question: are the cells degrading at a different pace or are they degrading differently? Many different degradation mechanisms can be associated with a similar capacity loss [3] and this could have major implications for the durability of the cells. Indeed, some degradation could remain silent in terms of capacity loss before it starts to induce loss at a greater pace [4]. In order to verify whether or not the cells are degrading under the same mechanisms, data at a similar 5% capacity loss for 4 cells will be compared (Figure 6): DCR-DCR@ 6 months, CR-CR@ 15 months, 45°C/70% SOC @ 18 weeks and 55°C/5%SOC @ 36 weeks.

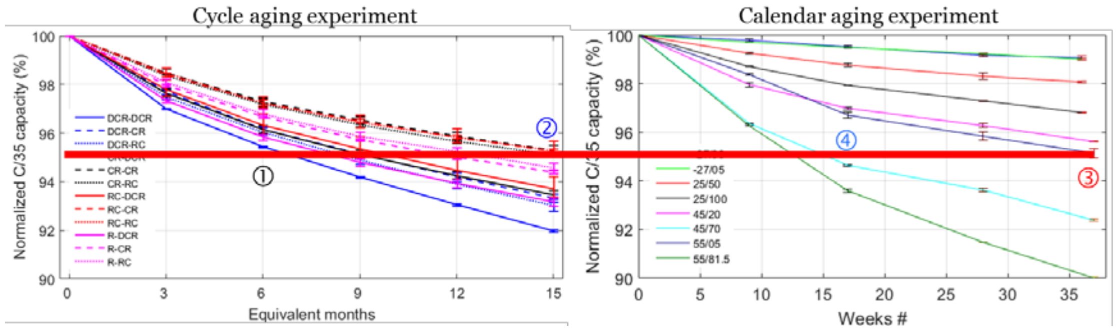

Figure 6: Capacity retention under cycle and calendar aging showcasing 4 distinct paths towards 5 % capacity loss.

Figure 7 presents the incremental capacity signatures of the 4 cells at 5% iso capacity loss. There are some differences in the electrochemical response of the cells and it is therefore clear that the different paths translate into different degradation mechanisms. The analysis using our emulation technique is in progress and it should allow us to predict differences in term of cell durability.

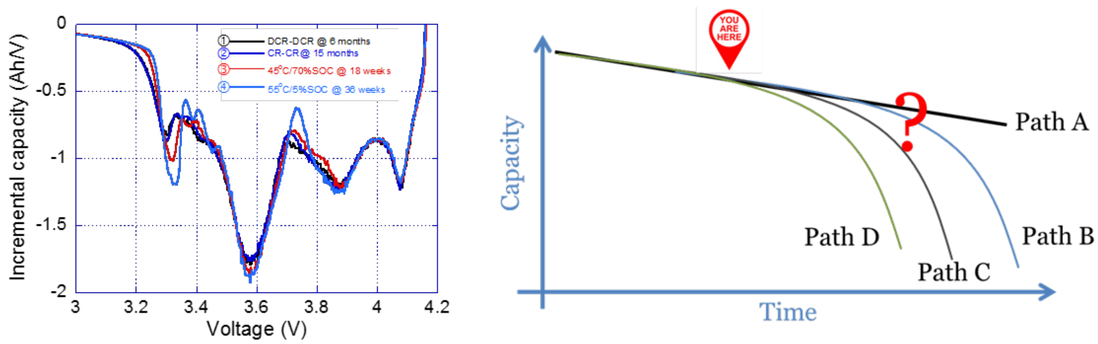

Figure 7: Incremental capacity curves of 4 different cells at 5% iso capacity loss and schematic representing the possible impact of different degradation paths on capacity retention,

VI. Testing progress assessment (Continue/Stop/Repeat/Refine).

In the initial test plan, it was thought that 1 year would suffice to degrade the cells enough to have clear trends on the impact of V2G/G2V cycles. The second year of testing was thought to be devoted to different conditions and/or different chemistries.

In the light of the results from Figure 1 and Figure 3, it appears that the cells degraded far less than anticipated. Moreover, with the current shutdown and the anticipated end of the project in early 2017, there may not be enough time to complete testing another matrix of experiments. Based on those observations and delays, testing of the cells will continue until the end of 2016 rather than launching any new cycling experiments.

Continuing the testing has two main benefits:

- First, it could validate the impact of the different degradation paths. The analysis of the data in Figure 7 might predict accelerated failure for some of the conditions. By continuing the test, some validation could be sought.
- Second, it will get the cells closer to their end of life at 20% capacity loss. The cells at EOL could then be used to assess the technical and economic viability of second use.

VII. Test status summary

As of May 31st 2016, the cells performing the cycling experiment were cycled nearly 700 times. The test is currently on hold because of the HNEI shutdown. The 8th RPT will be launched as soon as we have the green light to resume testing. The cells performing calendar aging all aged at least 45 weeks. They are all still at temperature and the 6th RPT will be launched as soon as testing resumes.

VIII. Invention Disclosure

While working to automate the analysis of the data, we invented a new method to estimate the SOH of the cells that should provide a significant leap forward compared to methods currently used in battery management systems. A provisional patent was filed on February 29th 2015. Further validation is in progress. Our invention addresses and solves the two main problems associated with SOC estimation: the gradual loss of accuracy with aging and the difficulty to diagnose cell aging without maintenance cycles. Table 1 presents a comparison of our method compared to recent patents and literature.

Table 1: SOH estimator comparison

US pat. #	First Filing Date	Assignee	Uses Coulomb counting	Infers SOC from OCV meas.	Estimates Q' as a result	Estimated Q' is accurate	1st principles method	Uses simple algebra	Does not restricts SOC range validity	Generates OCV = f(SOC) curves	Updates OCV = f(SOC)	Correlates Q' to LLI, LAMPE, LAMNE
US 6,892,148 B2	May 2, 2003	Texas Instruments	Y	Y	Y	N		N		N	N	N
US 2015/0268309 A1	Mar 20, 2014	Hyundai	Y	Y	Y[1]	N[1]	N	N	N[2]	N	N	N
US 9,081,068 B2	Jul 13, 2015	Apple	Y	Y	Y	N			N	N	N	N
US 8,046,181 B2	Aug 8, 2008	LG Chem	Y	Y	Y	N	N	Y	Y	N	N	N
Tong2015	Oct 30, 2014	In JPS	Y	Y	Y	Y	N[3]	N[3]				
Wang2016	May 16, 2015	In JPS	N	N	N		Y[4]	N[4]	N	N		Y[4]
Our invention		UH	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y

[1] The Hyundai patent estimates the new no-load capacity Q' as the average value of a number of Qr measurements. However the OCV = f(SOC) does not appear to be updated. Meaning the estimate for Q' is likely to be wrong.

[2] The Hyundai patent restricts the applicability of the method to a range of SOC from 0 to 50%.

[3] The UC Davis method uses Extended Kalman Filter, Recursive Least Square and Parameter Varying Approach. Heavy on computation and not physics based.

[4] The Harbin Institute of technology method uses emulated battery voltage from active materials and tracks specific markers at end of charge and discharge. More of a visual approach as popularized by Dr. Dubarry.

IX. Conclusions

Overall, the proposed testing plan is being followed and trends have started to emerge. Intensive V2G usage (1 hour at a quarter of the car's maximum power) seems to induce 50% additional capacity loss. Interestingly, it also appears that charging twice a day is beneficial to the cells. Regarding calendar aging, the high temperature and high SOC induced more degradation. A model accounting for time, temperature and SOC was proposed. The analysis of the incremental capacity signature is in progress.

Since degradation path dependence was observed, we would recommend extending the current experiment by 6 months in order to further understand this dependence by inducing more degradation on the cells.

X. Acknowledgements

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XI. References

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[3] M. Dubarry, A. Devie, B.Y. Liaw, Journal of Energy and Power Sources, 1(**5)** (2014) 242-249.
[4] M. Dubarry, C. Truchot, B.Y. Liaw, J. Power Sources, 219(2012) 204-216.