A Study Of The Relaxation Patterns Of Commercial {Gr,Si}//NMC-811 and Gr//LFP Cells

Alexa Fernando and Matthieu Dubarry

HNEI Hawai'i Natural Energy Institute, School of Ocean and Earth Science and Technology, University of Hawai'i at Mānoa

matthieu@hawaii.edu

Introduction

Deployed battery systems often have sporadic usage with no constant current or pattern, making controls complex.
Investigating **voltage relaxation** is interesting because it is controllable, independent of usage, and can be used to determine **state-of-charge (SoC)**.
Knowledge of parameters affecting voltage relaxation needs to be further developed as there is no standardized method for determining adequate rest duration for accurate OCV determination.
This work aims to discuss the impact of depth-of-discharge (DoD), rate, and temperature on **voltage relaxation duration**, as well as investigate the link between electrochemical voltage reactions and rest behavior based on experimental data at the full- and half-cell levels.
Gaining a better understanding of voltage relaxation behavior is important for developing and testing models of the rest period that could be used for online battery diagnosis and prognosis.

Objective & Significance

Voltage relaxation data from the half-cells and full-cells was analyzed to:

- determine the impact of each active material on the full-cell relaxation
- identify patterns in how the relaxation varies depending on the testing conditions.

Since relaxation data is monotonic and difficult to describe, this study also investigated different characterization approaches in order to provide guidance on the amount of time LFP and NMC-811 based batteries require to reach OCV.

Experimental

Two types of commercial 18650 full-cells were tested in this study:
a **Graphite / Li. Iron Phosphate (LFP)** and a **{Si, graphite}/Nickel Manganese Cobalt oxide (NMC811)**.
Half-cells were built from the positive and negative electrodes harvested from the commercial full cells.
Full-cells and half-cells were subjected to the same testing protocol designed to investigate the effect of DoD in charge/discharge, the impact of the charge/discharge schedule, and the impact of the charge/discharge at constant DoD.

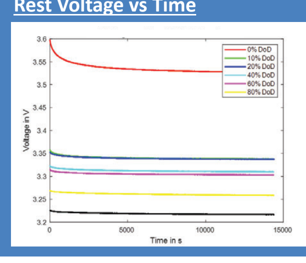
The full- and half-cells were cycled at various rates with incremental cutoffs at different DoDs ranging from 0-100%.
The residual capacity steps ensure that the starting conditions are the same for each segment and independent of the previous step, as opposed to a classic GITT test where the rest could be influenced by the rest/current before as the cell got more time to equilibrate.

Methodology – How Can Relaxation Be Characterized?

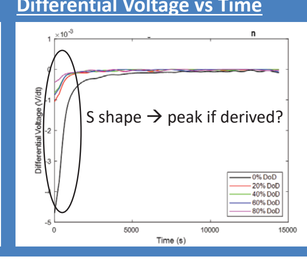
- There is currently no standardized method for characterizing relaxation data.
- It is important to characterize voltage relaxation so that we can extract important parameters that can be used for battery diagnosis, prognosis, and modelling.
- The method should be able to be 'blindly' applied to relaxation data to acquire information about the cell.
- A variety of different methods for plotting rest data have been explored in this study.

- The original voltage vs time curves does not allow for precise analysis of the relaxation behavior, as there are no quantifiable features of interest.
- Differential voltage vs time curves have been shown to detect lithium plating, but are not useful for quickly analyzing and quantifying the resulting relaxation behavior and for comparing curves to one another.
- Hard to extract quantifiable features from these plots.

Rest Voltage vs Time

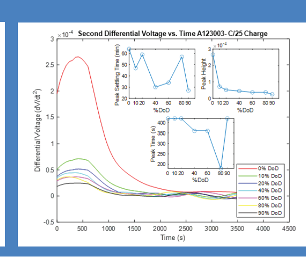


Differential Voltage vs Time

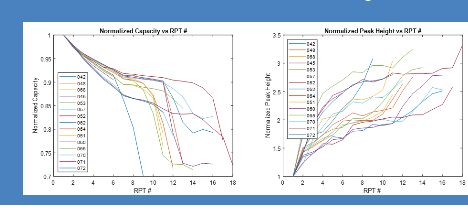


Second Differential Voltage vs Time

- Second differential voltage vs time showed potential for extracting features from the relaxation data.
- However, the peaks in these curves are dependent on heavy filtering, so an accurate analysis is unreliable and some data is lost.

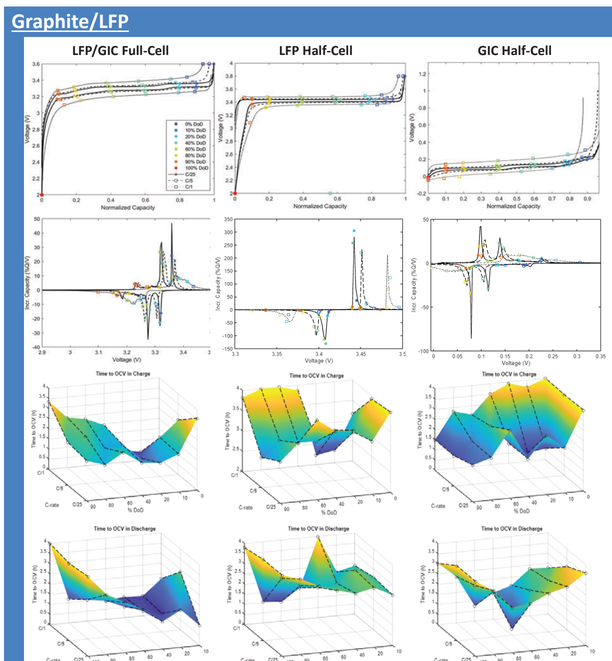


- Peak height showed a correlation with capacity loss, but was not efficient in detecting knees.



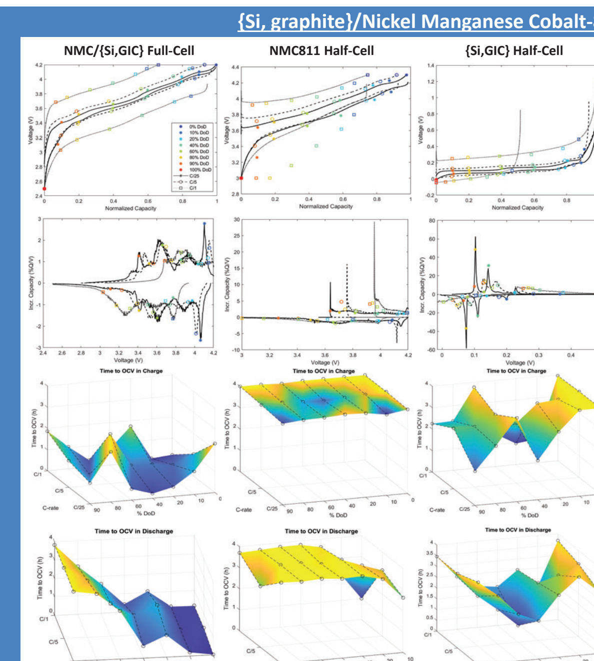
Effect of DOD, rate, and regime – Full-Cell vs Half-Cell

Graphite/LFP



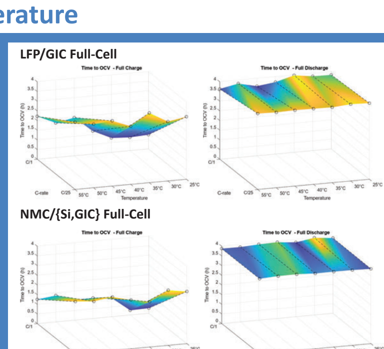
- The time it takes for relaxation to reach its final open-circuit voltage value was studied as a function of rate and DoD for both charge and discharge in order to identify patterns in the data and determine if the relaxation time can be reduced from the 4-hour period commonly used in research.
- Incremental capacity plots are shown to determine if the electroactive phases at which the cell is charged/discharged to has an impact on its relaxation behavior.
- Data shows that relaxation behavior is highly complex and the rest time is dependent on both DoD and rate.
- Rest time is also chemistry dependent; the LFP/graphite cell behaved differently than the NMC/{Si,graphite} cell.
- Relaxation time after a full discharge takes longer than the relaxation time after a full charge to reach OCV.
- Relaxation at the same DoD does not take the same amount of time to reach open-circuit voltage in charge and discharge, as the diffusion of lithium ions during the rest period changes direction depending on the direction of the current.
- There are no clear patterns in the time it takes to reach open-circuit voltage as a function of DoD and rate. For some points in the data, a 4-hour relaxation period was not long enough for the rest voltage to settle to its equilibrium OCV.

{Si, graphite}/Nickel Manganese Cobalt-811



Effect of Temperature

- A full charge and discharge cycle at C/1 and C/25 was performed at high temperatures ranging from 25°C - 55°C in 5°C increments on full-cells of both chemistries.



- Data does not indicate any trends or large changes in relaxation behavior dependent on increasing temperatures during charge and discharge for both chemistries.

Get OCV from extrapolation?

- In deployed systems, there may not be enough time for rest to reach OCV.
- Modeling from limited relaxation data could mitigate this issue.
- The complex nature of relaxation voltage makes modeling difficult.

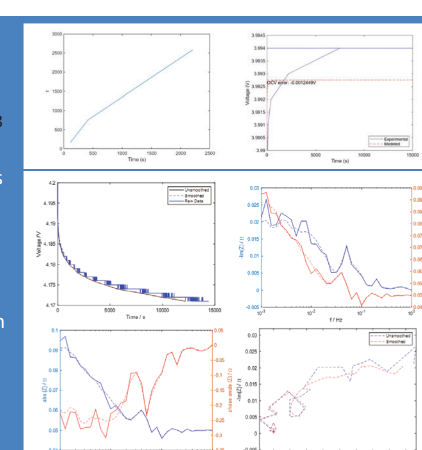
Rapid OCV Prediction Modeling — Pei L. et al. J. Power Sources 253 (2014) 412-418

- Based on an ECM (second-order RC circuit) that accounts for a linearly changing time-constant.
- In some cases, the model can predict the OCV and model the shape of the relaxation curve from just 15 minutes of rest data.
- When tested on data from various chemistries and DoD's, the model is inaccurate and unreliable.

Impedance Modeling From Time-Domain Relaxation Data — Bessler W. J. Electrochem 154 (2007) B1186

- Fourier transforms can be applied to time-domain relaxation data to obtain electrochemical impedance.
- Allows for analyzing experimental data without ECMs or traditional frequency-domain EIS measurements, which are time-consuming.
- From electrochemical impedance, the distribution of relaxation times (DRT) can be extracted, then a parameterized model could be created.
- Actual experimental data is too noisy for this technique to provide meaningful results and thoughtful analysis.

Schmidt J. et al. J. Power Sources 221 (2013) 70-77
Goldammer E. and Kowal J. Batteries (2021) 7,36



Conclusions & Perspective

- ✓ Relaxation is highly complex and dependent on rate, depth-of-discharge, and chemistry.
- ✓ Proving the complexity of relaxation informs modeling and characterization techniques, as they must include parameter-dependency.
- ✓ Reducing the rest time to reach open-circuit voltage is not straight-forward, and there is no 'one-size fits all' approach.
- ✓ Further testing includes relaxation data from cells cycled in low temperature conditions (15°C to - 15°C), including half-cells.

Acknowledgments

This research was funded by ACCURE Battery Intelligence and by the Office of Naval Research (ONR), grant # N00014-19-1-2159.

Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the sponsor.

University of Hawai'i Mānoa — School of Ocean and Earth Science and Technology — HNEI Hawai'i Natural Energy Institute, School of Ocean and Earth Science and Technology, University of Hawai'i at Mānoa — PakaLi+ Battery Laboratory