Thermodynamic Investigations of Lithium- and Manganese-Rich Transition Metal Oxides

Wenquan Lu (PI)

Qingliu Wu, Dennis Dees, Kevin Gallagher, Ira Bloom, and Anthony Burrell

Electrochemical Energy Storage
Chemical Sciences and Engineering Division
Argonne National Laboratory

Vehicle Technologies

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Vehicle Technologies Program

Overview

Timeline

- Start – Oct. 2012
- Finish – Sep. 2014
- Percent complete: 25%

Barriers

- Lithium manganese rich transition metal oxides (LMR-NMC) are viewed as the next generation high energy cathode material for lithium ion batteries. Mitigation of the voltage fade issue is critical for its successful commercialization.

Budget

- Part of Voltage Fade ($4M total project funding in FY2013)
- 100% DOE

Partners and Collaborators

- Voltage Fade Participants (Anthony Burrell, ANL)
- Cell Fabrication Facility (Andrew Jansen, ANL)
- Illinois Institute of Technology (Jai Prakash)

Objectives

- The entropy change will be investigated to monitor the structural transitions of the LMR-NMC material during charge and discharge, leading to the better understanding of the root cause of voltage fade.

- In addition, the kinetics of LMR-NMC, such as lithium ion diffusion and electronic conductivity, will be studied to identify their role in voltage fading.

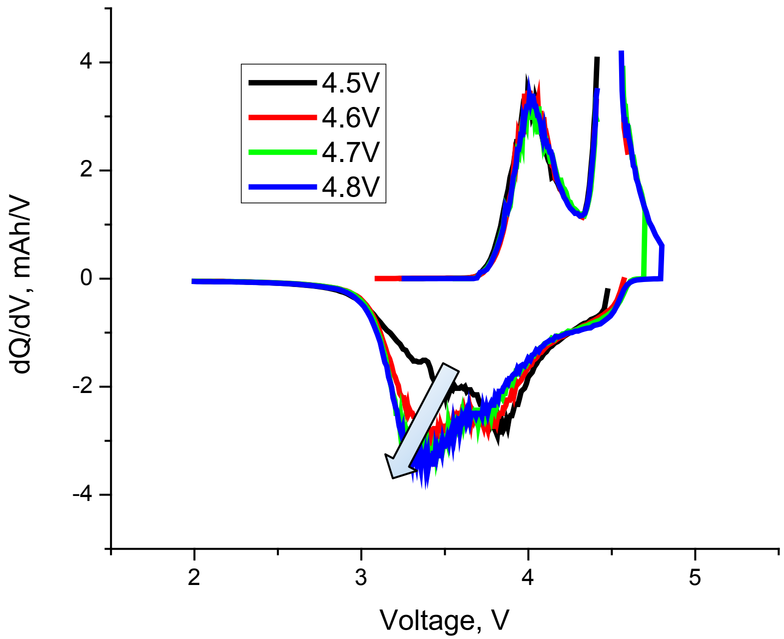
Milestones

- Formation effect on voltage fade of LMR-NMC (HE5050, Toda) —— Completed
- Entropy change investigation of LMR-NMC (HE5050) —— On target
- Thermal investigation of LMR-NMC —— Initiated

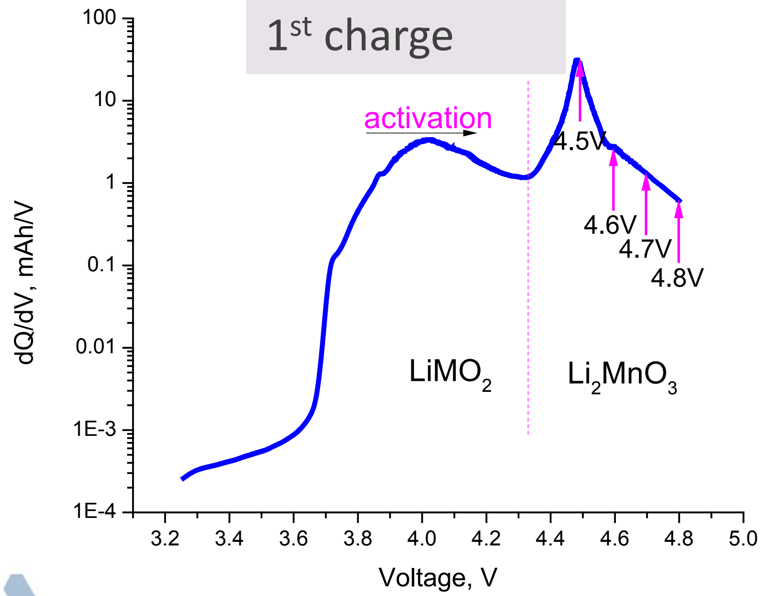
Formation effect

- **Why study formation effect?**
  - A lot of scattered information from various researches conducted using varying test conditions.
  - Strong need to determine the effect of formation cut-off voltage, related to the depth of Li_2MnO_3 activation, on voltage fade using standard test protocol with a systematic approach.

dQ/dV of First formation

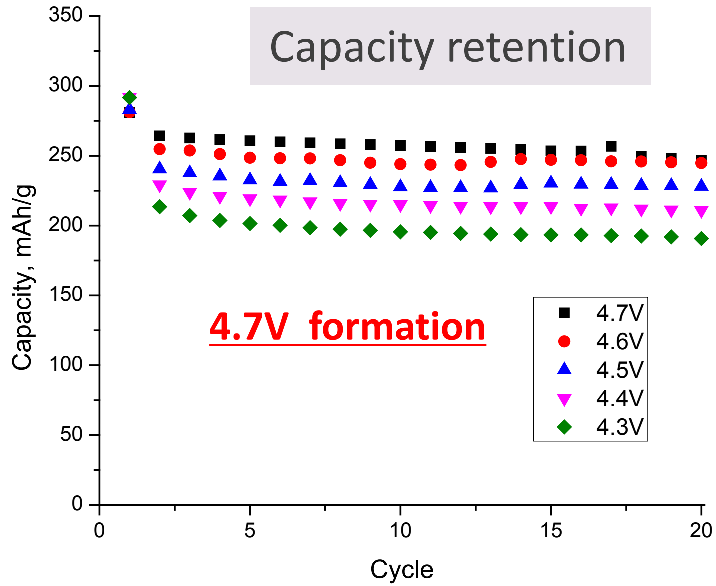


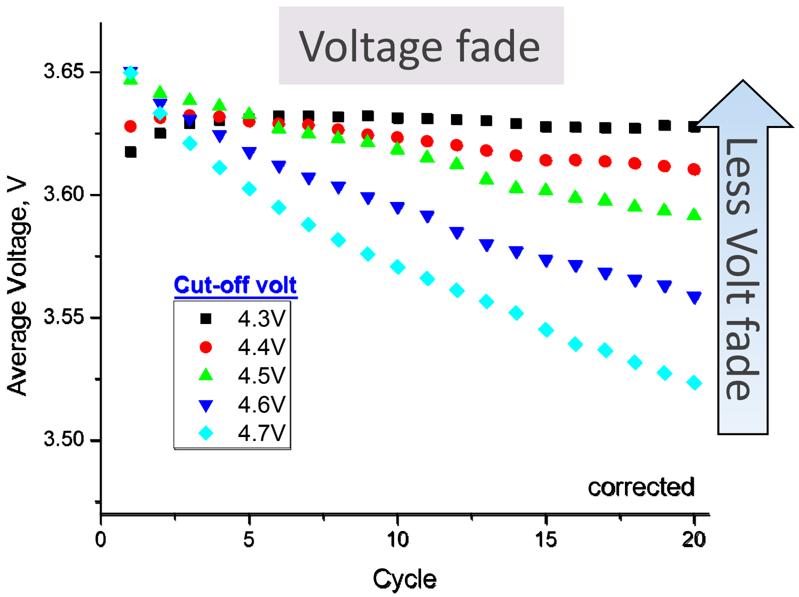
Li/HE5050 cell
1st charge



- Four different formation cut-off voltages, 4.8V, 4.7V, 4.6V, and 4.5V, were investigated. Under each formation cut-off voltage, a lower or equal cut-off voltages was applied for cycling tests.
- Increasing the formation voltage also increase the capacity obtained at lower reduction potentials.

Voltage Fade with Various Cycling Cut-off Voltages



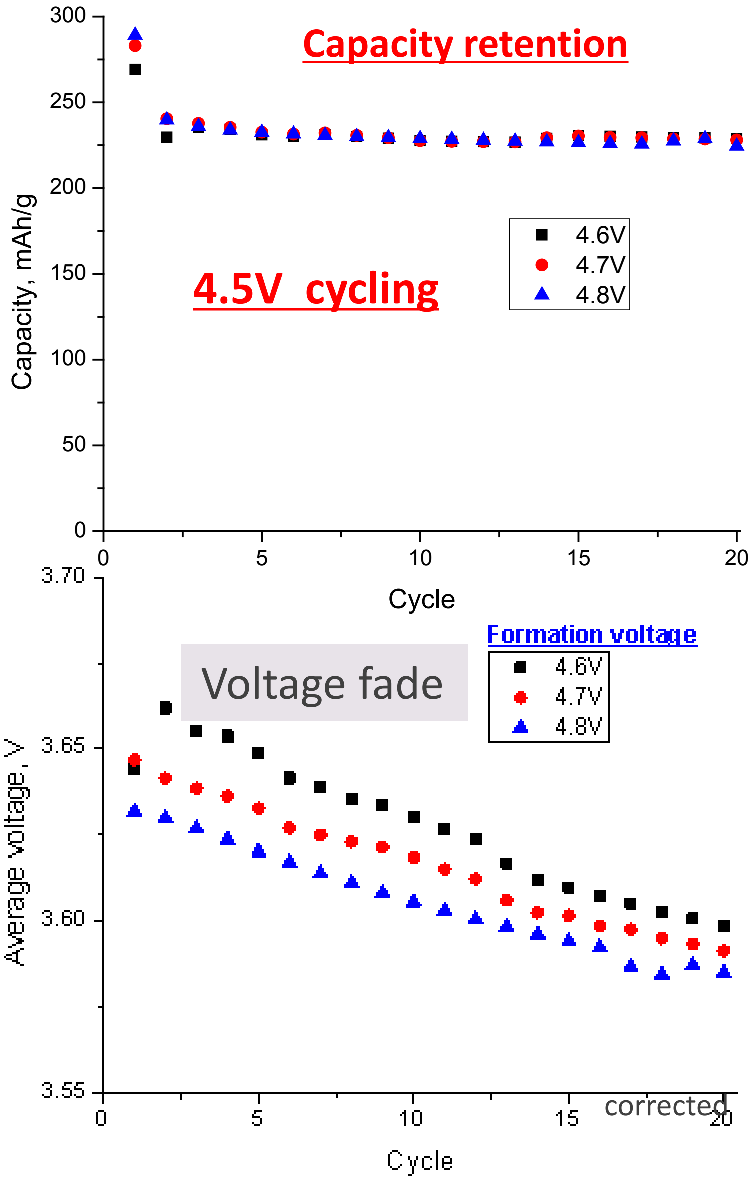


Li/HE5050 cell
1.2M $LiPF_6$ EC/EMC (3/7)

Formation:
2.0V to 4.7V
10mA/g
Cycling:
2.0V to cut-off
20mA/g

- With 4.7V formation voltage, no clear capacity fading difference was observed regardless of cycling cut-off voltage.
- The lower the cycling cut-off voltage is, the less voltage fade. No voltage fade observed when 4.3V was used as cycling voltage.

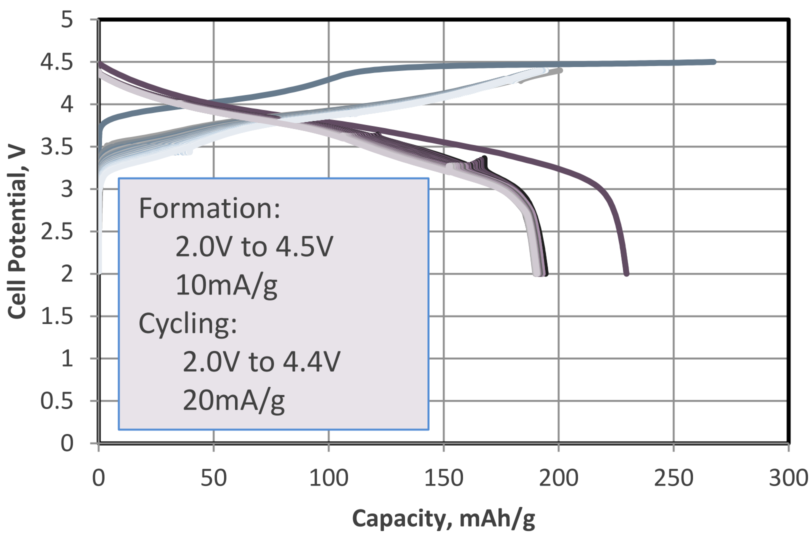
Voltage Fade with Various Formation Cut-off Voltages

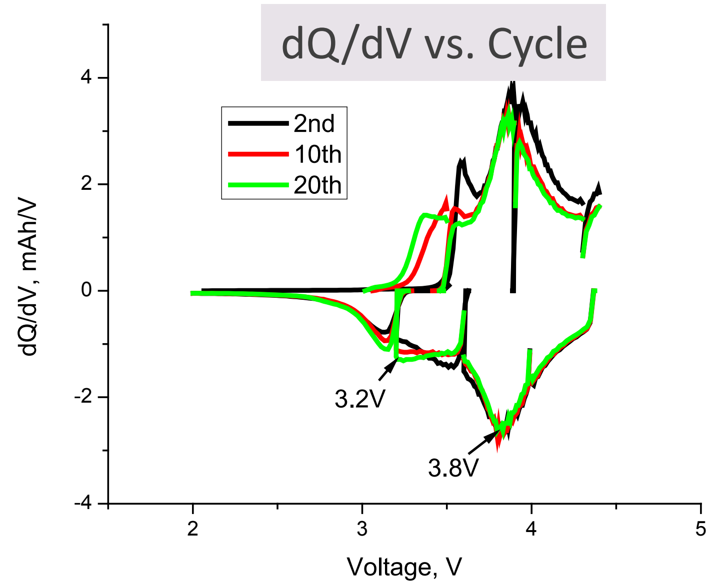


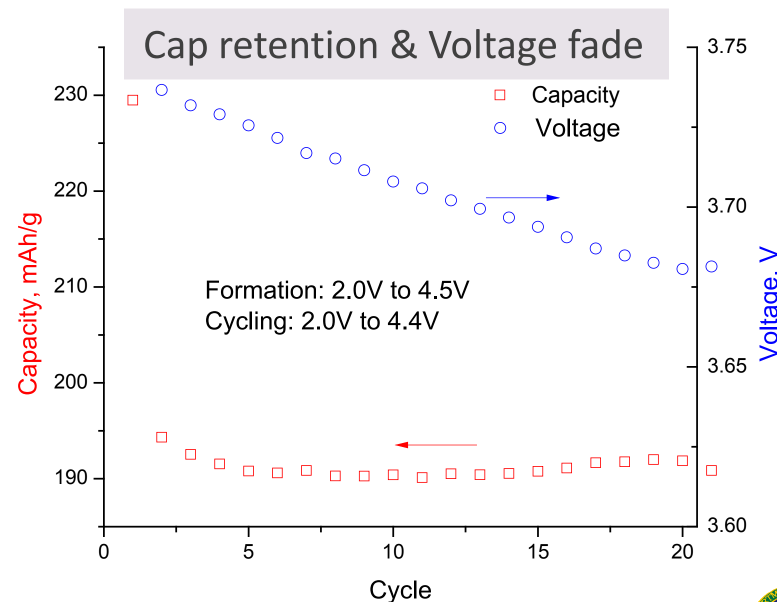
Li/HE5050 cell 1.2M LiPF6 EC/EMC (3/7)
Formation: 2.0V to cut-off 10mA/g Cycling: 2.0V to 4.5V 20mA/g

- Same reversible capacity with same cycling cut-off voltage regardless of various formation cut-off voltages.
- The formation cut-off voltages affect both voltage fade and electrode average voltage. The higher formation cut-off voltage will cause
  - lower voltage fade, and
  - lower starting average voltage.

Voltage Fade and Redox Potential Shift







- After 4.5V formation, no capacity fading with 4.4V cycling cut-off voltage observed.
- No capacity change related to redox peak at 3.8V.
- Therefore, voltage fade can be attributed to the shift of lower redox potential at 3.2V.

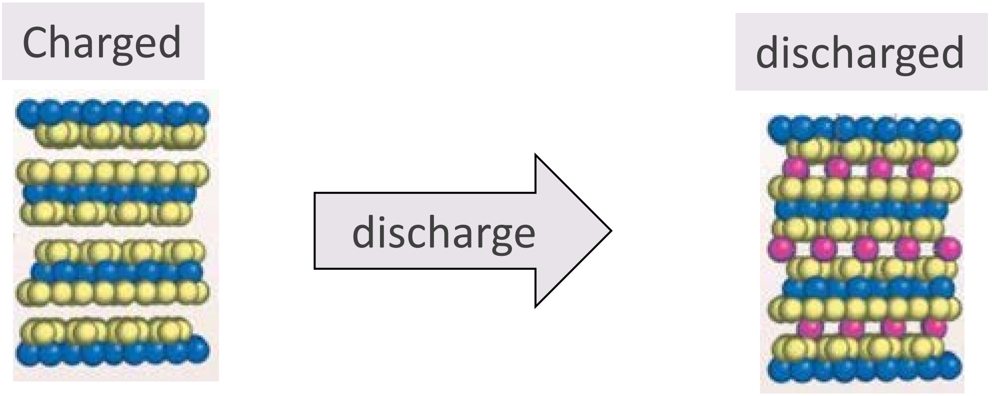
Entropy Change and Open Circuit Voltage (OCV)

Why entropy change (ΔS)

- Entropy change is defined as the index of energy dispersal, or a measure of the molecular randomness or disorder of a system.
- Entropy change is directly related to cell potential as given by the function below:

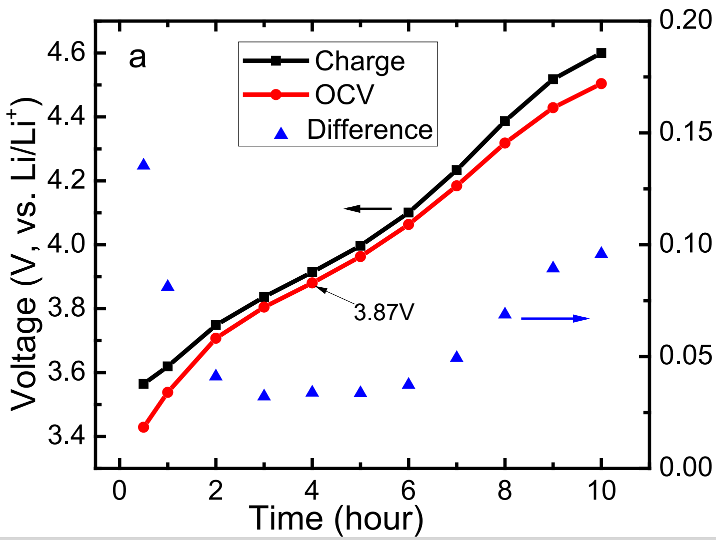
$$\Delta S = nF(dE/dT)_p$$

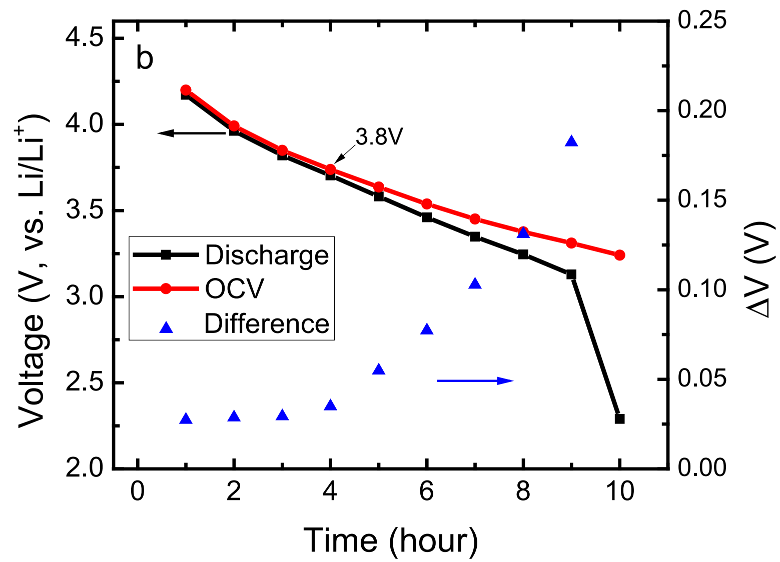
- Entropy change measurement allows us to find out the root cause of voltage fade for LMR-NMC at macrostate level.



$$Li_{1-x}MO_2 \quad + \quad xLi \quad \rightarrow \quad LiMO_2$$

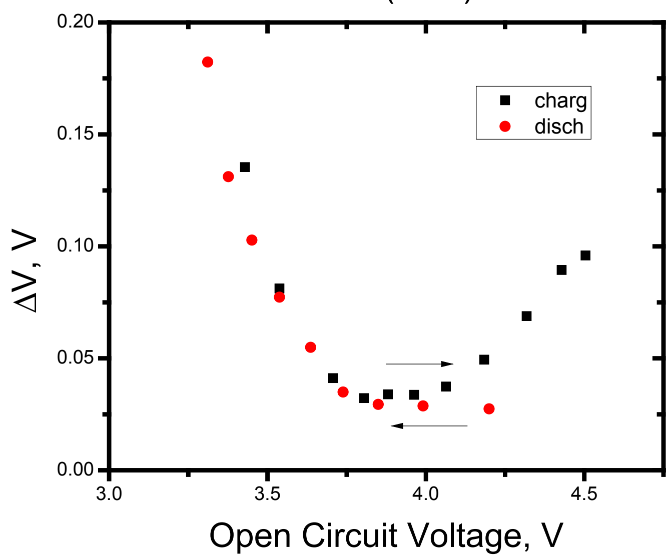
Open Circuit Voltage vs. State of Charge (OCV vs. SOC)





The Li half cell was charged/discharged at C/10 rate. OCV was taken after 3 hours rest.

- Charge: High over-potential at both low and high SOC.
- Discharge: high over-potential at only low SOC.
- Over-potential separation from charge to discharge at high SOC.



OCV vs. Temperature

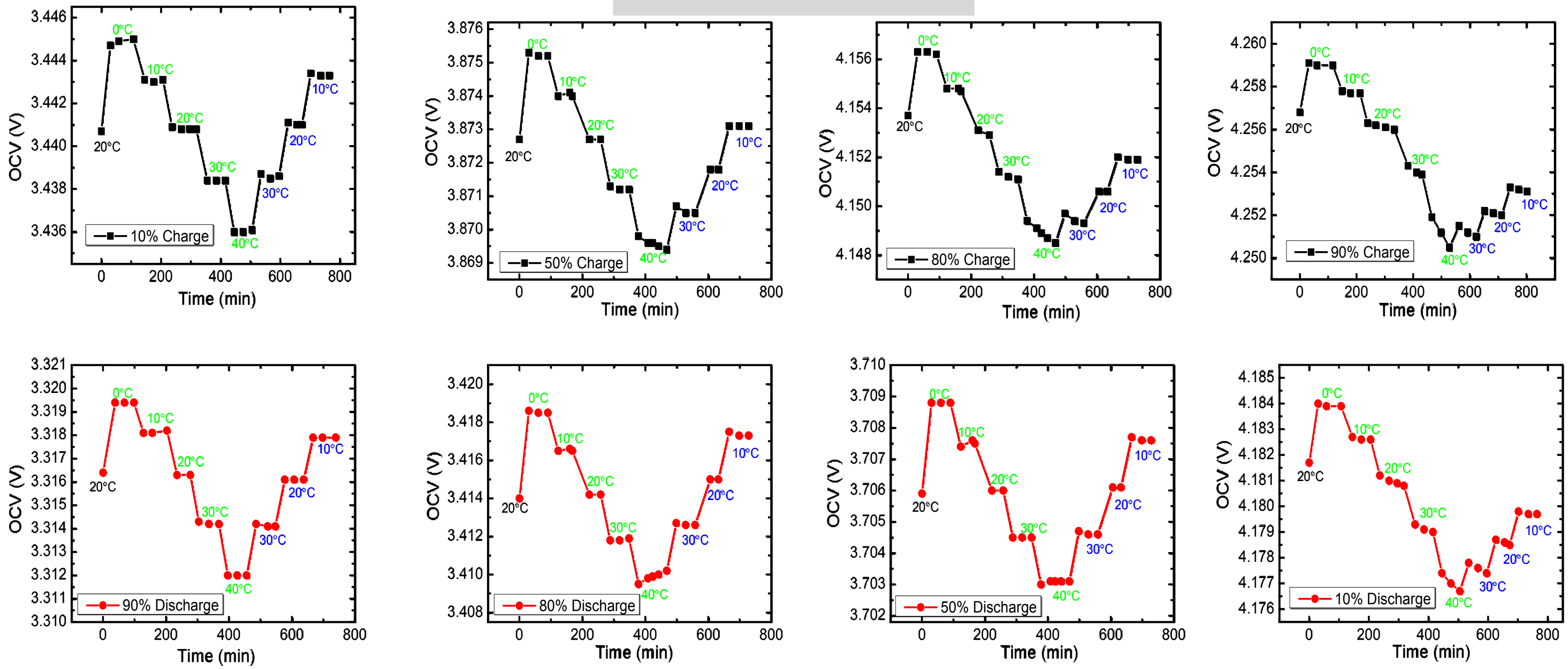
Low SOC

3hr hold at each temperature for each SOC.

High SOC

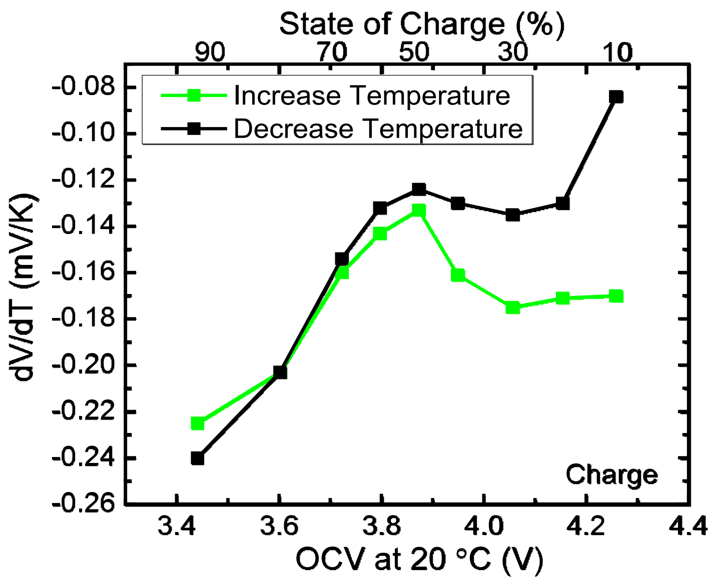
charge

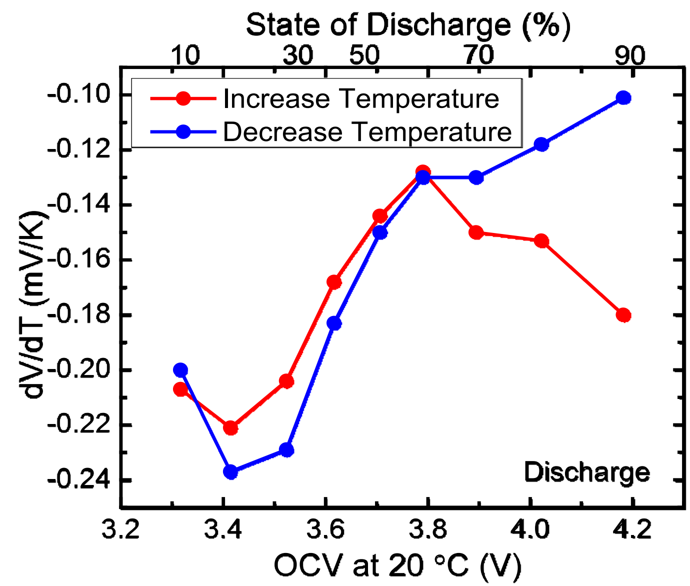
discharge



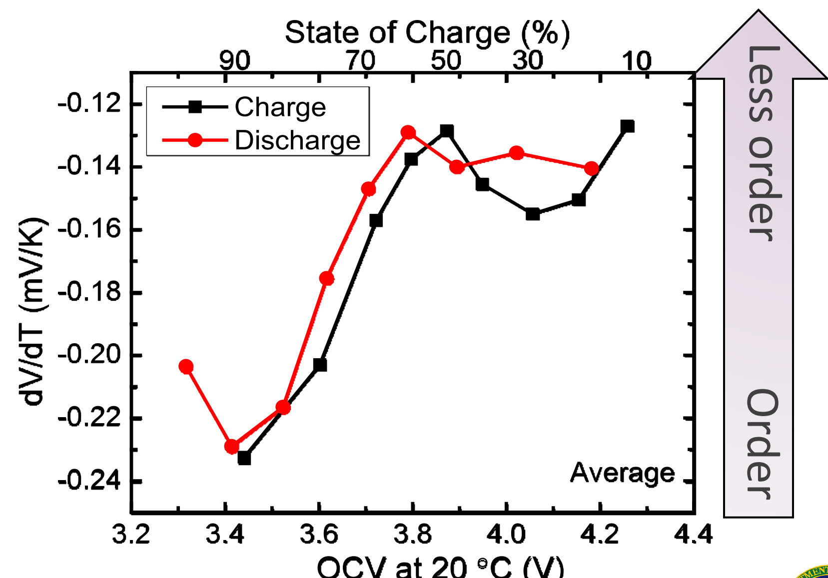
- Temperature steps:
  - 0°C -> 10°C -> 20°C -> 30°C -> 40°C -> 30°C -> 20°C -> 10°C.
- At low SOC, OCV is stable at all temperatures.
- At high SOC, OCV **isn't** stable at elevated temperatures.

Entropy Change at Various SOC

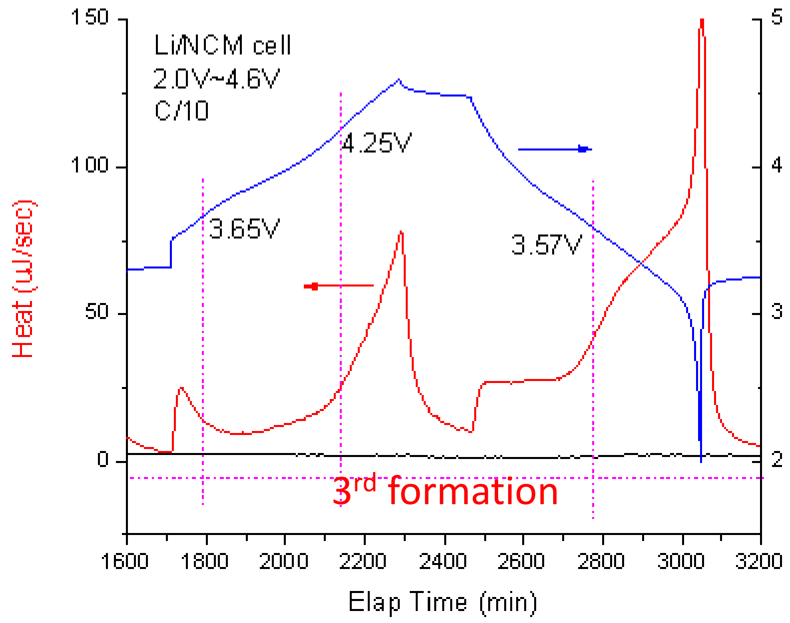


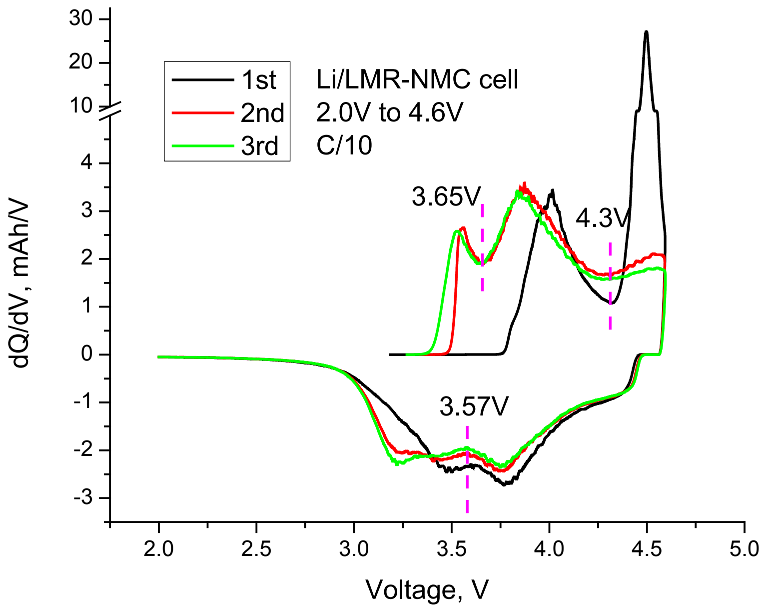


- LMR-NMC becomes less ordered at delithiated state.
- Overlapped entropy change, especially at lower SOC, indicates reversible chemical process during charge and discharge.



Isothermal Micro Calorimetry (IMC) Study on LMR-NMC





- Heat flow during charge/discharge consists of joule heat and entropy heat.
- The heat flow characteristics reflect the structure changes of the electrode material.
- During charge, three heat flow regions are apparent at low, middle, and high SOC. More heat is released at both low and high SOC.
- During discharge, two heat regions were observed at high and low SOC.

Future Plan

- The entropy change of the LMR-NMC electrode after formation cycles was measured at various state of charge. We will continue to investigate the entropy change of the LMR-NMC during the voltage fade process.
- The Isothermal micro calorimetry investigation of LMR-NMC will be continued.
- Lithium ion diffusion at various state of charge (SOC) will be studied using electrochemical impedance spectroscopy.
- The entropy change investigation, together with formation effect on LMR-NMC, suggested an order/disorder change of LMR-NMC during charge and discharge. The detailed phase transition mechanism is being studied with structural study under the Voltage Fade project.

Summary

- The formation effect on voltage fade of LMR-NMC was systematically investigated. The results clearly indicate that the voltage fade is affected by both formation and cycling cut-off voltages.
  - After same cut-off voltage formation (4.7V vs. Li/Li^+), the lower the cycling cut-off voltage is, the less voltage fade. No voltage fade observed when 4.3V was used as cycling voltage.
  - With the same cycling cut-off voltage (4.5V vs. Li/Li^+), the higher the formation cut-off voltage, the lower the voltage fade, however, at expense of lower average voltage.
  - We also noticed that the cell capacity was proportional to the cycling voltage, but less affected by the formation voltage. However, increasing the formation voltage increase the capacity obtained at lower reduction potentials.

Summary

- The entropy change after formation was measured during the charge and discharge processes:
  - The entropy change of LMR-NMC increases linearly at lower states of charge, but, relatively flat at higher states of charge.
  - The distinct deference in these two regions suggests a different configuration of the LMR-NMC at low and high states of charge.
  - At higher states of charge, the voltage is not stable at elevated temperature.
- Heat flow of LMR-NMC was measured using isothermal micro calorimeter during charge and discharge.
  - Different heat flow feature during charge and discharge suggest an irreversible process.

Acknowledgments

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