Characterization Studies of Li_2MnO_3-$LiMO_2$ (M=Mn, Co, Ni) Cathodes

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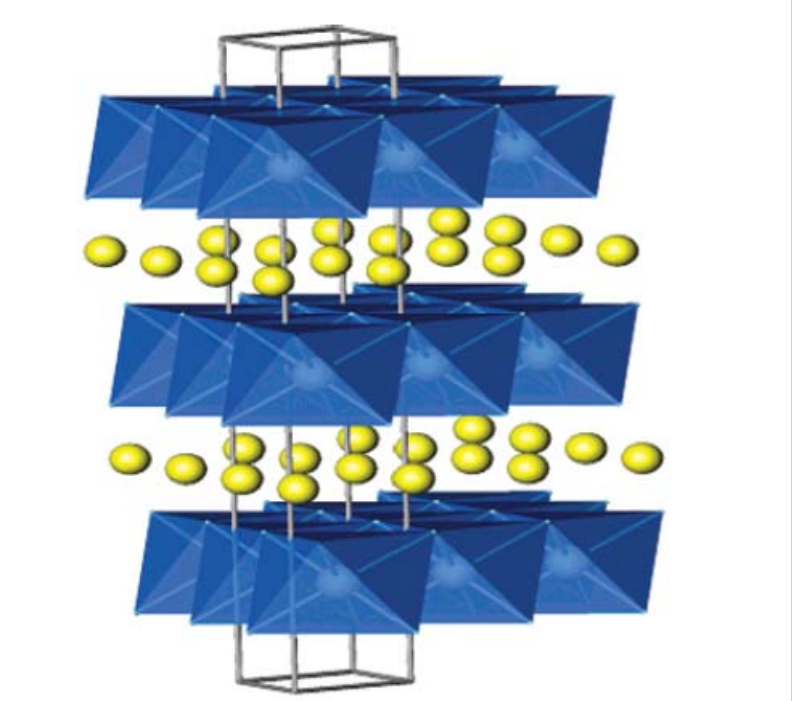
Space-Rated Li-Ion Batteries for NASA's ETDP

- Specific Aims/objectives (JPL):
  - To develop advanced components and materials, i.e., electrolytes, electrodes and cell components, for improving the performance and safety
    - Develop cathodes with high specific energy (1000 Wh/kg, i.e., high specific capacity and/or high voltage), with good to moderate cycle life and improved thermal stability
    - Develop electrolytes with wide operating temperature range and reduced flammability.
    - Develop stable electrolytes against high voltage cathodes.
  - Develop a safe rechargeable lithium chemistry with significantly high specific energy in excess of 250 Wh/kg at cell level
  - Assess the performance of High Specific Energy Lithium Rechargeable cells

High Specific Energy Cathodes Materials

- **Strategy**
  - **Layered oxide compositions of solid solutions of Li_2MnO_3 and $LiMO_2$ (M = Mn_x, Ni_y, Co_z) exhibit capacities as high as 250 mAh/g on cycling from 4.8V – 2V.**
- **Problems**
  - **Huge irreversible capacity loss**
    - **40 − 100 mAh/g in the first cycle,**
  - **Low power densities**
    - **Capacity decreases from ~ 250 mAh/g atC/20 to 210 mAh/g atC/5**
  - **Poor low temperature performance**
- **Prepared by sol-gel synthesis from metal acetates or co-precipitation of metal hydroxides**
- **In some cases, incorporate coating on cathode particles post-firing**
  - **Includes metal oxides, phosphates, fluorides**

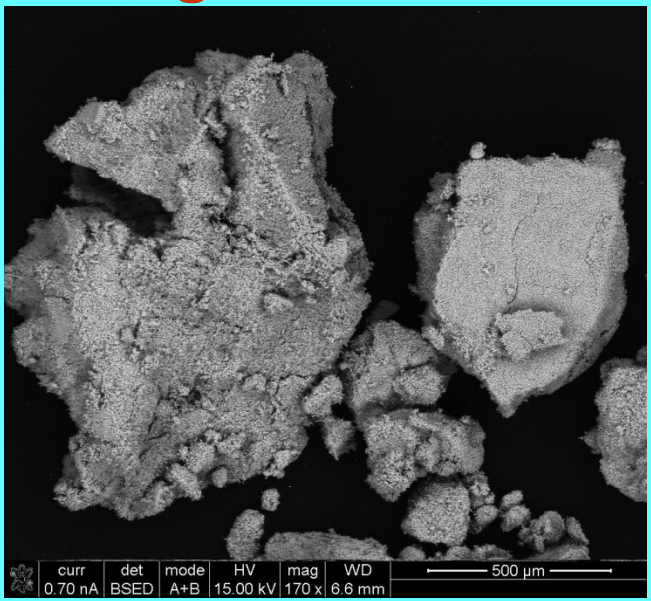


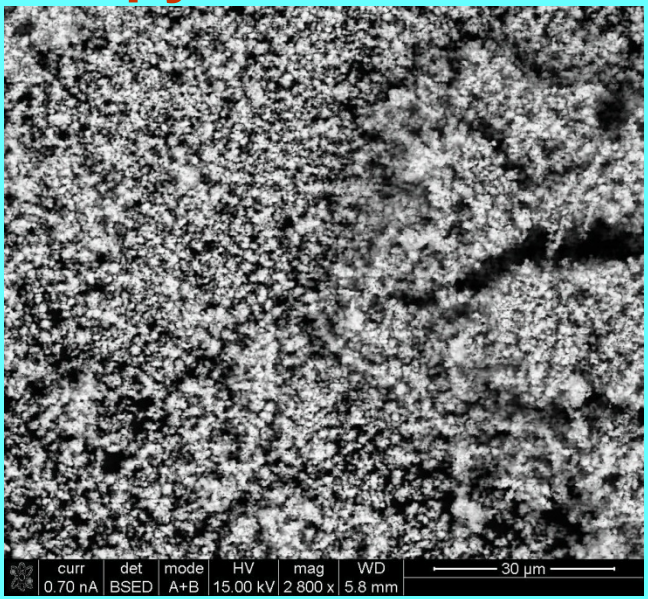
- Layered structure of $LiCoO_2$, $LiNiO_2$, and $LiNi_yMn_yCo_{1-2y}O_2$, showing the Li^+ between the transition-metal oxide sheets. The actual stacking of the metal oxide sheets depends on the transition metal and the anion.

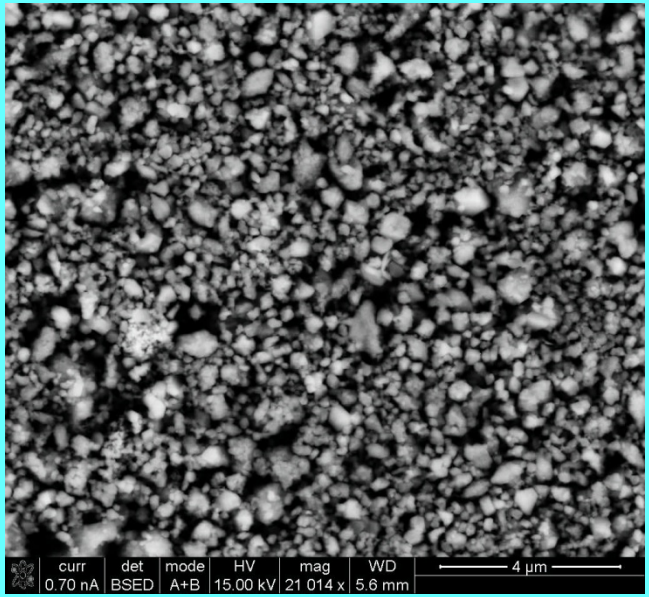
Scanning Electron Microscopy

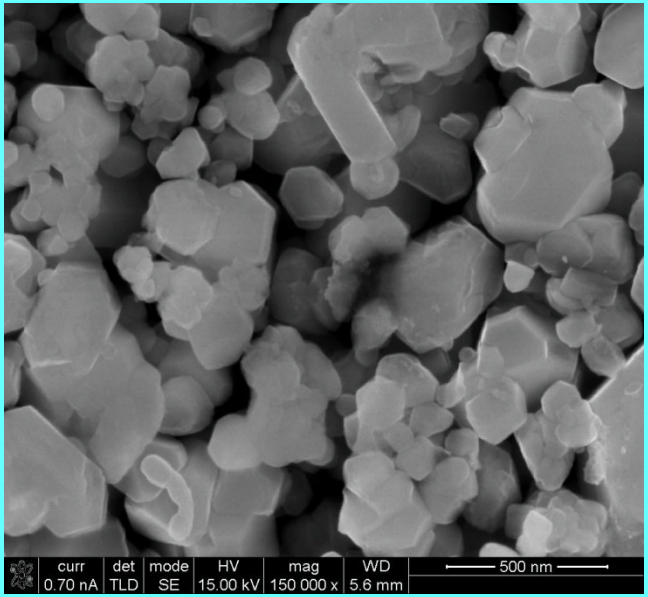
SEM of as-prepared cathode particles:

- Macroscopic particles observed on the order of 10- 500 μm with very wide particle size distribution
- Large particles are likely poorly adhered and may be broken apart with simple mechanical mixing based on quantitative particle size measurements
- Macroscopic particles consist of sub-particles on the order of 100 – 500 nm









Particle Size Distribution Measurements

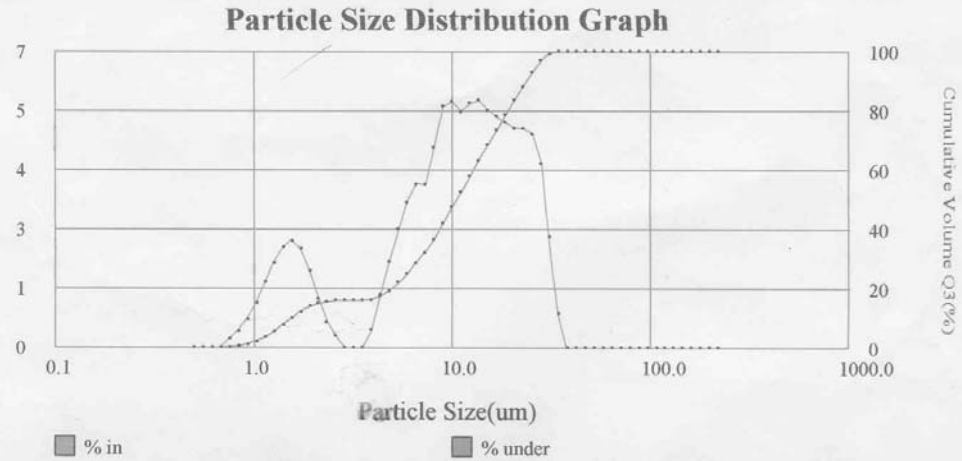
Particle Size Distribution:
After air milling cathode powders, observe generally bi-modal distribution centered at ca. 1.2 μm and 12 μm

Record Num: 8
Sample Provider: Howard Industries
Dispersant Name: air

Sample Name: NEI D3 sample1 070909
Operator: D Powell
Notes:

Record Number: 8 | MeasDate: 7/9/2009 | MeasTime: 10:10:47 AM

x10: 1.55 um | x50: 10.51 um | x90: 23.71 um

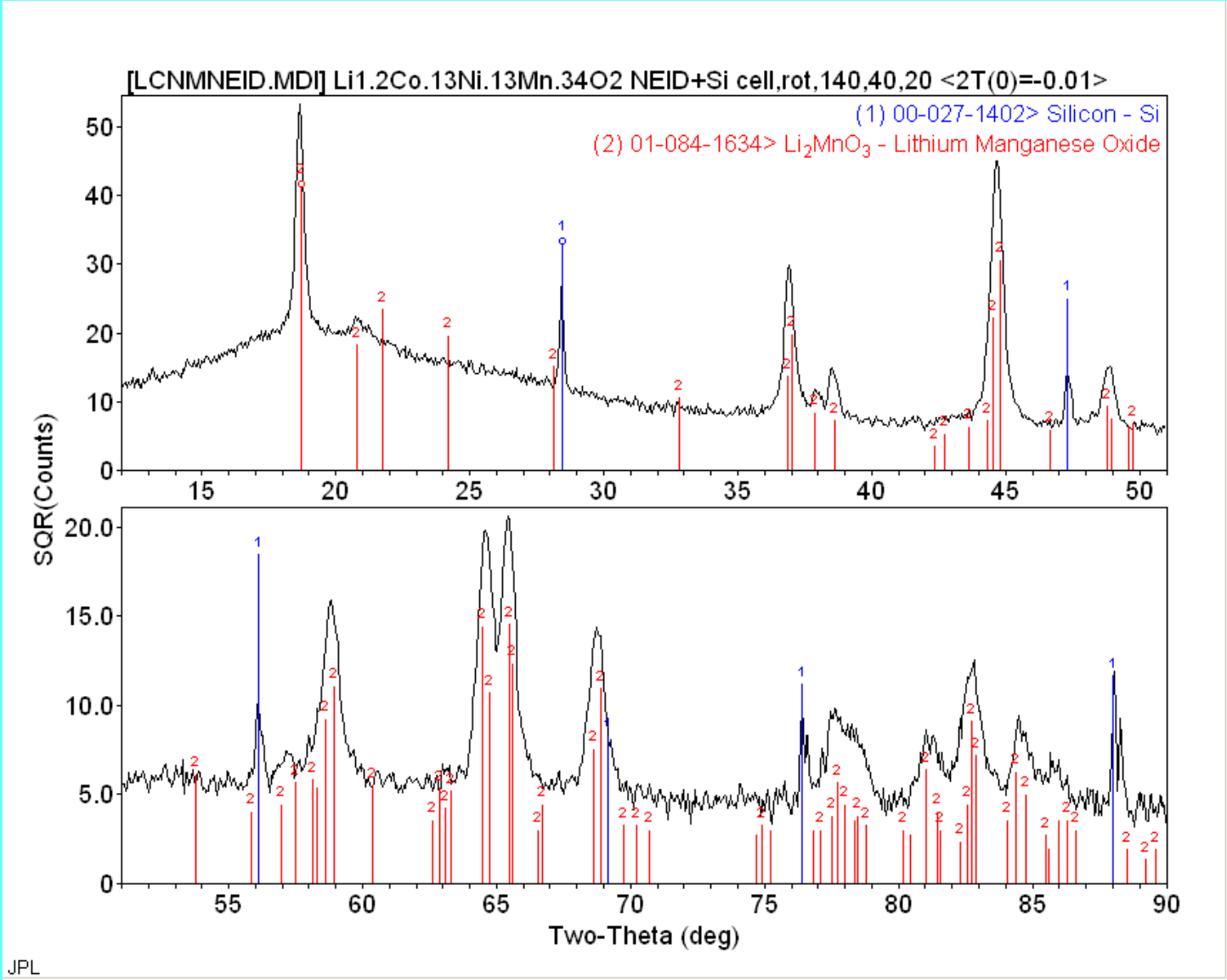


Size(um)	% in	% under	Size(um)	% in	% under	Size(um)	% in	% under	Size(um)	% in	% under
0.50	0.00	0.00	2.35	0.56	15.52	11.04	5.18	52.46	51.90	0.00	100.00
0.55	0.00	0.00	2.61	0.26	15.78	12.24	5.36	57.82	57.54	0.00	100.00
0.61	0.00	0.00	2.89	0.00	15.78	13.57	5.42	63.24	63.79	0.00	100.00
0.68	0.00	0.00	3.20	0.00	15.78	15.05	5.21	68.45	70.73	0.00	100.00
0.76	0.19	0.19	3.55	0.00	15.78	16.68	5.07	73.52	78.41	0.00	100.00
0.84	0.36	0.55	3.94	0.39	16.17	18.50	4.95	78.47	86.93	0.00	100.00
0.93	0.63	1.18	4.36	1.18	17.35	20.51	4.82	83.29	96.38	0.00	100.00
1.03	0.98	2.16	4.84	1.90	19.25	22.74	4.80	88.09	106.85	0.00	100.00
1.14	1.42	3.58	5.36	2.60	21.85	25.21	4.69	92.78	118.47	0.00	100.00
1.27	1.86	5.44	5.95	3.20	25.05	27.95	4.03	96.82	131.34	0.00	100.00
1.40	2.21	7.66	6.59	3.59	28.64	30.98	2.42	99.24	145.61	0.00	100.00
1.56	2.35	10.01	7.31	3.57	32.20	34.35	0.76	100.00	161.44	0.00	100.00
1.72	2.18	12.18	8.10	4.37	36.58	38.08	0.00	100.00	178.93	0.00	100.00
1.91	1.70	13.88	8.98	5.30	41.88	42.22	0.00	100.00	198.44	0.00	100.00
2.12	1.08	14.96	9.96	5.40	47.28	46.81	0.00	100.00	220.00	0.00	100.00

X-Ray Diffraction Studies

X-Ray diffraction data:

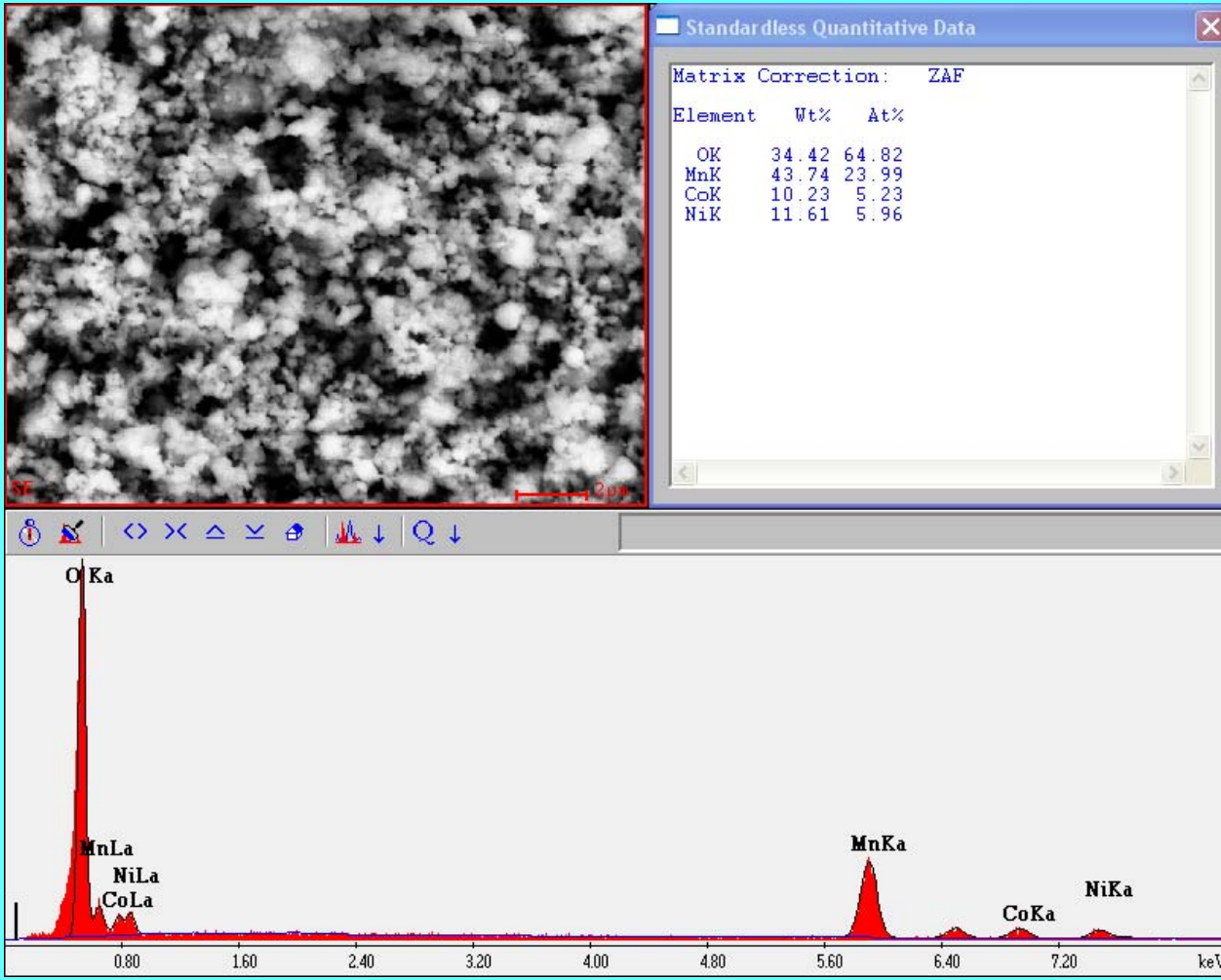
- Well indexed to Li_2MnO_3 lattice (solid solution of Li_2MnO_3 and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$)
- Superlattice peaks associated with cation ordering observed at ca. 21º)



Energy Dispersive Spectroscopy Studies

Energy Dispersive Spectroscopy Data:

•Demonstrates predicted transition metal ratios:
predicted: Mn:Ni:Co = 68:16:16
Measured: Mn:Ni:Co = 68:17:15
•Highly sensitive to scan area: small scan size reveals anisotropic x-ray emission and concomitant skew in composition



Experimental Details

Performance Verification of Cathode Formulations:

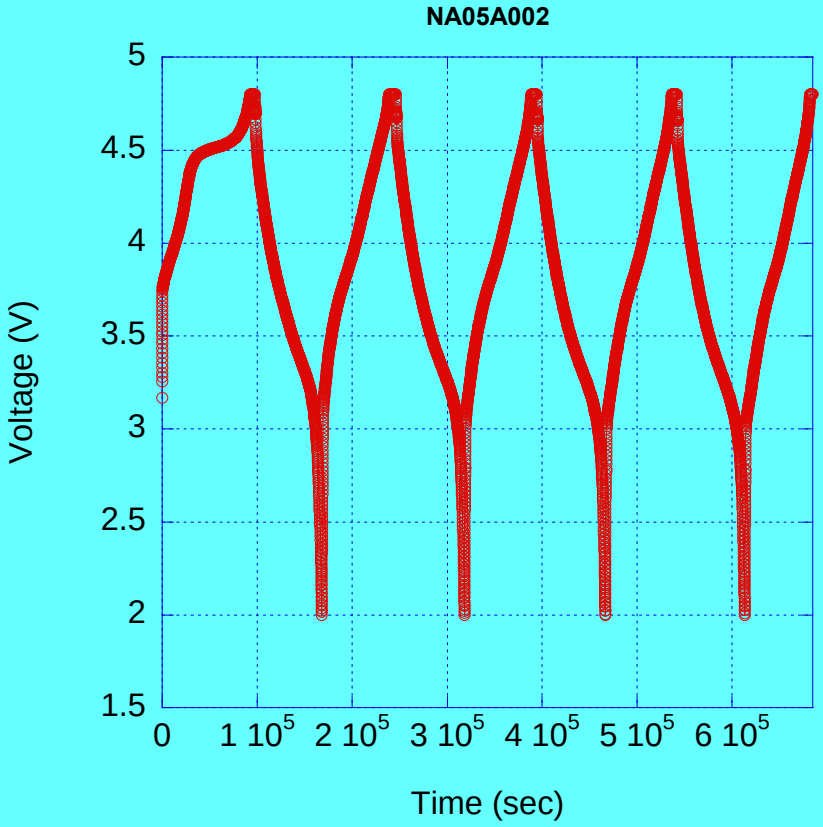
(1) **Results in coin cells**

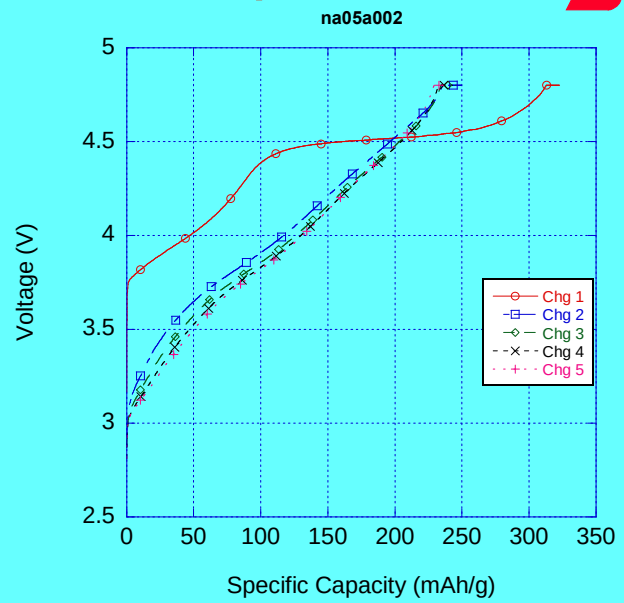
- Size 2032 coin cells (two electrode design)
- Cathode: 80% active, 10% PVDF, 10% C black
- Anode: Lithium foil in excess
- Electrolyte: 1M $LiPF_6$ in 1:1:1 (EC:DEC:DMC)
- Separator: 20 μm Setella

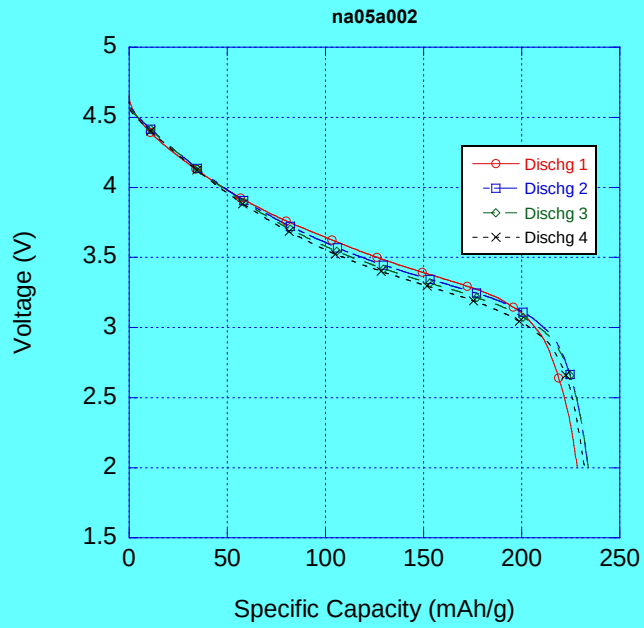
(2) **Results in three electrode cell**

- ~ 400 mAh cell size, jelly roll design
- Lithium metal reference and counter electrode
- Cathode: 80% active, 10% PVDF, 10% C black
- Electrolyte: 1M $LiPF_6$ in 1:1:1 (EC:DEC:DMC)
- Separator: 20 μm Setella

Coin Cell Results (Formation)

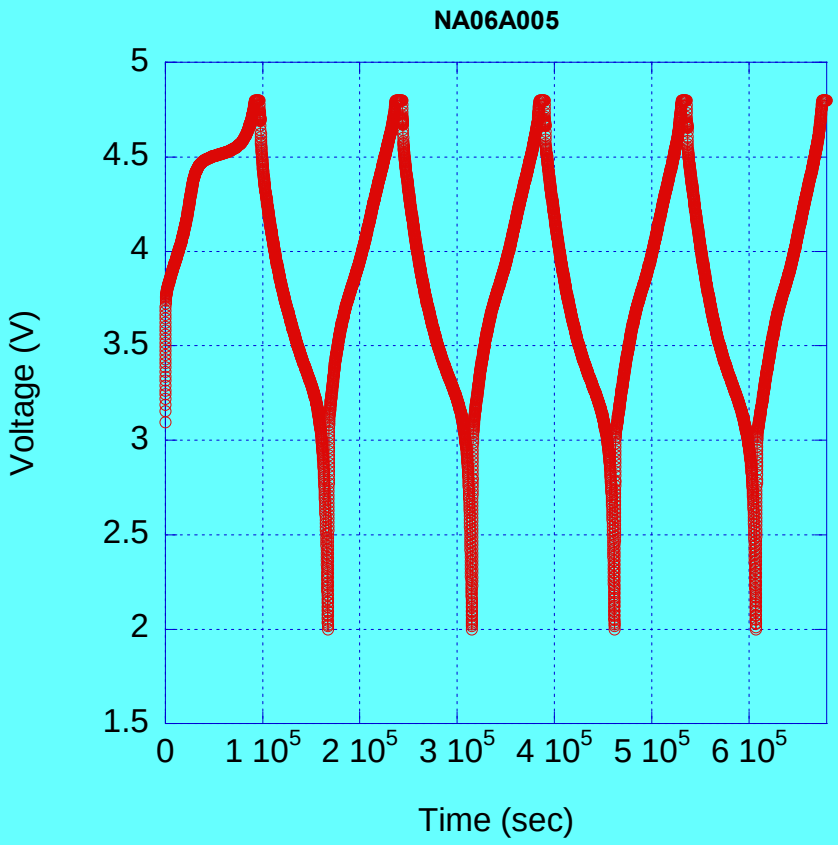


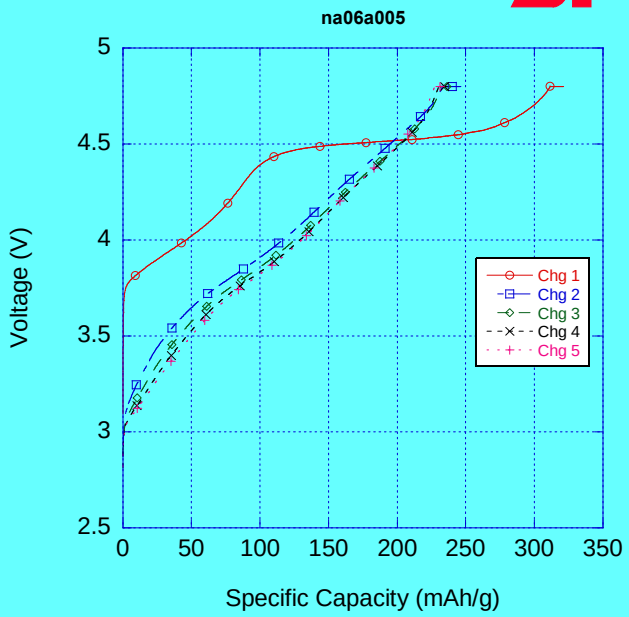


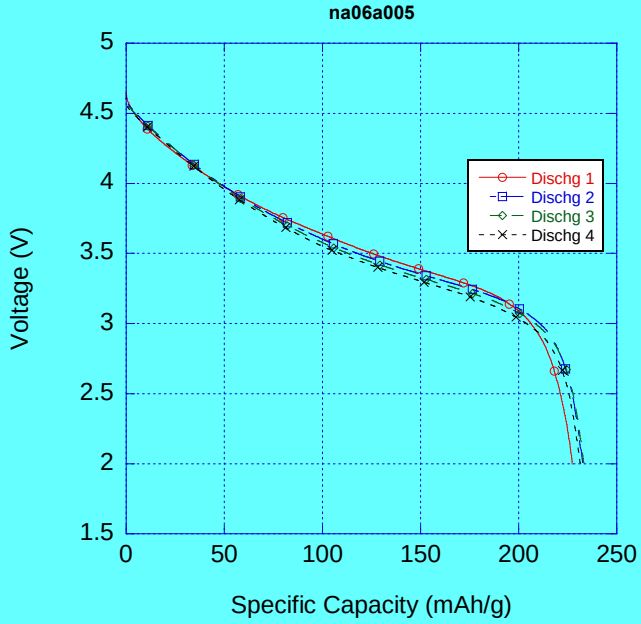


Cycle	Sp. Chg Cap. (mAh/g)	Sp. Dischg Cap. (mAh/g)	Efficiency %
1	323	228	70.6
2	250	234	93.6
3	245	234	95.5
4	243	232	95.5

Coin Cell Results (Formation)

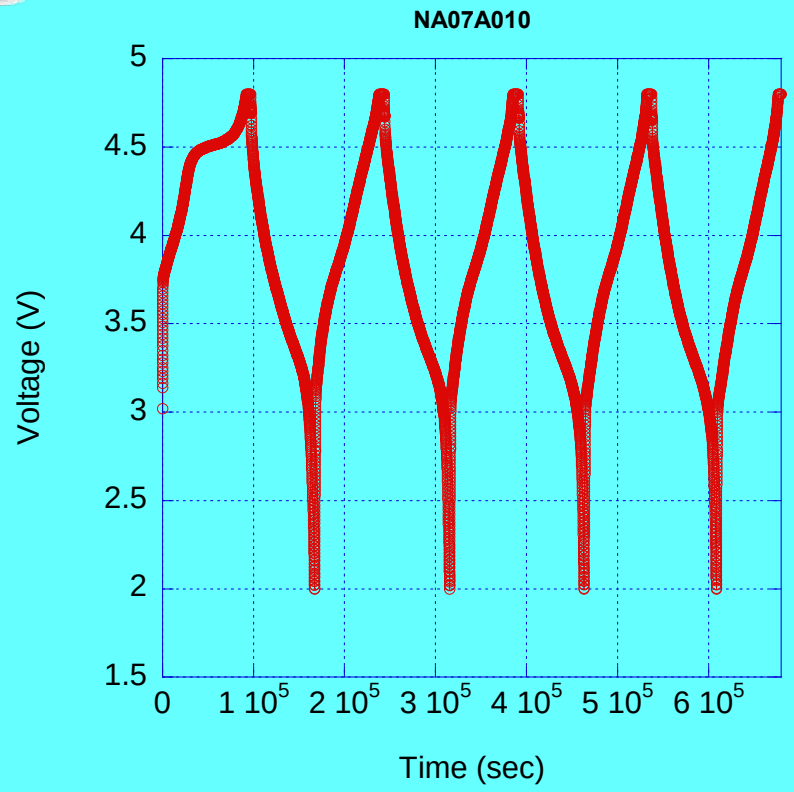


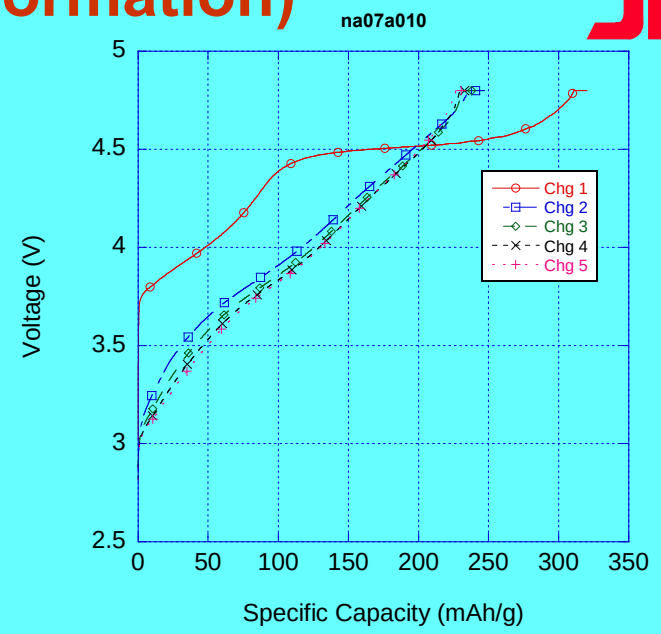


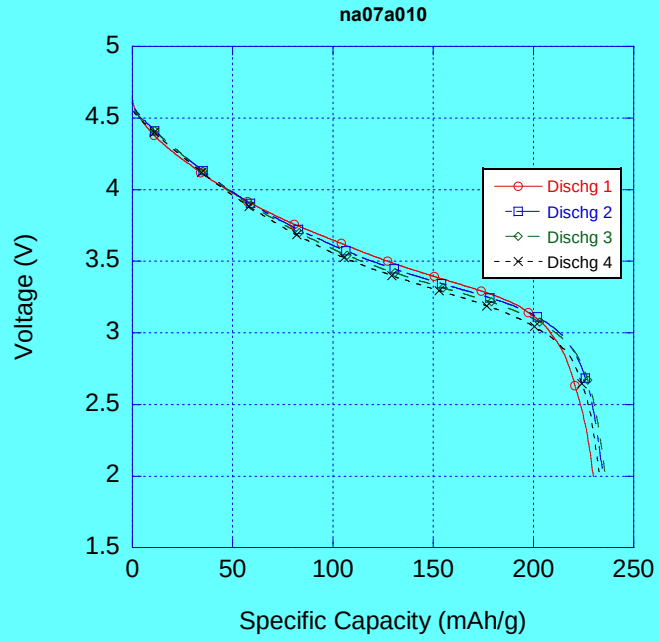


Cycle	Sp. Chg Cap. (mAh/g)	Sp. Dischg Cap. (mAh/g)	Efficiency %
1	321	227	70.7
2	246	233	94.7
3	243	233	95.9
4	240	231	96.3

Coin Cell Results (Formation)

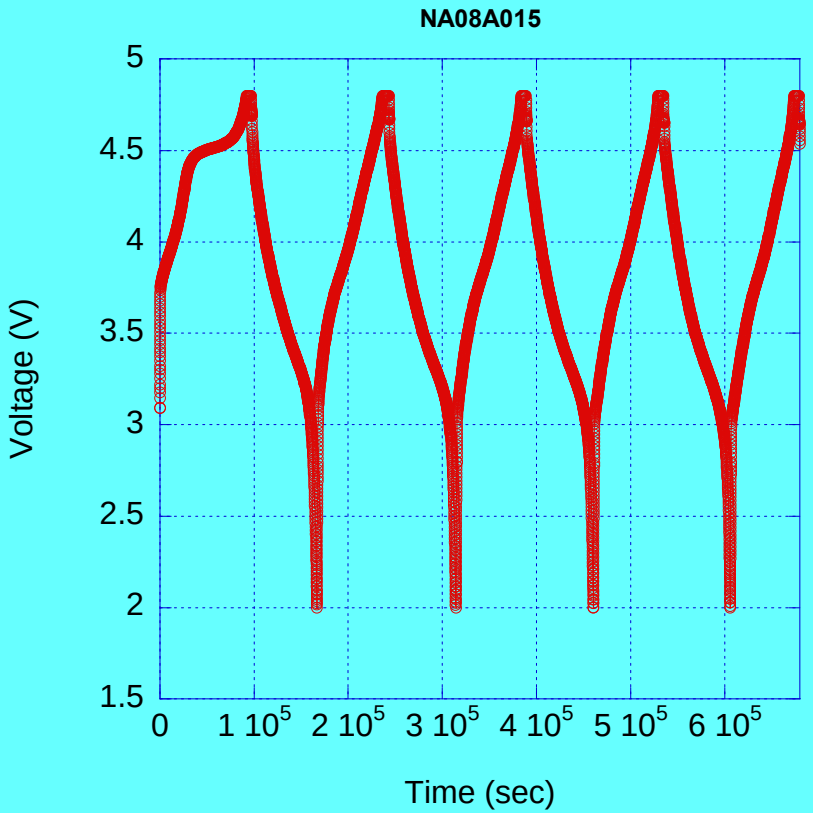


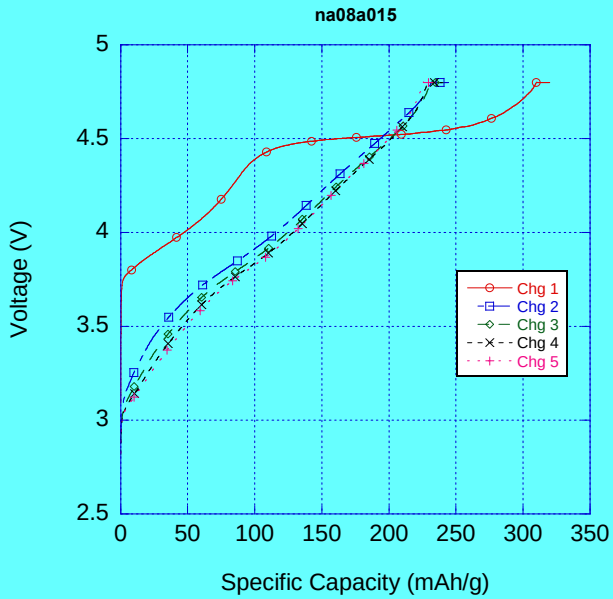


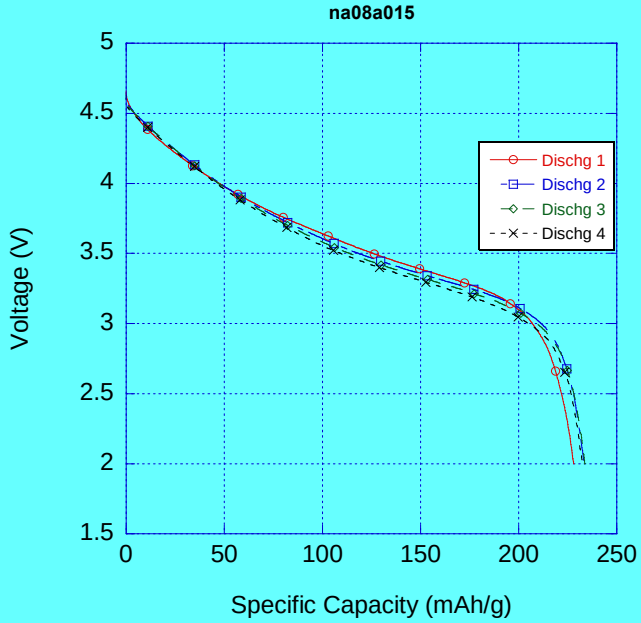


Cycle	Sp. Chg Cap. (mAh/g)	Sp. Dischg Cap. (mAh/g)	Efficiency %
1	320	230	71.9
2	247	235	95.1
3	244	236	96.7
4	240	233	97.1

Coin Cell Results (Formation)

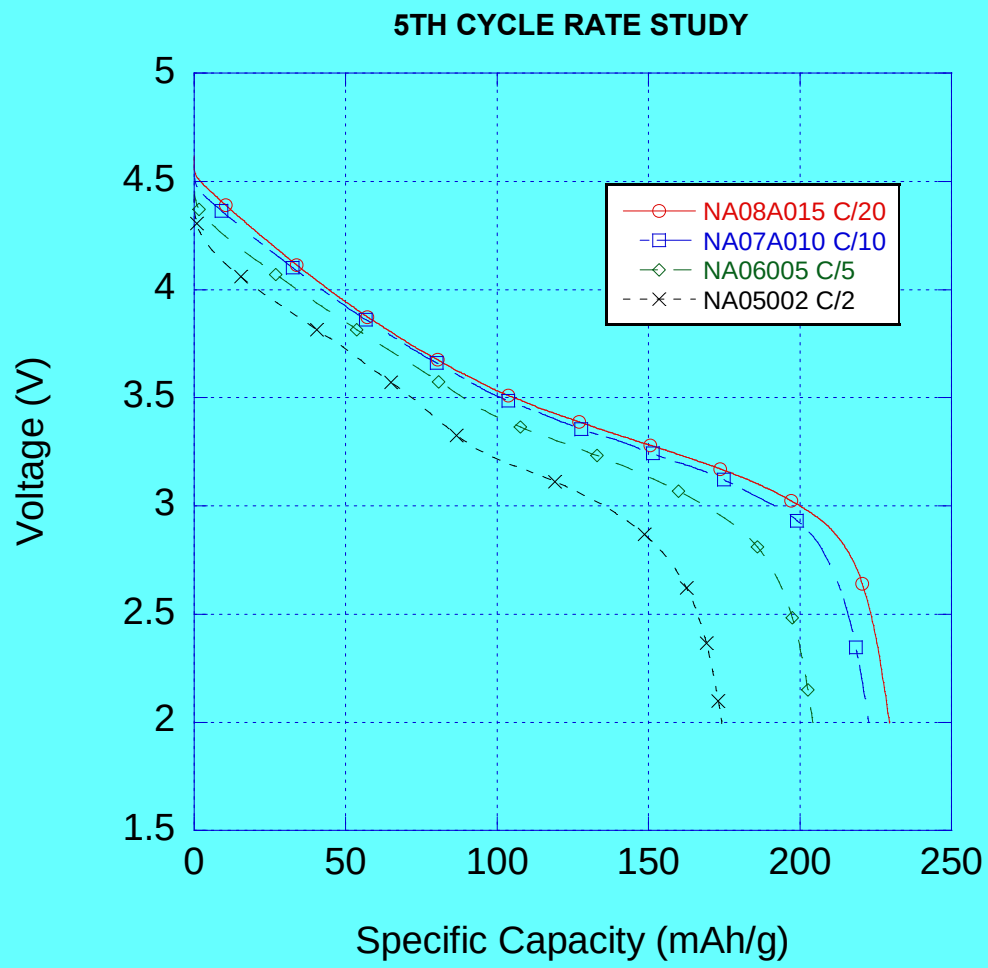






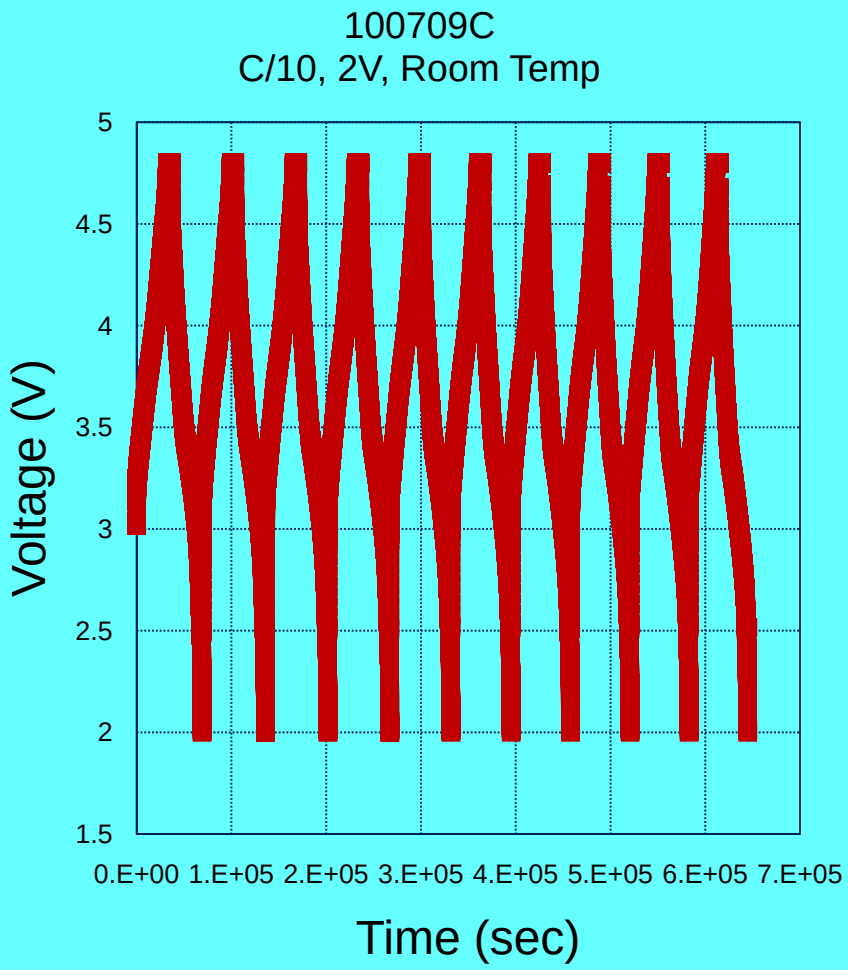
Cycle	Sp. Chg Cap. (mAh/g)	Sp. Dischg Cap. (mAh/g)	Efficiency %
1	320	228	71.3
2	244	233	95.5
3	241	234	97.1
4	240	232	96.7

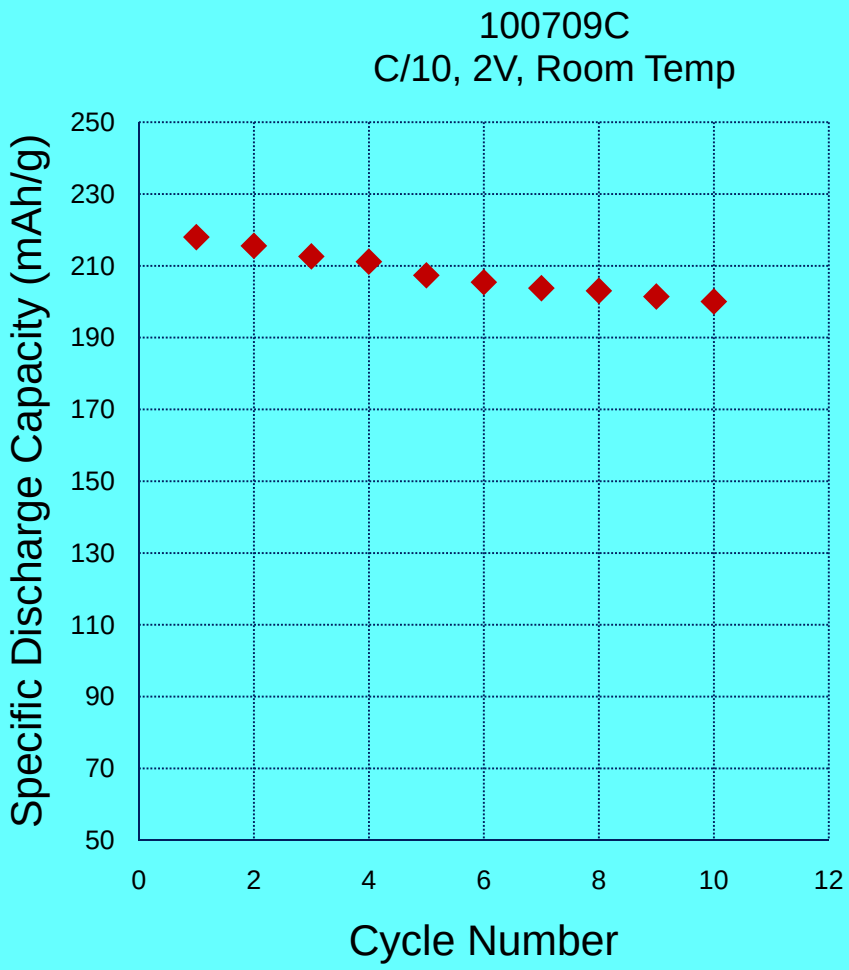
Coin Cell Results (Rate Study)



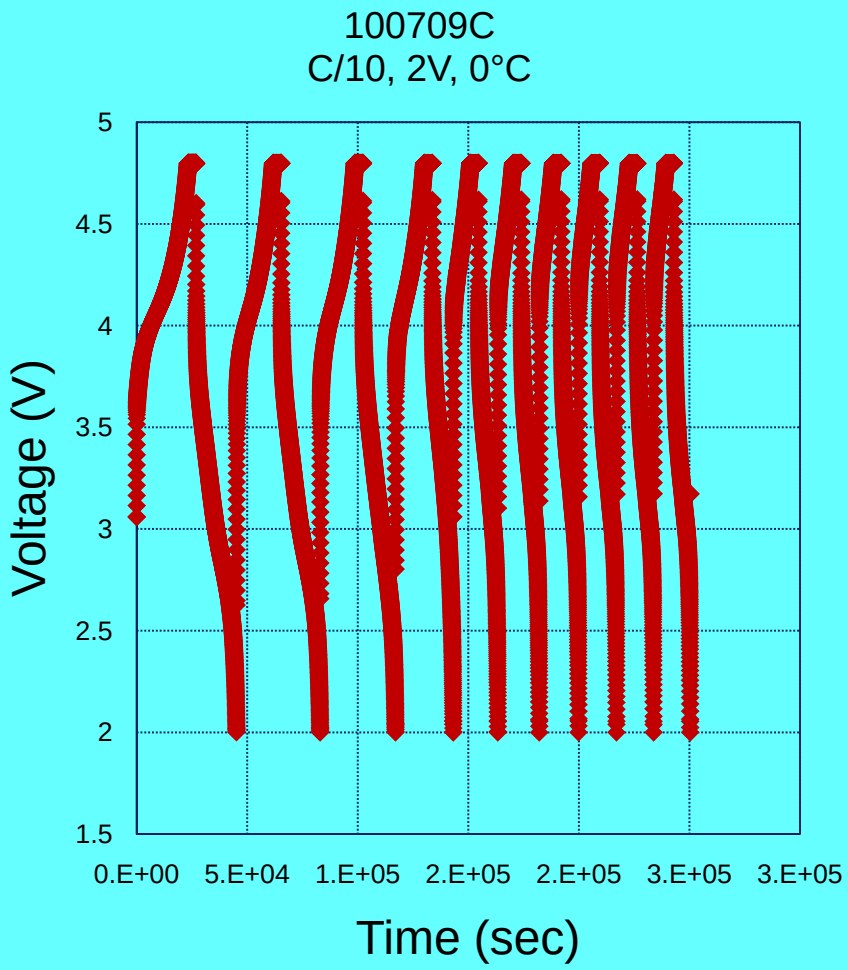
Cell	Rate	Sp. Dischg Cap. (2V) (mAh/g)	Sp. Dischg Cap. (3V) (mAh/g)
NA08015	**C/20**	**230**	**200.0**
NA06005	**C/10**	**223**	**192.0**
NA07010	**C/5**	**204**	**168.0**
NA05002	**C/2**	**174**	**134.0**

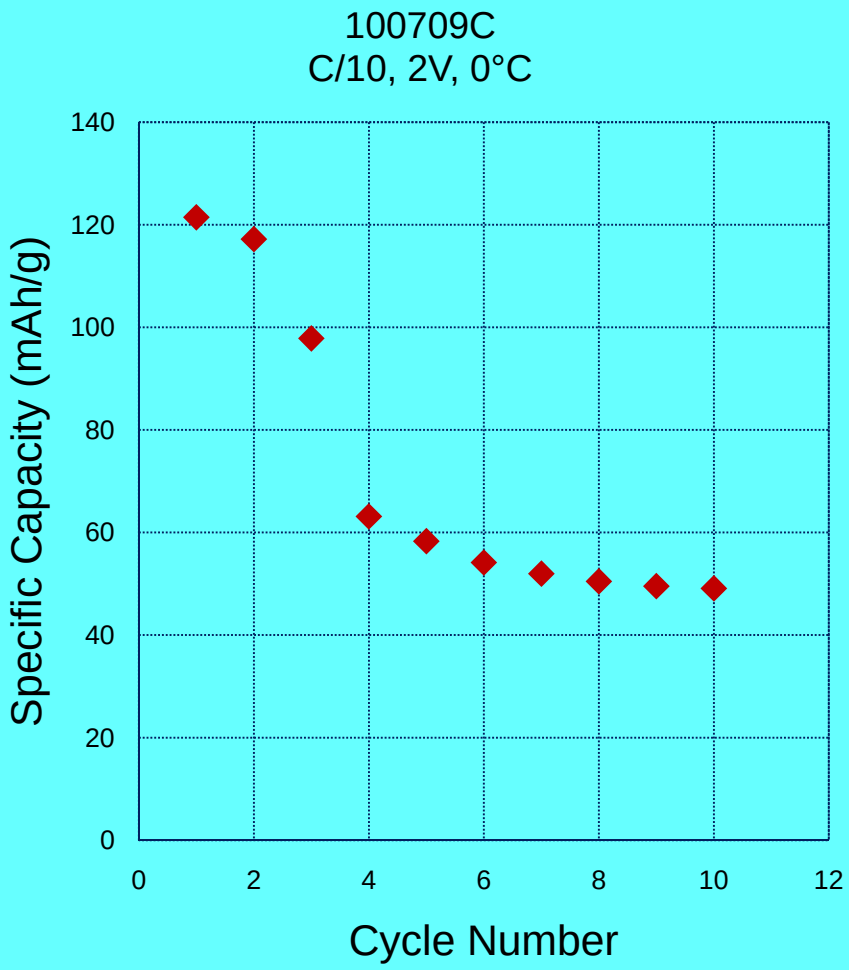
Coin Cell Results (Room Temperature, C/10)



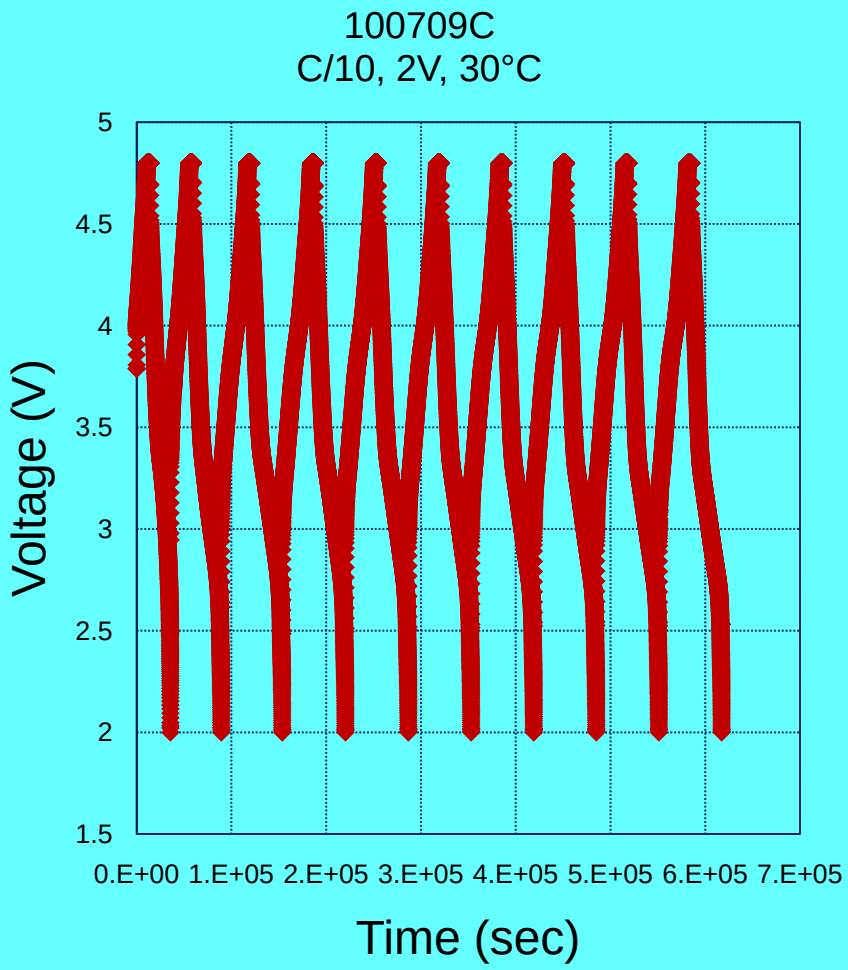


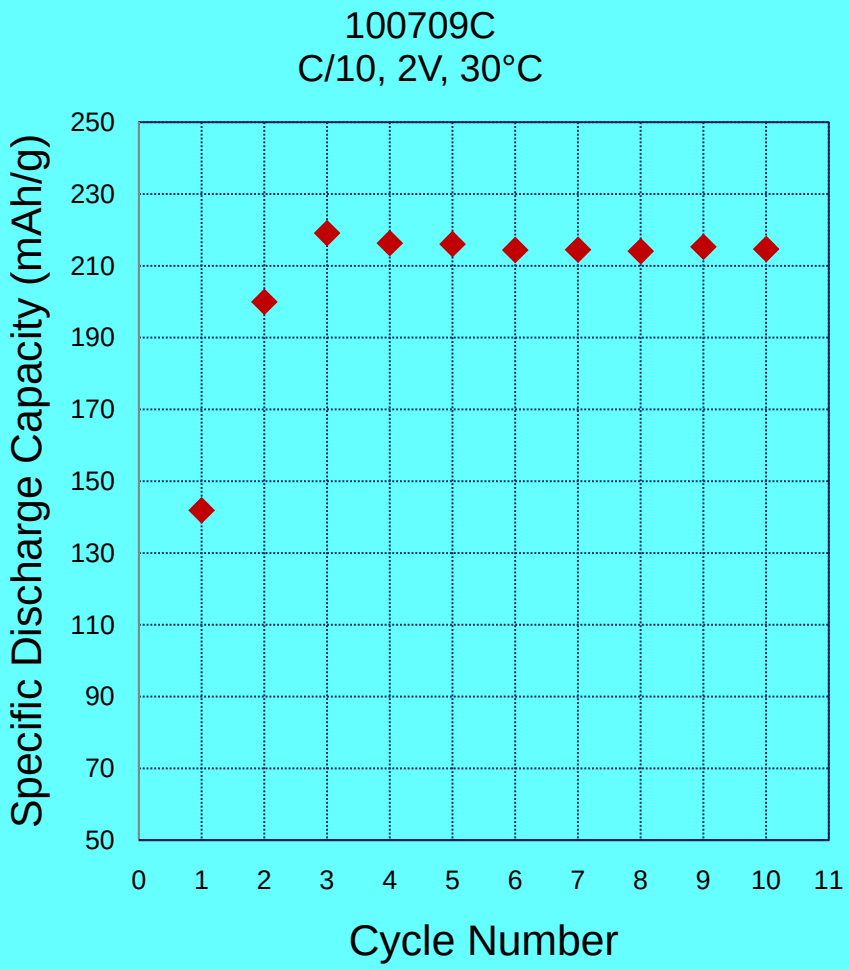
Coin Cell Results (KPP Conditions: 0°C, C/10)



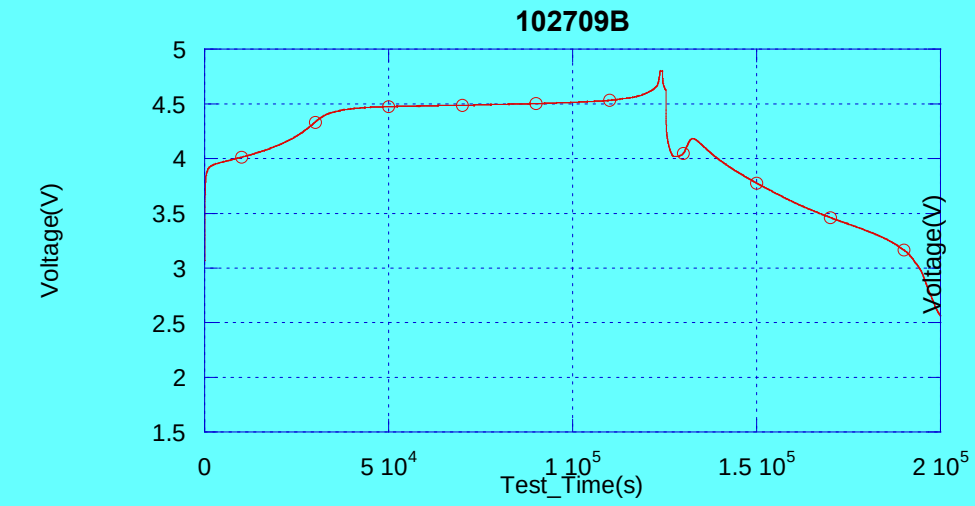


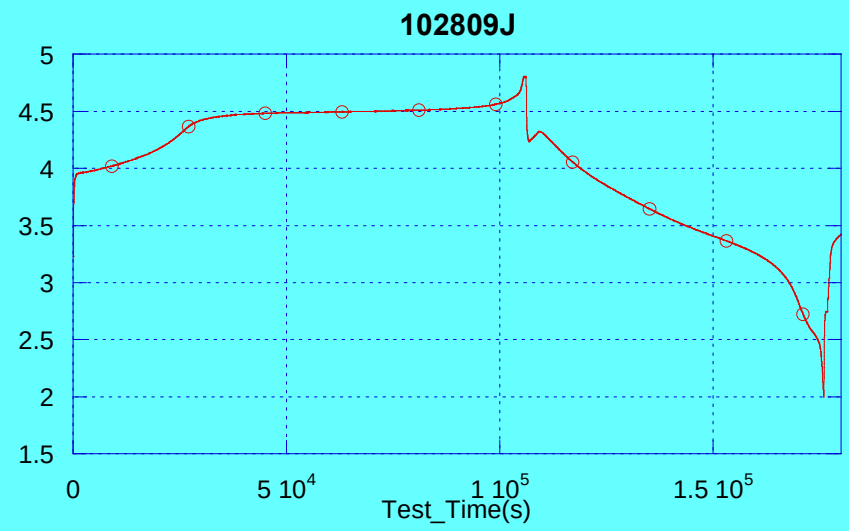
Coin Cell Results (30°C, C/10)

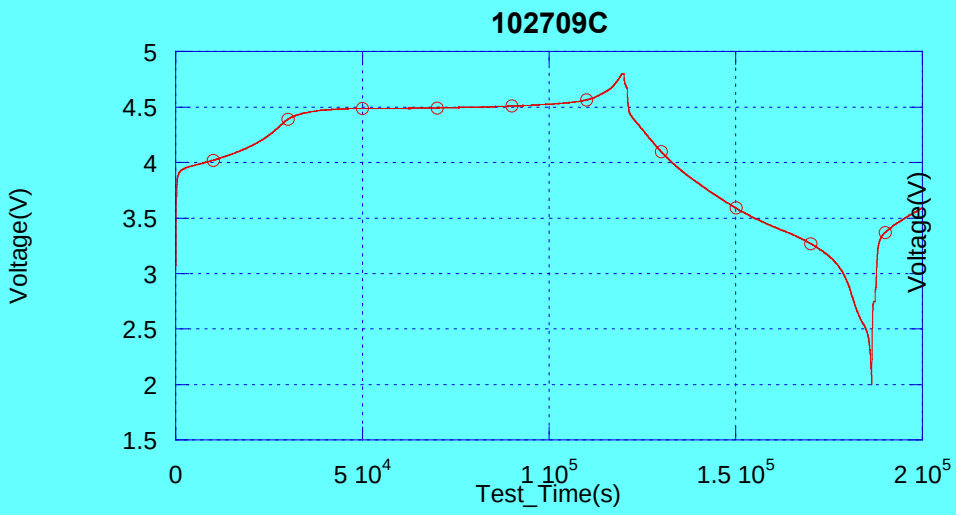


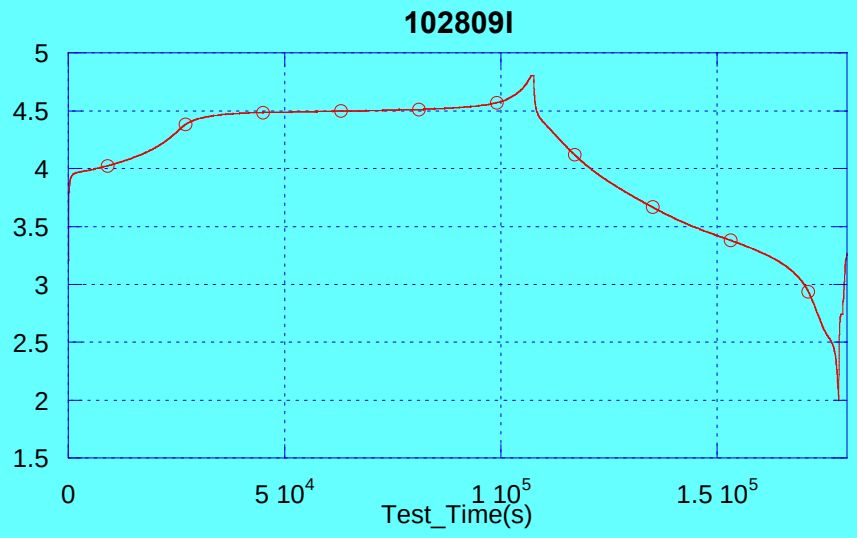


Formation Cycling: Evidence for voltage delay?

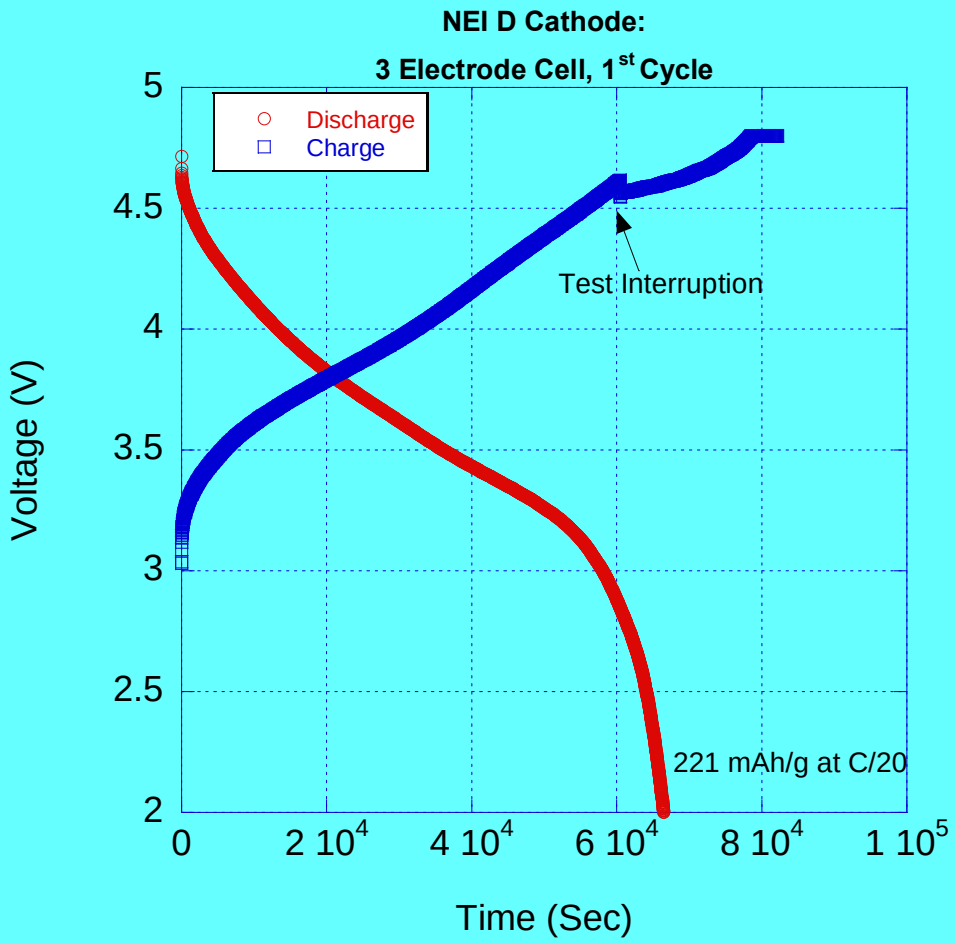




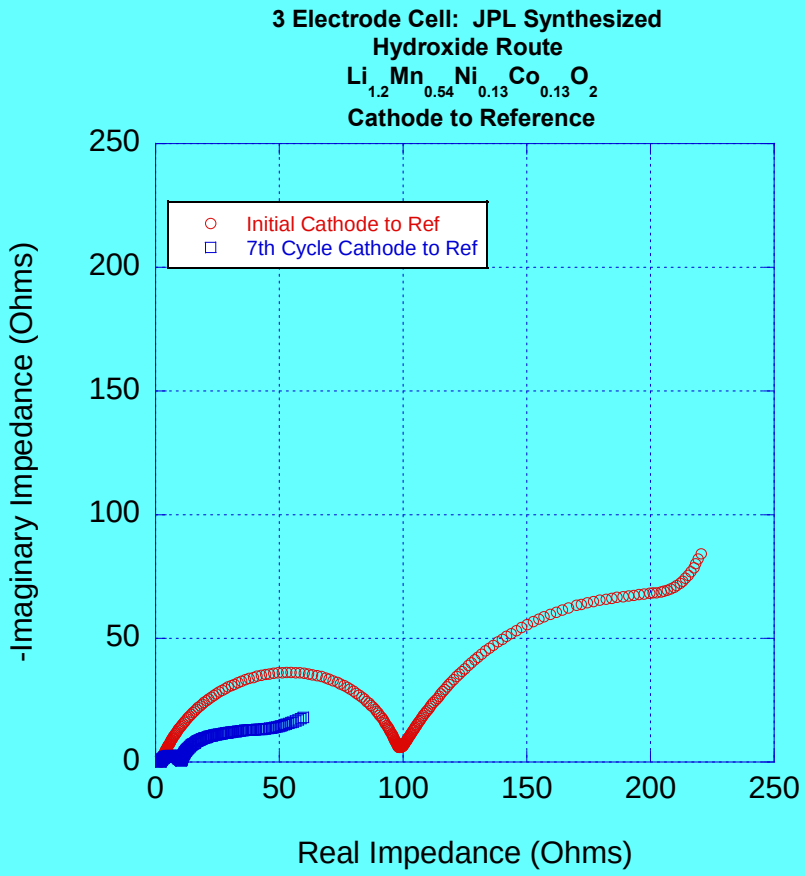


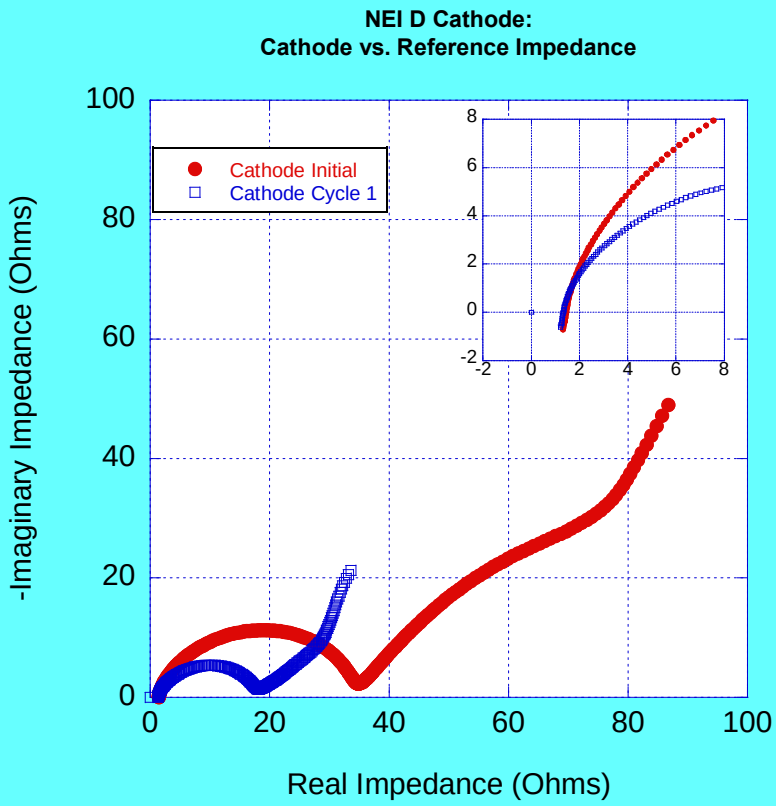


3 Electrode Cells (Formation)

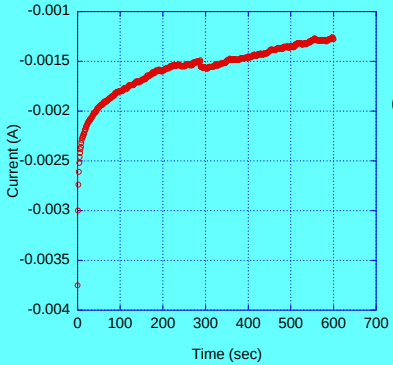


3 Electrode Cells (Electrochemical Impedance Spectroscopy)

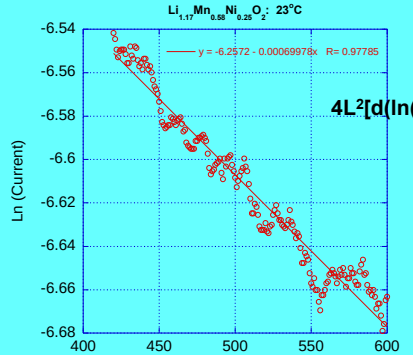




3 Electrode Cells (Potentiostatic Intermittent Titration Technique)

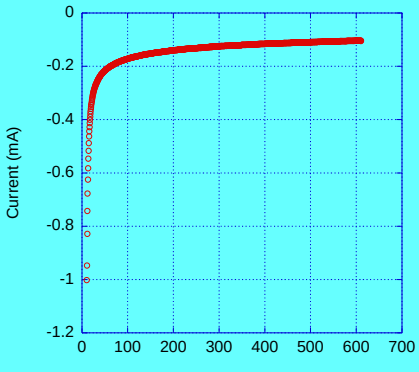


$d(\ln(I))/dT|_{t=420\text{-}600s}$ →

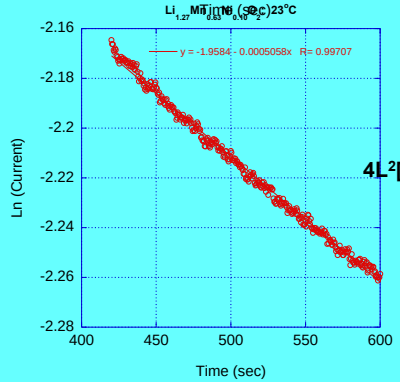


$4L^2[d(\ln(I))/dT|_{t=420\text{-}600s}]/\pi$ →

Baseline $Li(Li_{0.17}Mn_{0.58}Ni_{0.25})O_2$ chemical diffusion coefficient at 23°C = 2.2×10^{-12} cm^2/s

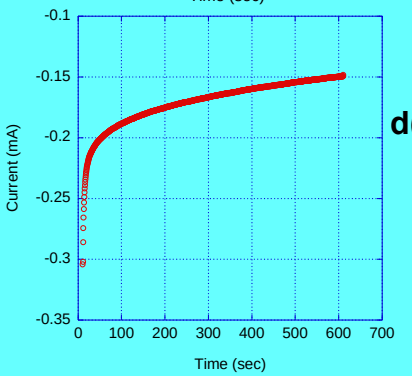


$d(\ln(I))/dT|_{t=420\text{-}600s}$ →

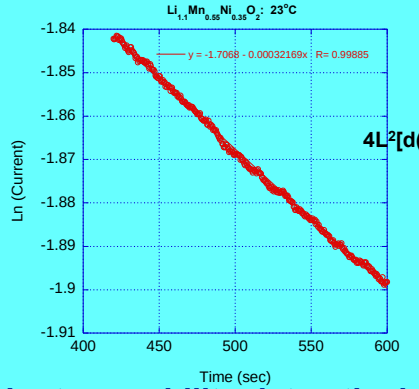


$4L^2[d(\ln(I))/dT|_{t=420\text{-}600s}]/\pi$ →

Li rich $Li(Li_{0.27}Mn_{0.63}Ni_{0.10})O_2$ chemical diffusion coefficient at 23°C = 1.6×10^{-12} cm^2/s



$d(\ln(I))/dT|_{t=420\text{-}600s}$ →



$4L^2[d(\ln(I))/dT|_{t=420\text{-}600s}]/\pi$ →

Li poor $Li(Li_{0.10}Mn_{0.55}Ni_{0.35})O_2$ chemical diffusion coefficient at 23°C = 1.0×10^{-12} cm^2/s

West et al., ECS Fall Meeting 2007

PITT data is consistent with previous EIS and rate capability data: the highest impedance cathode material is the Li poor composition, and the highest rate capability cathode material is the baseline composition. The diffusion coefficient values fall about an order of magnitude lower than $LiCoO_2$.

Summary

- Candidate cathode materials for high specific energy batteries are evaluated by:
  - Physical techniques including:
    - SEM
    - XRD
    - EDS
  - Electrochemical techniques including:
    - Formation cycling/cycling as a function of temperature
    - Rate studies
    - EIS
    - PITT
- Coin cell studies offer high degree of reproducibility cell to cell
- Several candidate materials operate at near 230 mAh/g under formation cycle conditions
- Cathode materials are highly rate sensitive
- Under KPP conditions (C/10, 0°C, 3V discharge cutoff) cathode performance falls sharply
- Additional studies are underway in-house and with ETDP partners to improve high rate and low temperature performance

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