Oak Ridge National Laboratory

Fast Formation Cycling of Graphite Anodes with Layered Low-Co Cathodes for High-Energy LIBs

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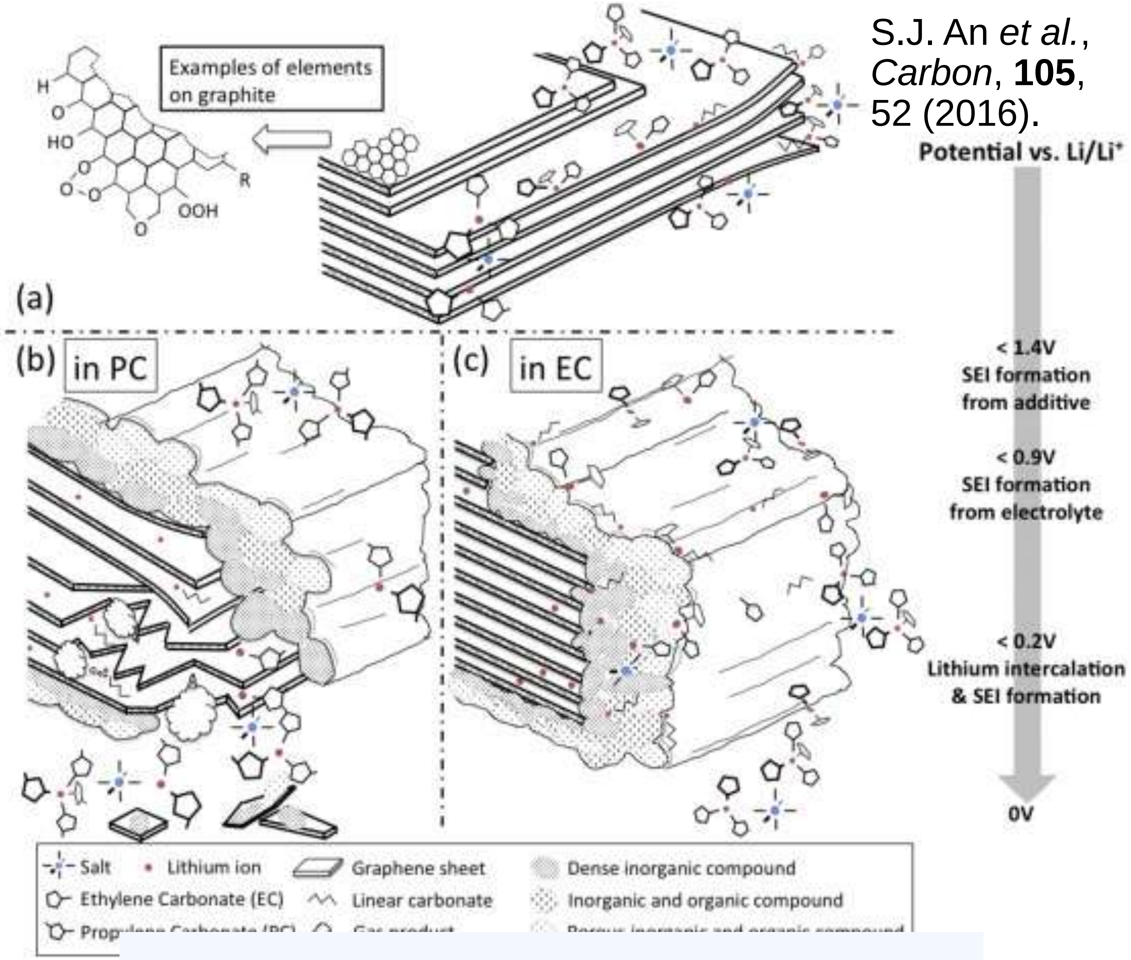
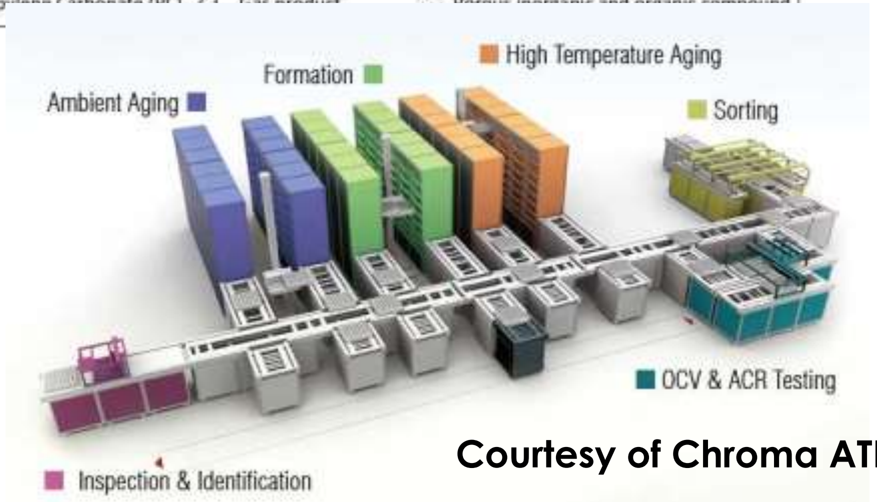
Basics of SEI Formation Cycling

- Typical Wetting and Formation Protocol:
  - Electrode wetting for 6-24h at room T
  - 1-2 formation cycles at 0.1-0.2C charge/discharge rates
  - Electrode wetting for 12-24 h at room T
  - 1-2 formation cycles at 0.2-0.5C
  - Electrolyte wetting for 12-24 h at 40-60°C
- Total time is ~3-7 days (not including the conditioning, or incubation, time).

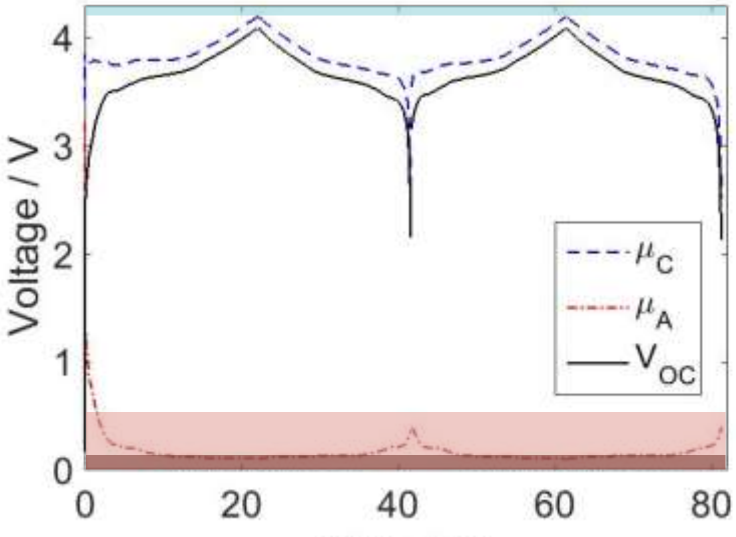
S.J. An *et al.*, *Carbon*, **105**, 52 (2016).

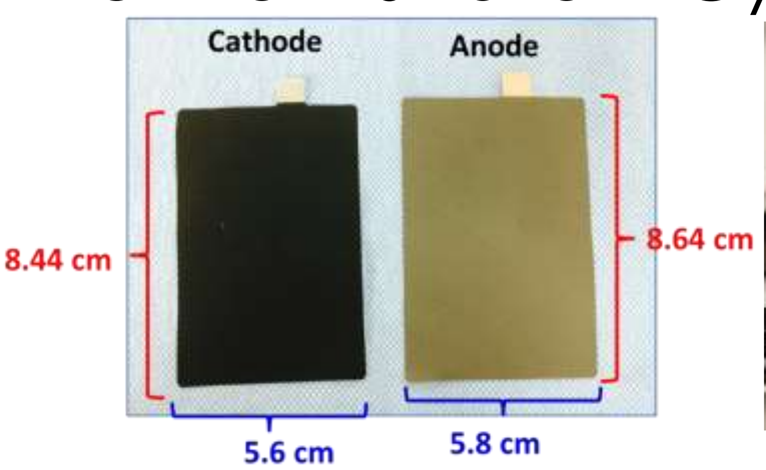


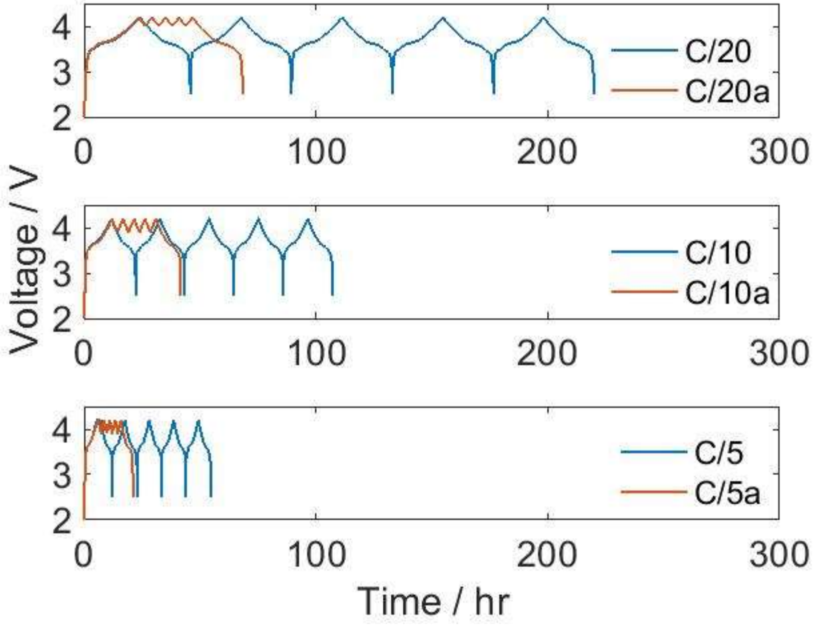


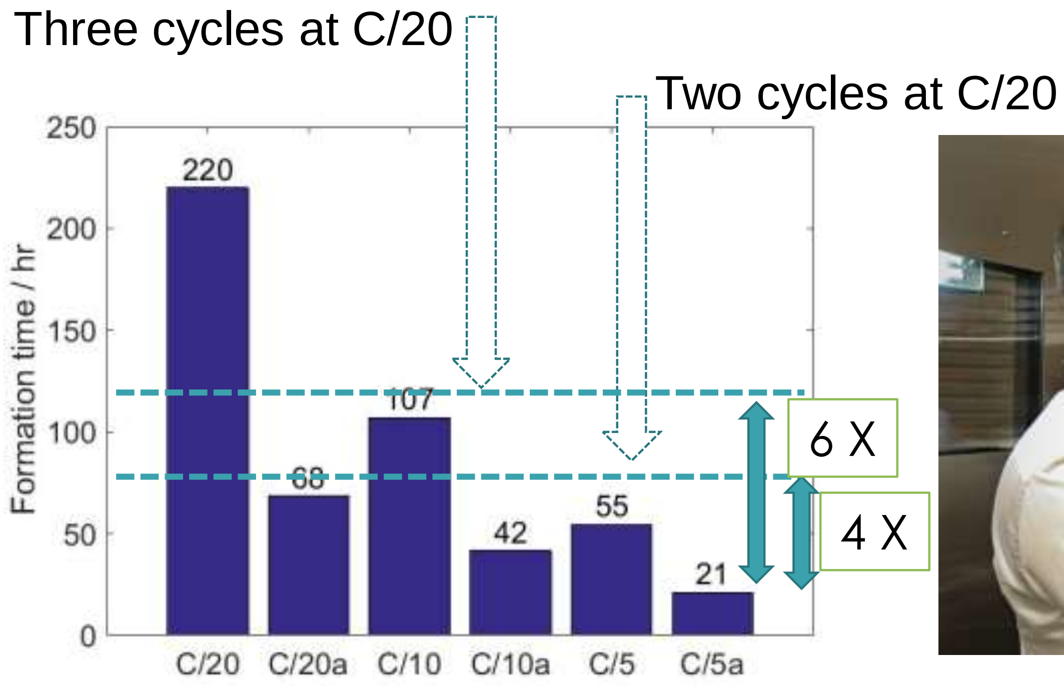
Courtesy of Chroma ATE

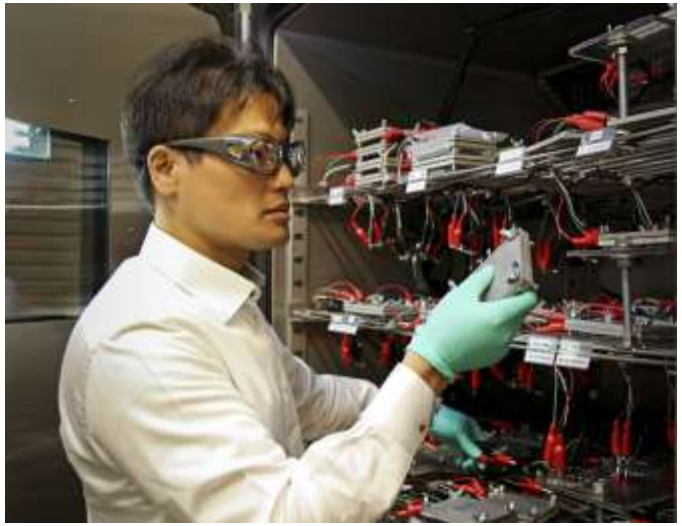
ORNL Baseline Formation Protocol Was Significantly Reduced in 2016 with Development of "Shallow Cycling"





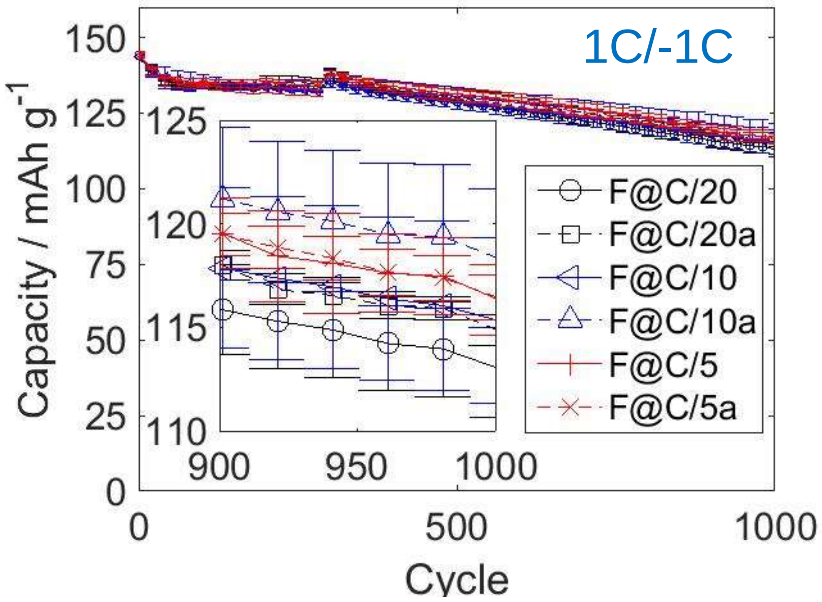


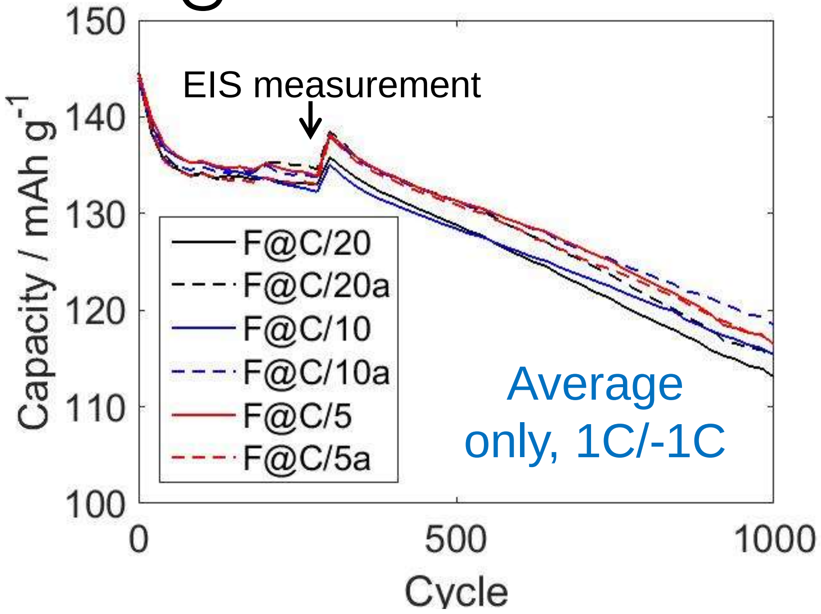


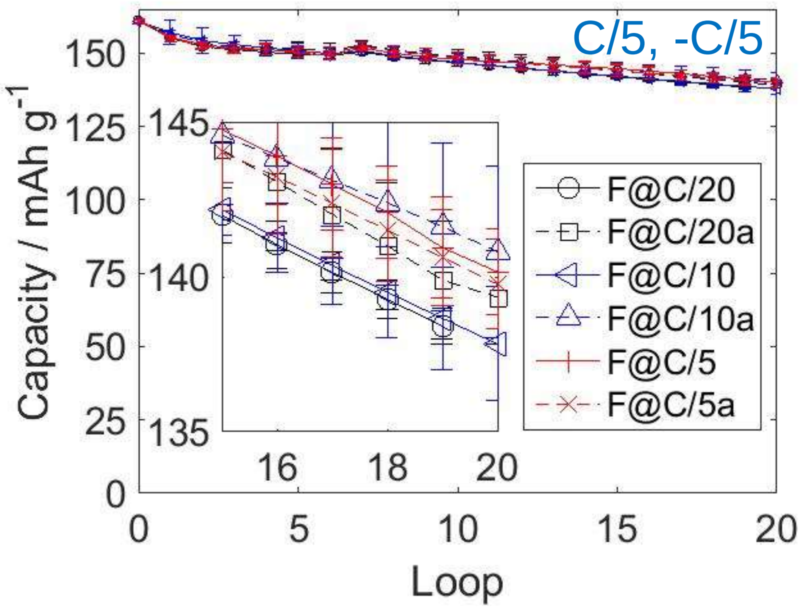


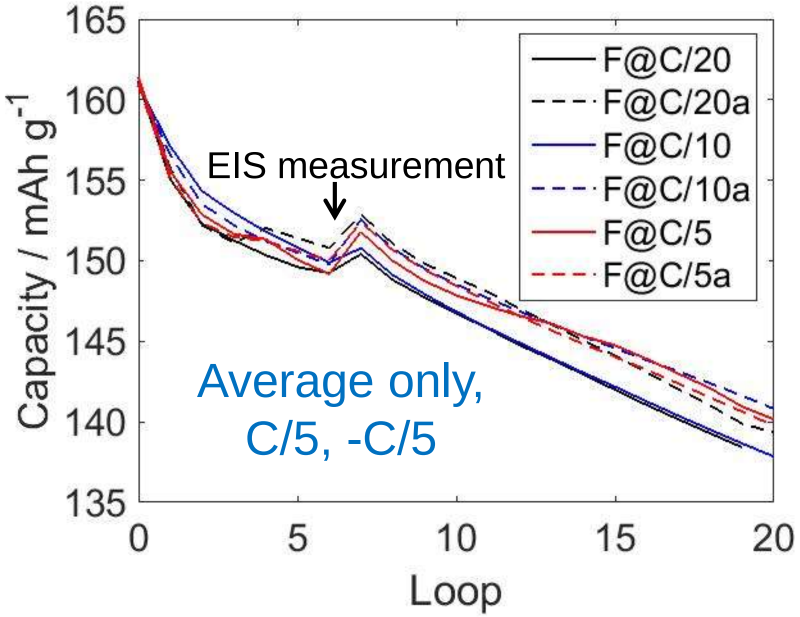
Capacity Fade with NMC 532 Was Found to Be Identical Through 1000 Cycles at Low and High Discharge Rates

- 1.5 Ah pouch cells
- ConocoPhillips A12 graphite
  - 6.36 mg/cm^2
  - 2.23 mAh/cm^2
- Toda America NMC 532
  - 12.02 mg/cm^2
  - 1.92 mAh/cm^2
- N/P = 1.16
- Celgard 2325
- 1.2 M $LiPF_6$ in EC:DEC (3:7 by weight

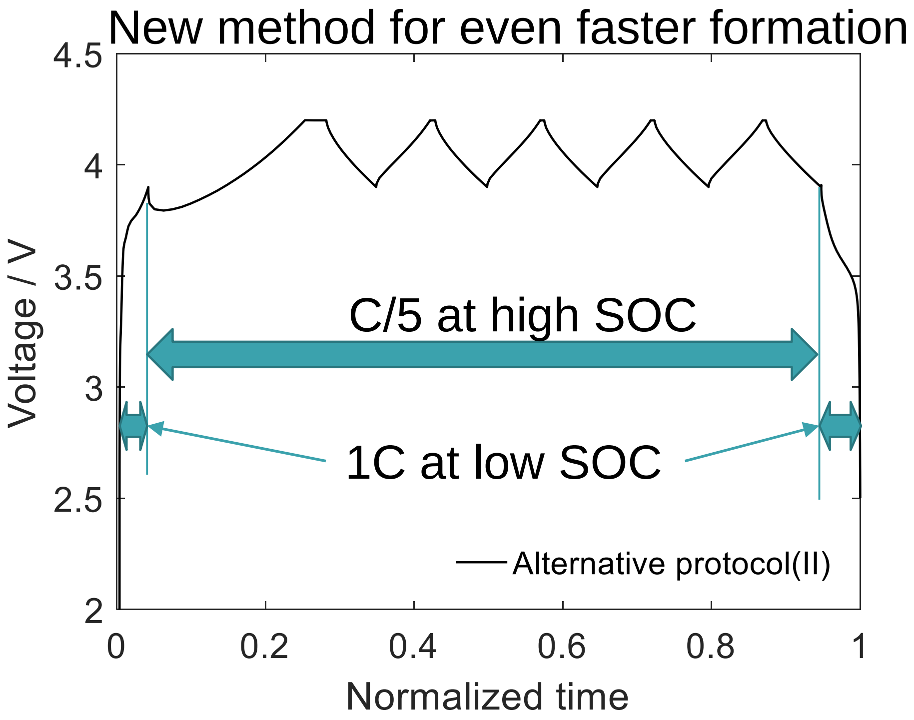


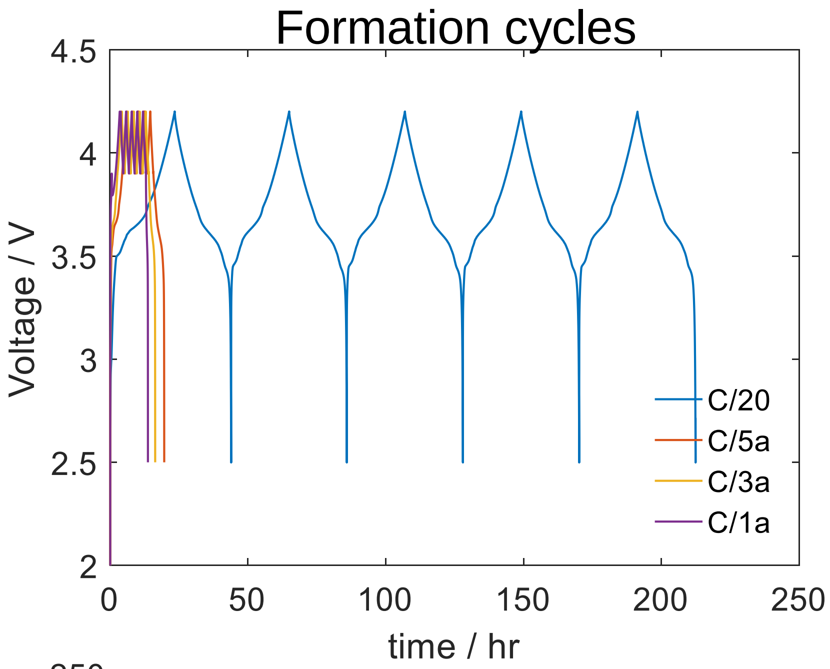


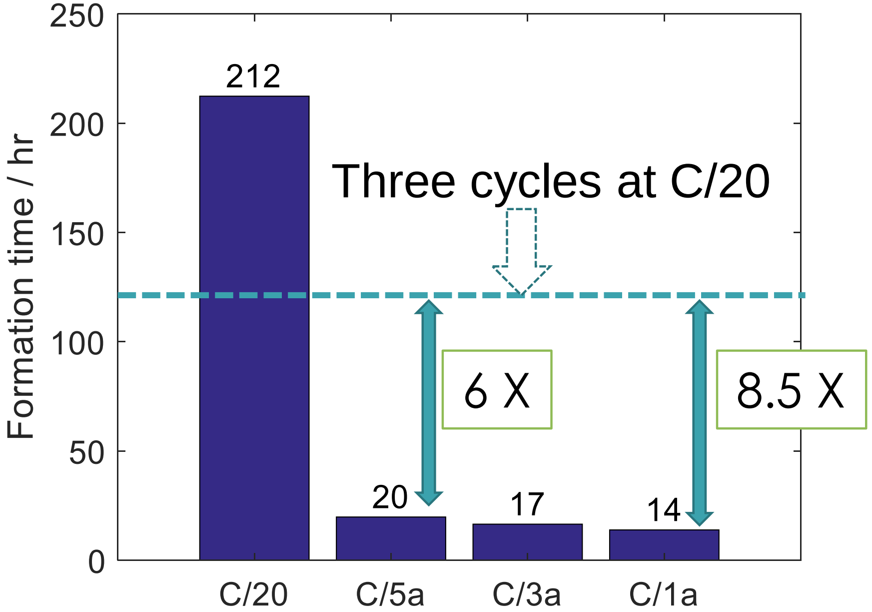




Additional Improvements Made to Fast Formation Protocol





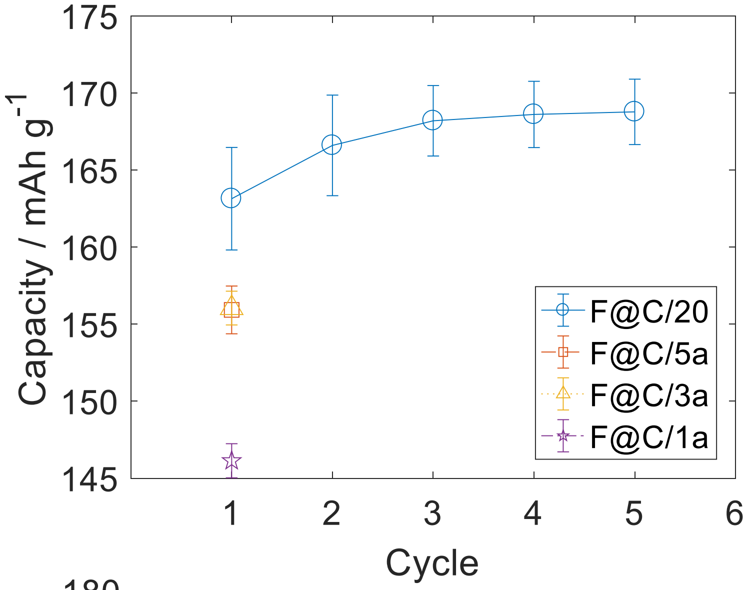


S.J. An, J. Li, Z. Du, C. Daniel, and D.L. Wood, III, "Fast Formation Cycling for Lithium Ion Batteries," *Journal of Power Sources*, **342**, 846–852 (2017).

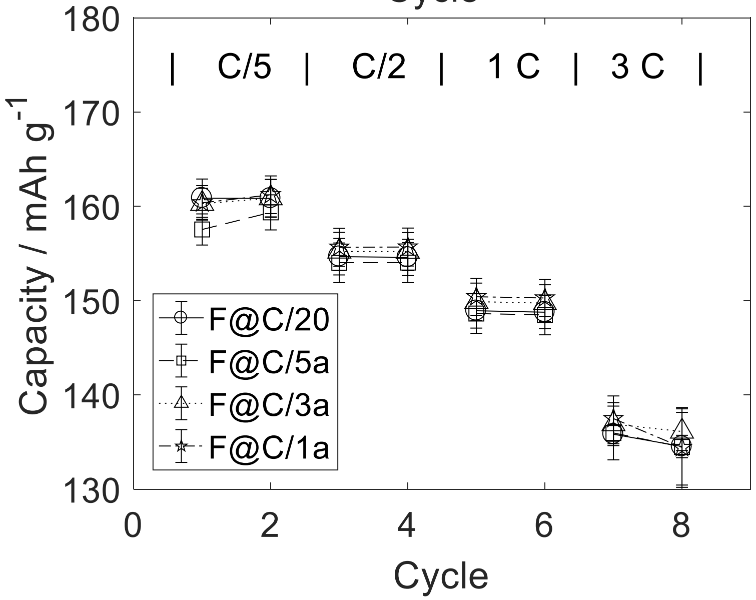
D.L. Wood, III, J. Li, and S.J. An, "Fast Formation Cycling for Rechargeable Batteries," Filed December 19, 2018, U.S. Patent Application No. 16/225,889 (UT-Battelle, LLC).

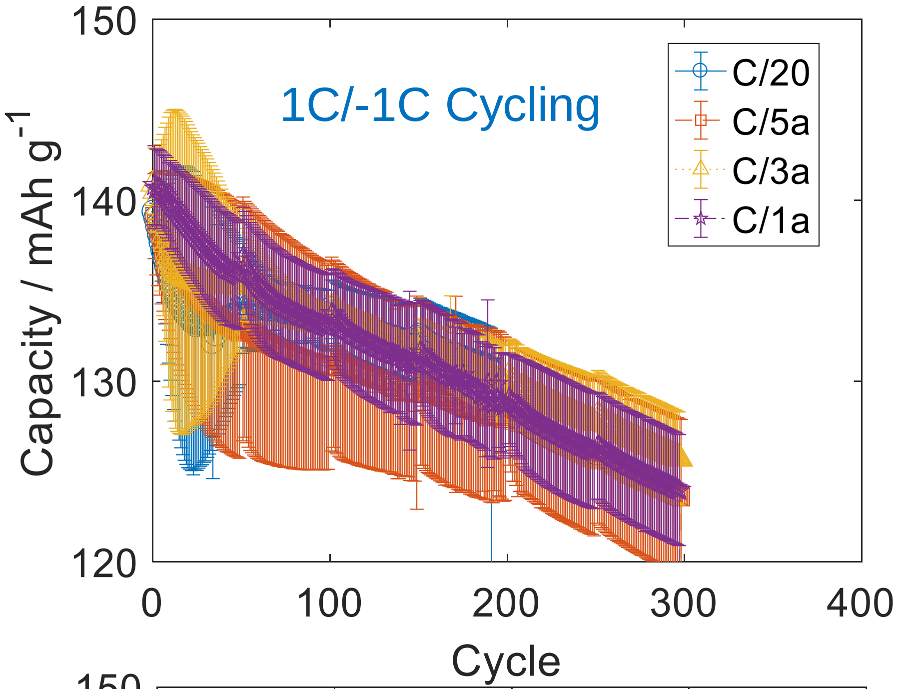
Differences Were Observed in First Charge Capacity, But Rate Capability and Long-Term Cycling Behavior Was Similar

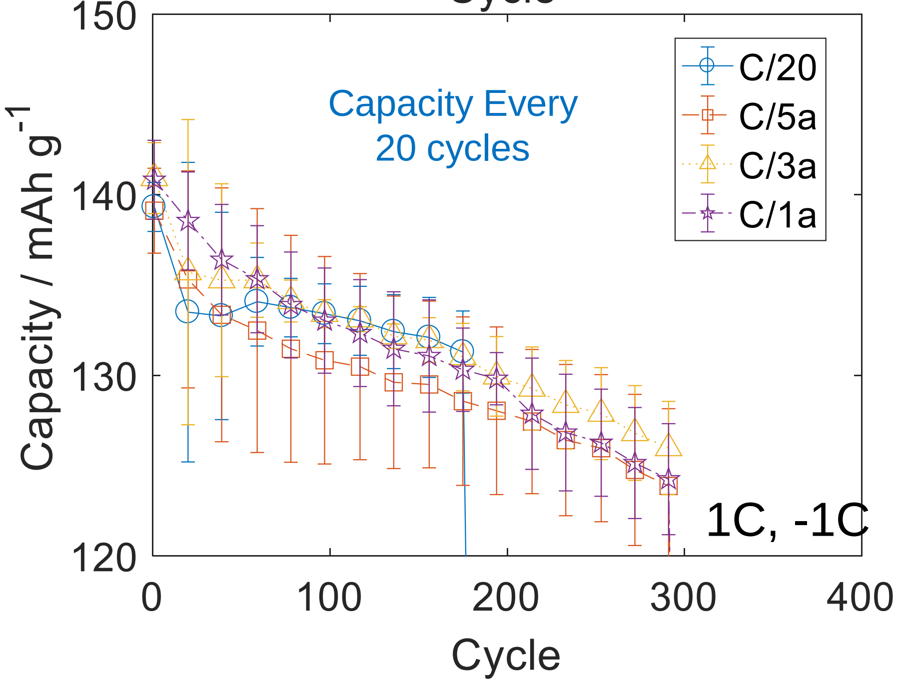
Formation Cycle(s) Capacity from Different Protocols



Rate Capability Data Immediately Following Formation Protocol





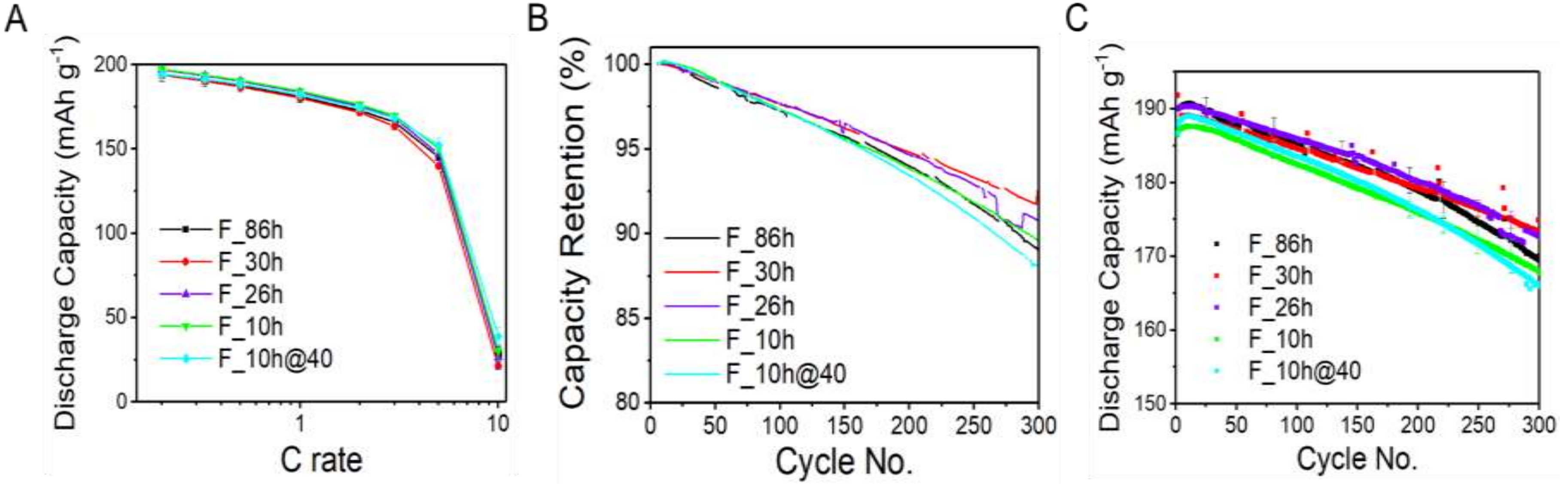


Graphite/NMC 811 Formation Protocol Test Matrix

Formation Protocol	Wetting Conditions	Cycling Conditions	Total Formation Time
F_86h	Tap Charge to 1.5V after vacuum seal, then rest for 6 hours at 30°C.	C/10 CCCV Charge to 4.2 V till Current <C/20, C/10 Discharge to 3.0 V, 4 Cycles. Cycling at 30°C .	86 hours
F_30h	Tap Charge to 1.5V after vacuum seal, then rest for 6 hours at 30°C.	C/2 CCCV Charge to 4.2 V till Current <C/20, C/2 Discharge to 3.0 V, 1 Cycle. C/2 CCCV Charge to 4.2 V till Current <C/20, C/2 Discharge to 3.0 V, 1 Cycle. Cycling at 30°C.	30 hours
F_26h	Tap Charge to 1.5V after vacuum seal, then rest for 6 hours at 30°C.	C/10 CCCV Charge to 4.2 V till Current <C/20, C/10 Discharge to 3.0 V, 1 Cycle. Cycling at 30°C.	26 hours
F_10h	Tap Charge to 1.5V after vacuum seal, then rest for 6 hours at 30°C.	C/2 CCCV Charge to 4.2 V till Current <C/20, C/2 Discharge to 3.0 V, 1 Cycle. Cycling at 30°C.	10 hours
F_10h@40	Tap Charge to 1.5V after vacuum seal, then rest for 6 hours at 40°C.	C/2 CCCV Charge to 4.2 V till Current <C/20, C/2 Discharge to 3.0 V, 1 Cycle. Cycling at 30°C.	10 hours

Capacity Fade Varied for NMC 811 Pouch Cells During Long-Term USABC Cycling

- 100 mAh (single-layer) pouch cells
- Superior Graphite SLC 1520T graphite
  - 8.3 mg/cm^2
  - 2.6 mAh/cm^2
- Targray NMC 811
  - 11.5 mg/cm^2
  - 2.3 mAh/cm^2
- N/P = 1.15
- Celgard 2325
- 1.2 M $LiPF_6$ in EC:EMC (3:7 by weight)

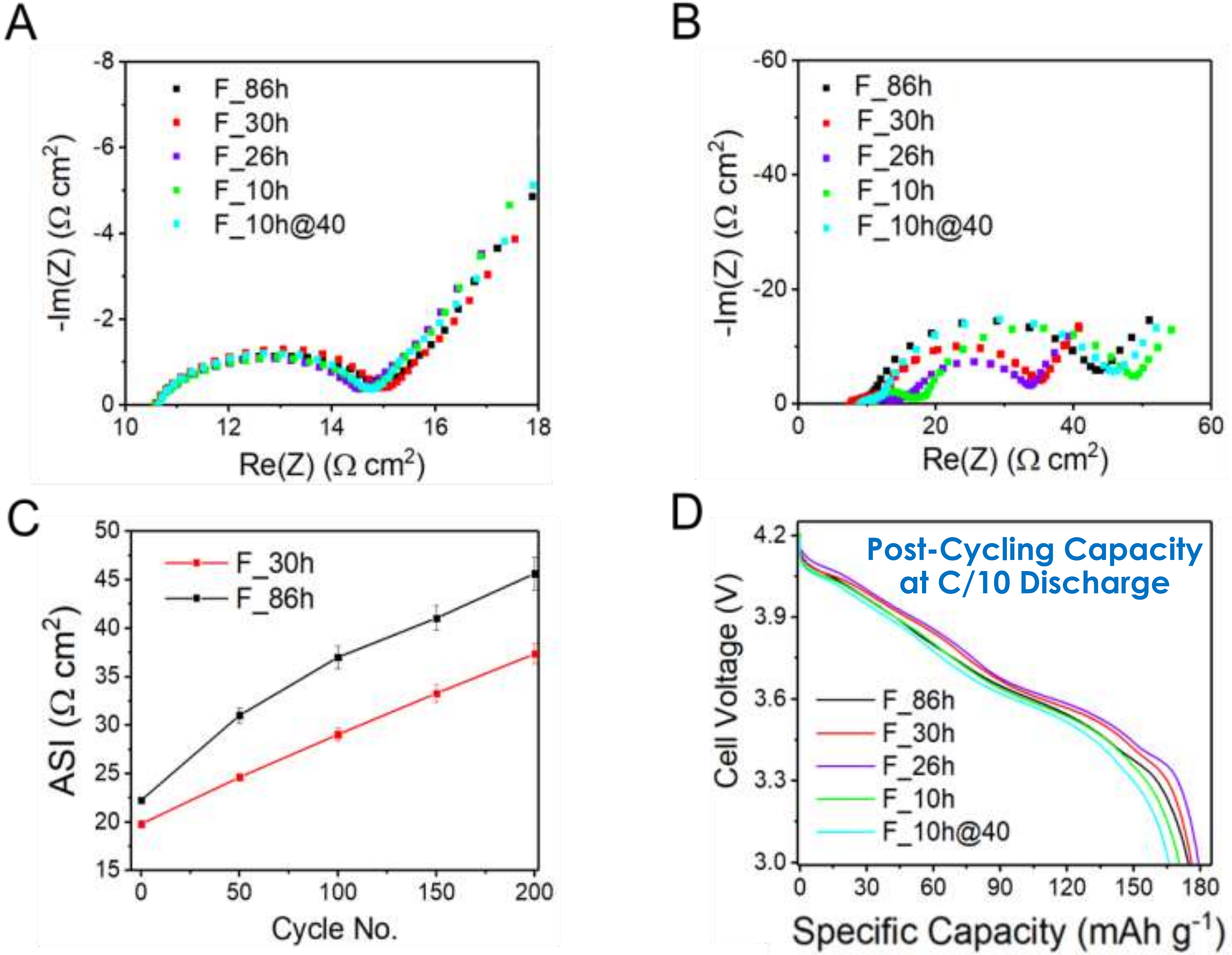


- All formation protocols resulted in excellent rate capability (76-79% of rated capacity at 5C discharge).
- F_26h and F_30h protocols resulted in the best capacity retention after 300 0.33C/-0.33C cyles.
- The two F_10h protocols performed the worst after long-term cycling.

C. Mao, S.J. An, H.M. Meyer, III, J. Li, M. Wood, R.E. Ruther, and D.L. Wood, III, "Balancing Formation Time and Electrochemical Performance of High Energy Lithium-Ion Batteries," *Journal of Power Sources*, **402**, 107–115 (2018).

Charge-Transfer and SEI Impedance Increased Significantly after Cycling for Two F_10h Protocols

- Cell impedance was similar for all cells immediately after formation.
- The area specific impedance (ASI) was substantially higher for the F_86h formation protocol than the optimum F_30h protocol.



Conclusions

- NMC 532 with Shallow Cycling Replacement
  - The proposed formation protocol with shallow cycling between 3.9-4.2 V shortened formation time by ≥6 times without compromising cell performance.
  - Rather, this methodology improved capacity retention, which will have a tremendous impact on the operating and capital cost of manufacturing LIBs.
- NMC 811 with Protocols at Different First Charge Rates
  - The shortest formation protocols (10 h) resulted in lithium plating, faster impedance growth, and the poorest long-term capacity and capacity retention.
  - Formation protocols that were intermediate in length (26-30 h) yielded the best long-term performance with minimal impedance rise.
  - Surprisingly, further increasing the time for the formation protocol did not offer any improvements.

Thank you for your attention!

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CP A12 / Toda NMC 532 Cell Information

	Composition	Size (loading) [porosity]
Anode	Electrode: 92 wt % A12 graphite (ConocoPhillips), 2 wt % C-65 carbon black (Timcal), 6 wt % polyvinylidene fluoride (PVDF, Kureha 9300) Current collector: Copper foil Tab: nickel	Electrode only 84.4 mm×56 mm× 65 µm (6.36 mg/cm^2) [55%]
Cathode	Electrode: 90 wt % $Li_{1.02}Ni_{0.50}Mn_{0.29}Co_{0.19}O_2$ (NMC 532 or NCM 523, TODA America Inc.), 5 wt % powder grade carbon black (Denka), 5 wt % PVDF (Solvay Solef® 5130) Current collector: Aluminum foil Tab: Aluminum	Electrode only 84.4 mm×56 mm× 64 µm (12.02 mg/cm^2) [55%]
Separator	Polypropylene–polyethylene–polypropylene (Celgard® 2325)	89 mm × 61 mm × 25 µm [39%]
Electrolyte	1.2 M $LiPF_6$ in EC:DEC (3:7 by weight, BASF)	–