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Near Zero Volt Tolerance in Lithium-ion Batteries Using Reversible Lithium Management – Addressing Cathode Over-insertion

Dr. Kyle R. Crompton, Michael P. Hladky, Jason W. Staub and Dr. Brian J. Landi

4/23/2018

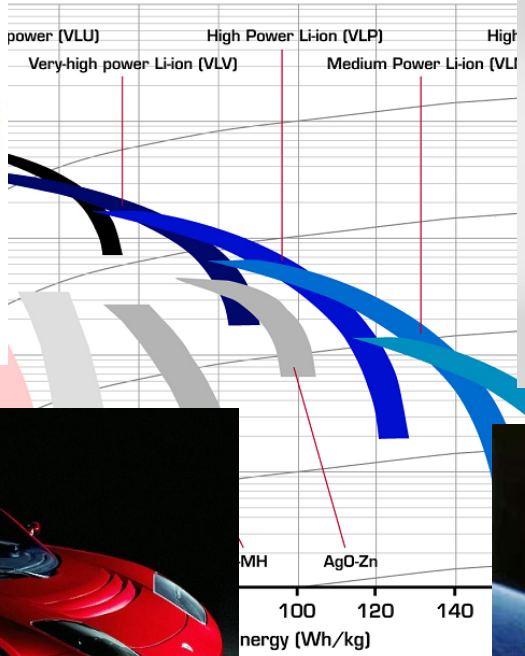
Outline

FA9453-14-1-0239

1. **Near Zero Volt (NZV) background, motivation and scale-up efforts**
2. Addressing cathode over-insertion concern with reversible lithium management approach

Li-ion batteries

Lithium ion batteries have increased energy and power density compared to other chemistries, making them the best choice for many portable electronic applications



Near zero volt tolerance - benefits

Lithium-ion cells are inactive when assembled into packs, transported, launched, or stored ship board

https://www.greencarreports.com/

http://money.cnn.com/2016/02/23/news/companies/lithium-ion-battery-ban-airplanes/

http://spacenews.com/spacex

https://defensesystems.com

Need improved safety and decreased maintenance requirements for these inactive lithium-ion cells

Near zero volt tolerance - benefits

What if a lithium-ion cell can be held in a near zero volt state when inactive without losing performance?

https://www.greencarreports.com/

http://money.cnn.com/2016/02/23/news/companies/lithium-ion-battery-ban-airplanes/

http://spacenews.com/spacex

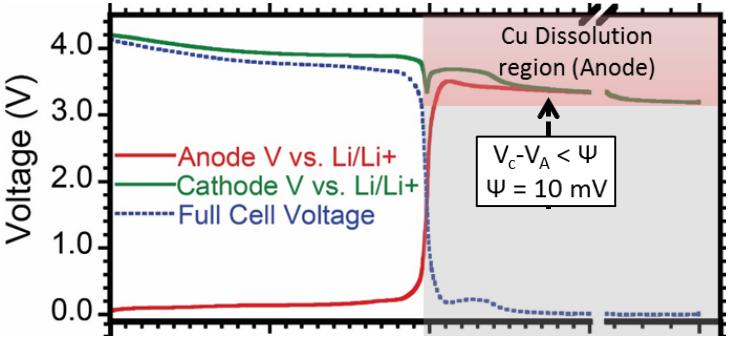
https://defensesystems.com

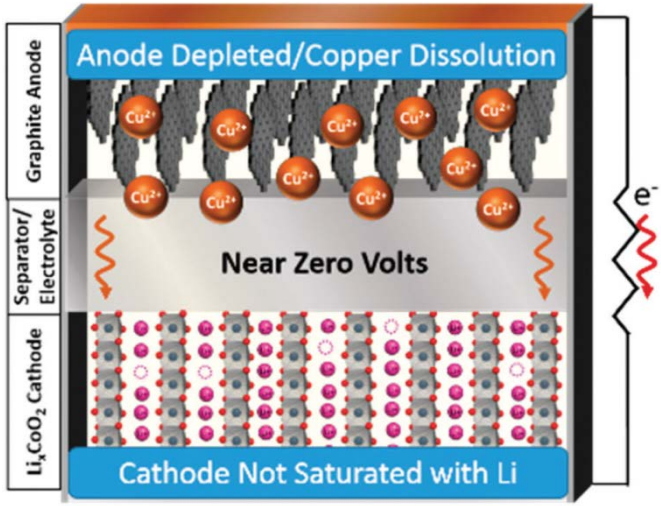
Safety of pack assembly, shipping, launch and ship board storage greatly increased with no need for voltage monitoring or trickle charging

Reversible lithium management to fabricate near zero volt tolerant cells

Conventional

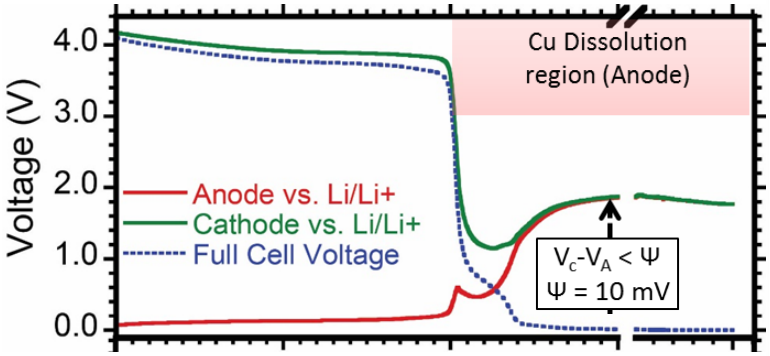
- Cu dissolution leading to degraded cell performance

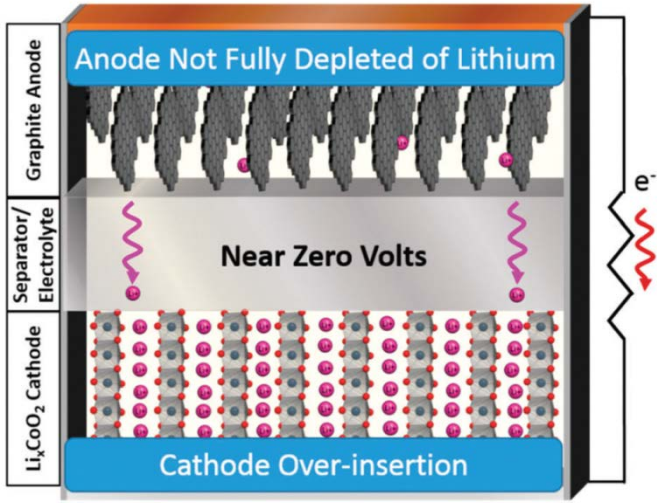




Reversible lithium managed

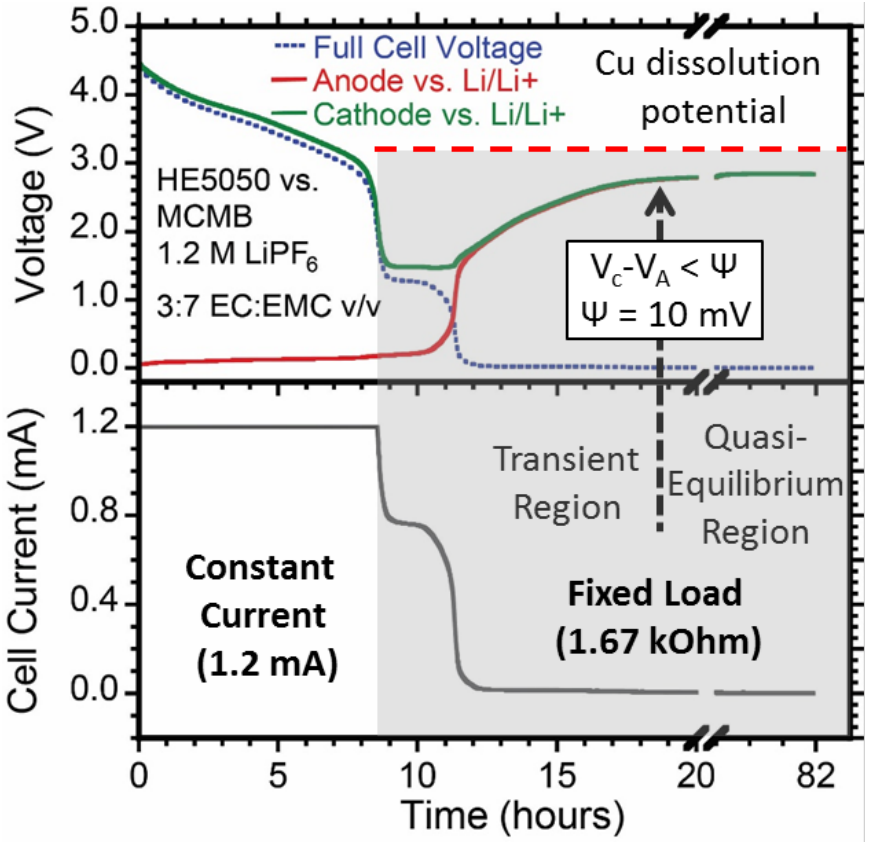
- No Cu dissolution due anode potential less than 3.0 V vs. Li/Li^+



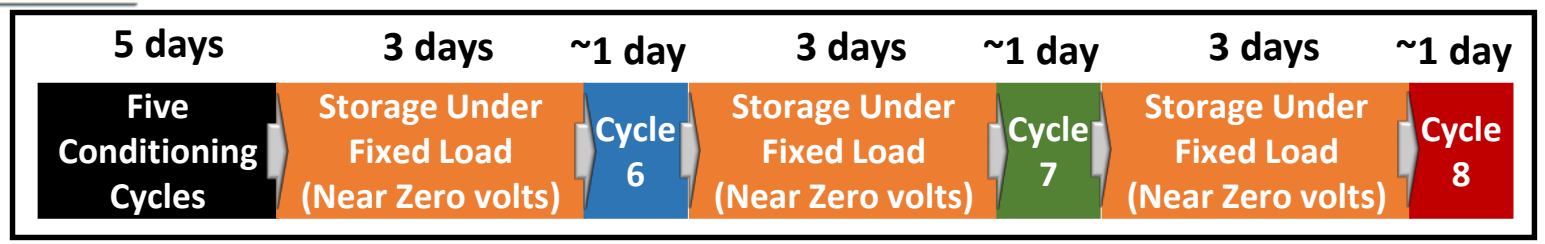


Reversible lithium management to fabricate near zero volt tolerant cells

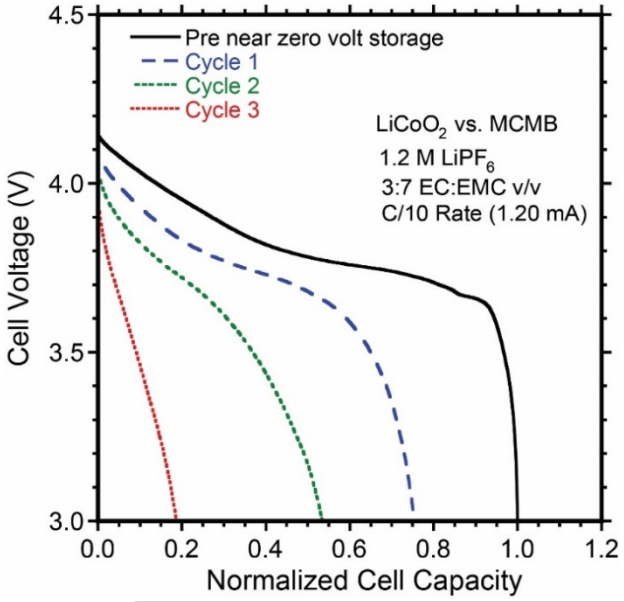
- Reversible lithium management technique does not require secondary materials, alternative current collectors or additives – *state of the art performance can be maintained*
- Has been demonstrated for $LiCoO_2$:MCMB, $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2$ (HE5050):MCMB, and $LiNiCoAlO_2$(NCA):MCMB cell chemistries



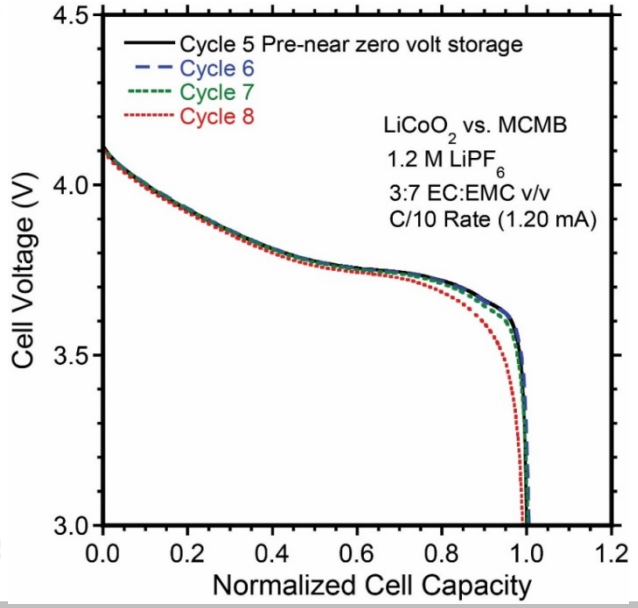
Capacity retention of reversible lithium managed cells after repeated NZVS



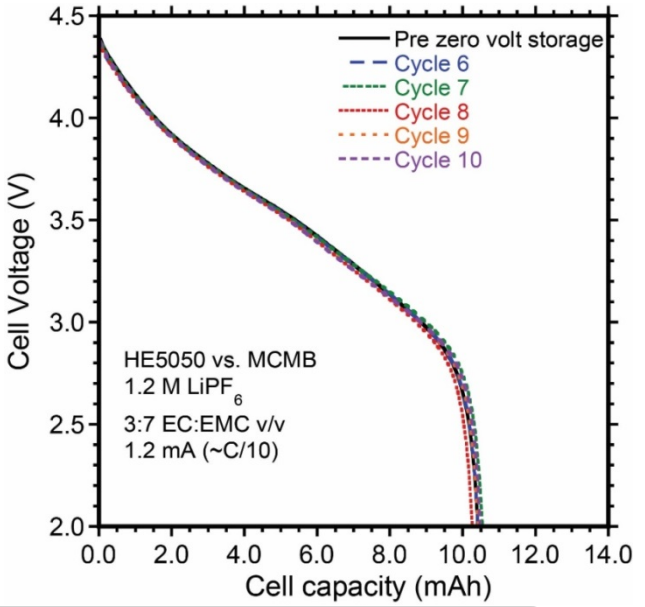
Conventional $LiCoO_2$:MCMB cell



Reversible Li managed $LiCoO_2$:MCMB cell



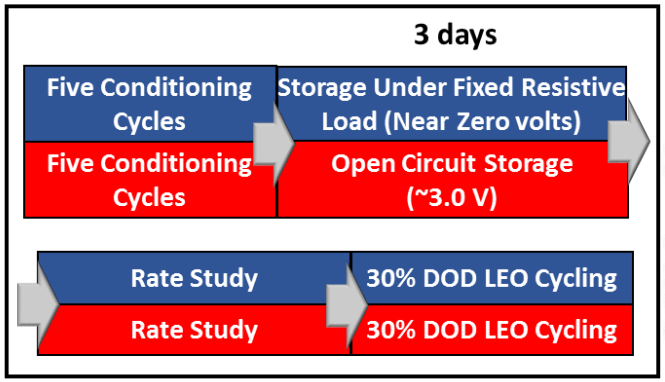
Reversible Li managed HE5050:MCMB cell



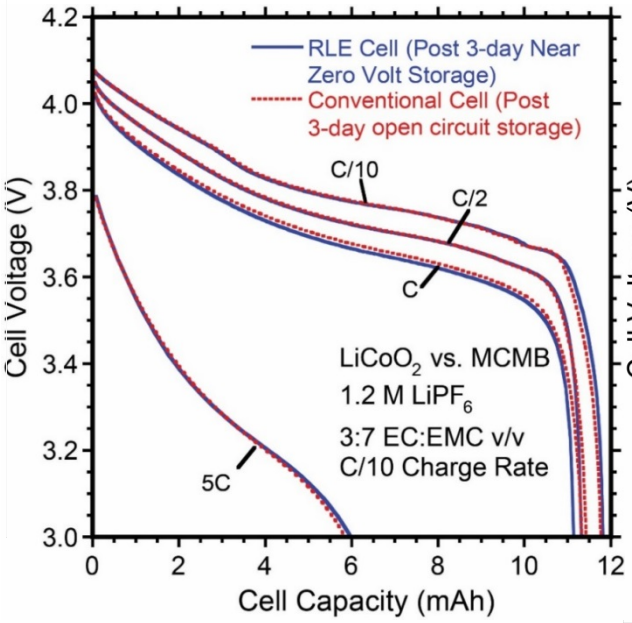
Capacity retention after NZVS in reversible lithium managed cells >99% at a C/10 rate

Reversible lithium management to fabricate near zero volt tolerant cells

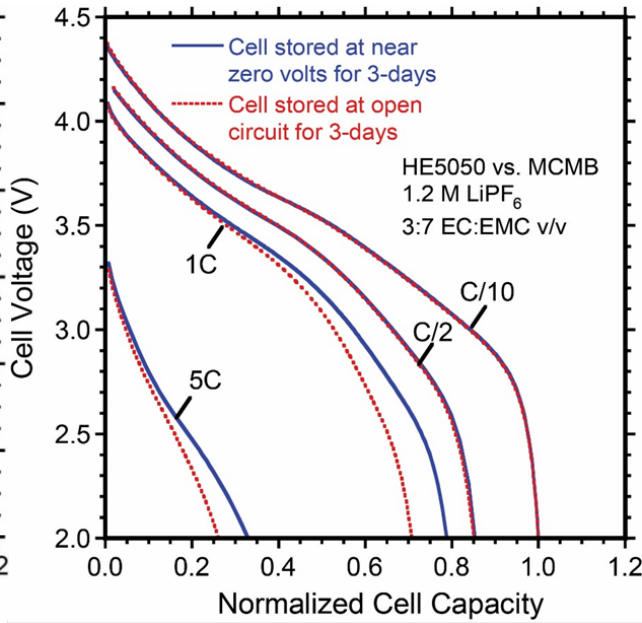
Cycling Schedule



$LiCoO_2$:MCMB cell



HE5050:MCMB cell

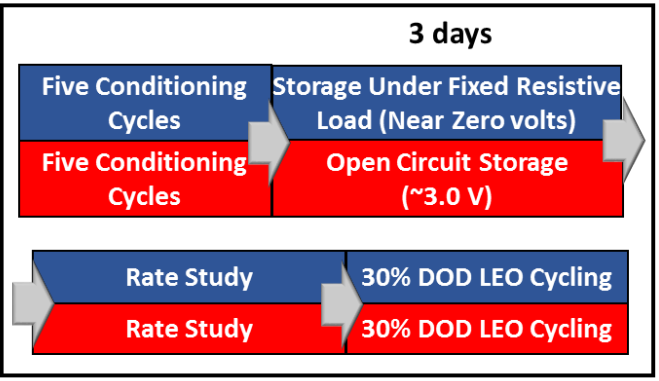


- Compared to baseline cell stored for 3 days at open circuit, reversible lithium managed cells stored at near zero volts for 3 days had nearly identical rate performance up to a 5C discharge rate

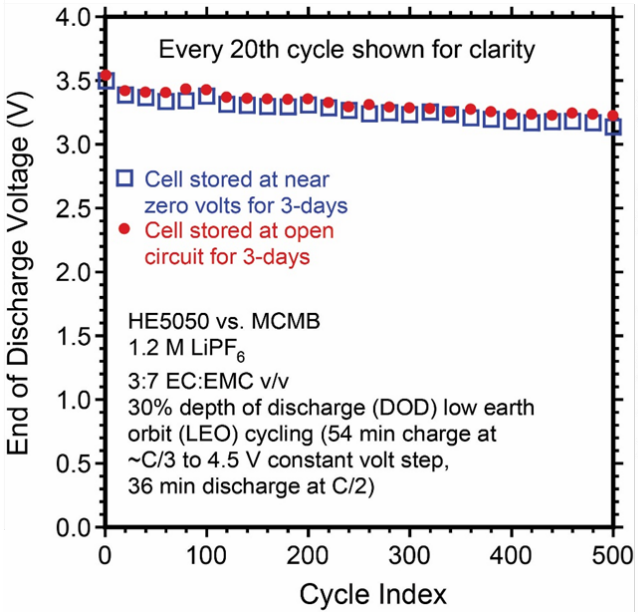
Rate study shows that near zero volt storage period did not adversely effect cell rate capability

Reversible lithium management to fabricate near zero volt tolerant cells

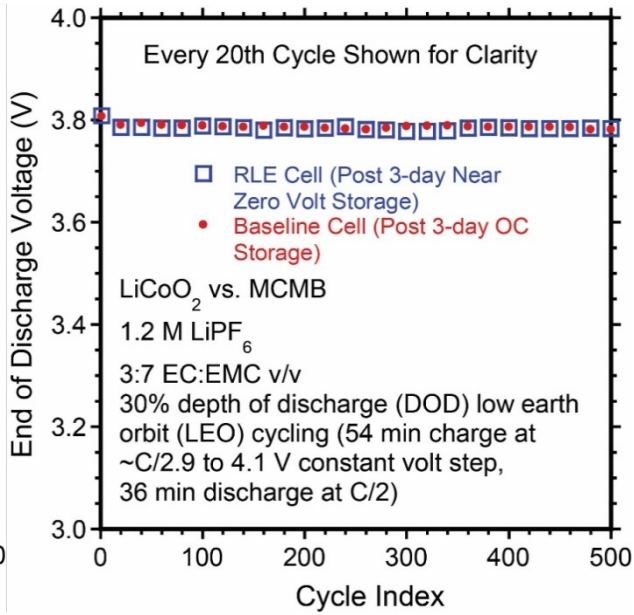
Cycling Schedule



$LiCoO_2$:MCMB cell



HE5050:MCMB cell



- Compared to baseline cell stored for 3 days at open circuit, reversible lithium managed cells stored at near zero volts for 3 days had nearly identical cycling performance to 500, 30% DOD LEO cycles

LEO shows that near zero volt storage period did not adversely effect cell cycling out to 1 month

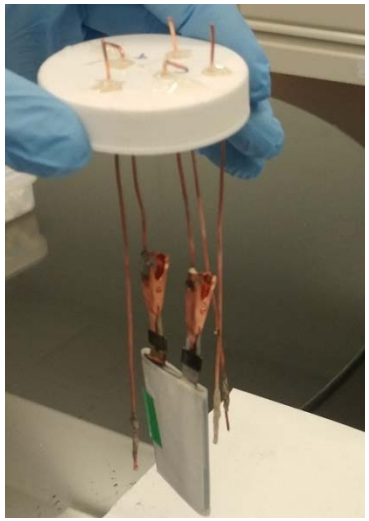
Scale up with bath lithiation

Rochester Institute of Technology Battery Prototyping Center

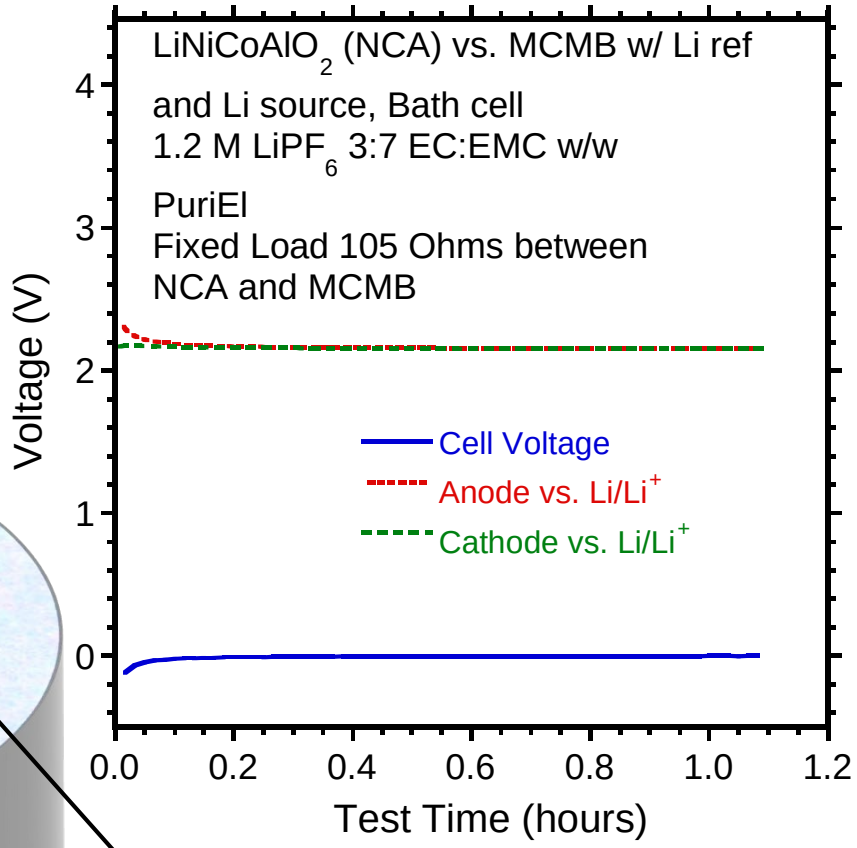
Images courtesy of: Dr. Matthew Ganter and Dr. Christopher Schauerman

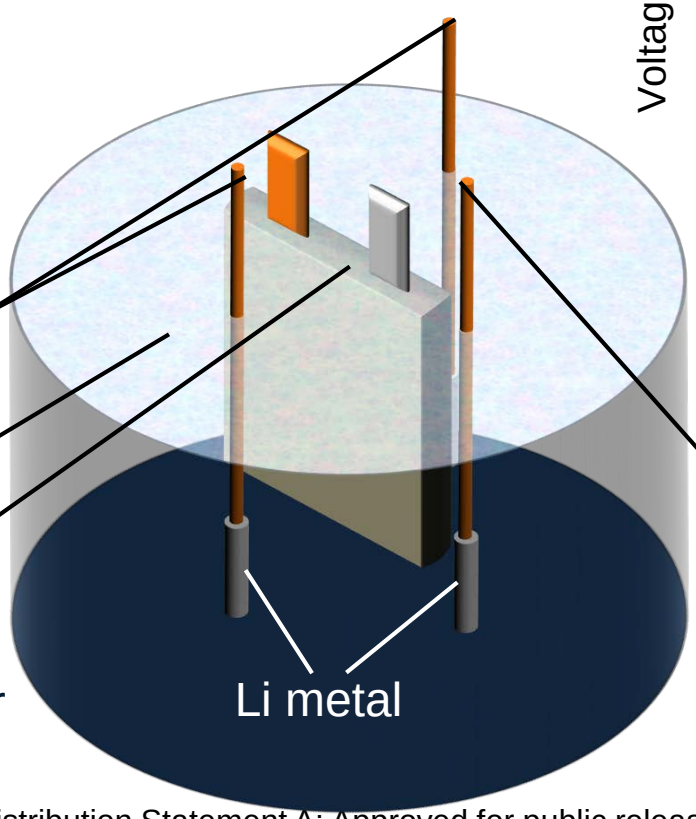
- Solith semi-automated pouch cell assembly equipment
- 10,000 ft^2 dry room, -60°C dewpoint
- Slurry mixing, coating, drying, calendaring and punching

Scale up with bath lithiation

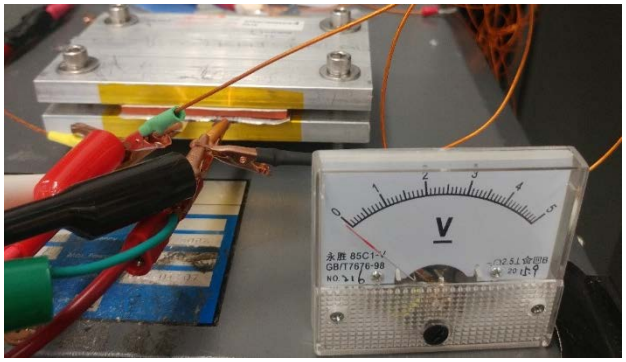


With addition of lithium ions to cathode/anode cell stack from lithium electrodes, EAP can be decreased to ~2.2 V vs. Li/Li^+, less than the copper dissolution potential

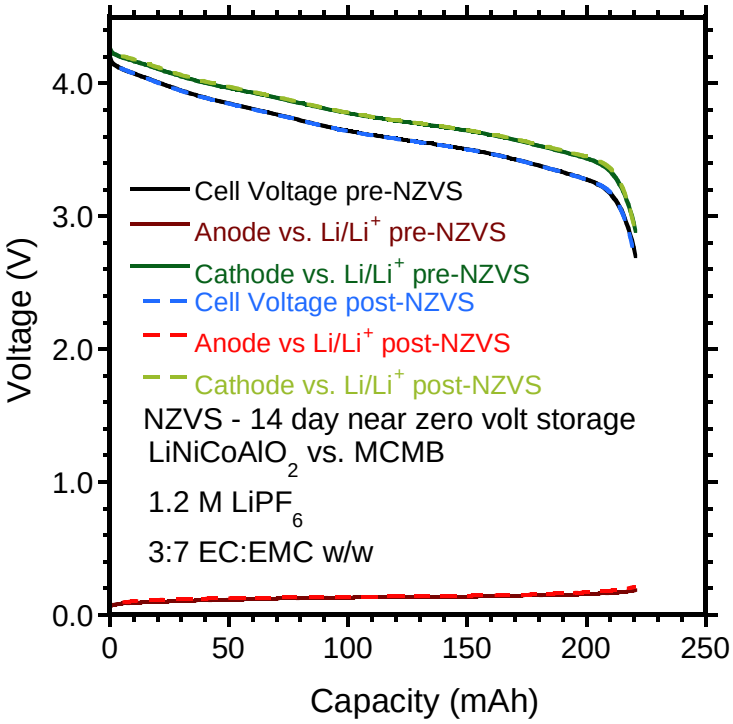


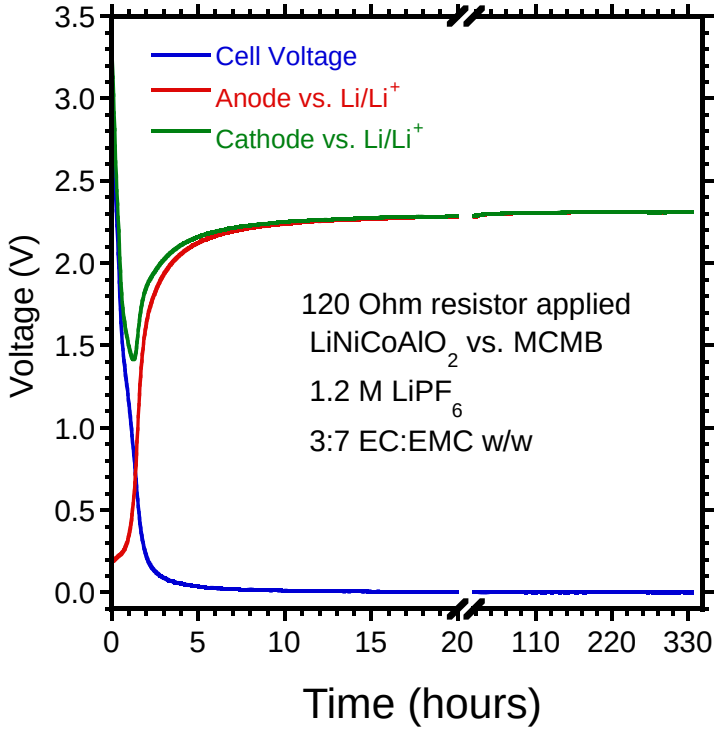


Scale up effort



Scaled to cell phone-sized battery –has steady EAP of ~2.3 V vs. Li/Li^+ for 14 days





Scale up to nearly a cell phone size battery form factor was successful and lithium management method can be integrated into BPC's semi-automated pouch cell line

Conclusions from prior work

- Reversible lithium management demonstrated to be effective in fabricating cells with tolerance to near zero volt storage in the beginning of cell life
  - Room temp and high temp (40-45°C)
- Reversible lithium management applied successfully to 3 different cell chemistries ($LiCoO_2$, $LiNiCoAlO_2$ and $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2$ (HE5050)) that resulted in cells that are highly tolerant to prolonged (up to 14 day) zero volt states

- Scale up to cell-phone sized pouch cell was successful and demonstrates the reversible lithium management approach is scalable

K. R. Crompton, *et al* J. Power Sources, vol. 343, pp. 109–118, 2017.

K. R. Crompton and B. J. Landi, Energy Environ. Sci., vol. 9, pp. 2219–2239, 2016.

K.R. Crompton, B.J. Landi U.S. Serial No. 15/481115, application.

Outline

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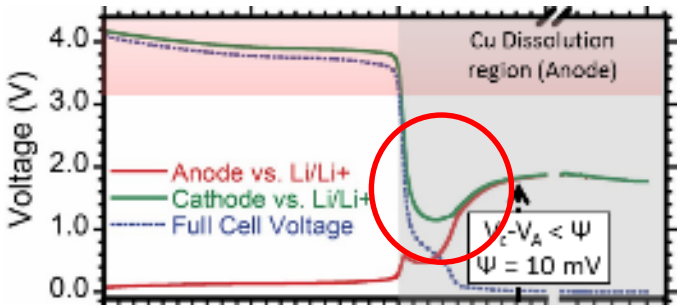
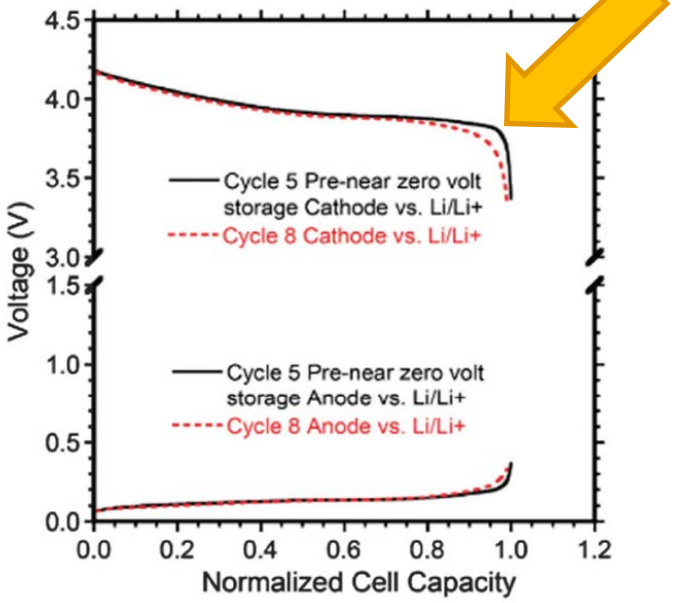
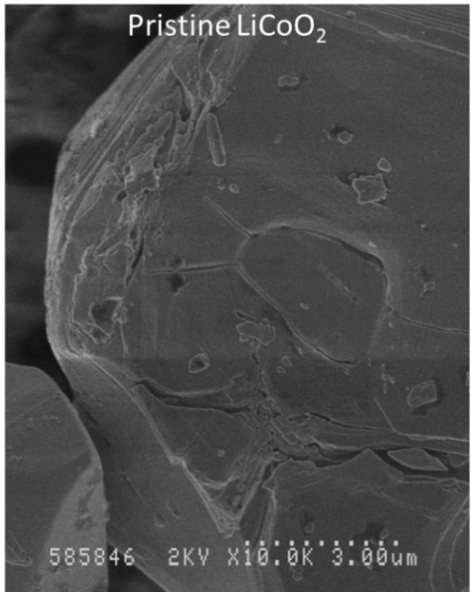
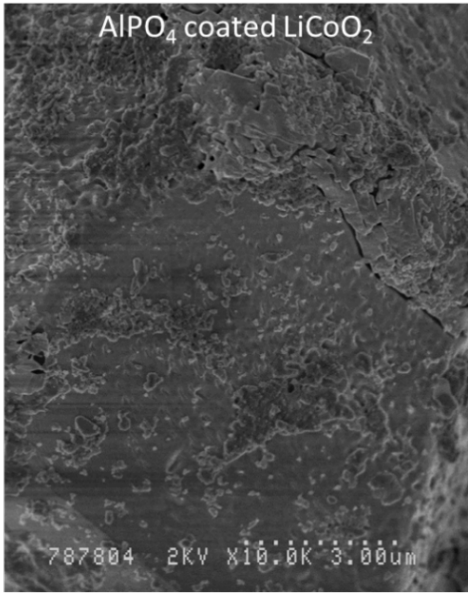
1. Near Zero Volt background, motion and scale-up efforts
2. **Addressing cathode over-insertion concern with reversible lithium management approach**

Addressing Cathode over-insertion







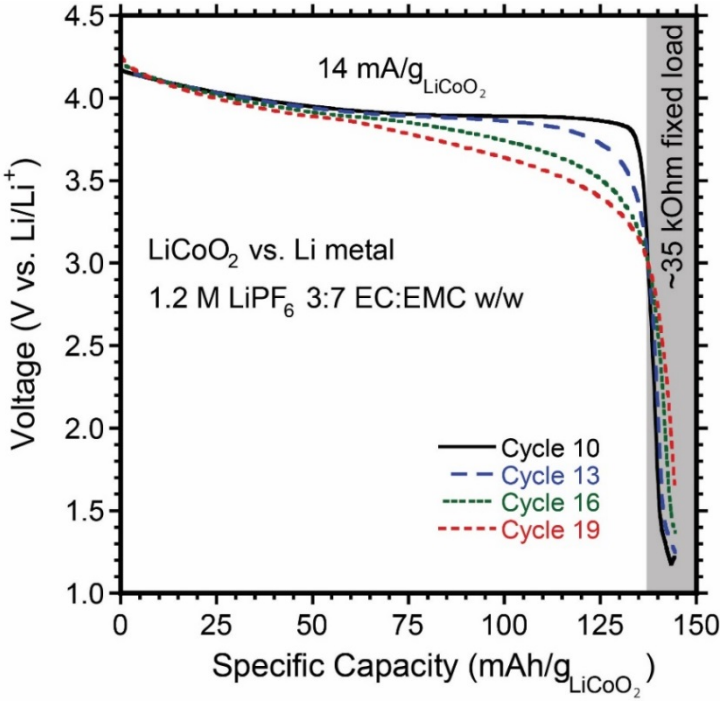


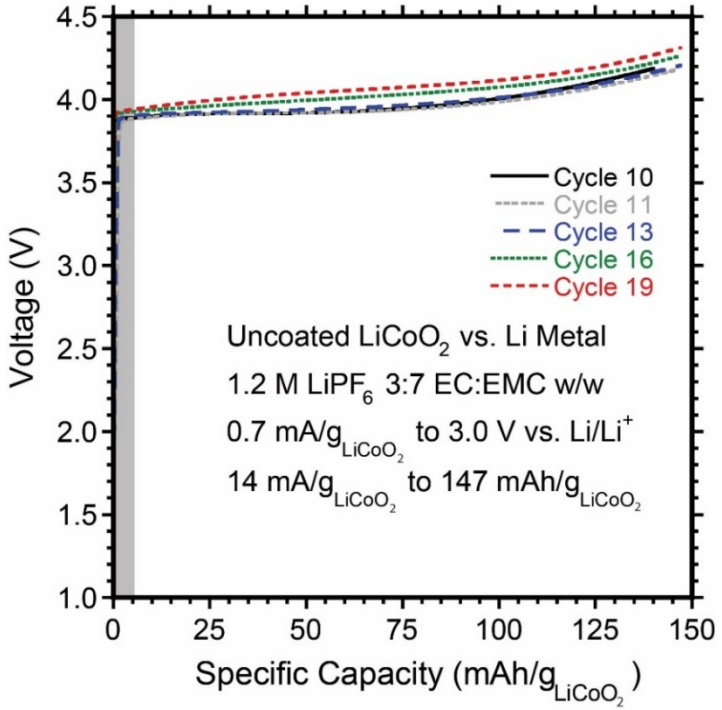
*** 5% over-insertion by fixed load, 0.7 mA/g_{LCO} charge to 3.0 V vs. Li/Li^+**

As-received $LiCoO_2$

*** 5% over-insertion by fixed load, 0.7 mA/g_{LCO} charge to 3.0 V vs. Li/Li^+**

10 conditioning cycles * 11 * 12 * Cycle 13 * 14 * 15 * Cycle 16 * 17 * 18 * Cycle 19 * C/200 recharge to 3.0 V vs. Li/Li^+



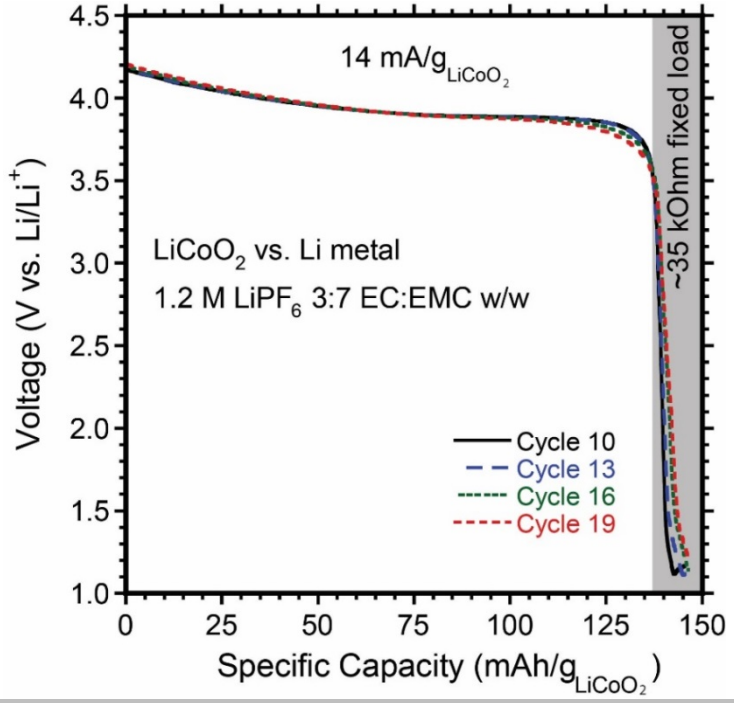


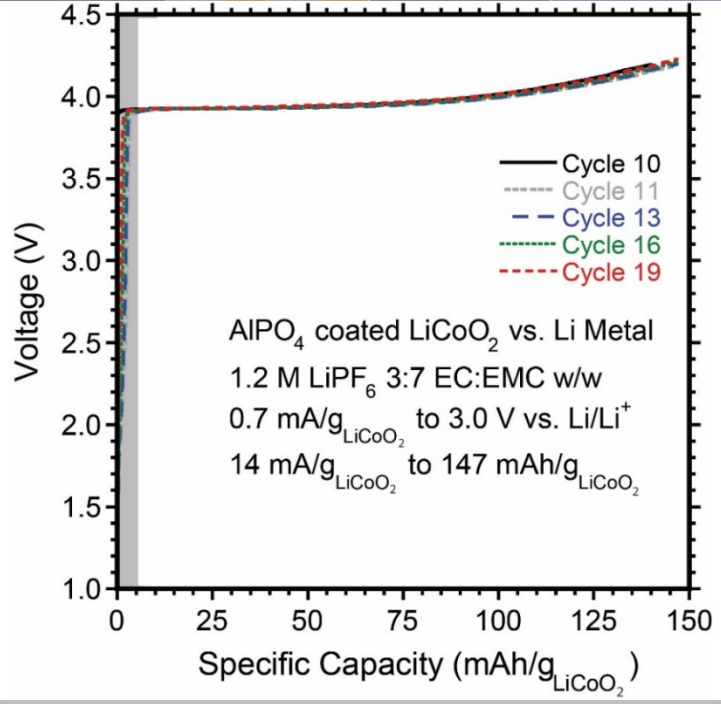
Repeated over-insertion leads to decrease and rounding of discharge voltage curve

$AlPO_4$ coated $LiCoO_2$

*** 5% over-insertion by fixed load, 0.7 mA/g_{LCO} charge to 3.0 V vs. Li/Li^+**

10 conditioning cycles * 11 * 12 * Cycle 13 * 14 * 15 * Cycle 16 * 17 * 18 * Cycle 19 * C/200 recharge to 3.0 V vs. Li/Li^+

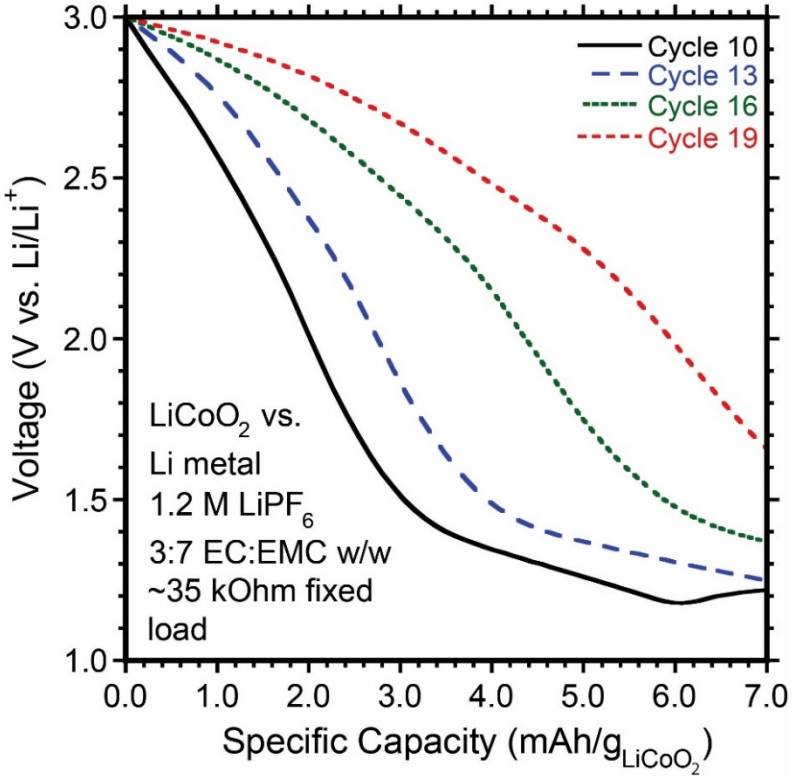




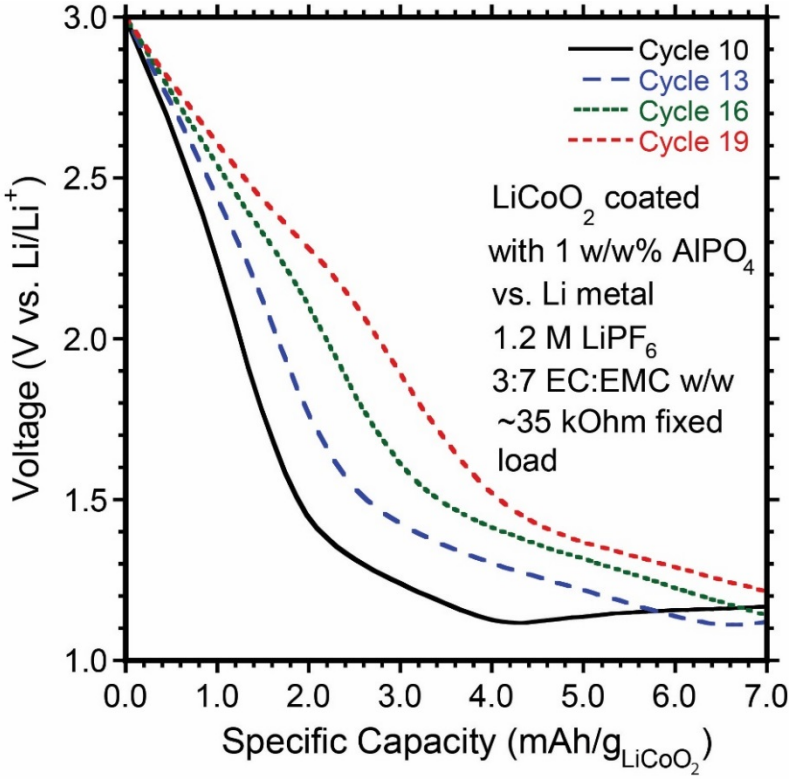
Discharge and charge voltage curve characteristics are maintained in $AlPO_4$ coated $LiCoO_2$ after 10 repeated over-insertion steps

Over-insertion curves

As-received $LiCoO_2$



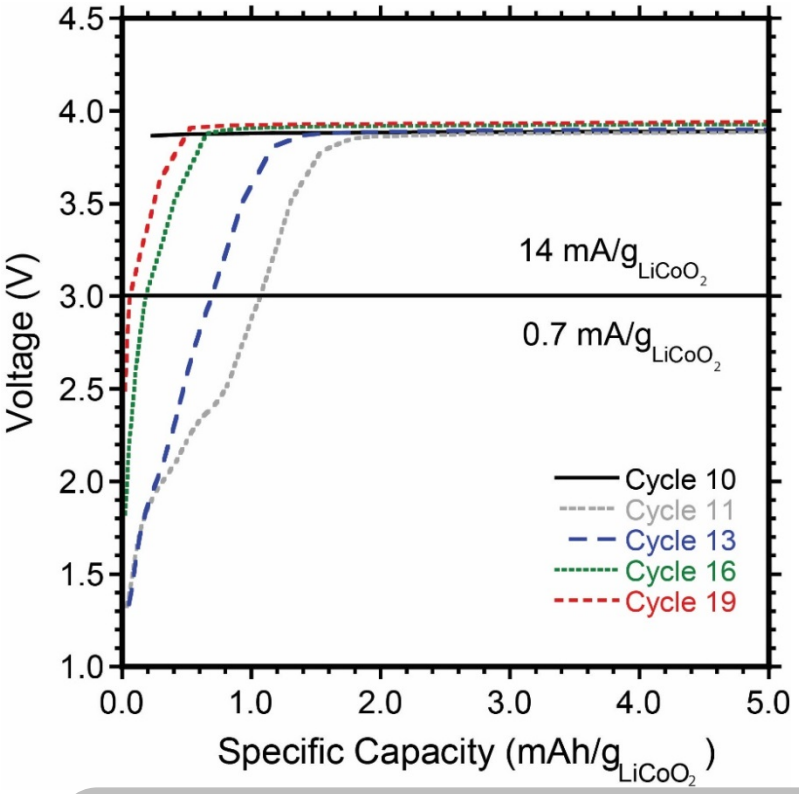
$AlPO_4$ coated $LiCoO_2$



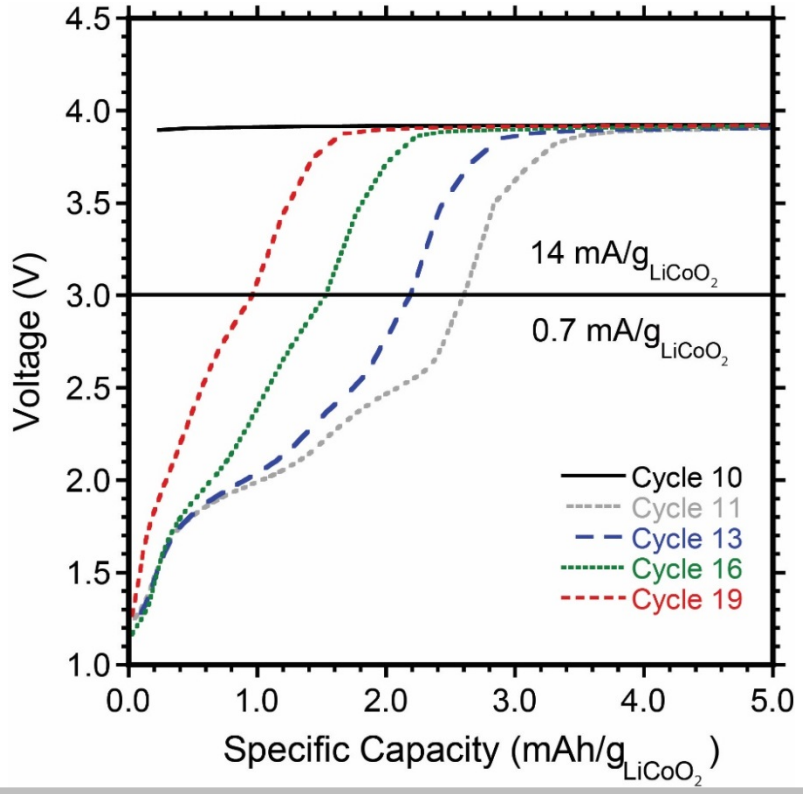
Over-insertion voltage curves more consistent in $AlPO_4$ coated $LiCoO_2$, suggesting irreversible transformation of $LiCoO_2$ by over-insertion is decreased

Initial charge step curves

As-received $LiCoO_2$



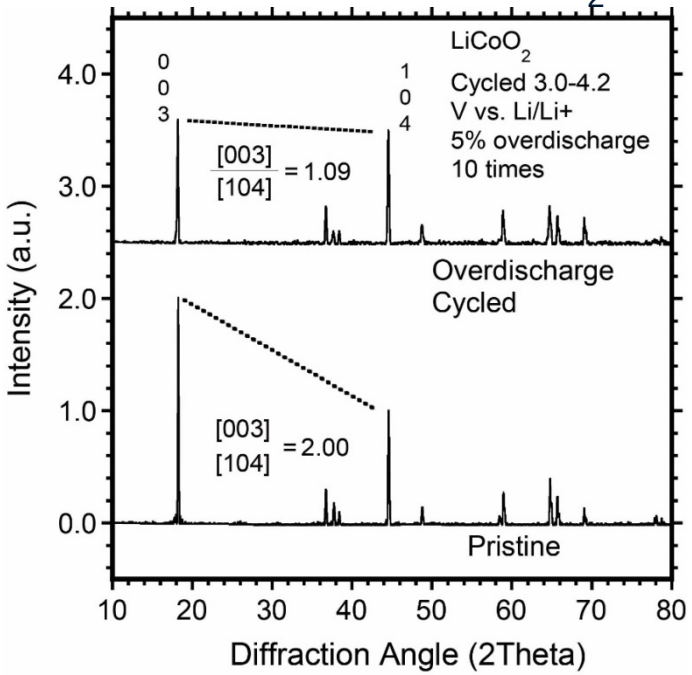
$AlPO_4$ coated $LiCoO_2$



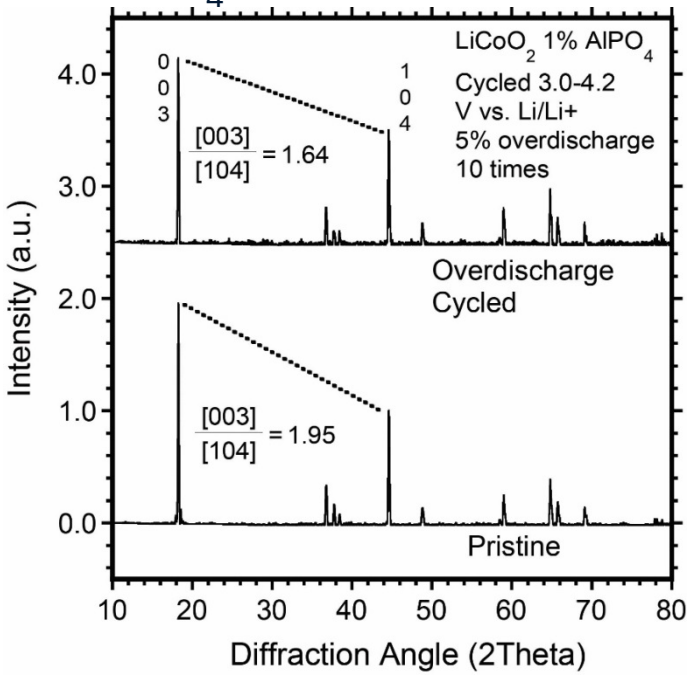
More significant plateau features in $AlPO_4$ coated $LiCoO_2$ indicate the $AlPO_4$ coating makes over-insertion processes more reversible

X-ray diffraction

As-received $LiCoO_2$



$AlPO_4$ 1% w/w coated $LiCoO_2$



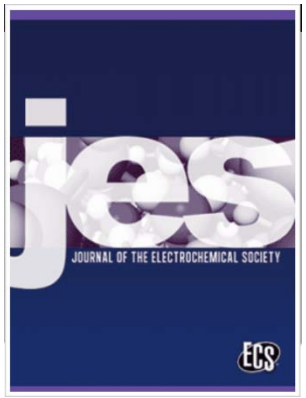
- Decrease in relative magnitude of [003] peak indicates Li^+ Co^+ exchange in the crystal structure[1-2], which is consistent with Li_2O formation found in a prior study[3]

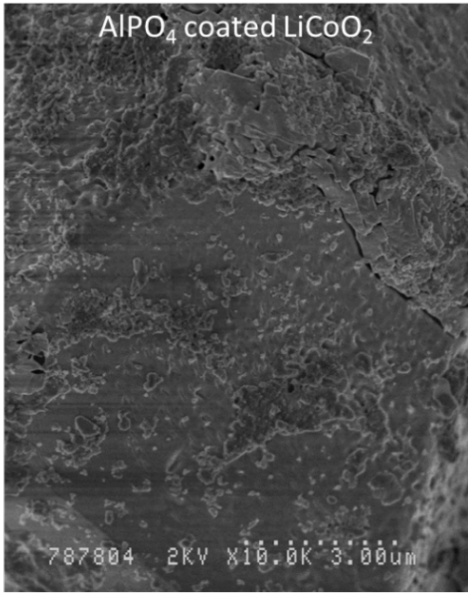
Data with support from previous studies suggests that the $AlPO_4$ coating suppresses irreversible cation exchange in the $LiCoO_2$ crystal during lithium over-insertion

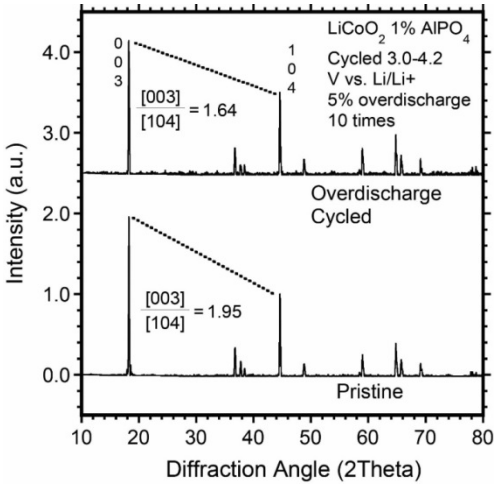
1. H. Wang, Y. Jang, B. Huang, D. R. Sadoway and Y. Chiang, J. Electrochem. Soc., 1999, 146, 473–480.
2. R. J. Gummow, M. M. Thackeray, D. W. I. F. and S. Hull, Mater. Res. Bull., 1992, 27, 327–337.
3. Shu, J. et al. A new look at lithium cobalt oxide in a broad voltage range for lithium-ion batteries. J. Phys. Chem. C 114, 3323–3328 (2010).

Conclusions

- Solution deposited $AlPO_4$ coating onto $LiCoO_2$ stabilizes material performance against repeated over-insertion of lithium
- XRD data shows that $AlPO_4$ prevents irreversible cation exchange in the $LiCoO_2$ crystal







K. R. Crompton, M. P. Hladky, J. W. Staub, and B. J. Landi, *J. Electrochem. Soc.*, **164**, A3214–A3219 (2017)

New Customer/Sponsor support capability

- With new lab we can perform
  - Half-cell performance testing of harvested electrodes from cell dissections
  - 3-electrode performance testing of harvested electrodes from cell dissections
  - Third-party testing of lithium-ion cell components (i.e. powders, electrodes, separators, electrolytes) as part of verification or lot acceptance protocols

Questions

Thank you!