# ENABLING HIGH-ENERGY/ VOLTAGE LITHIUM-ION CELLS: ELECTROLYTES AND ADDITIVES

ES252

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2017 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

# OVERVIEW

## Timeline

- Start: October 1, 2014
- End: Sept. 30, 2018
- Percent complete: 65%

## Budget

- Total project funding:
  - FY16 - $4000K
- ES252, ES253, and ES254

## Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

## Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

# PROJECT OBJECTIVES - RELEVANCE

**Energy fade during calendar-life and cycle-life aging limits the commercial viability of lithium-ion cells for transportation applications**

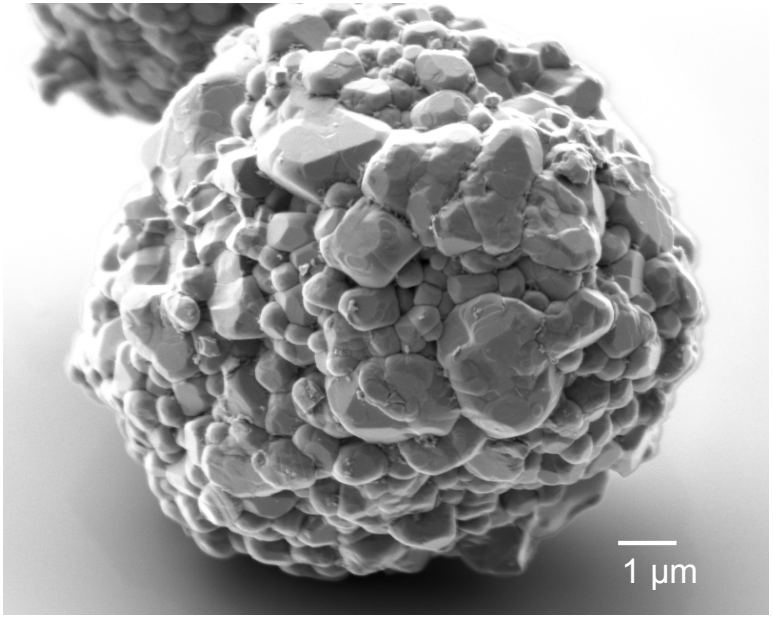
- High-performing, high-energy, safe and long-life batteries are needed to reduce petroleum consumption in vehicular applications
- Performance targets of plug-in electric vehicle (PEV) and electric vehicle (EV) batteries can be met by cells containing layered-oxide-based positive electrodes
- To achieve the energy and power density targets, cells with these electrodes must be cycled to voltages that exceed 4.5 V vs. $Li/Li^+$
- On extended cycling at these voltages, capacity loss, impedance rise and voltage fade reduce the cell's energy and power output
- Our approach is to determine reasons for this loss in performance and to develop solutions (*novel electrolytes and electrolyte additives in this presentation*) to minimize the degradation.

# APPROACH - PROJECT

- Determine factors that contribute to performance decline (capacity fade, impedance rise) in the baseline NMC532/Graphite cells
  - Use various diagnostic tools and techniques to determine cell constituents and reaction mechanisms associated with this performance loss
- Identify additives, which when incorporated into our baseline electrolyte (Gen2) consisting of 1.2M $LiPF_6$ in EC:EMC (3:7 w/w), reduces cell degradation
  - Provide an understanding of electrolyte-additive mechanisms through experimental and computational techniques
- Identify novel electrolyte systems that outperform the baseline Gen2 electrolyte
  - Examine fluorinated electrolytes which are known for high-voltage stability
  - Conduct diagnostic studies to explain their performance characteristics
- Establish protocols to examine oxidative stability of electrolytes
  - Investigate and model the parasitic currents observed at high cell voltages
- Develop electrochemical models to explain electrode and cell performance and performance loss in high-energy/high-voltage lithium ion systems
  - Expand and improve data base and modeling capabilities
- Report and publish the knowledge gained, so as to accelerate the development of high energy, high voltage cells that are suitable for vehicular applications.

# ELECTRODES FABRICATED AT THE CAMP FACILITY ARE USED FOR VARIOUS TESTS

## Baseline Cells: NMC532-based positive & graphite-based negative electrodes

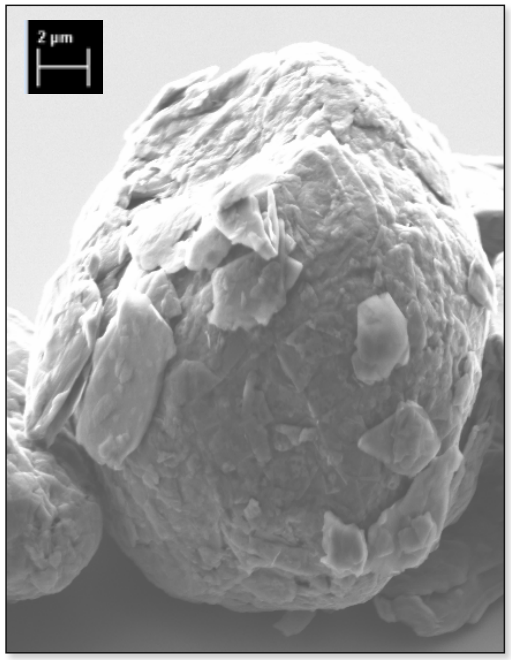



Positive Electrode contains

- 90 wt% NMC532 Oxide
- 5 wt% C45 carbon
- 5 wt% PVdF binder

Baseline Electrolyte

- 1.2 M $LiPF_6$ in EC/EMC (3:7)



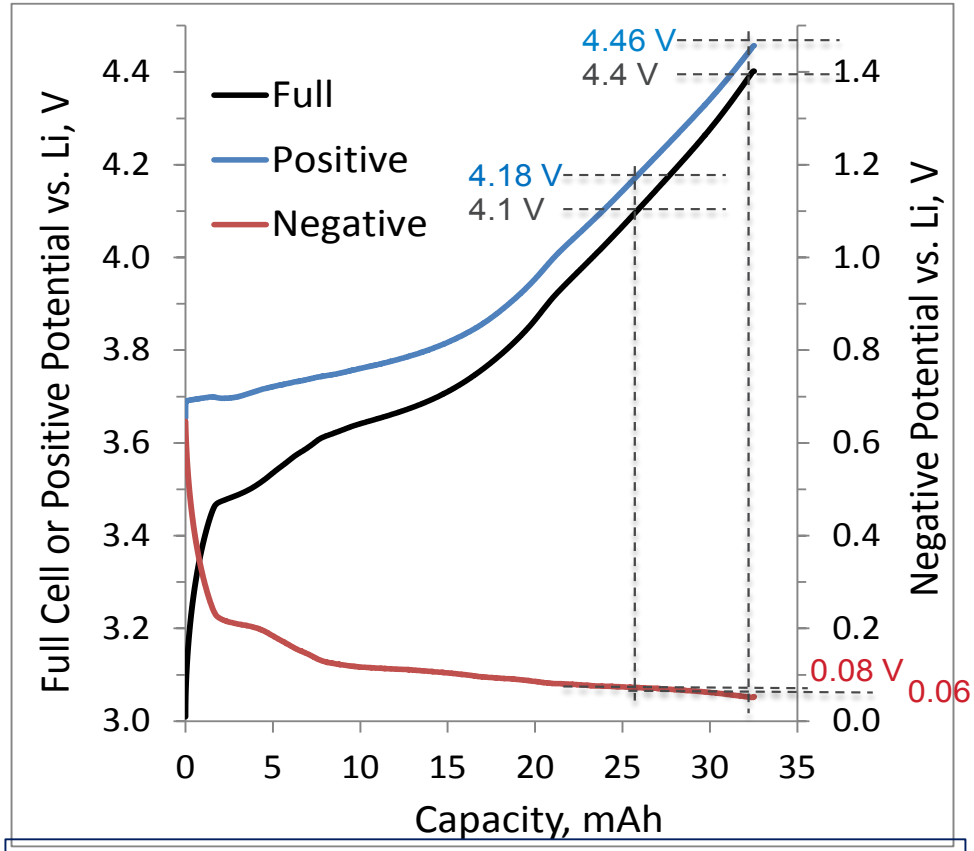

Negative Electrode contains

- 92 wt% A12 Graphite
- 2 wt% C45 carbon
- 6 wt% PVdF binder

# PERFORMANCE DEGRADATION OF CELLS WITH THE BASELINE CHEMISTRY

## Current Understanding

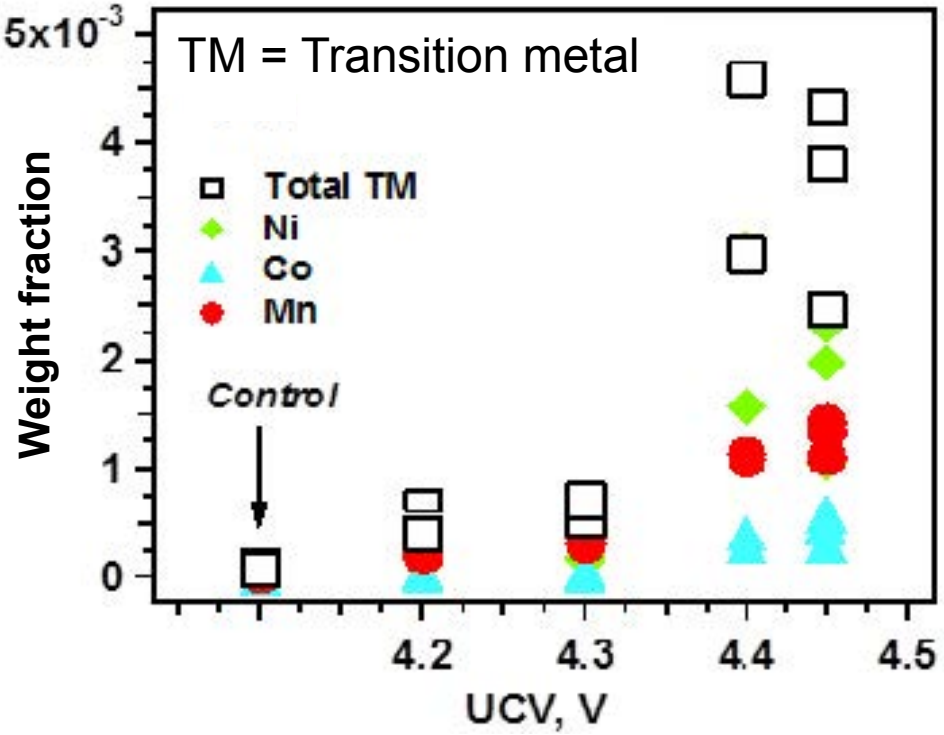
- Cell capacity loss (measured at low rates) arises from $Li^+$ trapping in negative electrode SEI.
- Impedance growth arises mainly at the positive electrode with major contributions from the electrode-electrolyte interface.



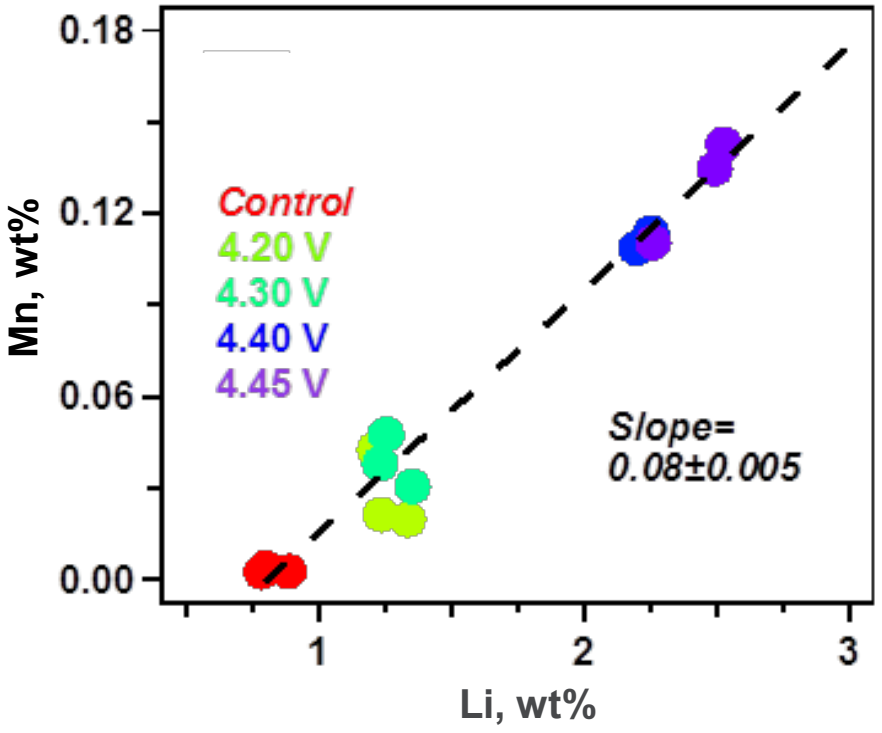

Why would an increase in positive electrode potential increase $Li^+$ ion trapping at the negative electrode?

# CELL CAPACITY LOSS INCREASES AS UPPER CUTOFF VOLTAGE (UCV) INCREASES

## TM content at negative electrode also increases with UCV



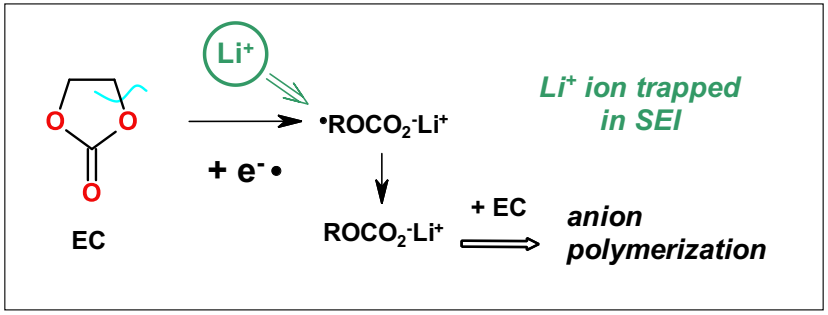

Higher TM content and greater variation at higher UCV

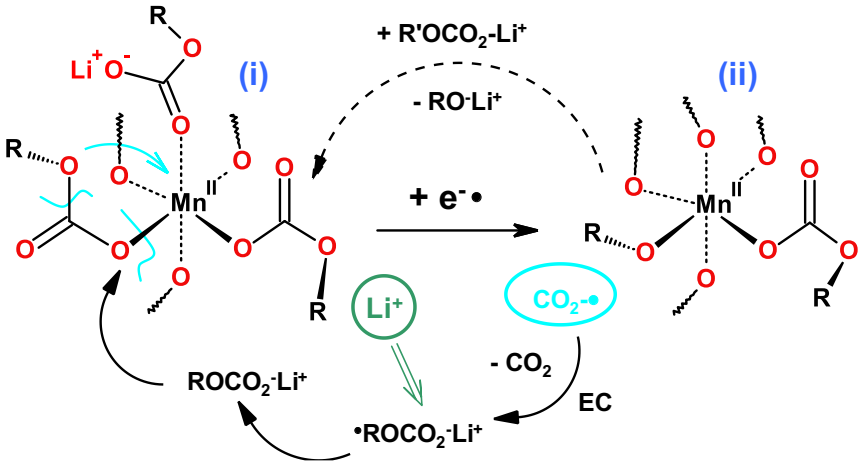



Correlation between Mn and Li content in negative electrode

# ELECTROCATALYSIS MECHANISM TO EXPLAIN THE INFLUENCE OF MANGANESE IONS

## For each Mn ion in SEI, ~ 100 $Li^+$ ions become trapped



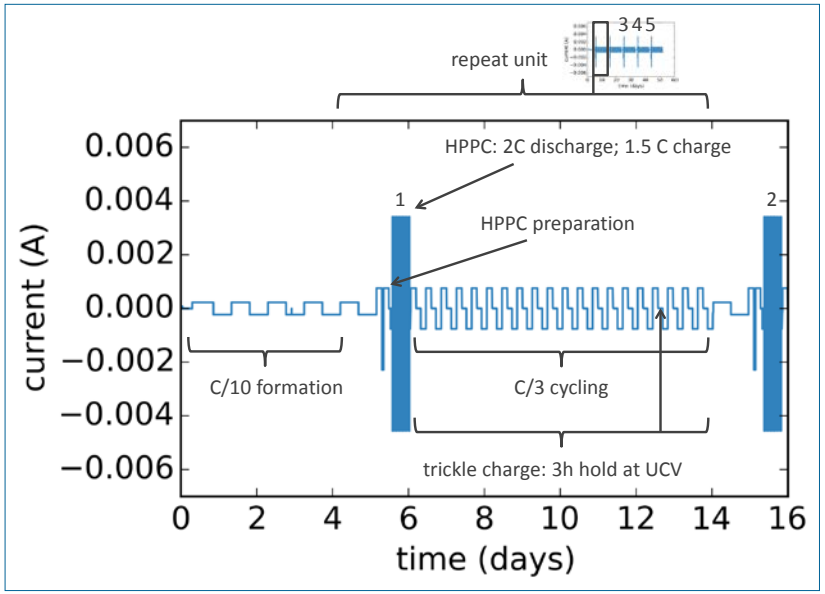




***Top***: The box shows the common reduction pathway that does not involve TM ion catalysis. Electron transfer to ethylene carbonate (EC) causes ring opening and the formation of a radical anion that pairs with a $Li^+$ ion and eventually becomes an open chain carbonate anion ($•ROCO_2^-Li^+$) that can initiate anion polymerization of EC.

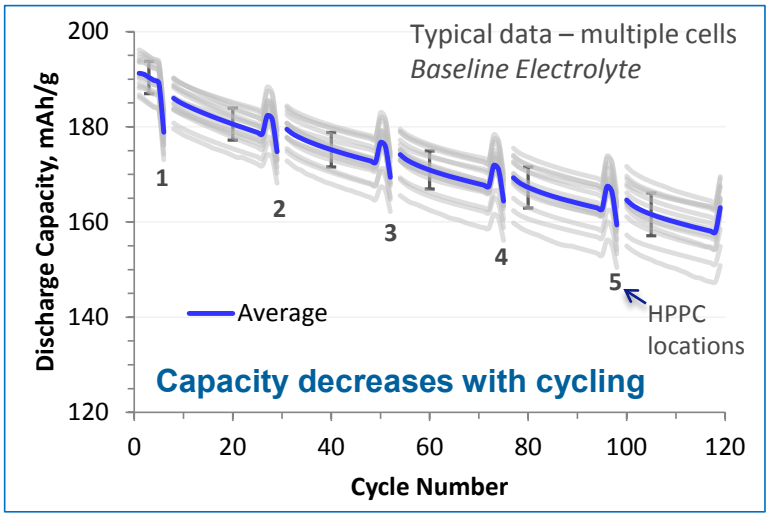
***Below***: complexation of such anions by $Mn^{II}$ in the SEI matrix yields an active center (complex i) that, after accepting an electron (complex ii), can reduce these anions straight to alkoxide anions ($RO^-$) and yield a carbon dioxide radical anion $CO_2^{-•}$ that diffuses through the outer SEI matrix towards the solvent and reduces it therein, converting to $CO_2$ and trapping lithium. In this way, reductive equivalents become "transferred" from the inner SEI outwards. As the carbonates replace oxides in the inner sphere of complex ii, there is a turnover of the electrocatalytic center (i).

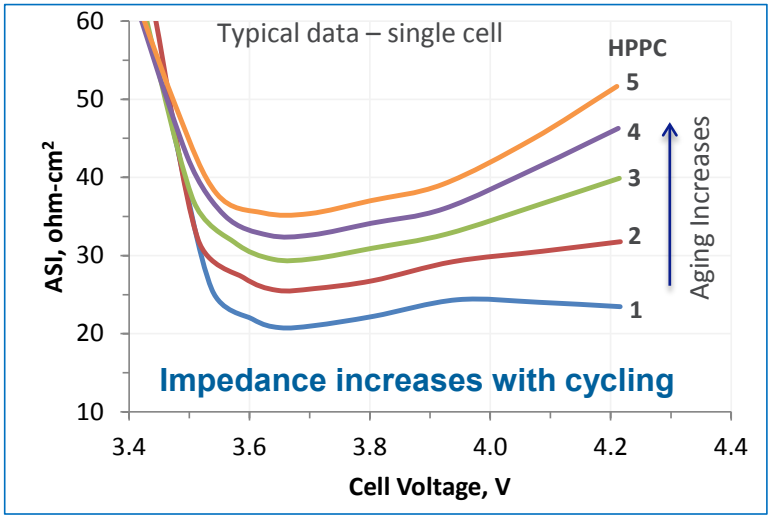
# STANDARD PROTOCOL USED TO TEST EFFECT OF ELECTROLYTES AND ADDITIVES

## Coin Cells, NMC532/Gr, 3-4.4 V, 30°C



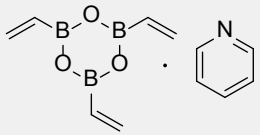
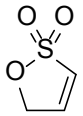
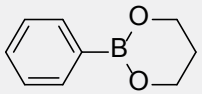
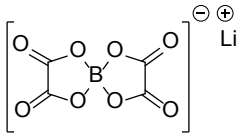
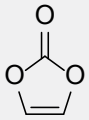

- Initial capacity (Cycles 1-4)
- Rate Information (Cycles 5&6)
- HPPC Impedance (Cycle 7)
- Aging @C/3 Rate (Cycles 8-26)
- Aging of “True” Capacity (Cycle 27)

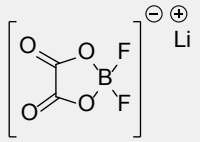
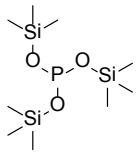
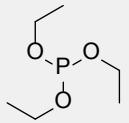


# ELECTROLYTE ADDITIVES FOR THE NEGATIVE AND POSITIVE ELECTRODES

## Selection rationale based on information in the research literature

| Negative additive | Structure | Wt % |
|---|---|---|
| 2,4,6-trivinylcyclotriboroxane (**tVCBO**) |  | 0.25 |
| Prop-1-ene-1,3-sultone (**PES**) |  | 2.0 |
| Phenyl boronic acid ethylene glycol ester (**PBE**) |  | 0.25 |
| Lithium bis(oxalato)borate (**LiBOB**) |  | 1.0 |
| Vinylene carbonate (**VC**) |  | 2.0 |

| Positive additive | Structure | Wt % |
|---|---|---|
| Lithium difluoro(oxalate)borate (**LiDFOB**) |  | 2.0 |
| Tris(trimethylsilyl) phosphite (**TMSPi**) |  | 1.0 |
| Triethyl phosphite (**TEPi**) |  | 1.0 |

**Could these compounds help form a robust SEI and lower capacity fade?**

**Could these compounds "protect the oxide" and lower impedance rise?**

# ENERGY FIGURE OF MERIT (ENERGY FOM)

**Baseline**
170.0

## Matrix of Additives

| Cathode additives | Anode additives: LiBOB | PBE | PES | tVCBO | VC |
|---|---|---|---|---|---|
| LiDFOB | 122.7 | 88.5 | 128.2 | 110.7 | 110.3 |
| TEPi | 116.1 | 84 | 77.6 | 96.9 | 147.3 |
| TMSPi | 114.8 | 168.7 | 154.2 | 203.6 | 200.4 |

Better


Worse

**Energy FOM** is the extrapolated cycle number at which the cell energy density (Wh/$kg_{oxide}$) decreases to ***80% of the baseline*** (Gen2) system.

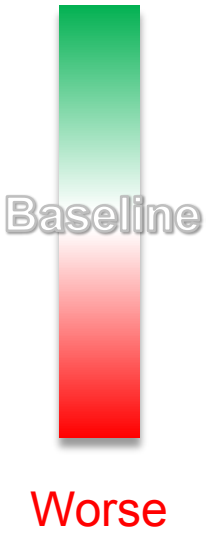
- Energy FOM for Gen2 cells is 170 cycles.
- Only the tVCBO + TMSPi and VC + TMSPi additive combinations have Energy FOMs better than that of the baseline electrolyte

# POWER FIGURE OF MERIT (POWER FOM)

**Baseline**
23.3

## Matrix of Additives

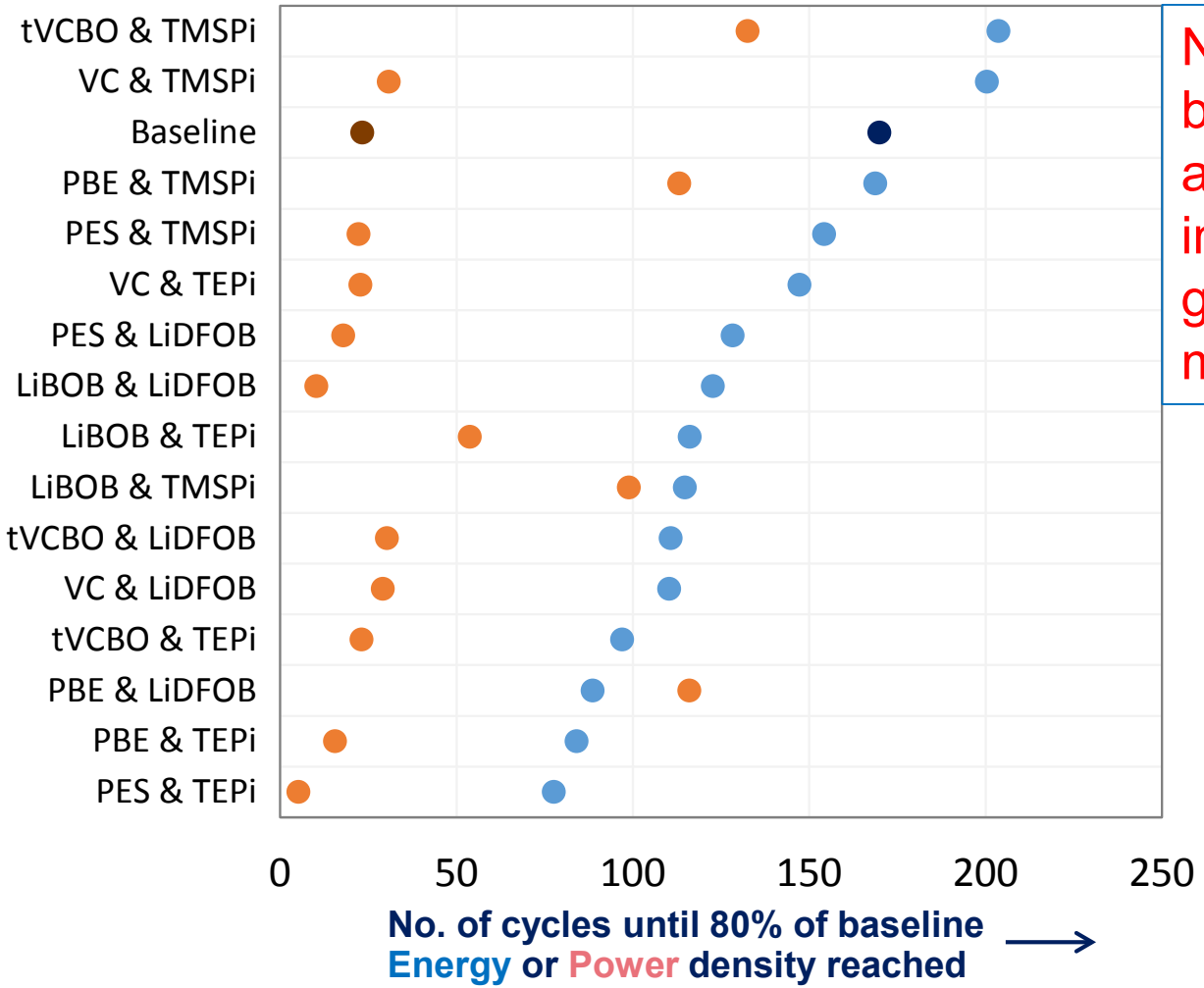
| Cathode additives | Anode additives: LiBOB | PBE | PES | tVCBO | VC |
|---|---|---|---|---|---|
| LiDFOB | 10.3 | 116 | 17.9 | 30.2 | 29.1 |
| TEPi | 53.7 | 15.5 | 5.2 | 23 | 22.8 |
| TMSPi | 98.8 | 113 | 22.2 | 133 | 30.8 |




**Power FOM** is the extrapolated cycle number at which power density at 80% state of charge decreases to ***80% of the baseline*** system.

- Power FOM for baseline (Gen2) cells is 23 cycles.
- Several combinations with TMSPi have high Power FOM values

# ENERGY FOM VS. POWER FOM

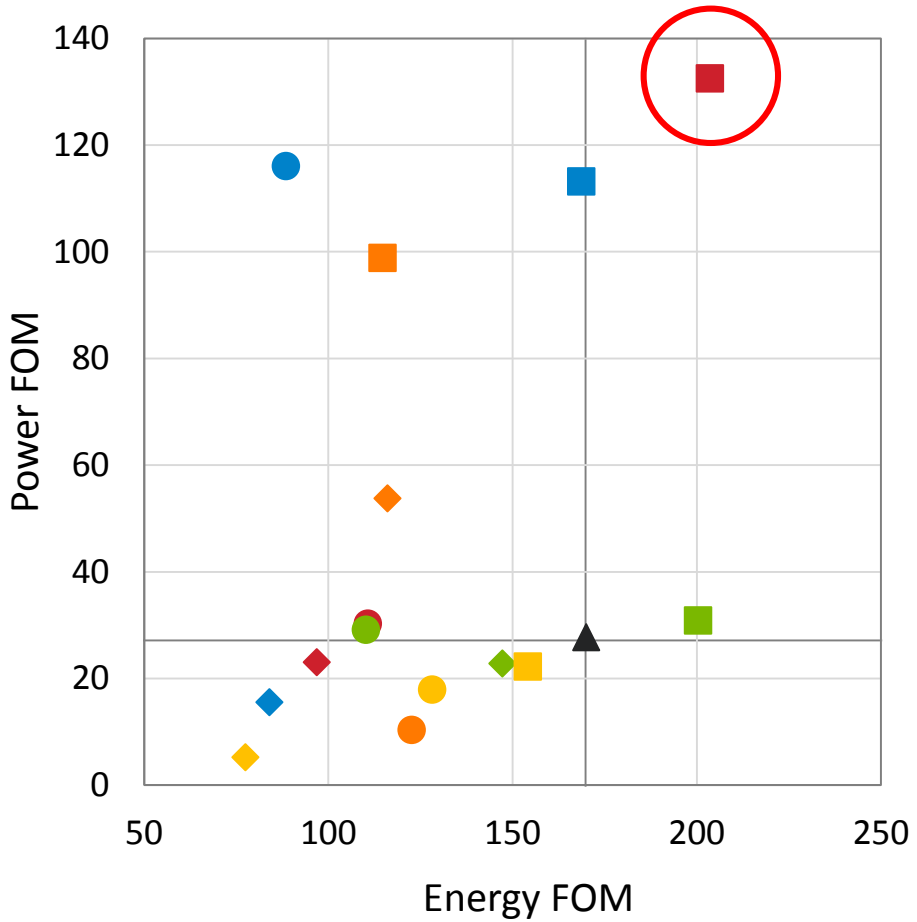



No apparent correlation between Energy FOM and Power FOM, which indicates that they are governed by separate mechanisms.

# ENERGY FOM VS. POWER FOM - REPLOTTED

| Anode | Cathode |
|---|---|
| VC | LiDFOB ◯ |
| PES | TMSPi □ |
| LiBOB | TEPi ◇ |
| PBE | |
| tVCBO | |

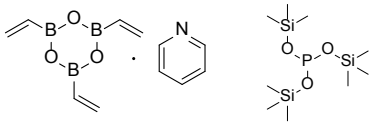
| | |
|---|---|
| - Energy<br>+ Power | + Energy<br>+ Power |
| - Energy<br>- Power | + Energy<br>- Power |




**Cells with the (0.25 wt% tVCBO + 1 wt% TMSPi) additive have the best Energy FOM and Power FOM**

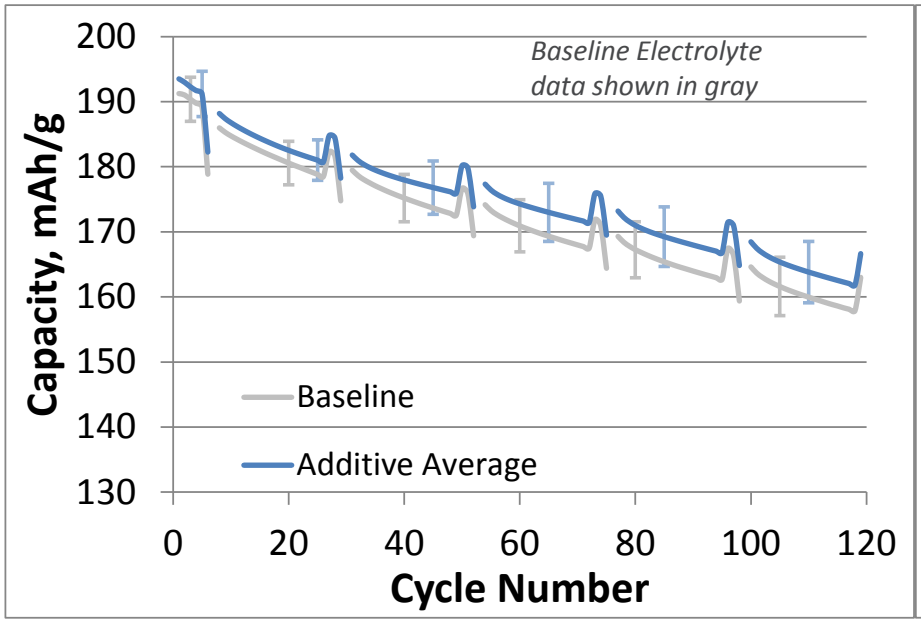
# EXAMPLE DATA FROM "BEST" ELECTROLYTE

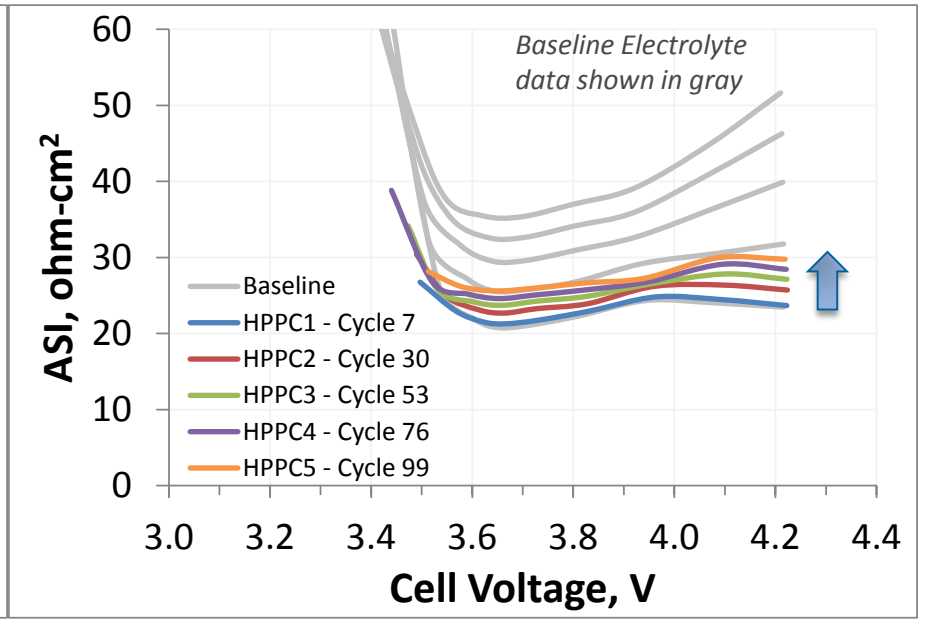
0.25 wt% tVCBO
+ 1.0 wt% TMSPi





| Electrolyte | Energy FOM | Power FOM |
|---|---|---|
| Baseline | 170 | 23 |
| tVCBO + TMSPi | 203 | 132 |



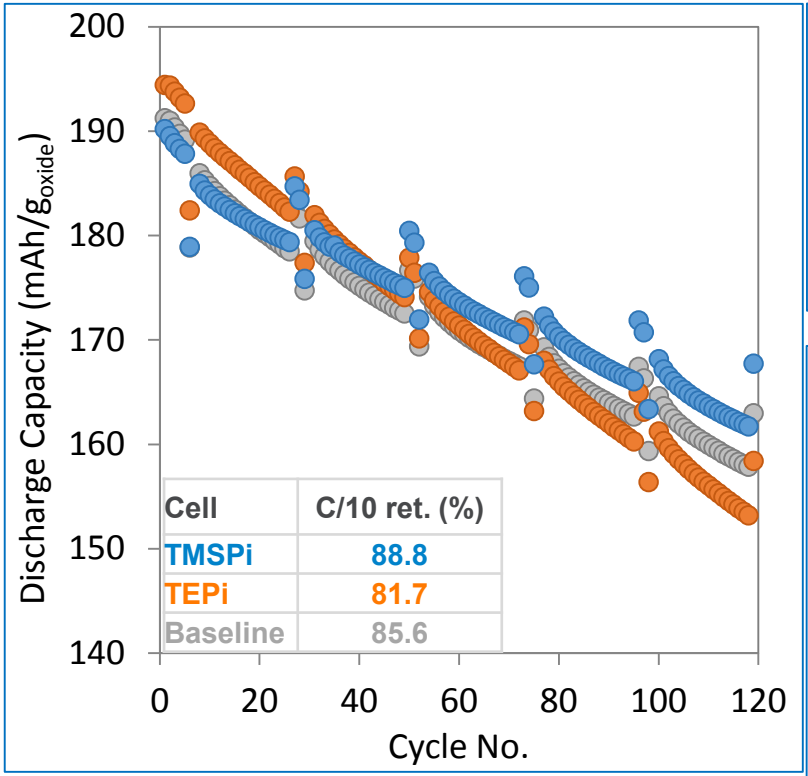




**Electrolyte additive improves cell capacity retention**

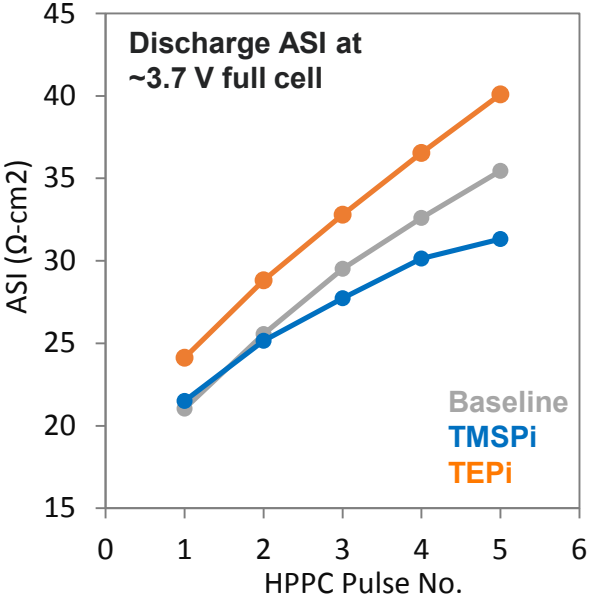
**Electrolyte additive lowers cell impedance rise**

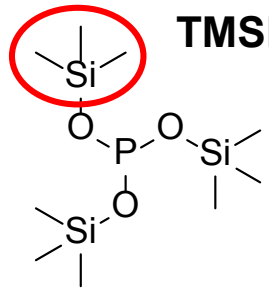
# TMSPI AND TEPI ARE STRUCTURALLY ANALOGOUS YET BEHAVE DIFFERENTLY

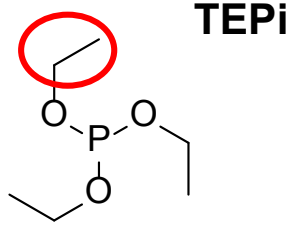
## Functional groups are different - Trimethyl silyl (TMS) vs. Ethyl




Cells with TMSPi display better capacity retention and lower impedance rise than the baseline. In contrast, cells with TEPi show poorer capacity retention and higher impedance rise. **Why the difference?**



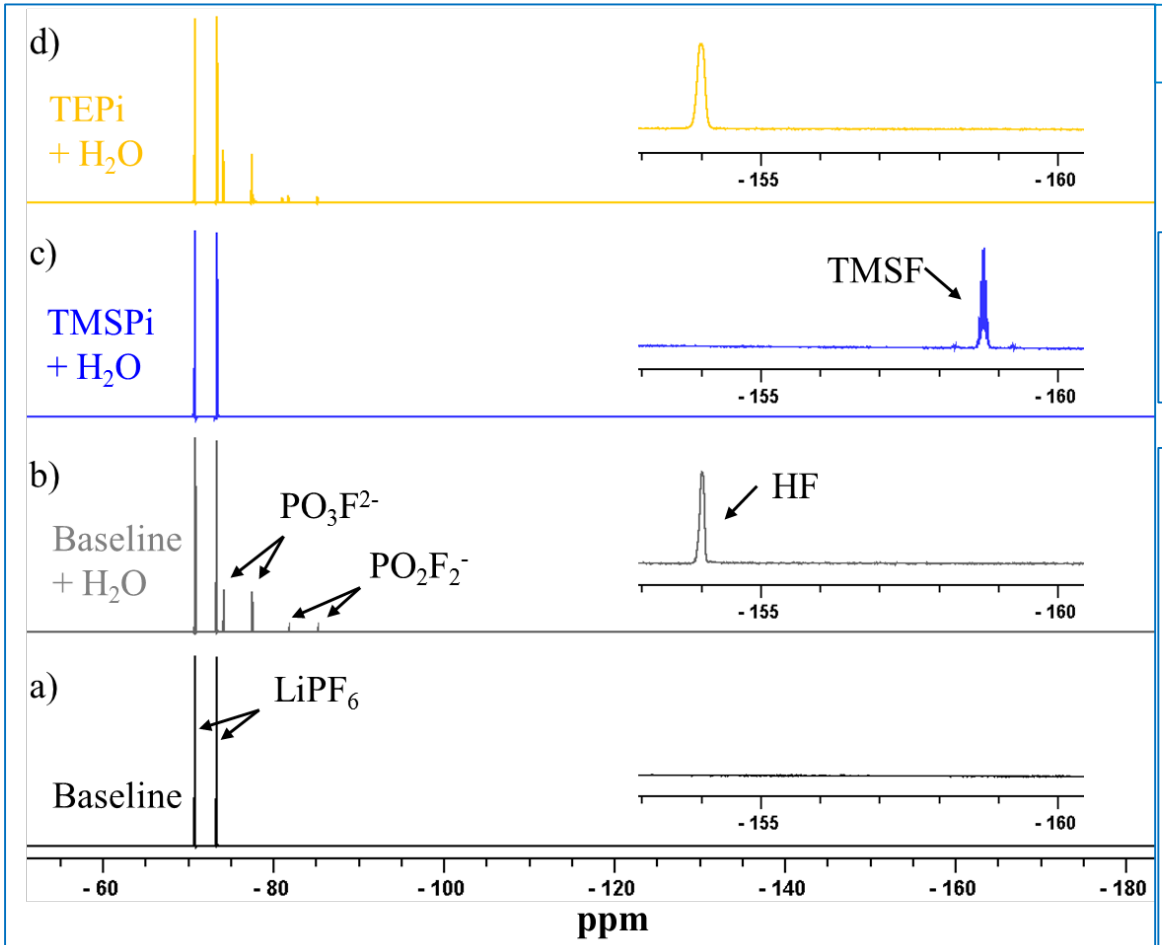



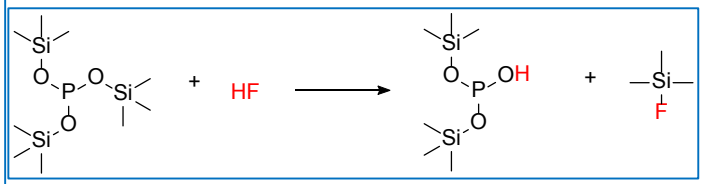

**Performance differences between TMSPi and TEPi**

# TMSPI (BUT NOT TEPI) IS ABLE TO SCAVENGE HF FROM ELECTROLYTE SOLUTIONS

## Water added to Baseline (Gen2) electrolyte to generate HF




**$^{19}$F NMR spectra**



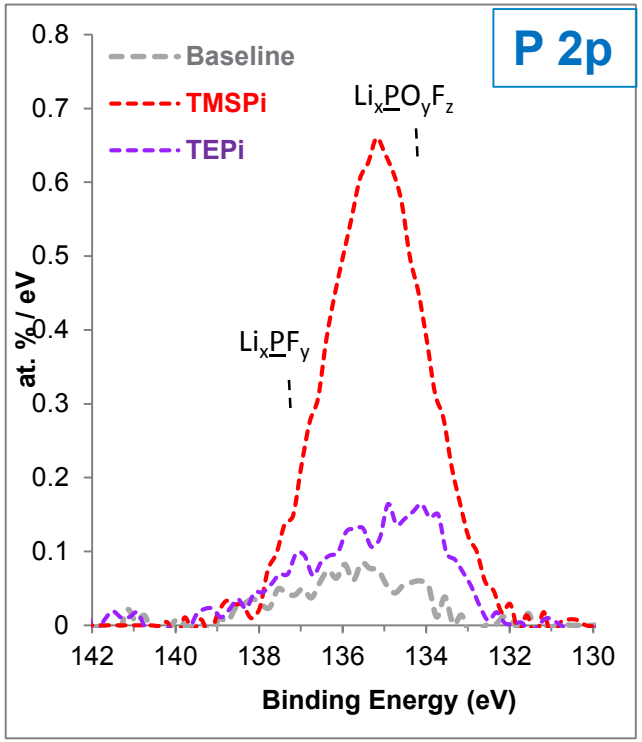

$LiPF_6$ hydrolysis species are generated when water is added to the baseline electrolyte.

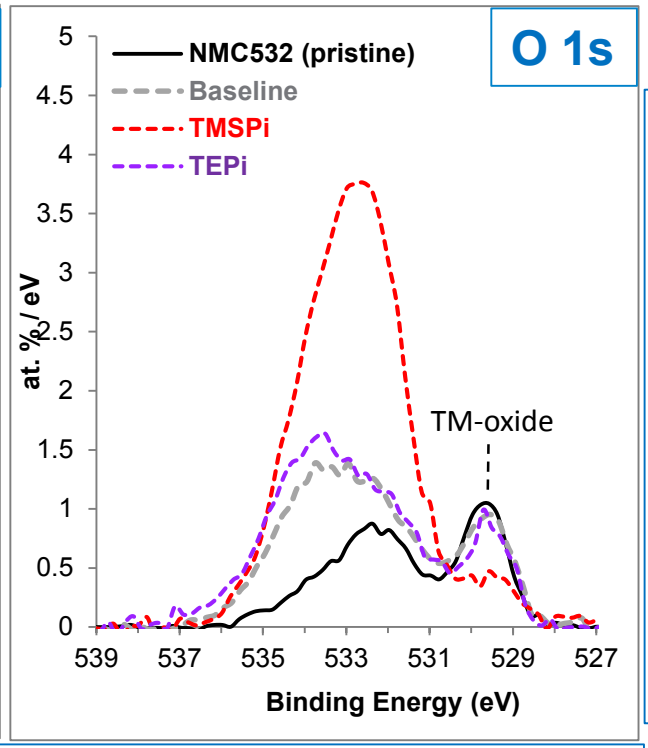
These species are also observed in solutions containing TEPi.

These species are **not** observed in solutions with TMSPi. Instead TMSF is observed (reaction with HF shown above).

# XPS DATA SHOW P AND O RICH FILMS ON OXIDE ELECTRODES FOR CELLS WITH TMSPI

## After cell formation – data acquired at Argonne's Post-Test Facility




### In addition

**ICP-MS data** show lower TM contents on graphite electrodes for cells with TMSPi.

In contrast, graphite electrodes from TEPi cells show TM contents that are higher than those of the baseline.

Oxide surface films also appear to be thicker with TMSPi.

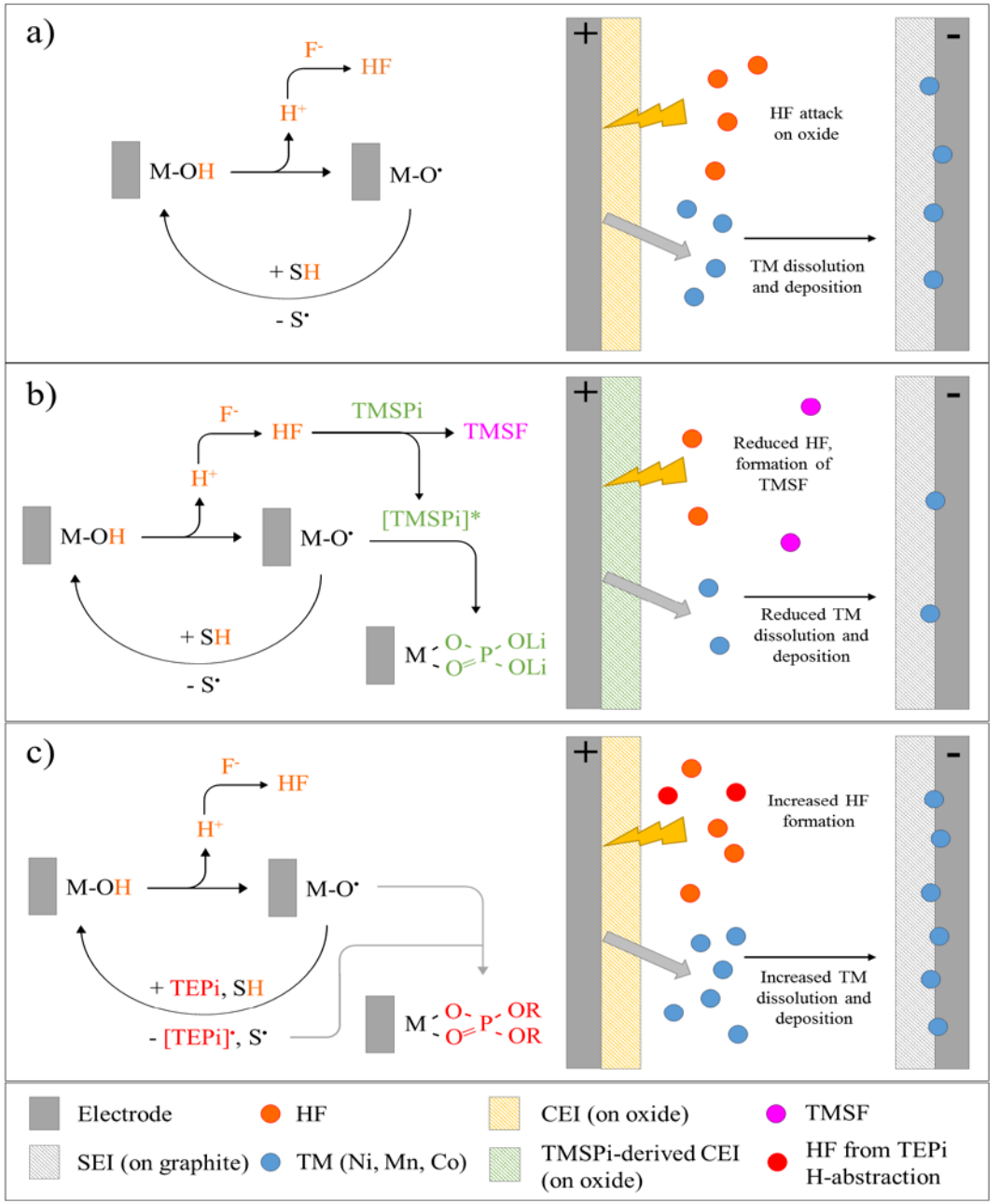
Surface films with TEPi are similar to that of the baseline.

# TMSPI VS. TEPI: DIFFERENCES IN MECHANISMS

Baseline Cell: Oxygen dangling bond centers (M-O• radicals) abstract hydrogen atoms from solvent molecules generating solvent radicals and transient M-OH species. The abstracted hydrogen reacts with fluorine species in the electrolyte to form HF that enhances TM dissolution from the oxide electrode.

TMSPi Cell: Reaction of TMS groups with HF leads to formation of TMSF and [TMSPi*], which bonds with M-O• species to form a **protective** film at the oxide surface.

TEPi Cell: Hydrogen abstraction from the TEPi alkyl groups generates HF which increases TM dissolution. The oxidized TEPi [TEPi]• eventually forms a P- and O-rich film at the oxide surface.

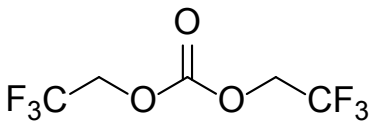


# FLUORINATED ELECTROLYTES SHOW HIGHER INITIAL IMPEDANCE

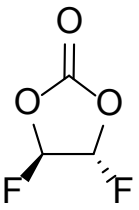
## NMC532/Gr, 3.0-4.4 V cycles

Gen2: 1.2M $LiPF_6$ in 3:7 w/w EC: EMC

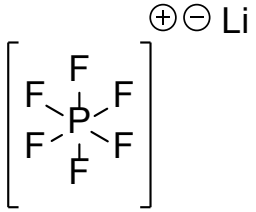
**FE3: 1M $LiPF_6$ in 3:7 w/w DFEC:HFDEC**

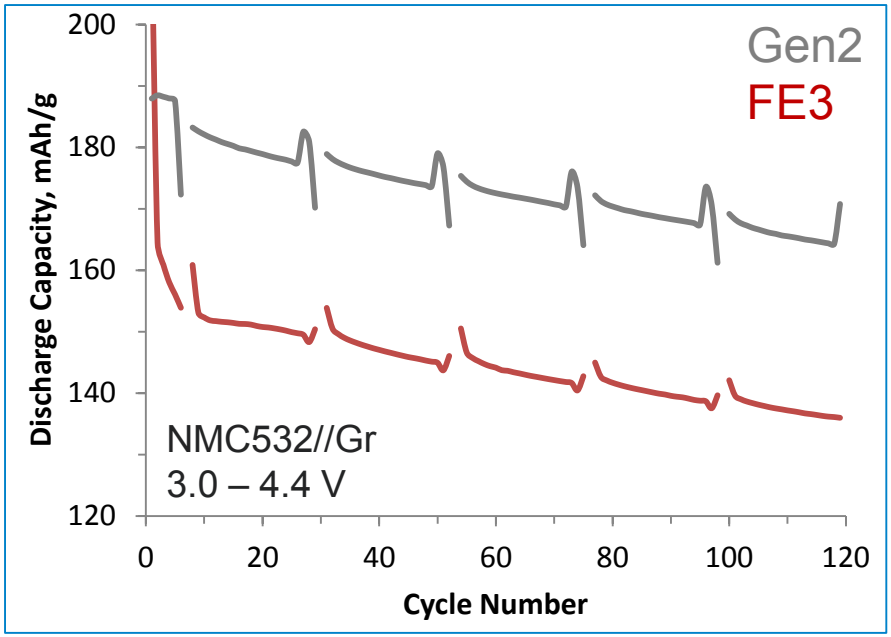


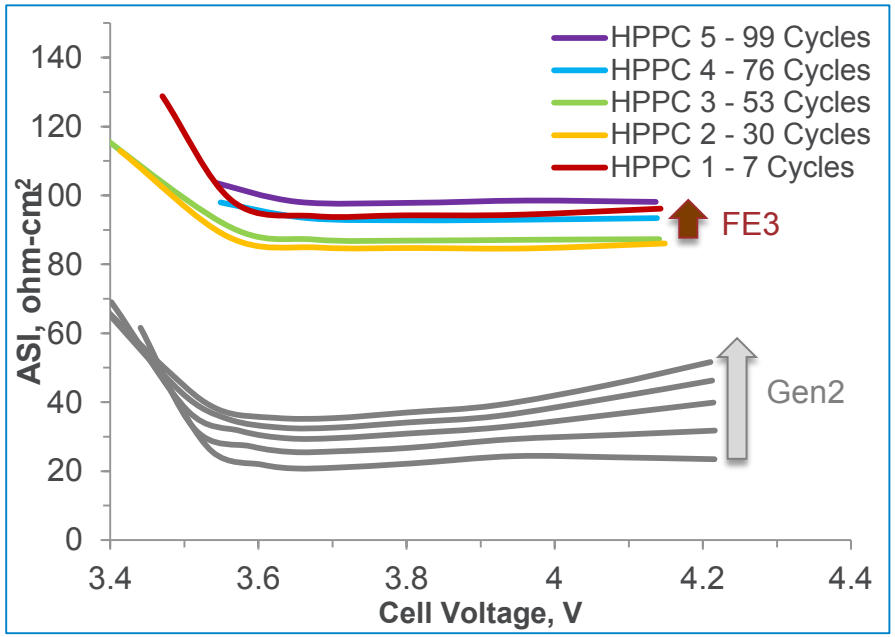

HFDEC




FEC



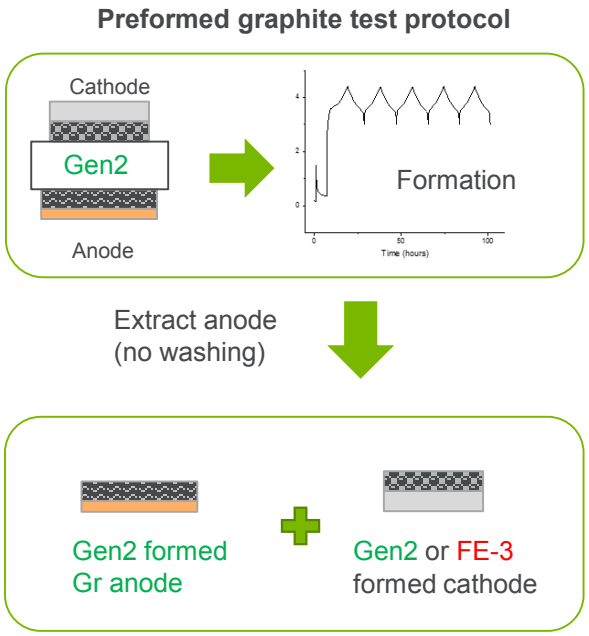

Although initial capacity is lower for FE3, capacity retention is similar to Gen2 cell

Although initial impedance is higher for FE3, impedance rise is slower than for Gen2 cell

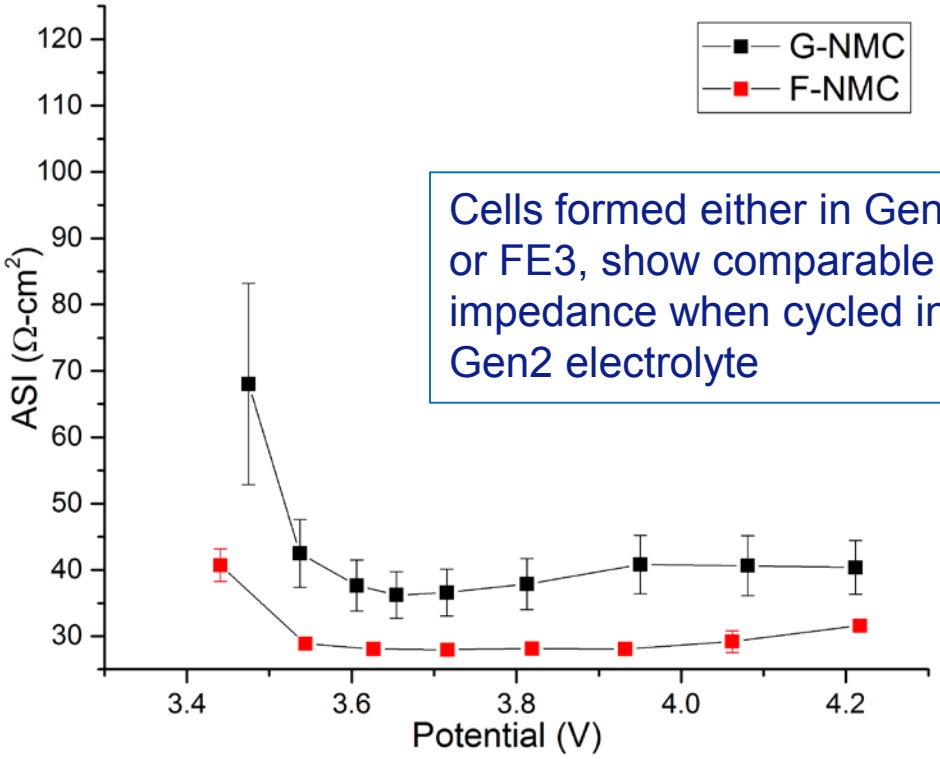
# IDENTIFYING SOURCE OF HIGHER INITIAL IMPEDANCE IN FE3 CELLS - 1

FE3: 1M $LiPF_6$ in 3:7 w/w DFEC:HFDEC

## Does higher impedance originate from LiF in cathode surface film?




1. Tap charge, 3.0-4.4V formation (5 cycles)
2. Preformed anode extracted (minimal LiF)
3. Preformed anode combined with Gen2-formed cathode (minimal LiF) or FE3 formed cathode (has LiF)
4. Evaluated with baseline electrolyte




Cells formed either in Gen2 or FE3, show comparable impedance when cycled in Gen2 electrolyte

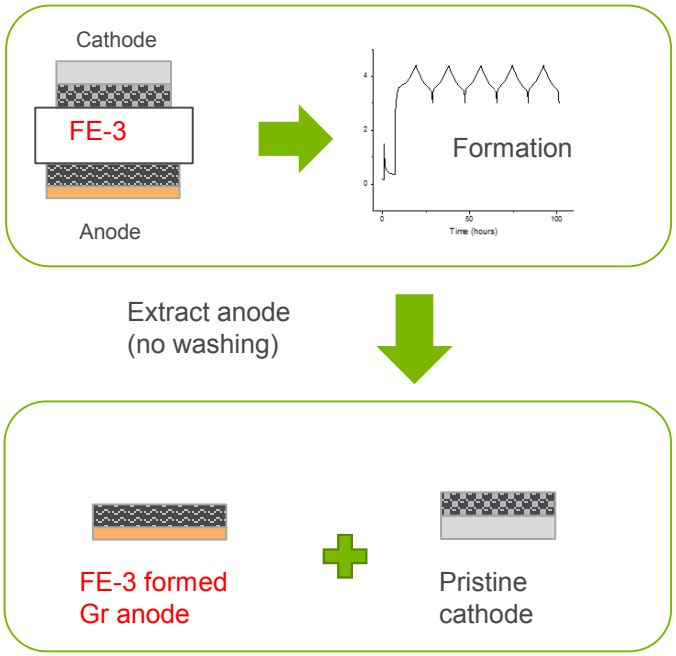
**Species (such as LiF) in cathode surface films are not the source of the high initial impedance observed in FE3 electrolyte**

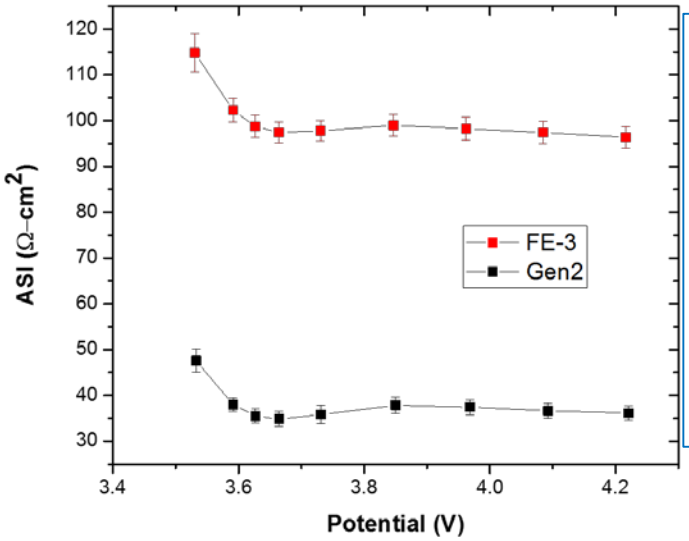
# IDENTIFYING SOURCE OF HIGHER INITIAL IMPEDANCE IN FE3 CELLS - 2

FE3: 1M $LiPF_6$ in 3:7 w/w DFEC:HFDEC

## Does higher impedance originate from LiF in anode SEI?

Preformed graphite protocol



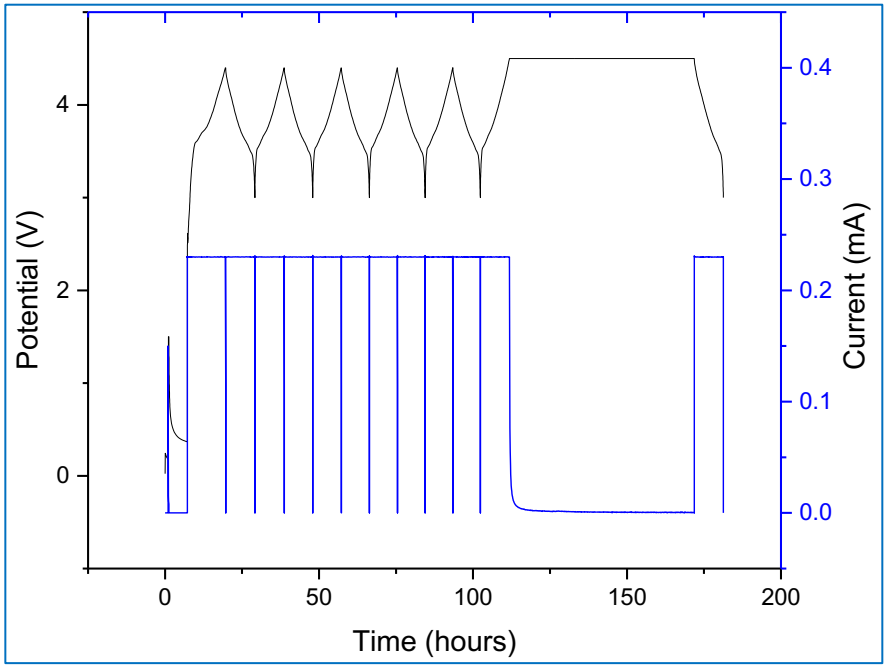

LiF-containing anode shows low impedance with baseline electrolyte, but high impedance with FE3 electrolyte

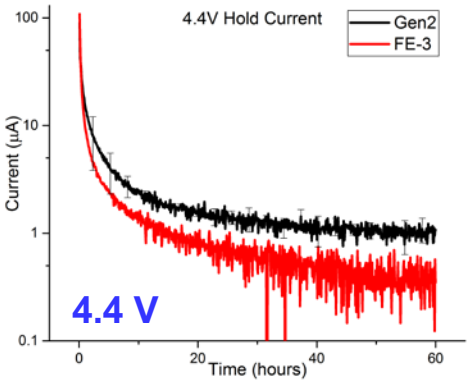
1. Tap charge, 3.0-4.4V formation (5 cycles)
2. Preformed anode extracted (has LiF)
3. Preformed anode combined with pristine cathode
4. Evaluated with FE3 and baseline electrolytes

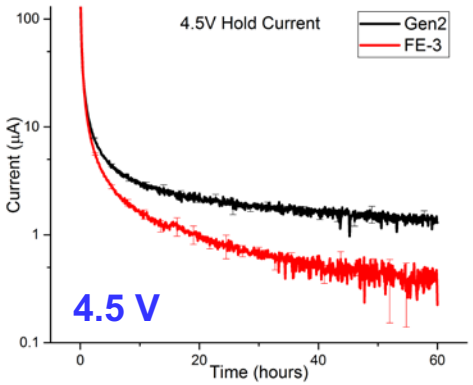
**Species such as LiF in anode are not the source of high initial impedance.**
Electrolyte bulk characteristics (such as resistivity) and electrode/electrolyte interface characteristics (such as solvation and desolvation) cause the high impedance.

# POTENTIOSTATIC HOLD TEST DEVELOPED TO EVALUATE FLUORINATED ELECTROLYTES

## Significantly lower oxidation current for FE3 compared to Gen2




After ~20 hours, polarization processes have relaxed and side reactions dominate the current signal. FE3 cells show lower side reaction currents than Gen2

**Test Protocol**

1. Tap charge, 3.0-4.4V formation (5 cycles)
2. Charge to 4.4 or 4.5V
3. Hold at terminal voltage for 60 h

**FE3 has better stability than Gen2 at the charged cathode surface**

# SUMMARY

- Used a systematic approach to characterize capacity loss as a function of increasing UCV for NMC532/Gr full cells and correlated this loss with transition metal deposition in the negative electrode.
  - Mn and Li contents in graphite anodes correlate well with the capacity fade. We note that ~$10^2$ extra $Li^+$ ions are trapped for every deposited $Mn^{II}$ ion
- Developed Energy and Power Figure of Merit (FOM) criteria to identify additive systems that outperform the baseline electrolyte
  - Cells with the (0.25 wt% tVCBO + 1 wt% TMSPi) additive mixture showed the best Energy FOM and Power FOM
- Examined reasons for the significant performance differences between TMSPi and TEPi additives, which are structurally analogous compounds
  - Determined that TMSPi effectively passivates the positive electrode, whereas hydrogen abstraction from the TEPi alkyl groups generates HF which increases TM dissolution (and thereby, capacity fade)
- Examined source of higher initial impedance of the fluorinated FE3 electrolyte
  - Determined that this higher impedance is an electrolyte characteristic
- Developed a potentiostatic hold test to evaluate electrolytes
  - Showed that fluorinated FE3 electrolyte has better anodic stability than the baseline electrolyte

# FUTURE WORK AND WORK IN PROGRESS

- "Sprints" have identified electrolyte systems that outperform the baseline electrolyte at high cycling voltages
  - Mechanistic details are being investigated. **For example**:
  - Dynamic interactions between TMSPi and the baseline electrolyte improve cell performance – how does this happen?
  - Some fluorinated electrolytes are beneficial while others perform poorly. What are the structure-function relationships that determine cell performance?
- EC-free systems are reported to improve cell performance at high voltages
  - Diagnostic experiments are underway to "understand" these improvements
- Additional efforts are being devoted to examine "cross-talk" in cells
  - Novel test protocols are being developed to quantitate effects of cross-talk
  - Cell chemistries that minimize transition metal deposition at the graphite electrode are being developed.
- Continue development of electrochemical models
  - Utilize EIS electrochemical model to study changes in interfacial transport and kinetic parameters with SEI and surface modifications
  - Complete modeling the parasitic current behavior at high cell voltages

Any proposed future work is subject to change based on funding levels

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***See also ES253, ES254***

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- S.J. An, J. Li, D. Mohanty, C. Daniel, B.J. Polzin, J.R. Croy, S.E. Trask, and D.L. Wood III, "Correlation of Electrolyte Volume and Electrochemical Perfomance of Li-Ion Pouch Cells with Graphite Anodes and NMC532 Cathodes, J. Electrochem. Soc. 164 (2017) A1195-A1202.
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- I. Bloom, R. Sahore, C. Peebles, D.P. Abraham, J. Gilbert, "Effect of Additives on the Performance of High-Voltage, NMC-based Cells: A Combinatorial Approach", J. Electrochem. Soc. 164 (2017) *under review*.


***See also ES253, ES254***

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- Battery Manufacturing Facility (BMF)
- Advanced Photon Source (APS)

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