

From Radiation to Aging: Multiscale Evolution of LiF & Interphases in Lithium Carbon-Monofluoride Batteries

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Space Power Workshop, April 23rd, 2026

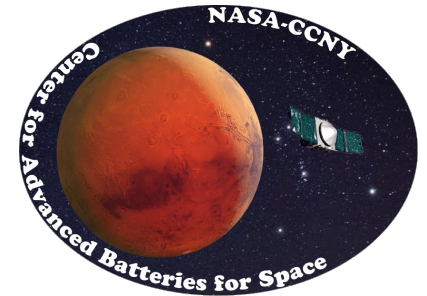
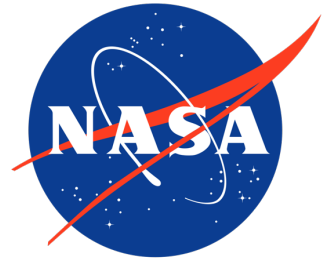
Acknowledgements



Dr. Lola Robinson
Now at 3M (Austin)



Dr. Theresa Schoetz
Now Prof. ChBE, UIUC



#80NSSC19M0199



CAREER: CBET-1847552



Dr. John-Paul Jones
JPL

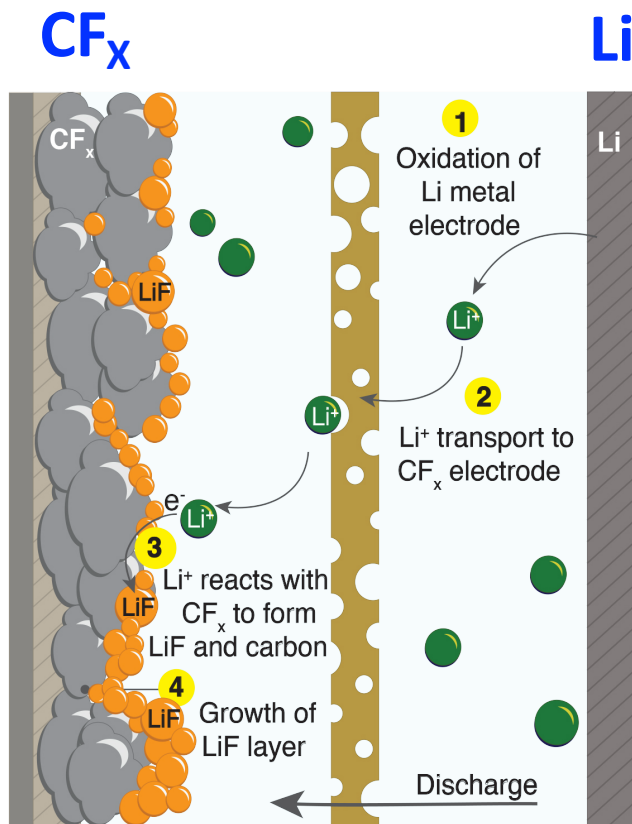


Dr. Will West
JPL



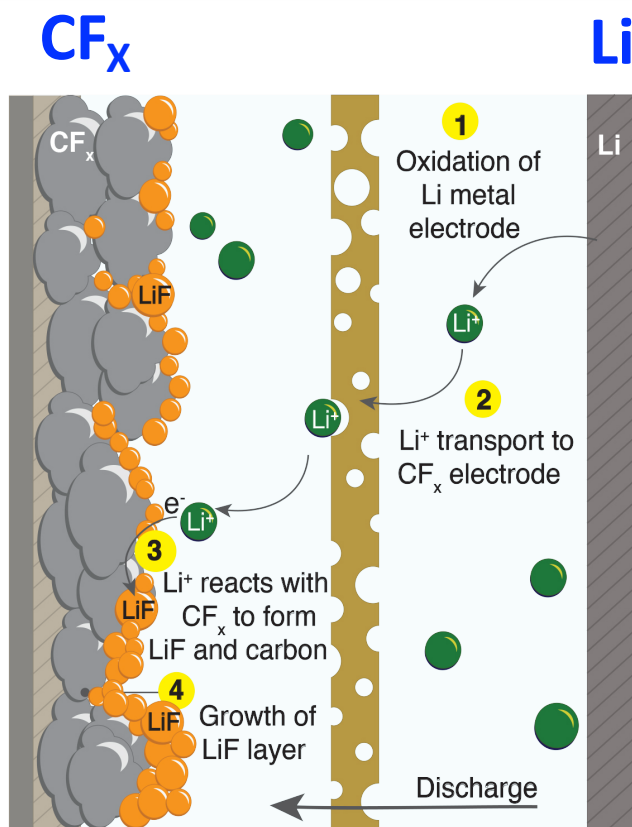
Dr. Erik Brandon
JPL

Li-CF_x: Highest Specific Energy Li Battery (Practical)

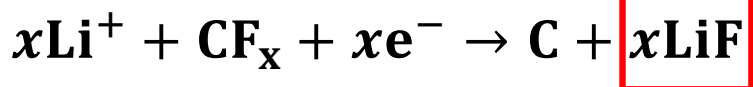
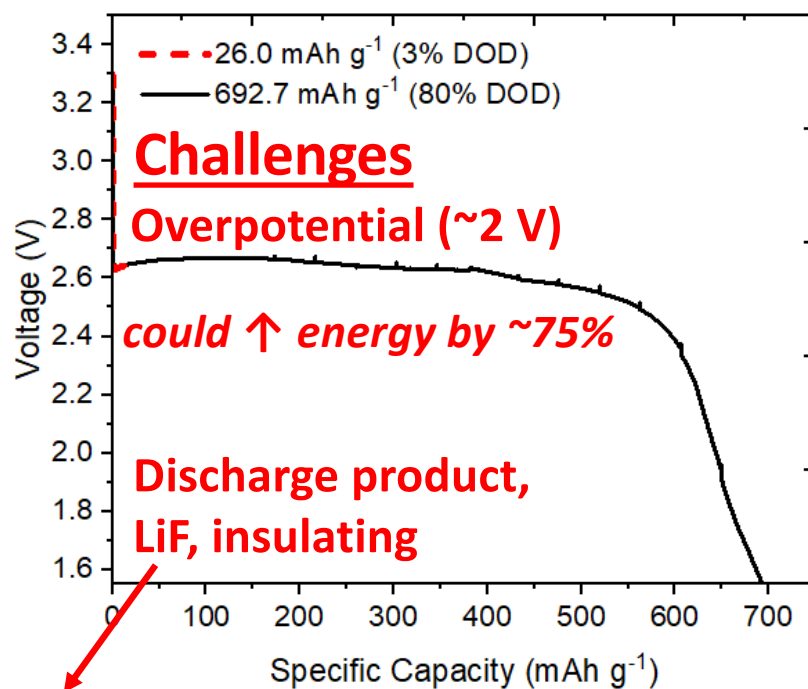


- **Theoretical discharge potential: 4.57 V**
- **Specific capacity: 865 mAh g⁻¹ for CF_x (x=1)**
- **Theoretical specific energy: 2180 Wh kg⁻¹**
- **Practical : Li-CF_x D-cell @ 2.5 V: ~ 700 Wh kg⁻¹**
- **Low self-discharge**
- ***Non-rechargeable (primary)***

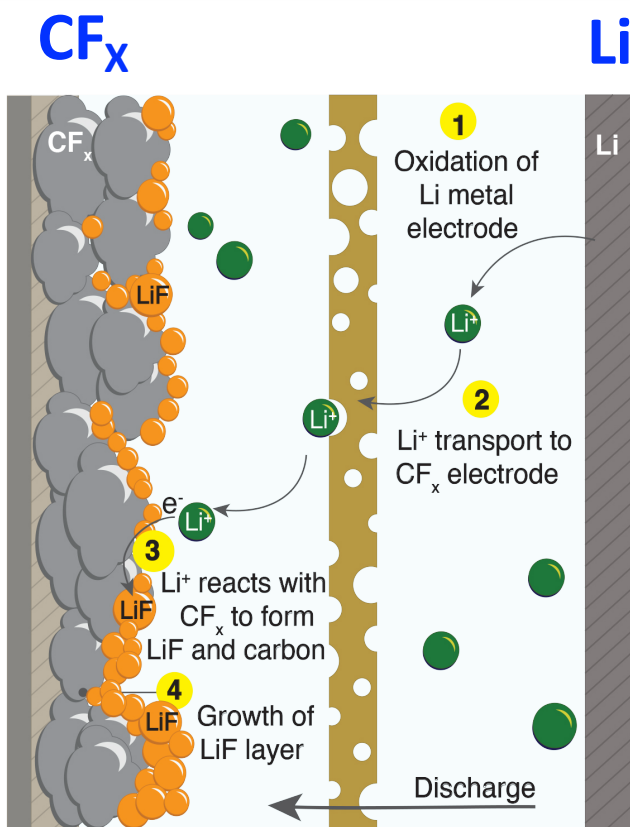
Li-CF_x: Highest Specific Energy Li Battery (Practical)



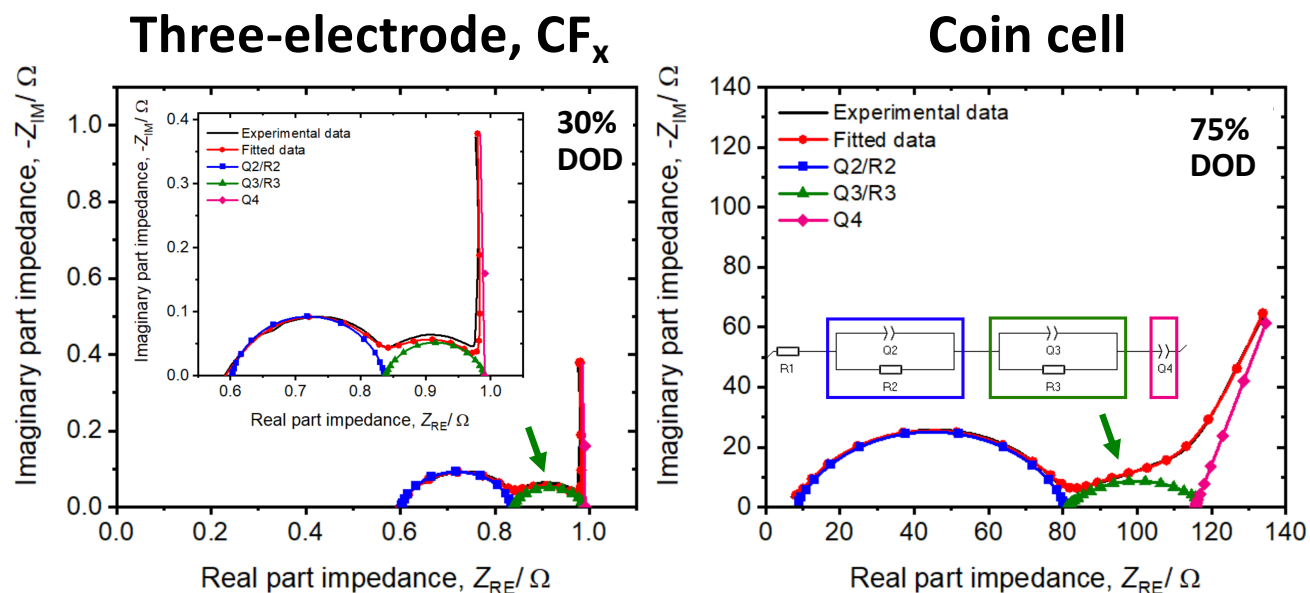
- Theoretical discharge potential: **4.57 V**
- Specific capacity: 865 mAh g⁻¹ for CF_x (x=1)



EIS Study: Electrode Interphases & LiF Interface



Electrochemical Impedance Spectroscopy

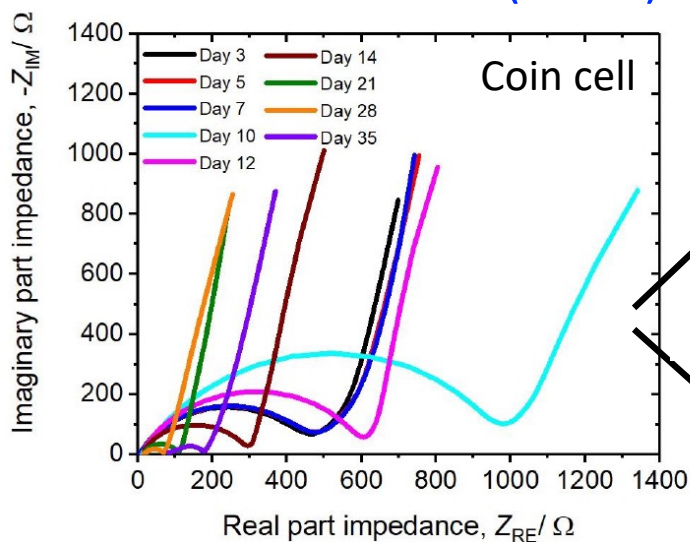


- EIS: quantitatively disentangle impedance contributions; studied at different DODs and aging periods
- Concluded **LiF** interface on the CF_x cathode associated with lower frequency (**Q3/R3**) element



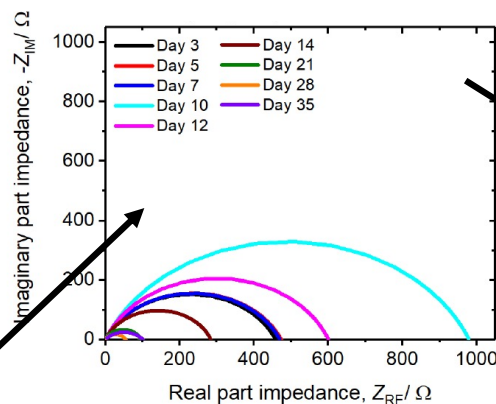
Impedance Evolves Non-Monotonically with Age

Cell aged after 3% DoD
+ heat treatment (55 °C)

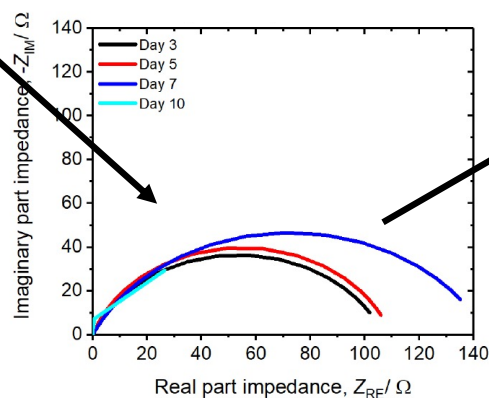


Non-monotonic
evolution of impedance

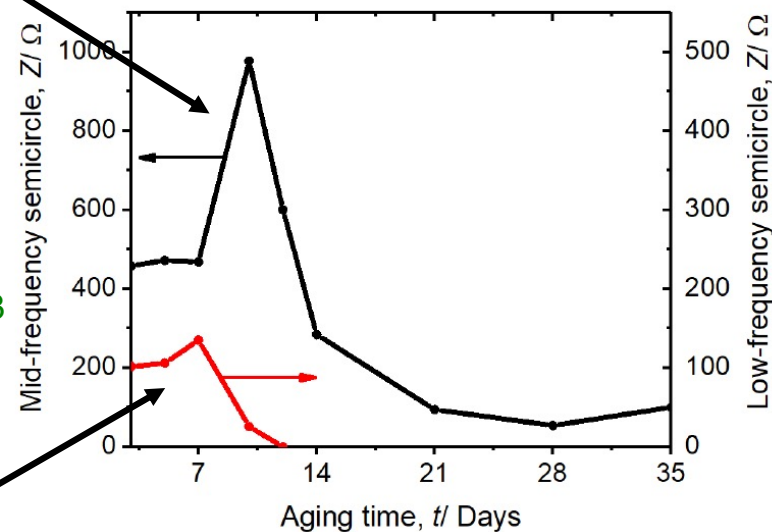
Mid-frequency Semicircle ($Q2/R2$)



Low-frequency Semicircle ($Q3/R3$)



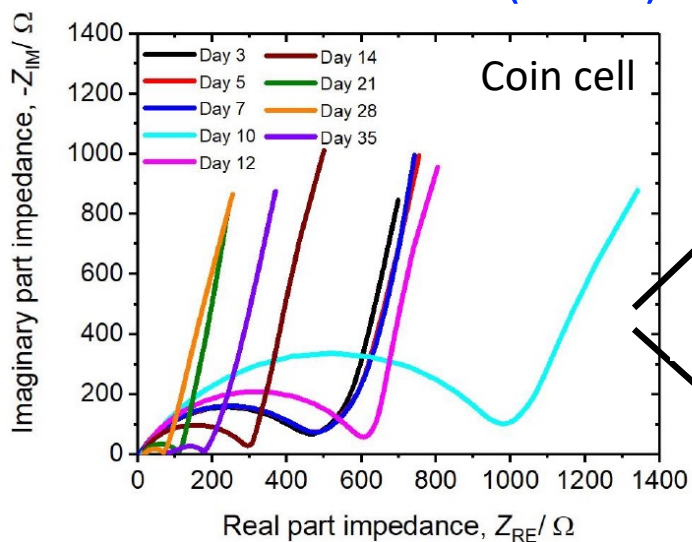
Local restructuring of
electrode interphases?



Impedance associated w/ LiF
disappears after ~10 days...

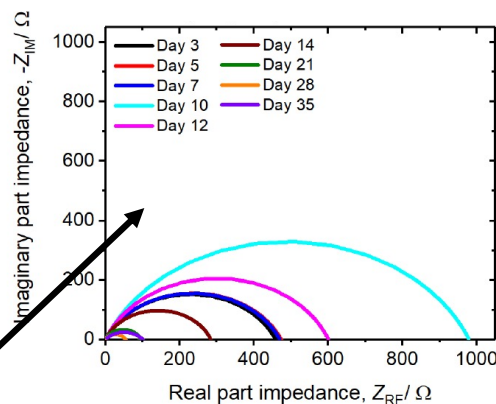
Impedance Evolves Non-Monotonically with Age

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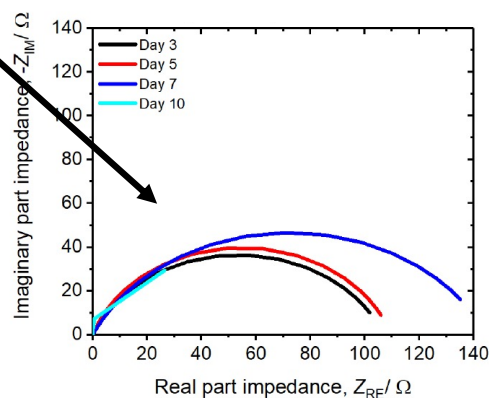


Non-monotonic
evolution of impedance

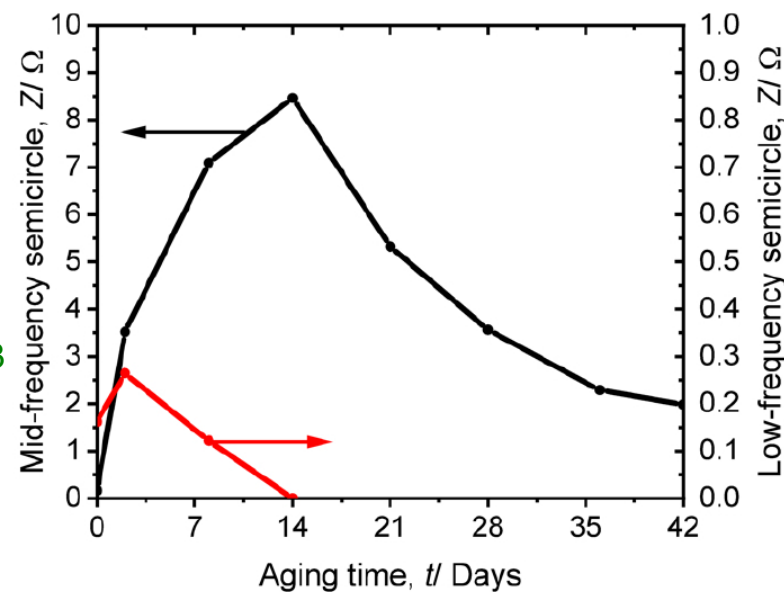
Mid-frequency Semicircle ($Q2/R2$)



Low-frequency Semicircle ($Q3/R3$)



Similar trend observed in
three-electrode cells

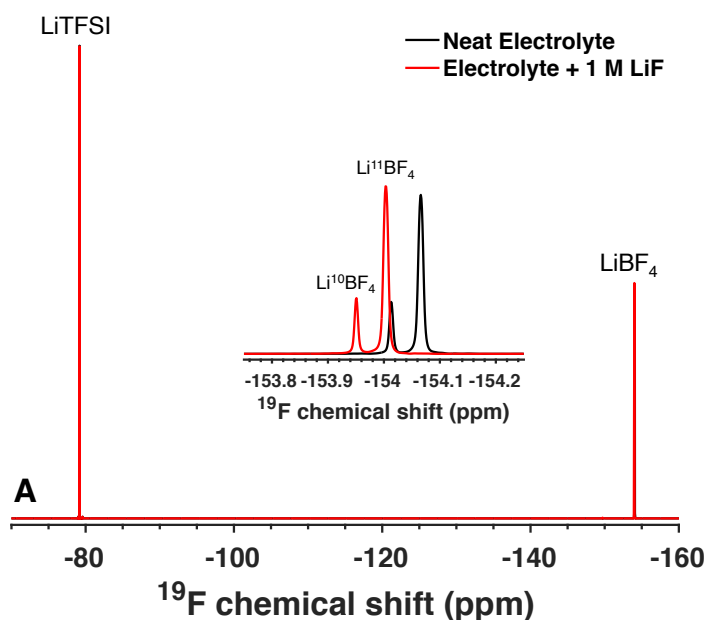


Impedance associated w/ LiF
disappears after ~10 days...

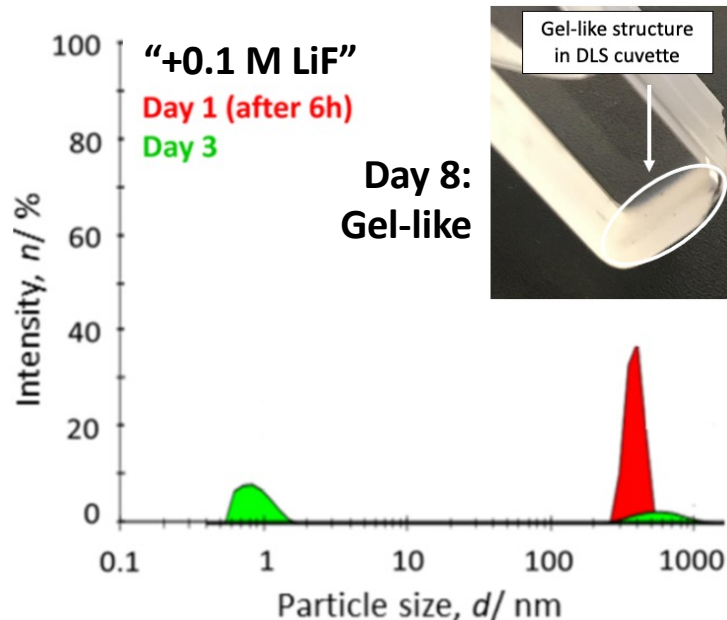
LiF Disperses Into Organic Electrolyte

Electrolyte: 0.75 M LiBF₄ PC:DME (0.3:0.7) + LiF visually disappears

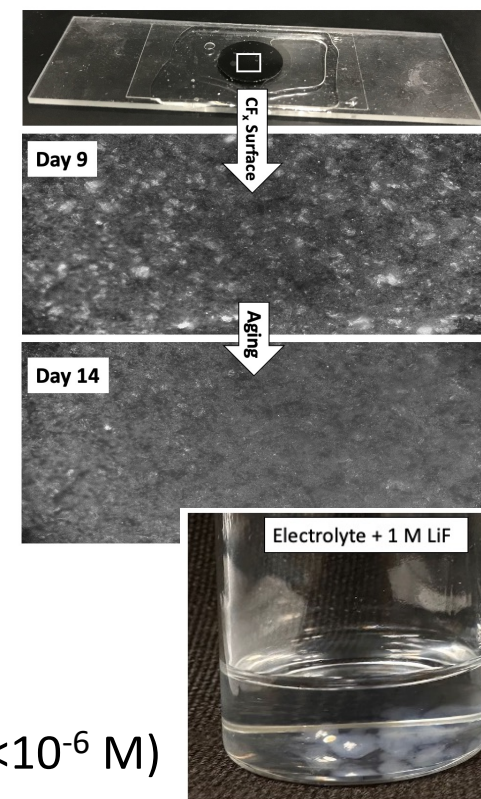
Liquid-state ¹⁹F NMR



Dynamic Light Scattering



Optical Microscopy



NMR & Conductivity: LiF *not* soluble at molecular level

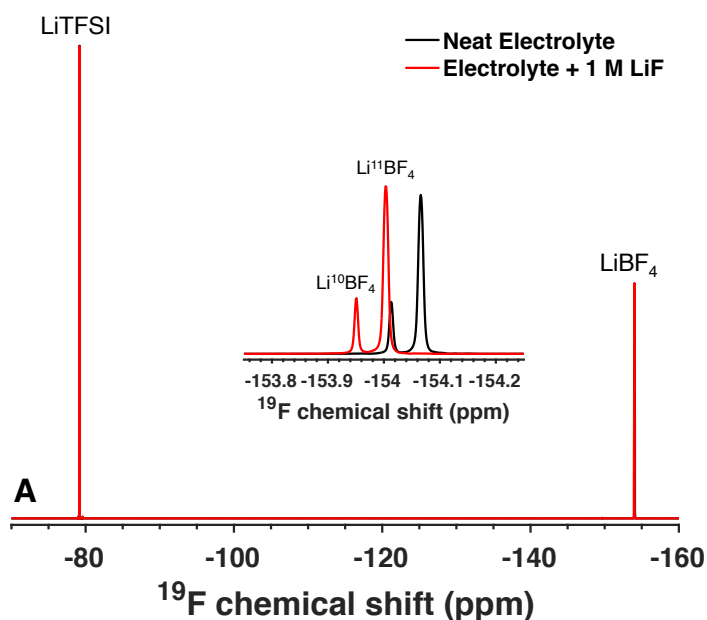
LiF solubility: 0.14 g L⁻¹ (~5.4 mM) in PC @ 25 °C; “insoluble” in DME (<10⁻⁶ M)

Schoetz, Robinson, Jones, Brandon, Messinger, et al., *ACS Appl. Mater. Interf.*, **2024**, *16*, 18722–18733.

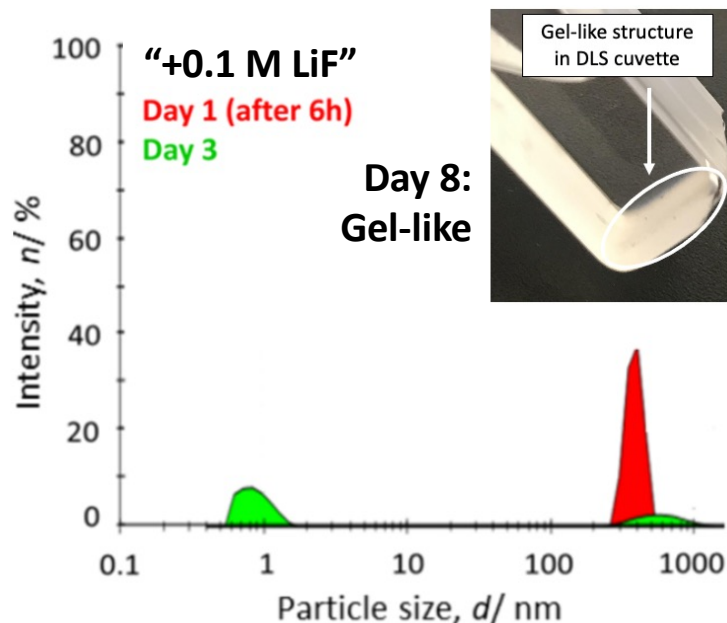
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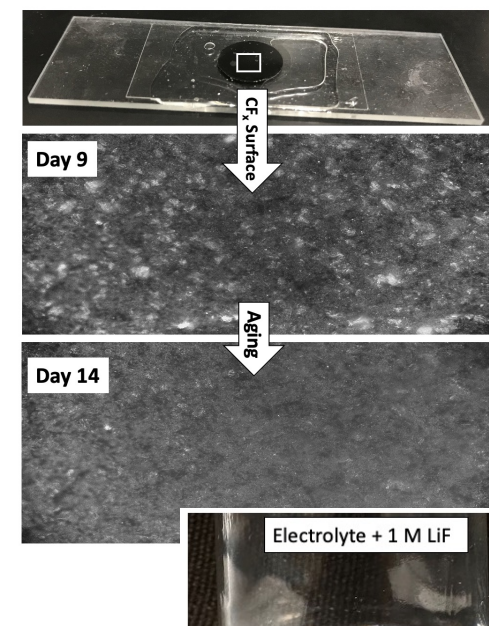
Liquid-state ¹⁹F NMR



Dynamic Light Scattering



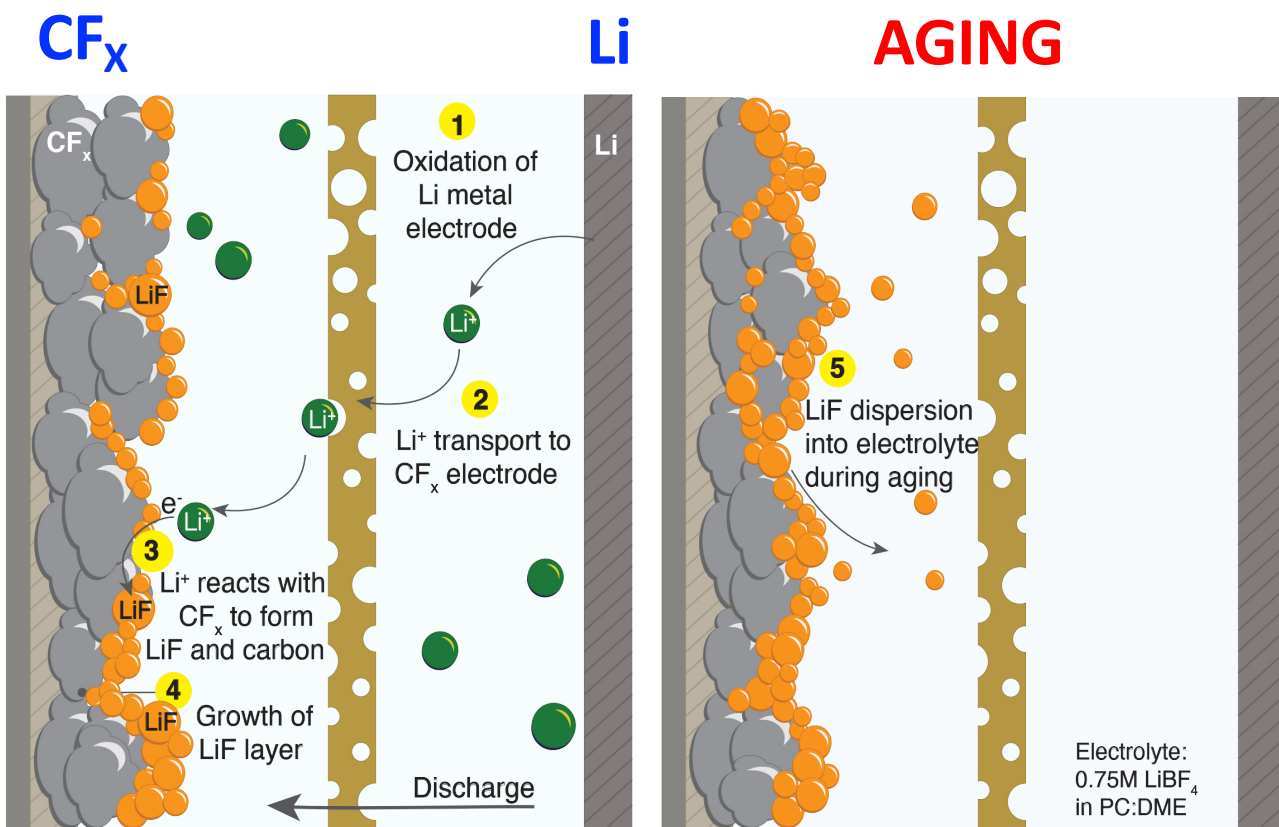
Optical Microscopy



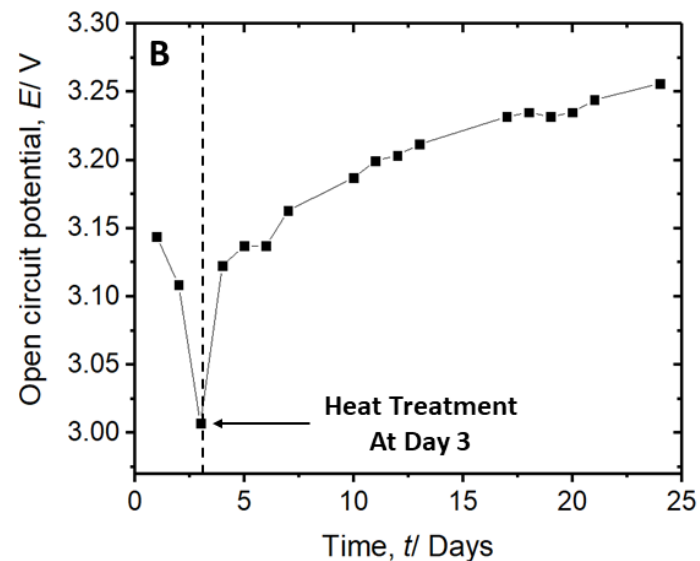
LiF forms *colloidal dispersion* in electrolyte; VdW forces drive gel formation
Driving force: interfacial free-energy of LiF lowers with wetting (“peptizes”)

Schoetz, Robinson, Jones, Brandon, Messinger, et al., *ACS Appl. Mater. Interf.*, **2024**, *16*, 18722–18733.

LiF Evolution Affects Open Circuit Potential



Open-circuit potential



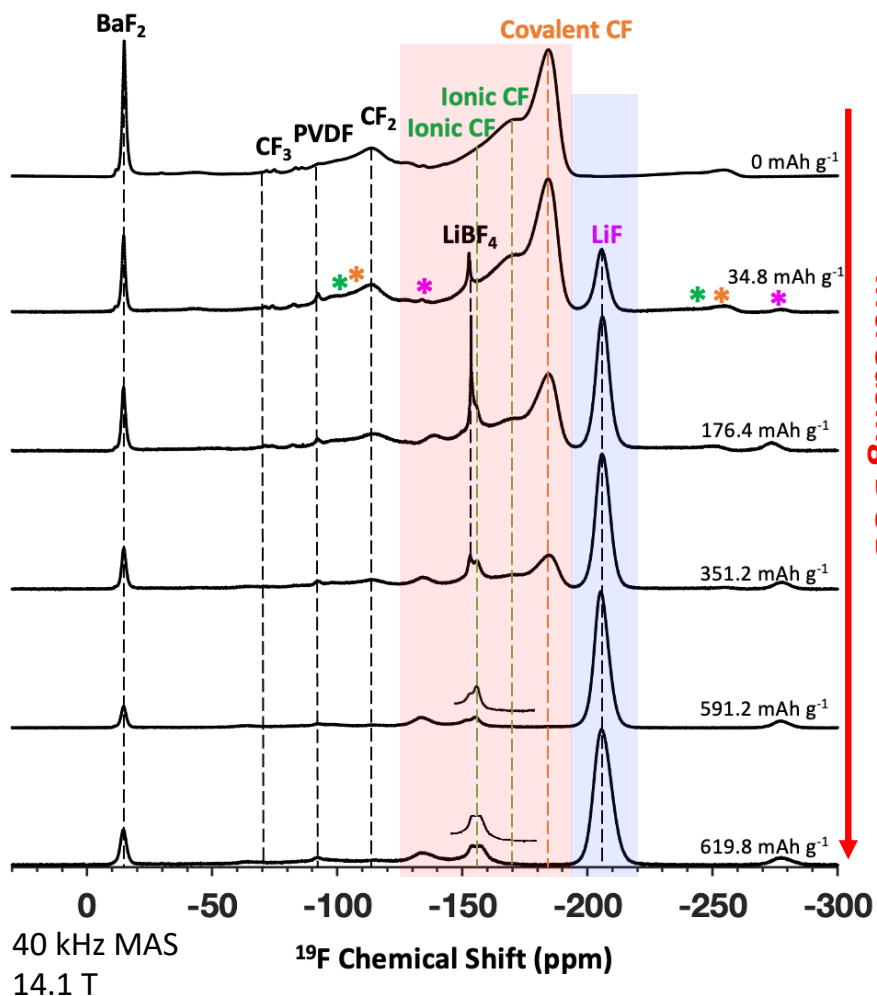
Relate Nernst & Kelvin equations:

$$E = E^{\circ} - \frac{2\sigma V_m}{zFr}$$

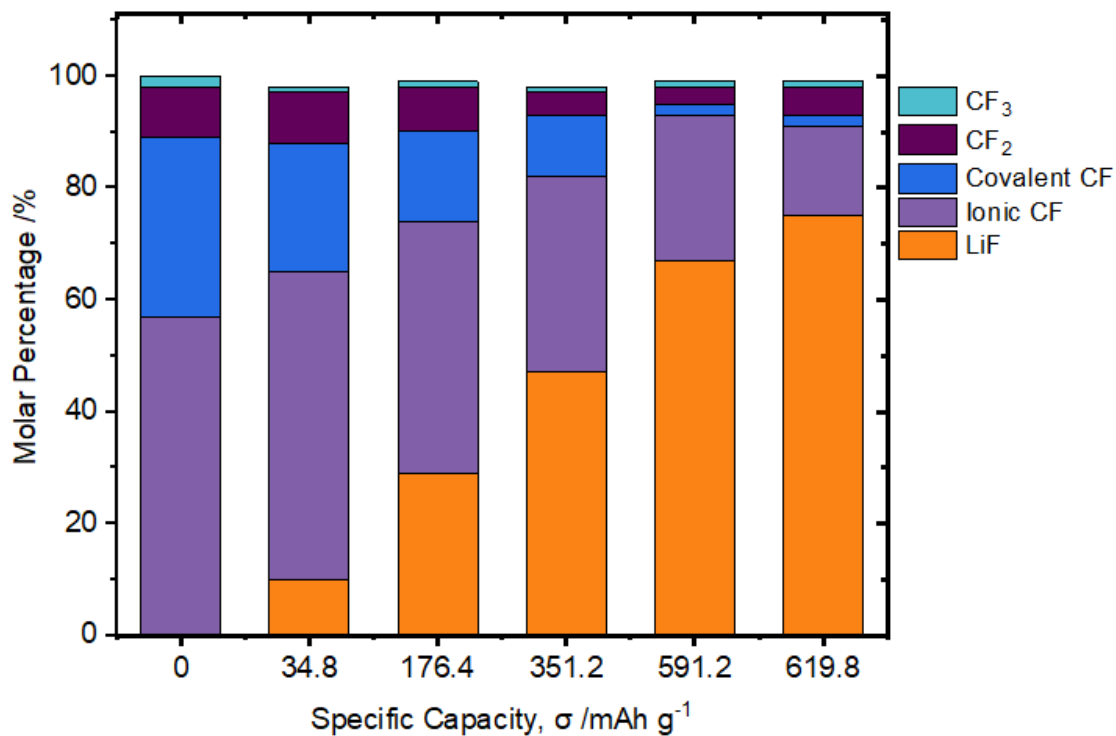
E ~ 1/r; decrease in LiF particle size will increase OCP

Schoetz, Robinson, Jones, Brandon, Messinger, et al., *ACS Appl. Mater. Interf.*, **2024**, 16, 18722–18733.

Solid-State ^{19}F NMR: LiF Formation + CF_x Defluorination

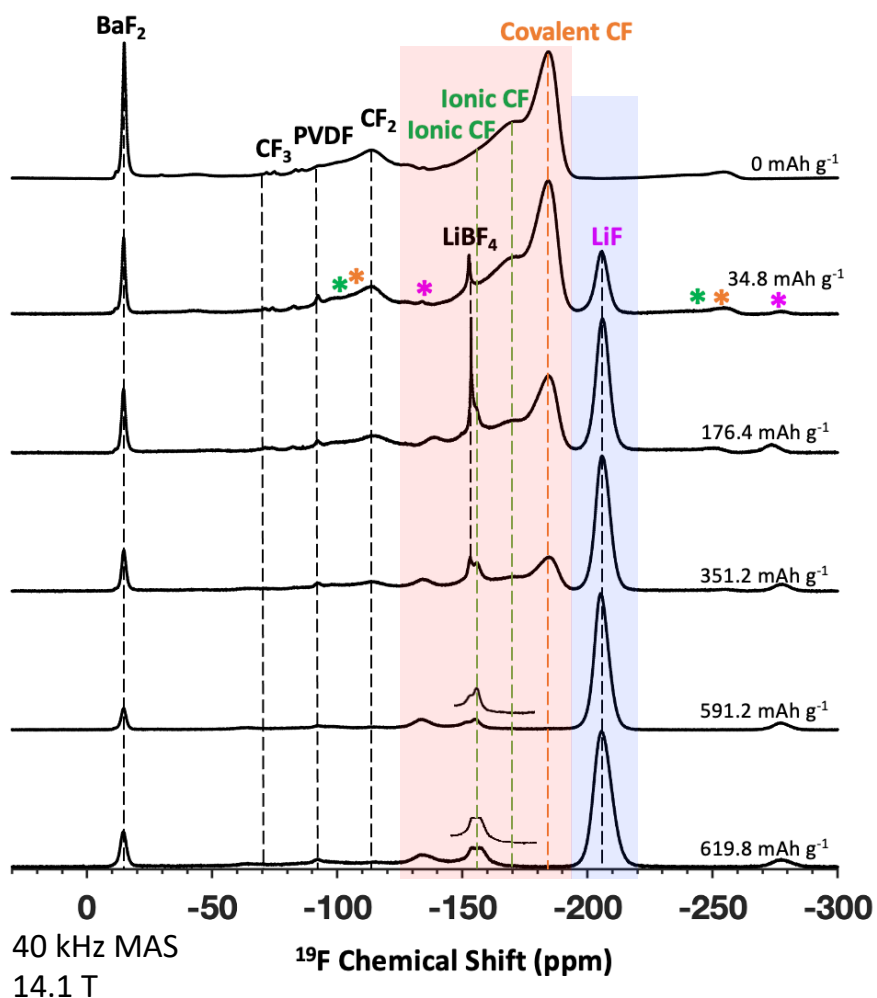


Molar percentages of ^{19}F moieties at different DOD



CF bonds with most ionic character are a limiting factor in achieving full theoretical specific capacity

Solid-State ^{19}F NMR: LiF Formation + CF_x Defluorination



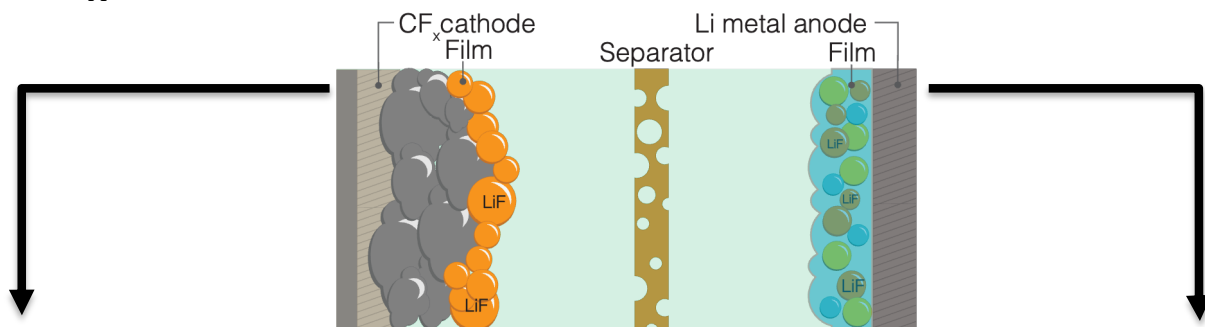
Solid-state NMR quantitatively consistent with electrochemical measurements

Specific Capacity / mAh g^{-1}	Molar percentage /%			
	DOD/%	LiF	Ionic CF	Covalent CF
0	0	0	57	32
34.8	4	10	55	23
176.4	20	29	45	16
351.2	41	47	35	11
591.2	68	67	26	2
619.8	72	75	16	2

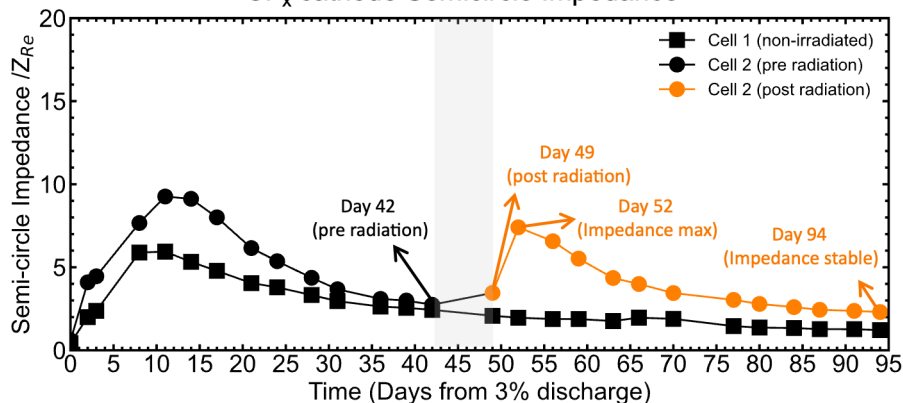
CF bonds with most ionic character are a limiting factor in achieving full theoretical specific capacity

Li-CF_x Cells + Gamma Radiation: Impedance Changes

Li-CF_x cells irradiated with gamma rays: **10 Mrad**

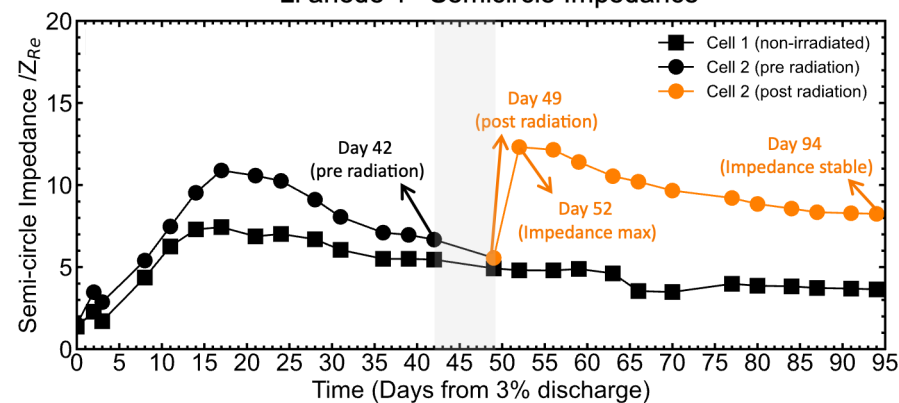


CF_x cathode Semicircle Impedance



CF_x film impedance increases, then returns to pre-radiation values

Li anode 1st Semicircle Impedance



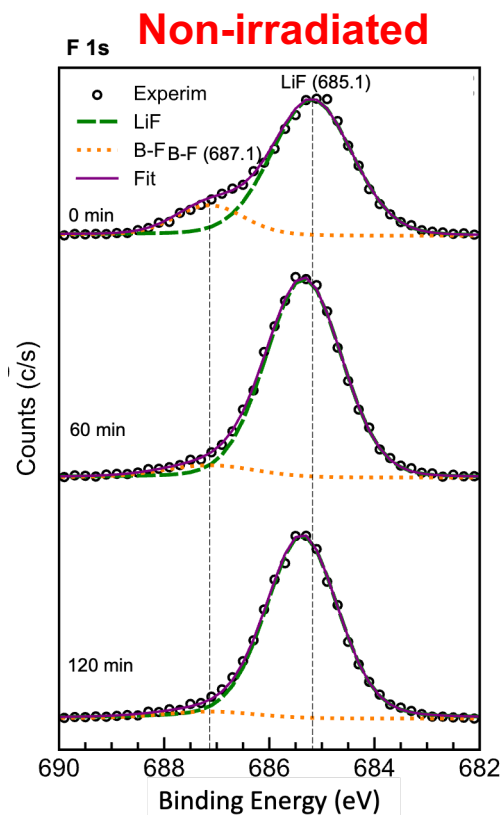
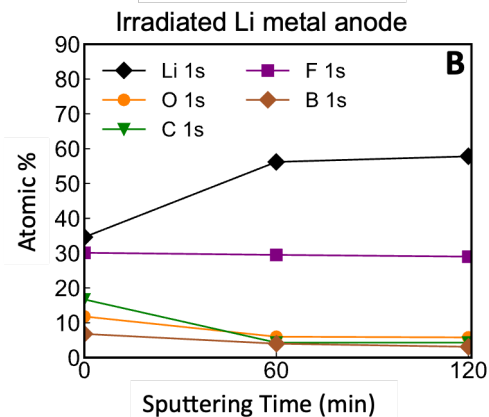
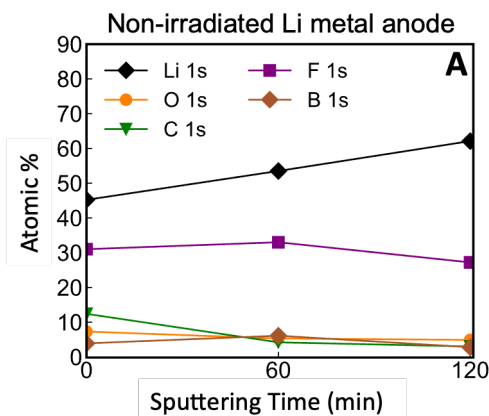
Li metal film: ~30% higher impedance after radiation exposure

Robinson, Jones, Brandon, Messinger, et al., *J. Power Sources*, 2026, 263, 238864.

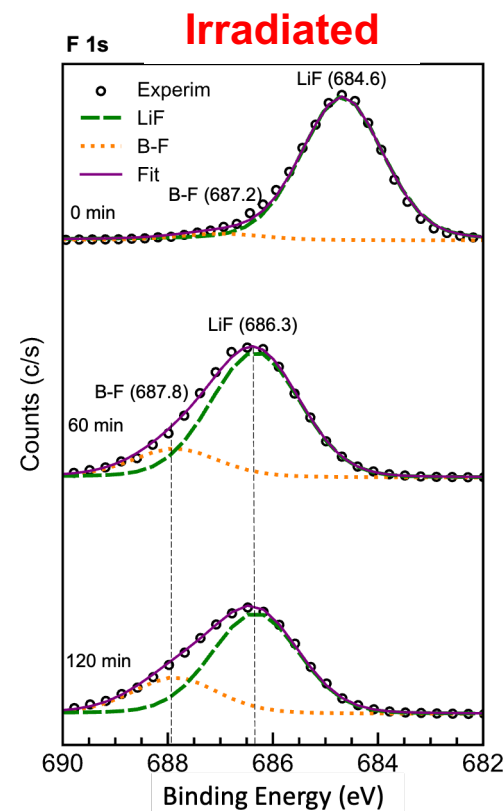
XPS Reveals Chemical Changes in Li Anode Film

Li & F dominant elements

XPS F 1s Depth Profiles



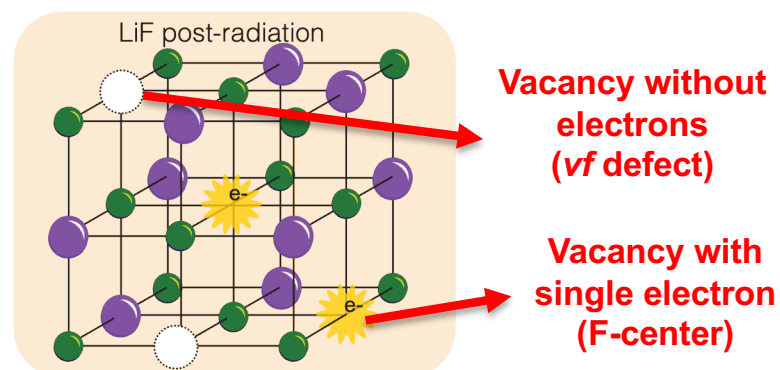
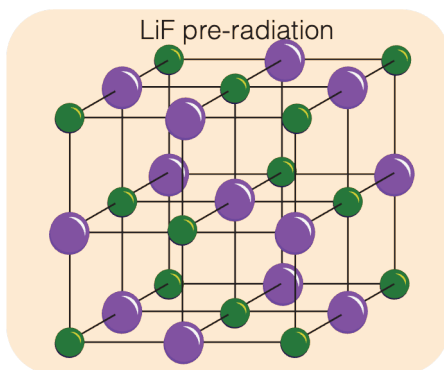
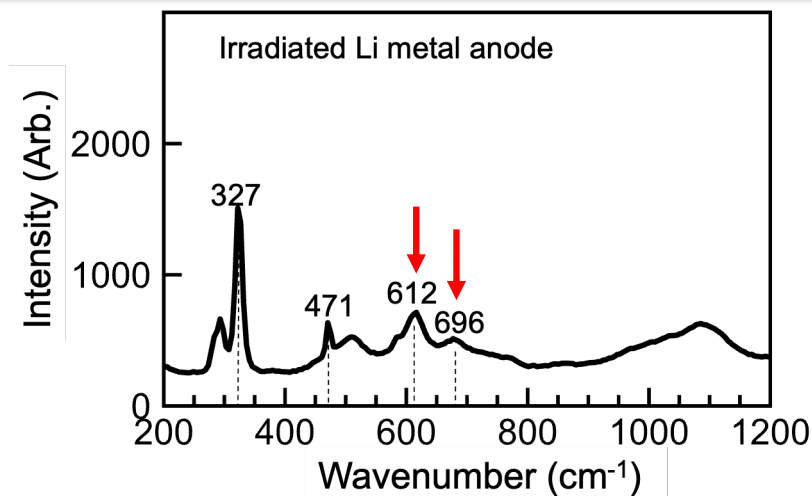
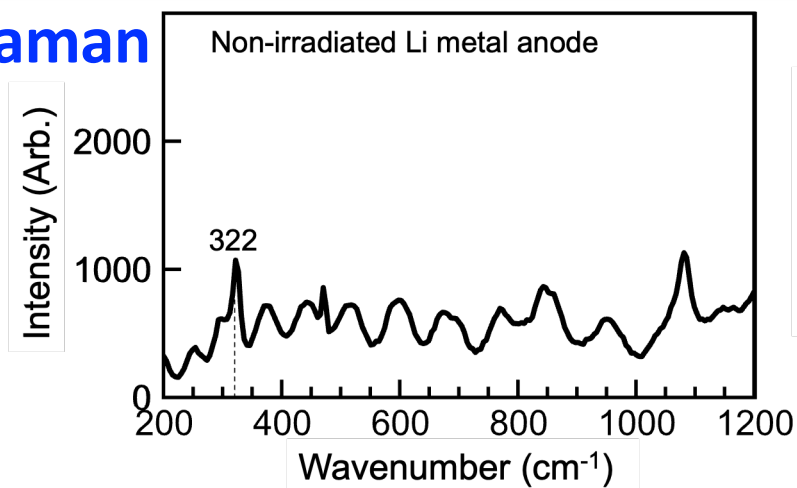
No shift in the binding energy of LiF throughout film depth



Shift in LiF binding energy upon sputtering: **why?**

Radiation-Induced Defects Alter LiF Electronic Structure

Raman



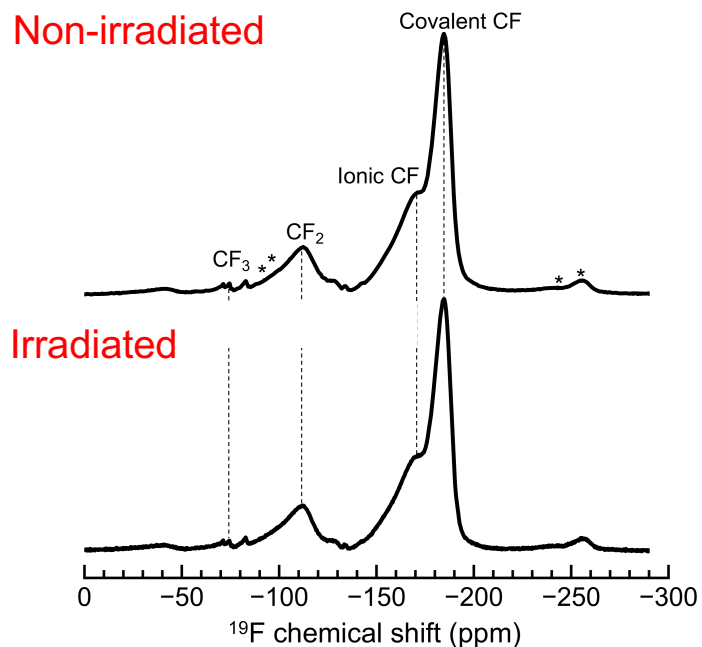
Sorokin et al. *Nucl. Insts. Methods Phys. Res. Sect. B* **2020**, 480, 33–37.

Robinson, Jones, Brandon, Messinger, et al., *J. Power Sources*, **2026**, 263, 238864.

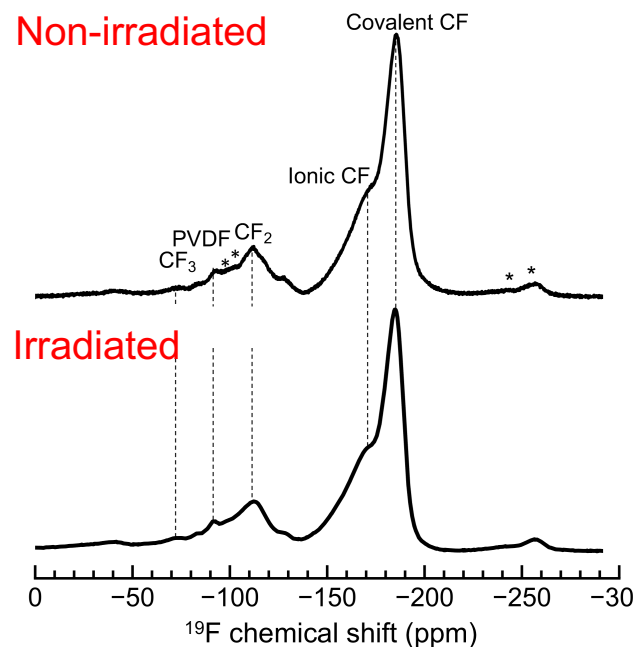
CF_x Remarkably Stable to Radiation at Molecular Level

Solid-state ¹⁹F NMR

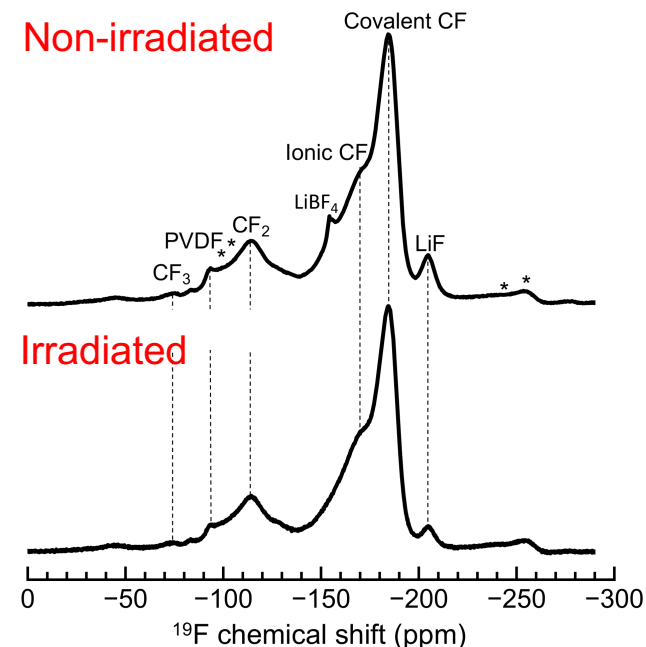
CF_x powder



CF_x electrodes



CF_x electrodes, 3% DOD + Heat Treatment



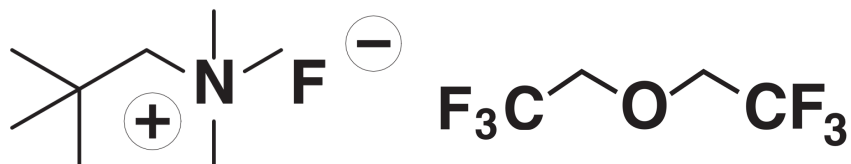
Robinson, Jones, Brandon, Messinger, et al., *J. Power Sources*, **2026**, 263, 238864.

Back to Overpotential: Let's Re-think CF_x ...

- *Q: can we reduce **overpotential** by fundamentally altering reaction mechanism?*
- **Hypothesis:** electrochemically defluorinate CF_x directly with F-ion electrolyte



Simon Jones
Flion Energy



0.75 M NP_1F salt in **BTFE**

Davis et al., *Science*, **2018**, 362, 1144–1148.

*Neopentyl-substituted
alkylammonium fluoride salt*

*Np-branch: improved solubility;
lack of β -hydrogen: inhibits
decomposition while drying*

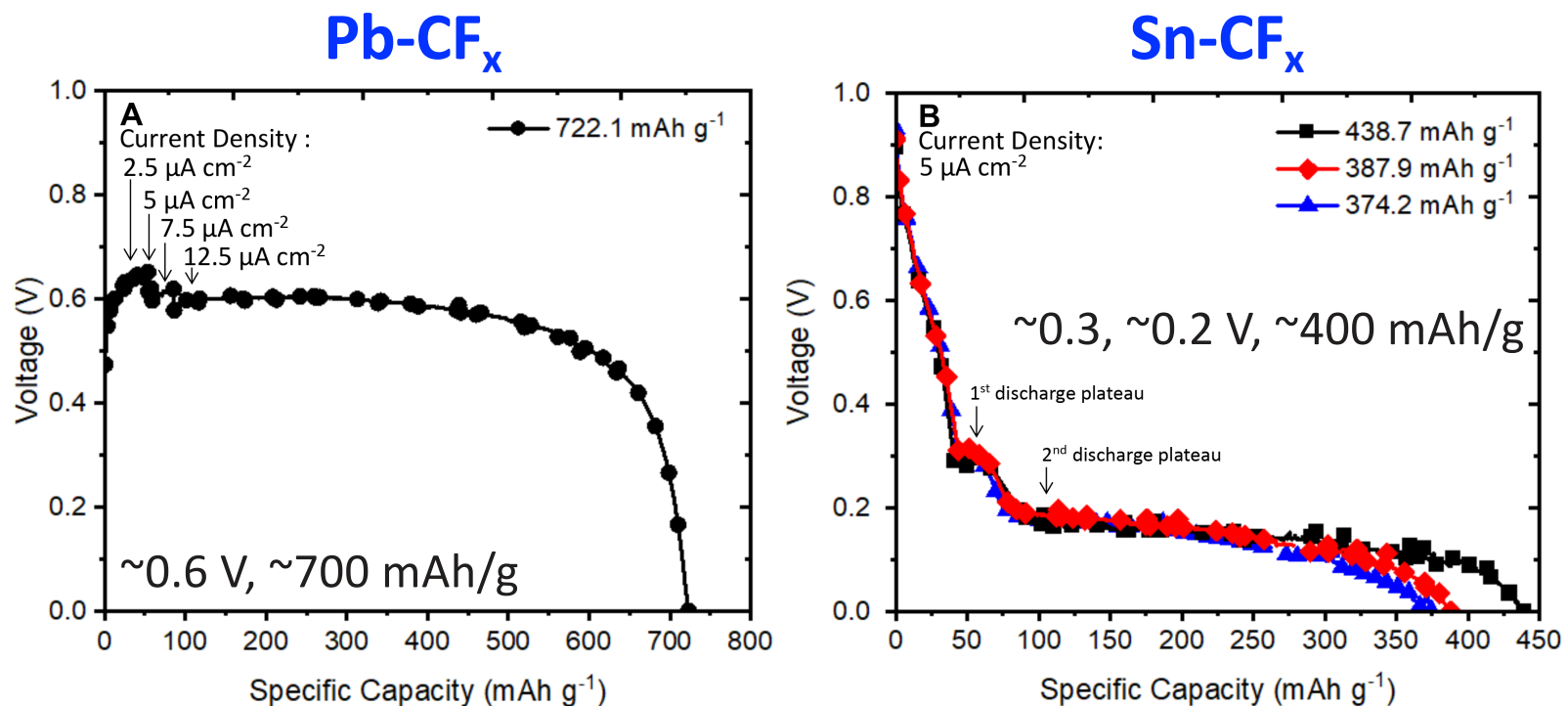
- **Approach:** couple CF_x cathode & metal anode w/ room-temp F-ion electrolyte
- **Challenge:** lithium metal reactivity w/ F-ion electrolyte
- **Solution:** pair w/ other metal anodes for proof-of-concept



Will West
NASA JPL

Primary F-ion Metal-CF_x Cells

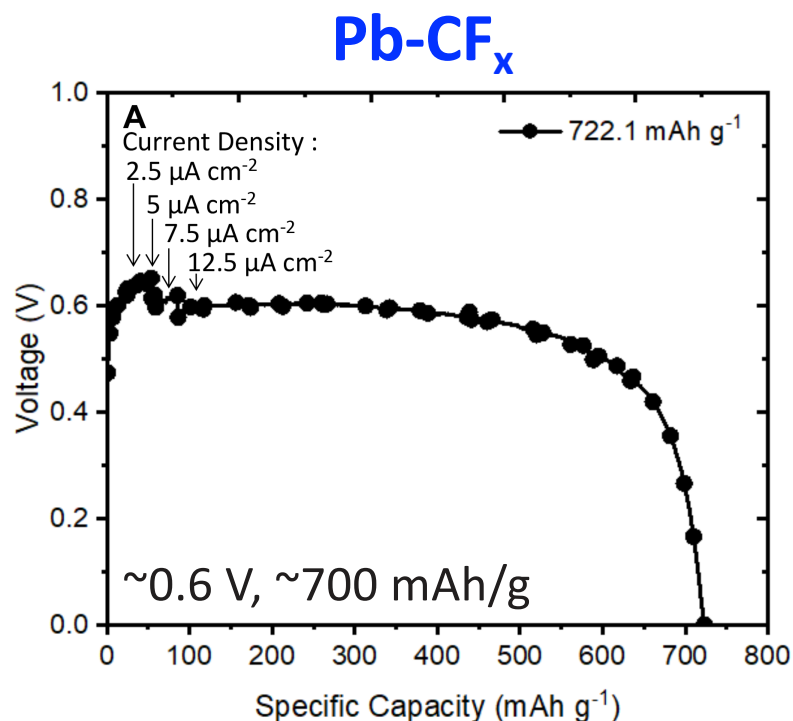
- F-ion CF_x cells successfully electrochemically discharged w/ Pb & Sn metal anodes



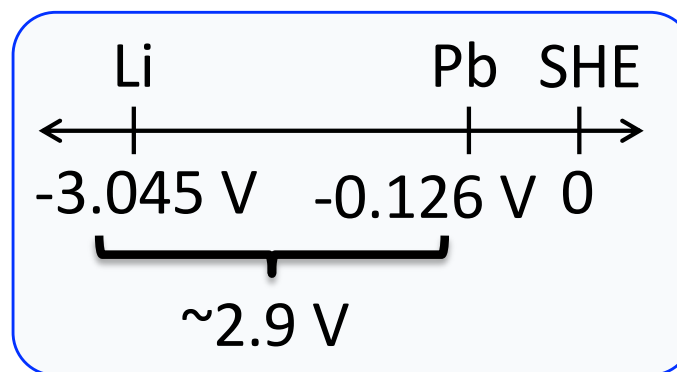
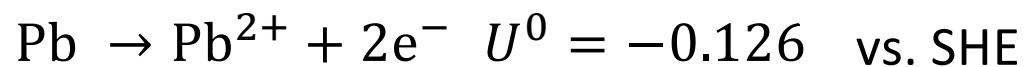
- First demonstration of F-ion primary batteries

Primary F-ion Metal-CF_x Cells

- F-ion CF_x cells successfully electrochemically discharged w/ Pb & Sn metal anodes



Electrochemical standard potentials



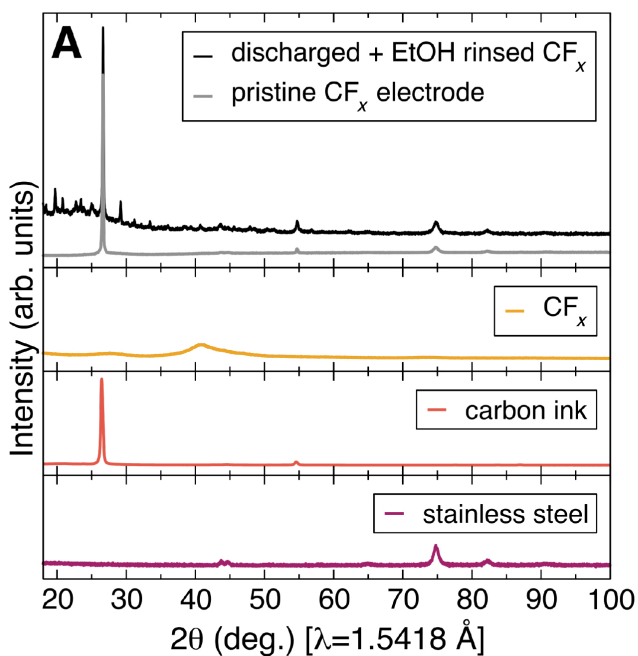
- Are hypothesized electrochemical half reactions occurring?
- Sn-CF_x reaction mechanism analyzed in detail

Back-of-the-envelope:
overpotential ↓ by ~1 V

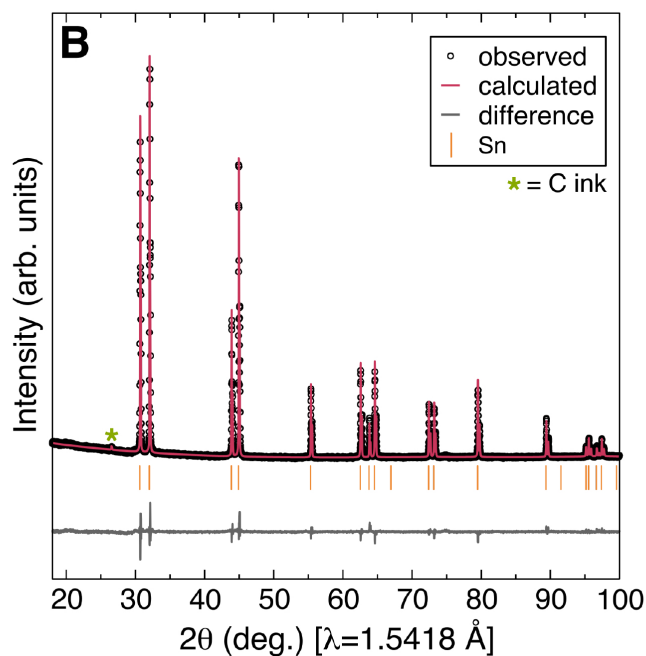
XRD of Sn-CF_x Electrode Materials: SnF₂ Forms

- XRD establishes that **crystalline SnF₂** forms upon electrochemical discharge

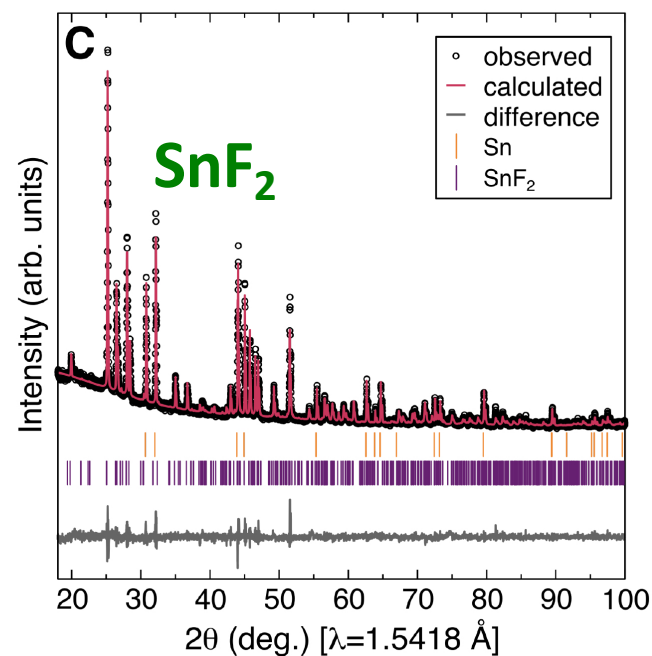
Discharged CF_x cathode



Pristine Sn anode



Discharged Sn anode

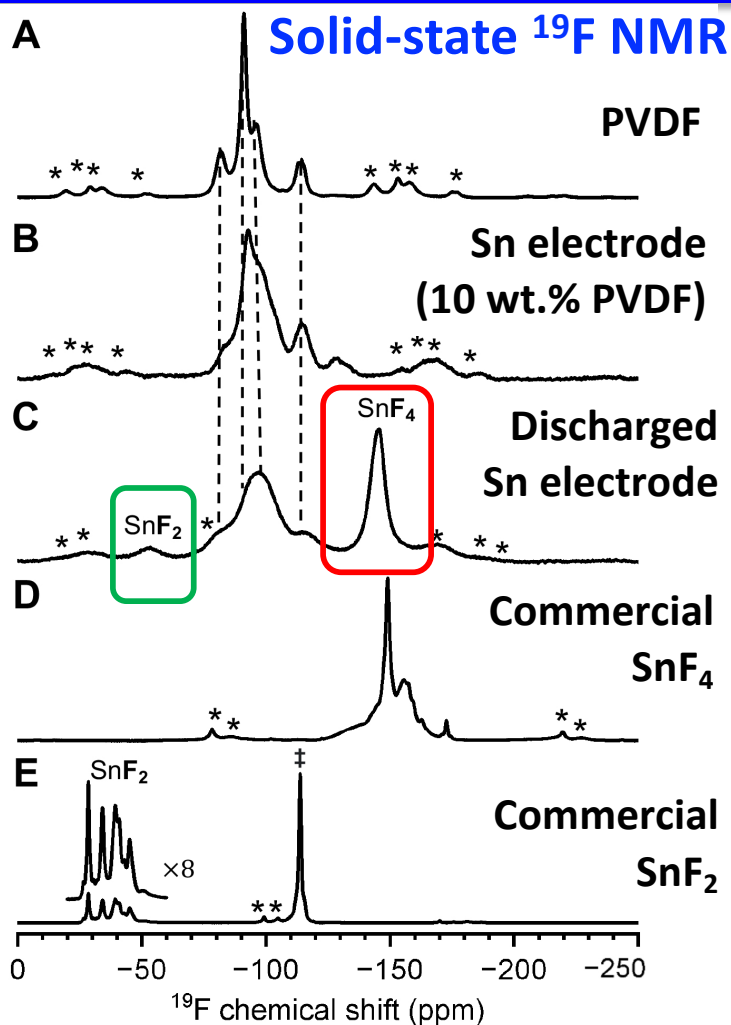


- *Yes, **crystalline SnF₂** does form – but always use multiple characterization methods...*

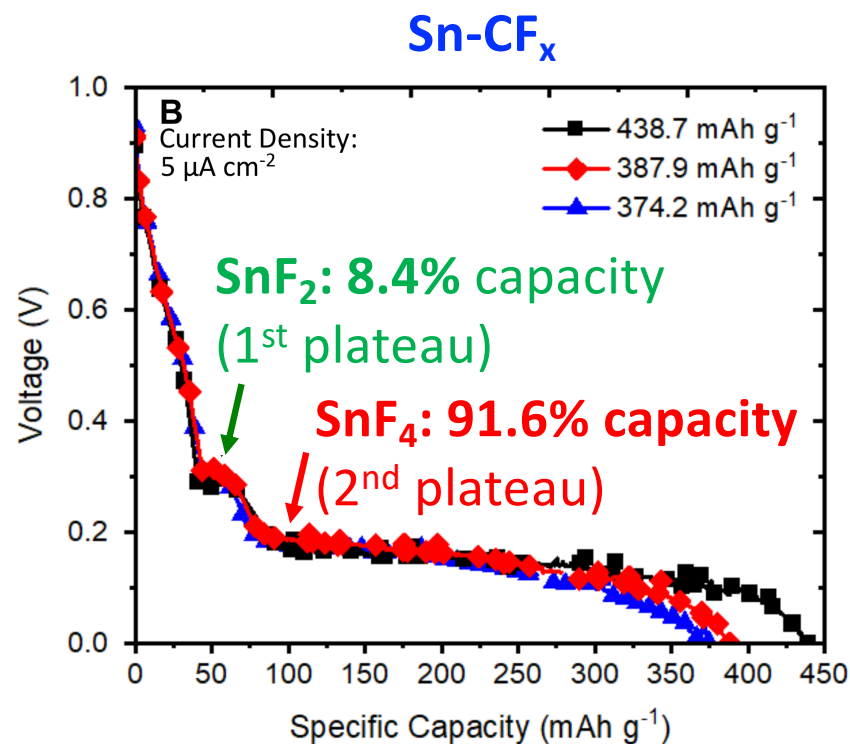
Solid-state NMR Reveals Reaction Products of Sn-CF_x Cell

SnF₄: 91.4%
¹⁹F signals
 (Sn species)

SnF₂: 8.6%
¹⁹F signals
 (Sn species)



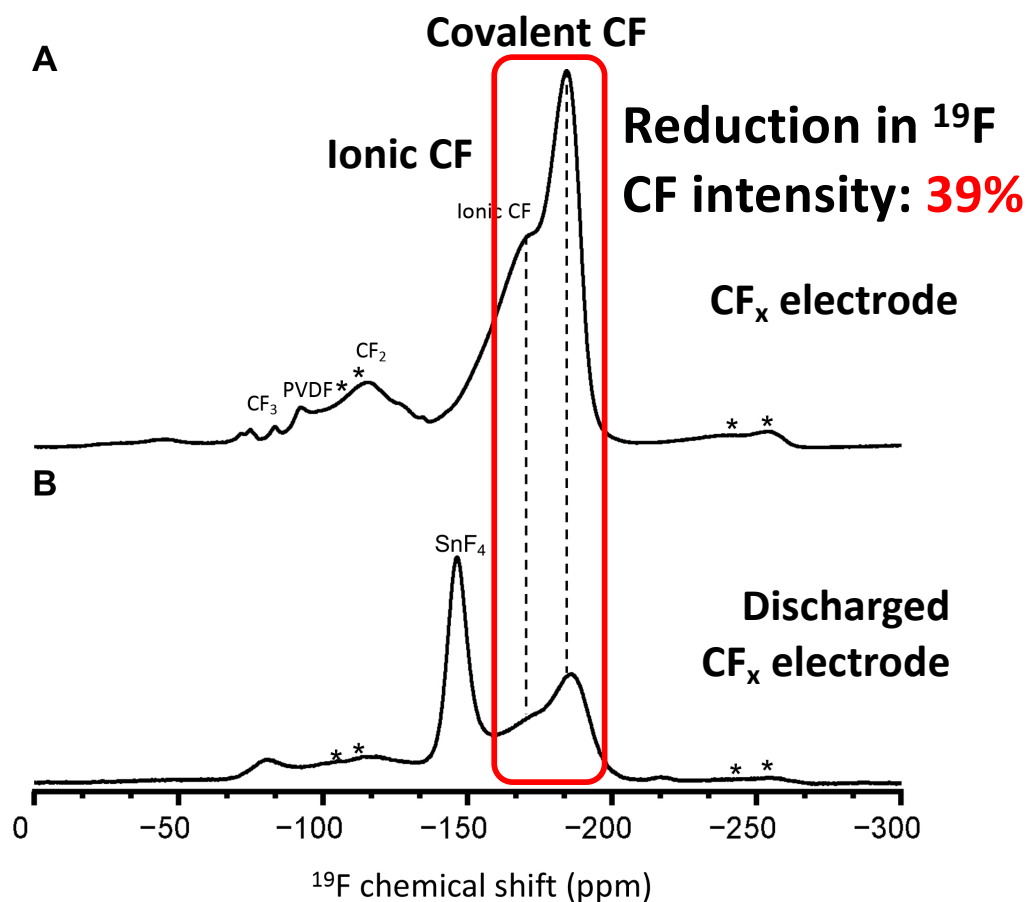
14.1 T, 40 kHz MAS



L. Robinson, Messinger*, Jones*, West*, et al.,
J. Phys. Chem. C. **2024**; 128, 14195–14205.

Solid-State NMR Confirms Electrochemical Defluorination of CF_x

Solid-state ^{19}F NMR



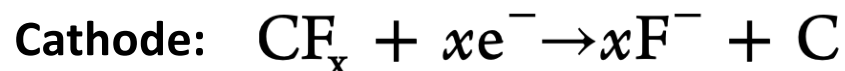
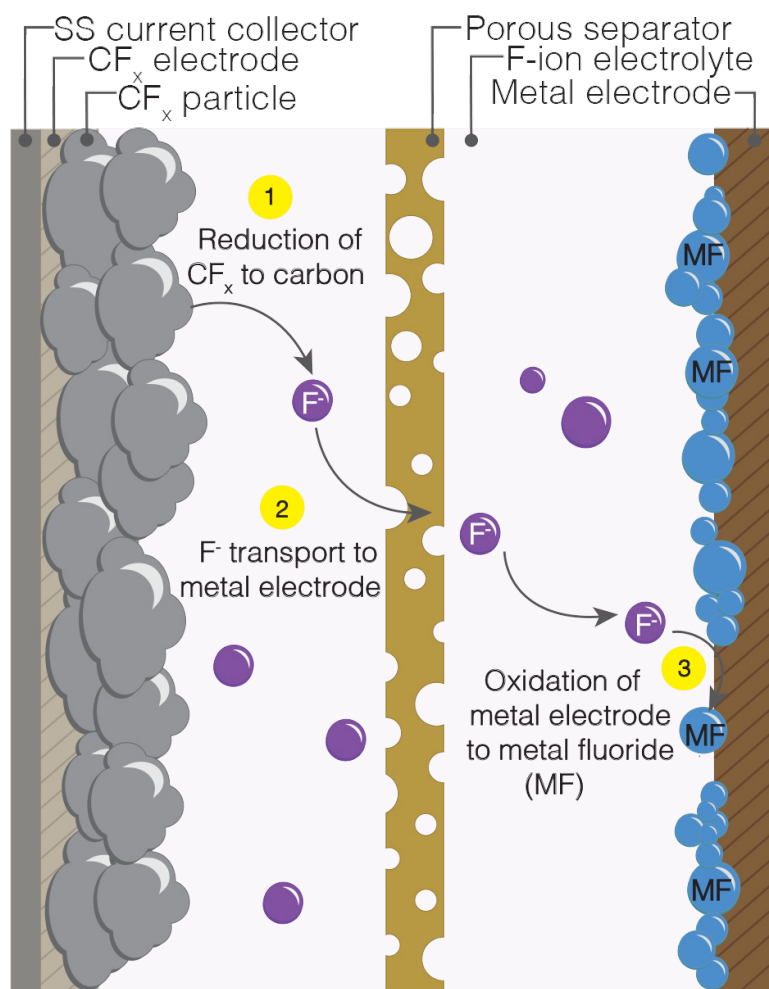
Fraction of theoretical specific capacity obtained: **36.4%**

Fraction of capacity due to Sn transport and reaction: **~3%**
(Consistent with ICP & XRF)

SnF₄: mass transport of Sn species from anode to cathode possible

L. Robinson, Messinger*, Jones*, West*, et al.,
J. Phys. Chem. C. **2024**; 128, 14195–14205.

Primary F-ion Metal-CFx: Electrochemical Defluorinate CFx



- **Demonstrated new electrochemical reaction mechanism** for CF_x electrodes
- First demonstration of **primary F-ion battery**
- **Future work:** address **Li metal reactivity** to enable F-ion based Li- CF_x cell w/ reduced overpotential

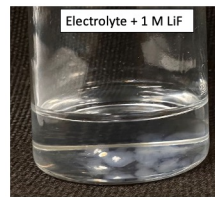
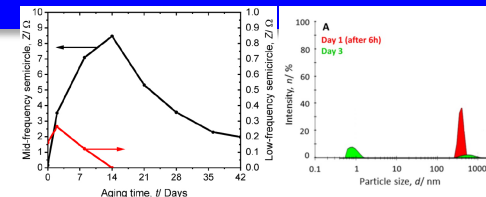


L. Robinson, Messinger*, Jones*, West*, et al.,
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Conclusions

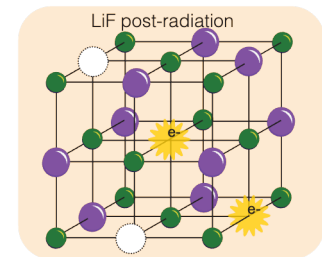
Li-CF_x: impedance, aging, & LiF evolution

- Non-monotonic impedance changes observed upon cell aging
- Electrochemically-formed LiF **disperses** into organic electrolyte, forms **colloidal dispersion** (particle diameter: order nm) that is metastable & subsequently gels
- Evolution/aging of LiF affects OCP & enables LiF mass transfer to Li metal anode



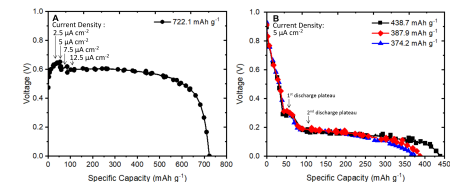
Li-CF_x: radiation

- **LiF**: gamma-ray radiation induces defects that alter its electronic structure
- **CF_x**: remarkably stable to gamma-ray radiation at a molecular level



F-ion metal-CF_x

- Electrochemically defluorinate CF_x directly without formation of metal fluoride at CF_x
- Metal fluoride forms at anode
- Reduces overpotential; back-of-the-envelope: ↓ by ~1 V



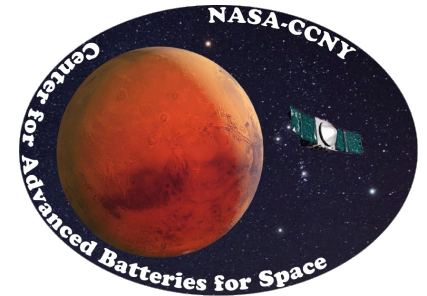
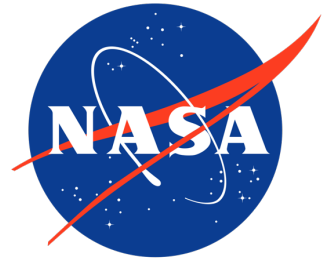
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