THE OHIO STATE UNIVERSITY

# Latent Effects of Radiation on Li-ion Batteries in Robots

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2017 American Nuclear Society Annual Meeting San Francisco

# Li-ion Batteries


*courtesy: Government of Canada, greentech media, ESA, NASA, Bloomberg*

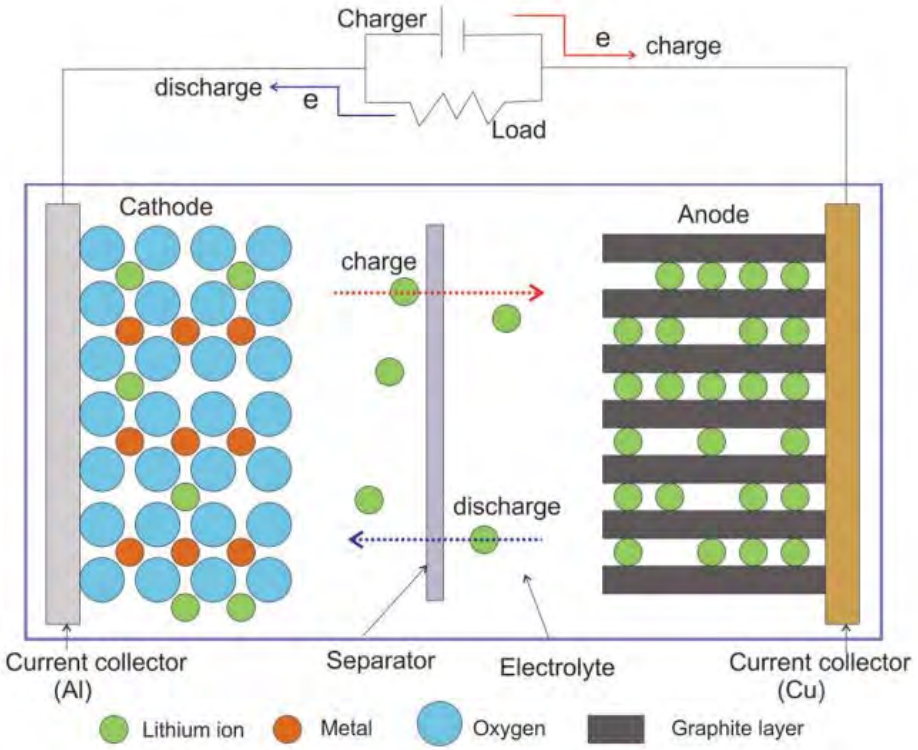
# Radiation Dose in Fukushima

"…What the company ultimately discovered, however, is that the amount of radiation pouring off the damaged reactor below the reactor pressure vessel is 530 sieverts per hour, vastly higher than had previously been communicated…"


https://techcrunch.com/2017/03/25/japanese-authorities-decry-ongoing-robot-failures-at-fukushima/

# Structure of LIBs

$LiFePO_4$




Courtesy: Dandan He, M.S Thesis

Graphite

$$C_6 + Li^+ + e^- \rightleftharpoons LiC_6$$

$$LiFePO_4 \rightleftharpoons Li^+ + e^- + FePO_4$$

## What matters in LIBs

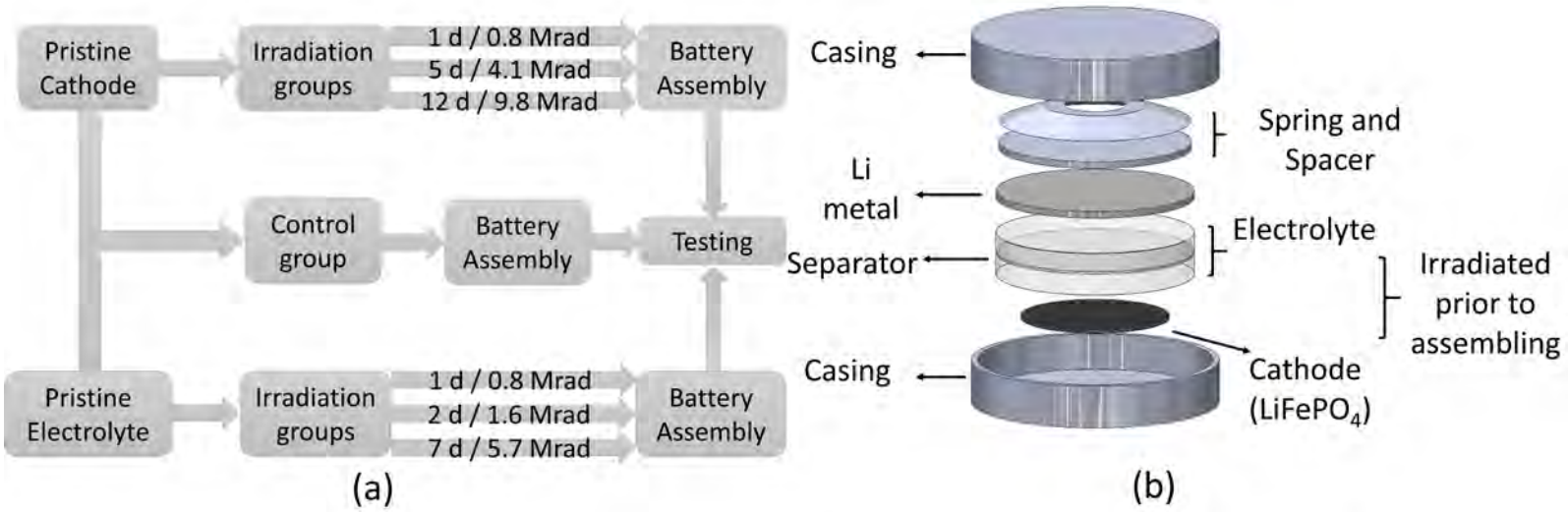
# Objectives

- Understand how lithium ion batteries (LIBs) are affected in radioactive environments

# 3 metrics for evaluation

- Capacity-How long
- Resistance-How fast
- Cyclic Performance-How many times

# Study begins…




- $LiFePO_4$ cathode and electrolyte of 1M $LiPF_6$ in EC/DMC 1:1 wt% were irradiated separately prior to assembly
- Co-60 irradiator with a dose rate ~30krad/hr (OSU Nuclear Reactor Lab)
- Each irradiation group contains at least 7 coin cells.

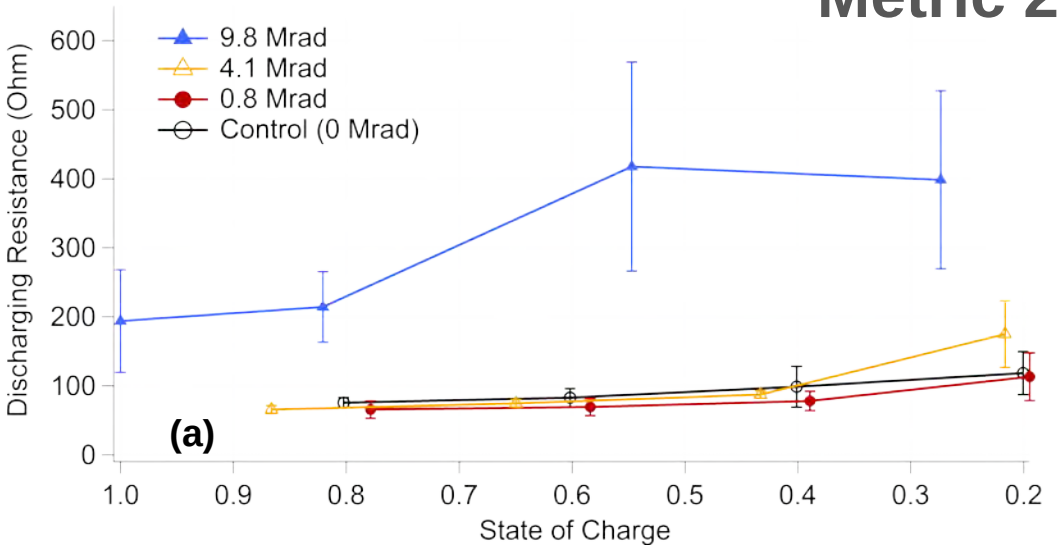
# Metric 1 - Capacity fade

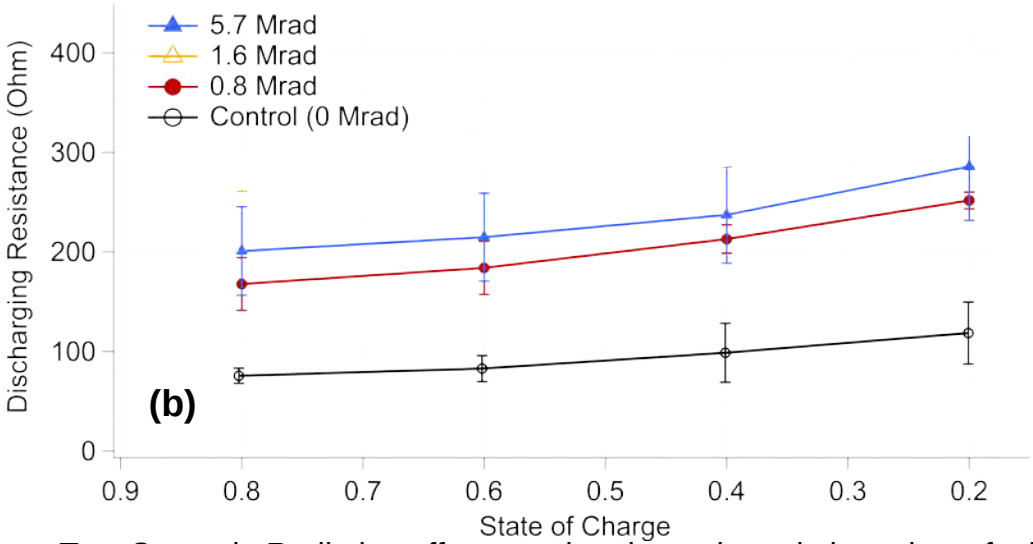
| Dose (Mrad) | Average Capacity (mA h) | Standard Deviation | Relative Standard Deviation |
|---|---|---|---|
| Control Group | | | |
| 0 | 1.50 | 0.11 | ±7.37% |
| Cathode Irradiation | | | |
| 0.8 | 1.54 | 0.094 | ±6.08% |
| 4.1 | 1.39 | 0.082 | ±5.90% |
| 9.8 | 1.10 | 0.09 | ±7.83% |
| Electrolyte Irradiation | | | |
| 0.8 | 1.43 | 0.056 | ±3.90% |
| 1.6 | 1.43 | 0.022 | ±1.53% |
| 5.7 | 1.33 | 0.048 | ±3.62% |

- Averaged over the living cells in each group
- Up to 26.7% fade for irradiated cathode groups
- Up to 11.2% fade for irradiated electrolyte groups

Tan, C., et al., Journal of Power Sources, 2016. **318**: p. 242-250.

# Metric 2 - Resistance measurement




- **Increase in resistance = loss in performance**
- Cells with irradiated cathodes
  - Resistance increases with dose
  - Low resistance in low and intermediate doses
- Cells with irradiated electrolyte
  - Resistance increase with dose
  - Even low dose group show 2-3 times as the control group
  - 1.6 Mrad group has the highest resistance.

Tan, C., et al., Radiation effects on the electrode and electrolyte of a lithium-ion battery. Journal of Power Sources, 2016. **318**: p. 242-250.

# What happened to our 1.6 Mrad group?

- **Highest resistance**
- **Highest failure rate**

- When we went back to check the notebook we found out that this 1.6 Mrad group was assembled 3 days after the irradiation, while the other two groups were assembled immediately after the irradiation.
- **We relate this further degraded performance to the latent effects of electrolyte.**

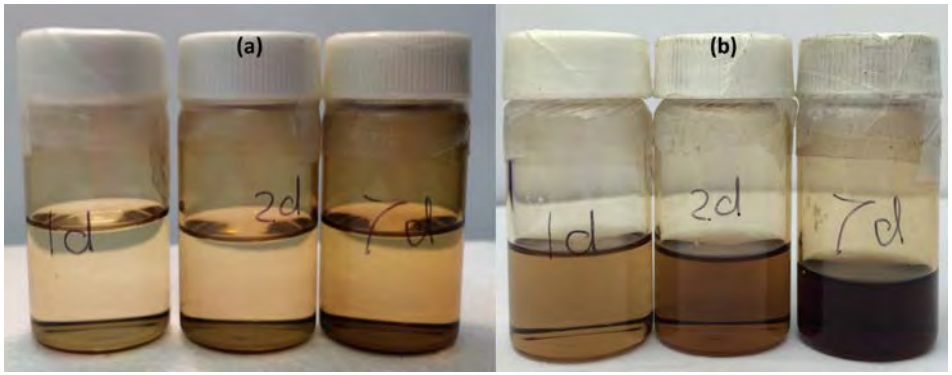
# Electrolyte Latent Effects


Plastic vials

Immediately post irradiation

54 days post irradiation

Pre-irradiation



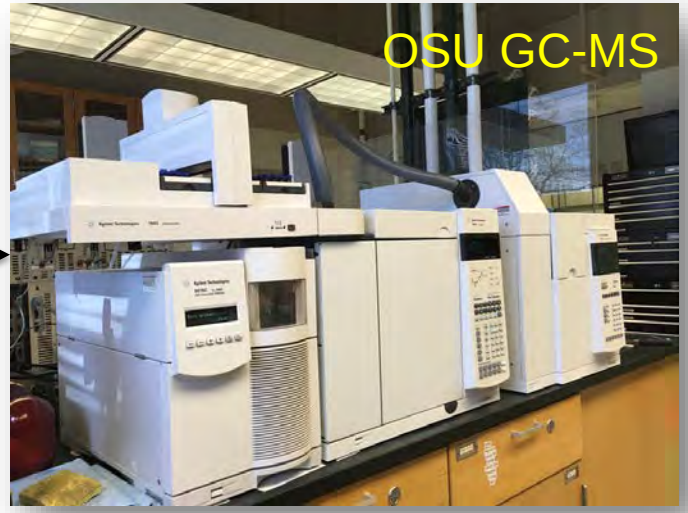

glass vials

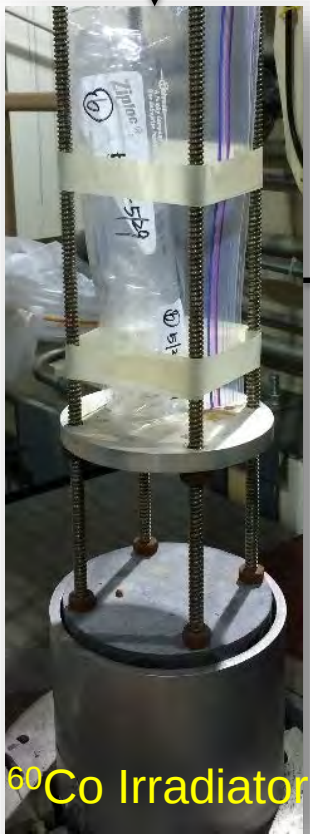
- The color of the electrolyte turned darker as the cumulative dose was increased.
- All three groups of electrolyte changed color gradually with time inside the glove box post-irradiation.

Tan, C., et al., Journal of Power Sources, 2016. **318**: p. 242-250.

# Investigation on LATENT EFFECTS

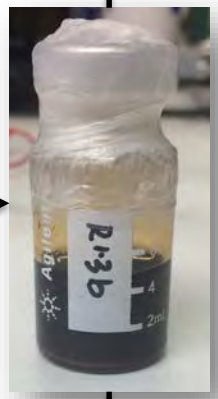
Sample preparation

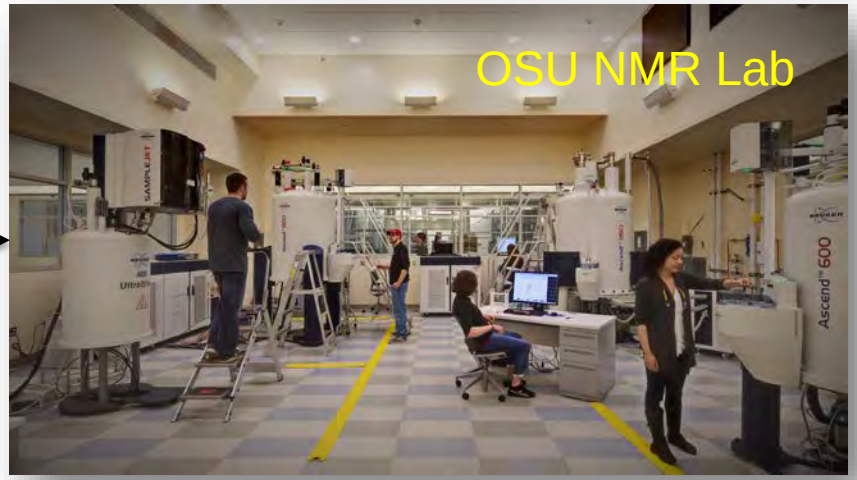



Irradiation
4.2 Mrad

Latent effects developing



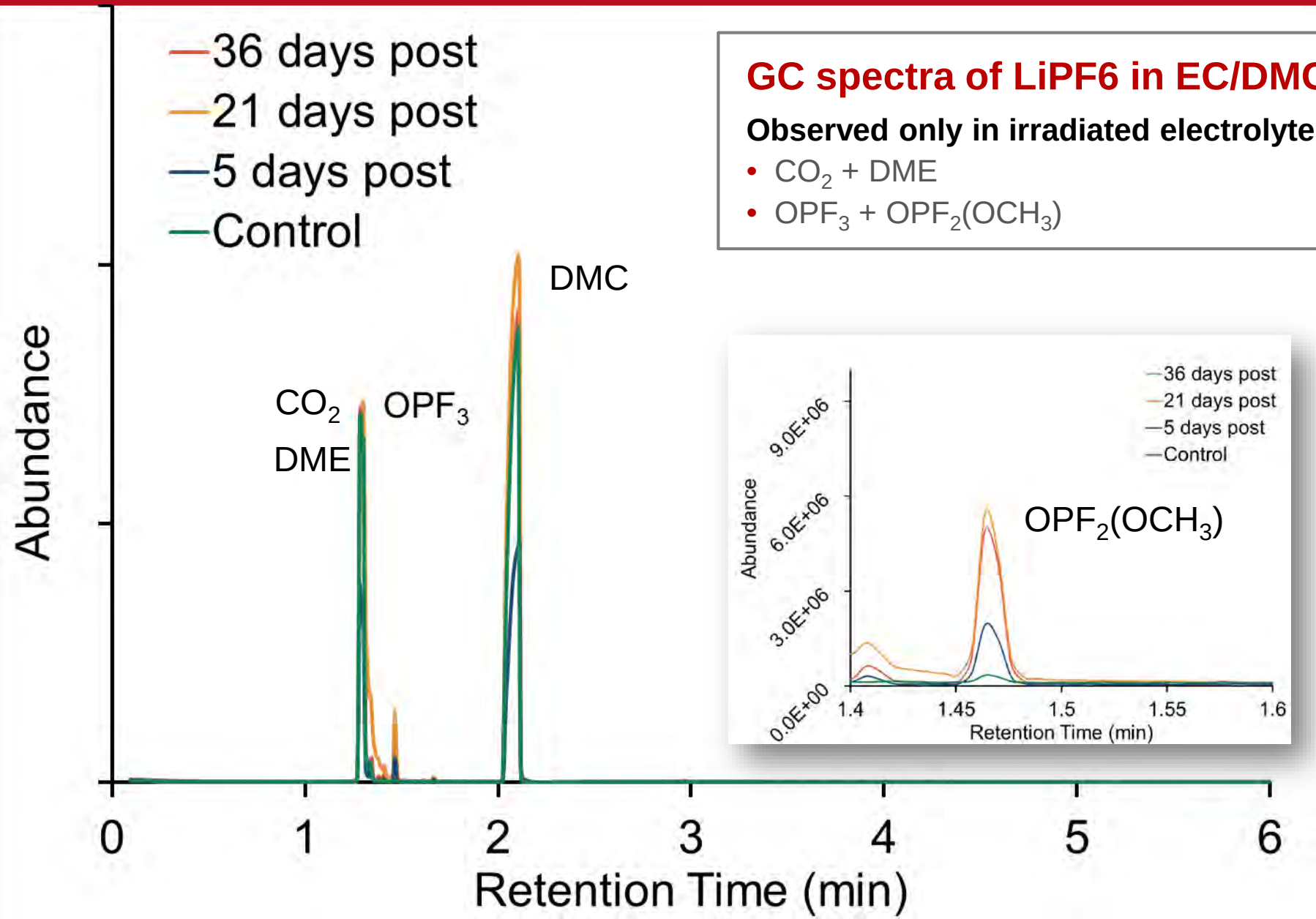



NMR pic courtesy: OSU Chemistry and Biochemistry NMR Lab

## GC spectra of LiPF6 in EC/DMC

**Observed only in irradiated electrolyte**

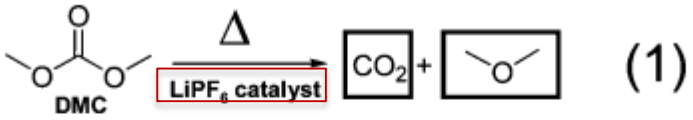
- $CO_2$ + DME
- $OPF_3$ + $OPF_2(OCH_3)$



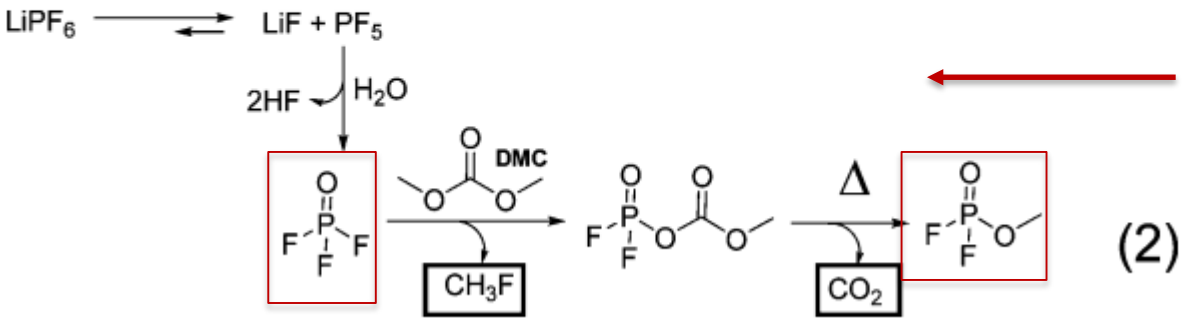
# GC-MS results

| PRODUCTS | LiPF6 in EC/DMC | | | | DMC | EC/DMC | LiPF6 in DMC | |
|---|---|---|---|---|---|---|---|---|
| | Control | 5 day post | 21 days post | 36 days post | | | 21 days | 36 days |
| $CO_2$ | ? | X | X | X | X | X | X | X |
| DME | - | X | X | X | X | X | X | X |
| $OPF_3$ | - | X | X | X | - | - | X | X |
| $OPF_2OME$ | - | X | X | X | - | - | X | X |

# Electrolyte decomposition mechanism




DME



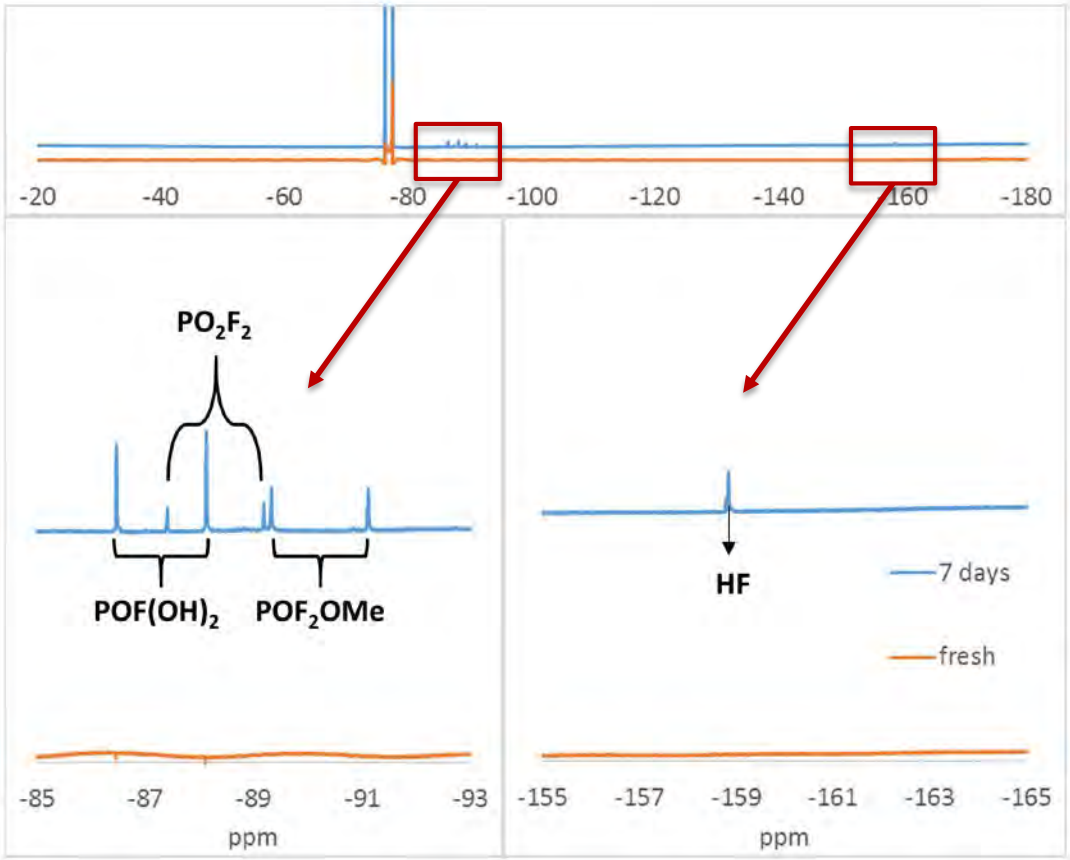

Thermal decomposition

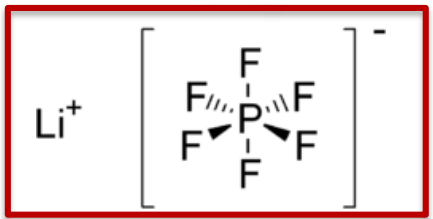
Gachot et al. Anal. Chem. 2011, 83, 478-485

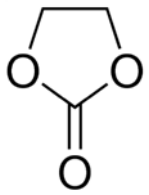
Picture adjusted contrast and brightness

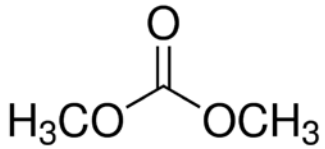
- Different to thermal decomposition, DMC was decomposed directly by gamma rays without $LiPF_6$.
- Amount of products increases with time after irradiation, but no increase from 21 days post to 36 days post.
- White precipitates (LiF?) only in $LiPF_6$ in EC/DMC samples
- Analysis ongoing

# Electrolyte Latent Effects
# Chemical Characterization-NMR(F, P, H)



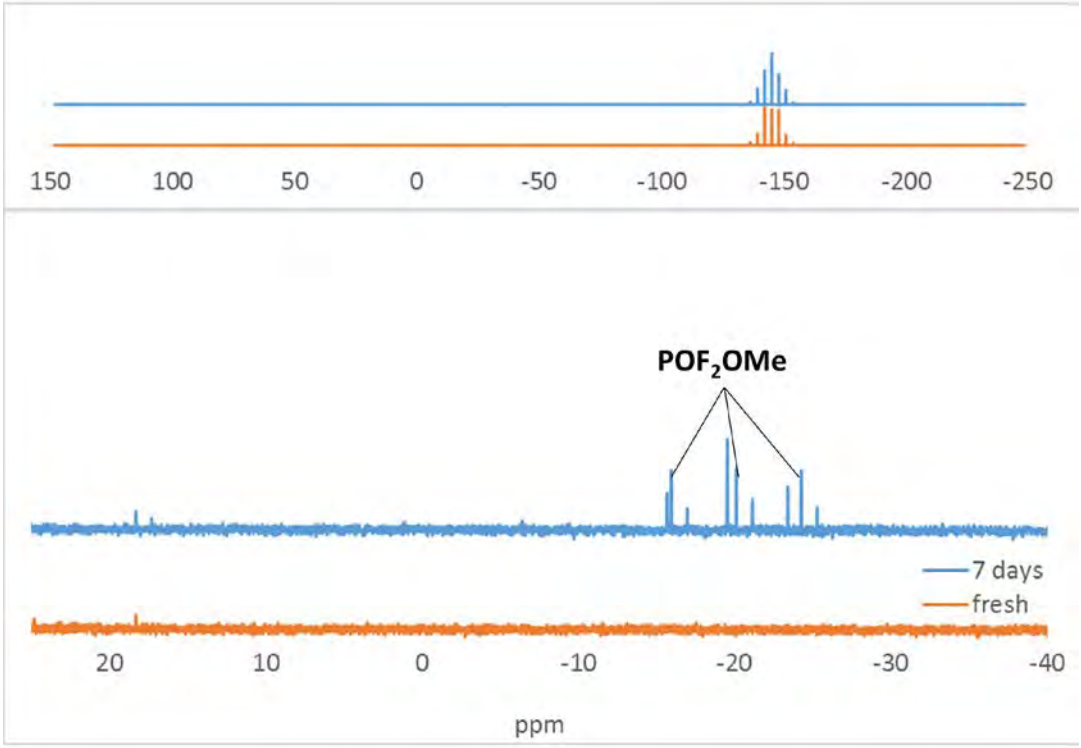




F-NMR

- After irradiation a pre-existing doublet grows and 2 more doublets appear in the irradiated electrolyte between -85 and -92 ppm. The inset shows the entire spectral window.
- $LiPF_6$ salt has been damaged.

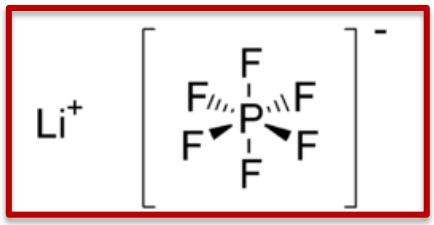
Tan, C., et al., Journal of Power Sources, 2016. **318**: p. 242-250.

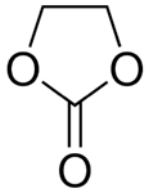
# Electrolyte Latent Effects
# Chemical Characterization-NMR(F, P, H)

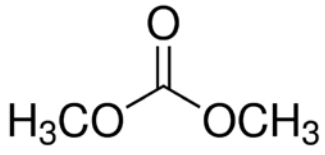



P-NMR

- After irradiation a triplet of triplets appears in the irradiated electrolyte between -14 and -26 ppm. The inset shows the entire spectral window.
- $LiPF_6$ salt has been damaged.

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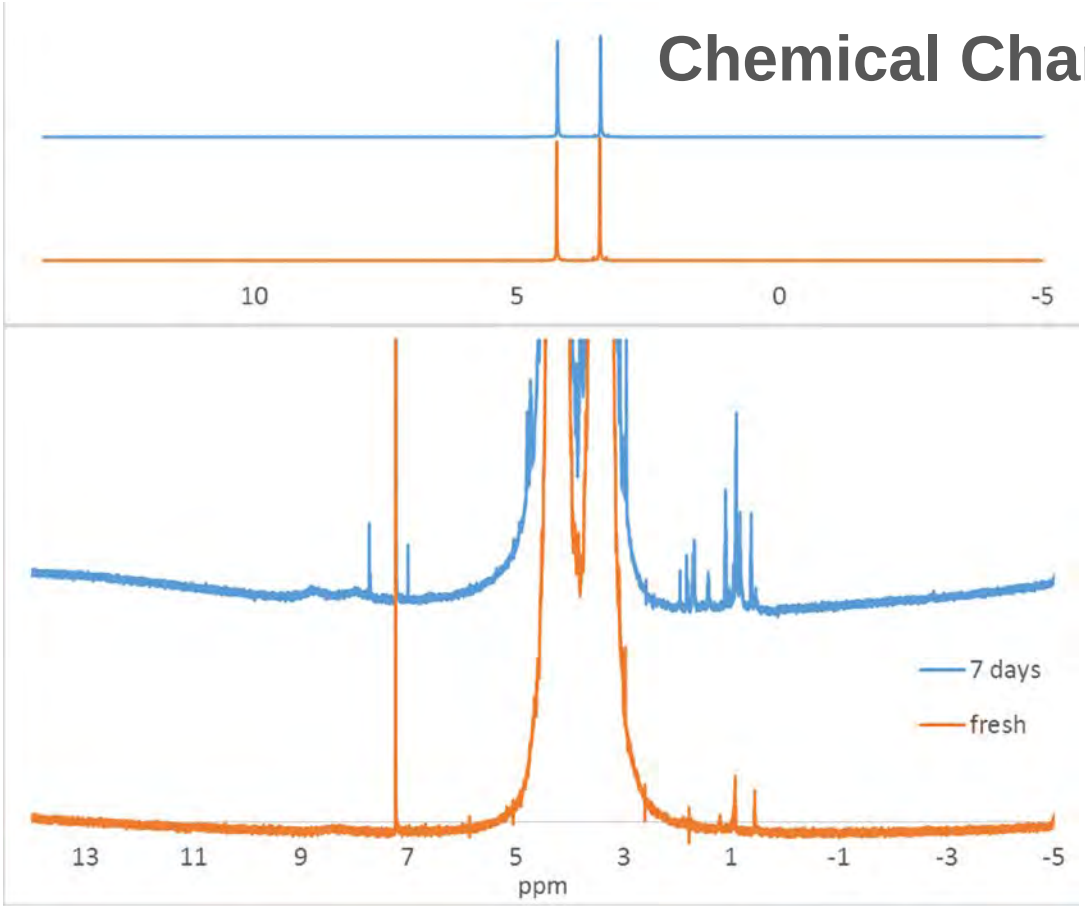
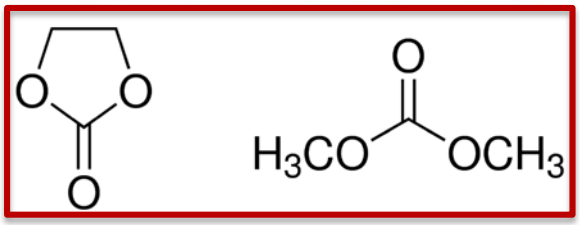
# Electrolyte Latent Effects
## Chemical Characterization-NMR(F, P, H)





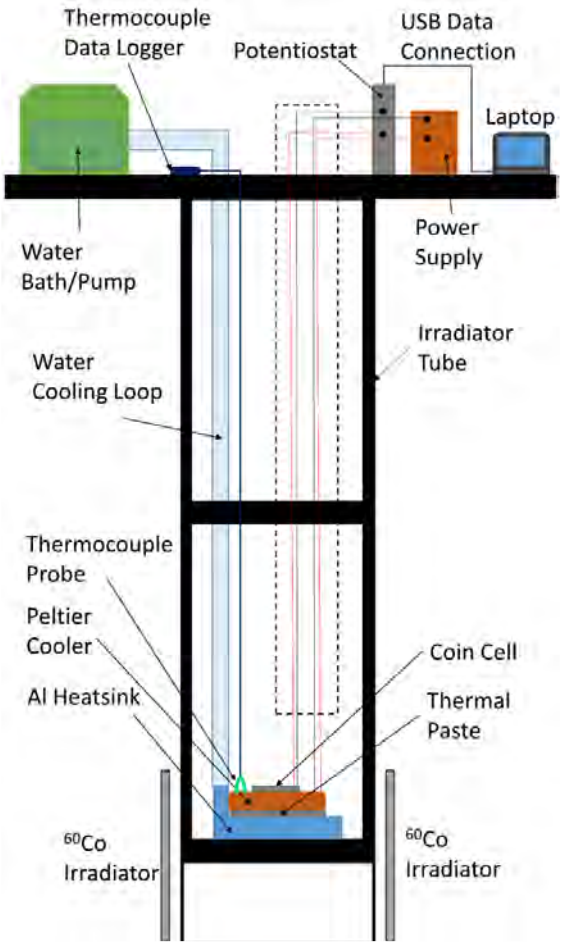



H-NMR

- Radiation is damaging both the salt as well as the EC/DMC solution since the only source of hydrogen is in the EC/DMC.

Tan, C., et al., Journal of Power Sources, 2016. **318**: p. 242-250.

# Latent effects illustrated from battery performance

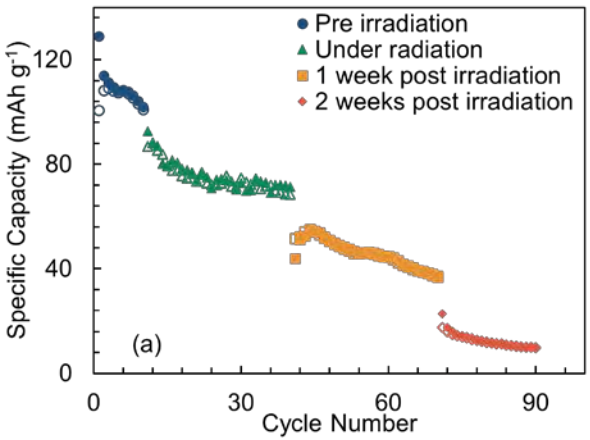


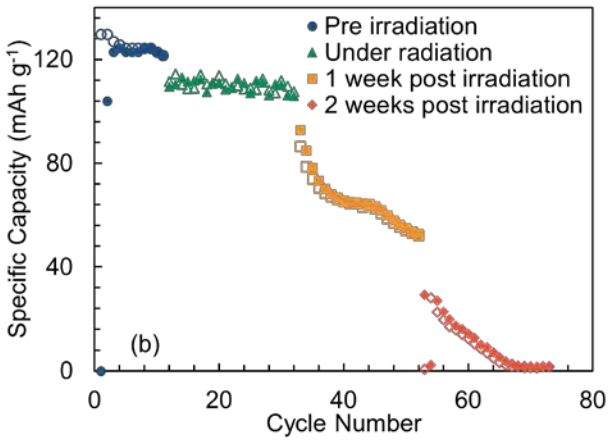

**In-situ battery cycling setup using $^{60}$Co irradiator**

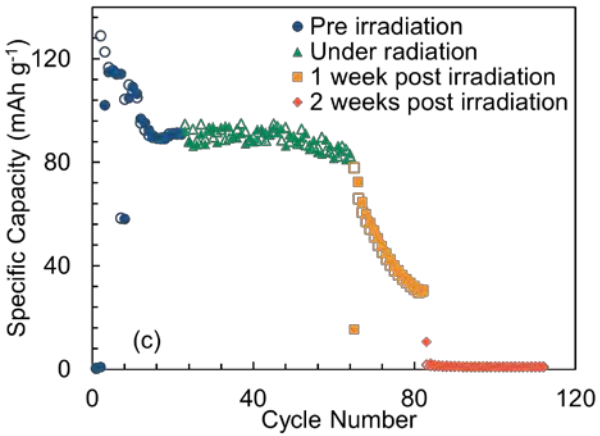
Tan et al., Journal of Power Sources, Volume 357, 31 July 2017, Pages 19-25.

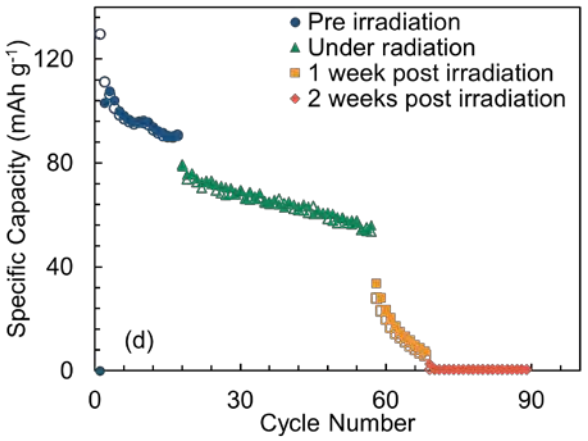
# In-situ capacity fading

2.2 Mrad



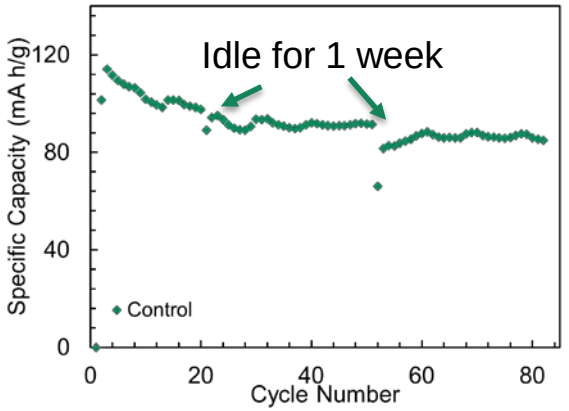




3.6 Mrad

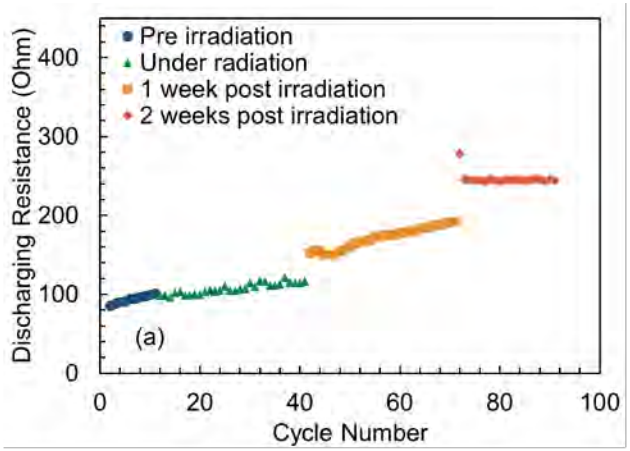
- Capacity fade not obvious during irradiation
- Rapid capacity fading after irradiation
- Shortened calendar life after irradiation
- Higher dose results in shorter life

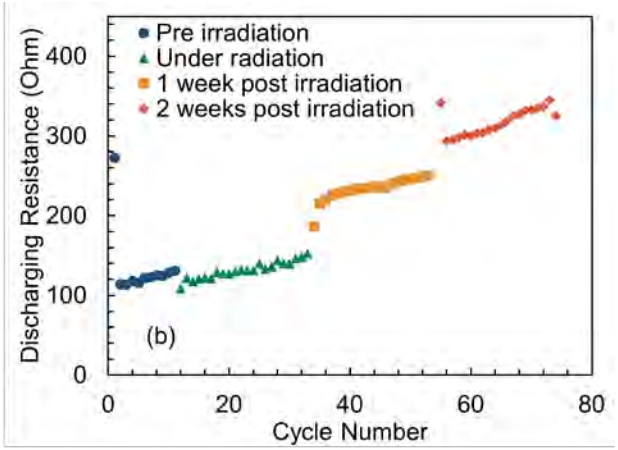


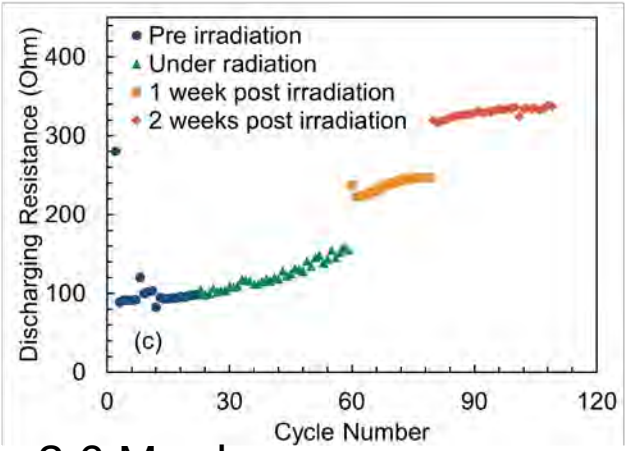

Tan et al., Journal of Power Sources, Volume 357, 31 July 2017, Pages 19-25.

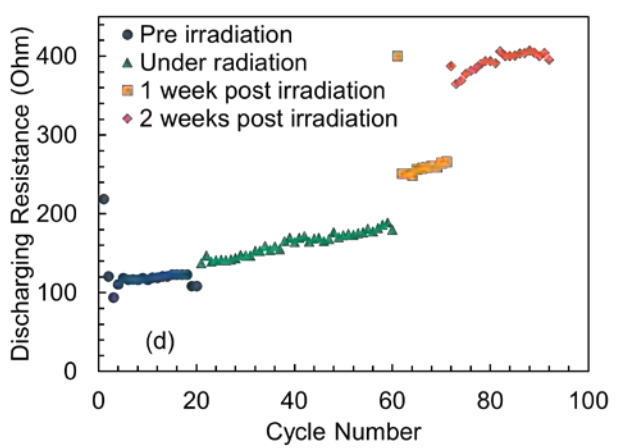
# In-situ resistance rise

2.2 Mrad



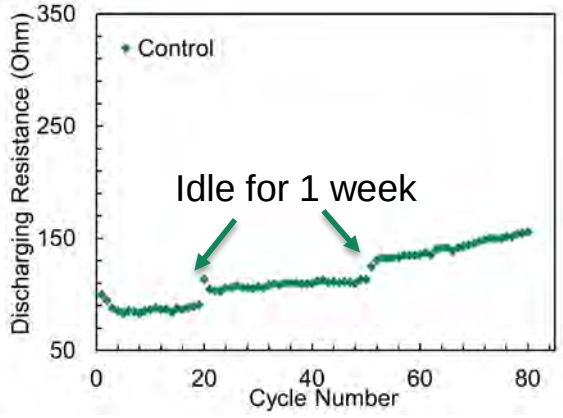



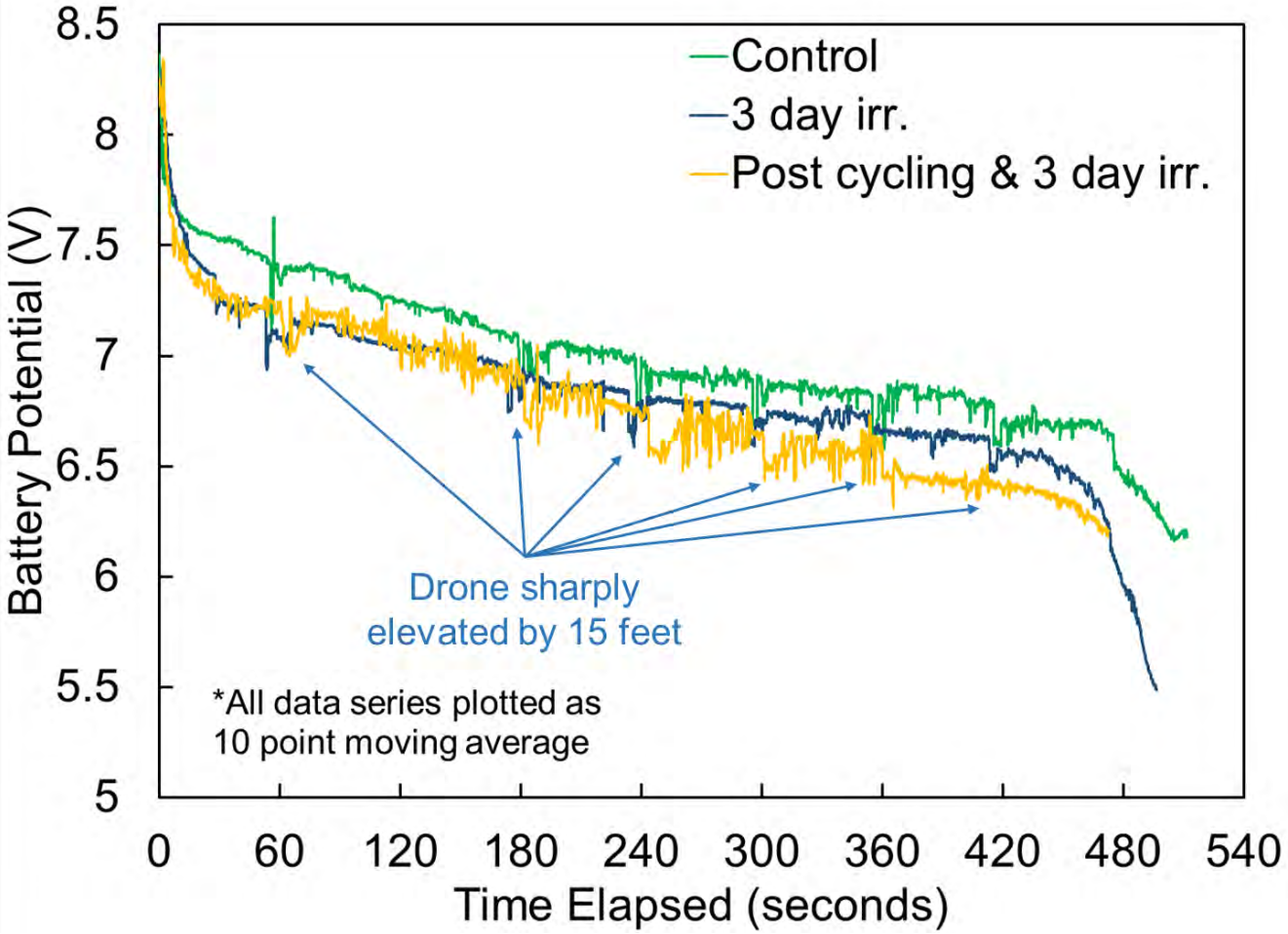

3.6 Mrad

- Resistance profile confirmed no change during irradiation
- Higher dose, higher post irradiation resistance




Tan et al., Journal of Power Sources, Volume 357, 31 July 2017, Pages 19-25.

# Drone test using irradiated LIB



## Conclusions

- Latent effects!
- Electrolyte will decompose after being irradiated and the process is similar to thermal decomposition but not the same
  - Analysis ongoing to identify decomposition pathways
- In-situ cycling proved that latent effects could be more damaging

# Acknowledgement

We would like to acknowledge

**Funding source - Defense threat reduction agency**

**OSU Nuclear Reactor Lab**

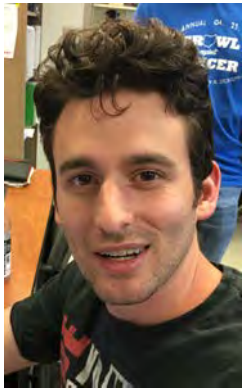
**OSU Center for Electron Microscopy and Analysis**

**OSU Chemistry and Biochemistry Analytical Lab**

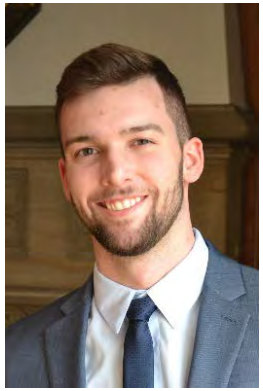
**OSU Chemistry and Biochemistry NMR Lab**

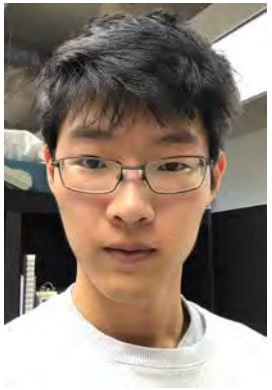
# Team members


Chuting Tan


Daniel Lyons

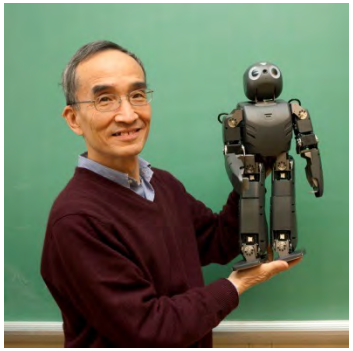

Nick Bashian


Chase Hemmelgarn


Wesley Thio


Jenna Glover


Prof. Raymond Cao


Prof. Yuan F. Zheng


Prof. Anne C. Co

# Thank you!