Lithium CF_x Batteries for High Radiation Environments

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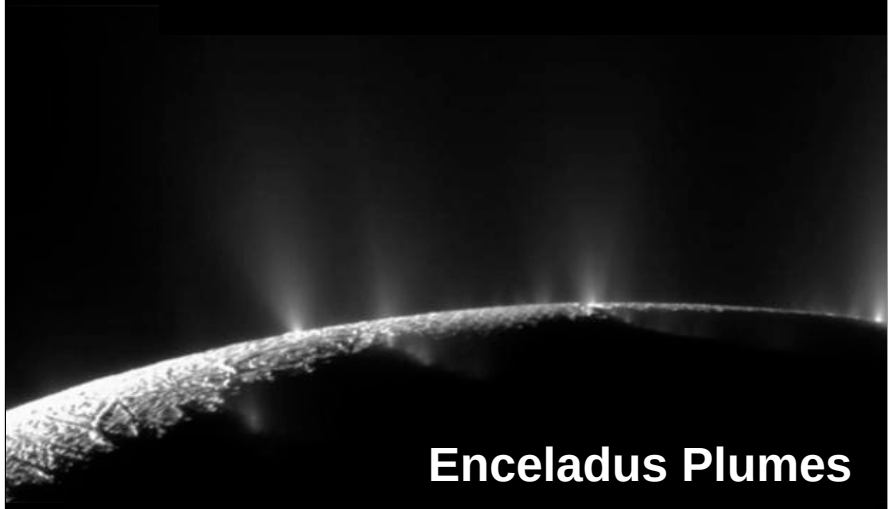
Increasing Interest in a lander for “Ocean Worlds”



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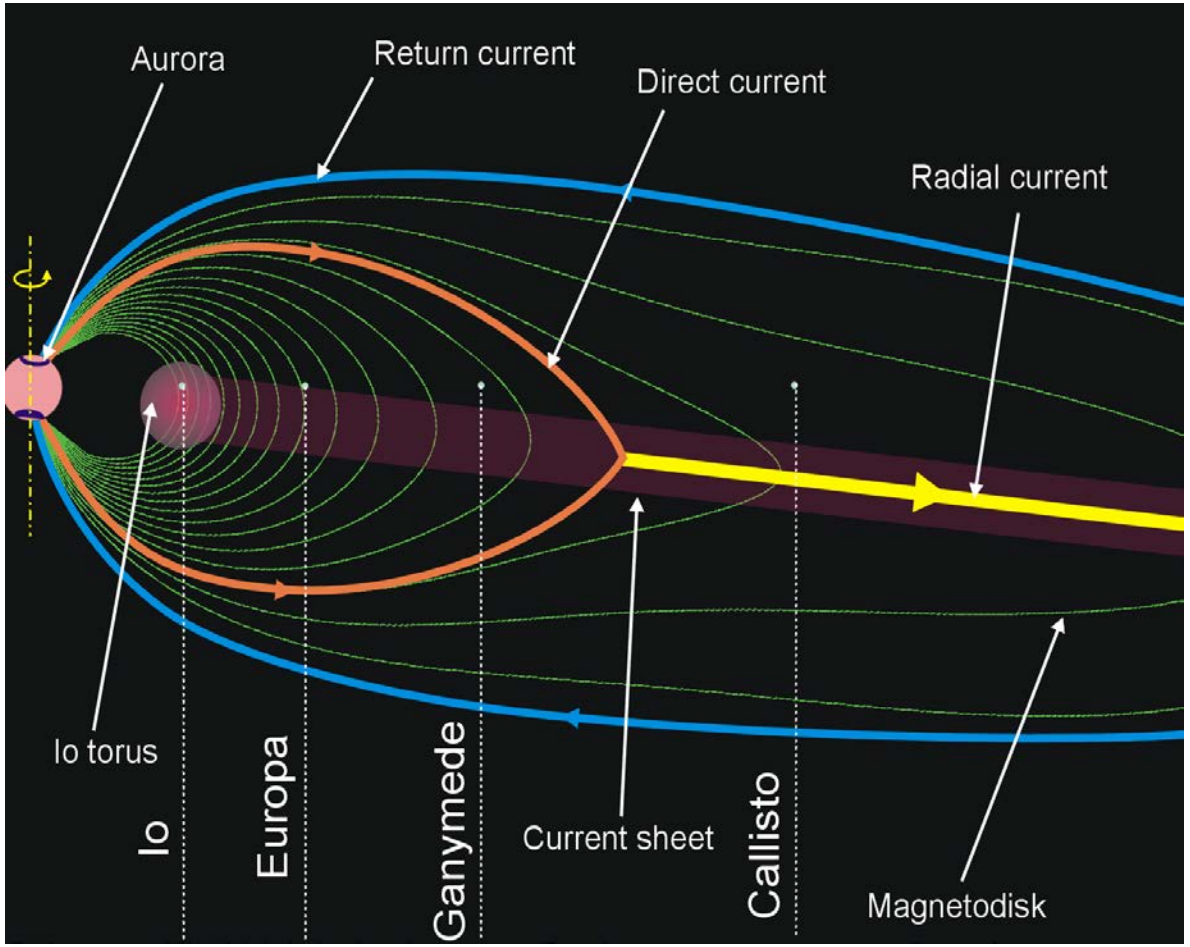
Radiation Testing

- Jupiter generates a high radiation environment
- Europa is directly in the path
- Possible sterilization procedure for planetary protection
- JPL high dose rate ^{60}Co source
  - 1.3 MeV gamma rays
  - ~100 rad/s
  - 1 MRad up to 15 MRad

Test articles:

- Rayovac Li/CF_X D-cells
  - $LiBF_4$ in PC+DME + $LiNO_3$
- EaglePicher Li/CF_X-MnO_2 D-cells
  - $LiClO_4$ in PC+DME+THF
- EaglePicher Li/CF_X D-cells
  - $LiClO_4$ in PC+DME
- 3-electrode Li/CF_X cells
- Cell components (cathode materials, salts, electrolytes, separators)



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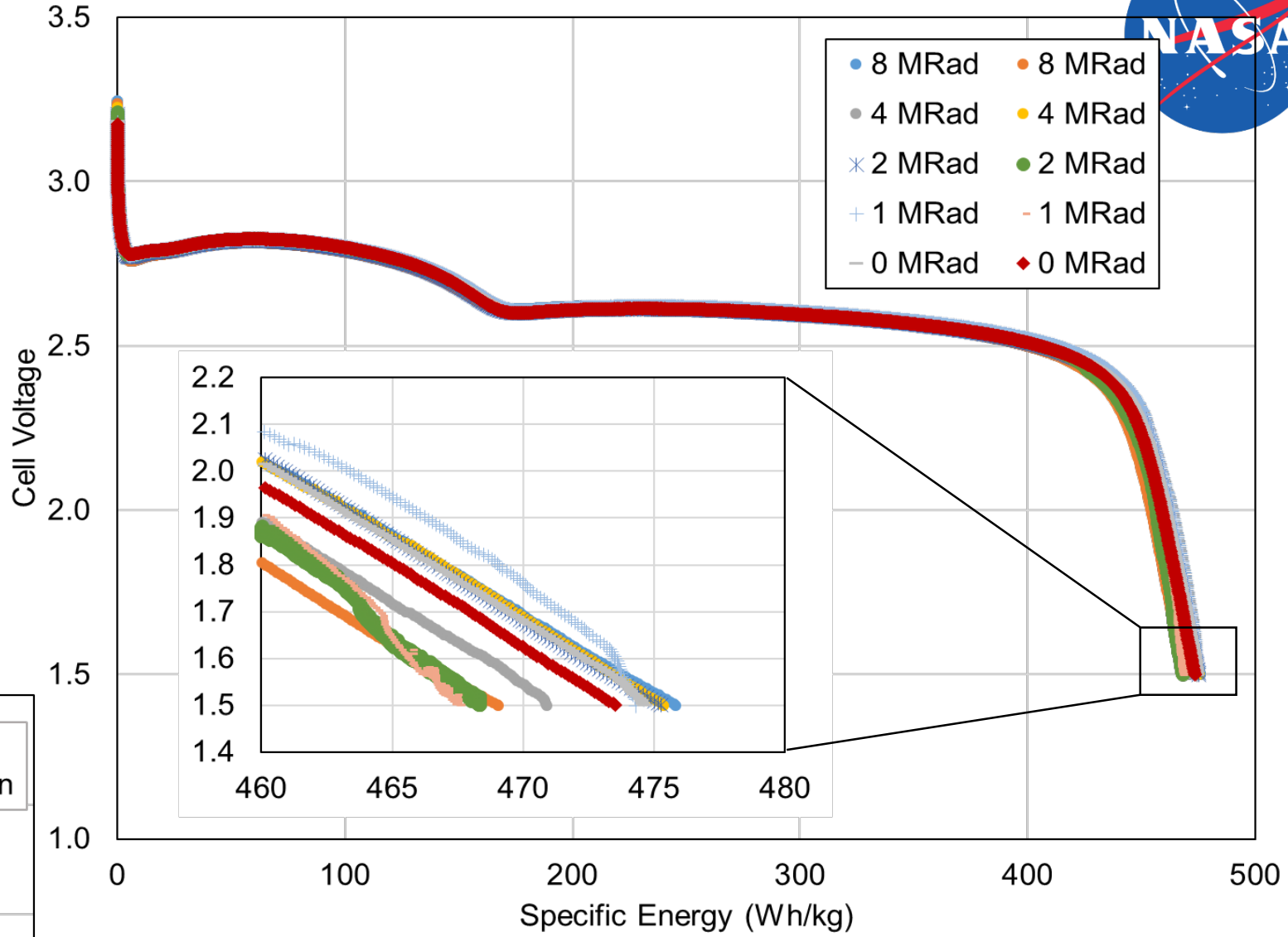
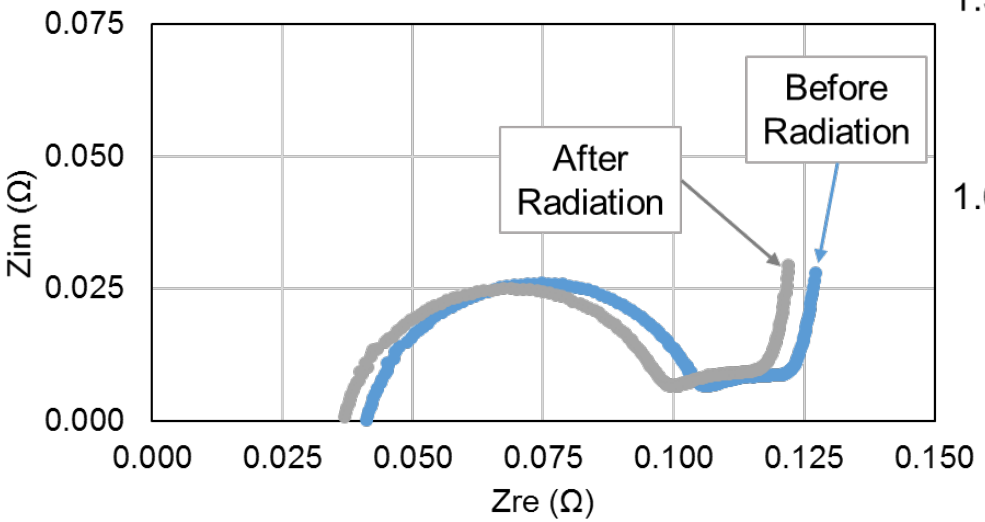
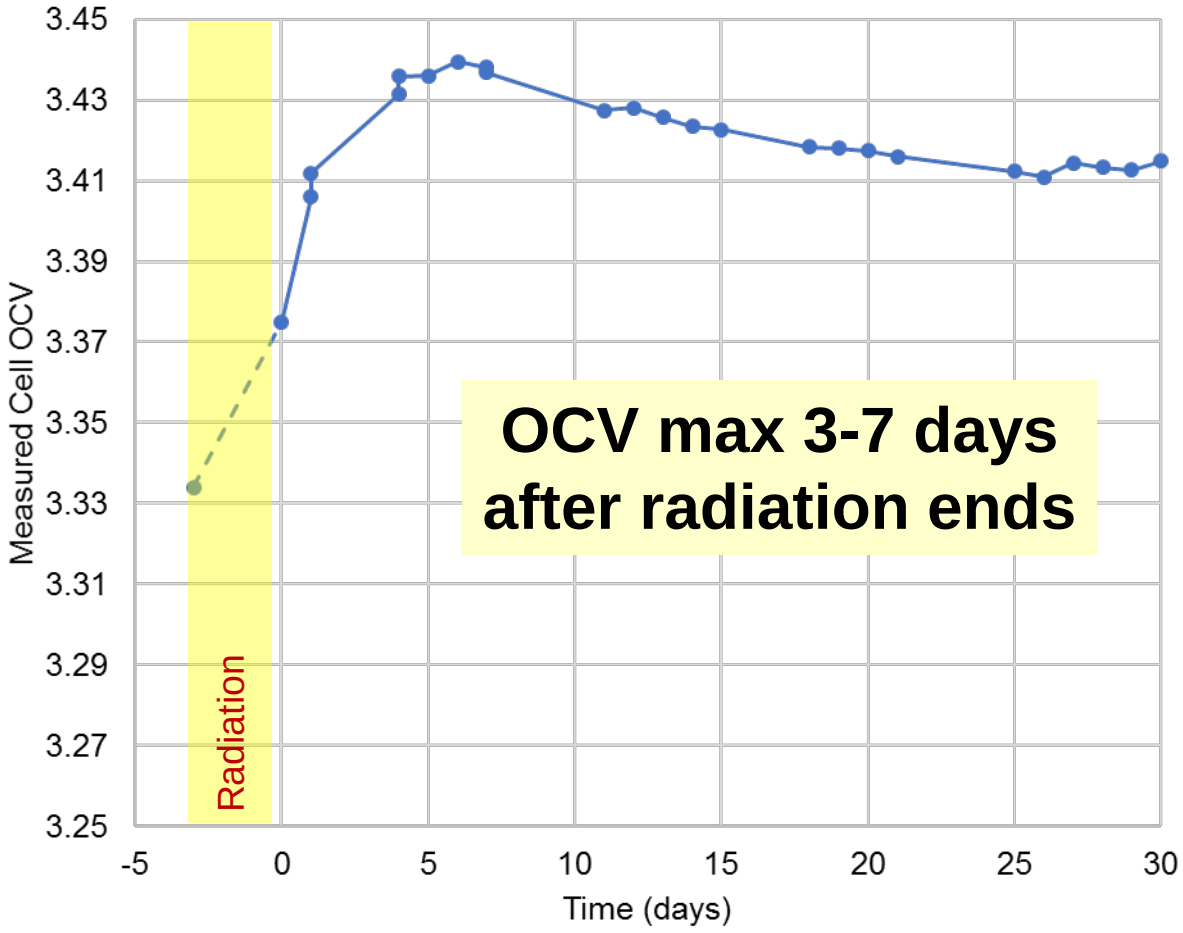
Li/CF_x-MnO_2 Radiation cell discharge performance at 250 mA, 21 °C

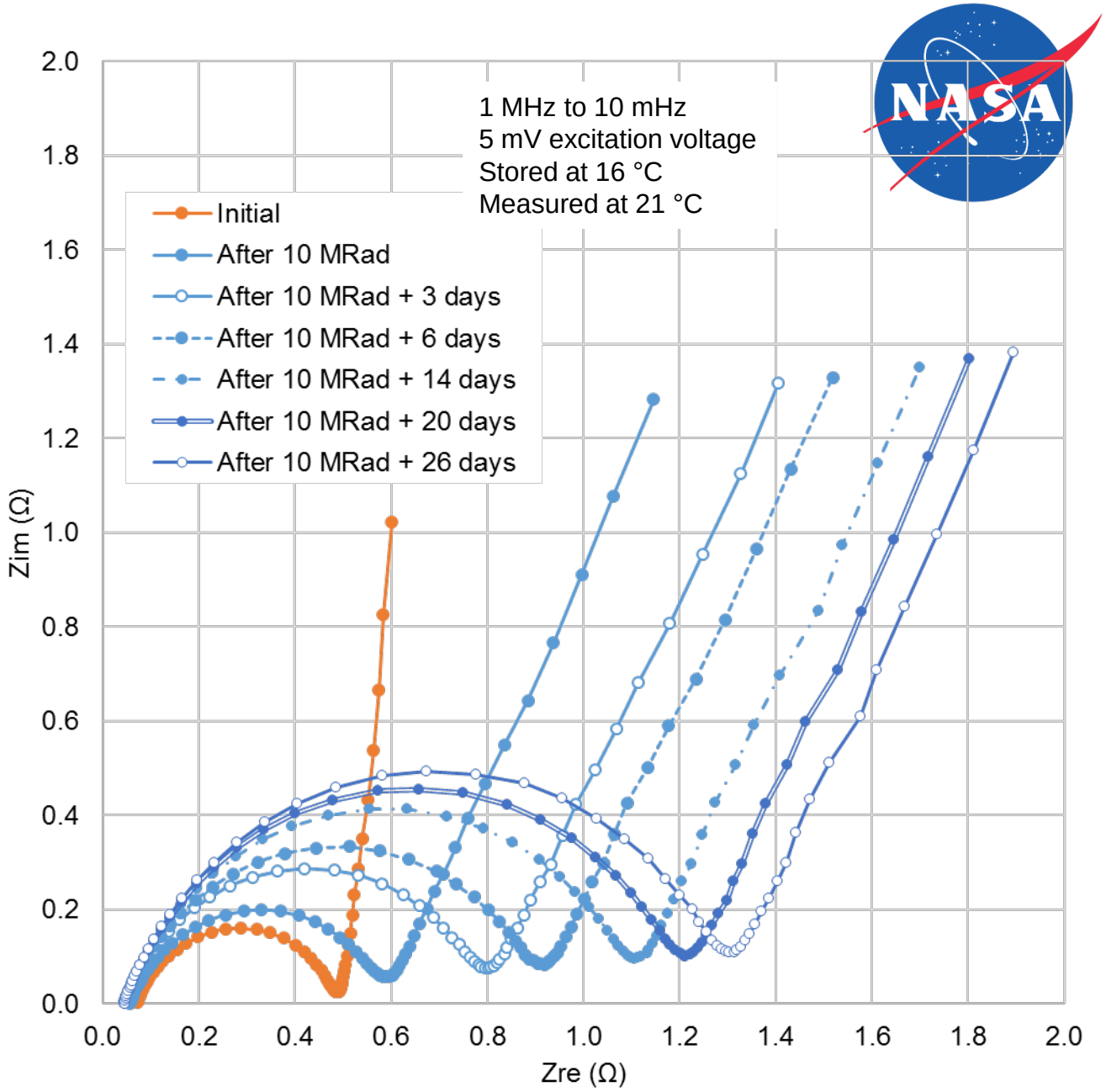
Radiation does not appear to impact capacity or energy



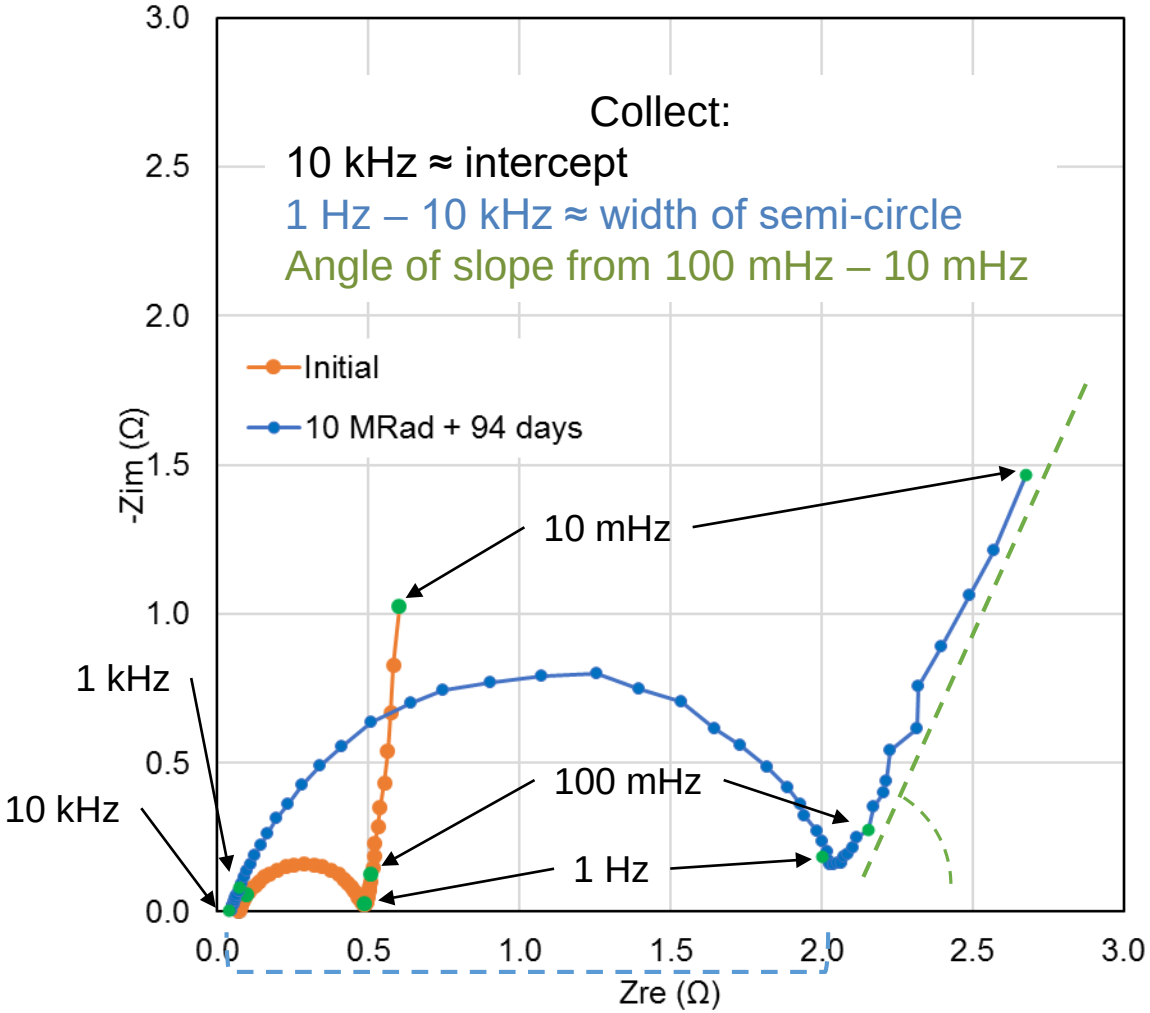


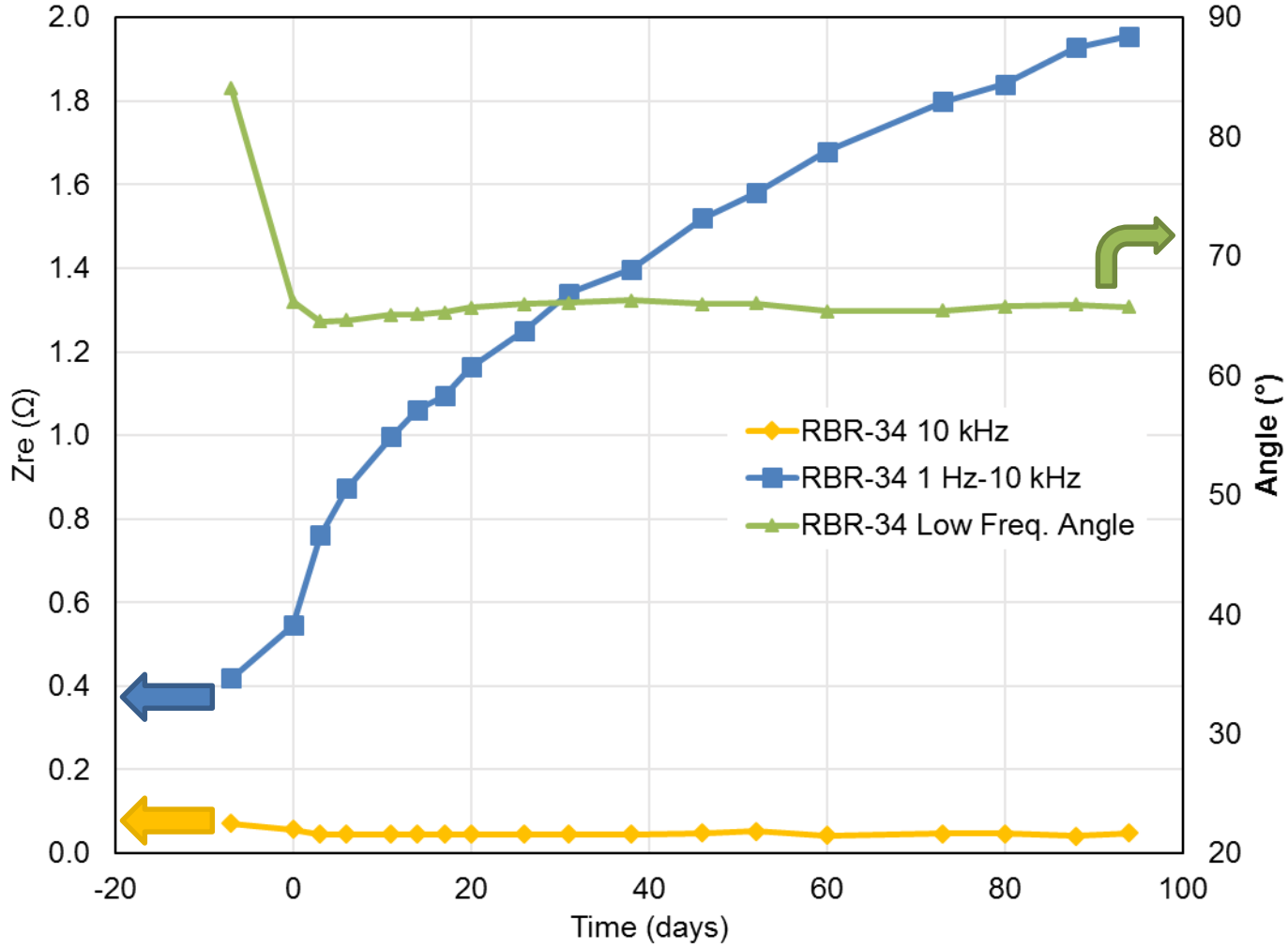
OCV and Impedance change drastically for Li/CF_x D-cell after 10 MRad





Quantifying EIS changes over time for Li/CF_x cells



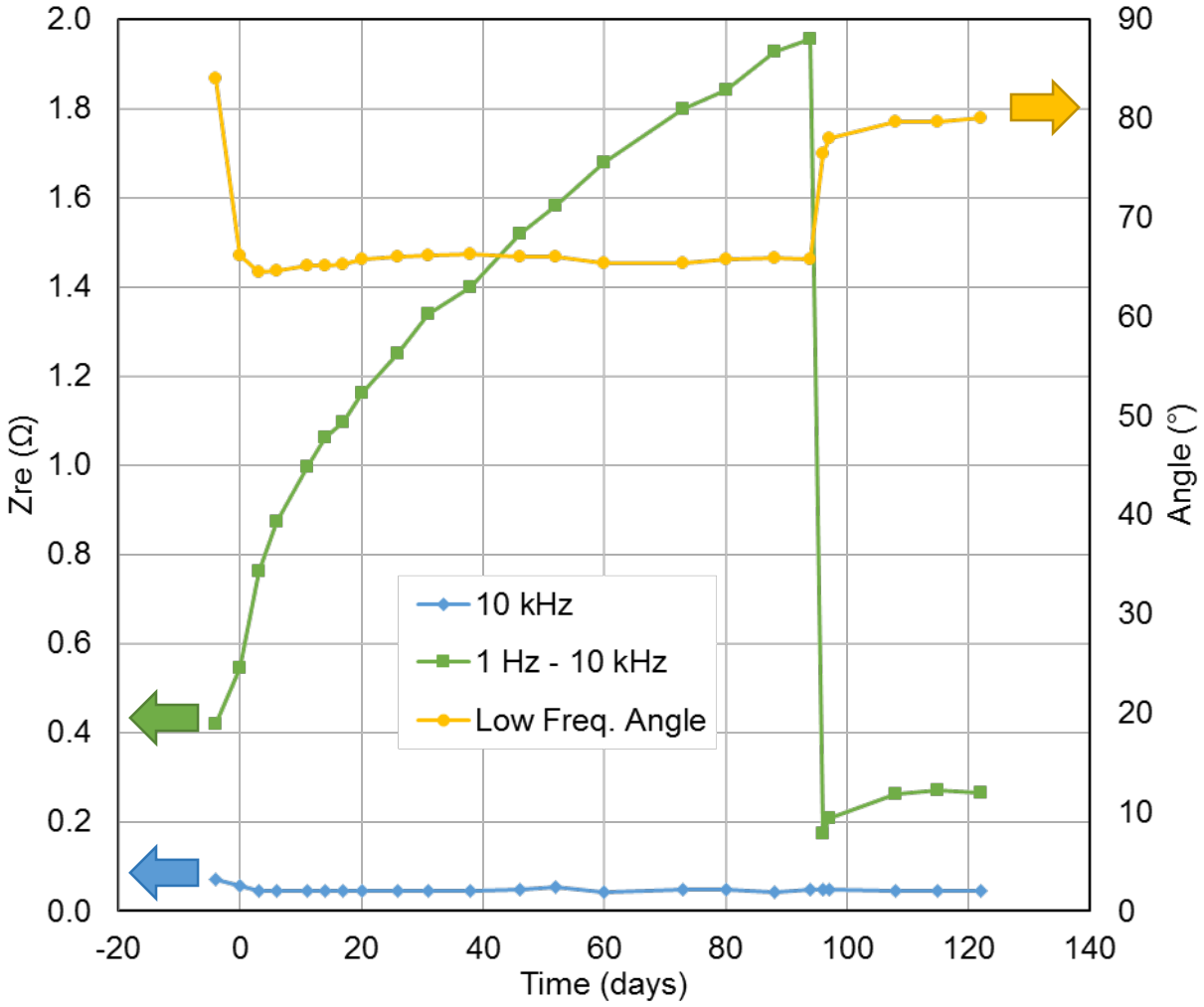


1 MHz to 10 mHz
5 mV excitation voltage

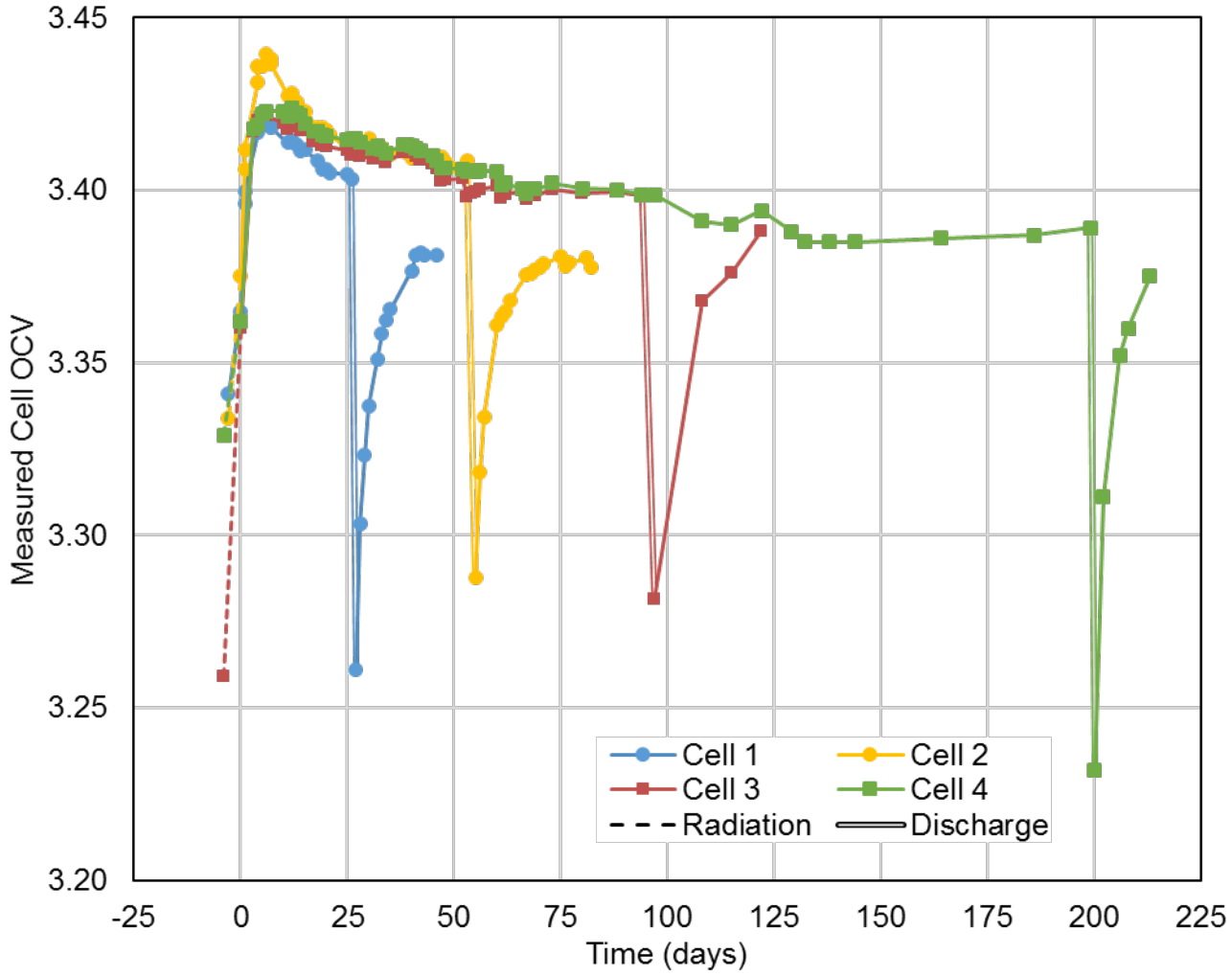
Stored at 16 °C
Measured at 21 °C

2% discharge effects on EIS and OCV

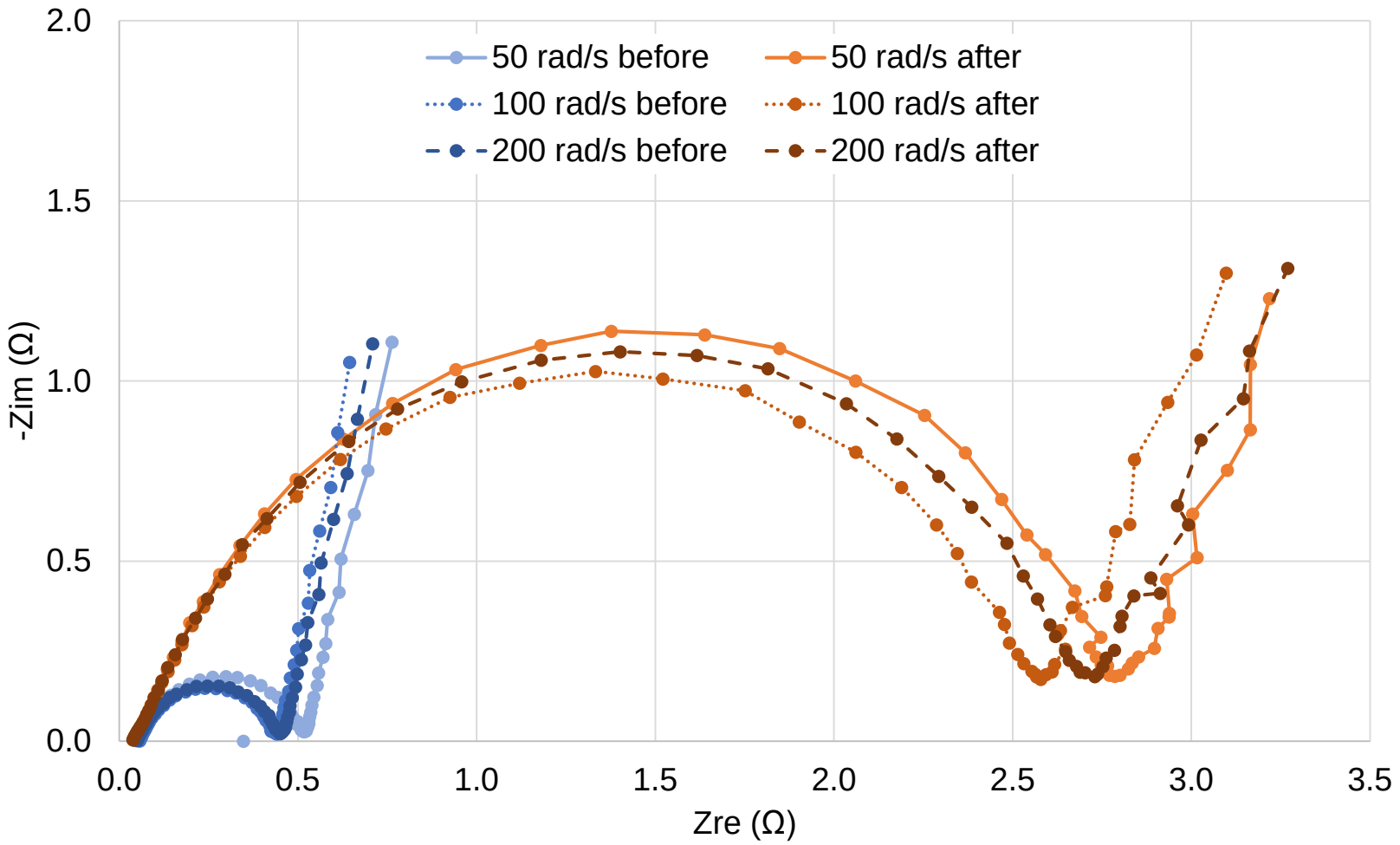
Semi-circle width decreases
Low freq. angle becomes steeper



OCV remains elevated
after discharge

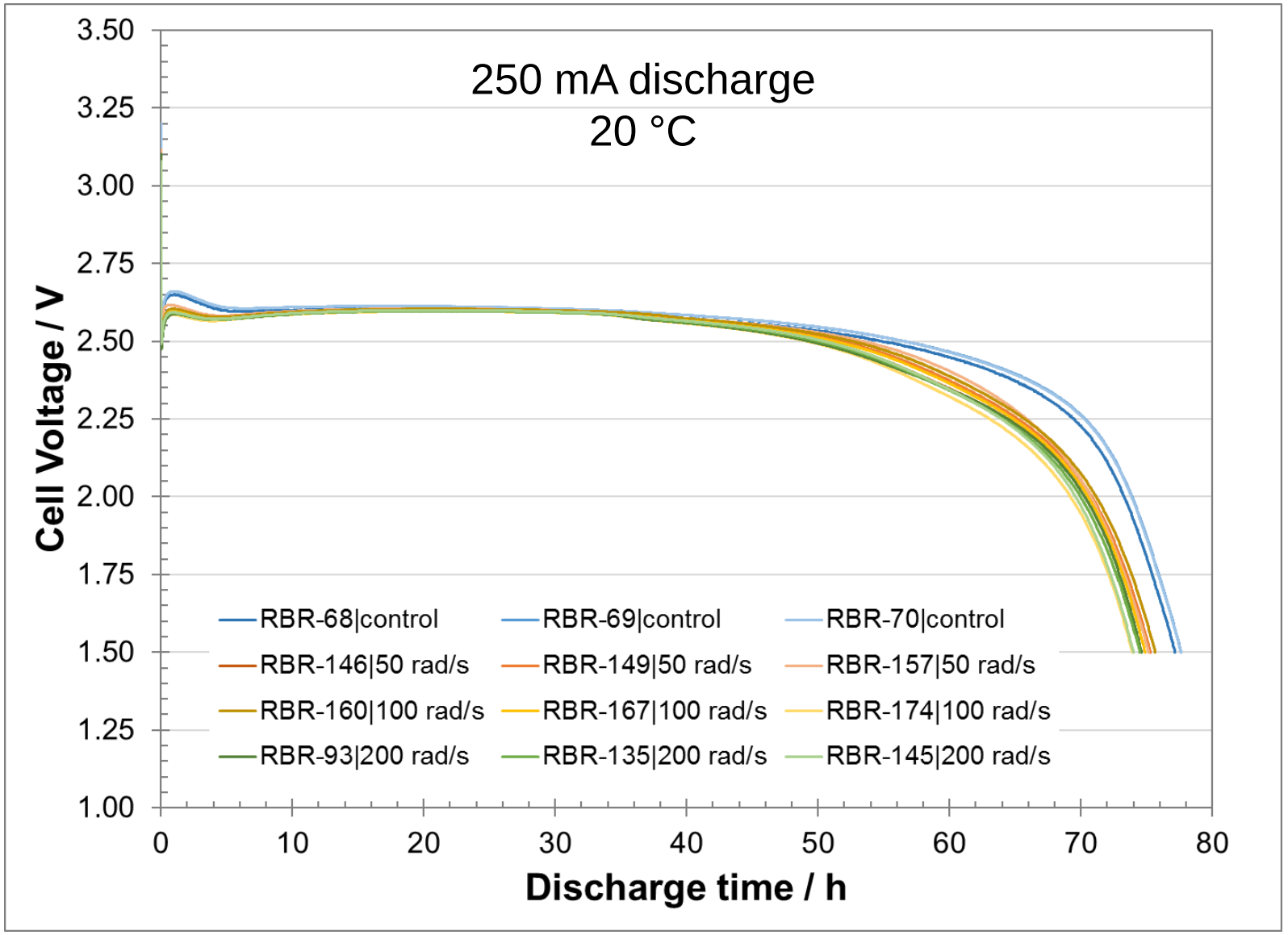


EIS Change as a Function of Radiation Dose Rate (10 Mrad total)

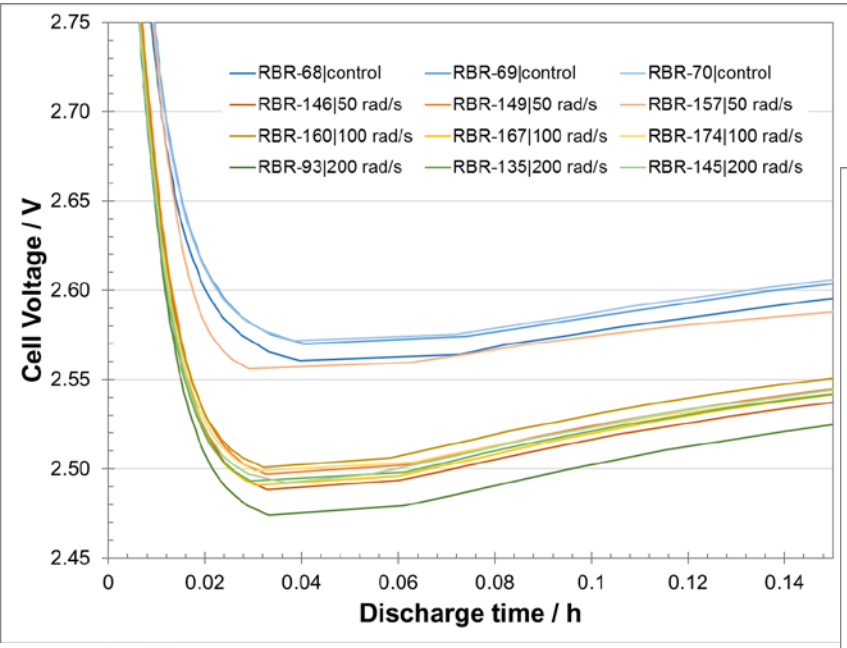


No correlation between impedance and dose rate observed

Discharge Performance as a Function of Radiation Dose Rate

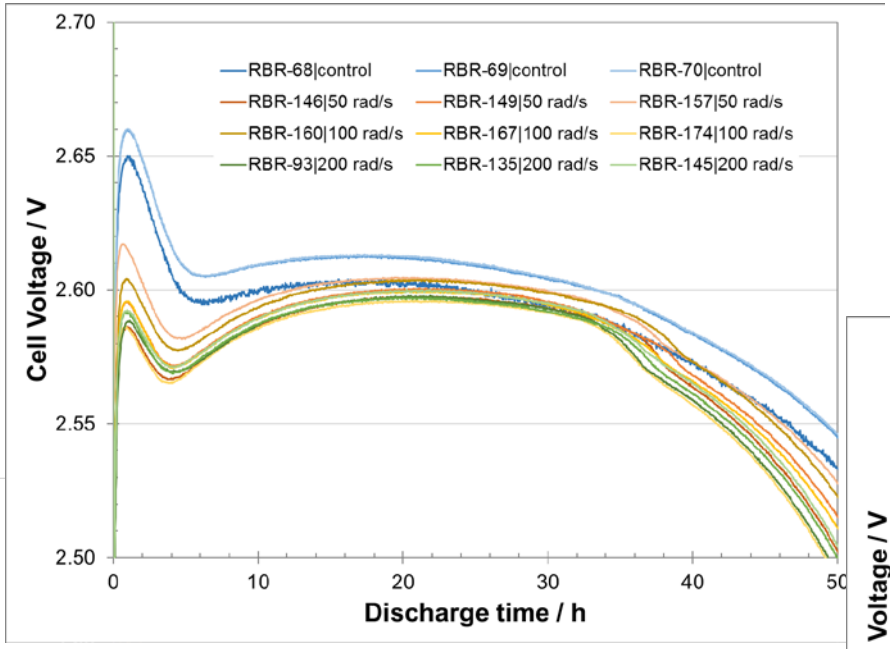


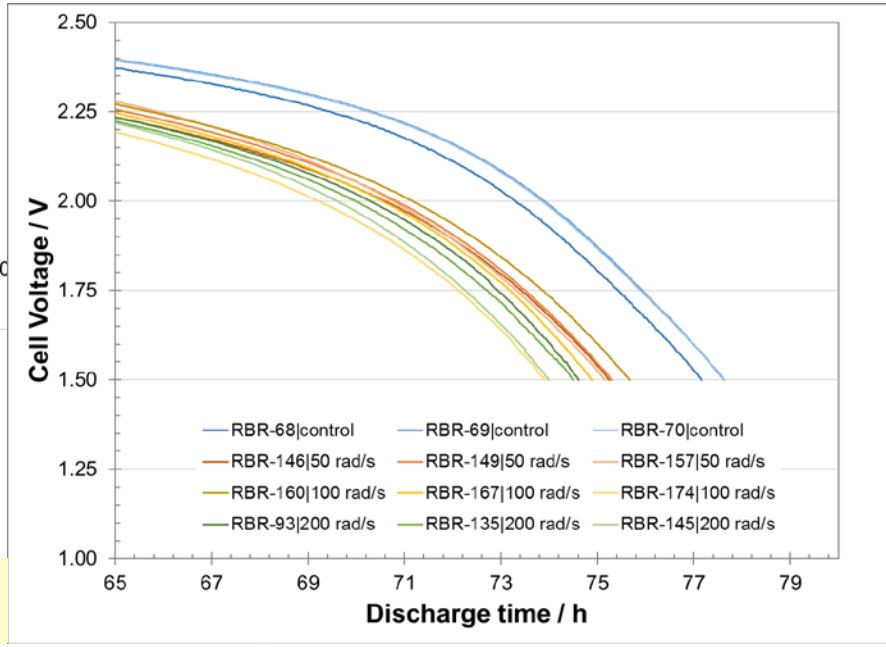
Discharge Performance as a Function of Radiation Dose Rate



250 mA discharge
20 °C

Lower voltage at all points during discharge



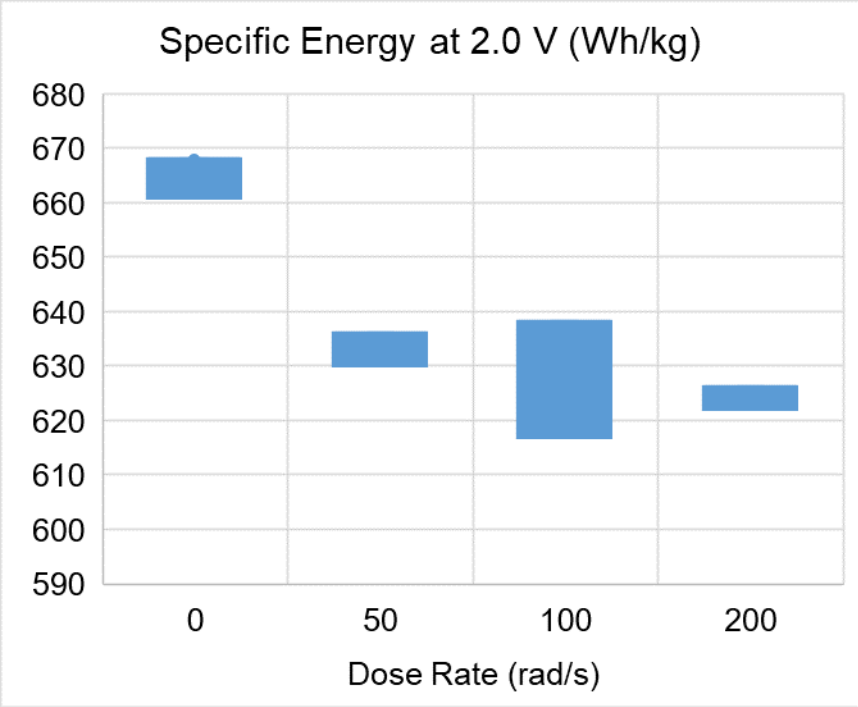


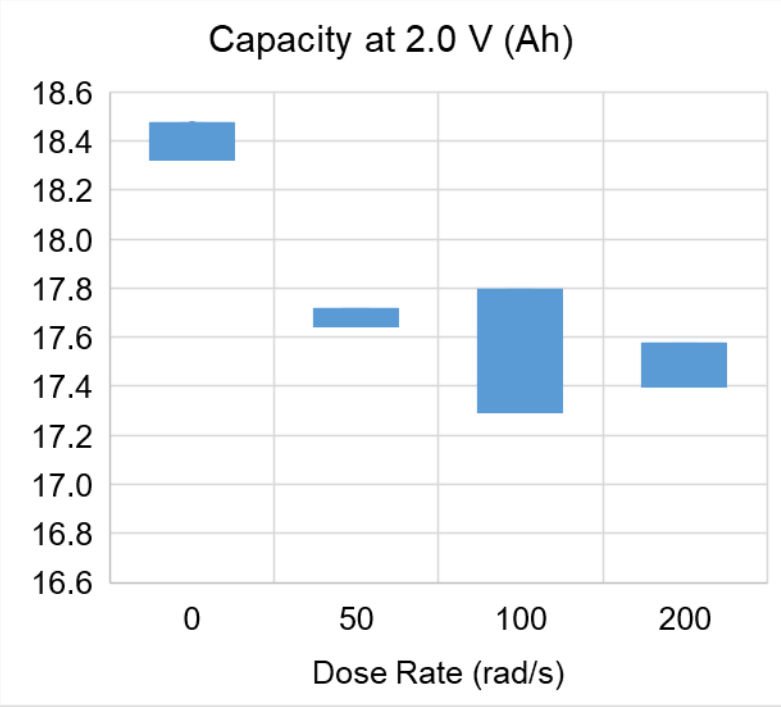
Less capacity delivered

Capacity and Energy Following Radiation

- Controls experienced very similar thermal history
- Capacity drops by 2-5 %
- Energy drops by 2-6 %

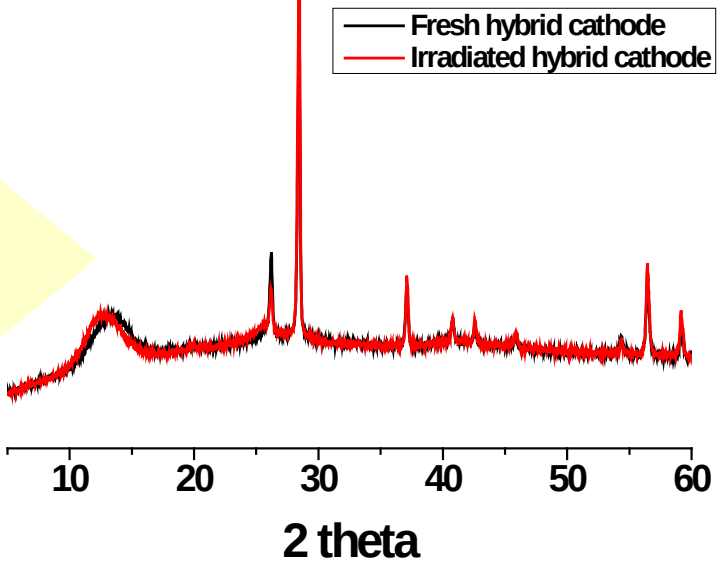
- Weak correlation between dose rate and discharge performance
- Selected 100 rad/s for future studies

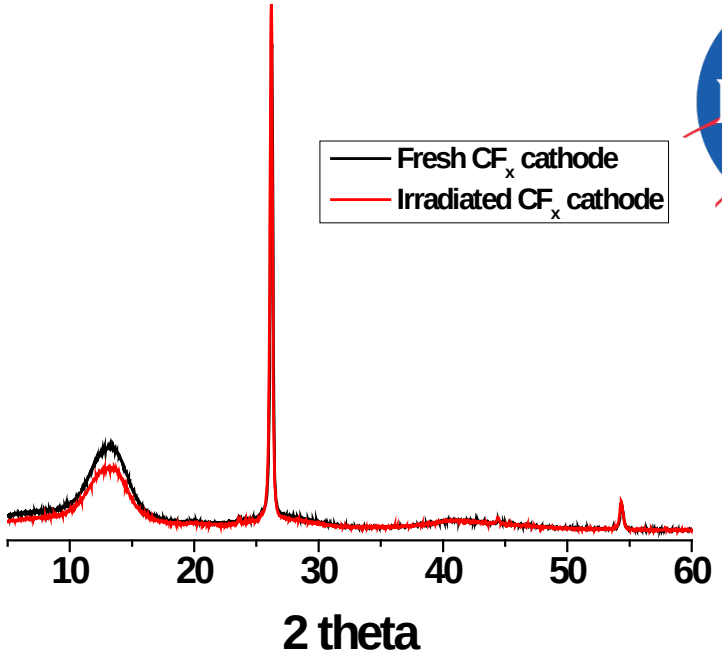


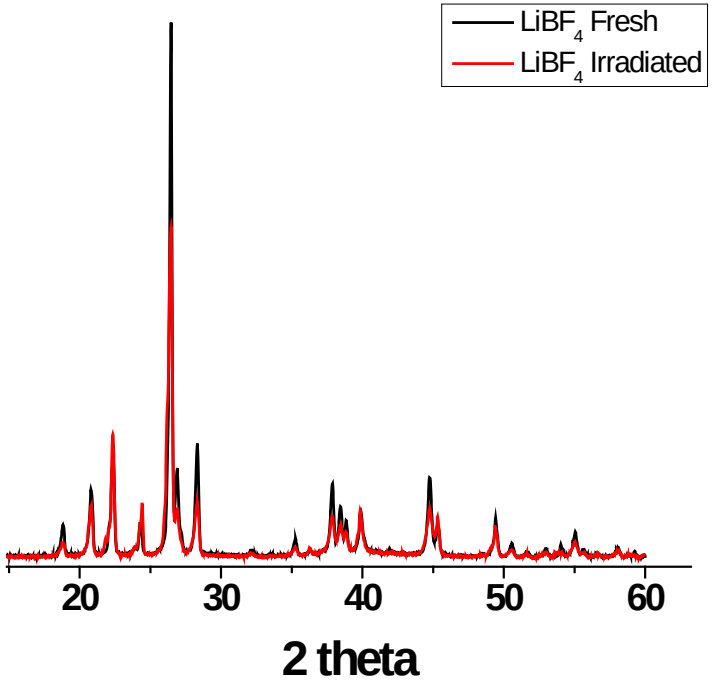


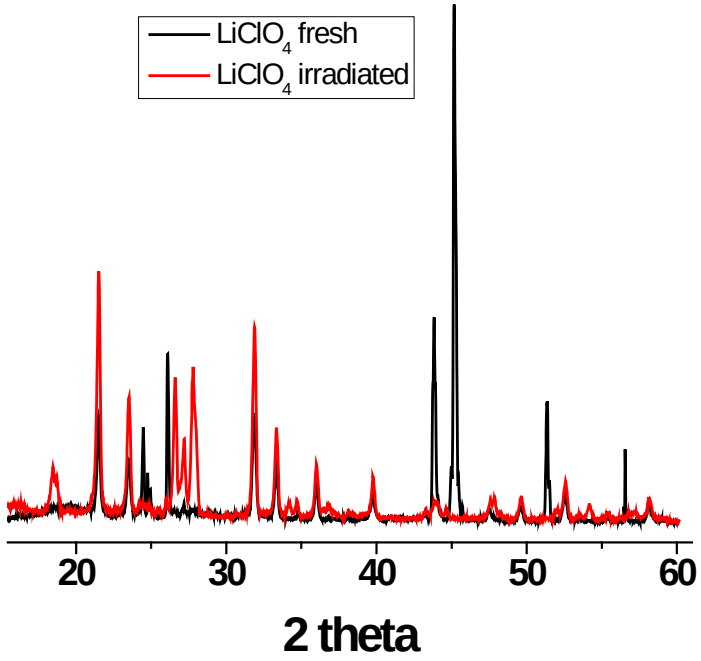
Materials testing – XRD analysis

Pure CF_X and CF_X-MnO_2 cathodes do not change significantly during exposure to 10 MRad



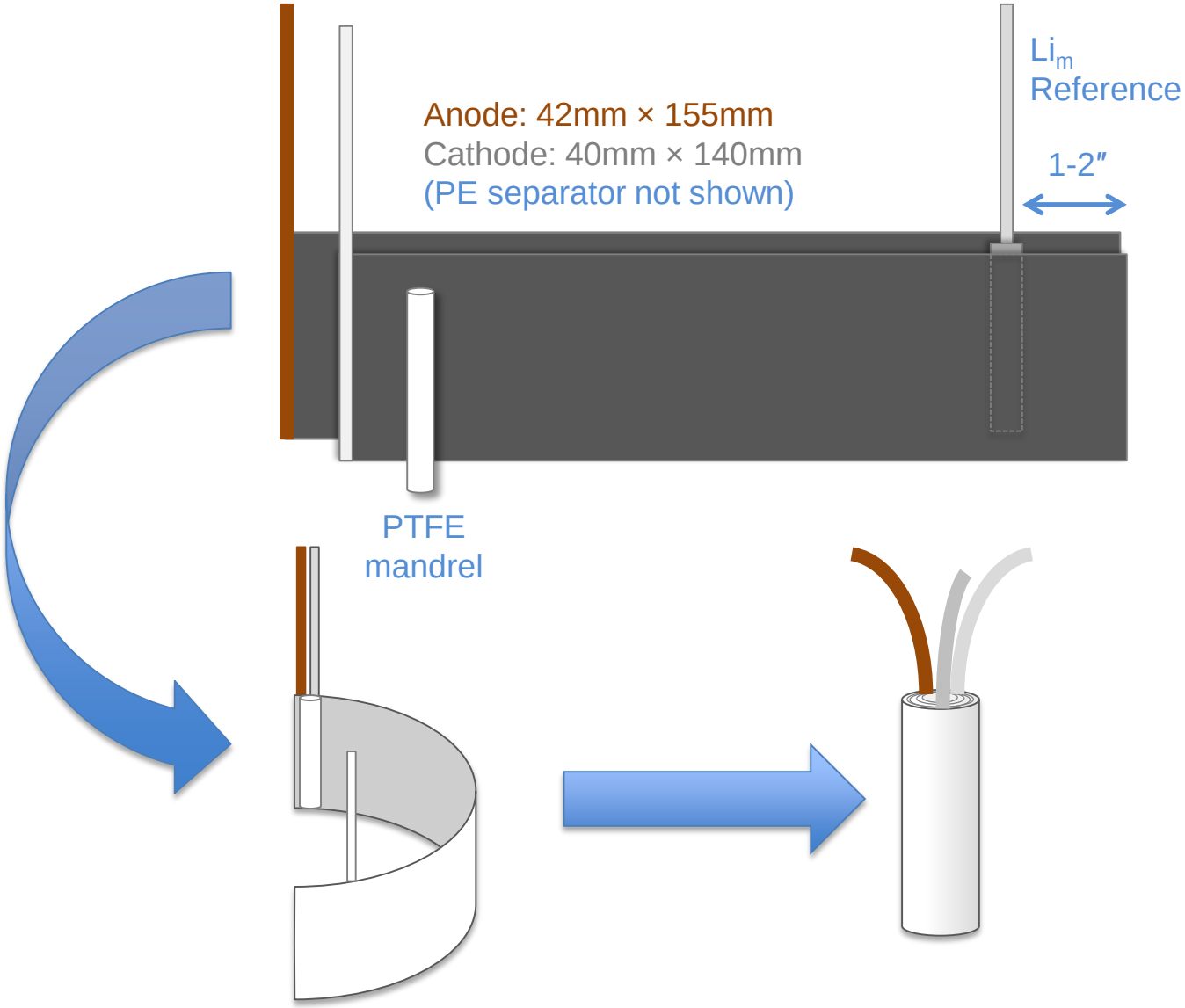






$LiClO_4$ appears to change due to 10 MRad, while $LiBF_4$ does not

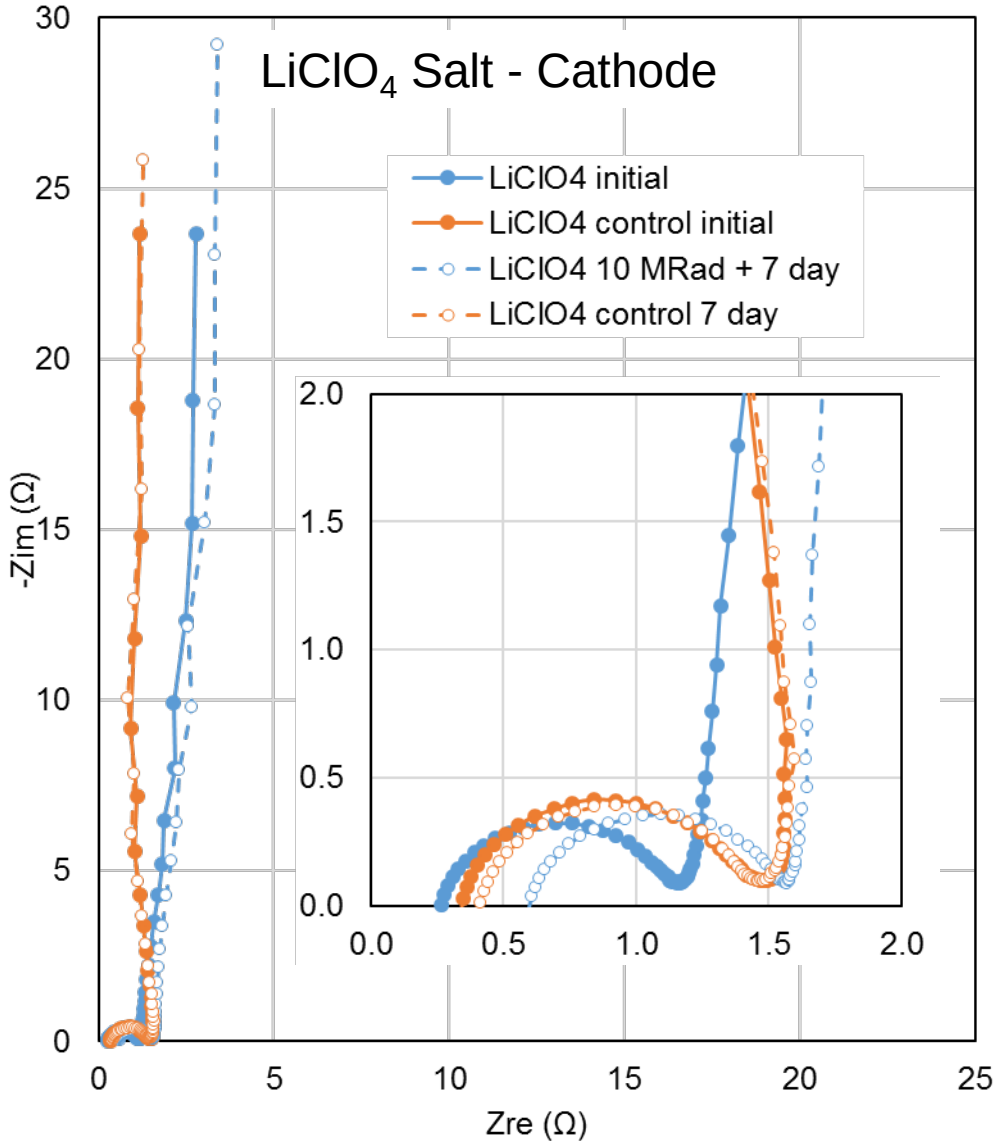
Build 3-electrode cells to understand effects on individual electrodes

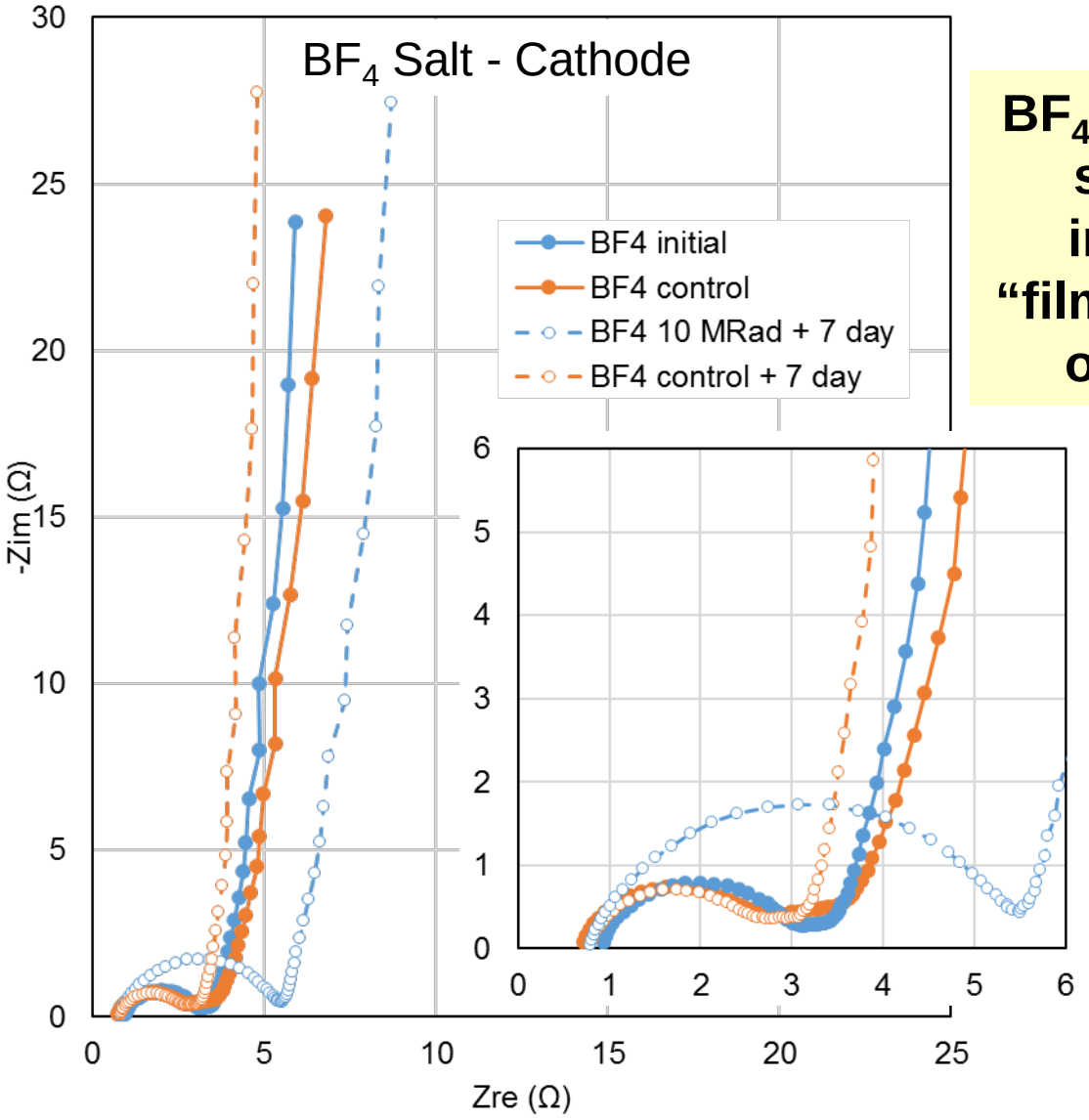


Experimental Design

- Li/CF_X-MnO_2 cells typically use $LiClO_4$ as an electrolyte salt
- Li/CF_X cells typically use $LiBF_4$ as an electrolyte salt
- Two cells with 0.75 M **$LiBF_4$** in PC+DME (3:7 by vol.)
- Two cells with 0.75 M **$LiClO_4$** in PC+DME (3:7 by vol.)
- Subject one of each to 10 MRad
- Keep one of each for control

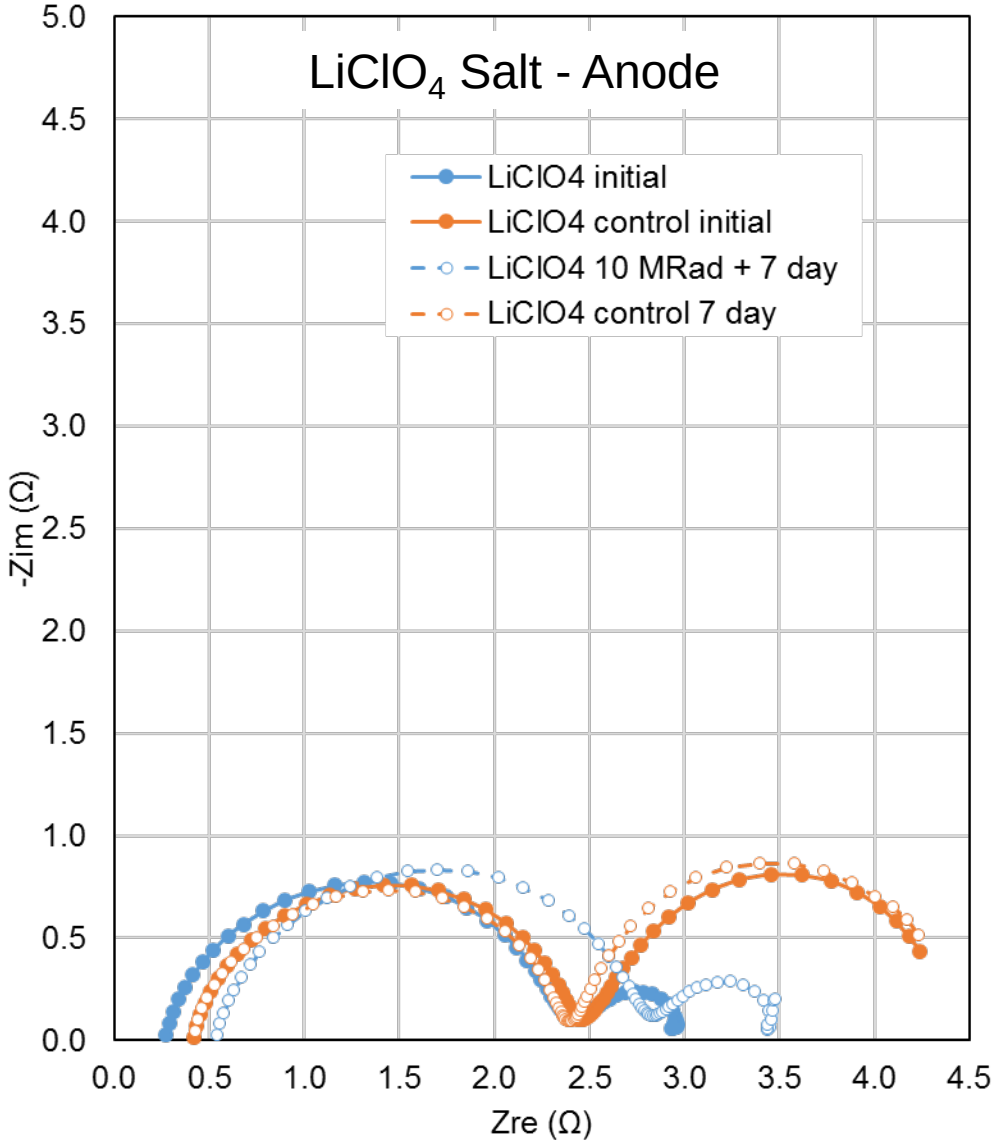
Film on cathode of Li/CF_x cell with $LiClO_4$ salt appears unaffected after 10 MRad

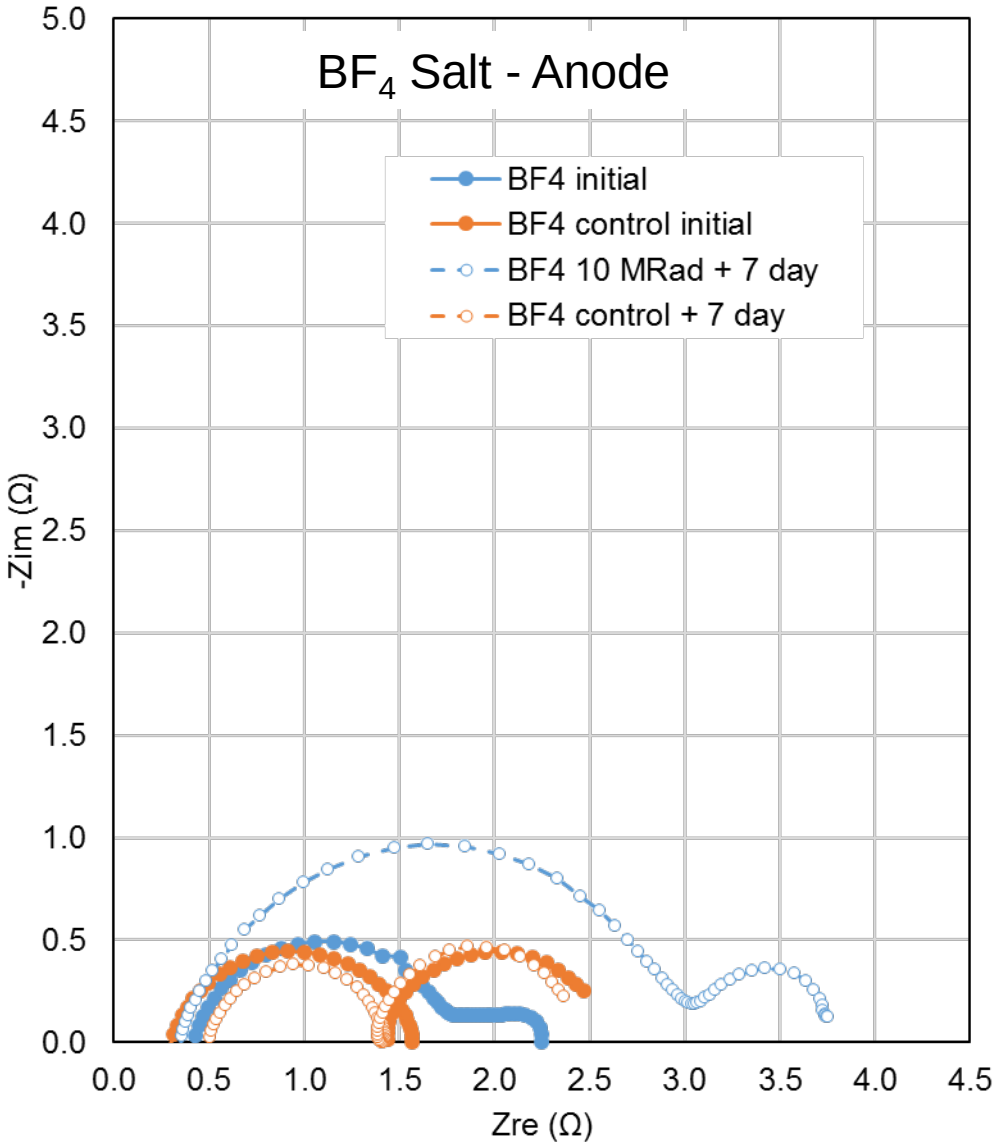




BF_4 salt leads to significant increase in "film" resistance on cathode

Film on anode of Li/CF_X cell with $LiClO_4$ salt appears unaffected after 10 MRad

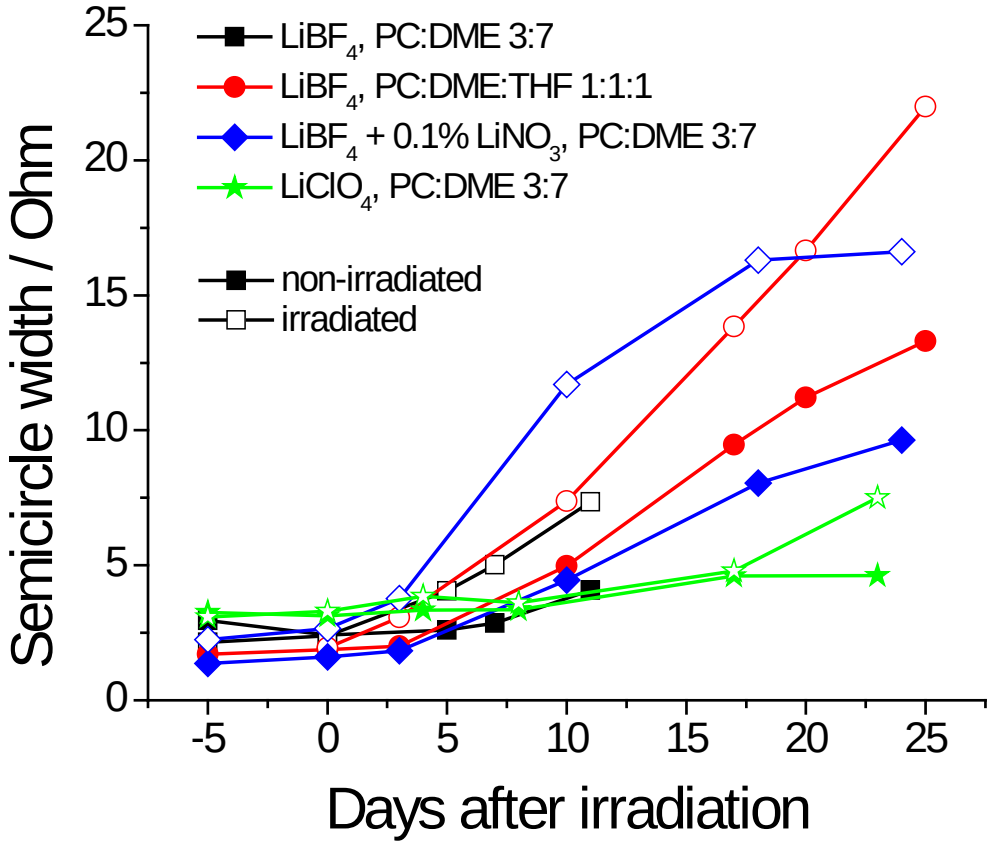


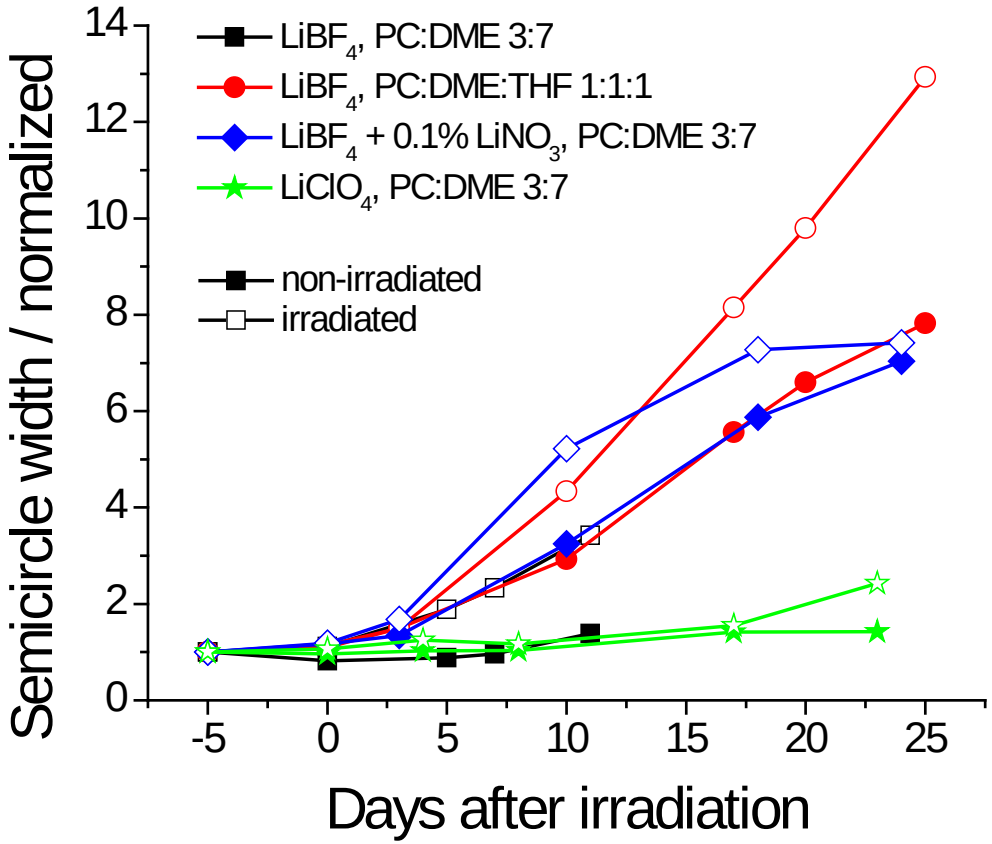


BF_4 salt leads to significant increase in "film" resistance on anode

Full Cell Analysis of Film Over Time in 3-Electrode Cells

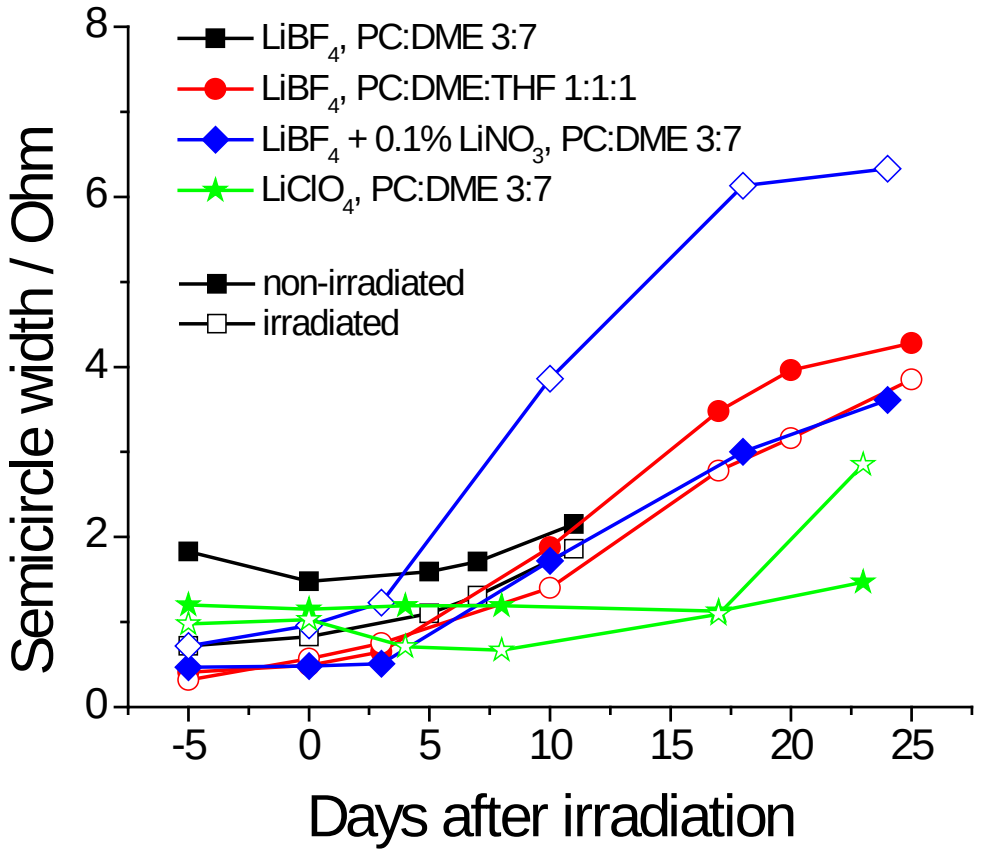
THF and $LiNO_3$ additive leads to rapid film growth following radiation

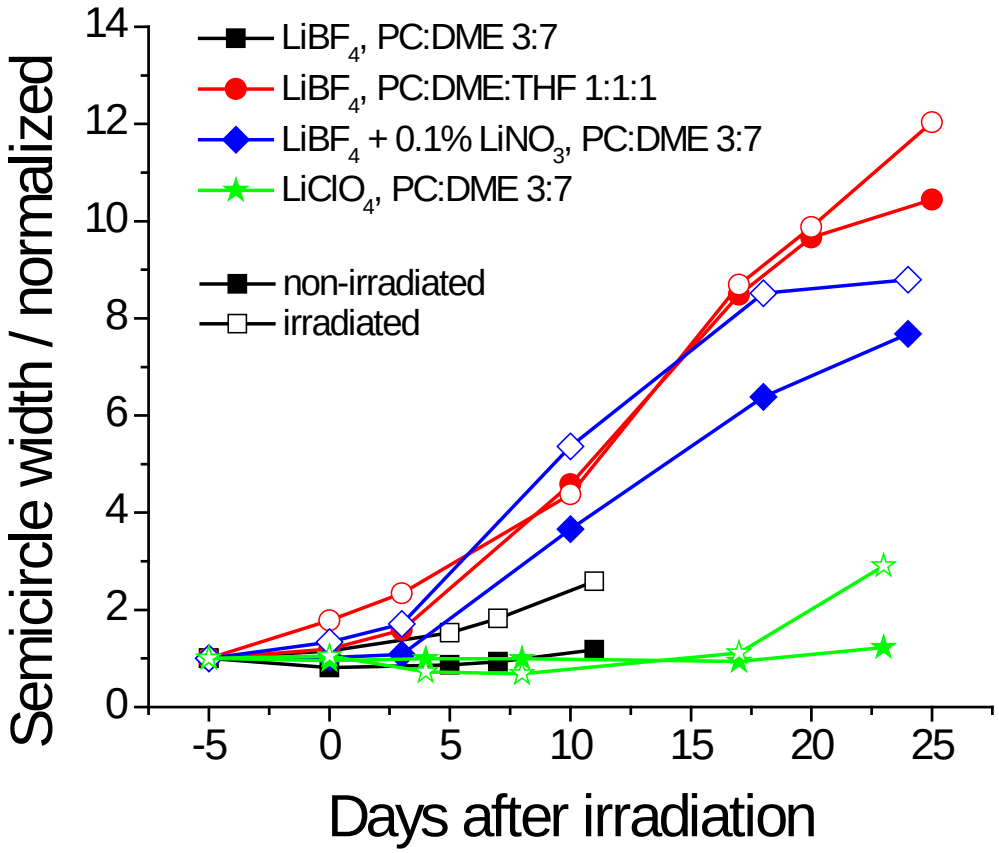




Cathode Analysis of Film Over Time in 3-Electrode Cells

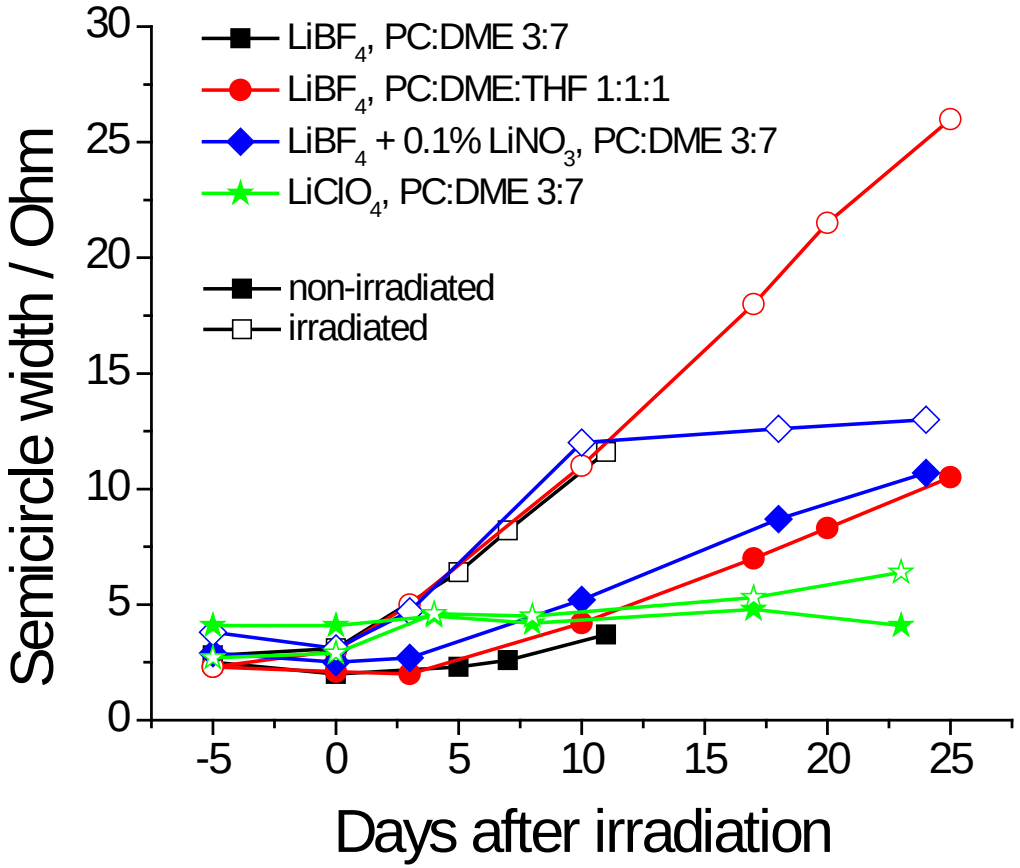
THF and $LiNO_3$ additive leads to rapid film growth following radiation

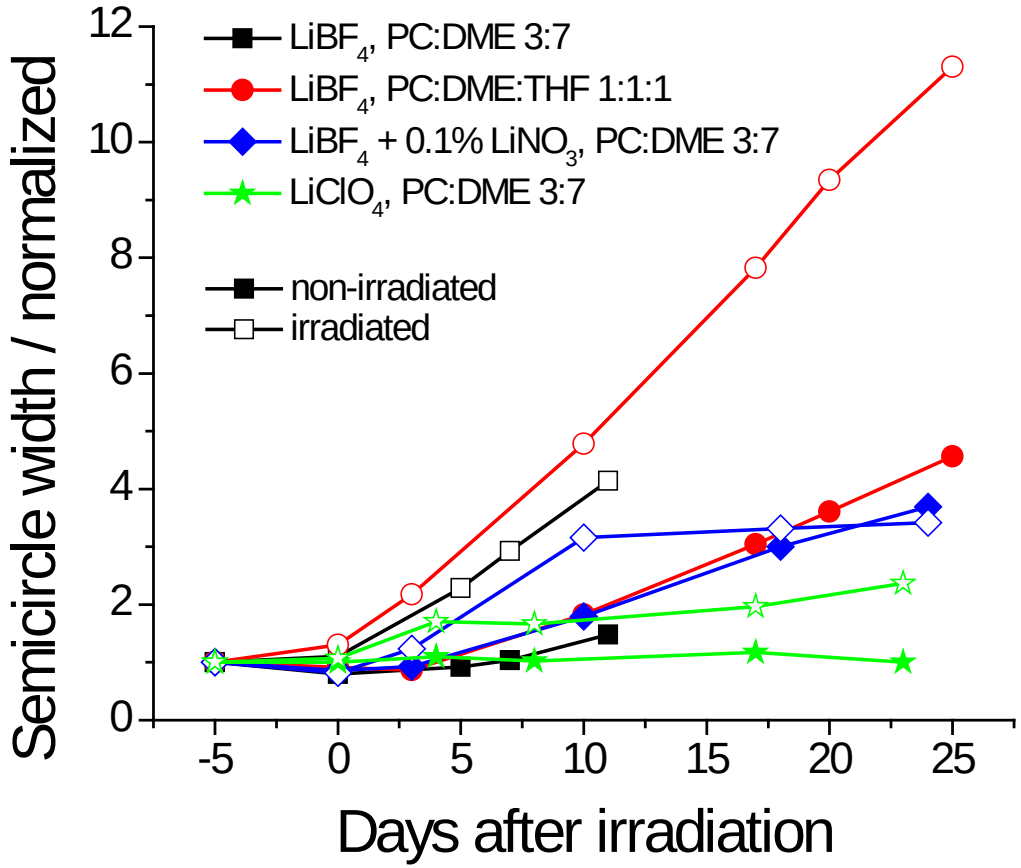




Anode Analysis of Film Over Time in 3-Electrode Cells

$LiNO_3$ additive limits film growth on anode





Conclusions

- Li/CF_X cells provide the highest available specific energy
- Degradation of the cell has been observed in Li/CF_X D-cells
  - Increased “film” resistance
  - Increased low frequency resistance
  - Increased cell OCV
  - Lower energy (2-6 %)
  - Lower capacity (2-5%)
- “Film” resistance grows in 3-electrode cells with $LiBF_4$ salt
  - Both anode and cathode are affected
  - Neither THF or $LiNO_3$ have a positive effect on film growth
- “Film” resistance remains constant in 3-electrode cells with $LiClO_4$ salt
  - Hope to incorporate other salts into prototype Li/CF_X D-cells

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Acknowledgements

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA), and was supported by the Planetary Science Division.