Radiation Effects on Lithium CF_x Batteries for Future Landers

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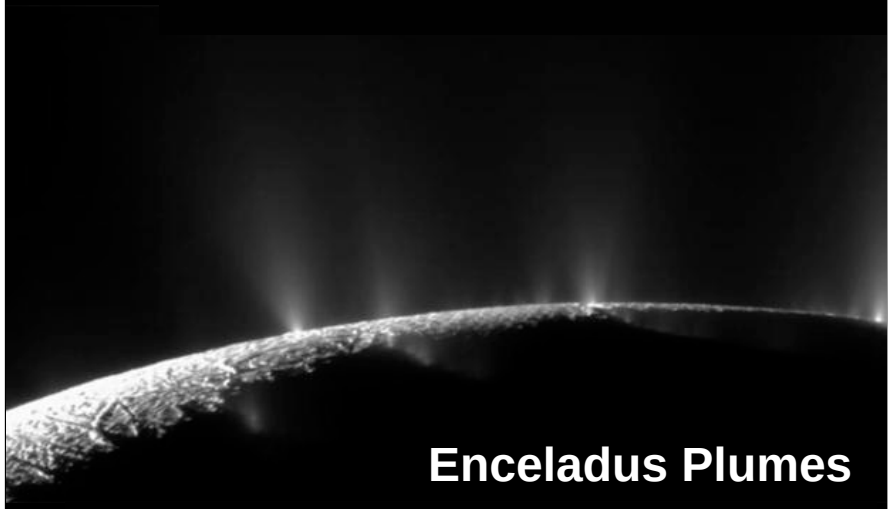
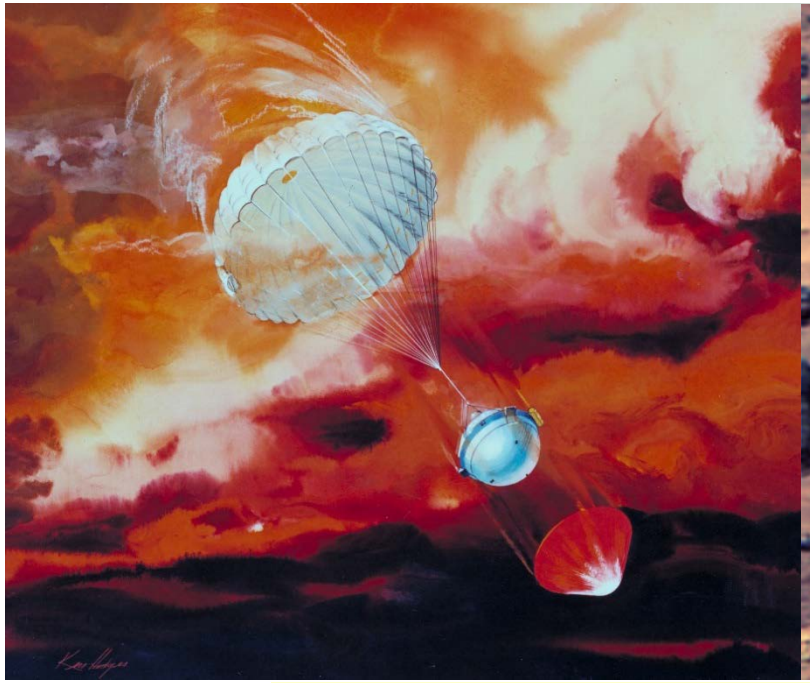
Space Power Workshop
Los Angeles, CA
Thursday, April 23, 2018

Increasing Interest in a lander for “Ocean Worlds”

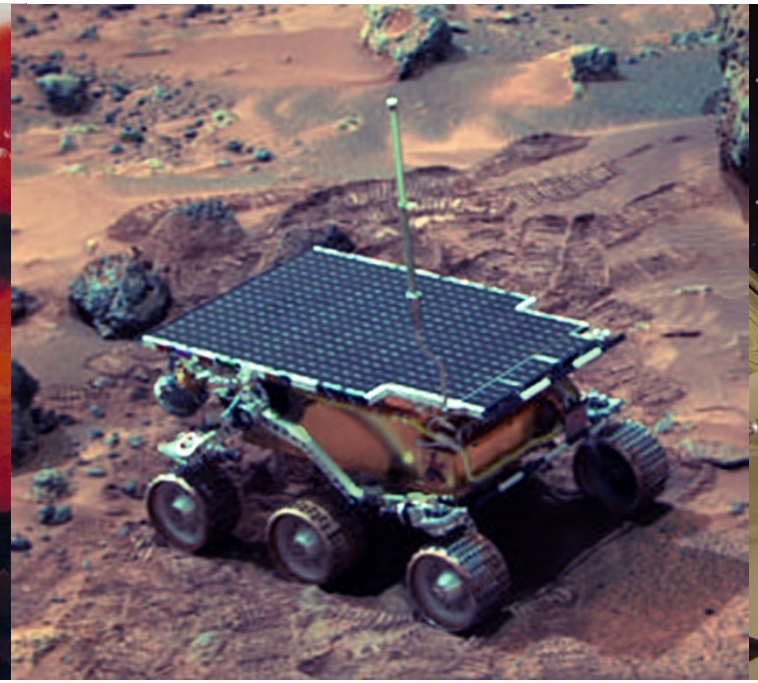


Three Examples of Primary Batteries for Space

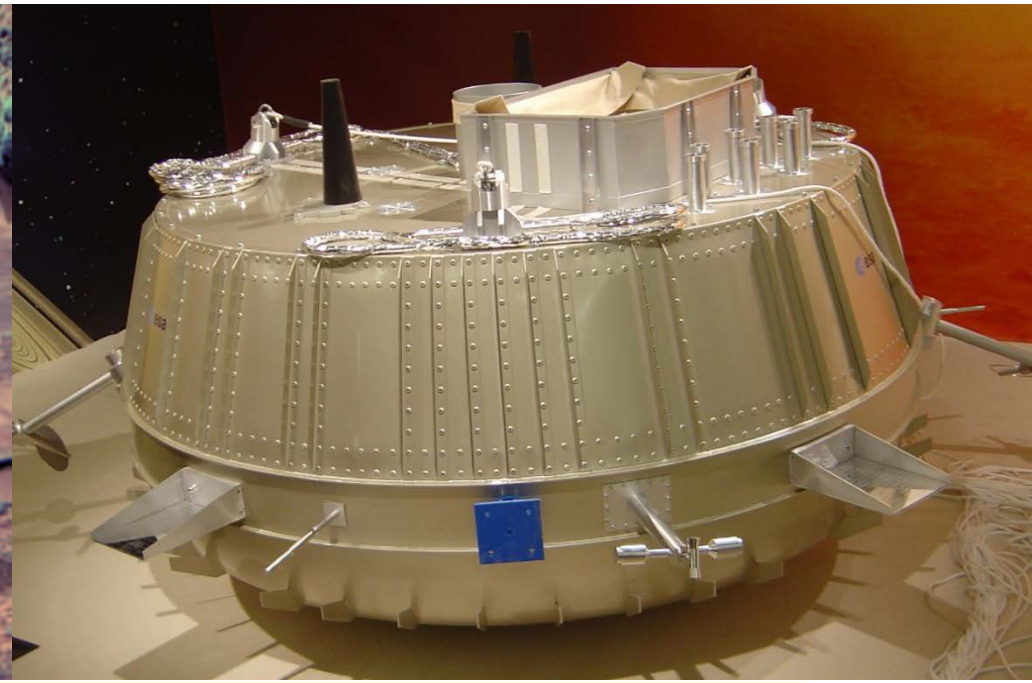
Galileo Probe 1989: Li/SO_2
~580 Wh
58 minutes



Sojourner Rover 1996: $Li/SOCl_2$
432 Wh
56 days (PV + battery)

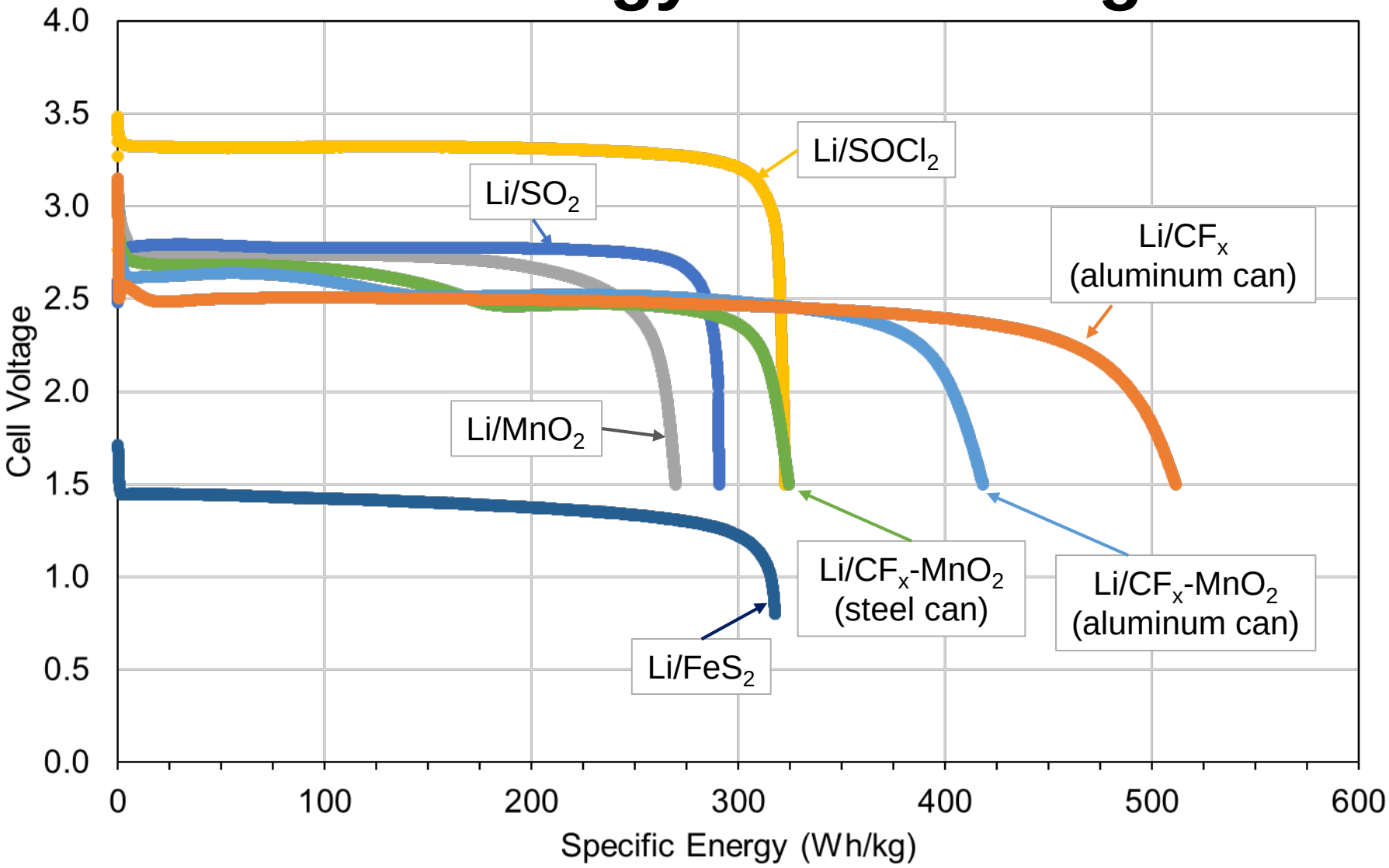


Huygens Probe 2004: Li/SO_2
~2700 Wh
153 minutes



A Europa Lander could require at least 480 hours of operation on battery power alone, therefore, high specific energy is critical to achieving mission objectives

Li/CF_x cells provide 50% more energy than heritage cells



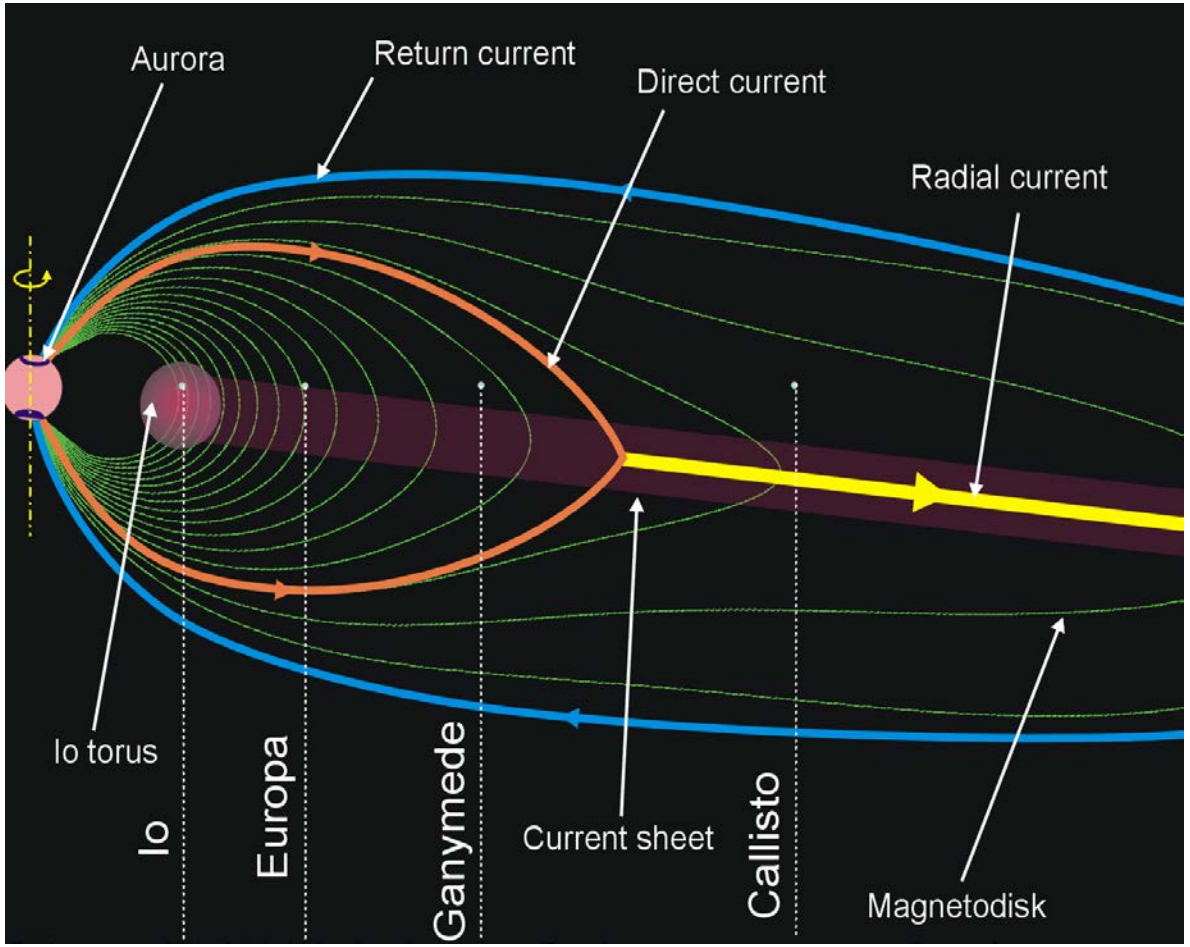
- Discharged at the same condition
- 0 °C, 250 mA
- Li/FeS_2 discharged at 100 mA due to size (AA instead of D)
- 2 Li/FeS_2 cells could be connected in series to provide comparable voltage

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
  - o 1.3 MeV gamma rays
  - o ~200 rad/s
  - o 1 MRad up to 15 MRad

Test articles:

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



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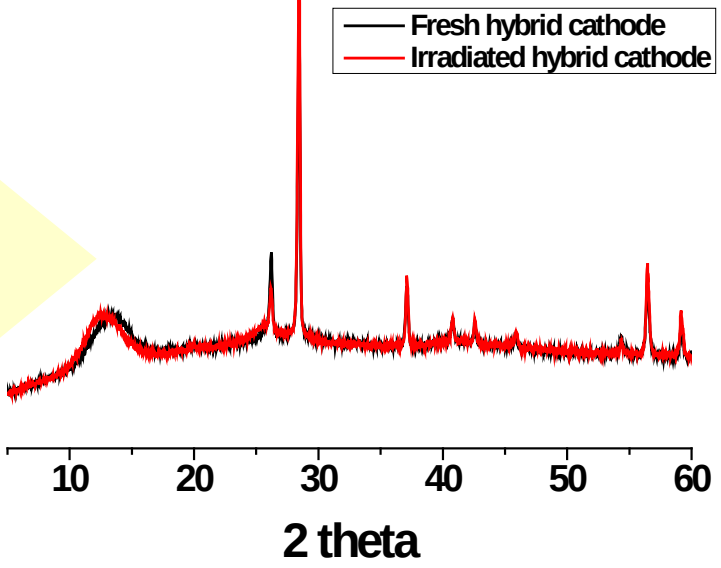
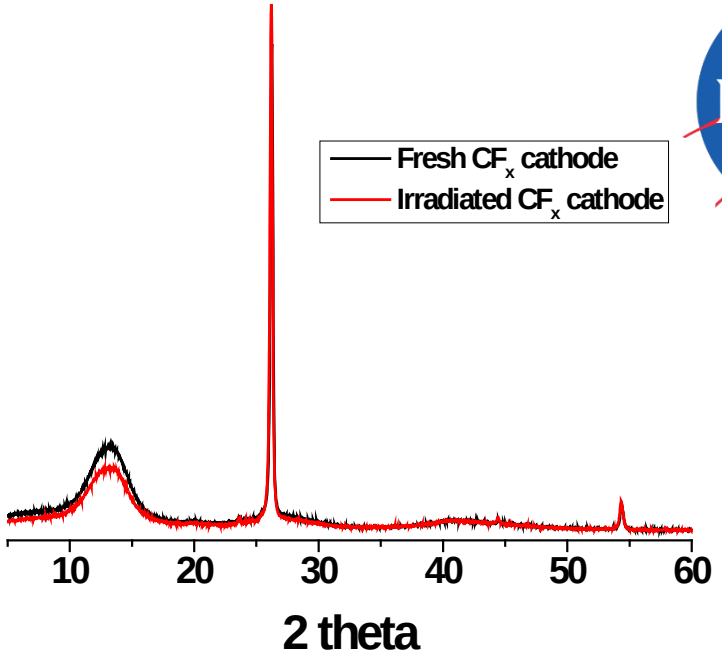
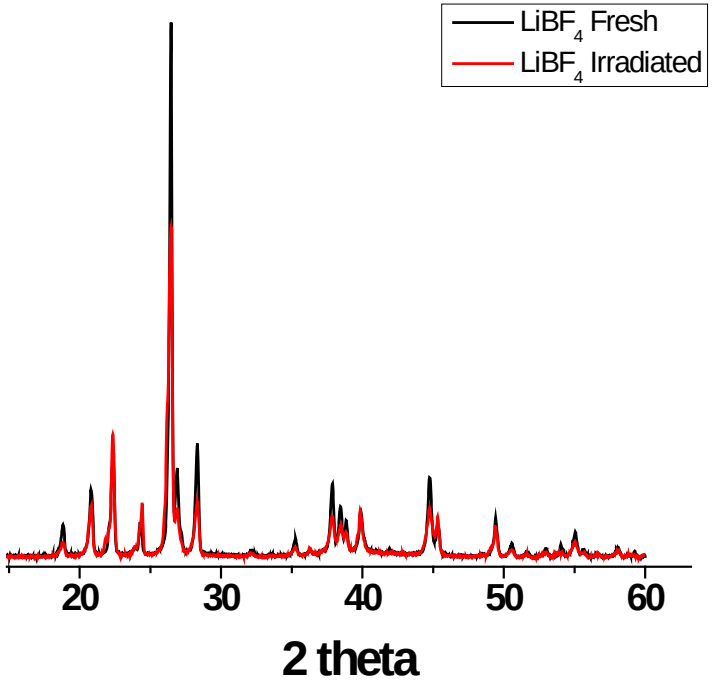
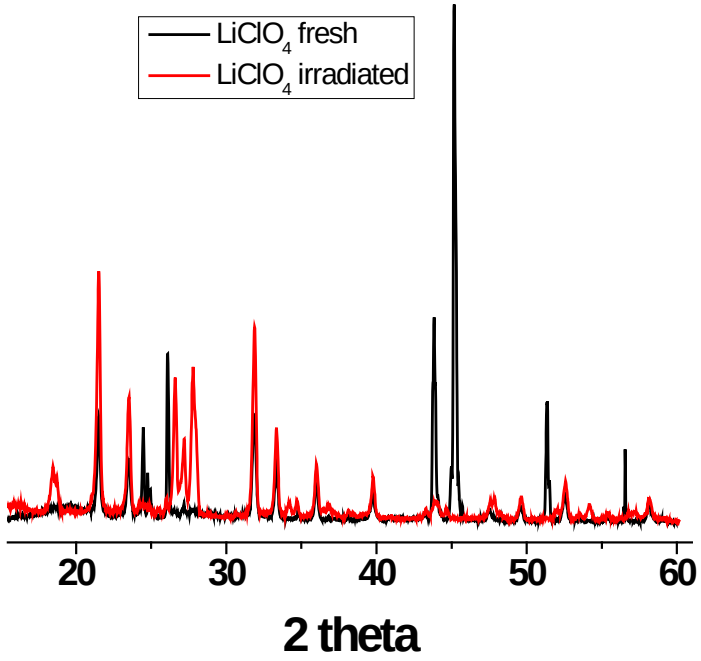
Materials testing – XRD analysis

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





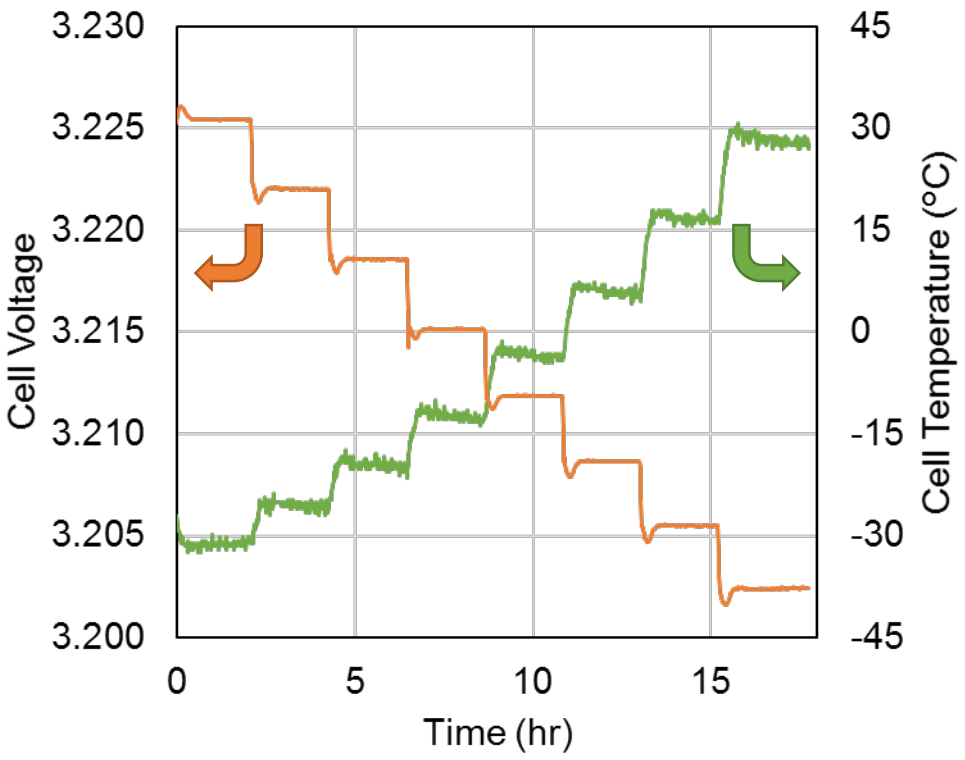




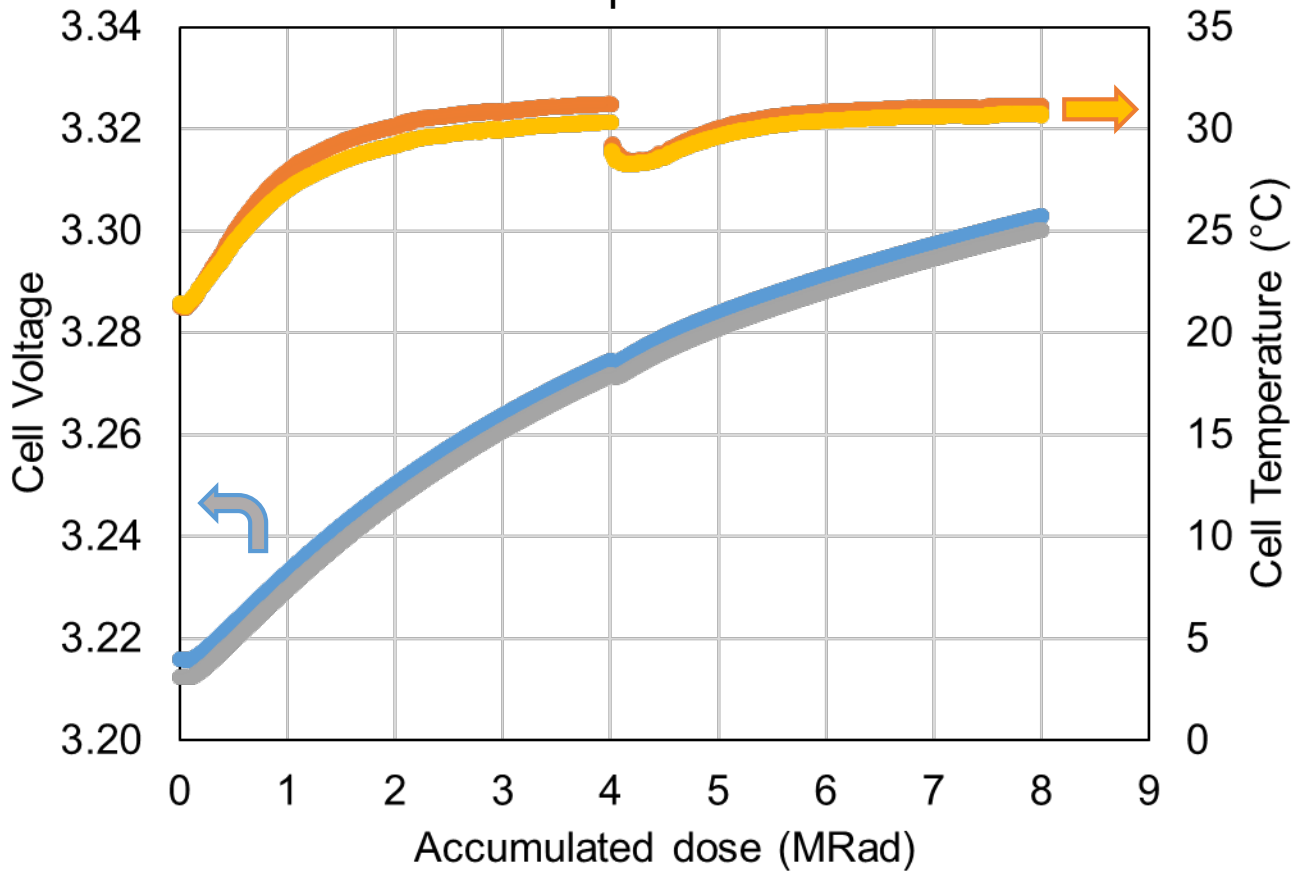
$LiClO_4$ appears to change due to 10 MRad, while $LiBF_4$ does not

Li/CF_x-MnO_2 cell voltages increase during radiation exposure

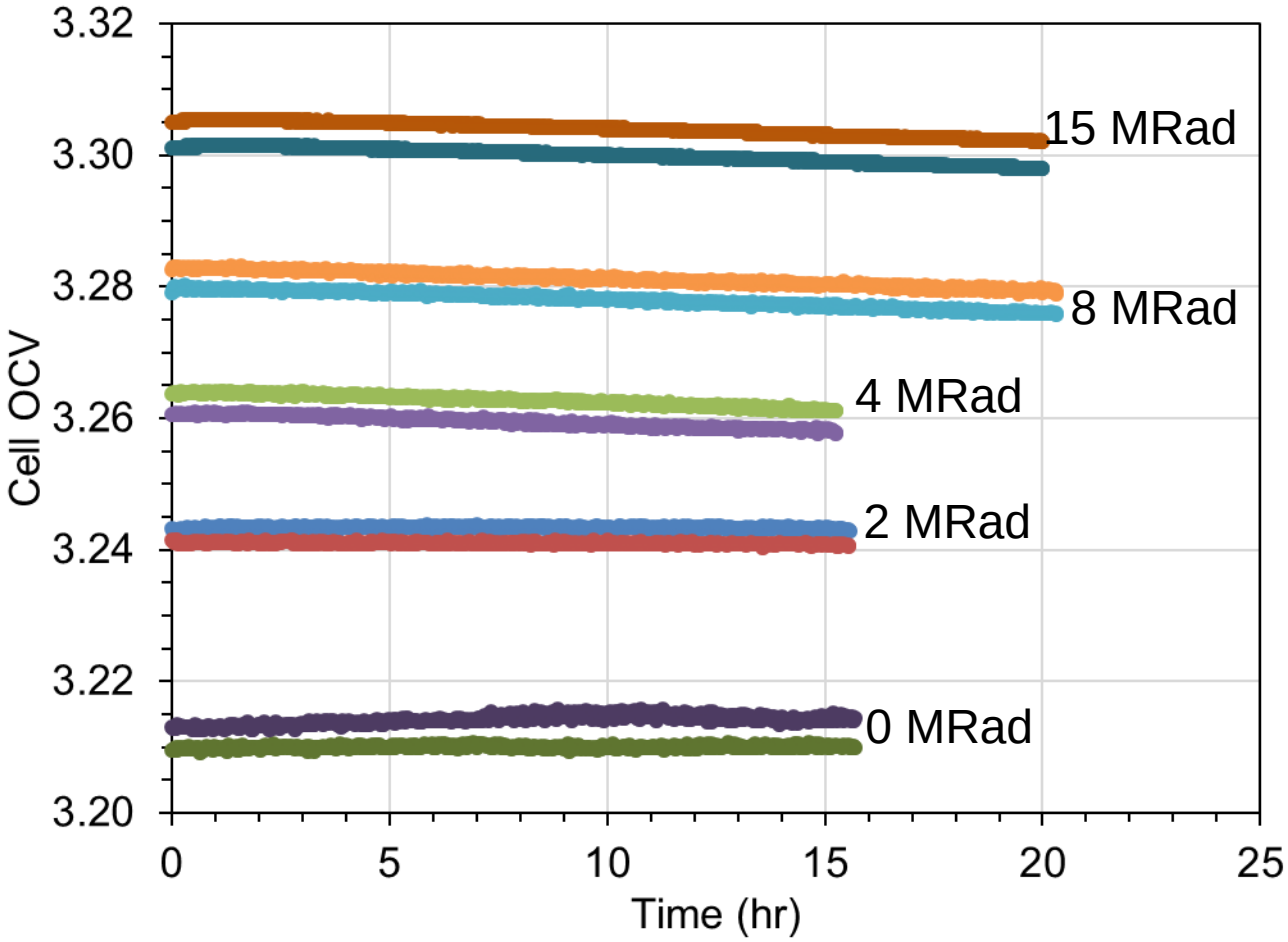
Temperature rise does not correlate with voltage increase in the absence of radiation



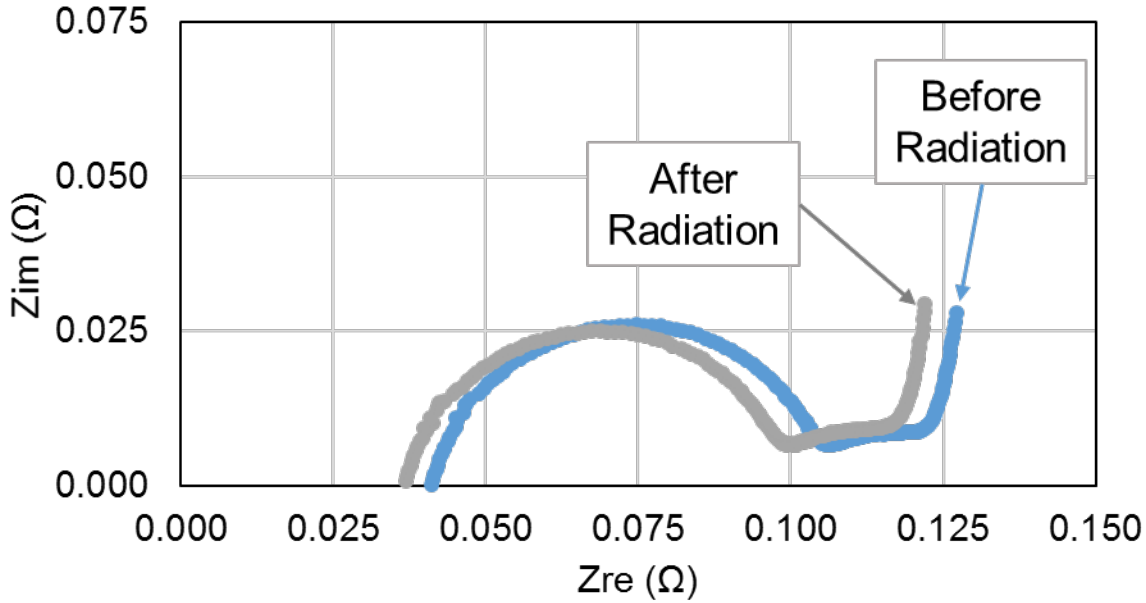
Cells increase by ~100 mV and 9 °C over the course of 8 MRad exposure



Rest OCV and Impedance Analysis of Li/CF_x-MnO_2 Cells

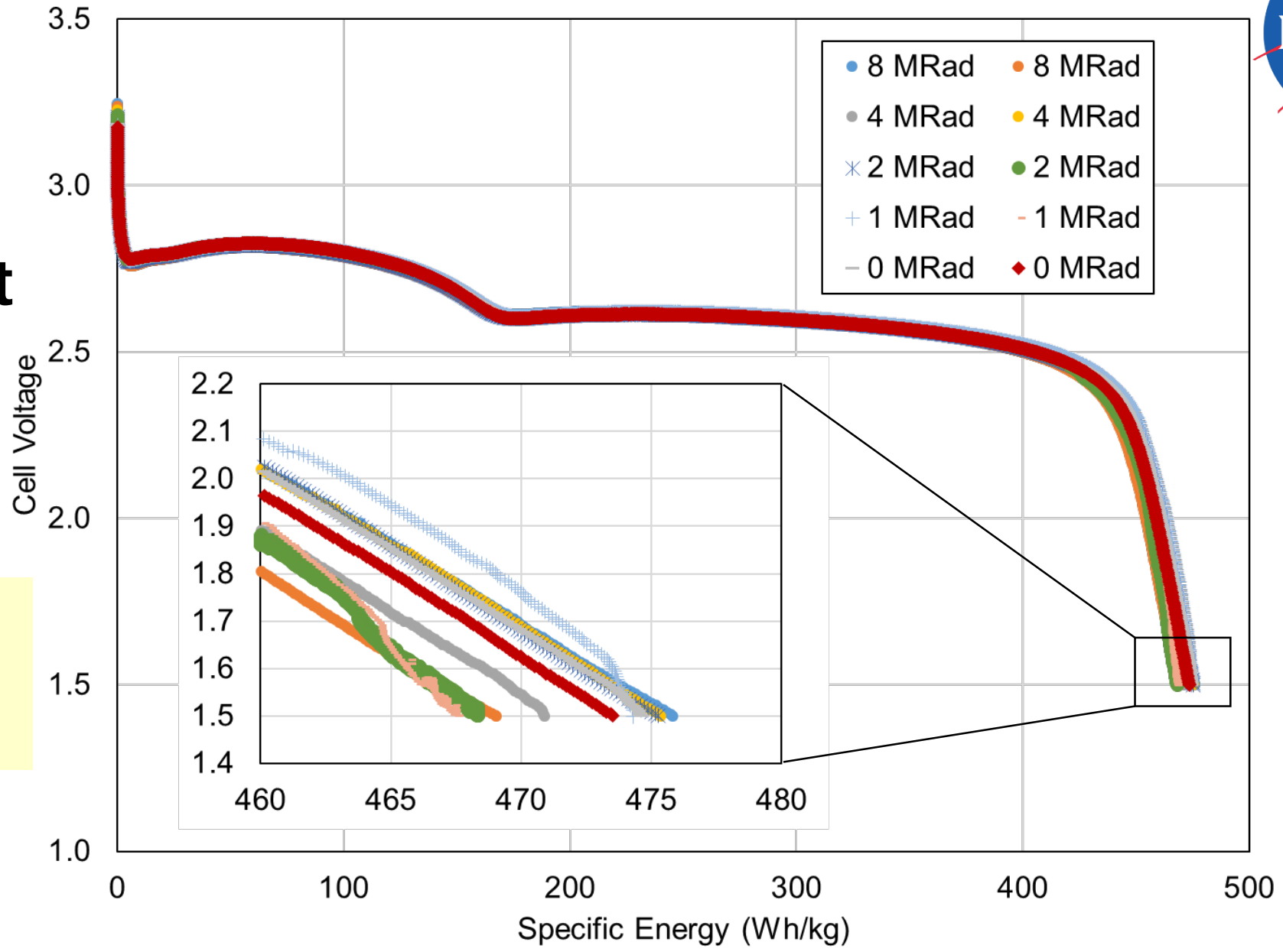


- OCV monitored for >15 hours
- Linear regression analysis shows a slight voltage drop (**0.18 to 0.2 mV/hr**) for higher dose cells (4, 8, 15 MRad)
- No change in impedance after radiation
  - Spectrum slightly shifted due to connections

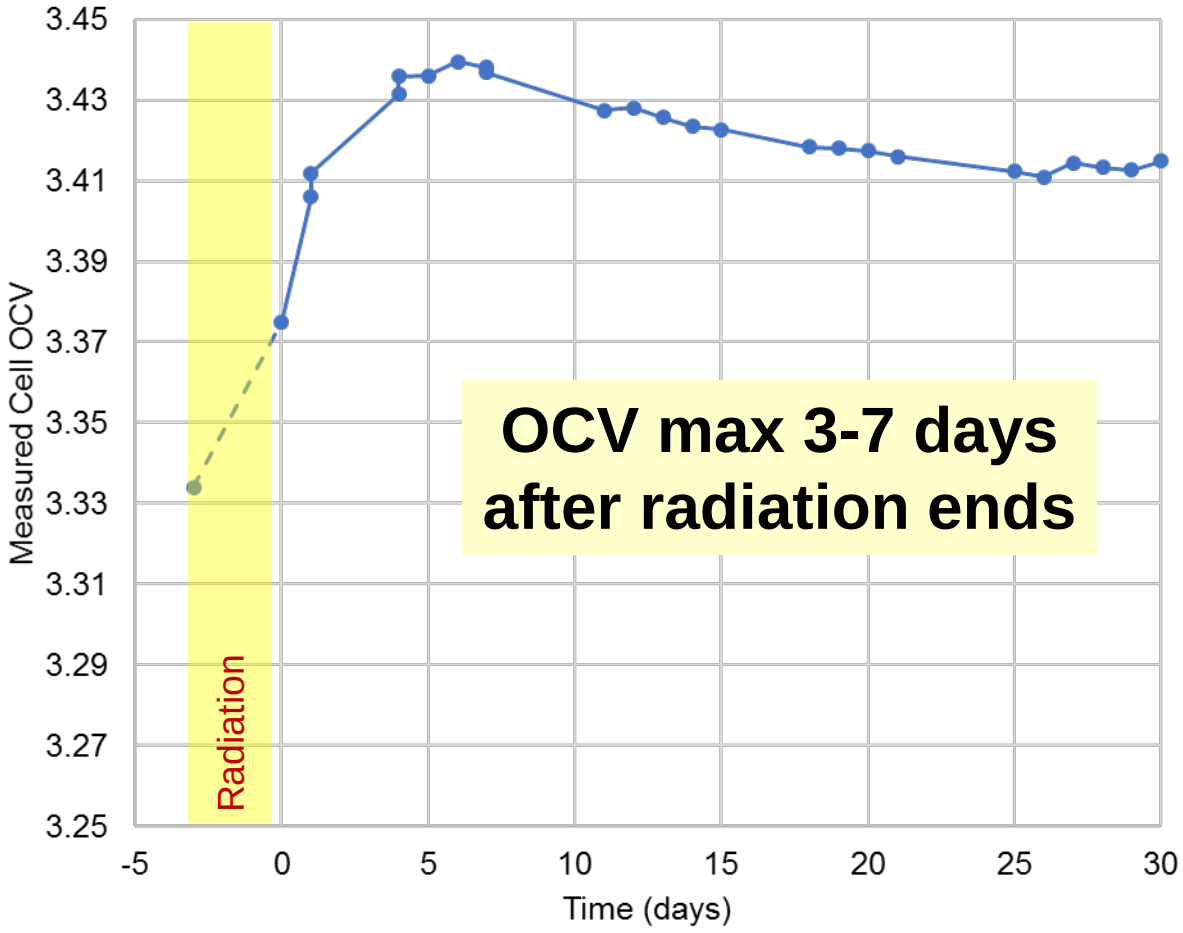


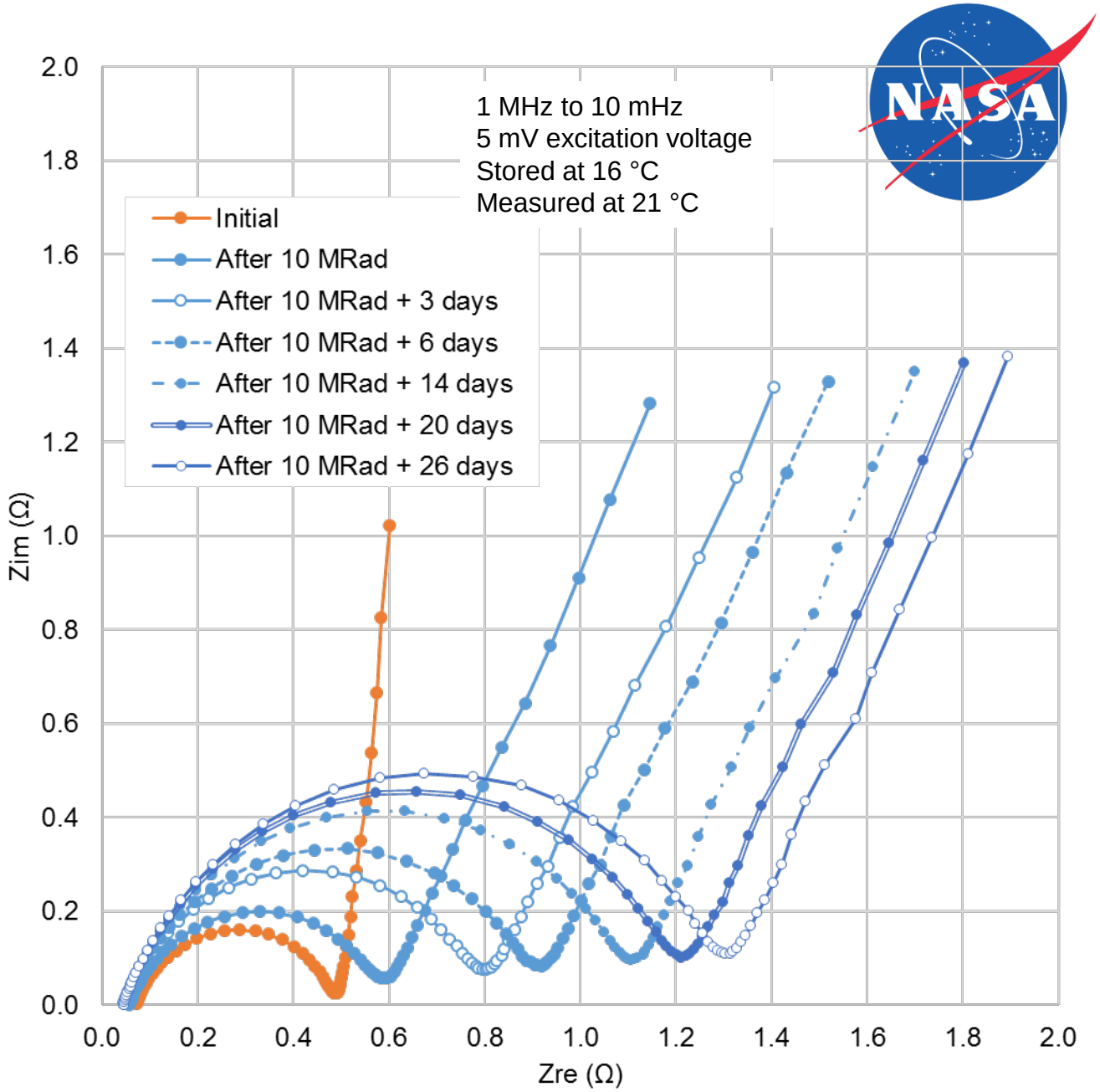
Li/CF_x-MnO_2 Radiation cell discharge performance at 250 mA, 21 °C

Radiation does not appear to impact capacity or energy



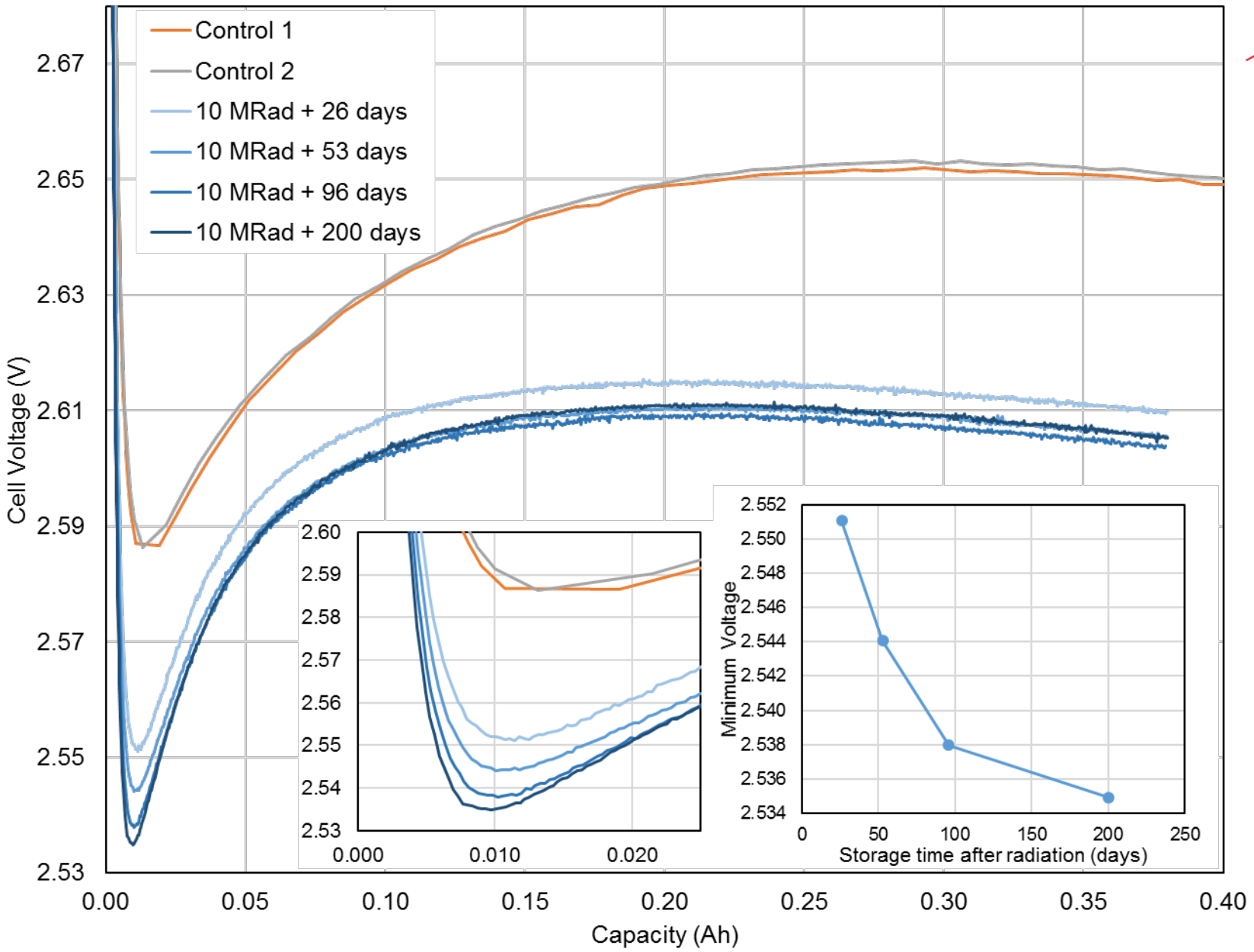
OCV and Impedance change drastically for Li/CF_x D-cell after 10 MRad



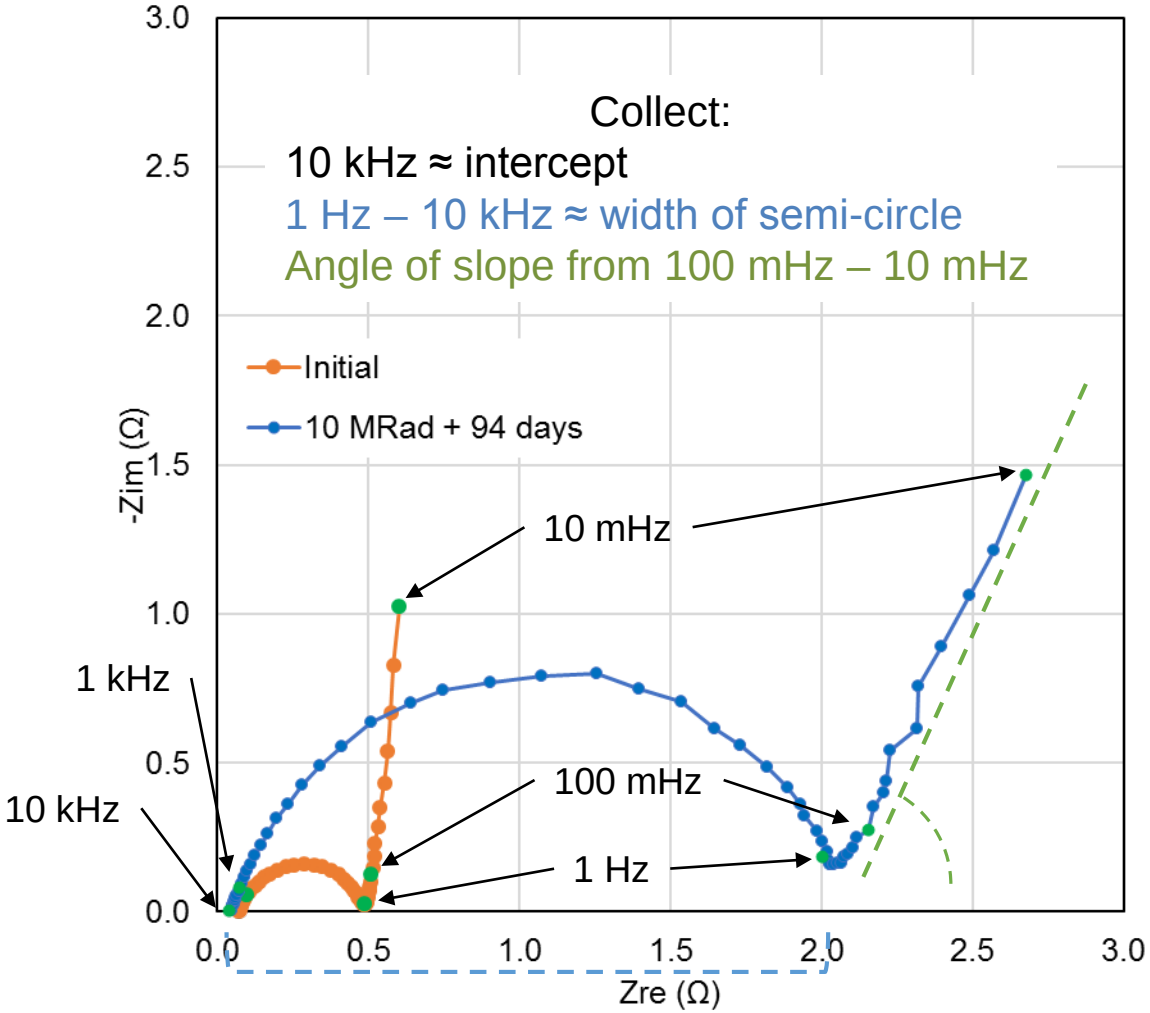


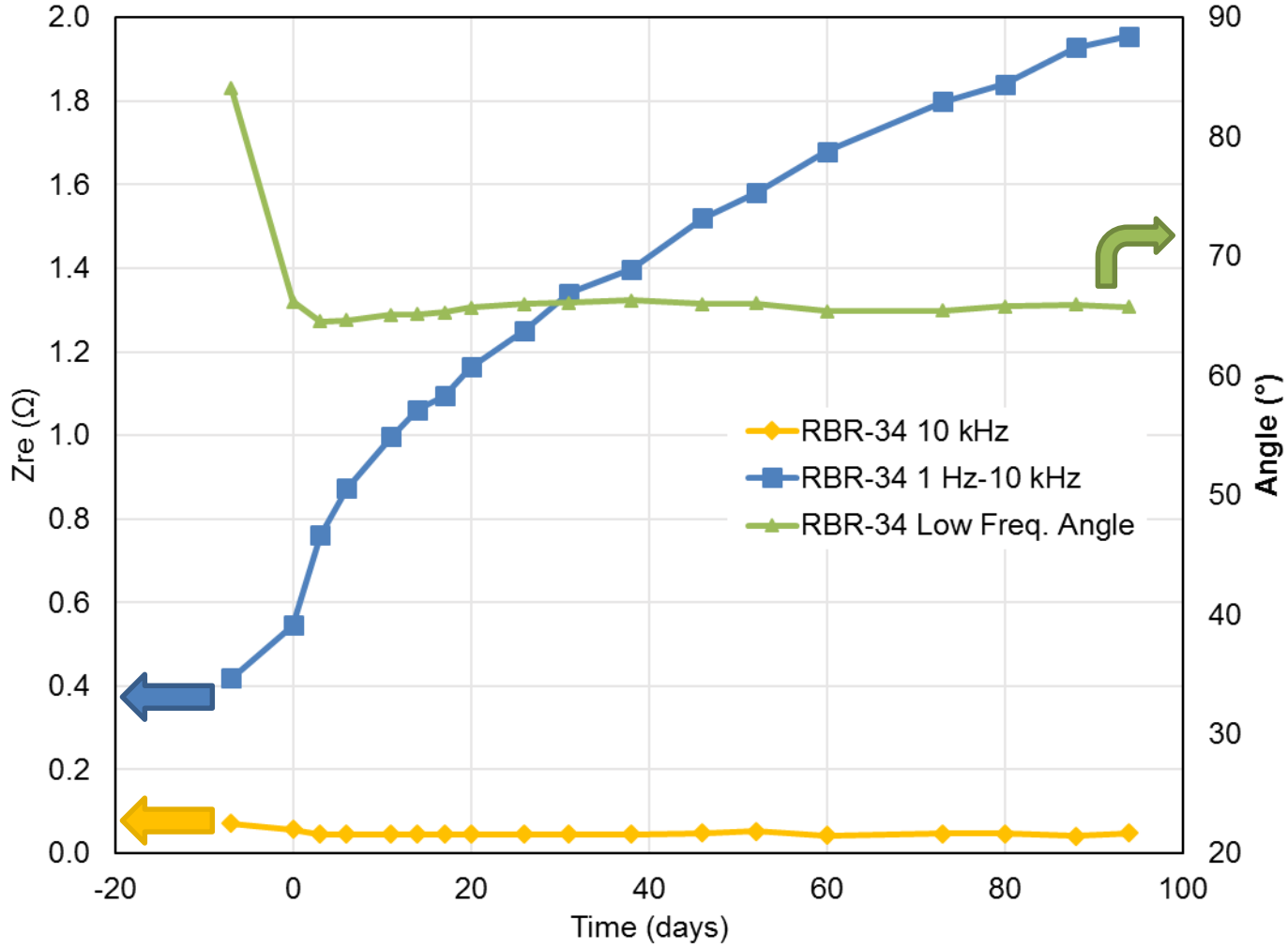
Discharge 2% of capacity at 250 mA, 21 °C to remove any film grown during radiation

Initial voltage drop affected by time after radiation



Quantifying EIS changes over time for Li/CF_x cells





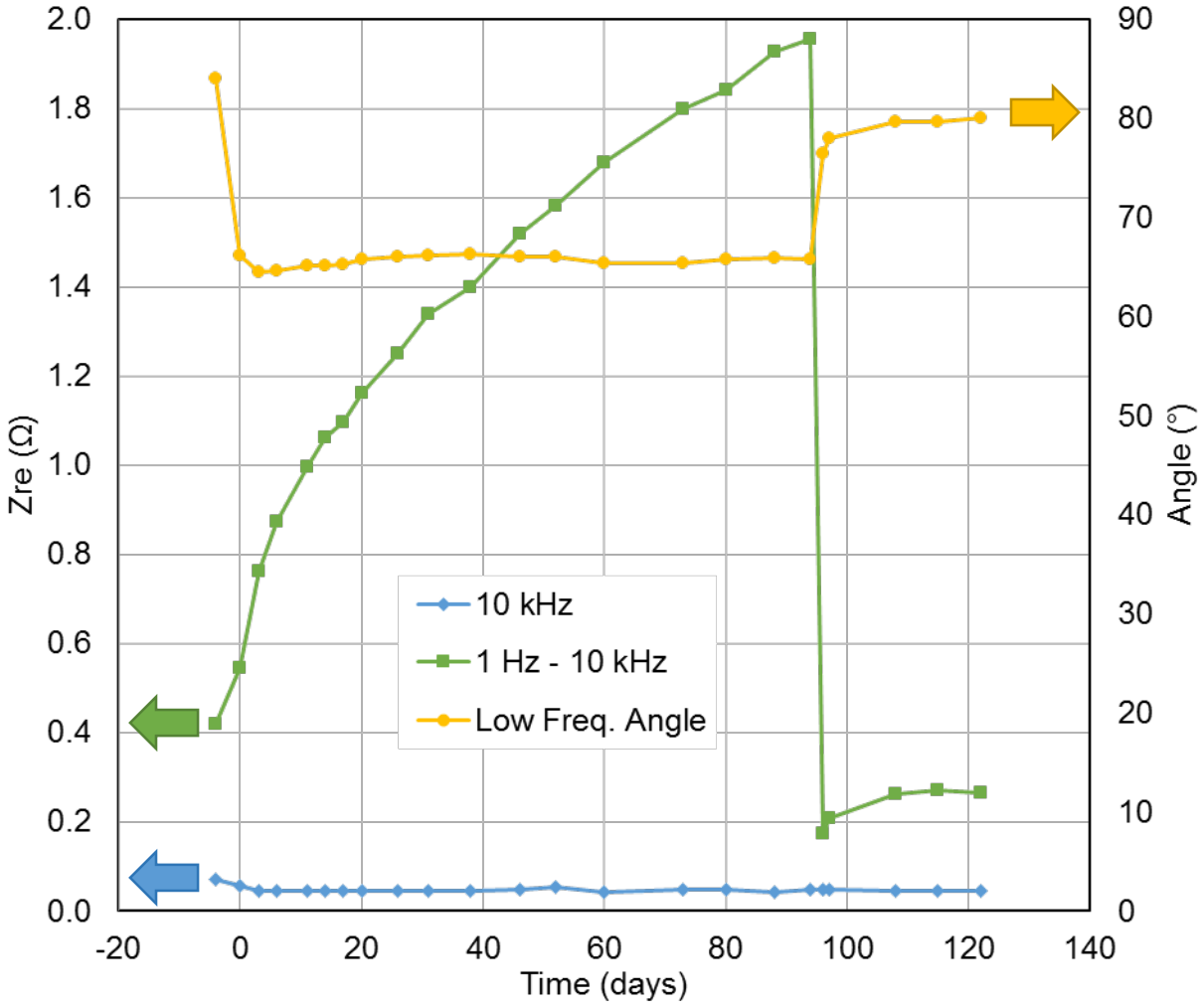
1 MHz to 10 mHz
5 mV excitation voltage

Stored at 16 °C
Measured at 21 °C

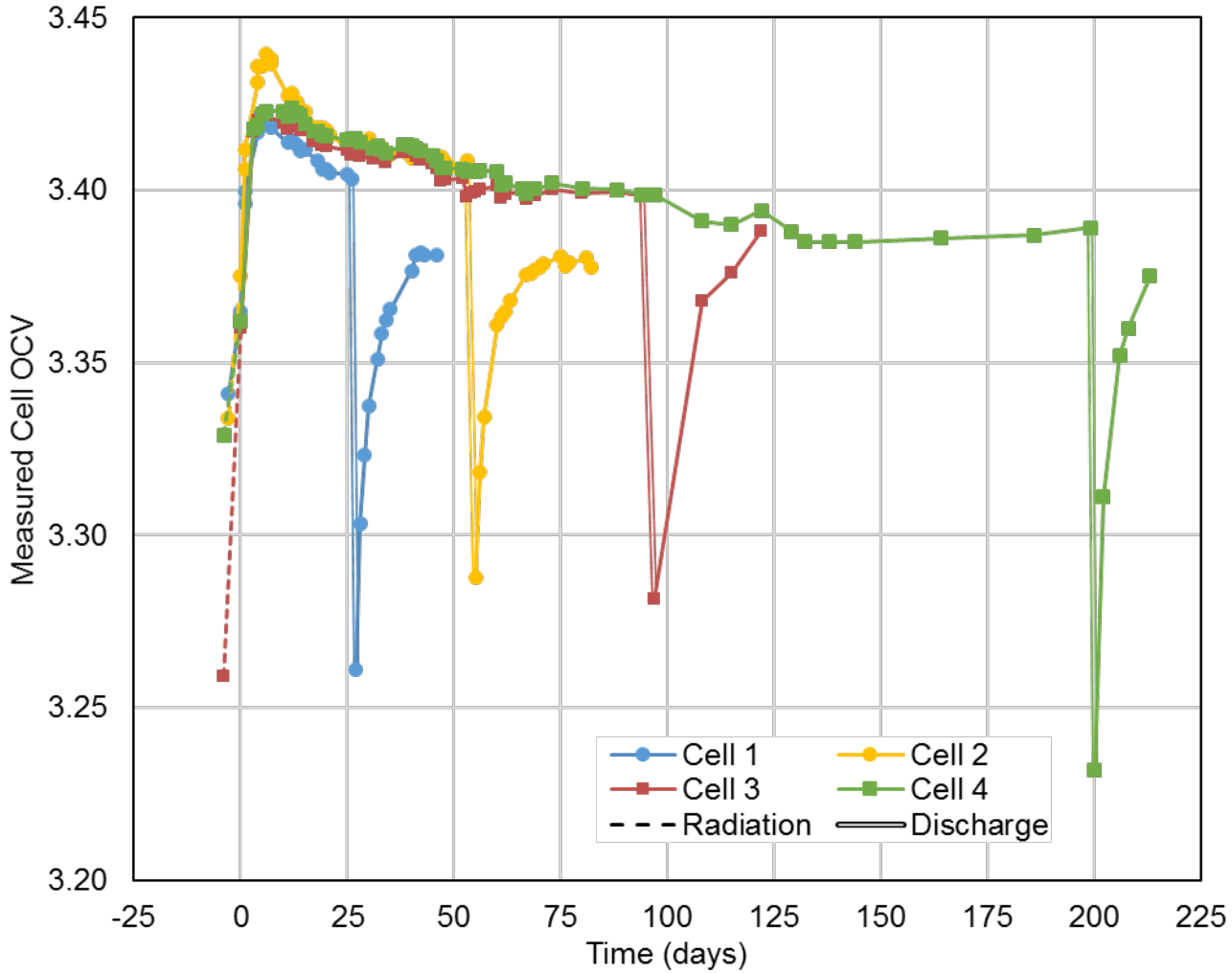
Pre-Decisional Information -- For Planning and Discussion Purposes Only

2% discharge effects on EIS and OCV

Semi-circle width decreases
Low freq. angle becomes steeper

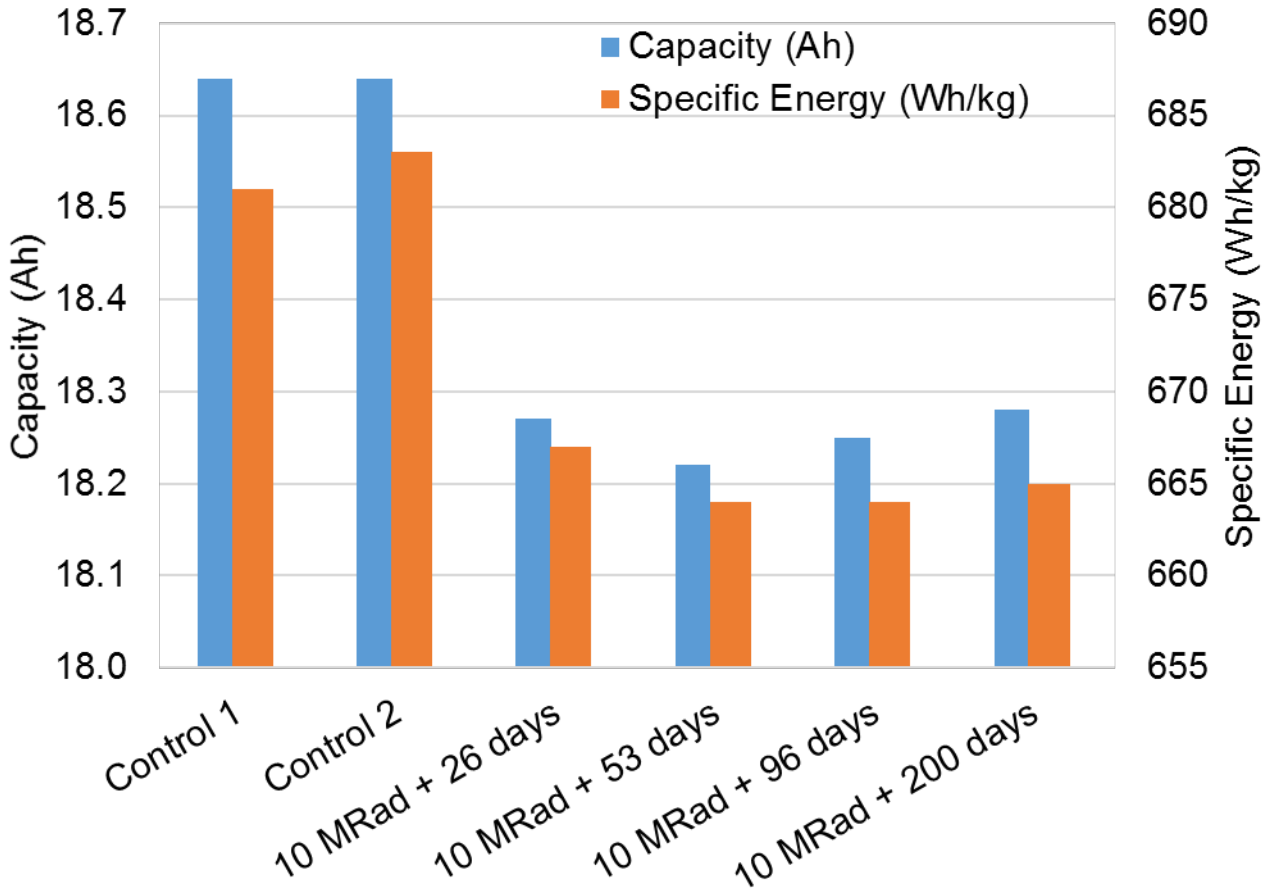


OCV remains elevated
after discharge

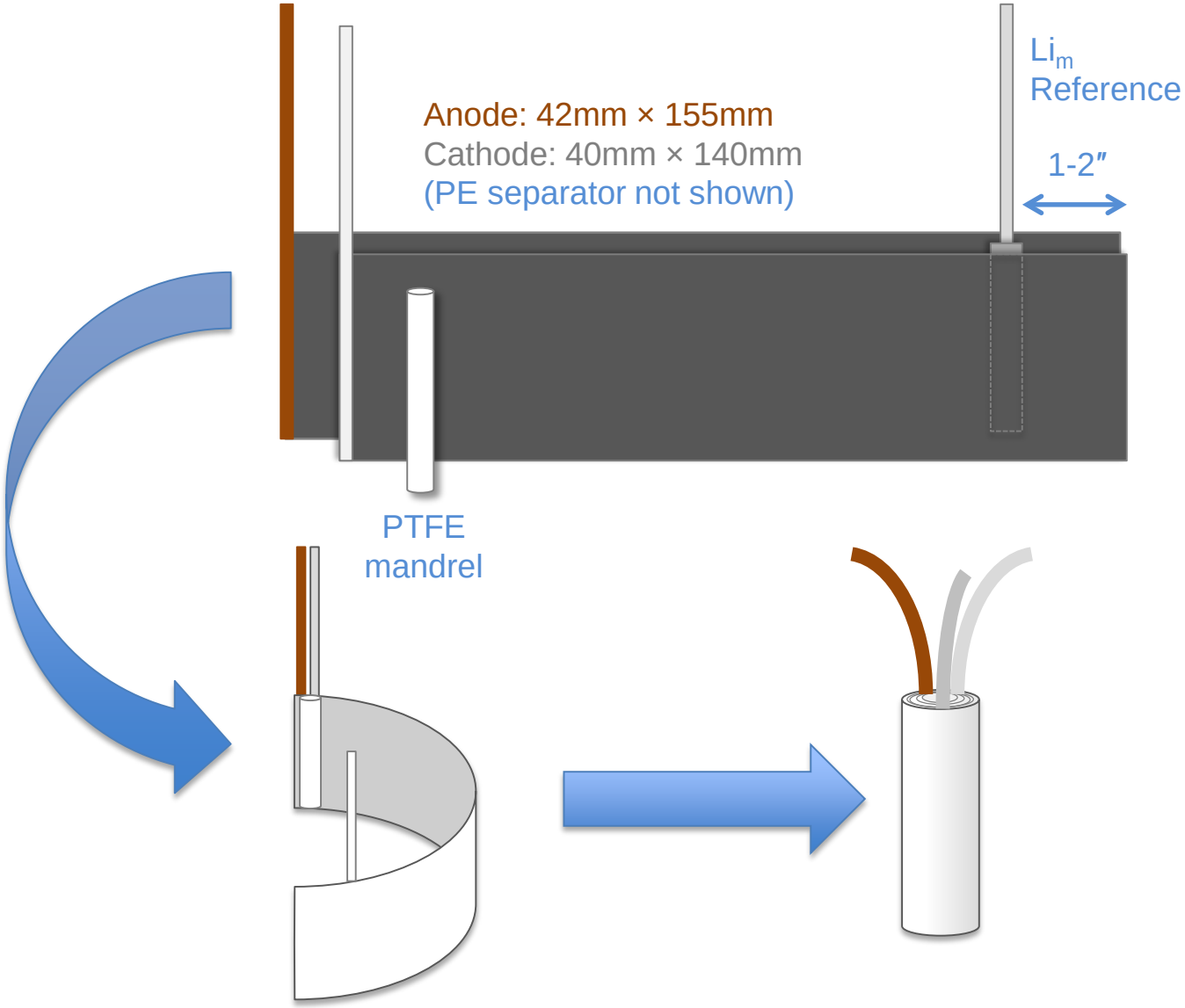


Total capacity and specific energy for Li/CF_x D-cells drops by ~2% after radiation

	Capacity (Ah)	Specific Energy (Wh/kg)
Non-irradiated average:	18.64	682
10 MRad average:	18.28	667
Drop:	1.94%	2.23%



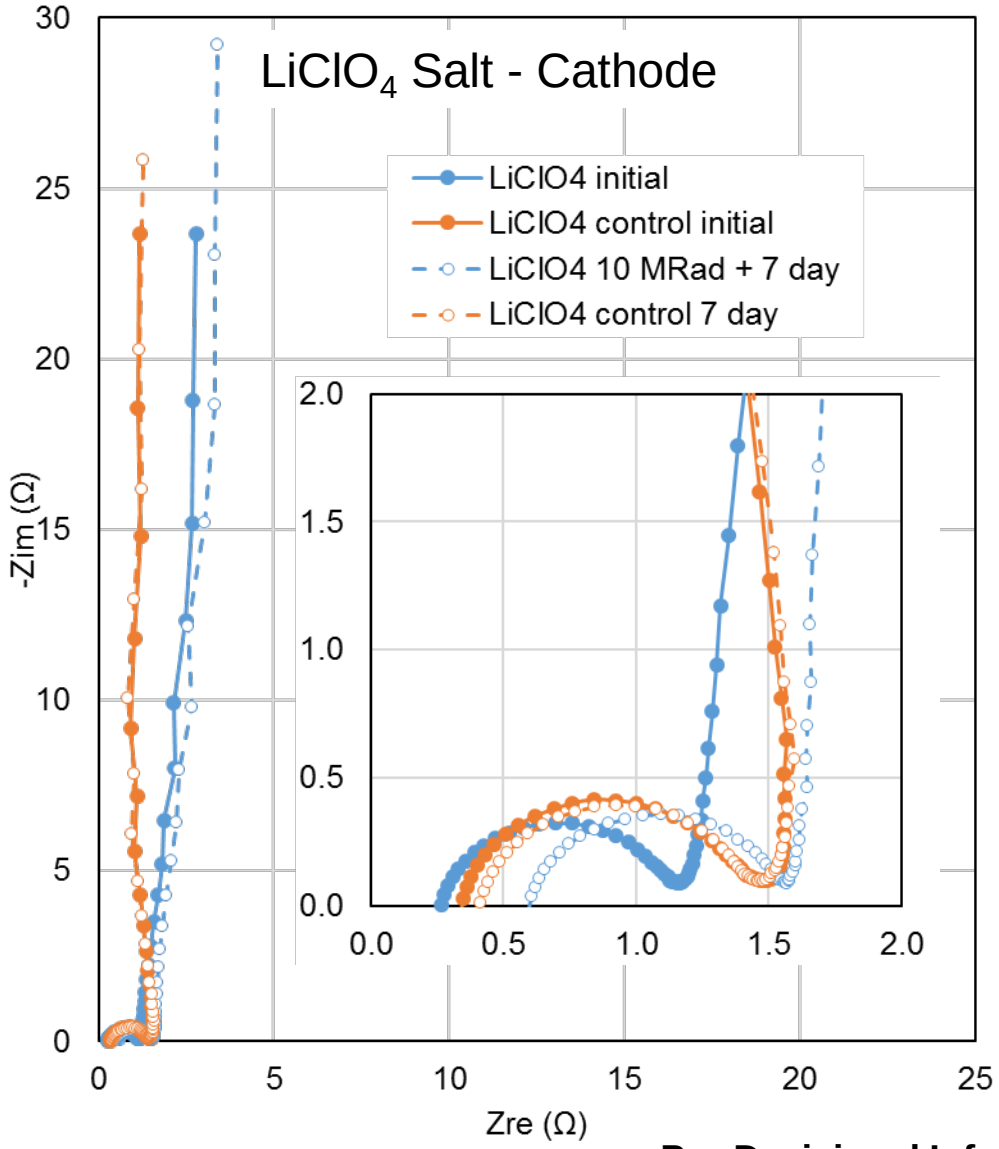
Build 3-electrode cells to understand effects on individual electrodes

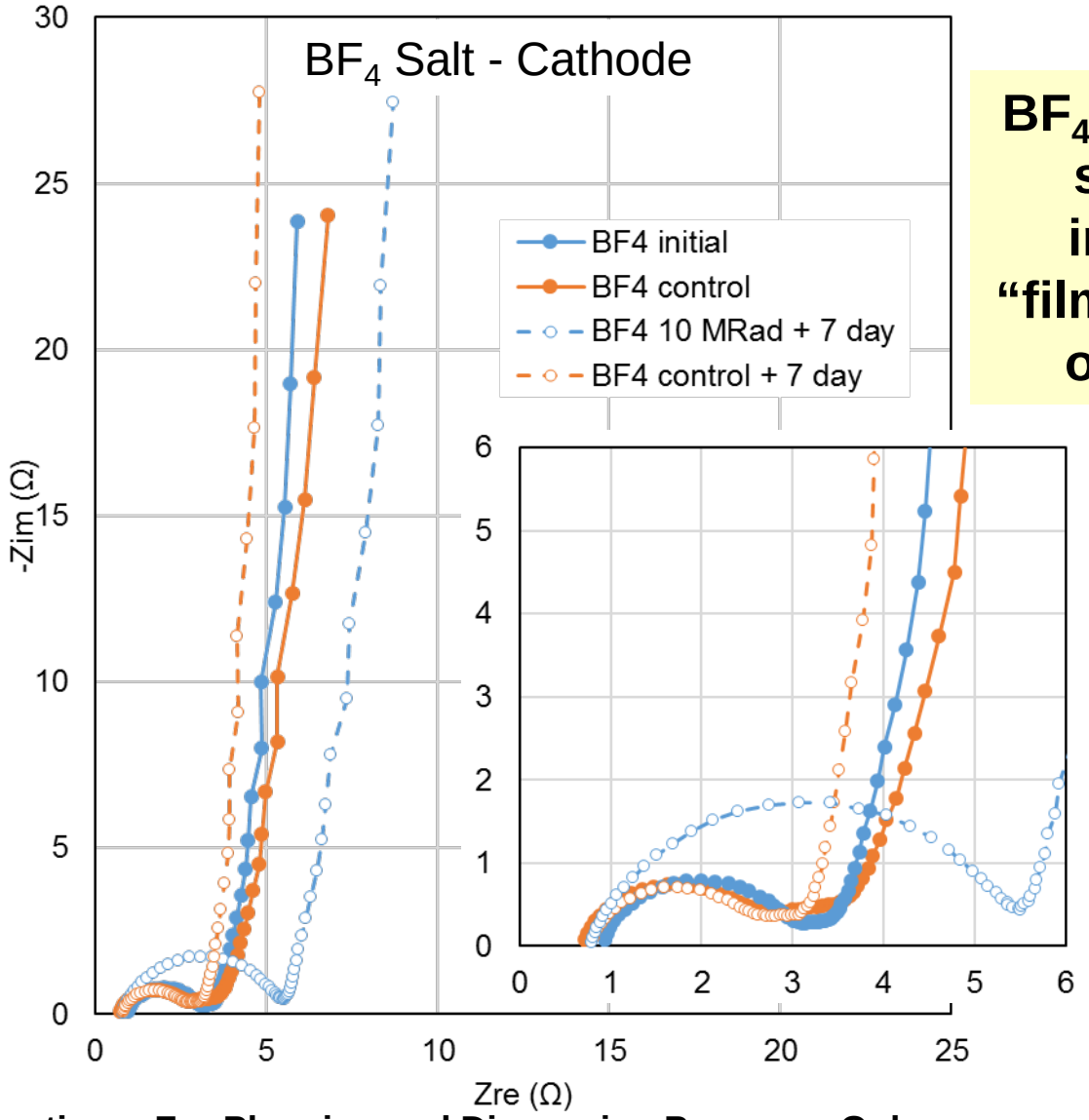


Experimental Design

- 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

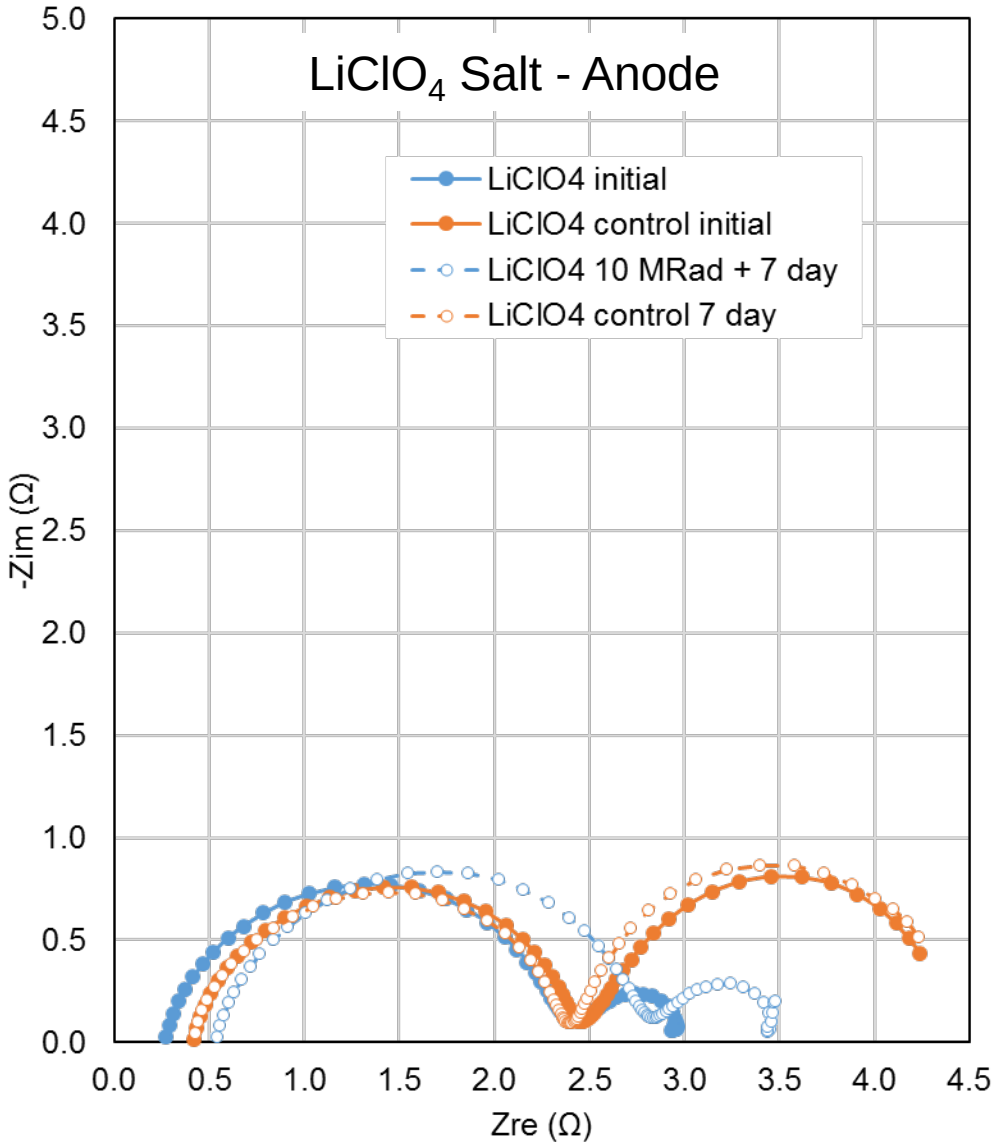
Film on cathode of Li/CF_x cell with $LiClO_4$ salt appears unaffected after 10 MRad

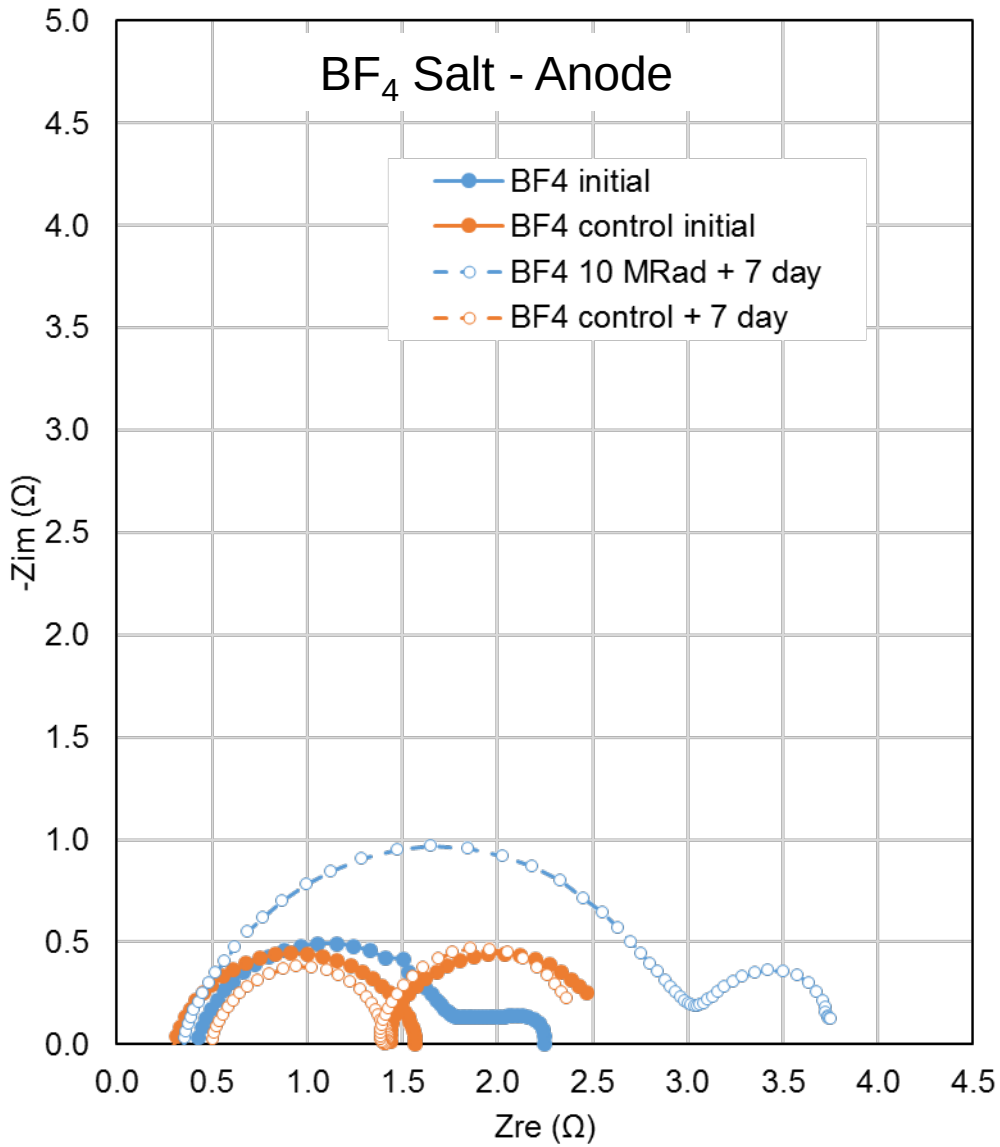




BF_4 salt leads to significant increase in "film" resistance on cathode

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

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
  - Lower capacity
- “Film” resistance grows in 3-electrode cells with $LiBF_4$ salt
  - Both anode and cathode are affected
- “Film” resistance remains constant in 3-electrode cells with $LiClO_4$ salt
  - Hope to incorporate other salts into prototype Li/CF_X D-cells

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.