Evaluation of Commercial High Energy Lithium Primary Cells for Wide Temperature Range Aerospace Applications

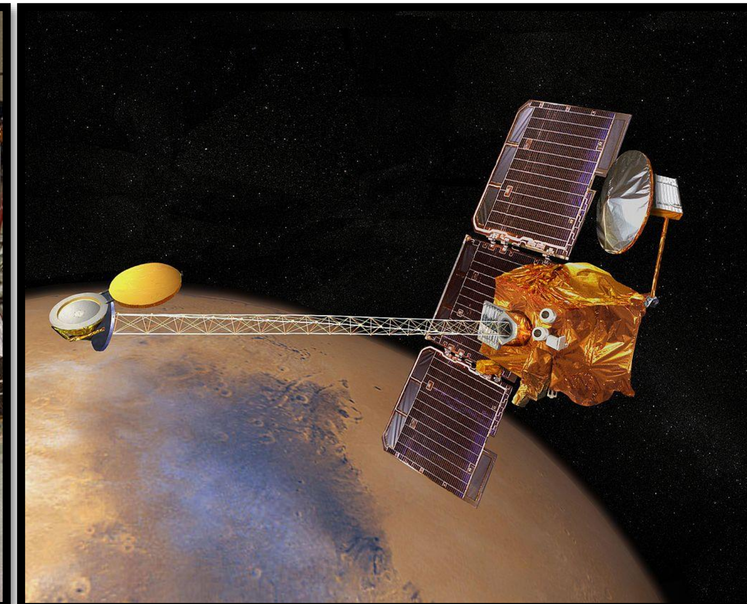
F. C. Krause, S. C. Jones, E. J. Brandon, R. V. Bugga, J.-P. Jones, W. C. West, J. Pasalic, K. J. Billings

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA

231st Meeting of the Electrochemical Society
New Orleans, Louisiana
31 May 2017

Batteries in NASA missions

History and Introduction: Pre-Lithium-Ion



- Voyager (1977), Galileo (1989), Cassini (1997): **RTG** power only
- Viking orbiters/landers (1975-76): PV/RTG + **Ni/Cd** batteries
- Mars Global Surveyor (1996), Mars Surveyor ’98, Stardust (1999), Genesis (2001), Mars Odyssey (2001): **Ni/H_2** batteries
  - Stardust, Genesis: also primary Li/SO_2
- Pathfinder (1996): **Ag-Zn**
  - Sojourner rover: primary $Li/SOCl_2$

Batteries in NASA missions
Lithium-ion

- Lithium-ion have powered many missions thanks to high specific energy and long life: Mars Exploration Rover (2003), Mars Express (2003), Phoenix Lander (2007), Kepler (2009) Grail (2011), Aquarius (2011), Mars Science Laboratory (2011), Juno (2011), NuSTAR (2012), SMAP (2014), Mars InSight Lander (2018), Mars Rover (2020)
    - MER lander also used primary Li/SO_2

- Secondary battery systems require available power: generally photovoltaic or radioisotope thermoelectric generator (RTG)

- When neither is available or practical, high energy primary batteries may be the best option

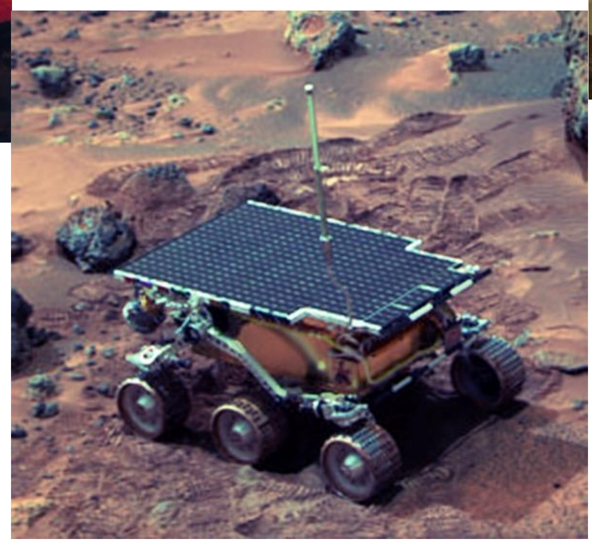
Images courtesy NASA/JPL-Caltech

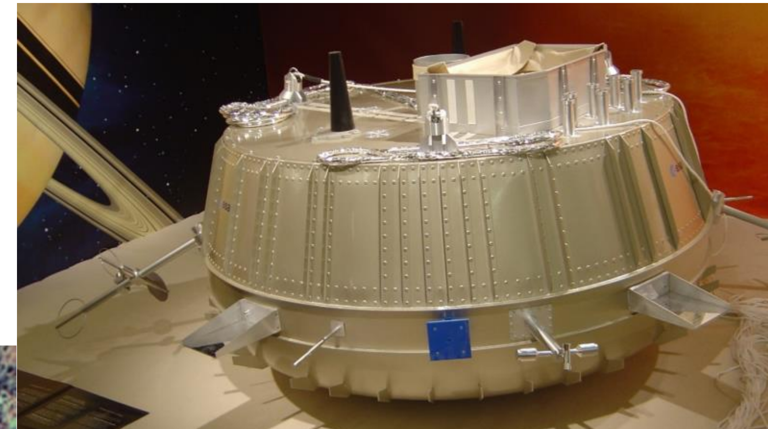
Lithium primary cells in NASA missions
Past examples

Images courtesy NASA/JPL-Caltech

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

Sojourner Rover (1996): Li/$SOCl_2$
150 Wh + PV
PV-only after batteries depleted





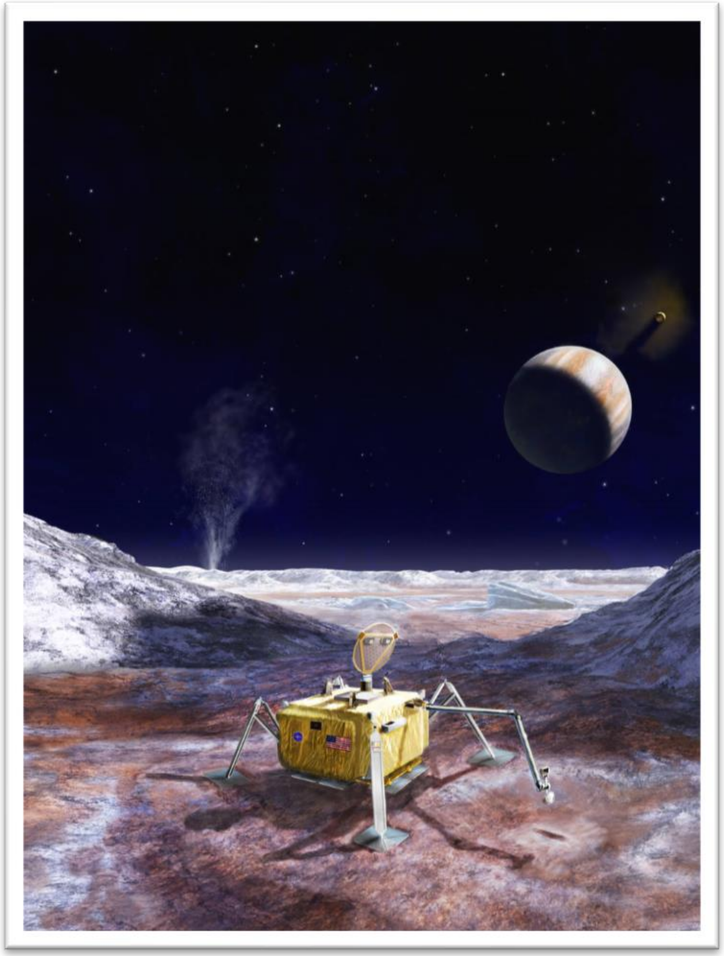
Huygens Probe (2004): Li/SO_2
~2700 Wh
153 minutes

→ **So far most primary-only battery systems have been for very short mission durations**

Ocean Worlds NASA missions
Mission requirements

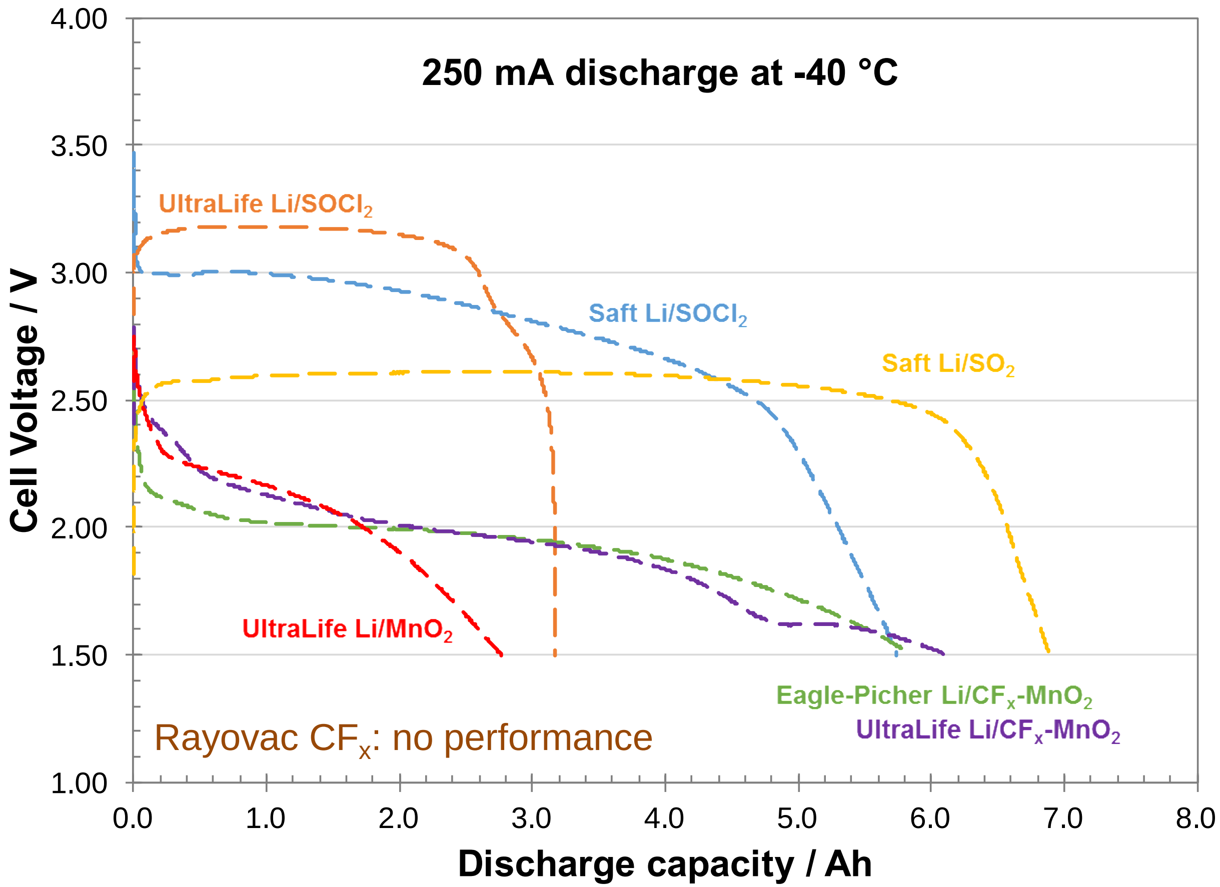
- ❖ Increasing interest in Ocean Worlds destinations, in particular for origin-of-life studies: Europa, Enceladus, Titan
- ❖ Theoretical Lander concept:
  - ➢ RTG not baselined
  - ➢ Insufficient solar exposure for PV
  - ➢ Very low temperature operation
  - ➢ Long cruise time/shelf life
  - ➢ Radiation tolerance
  - ➢ Planetary protection
  - ➢ Mission duration
    - ➢ 20-30 days desirable

A targeted operation time of 480 hours would require much higher energy density batteries than previous primaries



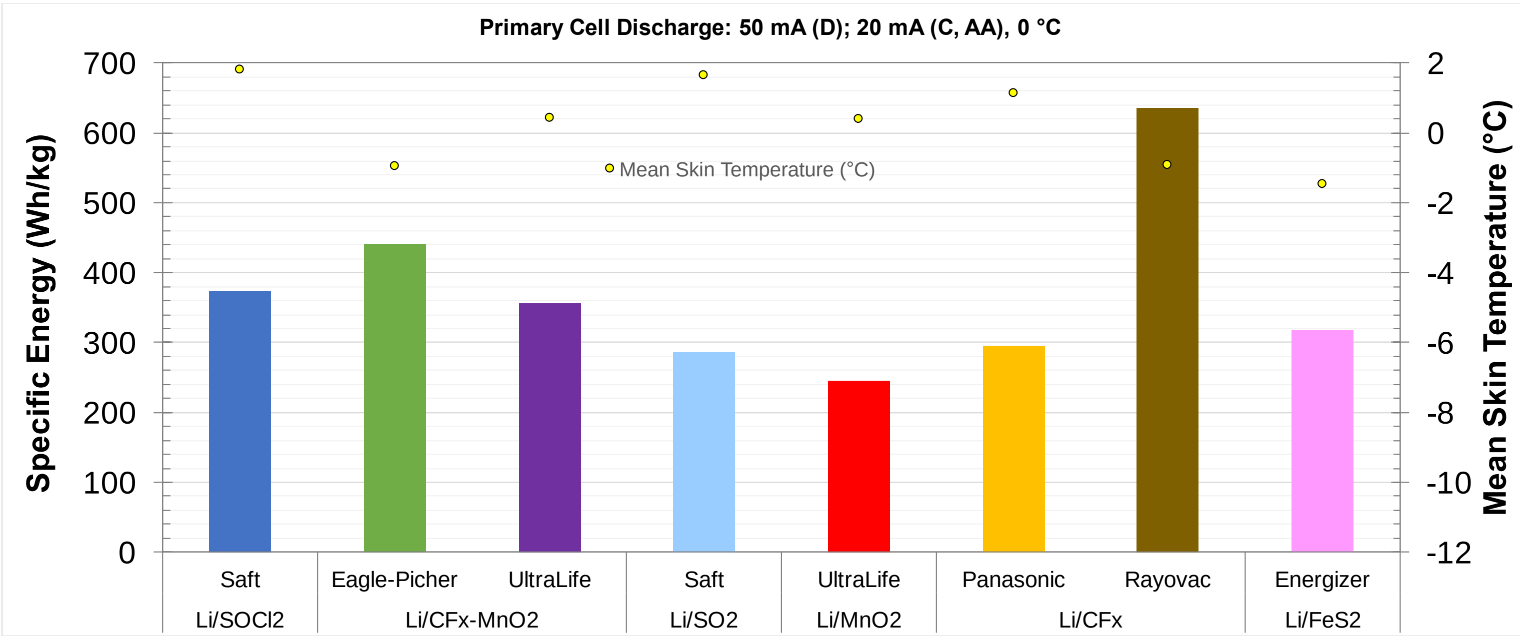
Artist's concept
Image courtesy NASA/JPL-Caltech

Lithium primary cells: D format
Summary of performance by chemistry



- Many lithium primary battery chemistries are available in the D-cell format
- Nameplate capacities range from 9 – 19 Ah
- Over the range of temperatures and rates of interest, the highest and lowest capacity cells switch places!
- Cell can materials vary: stainless steel, aluminum; significant effect on mass
- Baseline of 0 ºC operation targeted; operation down to -40 ºC is desirable

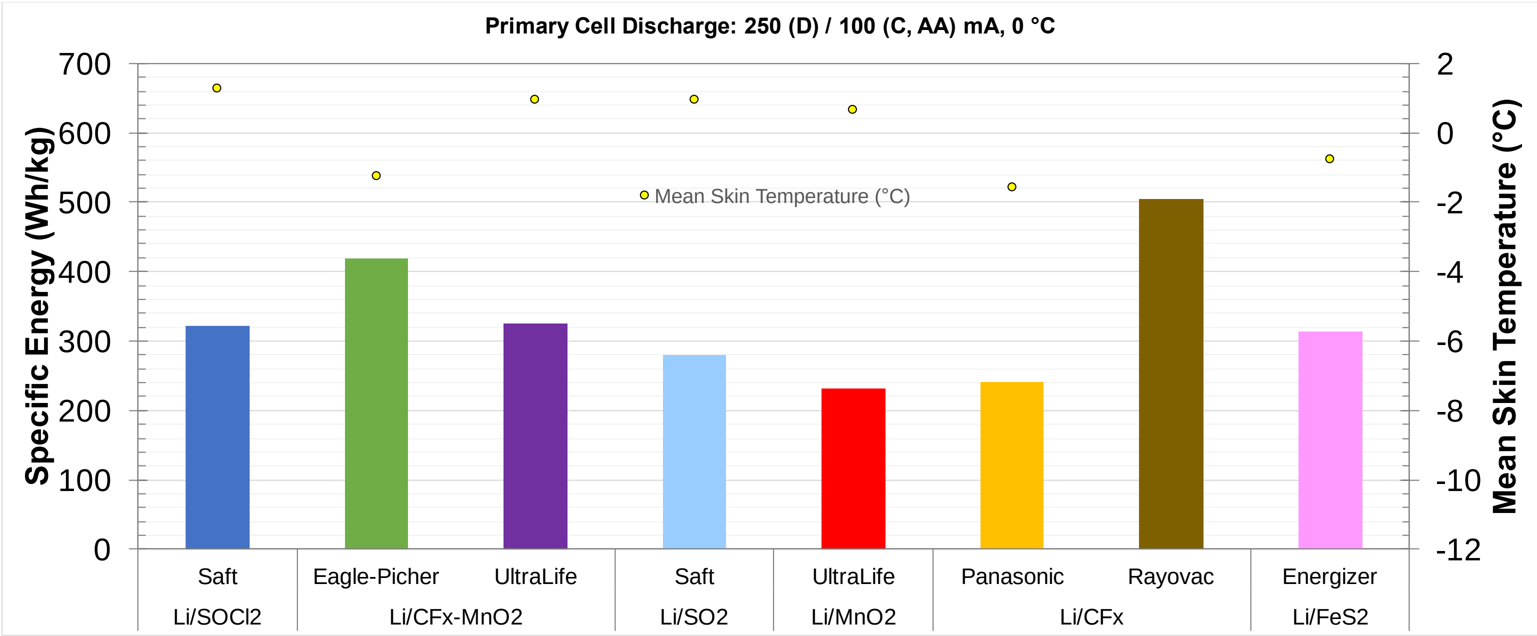
Lithium primary cells: D format
Summary of performance by chemistry



- **~C/300 discharge at 0 ºC**
- Rayovac Li/CFx cells have the highest specific energy at 0 ºC
- E-P Li/CF_x-MnO_2 hybrid cells have lower but still good energy
- Other chemistries/manufacturers are undistinguished

Lithium primary cells: D format

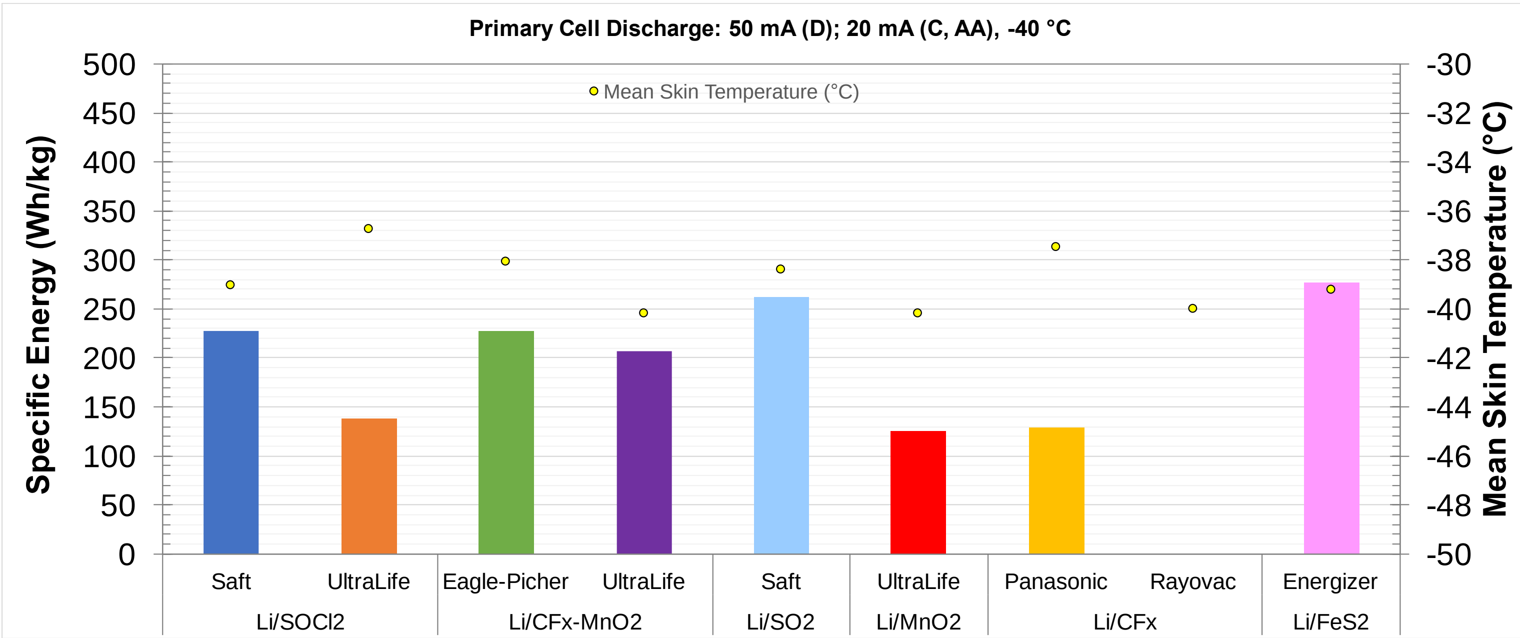
Summary of performance by chemistry



- **~C/60 discharge at 0 ºC**
- Rayovac Li/CFx cells have the highest specific energy at 0 ºC
- E-P Li/CF_x-MnO_2 hybrid cells have lower but still good energy
- Other chemistries/manufacturers are undistinguished

Lithium primary cells: D format

Summary of performance by chemistry

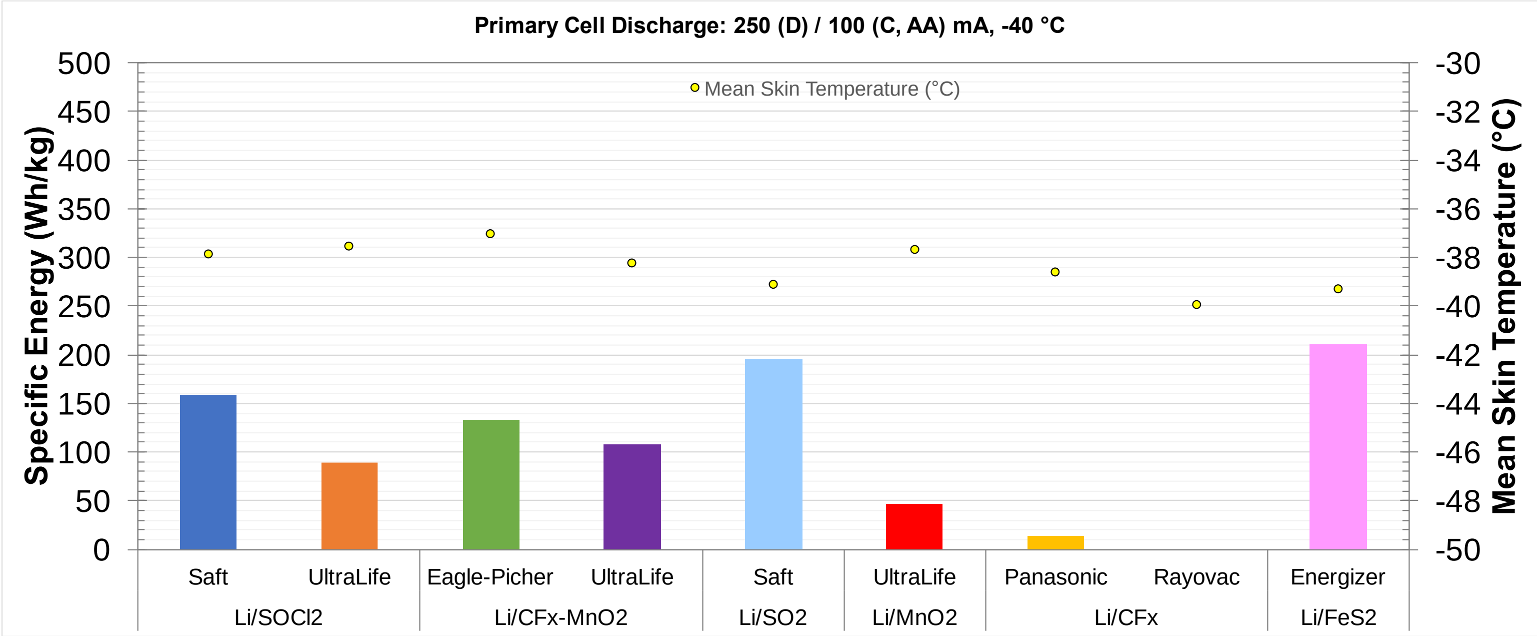


- **~C/300 discharge at -40 ºC**

- Despite excellent energy at room temperature, Li/CF_x cells are poor or non-functional at -40 ºC
- Li/CF_x-MnO_2 hybrid cells, on the other hand, have good energy over a large temperature range
- In spite of small size (AA) and low voltage (< 1.5 V), Li/FeS_2 offer excellent energy at -40 ºC

Lithium primary cells: D format

Summary of performance by chemistry

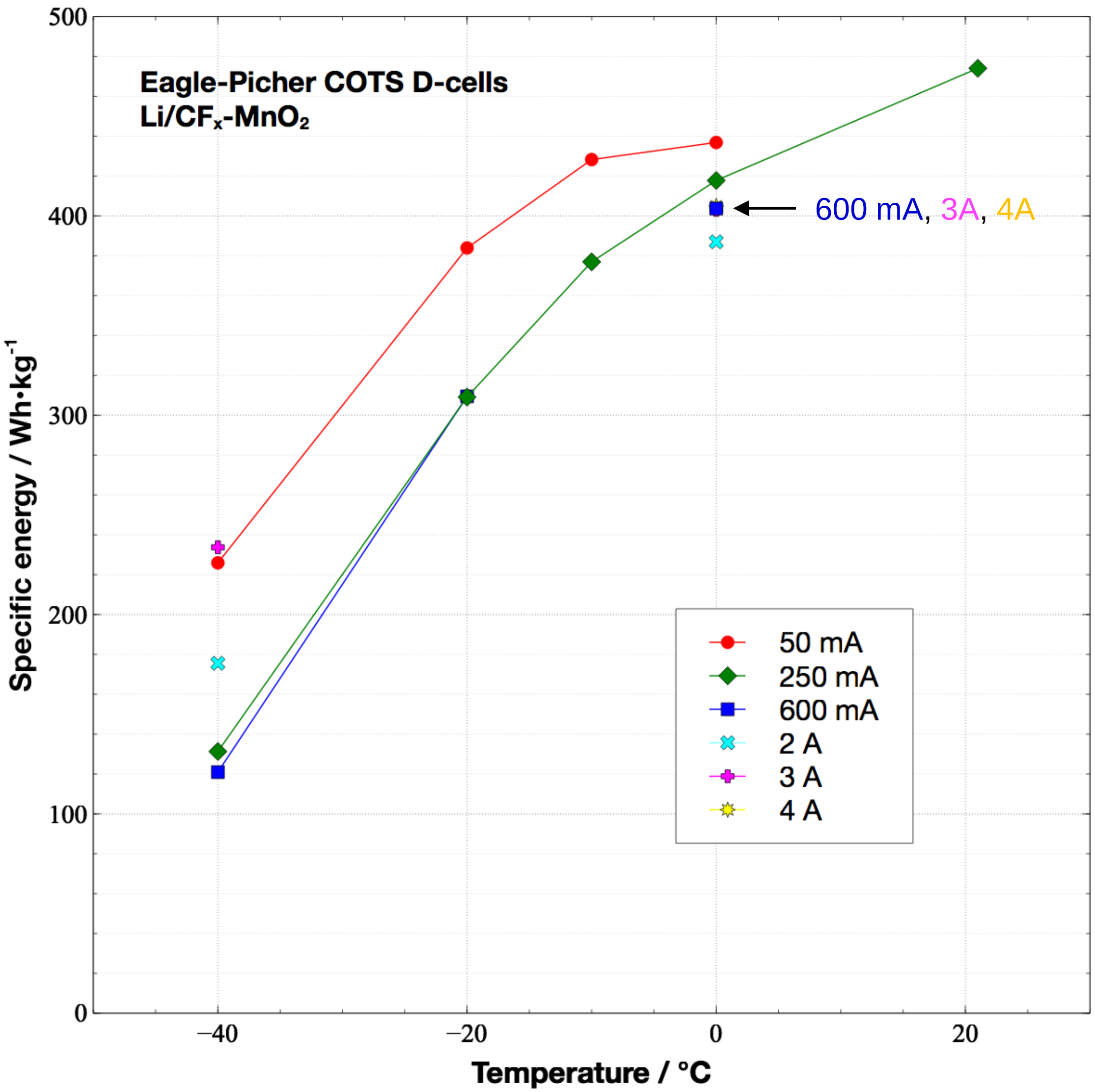


- **~C/60 discharge at -40 ºC**
- Despite excellent energy at room temperature, Li/CF_x cells are poor or non-functional at -40 ºC
- Li/CF_x-MnO_2 hybrid cells, on the other hand, have good energy over a large temperature range
- In spite of small size (AA) and low voltage (< 1.5 V), Li/FeS_2 offer excellent energy at -40 ºC

- ***At moderate rates over a broad temperature range, Li/CF_x-MnO_2 hybrid cells appear to be the most versatile option***

Eagle-Picher Li/CF_x-MnO_2 cell discharge testing

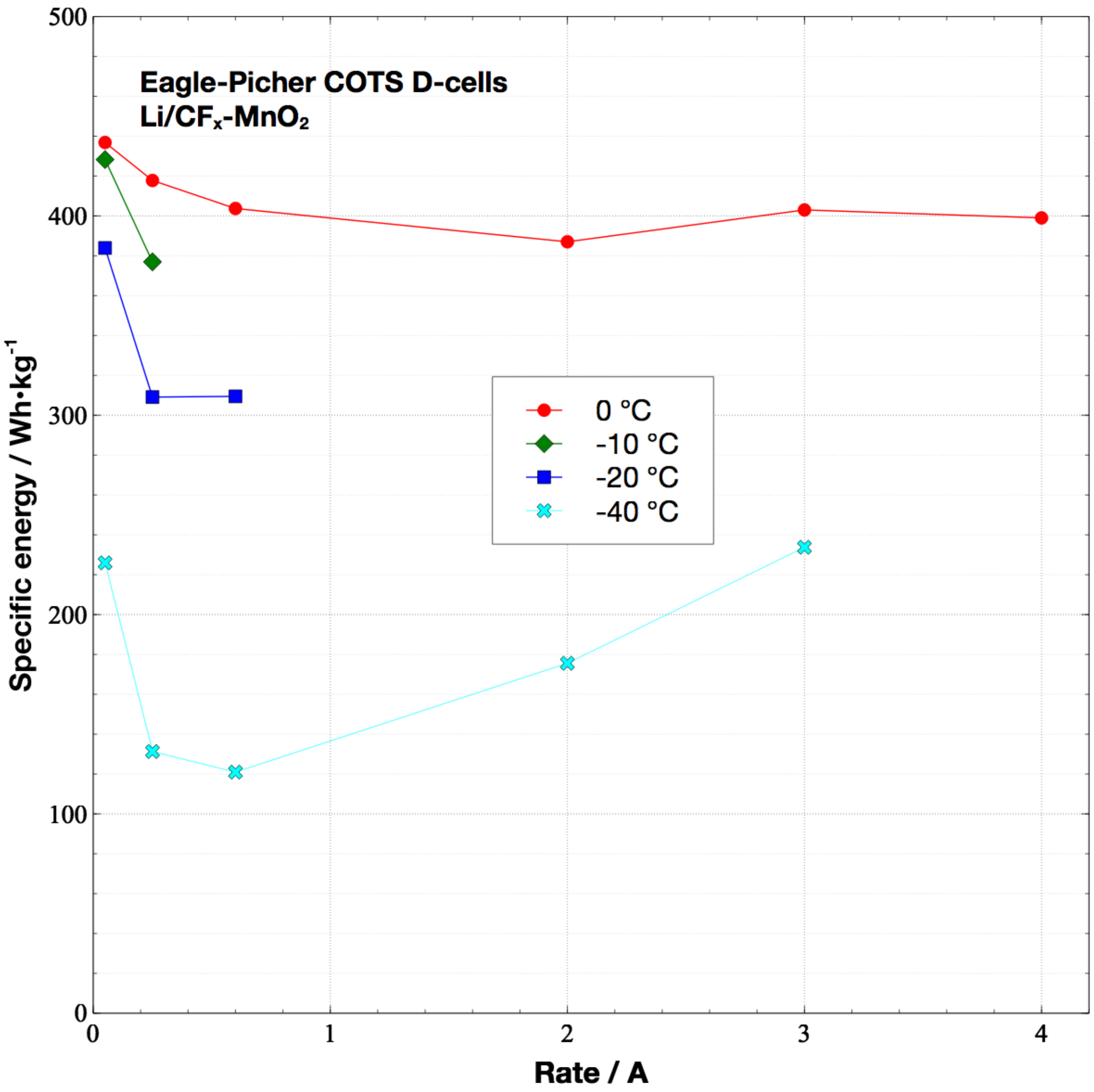
Temperature and rate study



- Rates ranged from 50 mA (~C/300) to 4 A (~C/3.75)
- Temperatures ranged from 21 ºC to -40 ºC
- Energy was strongly temperature dependent, and lower temperatures induced greater discharge rate dependence as well

Eagle-Picher Li/CF_x-MnO_2 cell discharge testing

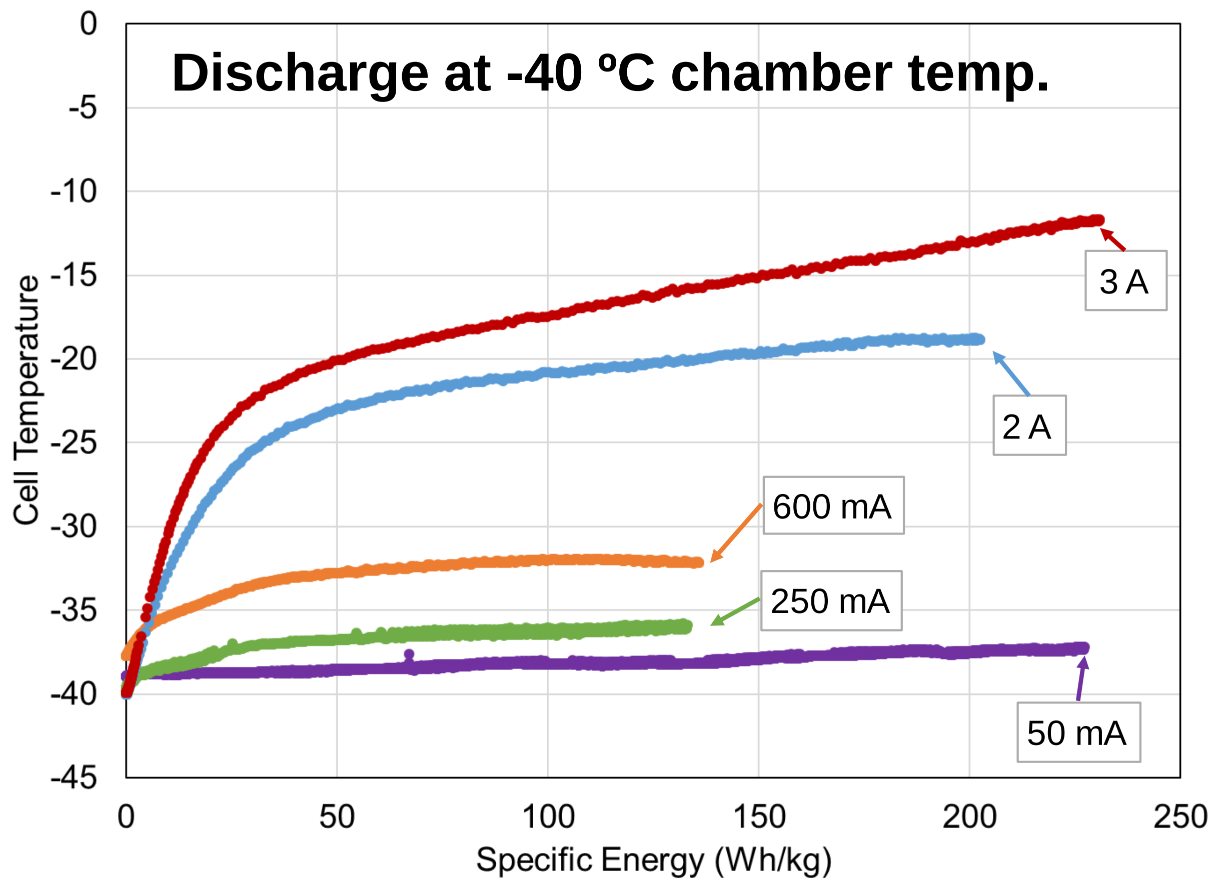
Temperature and rate study



- Rates ranged from 50 mA (~C/300) to 4 A (~C/3.75)
- Temperatures ranged from 21 ºC to -40 ºC
- 0 ºC is relatively rate-agnostic, while lower temperatures show a bathtub-like dependence with 50 mA and 3 A being nearly equivalent
- This behavior is explained by self-heating

Eagle-Picher Li/CF_x-MnO_2 cell discharge testing

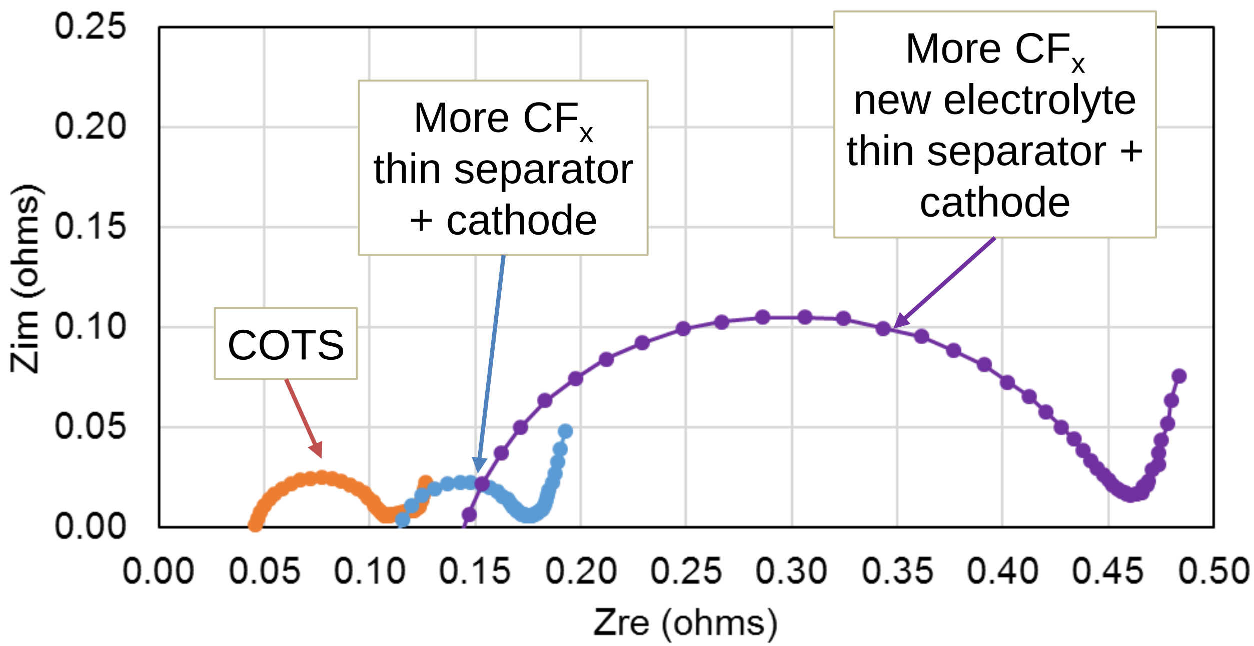
Temperature and rate study



- Cells are roughly 50% efficient (discharged energy vs. dissipated heat)
- At high rates, self-heating is poorly compensated by the chamber environment and high cell temperature leads to good performance
- At moderate rates, self-heating is not enough to compensate for increased resistance

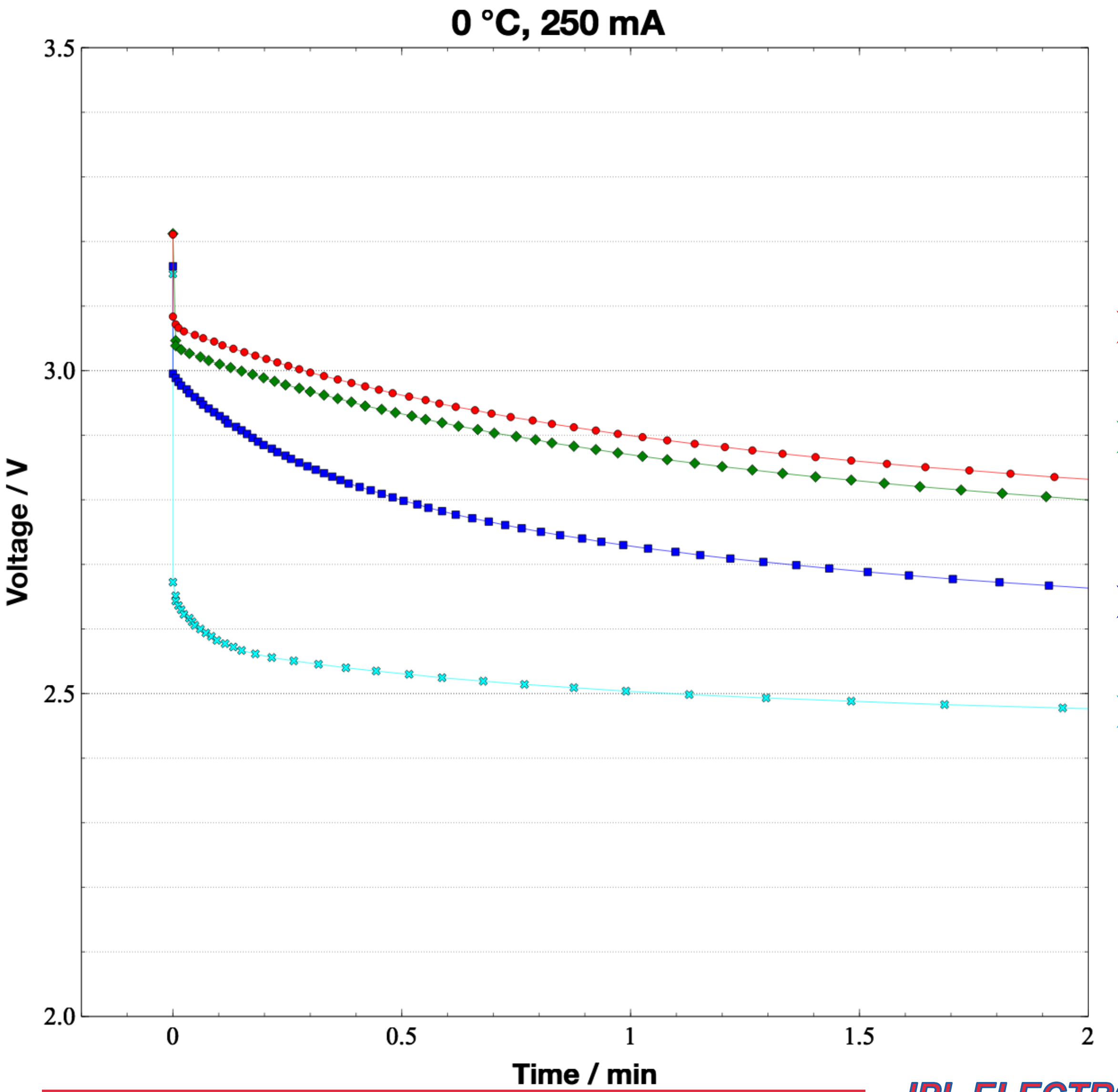
Eagle-Picher Li/CF_x-MnO_2 cells: improvements
Modifications to cathode and electrolyte

- **JPL worked with Eagle-Picher to create modified Li/CF_x-MnO_2 D-cells targeting improved low-temperature performance**
- **Modifications were made to the separator, cathode, and electrolyte**
- **Initial EIS of these cells revealed noticeable differentiation**



Eagle-Picher Li/CF_x-MnO_2 cells: improvements

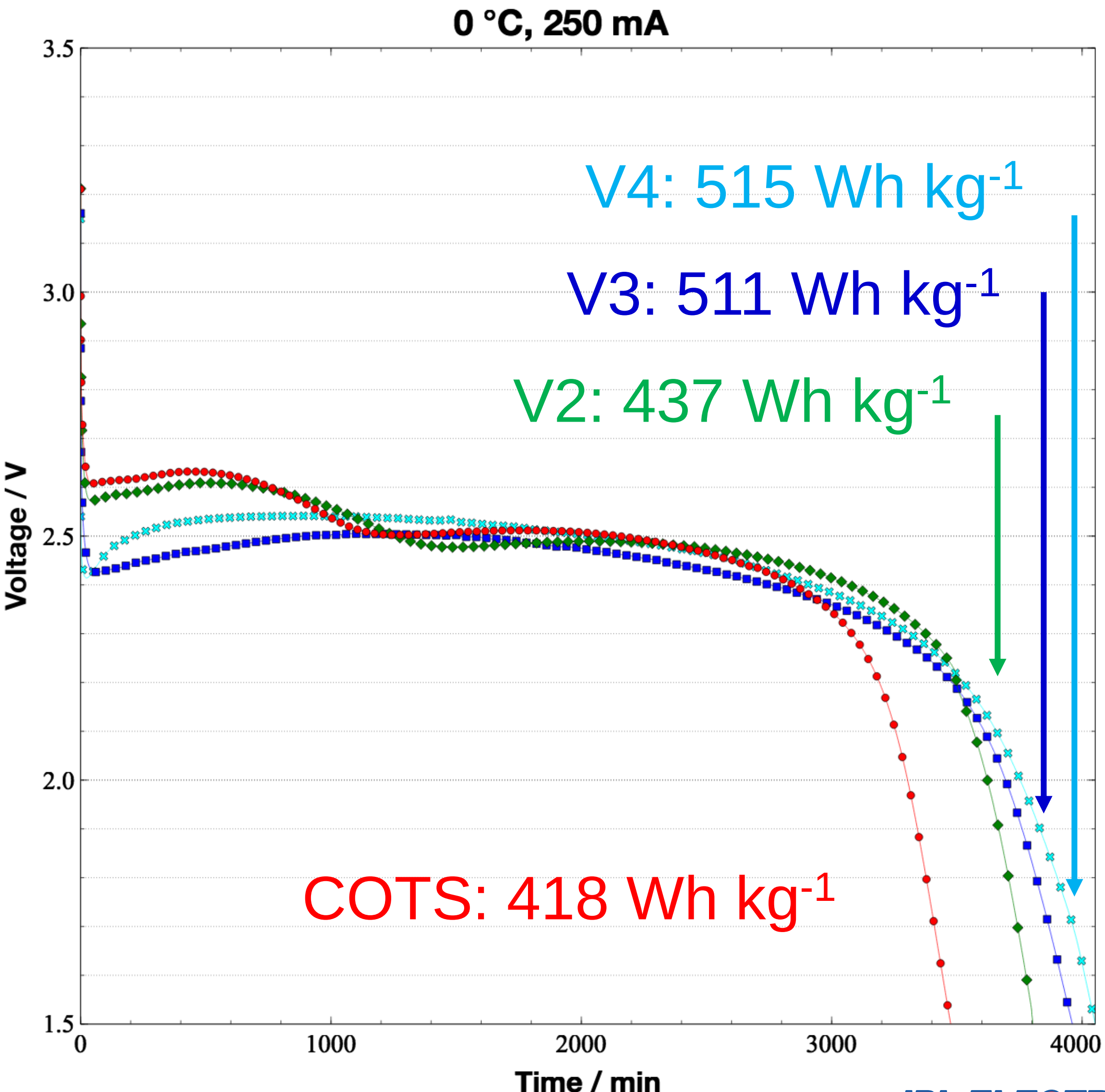
Modifications to cathode and electrolyte



- **COTS**: standard cathode
- **Version 2**: modified coating of standard cathode
- **Version 3**: higher CF_x cathode
- **Version 4**: higher CF_x cathode, JPL electrolyte

Eagle-Picher Li/CF_x-MnO_2 cells: improvements

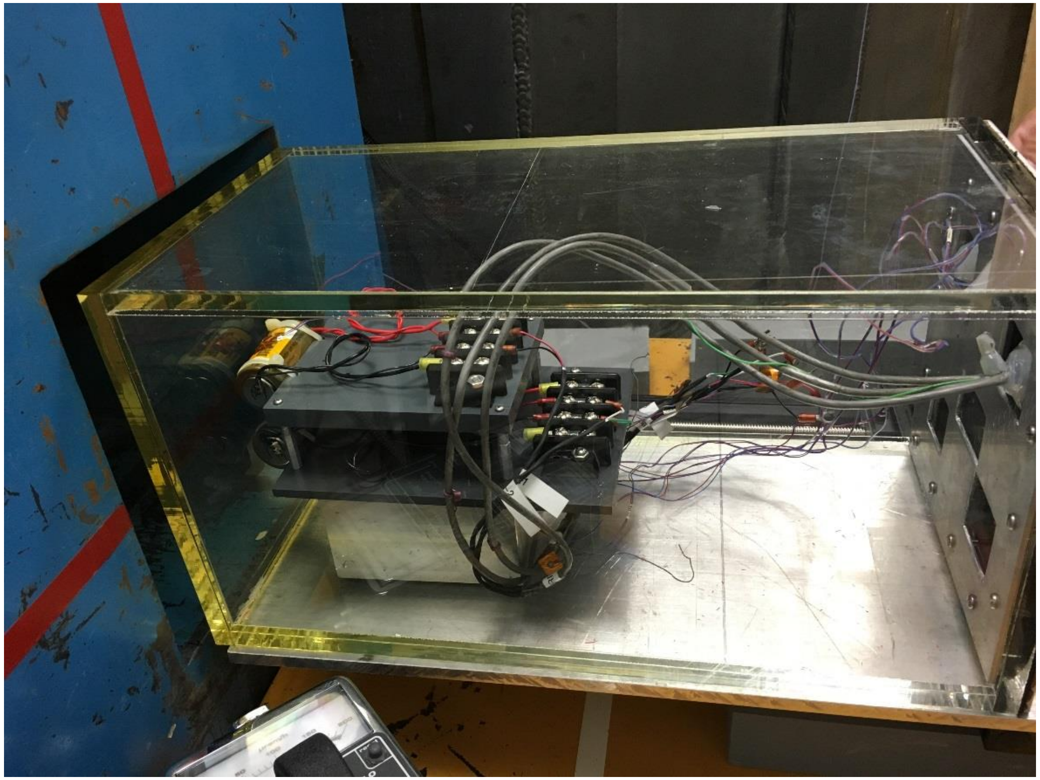
Modifications to cathode and electrolyte



- **COTS**: standard cathode
- **Version 2**: modified coating of standard cathode
- **Version 3**: higher CF_x cathode
- **Version 4**: higher CF_x cathode, JPL electrolyte

Eagle-Picher Li/CF_x-MnO_2 cells: radiation exposure

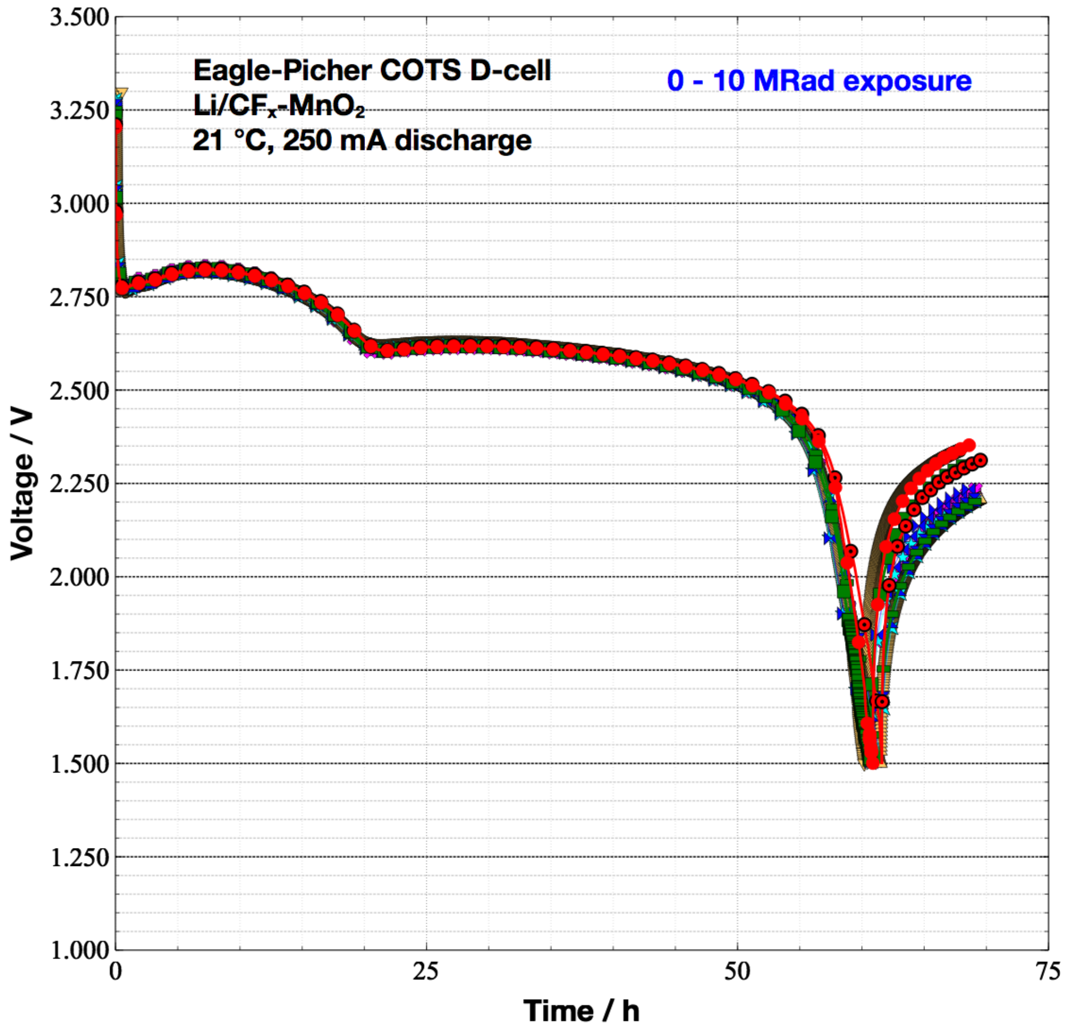
JPL ^{60}Co source



- Radiation: a hazard during cruise and within Jupiter's magnetosphere
- Radiation exposure may be used for planetary protection since dry-heat microbial reduction (DHMR) is not suitable
- Typical Li cells would not survive the necessary time and temperature for DHMR
- 1.3 MeV gamma source irradiates the cell at ~200 rad/s

Eagle-Picher Li/CF_x-MnO_2 cells: radiation exposure

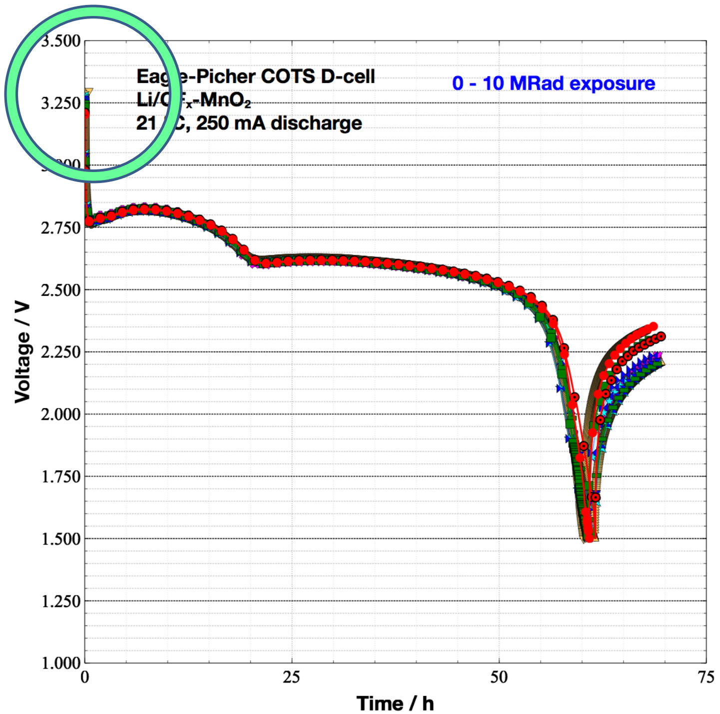
No irradiation → 10 Mrad exposure

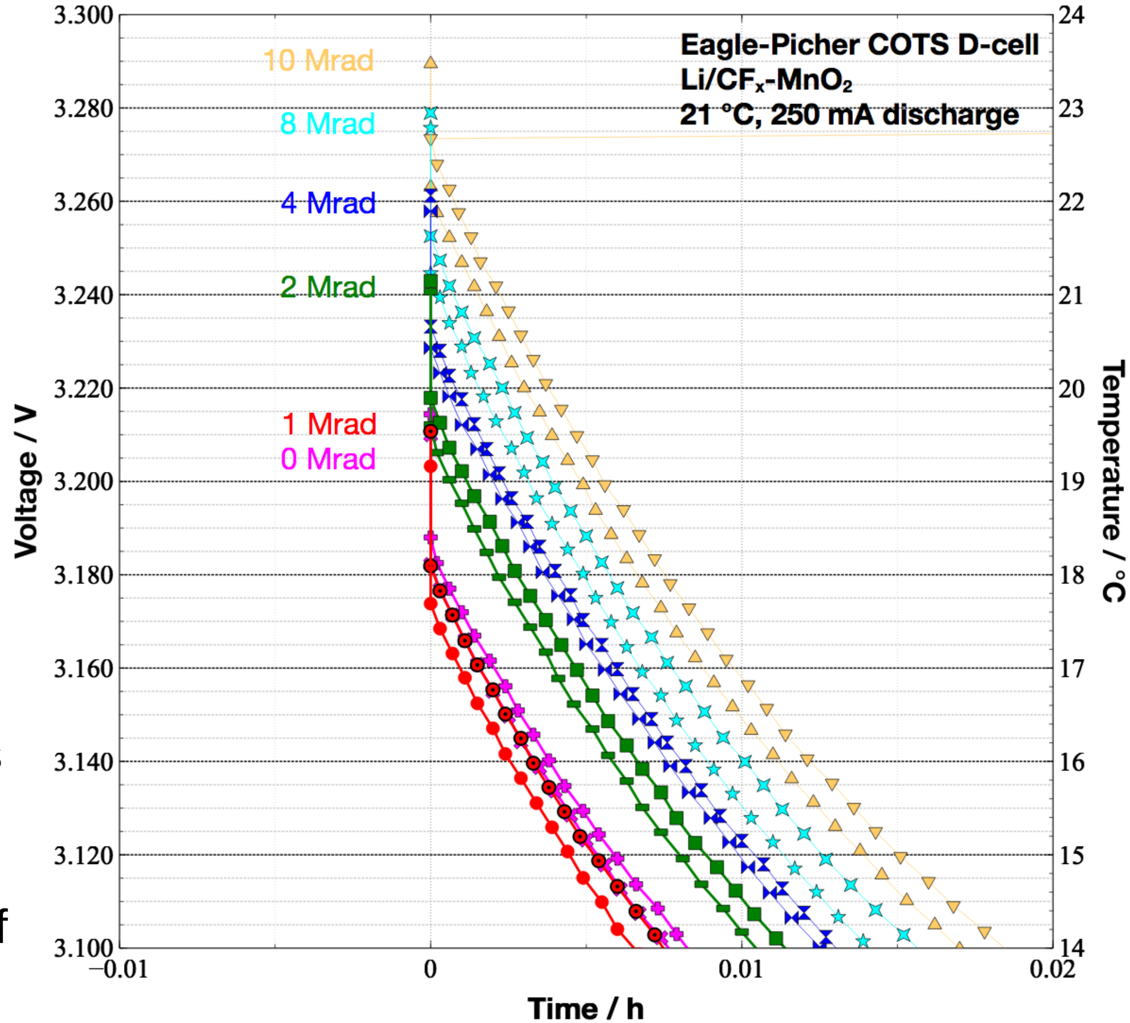


- 10 cells were irradiated to either 1, 2, 4, 8, or 10 Mrad
- Discharge at 21 ºC, 250 mA, along with two non-irradiated cells
- Very similar discharge performance
- Discharge profiles show no significant changes up to 10 Mrad exposure

Eagle-Picher Li/CF_x-MnO_2 cells: radiation exposure

No irradiation ➞ 10 Mrad exposure

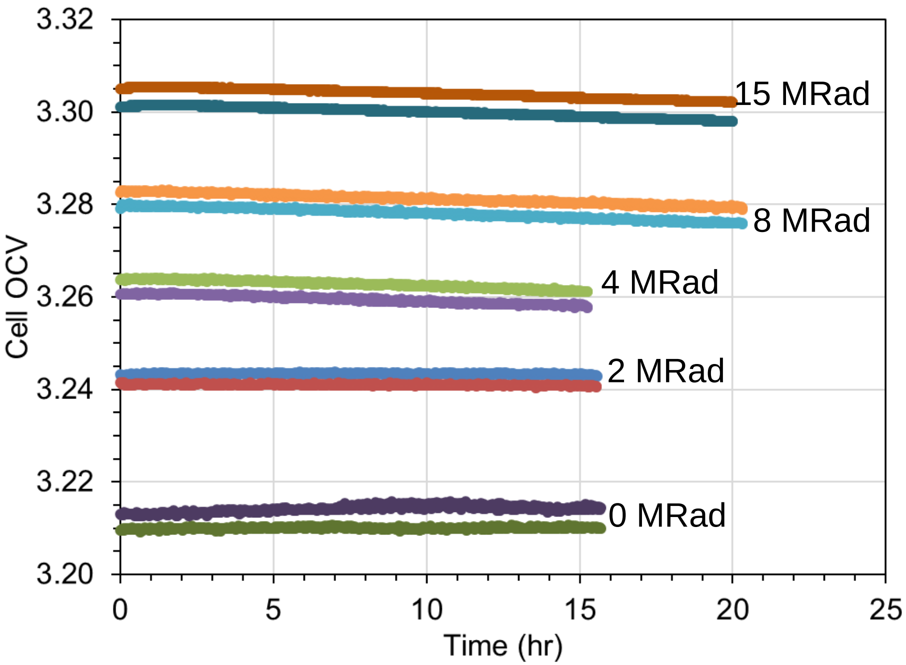


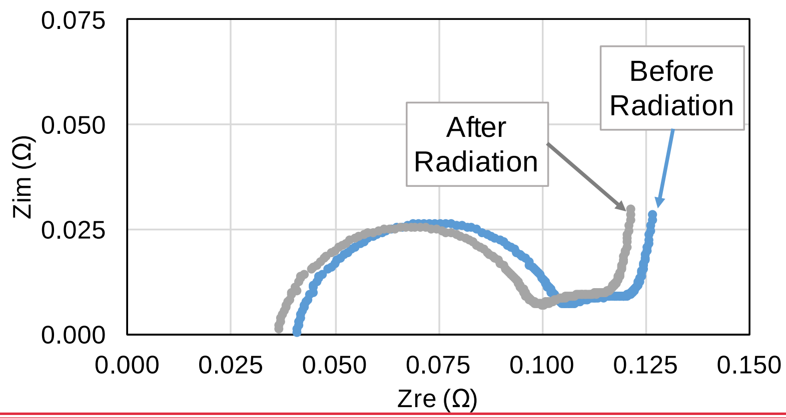


- Instantaneous voltage drop is similar for all cells
- Unexplained rise in OCV proportionate to the degree of irradiation

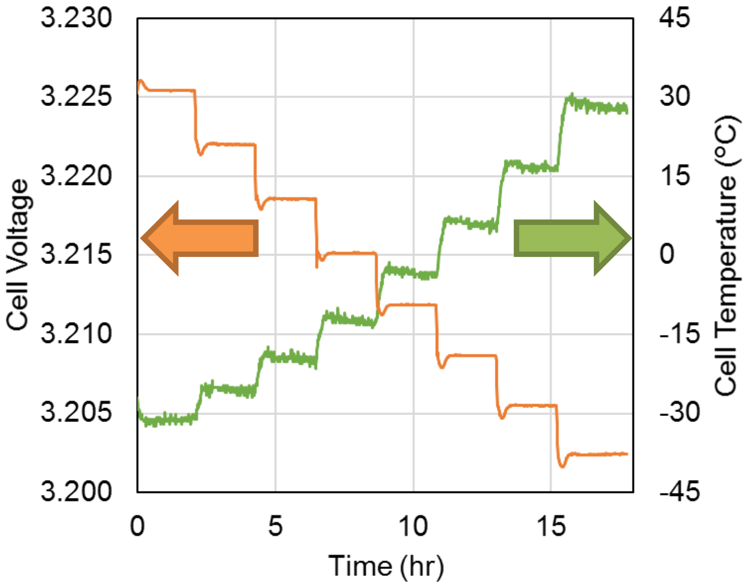
Eagle-Picher Li/CF_x-MnO_2 cells: radiation exposure

Effects of Irradiation on OCV and Impedance





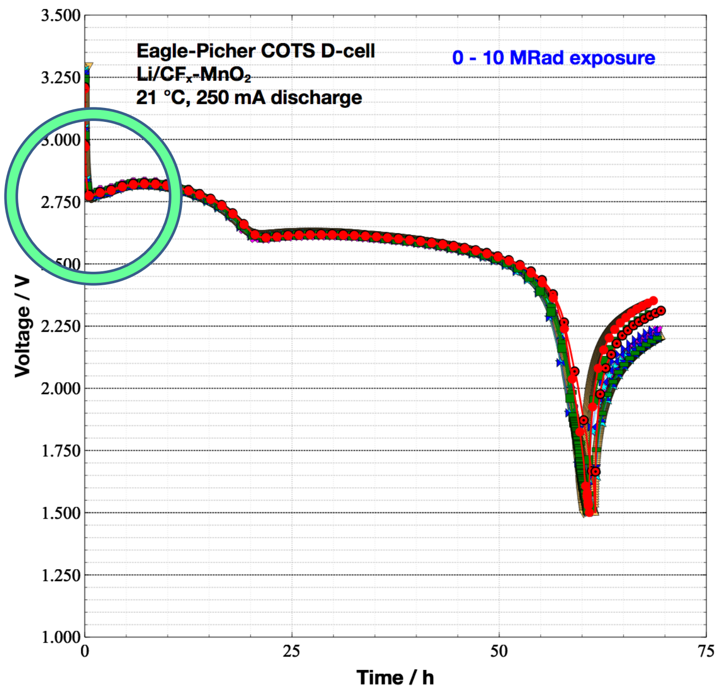
- Rise in OCV proportional to irradiation
- Irradiation also causes cell heating; however, manually heating a non-irradiated cell in a stepwise fashion reveals that increased temperature causes lower OCV:

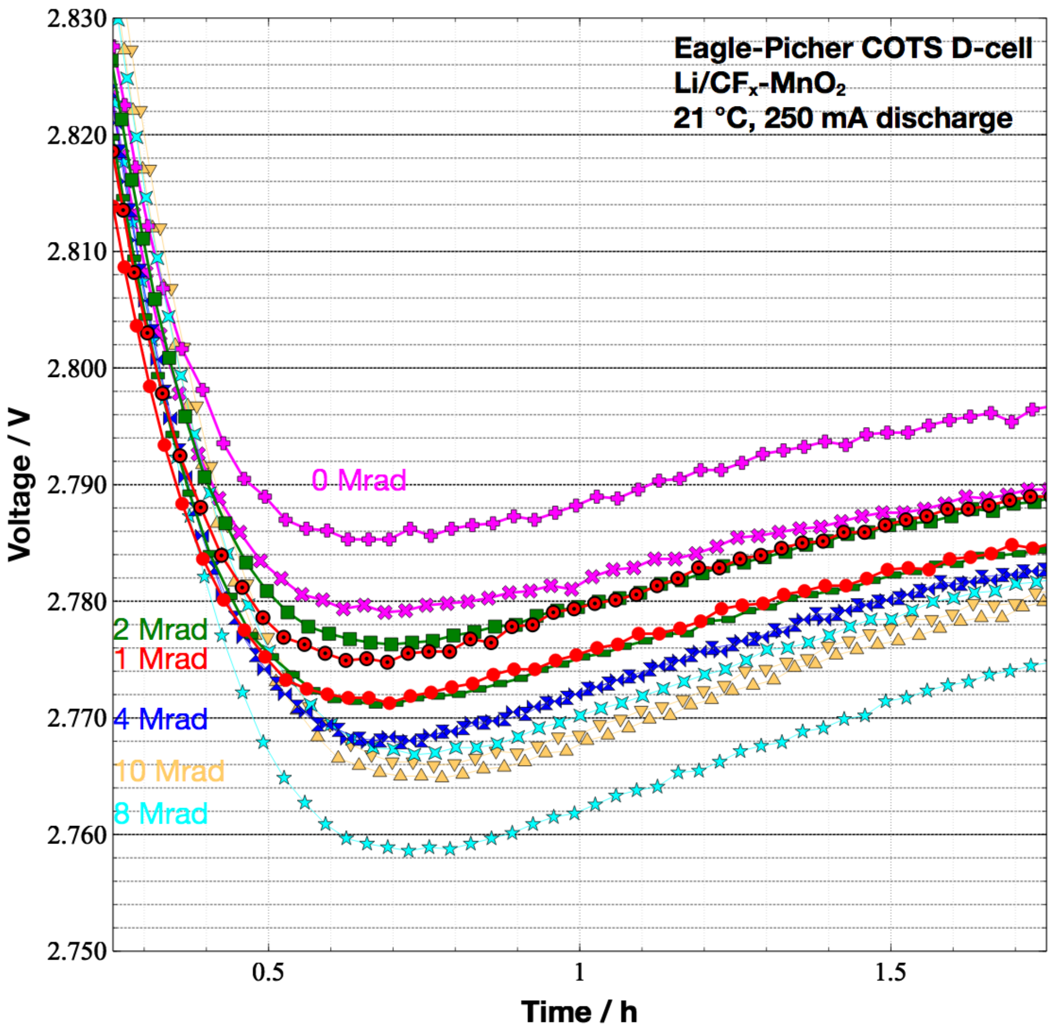


- Temperature is not the cause of OCV rise
- No change in impedance after radiation

Eagle-Picher Li/CF_x-MnO_2 cells: radiation exposure

No irradiation ➞ 10 Mrad exposure

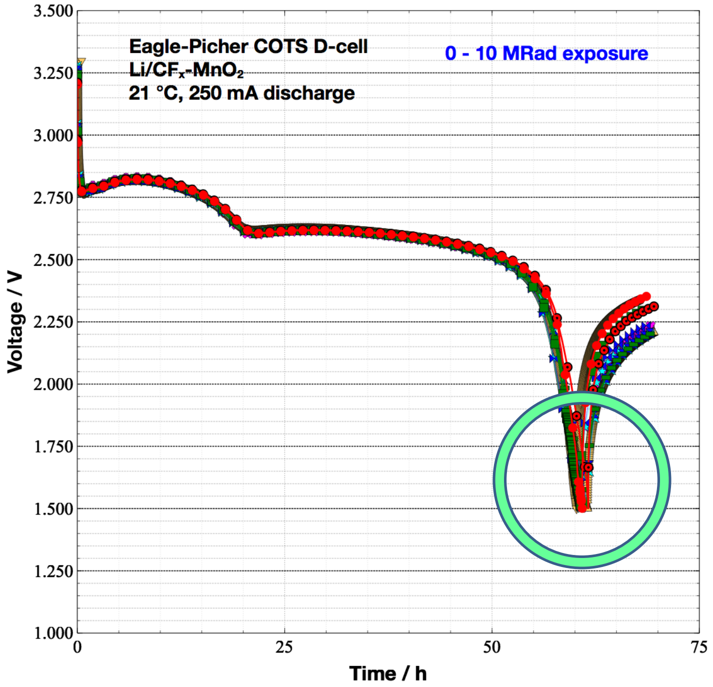


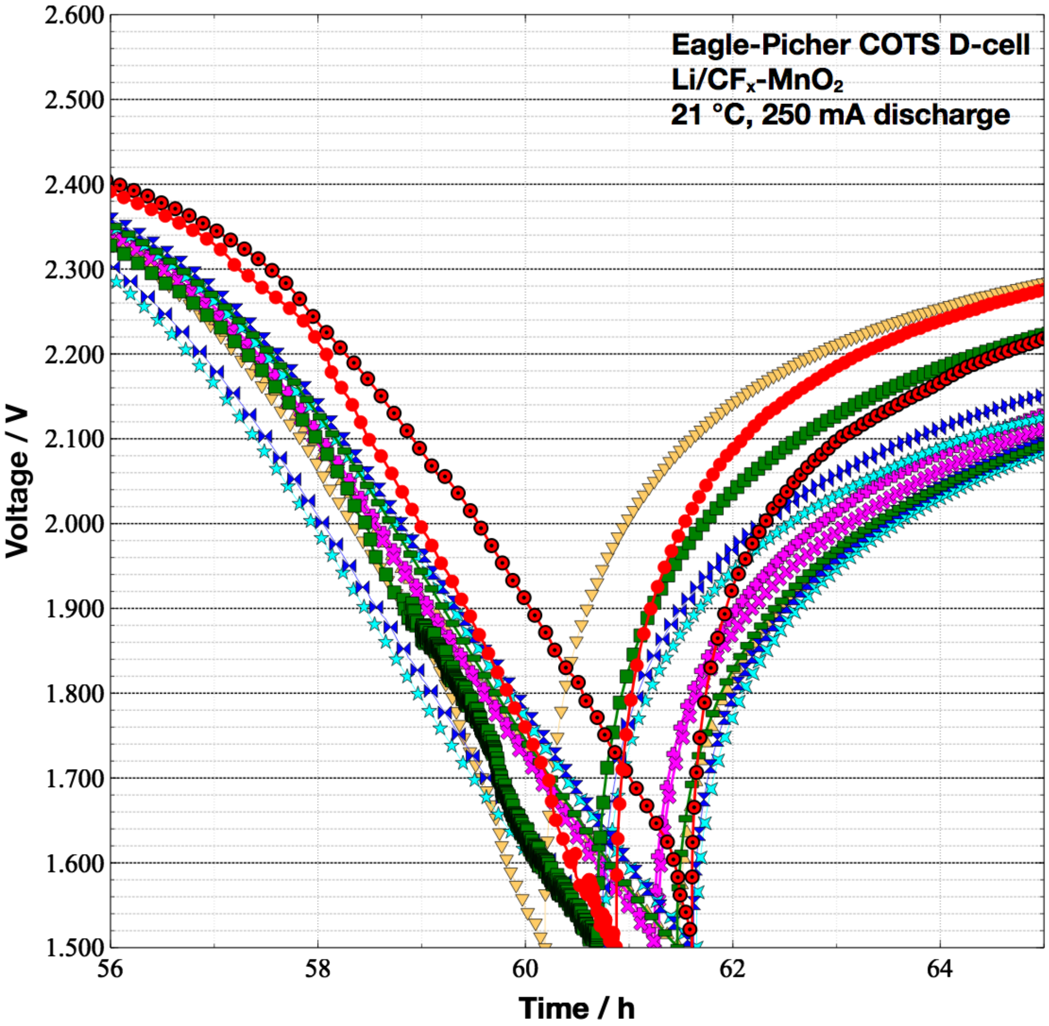


- Weak correlation between radiation exposure and depth of initial voltage drop
- Trend does **not** persist throughout discharge

Eagle-Picher Li/CF$_x$-MnO$_2$ cells: radiation exposure

No irradiation → 10 Mrad exposure





- **No impact** of radiation exposure on final capacity
- Spread is in line with expected cell-to-cell variation

Lithium primary batteries for broad temperature ranges

Conclusions

- New battery systems with higher specific energy than the state-of-the-art are required for future missions to Ocean Worlds
- Li/CF_x-MnO_2 offers good performance over the 0 to -40 ºC range
- Further optimization of this hybrid chemistry through cathodes, separators and electrolytes has shown improvements at low temperatures
- For the anticipated mission environments of 0 ºC, Li/CF_x cells offer the greatest energy density, >**600 Wh/kg** at 0 ºC and >**700 Wh/kg** at room temperature
- The CF_x-based primary cells showed good radiation tolerance based on discharge capacities; however, we observed unusual voltage rise and component instability, which need to be studied further

Artist's concept
Image courtesy NASA/JPL-Caltech

Acknowledgement

The work described herein was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) and supported by the NASA's Space Technology Mission Directorate Game Changing Development Program.

F. C. Krause, S. C. Jones, E. J. Brandon, R. V. Bugga, J.-P. Jones, W. C. West, J. Pasalic, K. J. Billings

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA

231st Meeting of the Electrochemical Society
New Orleans, Louisiana
31 May 2017