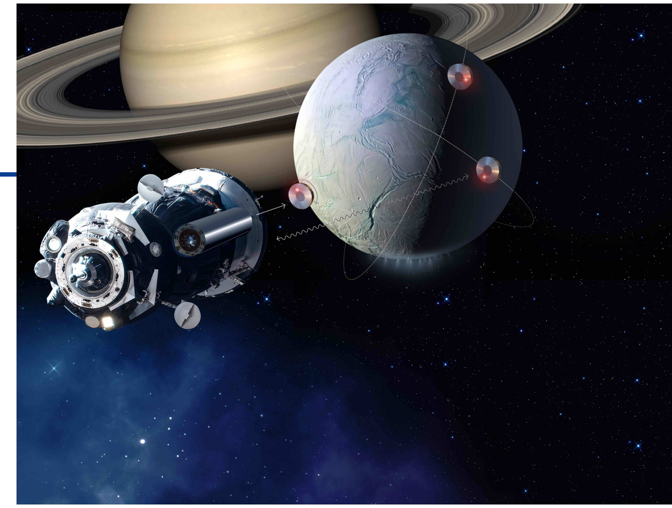

Recent Results from Li/CF_x Battery Cell Development for Robotic Space Missions

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New York , NY

Space Power Workshop
April 23, 2024

Full Li/CF_X Cell Development Team

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- Charlie Krause
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- Leo W. Gordon
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EaglePicher Technologies
- Mario Destephan
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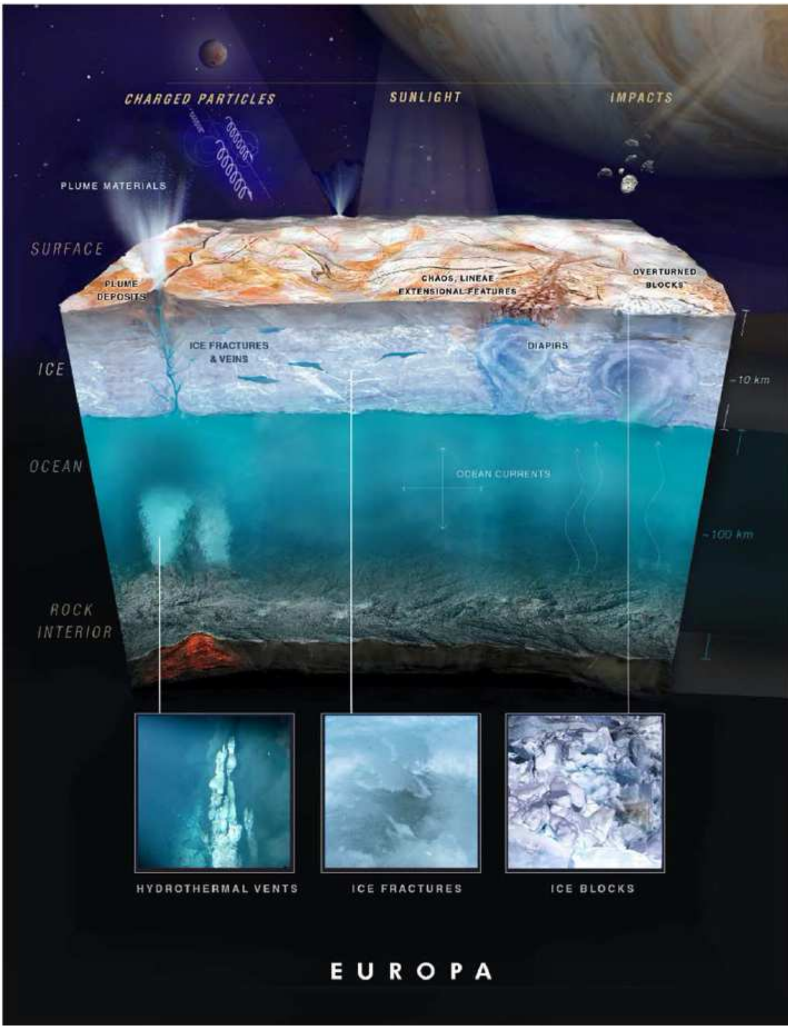
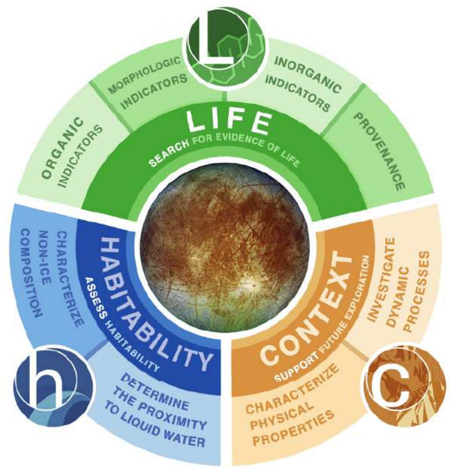
- Jackie Kennedy

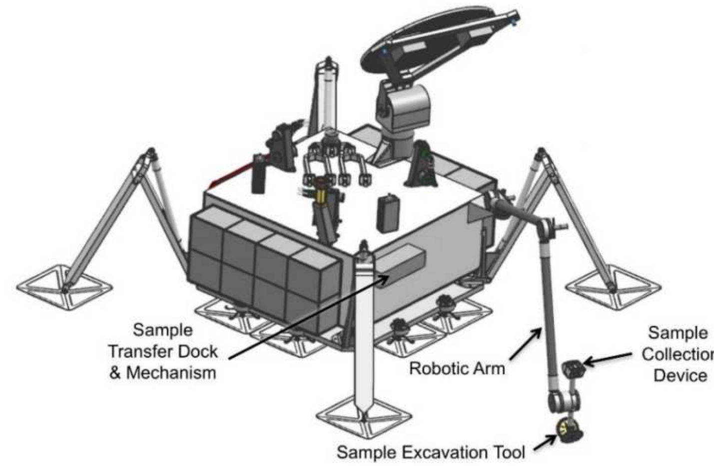
Sandia National Laboratory
- Don Hansen
- Maryla Wasiolek
- Loraine Torres-Castro
- Nathan Brenner

Rayovac
- Bill Bushong
- Sarah Wescott
- Greg Davidson

Europa Lander Mission Concept







- A mission concept to land on Europa
- Europa is an ocean world within our solar system, believed to harbor significant liquid water under an icy shell
- Mission objectives:
  - Assess habitability
  - Search for evidence of life
  - Characterize the surface to support future exploration

Europa Lander Primary Battery Mission

- **Primary battery only mission**
  - 50 kWh total energy
  - ~100 kg battery mass
  - 20-30 days mission to achieve primary science objectives

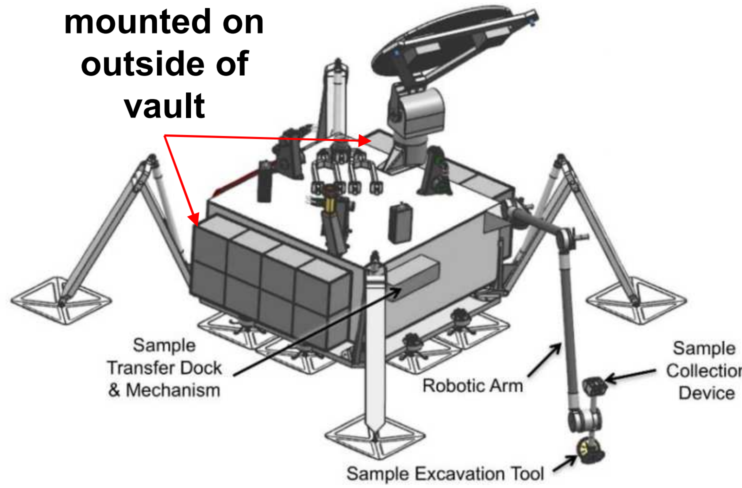
- **Initial target of 500 Wh/kg battery**
  - 4X battery modules
  - ~12.5 kWh each

- **Estimate ~700 Wh/kg required for the cell specific energy**
  - 75% allocated for cell mass
  - 25% overhead for battery packaging/structure

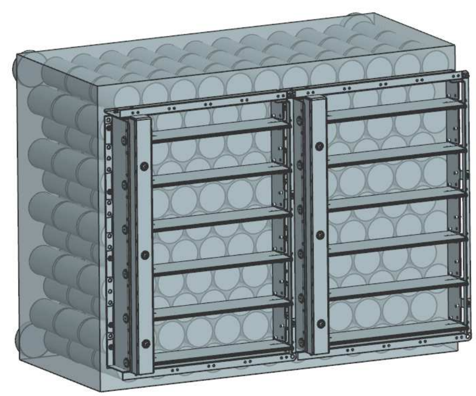
- **Must also consider de-ratings for losses and design principles**

- **Identify opportunities to increase specific energy**
  - Provide extra margin on the mission timeline
  - Extend timeline on the surface for additional science activities

Batteries mounted on outside of vault

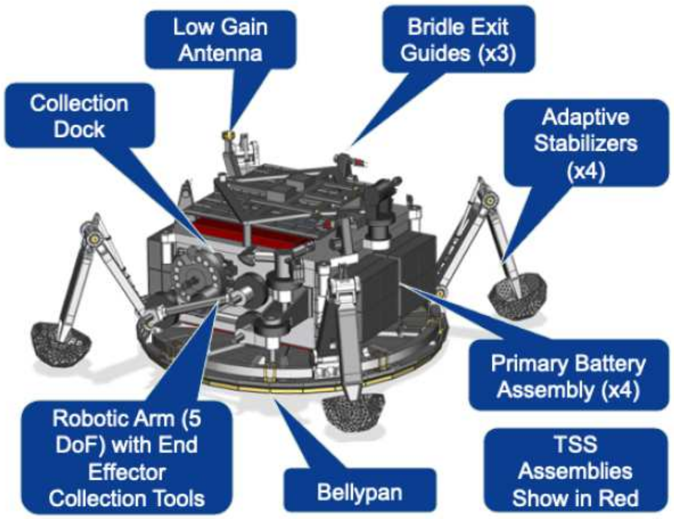


Notional Lander Concept



Initial battery module design (~12.5 kWh)

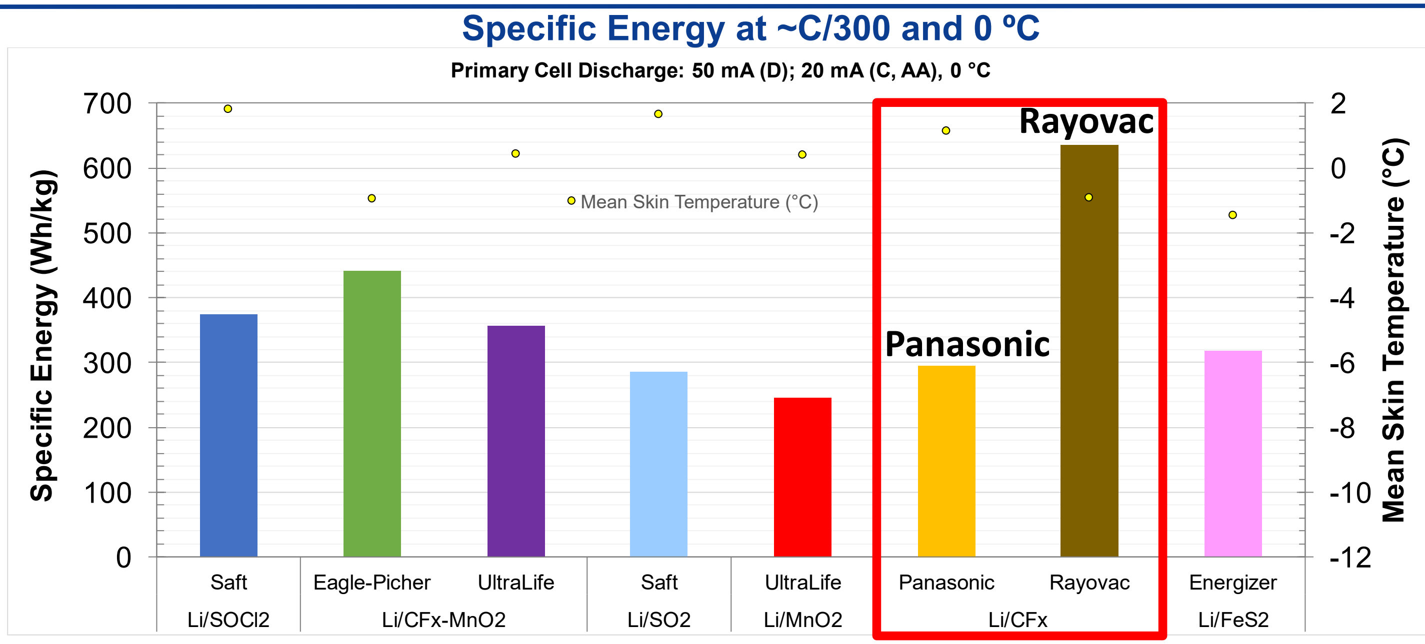
Defining Europa Lander Battery Needs



Parameter	Values	Comments
Operational temperature	0 to +70°C	Significant waste heat from avionics and cells
Non-operational temperature	-40 to +70°C	During cruise stored at 0ºC
Peak power	~510 W	Sampling
Minimum power	~20 W	Sleep
Radiation tolerance	2-3 Mrad	JOI and Landing
Storage Duration	7-11 years	Pre-launch, cruise and JOI

- Initially assume 12s26p module design operating over 24 – 31V
- Max. power is 510W / 24V = 21A / 26p strings = **800 mA / cell** (sampling warm-up power mode)
- Min. power is 20W / 31.2V = 0.640 A / 26p strings = **25 mA / cell** (sleep mode)
- Currents may be <25 mA, due to a lower sleep power mode, use of more strings or both

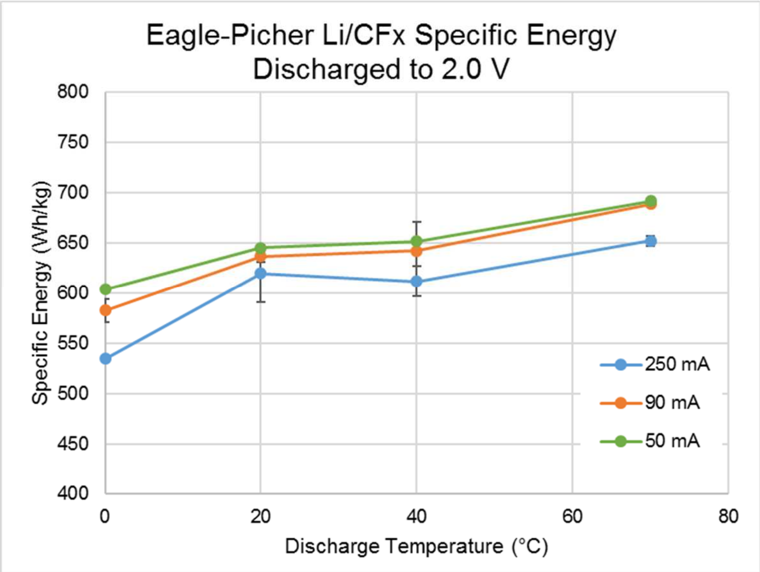
Initial COTS Screening for High Specific Energy Options (2018)

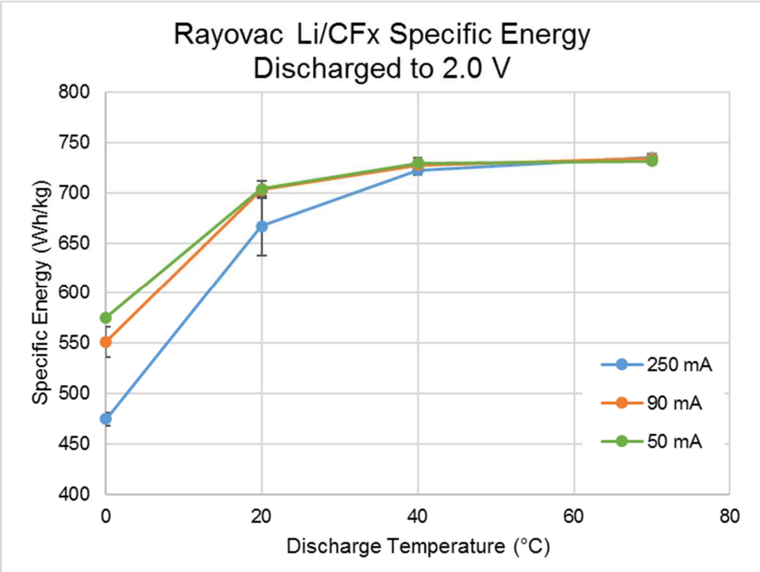


- Cell specific energy target is ≥700 Wh/kg
- Li/CF_x only realistic option to meet mission requirements
- At the time, the only off-the-shelf Li/CF_x option was a C-Cell offered by Panasonic

“High Specific Energy Lithium Primary Batteries as Power Sources for Deep Space Exploration” F. C. Krause et al. *J. Electrochem. Soc.*, 165 (10) A2312-A2320 (2018).

Europa Lander Li/CF_x D-Cell Design Build 1 Performance Recap (2018-2020)



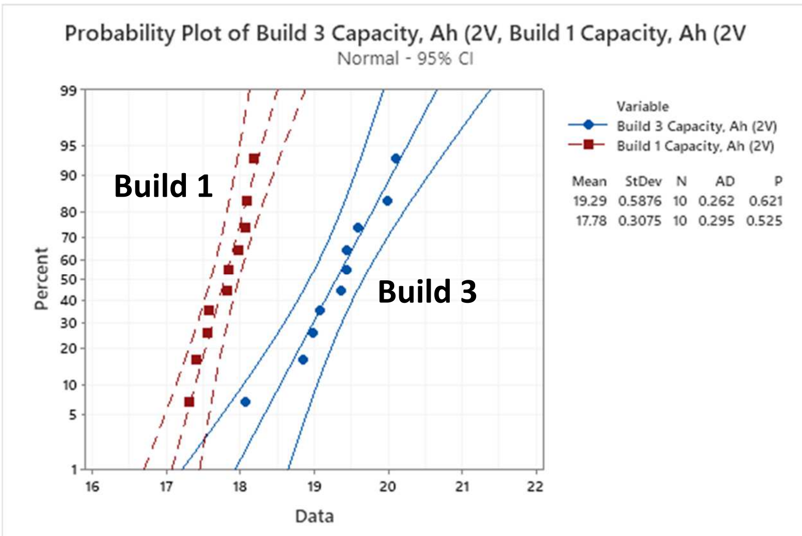


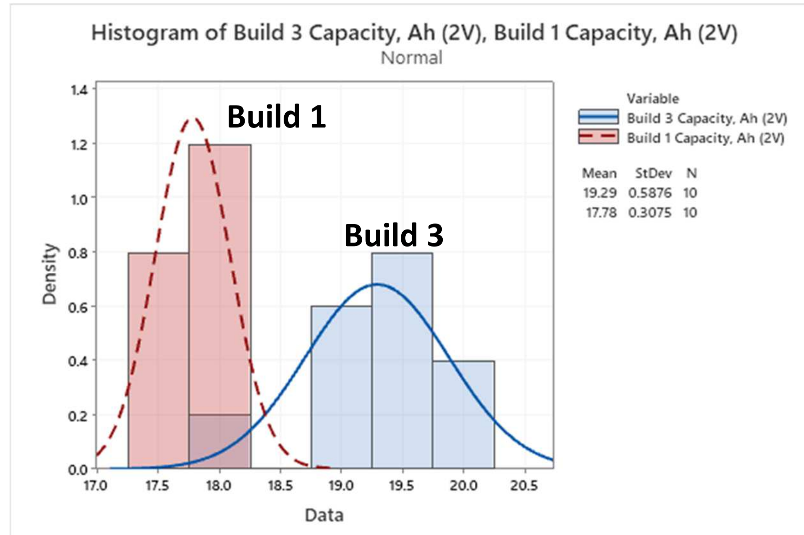
Europa Lander Cell (EPT Version)
~ 525 - 700 Wh/kg

Europa Lander Cell (Rayovac Version)
~ 475 - 725 Wh/kg

- Focus on high loading, pure CF_x cathodes to increase capacity
- Use aluminum casing to reduce cell mass and increase specific energy
- Characterize and use generated heat for cell thermal management
- Developed cell technology through three successive generations or “builds”

Li/CF$_x$ D-Cell Capacity Dispersion, EaglePicher Version Build 1 vs. Build 3 (2018 vs. 2024)

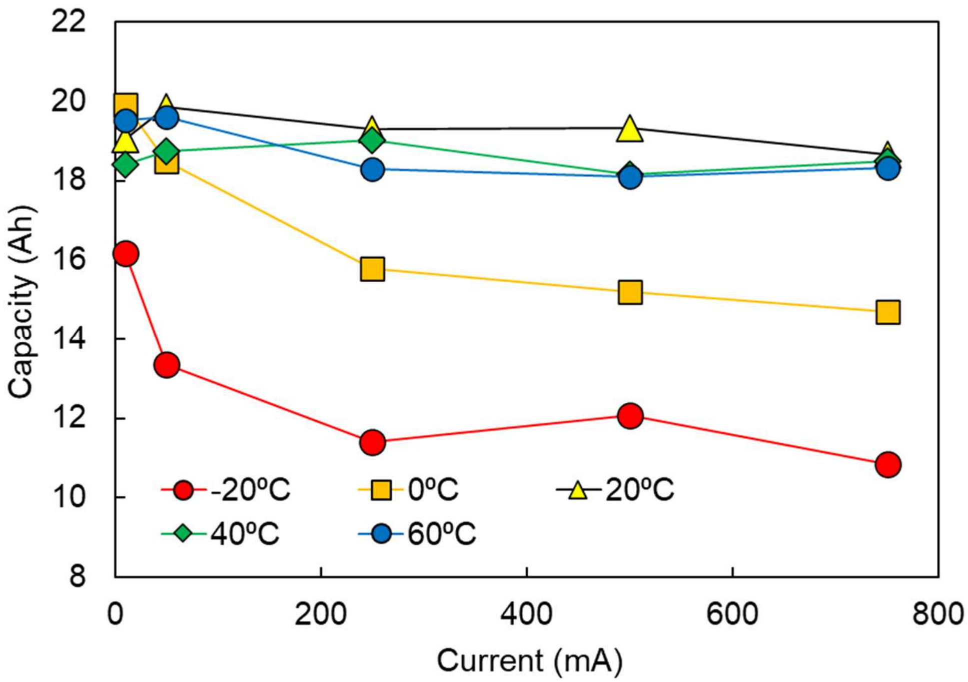


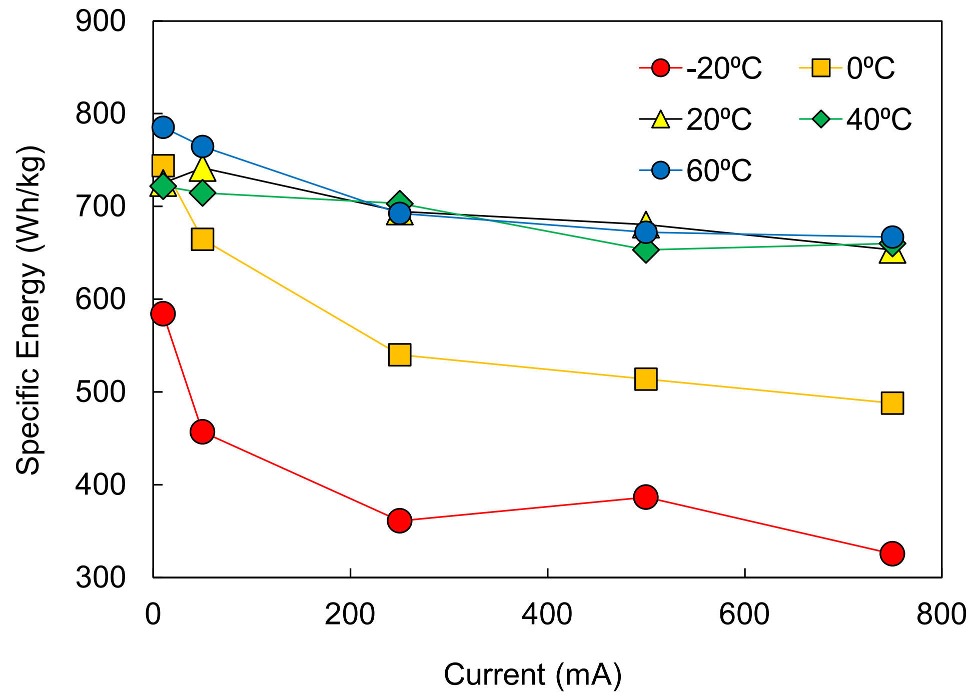


ID	Mean Capacity (Ah)	Standard Dev.
Build 1	17.78	0.3075
Build 3	19.29	0.5876

- Rayovac discontinued further development, proceeded with EaglePicher Technologies
- Improved capacity for Build 3 vs. Build 1, but with wider spread in mean values
- Can improve dispersion with improved manufacturing controls following scale-up

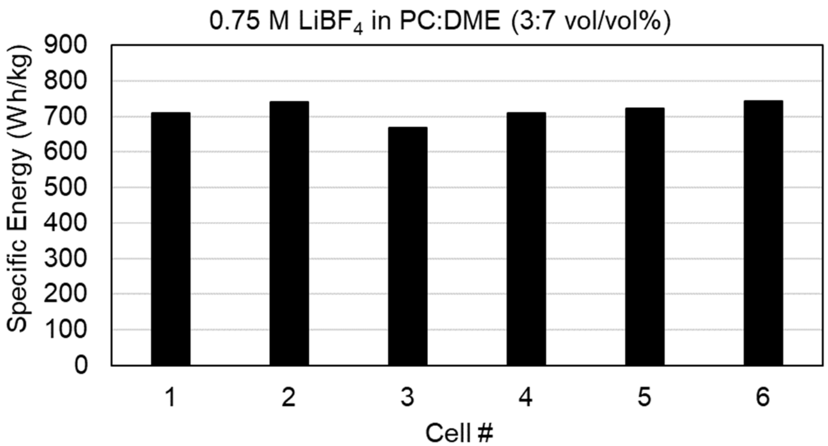
Europa Lander Build 3 Cell Performance

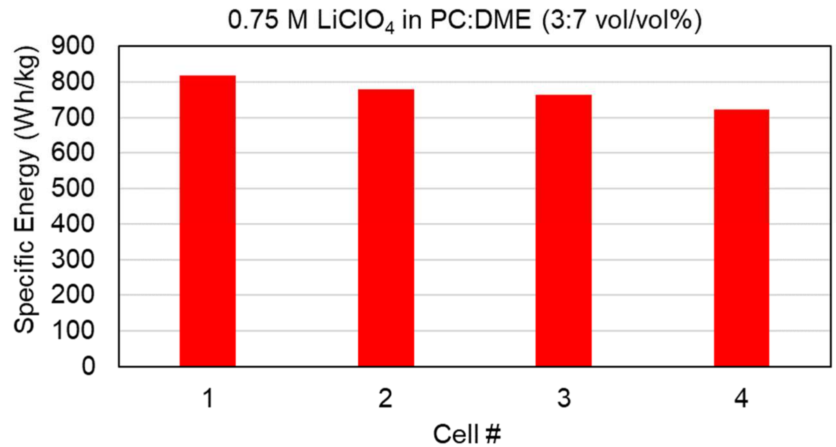


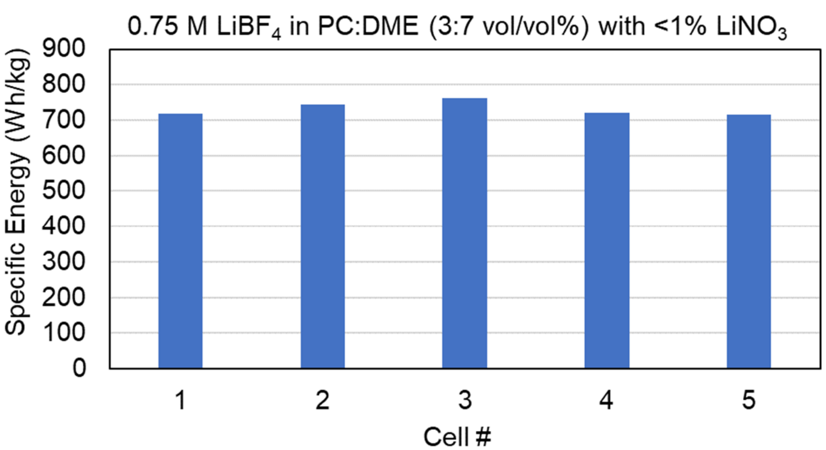


- Achieving 20 Ah at 20°C and 700 Wh/kg across range of temperatures and rates
- Approaching 800 Wh/kg at low rates and high temperatures

Investigation of Build 3 Cell Design using Alternative Electrolytes





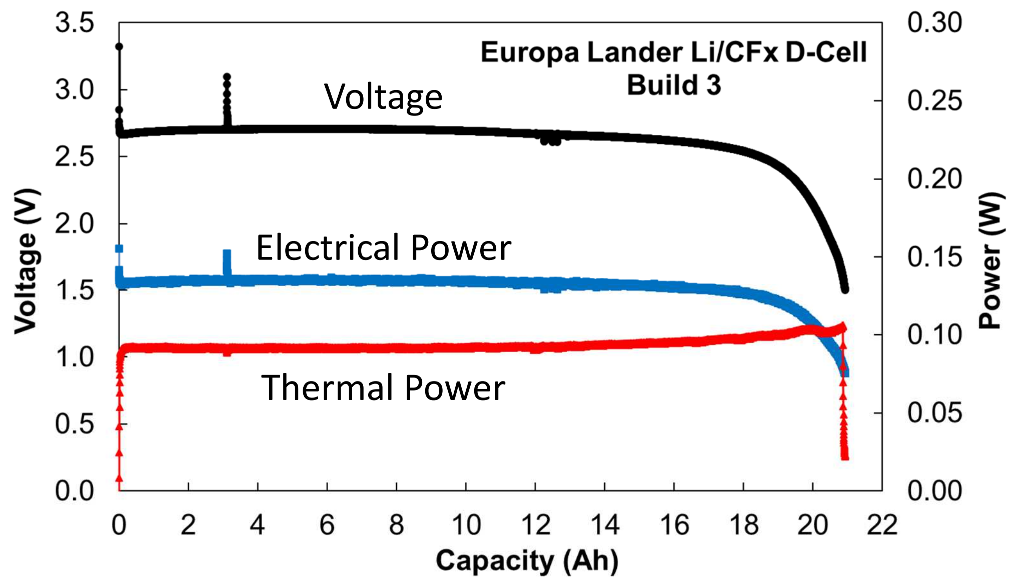


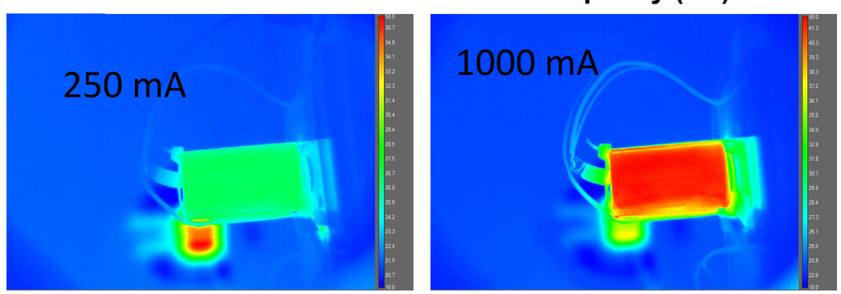
Electrolyte	Capacity (Ah)	3σ	Energy (Wh)	3σ	Specific Energy (Wh/kg)	3σ
Baseline	18.75	2.12	51.12	5.52	716	76
Custom 1	20.16	2.62	55.04	7.29	771	101.7
Custom 2	19.18	1.45	52.2	3.74	732	54

- **Baseline: 0.75 M $LiBF_4$ in PC:DME (3:7 vol/vol%)**
- **Custom 1: 0.75 M $LiClO_4$ in PC:DME (3:7 vol/vol%)**
- **Custom 2: 0.75 M $LiBF_4$ in PC:DME (3:7 vol/vol%) with <1% $LiNO_3$**

Evaluation of Thermal Power
Europa Lander Build 3 Cell Design

$$Li + CF_x \rightarrow LiF + C + heat$$



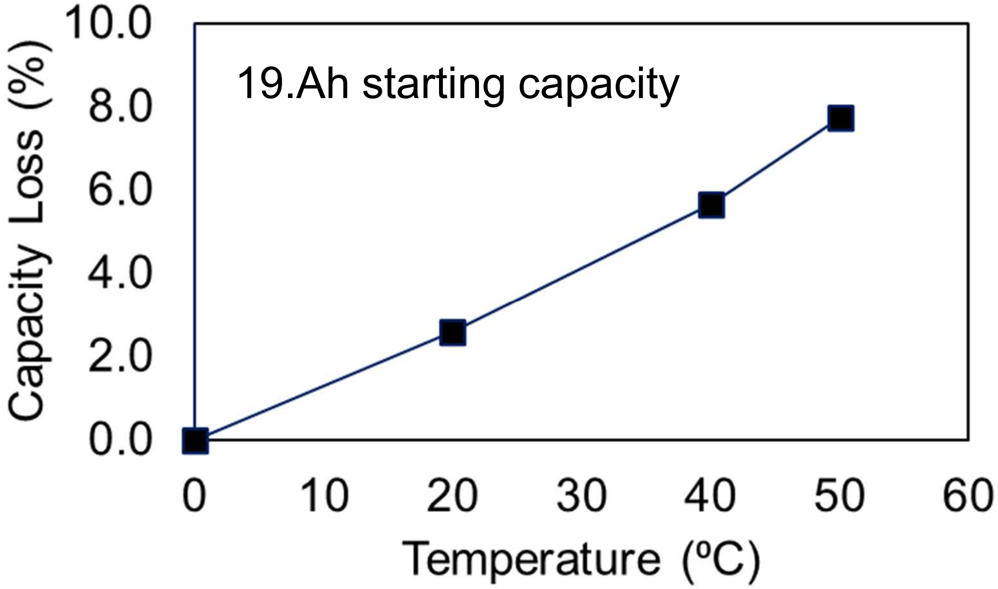


Cell thermal imaging at different discharge rates (Build 1 Cells)

~55 to 45% ratio of electrical to thermal power output

Europa Lander Build 3 Cell Storage Testing

Cells stored at 20, 40, 50ºC for 1 and 1.5 years
5 cell per storage condition



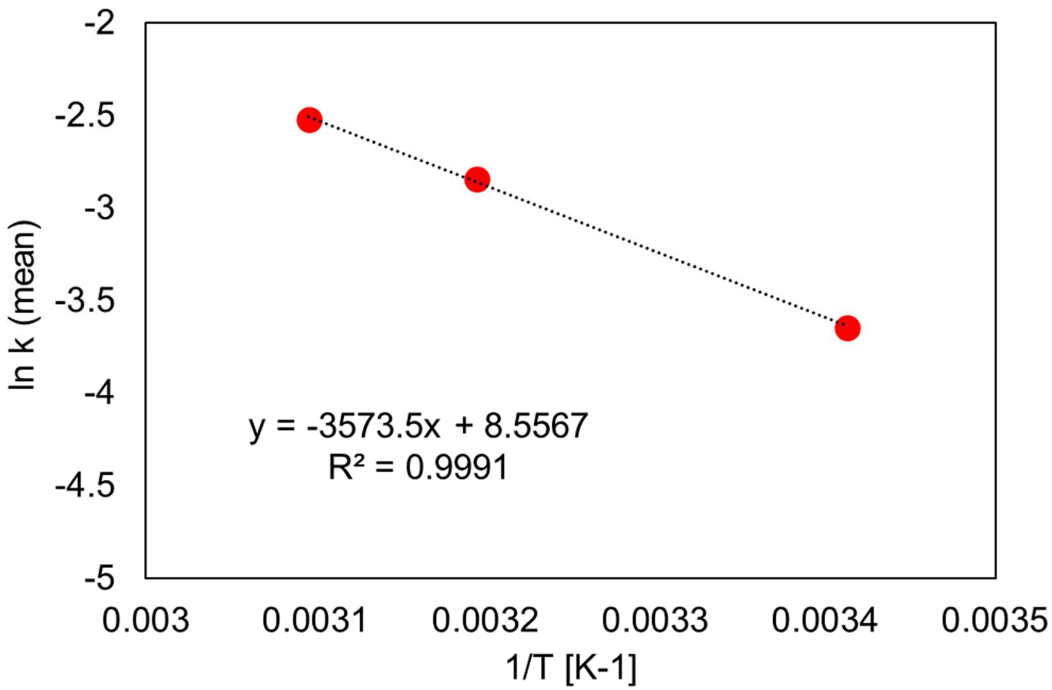
Capacity loss after 1.5 years of storage

Temp.	1 year	1.5 years
20	1.5	2.6
40	4.6	5.7
60	4.1	7.7

~1.6% annual capacity loss at 20ºC

Estimated at ~0.5% at 0ºC

Arrhenius Analysis for Self-Discharge Process



- Each ln k vs. 1/T data point an average of 5 rate constants over 1.5 years of storage
- Activation energy in range of typical self-discharge processes for other battery chemistries

$$c(t) = c(0) - kt$$

c(0): initial capacity (Ah)
c(t): capacity at time t (Ah)
k: rate constant (Ah/year)
t: time (years)

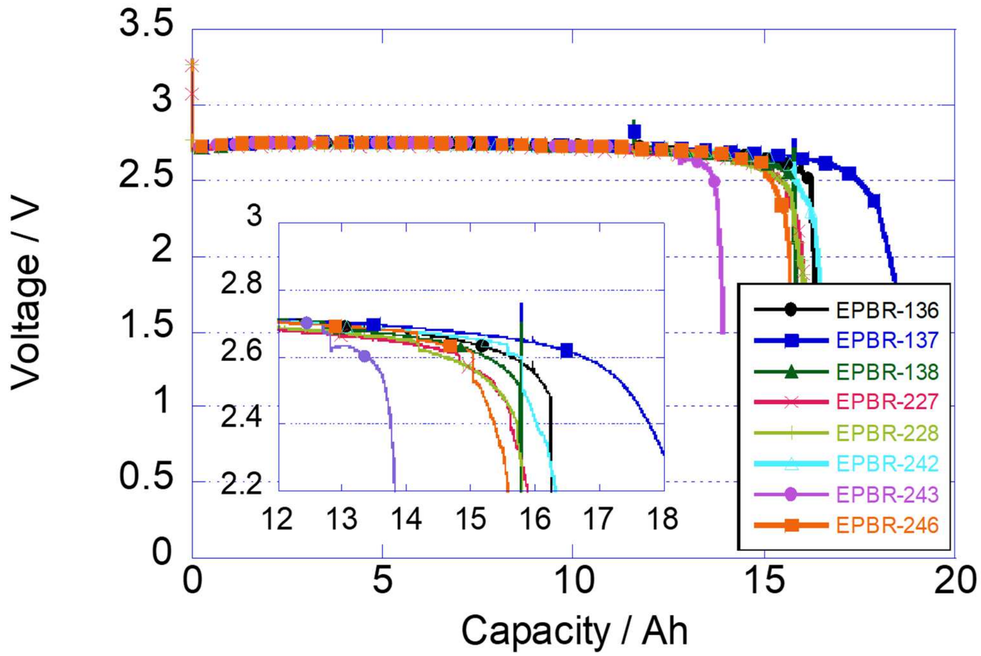
$$\ln k = \ln k_0 - \frac{E_a}{RT}$$

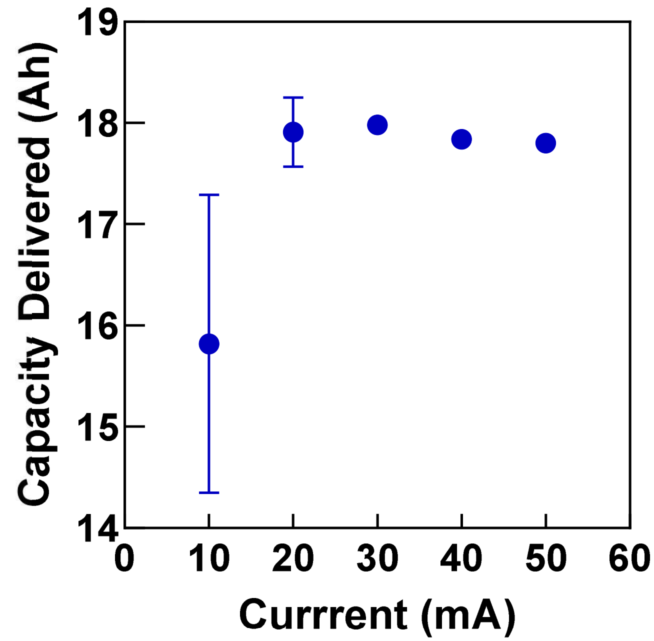
E_a: activation energy (J/mol)
R: gas constant (J/mol-K)
T= absolute temperature (K)

Build 1: E_a: 31.5 kJ mol^{-1}

Build 3: E_a: 29.7 kJ mol^{-1}

Unexpected Low Capacity Delivered at Very Low Rates





- 10 mA discharge at 20ºC resulted in capacities in 14-19 Ah range
- Converges to high capacity with little spread at currents ≥20 mA

"Anomalous Behavior During Low Rate Discharge of Li/CF_X Cells," H.L. Seong et al. 2022 J. Electrochem. Soc. 169 060550

Rate Dependent Li Anode Utilization

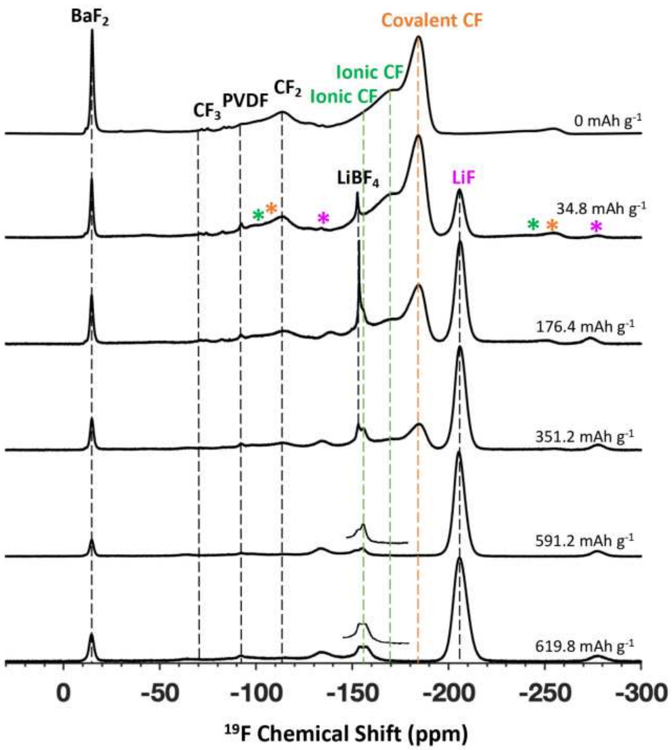
Discharged at 10 mA and 20°C (~13.25 Ah)

Discharged at 250 mA and 20°C (~19 Ah)

Li anode utilization is poor at very low rates

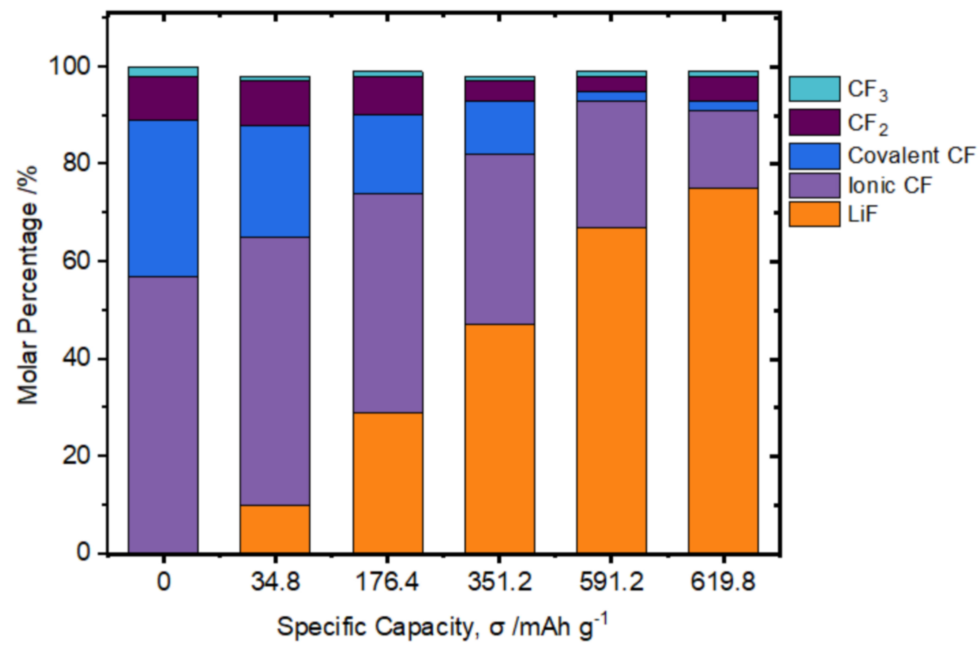
“Anomalous Behavior During Low Rate Discharge of Li/CF_X Cells,” H.L. Seong et al. 2022 J. Electrochem. Soc. 169 060550

Preferential Discharge of C-F and Formation of LiF



Solid-state [19]F MAS NMR spectra of CF_x electrodes from Li-CF_x coin cells galvanostatically discharged to different DOD.

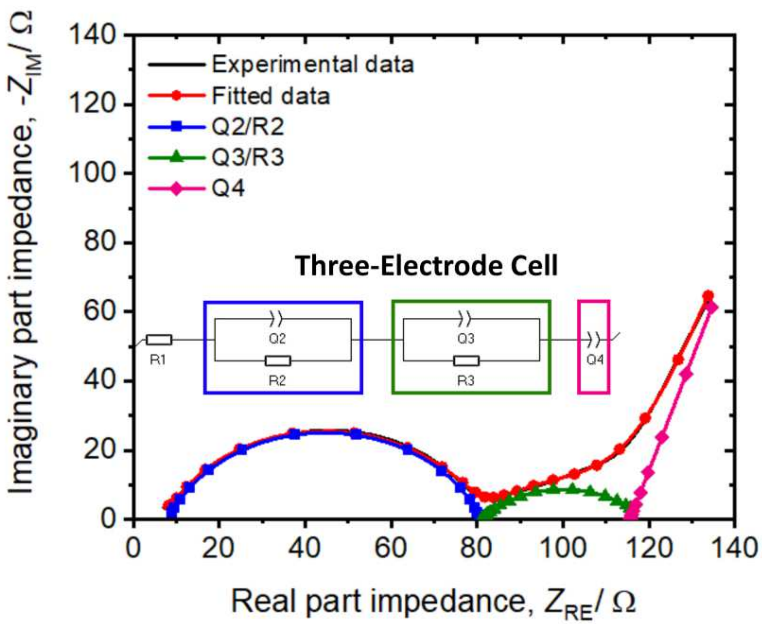
$$Li + CF_x \rightarrow LiF + C + heat$$



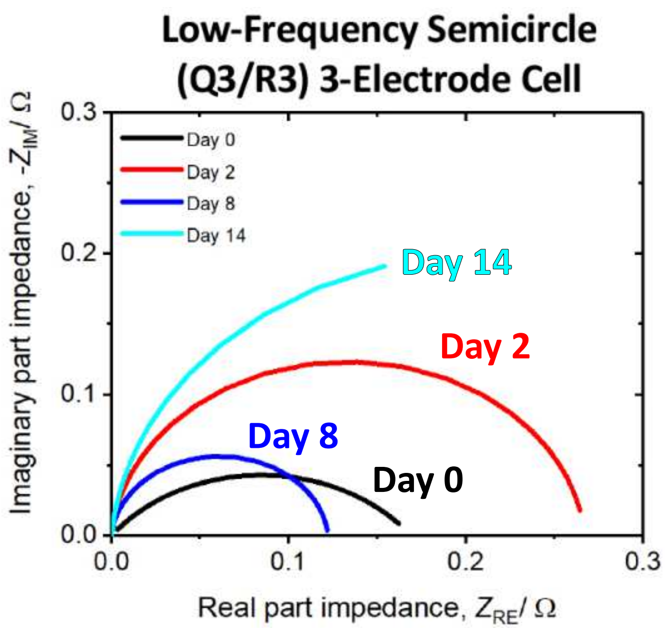
Molar percentages of 19F moieties obtained from deconvoluting solid-state 19F MAS NMR spectra of the CFx electrodes discharged to different DOD.

“Elucidating the Role of Electrochemically Formed LiF on Discharge and Aging in Li-CFx Batteries,” T. Schoetz, L. Robinson, *et al. ACS Appl. Mater. Interfaces*, 2024 (accepted for publication)

Monitoring Cell Aging With Electrochemical Impedance Spectroscopy



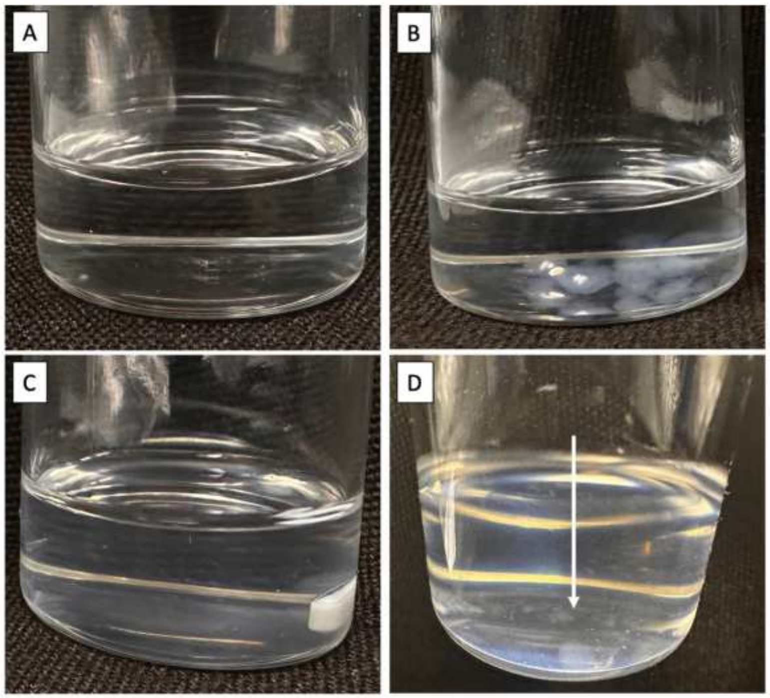
Li/CF_x two-electrode cell discharged to 75% DOD



Low-frequency semicircle for the three-electrode cells

By Day 21, Q3/R3 semi-circle disappears in custom 3-electrode cells
What causes this feature to grow, then disappear?

A New Model for LiF in Li/CF_x: Dispersion in Electrolyte

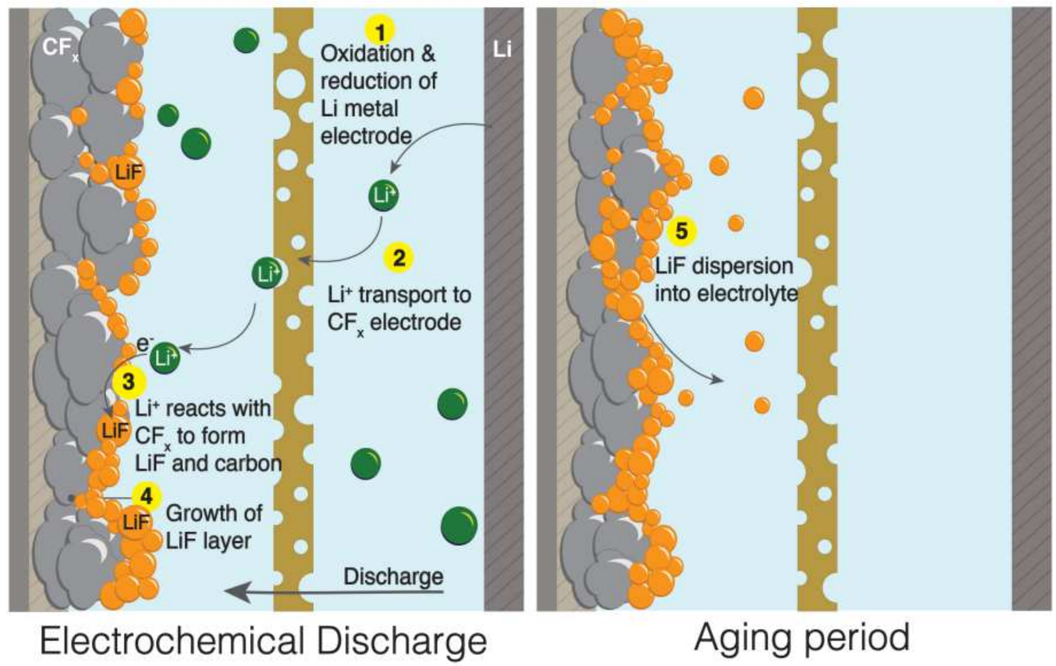


A: Pristine electrolyte

B: 1 M LiF added to electrolyte

C: 1 M LiF in the electrolyte after magnetic stirring

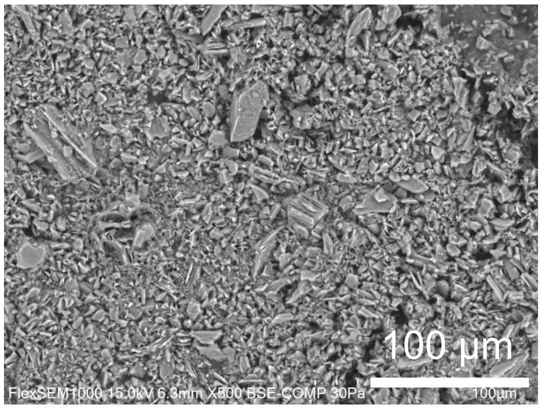
D: Gel-like structure settled from mixture

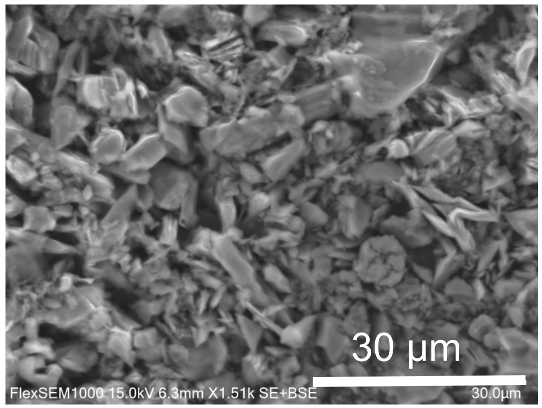


1. Discharge to release electrons to circuit
2. Li transport to CFx cathode
3. LiF formation
4. Growth of LiF layer (detected by EIS)
5. LiF dispersion into electrolyte (as seen to the left)

Improved CF_x Cathode Materials: AETC Materials

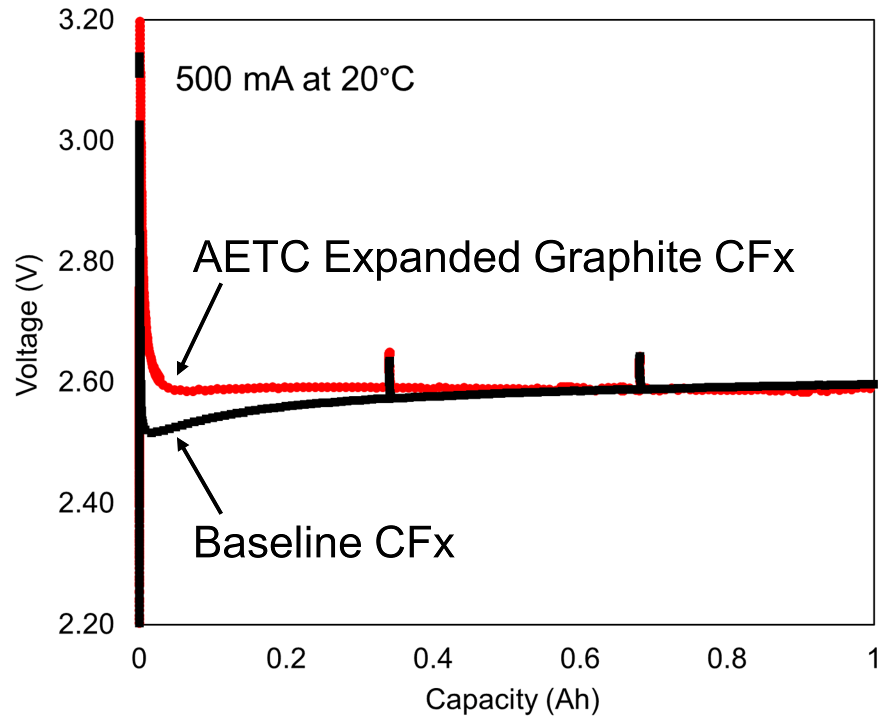
SEM Images:





BET Surface Area (JPL): 133 m^2/g

	AETC material at 2.0V	
Test condition	**Ah**	**Wh/kg**
250mA, 20°C	18.2	627.7
500mA, 20°C	18.1	607.7
750mA, 20°C	17.5	580.3
250mA, -20°C	10.5	321.5
250mA, 60°C	19.1	682.4



Reduced voltage delay with AETC higher conductivity expanded/delaminated graphite

Progress of Europa Lander Battery Cell Development 2018 - 2024

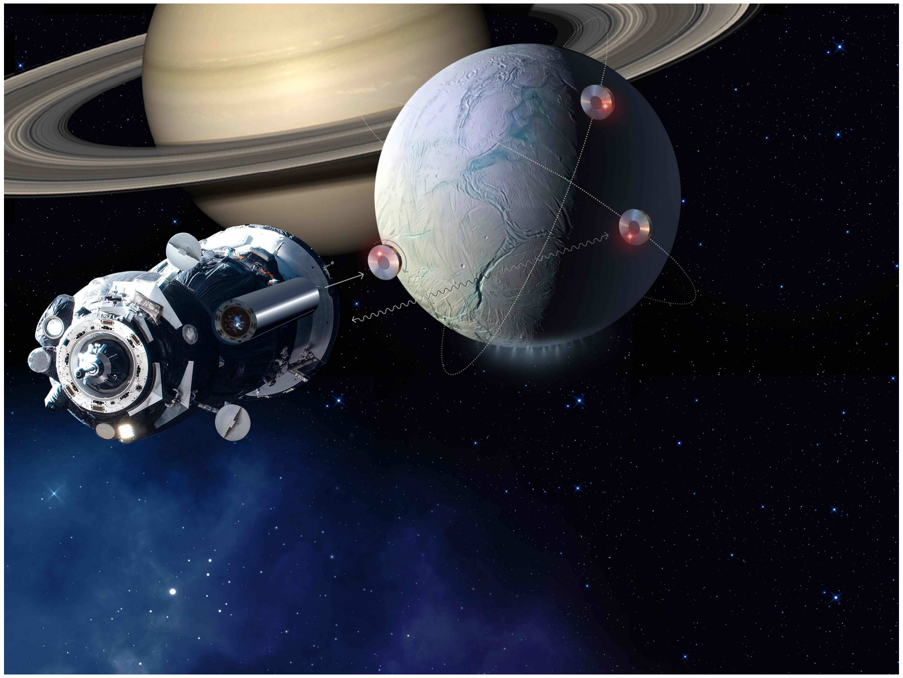
	Capacity (Ah)	Energy (Wh)	Cell Specific Energy at 20^{o}C and 250 mA to 2V cut-off (Wh kg^{-1})
Initial COTS cell design	16.98	43.3	614
Europa Lander Build 1	17.78	45.1	654
Europa Lander Build 2	17.80	42.8	657
Europa Lander Build 3	19.29	49.5	695
Baseline to Build 3 Increase	**+2.31**	**+6.2**	**+81**

Battery Design 1: 1248 cells → ~8 kWh additional energy vs. COTS (Baseline design)
Battery Design 2: 1584 cells → ~10 kWh additional energy vs. COTS (Mission Life Extension)

Battery Design	# of Cells	Cell Mass (kg)	Battery Mass	BOL Energy
1	1248	89	119	61,855
2	1584	112	150	76,626

Conclusions and Path Forward

- Europa Lander investments in Li/CF_x technology since 2018 have resulted in significant cell level performance enhancements
- Achieving specific energies in the 750 – 800 Wh/kg range
- Europa Lander mission concept future uncertain, but many other space applications on the horizon including GIRO
- Focus on assembling and testing space rated modules with EaglePicher Technologies
- Focus on continued cell improvements with new electrolytes and new electrodes, based on improved fundamental understanding of cell chemistry



Gravity Imaging Radio Observer (GIRO)

Acknowledgements

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This work was supported by the NASA Science Mission Directorate