

# Carbon Monofluoride ( $CF_x$ ) Based High Voltage Thermal Battery Cathode



PRESENTED BY

Brian Perdue Chris Aplett Linda Johnson Eric Allcorn



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

# The Problem: Not Enough Power (Size Weight and Power SWaP) in Thermal Batteries

“Since future systems are likely to require continued growth of battery energy and power densities, there must be significant advances in battery technology” - Navy

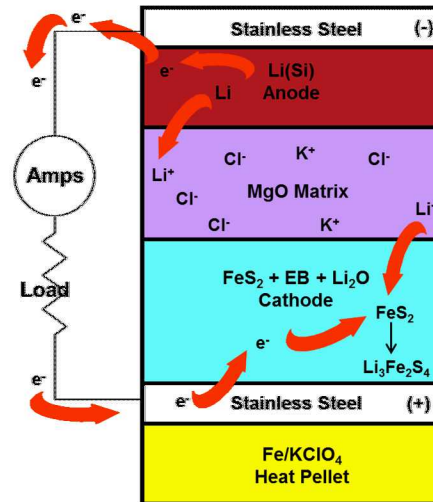
Routes to Higher specific energy and/or power

- Use of lower melting point or lower resistivity electrolytes
- Use of more thermally stable cathodes
- Use of more energetic pyrotechnic sources
- Development of better insulations
- Use of advanced structural alloys or composites
- Development of higher voltage cathodes
- Development of lower voltage anodes

## Current Li Primary Chemistries

Chemistry	Voltage (V)
SOCI <sub>2</sub> (liquid)	3.6
SO <sub>2</sub> (liquid)	3
CF <sub>x</sub>	3.1
MnO <sub>2</sub>	3.15
FeS <sub>2</sub>	1.9
CoS <sub>2</sub>	1.9

If we look at **mature primary chemistries** (high TRL) liquid systems are out and oxides can decompose at elevated temperature CF<sub>x</sub> is the next viable option for a substitution



- Ions don't diffuse very fast in a solid
- If the separator is a solid, then the battery is inert...shelf-life >25yrs
- When the separator melts, the battery “goes live”
- Need a lot of heat (>350°C)
- Most thermal batteries operate around 550°C

If you want more power, you must modify the cathode!

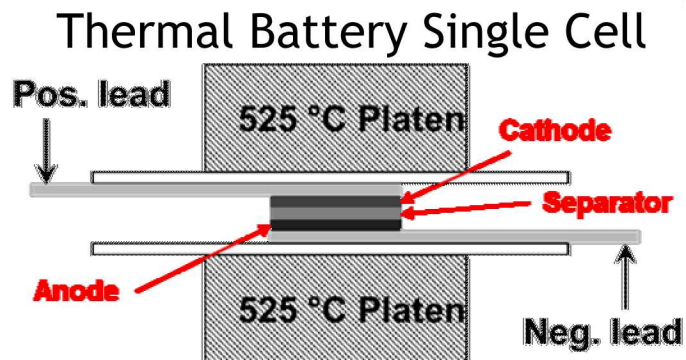
# The Benefits and Payoff of Switching to $\text{CF}_x$



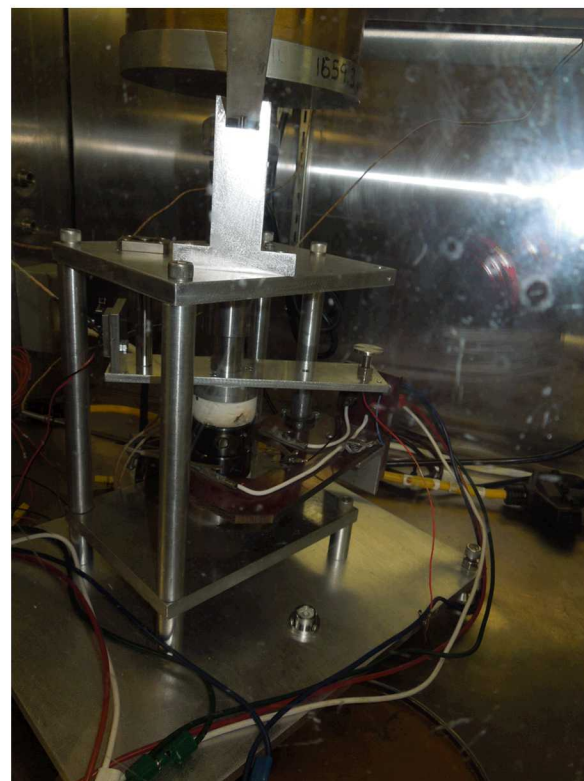
- By converting thermal batteries to the  $\text{CF}_x$  chemistry, the voltage has the potential to increase from the present  $\sim 1.9$  V to  $\sim 3.2$  V ( $\sim 68\%$  increase) per cell with a concurrent increase in capacity from 360 mAh/g to over 600 mAh/g ( $\sim 67\%$  increase). Could potentially result in ***a >2.5X improvement in energy density over  $\text{FeS}_2$***
- Can be a ***substitution*** for current thermal battery chemistries that is higher in energy density resulting in ***reduced Size, Weight, and increased Power (SWaP)***

## 4 Design of Experiments and Testing

- Anode pellets used in this study were Li-Si alloy anode with **44wt% Li in Si**.
- Separator pellets consisted of a mixture of 65 wt% binder material and 35 wt% percent of the molten salt eutectic
  - Binders **MgO**,  $\text{Al}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$  Boron Nitride/Carbide
  - Electrolyte **LiCl:KCl (CLiK)**,  $\text{LiCl}:\text{LiBr}:\text{KBr}$  (LM),  $\text{LiF}:\text{NaF}:\text{KF}$  (FLiNaK)
- Cathode pellet mixture consisted of a of ratio of 75 wt% active material, 10 wt% binder material and 15wt% eutectic.
  - Two active materials **CF<sub>0.96</sub>**, **CF<sub>1.01</sub>**
- Electrochemical Evaluation
  - Single cells were tested in the thermal battery single cell tester and subjected to a compressive 9.6 kg load. Electrochemical measurements were collected with a Maccor battery tester.
  - Items in **bold** were used in the “drop in replacement” study



Thermal Battery Single Cell Tester



## 5 “Drop in Replacement” Testing

- In order to test the feasibility of the  $CF_x$  chemistry in a thermal battery environment,  $CF_x$  was first tested using the established material set currently used by the  $FeS_2$  chemistry.
- In this instance a low level of fluorination was chosen  $CF_x < 1$  to **decrease the lubricity** of the active material and increase chances of pelletization.
  - The consequence of this choice is that the voltage of these cells will not be as high as possible, however they would still demonstrate a substantial increase in voltage over the current  $FeS_2$  chemistry.
- LiCl:KCl electrolyte is not the ideal electrolyte for  $CF_x$  as chlorine has the potential to cause parasitic side reactions. Cells with the drop in replacement formulation were subjected to different current densities ranging from  $0.05\text{mA}/\text{cm}^2$  to  $25\text{mA}/\text{cm}^2$  at temperatures ranging from  $375^\circ\text{C}$  to  $450^\circ\text{C}$ .

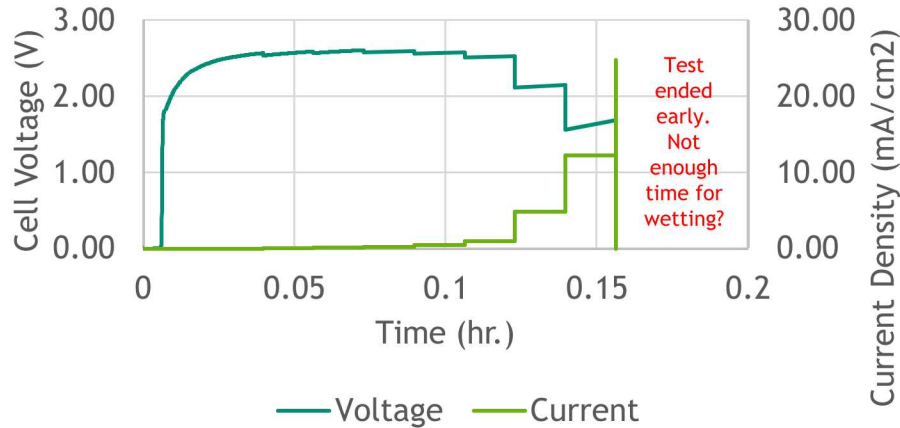
### Pelletization Challenges

- Pressing  $CF_x$  pellets shows very different behavior in the pelletization process when compared to other mixtures.
  - $CF_x$  has a much narrower functional range of press tonnage: increasing pressure does not result in more effective packing of material in the pellet due to flowing and breakage; too little pressure results in no formation of a pellet at all.
  - This is exacerbated by increasing the F content in  $CF_x$ . Increasing Fluorene makes  $CF_x$  more Teflon like...  
**We are trying to pelletize a lubricant!**

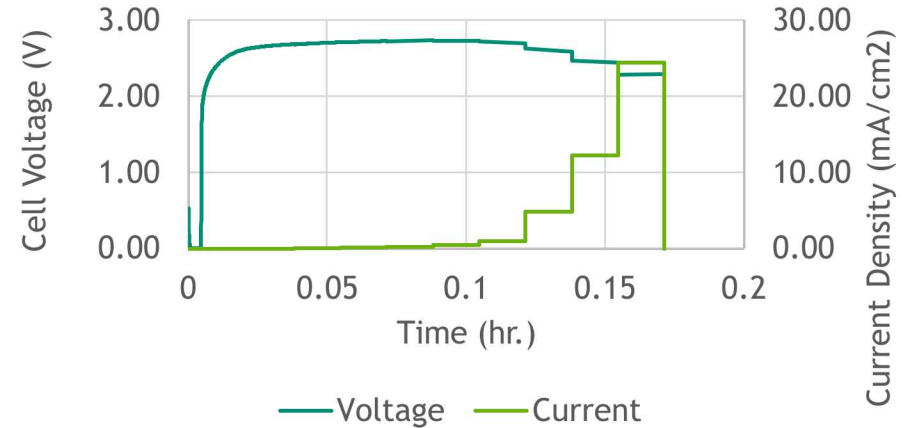
Pelletization of a lubricant will be a key challenge

# “Drop in Replacement” Testing continued

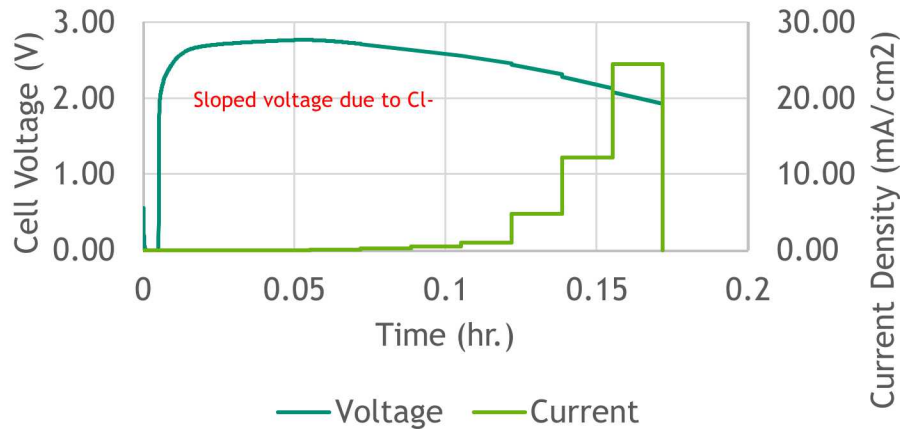
## Operating Temperature 375°C



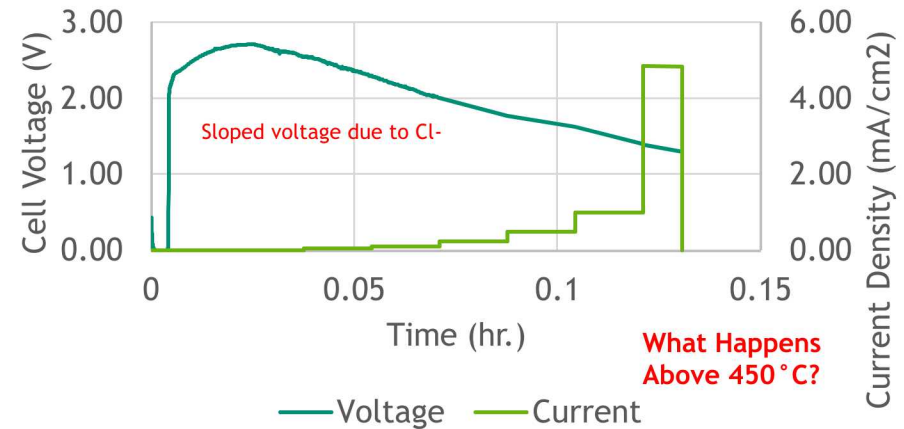
## Operating Temperature 400°C



## Operating Temperature 425°C



## Operating Temperature 450°C

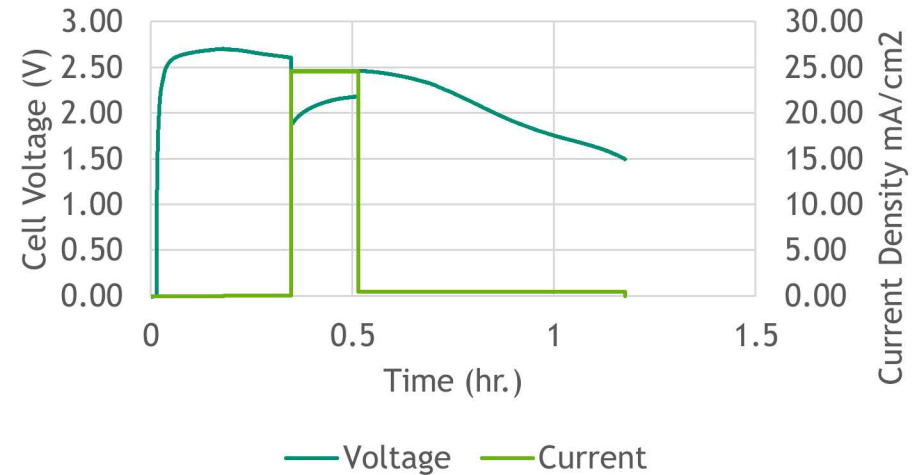


Initial results show  $CF_x$  is stable @ high temp in a molten salt and can support current!

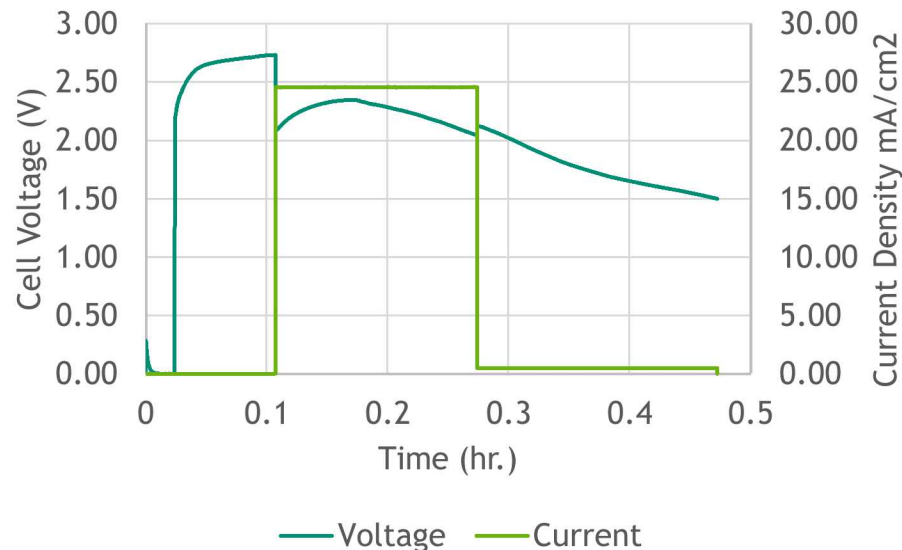
# “Drop in Replacement” Testing continued

- Initial electrochemical performance looked promising!
- With remaining three samples attempted to increase current density and runtime
  - With success!

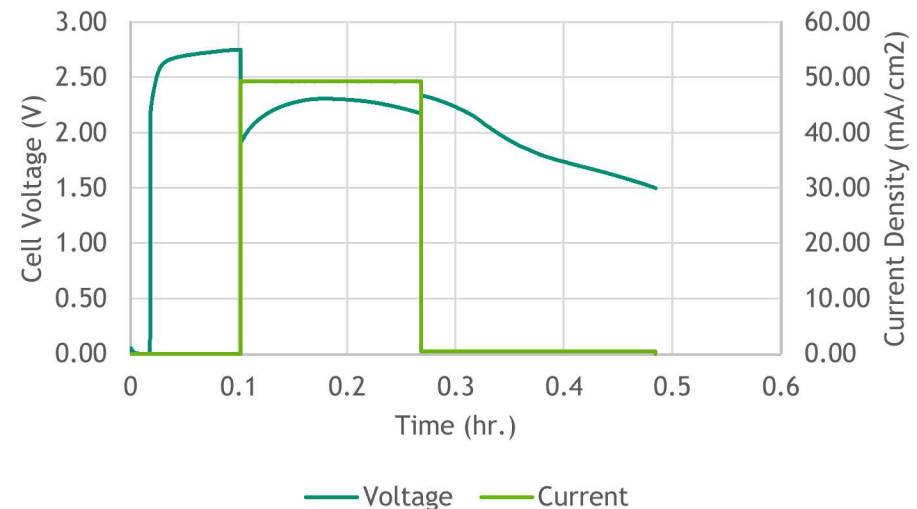
Operating Temperature 375°C



Operating Temperature 400°C



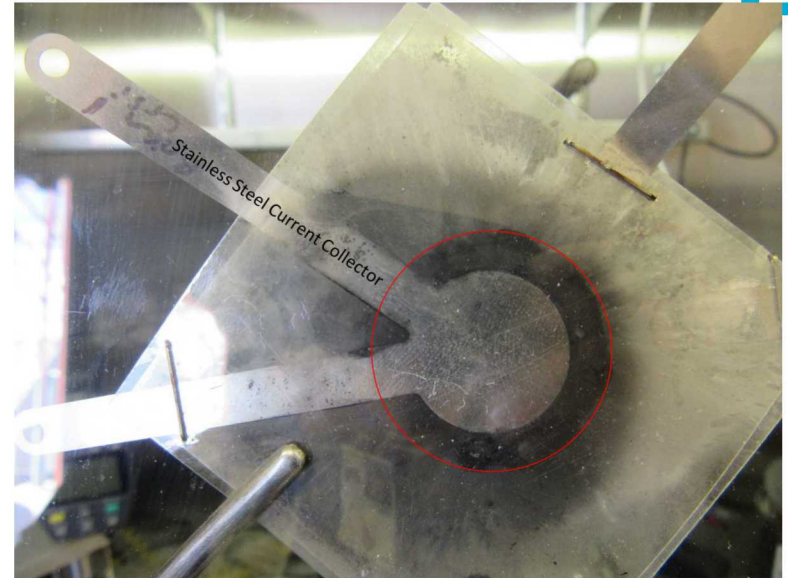
Discharge Profile CF<sub>x</sub> MgO Binder LiCl:KCl Eutectic at 400°C



CF<sub>x</sub> was able to support 50 mA/cm<sup>2</sup> for 15 min and stayed above 1.8V!

## 8 Gas Generation Investigation

- So what happened when the temperature increased beyond 450°C?
  - **Gas generation!**
- When performing the original electrochemical performance evaluation, gas evolution was observed.



- Chemistry that generates gas in hermetically sealed thermal battery will exclude its use
- Thermogravimetric analysis (TGA) was performed to identify the gases generated by the side reactions
- Mixtures of CF<sub>x</sub> and potential binder systems were made and tested with TGA to measure their thermal stability and potential for gas generation

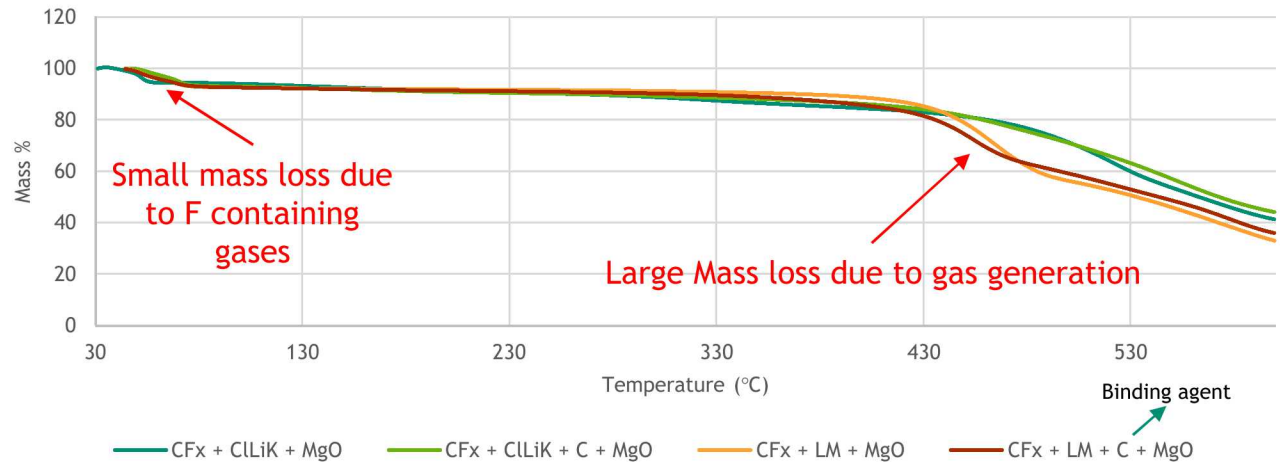
# 9 Gas Generation Investigation Continued

○ Cathode powder mixtures of  $CF_{0.96}$  MgO and electrolyte analyzed with TGA

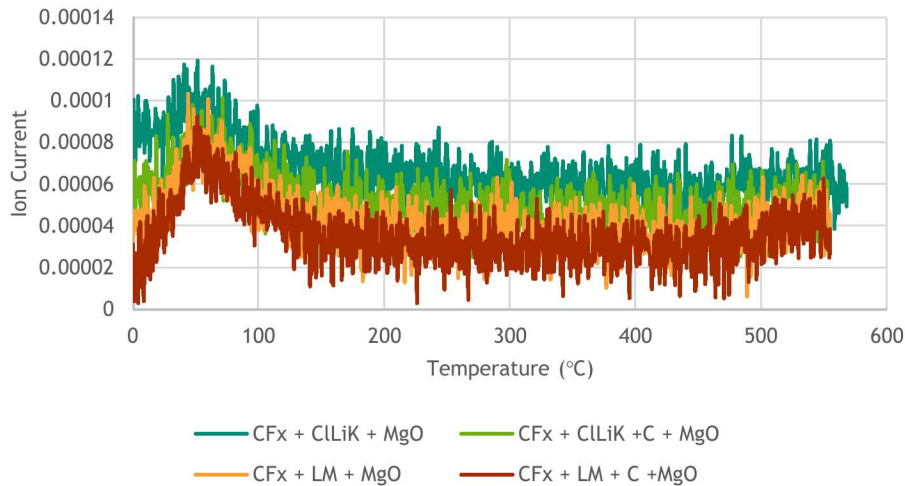
○ Gas generation! CF!!! And  $CO_2$

○ A low melting electrolyte with Br generated more gas but could increase the functional temperature range

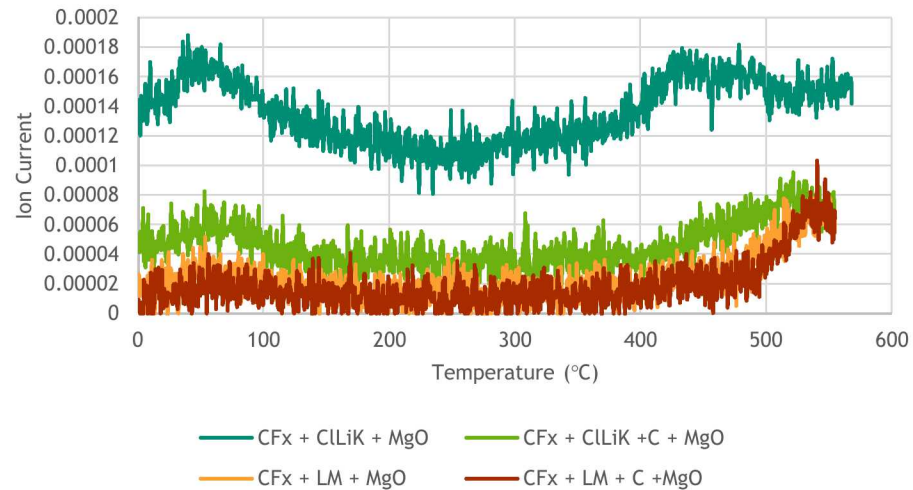
TGA of Drop in Replacement formulations



Mass Spec TGA Samples CF Spectrum



Mass Spec TGA Samples CO2 Spectrum

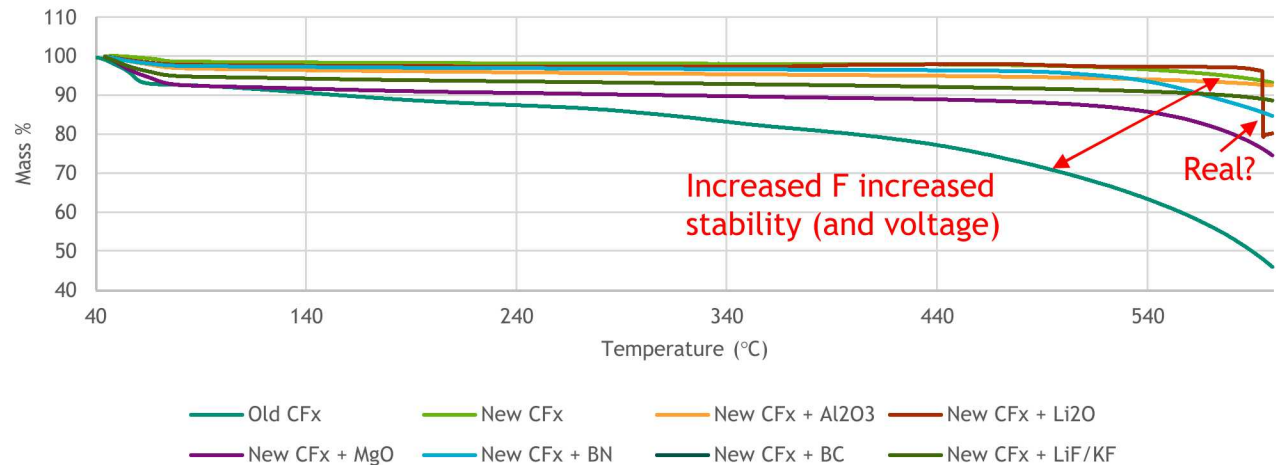


**MgO is incompatible with  $CF_x$ !**

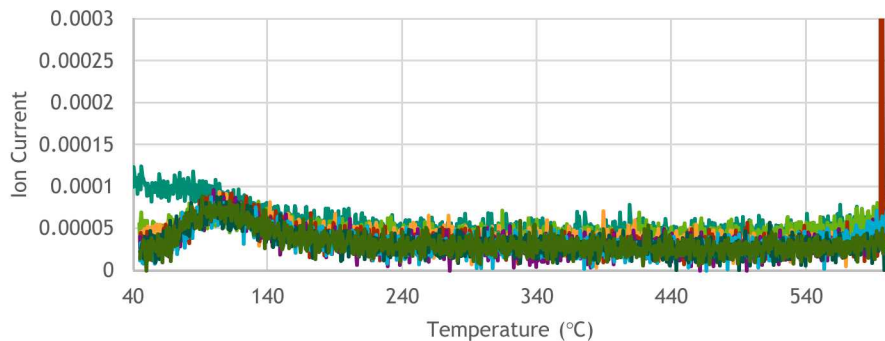
# Gas Generation Investigation Continued

- Tested  $CF_{0.96}$  and  $CF_{1.01}$  to gauge thermal stability
- Due to the MgO incompatibility tested  $CF_{1.01}$  with different binders
  - BN and BC while compatible have too high conductivities at high temp
- Tested F based electrolyte against  $CF_{1.01}$  to probe high temperature compatibility

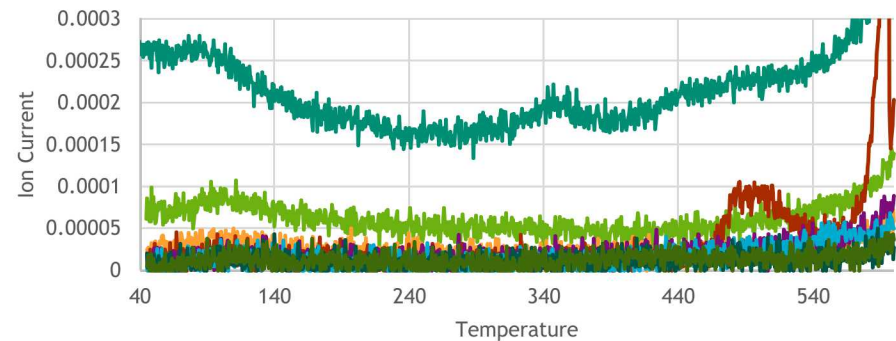
TGA of  $CF_x$  and Potential Binders



Mass Spec TGA Samples CF Spectrum



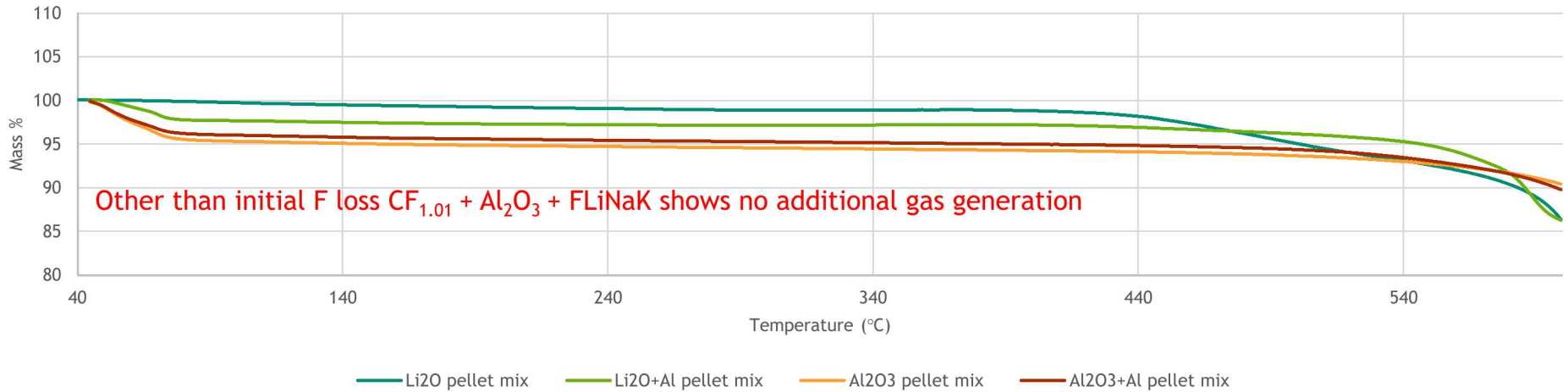
MS of TGA Samples CO<sub>2</sub> Spectrum



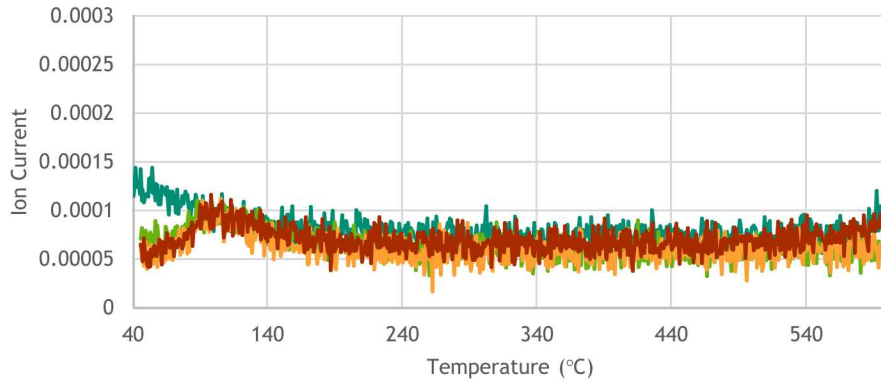
**Li<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> look like promising candidates!**

# Gas Generation Investigation Continued

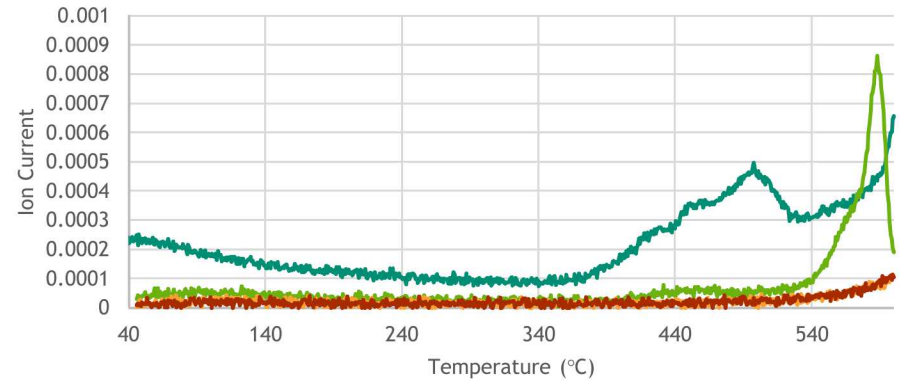
TGA of Thermal Battery Cathode Formulation (CFx + Binder + Electrolyte)



Mass Spec of TGA samples CF Spectrum



Mass Spec of TGA samples CO2 Spectrum

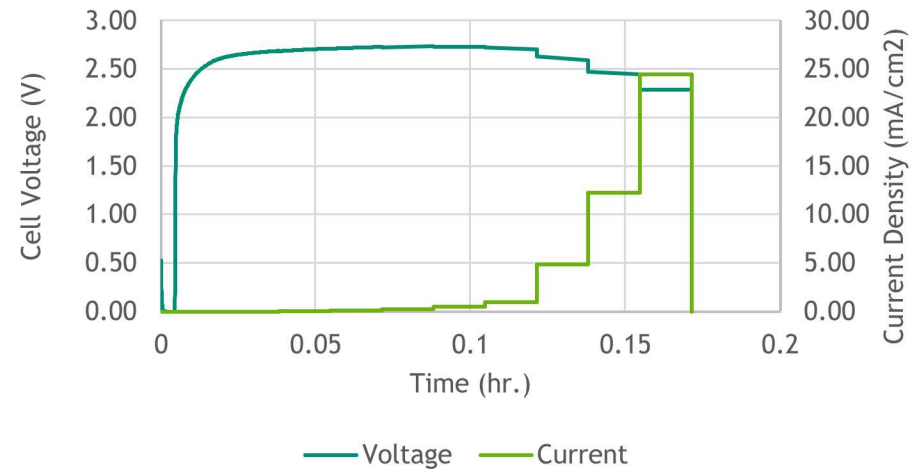


**Al<sub>2</sub>O<sub>3</sub> most viable path forward!**

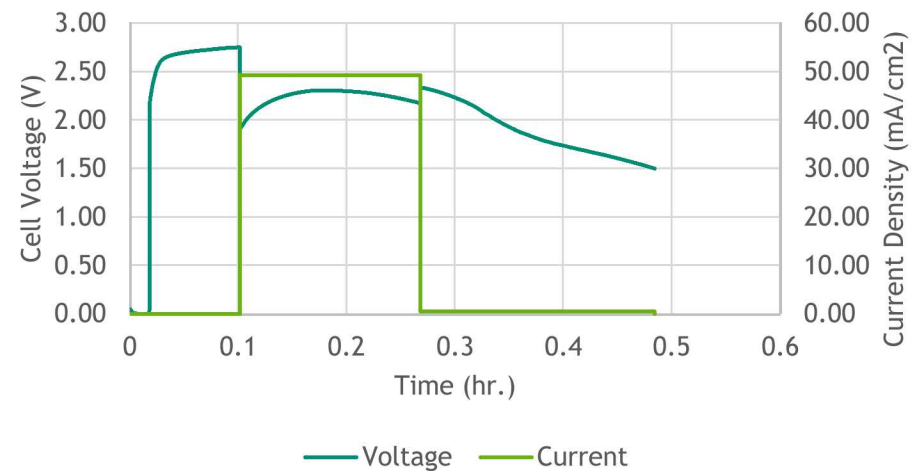
## 12 Technical Accomplishments

- $CF_x$  mixed and pelletized with relevant ratios for drop in replacement
- Tests show that  $CF_x$  “drop in replacement” formulation **can support the 50 mA/cm<sup>2</sup>**
- Additional testing also shows **increased thermal stability** (flat open circuit voltage) **and voltage** (cell voltage above 1.8V) **over current chemistry**
- A projected battery build would have a **stack height** reduction of almost **50%**.

Pulsed Load of CFx MgO Binder LiCl:KCl Eutectic at 400°C



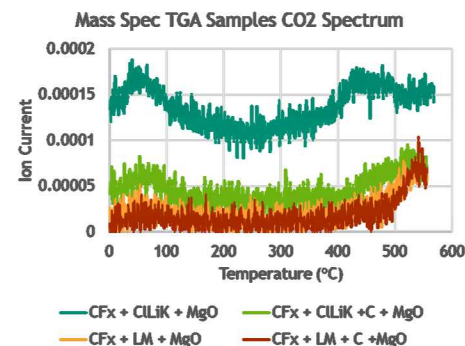
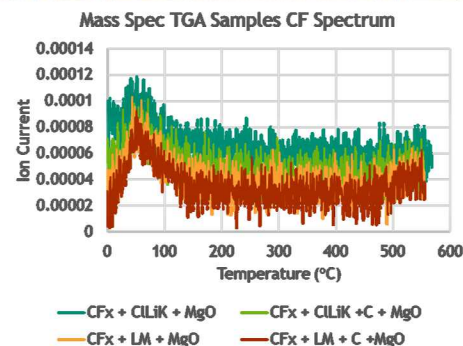
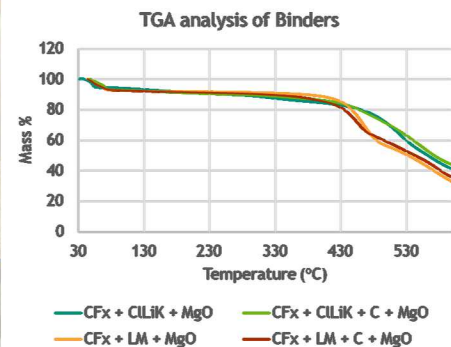
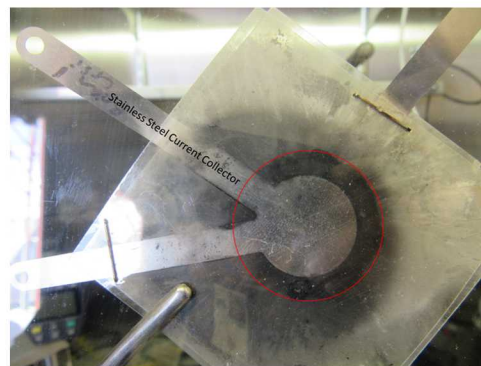
Discharge profile against CFx MgO Binder LiCl:KCl Eutectic at 400°C



## Technical Challenges

### Chemical incompatibilities leading to gas generation

- Safety concerns: F containing gases produced
- Facilities may not be equipped for potential F gas exposure (10% by mass F containing gas generated!)
- CO<sub>2</sub> is also a byproduct
- CF and CO<sub>2</sub> both disrupt cell continuity (loss of voltage or short) as well as create a rupture hazard in a full battery



### Traditional MgO separator will not work with CF<sub>x</sub>.

- Through screening, Al<sub>2</sub>O<sub>3</sub> may be used but gas can still be generated at higher temperatures

### Pelletization of a Lubricant

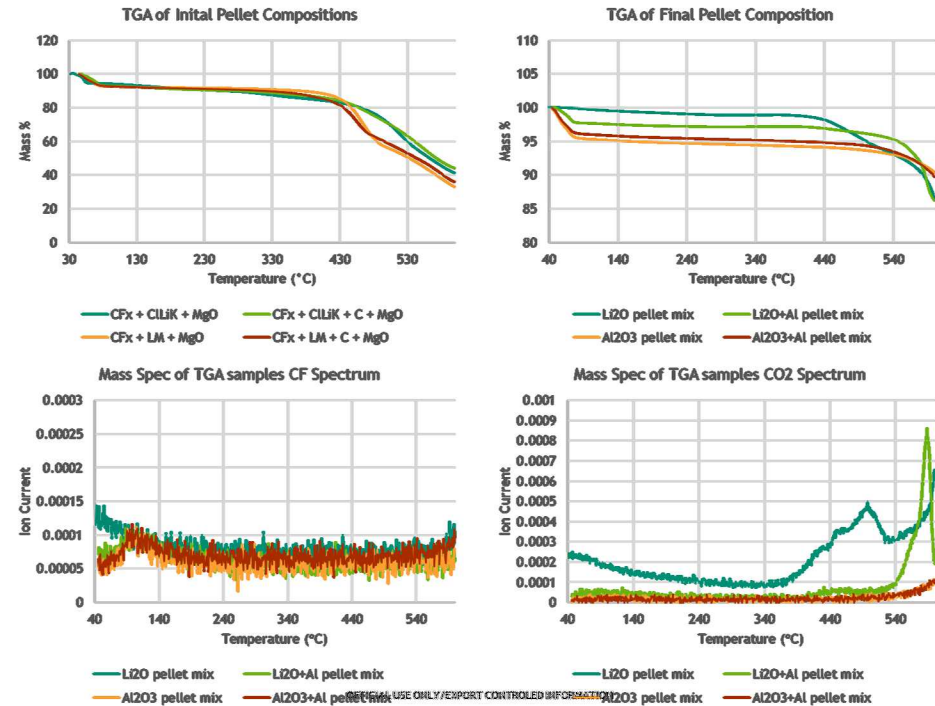
- Two formulations of CF<sub>x</sub> were investigated one with low fluorination but could be pelletized and another with high fluorination but could not be pelletized
  - Increased F content increases voltage and thermal stability however makes the cathode more Teflon like which makes pelletization difficult

### These issues are related!

- Pellets with low binding strength break apart by generated gas causing a loss in voltage or short

## Gas issues

- CO<sub>2</sub> has been minimized by eliminating Cl containing electrolytes and switching binder systems.
- It does not seem that fluorene containing gas biproducts can be eliminated. However pretreating the pellet mix at 150°C will release the gas before palletization
  - Currently unknown effects on performance



## Pelletization

- Potential cross-cutting effort!
  - Powder processing and modeling to tackle this issue.

## Relevant Impacts!

- This could potentially replace FeS<sub>2</sub>.** Leading to either higher power or reduced size for

Thank you for your time

Questions?

This work was funded by the Sandia Laboratory Directed Research and Development Program