Design and Testing of an Ultra-Low Temperature Primary Battery Chemistry for Titan

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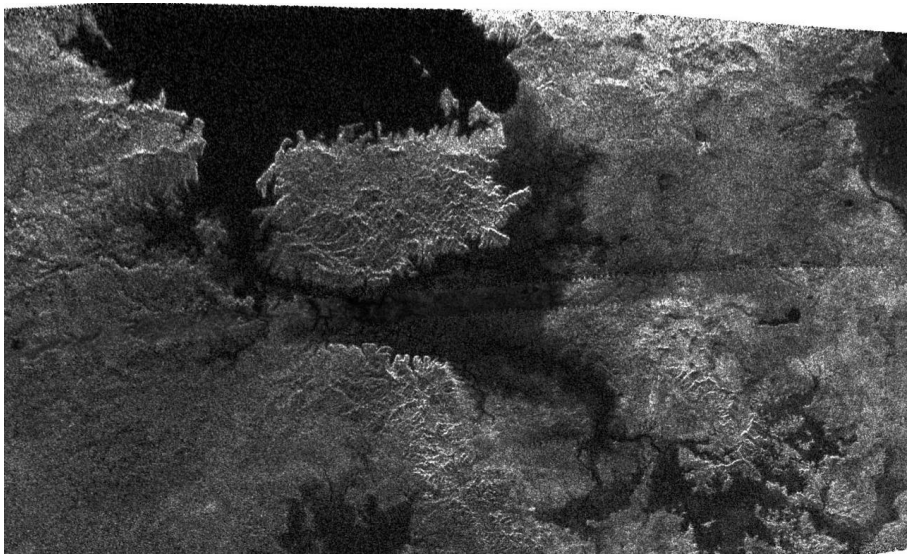
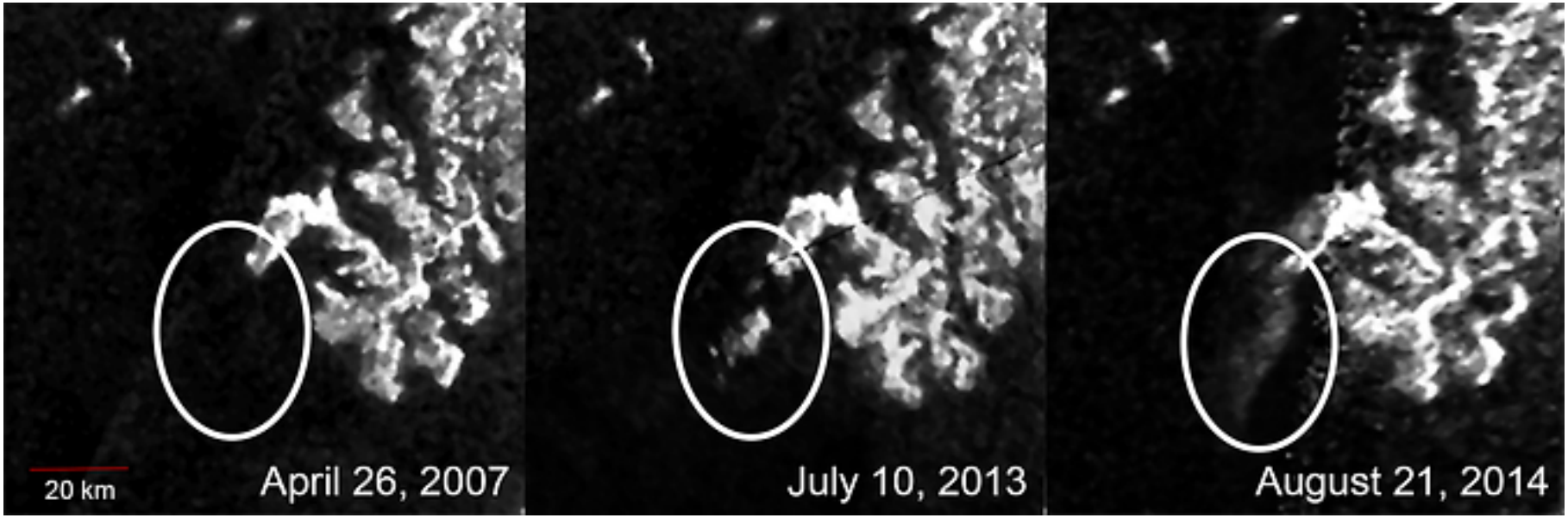
Motivation: Titan as a Science Target

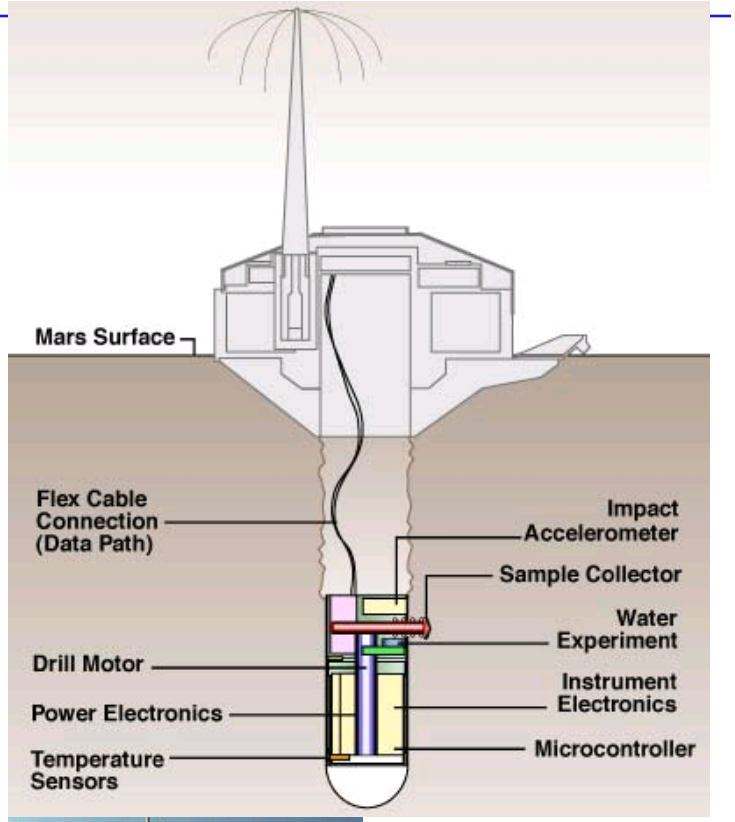


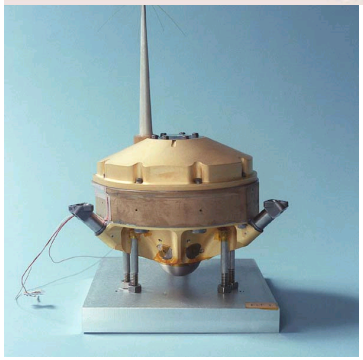
- Aside from Earth, only other known solar system body with dynamic “hydrology” of liquid methane and ethane rainfalls, rivers, gullies, and oceans.
- Transient features: surface darkening associated with precipitation and receding sea shorelines associated with evaporation.



Background: Mars DS2 Spacecraft

- Launched on January 1999
- Design:
  - No parachute:
  - Drill scoops soil sample
  - Heat, vaporize, and analyze for H_2O
  - Transmit science data





DS2 spacecraft

Background: Mars DS2 Battery

- Lithium-Thionyl Chloride Chemistry
  - Anode: Li
  - Electrolyte (catholyte): 0.5M $LiGaCl_4$ in $SOCl_2$,
  - Cathode: Carbon
  - Reaction: $4Li + 2SOCl_2 \rightarrow 4LiCl + SO_2 + S$
- Operation temperature: -80°C
- Battery voltage: 6-14V (4 cells)
- Battery Capacity:
  - 550 mAhr @ -80°C
- Shelf Life: 2.5 Years

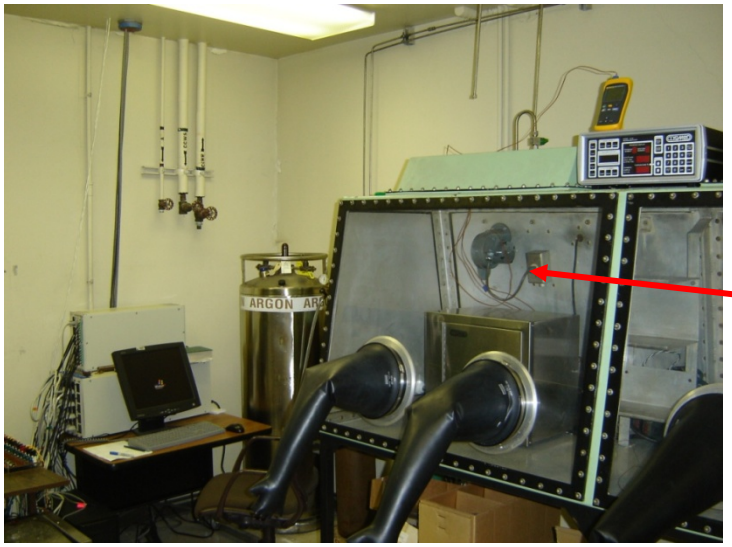
DS2 lithium-thionyl chloride cells and batteries

Motivation for Extreme Environment Power Sources Research

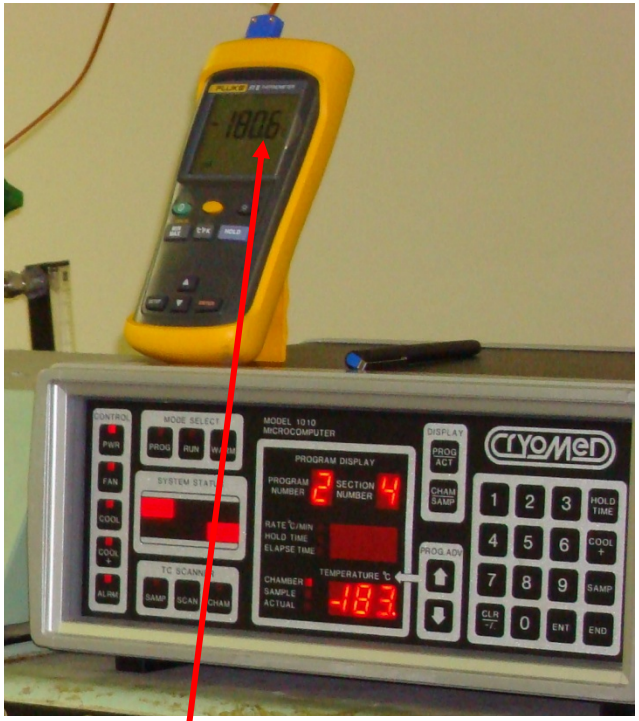
- How do we get power on Titan at -160°C?
  - **Not solar**: Not with currently available solar tech: Maximum solar flux is only 34 W/m^2 vs. 1371 W/m^2 at low earth orbit
  - **Not standard battery:** Record lowest temperature battery is -80°C
  - **Heaters are undesirable**
  - **Radioisotope thermoelectric generators:** Can have cost and mass drawbacks

- Develop new ultra-low temperature battery cells
  - Design principles:
    - Avoid solid-state diffusion
    - Avoid freeze-up of electrolyte solvents
    - Find new reactants with vastly lower melting points
    - Identify electrode passivation schemes, co-solvents and other additives for improved performance
- Approach: Examine liquid catholyte primary cell
  - Anode: Li
  - Catholyte (non-electronically conductive reactant reduced at C current collector)
  - Example: $2Li + 2SO_2 \rightarrow Li_2S_2O_4$

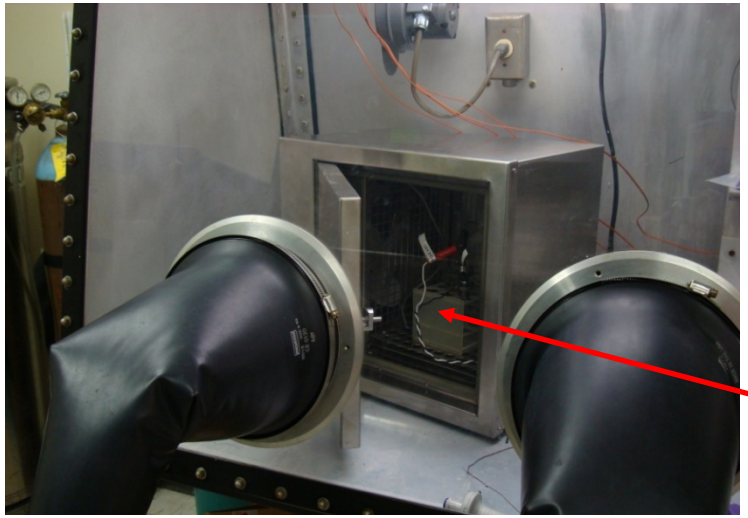
Construction of Low Temperature Inert Gas Battery Test Bed



Liquid argon fed chamber in argon glove box

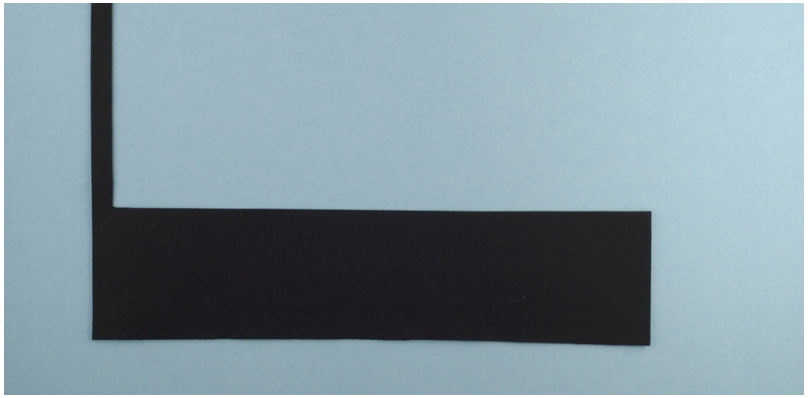


Operation demonstrated at -180°C

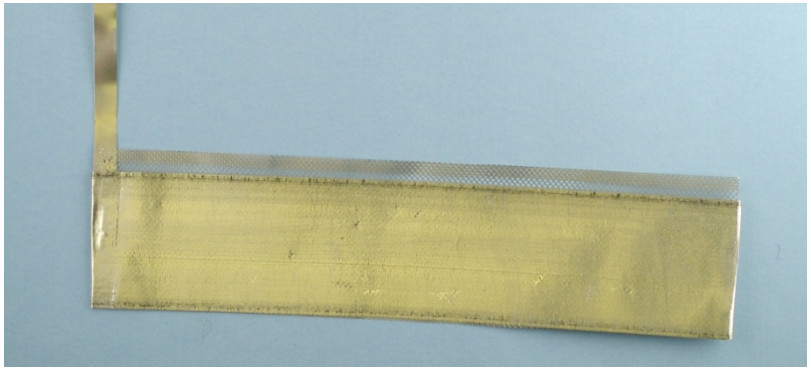


Chamber with battery cell

Cell Design

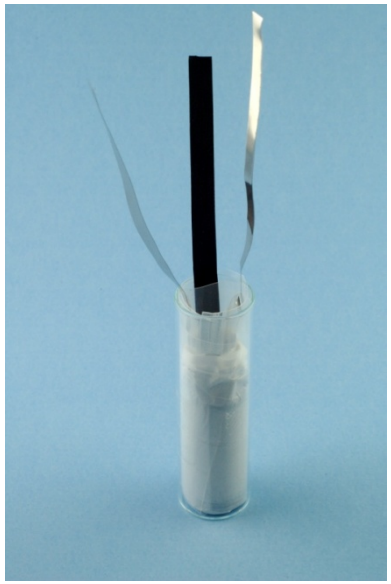


Cathode current collector 660 μm carbon
mass = 1.5g
area = 1.5” x 6.375”



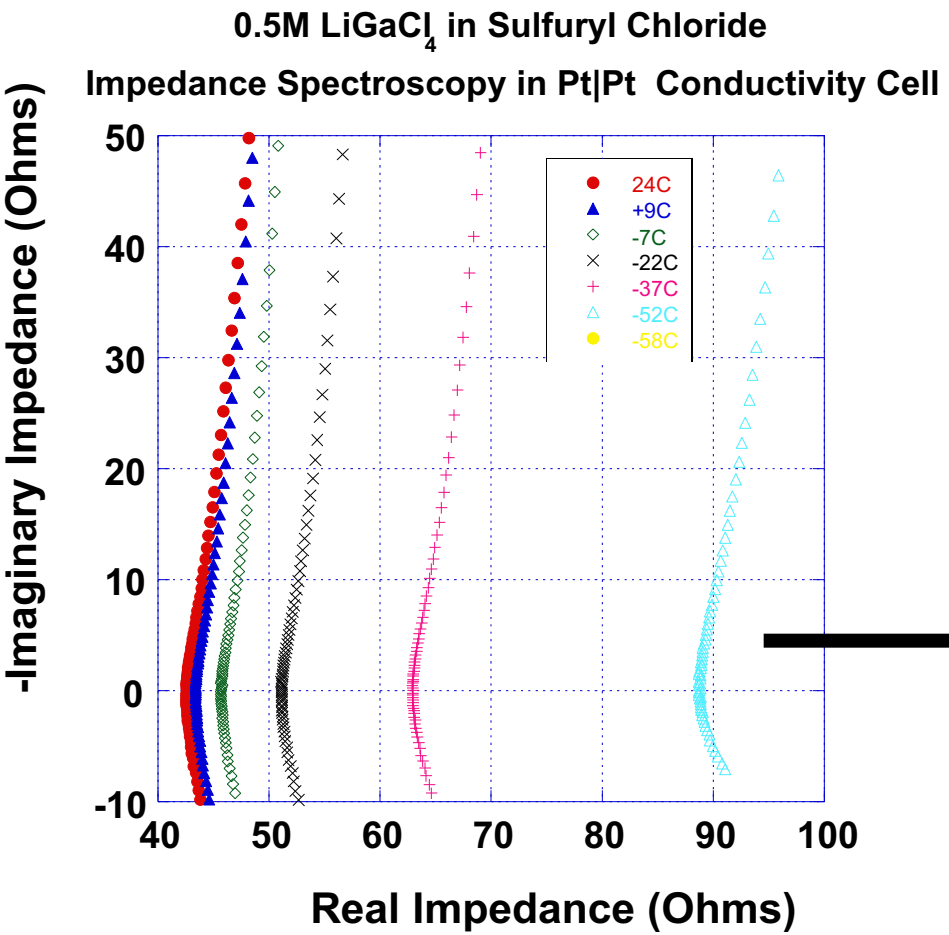
Li foil on Ni mesh counter electrode

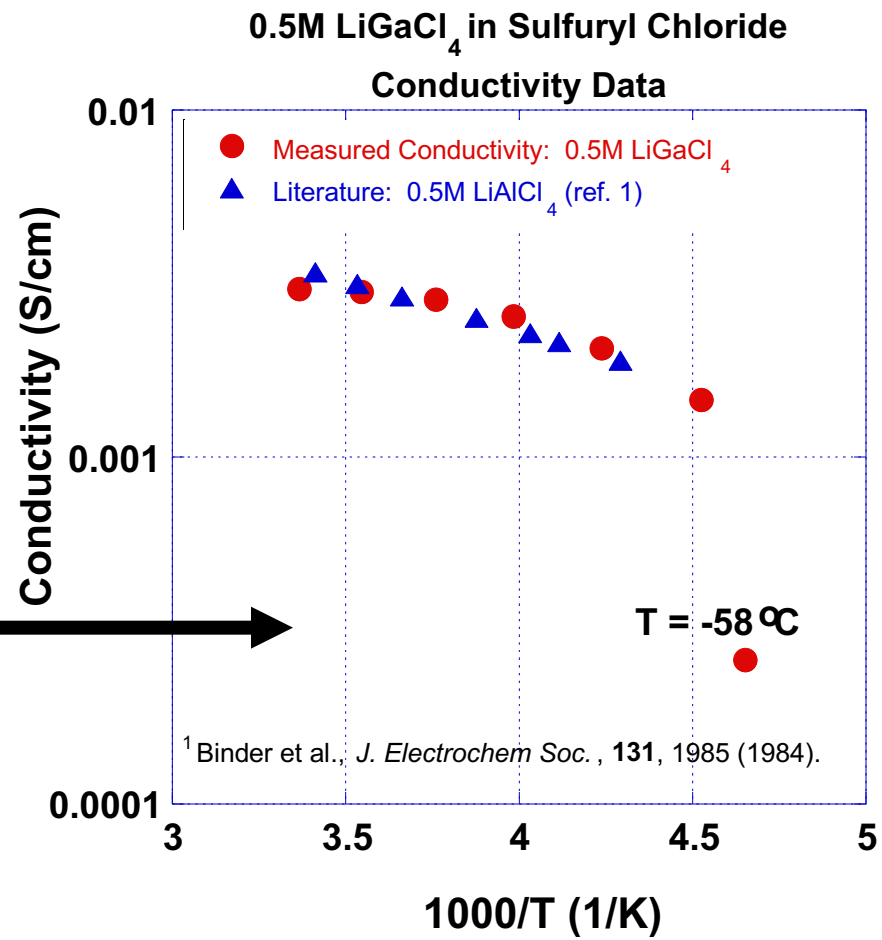
Electrodes in in 20 μm Tonen separator



Spiral cell in vial. Condense gas, fill cell.

Conductivity: Sulfuryl Chloride

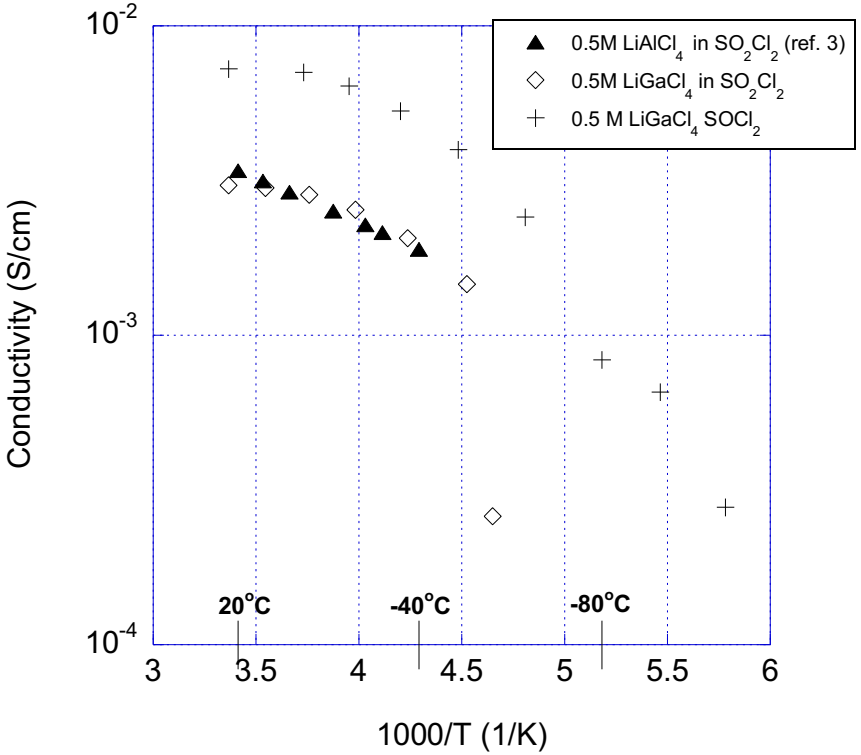


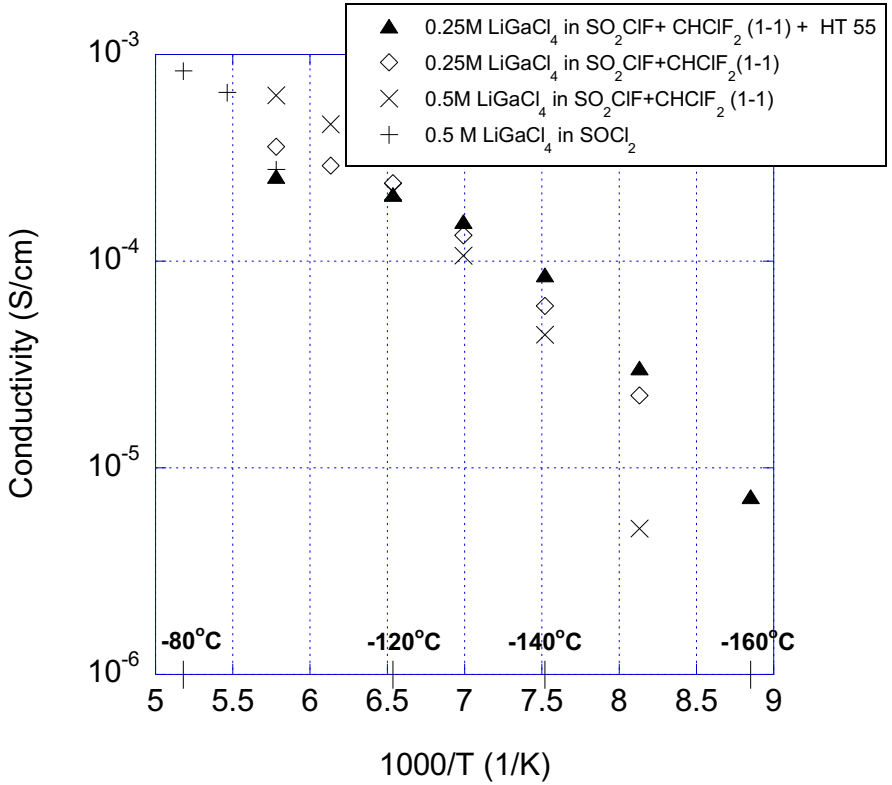


[1] Binder et al., *J. Electrochem Soc.*, **131**, 1985 (1984).

Conductivity measurements are similar literature reports

Conductivity of Various Catholytes



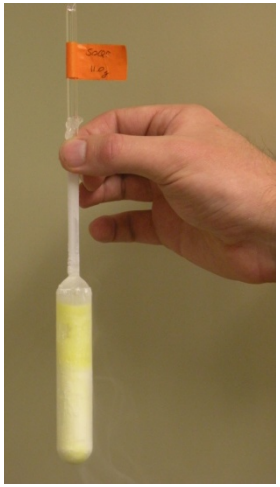


Many formulations examined, varying catholyte, co-solvent, and additives.

"Optimized" Catholyte System

- Base catholyte: Sulfuryl chloride fluoride (SO_2ClF); m.p. -125°C, b.p. 7°C
  - SOClF disproportionates with storage, SO_2F_2 low b.p., and not likely to reduce readily by Li
- Co-solvent: chlorodifluoromethane; m.p. ($CHClF_2$); m.p. -175°C, b.p. -41°C
  - Wide range of alkanes, halocarbons,* chloroethane-butylnitrile binaries examined
- Salt: $LiGaCl_4$
  - Better low temperature conductivity than $LiAlCl_4$
- Surfactant: 3 vol % of perfluoroether: Galden HT55
  - Below -120°C, 1:1 SO_2ClF:$CHClF_2$ phase separates
  - Addition of a perfluoroether suppresses the temperature of phase separation
- Halogen Passivation: Bromine (Br_2)
  - Li-$SOCl_2$ cells with BrCl, Cl_2 additives show reduced voltage delay

USC Purified SO_2ClF

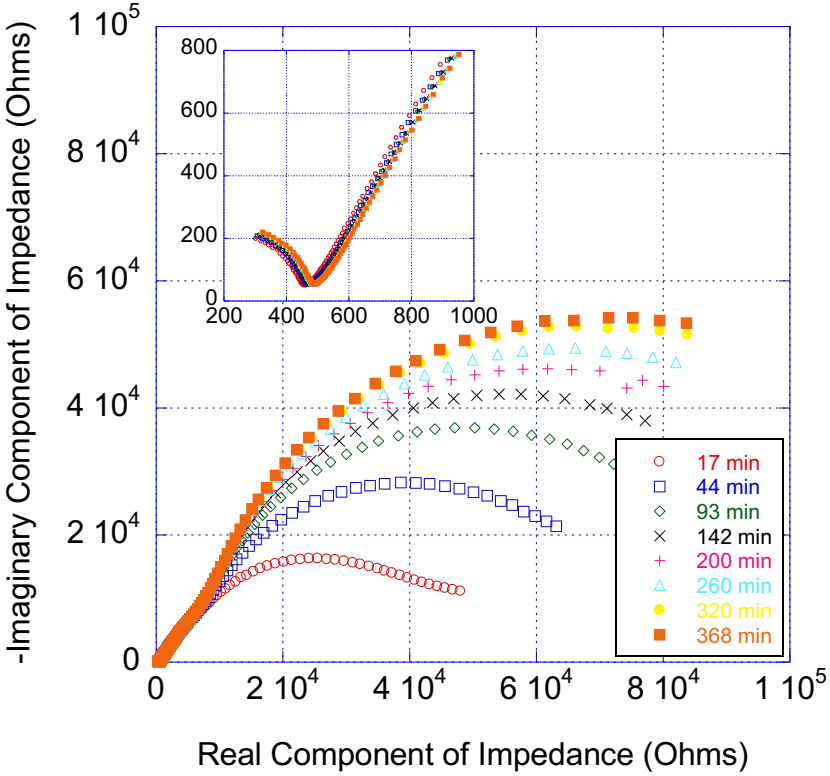


USC Synthesized SOClF

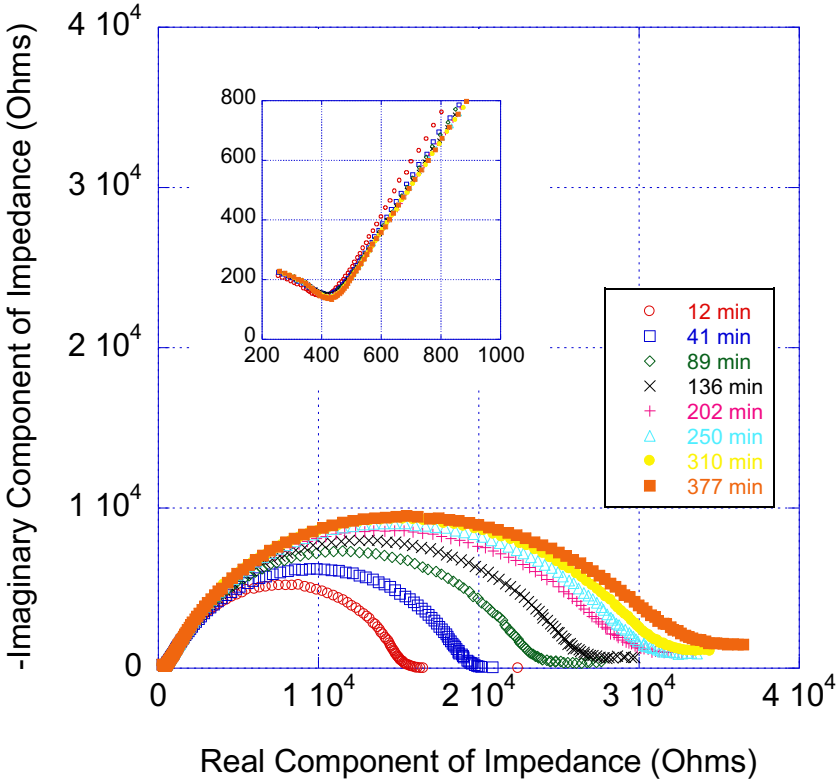
*See Rustomji et al., *Science,* **356**, 1 (2017).

EIS of Anode-Catholyte Interface, with and without Br_2

No Br_2

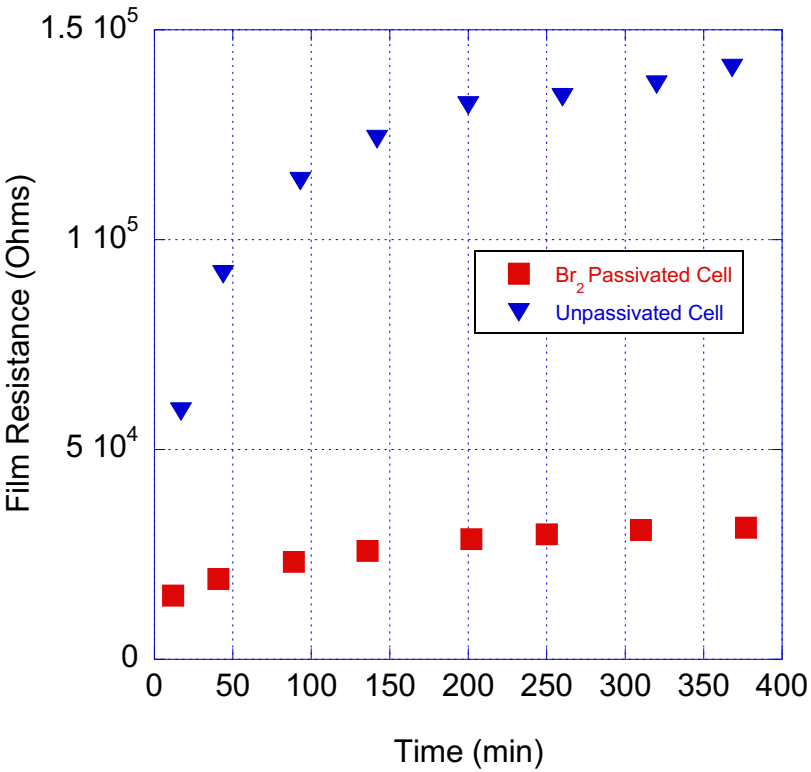


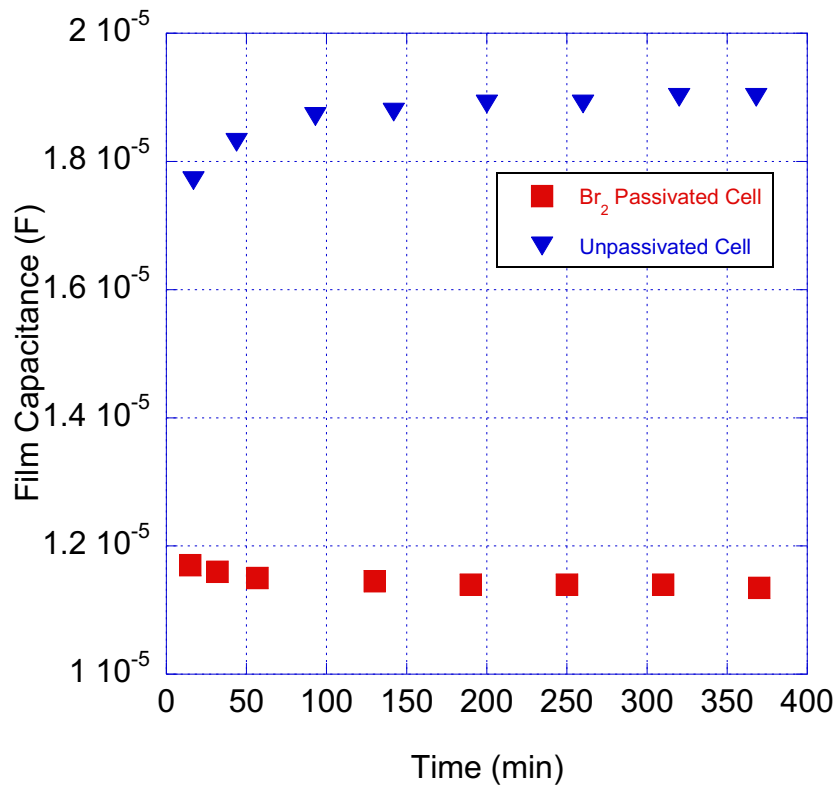
Br_2 additive



High frequency relaxation time invariant (solution impedance, insets). Low frequency relaxation strongly time dependent (passive film impedance).

Fitted Resistance-Capacitance of Anode

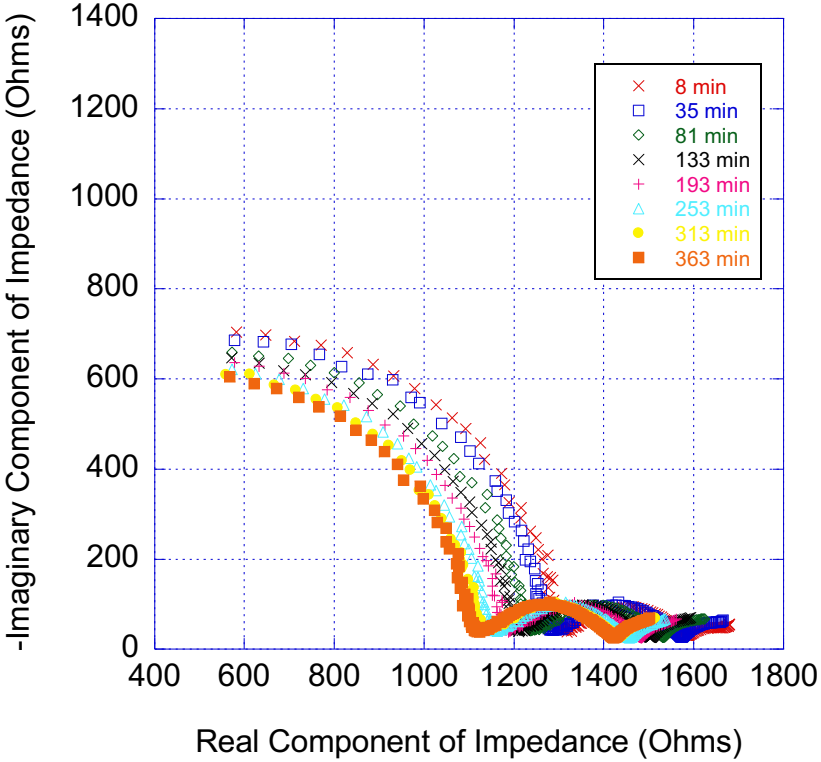




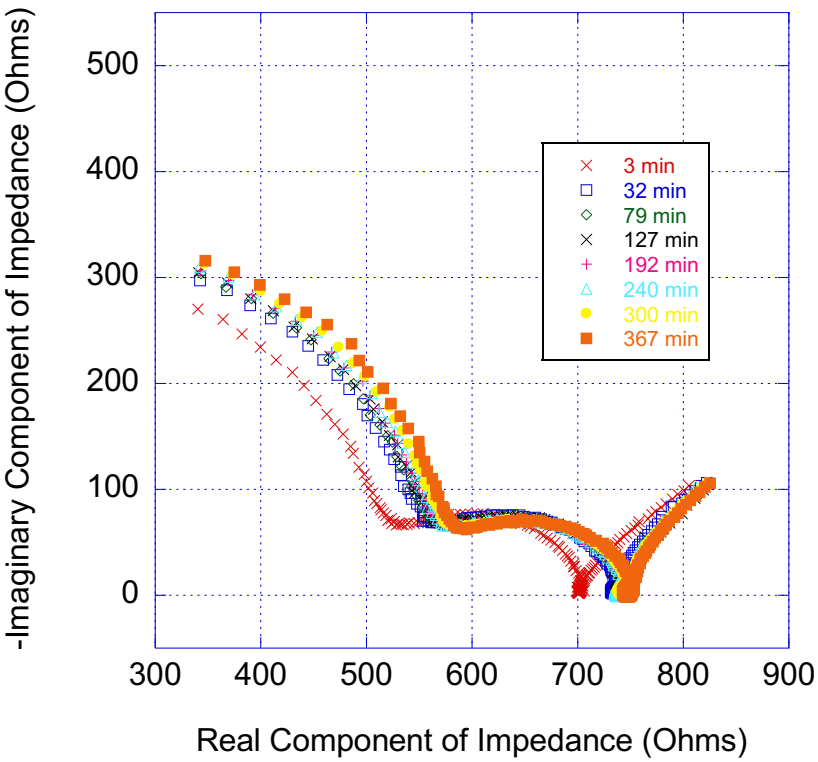
Br_2 reduces film resistance and capacitance. Br_2 slows film impedance growth.

EIS of Carbon-Catholyte Interface, with and without Br_2

No Br_2

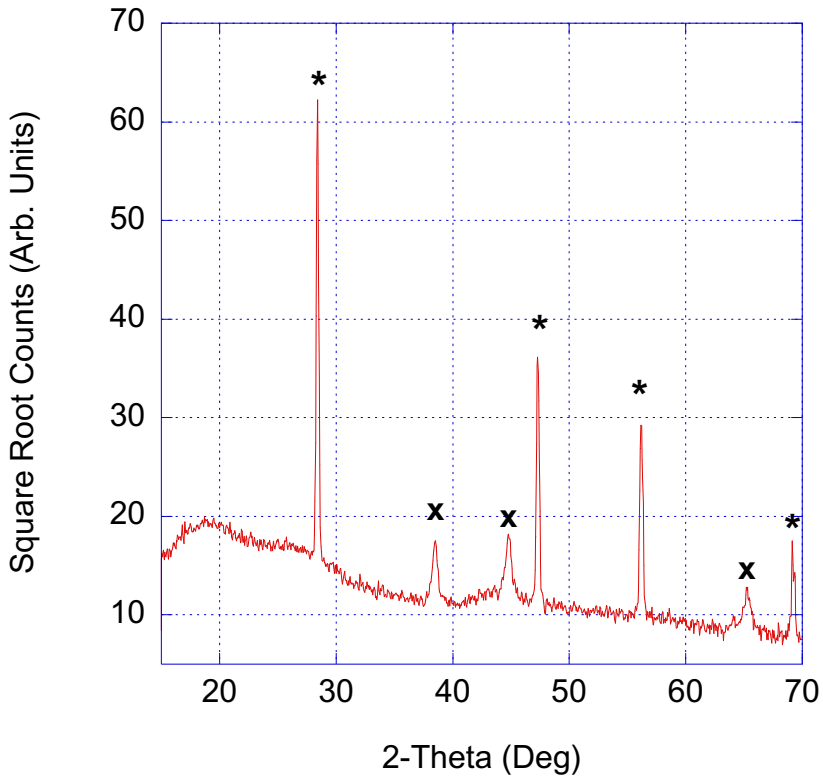


Br_2 additive



Some decrease in electrode impedance for the unpassivated cell, likely delayed wetting. Br_2 may serve to better wet the electrode.

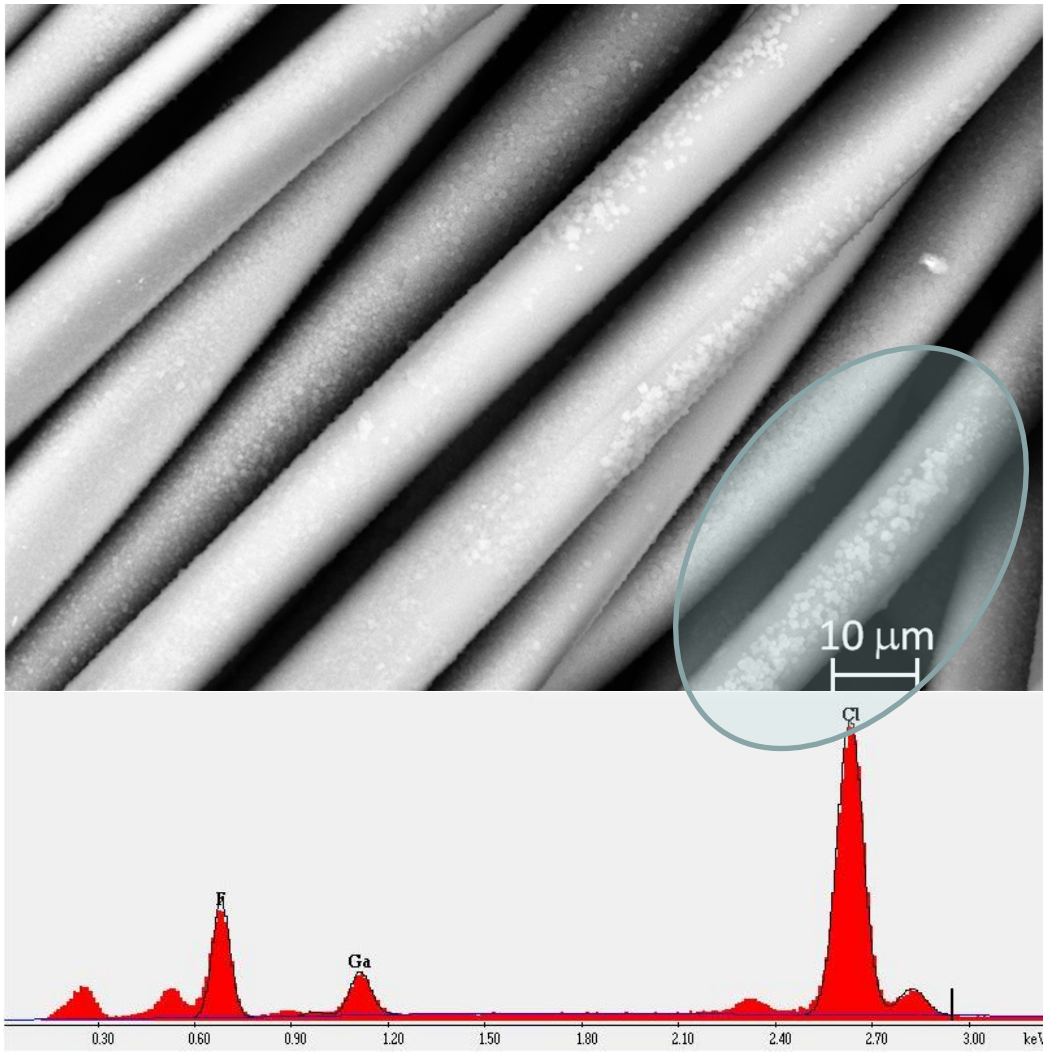
XRD of Reaction Product



XRD of reaction product (and Si reference). Asterisks identify Si reflections, X identify LiF reflections.

- In a complete reaction, the ratio of LiF:LiCl would have to be 1:1.
- Crystalline LiF observed in reaction product, but no LiCl.
- Likely LiCl is hydrated and amorphous (much more hygroscopic than LiF).
- Born Haber calculations were carried out for the stepwise formation of LiF and LiCl.
- The formation of LiF is favored by about 238 kJ/mol over that of LiCl.
- Thermodynamics strongly favor the formation of LiF in an incomplete reaction.

Cell Reaction Study: SEM-EDS of Carbon Current Collector



- Proposed mechanism:

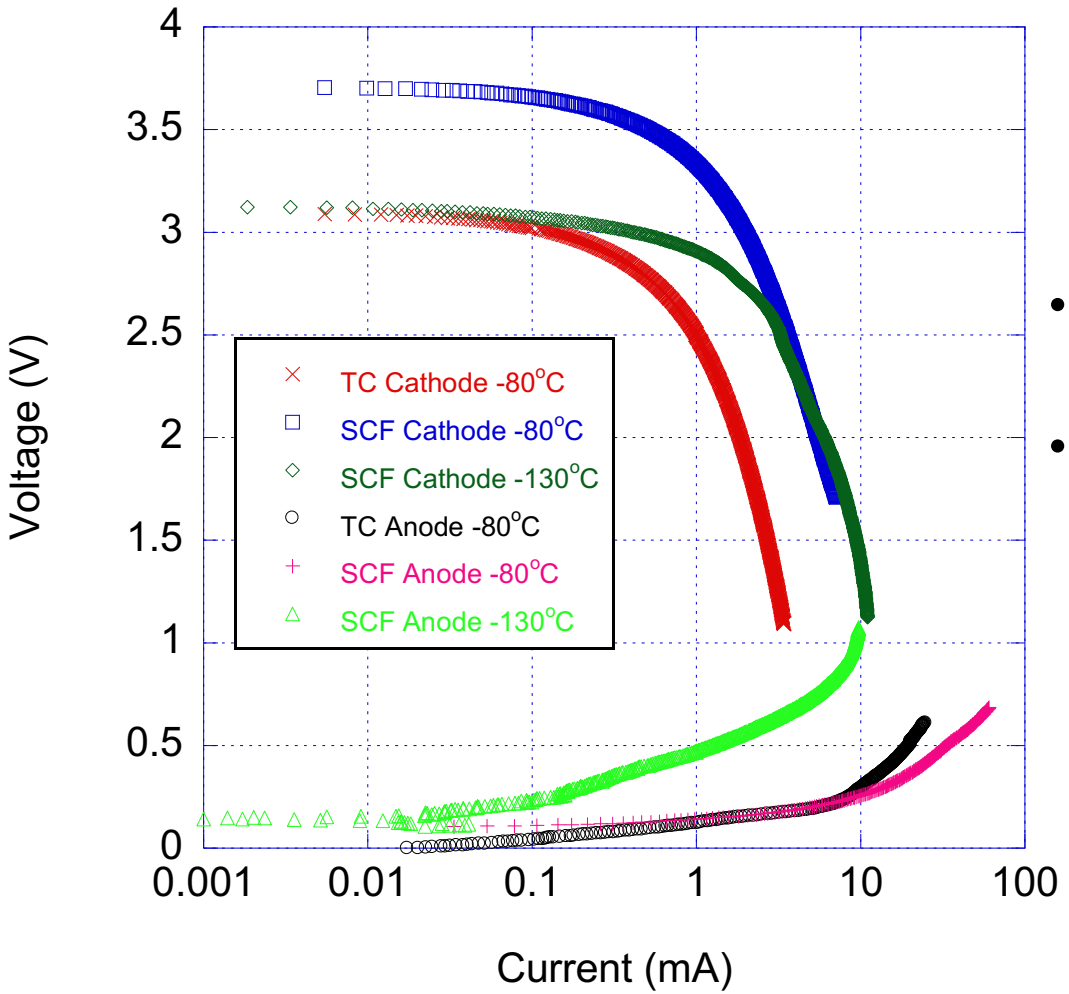
anode: $2Li \rightarrow 2Li^{+} + 2e^{-}$

cathode: $SO_2ClF + 2e^{-} \rightarrow SO_2 + Cl^{-} + F^{-}$

overall: $2Li + SO_2ClF \rightarrow SO_2 + LiCl + LiF$

- After discharge, rinse C electrode, carry out EDS study
- LiF:LiCl = 3.2:1 (well above predicted 1:1)

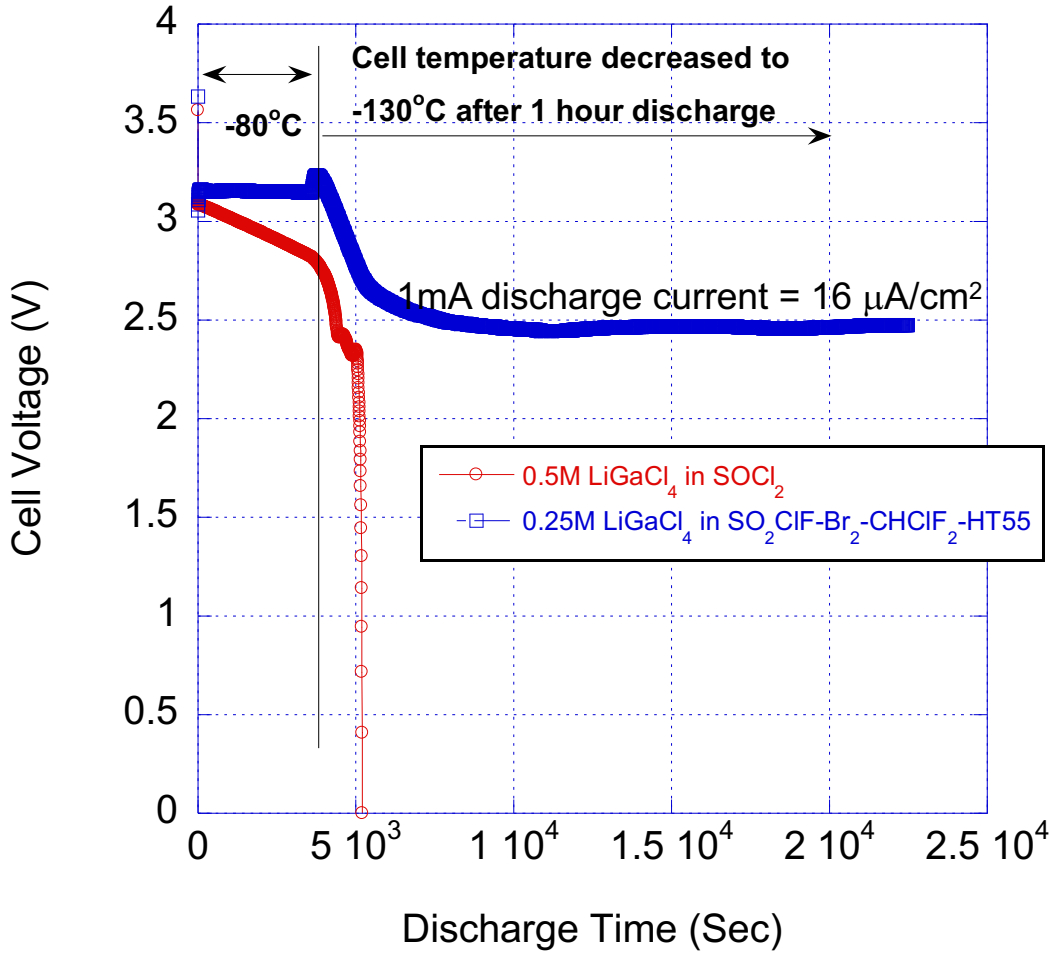
3 Electrode Cell Study of Tafel Polarization



- Polarization of electrodes dominated by cathode
- At lower temperature, the anode polarization becomes more significant

TC denotes the cell with 0.5 M $LiGaCl_4$ in $SOCl_2$ formulation and SCF denotes the cell with Br_2 passivated 0.25 M $LiGaCl_4$ in 1:1 SO_2ClF:$CHClF_2$–HT55 formulation

Cell Discharge Studies



New formulation discharges with minimal polarization at -130°C and as low at -145°C: ***lowest operating temperature battery ever reported.***

W. C. West, A. Shevade, J. Soler, J. Kulleck, M. C. Smart, B. V. Ratnakumar, Matthew Moran, Ralf Haiges, Karl O. Christe, and G. K. Surya Prakash, *J. Electrochem. Soc.,* 157, A571 (2010).

Summary

- New ultra-low temperature battery formulations have been identified.
- First demonstration of cell operation below -130°C, about 60°C lower than any other battery system reported.
- Br_2 addition results in dramatic decrease in film impedances.
- Analyses of reaction products and thermodynamics of stepwise reactions suggest incomplete reduction of sulfuryl halide to lithium halides.
- Future work will focus on vacuum filling in larger commercially prepared cells.

2020 Conference on Advanced Power Systems for Deep Space Exploration

27 - 29 October 2020
Pasadena, California

https://www.usasymposium.com/deepspace/default.php

Acknowledgements

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