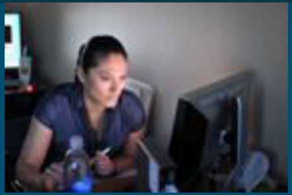
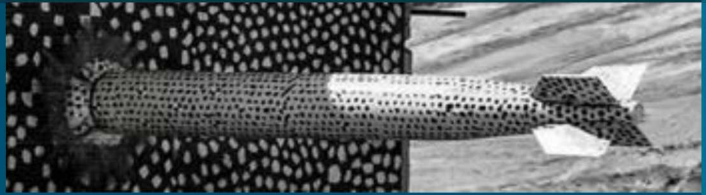
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Sandia National Laboratories

SAND2020-9883C

Printable Ink Development for Molten Salt Battery Electrodes





PRiME 2020

Molten Salts and Ionic Liquids

L02-2957

Presented by

David Herman, Adam Cook, Bertha Montoya, William Reinholtz, Teal Harbour, Raegan Johnson-Wilke, 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.

Outline

- Background
- Printable ink development
- Slot die printing
- Analysis and characterization
- Electrochemical performance
- Summary

Background – Thermally-activated, molten-salt batteries

Thermal batteries are primary, reserve power sources that use molten salt electrolytes

- Benefits :
  - Inert during long-term storage (electrolyte is solid/non-conducting at ambient temperature)
  - High power density

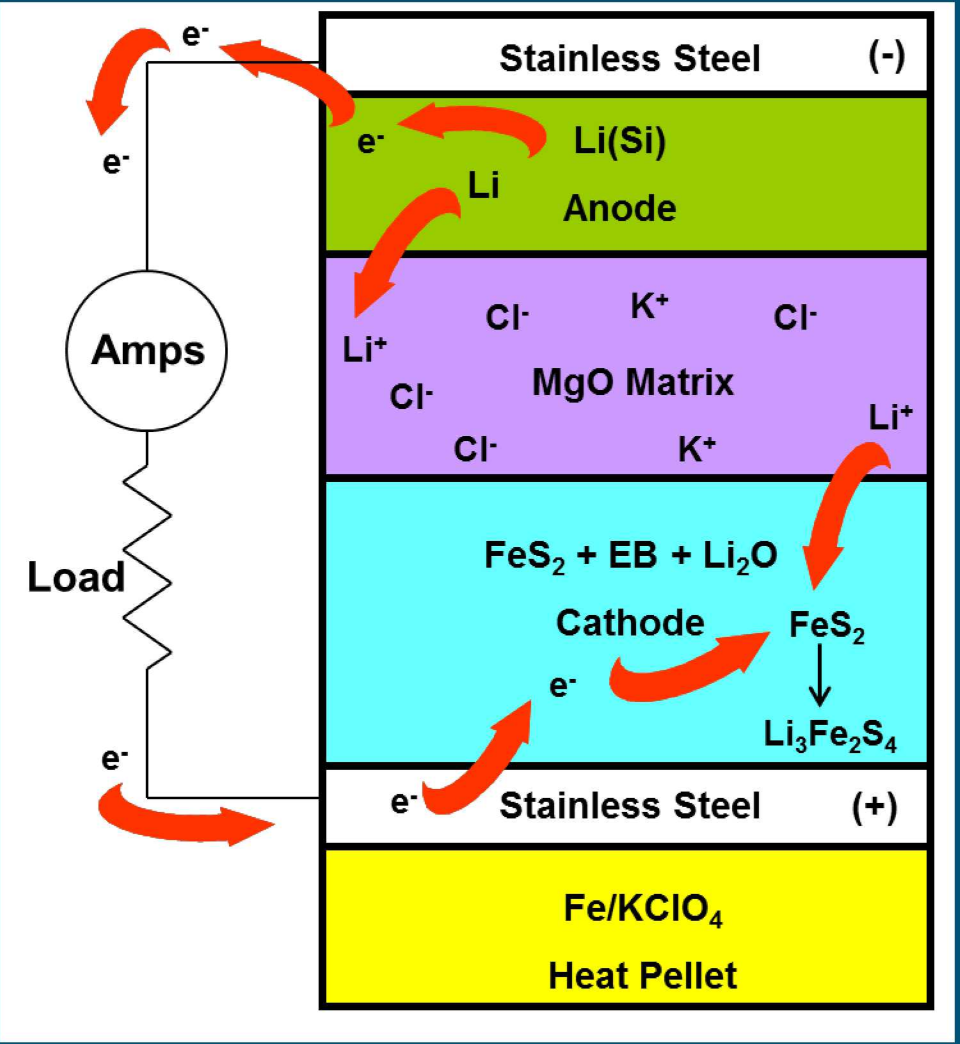
A typical Li-FeS_2 thermal battery cell consists of:

- Lithium alloy anode
- Combined MgO and electrolyte salt separator
- FeS_2 cathode
- Heat source
- Approximately 2V per cell

Electrolyte salts melt when activated at high temperatures

- High ionic conductivity
- Rapid power delivery

Standard manufacturing utilizes pressed-pellet materials



Li-FeS_2 cell

Background – motivation for printed-film batteries

Disadvantages of standard pressed-pellet manufacturing

- Labor intensive with lower throughput – components have higher variability and lower yields
- Pellets restrict the cells to a circular form factor (cylindrical batteries)
- Extra material required to produce robust pellets (reducing the power density)

Benefits of printed-electrode manufacturing

- Continuous process – reduced labor cost and higher, more consistent output
- Can be cut/punched into custom, non-circular form factor
- Reduced excess material – only as thick as needed to meet power demands (less weight, better power density)


Pellet production


Pressed-pellet cell


Continuous electrode printing


Printed-electrode cell

Printable ink development – desired properties

Particle size and stability
- Small enough to prevent clogging during printing
- Ink remains stable - no separation or sedimentation of slurry particles/solvent

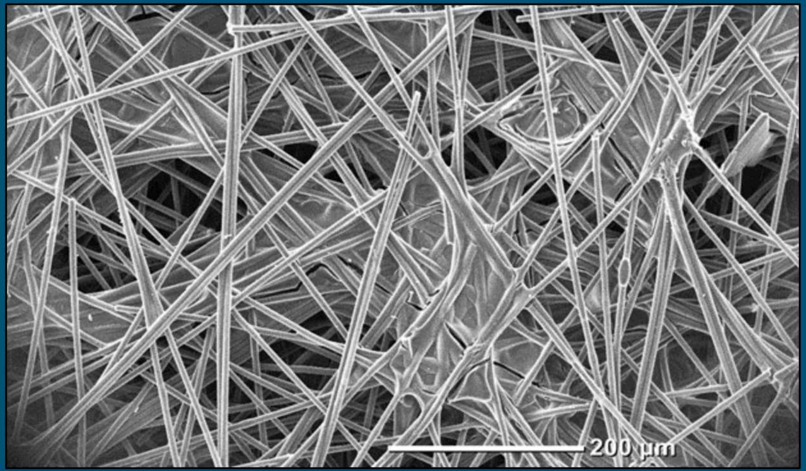
Viscosity
- Sufficiently high viscosity to prevent absorption into substrate
  - Porous carbon-fiber paper with cathode film as substrates
- Shear-thinning for easy extrusion under pressure and stable wet film

Ease and repeatability - scale-up to larger batches of ink

***Initial unsuccessful separator/electrolyte inks**

Precursor materials (MgO and LiCl-KCL eutectic) were blended and fused into 'electrolyte binder' (EB) powder
- EB was milled from stock 300 μm particle size down to <10 μm
  - Milling potentially alters the morphology of MgO particles, degrading the separator performance
- Using pure solvent
  - Salts gradually dissolve in solvent causing particle aggregation and filter pressing of particles – unable to print

Uncoated carbon paper substrate (SEM image)



Print failure due to clogged slot die

Printable ink development - Slurry preparation

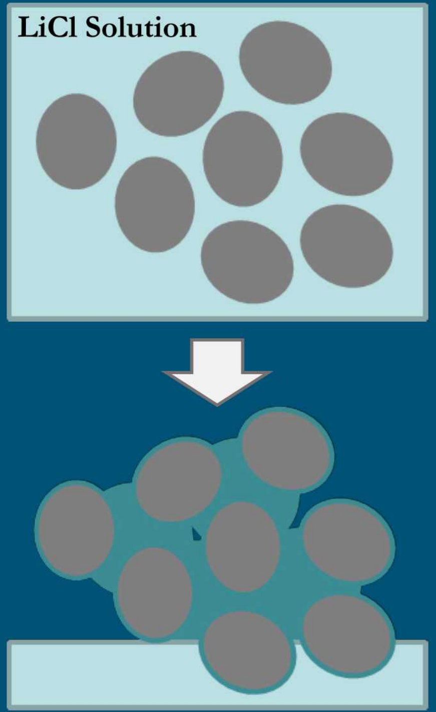
Separator slurries utilize the existing pellet-based materials and chemistry
- Magnesium oxide (MgO) powder provides separator structure
- LiCl-KCl eutectic salt blend is used as the electrolyte
  - Eutectic salt melts <360ºC, providing high ionic conductivity at battery operating temperatures (>500ºC)

EB powder and DMSO blended with high-shear rotor-stator, followed by high-torque stirring for approximately 100 hr
- No milling needed to reduce particle/agglomerate size
- Batches remain in stable/printable condition for weeks as long as they are continually stirred

Optimal LiCl added

Extended mixing

- Dimethyl sulfoxide (DMSO) used as carrier solvent
  - Compatible with materials, LiCl is soluble
  - Boiling point low enough for complete drying
- Added LiCl (pre-dissolved in DMSO) functions as binder
  - Chemically compatible with electrolyte
  - No off-gassing or reactions at operating temperature



EB powder added to DMSO with pre-dissolved LiCl

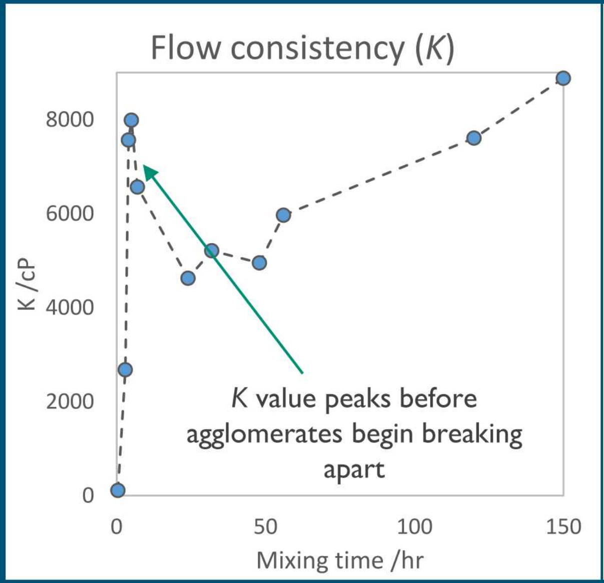
Precipitated salt binds the dry film

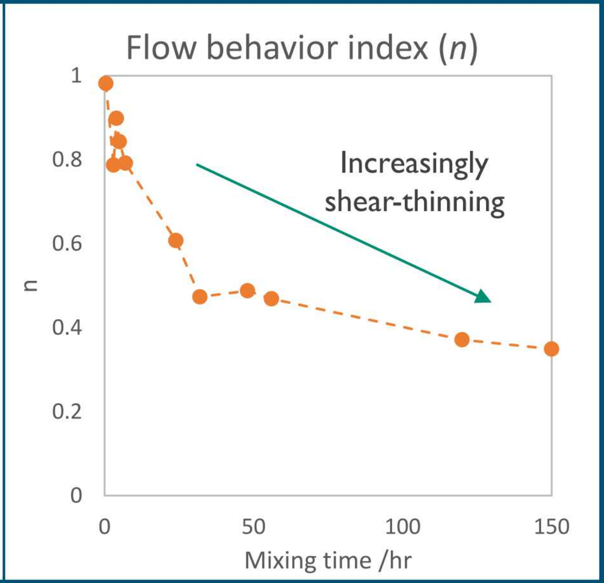
Printable ink development - Rheology

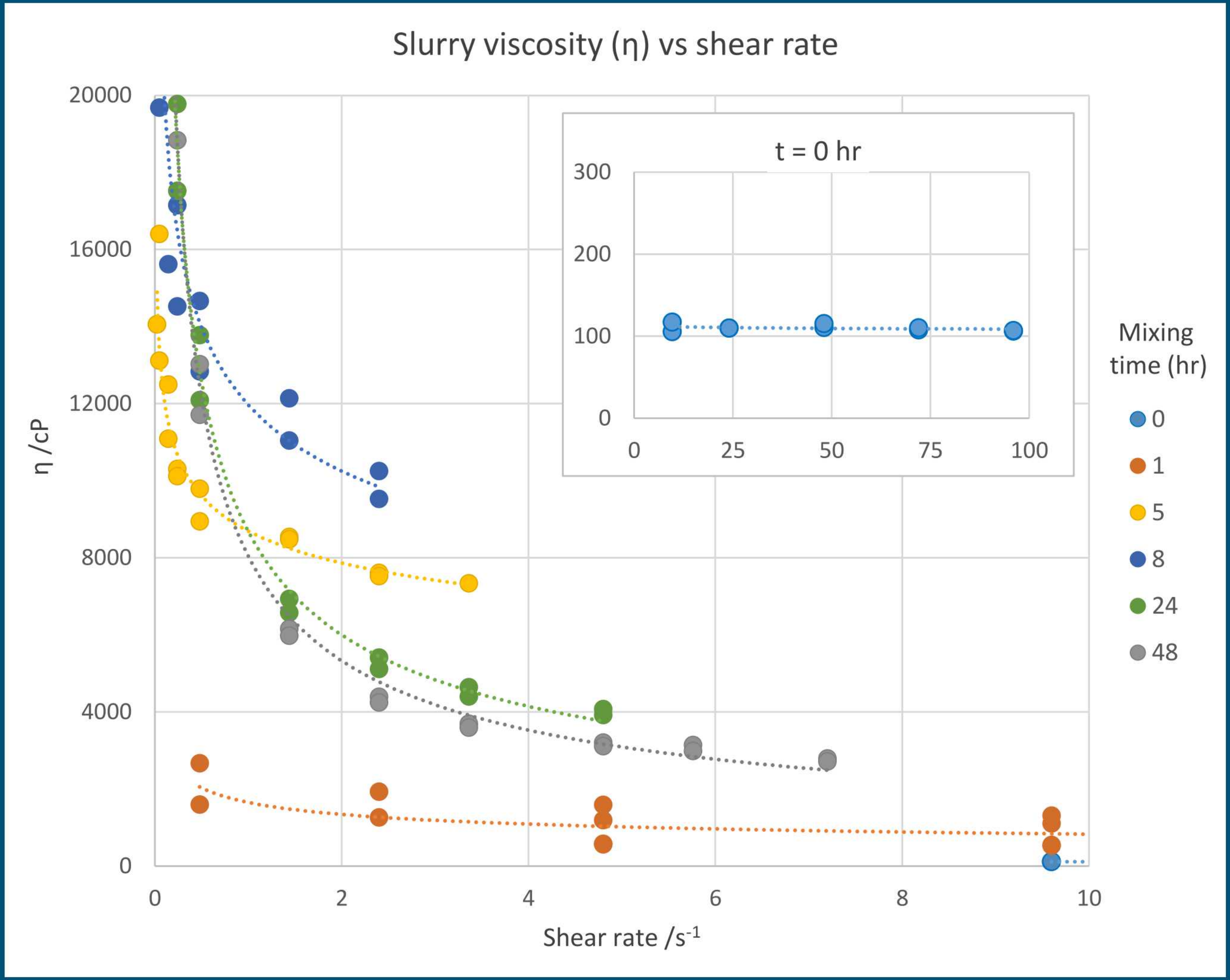
Ink behaves as a power-law fluid: $\eta = K\dot{\gamma}^{(n-1)}$
- η – apparent viscosity (cP)
- $\dot{\gamma}$ – shear rate (s^{-1})
- n – flow behavior index
- K – flow consistency

n stabilizes around 0.3 (shear thinning)

K increases with extended mixing (solvent evaporation)





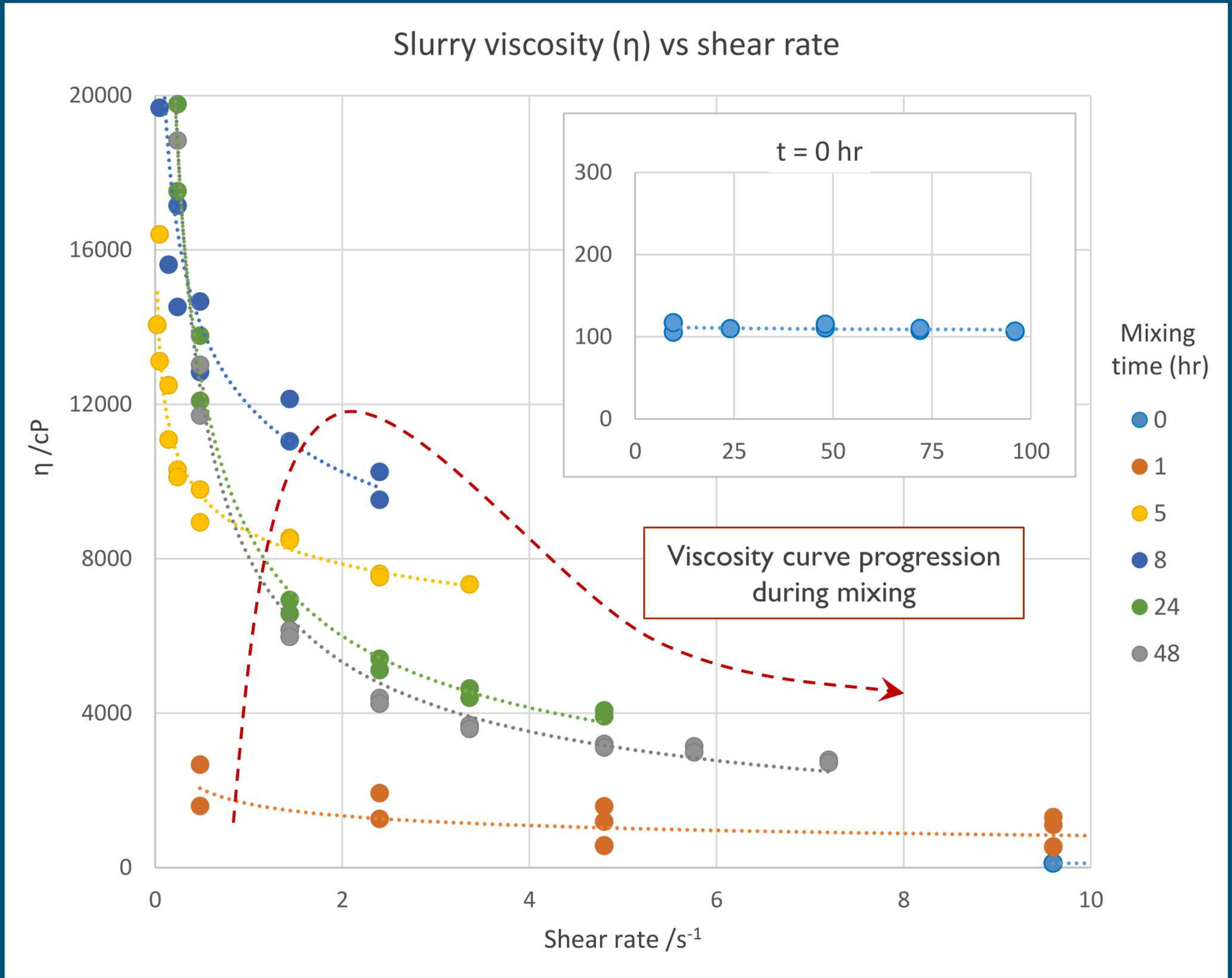


Viscosity as measured using cup-and-bob rheometer

Printable ink development -Rheology

Rheological behavior develops over >48 hr mixing

- Viscosity is independent of shear rate immediately after initial blending
  - Viscosity increases rapidly as salts dissolve in DMSO
  - Slurry develops highly shear-thinning behavior after prolonged mixing, apparent viscosity follows power-law model
    - DMSO and LiCl initially forms an adduct phase – quickly increasing effective viscosity
    - Salt/MgO agglomerates slowly break apart as the salt dissolves – resulting in increasingly shear-thinning with extended mixing
- Final slurry has small particle size (<25 μm)
  - MgO and salt aggregates slowly break apart during mixing
  - Small particles prevent filter-pressing and clogging of the slot die during printing

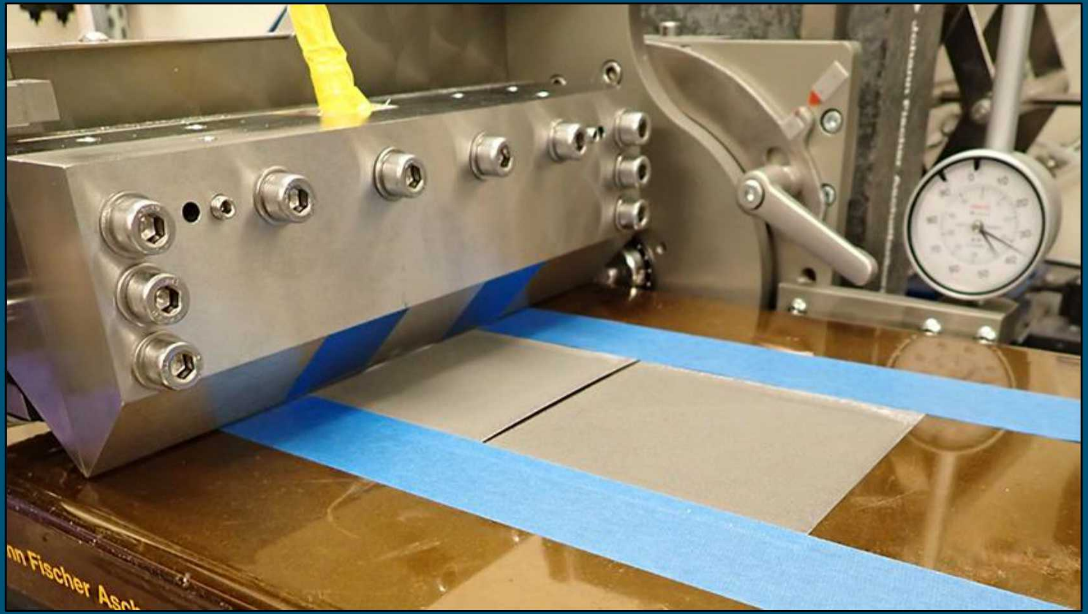


Slot die printing

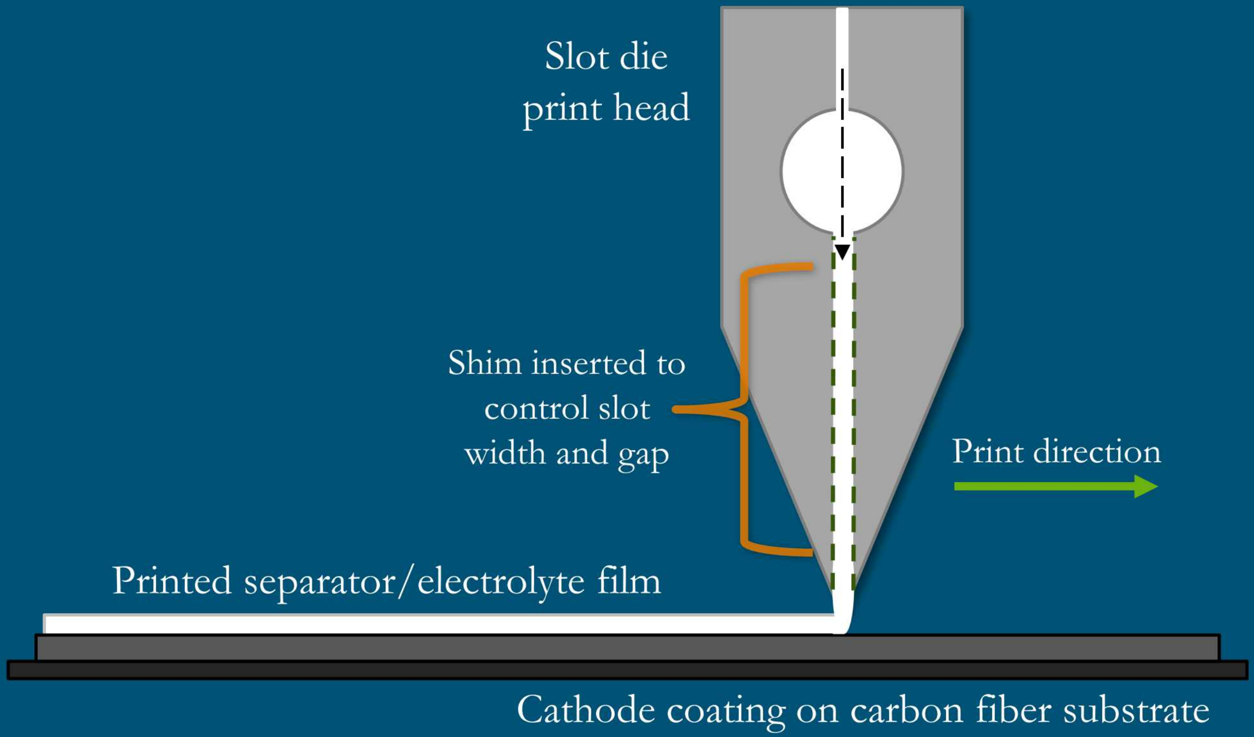
Separator films were printed directly on pre-prepared cathode coatings with carbon fiber substrates

Slot die printing allows for multi-variable control of wet film coatings

- Adjustable substrate speed, slurry flow rate, and die head position (height, width, angle, shim size)
  - Separators were printed with a 300 μm shim, with ~200 μm gap above the substrate
  - Additional separator layers can be printed – initial separator layer dried for 1 hr before second coating



Slot die set-up

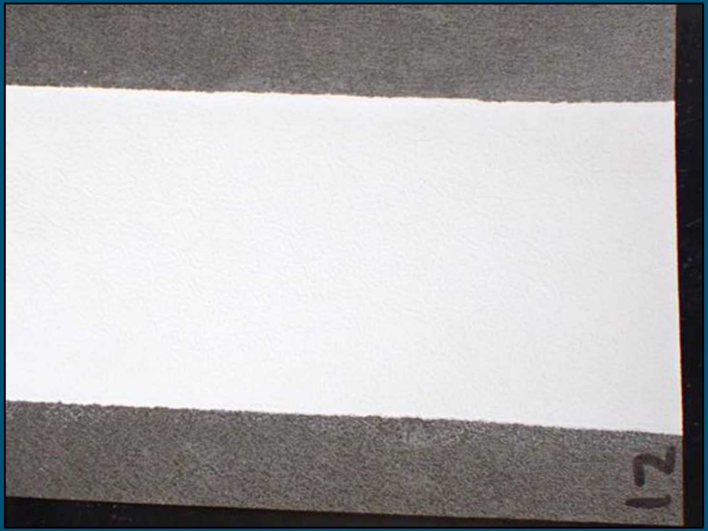


Slot die printing

Cathode substrates

Printing in progress

Wet film



Dried separator on cathode

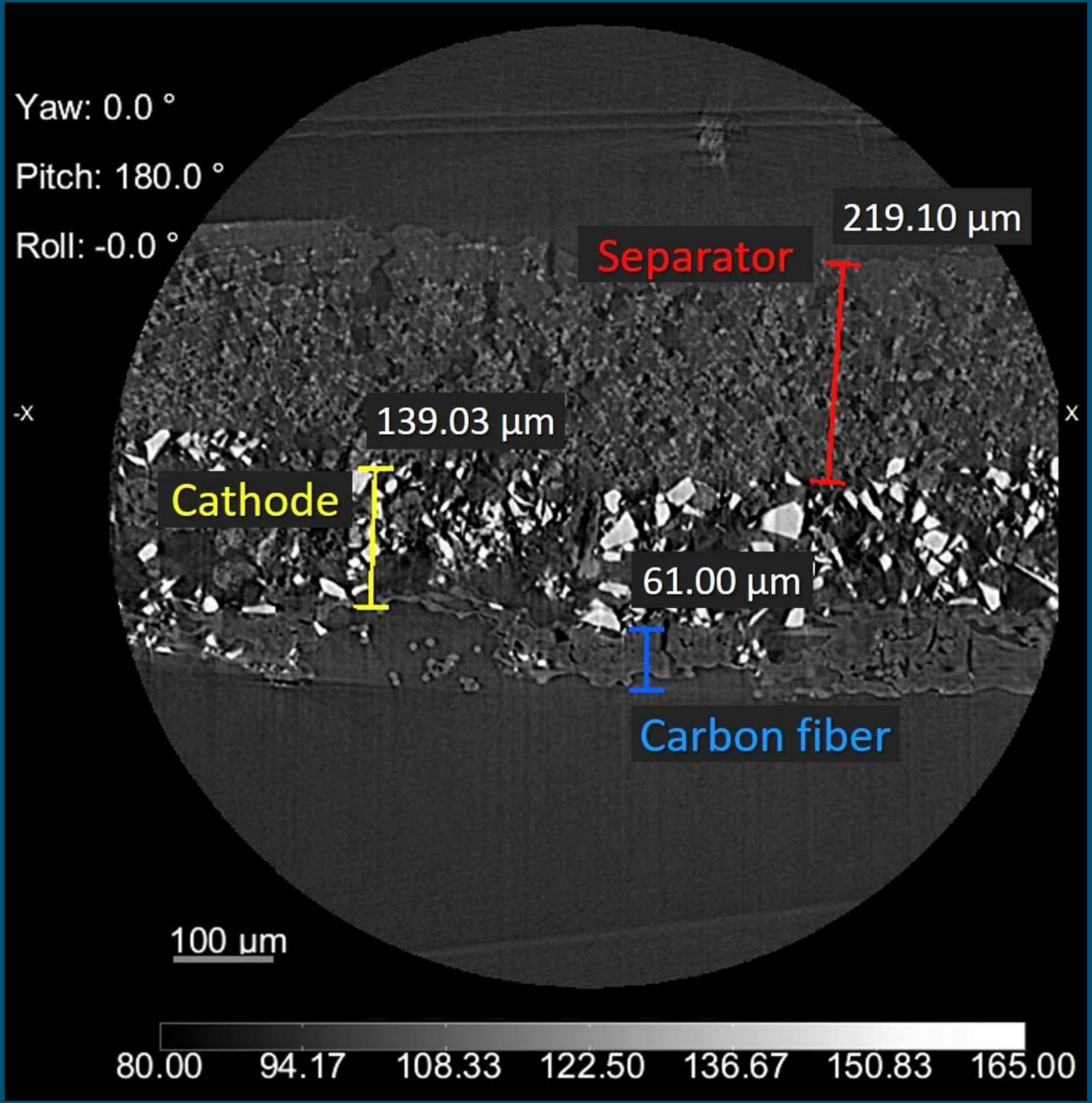
Separator films print smoothly and uniformly

- Easy to handle
- No clogging and ink remained consistent during entire process

Two-stage final drying procedure – dries without discoloration or cracking

- Lower temperature (110ºC) convection drying to remove majority of DMSO
- Higher temperature (150ºC) vacuum drying to completely remove any remaining DMSO
  - Avoids cathode degradation at high temperatures

Analysis and characterization - Micro-CT imaging

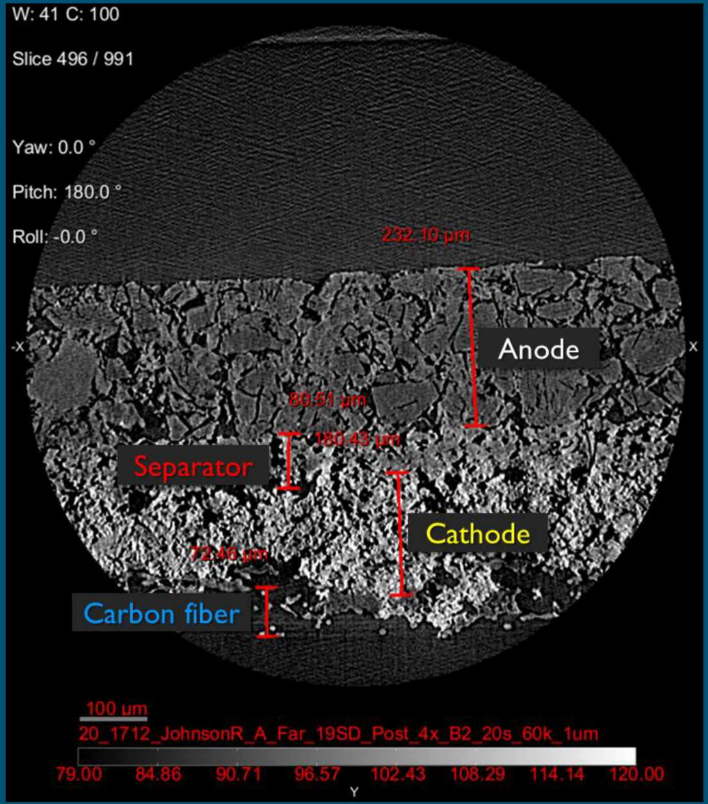


Cross-sectional imaging with micro-CT shows distinct separator and cathode layers

- Separator layer thickness is generally uniform
- Minimal migration of active cathode material into the separator layer
- Some void space/defects present in separator film

Single-cell cross section after discharging

- Electrode and separator layers remain distinct and intact
- Thickness reduced due to electrolyte melting and compression of films



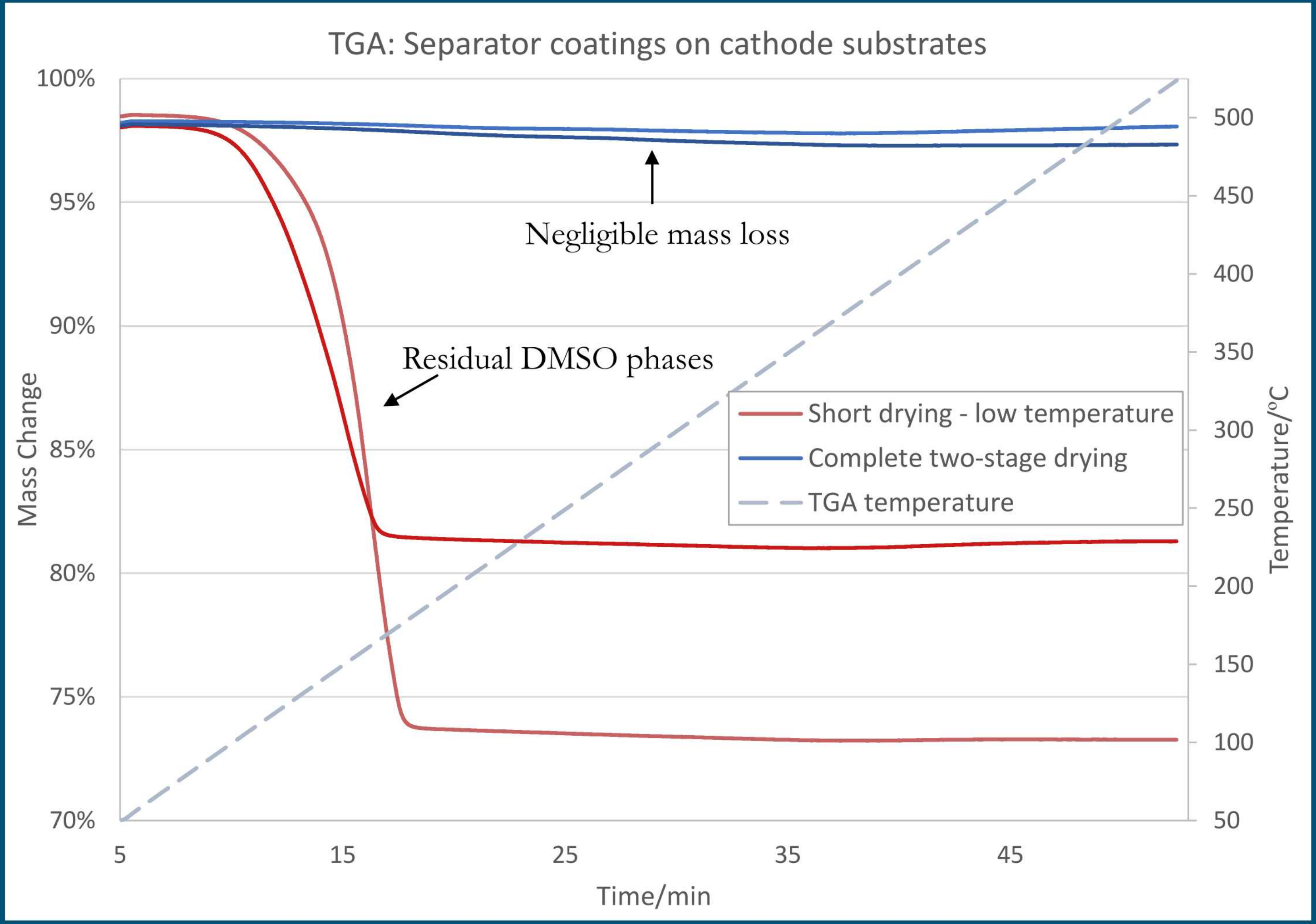
Analysis and characterization – TGA

Proper drying is crucial

- Prevent vaporization during battery activation
- Improve electrochemical performance of separator

Thermogravimetric analysis (TGA) was used to ensure drying procedure sufficiently removed the solvent from separator coating

- Two-stage drying procedure
  - Lower temperature (110ºC) convection drying to remove majority of DMSO
  - Higher temperature (150ºC) vacuum drying to completely remove any remaining DMSO
- TGA shows no mass loss after full two-stage drying process
  - Measurements after short/intermediate indicate residual DMSO and LiCl:DMSO adduct phases – resulting in mass loss below 200ºC



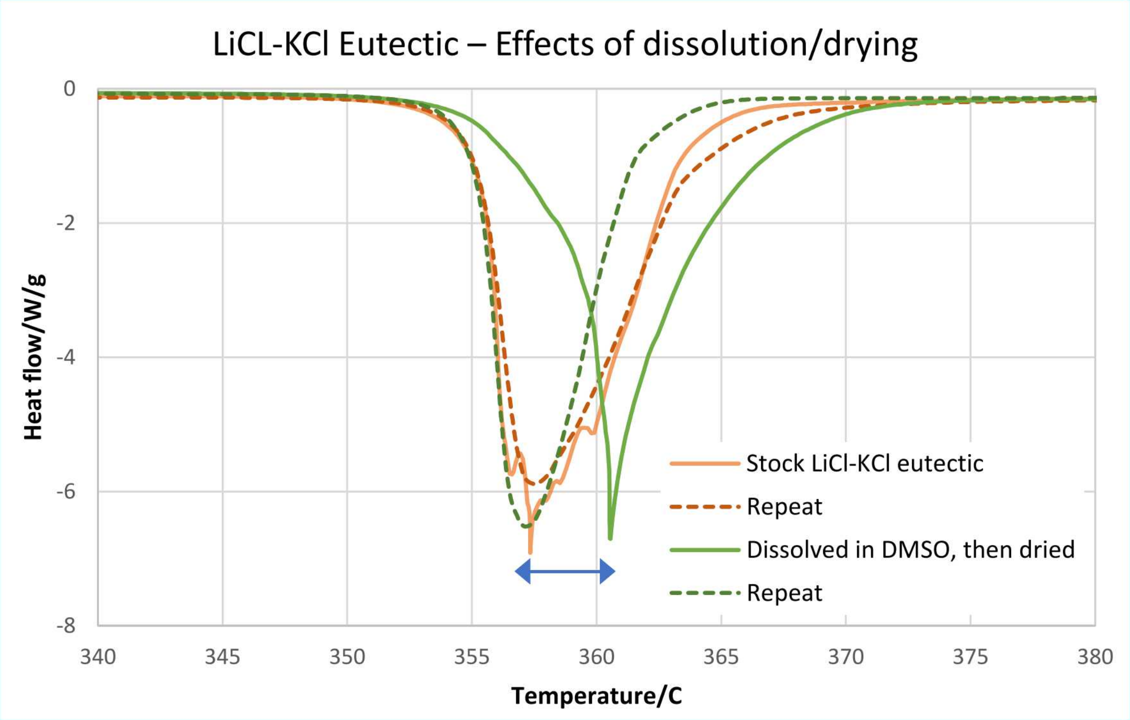
Analysis and characterization – DSC

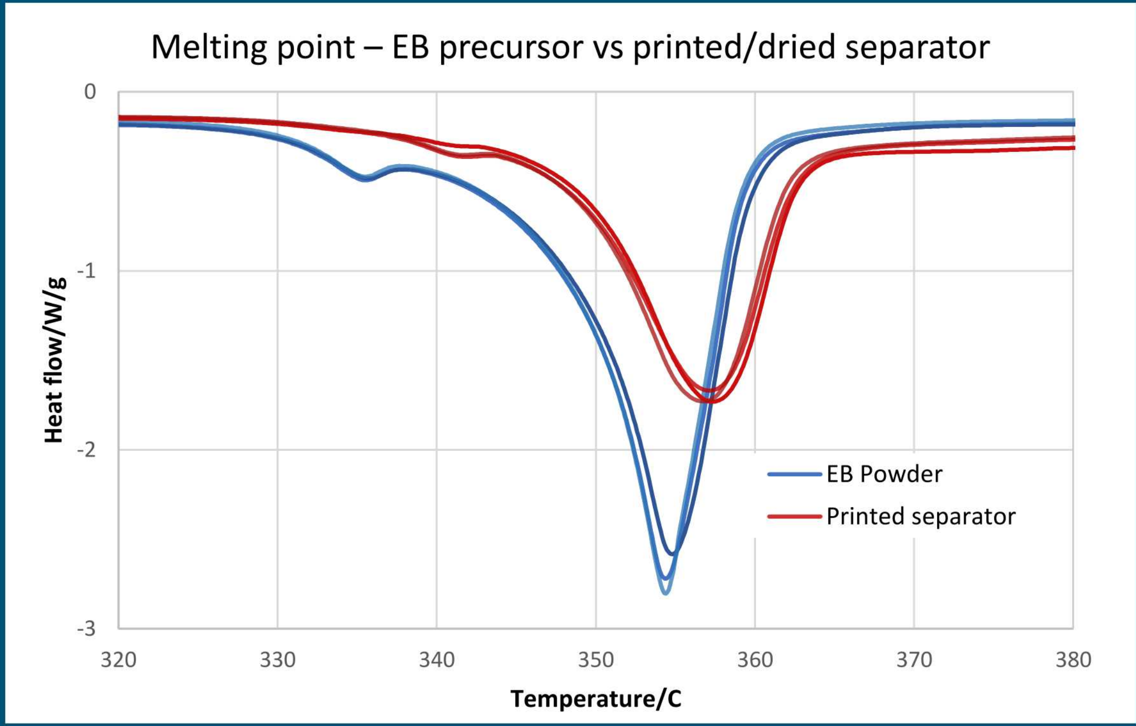
Differential scanning calorimetry (DSC) used to determine differences in the electrolyte melting behavior

- Eutectic LiCl-KCL melting point shifts ~5ºC after dissolving in DMSO and drying
  - Due do asymmetric solubility of LiCl/KCL in DMSO
- Repeating the temperature cycle shows samples return to eutectic point
  - Shift is different solubility/crystallization of salts, not residual DMSO adducts

EB vs printed separator

- Melting onset and peak is shifted higher (<5ºC) compared to standard EB powder
  - Additional pre-dissolved LiCl alters the LiCl:KCl ratio
- Still melts below 360ºC
  - Not significant enough to affect battery performance (operating >500ºC)





Electrochemical performance - Single-cell testing

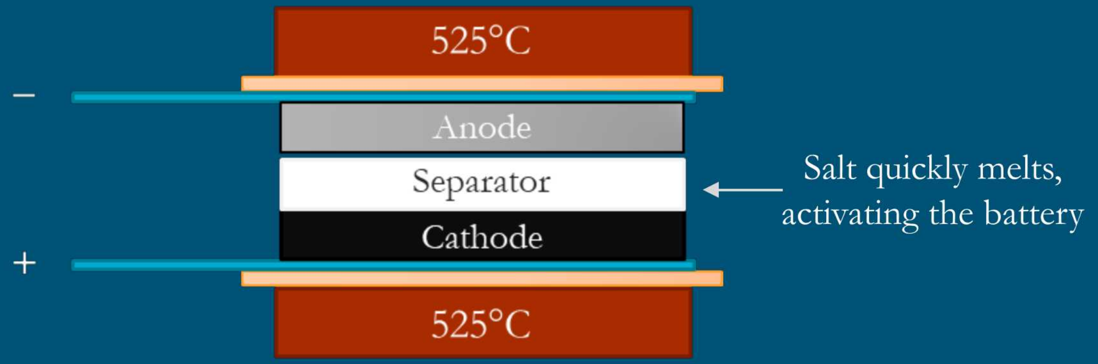
Individual electrodes are cut/punched out from the multi-layer films

- Single cells are assembled between stainless steel current collectors with attached electrode leads
- Cell tester consists of weighted, pre-heated platens to provide compressive force and rapidly heat the cell to desired operating temperature

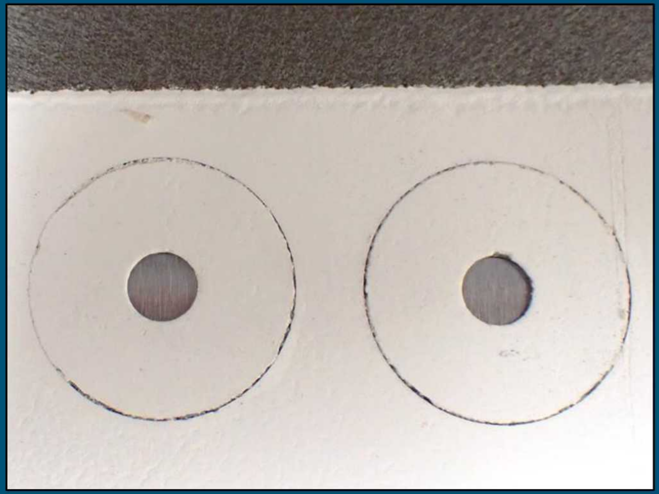
Voltage is monitored and a current test profile is applied

- Initial open circuit hold, followed by low baseline current (50 mA/cm^2) with multiple high-current pulses up to 2 A/cm^2
  - Pulsed current used to determine cell polarization under load
  - Delivered capacity determined above voltage threshold of 1.65 V

Single cell schematic



Separator-coated cathodes cut to desired size

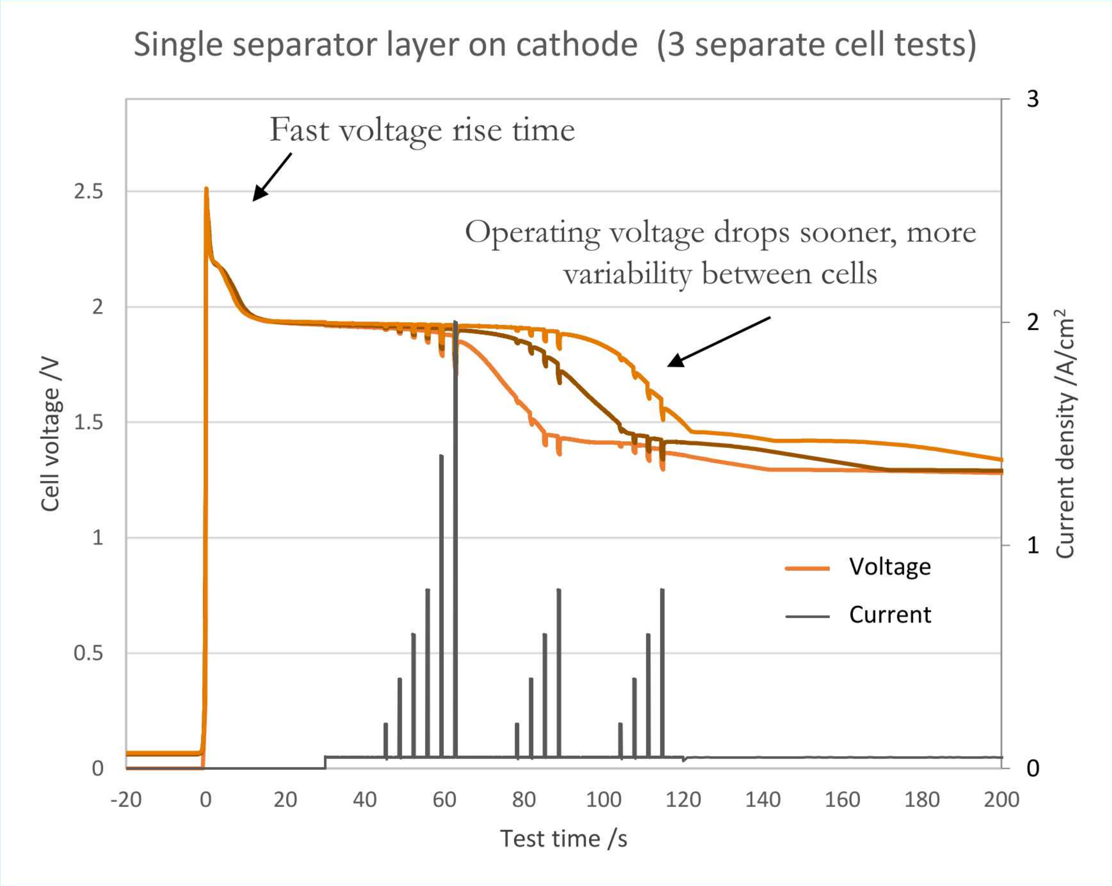


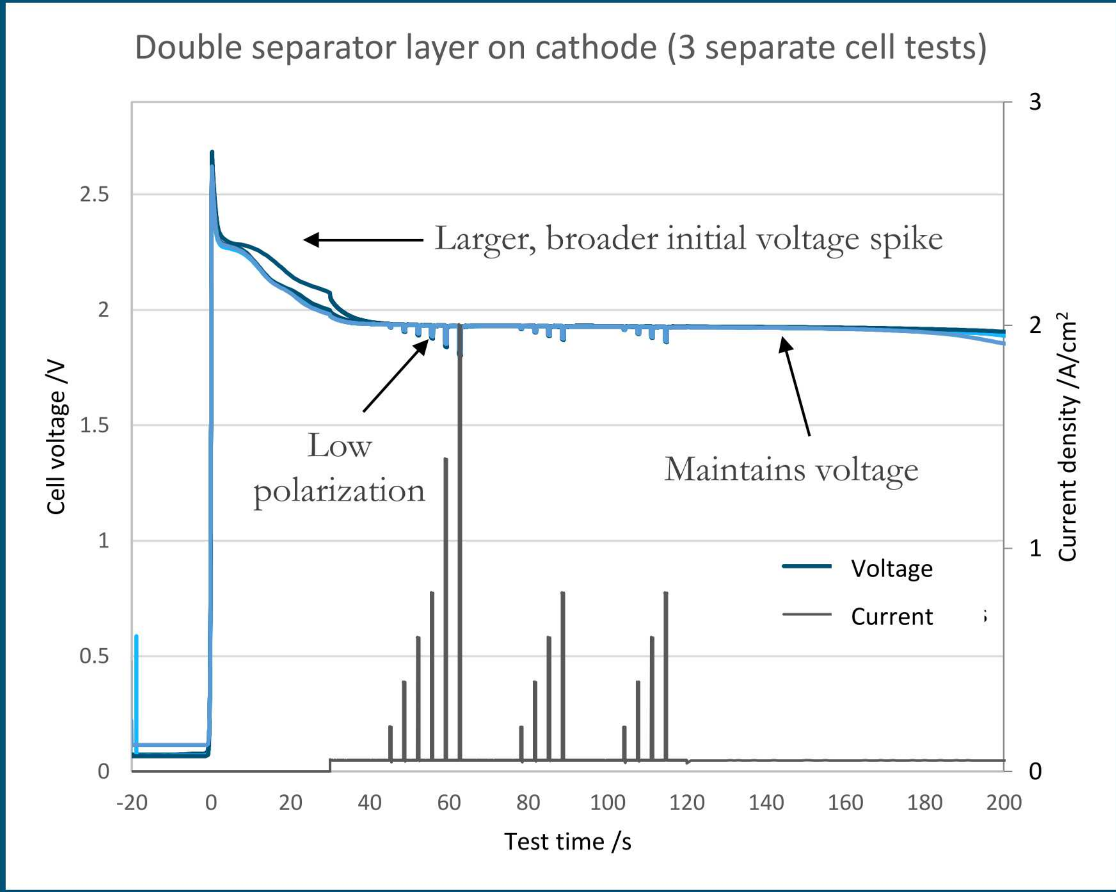
Electrochemical performance - Single-cell testing

- Printed separator on cathode with LiSi anode
- Tests conducted at 525°C
- Dry/inert glovebox atmosphere

Tested both single and double-layer separators printed directly on cathode films

- Single layer – approx. 220 µm dry separator thickness
- Double layer - approx. 350 µm





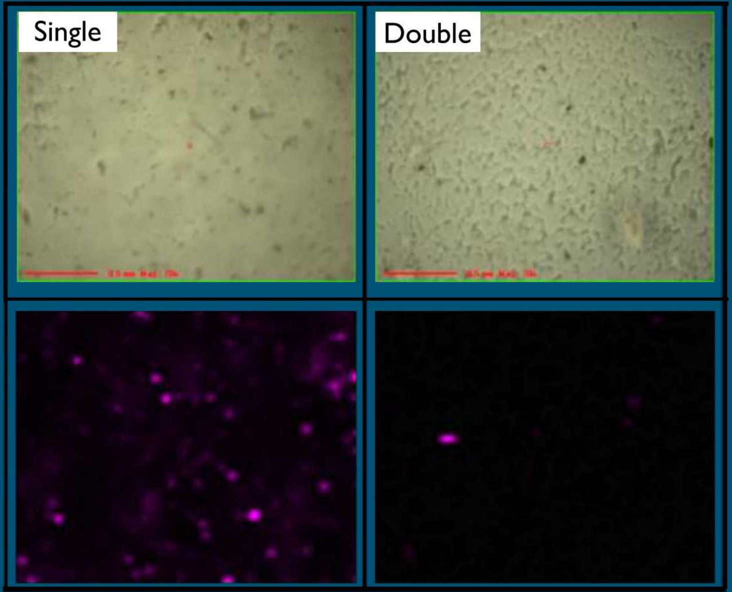
Electrochemical performance

Both sets of single cells have low polarization/resistance
- 21-27 mOhm (superior to typical pellet performance)

Significant differences between single/double separator coating
- Single-layer discharges without failure
  - Lower delivered capacity (<100 mAh/g)
  - Possible soft-shorts/defects causing quick discharge
- Double-layer delivers nearly 200 mAh/g (normalized by cathode active mass)
  - Approaches typical all-pellet performance (~225 mAh/g)
  - Second layer reduces defects in first layer (XRF elemental mapping)
  - Increase in initial high-voltage operation (undesirable)
    - Repeated wetting/drying possibly affects active materials in cathode

Printing second separator layer

Optical images (top) and XRF iron maps (bottom) showing pinhole defects (colored purple) for single and double separators



Single cell tests

Single-layer separator (~220 μm thick)			
Cell#	Delivered capacity (mAh/g)	Resistance (Ohm)	Max Voltage (V)
1	57.6	0.021	2.49
2	79.2	0.023	2.48
3	92.2	0.023	2.51

Double-layer separator (~350 μm thick)			
Cell#	Delivered capacity (mAh/g)	Resistance (Ohm)	Max Voltage (V)
1	200.3	0.027	2.69
2	192.5	0.023	2.61
3	204.5	0.022	2.61

Summary

Printable separator/electrolyte binder (EB) inks were developed for molten salt (thermally-activated batteries)

- Slurries utilize the existing pellet-based battery chemistry (LiCl-KCL electrolyte and MgO separator)
- Additional pre-dissolved LiCl leads to small particle size without complete dissolution of eutectic salt electrolyte

EB slurries undergo complex viscosity changes during processing

- Extended mixing results in smooth, stable, shear-thinning slurry
- Printed separators are uniform in appearance and thickness

Electrodes and separators can be efficiently assembled with multi-step slot-die printing process

- Separator can be printed directly on pre-printed cathode coatings
- Multiple separator layers can be added as desired

Printed multi-layer coatings can be cut to desired/custom form factor

- Single-cell electrochemical testing results show desired capacity and low polarization
- Multiple separator layers improve overall performance

Questions?

Contacts

- David Herman: dherman@sandia.gov
- Eric Allcorn: eallcor@sandia.gov

Acknowledgments:

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and 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.