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AgI Electrolytes for Printable Thermal Batteries

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Solid State Silver-Iodine Batteries

- Similar to the molten salt batteries, the solid-state silver-iodine battery is shown to have Minimal conductivity at room temperature, which extends its shelf life.
- It also shows a higher performance at a higher temperature, though it is significantly lower than the operating temperature of a molten salt battery.
- This is linked to the phase transition from the ß-AgI structure to the α-AgI structure, which takes place around 150˚C.
- Battery chemistry:

∗ **Anode:** $Ag \rightarrow Ag^+ + e^-$ (-0.80 V)*

∗ **Cathode:** $2\ Ag^+ + I_2 + 2e^- \rightarrow 2AgI$ (+0.15 V)*

∗ **Overall:** $2Ag + I_2 \rightarrow 2AgI$ (+0.95 V)*

*maximum theoretical room temperature aqueous

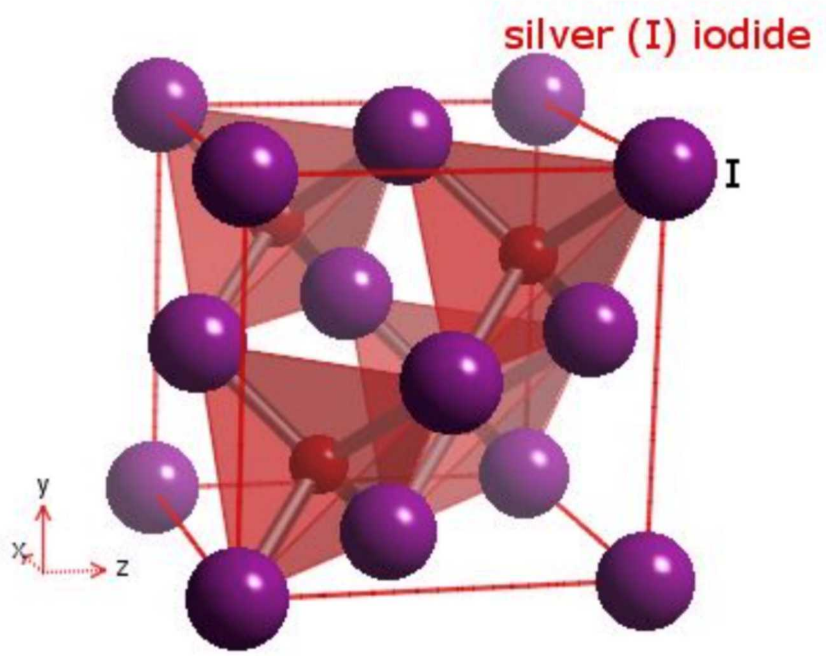
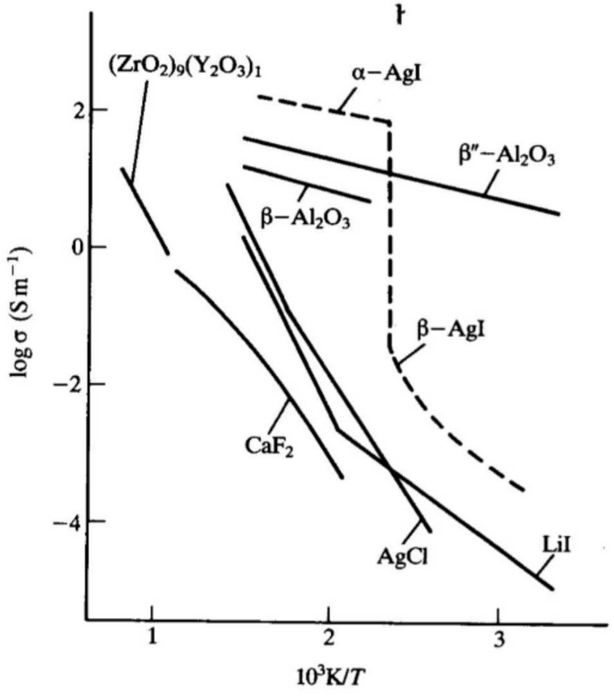


Table 2. Comparison of silver-iodine versus lithium-iodine batteries

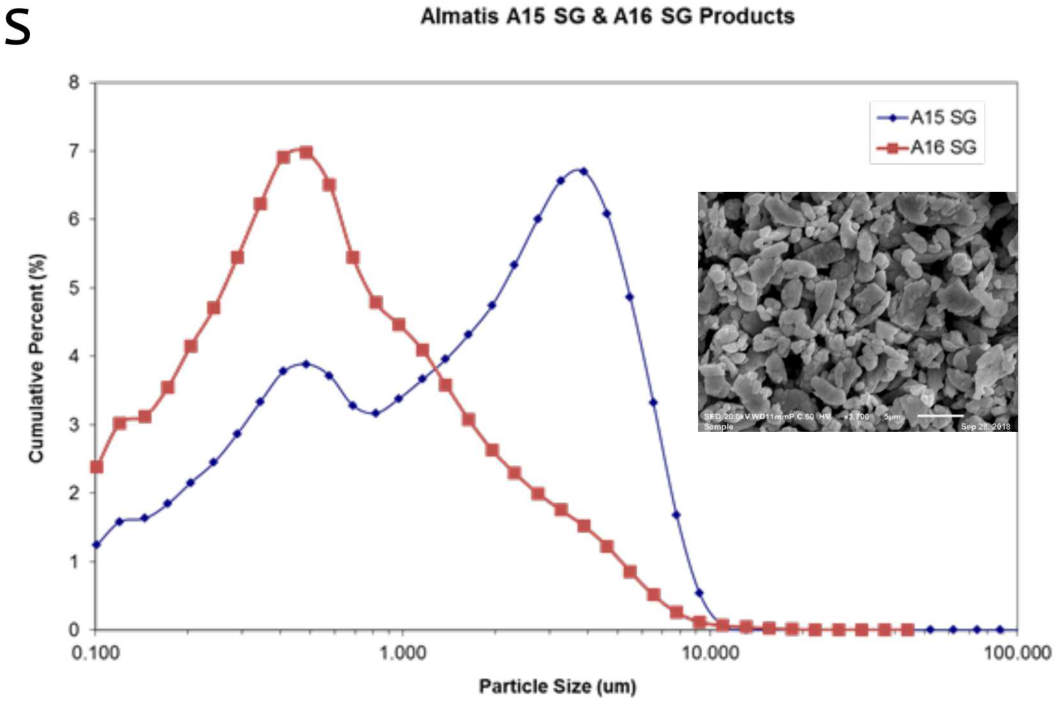
System comparison	Silver-Iodine Battery	Lithium-Iodine Battery
Anode capacity, mAh/cm^3	2609	2047
Volumetric capacity, mAh/cm^3	882	549
Cell voltage, V	0.7	2.8
Volumetric energy density, mWh/cm^3	599	1536
Electrolyte conductivity, S/cm	~$1.0 \cdot 10^{-1}$	~$1.0 \cdot 10^{-7}$

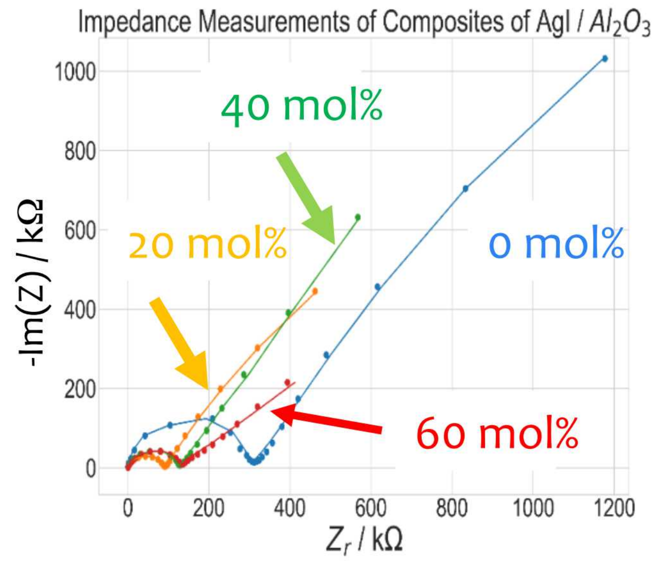
Takeuchi et al -Patent WO2017023884A1

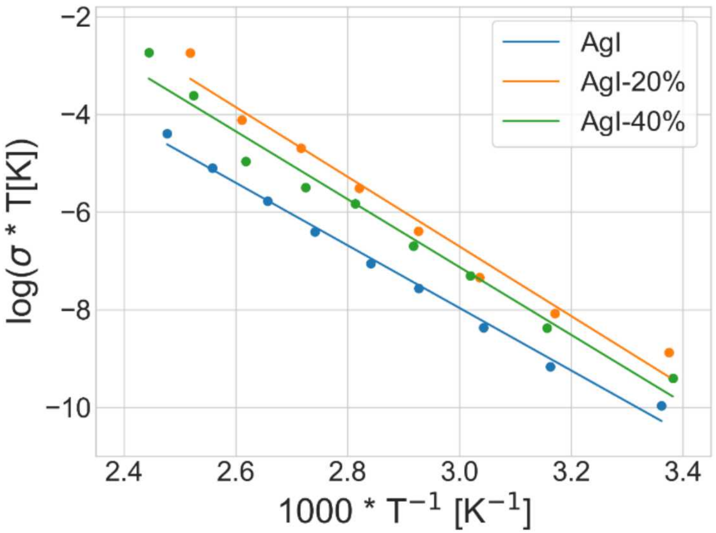


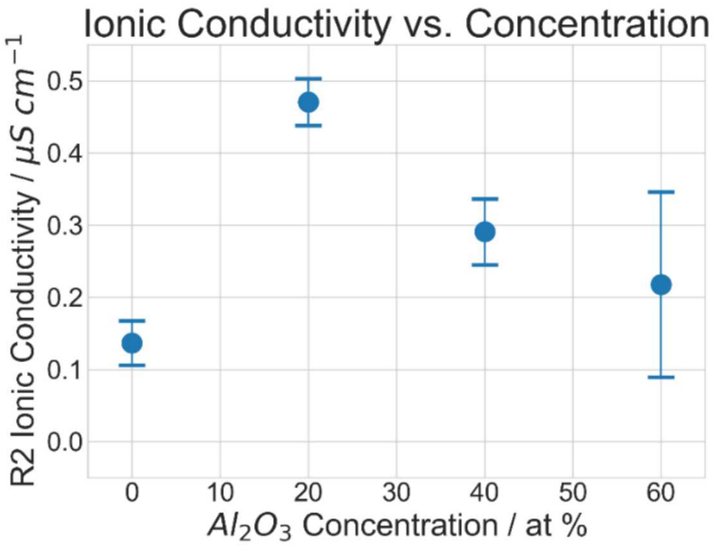
AgI/Al_2O_3 Composites

- Vacancy enhancement at composite interfaces has been suggested to enhance the conductivity of AgI.[1,2]
- Almatis A16 alumina (0.5 μm, α-phase) was ball milled into AgI and Pt/AgI-Al_2O_3/Ag cells were printed.
- Impedance measurements obtained at room temperature and fit to R1-R2||Q2-R2||Q3 equivalent circuit.
- 4.5x enhancement in ionic conductivity observed at 20%.
- Demonstrates the ability to deposit composites with AM which are difficult for traditional vapor techniques to co-deposit.









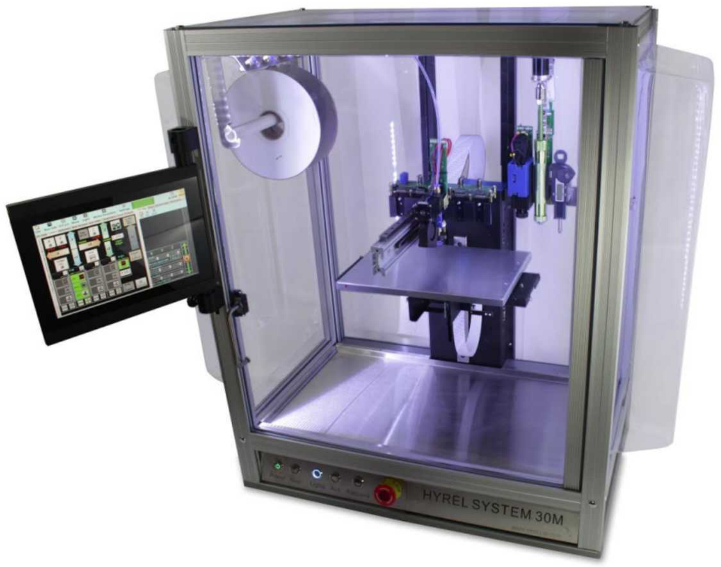
[1] J.-S. Lee, S. Adams, J. Maier, J. Electrochem. Soc. 147 (2000) 2407.
[2] J.-S. Lee, S. Adams, J. Maier, J. Phys. Chem. Solids 61 (2000) 1607–1622.

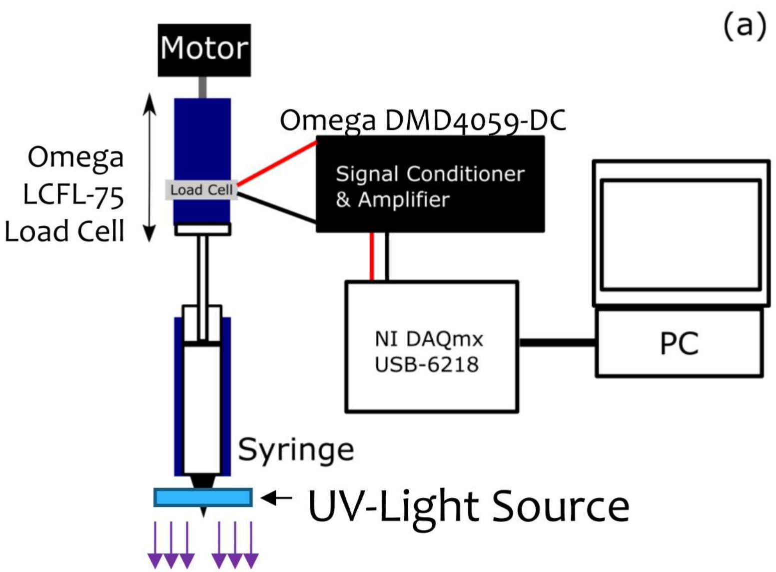
Materials Deposition by Additive Manufacturing

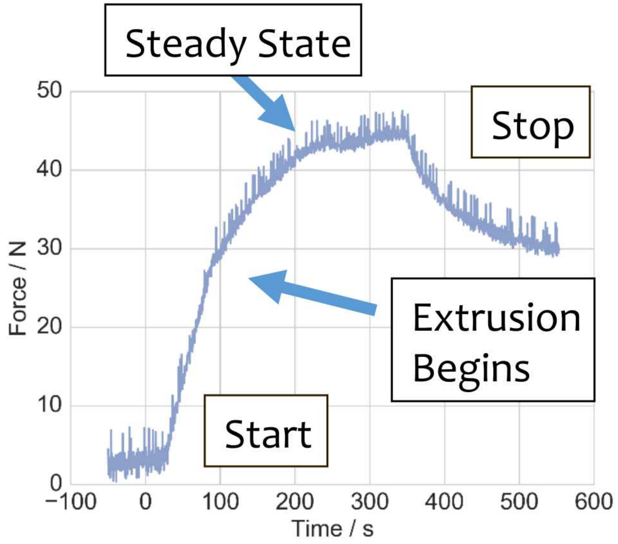
Hyrel System 30M printer – Supports several material types including pastes, gels, and plastic filaments.

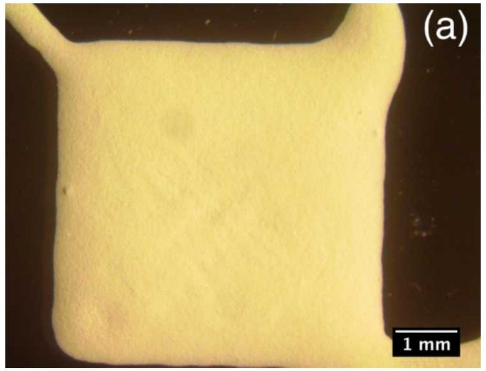
CSD-5 – 5mL Syringe head with 365 nm UV LEDs.

Modification of print head with a load cell to support force sensing.









Deposited AgI film prior to burnout

AgI powder processing:

- Milled in 0.5 mm YSZ milling media with 0.5 w% oleic acid for 4 hours in EtOH
- Crushed and sieved with 425 mm sieve.

Paste formulation:

- 65 wt% AgI
- ESL 473 Vehicle: 401 Thinner (3.5:1 by weight)
- Deposit at write speed of 7 mm/s with 0.41 mm nozzle.

Resin Burnout:

- 2 hour holds at 100, 200, 325C in air atmosphere.

Thick Film Silver Iodine Battery Preparation

Anode Preparation

- Conductive silver paste hand-printed onto either alumina composite or glass slide

Furnace Treatment

Ramp 1: 1˚C per minute to 100 ˚C

Hold 1: 100 ˚C for 2 hours

Ramp 2: 3˚C per minute to 25 ˚C

Electrolyte Preparation

#2: AgI solid state electrolyte from AgI paste

- Printed onto surface of Ag anode
- Hand printed or 3D printed with Hyrel™ 3D Printer
  - Hand printing resulted in cracking and peeling of AgI
  - 3D printing resulted in smooth deposited layer
- Heat treated for solidification:

Ramp 1: 1˚C per minute to 100 ˚C

Hold 1: 100 ˚C for 2 hours

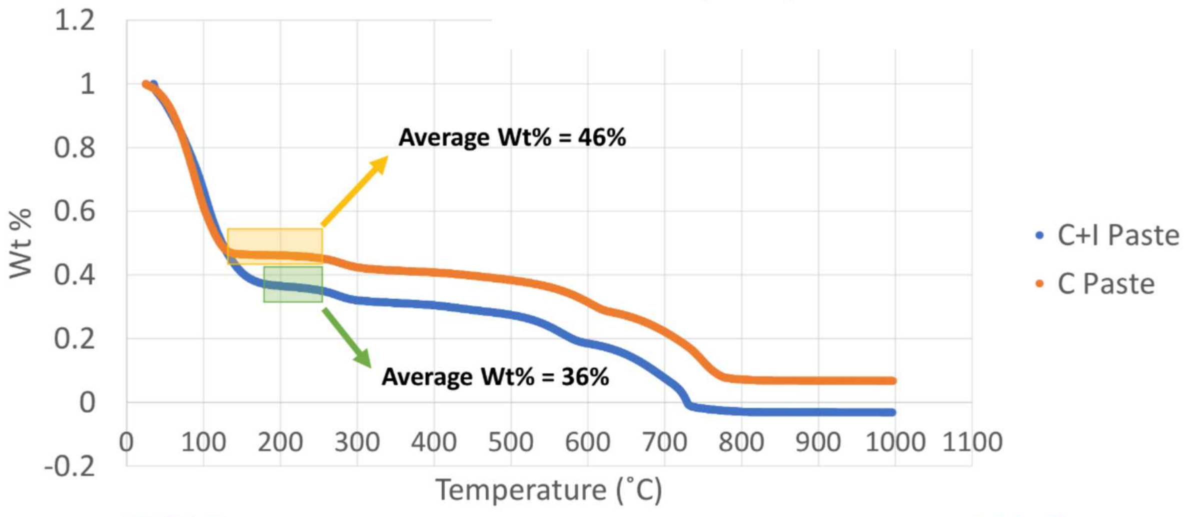
Ramp 2: 0.1˚C per minute to 200 ˚C

Hold 2: 200 ˚C for 2 hours

Ramp 3: 0.1˚C per minute to 325 ˚C

Hold 3: 325 ˚C for 2 hours

Ramp 3: 3˚C per minute to 25 ˚C



~10 Wt% of carbon iodide paste can be attributed to iodine, or 54 At%.
(Iodine B_P = 184.3 ˚C)

Cathode Preparation

Tested Cathodes:

1. Carbon Norit paste with absorbed I_2
2. PVP-I_2 powder with Vulcan XC 72 and Glycerol

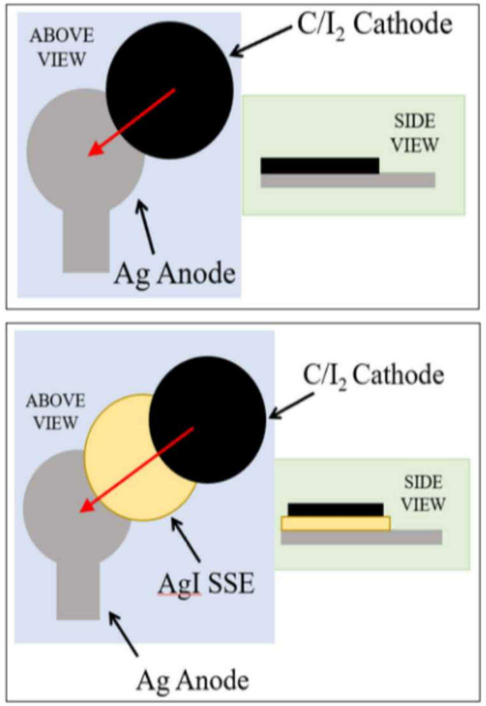
Cathode Challenges:

1. Carbon Paste

- Low conductivity
- Contact between silver and C-I_2 paste causes short circuit

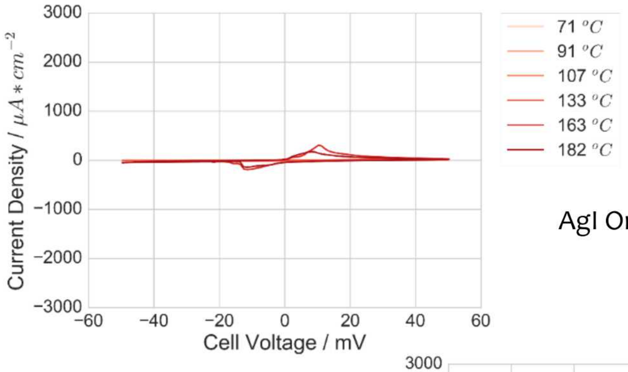
2. PVP-I_2 paste with Vulcan XC 72 and glycerol

- Glycerol compound volatilization/drying not optimized

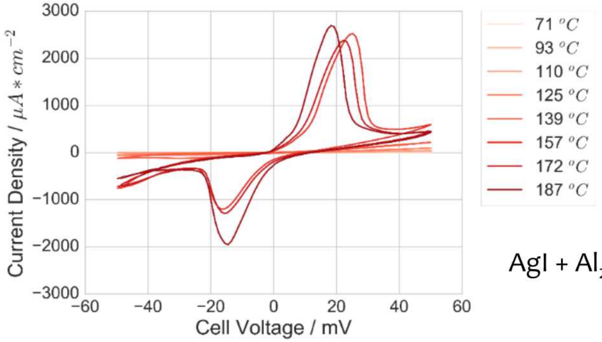


Solid State Silver-Iodine Battery Testing

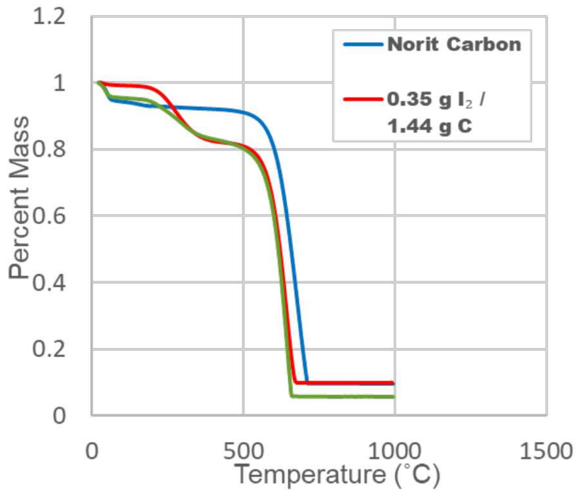
*6 **Summary:** Similar to molten salt batteries, the solid-state silver-iodine battery is shown to have low conductivity – extending shelf life – with higher performance at elevated temperature linked to a phase change in the electrolyte. This phase change is solid → liquid in molten salt batteries but in the silver-iodine system is a solid state α → β transition at roughly 150°C.

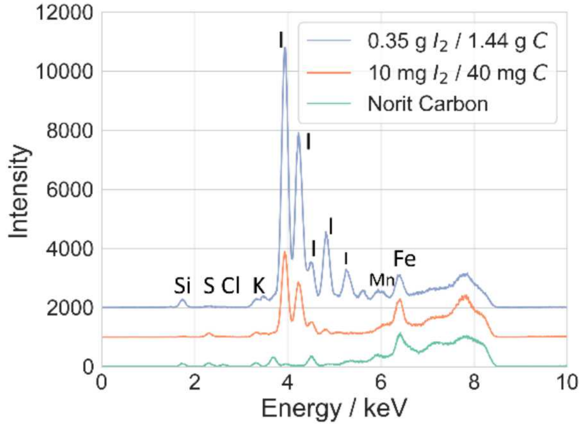


AgI Only



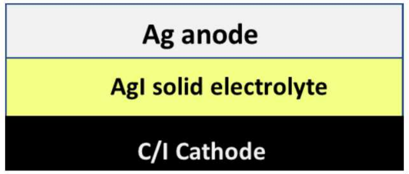
AgI + Al_2O_3

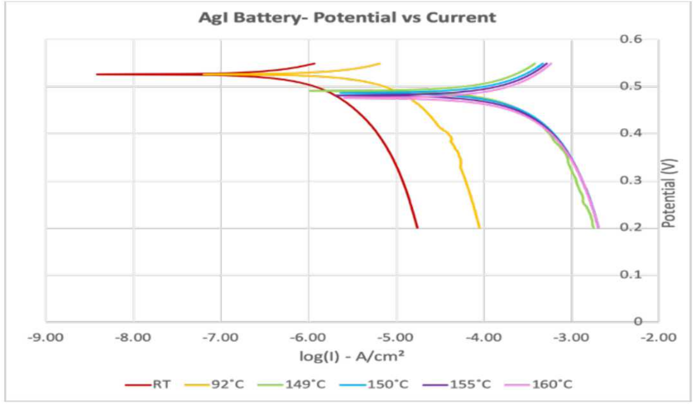




Characterization of I/C cathodes

Silver Anode Electrodeposition





Battery Fabrication and Testing

- Separate powder components layered and pressed together in a hydraulic press
- Batteries show > 0.5V with more than two order of magnitude increase in delivered current above the phase transition temperature

Summary

* Demonstrated low-temperature thermal battery chemistry
  * Alumina addition to increase AgI conductivity by 450%
  * Additive manufacturing of AgI separator layer for improved uniformity
  * Two iodine cathode fabrication techniques tested with successful iodine incorporation but limited performance success

Acknowledgements:

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