ES324
Dual Function Solid State Battery with Self-forming Self-healing Electrolyte and Separator

PI: Esther S. Takeuchi
Co-PIs: Kenneth J. Takeuchi, Amy C. Marschilok

Research Foundation for SUNY Stony Brook University
DE-EE0007785

2019 DOE VTO Annual Merit Review

Stony Brook University

Project Overview

Timeline

- Start Date: October 1, 2016
- End Date: September 1, 2019
- 83% complete

Barriers Addressed

- **Safety**: Pin holes-induced short circuit
- **Electrode/Electrolyte interface**: High interface impedance
- **Energy density**: Low Wh/L or Wh/kg

Budget

Total project funding	$1,200,000
DOE Share	$1,065,975
Contractor Share	$ 134,025
FY19 funding	$ 400,000

Partners

- Project Lead: Esther S. Takeuchi

Stony Brook University

Relevance

The proposed concept is a solid state battery utilizing lithium iodide (LiI) as the electrolyte with lithium metal as the anode and iodine as the cathode with the opportunity to meet the DOE Targets.

System characteristics	**Li/I_2**	**DOE Target**
Anode, mAh/cc	2047	
Volumetric energy density, Wh/L	1536	400
Gravimetric energy density, Wh/kg	560	250
Cell Voltage, V	2.8	

Objective 1: Develop a LiI based electrolyte conductivity of $>10^{-3}$ S/cm at 30^{o}C.

Objective 2: Form Li/I_2 batteries through the charging of the composite solid state electrolytes; determine relationship of coulombic efficiency to electrolyte type.

Objective 3: Determine the role of the anode:electrolyte interface as a function of electrolyte composition and cell test parameters through in-situ and ex-situ analyses.

Resources

Stony Brook University

Personnel

Prof. Esther Takeuchi (PI)

- Overall project planning for project reassignment and task reallocation
- Lead cell design efforts

Prof. Kenneth Takeuchi (Co-PI)

- Lead materials characterization efforts and development of analysis methods

Prof. Amy Marschilok (Co-PI)

- Lead cell testing and functional characterization efforts

Graduate student researchers

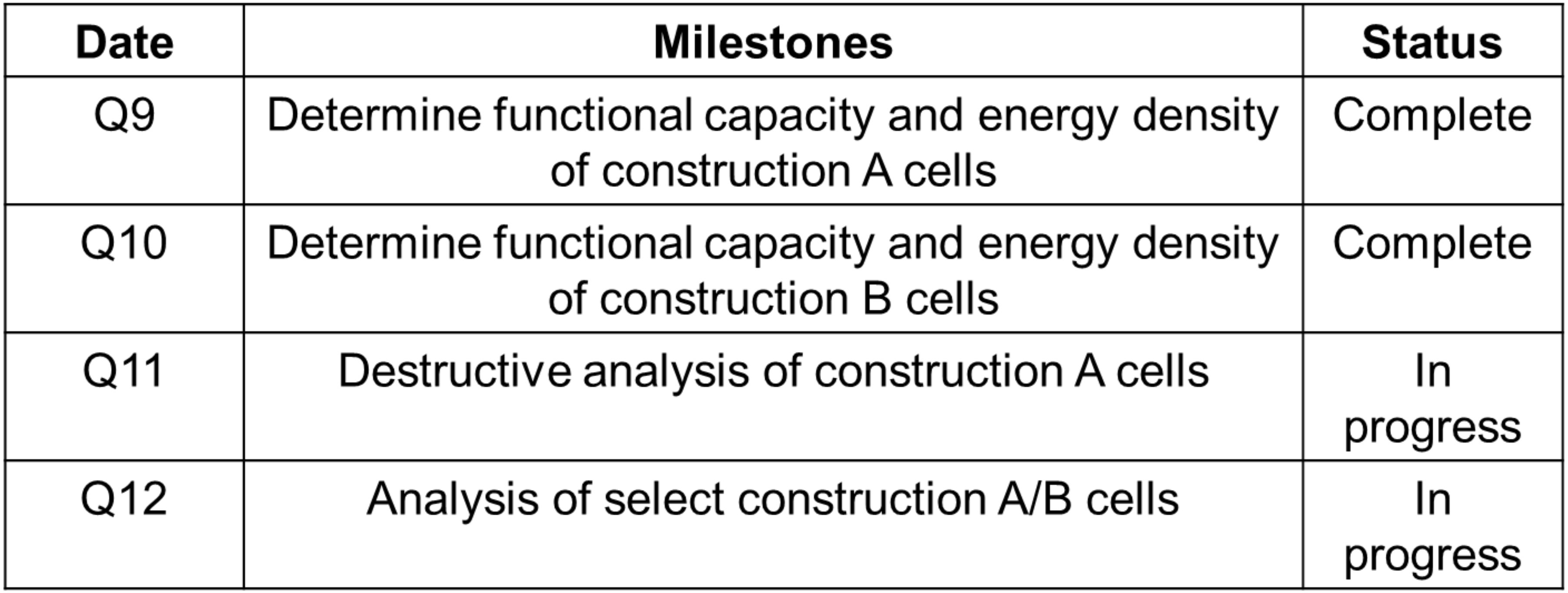
- Execute data collection and data analysis tasks

Facilities

Laboratories within the Chemistry Department and Advanced Energy Research and Technology Center at Stony Brook University

- Extensive materials synthesis and characterization tools
- Cell assembly capability in both glovebox and dry room
- Electrochemical potentiostats, cyclers, AC impedance instruments

Milestones for FY19



Date	Milestones	Status
Q9	Determine functional capacity and energy density of construction A cells	Complete
Q10	Determine functional capacity and energy density of construction B cells	Complete
Q11	Destructive analysis of construction A cells	In progress
Q12	Analysis of select construction A/B cells	In progress

Approach

The proposed solid state battery utilizes lithium iodide (LiI) combined as the electrolyte with lithium metal as the anode and iodine as the cathode with the proposal of a self-forming self-healing separator/electrolyte.

Mechanism of **Li/I_2 solid state battery**:

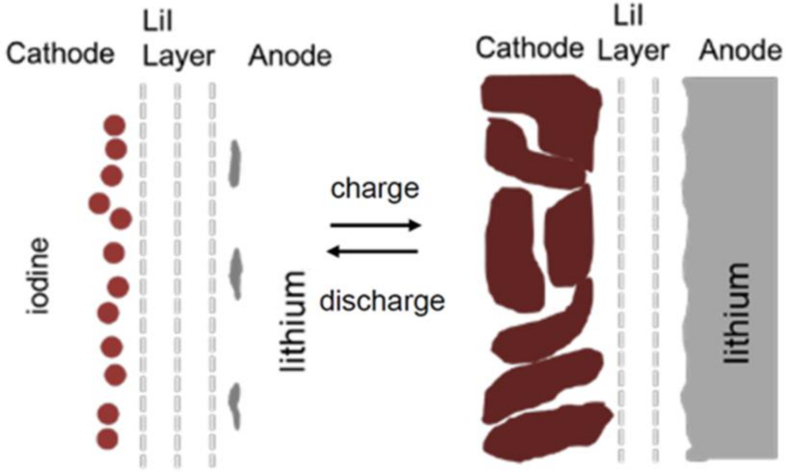
Charge:

$Li^+ + e^- \rightleftharpoons Li$ (anode)

$I^- \rightleftharpoons \frac{1}{2} I_2 + e^-$ (cathode)

Discharge:

$\frac{1}{2} I_2 + Li \rightleftharpoons LiI$



<u>Benefits of approach:</u>

High volumetric energy density

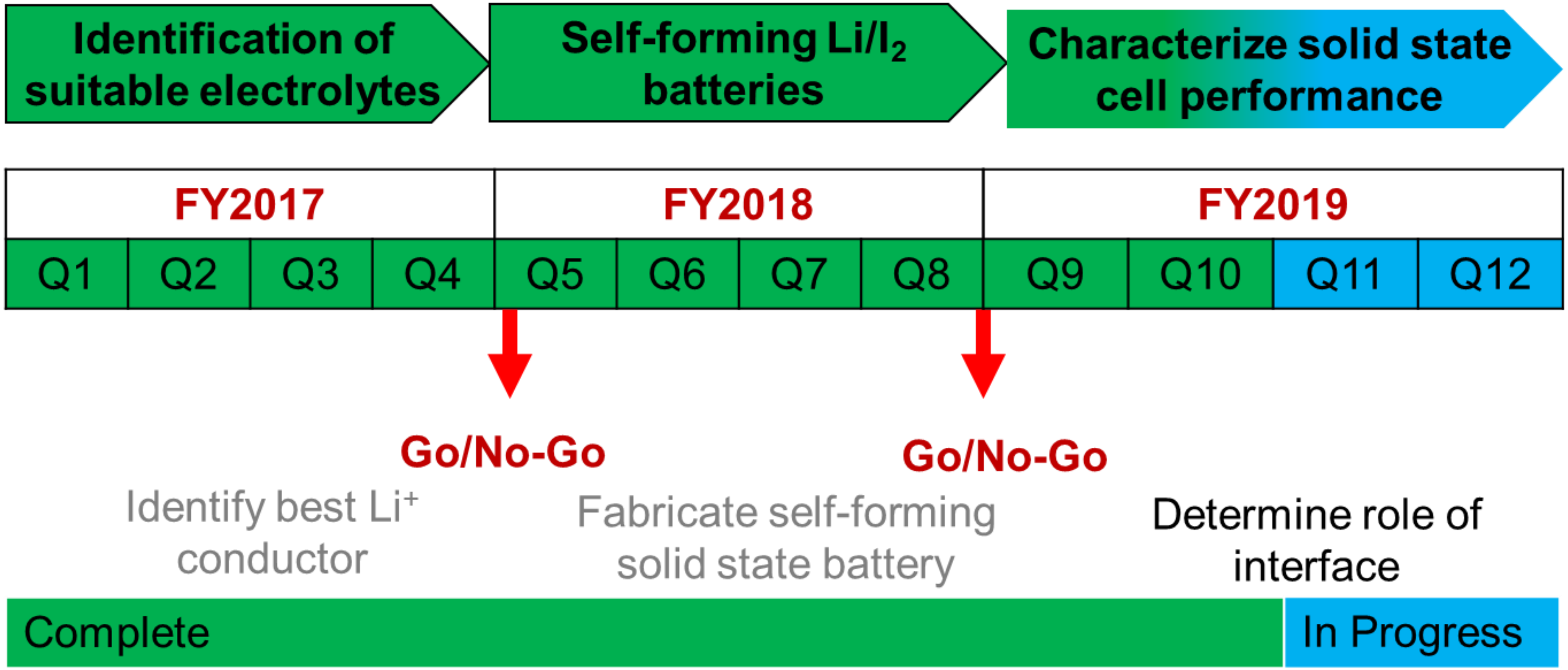
High gravimetric energy density

Facile assembly, few parts required

No flammable electrolyte

Self-forming, self-healing separator/electrolyte to provide high reliability

Project Objectives and Project Status



Identification of suitable electrolytes

Self-forming Li/I_2 batteries

Characterize solid state cell performance

FY2017				FY2018				FY2019			
Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12

Go/No-Go

Identify best Li^+ conductor

Go/No-Go

Fabricate self-forming solid state battery

Determine role of interface

Complete

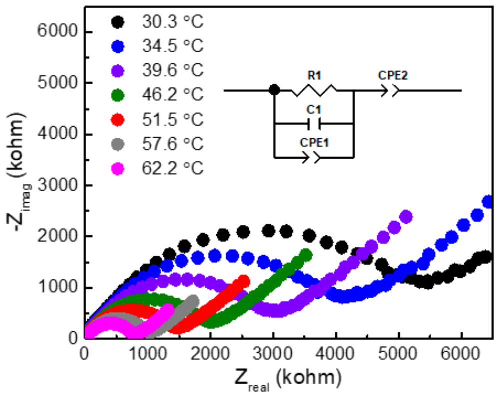
In Progress

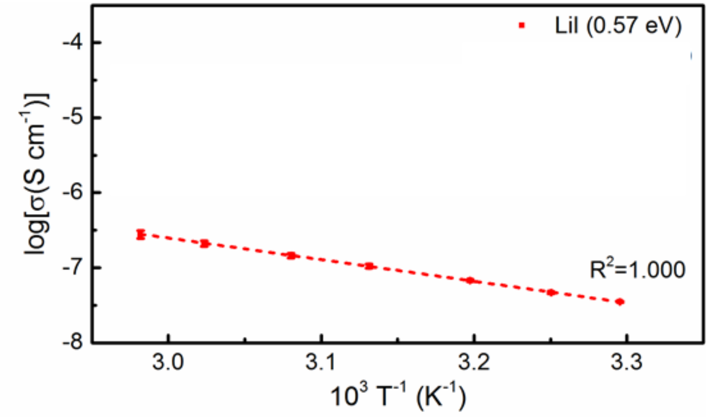
Currently:

- Studying the effects of the interface on Coulombic efficiency
- Evaluating role of self-healing capability

Technical Accomplishments and Progress

Characterization of pure LiI cation conductor as solid electrolyte, Conductivity ~ 10^{-7} S/cm





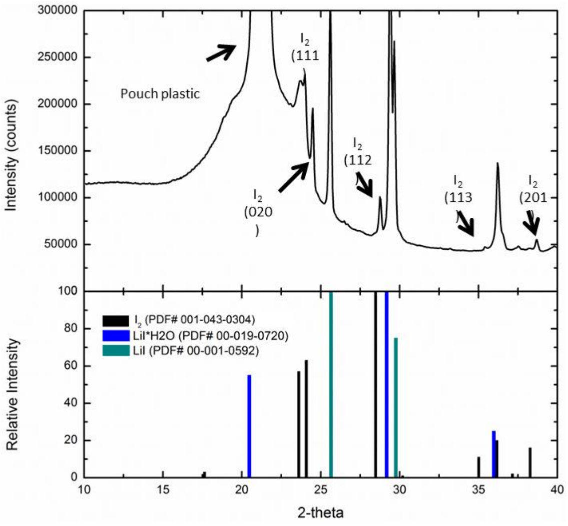
$$R = \frac{\rho l}{S}$$

$$\sigma = \frac{l}{RS}$$

$$\sigma = \sigma_0 e^{-E_a/k_BT}$$

$$ln\sigma = ln\sigma_0 - E_a/k_BT$$

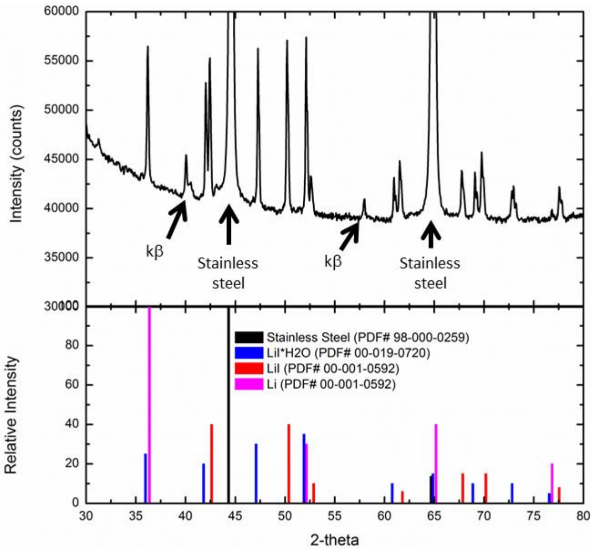
Verification of successful cell formation under potential hold.



Cells charged under potential hold.

Left: I_2 clearly identified by XRD on oxidized side of solid state electrolyte (SSE)

Right: peaks consistent with Li formation observed on reduced side of SSE.

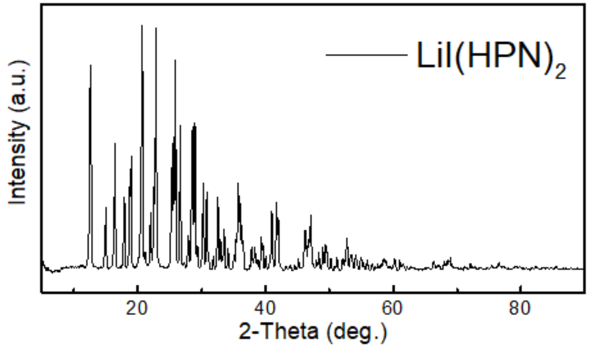


Technical Accomplishments and Progress

Preparation of LiI- $LiI(HPN)_2$ composite SSE

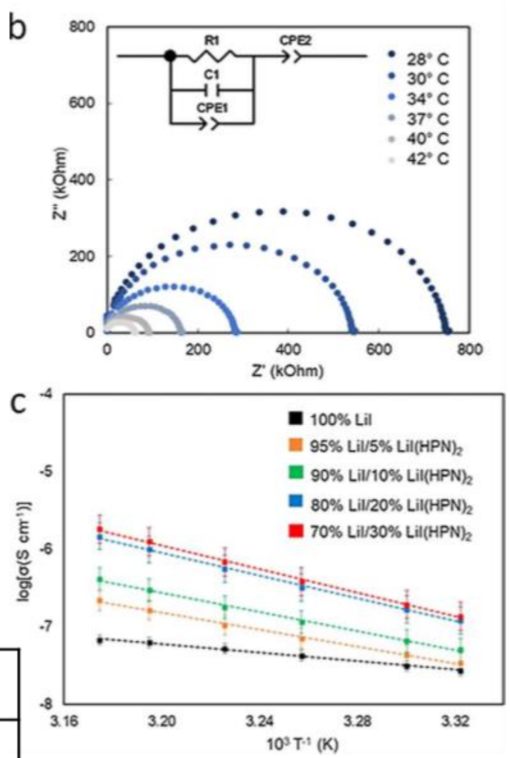
LiI(3-hydroxypropionitrile)$_2$ – anion conductor

Chemical formula: $LiI(C_3H_5NO)_2$



Pure $LiI(HPN)_2$ was synthesized and characterized by XRD

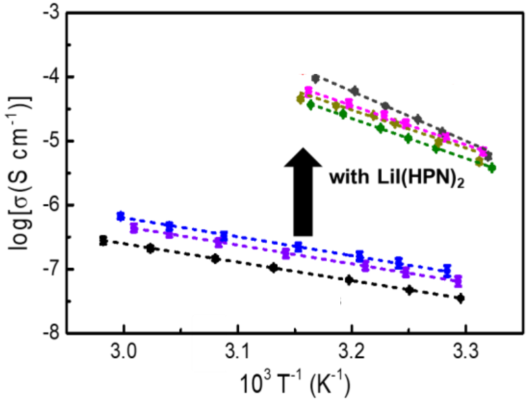
Sample	Conductivity (S/cm, 30 °C)
LiI	**$(3.5 \pm 0.1) \times 10^{-8}$**
LiI:HPN = 2:1	$(1.4 \pm 0.5) \times 10^{-5}$
LiI:HPN = 2.25:1	$(1.1 \pm 0.2) \times 10^{-5}$
LiI:HPN = 1:4	**$(1.0 \pm 0.1) \times 10^{-3}$**



Prepared series of composites with LiI and LiI:HPN (2:1)

Determined conductivity as a function of temperature

LiI-$LiI(HPN)_2$ solid electrolytes are 1-3 orders of magnitude higher conductivity relative to LiI.



Technical Accomplishments and Progress

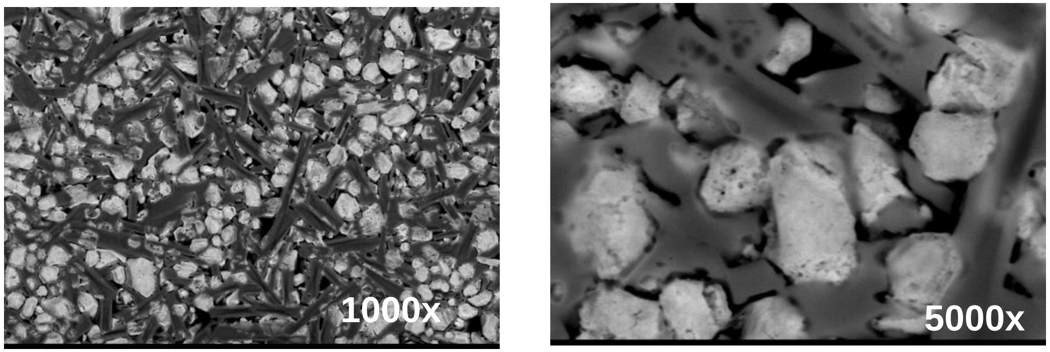
SSE composed of LiI and LiI(HPN)$_2$

SEM Backscatter Imaging:

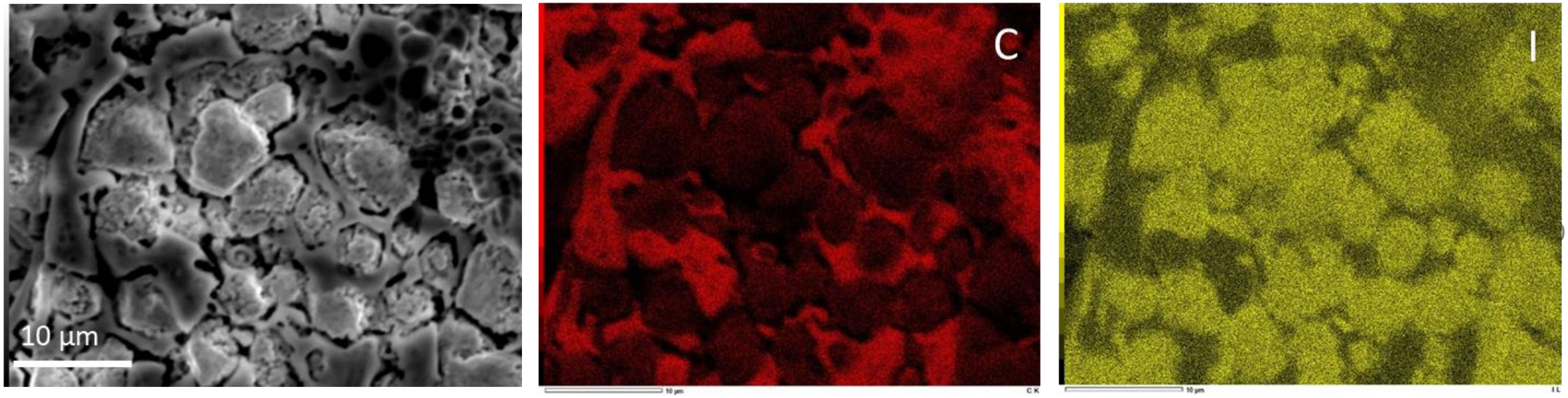
Verified consistent morphology on surface and throughout electrode thickness

LiI(HPN)$_2$ is irregularly shaped and surrounds aggregates (~ 5-6 microns) of LiI

SEM Solid Electrolyte Surface



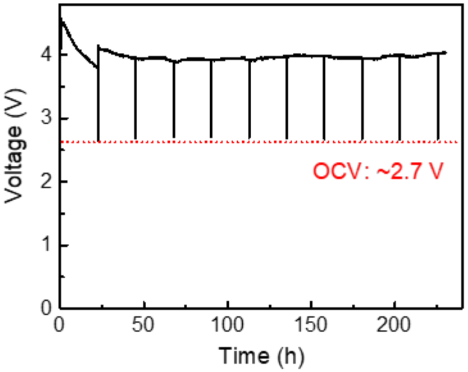
LiI(HPN)$_2$ can be clearly distinguished from LiI via EDS mapping for Carbon (center panel) and Iodine (right panel)



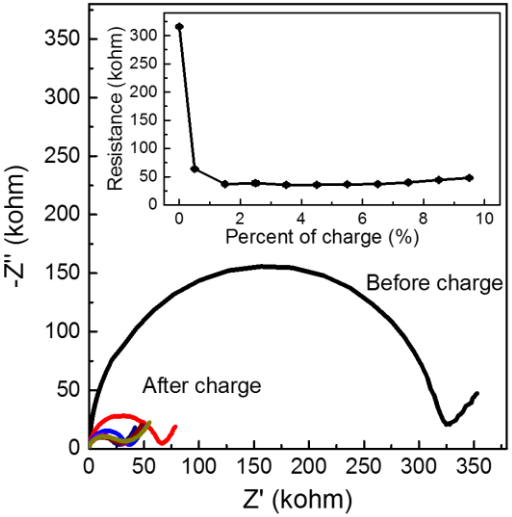
Technical Accomplishments and Progress

Successful construction of self-forming battery demonstrated

Determined 9 fold decrease in impedance after 1.5% charge



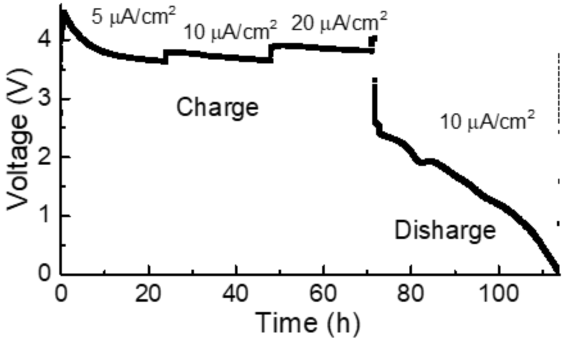
Intermittent charge of 80%LiI-20%LiI(HPN)$_2$ cell under 10 μA/cm^2

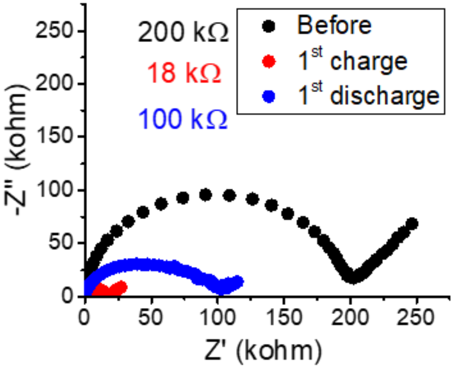


Depth of charge	Impedance
0	316 kΩ
0.5%	64 kΩ
1.5%	37 kΩ

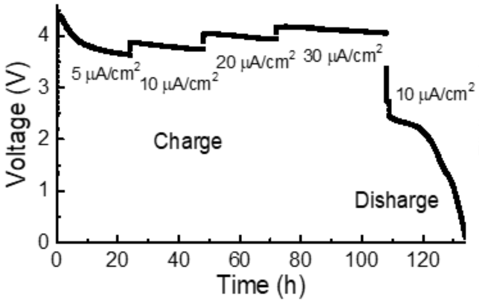
Decreased resistance upon charge enables step charging

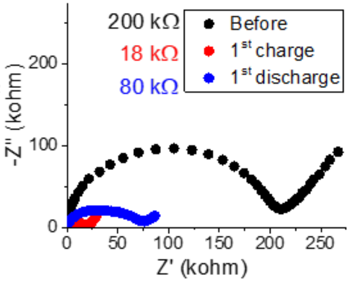
Charge capacity: ~0.68 mAh (~5%)





Charge capacity: ~1.36 mAh (~10%)





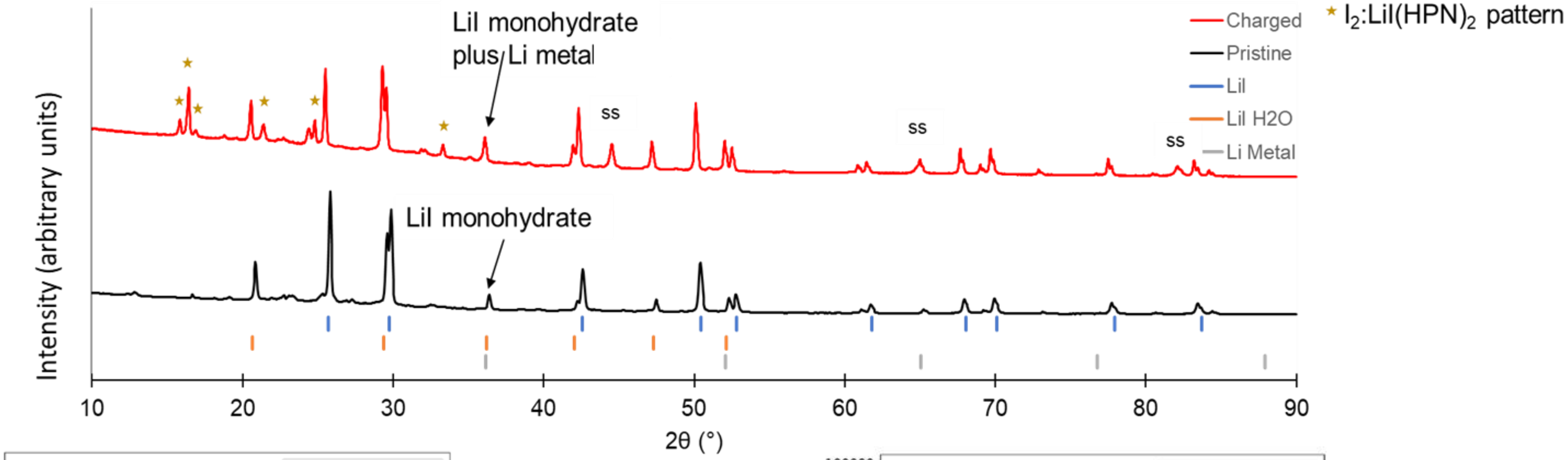
A. Abraham, J.P. Huang, P.F. Smith, A.C. Marschilok, K.J. Takeuchi, E.S. Takeuchi, *J. Electrochem. Soc.*, **2018,** *165(10),* A2115.

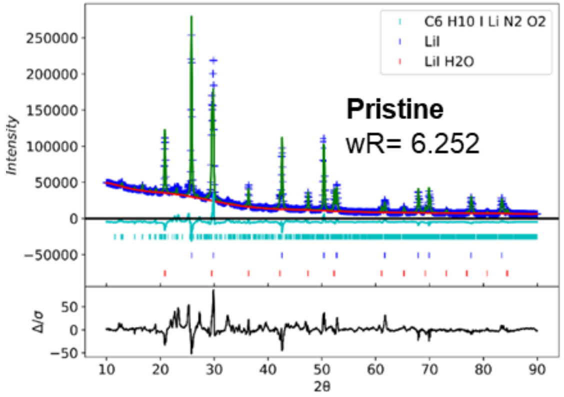
Solid Electrolyte Characterization: Post-charging XRD

XRD obtained of the negative side of the de-crimped solid electrolyte coin cell post charging to 58% capacity

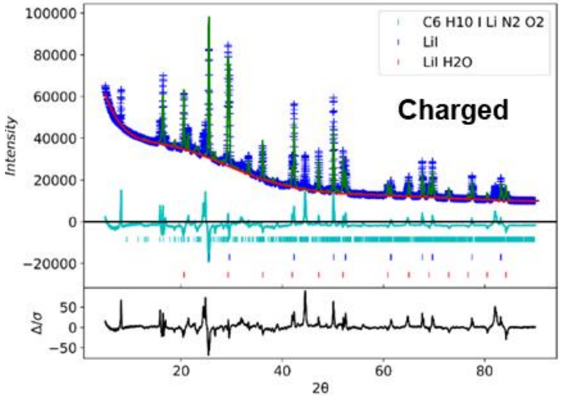
Compared to the pristine solid electrolyte, peaks (starred) were observed corresponding with the I_2-LiI$(HPN)_2$ complex

An increase in intensity was observed at 36.1° 2θ, which is associated with both the LiI monohydrate and strongest observable peak with Li metal. The increase of intensity would be consistent with formation of Li metal.





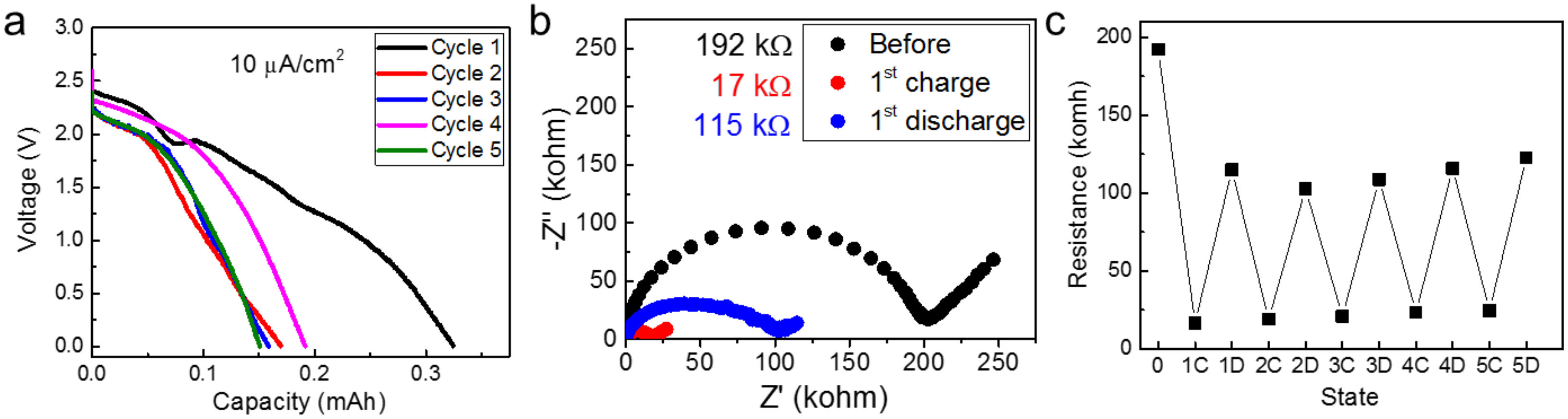
Weight Fraction:
LiI: 0.53 ± 0.01
LiI H_2O: 0.374 ± 0.003
LiI$(HPN)_2$: 0.09 ± 0.01



The presence of I_2:LiI$(HPN)_2$ peaks in the charged sample is observed.

Impedance Response to Charge/Discharge

The impedance changes as a function of charge and discharge.



Discharge capacity > 0.15 mAh at a current density of 10 μA/cm^2

The impedance values after charge/discharge are lower than the impedance before test, implying improved electrode/electrolyte interface after charging

Investigations of interfacial impact on Coulombic efficiency

Possible factors considered regarding Coulombic efficiency:

Lithium metal surface not fully formed on charge

- Investigate addition of thin lithium metal foil to negative interface

Decrease interfacial resistance of solid electrolyte and current collector

- Add thin layer of Au on surface of current collector

Iodine diffuses after formation

- Add carbon (CNTs) to adsorb iodine after formation at positive interface
- Incorporate iodine – P2VP on cathode interface

Formation of lithium dendrites and shorts results in lower efficiency

- Increase surface area for lithium deposition by adding CNT substrate
- Mimics anode of lithium ion cell versus lithium metal cell

Studies on interface modification – 5 configurations

Cell Construction A Studies

AI. Stainless steel/electrolyte/stainless steel

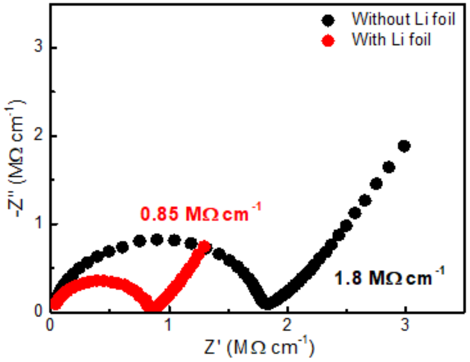
AII. Lithium/electrolyte/stainless steel

AIII. Lithium/electrolyte/Au

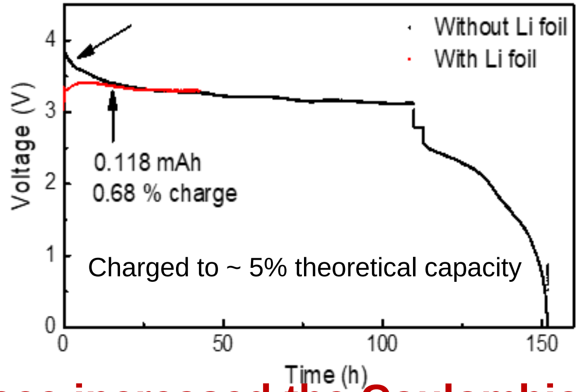
AIV. Au/electrolyte/Au

Modification of the interface: Impact on impedance and initial charge

Li metal at the anode ***lowers initial interfacial resistance***

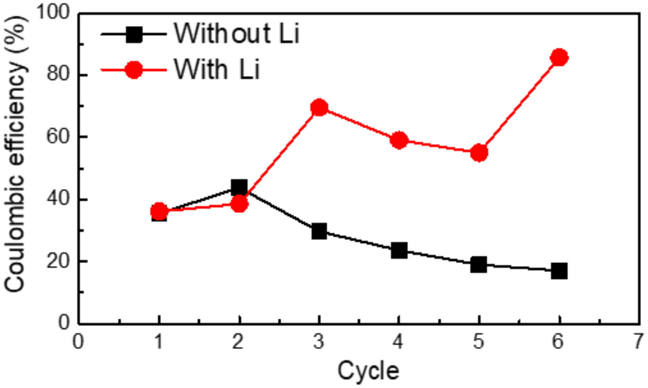


First cycle of LiI /LiI(HPN)$_2$ cell with and without Li foil



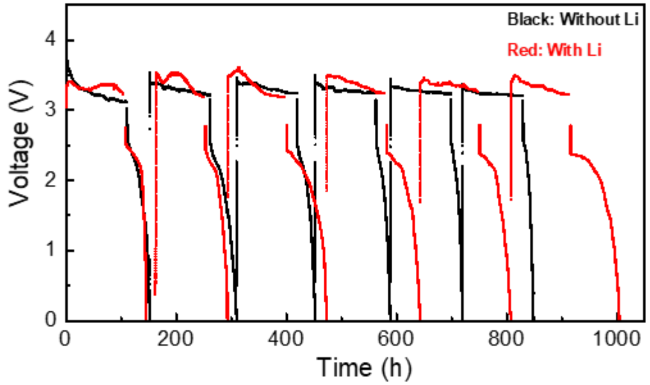
After ~0.7% charge, voltages of the two cells are similar, which may be attributed to in-situ formation of Li metal at the negative interface making both cells more similar.

Addition of Li metal interface increased the Coulombic efficiency of solid electrolyte cells



Cycle	1	2	3	4	5	6
DOD	1.8 % (0.31 mAh)	2.2 % (0.38 mAh)	1.5 % (0.26 mAh)	1.2 % (0.20 mAh)	0.93 % (0.16 mAh)	0.87 (0.15 mAh)
Coulombic efficiency	35 %	44 %	30 %	24 %	19 %	17 %

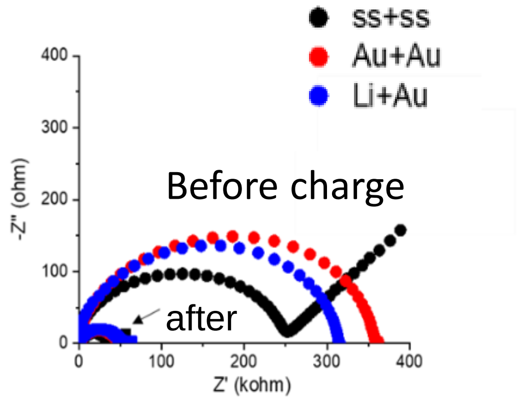
Without Li foil

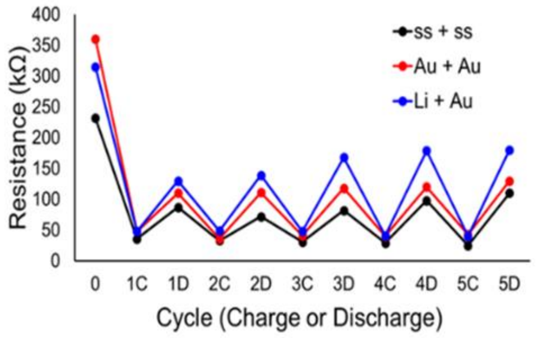


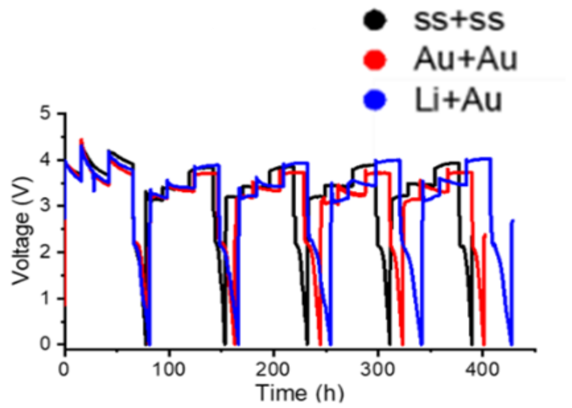
Cycle	1	2	3	4	5	6
DOD	1.8 % (0.29 mAh)	1.9 % (0.31 mAh)	3.5 % (0.57 mAh)	2.9 % (0.48 mAh)	2.8 % (0.45 mAh)	4.3 % (0.70 mAh)
Coulombic efficiency	36 %	39 %	70 %	59 %	55 %	86 %

With Li foil

Impact on the interface on Coulombic efficiency

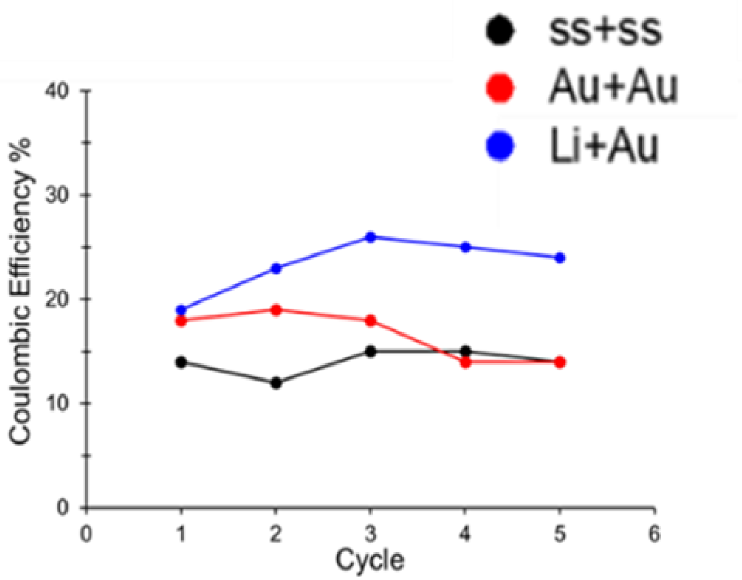






All designs showed a reduction in resistance on charge, with a gradual increase of resistance upon subsequent discharge cycles.

On full discharge, all three cell designs returned to lower resistance compared to their initial resistance values.



The cells with the lithium and gold interfaces had the highest Coulombic efficiency even though the resistance on discharge was the highest among the group.

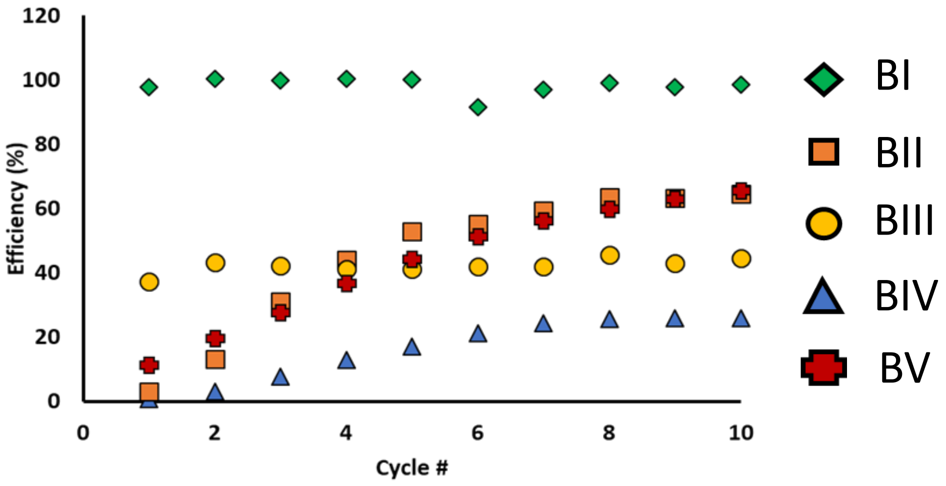
These results imply that there is some loss of active lithium leading to inefficiency that is offset by inclusion of supplemental lithium metal in the cell design.

Long-Term Cycling – 5 configurations

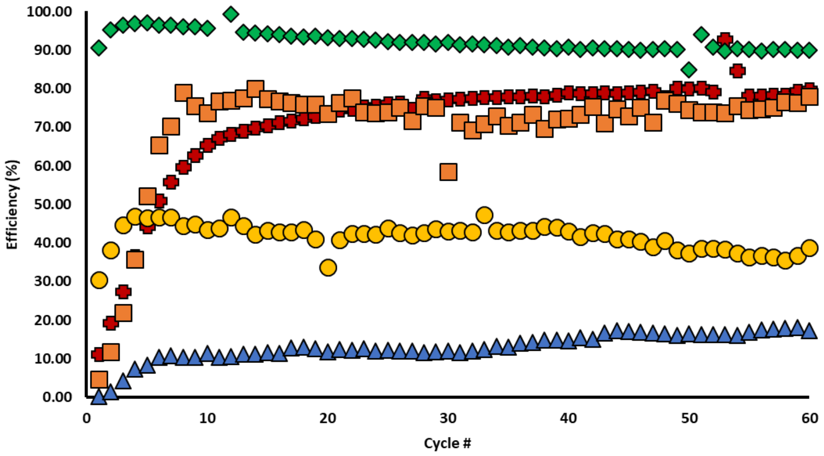
Cell Construction B consisted of 5 configurations (BI through BV)

Extended cycling displays dependence of efficiency and shorting behavior upon cell design

Cycles 1-10



Cycles 1-60



Configuration BI demonstrated > 90% efficiency for longer term cycling (over 60 cycles)

Configuration BII and BV showed marked improvement after continuous cycling

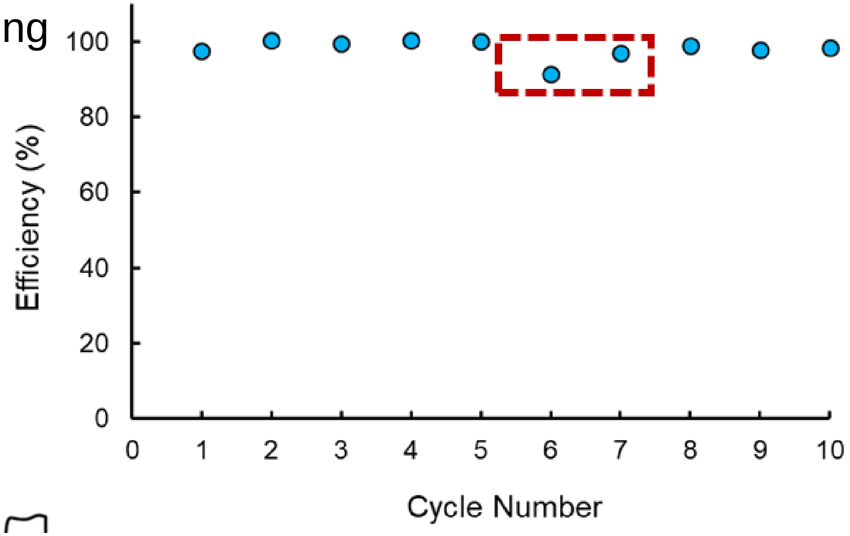
Demonstration of self healing

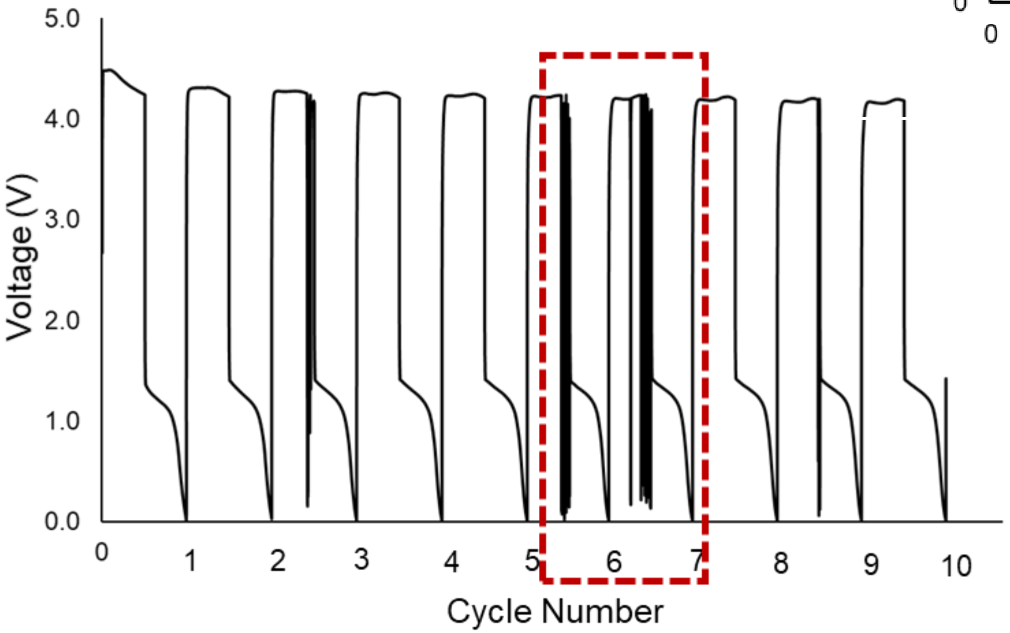
Cell shorting can be observed during charging

After a shorting event, the cell recovers

Continued cycling is possible

Confirmation of Hypothesis of self-healing

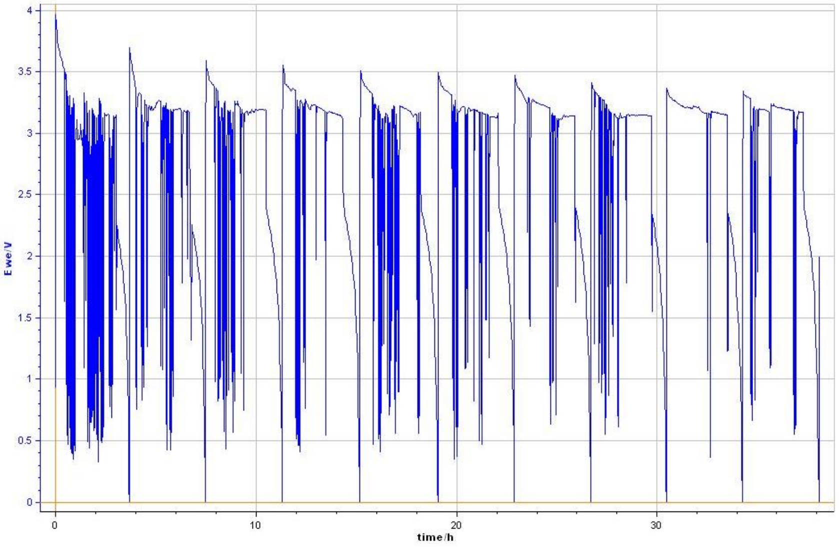




Demonstration of self healing

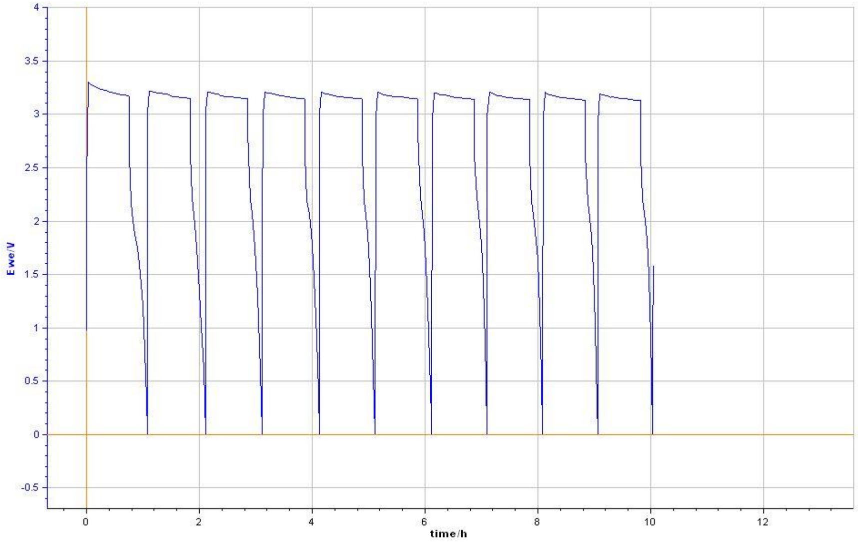
In addition to recovering from shorting behavior during cycle tests, it has been demonstrated that prior shorting behavior in a cycle test does not necessarily carry over to the next cycle test

This test run first



Current density: 2X

This test run second



Current density: 1X

Responses to Reviewer’s Comments; Collaborators; Remaining Challenges and Barriers

Responses to Reviewer Comments: N/A

Collaborations: User proposal systems actively used for interaction with Brookhaven National Laboratory and the Advanced Photon Source at Argonne National Laboratory.

Remaining Challenges and Barriers
Decrease the electrode-electrolyte interfacial impedance.
Develop modified cell construction to lower impedance and deliver higher efficiency cycling.
Utilize characterization techniques (ex-situ and in-situ) in order to probe the cell mechanisms.

Proposed Future Research

- Further investigate the role of the cathode-electrolyte interface to increase conductivity and improve efficiency.
- Continue to develop next generation cell construction (cell design B) for effective cycling of the self-forming battery.
- Utilize multiple characterization techniques to investigate cell interfaces and charged/discharged products.

Any proposed future work is subject to change based on funding levels

Summary

Program is on schedule.

Cell design and testing is under development and on track.

Electrolyte demonstrated based on salt-polymer hybrid increased conductivity by 1-2 orders of magnitude.

Demonstrated the use of step-charge to decrease total charge time.

Methods to decrease cathode/electrolyte interfacial impedance were demonstrated.

Self-formed Li anode and I_2 cathode were verified.

This solid state cell design enables self-healing. Demonstrated cell recovery after the formation of an internal short to effectively cycle.

Simple construction is possible using solid electrolyte to create the uncharged cell.

Uncharged cells can have very long shelf-life.

Theoretical volumetric energy density (1536 Wh/L)

Theoretical gravimetric energy density (560 Wh/Kg)