BAT324

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

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Research Foundation for SUNY Stony Brook University

DE-EE0007785

2018 DOE VTO Annual Merit Review

Stony Brook University

Project Overview

Timeline

- Start Date: October 1, 2016
- End Date: September 1, 2019
- 40% 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
FY17 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) combined with silver iodide (AgI) as the electrolyte with lithium (silver) metal as the anode and iodine as the cathode with the opportunity to meet the DOE Targets.

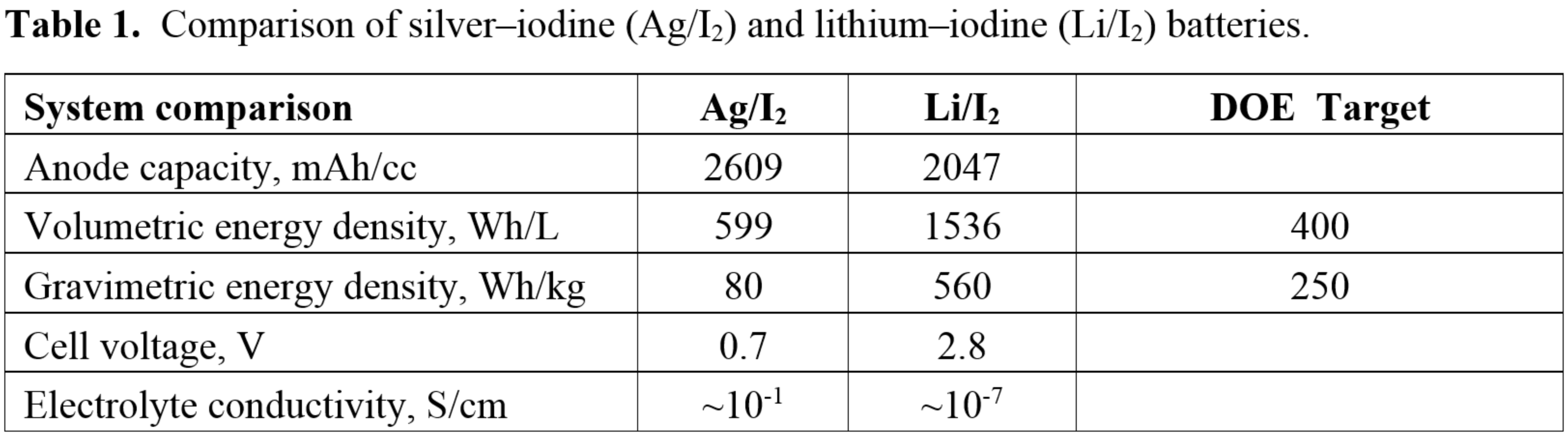


Table 1. Comparison of silver–iodine (Ag/I_2) and lithium–iodine (Li/I_2) batteries.

System comparison	**Ag/I_2**	**Li/I_2**	**DOE Target**
Anode capacity, mAh/cc	2609	2047	
Volumetric energy density, Wh/L	599	1536	400
Gravimetric energy density, Wh/kg	80	560	250
Cell voltage, V	0.7	2.8	
Electrolyte conductivity, S/cm	$\sim10^{-1}$	$\sim10^{-7}$	

Objective 1: Develop a LiI/AgI based electrolyte conductivity of $>10^{-3}$ S/cm at 30°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 Ag ion in 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 FY18

Date	Milestones	Status
Q5	Identify 3 most conductive electrolytes	Complete
Q6	Demonstrate cell construction A	Complete
Q7	Demonstrate construction A cell with most conductive electrolytes	On-track
Q8	Affirm formation of Li and I_2 at anode and cathode	On-track

Approach

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

Mechanism of **Ag-Li/I$_2$ solid state battery**:

Charge:

$$Li^+ + e^- \rightleftharpoons Li \text{ (anode)}$$

$$Ag^+ + e^- \rightleftharpoons Ag \text{ (anode)}$$

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

Discharge:

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

$$\tfrac{1}{2} I_2 + Ag \rightleftharpoons AgI$$

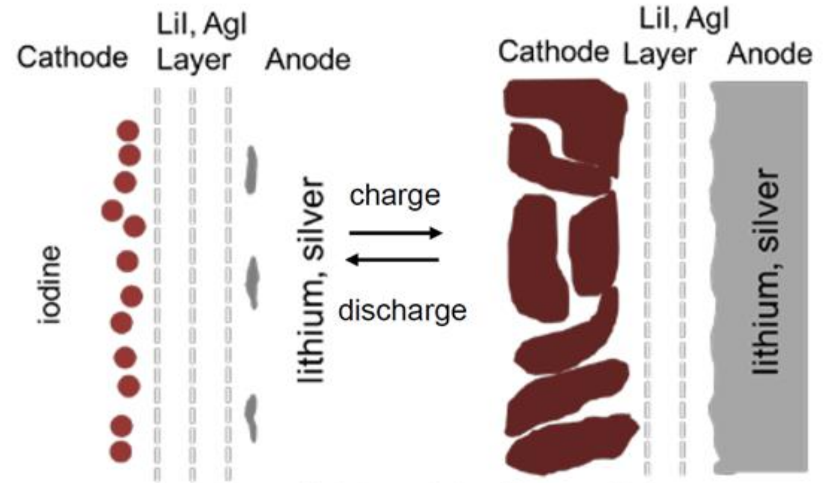


Figure 1. Silver-lithium/ iodine solid state dual function battery.

Benefits of approach:

High volumetric energy density

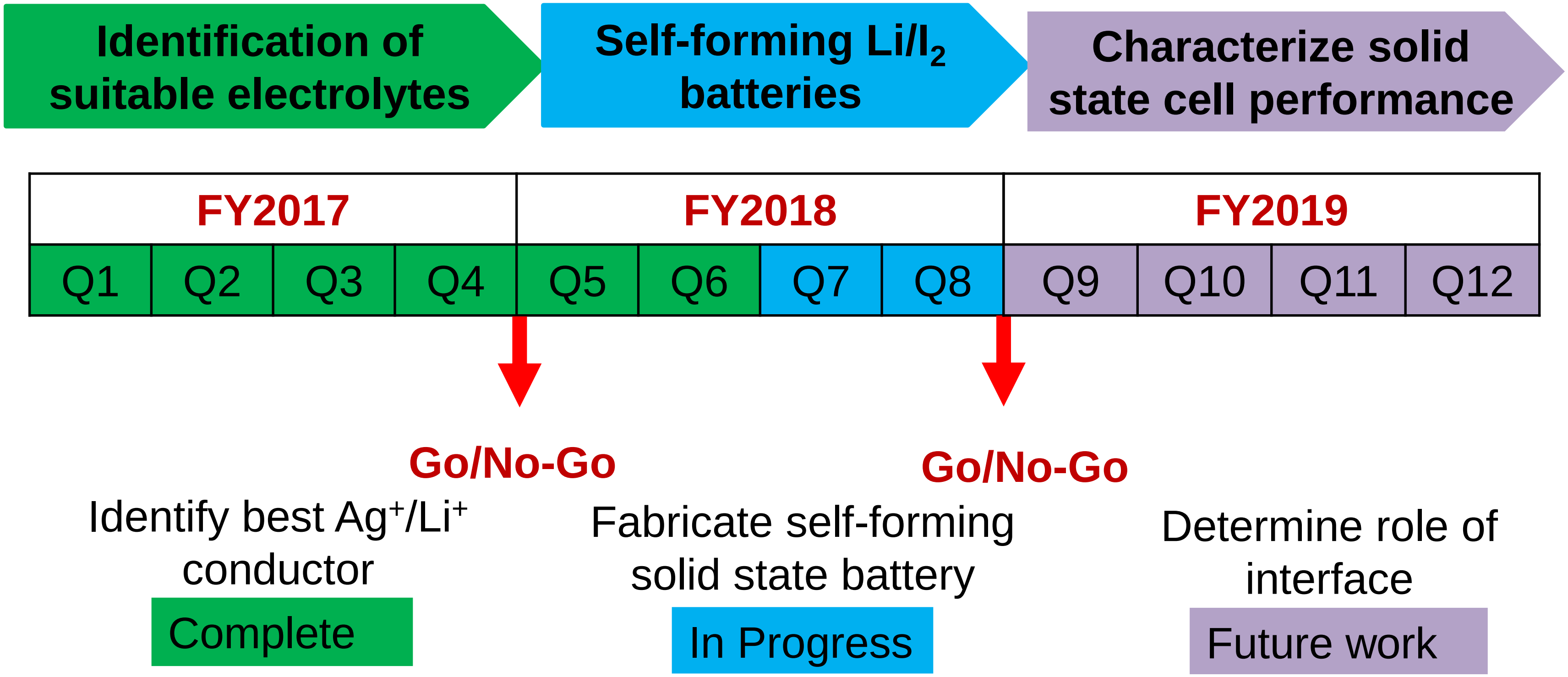
High gravimetric energy density

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

Go/No-Go

Identify best Ag$^+$/Li$^+$ conductor

Complete

Fabricate self-forming solid state battery

In Progress

Determine role of interface

Future work

Currently:

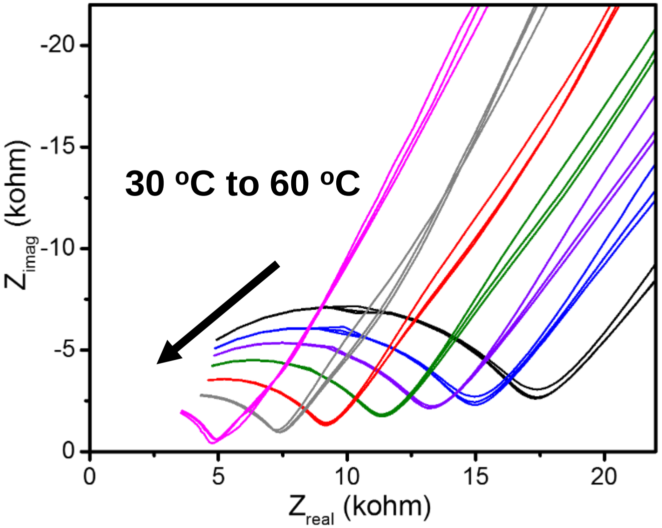
- Developing cell construction for self-forming Li/I$_2$ batteries.
- Optimizing electrolyte by incorporating polymer
- Optimizing electrode/electrolyte interfaces

Technical Accomplishments and Progress

Electrolyte conductivity measurement methods affirmed

Bulk resistance R measured by AC impedance
Triplicate data collected from 30 to 60°C

lnσ shows a linear relationship with 1/T.



400 kHz to 1 Hz

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

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

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

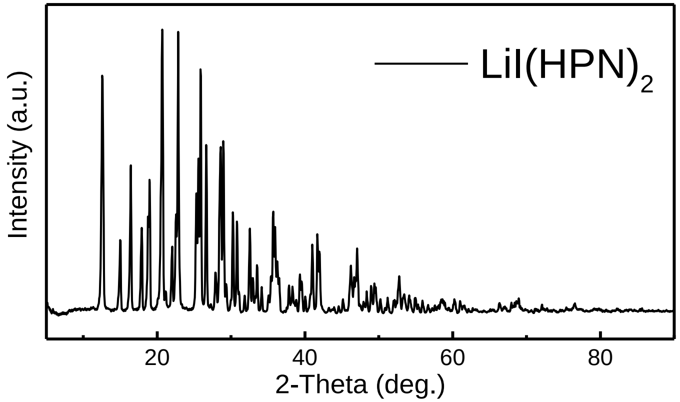
$$ln\sigma = ln\sigma_0 - E_a/k_B T$$

R is the bulk electrolyte resistance, ρ is the resistivity, *l* is the electrolyte thickness, S is the surface contact area, σ is the conductivity, E_a is the activation energy, K_B is the Boltzman constant and T is the temperature.

Equations adapted from: B.J. Neudecker, W. Weppner, *J. Electrochem. Soc.*, 1996, **143(7),** 2198-2203.

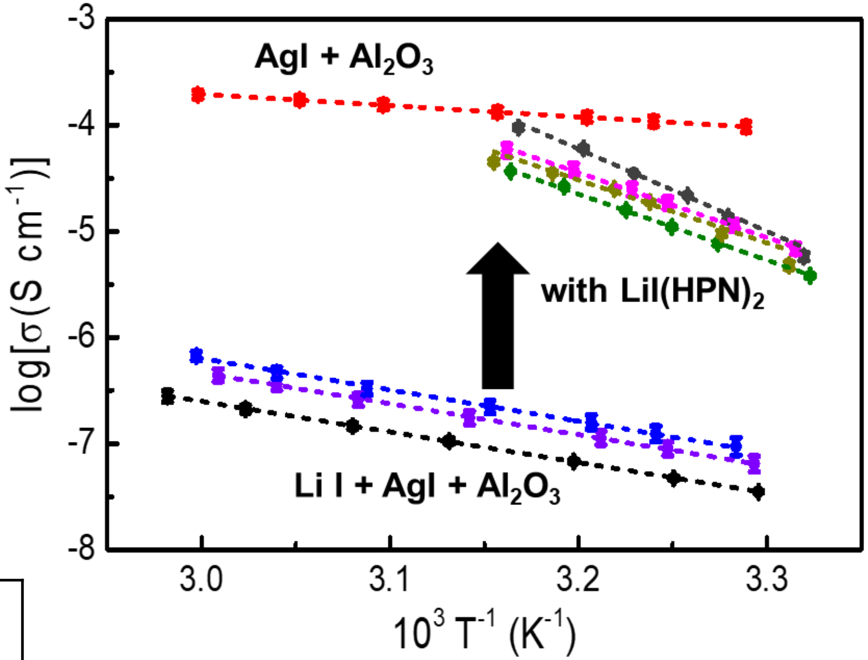
Technical Accomplishments and Progress

Demonstrated incorporation of polymer in solid electrolyte: LiI-LiI(HPN)$_2$ solid electrolytes are 1-2 orders of magnitude higher conductivity relative to LiI.



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

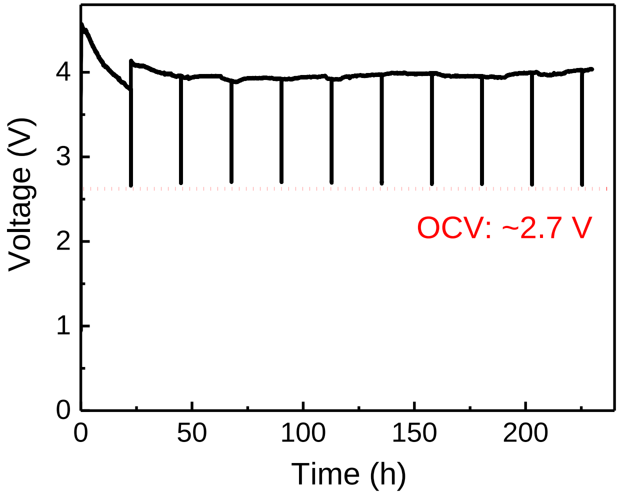
Sample	Conductivity (S/cm, 30 °C)
LiI	**(3.5 ± 0.1) × 10^{-8}**
LiI:HPN = 2:1	(1.4 ± 0.5) × 10^{-5}
LiI:HPN = 2.25:1	(1.1 ± 0.2) × 10^{-5}
LiI:HPN = 1:4	**(1.0 ± 0.1) × 10^{-3}**

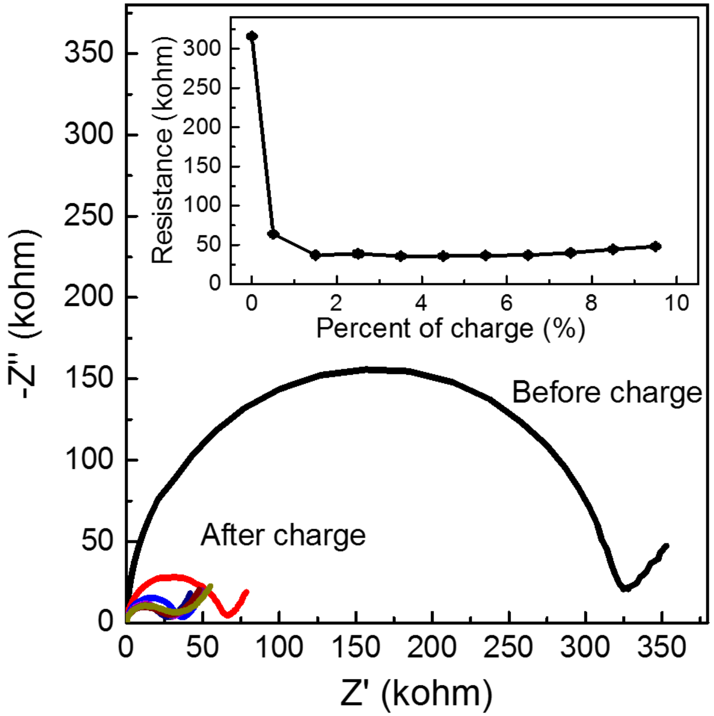


Electrolyte with conductivity ≥10^{-3} S/cm was identified

Technical Accomplishments and Progress

Cell construction A demonstrated, determined impedance as a function of charge





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

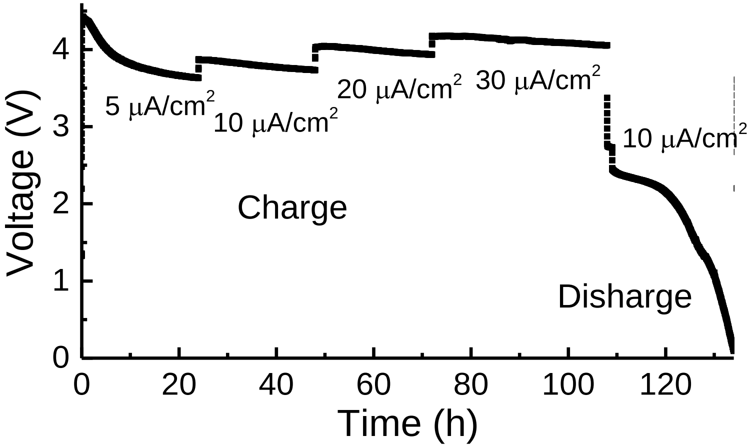
Depth of charge	**Impedance**
0	316 kΩ
0.5%	64 kΩ
1.5%	37 kΩ

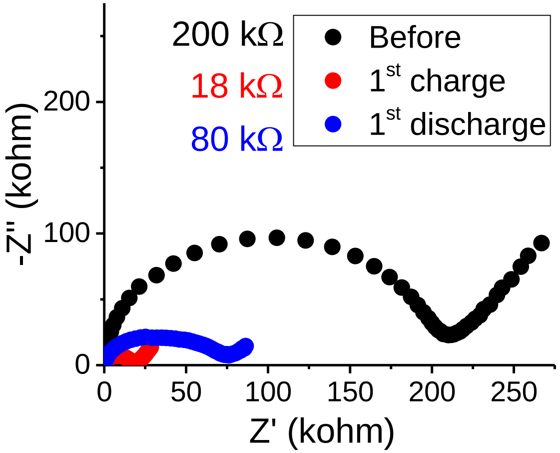
9 times decrease in impedance after 1.5% charge

Cell charge decreases resistance by more than amount due to decrease in electrolyte thickness.

Technical Accomplishments and Progress

Demonstrated feasibility of step charging





Discharge-charge curves (10% charge)

Nyquist plots before and after charge/discharge

80%LiI + 20%LiI(HPN)$_2$

Charge:
5 μA/cm^2
10 μA/cm^2
20 μA/cm^2
30 μA/cm^2

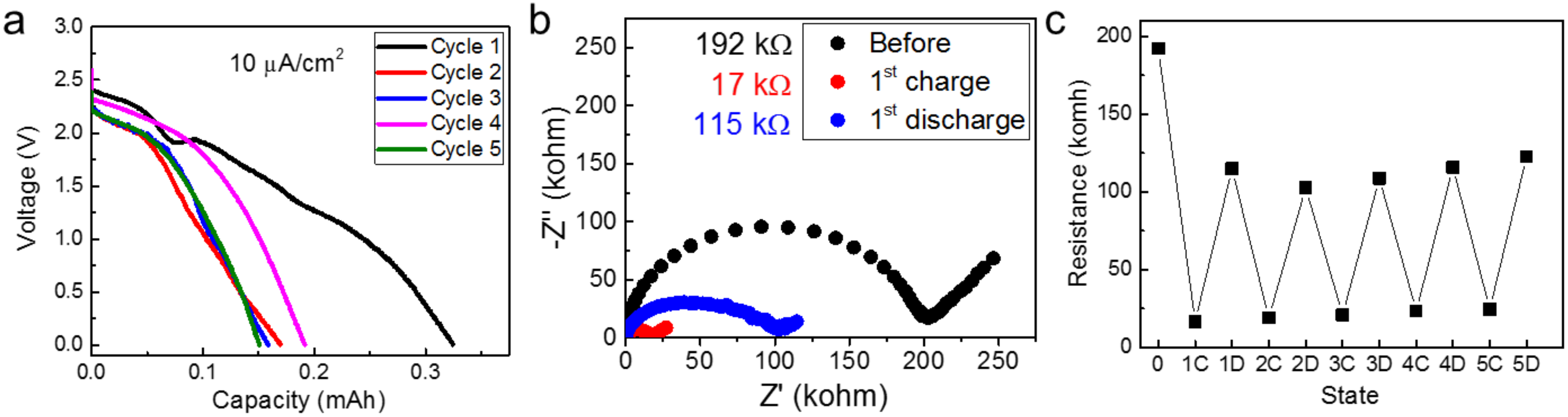
Discharge:
10 μA/cm^2

Charged capacity: ~1.36 mAh (~10%)

Decreased resistance on charging enables step charging to decrease total charge time by ~ 3X.

Technical Accomplishments and Progress

Determined evolution of impedance as a function of charge and discharge



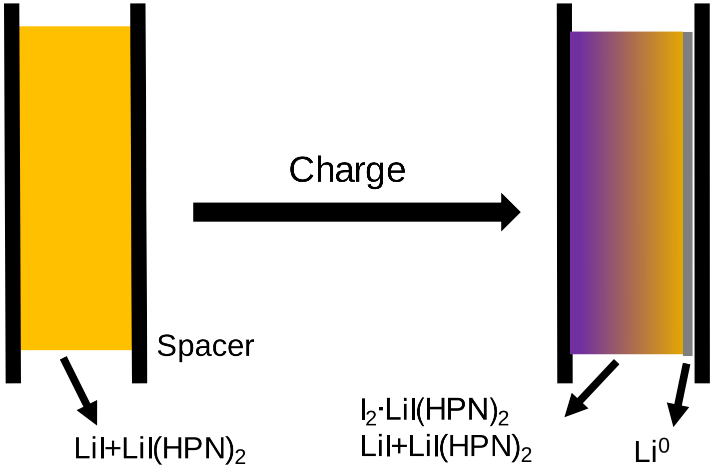
Electrochemistry of 80%LiI-20%LiI(HPN)$_2$ cell

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

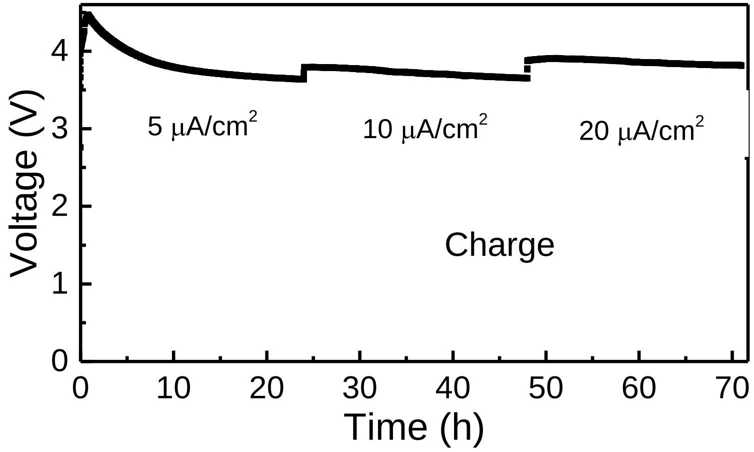
The Impedance values after charge/discharge are lower than the impedance before test, implying improved electrode/electrolyte interface after charging

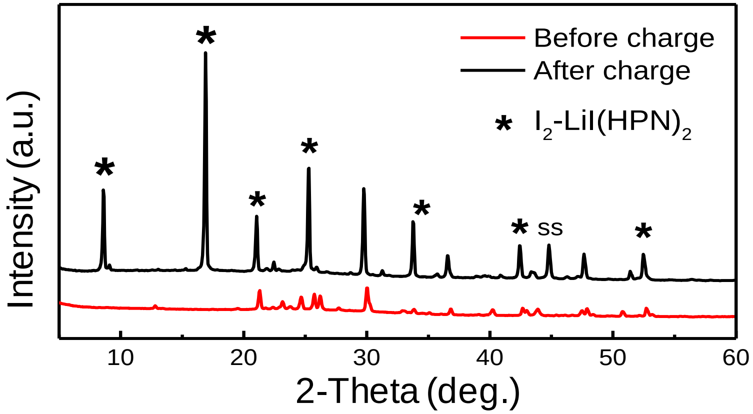
Technical Accomplishments and Progress

Cell construction A demonstrated, verified formation of I_2 at cathode upon initial charging



Schematic of cell after charge

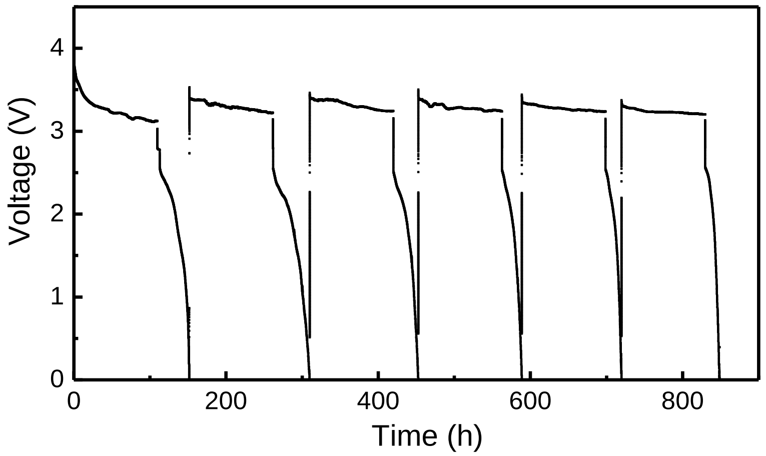


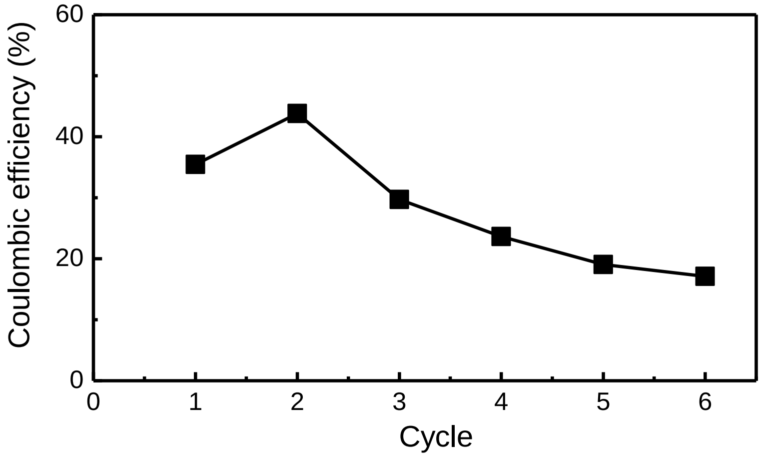


X-ray diffraction shows presence of iodine

Technical Accomplishments and Progress

Determined coulombic efficiency of cell construction A



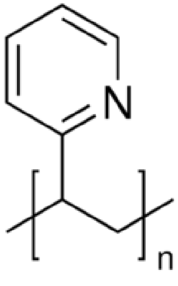


86%LiI + 14%LiI(HPN)$_2$

Current density: 10 μA/cm^2
Charged capacity: ~5% of theoretical

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 %

Technical Accomplishments and Progress

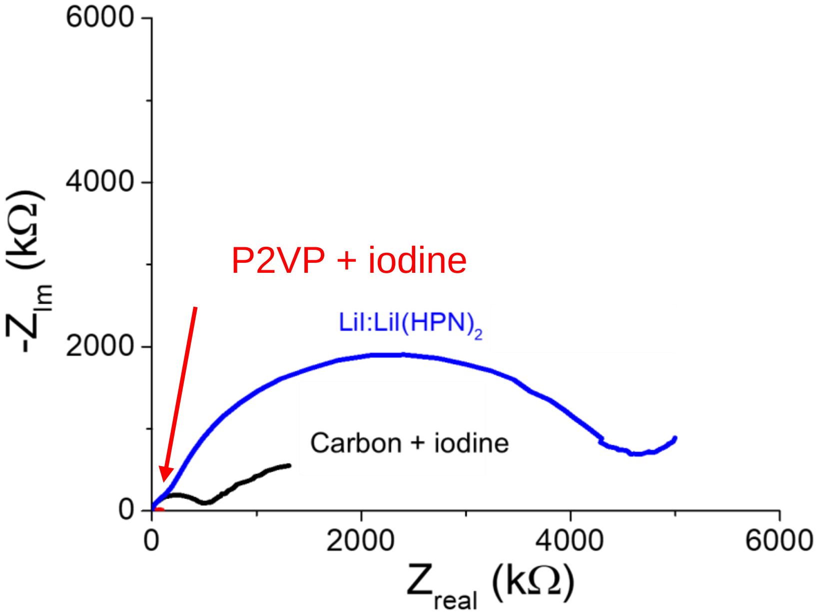


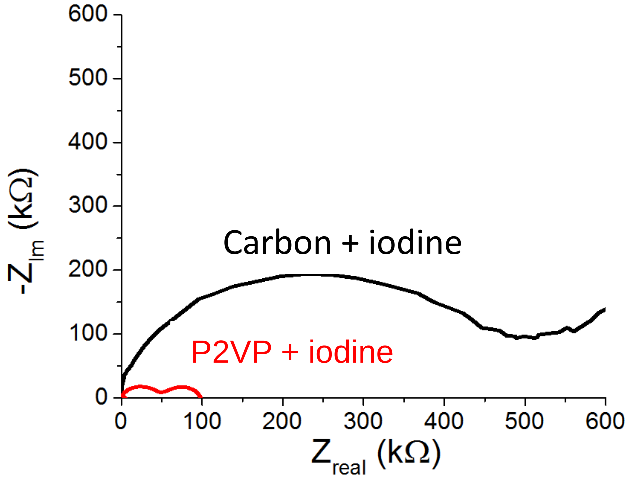
P2VP

Reduced cathode-electrolyte interfacial resistance through modification of the interface

Modifications of the cathode- electrolyte interface included, carbon, carbon + iodine and poly 2-vinyl pyridine (P2VP) + iodine

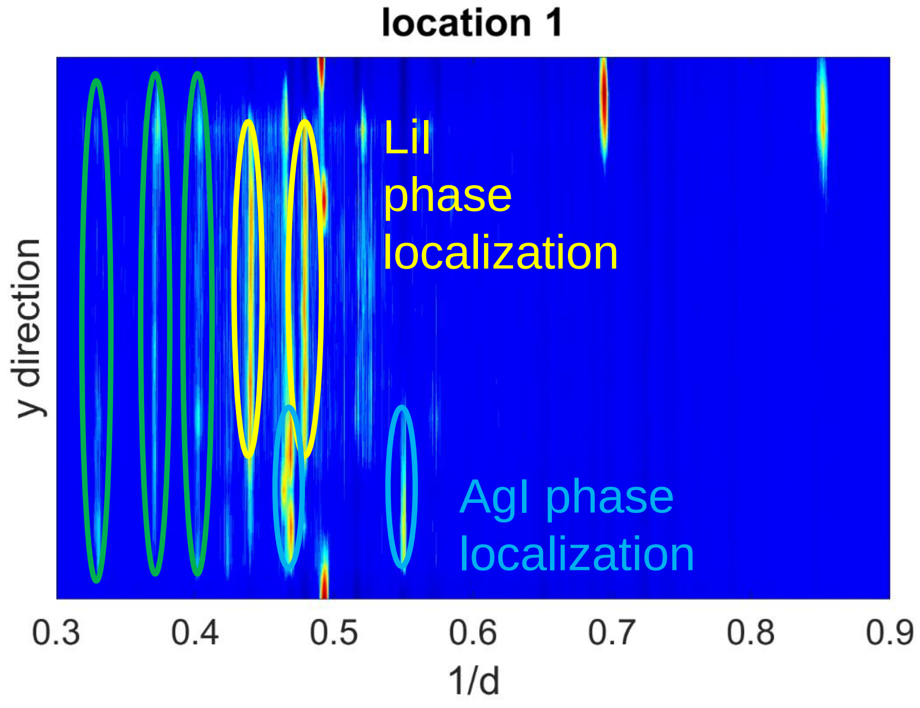
P2VP + iodine form a conductive charge transfer complex. This method was effective in reducing the overall impedance of the cell.

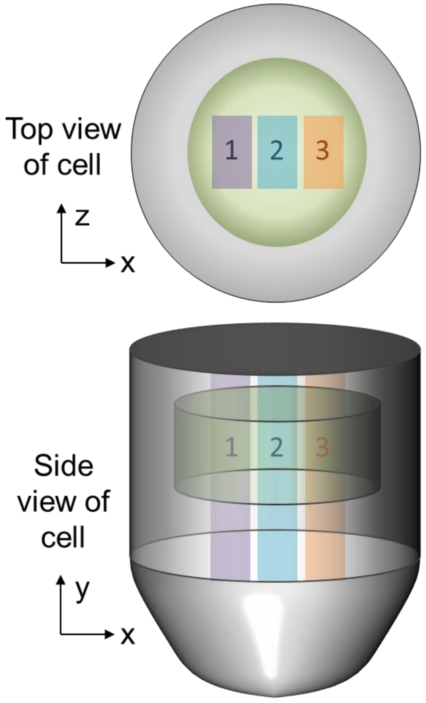




Technical Accomplishments and Progress

Demonstrated in-situ Energy Dispersive X-Ray Diffraction (EDXRD) to identify phase localization on charge





Experimental set-up

Fully sealed coin cells were examined by synchrotron EDXRD.

Three locations were scanned with 25 scans per location per depth of discharge.

Phase localization of LiI, AgI within the electrolyte could be observed.

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

- Investigate the role of the polymer to improve cathode/electrolyte interface and increase conductivity.
- 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.

Summary

Program is on schedule.

- Cell design and testing is under development and on track.
- Electrolyte demonstrated based on salt-polymer hybrid and 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.
- In-situ measurements could identify phase localization within the solid electrolyte.