ES324
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

2017 DOE VTO Annual Merit Review

Stony Brook University

Project Overview

Timeline

- Start Date: October 1, 2016
- End Date: September 1, 2019
- 35% complete

Barriers

- **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 EV Everywhere 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	EV Everywhere 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	$\sim10^{-1}$	$\sim10^{-7}$	

Relevance

Relevance

- Self-forming, self-healing LiI/AgI based electrolyte is aimed at addressing potential safety issues caused by short circuit.
  Barrier: *Safety*-pin hole induced short circuit

- Formed Ag metal will decrease anode/electrolyte interface impedance.
  Barrier: *Electrode/Electrolyte interface*-High interface impedance

- The proposed materials will provide high energy densities.
  Barrier: *Energy Density*-Low Wh/L or Wh/kg

Objective 1: Develop a LiI/AgI 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 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

Three 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 FY17 and FY18

Date	Milestones	Status
November, 2016	All reagents procured, water content verified	Complete
December, 2016	Develop methodology for AC impedance measurement as a function of temperature	Complete
December, 2016	Identify 4 most conductive Ag containing LiI solid electrolytes for further study	Complete
January, 2017 (Go/No-Go)	At least one electrolyte with conductivity $\geq 10^{-3}$ S/cm	Complete
February, 2017	Identify 3 most conductive Ag containing LiI solid electrolytes with or without $LiI(HPN)_2$	Complete
May, 2017	Develop cell construction A (current collectors, tab configuration, etc.) for Li/I_2 batteries with or without P2VP	On-track
August, 2017	Prepare construction A cells with 3 most conductive electrolytes from Subtask 2.1.0	On-track
October, 2017 (Go/No-Go)	Formation of Li^0, Ag^0 at anode and iodine at cathode with charging	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:

$Li^+ + e^- = Li$ (anode)

$Ag^+ + e^- = Ag$ (anode)

$I^- = 1/2 I_2 + e^-$ (cathode)

Discharge:

$1/2 I_2 + Li = LiI$

$1/2 I_2 + Ag = AgI$

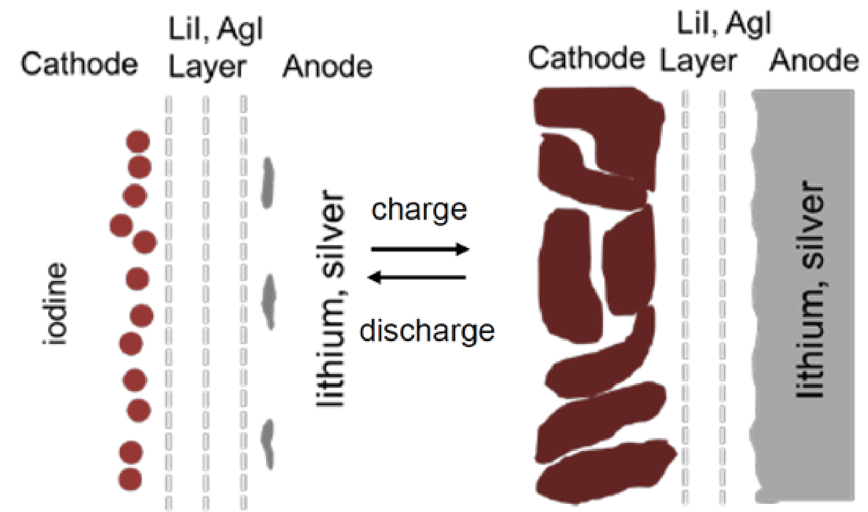


Figure 1. Silver-lithium/ iodine solid state dual function battery.

FY17/18 Approach

Identification of suitable electrolytes

Self-forming Li/I_2 batteries

FY2017				FY2018			
Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8

FY2019

Identify best Ag^+/Li^+ conductor

Complete

Go/No-Go

Fabricate self-forming solid state battery

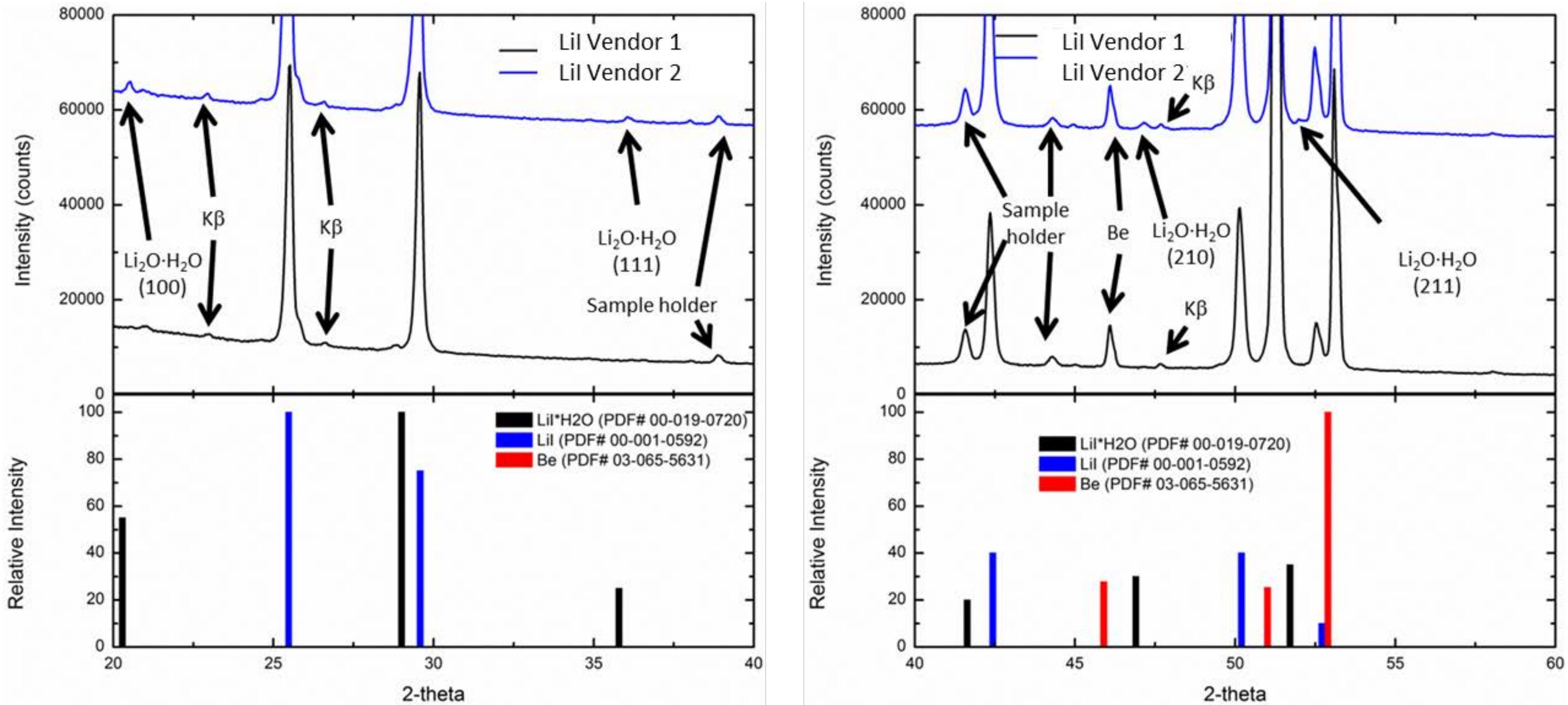
In Progress

Go/No-Go

- Develop conductive Ag containing LiI solid electrolytes.
- Develop cell construction for self-forming Li/I_2 batteries.
- Optimize cathode/electrolyte interface by incorporating P2VP.
- Determining Li^0, Ag^0 at anode and iodine at cathode with charging.

Technical Accomplishments and Progress

Summary: Reagents procured and water content verified. Hydrate peaks not observed in ultra dry LiI. (Milestone 1.1.0)

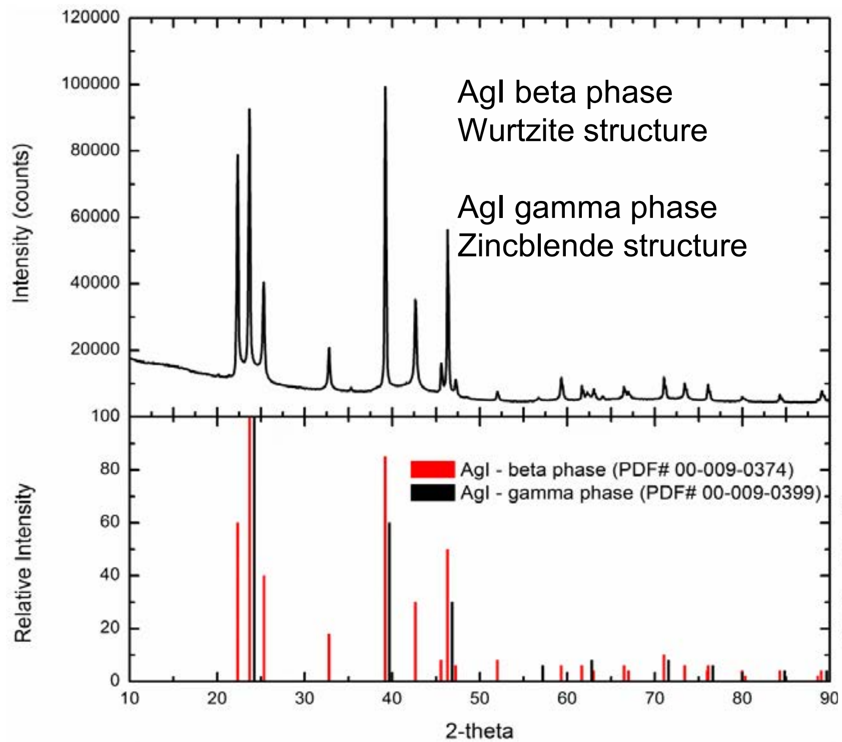


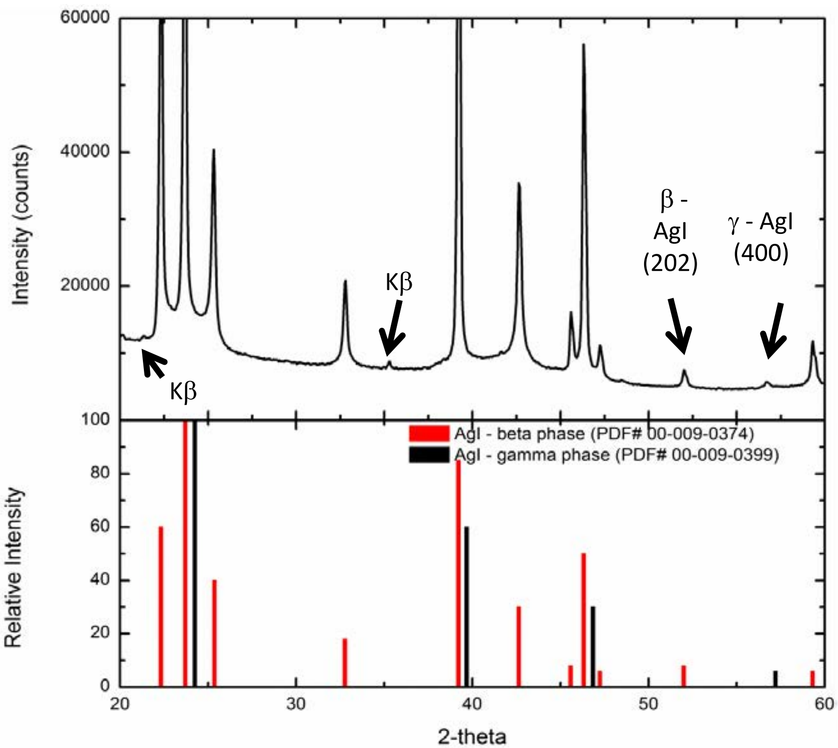
Karl Fisher method used to determine water content

	LiI	Dried LiI	LiI from ampule	AgI
Water content (ppm)	199	104	8.0	54

Technical Accomplishments and Progress

Summary: Reagents procured and water content verified. Both beta and gamma phases of AgI detected. (<u>Milestone 1.1.0</u>)

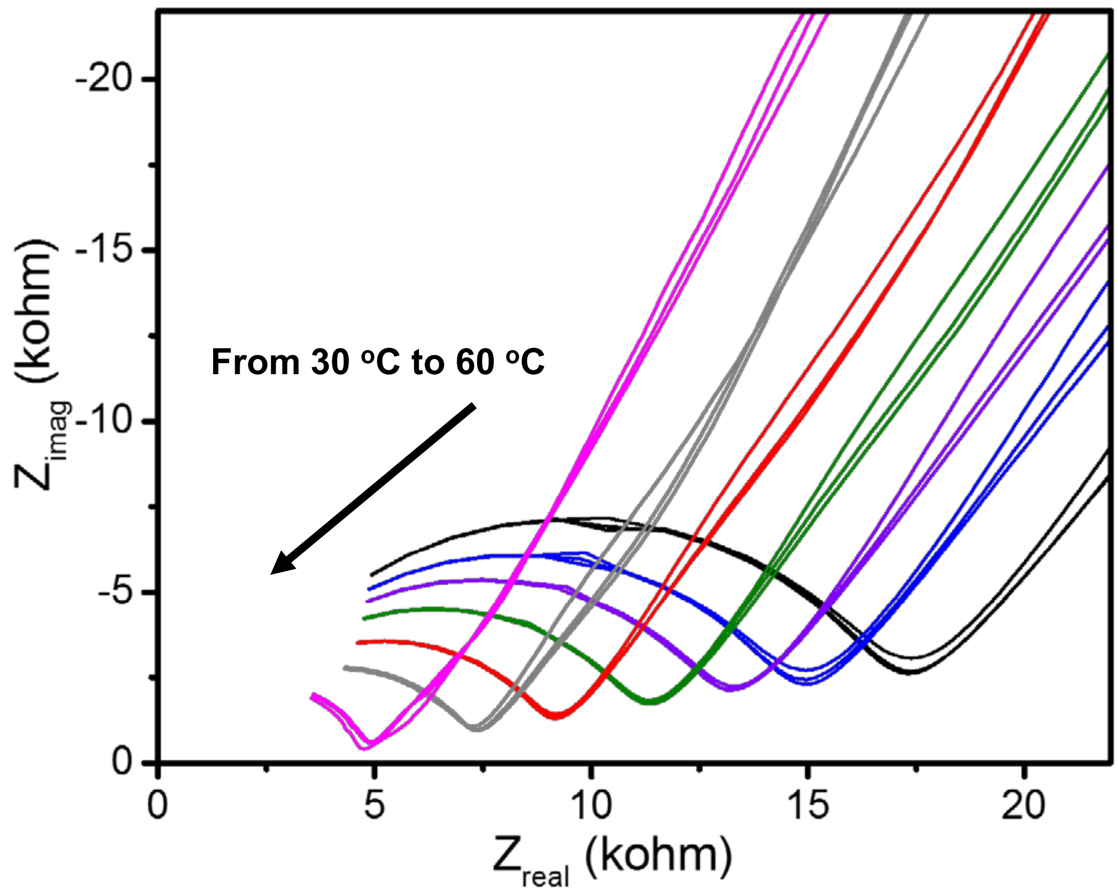




Technical Accomplishments and Progress

Summary: Method development demonstrates reproducibility. (Milestone 1.1.4)

- Impedance data were collected under at seven temperatures between 30 and 60^{o}C.
- Three samples were independently run under each condition; this example is AgI.
- Variation from sample to sample is small.



400 kHz to 1 Hz

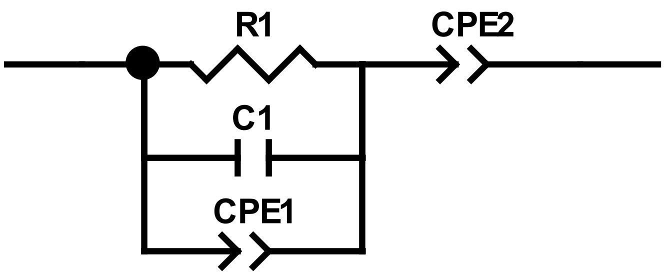
Technical Accomplishments and Progress

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

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

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

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



Summary: Equivalent circuit modeling of AC impedance data allows for determination of conductivity as a function of temperature. (Milestone 1.1.4)

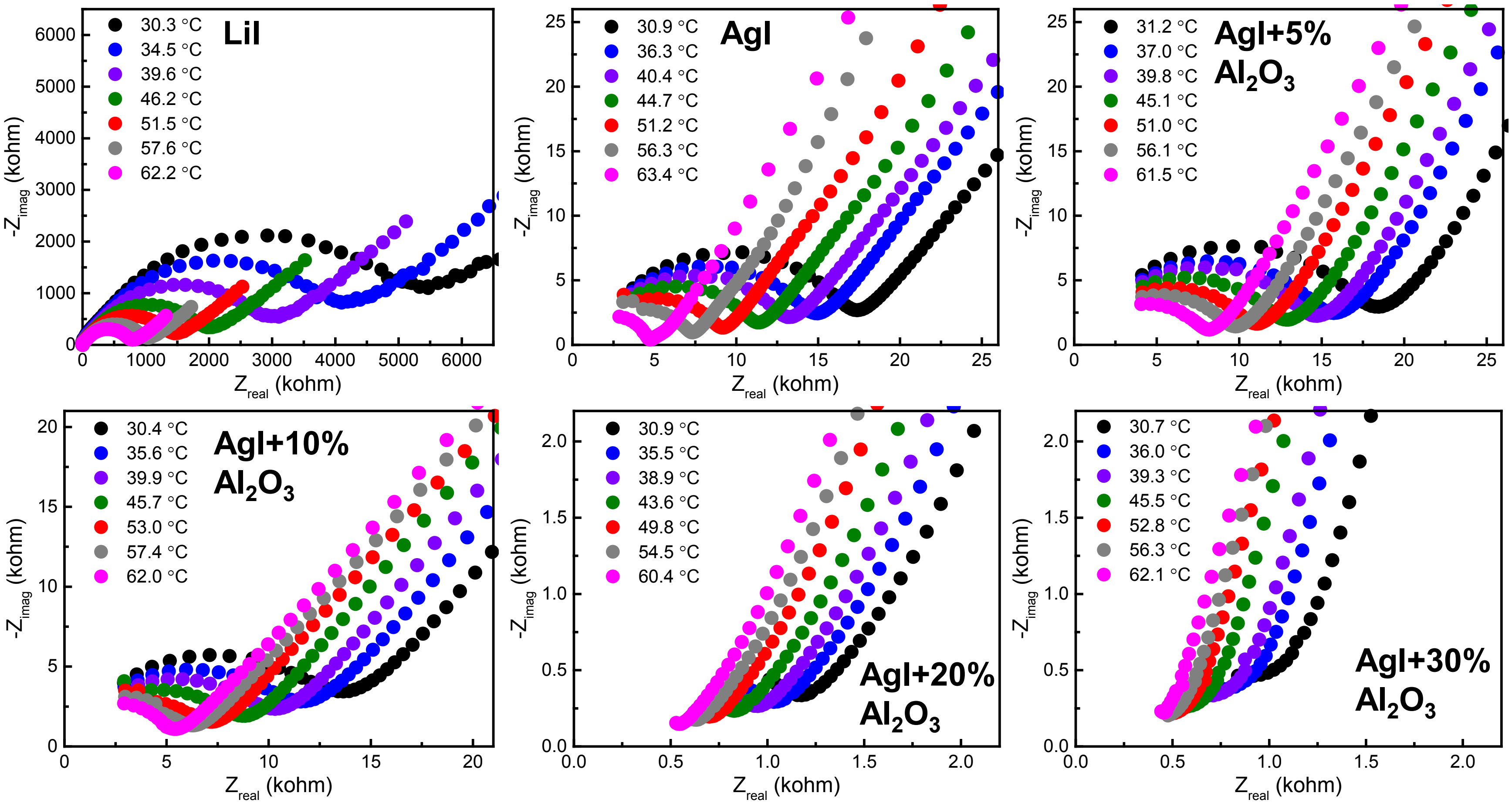
The bulk resistance R can be measured by AC impedance technique.

lnσ shows a linear relationship with 1/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.

Neudecker, B. J., and W. Weppner. J. Electrochem. Soc. 143.7 (1996) 2198-2203.
Poulsen, Finn W. S. S. Ionics 2.1 (1981) 53-57.

Technical Accomplishments and Progress

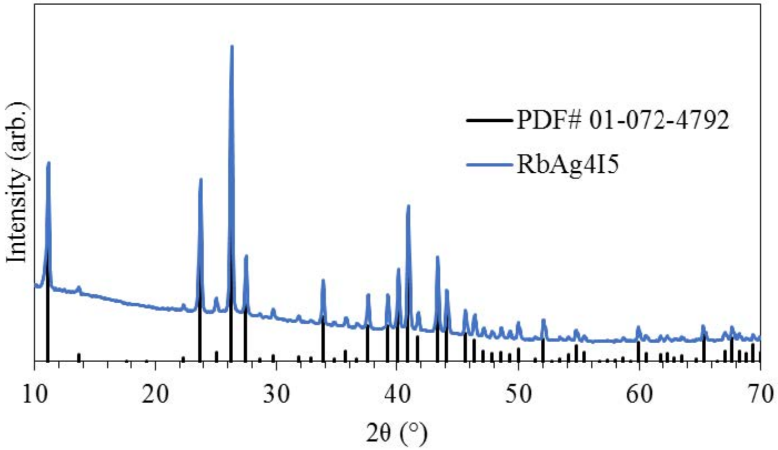


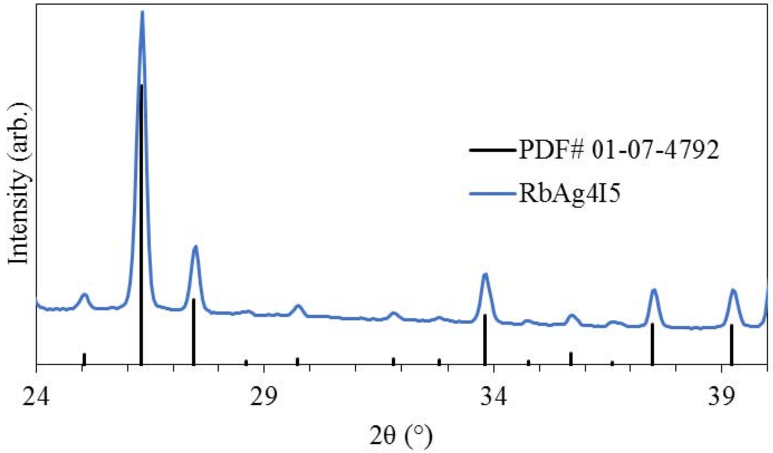
AC impedance of Ag^+/Li^+ conductors

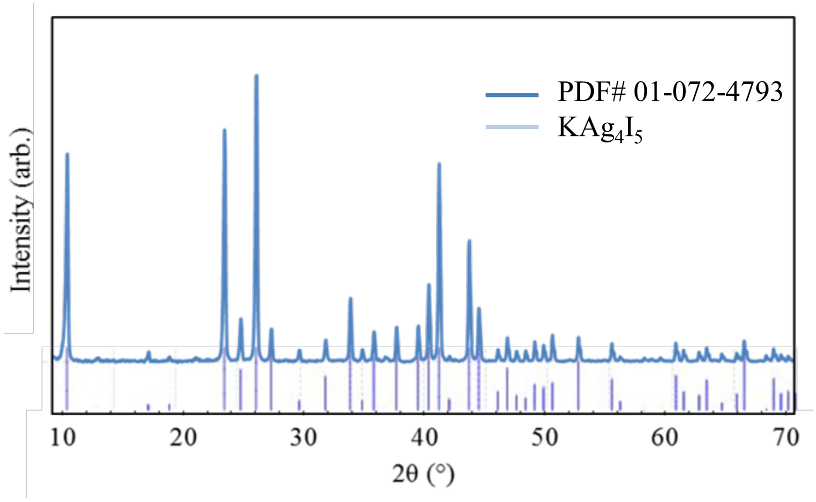
Summary: Addition of alumina shown to reduce measured impedance of AgI ion conductor. (Task 1.1.2)

Technical Accomplishments and Progress

Summary: Successful synthesis of ion conductors MAg_4I_5 (M = Rb, K).
(Addresses tasks 1.1.5 to 1.1.8)







MAg_4I_5 (M= Rb, K) was prepared and the XRD pattern recorded.

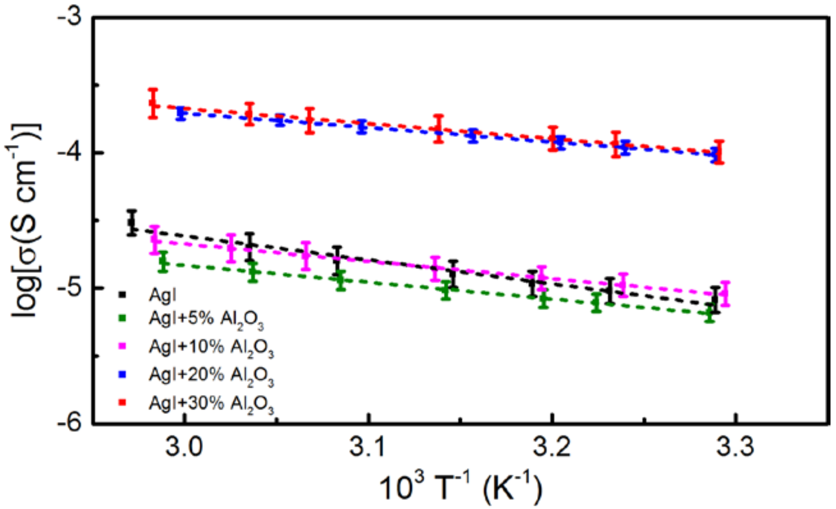
Pattern is consistent with reference pattern for $RbAg_4I_5$, and for $KAg_{3.925}I_5$ phase
No impurity phases were noted.

Technical Accomplishments and Progress

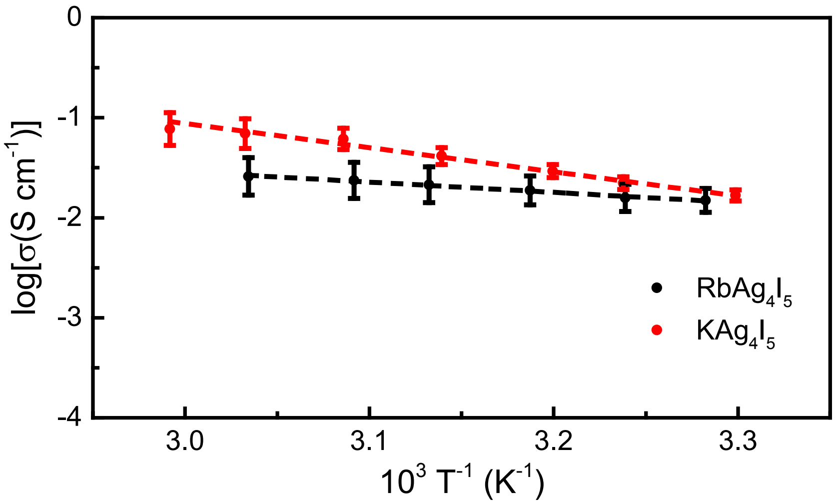
Conductivities of Ag^+ ion conductors

Summary:

- The addition of 20% and 30% Al_2O_3 significantly increases conductivity.
- Electrolytes identified with conductivity > 10^{-3} S/cm



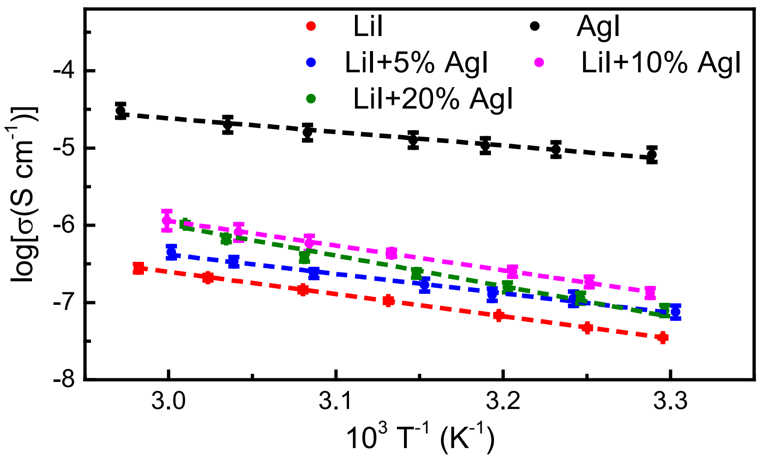
Conductivities of AgI with 0, 5, 10, 20, 30% Al_2O_3 added; 20% and 30% Al_2O_3 significantly increase conductivity.

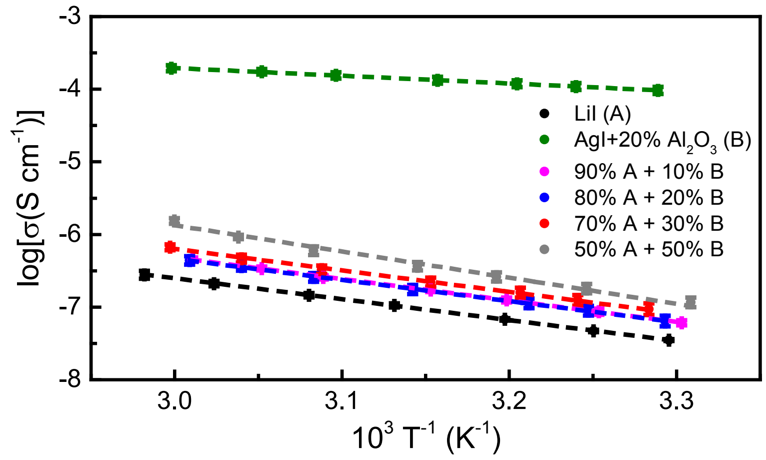


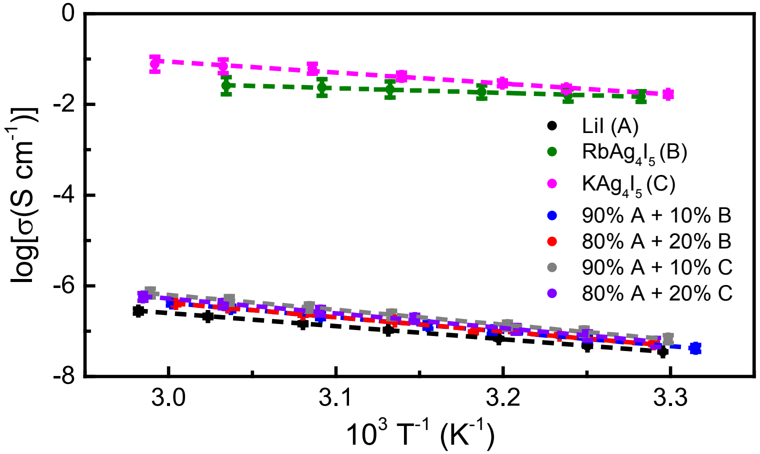
Conductivity (30 °C)
$RbAg_4I_5$: 1.5 × 10^{-2} S/cm
KAg_4I_5: 1.7 × 10^{-2} S/cm

Technical Accomplishments and Progress

Conductivities of AgI containing LiI electrolytes







Silver containing LiI electrolytes

Type1: x% LiI + y% AgI

Type2: x% LiI + y% AgI + z% Al_2O_3

Type3: x% LiI + y% MAg_4I_5 (M=Rb or K)

Summary: The addition of LiI in Ag^+ conductor decreases overall conductivity.

Responses to Reviewer's Comments

N/A

This is a new project

Collaborations with Other Institutions

User proposal submitted for access to a Brookhaven National Laboratory endstation currently installed at the Advanced Photon Source at Argonne National Laboratory.

Time has been allocated and measurements will be made within FY2017.

Remaining Challenges and Barriers

- Anode/electrolyte interface may be improved by formed Ag^0, while cathode/electrolyte interface will be addressed by addition of polymer. (**Will be addressed in Task 1.2.0**)
- Charge step of silver containing LiI electrolyte involves two oxidation reactions (AgI and LiI). (**Will be addressed in Task 2.1.3**)
- Iodine is volatile, and diffused iodine can lower capacity. (**Will be addressed in Task 2.1.4**)
- The role of Ag^0 at anode interface will be investigated. (**Will be addressed in Task 3.2.2**)

Proposed Future Research

- Include polymer to improve cathode/electrolyte interface and increase conductivity. **Task 1.2.0**
- Design appropriate electrochemical test parameters to clarify AgI reduction/oxidation and LiI reduction/oxidation. **Task 2.1.3**
- Develop a appropriate cell construction for effective cycling of the self-forming battery to minimize free volume for iodine. **Tasks 2.1.2, 2.1.4, 2.2.0**
- Utilize multiple characterization techniques to investigate cell interfaces and charged/discharged products. **Tasks 3.2.0, 3.2.1, 3.2.2.**

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

Summary

Program is on schedule.

- Materials have been obtained and characterized.
- Measurement methods have been demonstrated.
- Preparation of candidate electrolytes is on track.
- Measurements of electrolytes are on track.
- Cell design and construction is under development and on track.