Lithium Superoxide-Based Batteries

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DOE merit review

June 1-4, 2020

Project ID# BAT-431

Overview

Timeline

- Start: 2018
- Finish: 2022
- 60 %

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: $ 1500 K
  - Contractor 0
- FY 18: $ 500 K
- FY 19: $ 500 K
- FY 20: $ 500 K

Partners

- Interactions/ collaborations
  - S. Vajda, ANL/Prague
  - S. Al-Hallaj and B. Chaplin, UIC
  - J. G. Wen, ANL
  - Y. Wu, Ohio State University
  - A. Ngo, ANL
  - K. Senjac UIC/ANL

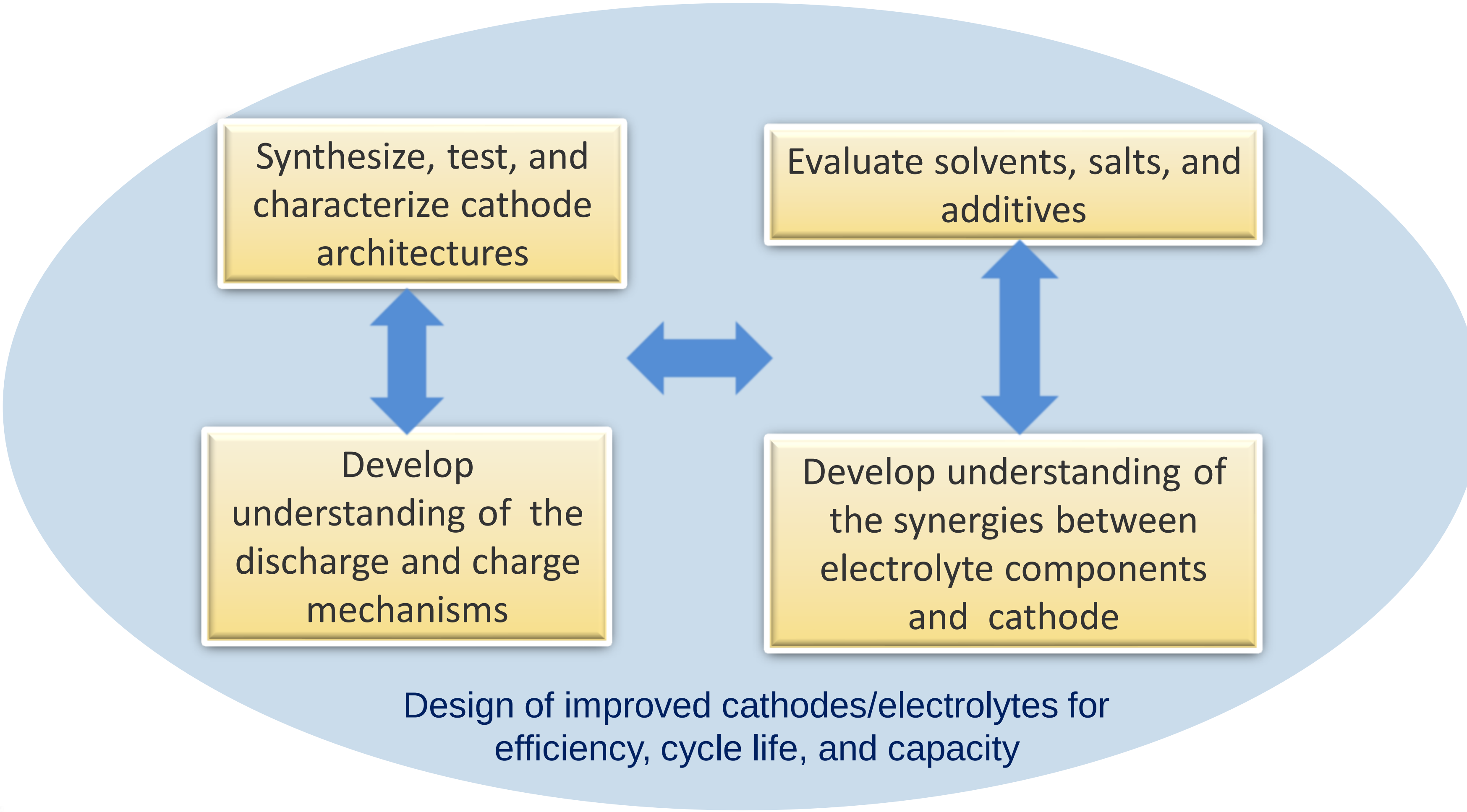
Project Objectives and Relevance

- Investigation of Li-O_2 batteries based on lithium superoxide to achieve understanding of discharge chemistry and how to enhance cycle life.
- Use an integrated approach based on experimental synthesis and state-of-the-art characterization combined with high level computational studies focused on materials design and understanding
- Li-air batteries based on lithium superoxide have the potential for being the basis for closed systems without need for an external O_2 source

FY18 Milestones

Month/ Year	Milestones
Dec/19	Investigate LiO_2 to Li_2O_2 conversion under different Ar conditions after LiO_2 formation on charge to help understand and control Li-O2 discharge chemistry, Q1 (**Completed**)
Mar/20	Synthesis and characterization of $IrLi_n$ alloys for templated lithium superoxide growth in Li-O_2 batteries, Q2 (**Completed**)
Jun/20	Investigate performance of Li-O_2 battery using cathode based on pre-formed $IrLi_3$ particles on rGO support, Q3(**Initiated**)
Sep/20	Investigate performance of Li-O_2 battery using cathode based on pre-formed IrLi particles on rGO support, Q4 (**Initiated**)

Strategy: an integrated experiment/theory approach that combines testing, understanding and design to develop lithium superoxide based Li-O2 batteries



Experimental methods

Synthesis

- New catalyst materials
- Electrolytes

Characterization

- In situ XRD measurement (Advanced Photon Source)
- TEM imaging
- FTIR, Raman
- SEM imaging
- Impedance measurements
- Titration

Testing

- Swagelok cells

Highly accurate quantum chemical modeling

- Periodic, molecular, and cluster calculations using density functional calculations
  - Static calculations
  - Ab initio molecular dynamics simulations (AIMD)
- Understanding discharge products
  - Li_2O_2 structure and electronic properties
  - LiO_2 structure and electronic properties
- Design of electrolytes
  - Reaction energies and barriers for stability screening
  - Electrolyte/surface interface simulations

Technical Accomplishments

Characterization and understanding of lithium superoxide based batteries

- LiO_2 to Li_2O_2 conversion under different Ar conditions
- Provides for new understanding of discharge mechanisms in Li-O_2 batteries

Synthesis of templates for lithium superoxide growth in Li-O_2 batteries

- Direct synthesis of Ir_3Li for templating LiO_2 instead of evolution from Ir nanoparticles on cycling
- Direct synthesis of a IrLi alloy particles for templating LiO_2

Performance of the new templating materials

- Identification of the discharge product
- Voltage profiles
- Implications for new Li-O_2 battery chemistries

Accomplishment: Characterization and understanding of lithium superoxide based batteries

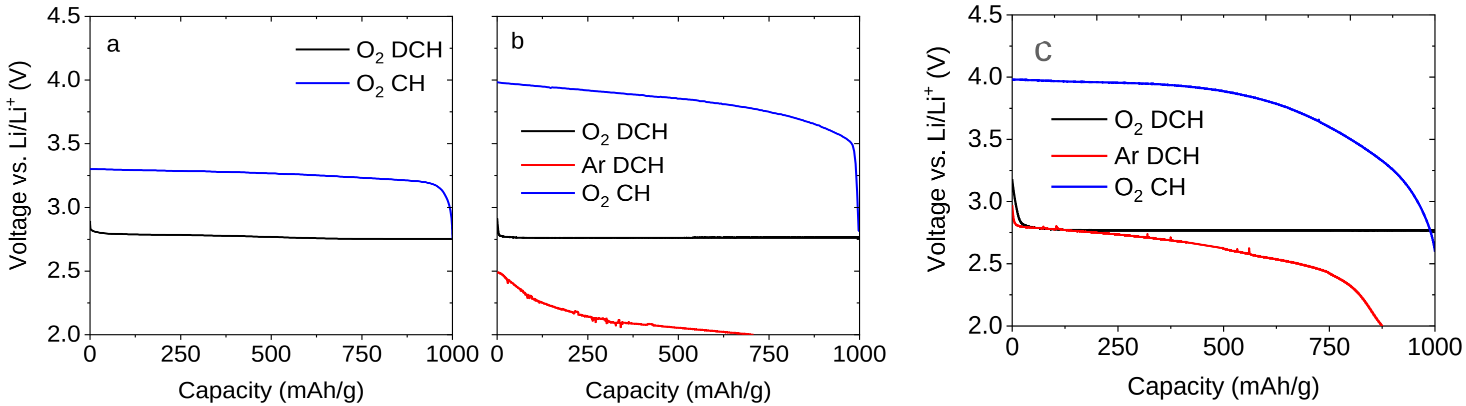
- LiO_2 to Li_2O_2 conversion under different Ar conditions after LiO_2 formation on charge
  - Purge of O_2 by Ar followed by flowing O_2
  - Purge of O_2 by Ar and then a fully closed cell
- Results
  - The two conditions lead to different discharge voltage profiles
  - However, the product remains the same – Li_2O_2
- Implications for charge transport in discharge products in Li-O2 batteries
  - Impedance measurement made on different discharge samples
  - In all cases LiO_2 shows better electronic conductivity than Li_2O_2
- Mechanistic understanding from the experiments
  - Surface mediated Li_2O_2 growth has a lower discharge potential than solution phase growth
  - This is true for these experiments, but is also probably true in general
- Preliminary results for a closed Li-O_2 battery, i.e. no source of O_2

LiO_2 to Li_2O_2 conversion under different Ar conditions after LiO_2 formation on discharge

Baseline: normal O_2 during discharge

Purge of O_2 by Ar followed by flowing Ar during discharge

Purge of O_2 by Ar and then a fully closed cell during discharge



a) Voltage profile of Li-O2 cell with Ir-rGO cathode, discharged at 100 mA/g current density in a constant flow of O2 (cell #1)

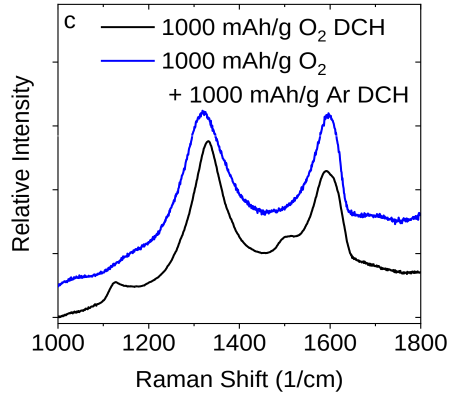
b) Voltage profile of Li-O2 cell with Ir-rGO cathode, discharged at 100 mA/g current density cathode in a constant flow of O2 directly followed by a constant flow of Ar (cell #2).

c) Voltage profile of Ir-rGO under O_2 followed by discharge in Ar in a fully closed cell

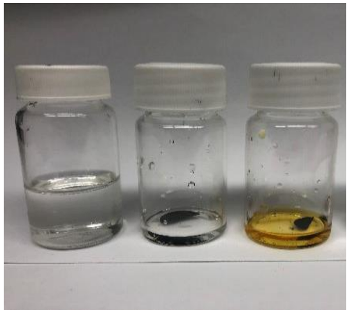
Notes: The Ar discharge is shown to start at 0 mAh/g to aid comparison of obtained capacity with the initial O2 discharge however, the actual discharge started after 1000 mAh/g of O2 discharge. All cells were recharged in O2 using a current density of 100 mA/g;

- The two conditions lead to different discharge voltage profiles however the product remains the same (Li_2O_2) but with different formation mechanism (see following four slides)

Characterization of product after LiO_2 to Li_2O_2 conversion under different Ar conditions



Raman spectra of discharged cathodes in O2 and with flowing Ar



$Ti(IV)OSO_4$ solutions resulting from titration with discharged cathodes. Left to right: $Ti(IV)OSO_4$ titrant, cell #1 titration solution, and cell #2 titration solution.

Titration[1,2] using $Ti(IV)OSO_4$:

1. Wang, Amine, Curtiss, et al ACS Energy Letters, **3**, 1105 (2018)
2. Wang, Amine, Curtiss, et al J. Phys. Chem. C 121, 9657 (2017)

Discharge conditions for titrations	Wt.% Li_2O_2
Baseline: normal O_2 during discharge (cell #1)	6
Baseline: normal O_2 during discharge (cell #1, repeat	5
Purge of O_2 by Ar followed by flowing Ar during discharge after 1st discharge in O2(cell #2)	98
Purge of O_2 by Ar and then a fully closed (no O2) cell during discharge after 1st discharge in O2 (cell #3)	98

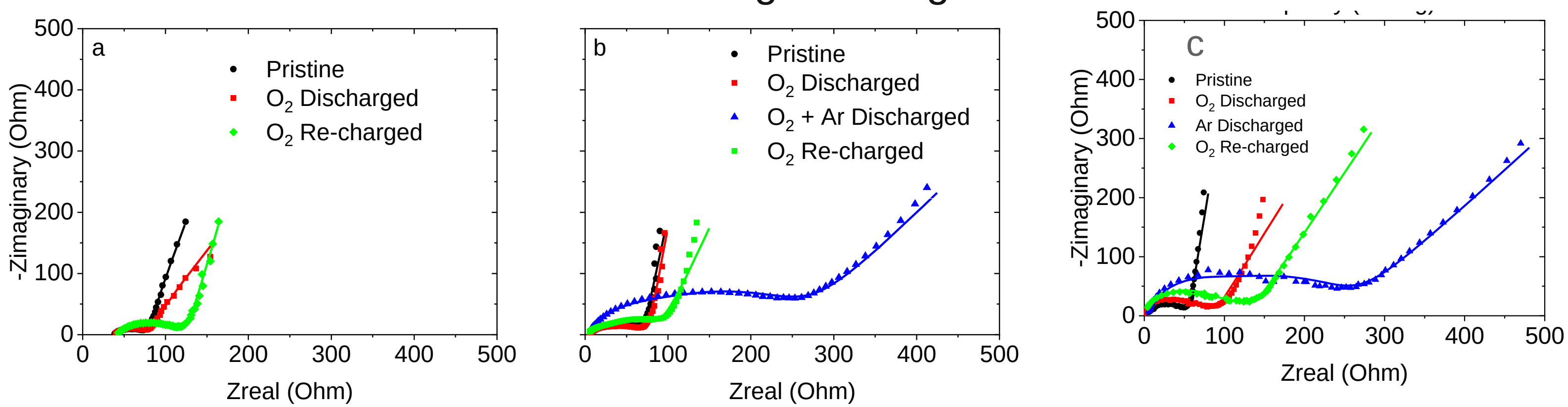
- Titration shows that during first discharge in O_2 the discharge product is LiO_2, after the second discharge under both Ar conditions the discharge product is Li_2O_2; Raman spectra confirm this

Impedance measurements of LiO_2 from O_2 discharge and of Li_2O_2 produced under different Ar conditions

Baseline: normal O_2 during discharge

Purge of O_2 by Ar followed by flowing Ar during discharge

Purge of O_2 by Ar and then a fully closed cell during discharge

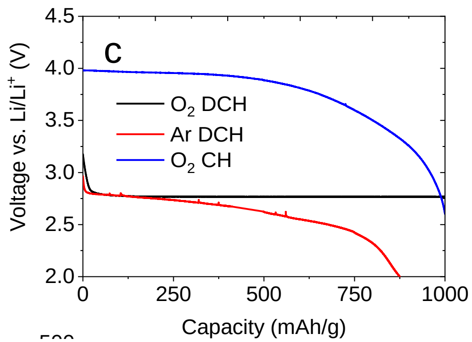


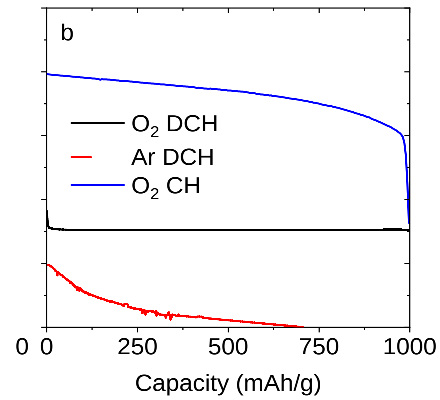
a) Nyquist plot obtained from pristine, post O_2 discharge and post charge; b) Nyquist plot obtained from pristine, post O_2 discharge, post flowing Ar discharge, and after charge.. c) Nyquist plot obtained from pristine, post O_2 discharge, post closed Ar discharge, and after charge.

Note: Experimental data and equivalent circuit model results are illustrated as shapes and solid lines, respectively, in Nyquist plots

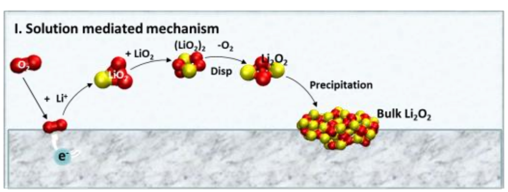
- In all cases LiO_2 shows better electronic conductivity than Li_2O_2 consistent with predictions from density functional theory

New mechanistic understanding of Li-O_2 discharge chemistry from Li_2O_2 produced under different Ar conditions

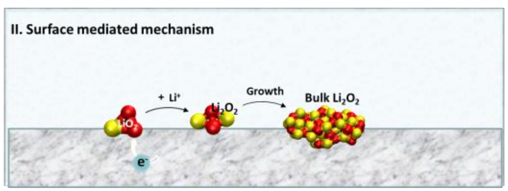




Fully closed under Ar results in mainly solution mediated growth (due to O_2 produced from disproportionation) and a higher discharge potential



Under flowing Ar results in only surface growth due to lack of any O_2 in electrolyte (from LiO_2 disproportion) and a lower discharge potential

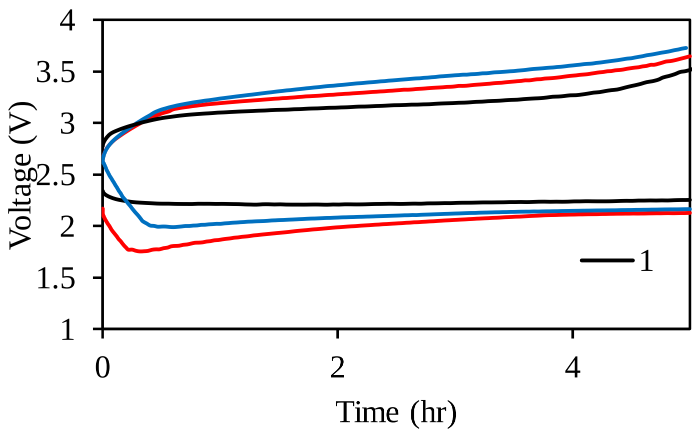


- Surface mediated Li_2O_2 growth has a lower discharge potential than solution phase growth
- This is true for these experiments, but is also probably true in general for discharge chemistry in a Li-O_2 battery.

Preliminary results for cycling (discharging and charging) a closed Li-O_2 battery, i.e. no external source of O_2

Desired reactions:

Discharge: $LiO_2 + Li^+ + e \rightarrow$ Li2O2 Charge: $Li_2O_2 \rightarrow LiO_2 + Li^+ + e$



$Li_2O_2 \rightarrow LiO_2 + Li^+ + e$ evidence: low charge potential; still under investigation

$LiO_2 + Li^+ + e \rightarrow Li_2O_2$ evidence: our previous studies based on discharge in Ar

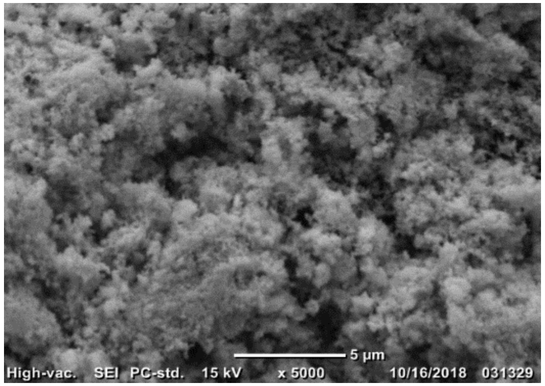
Cycling in argon after initial 10 h O_2 DCH. After argon purge first step was DCH; current density of 32 mA/g

- Preliminary results show that at low charge rates it is possible to discharge and charge a closed Li-O_2 battery (i.e. no external source of O_2)

Accomplishment: Successful synthesis of metal alloy particles for directing lithium superoxide growth

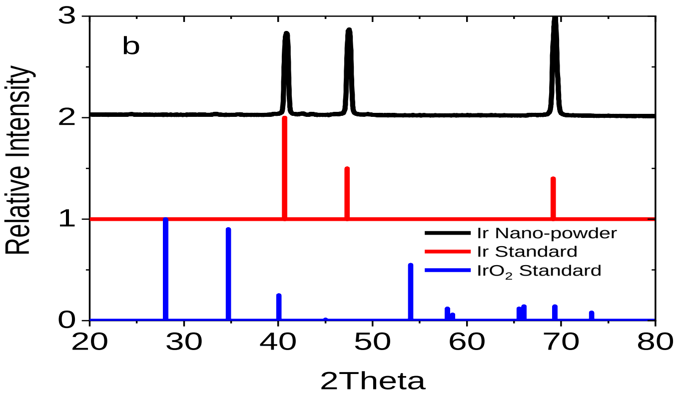
- Previous studies of lithium superoxide based Li-O2 batteries have been based on Ir nanoparticles on an reduced graphene oxide (rGO) cathode that form $IrLi_3$ during cycling, which act as templates for growth of LiO2 instead of the more stable Li_2O_2 product
  - Ir nanoparticles with a range of sizes (2-500nm) : Lu, Amine, Curtiss, et al Nature **529**, 377 (2016).
  - Size selected Ir clusters (Ir_n, n = 2-8) Lu, Vajda, Amine, Curtiss et al J. Phys. Chem A **123**, 10047 (2019).
- In this work we have synthesized and characterized particles of the IrLi3 alloy using a high temperature method to provide a “direct” LiO2 templating cathode in $Li\text{-}O_2$ batteries
  - Characterization has been carried out to confirm the structure and determine the size of the particles
  - Based on calculations that a 1:1 alloy will also be a good template, we have also synthesized a IrLi alloy

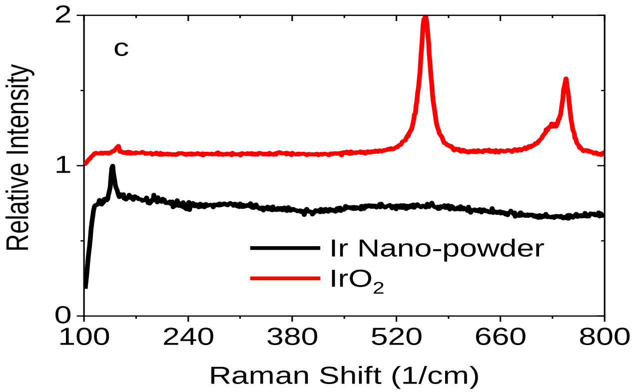
Baseline results for Ir nanopowder used for synthesis of IrLi alloys



SEM of Ir nanopowders

XRD



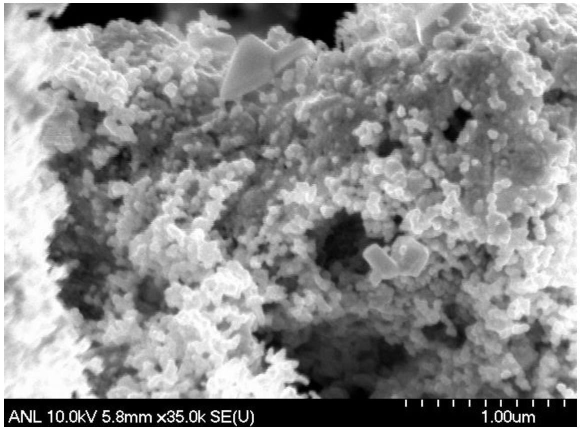


Raman

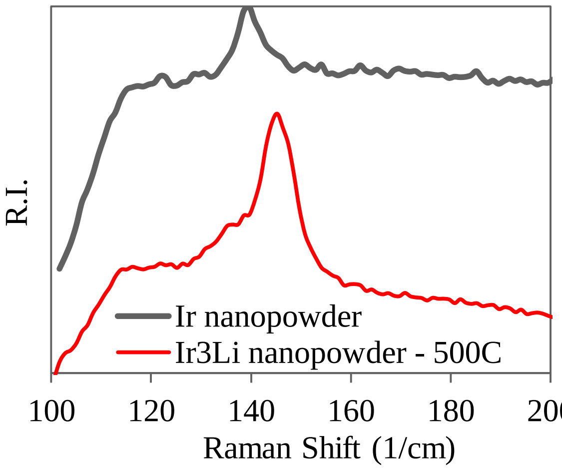
- Characterization results for Ir nanopowder used in high temperature synthesis

High temperature synthesis and characterization of Ir3Li

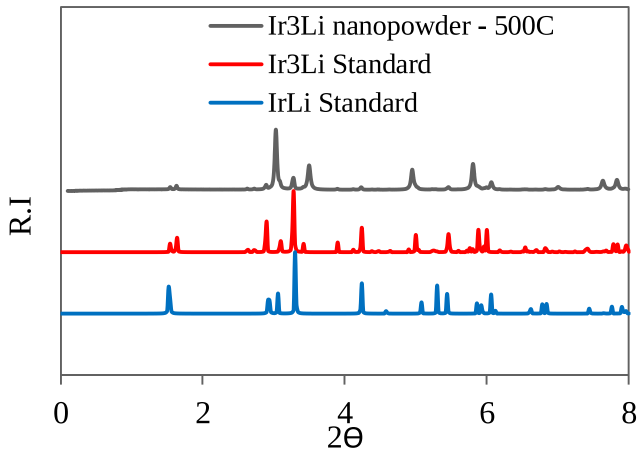
- Ir_3Li synthesis goal is to make small particles for the rGO cathode
  - conditions: 500 °C and 3:1 Ir:Li starting reactants



SEM of resulting alloy



XRD of resulting alloy

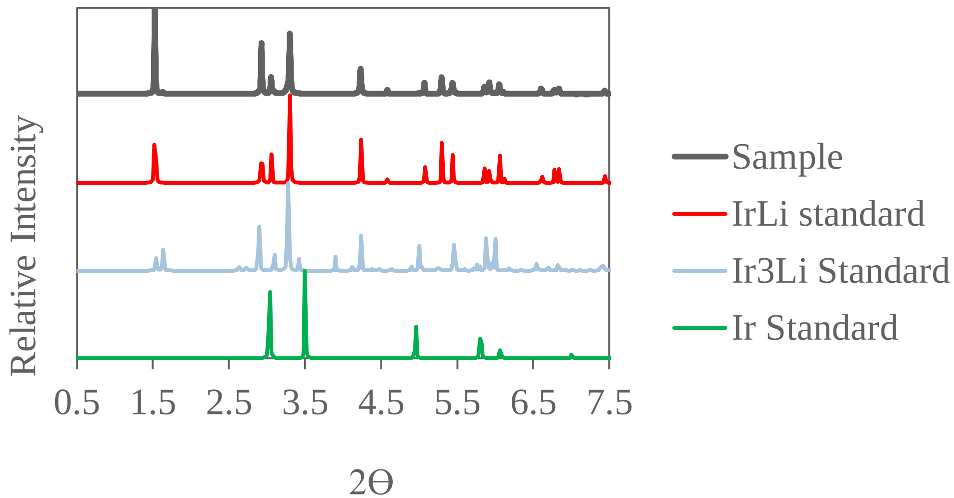


Raman of resulting alloy

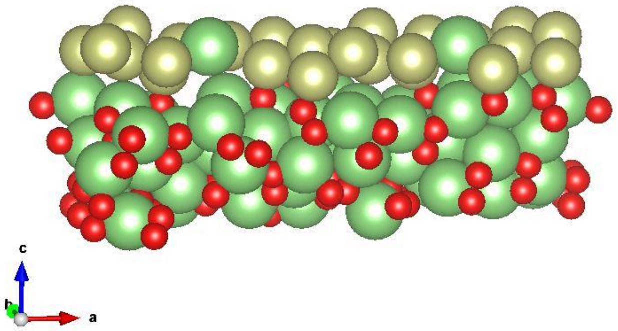
- Size of IrLi3 particles depends on synthesis conditions; by using the right conditions particle size of <1µm has been achieved

High temperature synthesis and characterization of IrLi alloy

- IrLi alloy synthesis
  - 500 °C in Ar, 1:1 Ir:Li



XRD of alloy sample



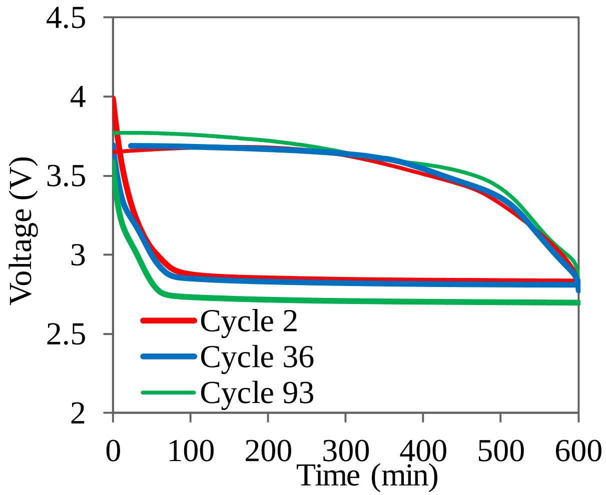
DFT calculation showing a good lattice match of 1:1 IrLi alloy with LiO2 of alloy

- XRD shows pure IrLi was synthesized for use in cathodes
  - Raman spectra is also consistent with IrLi
  - SEM and TEM is underway

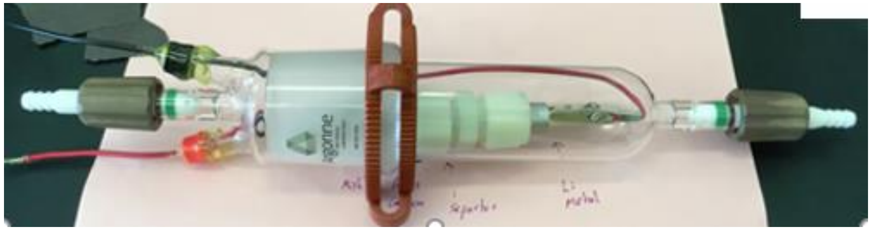
Accomplishment: Synthesized IrLi particles that were successful in directing lithium superoxide growth in Li-O_2 cells

- In this work we have used rGO to as a support for our synthesized $IrLi_n$ particles and used the resulting rGO/$IrLi_n$ materials as a cathodes in Li-O_2 batteries
  - The cathodes were used with a TEGDME/TFSI electrolyte in a Li-O_2 battery
  - Performance of the cathodes was evaluated and discharge product characterized
- The discharge product from both IrLi and $IrLi_3$ based cathodes was found to be lithium superoxide and capable of being cycled in the Li-O2 batteries with O2 source
  - These results have shown then it is possible to stabilize growth of lithium superoxide in a Li-O2 batteries by a templating action of pre-formed IrLi3 particles as well as the IrLi alloy
  - Hence, it is not necessary to use an Ir nanoparticles that evolve into $IrLi_3$ particles during cycling

Performance of Li-O_2 battery using cathode based on pre-formed $IrLi_3$ particles on rGO support



Voltage profile

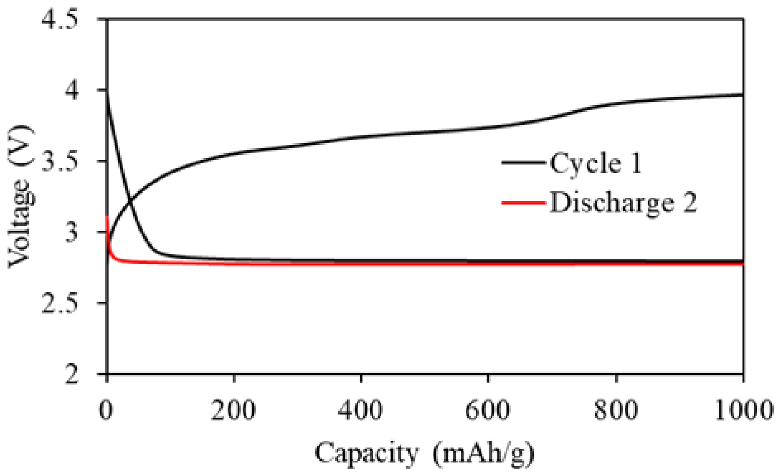


Sample	Wt.% Li_2O_2 ± 2%
rGO	33
Ir_3Li-rGO	0

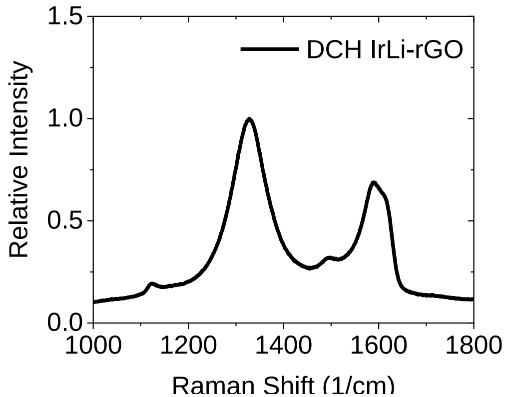
Titration data after 1.5 cycles for a rGO and Ir3Li-rGO cathodes

- Pre-formed $IrLi_3$ particles (<1μm in size) are found to result in LiO_2 discharge product with low charge potentials during cycling

Performance of Li-O_2 battery using cathode based on pre-formed IrLi (1:1 alloy) particles on rGO support



Voltage profile



Titration Sample	Wt.% Li2O2
IrLi-rGO	0

Raman and titration after 1.5 cycles confirm LiO_2 as discharge product and no Li_2O_2 formation

- Pre-formed IrLi (1:1 alloy) particles are found to result in LiO_2 discharge product during cycling

Response to last year reviewer's comments

No comments from last year.

Proposed Future Work

- Investigation of other electrolytes for stabilization of lithium superoxide in Li-O_2 batteries
  - Extend the lifetime of the discharge product for better cycle life
- Investigation of additives to electrolytes
  - Provide protection of the lithium anode for longer cycle life
- Search for lower cost materials to template lithium superoxide in Li-O_2 batteries
  - Use computational simulations to find materials with good lattice matches with lithium superoxide
  - Synthesize or purchase the materials for testing in cathodes

Collaborations with other institutions and companies

- S. Vajda, A. Halder, ANL
  - Development of new cathode materials based on supported size-selected metal cluster
- S. Al-Hallaj, B. Chaplin UIC
  - Characterization of discharge products and cathode materials
- J. G Wen ANL
  - TEM characterization of discharge products and catalysts
- K. C. Lau, California State University, Norridge
  - Computations

Remaining Challenges and Barriers

- Discovery of new electrolytes for lithium superoxide Li-O_2 batteries that can extend the lifetime of the discharge product for longer cycle life
- Investigation of additives to electrolytes for protection of the lithium anode for longer cycle life
- Search for lower cost materials to template lithium superoxide in Li-O_2 batteries

Summary

- Investigation of LiO_2 to Li_2O_2 conversion during discharge under different Ar conditions in lithium superoxide based batteries
  - Has provided a new understanding of surface mediated vs solution phas discharge mechanisms in Li-O_2 batteries
  - Prelimnary results on charging and discharging a lithium superoxide battery without an O_2 source
- Synthesis of templates for facilitating lithium superoxide growth in Li-O_2 batteries
  - Direct synthesis of Ir_3Li particles for templating LiO_2 instead of evolution from Ir nanoparticles on cycling
  - Direct synthesis of a IrLi alloy particles for templating LiO_2
- Performance of the new pre-formed $IrLi_n$ alloys in cathodes for Li-O_2 batteries materials
  - Identification of the discharge product as LiO_2
  - Voltage profiles showing cycling of the lithium superoxide batteries based on pre-formed $IrLi_n$ alloys