Investigation of Lithium Superoxide-Based Batteries

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DOE merit review

June 1-4, 2020

Project ID# BAT-431

Overview

Timeline

- Start: 2019
- Finish: 2023
- 60 %

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: $ 1280 K
  - Contractor 0
- FY 18: $ 400 K
- FY 19: $ 450 K
- FY 20: $ 430 K

Partners

- Interactions/ collaborations
  - M. Asadi, IIT
  - S. Al-Hallaj and B. Chaplin, UIC
  - J. G. Wen, ANL
  - K. C. Lau University of California-Northridge
  - M. Asadi, IIT

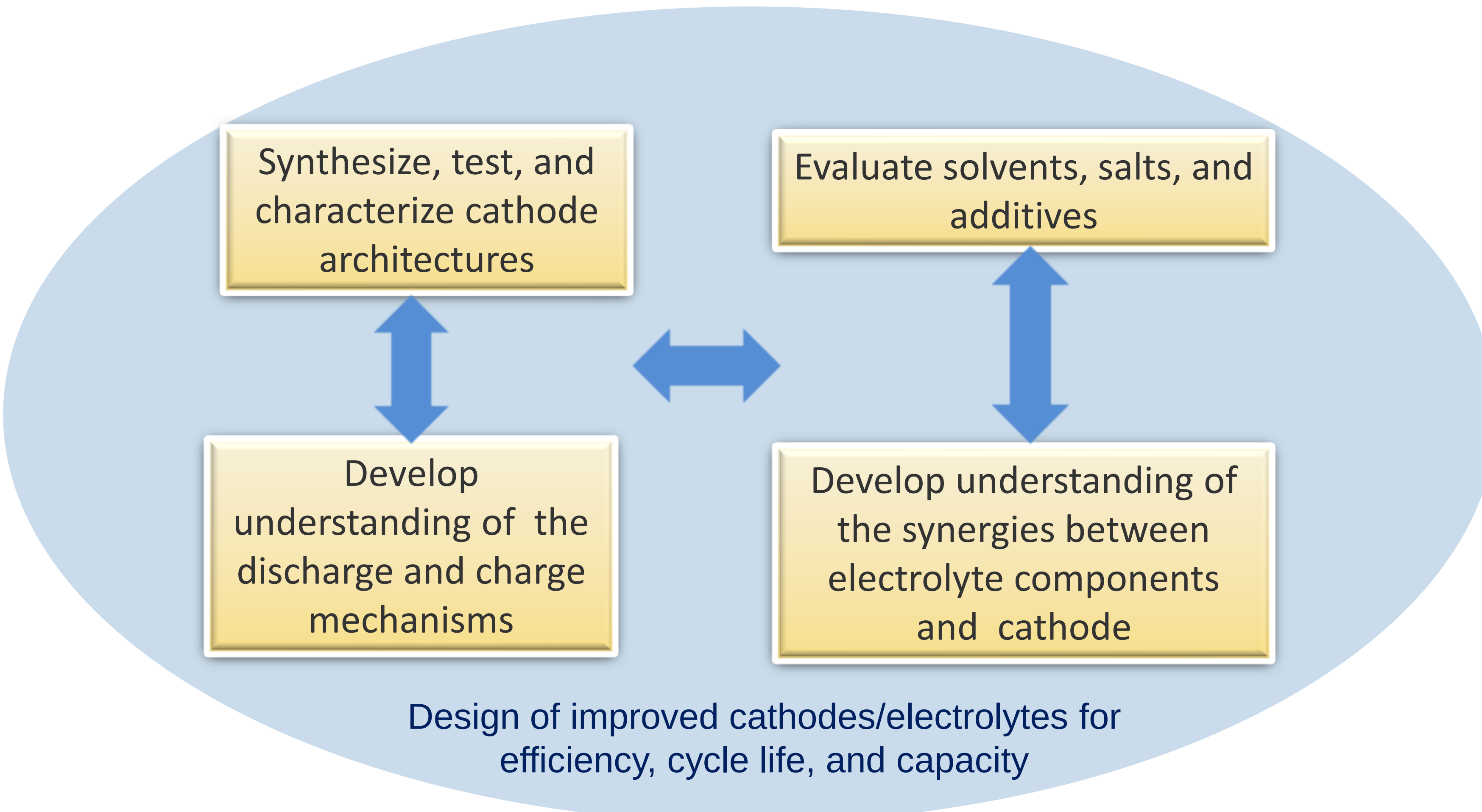
Project Objectives and Relevance

- 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

Milestones

Month/ Year	Milestones
Jun/20	Characterization of electronic properties of high temperature synthesized Ir_3Li, (**Completed**)
Sep/20	Voltage profiles and characterization of discharge product by titration and other techniques in an Ir_3Li cell, (**Completed**)
Dec/21	TEM studies of large LiO_2 particles, investigation of stability and formation mechanism, (**Completed**)
Mar/21	Investigate performance of Li-O_2 battery using cathode based on bulk high temperature synthesized IrLi particles on rGO support, (**Initiated**)

Strategy: an integrated experiment/theory approach that combines testing, understanding and design to develop lithium superoxide based Li-O_2 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

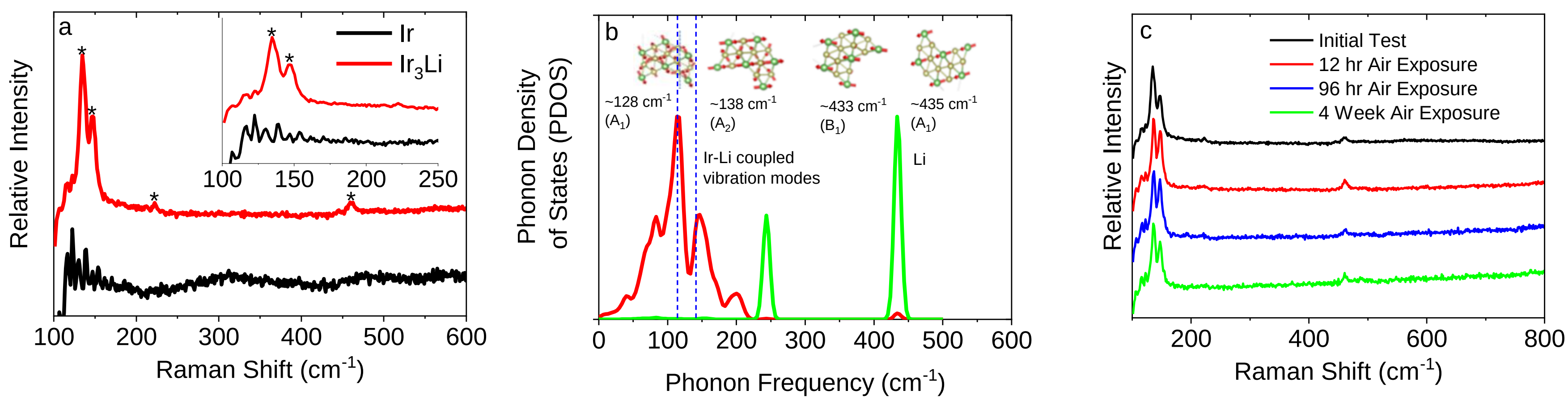
Background

- Previous studies of lithium superoxide based Li-O_2 batteries have been based on Ir nanoparticles on a reduced graphene oxide (rGO) cathode that partially form Ir_3Li during cycling, which act as templates for growth of LiO_2 instead of the more stable Li_2O_2 product
  - Ir nanoparticles and different sizes : 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 both cases Li is partially incorporated into Ir particles during discharge
- In this work we have synthesized (at high temperatures) and characterized bulk $IrLi_3$ and IrLi alloys using a high temperature method to use in LiO_2 batteries

Summary of Technical Accomplishments

1. **Characterization of electronic properties of Ir_3Li particles relevant to use as catalysts in Li-O_2 cells**
   - Bulk Ir_3Li was found to have comparable conductivity to iridium metal
   - Possess metal-like magnetic properties, and have an affinity toward O_2.
2. **Micron sized Ir_3Li particles are used to stabilize large LiO_2 particles of over 200 nm for first time**
   - Use of large Ir_3Li particles in a Li-O_2 cell promotes a nucleation and growth mechanism that results in large ultra-nanocrystalline LiO_2 particles in the discharge product
   - The large LiO_2 particles are more stable than previously grown small LiO_2 particles in Li-O_2 cells
3. **IrLi alloy found to give good cycling performance in a Li-O_2 cell with LiO_2 as the discharge product**
   - 100 cycles with confirmation of LiO_2 as a product

Characterization of Bulk Ir_3Li Synthesized at High Temperatures (500 nm to 5 microns): Raman spectroscopy and stability

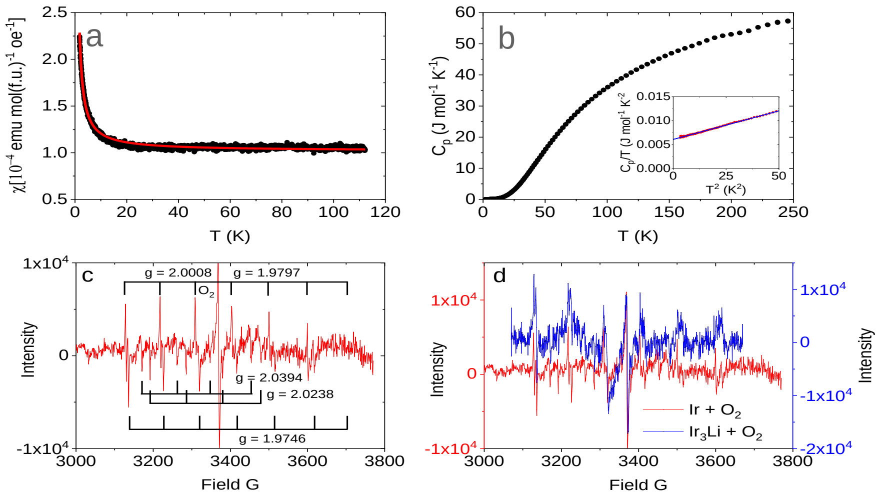


(a) *Raman shift of Ir starting material and synthesized Ir_3Li.*
(b) *Calculated phonon density of states of Ir_3Li with Ir-Li coupled modes (red trace) and vibration modes dominated by Li (green trace).*
(c) *Raman spectra of Ir_3Li powder during extended exposure to air.*

- These results show that Raman spectroscopy can be used to differentiate Ir_3Li from Ir.

- Raman measurements performed on the sample after 12 hr, 96 hr and 4 weeks of exposure found that the Raman spectra was similar in all cases indicating that bulk Ir_3Li is stable in air for extended periods.

Characterization of Bulk Ir_3Li (500 nm to 5 microns): Magnetic susceptibility, heat capacity, and EPR



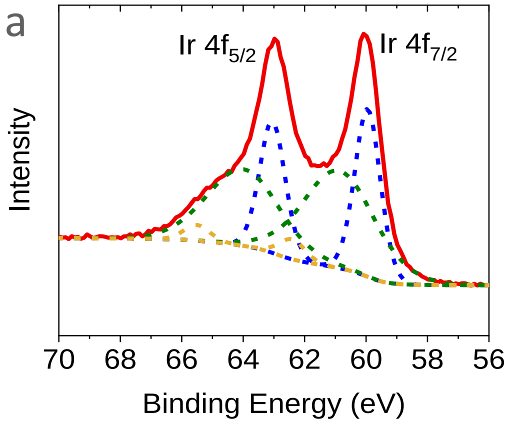
- (a) *Magnetic susceptibility of Ir_3Li (black trace) with fitted curve (red trace)*
- (b) *heat capacity of Ir_3Li*
- (c) *EPR spectrum of iridium powder in O_2 atmosphere at 200 K*
- (d) *Ir_3Li and Ir EPR spectrum in O_2 atmosphere at 100 K and 200K, respectively.*

- The magnetic susceptibility measurement together with heat capacity indicate that the temperature dependent behavior of Ir_3Li is metallic, which is support for the ORR/OER properties of Ir_3Li.

- The EPR results suggest that both Ir and Ir_3Li attract oxygen.

Characterization of Bulk Ir_3Li (500 nm to 5 microns): XPS and AFM

a



b

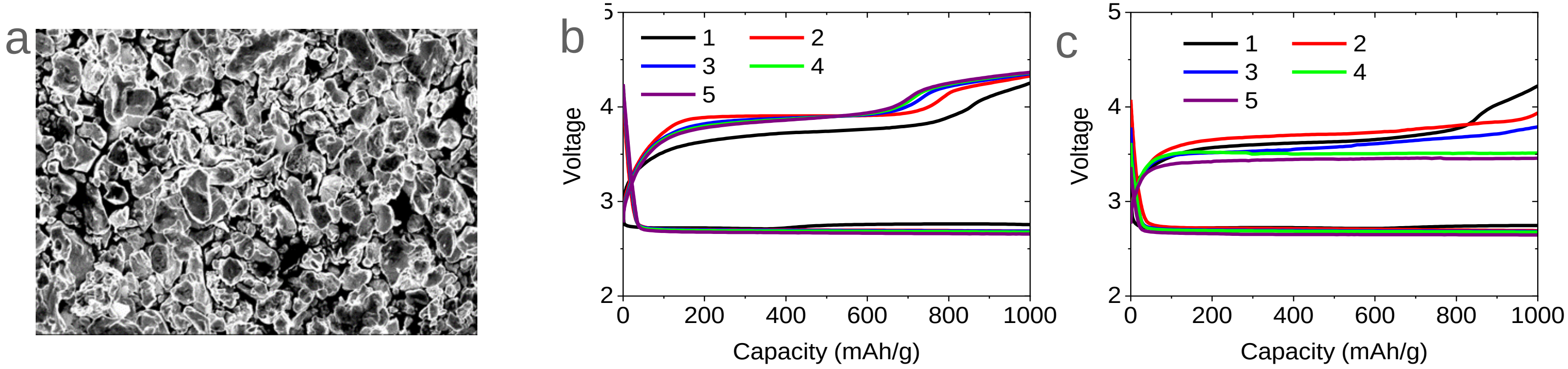
(c) XPS spectra of Ir_3Li powders showing three components of a Ir $4f_{7/2}$ peak at binding energy (BE) 59.95 eV [Ir_3^- blue trace], 60.89 eV [Ir(0) green trace], and 63.99 eV [unknown impurity], respectively.

(d) 5 x 5 µm current image of conductive AFM scan indicating high conductivity in bright color throughout the sample.

- This XPS analysis suggests a charge distribution of Li ~ +0.81e and Ir ~ -0.25e. The negative Ir charge provides a higher tendency to donate electrons. The ORR reaction may be more facile when occurring on Ir3Li compared to IR.

- From AFM measurements the Ir_3Li conductivity was determined as $2.5{\cdot}10^7$ S/m, which is similar to that of Ir metal. These results demonstrate the highly conductive nature of Ir_3Li needed for a cathode material.

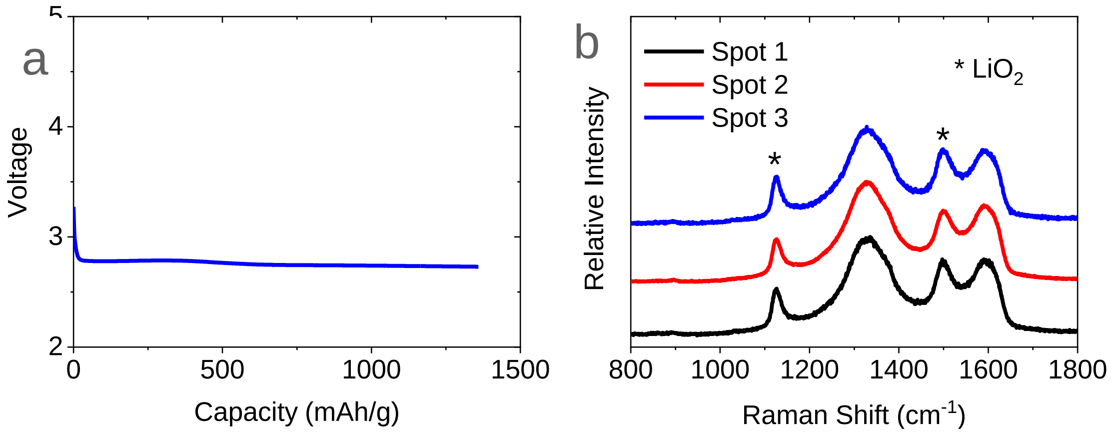
Li-O_2 cell performance with micron size Ir_3Li particles



(a) SEM image of Ir_3Li powders post grinding with mortar and pestle. Scale bar is 10 μm.
(b) The first five cycles of a Li-O_2 cell with rGO/GDL cathode, 1 M Li triflate in TEGDME electrolyte and current density 0.05 mA/cm^2, showing a two-plateau charge profile
(c) The first five cycles of a Li-O_2 cell with Ir_3Li-rGO/GDL cathode showing an initial high charge potential toward the end of the 1st charge cycle which tapered down and reached a charge potential below 3.5 V by the fourth cycle. Same electrolyte and current density as in (b) were applied.

- Ir_3Li particles used in the cathode of the Li-O_2 cell ranged from 200 nm to 5 microns
- Voltage profiles show low charge potentials similar to previous Li-O_2 cells based on much smaller Ir nanoparticles that gave LiO_2 discharge product

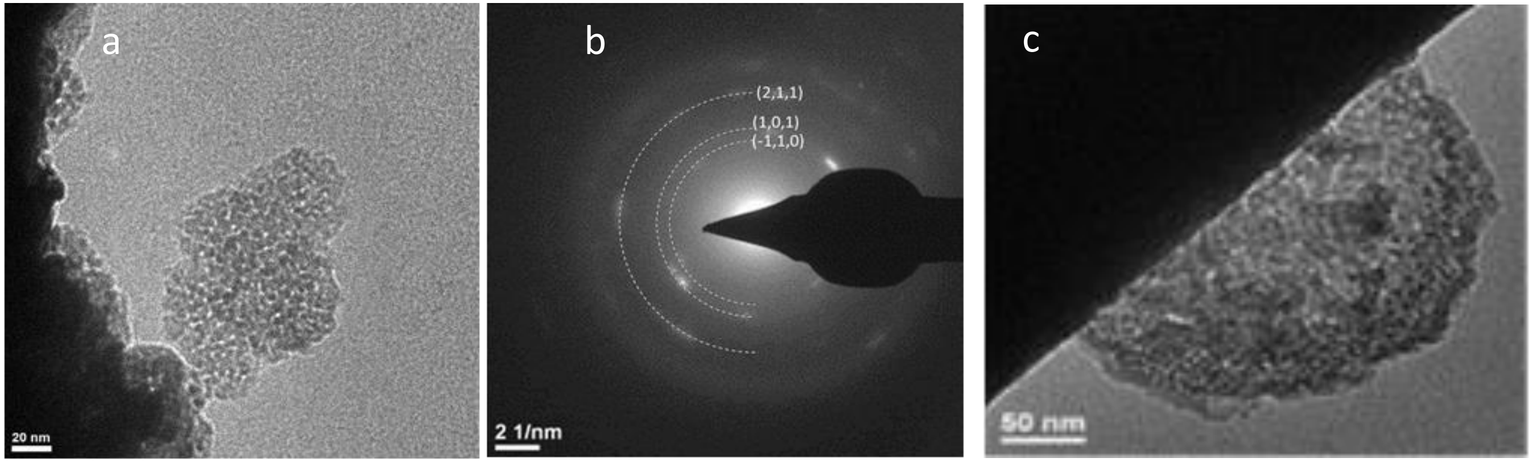
Characterization of the Ir_3Li- based Li-O_2 cell discharge product by Raman and titration



(a) Deep discharge of Ir_3Li-rGO cathode in a Li-O_2 cell showing the discharge potential ~2.75 V for use in characterization
(b) Raman spectra of deep discharged Ir_3Li-rGO cathode in a Li-O_2 cell showing strong LiO_2 peaks at different areas.

- Raman spectra were collected on several different areas and demonstrated strong LiO_2 characteristic peaks at 1125 and 1505 cm-1, along with the characteristic rGO/graphitic peaks at 1328 and 1596 cm-1
- Titration analysis with Ti(IV)OSO_4 followed by UV-Vis of the titrant indicated that the presence of Li_2O_2 was negligible on the discharged cathode consistent with the presence of LiO_2

Characterization of the LiO_2 discharge product by

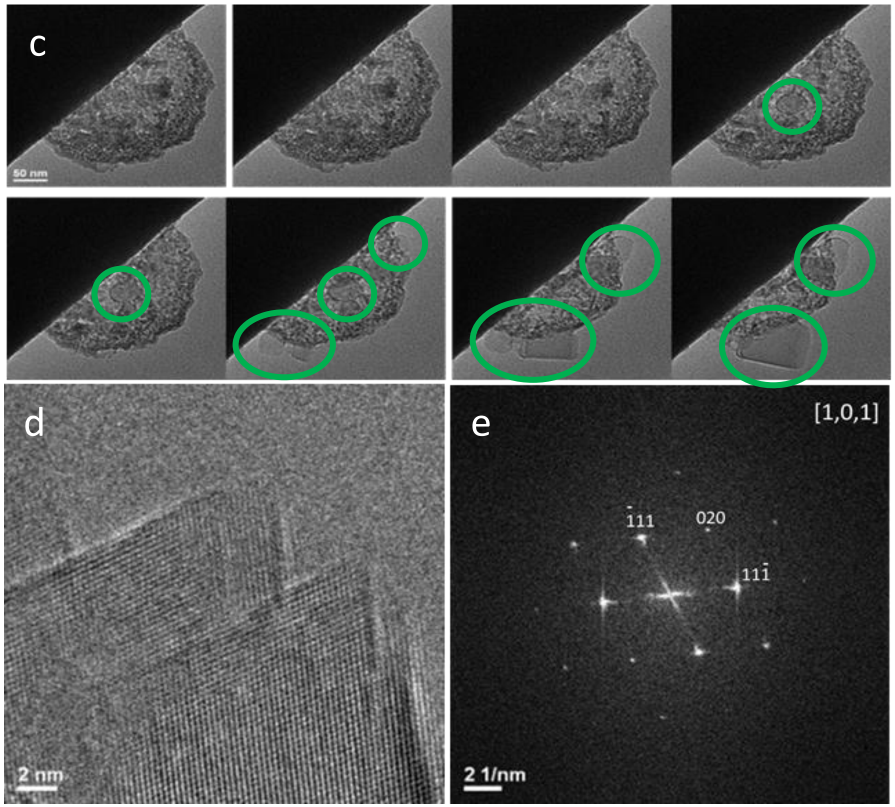


(a) Low resolution TEM image of discharge product particles of a representative ~80x 100 nm large raspberry shaped discharge product that was attached to the cathode surface
(b) electron diffraction pattern of discharge product particle in (a)
(c) Low resolution TEM image of discharge product particles of a representative ~200 nm large raspberry shaped discharge product that was attached to the cathode surface

- The discharge product morphology is made up of small primary particles (~5 nm) that appear to be connected together via amorphous regions to form much larger secondary particles (100-200 nm)

- Selected area electron diffraction (SAED) was performed on the raspberry shaped particle. The diffraction pattern of the particle is consistent with that of ($\bar{1}10$), (101), and (211) LiO_2 surfaces.

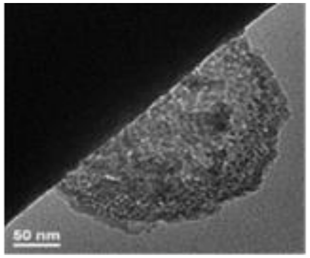
Conversion of large ultra-nanocrystalline LiO_2 particles to Li_2O particles



(c) TEM image snapshots during electron beam irradiation of discharge product particle
(d) high resolution image of particle formed during electron beam irradiation of discharge product (cubic particle circled in green in last video tile)
(e) Electron diffraction pattern of particle formed during electron beam irradiation of initial discharge product showing that LiO_2 is converted to Li_2O (cubic particle)

- The LiO_2 particles show no change under low electron beam accelerating voltage (80 kV), however, they undergo reaction during a high voltage electron beam (200 kV)
- The LiO_2 is converted to Li_2O during irradiation, further evidence for the LiO_2 in the discharge product.

Summary: Stability and Growth Mechanism of LiO_2 Ultrananocrystalline Particles



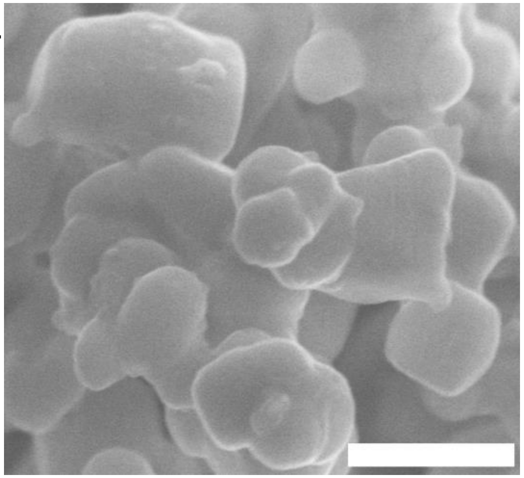
- First time such large LiO_2 particles have been found in discharge products
  - *Remarkably stable compared to previous LiO_2 found in discharge products, which have a relatively short lifetime from disproportionation.*
  - *Evidence for stability is that the 80 kV electron beam doesnot change them; and time between discharge and the TEM experiments*

- The growth of these large particles may be due to the use of large (up to 2 micron size) Ir_3Li particles for the cathode that results in ORR as well as nucleation/growth on the same substrate.
  - *This is in contrast to previous studies where cathodes have been based on small Ir nanoparticles loaded onto an rGO support where ORR and nucleation/growth are probably occurring on separate surfaces*

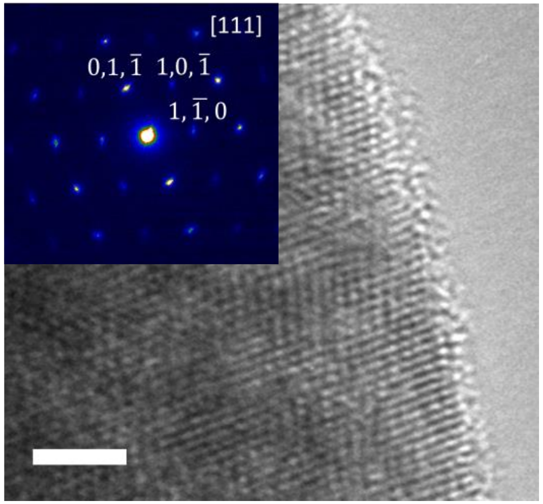
- Mechanism probably involves the primary nucleation and growth of crystalline particles from solution, and subsequent diffusion-controlled agglomeration of these primary particles or 'secondary nucleation' of new particles on primary particles

IrLi particles synthesized at high temperature: characterization

(a)



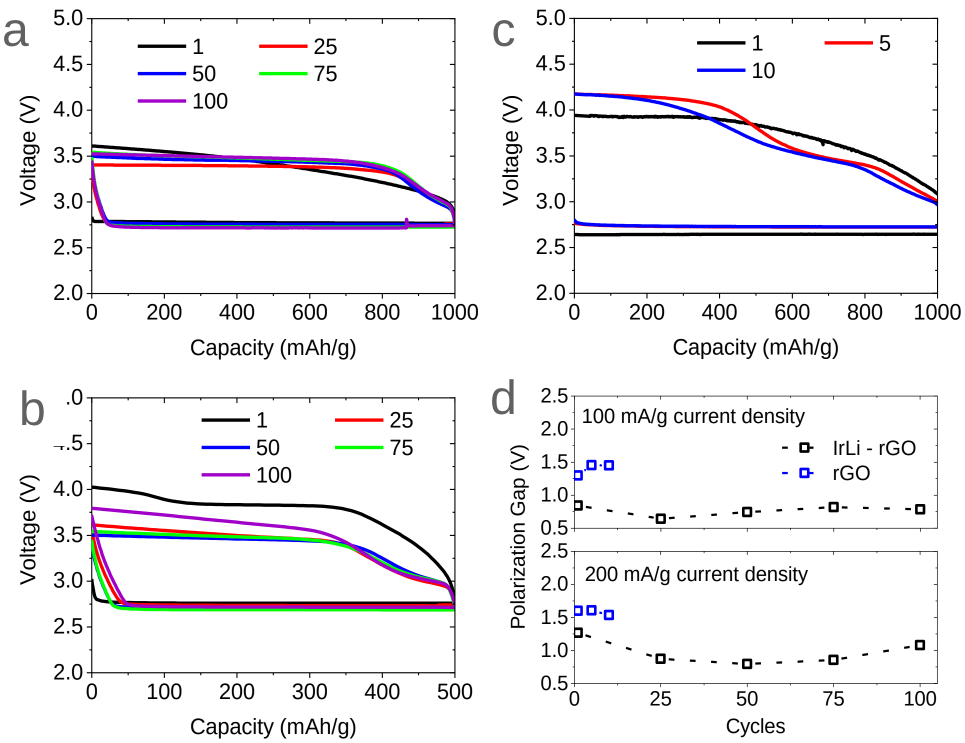
(b)



a) SEM and (b) TEM images of IrLi nanopowder synthesized by thermal treatment of Ir nanopowder and Li foil. TEM inset shows electron diffraction of IrLi particle. Scale bars in a and e are 500 nm and 2 nm, respectively

- SEM and TEM used to identify IrLi particles and their size (100-500 nm)

IrLi particles synthesized at high temperature and used in a Li-O_2 battery with a rGO support



(a) galvanostatic cycling of IrLi-rGO cathode in Li-O_2 cell at a current density of 100 mA/g and a capacity of 1000 mAh/g

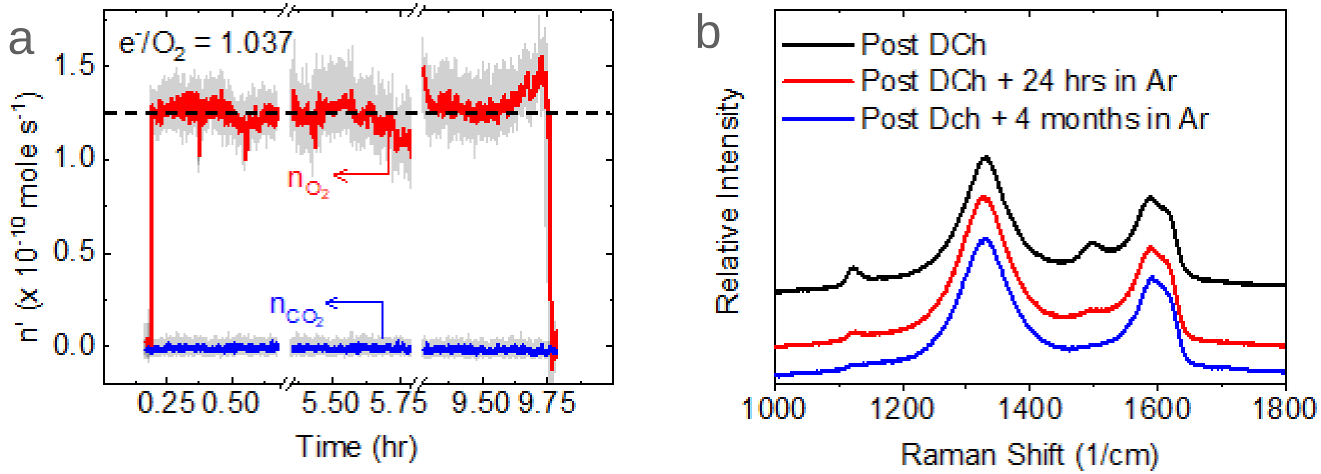
(b) galvanostatic cycling of IrLi-rGO cathode in Li-O_2 cell at a current density of 200 mA/g and a capacity of 500 mAh/g.

(c) galvanostatic cycling of rGO cathode in Li-O_2 cell at a current density of 100 mA/g and a capacity of 1000 mAh/g.

(d) maximum charge polarization overpotentials calculated from IrLi-rGO and rGO cathode cycling at 100 mA/g and 200 mA/g current densities.

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

Characterization of Li-O_2 battery based on cathodes with synthesized IrLi particles: DEMS and Raman

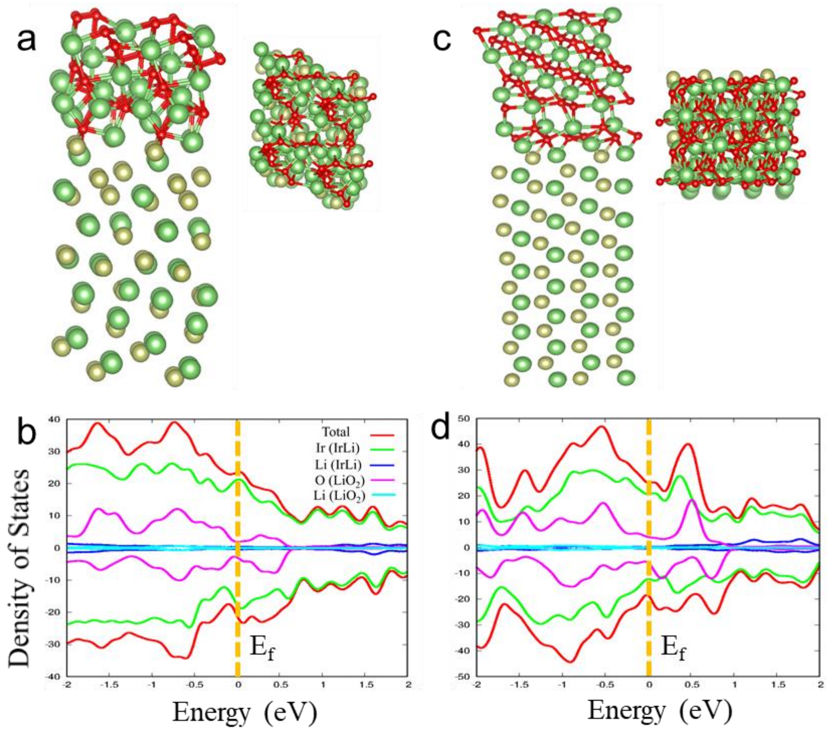


(a) molar quantiles of the evolved O_2 at the 10th charge cycle in three-time intervals (first 30 minutes, mid 30 minutes, and last 30 minutes) calculated from In-situ DEMS experiment of IrLi-rGO cell.

(b) Raman spectra of discharged IrLi-rGO cathode directly after removal from cell, and after ageing in Ar atmosphere for 24 hr and 4 months, post removal from cell.

- DEMS measurements are consistent with 1 electron/O2 reaction consistent with LiO_2 formation
- Raman shows LiO_2 peaks that are present still after 24 hours, disappear after 4 months due to disproportionation.

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



Two epitaxial growth interfaces of crystalline LiO_2 on IrLi facets.

(a) Crystalline LiO2 in (111) orientation on a (111) facet of IrLi with the electronic density of states (DOS) shown by c.

(c) Crystalline LiO2 in (101) orientation on a (110) facet of IrLi with electronic DOS shown by d.

- Based on DFT calculations on the interface between LiO_2 and IrLi, we find some crystalline faces have good lattice matches, as would be required for epitaxial growth of crystalline LiO_2.

Accomplishment: LiO_2 battery with long cycle life using IrLi nanoparticles

- IrLi nanoparticle synthesis was carried out by high temperature synthesis
- $Li-O_2$ batteries employing IrLi-rGO cathodes were cycled up to 100 cycles at moderate current densities with sustained low charge potentials (<3.5 V).
- Various techniques including SEM, DEMS, TEM, Raman, and titration were implemented to demonstrate a film-like LiO_2 discharge product and an absence of Li_2O_2.
- The formation of crystalline LiO_2 can be stabilized by epitaxial growth on IrLi facets of IrLi nanoparticles on the cathode surface based on first-principles calculation.

- These results demonstrate that by finding appropriate surfaces in alloys lithium superoxide can be stabilized and efficiently cycled in $Li-O_2$ batteries
  - This is the second cathode material that has been shown to stabilize LiO_2

Response to last year reviewer's comments

No comments from last year.

Proposed Future Work

- Stability of large lithium superoxide nanoparticles
  - Our preliminary results show that the large raspberry shaped LiO_2 particles may be quite stable
  - Investigate optimization of Li-O_2 cell cathode material to increase size and stability of the particles
- Closed Li-O_2 battery based on lithium superoxide, i.e. no external source of O_2
  - Investigate the possibility of using these large nanoparticles in a closed system
  - Examine coatings from electrolyte additives on the particles to extend life and enable a closed system
- 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. 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

M. Asadi, IIT

- Characterization of gaseous products

Remaining Challenges and Barriers

- Discovery of new electrolytes for lithium superoxide $Li\text{-}O_2$ 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 $Li\text{-}O_2$ batteries

Summary of Technical Accomplishments

1. **Characterization of electronic properties of Ir_3Li particles relevant to use as catalysts in Li-O_2 cells**
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2. **Micron sized Ir_3Li particles are used to stabilize large LiO_2 particles of over 200 nm for first time**
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   - The large LiO_2 particles are more stable than previously grown small LiO_2 particles in Li-O_2 cells
3. **IrLi alloy found to give good cycling performance in a Li-O_2 cell with LiO_2 as the discharge product**
   - 100 cycles with confirmation of LiO_2 as a product
   - Results show that other surfaces can be found to stabilize LiO2