Investigation of Lithium Superoxide-Based Batteries

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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

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones</th>
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<tbody>
<tr>
<td>Jun/20</td>
<td>Characterization of electronic properties of high temperature synthesized Ir$_3$Li, <strong>(Completed)</strong></td>
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<tr>
<td>Sep/20</td>
<td>Voltage profiles and characterization of discharge product by titration and other techniques in an Ir$_3$Li cell, <strong>(Completed)</strong></td>
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<tr>
<td>Dec/21</td>
<td>TEM studies of large LiO$_2$ particles, investigation of stability and formation mechanism, <strong>(Completed)</strong></td>
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<tr>
<td>Mar/21</td>
<td>Investigate performance of Li-O$_2$ battery using cathode based on bulk high temperature synthesized IrLi particles on rGO support, <strong>(Initiated)</strong></td>
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Strategy: an integrated experiment/theory approach that combines testing, understanding and design to develop lithium superoxide based Li-O$_2$ batteries

Design of improved cathodes/electrolytes for efficiency, cycle life, and capacity

- Synthesize, test, and characterize cathode architectures
- Evaluate solvents, salts, and additives
- Develop understanding of the discharge and charge mechanisms
- Develop understanding of the synergies between electrolyte components and cathode
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$_2$O$_2$ 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-O₂ batteries have been based on Ir nanoparticles on a reduced graphene oxide (rGO) cathode that partially form Ir₃Li during cycling, which act as templates for growth of LiO₂ instead of the more stable Li₂O₂ product
  - In both cases Li is partially incorporated into Ir particles during discharge
- In this work we have synthesized (at high temperatures) and characterized bulk IrLi₃ and IrLi alloys using a high temperature method to use in LiO₂ batteries
Summary of Technical Accomplishments

1. Characterization of electronic properties of Ir₃Li particles relevant to use as catalysts in Li-O₂ cells
   - Bulk Ir₃Li was found to have comparable conductivity to iridium metal
   - Possess metal-like magnetic properties, and have an affinity toward O₂.

2. Micron sized Ir₃Li particles are used to stabilize large LiO₂ particles of over 200 nm for first time
   - Use of large Ir₃Li particles in a Li-O₂ cell promotes a nucleation and growth mechanism that results in large ultra-nanocrystalline LiO₂ particles in the discharge product
   - The large LiO₂ particles are more stable than previously grown small LiO₂ particles in Li-O₂ cells

3. IrLi alloy found to give good cycling performance in a Li-O₂ cell with LiO₂ as the discharge product
   - 100 cycles with confirmation of LiO₂ as a product
Characterization of Bulk Ir₃Li Synthesized at High Temperatures (500 nm to 5 microns): Raman spectroscopy and stability

(a) Raman shift of Ir starting material and synthesized Ir₃Li.
(b) Calculated phonon density of states of Ir₃Li with Ir-Li coupled modes (red trace) and vibration modes dominated by Li (green trace).
(c) Raman spectra of Ir₃Li powder during extended exposure to air.

- These results show that Raman spectroscopy can be used to differentiate Ir₃Li 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 Ir₃Li is stable in air for extended periods.
Characterization of Bulk Ir$_3$Li (500 nm to 5 microns): Magnetic susceptibility, heat capacity, and EPR

- The magnetic susceptibility measurement together with heat capacity indicate that the temperature dependent behavior of Ir$_3$Li is metallic, which is support for the ORR/OER properties of Ir$_3$Li.

- The EPR results suggest that both Ir and Ir$_3$Li attract oxygen.
Characterization of Bulk Ir$_3$Li (500 nm to 5 microns): XPS and AFM

(c) XPS spectra of Ir$_3$Li 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 $\sim$ +0.81e and Ir $\sim$ -0.25e. The negative Ir charge provides a higher tendency to donate electrons. The ORR reaction may be more facile when occurring on Ir$_3$Li compared to IR.

- From AFM measurements the Ir$_3$Li 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$_3$Li needed for a cathode material.
Li-O$_2$ cell performance with micron size Ir$_3$Li particles

(a) SEM image of Ir$_3$Li 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$_3$Li-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$_3$Li 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$_3$Li- based Li-O$_2$ cell discharge product by Raman and titration

(a) Deep discharge of Ir$_3$Li-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$_3$Li-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$_2$O$_2$ was negligible on the discharged cathode consistent with the presence of LiO$_2$
Characterization of the LiO₂ discharge product by TEM

- 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 (110), (101), and (211) LiO₂ surfaces.

(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
Conversion of large ultra-nanocrystalline LiO$_2$ particles to Li$_2$O particles

- 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$_2$O during irradiation, further evidence for the LiO$_2$ in the discharge product.

(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$_2$O (cubic particle)
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 does not 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$_3$Li 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

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

(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.

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IrLi particles synthesized at high temperature and used in a Li-O₂ battery with a rGO support

(a) galvanostatic cycling of IrLi-rGO cathode in Li-O₂ 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-O₂ cell at a current density of 200 mA/g and a capacity of 500 mAh/g.

(c) galvanostatic cycling of rGO cathode in Li-O₂ 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 IrLi₃ particles (<1 μm in size) are found to result in LiO₂ 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 LiO$_2$ in (111) orientation on a (111) facet of IrLi with the electronic density of states (DOS) shown by c.

(c) Crystalline LiO$_2$ 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$_2$. 

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Accomplishment: LiO₂ battery with long cycle life using IrLi nanoparticles

- IrLi nanoparticle synthesis was carried out by high temperature synthesis
- Li-O₂ 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 LiO₂ discharge product and an absence of Li₂O₂.
- The formation of crystalline LiO₂ 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-O₂ batteries
  - This is the second cathode material that has been shown to stabilize LiO₂
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-O₂ 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-O₂ batteries
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3. IrLi alloy found to give good cycling performance in a Li-O₂ cell with LiO₂ as the discharge product
   - 100 cycles with confirmation of LiO₂ as a product
   - Results show that other surfaces can be found to stabilize LiO₂