Lithium-Air Batteries

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Project ID# BAT-286

Overview

Timeline

- Start: 2015
- Finish: 2020
- 65 %

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: $ 2400 K
  - Contractor 0
- FY 16: $ 400 K
- FY 17: $ 500 K
- FY 18: $ 500 K

Partners

- Interactions/ collaborations
  - S. Vajda, ANL
  - S. Al-Hallaj and B. Chaplin, UIC
  - D. Miller and J. G. Wen, ANL
  - Y. Wu, Ohio State University
  - A. Salehi, UIC
  - Anh Ngo, ANL

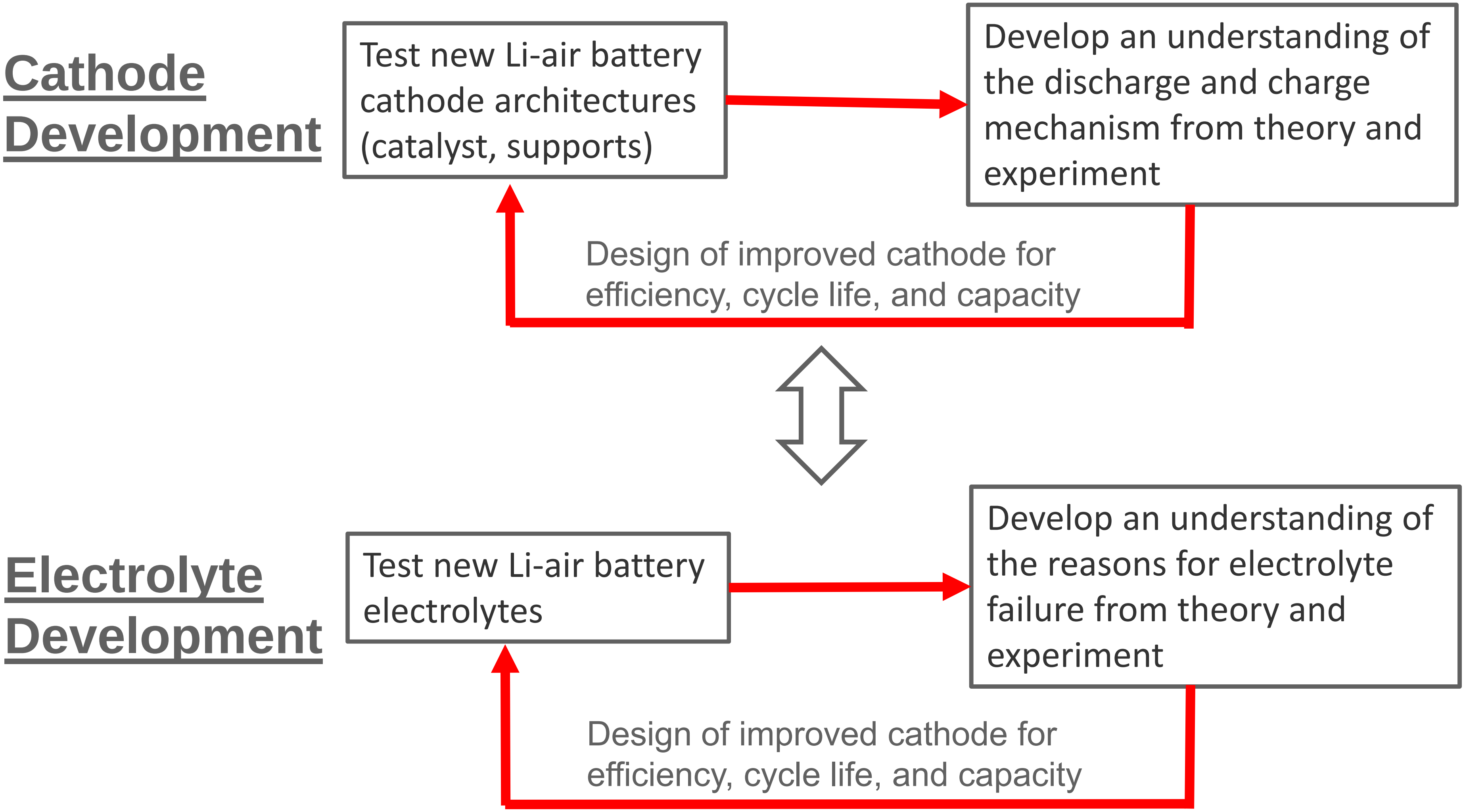
Project Objectives and Relevance

- Development of Li-air batteries with increased capacity, efficiency, and cycle life through use of new electrolytes that act in conjunction with new cathode architectures
- 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 have the potential for very high energy density and low cost

FY18 Milestones

Month/ Year	**Milestones**
Dec/17	Investigation of highly uniform Pt_3Co nanoparticles in biphasic nitrogen-doping cobalt@graphene heterostructures as cathode materials. Q1 (**Completed**)
Mar/18	Computational studies of dependence of stability and composition of discharge products in Li-O2 batteries on ether-based electrolytes. Q2 (**Completed**)
Jun/18	Use of highly uniform small Ir clusters supported on reduced graphene oxide to study formation of Ir_3Li alloys for lithium superoxide based batteries. Q3(**Initiated**)
Sep/18	Investigation of dependence of discharge composition on type of ether used electrolytes from experimental studies. Q4 (**Initiated**)

Strategy: an integrated experiment/theory approach that combines testing, understanding and design to develop cathodes and electrolytes for Li-O_2 batteries



Cathode Development

Test new Li-air battery cathode architectures (catalyst, supports)

Develop an understanding of the discharge and charge mechanism from theory and experiment

Design of improved cathode for efficiency, cycle life, and capacity

Electrolyte Development

Test new Li-air battery electrolytes

Develop an understanding of the reasons for electrolyte failure from theory and experiment

Design of improved cathode for efficiency, cycle life, and capacity

Experimental methods

Synthesis

- New catalyst materials
- New carbon materials
- Electrolytes

Characterization

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

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)
  - Assessment with high level theories (e.g. G4 theory)
- 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
  - Ion pair formation
  - Electrolyte/surface interface simulations
- Design of oxygen reduction and oxygen evolution catalysts
  - Density of states
  - Adsorption energies

Technical Accomplishments

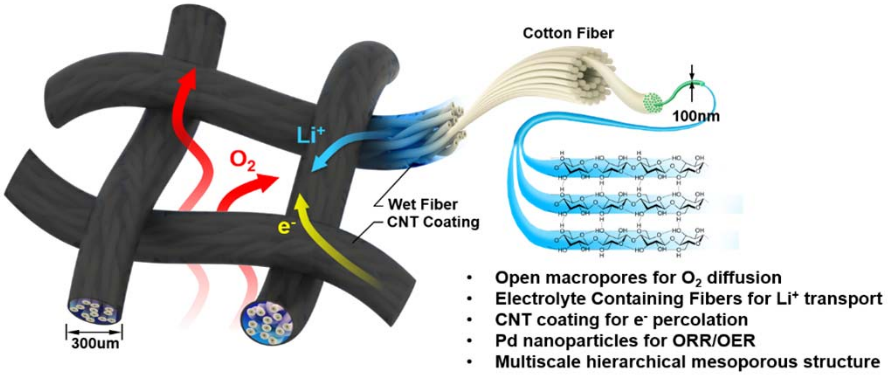
I. New cathode materials
  - A novel Li-O_2 cathode based on a triple phase structure using textile coated with carbon nanotubes
  - Metal-organic framework derived cathode for Li-O_2

II. Lithium superoxide
  - Identification of LiO_2 by Raman spectroscopy
  - Lithium superoxide based Li-O_2 battery using a cathode with Ir_8 clusters on reduced graphene oxide (rGO)

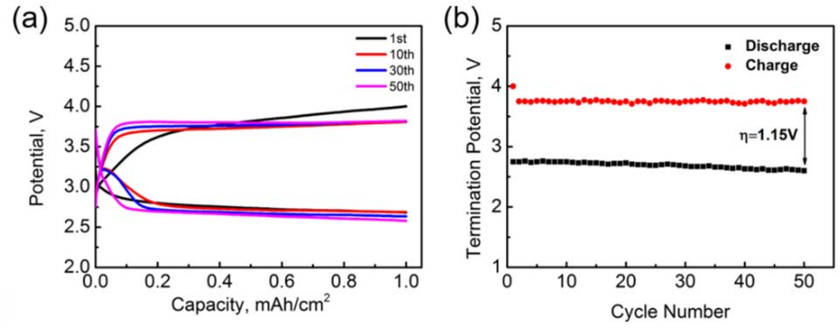
III. Electrolytes
  - Dependence of LiO_2 formation on type of electrolyte

A novel Li-O_2 cathode based on a novel triple phase structure by using a common textile

- Cathode is based on that of a textile, i.e., the surface is densely coated layer of carbon nanotubes (CNT)
  - hierarchical networked structure leads to decoupled pathways for electrolyte and oxygen gas
  - facilitate the transport of both components, significantly improving battery performance.
- Li-O_2 battery has a high discharge capacity of 8.6 mAh/cm^2, low overpotential of 1.2 V, and stable operation of over 50 cycles.
- Characterization of discharge product: XRD results indicate the formation of Li_2O_2; Raman spectroscopy and XPS were employed to analyze the discharge product and indicated Li_2O_2



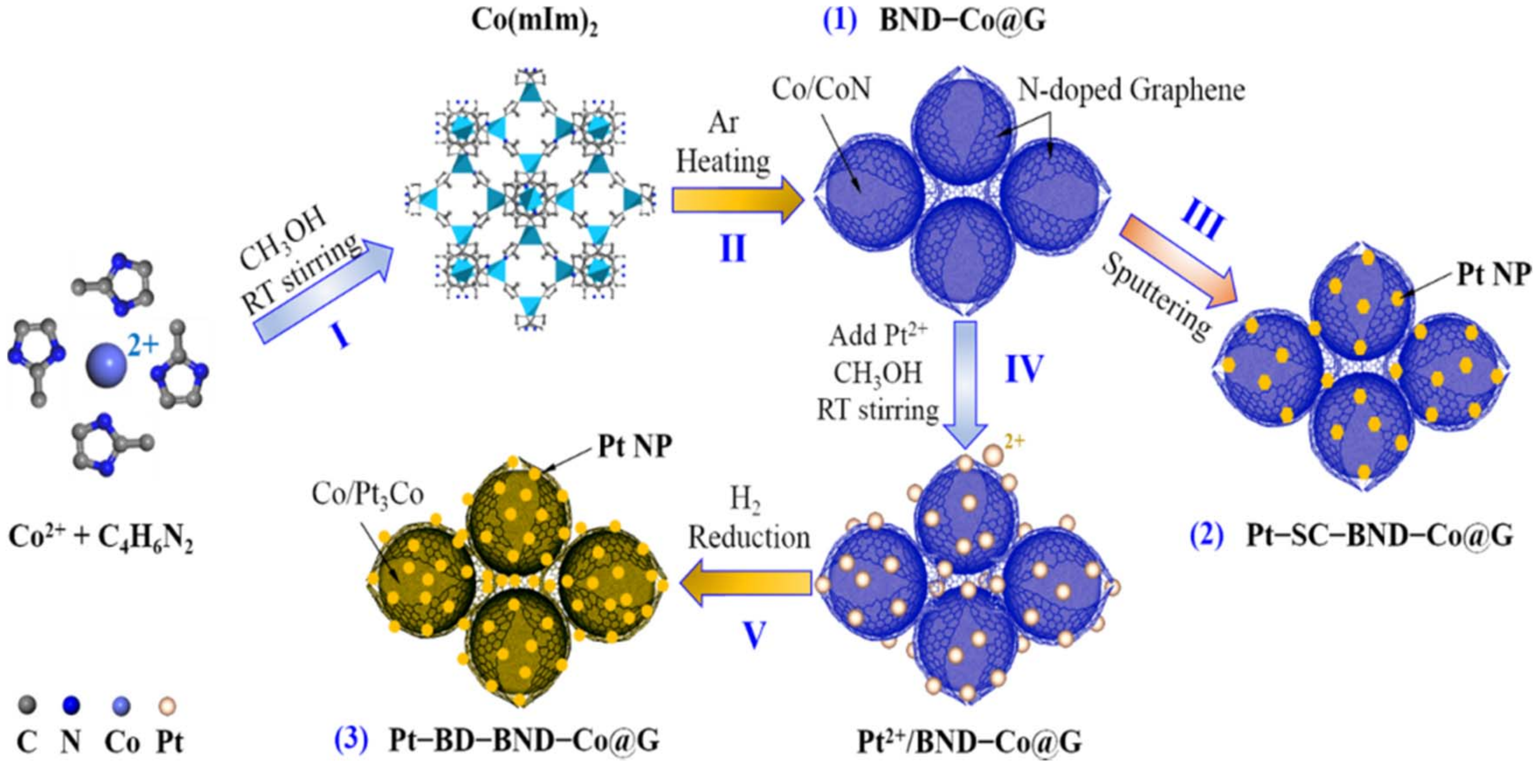
Schematic of the wet textile based air cathode with decoupled pathways for electrolyte and oxygen.



(a) discharge/charge profile for the 50 cycles
(b) termination voltage of charge/discharge for 50 cycles

Metal-organic framework derived cathode for Li-O_2

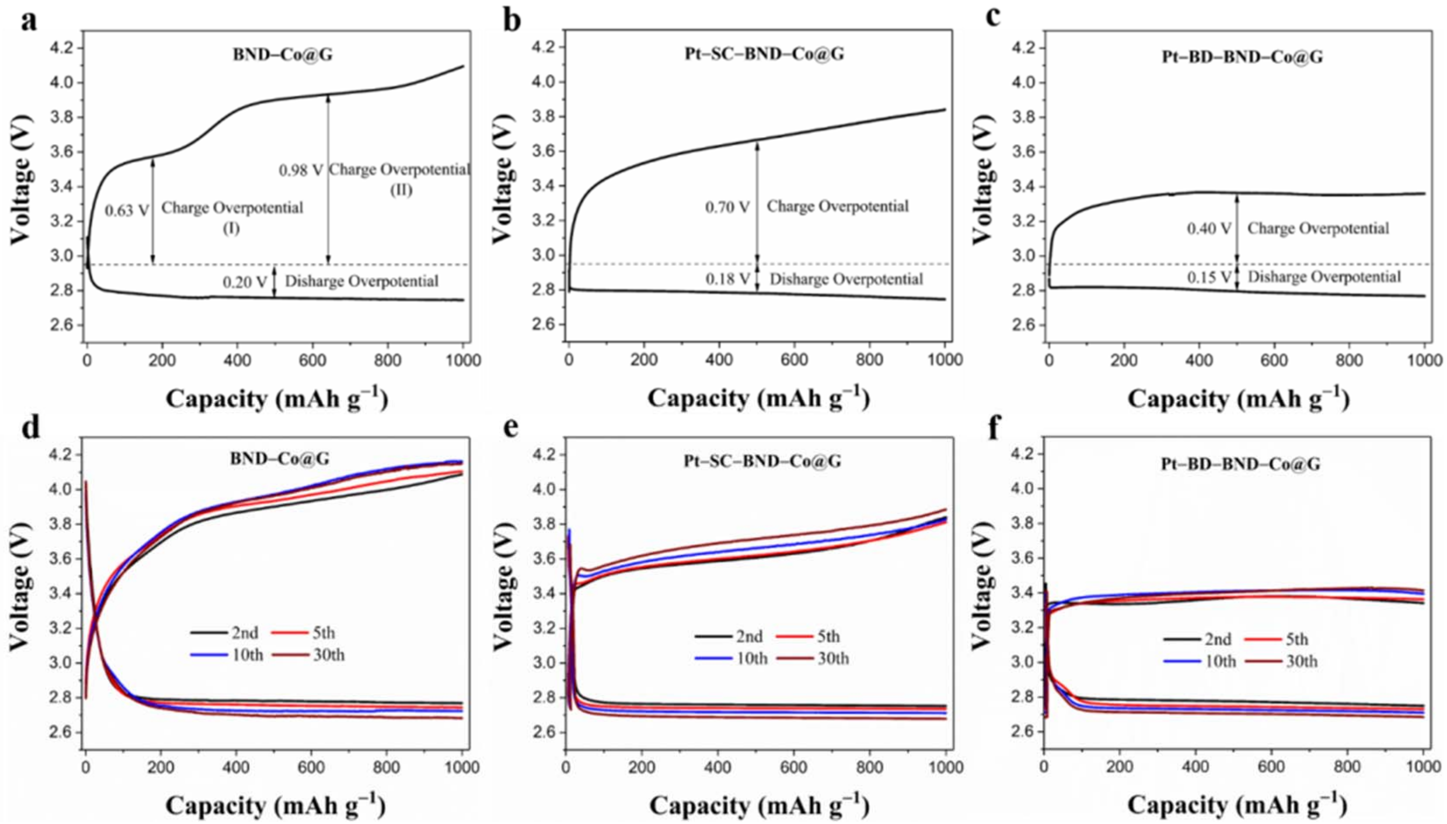
- We have used a bulk-doping approach to encapsulate platinum nanocomponents into a cobalt-based zeolitic imidazolate framework (ZIF)
- The fabricated cathode architectures feature highly uniform Pt and Pt_3Co nanoparticles within three different heterostructures shown below.



Schematic of Pt modified MOF-derived catalysts.
BND−Co@G = biphasic N-doped cobalt@graphene
Pt−SC−BND−Co@G = Pt surface-coating BND−Co@G
Pt−BD−BND−Co@G = Pt bulk-doping BND−Co@G

Metal-organic framework derived cathodes for Li-O_2: voltage profiles

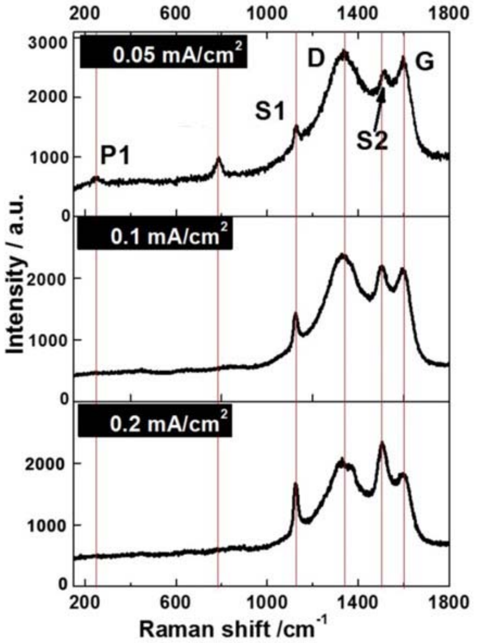
- The improvement in the materials for optimizing catalytic properties and maximizing active regions has enabled promising electrochemical performance in our testing.
- This has included higher specific capacity and a dramatic reduction in charge overpotential to 0.4 V in the case of the Pt−BD−BND−Co@G



Voltage profiles of cathodes in the Swagelok-typed Li-O_2 cells

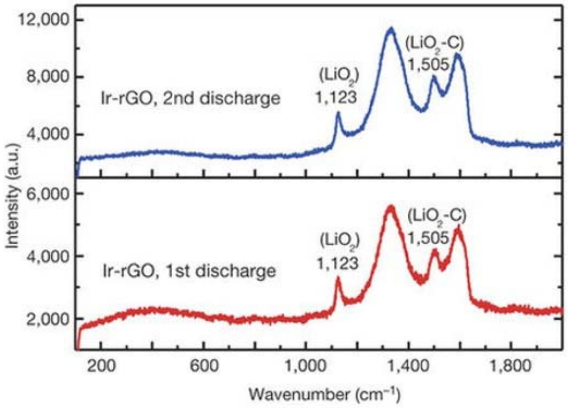
Identification of LiO_2 by Raman spectroscopy: two peaks

- There have been numerous assignments of Raman peaks at ~1123 and 1505 cm-1 to LiO_2 by us and others (for a review see Halder et al ACS Energy Letters 2018)
  - Peaks are found in discharge product of a Li-O_2 cell under some conditions
  - The 1123 cm-1 peak is from O_2 stretching frequency
  - The 1505 cm-1 peak is from coupling of coupling of LiO_2 to a carbon surface
- Other evidence has been reported that also confirms LiO_2 presence in some cases including DEMS, EPR, XRD, titration, Electron diffraction, XPS.



Raman peaks for LiO_2 (S1, S2) and Li_2O_2 (P1,P2) with an activated carbon cathode (JACS 2014)

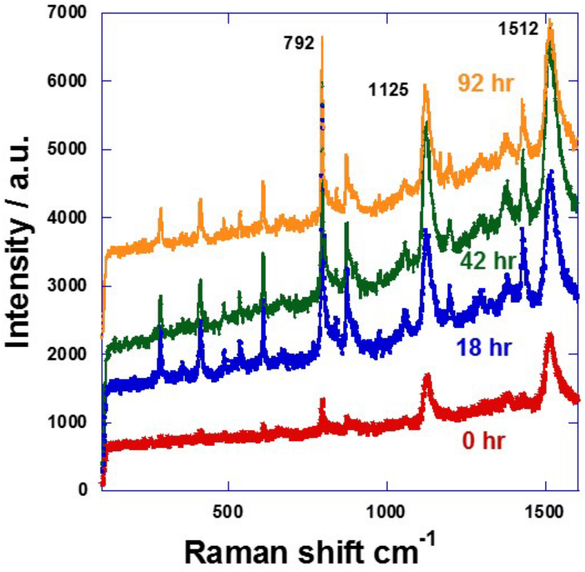
Raman peaks for LiO_2 with an Ir-rGO cathode (Lu, Amine, Curtiss, et al Nature 2016)



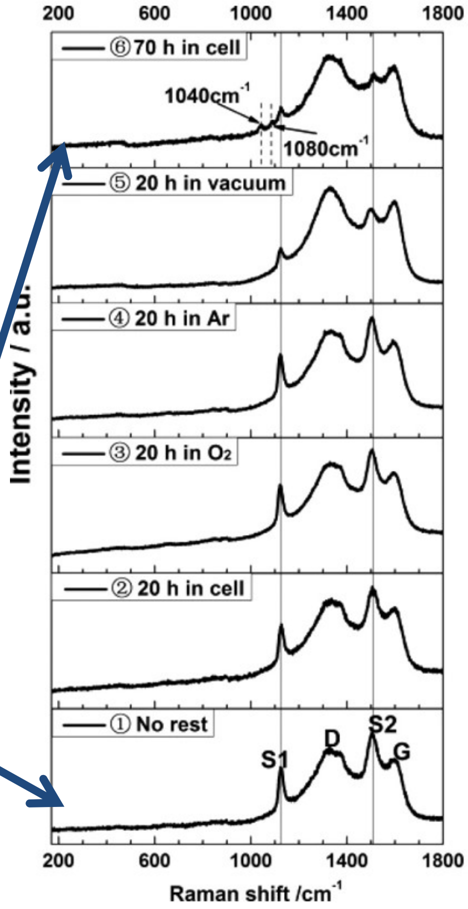
- **Conclusion: strong evidence for presence of LiO_2 as a component in some Li-O_2 cells.**

Identification of LiO_2 by Raman spectroscopy: PVDF binder?

- There has been some question as to whether the LiO_2 peaks may actually be due to degraded PVDF binder due to the fact that it has peaks close to these in Raman spectra
  - However, the peaks only appear if the binder has not been heated to ~100 C to drive off the water that can cause degradation
- We carried out ageing experiments to determine whether the LiO_2 and PVDF peaks are the same and whether the LiO_2 peaks have been missassigned (see Halder, Amine, Curtiss et al, ACS Energy Letters 2018)



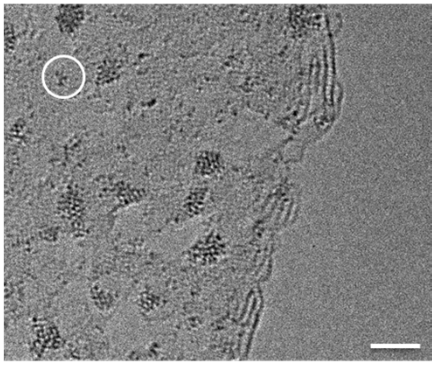
PVDF binder (not heated) Raman peaks are similar to LiO_2, but donot change with aging, unlike LiO_2 peaks which decrease with aging



- **Conclusion: With proper preparation of PVDF binder LiO_2 peaks are correctly assigned.**

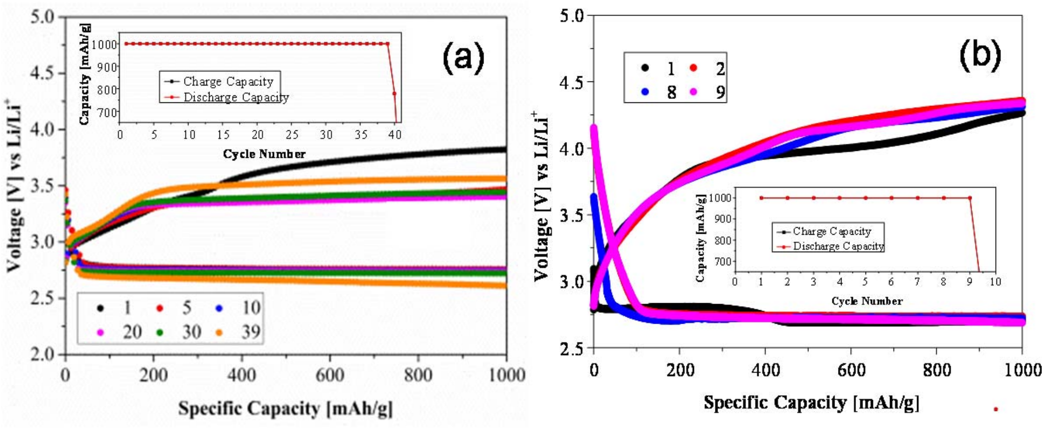
Lithium superoxide based Li-O_2 battery using a cathode with on Ir nanoparticles: follow-up on role of Ir

- In previous work (Lu, Amine, Curtiss et al, Nature 2016) we reported on a Li-O_2 cathode with Ir nanoparticles on an rGO cathode that gives LiO_2 as the discharge product based on DEMS, XRD, EPR, Raman, and titration data
- The Ir nanoparticles become an Ir_3Li intermetallic that seem to template crystalline LiO_2 growth
- This significantly reduces the charge overpotential from >4 V for rGO to under 3.5 V
- Cell configuration: tetraglyme (ether) and LiTFSI electrolyte; lithium anode



Cathode: Ir nanoparticles on rGO

Voltage profiles



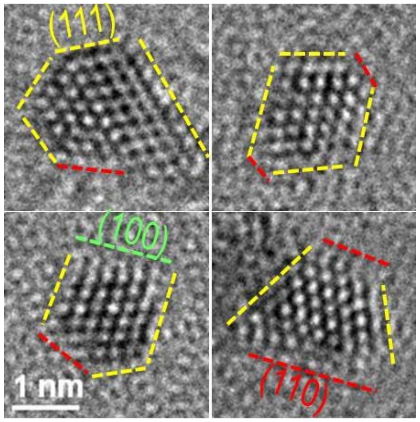
Ir-rGO

rGO

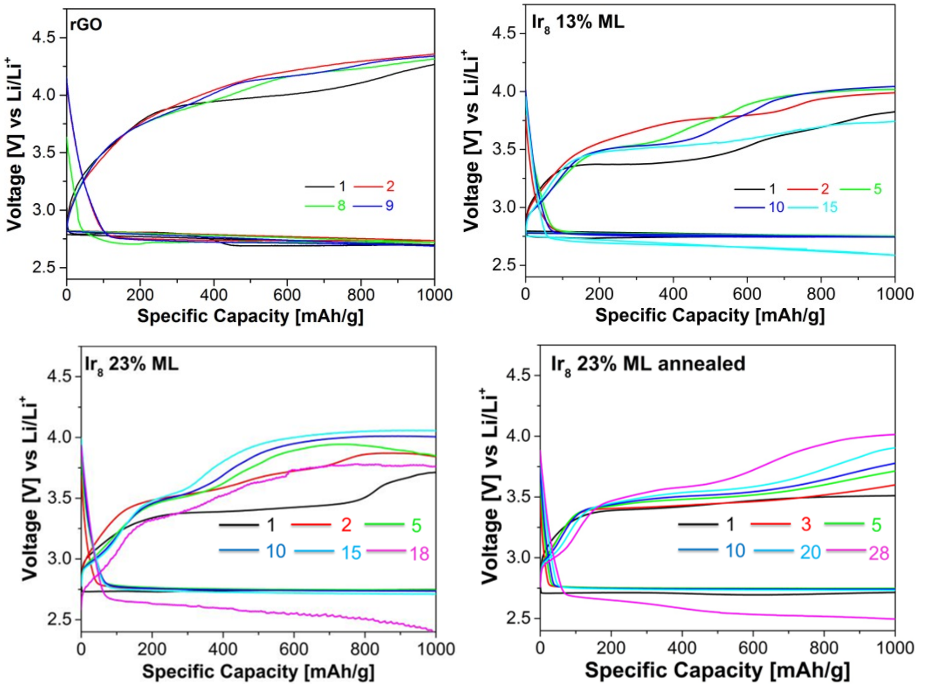
- **Conclusion: Ir nanoparticles are responsible for LiO_2 formation and lowered charge potential, but which size Ir nanoparticle is responsible is unclear since there is a range of sizes.**

Lithium superoxide based Li-O_2 battery with a cathode based on size-specific Ir_n clusters

- Size selected Ir clusters to determine size dependence of LiO_2 formation
  - Ir_2, Ir_4, Ir_8 clusters with different coverages on rGO; also annealed to larger sizes
- Annealed Ir_8 clusters (~1.5 nm nanoparticles) give lowest charge potential and were chosen for further characterization
- Characterization showed the discharge product to be lithium superoxide
  - From DEMS, Raman, titration



HRTEM image of 23% ML Ir_8-rGO cathode after annealing under vacuum for 24 hours at 100 ˚C showing ~1.5 nm NPs

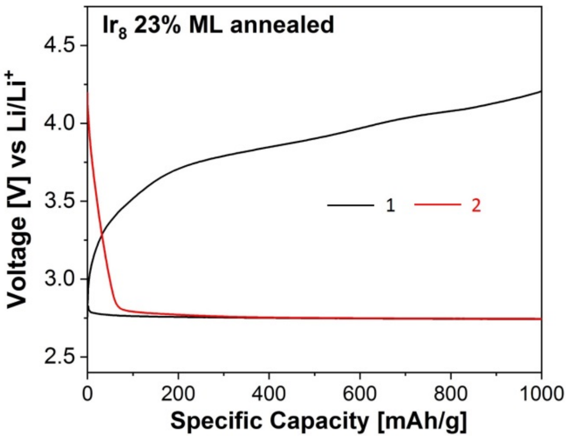


Voltage profiles for rGO and Ir_8 clusters on rGO with different coverages and preparation

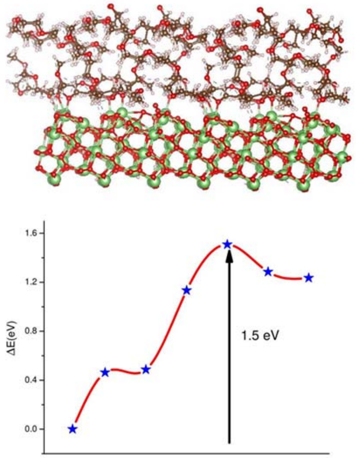
- **Conclusion: 1.5 nm Ir nanoparticles (NPs) give LiO_2 similar to our previously published non-uniform Ir NPs; work is underway to learn more about the effect of electrolyte and the role of the NPs.**

Dependence of LiO_2 formation on type of electrolyte

- LiO_2 formation dependence on electrolyte was investigated with the Ir_8 annealed cathode that gave LiO_2 in TEGDME based electrolyte; all other conditions remained the same.
- Two other electrolytes were investigated (DME and DMSO)
- Both electrolytes gave higher charge potentials indicative of more Li_2O_2 formation
  - Li_2O_2 formation confirmed by titration and lack of Raman peaks for LiO_2
- Computational studies were carried out to determine how the electrolyte can stabilize Li-O_2 formation at the interface
  - All three electrolytes gave large barriers (1.5-1.8 eV) for O_2 dissolution from the LiO_2 surface; thus this doesnot explain the electrolyte dependence



Voltage profile for DME based electrolyte: much higher charge potential than TEGDME



DFT calculation for the barrier to O2 dissolution from LiO2 surface

- **Conclusion: There is a strong electrolyte dependence on the formation of LiO_2 with TEGDME favoring LiO_2 formation. We are investigating possible differences in LiO_2 disproportionation rates as an explanation**

Response to last year reviewer’s comments

No comments from last year.

Proposed Future Work

- Systematic studies of electrolytes including highly concentrated electrolytes, ionic liquids, and blends.
  - Effect on discharge product composition, cycle life, and efficiency
  - Understand effect on disproportionation
  - Investigate redox mediators
  - Computational studies to help design new electrolytes
  - Design new electrolytes for optimal Li-O_2 performance
- New electrodes for Li-O_2 cells
  - Explore alternative catalyst to Ir that stabilize LiO_2
  - Explore lithium anode protection to prevent anode corrosion and extend cycle life

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
- Y. Wu, Ohio State University
  - Development of electrolytes for Li-air batteries.
- A. Salehi, University of Illinois-Chicago
  - Li anode protection
- A. Ngo, ANL
  - Computations
- K. C. Lau, California State University, Norridge
  - Computations

Summary

I. New cathode materials

- A novel Li-O_2 cathode for low charge potentials was developed with a novel triple phase structure based on a densely coated layer of carbon nanotubes (CNT) on textile fibers to create a hierarchical networked structure leading to decoupled pathways for electrolyte and oxygen gas
- We have used a bulk-doping approach to encapsulate platinum nanocomponents into a metal organic framework and found that certain types have low charge potentials.

II. Lithium superoxide

- The assignment of two Raman peaks to LiO_2 has been validated by eliminating degraded PVDF binder as a possible source of the peaks
- A Li-O_2 battery using a cathode based on Ir_8 clusters has been found to result in LiO_2 as the discharge product. The results help to establish the mechanism for formation of LiO_2 in the cell.

III. Electrolytes

- The formation of LiO_2 in a Li-O_2 cell is found to have a surprising dependence on the choice of electrolyte. This opens the way to further optimizing the performance by electrolyte modification.