Development of Novel Electrolytes and Catalysts for Li-Air Batteries

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DOE merit review

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Project ID# ES286

Overview

Timeline

- Start: 2014
- **Finish: 2018**
- **60%**

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: 1200
  - Contractor 0
- FY 14: $ 400 K
- FY 15: $ 400 K
- FY 16: $ 400 K

Partners

- Interactions/ collaborations
  - Y K. Sun, Korea
  - S. Vajda, ANL
  - S. Al-Hallaj, UIC
  - D. Miller, ANL
  - Y. Wu, Ohio State University

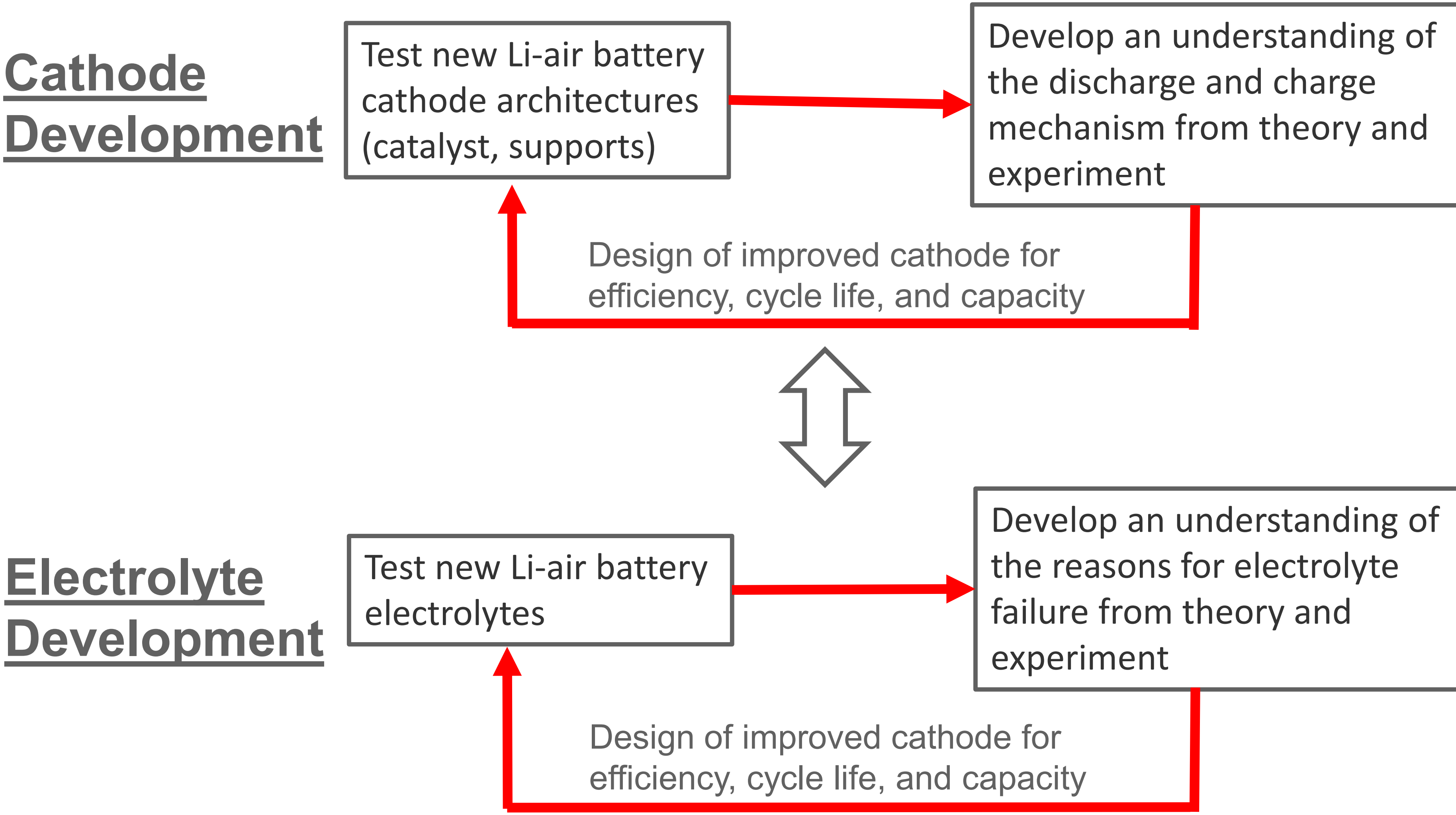
Project Objectives and Relevance

- 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

Milestones

Month/Year	Milestones
Dec/15	Development of new cathode materials based on Pd nanoparticles and ZnO coated carbon that can improve efficiency of $Li\text{-}O_2$ batteries through control of morphology and oxygen evolution catalysis. ***Completed.***
Mar/16	Investigation of use of catholytes to control the lithium superoxide content of discharge products of $Li\text{-}O_2$ batteries to help improve efficiency and cycling. ***On schedule.***
Jun/16	Computational studies of electrolyte stability with respect to superoxide species and salt concentrations for understanding and guiding experiment. ***On schedule.***
Sep/16	Investigations of mixed K/Li salts and salt concentration on the performance of $Li\text{-}O_2$ batteries with goal of increasing cycle life. ***On schedule.***

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



- Cathode development has been the major priority of the project so far as our strategy is to control charge overpotentials and then work on electrolytes

Experimental methods

Synthesis

- New catalyst materials
- New carbon materials
- Electrolytes

Characterization

- In situ XRD measurement (Advanced Photon Source)
- TEM imaging (ANL Electron Microspopy Center)
- FTIR, Raman
- SEM imaging

Testing

- Swagelock cells

Highly accurate quantum chemical modeling

- Periodic, molecular, and cluster calculations using density functional calculations
  - Static calculations
  - Ab initio molecular dynamics simulations
  - 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

Cathode materials

I. <u>Lithium peroxide based discharge products:</u> discovered cathode materials with improved catalysts for Li_2O_2 formation and decomposition with improved efficiency and longer cycle life

II. <u>Lithium peroxide/superoxide discharge products:</u> Discharge product characterization has led to cathode materials that stabilize LiO_2 in the discharge product, which provides a new way to reduce charge overpotential

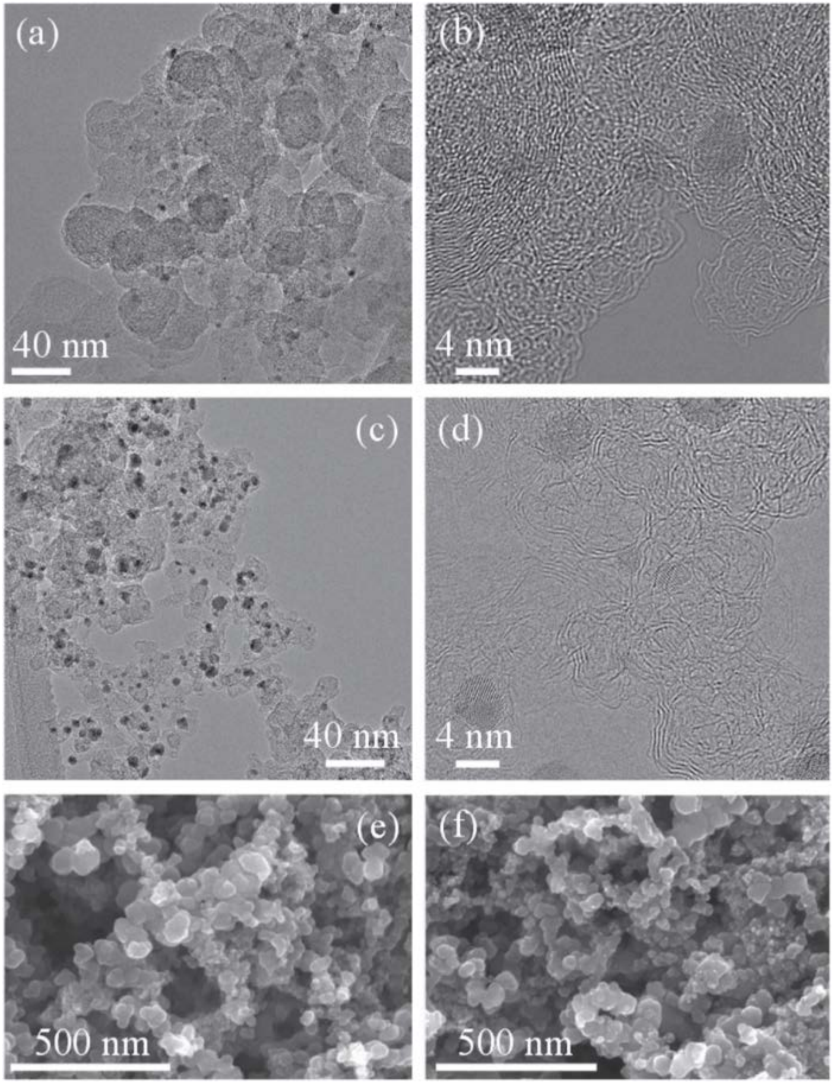
  - Has led to the first lithium superoxide based battery

Electrolytes

III. Screening methods for finding electrolytes with greater stability that will be used in future electrolyte development

IV. Enhanced Li anode lifetime in Li-O2 batteries through mixed K/Li salts

New cathode materials: Characterization of Pd nanoparticles on ZnO-passivated carbon



TEM

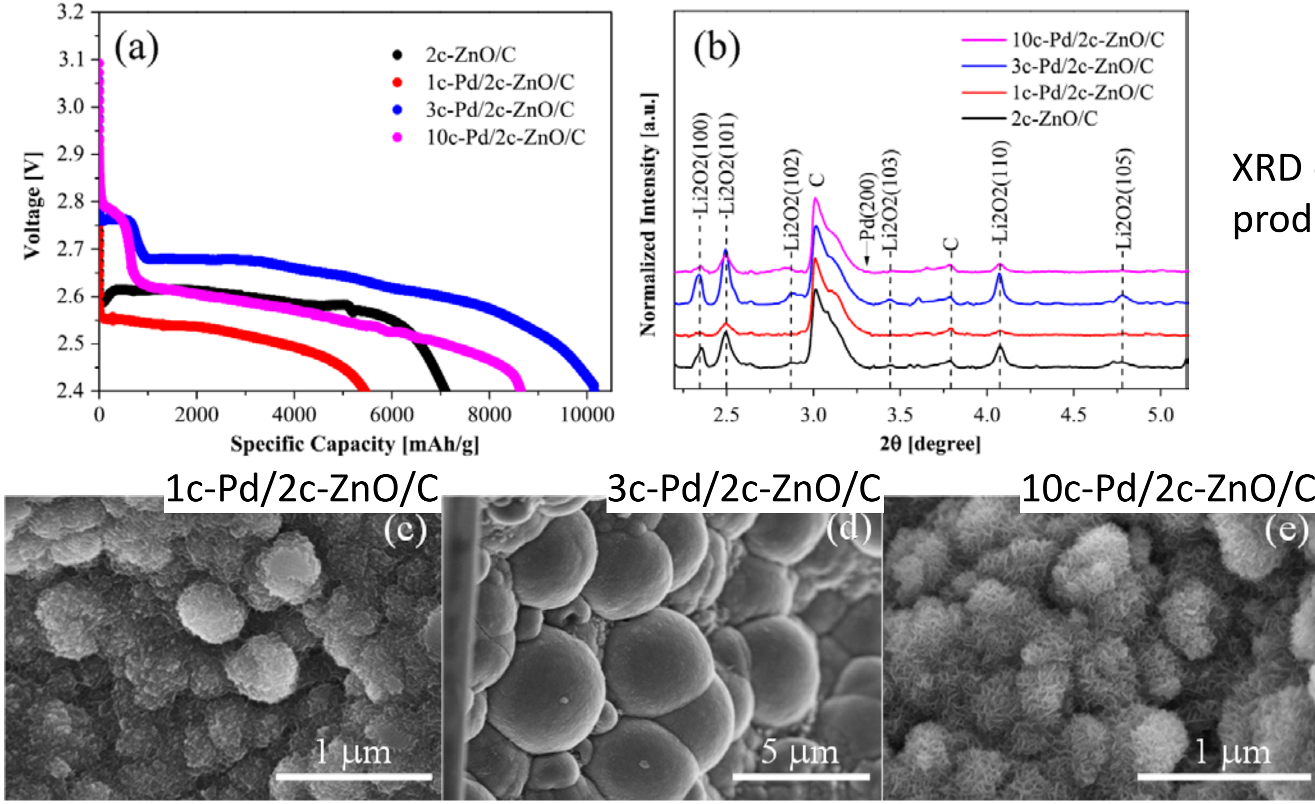
- Transmission electron microscopy (TEM) show crystalline nanoparticles decorating the surface of the ZnO-passivated porous carbon support in which the size can be controlled in the range of 3–6 nm, depending on the number of Pd Atomic Layer Deposition (ALD) cycles.
- The ZnO-passivated layer effectively blocks the defect sites on the carbon surface, minimizing the electrolyte decomposition

New cathode materials: Discharge results for Pd nanoparticles on ZnO-passivated carbon

Discharge performance

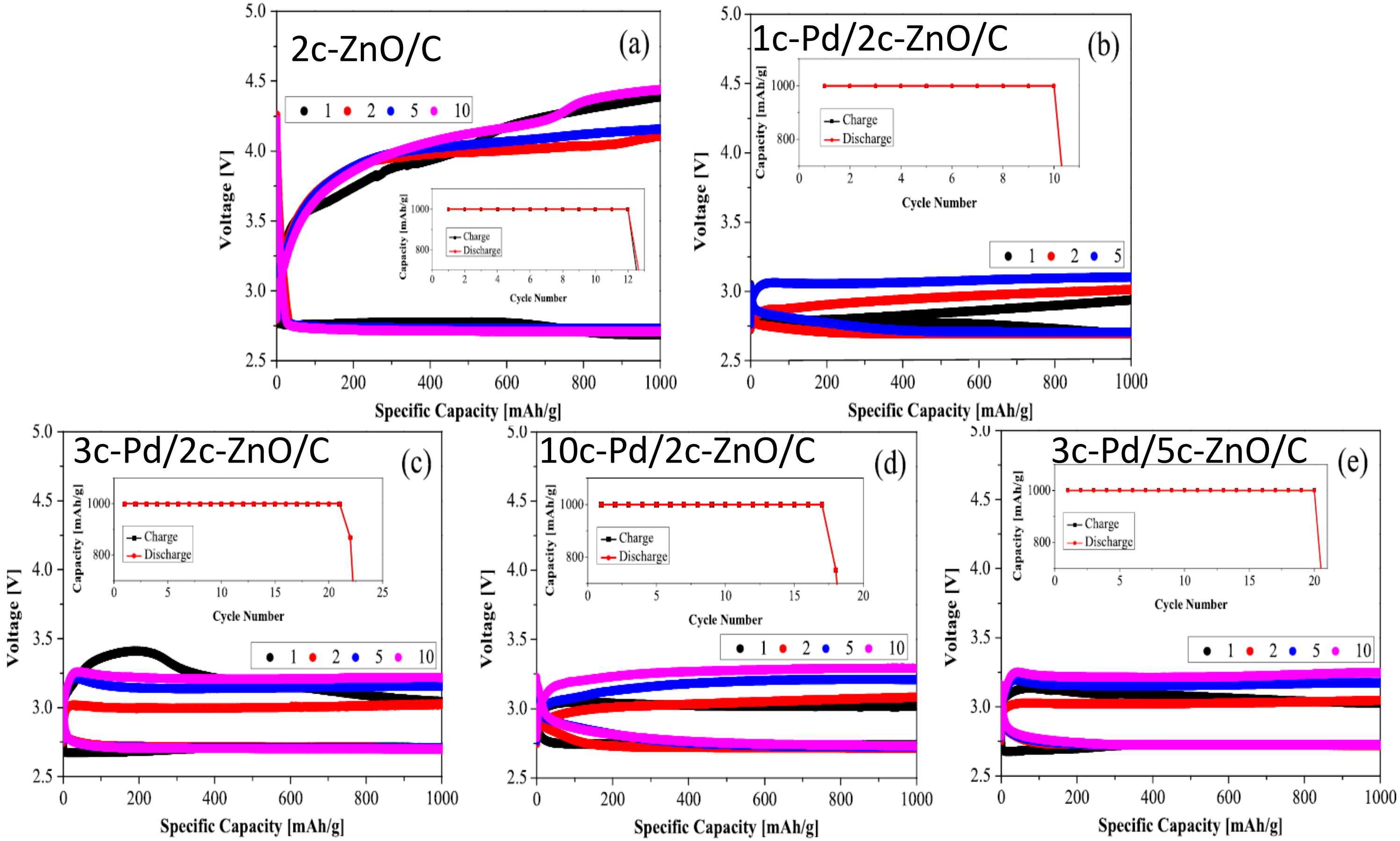
XRD of discharge product

SEM images



- Oxygen reduction reaction during discharge in the Li-O_2 cell is significantly altered when Pd nanoparticles on ZnO-passivated carbon are used as the electrocatalyst as evidenced by the higher capacity in the case of 3c and 10c ALD-Pd samples
- Also leads to a different morphology of the discharge products

New cathode materials: Voltage profile of Pd nanoparticles on ZnO-passivated carbon

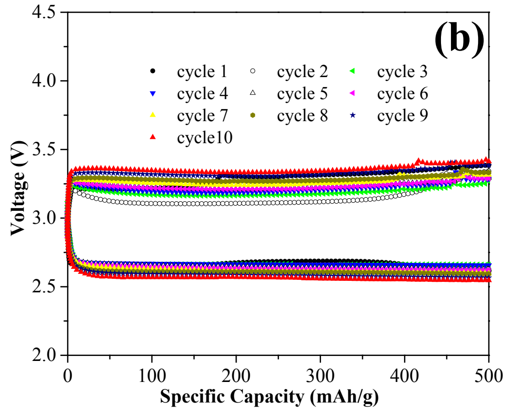


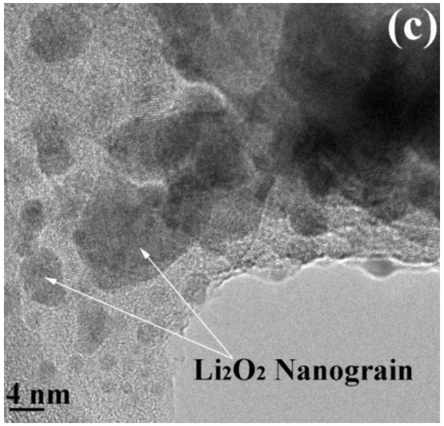
- Compared to the ZnO/C cathode, the ZnO-passivated greratly reduces the charge overpotential!

New cathode materials: Other cathode materials we have found that give low charge potentials

Pd/Al2O3/C

Lu et al, Nature Communications, 2013

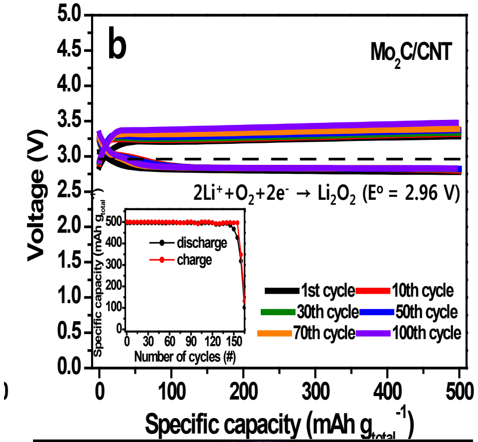


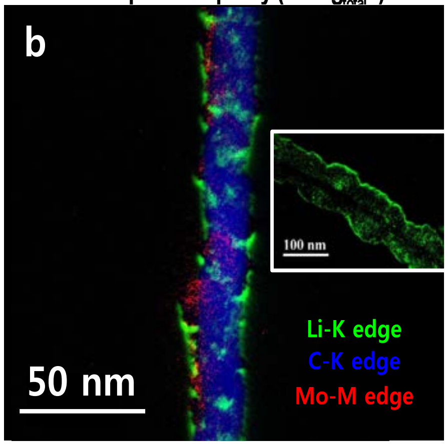


- Nanocrystalline discharge products promotes electronic conductivity and lower charge overpotentials

Mo2C/CNT

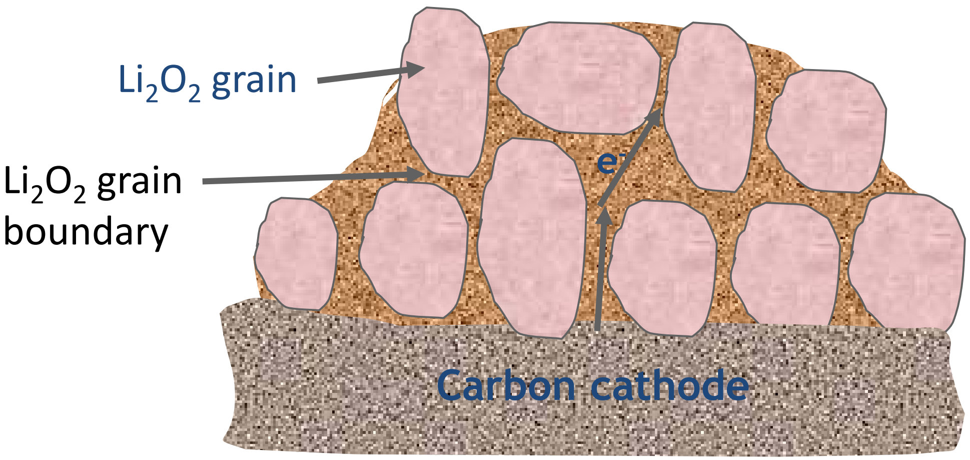
Kwak et al, ACSNano, 2015



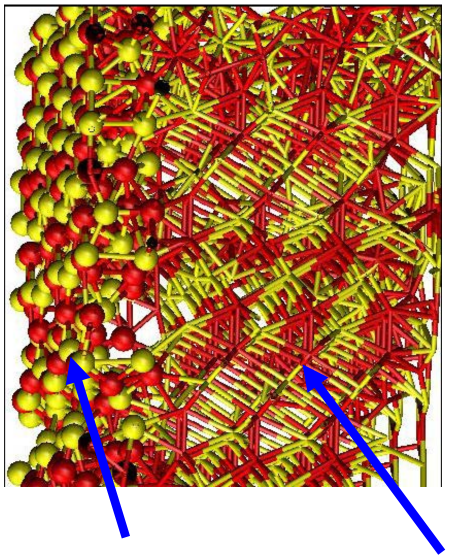


- Small Li2O2 particles promotes low charge potentials, longer cycle life

New cathode materials: Explanation for Pd results



DFT calculations for a model of nanocrystalline Li_2O_2

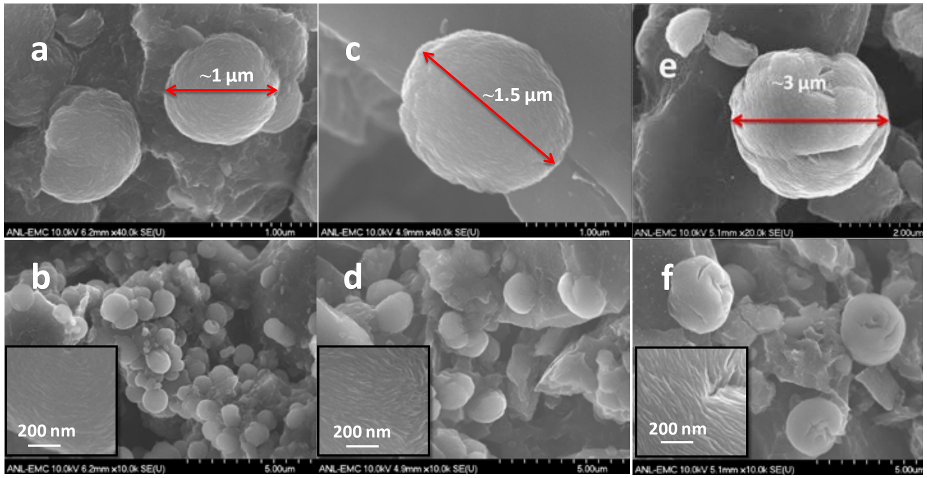


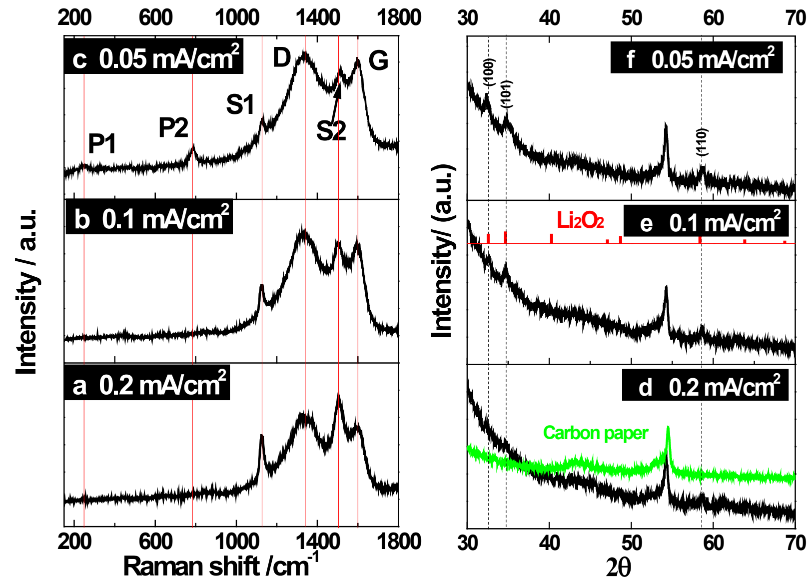
Grain boundary: amorphous LiO_2 or Li_2O_2 (spin, short O-O distances, conducting)

Grains: crystalline Li_2O_2

- **Nanocrystalline lithium peroxide discharge product may provide good electronic conductivity for charge**
- **Can LiO_2 be incorporated into discharge product to increase electronic conductivity?**

Stabilization of LiO_2: Background



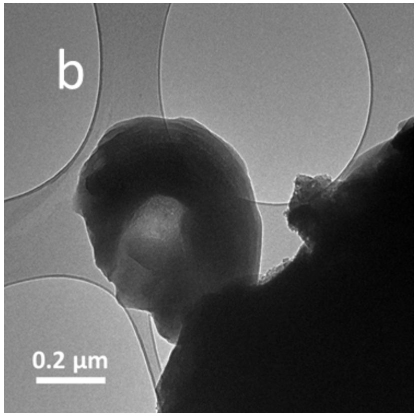


Raman peak at 1125 cm^{-1} (S1) is evidence for more LiO_2-like component at faster discharge current densities

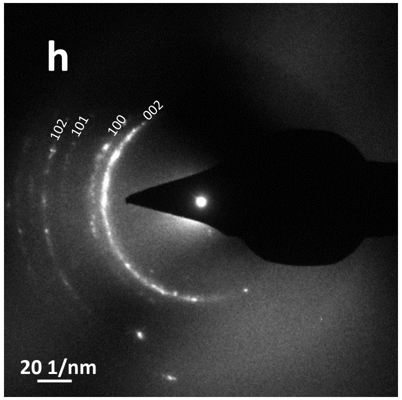
- In a series of papers[1-3] we have shown that a Li-O_2 battery based on an activated carbon cathode can result in a discharge product containing both lithium peroxide and lithium superoxide.
- **Faster discharge rate and slow disproportionation kinetics → more LiO2-component (lower charge overpotential)**

1. Zhai, D. et al., J. Phys. Chem. Lett. (2014).
2. Zhai, D. et al., J. Am. Chem. Soc. (2013).
3. Yang, J. et al., Phys. Chem. Chem. Phys. (2013)

Stabilization of LiO_2: Evidence for LiO2 in discharge product



TEM image of toroid from activated carbon cathode

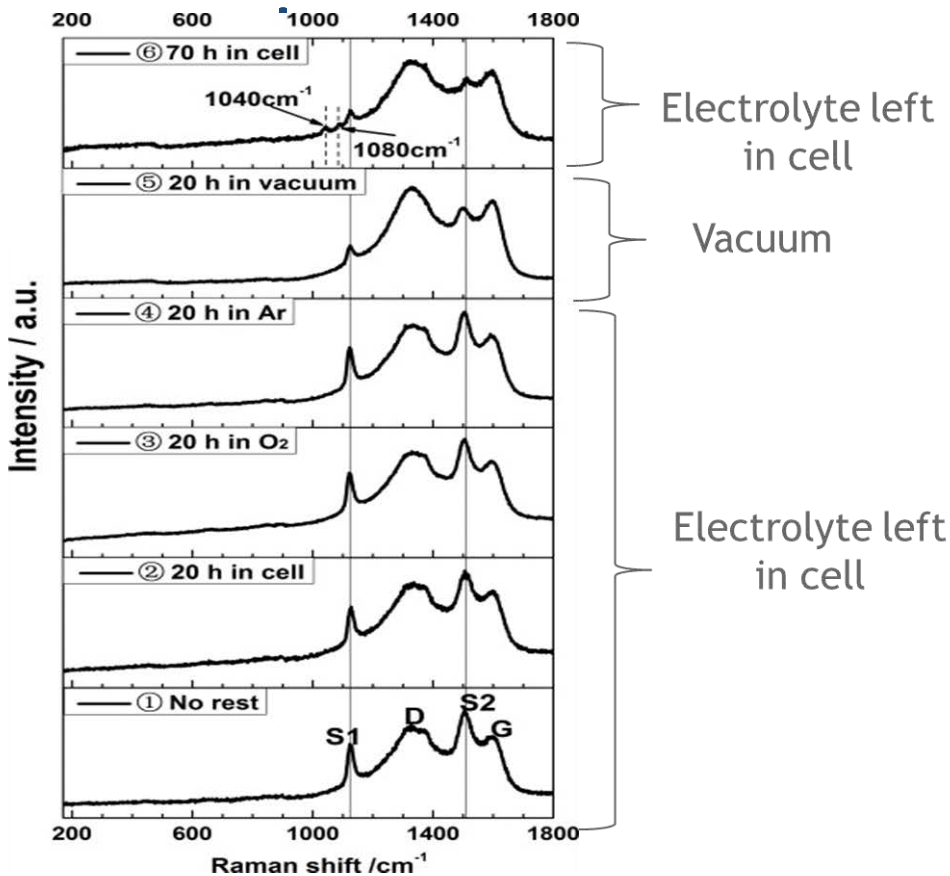


Electron diffraction pattern of toroid showing LiO_2 crystal structure

- In our latest paper[1] on this topic we have found that interfacial effects can suppress disproportionation of a LiO_2 component in the discharge product.
- High-intensity X-ray diffraction and transmission electron microscopy measurements are first used to show that there is a LiO_2 component along with Li_2O_2 in the discharge product

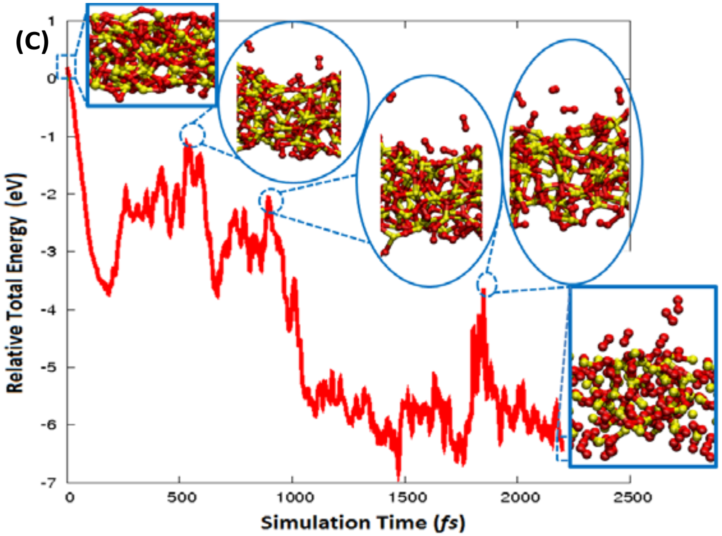
Stabilization of LiO_2: Ageing of discharge product from activated

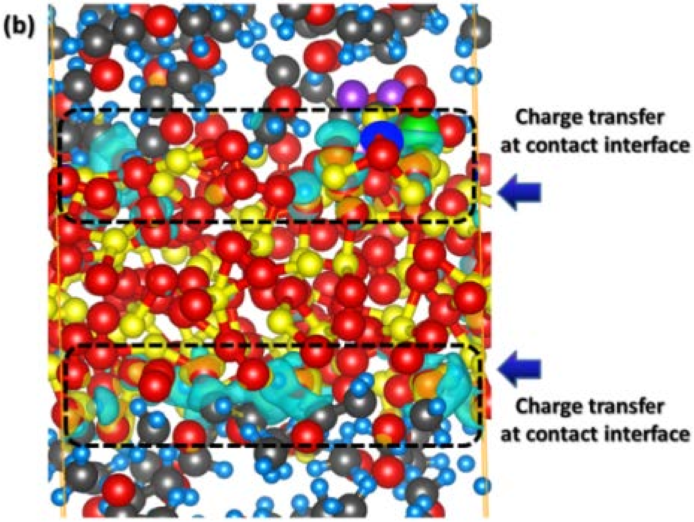
- 20 hrs in cell under Ar, O2 no change in 1125 cm- peak
- 20 hrs in cell under vacuum 1125 peak significantly decreases
- 70 hr in cell 1125 cm-1 peak decreases (electrolyte decomposes?



- The stability of the discharge product was then probed by investigating the dependence of the charge potential and Raman intensity of the superoxide peak with time.
- The results indicate that the LiO_2 component can be stable for possibly up to days when an electrolyte is left on the surface of the discharged cathode

Stabilization of LiO_2: Effect of electrolyte from DFT calculations

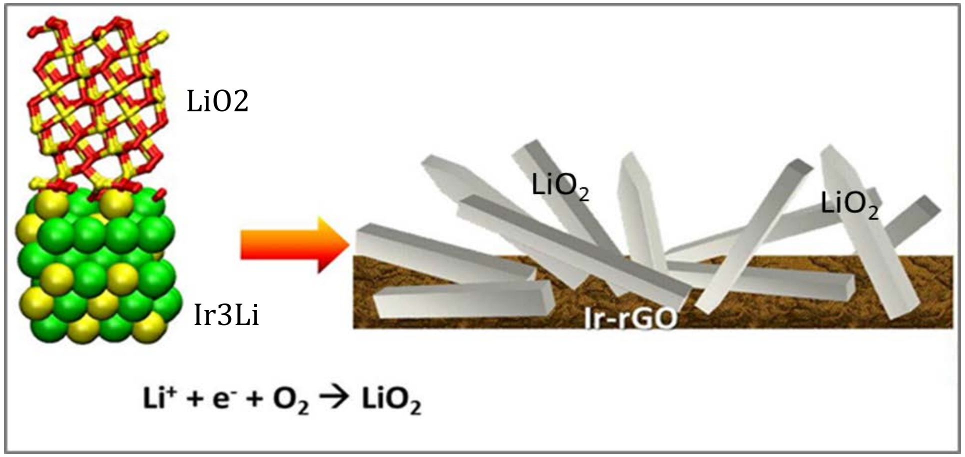




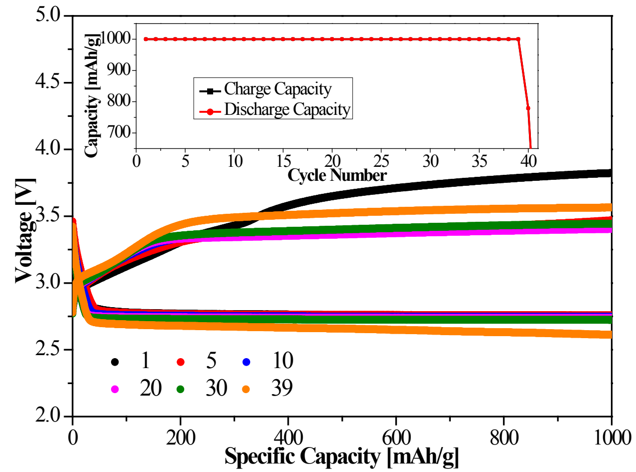
Ab initio molecular dynamics simulations: fast desorption of O_2 occurs from amorphous surface in vacuum (left); presence of electrolyte slows down desorption of O_2 (right)

- Density functional calculations on amorphous LiO_2 reveal that the disproportionation process will be slower at an electrolyte/LiO_2 interface compared to a vacuum/LiO_2 interface.

Stabilization of LiO_2: Templated growth



Templated nucleation and growth of crystalline LiO_2

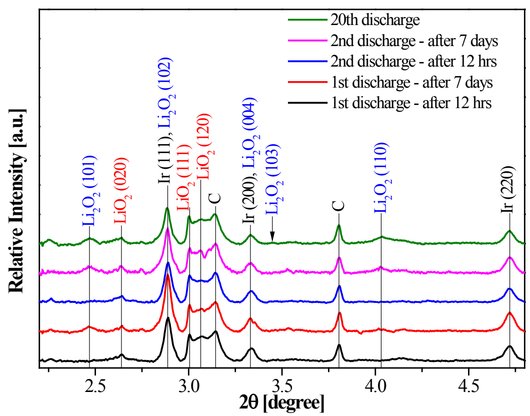


Voltage profile for Ir-rGO cathode

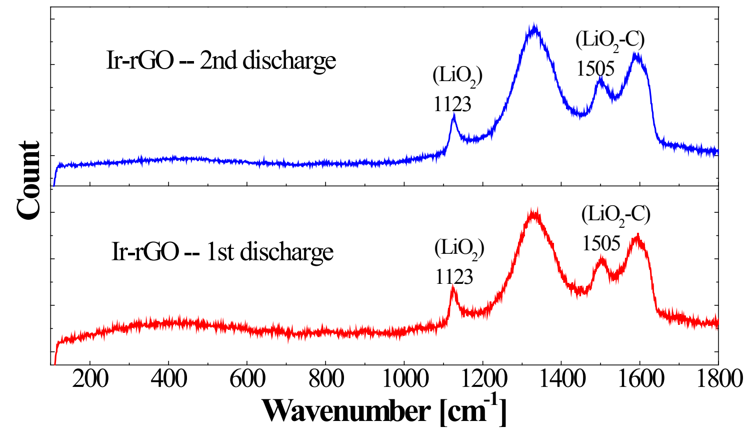
- Our studies[1] have revealed an approach to electrochemically synthesize LiO_2
  - The lattice match of crystalline LiO_2 with a Ir_3Li intermetallic component of the cathode can act as a template for electrochemical nucleation/growth of crystalline LiO_2
  - Stabilization of the LiO_2 is due to formation of crystalline LiO_2 and the presence of an electrolyte at the interface
- Performance of LiO_2 in a $Li\text{-}O_2$ battery was as good (efficiency, cycle life) as Li_2O_2 based $Li\text{-}O_2$ batteries and opens up new opportunities

1. Lu et al, Nature, 2016, **529** 377-382.

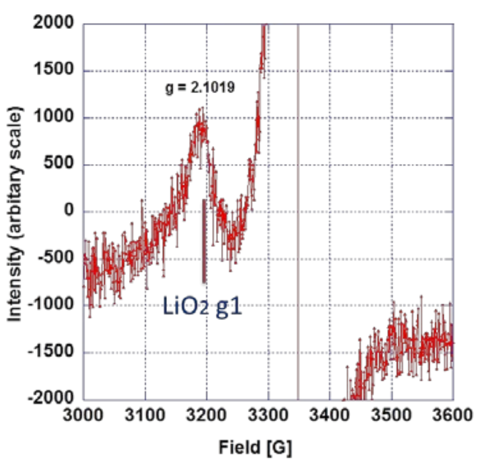
Characterization of Ir-rGO discharge product from experiment and theory



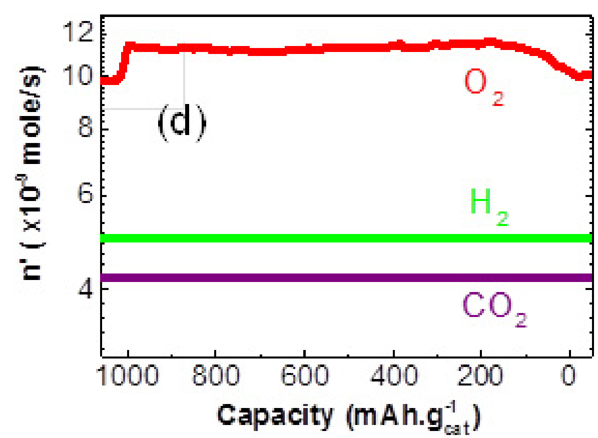
XRD shows LiO2 peaks and no Li2O2



Raman shows LiO2 peaks



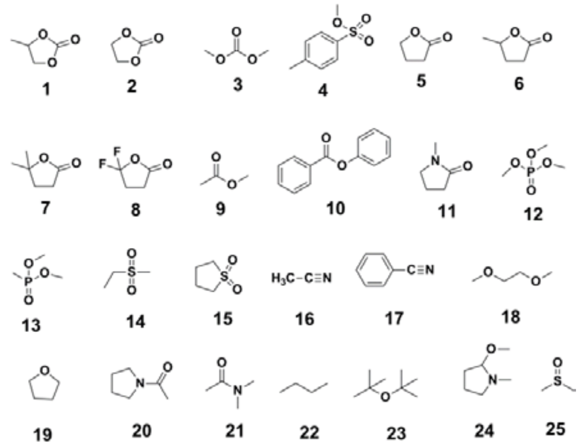
EPR spectrum consistent with LiO2

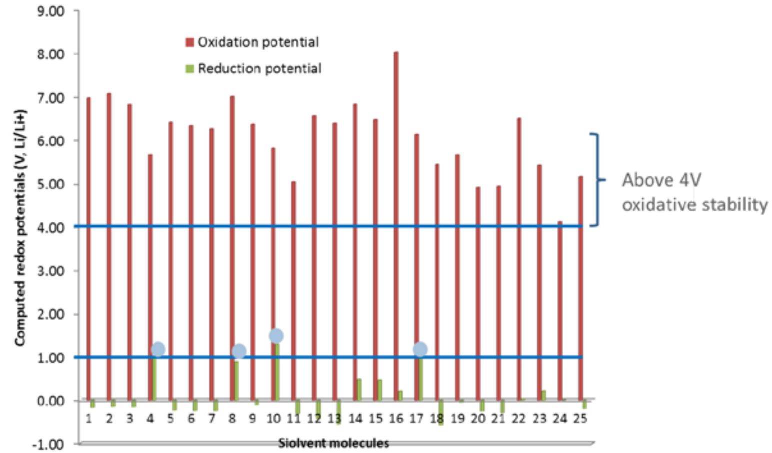


Differential electrochemical mass spectrometry (DEMS) shows 1 e per O2 on charge and discharge

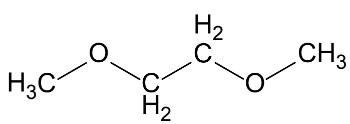
- Much evidence for LiO2 (and no Li2O2) for the Ir-rGO cathode

Predictions of electrolyte stability: examples of computational screening

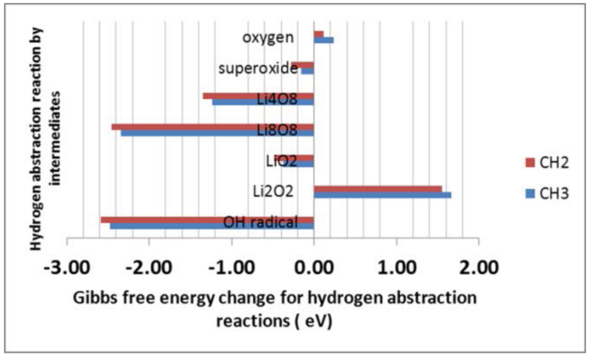




- Solvent molecules require ~4.5 V oxidative stability and ~1.0 V reductive stability



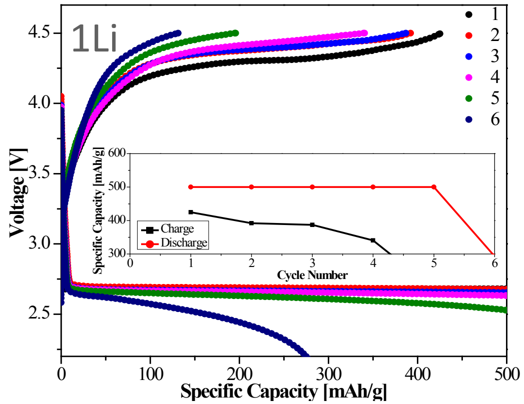
Dimethoxy Ethane (18)

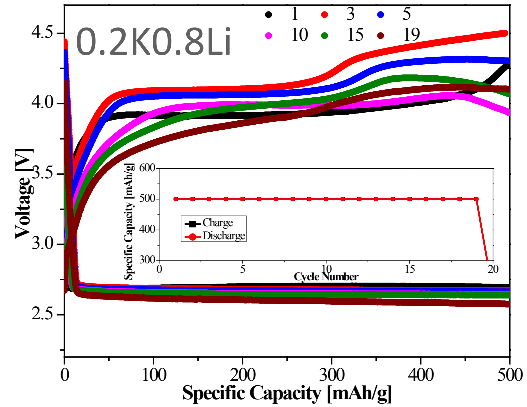


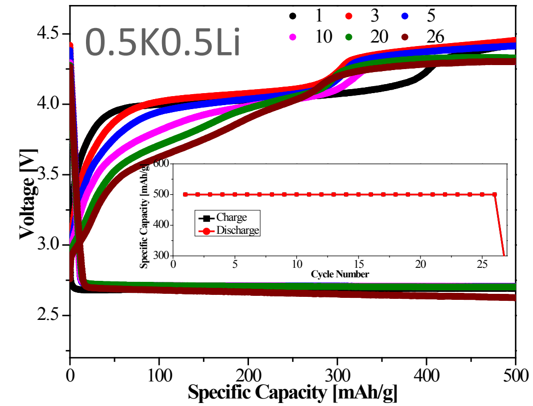
- Hydrogen abstraction reactions by OH radical, $(Li_2O_2)_4$, $(LiO_2)_4$, and superoxide are thermodynamically favorable in solution

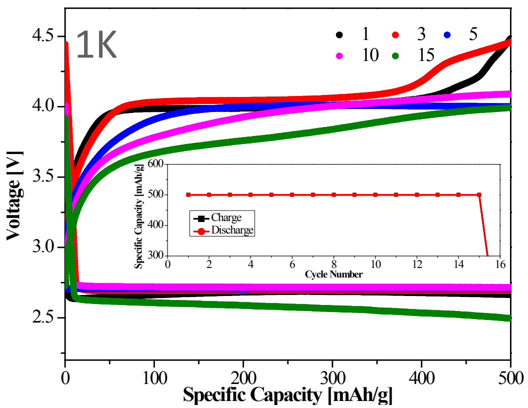
Rajeev Assary

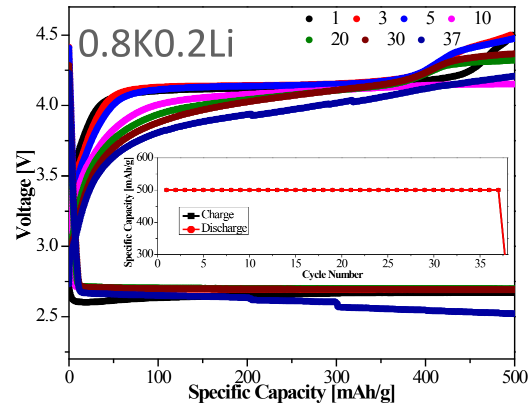
Mixed K/Li salts: The effect of salts on the performance of a Li-O_2 battery











Electrolyte: TEGDME + salt mixtures

- 1K : 1 M KCF3SO3
- 0.8K0.2Li: 0.8 M KCF3SO3 + 0.2 M LiCF3SO3
- 0.5K0.5Li: 0.5 M KCF3SO3 + 0.5 M LiCF3SO3
- 0.2K0.8Li: 0.2 M KCF3SO3 + 0.8 M LiCF3SO3
- Li: 1 M LiCF3SO3

Cathode: Graphitized Carbon Black (no catalysts)

Anode: Li metal

Capacity-controlled cycles (500 mAh/g)

- Cyclabilities and coulombic efficiencies are increased!
  - 0.8K0.2Li has the best cyclability (37 cycles vs. 5 cycles for 1Li)
- Charge potentials are slightly reduced
  - Catalysts are still necessary

Response to last year reviewer's comments

The comments needing responses are listed below:

Comment: "Palladium (Pd) and molybdenum carbide (Mo2C) catalysts are expensive, the reviewer observed, recommending that cheaper alternatives be developed and the result be demonstrated in a full cell configuration."

Response: Once we have achieved cathodes materials with good cycle life and low charge potential we will work on cheaper alternative

Comment: "Noting that development of new electrolytes and cathodes was proposed, the reviewer saw no strategy explained for developing materials nor what sort of materials were envisioned."

Response: Our strategy might not have been well explained in the previous review. On slide 5 we have clarified our strategy. We note that this strategy has resulted in new cathode materials with reduced charge overpotentials and longer cycle life.

Collaborations with other institutions and companies

- S. Vajda, ANL
  - Development of new cathode materials based on supported size-selected metal cluster
- S. Al-Hallaj, UIC
  - Characterization of discharge products and cathode materials
- D. Miller, ANL
  - TEM characterization of discharge products and catalysts
- Y. Wu, Ohio State University
  - Development of electrolytes for Li-air batteries.
- Y K. Sun, Korea

  Development of new cathode materials based on metal nanoparticles and novel carbons

Proposed Future Work

New catalysts developed in this project provide the basis for improvement of efficiency, cycle life, and capacity of Li-air batteries using a combined experiment/theory approach

- Determine the cause of degradation of the electrolytes and catalysts in these cathode materials that seems to limit performance
- Design new electrolytes that are more stable in the Li-O_2 batteries
- Synthesize, test, and evaluate new electrolytes and catalysts for Li-air batteries
- Design new cathode materials that do not degrade in the Li-O_2 batteries

Summary

Cathode materials

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