Development of Novel Electrolytes and Catalysts for Li-Air Batteries

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DOE merit review

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Project ID# ES-066

Overview

Timeline

- Start: 2014
- **Finish: 2016**
- **40%**

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/14	Electrolyte choice for development of baseline cathode materials. *Completed.*
Mar/15	Cathode material with low charge overpotential developed and tested . *Completed.*
Jun/15	Improve cycle life to over 100 cycle with high efficiency. *On schedule.*
Sep/15	*Develop novel cathode material structure to partially stabilise lithium superoxide phase.* ↪ *On schedule.*

Strategies

1. Design and test of new Li-air battery cathode architectures (catalyst, supports) for low charge overpotentials
2. Determine from experiment and theory the cause of poor cycling in these cathodes
3. Design and develop new electrolytes that are more stable to decomposition in the Li-air batteries to increase cycle life
4. Design and develop new cathode materials for longer cycle life and increased capacity

Approach: 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

Approach: highly accurate quantum chemical modeling methods

- 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
  - Electron transfer rates

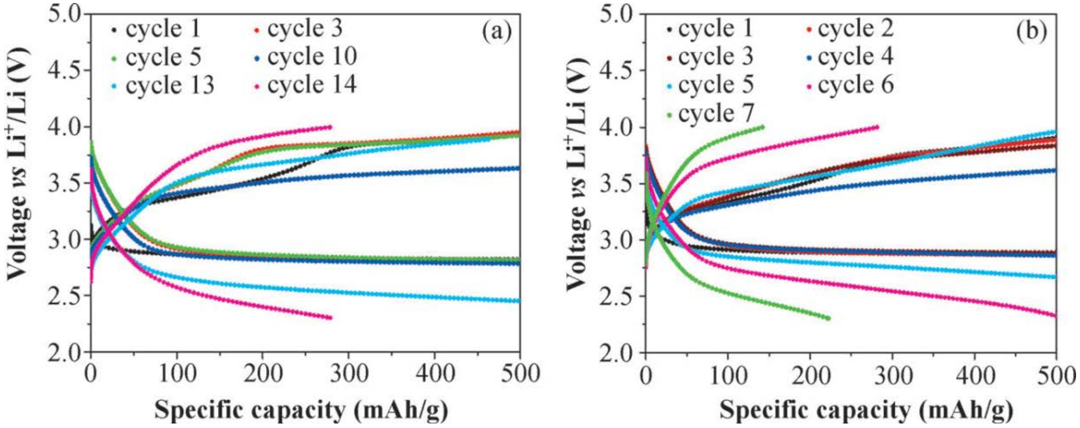
Technical Accomplishments

- Selection of electrolyte for development of catalysts
- Three new cathode materials developed, which can be used as a basis for discovery of more stable electrolytes and improved catalyst for longer cycle life, increased efficiency, and increased capacities
    1. $Pd/Al_2O_3/C$
    2. Mo_2C/CNT
    3. Activated carbon
- Evidence for an oxygen cross-over effect that degrades the lithium anode and shortens lifetime

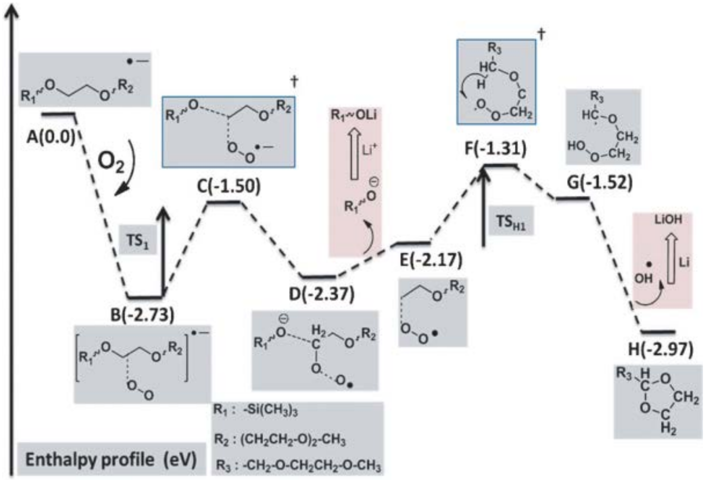
Selection of electrolyte for development of catalysts – solvent

Motivation: The development of cathodes with low charge overpotentials is needed to avoid decomposition of electrolytes at high charge potentials to enable electrolyte development

- Ethers are widely used for Li-air batteries – stable against superoxide anion and lithium superoxide
- Investigated O_2 cross-over to Li anode effect for several ethers
  - Siloxane-based electrolyte undergoes a relatively easier reductive decomposition at anode compared to tetraglyme, consistent with theory



Comparison of voltage profile for tetraglyme (left) and 1NM3 siloxane ether (right)

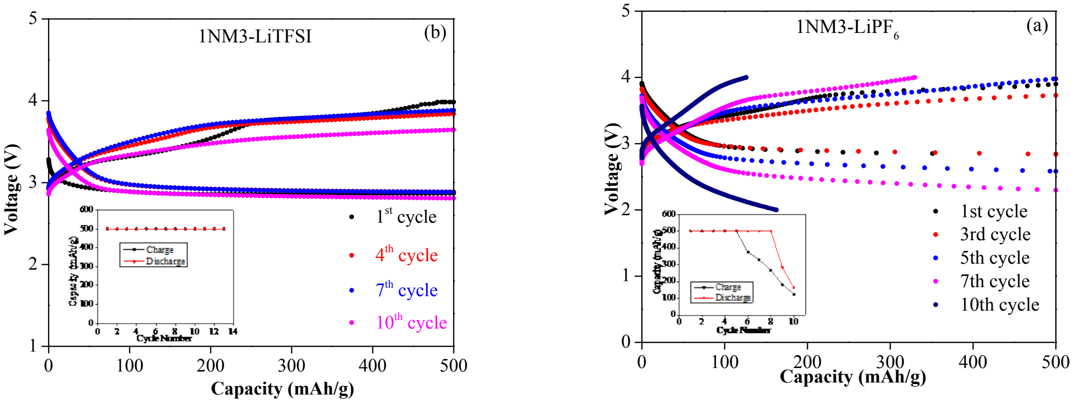


Reaction mechanism from DFT for decomposition of siloxane based ether at anode

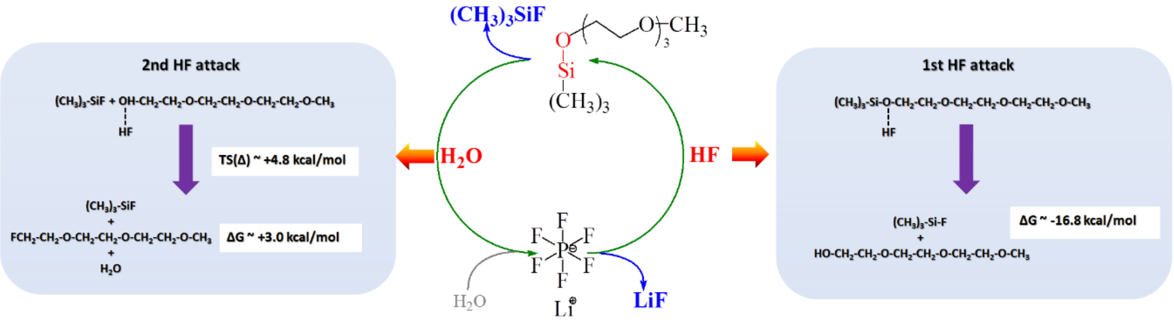
Selection of electrolyte for development of catalysts – salt

- Comparison of salt performance in an ether based electrolyte
  - $LiPF_6$ is less stable with evidence for decomposition
  - LITFSI, $LiCF_3SO_3$ are more stable
- Electrolyte chosen for catalyst development: TEGDME, LiTFSI electrolyte

Voltage profiles for LiTFSI (left) and $LiPF_6$ (right) salts showing poorer performance for $LiPF_6$

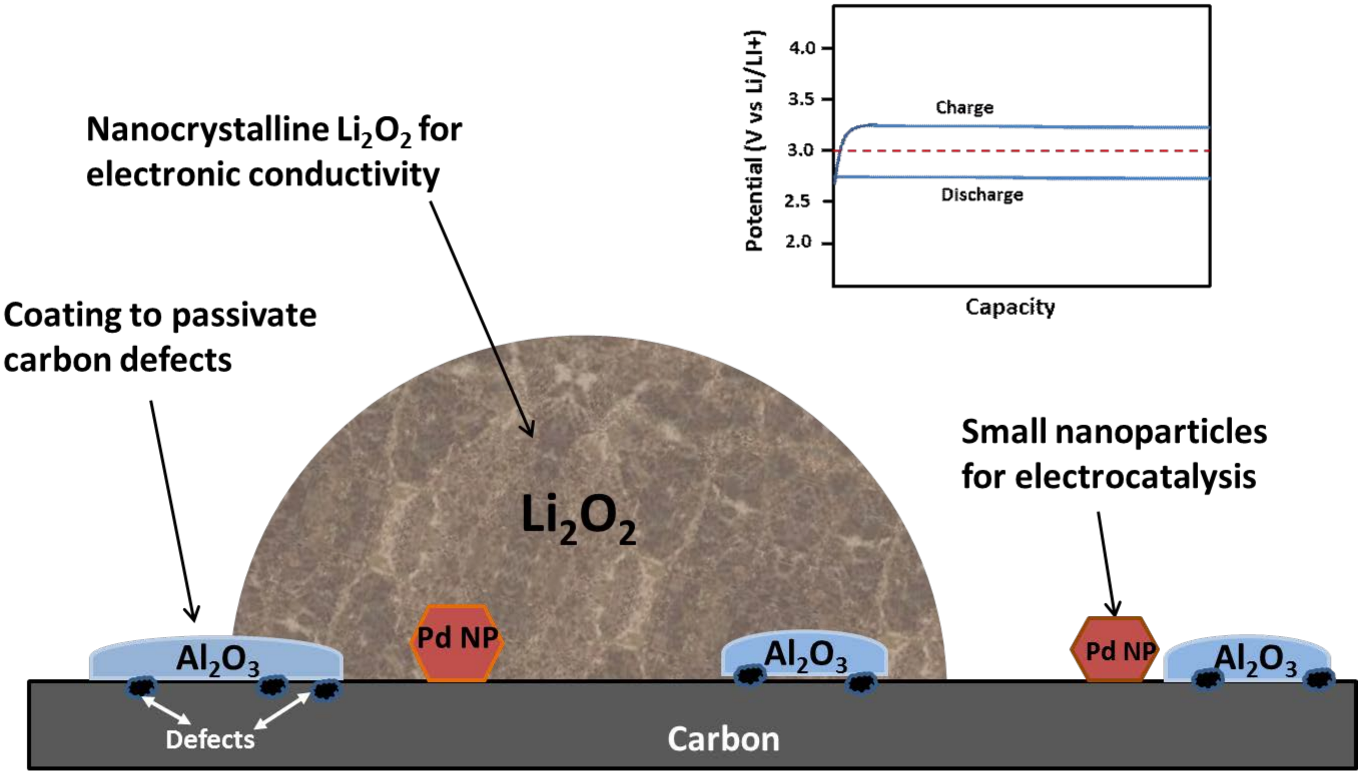


Reaction mechanism for $LiPF_6$ decomposition involving HF attack of electrolyte



Cathode #1: Pd/Al_2O_3 -- low charge potential based on a Li-O_2 cell with three combined concepts

- Atomic layer deposition (ALD) coating on super P carbon based cathode
- Small Pd nanoparticles
- Nanocrystalline discharge product



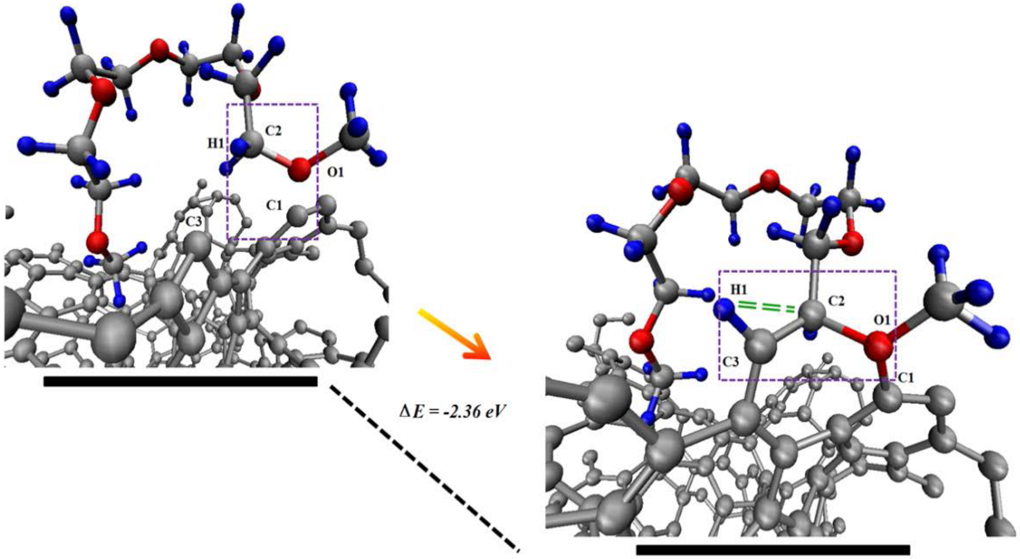
Nanocrystalline Li_2O_2 for electronic conductivity

Coating to passivate carbon defects

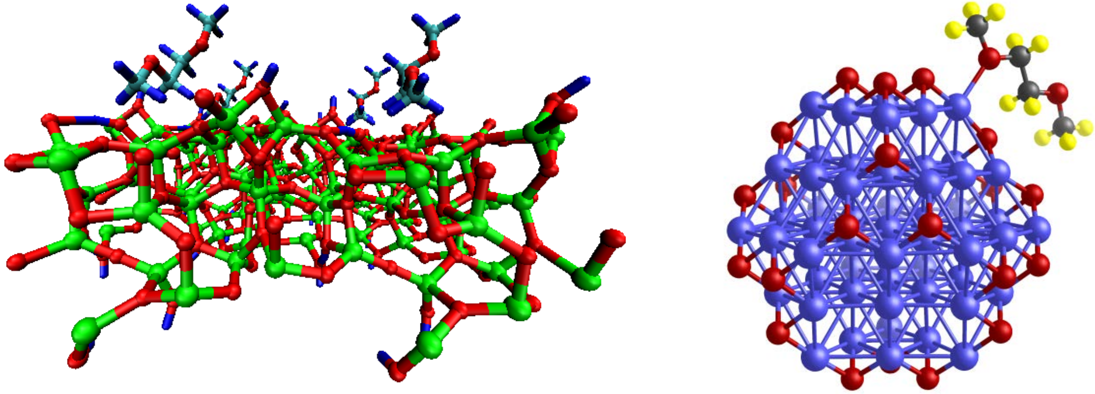
Small nanoparticles for electrocatalysis

Aluminum oxide coating prevents decomposition on defect sites from DFT calculations -- confirmed by experiment

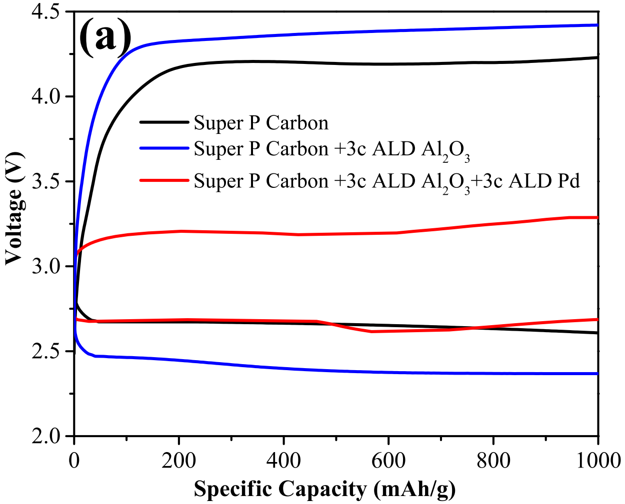
DFT calculations indicate carbon defect sites cause ether molecule (TEGDME) to decompose

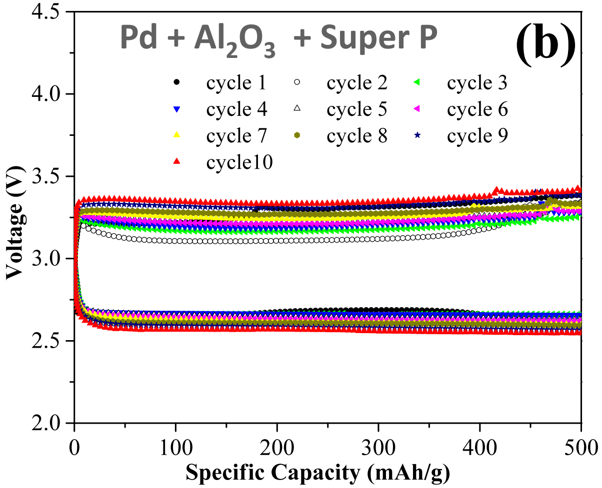


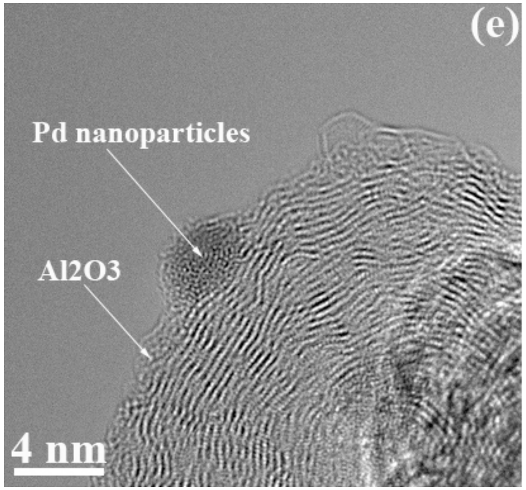
DFT calculations indicate ether molecules donot decompose on alumina or Pd NP surfaces



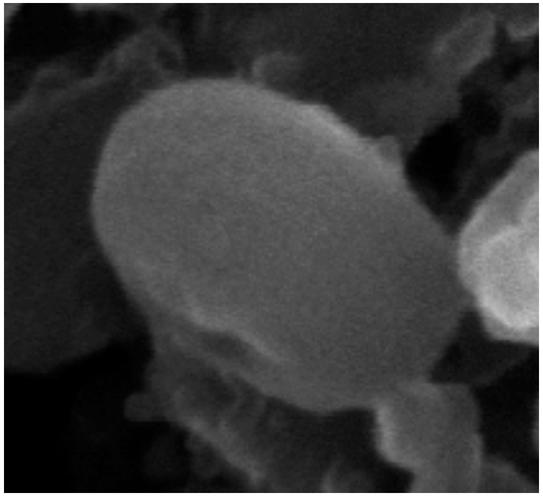
Low charge overpotential with Pd nanoparticles on an Al_2O_3 coated super P carbon (30% Al_2O_3 coated, ~0.5 nm thick, TEGDME, LiTFSI electrolyte)





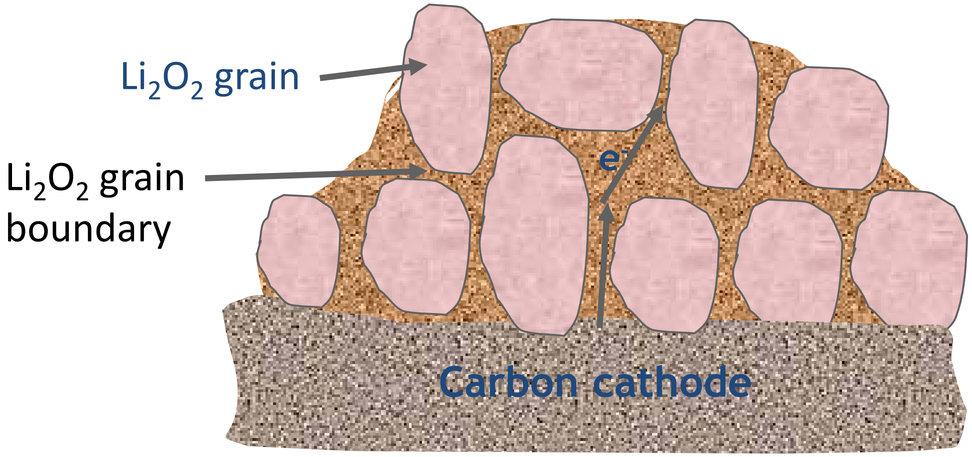


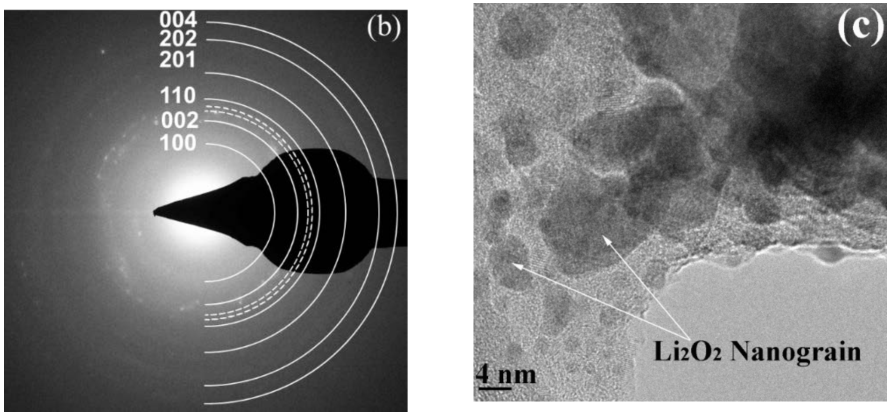
Pd NP + Al_2O_3 + Super P



Toroid in discharge product

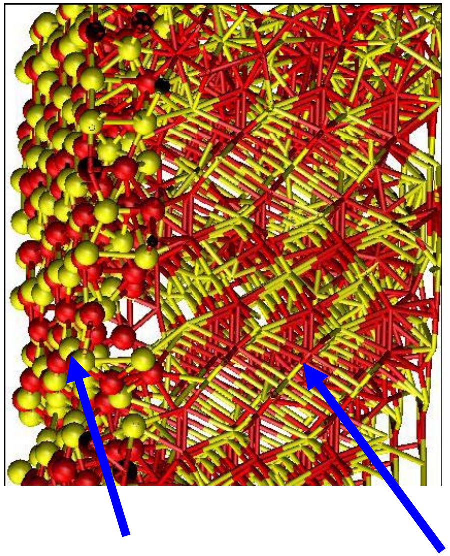
Nanocrystalline lithium peroxide discharge product may provide good electronic conductivity for charge





ED pattern (b, nanocrystalline Li2O2) and TEM image (c) for toroid in discharge product with cathode based on Pd NP + Al_2O_3 + Super P

DFT calculations for a model of nanocrystalline Li_2O_2



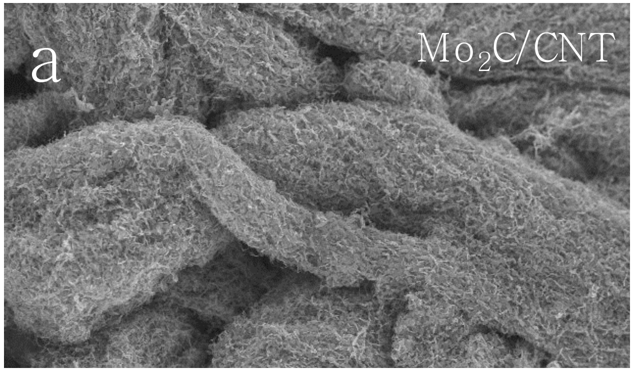
Grain boundary: amorphous Li_2O_2 (spin, short O-O distances, conducting)

Grains: crystalline Li_2O_2

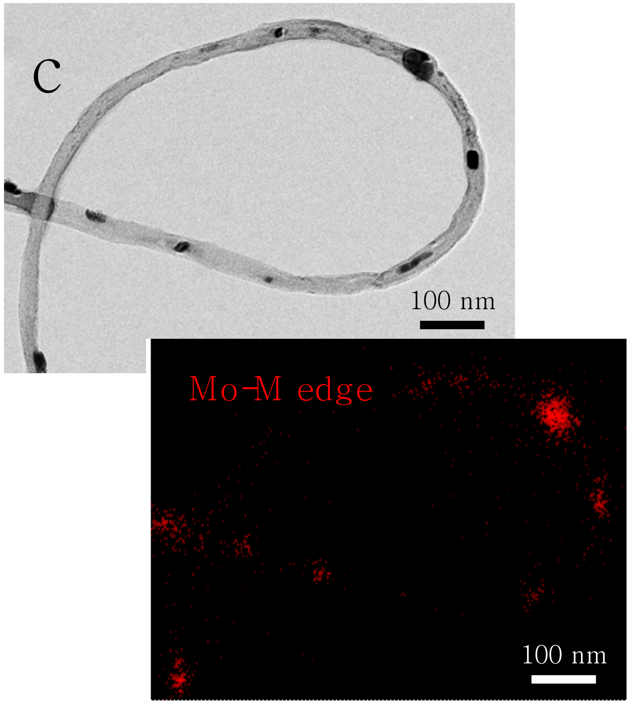
Pd/Al_2O_3/C cathode leads to nanocrystalline Li_2O_2 morphology (small grains with grain boundaries) that gives low charge overpotential (~3.2 V) for ~10 cycles

Cathode #2: Mo_2C/CNT-- low charge potential

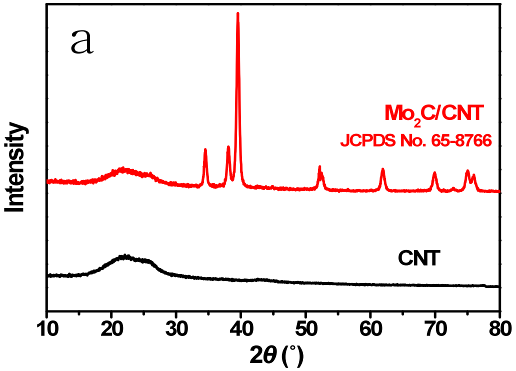
- Good ORR catalyst (Mo_2C) dispersed on CNTs
- Formation of a well-dispersed lithium peroxide nanolayers (Li_2O_2)
- Collaboration with Y. K. Sun, Korea



SEM images of Mo_2C/carbon nanotubes

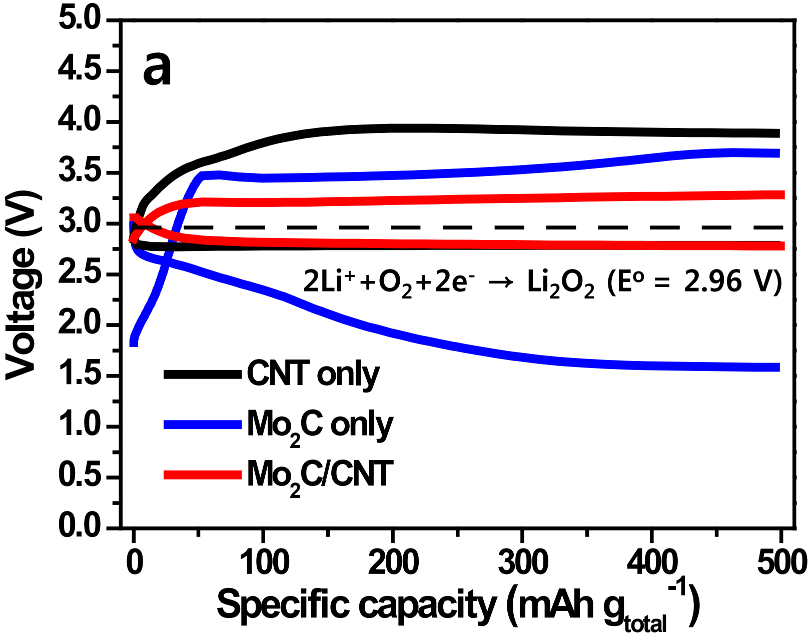


TEM image and EDX maps (Mo elements) of Mo2C/carbon nanotubes

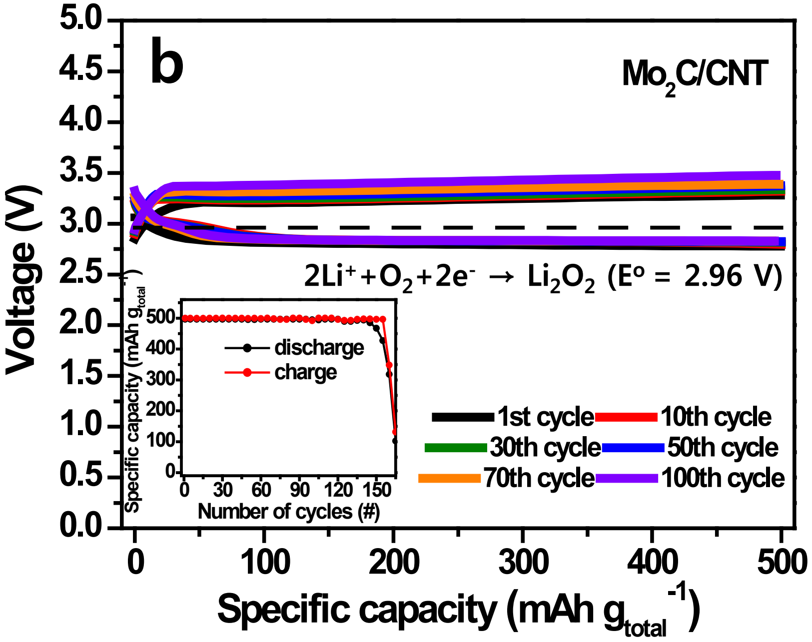


XRD pattern of Mo_2C/ carbon nanotubes

Voltage profiles for MoC_2/CNT cathode (TEGDME, LiTFSI electrolyte)



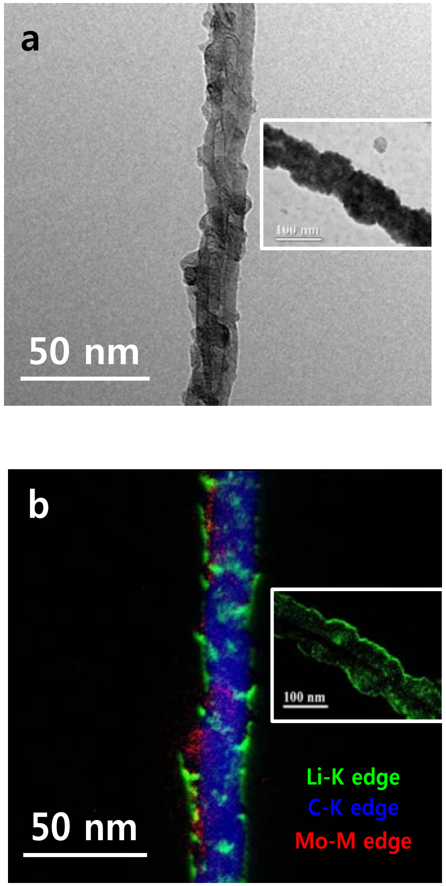
Voltage profiles showing Mo_2C/CNT has a charge overpotential (~88% roundtrip efficiency)

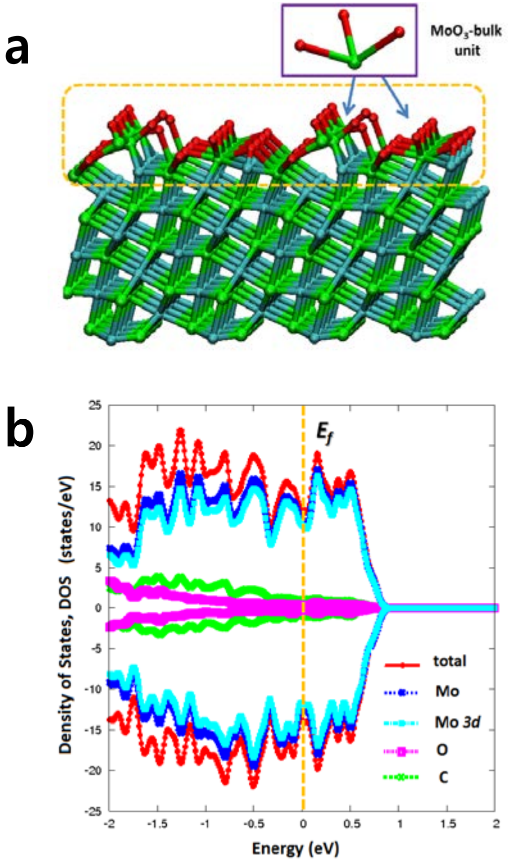


Voltage profiles showing Mo_2C/CNT has a long cycle life (>100 cycles) compared to Pd results

Evidence for Li_2O_2 morphology using HR-TEM & DFT calculation showing Mo as site of ORR

HR-TEM image (top) and EF-TEM (bottom) maps of the Mo2C/carbon nanotube electrode after 1st discharge



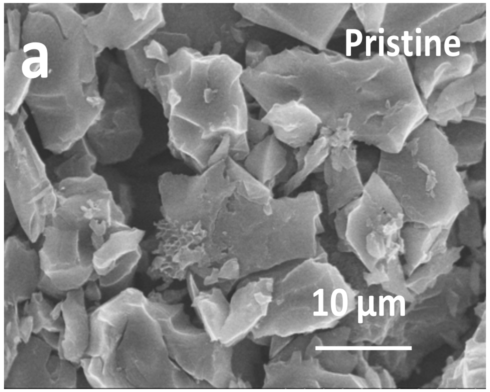


DFT calculations show Mo is the likely site for ORR

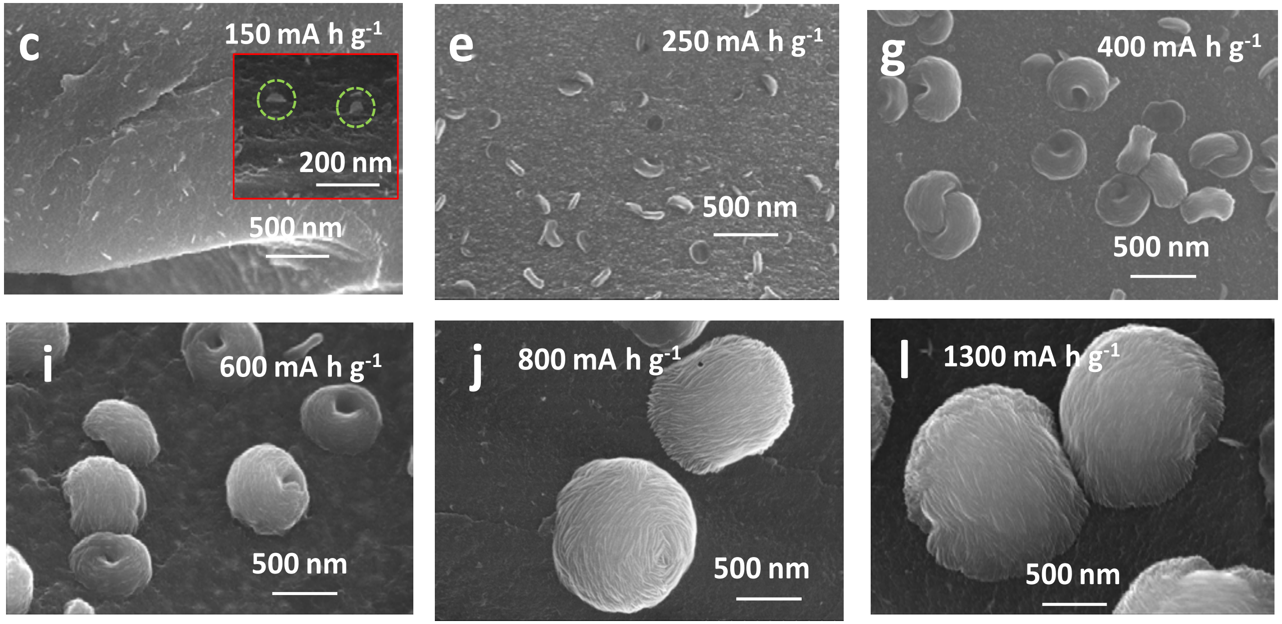
Mo_2C/CNT cathode leads to well-dispersed Li_2O_2 nanolayers which gives low charge overpotential (~88% round-trip efficiency) for 100 cycles

Cathode #3: Activated carbon cathode – evidence that some cathode materials can give a discharge product with LiO_2

- Large surface area carbon cathode
- Mixture of LiO_2 and Li_2O_2
- Results in two plateau charge potential

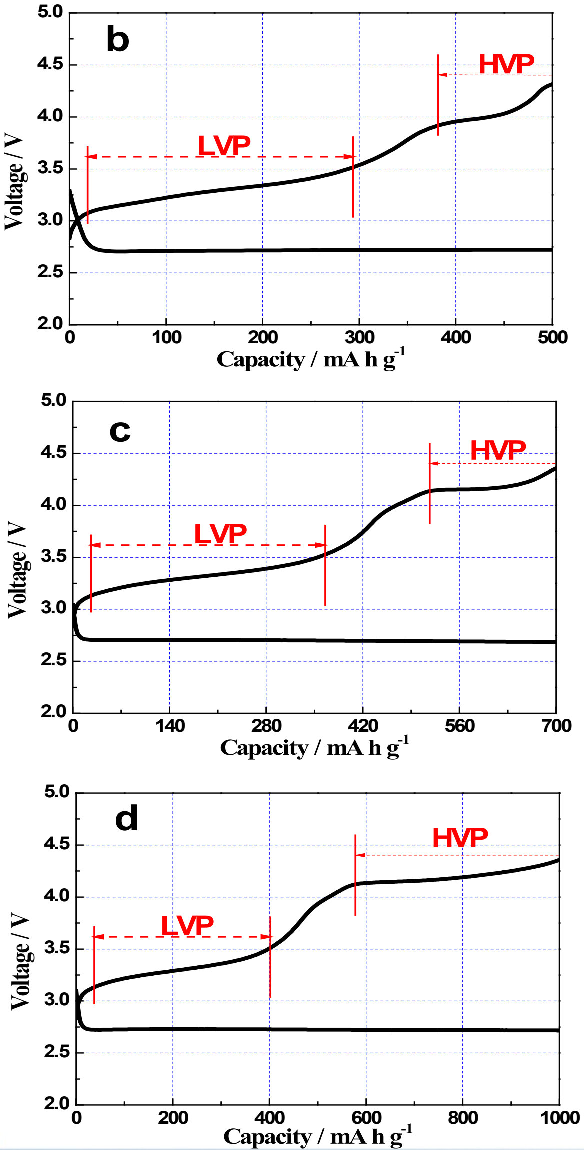


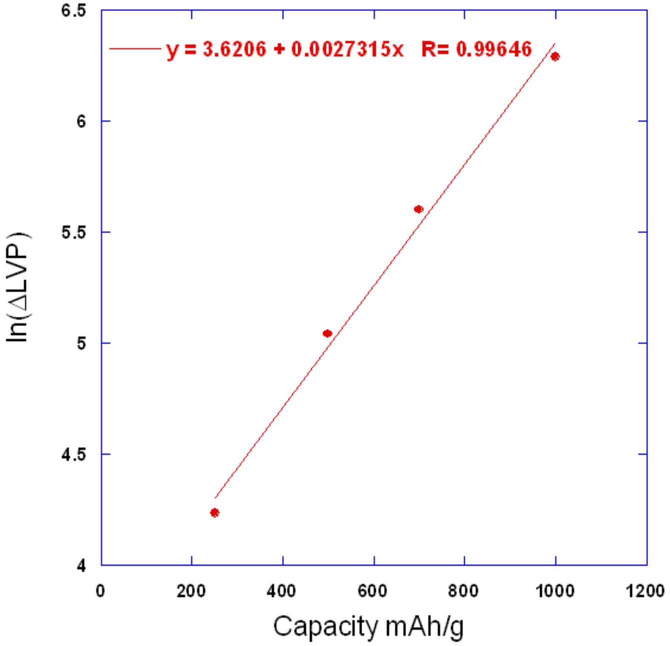
Pristine activated carbon cathode



SEM images of growing discharge Li-air products with time

Charge potentials have two plateaus that are dependent on capacity (time)



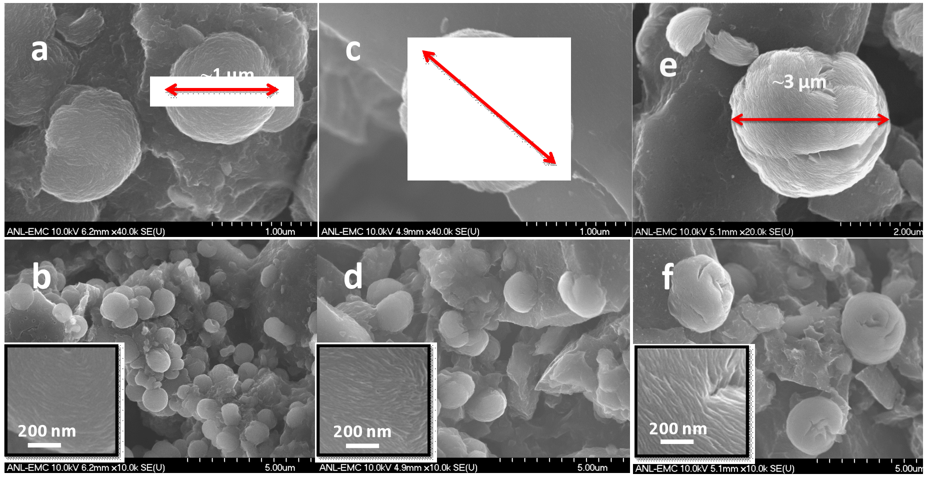


- Kinetics analysis is consistent with a first-order reaction (disproportionation) with LiO_2 component corresponding to the lower plateau

Raman evidence for “late” (slow) disproportionation in Li-O_2 cells under some conditions

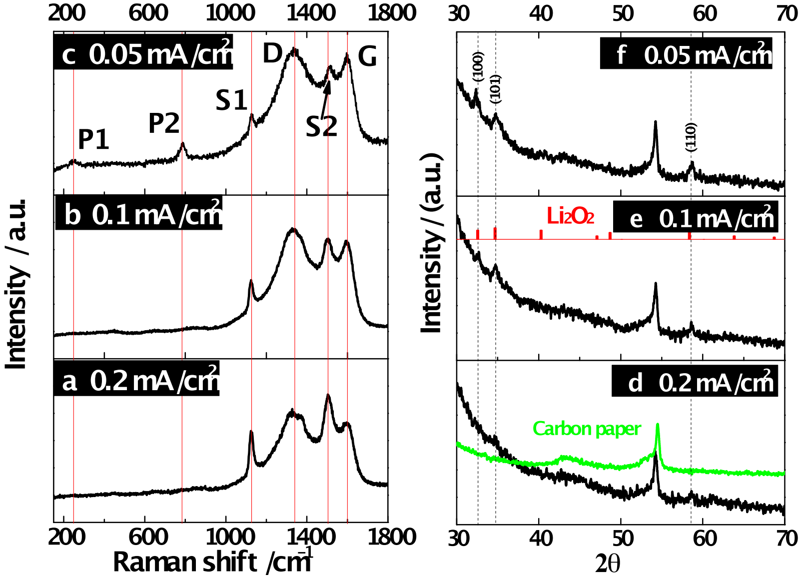
- Disproportionation
  - $2LiO_2 \rightarrow Li_2O_2 + O_2$
  - $(LiO_2)n \rightarrow (Li_2O_2)n/2 + n/2O_2$

0.2 mA/cm² 0.1 mA/cm² 0.05 mA/cm²



decreasing discharge current density

SEM images of toroids in Li-O_2 cell as a function of current density (cathode is activated carbon)

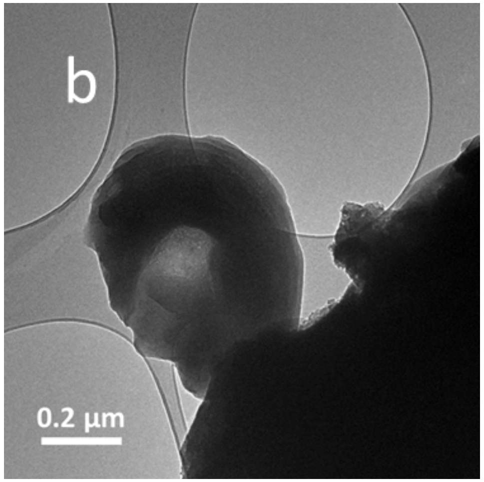


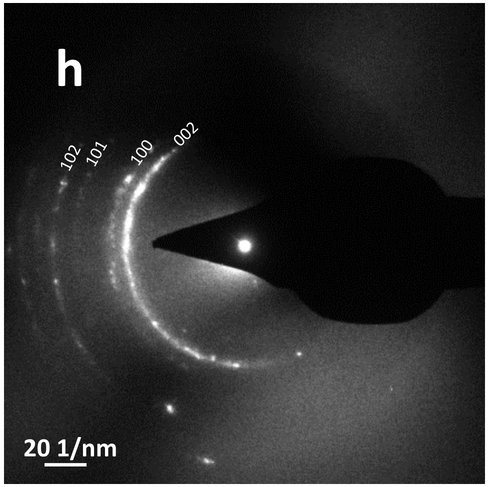
Raman peak at 1125 cm^{-1} (S1) is evidence for more LiO_2-like component at faster discharge current densities

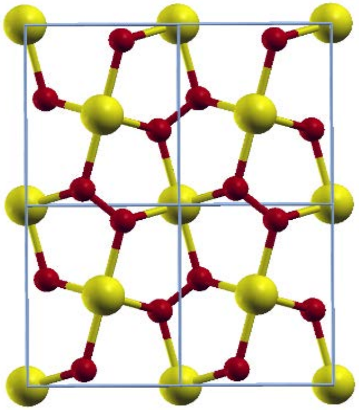
DFT calculations indicate that the 1505 cm-1 peak (S2) is from distortion of the graphitic ring stretching due to coupling with the LiO_2 bonding to it.

Faster discharge rate and slow disproportionation kinetics → more LiO2-component (lower charge overpotential)

Electron diffraction evidence for LiO_2 component in discharge product in activated carbon cathode



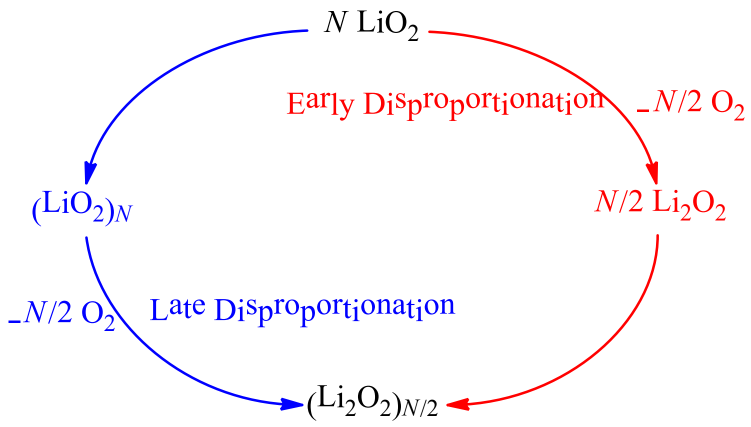




DFT predicted LiO_2 crystal structure (JPCC 2012)

- Electron diffraction indicate a mixture of Li_2O_2 and LiO_2
  - Partial disproportionation
  - Identified from DFT structure of bulk LiO_2 since no experimental structure is known (Lau et al, J. Phys. Chem. C, 2012)

LiO_2 disproportionation



$N\ LiO_2$

Early Disproportionation $-N/2\ O_2$

$(LiO_2)_N$

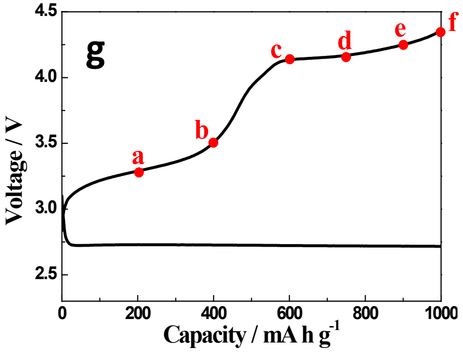
$N/2\ Li_2O_2$

$-N/2\ O_2$ Late Disproportionation

$(Li_2O_2)_{N/2}$

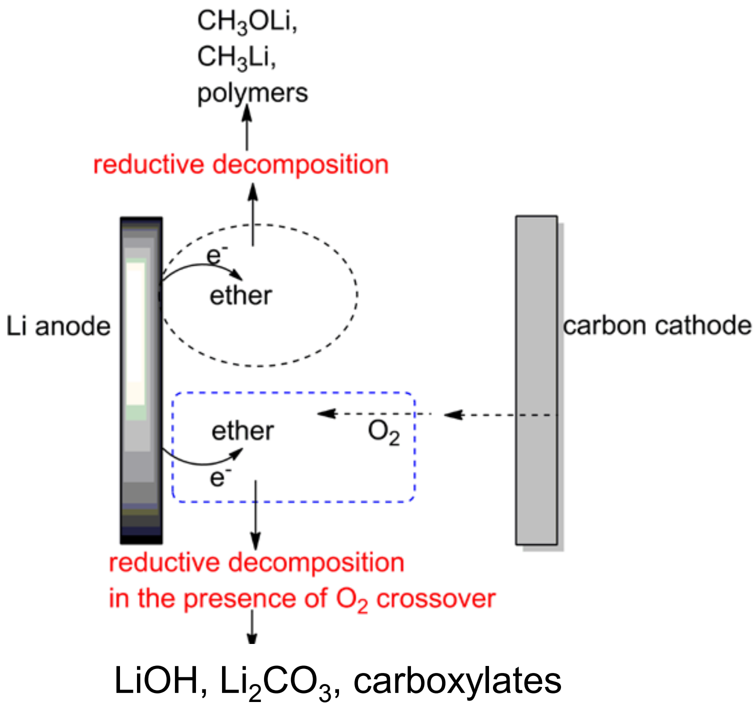
Early (fast) disproportionation will lead to dimer disproportionation (small DFT barrier) and Li_2O_2 deposition – surface growth or via solution

Activated carbon cathode: Late (slow) disproportionation leads to bulk LiO_2 growth and then partial disproportionation characterized by low plateau (LiO_2)



Activated carbon cathode suggests that controlling discharge product composition can also be used to lower charge overpotential in addition to morphology control found for Pd and Mo_2C cathodes

Oxygen crossover effect at the lithium anode in a TEGDME Li-O_2 cell



CH_3OLi,
CH_3Li,
polymers

reductive decomposition

Li anode

e^-

ether

carbon cathode

ether

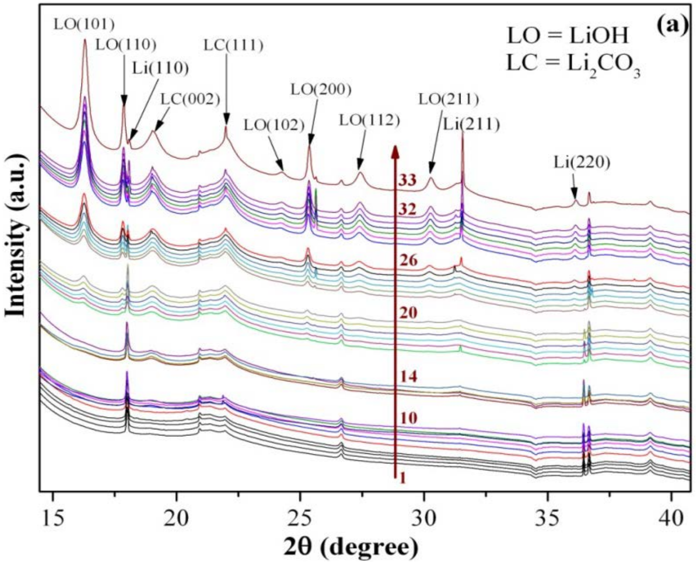
O_2

e^-

reductive decomposition
in the presence of O_2 crossover

LiOH, Li_2CO_3, carboxylates

DFT calculations predict reductive decomposition ether in the presence of O_2



In situ XRD measurements of Li anode in a TEGDME Li-O_2 cell showing LiOH formation

Presence of O_2 in Li-O_2 cells will lead to different decomposition mechanisms of ethers than Li-ion batteries - may effect cycle life

Response to last year reviewer's comments

This project is a new start and
no comments from 2014 AMR are available

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 (Pd, Mo_2C, activated carbon) 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-air batteries
- Design new cathode materials that do not degrade in the Li-air batteries
- Synthesize, test, and evaluate new electrolytes and catalysts for Li-air batteries

Summary

- Electrolyte selected for cathode development on basis of experiment and theoretical studies
- Three new cathode materials developed, which can be used as a basis for discovery of more stable electrolytes and improved catalyst for longer cycle life, increased efficiency, increased capacities
  1. $Pd/Al_2O_3/C$
  2. Mo_2C/CNT
  3. Activated carbon
- Evidence for an oxygen cross-over effect that degrades the lithium anode and shortens lifetime