Lithium-Air Batteries

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Argonne National Laboratory
DOE merit review
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Project ID# BAT-286

Overview

Timeline

- Start: 2016
- Finish: 2020
- 80 %

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: $ 2400 K
  - Contractor 0
- FY 17: $ 400 K
- FY 18: $ 500 K
- FY 19: $ 500 K

Partners

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

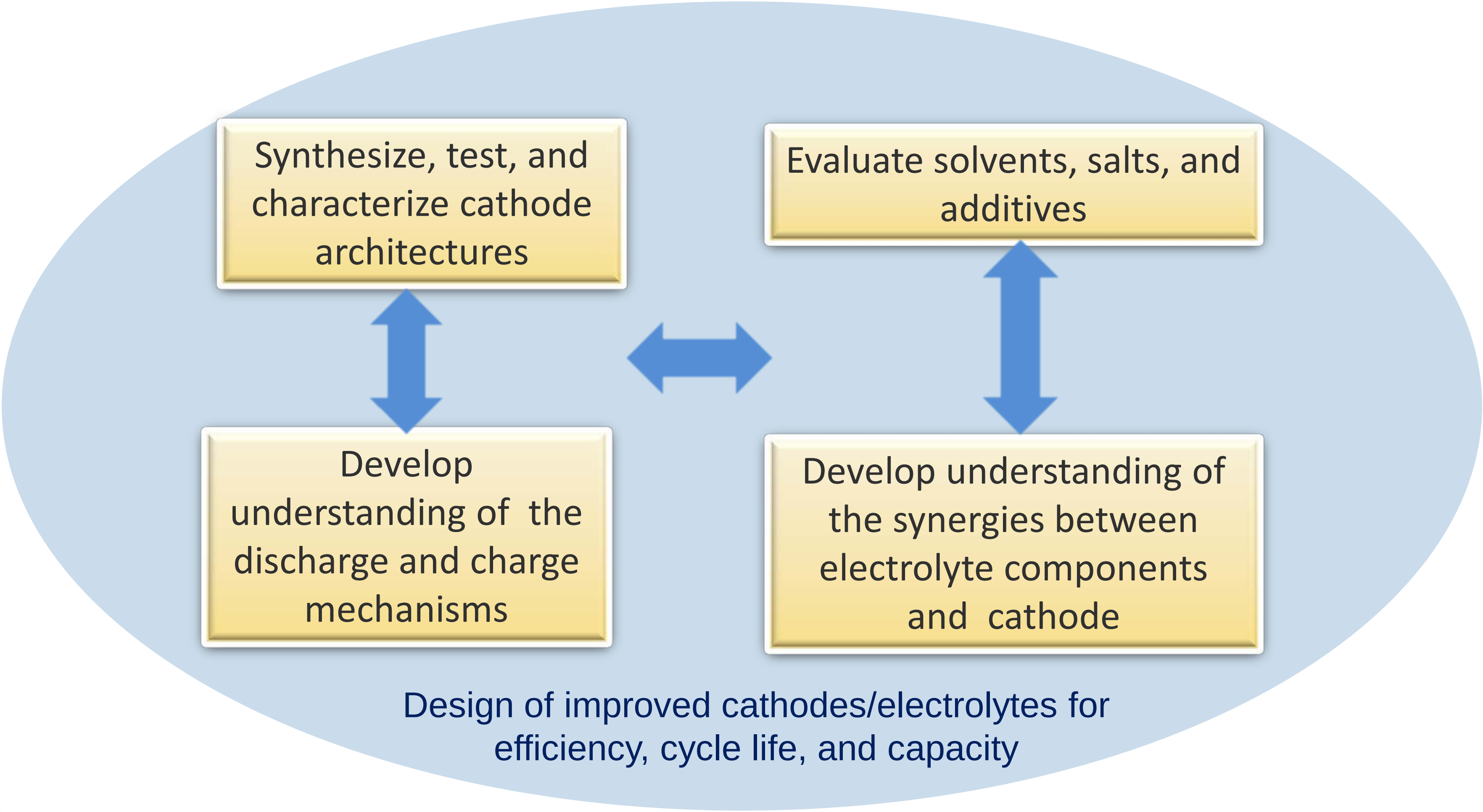
Project Objectives and Relevance

- 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/18	Synthesis and testing of low-cost transition metal catalysts that give low charge potentials in Li-O_2 batteries Q1 (**Completed**)
Mar/19	Characterization of Li_2O_2 and LiO_2 via Electrochemical Impedance Measurements Q2 (**Completed**)
Jun/19	Investigation of dependence of discharge product properties on electrolytes with mixtures of Na and Li salts . Q3(**Initiated**)
Sep/19	Computational and experimental studies of new electrolyte additives for increased efficiency Li-O2 batteries.Q4 (**Initiated**)

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



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

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

Experimental methods

Synthesis

- New catalyst 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)
- 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
- Design of oxygen reduction and oxygen evolution catalysts
  - Density of states
  - Adsorption energies

Technical Accomplishments

Cathode

- Developed new CoNi nanoparticle catalyst for low charge potentials

Characterization and understanding

- Use of impedance studies of discharge products has led to evidence for first time of good electronic conductivity of superoxide and correlation with charge potentials
- Derived an understanding of importance of mass and charge transport in Li_2O_2 formation through use of impedance, XRD, and computational studies

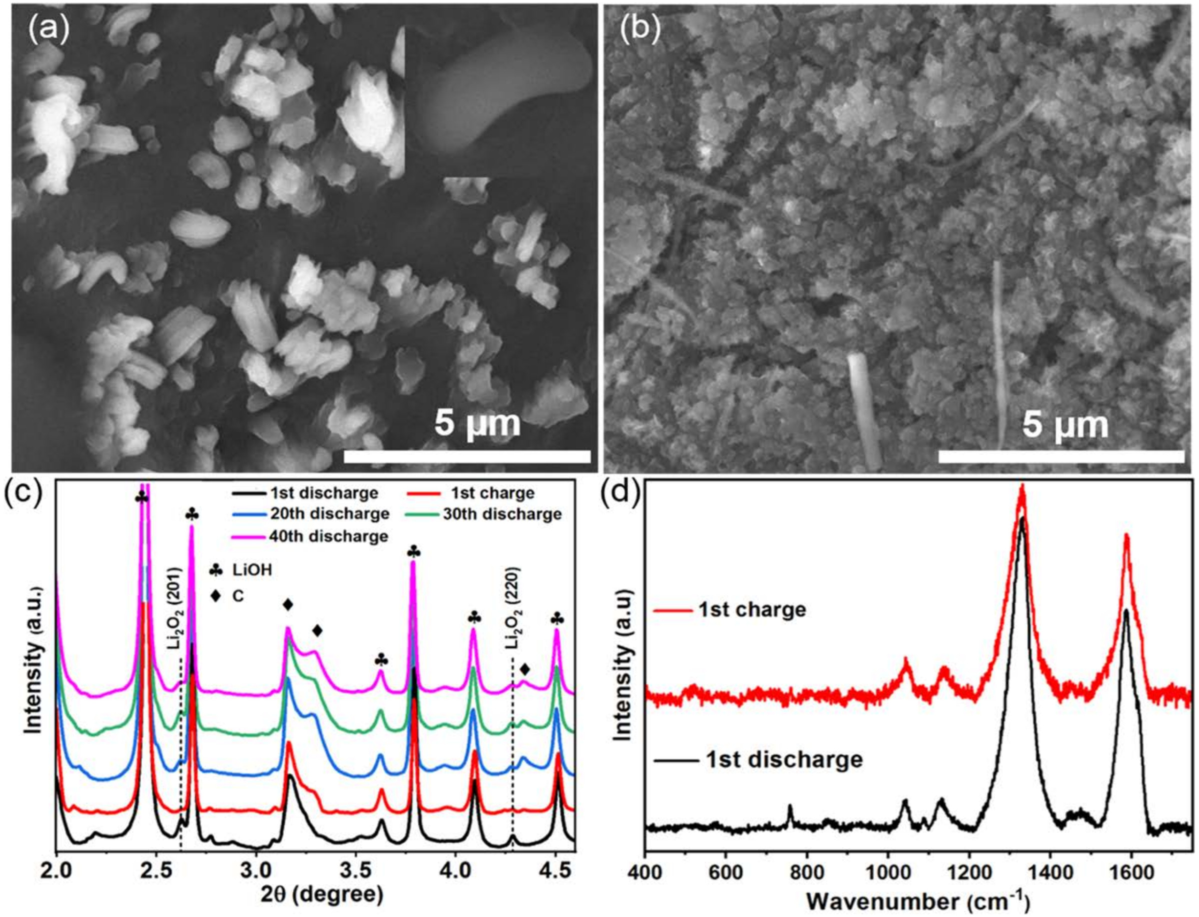
Electrolytes

- Identified a stable benzonitrile solvent and demonstrated longer cycle life

Accomplishment: Development of Non-Noble Metal Nanoparticles for Li–O_2 Batteries with Low Charge Potentials

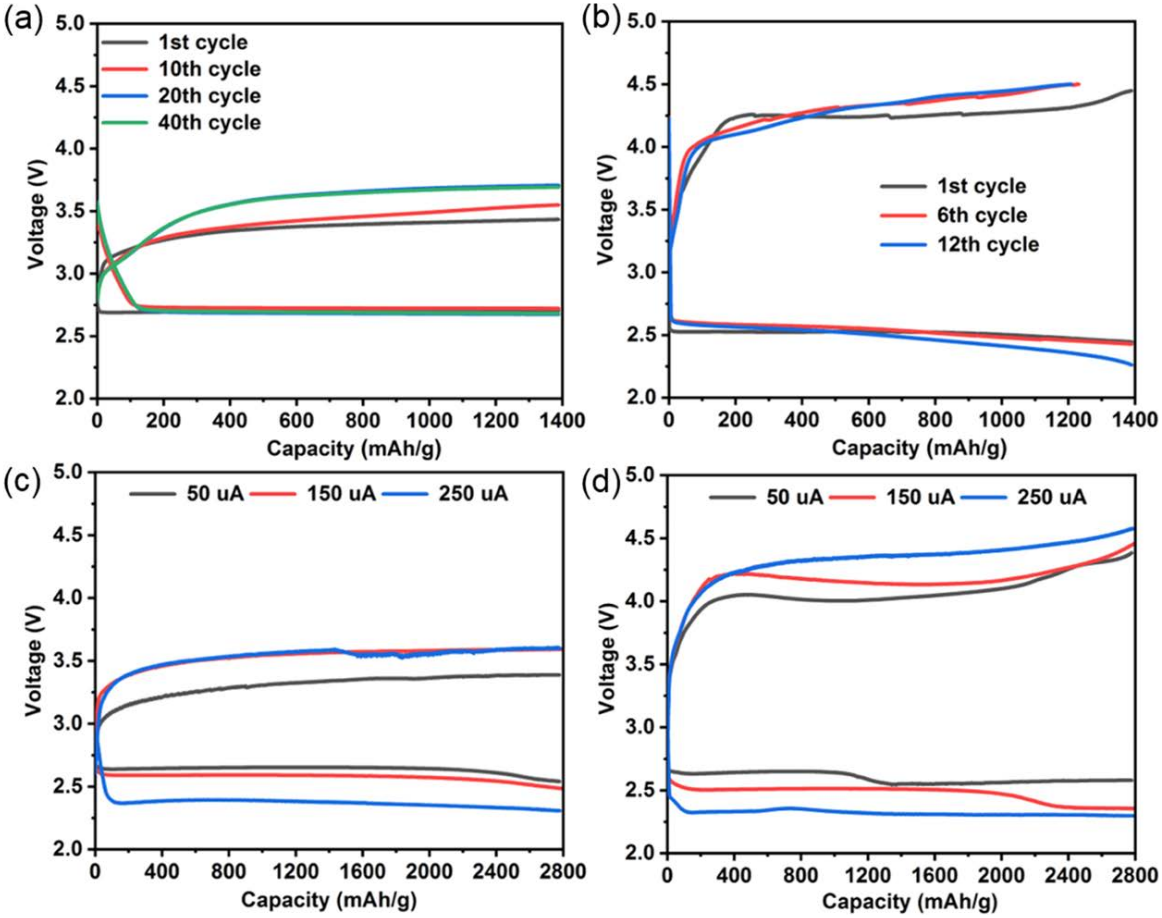
- It is desirable to explore low-cost and effective alternative catalysts for Li-O2 batteries.
- We designed a simple approach to prepare ultrafine cobalt and nickel nanoparticles dispersed in a porous LiOH structure (denoted as $Co_2Ni@LiOH$) by an *in situ* lithiation strategy.
- We lithiated cobalt–nickel layered double hydroxide (Co–Ni LDH) nanoplates by a discharge process under argon in a Swagelok cell, which leads to the formation of cobalt and nickel metal nanoparticles in a LiOH composite ($Co_2Ni@LiOH$).
- Then, the $Co_2Ni@LiOH$ composite-based electrode was directly employed as the cathode in a Li–O_2 cell after filling the glass chamber with pure oxygen.
- The metal particles have ultrafine size (∼2 nm) and the composite has a uniform 3D porous structure with enhanced surface area and good electrical conductivity.

Characterization of Li-O_2 battery with Co_2Ni@LiOH cathode



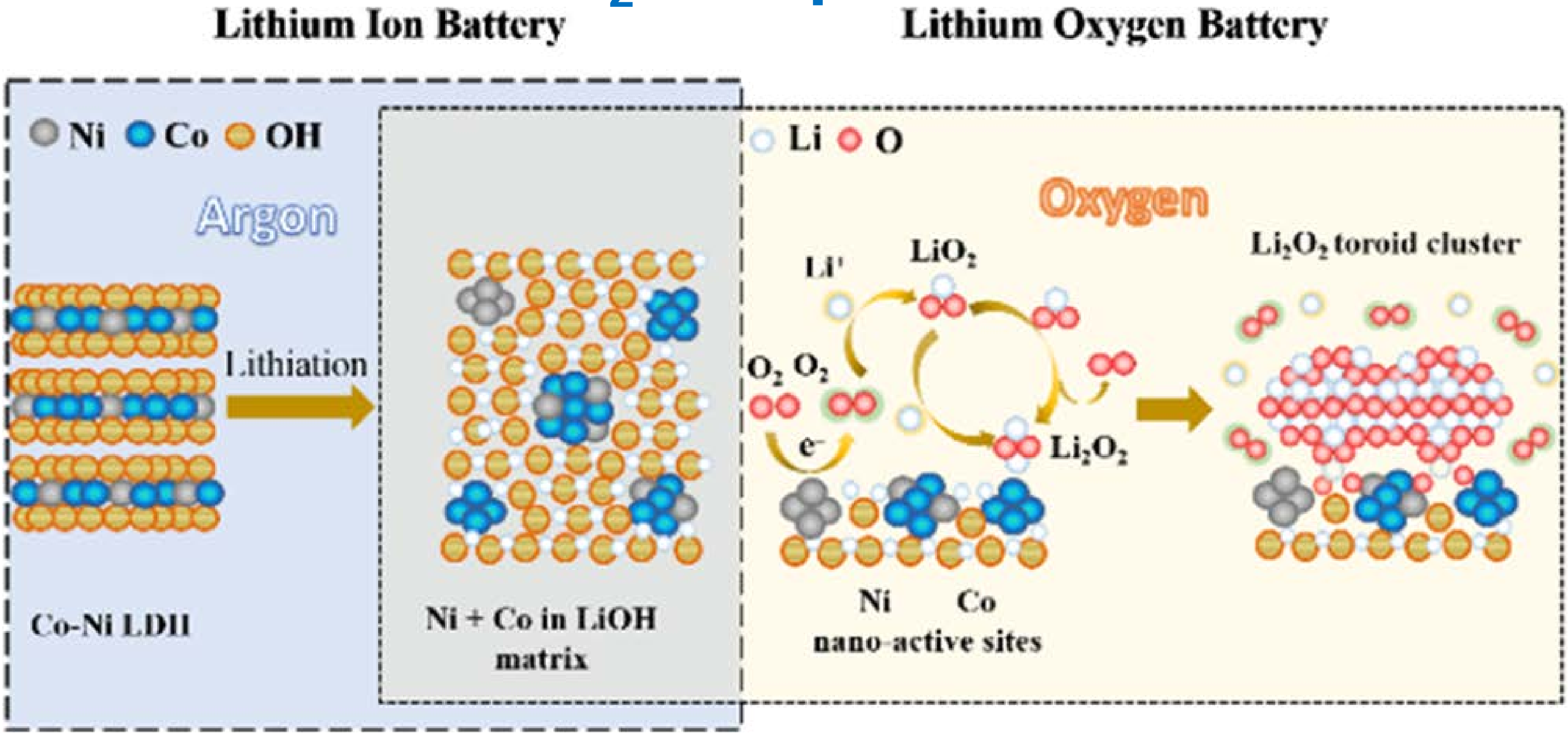
SEM of (a) 1st discharge and (b) charge products in Li−O_2 batteries with the Co_2Ni@LiOH cathode. (c) XRD of the 1st, 20th, 30th, and 40th discharge and the 1st charge products, (d) Raman spectrum of the 1st discharge and charge products in Li−O_2 battery

Voltage profiles of different cathodes based on porous LiOH



a) First 40 cycles of Li−O_2 battery with the Co_2Ni@LiOH cathode and (b) first 12 cycles of Li−O2 battery with the pristine Co−Ni LDH cathode. Rate performance of (c) Co_2Ni@LiOH-0.1V cathode and (d) pristine Co−Ni LDH cathode

Schematic of Li-O_2 battery mechanism based on $CoNi_2$ nanoparticles



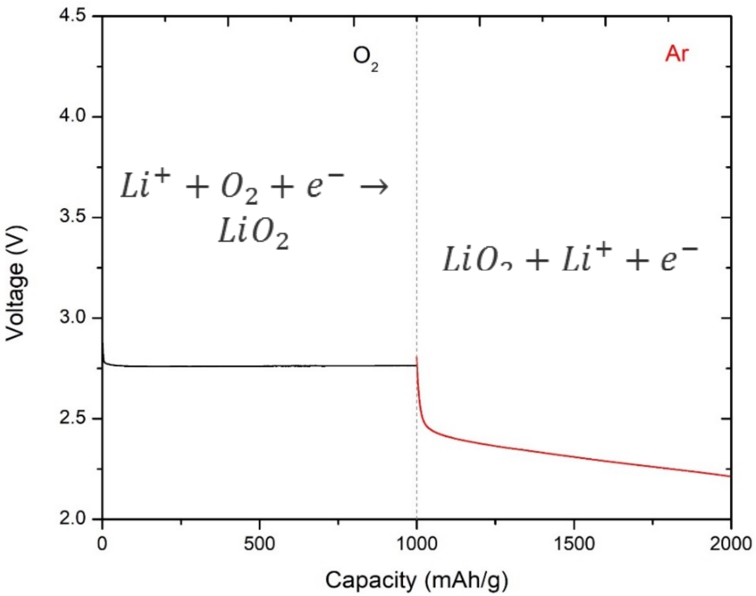
Lithiation of cobalt−nickel layered double hydroxide (Co−Ni LDH) nanoplates by a discharge process under argon, which leads to the formation of cobalt and nickel metal nanoparticles in a LiOH composite (Co_2Ni@LiOH).

Oxygen reduction and formation of Li_2O_2 toroids in a LiOH/Co_2Ni composite.

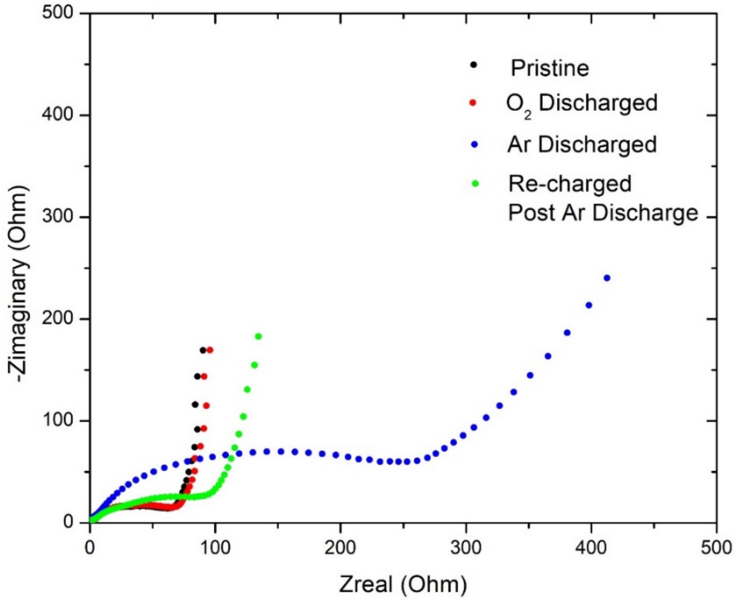
Performance of Co_2Ni Nanoparticles in Li−O_2 Batteries

- The Co_2Ni@LiOH exhibits a high discharge voltage of 2.7 V and a very low charge potential of 3.4 V at a current density of 50 µA cm^{-2},
  - results in a much higher roundtrip efficiency of ∼79% compared with that of pristine Co−Ni LDH (∼59%).
- The Co_2Ni@LiOH-based Li−O_2 cell is stable and can last 40 cycles with a 3.6 V charge potential at the current density of 50 µA cm^{-2}
- After the 1st discharge, the SEM image shows that the Co_2Ni@LiOH electrode is covered by toroidal structures, the common morphology for Li_2O_2.
- The well-aligned network facilitates the oxygen diffusion and the electrolyte penetration into the electrode.
- The enhanced electrical conductivity network improves the charge transport kinetics and more active sites are exposed, which facilitates the adsorption and dissociation of oxygen during the oxygen reduction reaction and the oxygen evolution reaction.

Accomplishment: Characterization of electronic conductivity of discharge products in Li-O_2 batteries by impedance measurements



Ir-rGO cathode used to grow LiO_2 in O_2 and subsequent growth of Li_2O_2 in Ar



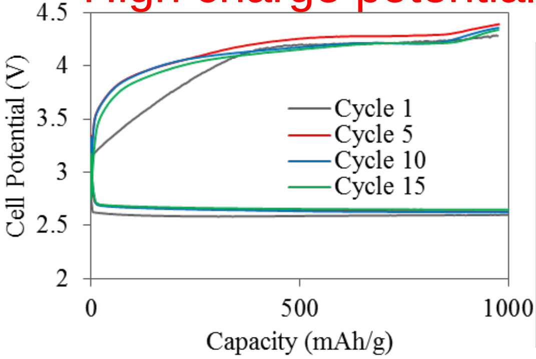
Impedance measurements of pristine cathode (black), LiO_2 covered cathode (red), and Li_2O_2 covered cathode (blue

- Impedance measurements show that LiO_2 has neglible resistance while Li_2O_2 has significant resistance!

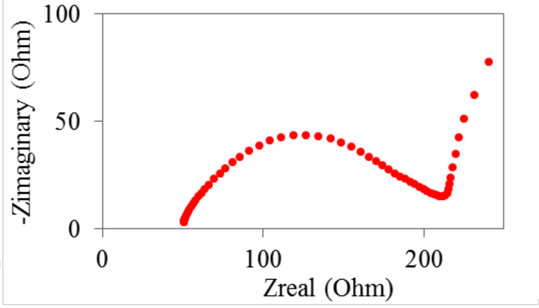
Correlation of impedance with charge potentials and nature of discharge product

rGO cathode

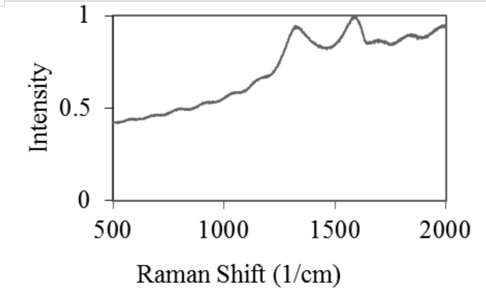
High charge potential



High impedance

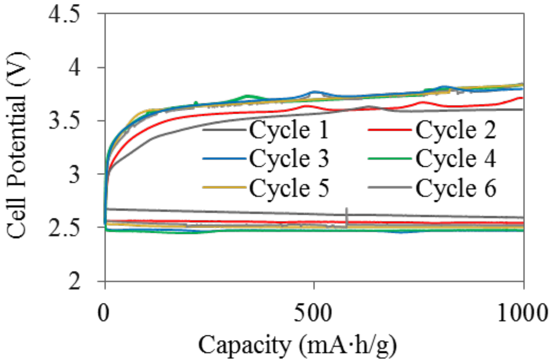


Li_2O_2

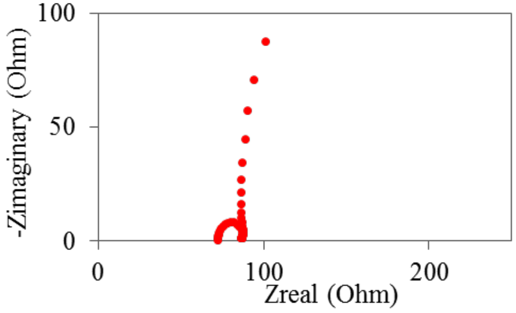


Ir-rGO cathode

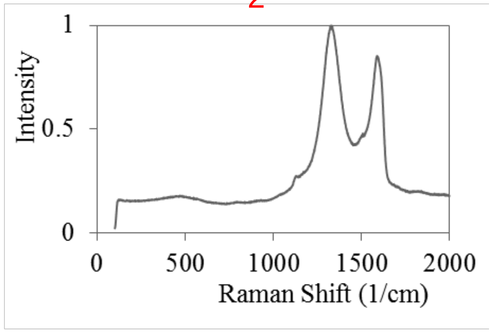
Low charge potential



Low impedance

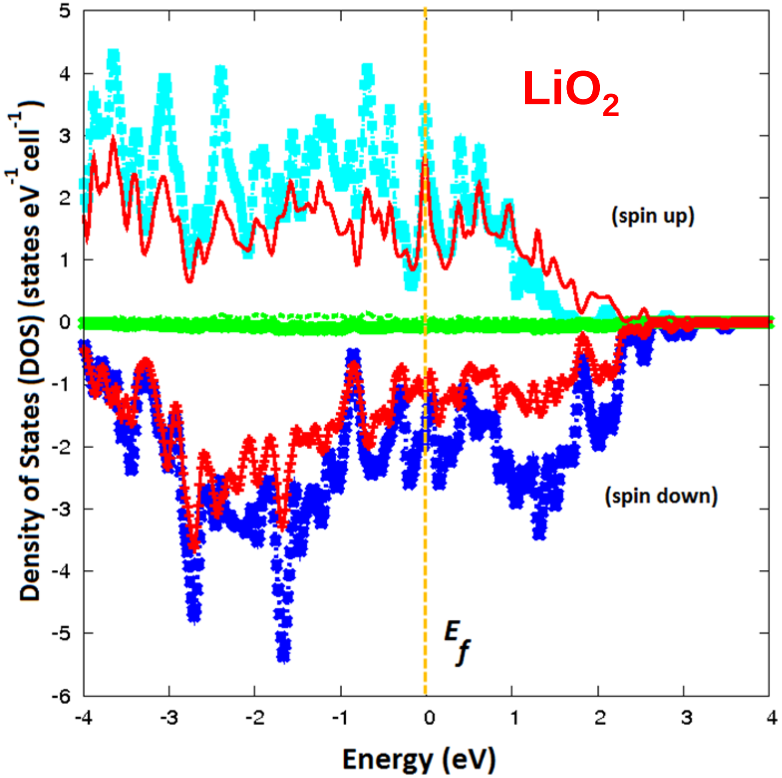


LiO_2



- Impedance measurements on rGO (Li_2O_2 discharge product) and Ir-rGO (LiO_2 discharge product) show difference in charge potentials that correlate with electronic conductivity of the two products.

DFT calculated density of states confirmed by impedance measurements



- DFT calculations had showed that LiO$_2$ is a half metal with no band gap compared to Li$_2$O$_2$ that has a large band gap.
- This DFT result is now confirmed by impedance measurements on the two discharge products and is consistent with the low charge potential found for products with LiO$_2$ present (Lu, Curtiss, Amine et al Nature, **529**, 377, 2016)

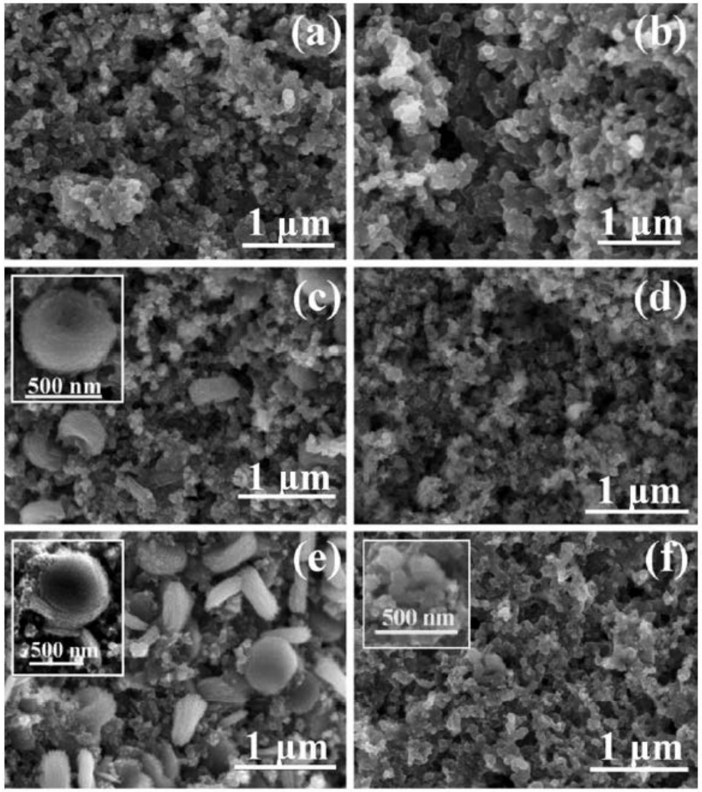
Accomplishment: Derived an understanding of importance of mass and charge transport in Li_2O_2 formation, the most common discharge product, through use of impedance, XRD, and computational studies

- Systematic study of the morphological transition of Li_2O_2 from a single crystalline structure to a toroid like particle during the discharge–charge cycle

- Evolution of Li_2O_2 at different stages of this process.
  - Evolution starts in the first monolayer of Li_2O_2, and is subsequently followed by a transition from particle growth to film growth if the applied current exceeds the exchange current for the oxygen reduction reaction in a Li-O_2 cell.

- A sustainable mass transport of the diffusive active species (e.g., O_2 and Li^+) and evolution of the underlying interfaces are critical for desirable oxygen reduction (discharge) and evolution (charge) reactions in a porous carbon electrode of a Li-O_2 cell.

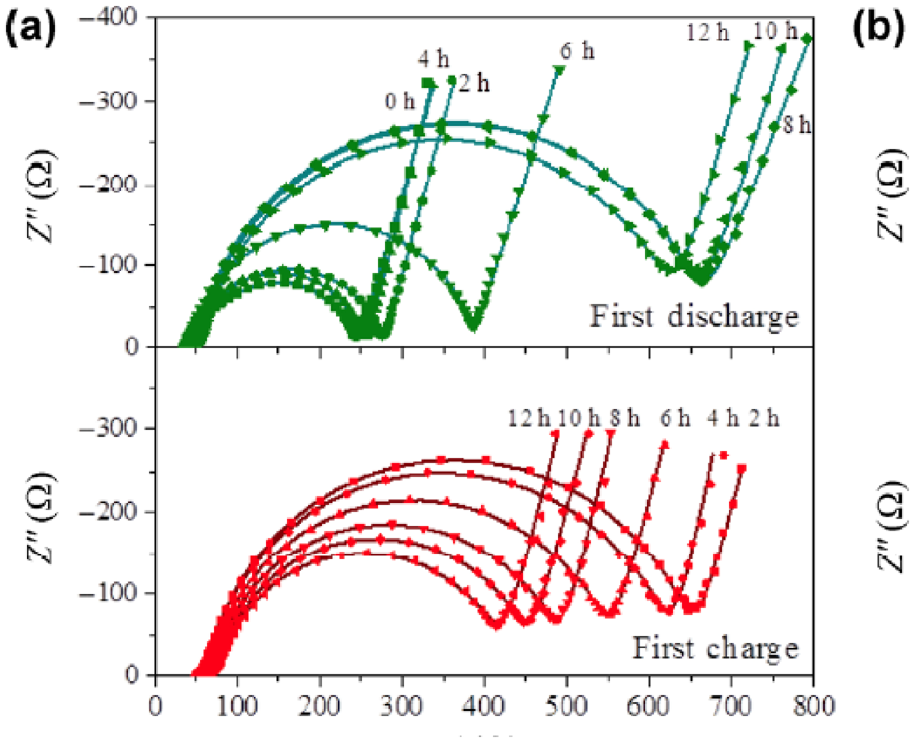
SEM images during discharge and charge of a Li-O_2 battery with a carbon black cathode and TEGDME electrolyte



<ins>SEM images of the graphitized carbon electrodes</ins>
(a) discharged for 400 mAh/g carbon,
(b) discharged and charged for 400 mAh/gcarbon each
(c) discharged for 600 mAh/g carbon
(d) discharged and charged for 600 mAh/g carbon each
(e) discharged for 1,200 mAh/gcarbon,
(f) discharged and charged for 1,200 mAh/g carbon each,

- Note that the SEM images show growth of toroids starting around 400 mAh/g capacity

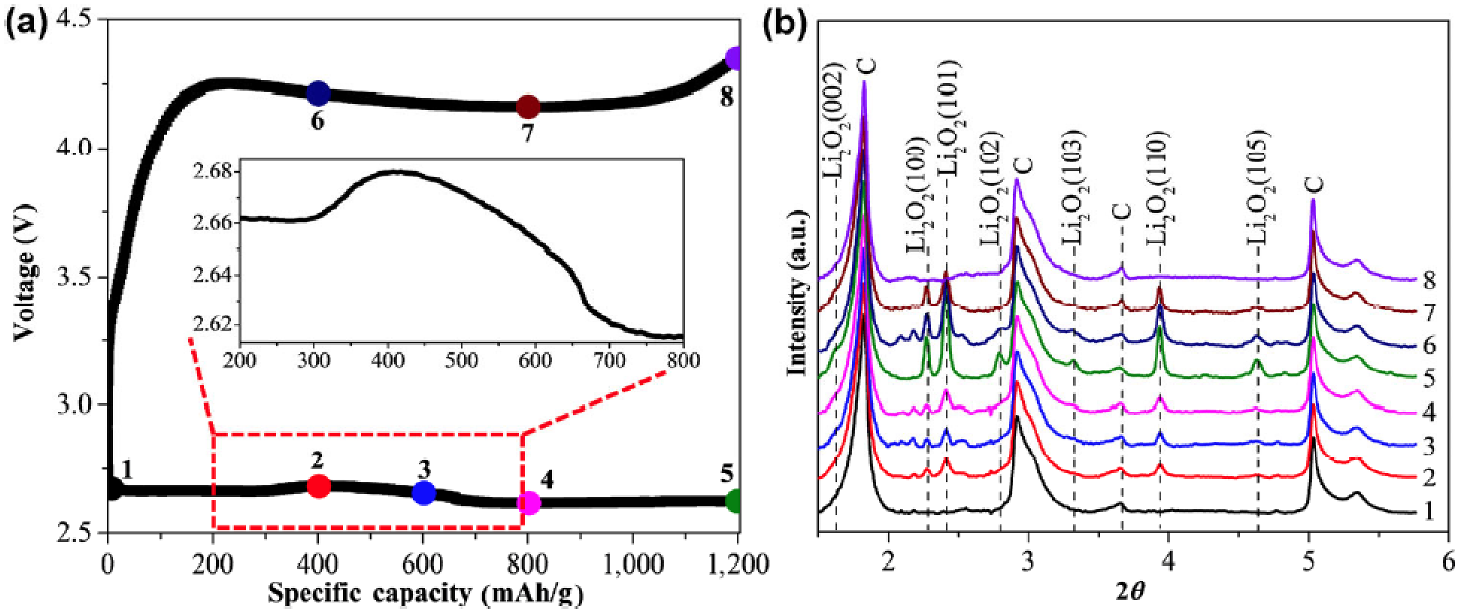
Impedance measurements during discharge and charge of a Li-O_2 battery with a carbon black cathode and TEGDME electrolyte



Impedance arcs for the first cycle, measured every 2 h.

- The gradually increasing impedance is most probably due to the accumulation of the insulating product Li2O2 on the cathode. The decrease upon charge agrees with the decomposition of Li2O2 during the charge process. This is in contrast to the Ir-rGO cathode that resulted LiO2 and little impedance.

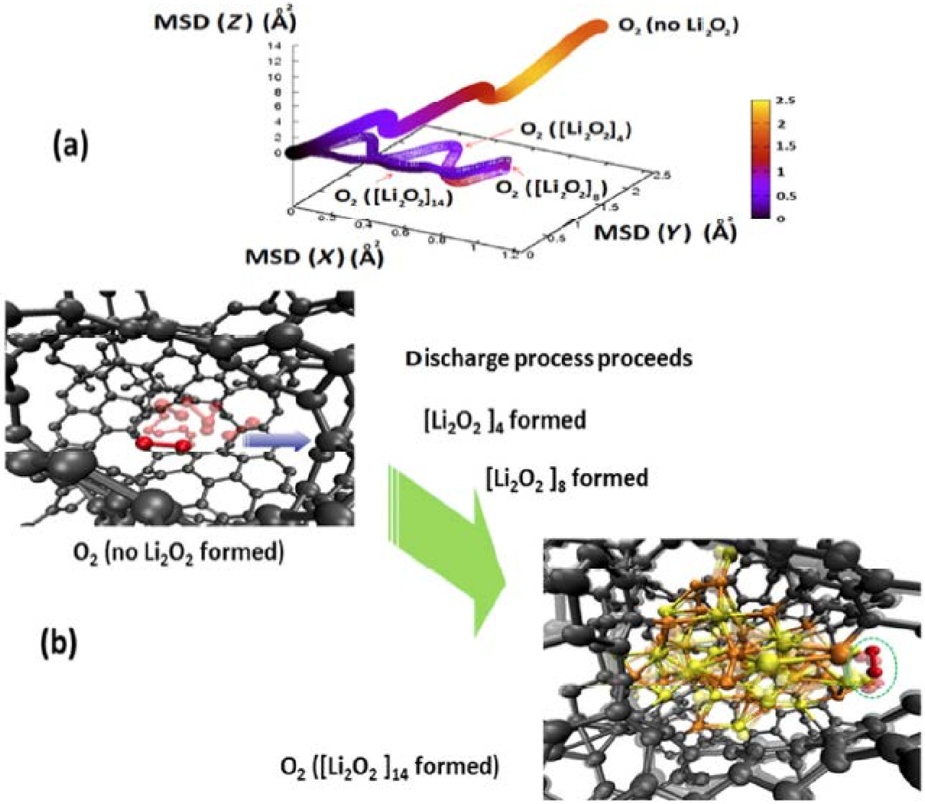
XRD and charge profile



(a) The voltage profile of a 1,200 mAh/g capacity-controlled cycle. (b) XRD spectra of graphitized carbon cathodes at different discharge or charge capacities.

- Li_2O_2 is the main discharge product.
- The intensity of the peaks increased when the capacity increased (patterns 1–5), implying a growth of the discharge product Li_2O_2.
- Note that there is a bump in the discharge voltage profile between 300 and 700 mAh/gcarbon when the Li_2O_2 nanoparticles start to form toroid-like morphologies.

DFT calculation of growth of Li_2O_2 particle



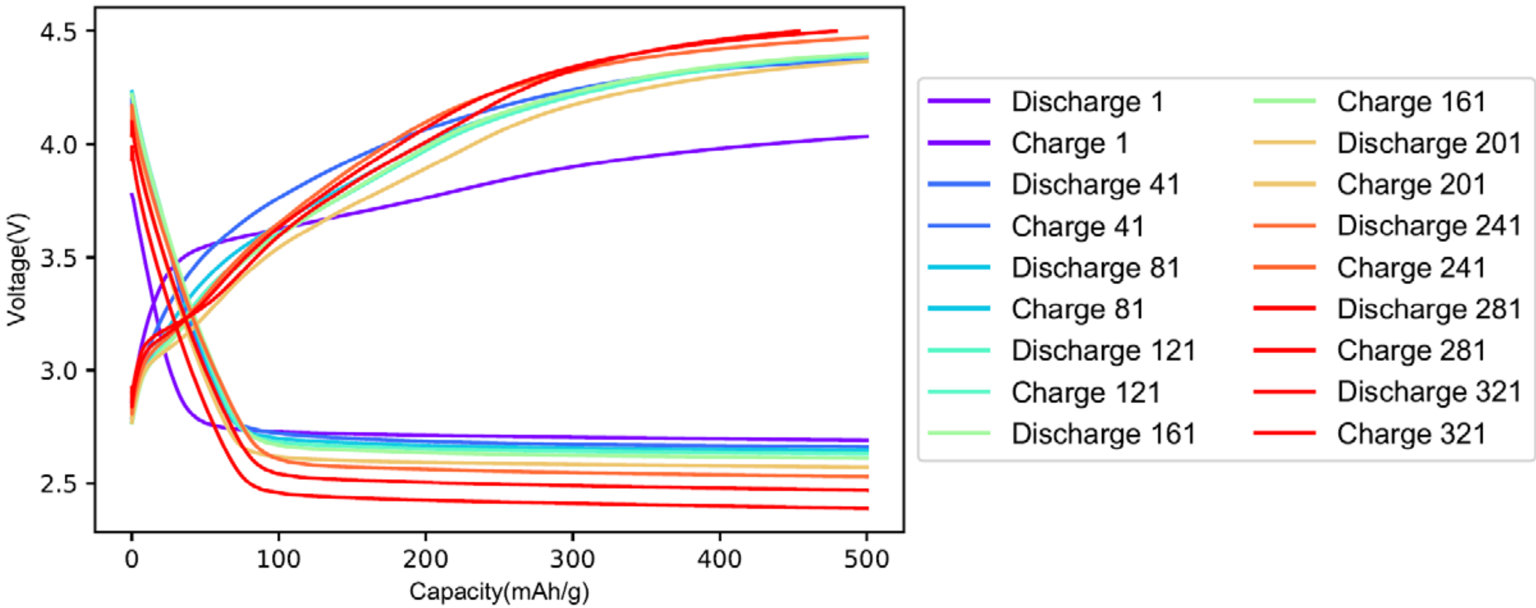
(a) The mean-square displacement (MSD) of the trajectory of an O_2 molecule during different stages of the discharge process.

(b) A selected snapshot of the atomic motion of free O_2 gas (red) and a chemically bonded O_2 species (red) when a Li_2O_2 cluster (yellow) is formed during the discharge process

- The calculations suggest that prior to the formation of Li_2O_2, the trajectories of both the active species (O_2 and Li^+) are found to be nearly linear and time dependent. However, the mobility of O_2 and Li^+ starts to diminish as the Li_2O_2 starts forming.

Accomplishment: A new low donor number electrolyte (benzonitrile) has been found to give long cycle life in a Li-O_2 battery

Charge profile for rGO cathode with 1M LiTFSI

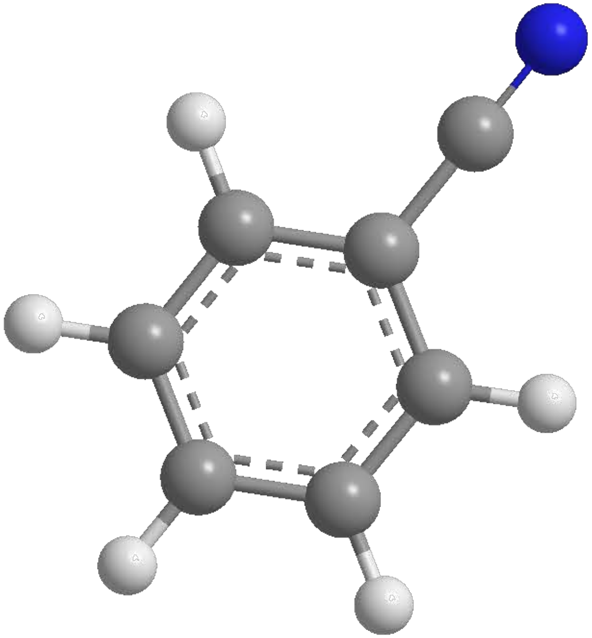


- Voltage profile shows long cycle life, but with high charge overpotential, probably due to the lack of a catalyst.

DFT calculations on donor number and redox potentials of the solvent

- Benzonitrile is computed to have low donor number of 12, a reduction potential of 0.7 eV, and an oxidation potential of 6.8 eV
- The low donor number suggests surface growth of the discharge product (Bruce et al, Nature Energy, 2016), which will reduce superoxide species in the electrolyte that can cause electrolyte decomposition
  - This may contribute to the long cycle life
- The low reduction potential and high oxidation potentials suggest that the solvent should be stable also.

- **The modification of this promising solvent by additives will be explored for reducing the charge potential and increasing the capacity**



Response to last year reviewer's comments

No comments from last year.

Proposed Future Work

- Systematic studies of electrolytes including concentrated electrolytes, additives, ionic liquids, and blends.
  - Effect on discharge product composition, cycle life, and efficiency
  - Understand effect on disproportionation
  - Computational studies to help design new electrolytes
  - Design new electrolytes for optimal Li-O_2 performance
- New electrodes for Li-O_2 cells
  - Design low cost catalysts to favor decomposition of Li_2O_2 and reduce polarization
  - 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.
- K. C. Lau, California State University, Norridge
  - Computations

Remaining Challenges and Barriers

- Discovery of electrolytes for Li-O_2 batteries that give low charge potentials as well as long cycle life
- Increasing capacity of Li-O_2 batteries while maintaining long cycle life.
- Developing a better understanding of the role of the electrolyte in cycle life.

Summary

Cathode

- Developed new CoNi nanoparticle catalyst for low charge potentials

Characterization and understanding

- Use of impedance studies of discharge products has led to evidence for first time of good electronic conductivity of superoxide and correlation with charge potentials
- Derived an understanding of importance of mass and charge transport in Li_2O_2 formation through use of impedance, XRD, and computational studies

Electrolytes

- Identified a stable benzonitrile solvent and demonstrated longer cycle life