# Investigation on Lithium Superoxide-Based Batteries

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DOE merit review

June 10-13 , 2019

Project ID: bat431

# Overview

## Timeline

- Start: 2017
- Finish: 2020
- 80%

## Barriers

- Barriers addressed
- Unstable electrolytes
- Electro-catalyst poisoning
- Reversibility of the reaction

## Budget

- Total project funding
  - DOE share: 1300
  - Contractor 0
- FY 17: $ 400 K
- FY 18: $ 400 K
- FY 19: $ 500 K

## Partners

- Interactions/ collaborations
  - J. Li, MIT
  - J. G. Wen, ANL
  - R. Shahbazian-Yassar, UIC
  - L. Hu, UM
  - S. Meng, UCSD
  - Y. Wu, OSU

# Project Objectives and Relevance

- Understand the conversion mechanism of alkali metal (Li, Na, K) superoxide based batteries
- 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
- Use conversion mechanism of oxygen redox to enable a closed lithium superoxide systems to eliminate volumetric energy density issues
- Explore the Na- and K- superoxide based battery systems.

# FY19 Milestones

| Month/ Year | Milestones |
|---|---|
| Dec/18 | **Investigation of light-anion redox nanolithia cathodes for Li-ion batteries.** ***Completed*** |
| Apr/19 | **Investigation of the sodium superoxide stabilization in sodium–oxygen batteries.** ***Completed*** |
| Jun/19 | **Finalized characterization of iridium clusters based cathode in lithium superoxide batteries.** ***Completed*** |
| Sept/19 | **Investigation of new nanostructured catalytic cathode for high-capacity sodium superoxide based sodium–oxygen batteries.** ***On going*** |
| Sept/19 | **Development of lithium ion battery using sodium superoxide and potassium superoxide as cathode in the absence of oxygen.** ***On going*** |

# Strategy: understanding the conversion mechanism of oxygen redox in Li-$O_2$ batteries and realizing lithium superoxide battery and using these new results to enable a closed Li-$O_2$ system

## Catalyst Development

Develop an understanding of the conversion mechanism of oxygen redox from theory and experiment

Develop a new kind of catalyst to stabilize the $LiO_2$ and enable conversion reaction between $LiO_2$ and $Li_2O_2$/$Li_2O$

Design new catalyst for efficiency, cycle life, and capacity

## Battery Development

Test new battery based on conversion reaction of oxygen redox

Find suitable electrolyte, catalyst and design new cathode to promote the new battery based on oxygen redox reaction

Design improved cathode for efficiency, cycle life, and capacity

# Experimental methods

Synthesis

- New catalyst materials
- New cathode materials

Characterization

- XAS measurements
- Raman
- SEM imaging
- In situ XRD measurement (Advanced Photon Source)
- TEM imaging

Testing

- Swagelok cells
- Coin cells
- Stainless steel cells

# Technical Accomplishments

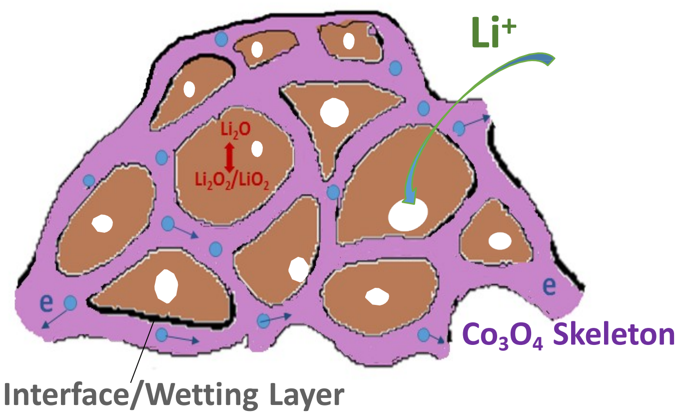
I. Demonstrate proof of concept of closed system between $Li_2O$, $Li_2O_2$ and $LiO_2$ without use of $O_2$ gas
  - Nanoporous substrate $Co_3O_4$ filled with $Li_2O$ served as a cathode in lithium closed battery.
  - Nanoporous substrate $Co_3O_4$ worked as a skeleton to promote the stable cycle between $Li_2O$, $Li_2O_2$ and $LiO_2$ without releasing/taking $O_2$ gas.

II. Lithium superoxide ($LiO_2$) stabilization
  - Ir clusters with suitable particle size were found to be able to stabilize the $LiO_2$ in Li-$O_2$ battery.
  - Mechanism of stabilization was elucidated.

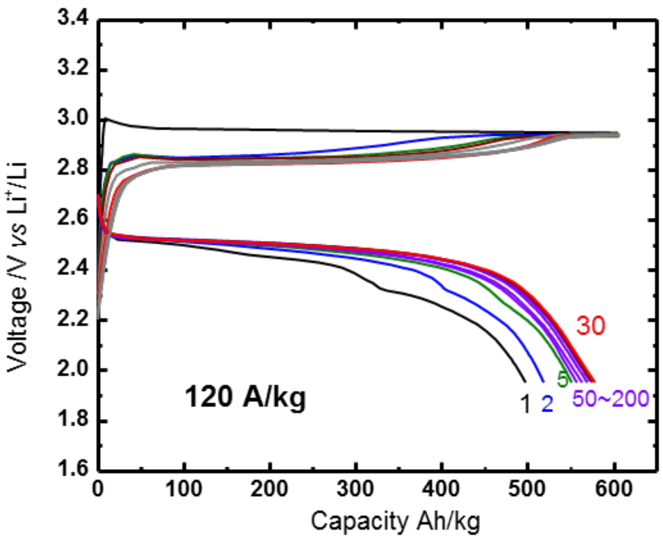
III. Stabilization of sodium superoxide ($NaO_2$) in Na-$O_2$ batteries
  - Cell environment was critical for the formation of discharge products in Na-$O_2$ batteries.
  - $NaO_2$ was successfully stabilized in a well-sealed Na-$O_2$ battery.

# Anion-redox nanolithia cathodes for Li-ion batteries

- Our studies have revealed an approach to realize light-anion redox cathode without $O_2$ evolution.
- Performance of this kind of nanolithia anion-redox cathode (energy density both based on weight and volume) is very promising
- Good performance (200 cycle with low polarization and no capacity fade) was obtained using a conventional electrolyte (1M $LiPF_6$/EC/DEC).

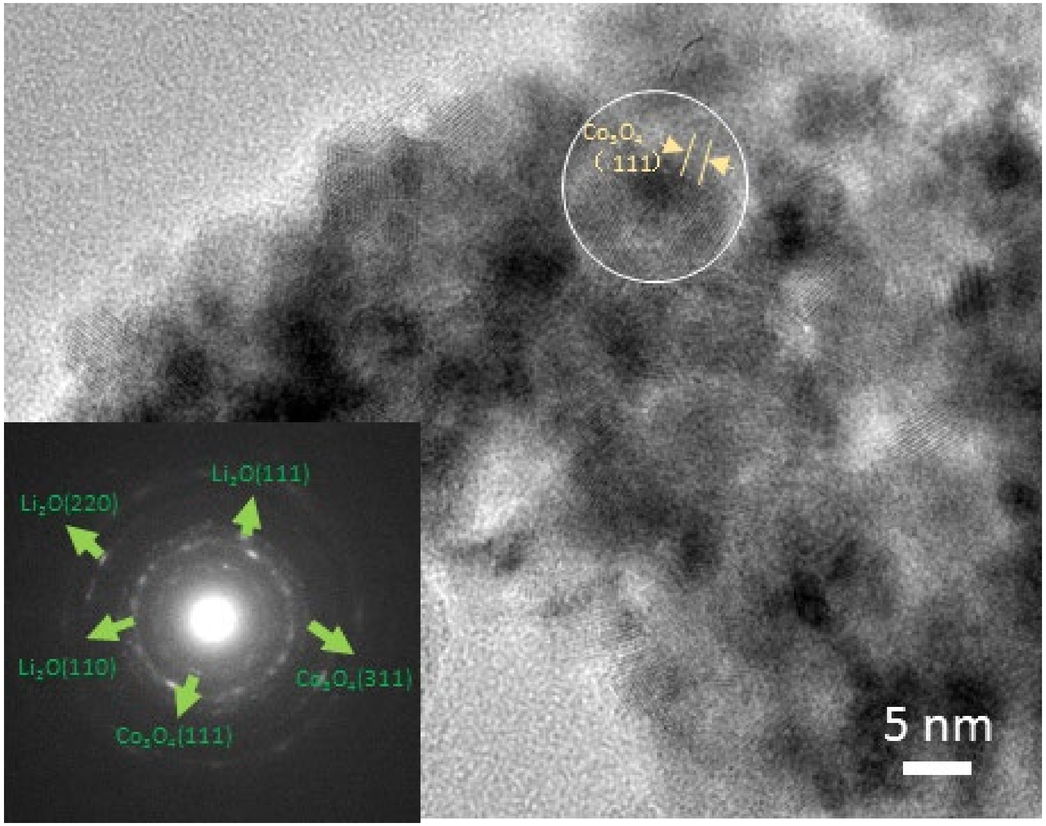



Schematic of $Co_3O_4$ skeleton wetted by amorphous $Li_2O/Li_2O_2/LiO_2$




Voltage profile for $Co_3O_4$ as a nanoporous substrate and filled with $Li_2O$ cathode

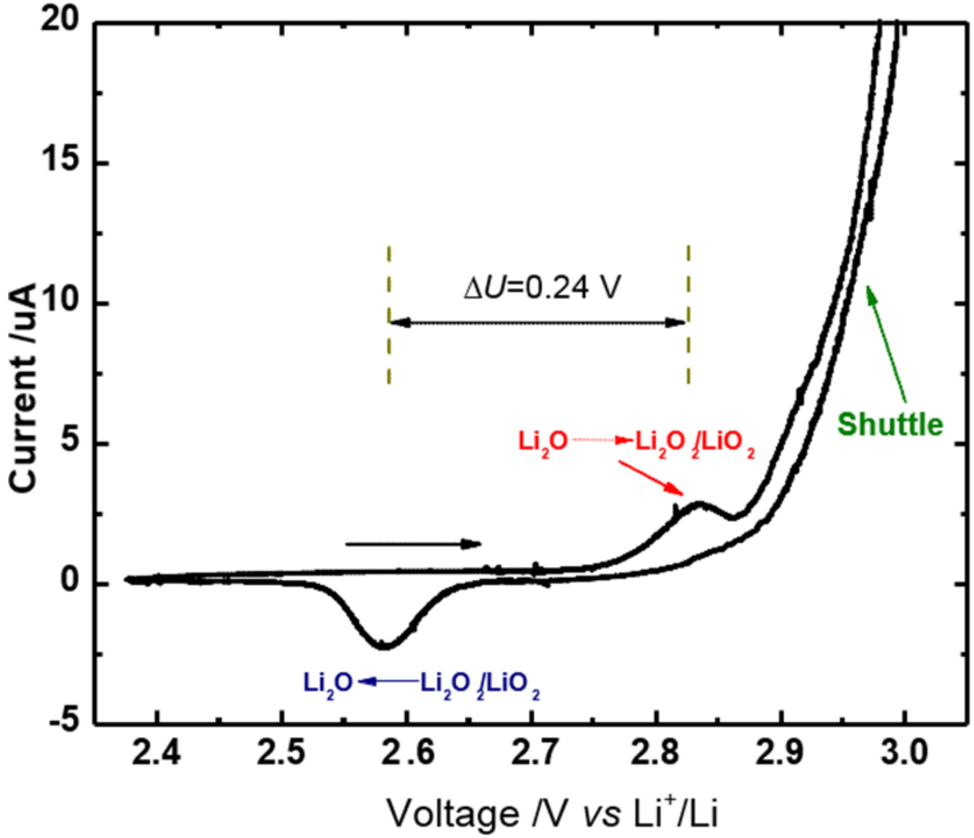
# TEM of $Li_2O$ and $Co_3O_4$ nanocomposite cathode




Transmission electron microscopy (TEM) of the nanocomposite $Li_2O$ and $Co_3O_4$ powder

- The cathode is a mixture of $Co_3O_4$ and $Li_2O$, and most of the $Li_2O$ nanoparticles are surrounded by a nonocrystalline $Co_3O_4$ skeleton.

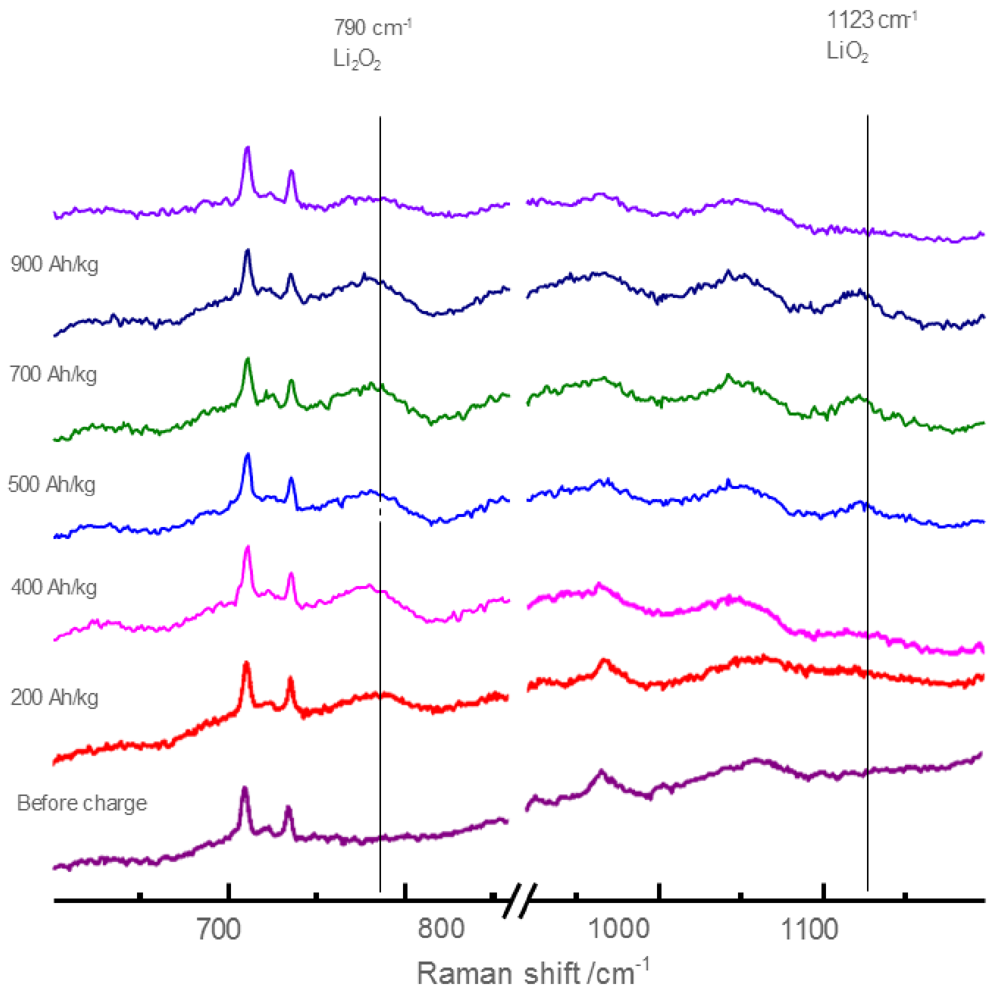
# Cyclic voltammogram of nanocomposite cathode




CV test $Li_2O$ and $Co_3O_4$ nanocomposite cathode between 2.35 and 3.0 V

- The oxidation peak is related to the charge process from $Li_2O$ to $Li_2O_2/LiO_2$, whereas the reduction peak is related to discharge from $Li_2O_2/LiO_2$ to $Li_2O$.
- The voltage difference between the oxidation and reduction peaks is only 0.24 V, one-fifth of that for the Li-air battery.

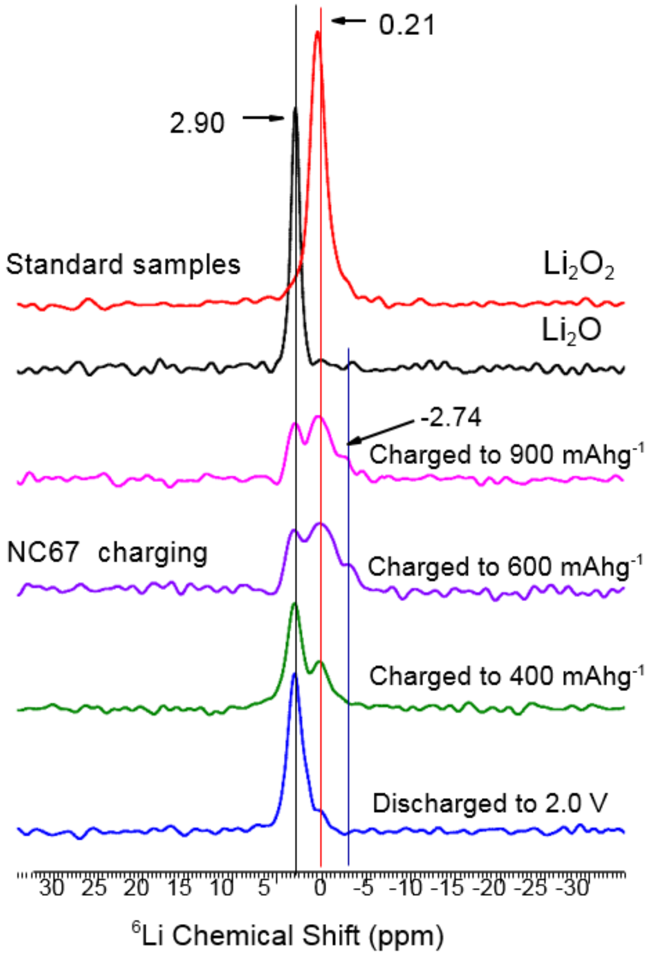
# Transformation of the nanolithia composite cathode




In situ Raman at different charge/discharge states

- The Raman spectra confirm that the peroxide and superoxide species exist in the confined amorphous solid

# $^6$Li NMR on the washed cathode at different SOCs



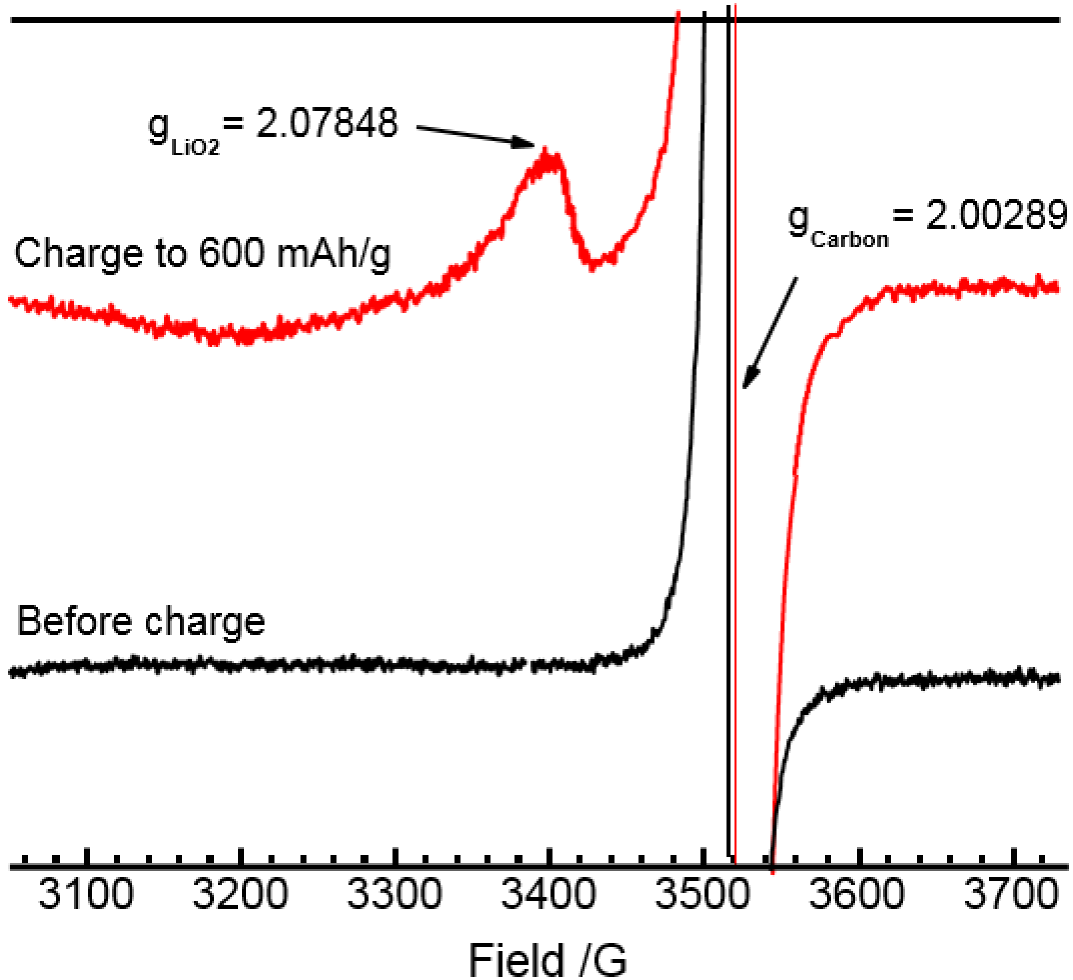

$^6$Li NMR of cathode at different SOC after DME washing

- NMR measurement during cycling shows that $Li_2O$ is oxidized during the charge process to form $Li_2O_2$

# ESR of the cathode before and after charge

- *ab initio* calculated ESR values for orthorhombic bulk $LiO_2$ (g = 2.085) prove the existence of an amorphous $LiO_2$ component.

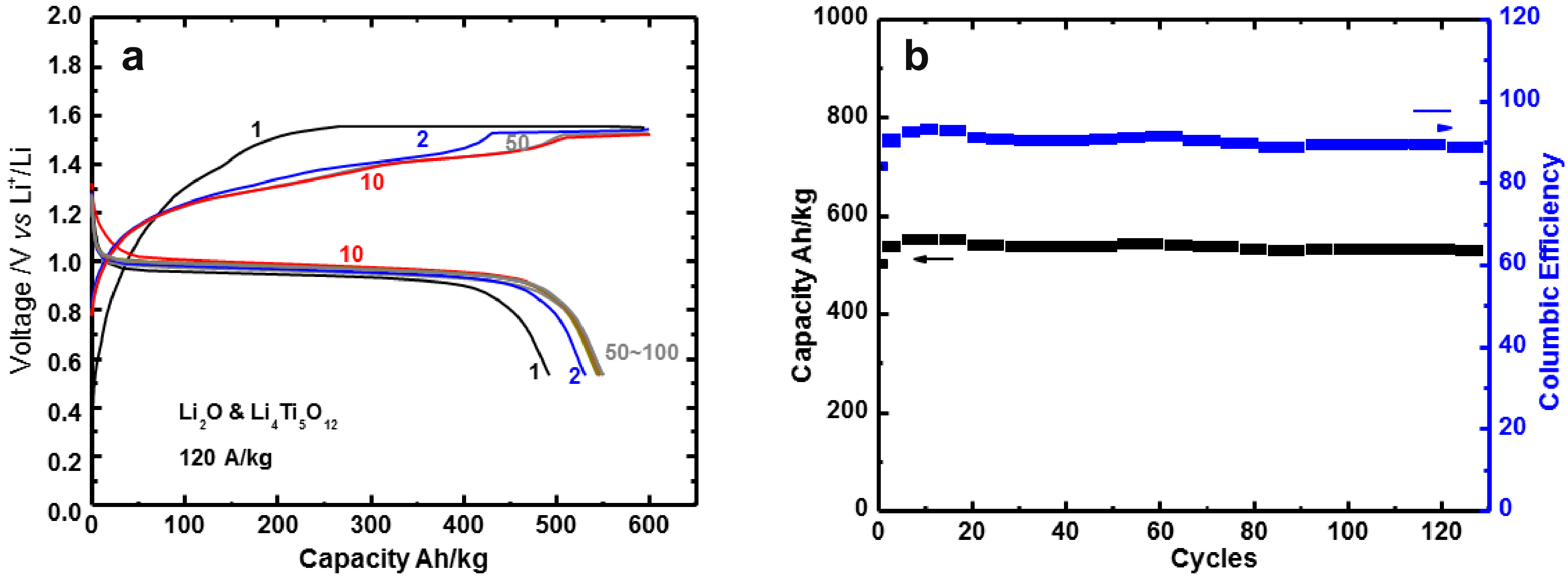
- Based on the NMR and ESR data, the deeply charged cathode electrode, contains an amorphous $Li_2O/Li_2O_2/LiO_2$ mixture stabilized by interfacial wetting.




Electron spin resonance (ESR) of the cathode before and after charge at 70 K.

# Electrochemical performance of a full-cell battery using an $Li_4Ti_5O_{12}$ anode

- **Full-cell capacity loss only 1.8% after 130 cycles**

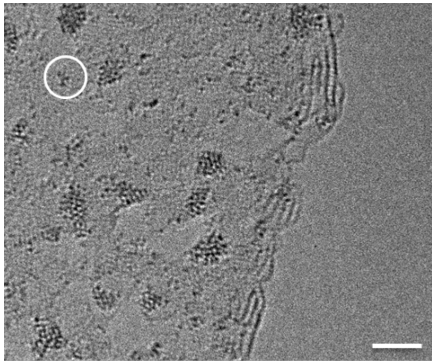



a, Charge/discharge curves b, cycling performance versus $Li_4Ti_5O_{12}$ anode, whose Li capacity is only 110% that of the NC-67 cathode capacity.

# Stabilizing Lithium superoxide using Ir nanoparticles catalyst: 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

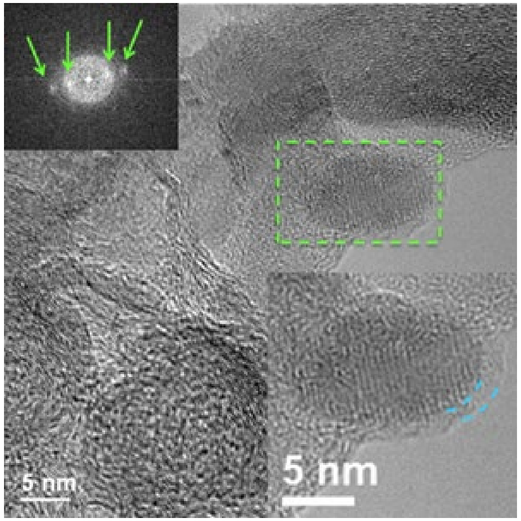
Cathode: Ir nanoparticles on rGO with a range of sizes that result in lithium superoxide as a discharge product

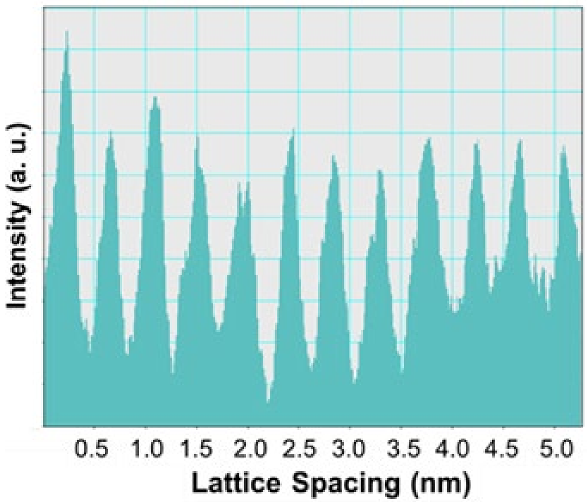


- **We have carried out follow-up studies of how the Ir nanoparticles become lithiated during discharge using Ir nanoparticles of size 1.5 nm**

# Lithium superoxide based Li-$O_2$ battery with a cathode based on 1.5 nm Ir clusters

- 1.5 nm nanoparticles give low charge potentials similar to our previous studies using a range of sizes
- Characterization showed the discharge product to be lithium superoxide
  - From DEMS, Raman, titration



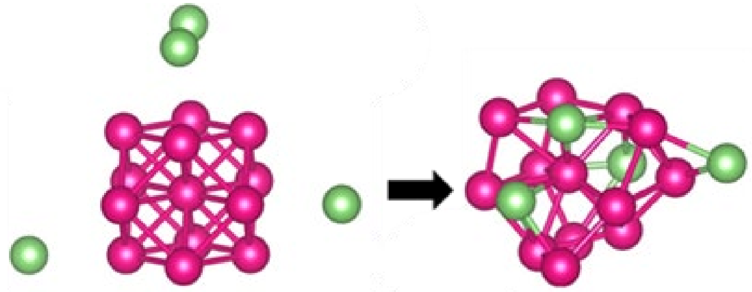




a) an individual ~5x10 nm particle formed after second discharge; the upper left inset shows a fast Fourier transform (FFT) on the nanoparticle surface with the diffraction peaks consistent with $Ir_3Li$; lower right inset shows a close up of the nanoparticle with a thin layer of ~1-2 nm marked by dashed cyan line on the surface of the nanoparticle, which may be due to the discharge product; b) the lattice spacing of ~4.1 Å for the nanoparticle in **(a)**, which is identical with that of $Ir_3Li$;.

- **TEM evidence shows that 1.5 nm Ir nanoparticles increasse in size to ~5-10 nm and Li becomes incorporated into the Ir to form $Ir_3Li$ that can act as a template for $LiO_2$ formation**

# Thermodynamics for Ir3Li formation from LiO2 and Ir

- The $Ir_3Li$ formation from interaction of $LiO_2$ and Ir was investigated computationally by two approaches



Ab initio MD simulation of a model cluster showing Li atoms (green) intercalating into a Ir cluster

***Formation energy for $LiO_2$ + 3Ir --> $Ir_3Li$ + $O_2$ -5.90 eV***

DFT energies of reactants indicate that the reaction of $LiO_2$(s) and Ir(s) is thermodynamically very favorable

- **The evidence indicates that the unstable nature of $LiO_2$, an initial discharge product, can react with Ir to form the $Ir_3Li$ intermetallic that generates the template for stabilization of further $LiO_2$ growth which will be used as cathode for the close system in the future**
  - **(LiO2 +Li -------Li2O2)**

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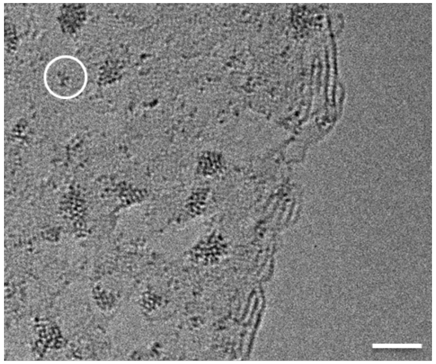

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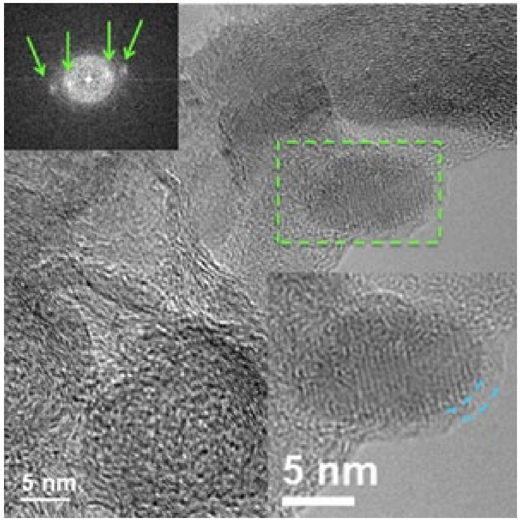


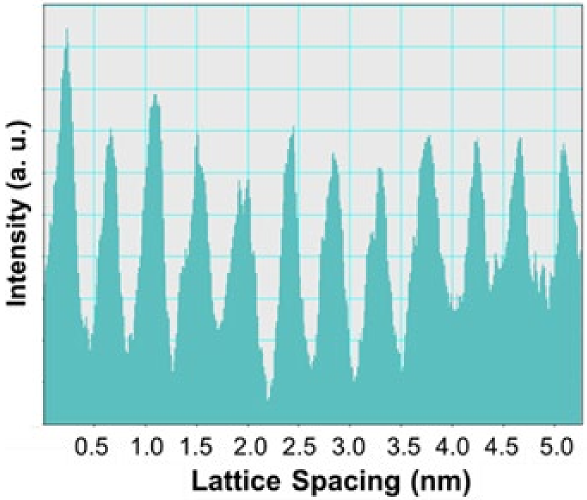


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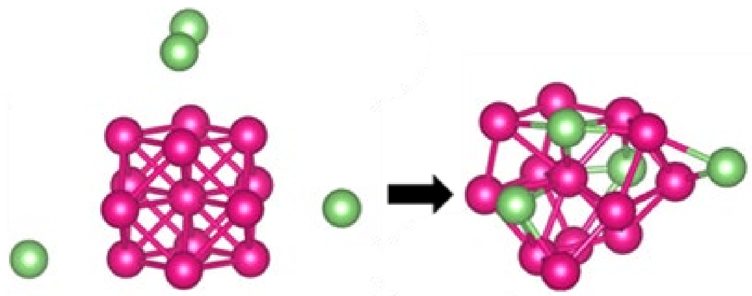

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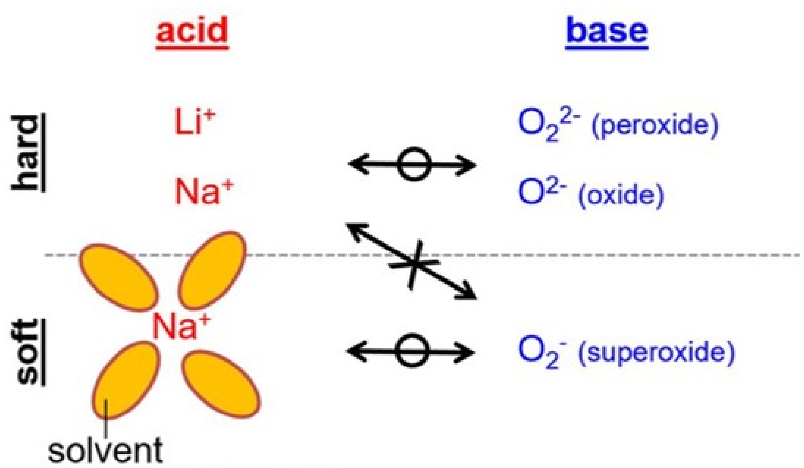
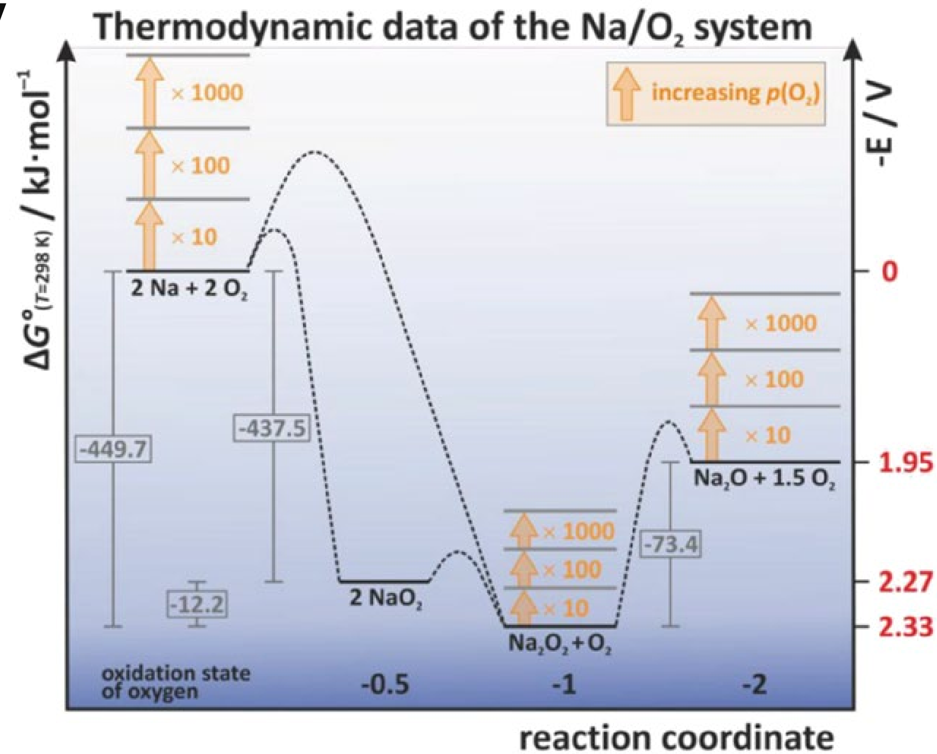
# Exploring novel $NaO_2$ based closed batteries

**Hard Soft Acids Bases (HSAB) Theory**




- HSAB theory predicts that the stability of $NaO_2$ is higher than $LiO_2$. $NaO_2$ could be a potential candidate for the close system.

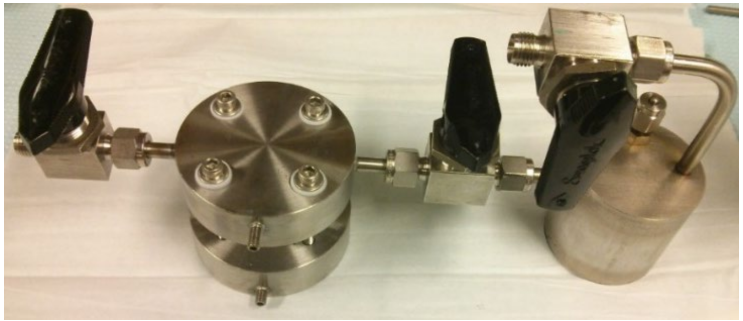
- The difference of 12.2 kJ $mol^{-1}$ between $NaO_2$ and $Na_2O_2$ indicates that it is possible to have both as the products in Na-$O_2$ batteries:

$Na + O_2 \leftrightarrow NaO_2$ ($E^0$=2.27 V, 1-electron transfer reaction)

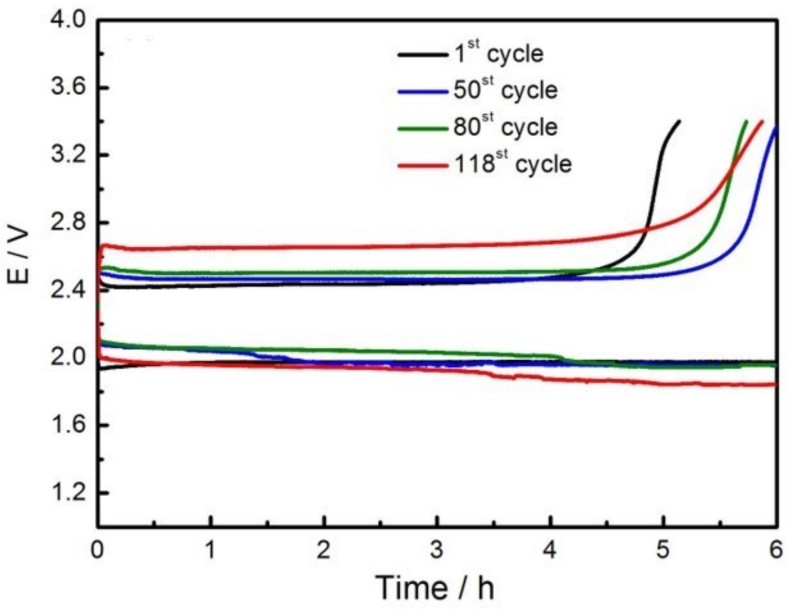
$2Na + O_2 \leftrightarrow Na_2O_2$ ($E^0$=2.33 V, 2-electron transfer reaction)

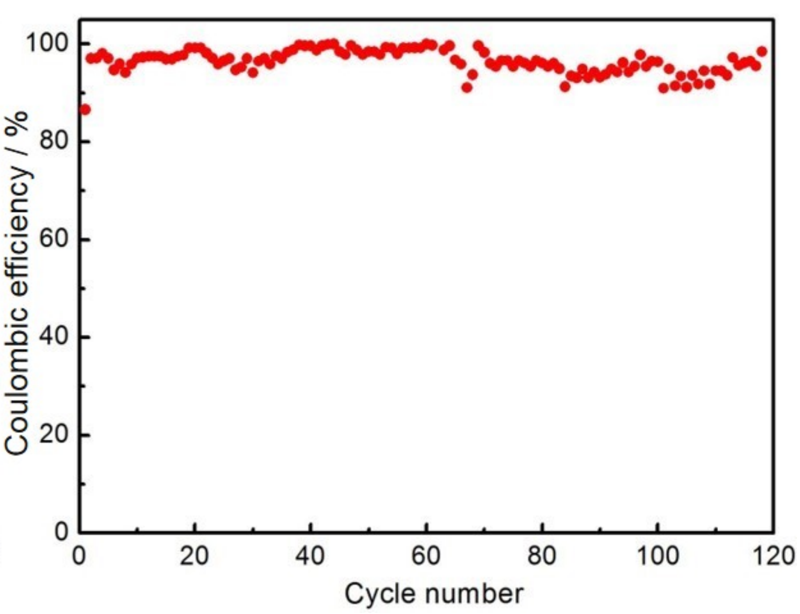
# Stabilizing $NaO_2$ in Na-oxygen batteries

**Stainless steel cell**



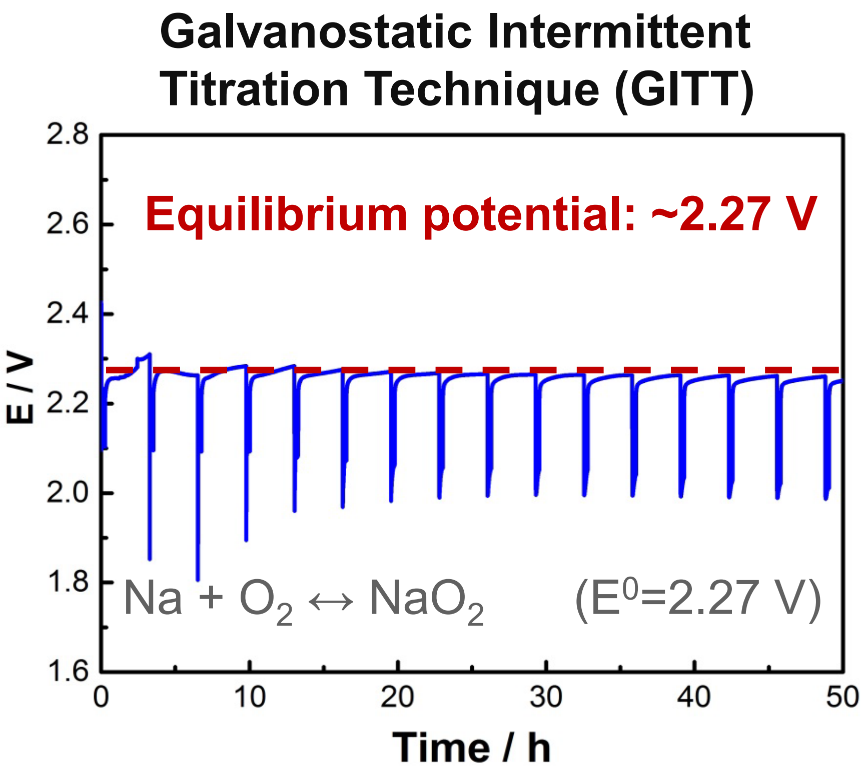
$Na\text{-}O_2$ cell assembly:
Anode-Na metal;
Cathode-porous carbon substrate and ultrahigh purity $O_2$;
Separator-glass fiber;
Electrolyte-1 M Na triflate in DEGDME.

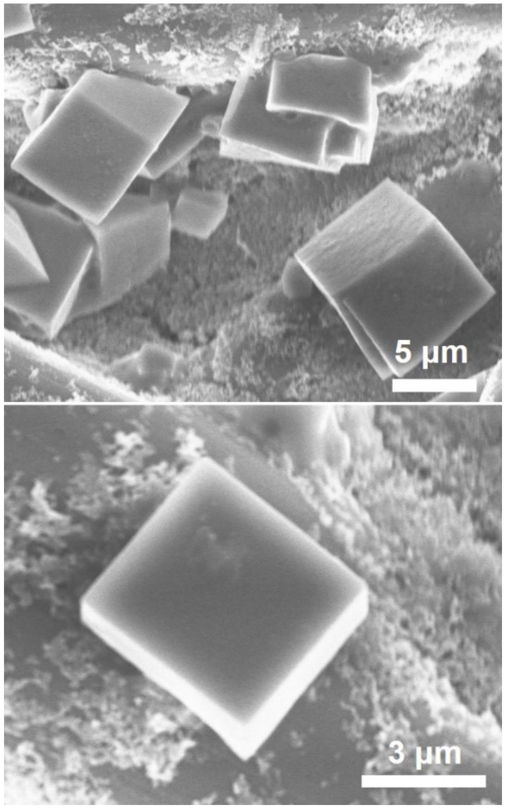



- The $Na\text{-}O_2$ battery shows a long cycle life of 118 cycles and it has a low charge overpotential.
- Coulombic efficiency of the $Na\text{-}O_2$ battery is mostly over 95%.

# Characterization of $NaO_2$ in Na-oxygen batteries

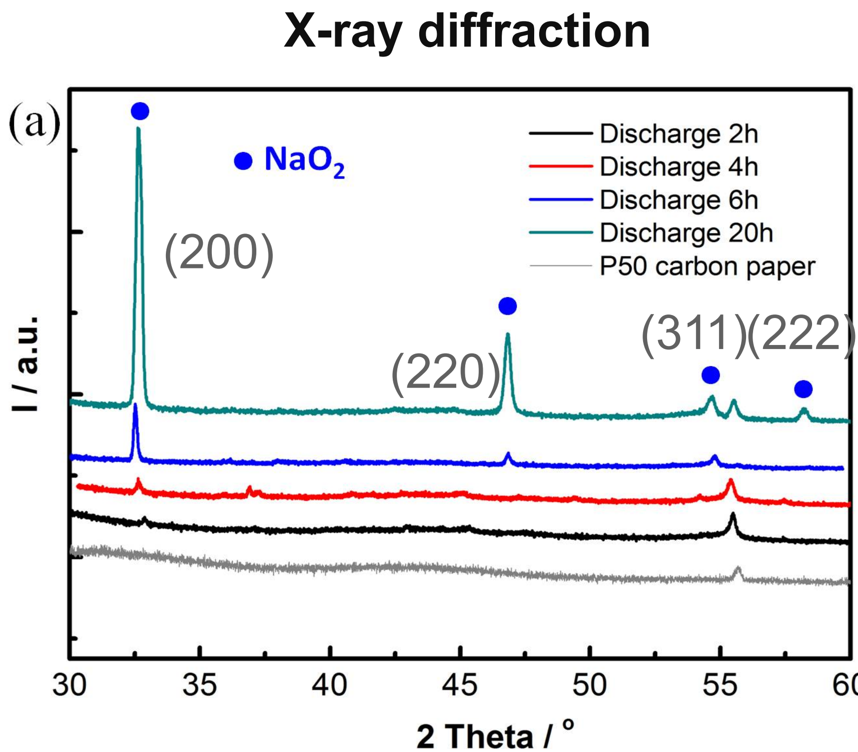


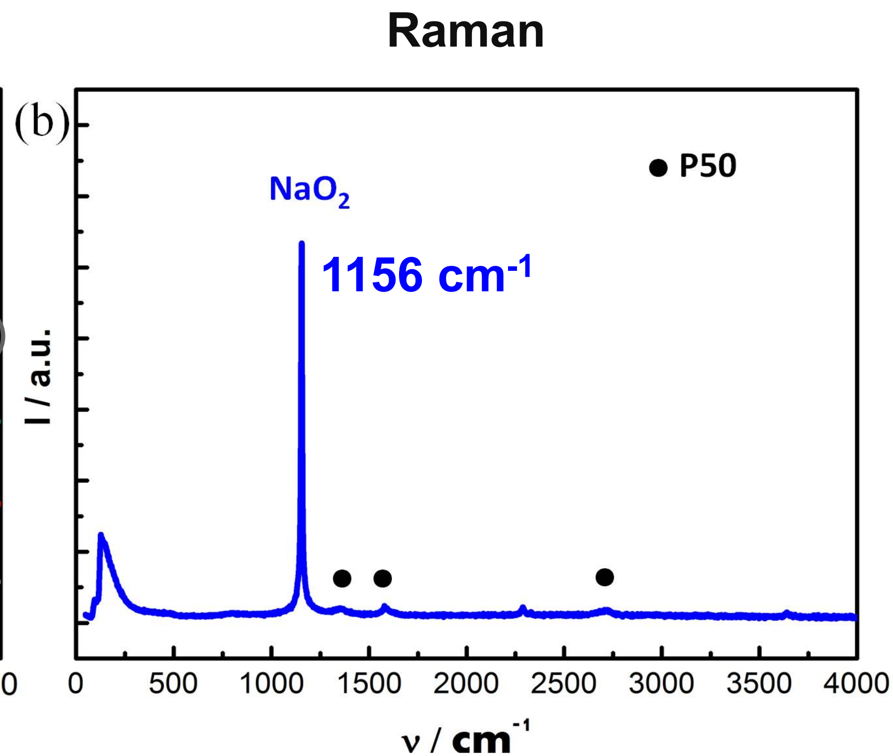




- GITT shows the equilibrium potential of the reaction in $Na-O_2$ battery is 2.27 V, which is consistent with the 1 electron transfer reaction of $NaO_2$ formation.

- SEM of the discharged air electrode shows the cubic morphology of the product, which is a typical structure of $NaO_2$.

# Characterization of $NaO_2$ in Na-oxygen batteries




- XRD and Raman show that $NaO_2$ is the sole discharge product. No other products are detected.
- We successfully achieve the 1 e transfer reaction:

$$\mathbf{Na + O_2 \leftrightarrow NaO_2}$$

# Na-$O_2$ Battery (Close System) - Next Step

**Since $NaO_2$ has been stabilized in Na-$O_2$ batteries, we will explore novel $NaO_2$ based closed batteries.**

| Discharge Product | Reaction | Delta G / KJ/mol | E° / V | z | Specific Capacity / mAh/g | Theor. energy density / Wh/kg |
|---|---|---|---|---|---|---|
| $NaO_2$ | $Na + O_2 \rightarrow NaO_2$ | -218.76 | 2.27 | 1 | 488.21 | 1108.22 |
| $Na_2O_2$ | $2Na + O_2 \rightarrow Na_2O_2$ | -449.72 | 2.33 | 2 | 689.00 | 1605.37 |
| $Na_2O$ | $2Na + ½\ O_2 \rightarrow Na_2O$ | -376.30 | 1.95 | 2 | 867.38 | 1691.38 |
| **$Na_2O_2$** | **$Na + NaO_2 \rightarrow Na_2O_2$** | **-230.96** | **2.39** | **1** | **344.69** | **823.83** |
| **$Na_2O$** | **$3Na + NaO_2 \rightarrow 2Na_2O$** | **-533.84** | **1.84** | **3** | **1297.26** | **2386.96** |
| **$Na_2O$** | **$2Na + Na_2O_2 \rightarrow 2Na_2O$** | **-302.88** | **1.57** | **2** | **864.84** | **1357.80** |

- High specific capacity and energy density.
- Can reach >500 Wh/kg on the cell level
- No $O_2$ involved in the reactions, avoid the crossover effect
- Use conventional Na-ion configuration

# Response to last year reviewer's comments

**No Comments from the Reviewers last year.**

# Collaborations with other institutions and companies

- J. Li, ANL
  - Development of new cathode materials based on $Co_3O_4$ as a substrate filled with $Li_2O$
- R. Shahbazian-Yassa, UIC
  - Characterization of discharge products and cathode materials
- J. G Wen, ANL
  - TEM characterization of discharge products and catalysts
- L. Hu, UM
  - Development of catalyst for Li-air batteries.
- S. Meng, UCSD
  - Development of new cathode materials based on $MoS_2$.
- Y. Wu, OSU
  - Stabilization of $NaO_2$ in Na-$O_2$ batteries.

# Summary

I. Anion-redox cathode in lithium ion battery

- Nanoporous substrate $Co_3O_4$ filled with $Li_2O$ served as a cathode in lithium closed battery.
- Nanoporous substrate $Co_3O_4$ worked as a skeleton to promote the stable cycle between $Li_2O$, $Li_2O_2$ and $LiO_2$ without releasing/taking $O_2$ gas.

II. Lithium superoxide ($LiO_2$) stabilization

- Ir clusters with suitable particle size were found to be able to stabilize the $LiO_2$ in Li-$O_2$ battery using various characterization techniques.
- Mechanism of stabilization was elucidated.

III. Stabilization of $NaO_2$ in Na-$O_2$ batteries

- $NaO_2$ was successfully stabilized in a well-sealed Na-$O_2$ battery.
- Stabilized NaO2 will be used as cathode for the close system ($NaO_2$+Na-----$Na_2O_2$)

# Proposed Future Work

- **Systematic studies of electrolytes in superoxide based batteries**
  - Effect on composition, cycle life, and efficiency
  - Computational studies to understand results
  - Design new electrolytes for optimal performance
- **Conversion reaction between $NaO_2$ and $Na_2O_2$**
  - Realizing the conversion reactions between $NaO_2$/$Na_2O_2$/$Na_2O$ in sodium ion battery
  - Optimizing the electrodes to improve the efficiency and cycle life
- **Potassium superoxide cathodes for Li-ion cells**
  - Investigating the feasibility of $KO_2$ cathodes for lithium closed cells
  - Optimizing size and loading of $KO_2$ to improve efficiency, capacity, and cycle life

Any proposed future work is subjected to change based on funding level