Lithium-Oxygen Battery Design and Predictions

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DOE merit review

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Project ID# BAT-420

Overview

Timeline

- Start: 2018
- Finish: 2021
- 40 %

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: $ 1350 K
  - Contractor 0
- FY 19: $ 500 K
- FY 20: $ 350 K
- FY 21: $ 500 K

Partners

- Interactions/ collaborations
  - B. Narayanan, University of Louisville
  - F. Khalili-Araghi, UIC
  - J. G. Wen, ANL
  - Robert Klie, UIC

Project Objectives and Relevance

- The objective of this work is to advance Li-O_2 battery concepts that operate in an air environment with long cycle life and high efficiency through novel design and predictions.
- A major goal of this work is to enable operation in an air environment and thus increase volumetric energy density needed for practical applications of Li-O_2 batteries
- The focus is on discovery of new combinations of electrolytes and additives that can promote the cathode functionality of 2-dimensional transition metal dichalogenide (TMDC) catalysts that have high activity for oxygen reduction and evolution.
- Li-O_2 batteries are considered a potential alternative to Li-ion batteries for transportation applications due to their high theoretical specific energy
- In this project we will also explore other new concepts for batteries operating on chemical transformations principles that can have practical applications.

FY20 Milestones

Month/ Year	Milestones
Dec/19	Investigate various salt combinations for $Li\text{-}O_2$ electrolytes for both lithium anode protection and low charge potentials for the performance of $Li\text{-}O_2$ batteries with use of computations to provide understanding. Q1 (**Completed**)
Mar/20	Investigate bromine-based redox mediators by experiment and theory for comparison with iodine-based redox mediators with MoS_2 cathode materials. Q2 (**Completed**)
Jun/20	Develop method for screening of additive and electrolytes by experiment and theory to develop a database of properties and performance data for optimizing $Li\text{-}O_2$ batteries by machine learning. Q3 (**Initiated**)
Sep/20	Investigate electrolytes and cathodes that can greatly increase $Li\text{-}O_2$ coin cell capacities compared to current capacities through optimization of oxygen reduction reactions. Q4 (**Initiated**)

Strategy

- The strategy is to use cathode materials based on 2-dimensional transition metal dichalcogenides (TMDCs) that we have found to be among the best oxygen reduction and evolution catalysts[*] and have shown exceptional performance in Li-O_2 electrochemistry.
- These cathode materials will be the basis of our strategy to carry out systematic studies of electrolyte blends and additives that will reduce charge potentials and enable long cycle life.
- In the initial stages we will focus on establishing this strategy for an O_2 atmosphere and then extend to a realistic air atmosphere.
- The strategy will use integrated experimental/theoretical investigation to develop an understanding of the complex reaction mechanisms.
- We will also utilize a high throughput screening strategy based on experiment and theory to develop a large database of properties and outcomes of electrolyte combinations that can be analyzed using artificial intelligence to predict electrolytes and additives that will have the best performance.

[*] Salehi-Khojin, Curtiss, et al Adv.Mater.2019, 31, 1804453

Experimental and computational methods

Synthesis of cathode materials

Chemical Vapor Transport method for the synthesis of bulk cathode materials; liquid phase exfoliation technique to produce nanostructured cathode materials

Characterization and Testing

DLS, AFM, TEM imaging, EDXXPS, Raman, XRD, SEM, DEMS imaging, impedance measurements, cyclic voltammetry (CV), high throughput screening, charge-discharge cycling experiments in Swagelok systems

Computation

Density functional theory (DFT), ab initio molecular dynamics (AIMD), classical molecular dynamics (CMD), periodic and cluster calculations, high throughput screening, machine learning and artificial intelligence for optimizing electrolyte/catalyst synergies and CMD potential development

Accomplishments

Two bifunctional additives found that give good performance for Li-O_2 battery operation in a dry air atmosphere

- InI_3, $InBr_3$ additives are both found to reduce charge potentials and have long cycle life with InI_3 having a smaller polarization gap and $InBr_3$ having a longer cycle life

Experiment and theory provide evidence how the In halide additives can act both redox mediators and react with Li anode surface to form a protective SEI layer

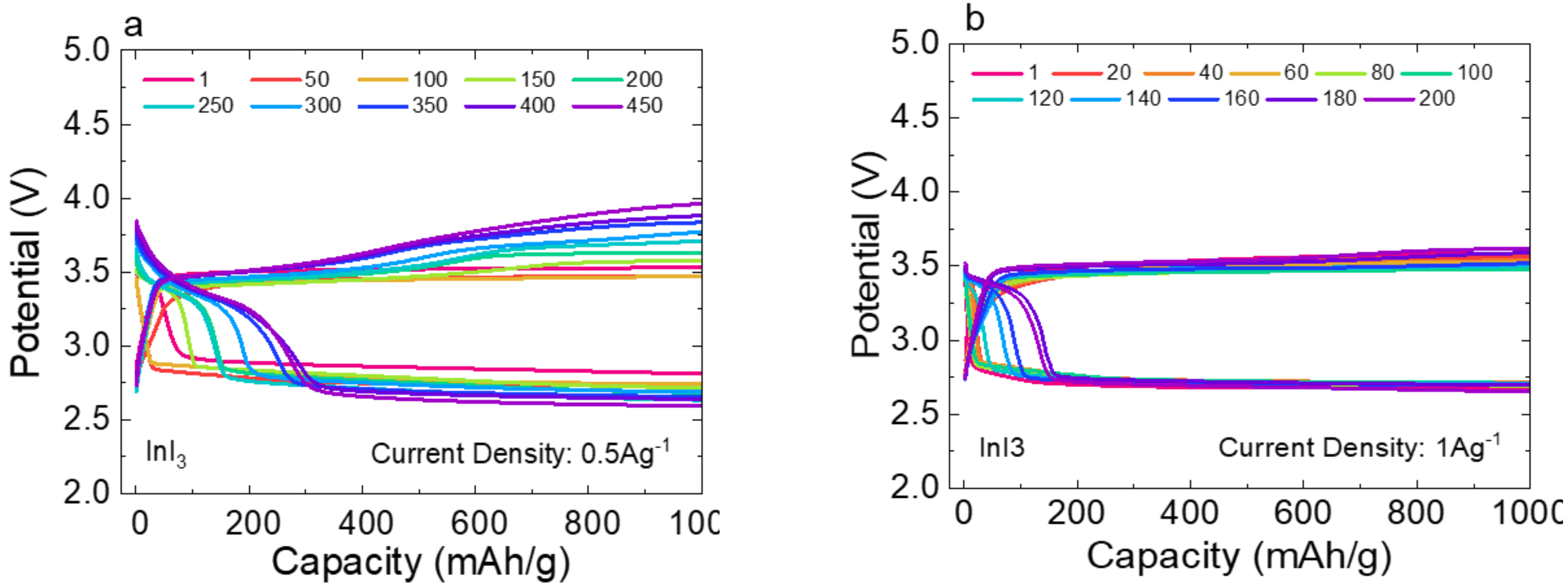
- TEM studies show the presence of a InI alloy on the Li surface
- Density functional calculations help understand the formation of the protective SEI layer and the redox mediator mechanisms

New more stable cathode TMDC materials have been synthesized and tested in Li-O_2 batteries and will be used in future studies of bifunctional additives

Systematic studies of redox mediator properties have been carried out and analyzed for finding new and improved additives

Accomplishment: Two bifunctional additives (InI_3 and $InBr_3$) found that give good performance for Li-O_2 battery operation in a dry air atmosphere

Discharge/Charge voltage profiles for InI_3. (a) 25mM InI_3 and current density of 0.5 Ag^{-1} (b) 25mM InI_3 and current density of 1 Ag^{-1}

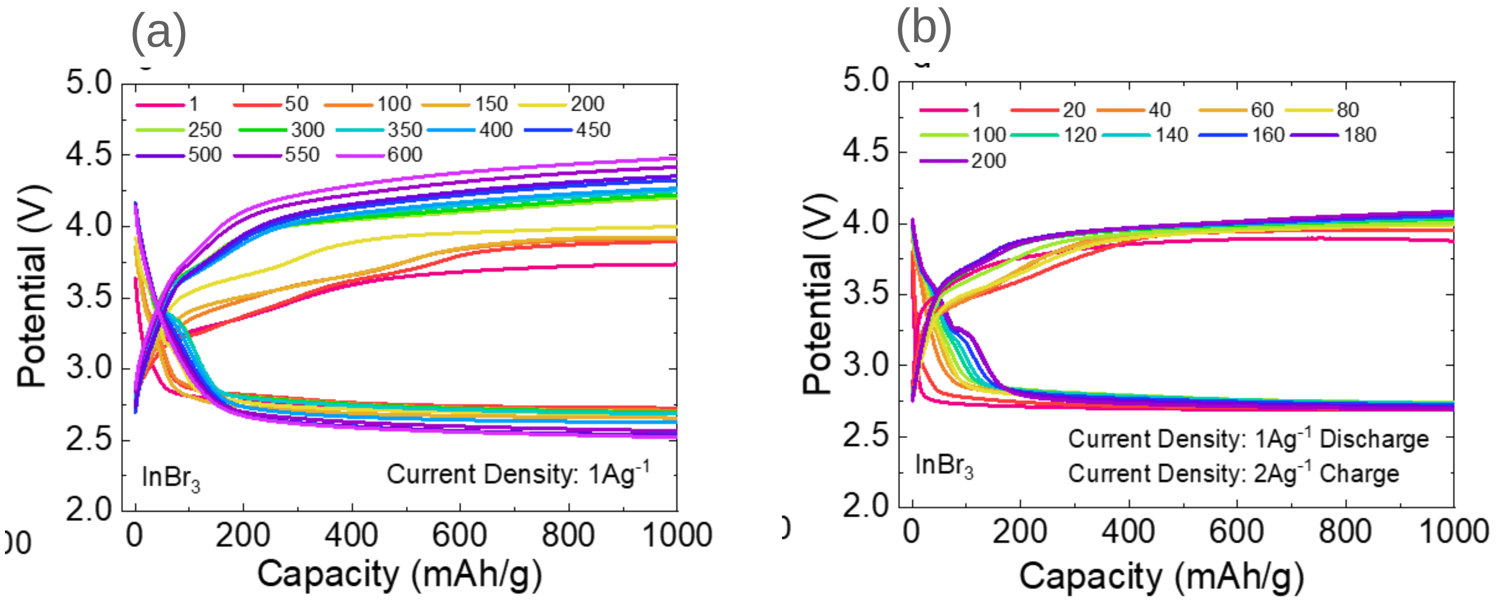


The cell configuration was based on a molybdenum disulfide cathode in a hybrid electrolyte of 10% ionic liquid (EMIM BF_4) and 90% DMSO and 0.1 M LiTFSI. The additives are noted above. The results are for a dry atmosphere.

- **These results indicate that an InI_3 additive can lower the charge potentials compared to without the additive (where the charge potential is >4 V) as well as maintain good cycle life in a dry atmosphere.**
- The InI_3 has a polarization gap of ~0.7 V (b in Figure) with a discharge current densities of 1 A/g and can run for 200 cycles before failing due to the discharge voltage decreasing

Accomplishment: Two bifunctional additives (InI_3 and $InBr_3$) found that give good performance for Li-O_2 battery operation in a dry air atmosphere

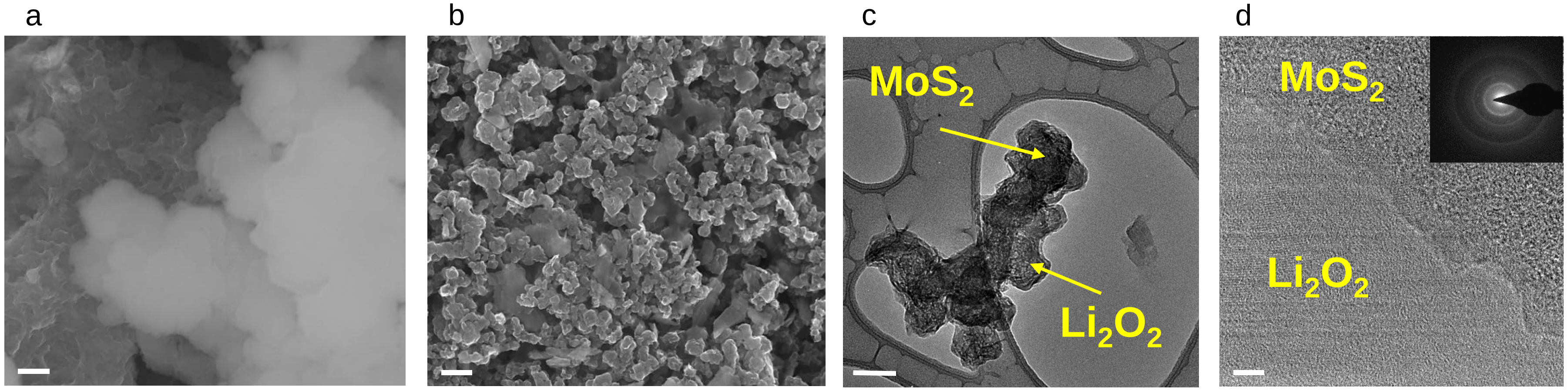
Voltage profiles for $InBr_3$. (a) 25mM $InBr_3$ and current density of 1 A g^{-1} (b) 25mM $InBr_3$ and current densities of 1 Ag^{-1} discharging 2 Ag^{-1} charging.



The cell configuration was the same as InI_3: based on a molybdenum disulfide cathode in a hybrid electrolyte of 10% ionic liquid (EMIM BF_4) and 90% DMSO and 0.1 M LiTFSI. The additives amounts are noted above. The results are for a dry atmosphere.

- **These results indicate that a $InBr_3$ additive can also lower the charge potentials compared to without the additive as well as maintain good cycle life in a dry atmosphere.**
- The $InBr_3$ has a polarization gap of ~1 V (b in Figure) compared to ~0.7 V for InI_3 for the same discharge current densities of 1 A/g.
- However, the $InBr_3$ additive enables a Li-O_2 cell with long life of ~600 cycles at charge/discharge current densities of 1 A g-1 (a in Figure) before failure at which point the charge potential has increased to ~4.4 V.

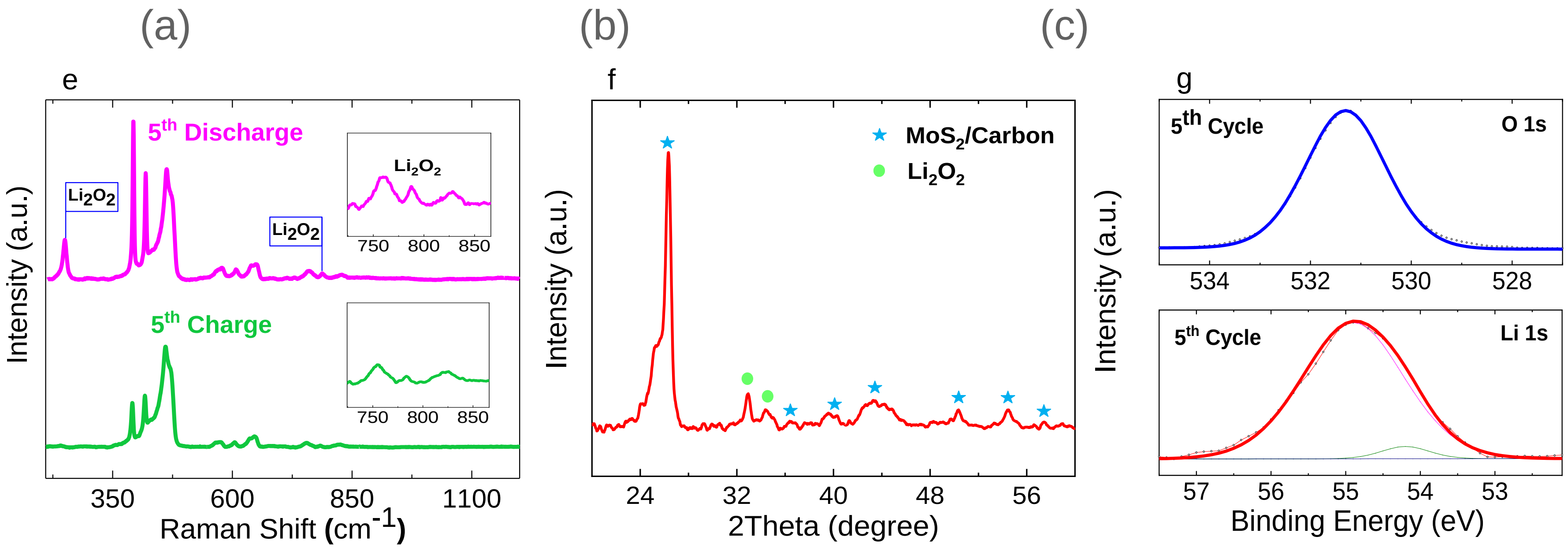
Characterization of discharge products from use of the bifunctional additive InI_3 that gives good performance for $Li-O_2$ battery operation in a dry air atmosphere



Characterization of cathode in InI_3 based system at the rate of 1A/g.
(a, b) SEM images of cathode surface after the 5th discharge and charge cycle, respectively (Scale bars: 200 nm).
(c, d) Low and high resolution TEM images of discharged cathode showing crystalline Li2O2 deposited on MoS2 cathode (Scale bars: 100 and 10 nm, respectively). Inset shows the electron diffraction pattern showing surfaces of polycrystalline Li2O2 and (1,1,1) and (0,0,2) MoS2 surfaces.

- **These characterization results based on TEM confirm the formation of Li_2O2 on a MoS_2 based cathode during discharge**

Characterization of discharge products from use of the bifunctional additives InI_3 that gives good performance for $Li\text{-}O_2$ battery operation in a dry air atmosphere



Characterization of cathode in InI_3 based system at the rate of 1A/g.

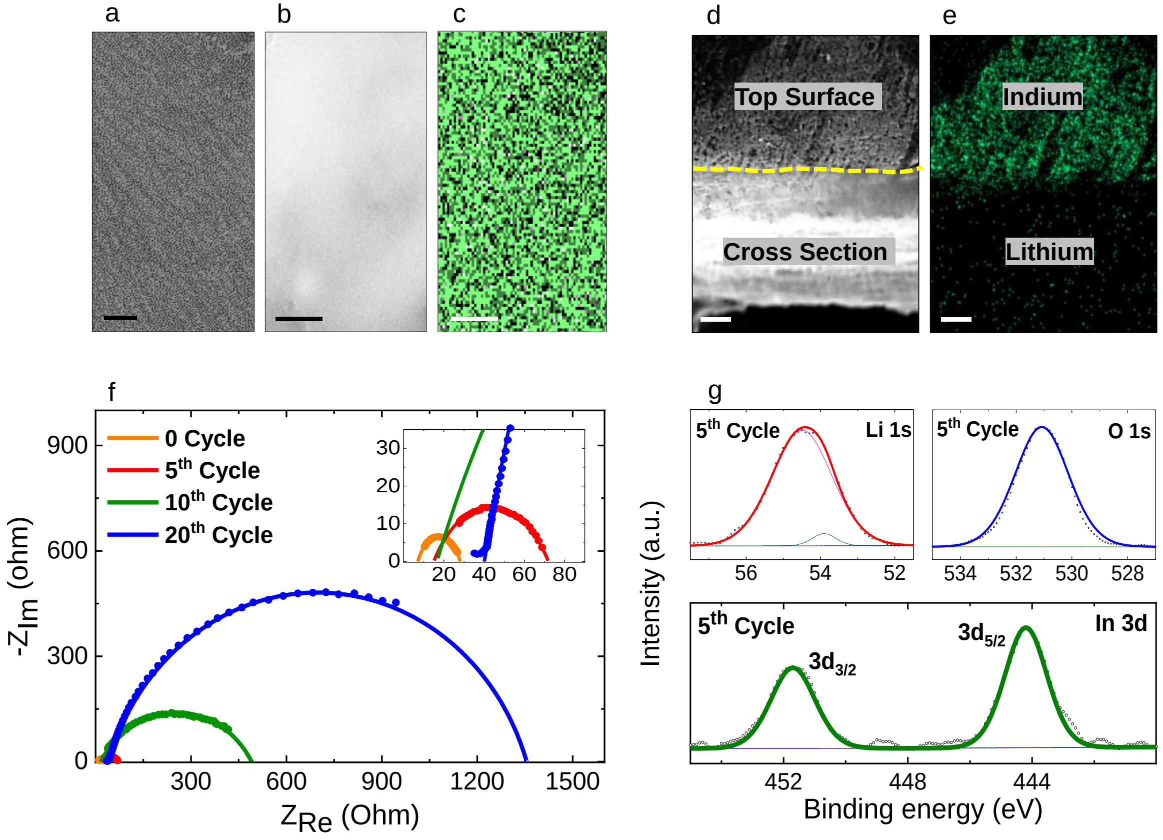
(e) Raman spectroscopy of the cathode after 5th discharge and charge cycle.

(f) X-ray diffraction pattern of the cathode after 5th discharge.

(g) XPS of the cathode including O 1s and Li 1s regions after the 5th discharge.

- **These characterization results based on XRD, and XPS additionally confirm the formation of Li_2O_2 during discharge; Raman confirms formation of Li_2O_2 during discharge and loss of Li_2O_2 after charge**

Characterization of the Li anode after running the cell with the LiI$_3$ additive



(a) Top-view SEM image of fresh anode (Scale bar: 500nm).

(b) Top-view SEM image of anode after the 5th discharge (Scale bar: 500nm).

(c) Top-view SEM-EDX composition mapping of anode for Indium element (Scale bar: 500nm).

(d) Cross-sectional SEM image of anode after the 5th discharge (Scale bar: 10µm).

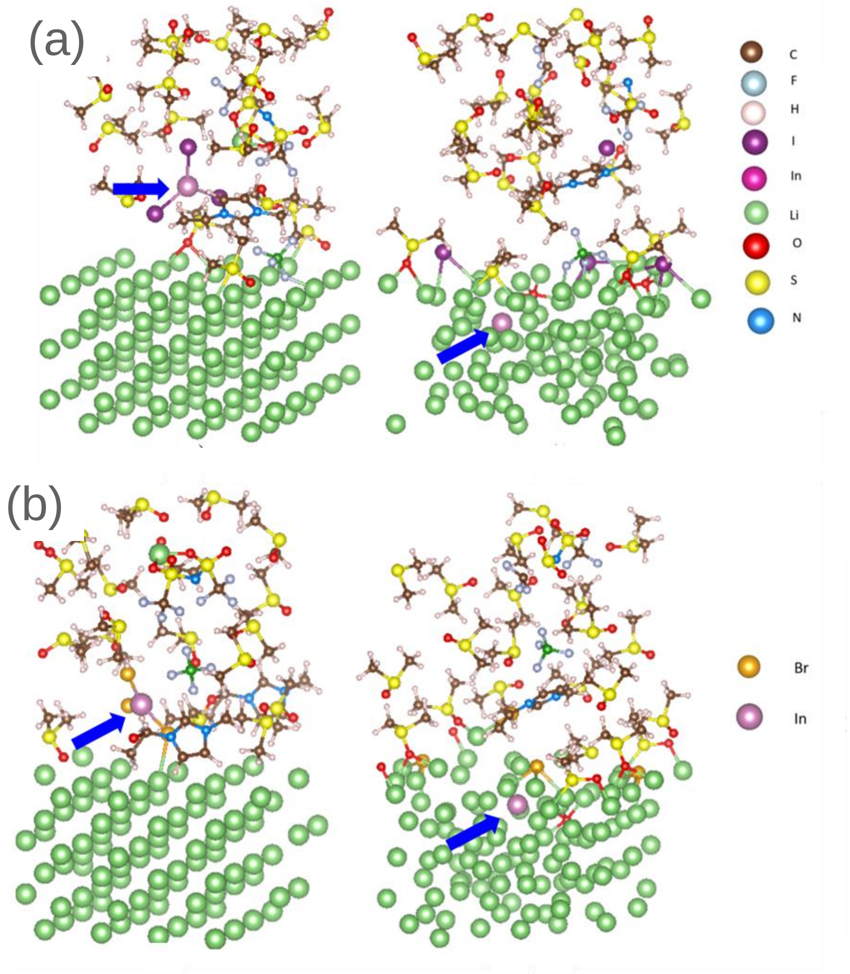
(e) Cross-sectional SEM-EDX composition mapping of anode after the 5th discharge for Indium (green) element showing it present in surface, but not in the interior. (Scale bar: 10µm).

(f) EIS measurements and fitted data for fresh and cycled anode surface. The dots represent the experimental data and lines represent the fitted data.

(g) XPS results of Li anode including O 1s and Li 1s regions after the 5th discharge and indium 3d after the 5th discharge.

- **Characterization (SEM-EDX, XPS) results show that that In has been incorporated into the top surface of the lithium anode**
- The SEM-EDX maps indicates ~26 wt% indium is present in the lithium surface region; XPS shows evidence of In in the anode.

Density functional studies of the reaction of InI_3 and $InBr_3$ with a Li surface



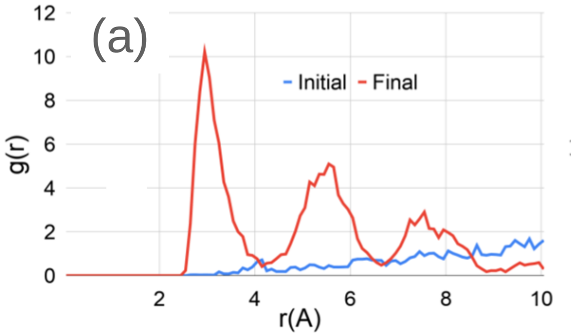
AIMD simulation of Li(100) interface with DMSO/IL electrolyte with a InX_3 molecule added to the electrolyte.

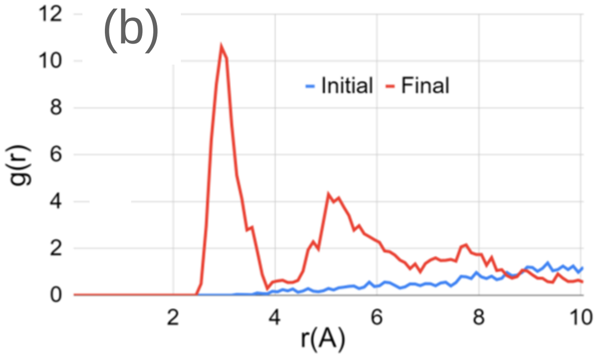
(a) initial (left) and optimized (right) structures for InI_3, arrow indicates the initial and final position of In atom;

(b) initial (left) and optimized (right) structures for $InBr_3$, arrow indicates the initial and final position of In atom;

- **Ab initio molecular dynamics (AIMD) simulations show that the InI_3 and $InBr_3$ will react with a Li surface with In adding to the surface and the I (or Br) reacting with the Li surface to form LiI (or LiBr) moieties on the surface**

Density functional studies of the reaction of LiI_3 with a Li surface



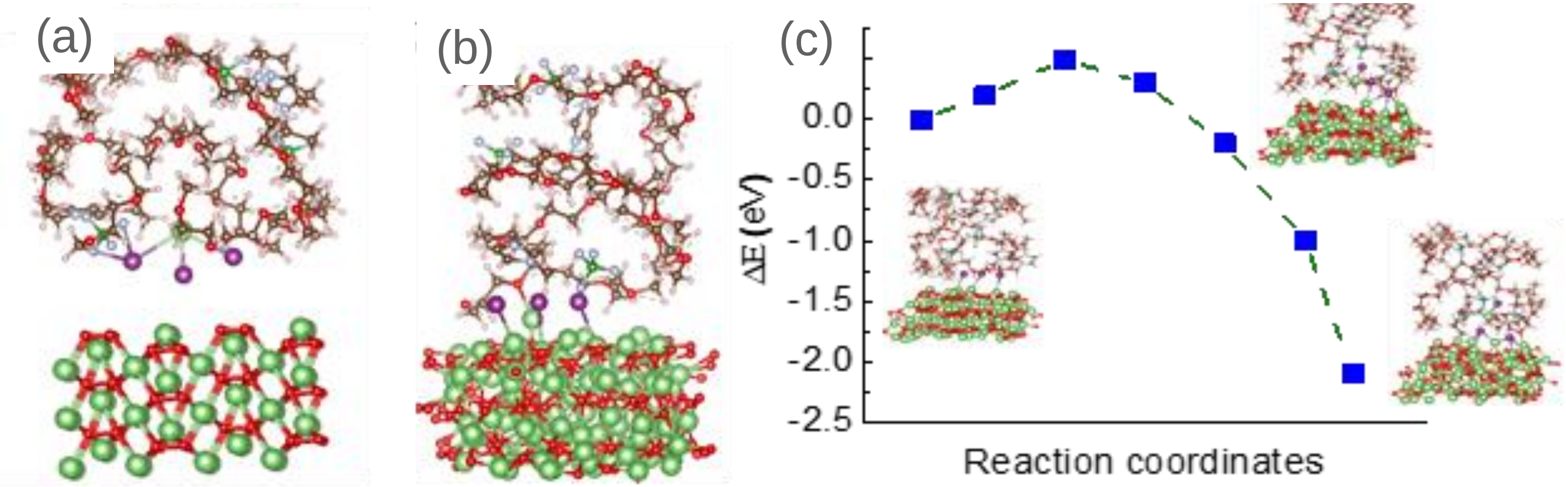


Calculation of pair distribution functions from the AIMD simulation of Li(100) interface with DMSO/IL electrolyte with a InX_3 molecule added to the electrolyte.

(a) pair distribution function g(r) for In atoms with respect to Li atoms from the surface for InI_3, final results (red color) indicate that In atoms are in Li;
(b) pair distribution function g(r) for In atoms with respect to Li atoms from the surface for $InBr_3$; final results (red color) indicate that In atoms are in Li.

- **Pair distribution functions show that as a result of the reaction of InX_3 with the Li surface the In atoms are incorporated into the Li surface.**

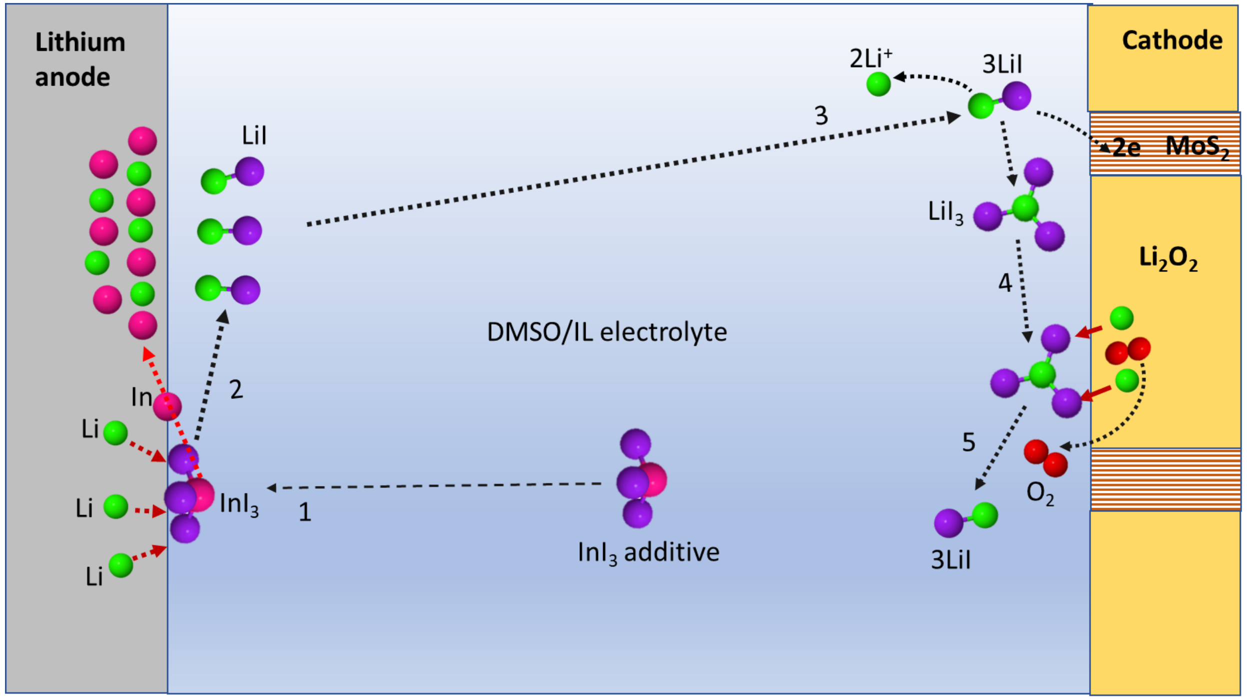
DFT studies of the LiI_3 decomposing Li_2O_2. The LiI_3 results from oxidation of LiI ($3LiI \rightarrow LiI_3 + 2Li^+ + e^-$) with the LiI coming from reaction of InI_3 with the Li surface



(a) initial structure of an AIMD simulation of electrolyte on a Li_2O_2 surface with an redox mediator, LiI_3
(b) optimized structure of electrolyte on a Li_2O_2 surface with a redox mediator, LiI_3, in the electrolyte,
(c) energy barrier obtained for removal of one LiI unit from interface in (e)

- **The DFT studies show that the barrier for removing one LiI from the Li_2O_2 surface is ~0.5 eV. This is the main step required for decomposition of Li_2O_2 by the redox mediator and confirms this type mechanism.**

Experiment and theory provide evidence how the In halide additives can act both redox mediators and react with Li anode surface to form a protective SEI layer

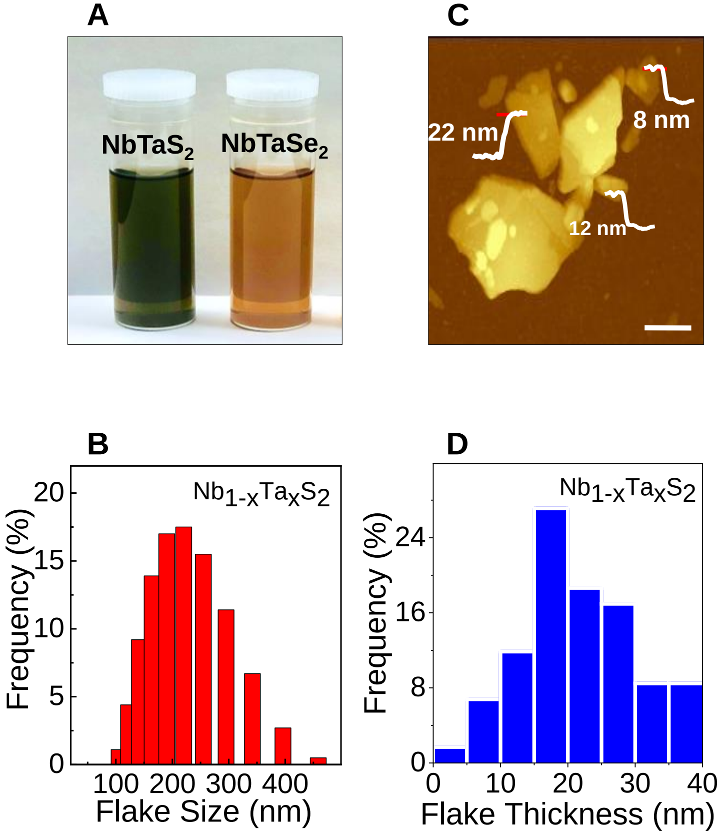


Lithium surface layer formation

Oxidation/Li_2O_2 decomposition

- **This schematic shows how the InI_3 additive functions in a Li-air battery: (1) reaction of InI_3 on lithium surface, (2) formation of the In surface protection layer and generation of LiI, (3) oxidation of LiI resulting in LiI_3, (4) decomposition of Li_2O_2 on the cathode surface by LiI_3, (5) regeneration of LiI**

Accomplishment: New quasi-binary TMDC alloys have been successfully synthesized and exfoliated into 2D structures providing for new Li-O_2 battery cathode catalysts



A) Dispersions of exfoliated nanoflakes of $Nb_{1-x}Ta_xS_2$ and $Nb_{1-x}Ta_xSe_2$ in isopropyl alcohol solvent.

B) Size distribution of synthesized $Nb_{1-x}Ta_xS_2$ alloy obtained by dynamic light scattering (DLS) measurements.

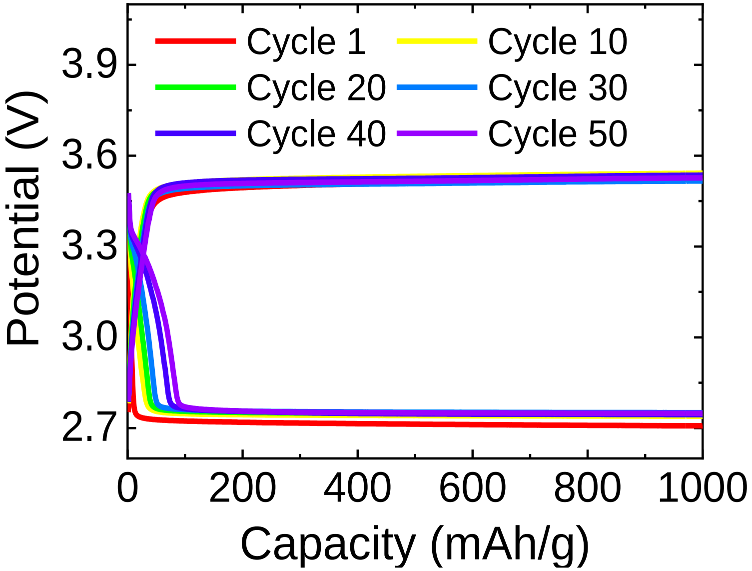
C) Typical AFM image of individual liquid-exfoliated flakes with the heights of 8 and 22 nm (Scale bar is 200 nm).

D) Frequency distribution of flake thickness obtained by AFM measurements on ~50 randomly selected exfoliated flakes.

- **These new quasi-binary TMDC 2D materials have excellent stability and will provide a large new exploration space for Li-O_2 batteries. A demonstration of their use in a Li-O_2 battery is shown in the next slide.**

One of the new quasi-binary TMDC alloys was tested in a Li-O_2 battery with a redox mediator and gave excellent performance.

Discharge-charge voltage profile for 50 cycles operation of Li-O_2 battery.



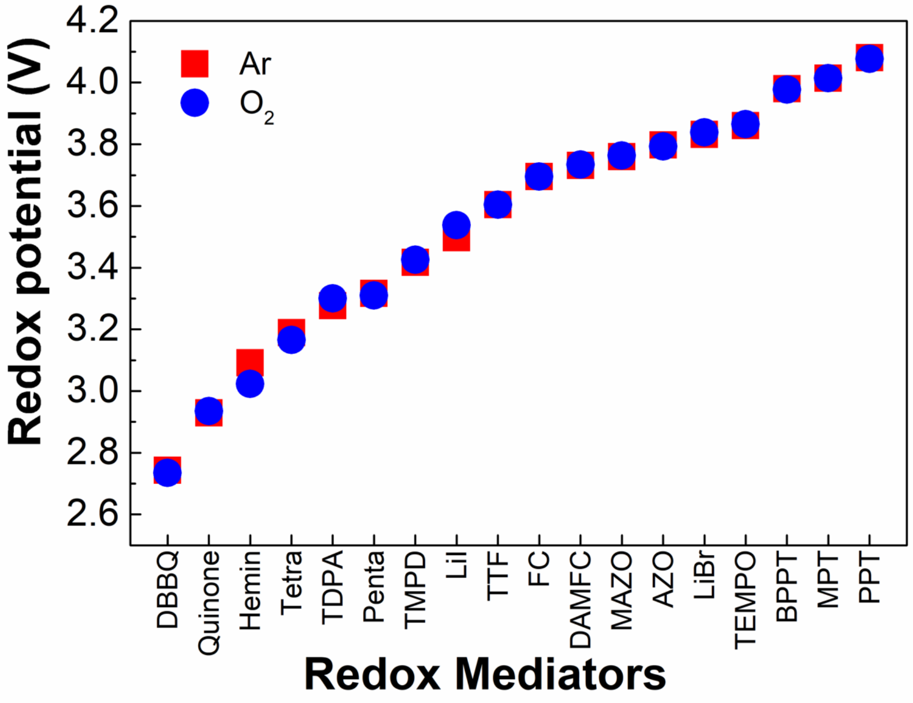
Cathode is based on $Nb_{1-x}Ta_xS_2$ nanoflakes coated on gas diffusion layer as the cathode.

The electrolyte consists of 0.1 M Lithium Bis (Trifluoromethanesulfonyl) Imide (LiTFSI) as lithium salt and 0.025 M Indium Iodide (InI_3) as a redox mediator in dimethyl sulfoxide (DMSO) solvent.

The battery was operated in a dry air environment at a fixed capacity of 1000 mAh/g with a 1000 mA/g rate.

- **The first discharge and charge curves are at ~2.7V and 3.5V, respectively. Throughout the 50 cycles of this battery's operation, there is no change in charge potential while surprisingly, the discharge curve gets closer to ~2.8V and approaches the equilibrium voltage (2.96 V)**
- This indicates an efficient reduction and evolution of oxygen corresponding to the formation and decomposition of Li_2O_2 products .

Accomplishment: Systematic studies of redox mediator properties have been carried out and analyzed for finding new and improved additives



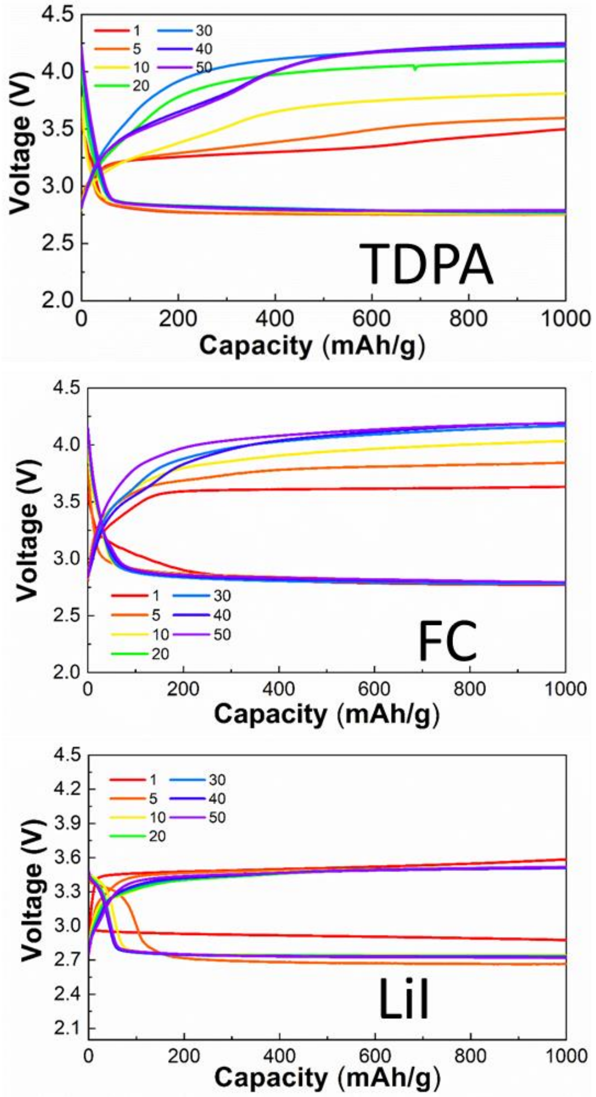
DBBQ: 2,5-di-tert-butyl-1,4-benzoquinone
Quinone: p-Benzoquinone
Hemin: Chloro(protoporphyrinato)iron(III)
Tetra: 5,10,15,20-Tetraphenyl-21H,23H-porphine iron(III) chloride
TDPA: tris[4-(diethylamino)phenyl]amine)
Penta: 5,10,15,20-Tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III) chloride
TMPD: tetramethyl-p-phenylenediamine
LiI: Lithium iodide
TTF: Tetrathiafulvalene
FC: Ferrocene
DAMFC: (Dimethylaminomethyl)ferrocene
MAZO: 1-methyl-2-azaadamantane-N-oxyl
AZO: 2-azaadamantane-N-oxyl
LiBr: Lithium Bromide
TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy
BPPT: 10-(4-biphenylyl)phenothiazine
MPT: 10-Methylphenothiazine
PPT: 10-isopropylphenothiazine

Redox potentials (vs Li^+/Li) of redox mediators measured from CV experiments in DMSO solvent.

- We have studied twenty four redox mediators in terms of their chemical characteristics such as redox potential with DMSO and TEGDME electrolytes. We also collected data on the separation of catholic and anodic peaks and intensities of the peaks, which correlates with reversibility and electron transfer rates.
- Nine of the best RMs were selected based on comparison of results from the CV studies. Galvanostatic cycling tests on these nine RMs (FC, LiI, TMPD, DAMFC, LiBr, Quinone, TTF, TDPA, DBBQ) were performed in Li-O_2 batteries – some results and conclusions are given in the next slide.

Systematic studies of redox mediator properties have been carried out and analyzed for finding new and improved additives

Voltage profile of three selected redox mediators (LiI, FC, and TDPA) measured in DMSO with MoS_2 as a catalysts.



- The results for all nine show that halides such as LiI and LiBr exhibit much better performance compared with the organic based on the charge potentials.
- The organic ones and transition metal complexes tend to have increasing charge potentials with number of cycles such as shown in the figure for TDPA and FC.
- The poorer results for the organic ones may be due to the reaction with singlet O_2, which may be present charge. DFT studies that were carried out confirmed this

Proposed Future Work

- Based on our successes in the past year, we will develop Li-O_2 batteries that can operate in a realistic air atmosphere with a low charge potential and a long cycle life.
- Two complementary strategies will be used.
  - The first will be systematic studies of new bifunctional additives to find ones that protect the Li anode, are stable, and enable easy decomposition of the discharge product.
  - The second will be a high throughput screening strategy based on experiment and theory to develop a large database of properties and outcomes of electrolyte combinations that can be analyzed using artificial intelligence to predict electrolytes and additives that will have the best performance.
- In addition, to low charge potentials and long cycle life we will also extend the studies to obtain larger capacities to enable large energy densities as well as higher charge rates

Remaining Challenges and Barriers

- The major challenge remains the discovery of electrolytes that work in combination with transition metal dichalgonide catalysts that can operate effectively in an air environment with high charge rates and higher capacities
- A second major challenge is to assess and optimize the Li-O2 lab scale batteries to be able to have practical applications outside the lab, which will be a future goal for this work.

Collaborations with other institutions and companies

- Robert Klie (UIC)
  - TEM studies of SEI of Li anodes and discharge product on cathodes
- J. G. Wen (ANL)
  - TEM studies of SEI of Li anodes and discharge product on cathodes
- Badri Narayanan (University of Louisville)
  - Machine learning for potentials for classical MD simulations
- F. Khalili-Araghi, UIC
  - Classical molecular dynamics simulations of bulk electrolytes
- Philip Yu, UIC
  - Artificial intelligence for Li-O2 batteries

Summary

Two bifunctional additives found that give good performance for Li-O_2 battery operation in a dry air atmosphere

- InI_3, $InBr_3$ additives are both found to reduce charge potentials and have long cycle life with InI3 having a smaller polarization gap and InBr3 having a longer cycle life

Experiment and theory provide evidence how the In halide additives can act both redox mediators and react with Li anode surface to form a protective SEI layer

- TEM studies show the presence of a InI alloy
- Density functional calculations help understand the formation of the protective SEI layer and the redox mediator mechanisms

New more active cathode TMDC materials have been synthesized and tested in Li-O2 batteries and will be used in future studies of bifunctional additives

Systematic studies of redox mediator properties have been carried out and analyzed for finding new and improved additives