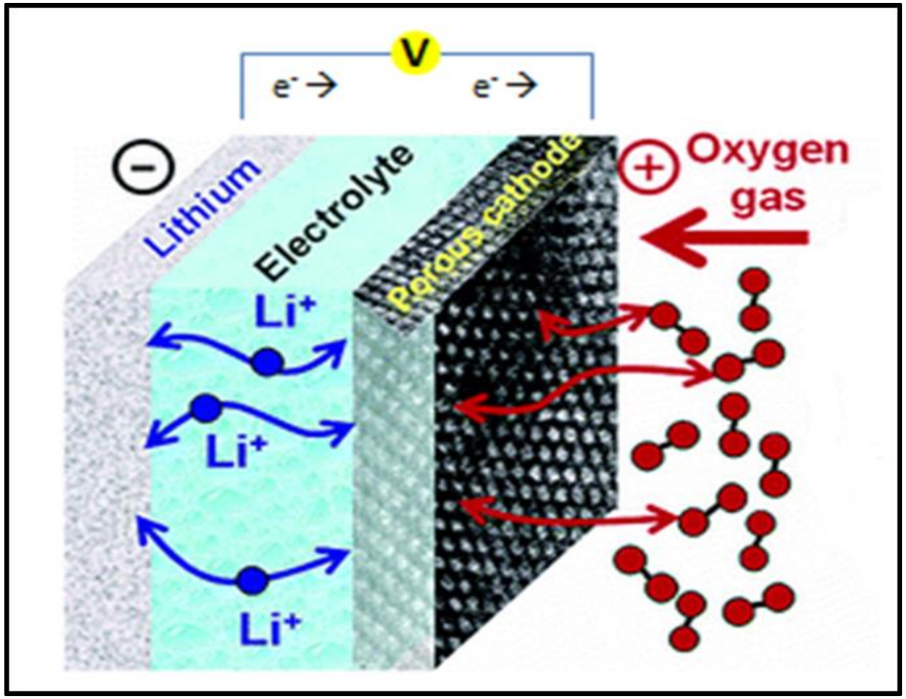
# Integrated Computational-Experimental Development of Lithium-Air Batteries for Electric Aircraft

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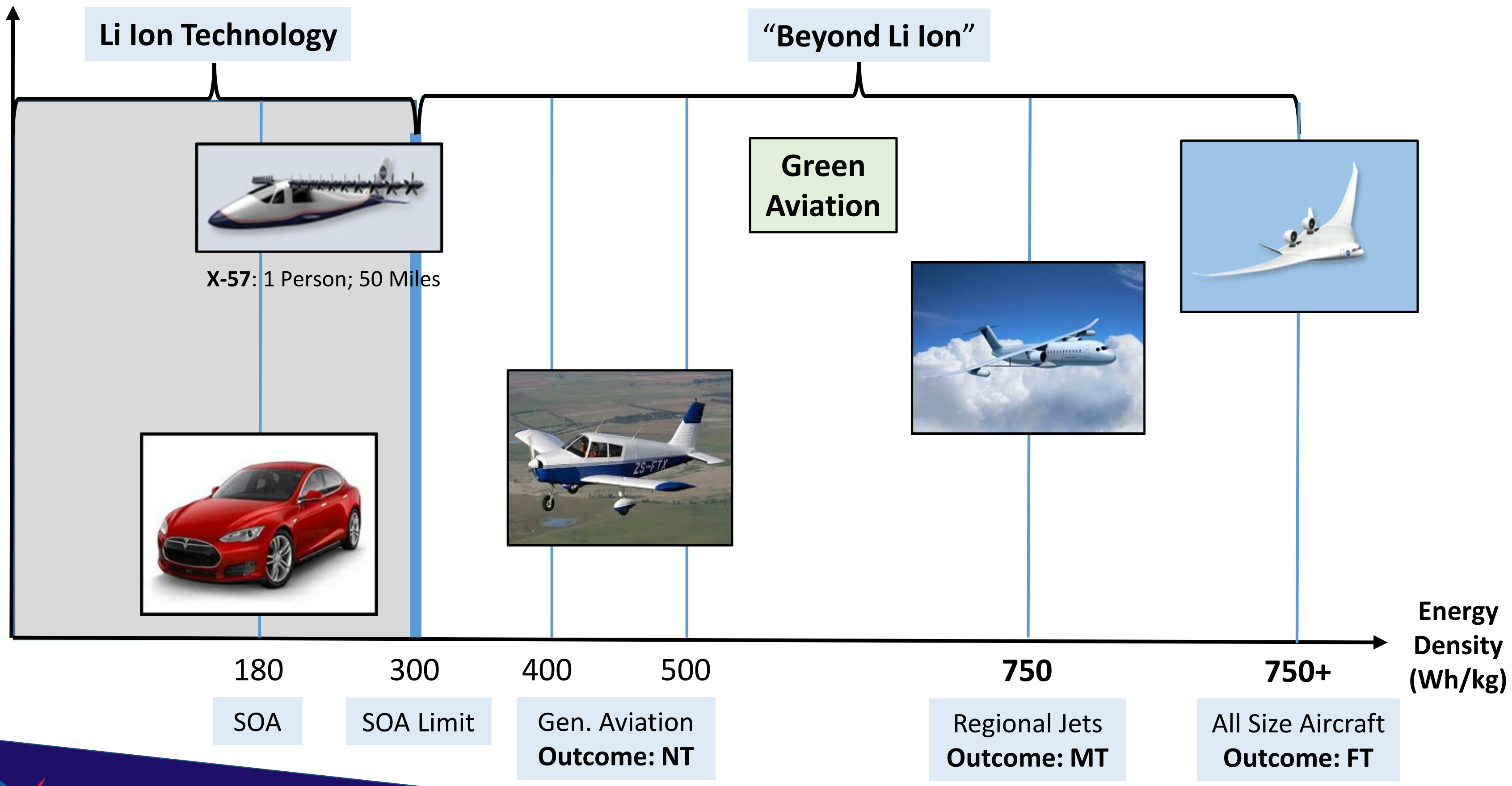
**External Partners**: NASA Armstrong, UC Berkeley, Stanford, Carnegie-Mellon, IBM Almaden

# Green Aviation Battery Requirements

## Major requirement is: High Energy Density

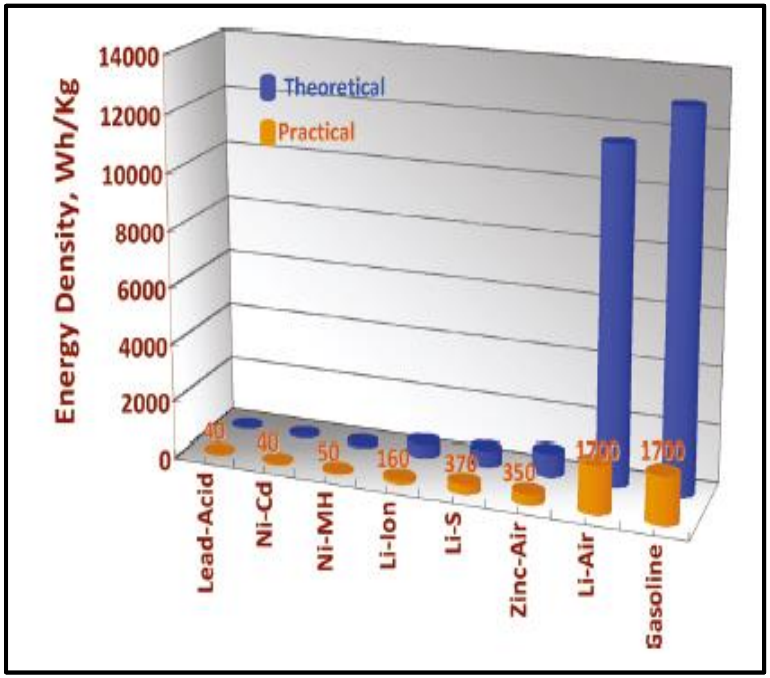
Other requirements are **rechargeable**, **safety**, power, recharge time, cost, etc.



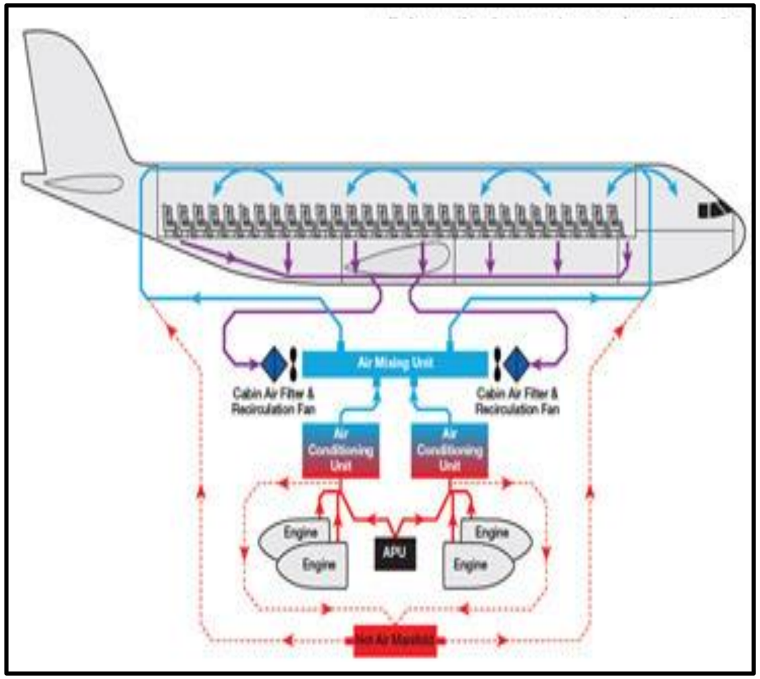
# Big Question

*Can we design and build a viable battery which satisfies the significant requirements of electric aircraft applications?*

## Li-Air batteries are a unique fit for electric aircraft applications

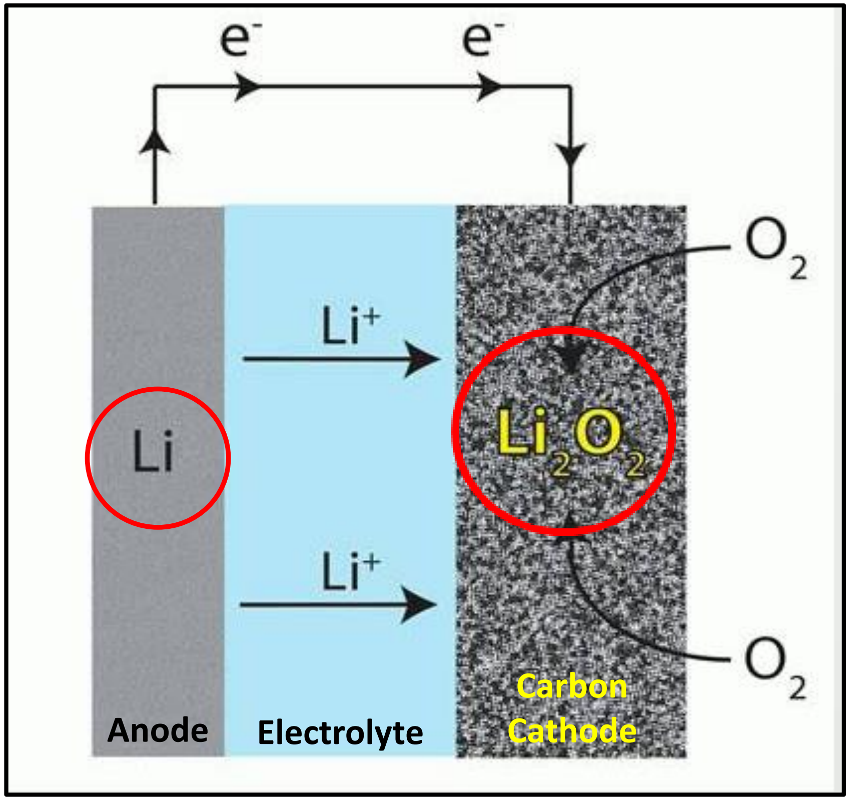



Li-Air has the highest theoretical battery energy density




Aircraft already have on-board oxygen systems needed for Li-Air batteries that can be leveraged for further **mass reduction**

# Major Li-Air Challenge




$Li_2O_2$ and Li are Hyper-Reactive

**Component decomposition is the limiting factor for Li-Air batteries**

# Feasibility Objective

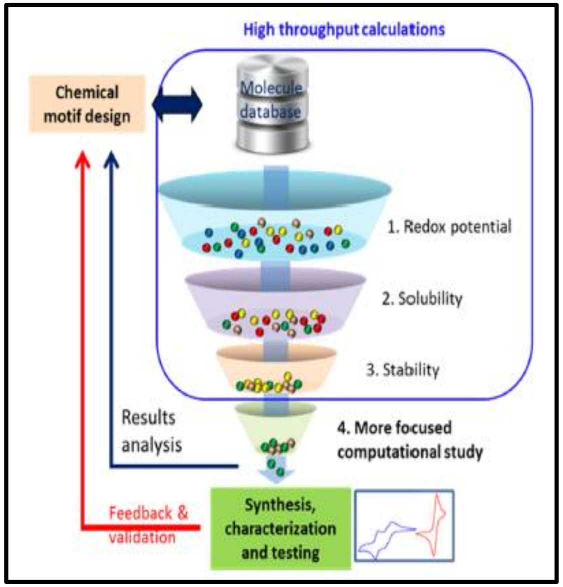
Design and fabricate *new stable components* for Li-Air batteries that achieve energy densities of 400+ Wh/kg and 100+ recharges and test them in an electric aircraft (UAV) flight

# I. Computation

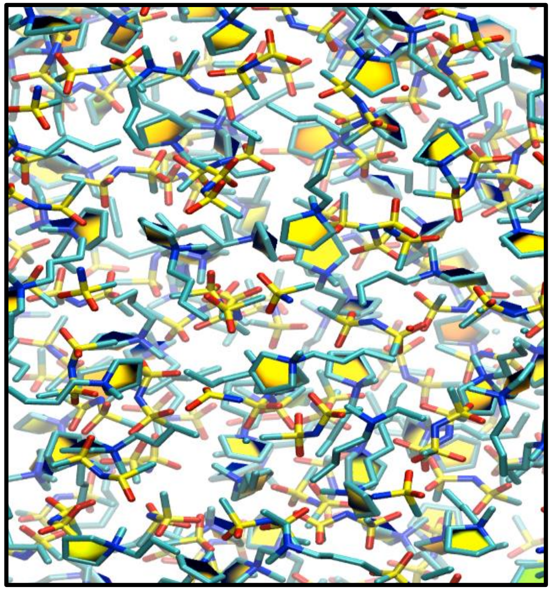
SOA Li-Air research uses highly empirical "trial-and-error" approach

**We are using predictive modeling at multiple scales leveraging NASA supercomputing to accelerate development**

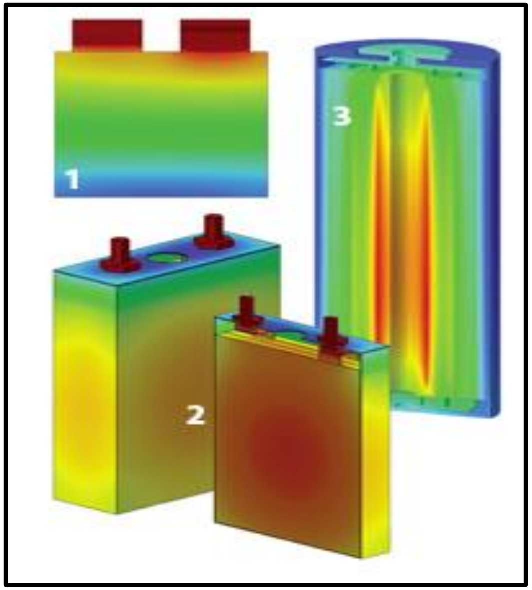
NASA Vision 2040 for Integrated Multiscale Materials and Systems Modeling and Simulations




High-throughput screening (ARC, CMU)



Materials simulations (ARC)




Multiphysics analysis (ARC, Purdue)

# II. New Materials

SOA Li-Air research uses commercial '*off-the-shelf*' materials (inadequate) for electrolytes

**We design, fabricate and integrate into Li-Air batteries new stable electrolytes tailored for this reactive environment**

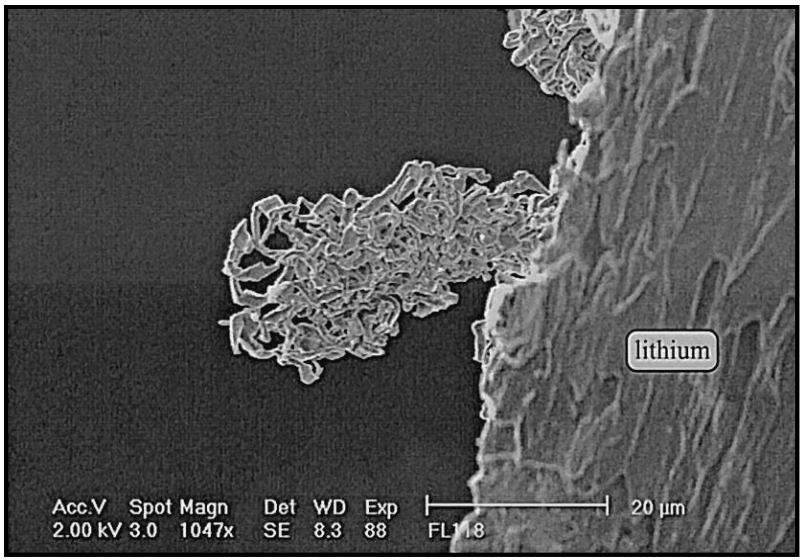
Advanced fabrication (GRC, Berkeley, IBM)

Unique characterization facilities (Berkeley, Stanford)

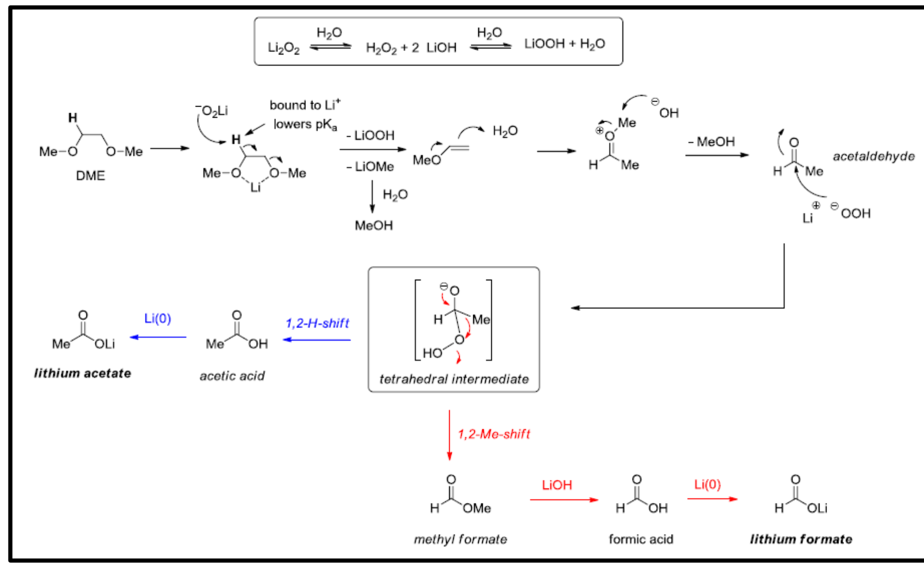
# III. Decomposition Mechanisms

SOA Li-Air research has very poor understanding of electrolyte decomposition mechanisms

We are coupling computational chemistry with experimentation to discover "***electrolyte design rules***"




Experimental analysis (GRC, IBM)




Chemical mechanistic pathways (ARC, IBM)

# IV. Electric Flight Test and Analysis

SOA Li-Air research confined to academic, laboratory studies

**We are modeling the system requirements, instrument, fly and analyze data from an electric flight test (UVA) with Li-Air batteries**

Electric flight systems modeling, instrumentation, flight and analysis (AFRC)

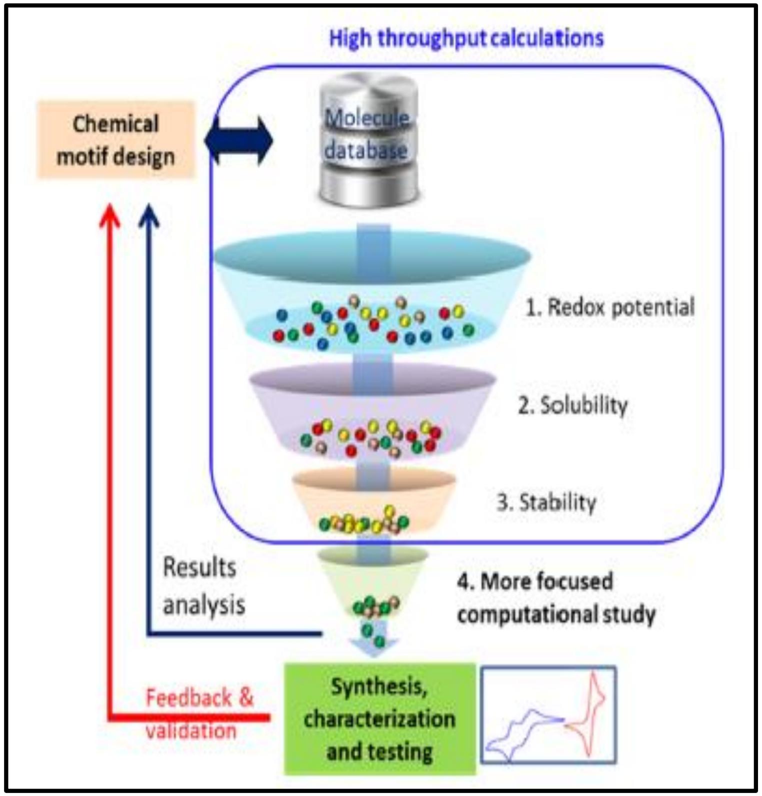
# Electrolyte Data Mining & Machine Learning

**Electrolyte Properties:**

Ionization potential, electron affinity
Boiling point, flash point, viscosity
Solvation energies
Acid dissociation constant $pK_a$

**"Descriptors" for Data Mining:**

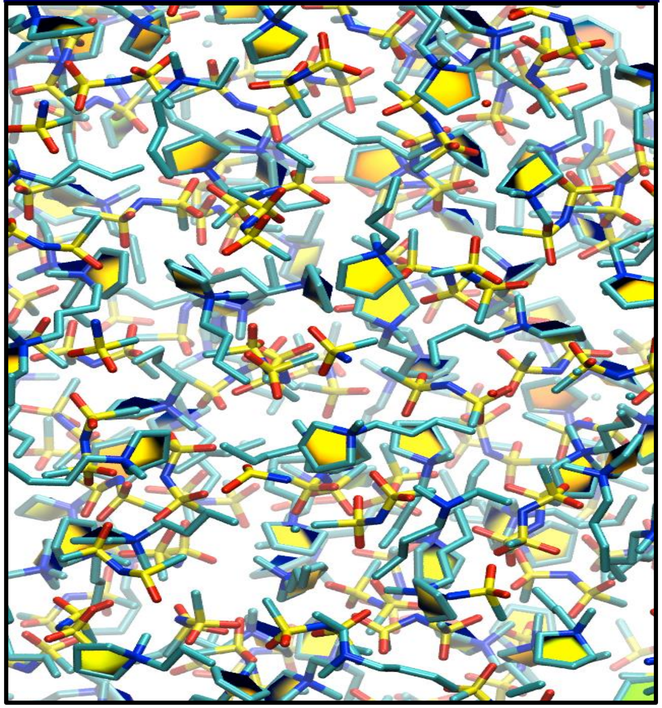
Boiling point >= 323 K
Flash point >= 323 K
Ionization potential <= -10.5 eV [ DME ~ -10.3]
Acid dissociation constant $pK_a$ => 30 [ ACN ~ 30]
$E_{sol}(Li^+)$ <= 10.0 kcal/mol [ACN ~ 12]
$E_{sol}(O_2)$ <= -1.8 kcal/mol [DME ~ -1.65]




**Databases with 10 million entries mined for Li-Air electrolyte properties**

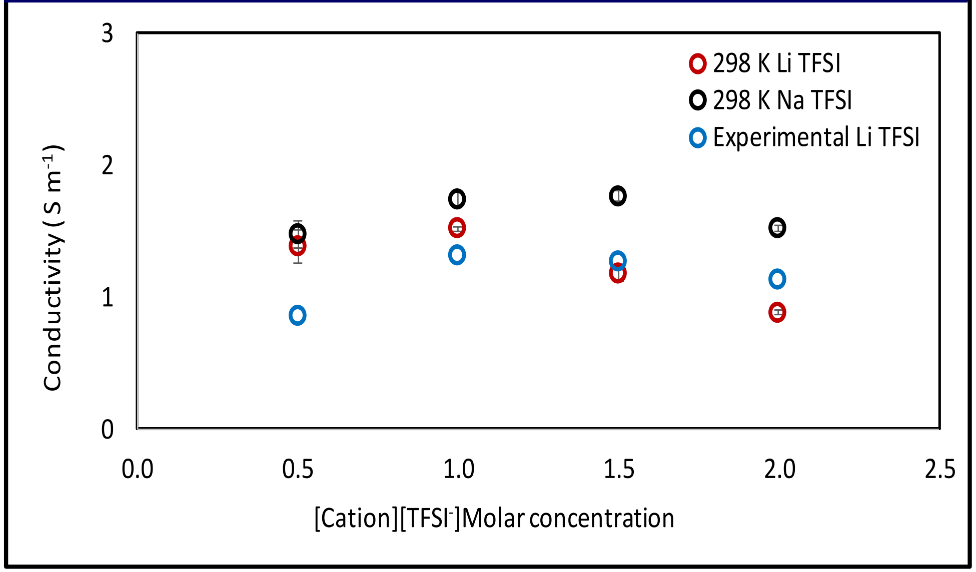
# Electrolyte Modeling

## Molecular Simulations



High fidelity molecular dynamics

## Transport Property: Ionic Conductivity




Excellent agreement between simulations and experiments

**Chemical structure-property relationships lead to design rules**

**Ultimately, we want to design component materials on the computer: *Virtual Design***

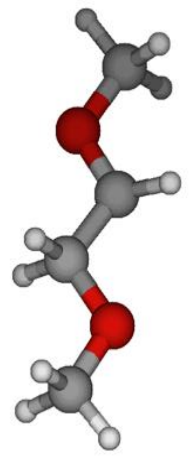
# Electrolyte Experimental Evaluation

| Family | Family Representatives | Progress/Advantages |
|---|---|---|
| | | |
| Glymes | DME (1,2-dimethoxyethane) / TEGDME | Current state-of-the-art |
| Ionic Liquids | EMIM TFSI | Poor lithium stripping |
| | PYR14 TFSI | Lower charge overpotentials, Low volatility<br>DEMS/NMR required |
| Phosphoramides | HMPA (Hexamethylphosphoramide) | High Donor Number,<br>Poor efficiency in DEMS |
| | Tris(N,N-tetramethylene)phosphoric acid triamide | High Donor Number,<br>Increased stability with anode over HMPA<br>NMR/DEMS required |
| Ureas | DMPU (1,3-Dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone) | Stable NMR against lithium peroxide,<br>Poor efficiency in DEMS |
| | DMI (1,3-Dimethyl-2-imidazolidinone) | Stable NMR against lithium peroxide<br>DEMS required |
| Fluorinated Compounds | Perfluorotetraglyme | Under investigation |

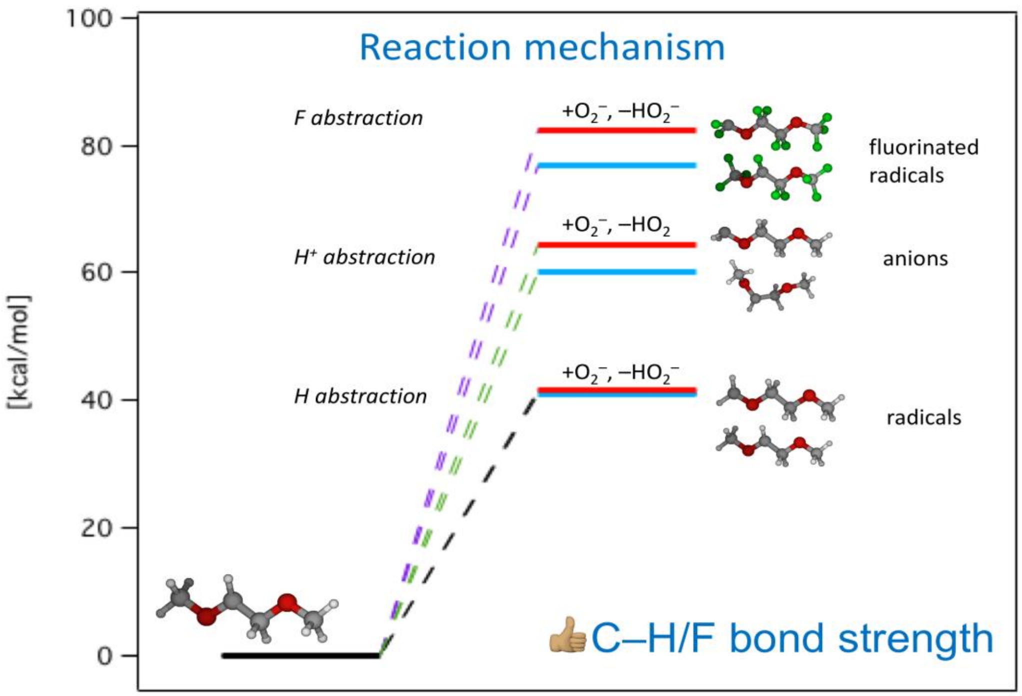
**New class of materials being considered: molten, <u>inorganic</u> electrolytes**

# Electrolyte Stability Chemistry

Decomposition initiates by H atom removal



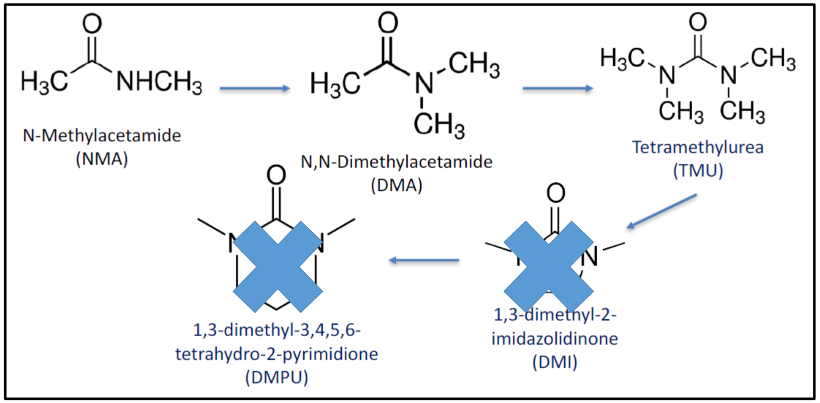
Li-Air Electrolyte:
DME



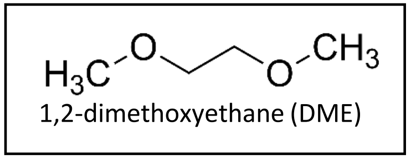

**Computational Chemistry**

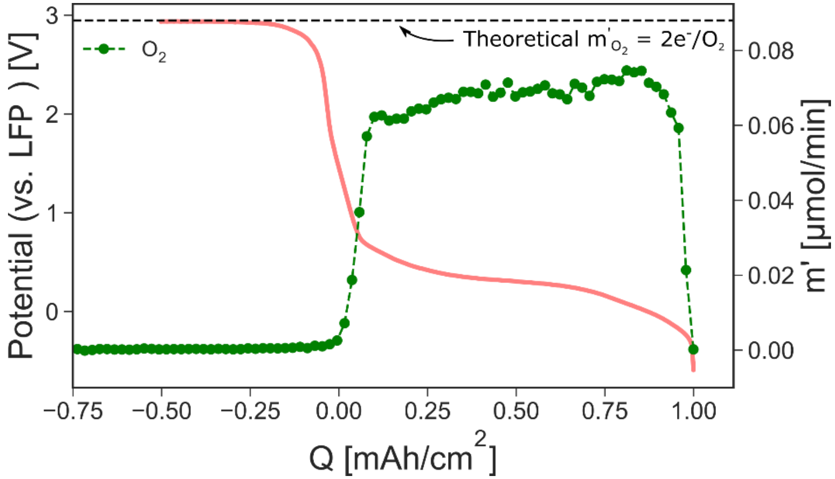
H atoms replaced by F atoms for more stable electrolyte – design rule

# Systematic Study of the Stability of New Electrolytes: Amides and Ureas




**Acetamides** and **ureas** are more stable in Li-$O_2$ cells compared to previous SOA electrolyte DME



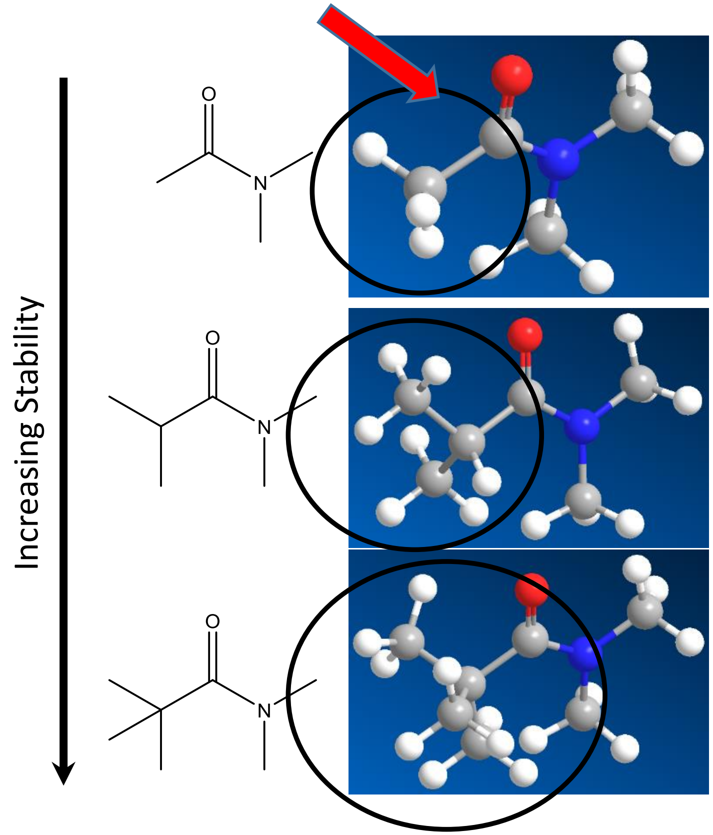

DEMS analysis of a Li-$O_2$ cell with **DMA**.
Molar flux of $O_2$ is closer to the theoretical rate showing improved performance.

# Acetamide and Urea Stability and their Degradation

| Solvent | $LiNO_3$ [M] | Cathode | OER/ORR | |
|---|---|---|---|---|
| 1,2-dimethoxyethane (**DME**) | 0.7 | XC72 (PTFE-bound) on SS-mesh | **0.78** | **<-SOA** |
| N-Methylacetamide (**NMA**) | 1 | | **0.96** | |
| N,N-dimethylacetamide (**DMA**) | 1 | | **0.97** | |
| Tetramethylurea (**TMU**) | 1 | | **0.85** | |

Reversibility quantified using OER/ORR (oxygen evolution/oxygen reduction).
Acetamides has OER/ORR ~25 % improvement to DME.
However, parasitic products are still form during cell operation.

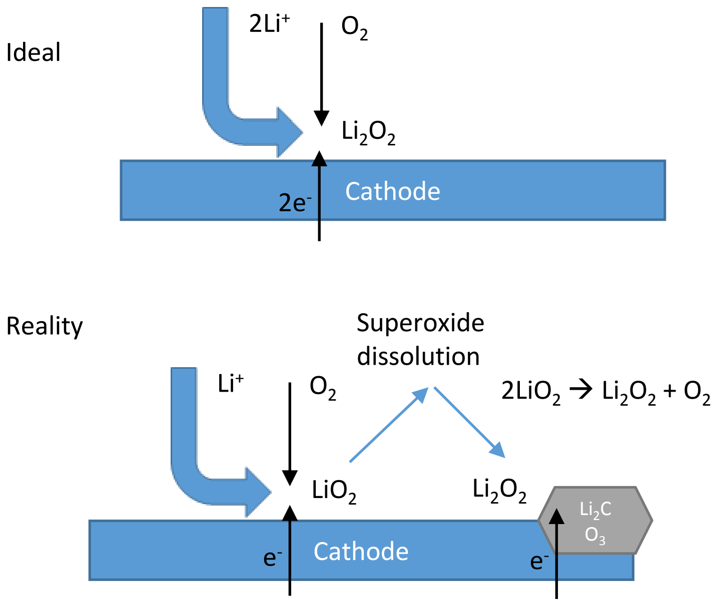
# Steric Hindrance Design Rule for DMA




**Hypothesis**: steric hindrance limits lithium superoxide attack

# Cathode Development

## Challenges



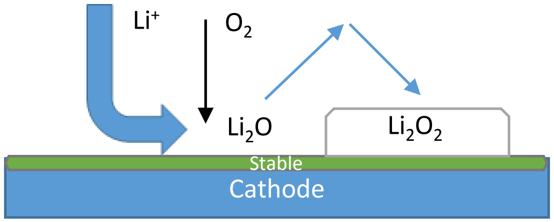

$Li_2O_2$ is formed in a two step process, with the first step forming lithium superoxide, that can escape into the electrolyte

- One-step $e^-$ transfer generates Lithium Superoxide ($LiO_2$) which is a strong nucleophile
- Dissolution of superoxide from cathode surface
  - Advantage: Allows for deposition of Li2O2 without direct $e^-$ transport
  - Disadvantage: Releases a highly reactive species into the electrolyte which must either recombine or react further
- Nucleophiles generated result in decomposition of carbon cathode and electrolyte forming $Li_2CO_3$ among other products
  - **~40% CO2 from Carbon Cathode 60% from Electrolyte[1]**
- $Li_2CO_3$ formed creates a passivation layer making it difficult to remove $Li_2O_2$, hurting reversibility
- $Li_2CO_3$ is removed at higher potentials, but generates $CO_2$ resulting in loss of active material ($O_2$)

1 McCloskey,B.D., et al. *J. Phys. Chem. Lett. 4, 17, 2989-2993*

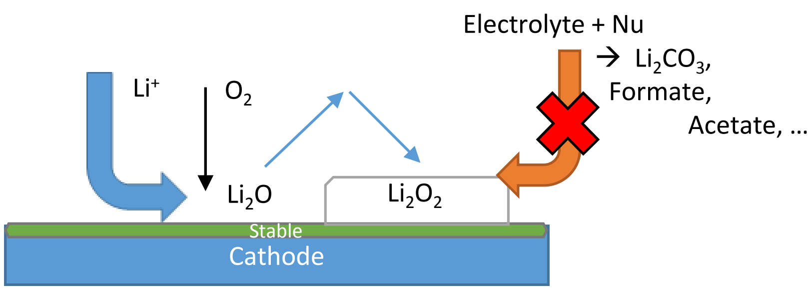
# Cathode Development

## Research Goals




Task 1:

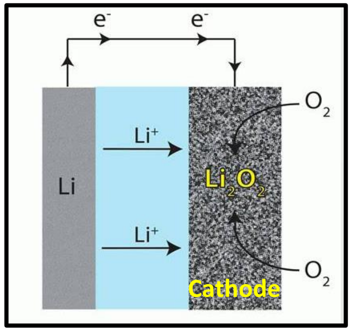
- Replace carbon cathode with oxidative resistive material

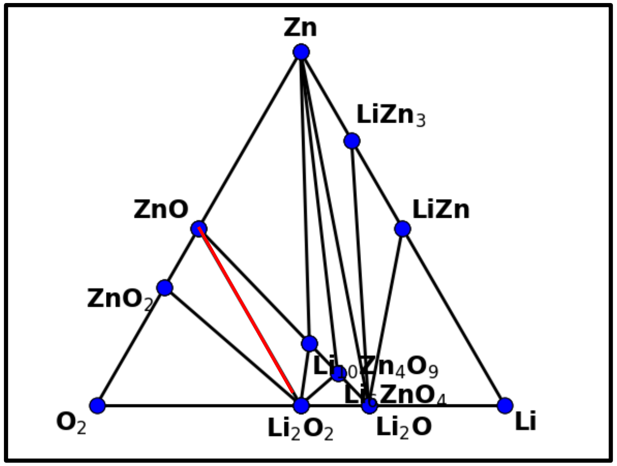



Task 2:

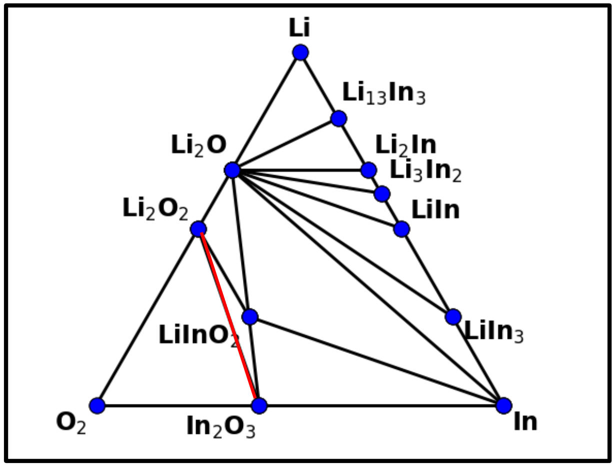
- Identify electrolytes with increased stability to nucleophilic attack/oxidation

# Cathode Coatings

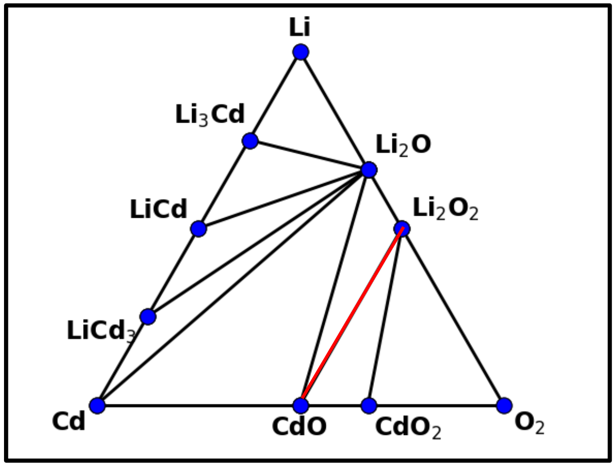



ZnO




$In_2O_3$

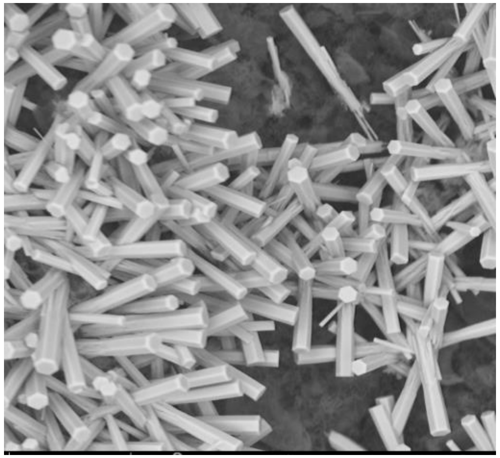



CdO

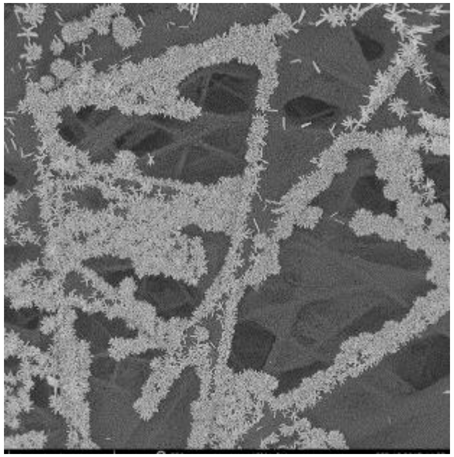
Phase diagrams suggest stable cathode coatings
Transparent conducting oxides (TCO) are especially promising

# Fabricated ZnO Coatings

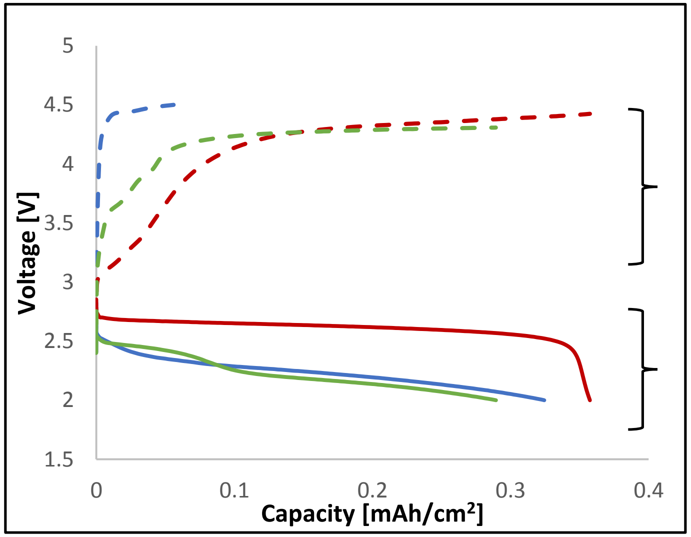
**Fabricated Morphologies**



***Rods***



***High Surface Area Layer***




Charge

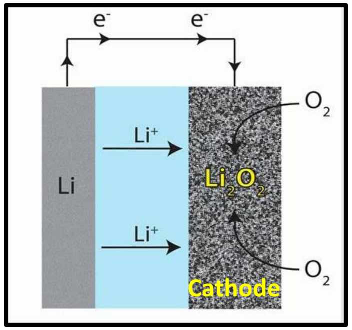
Discharge

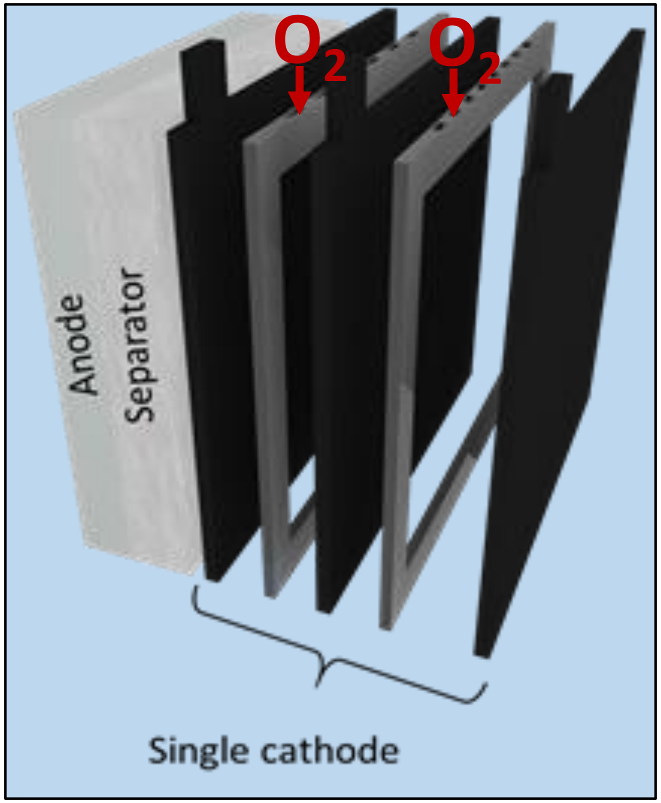
ZnO   Carbon   ZnO+5%Carbon

ZnO is stable but has lower electrical conductivity

**Next step**: doping ZnO to improve conductivity and maintain stability

# Li-Air Battery Pack for Electric Aircraft




**Alternating $O_2$ and cathode layers**

**Novel Li-Air battery <u>architectures</u> for high power needed by aircraft**
**Oxygen must be delivered efficiently to cathode surface**

# Summary

- **Big Question**: Can we design and build a viable battery which satisfies the significant requirements of electric aircraft applications?
- **Li-Air Batteries** have high theoretical energies and can leverage onboard oxygen systems
- **Major Challenge of Li-Air:** Electrolytes are limiting factor for practical energy densities, rechargeability and safety
- **Feasiblity Objective**: Design and fabricate new stable electrolytes for Li-Air batteries with energy densities of 400+ Wh/kg and 100 recharges and test them in an electric (UAV) flight
- **Li-Air Dream Team**: Unprecedented team of experts from NASA, DOE, academia, industry
- **Technical Thrust Areas:** Computation, New Materials, Mechanisms, Flight Application
- **Progress:**
  - Electrolyte data mining; materials simulations; computational chemistry
  - Electrolyte evaluation: inorganic electrolytes may be promising
  - Cathode coatings: transparent conducting oxide coatings may be promising
  - Li-Air cell/pack architectures will be required for high power

# Acknowledgements

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