# Efficient Rechargeable Li/$O_2$ Batteries Utilizing Stable Inorganic Molten Salt Electrolytes

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*Annual Merit Review*
*DOE Vehicle Technologies Program*
*Arlington, VA*
*June 10, 2015*

ES233

# Overview

## Timeline

- Project start date: 10-01-2014
- Project end date: 09-30-2017
- Percent complete: 16.6%

## Budget

- Total project funding
  - DOE share: $1,500,000
  - Liox share: $375,000
- Funding received
  - FY14: $125,000
  - FY15: $500,000

## Barriers

- Barriers addressed for Li/Air
  - Electrolyte stability
  - Fast electrode kinetics and high reversibility
  - Air tolerance

## Partners

- National Laboratories
  - Lawrence Berkeley
- Academia
  - Caltech

# Relevance

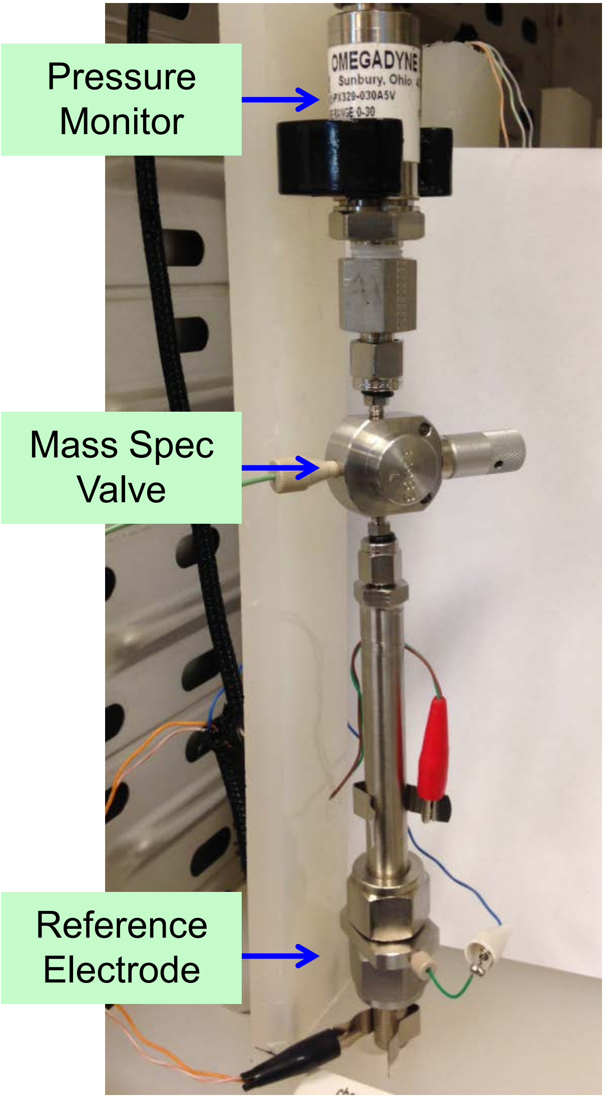
## Relevance

- Despite promise based on extremely high theoretical capacity, current Li-air battery technology fails:
  - Unstable, volatile electrolytes
  - High voltage hysteresis, poor cycle life
  - Low power density and intolerance to air ($H_2O$, $CO_2$), necessitating costly and heavy gas handling and $O_2$ purification equipment
- Radical new approach is needed to solve these problems

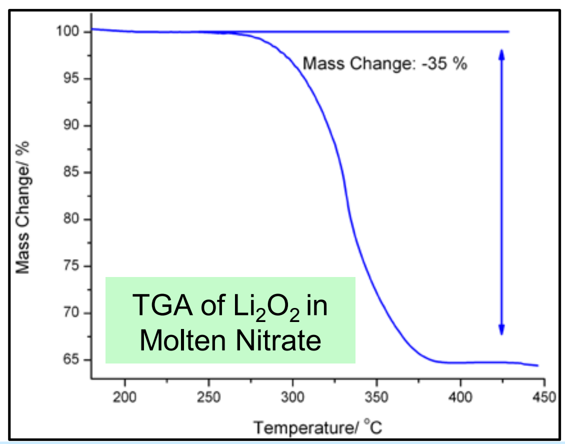
## Objectives

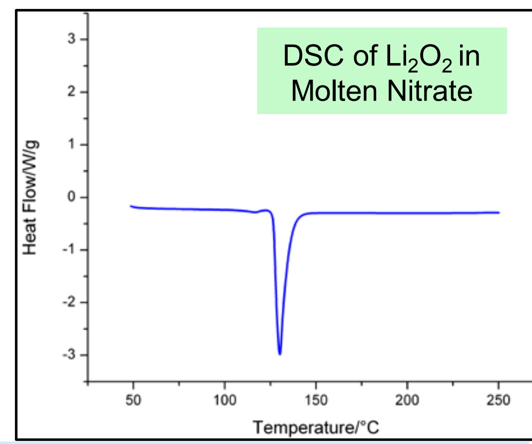
- Demonstrate inert, nonvolatile electrolytes
- Demonstrate long-term, higher rate, low voltage hysteresis cycling enabled by enhanced solubility of discharge products
- Demonstrate very high capacity, reversible, 4 electron $Li/O_2$ cells ($Li_2O$ discharge product)
- Demonstrate Li-air battery cycling in ambient air without the need for $O_2$ purification

# Approach and Deployment Strategy I

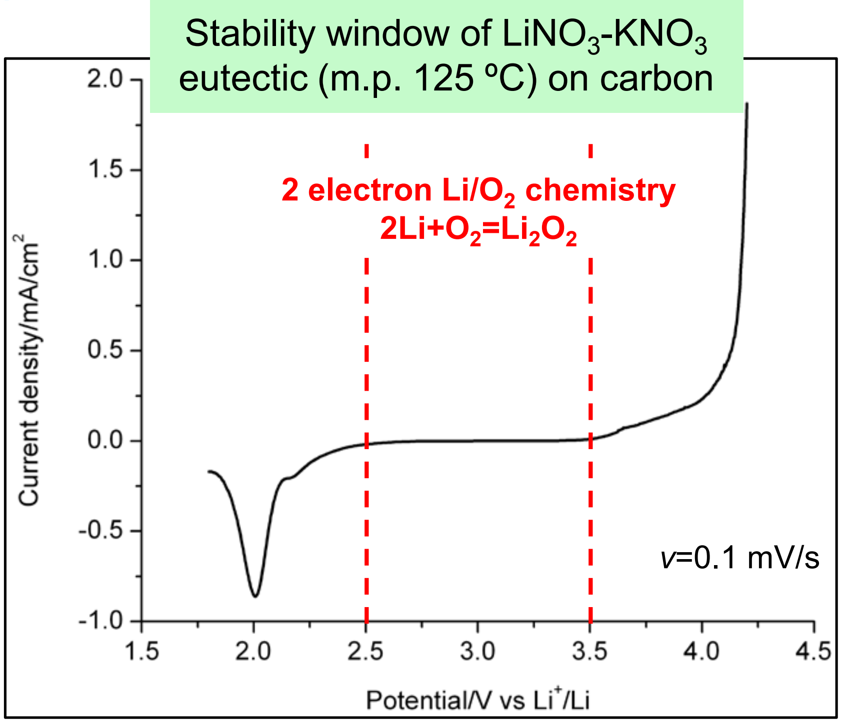


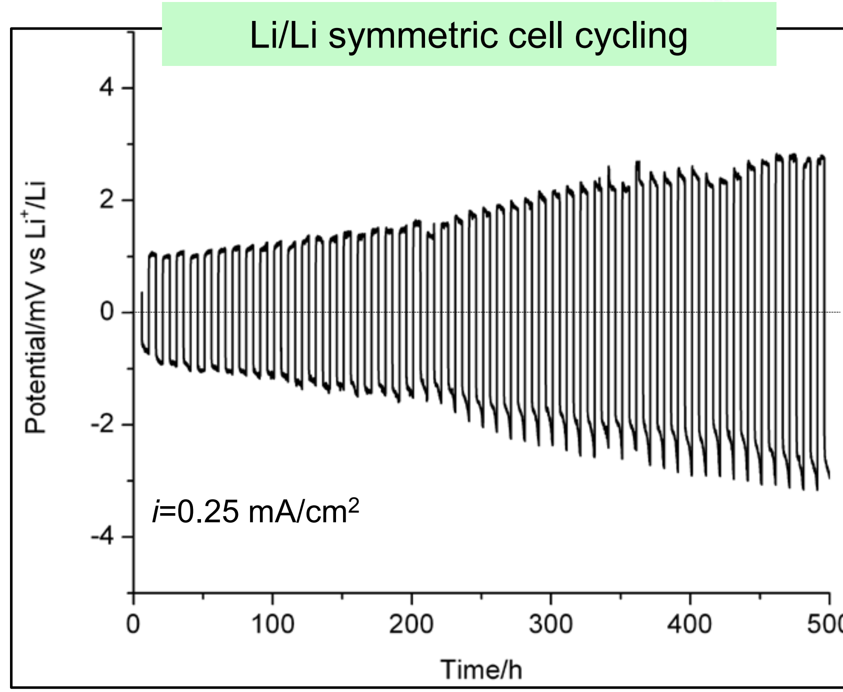

- **Approach:** Replace volatile, unstable and/or air-intolerant aqueous or organic electrolytes with inert molten nitrate electrolytes and operate cell above liquidus temperature (> 80 °C)
- **Strategy:** Improved reversibility and rate capability since discharge products ($Li_2O_2$, $Li_2O$, LiOH and $Li_2CO_3$) are stable and sparingly soluble in molten nitrate electrolytes; Electrode kinetics and mass transport are faster at elevated temperature
- **Research methodology:** Combine quantitative gas analysis (pressure monitoring, mass spectrometry) with precise coulometry to analyze air electrode processes



# Approach and Deployment Strategy II




- Nitrate reduction and SEI formation reaction: $2Li^+ + LiNO_3 + 2e^- \rightarrow Li_2O + LiNO_2$
- $E$ = 2.44 V vs. $Li^+$/Li at 150 ºC (sluggish kinetics on carbon)
- "Conventional", nonaqueous $Li/O_2$ electrochemistry between 2.5 and 3.5 V
- Low overpotential (>4 mV) Li metal cycling in eutectic for >500 hrs
- SEI layer is pseudo-stable. $Li_2O$ is sparingly soluble
- Coulombic efficiency for Li plating and stripping on Cu is >95%

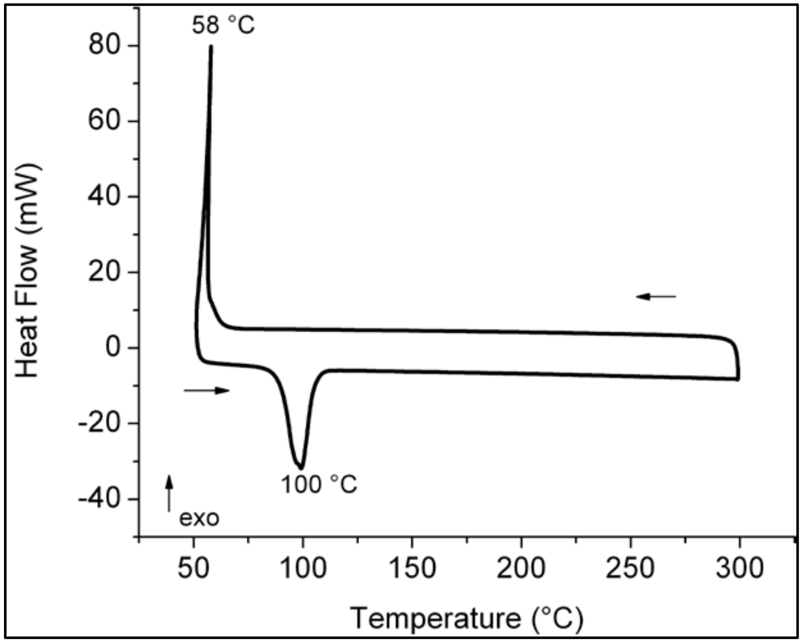
# Milestones: FY2014 and 2015

| | |
|---|---|
| A (Dec 14) | Demonstrate alkali metal eutectic compositions having eutectic points below 120 °C **Complete** |
| B (Dec 14) | Measure ionic conductivity and $Li^+$ transference number in eutectic compositions **Complete** |
| C (Mar 15) | Measure diffusion coefficients and solubilities of $O_2$, $Li_2O_2$ and $Li_2O$ **Complete** |
| D (Mar 15) | Synthesize oxidation-resistant carbons **Complete** |
| E (Jun 15) | Go/No-Go: Quantify $e^-/O_2$ and OER/ORR ratios for baseline carbon air electrodes **Complete** |
| F (Jun 15) | Quantify $e^-/O_2$ and OER/ORR ratios for oxidation-resistant carbon air electrodes **Ongoing** |
| G (Sep 15) | Measure diffusion coefficients and solubilities of $H_2O$, $CO_2$, LiOH and $Li_2CO_3$ **Ongoing** |
| H (Sep 15) | Synthesize metals and metal alloys of high air electrode stability and/or catalytic activity **Ongoing** |

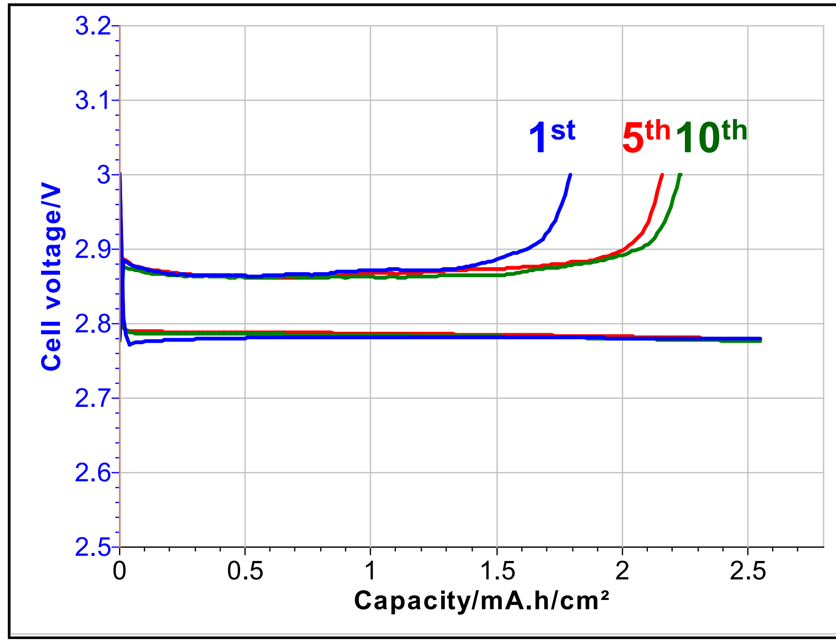
# Technical Accomplishments and Progress

## Milestone A & B (Demonstrate eutectic compositions containing $Li^+$ having eutectic points below 120°C; measure ionic conductivity and $Li^+$ transference number in eutectic compositions)

DSC curve (5°C/min; under Ar) of $LiNO_3$-$KNO_2$-$CsNO_3$ eutectic




$Li/O_2$ cell cycling at 120°C at 0.25 mA/cm$^2$ in $LiNO_3$-$KNO_2$-$CsNO_3$ eutectic



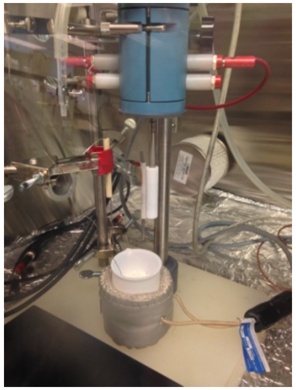

| Eutectic | M.P. (°C) | *t*+ | $\sigma_{150°C}$ (mS/cm) |
|---|---|---|---|
| $LiNO_3$-$KNO_3$ | 125 | 0.68 | 88 |
| $LiNO_3$-$KNO_2$-$CsNO_3$ | 90 | 0.28 | 115 |

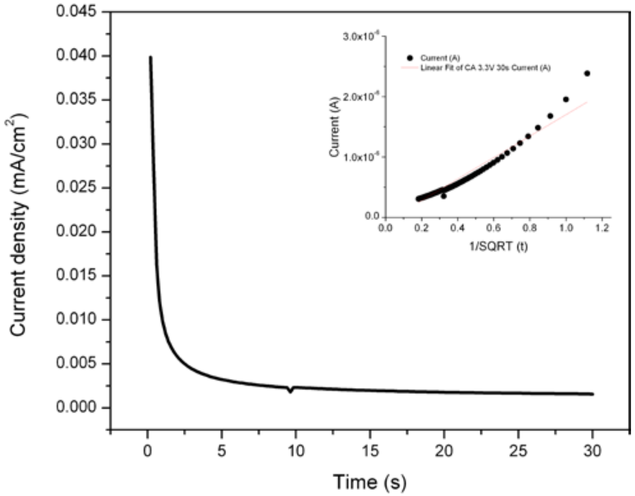
- Very low overpotential and coulombic efficiency improving with increasing cycle number are general characteristics of molten nitrate $Li/O_2$ cells

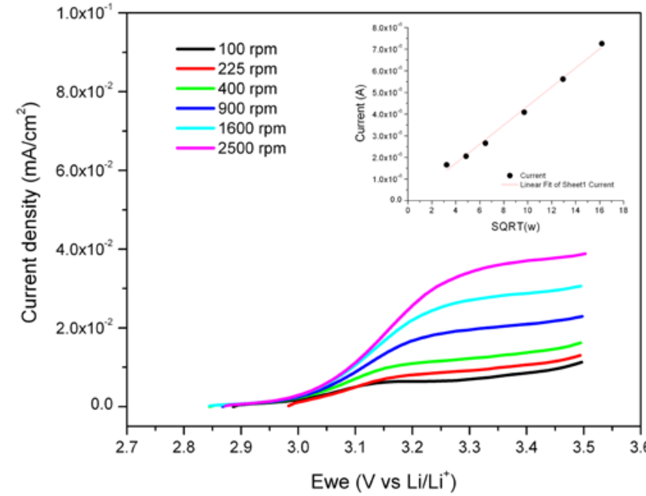
# Technical Accomplishments and Progress

## Milestone C (Measure diffusion coefficient and bulk concentration of $O_2$, $Li_2O_2$ and $Li_2O$ at 150 °C in (Li,K)$NO_3$ eutectic)

Levich-Cottrell analysis






$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}}$$

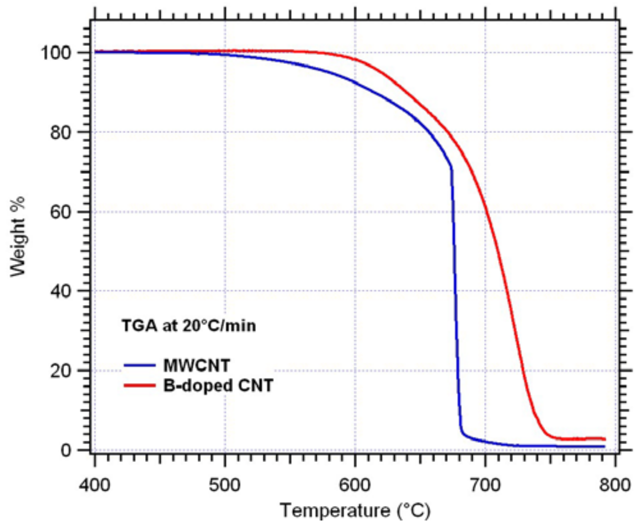
$$I_L = (0.620)nFAD^{\frac{2}{3}}w^{\frac{1}{2}}v^{\frac{-1}{6}}C$$

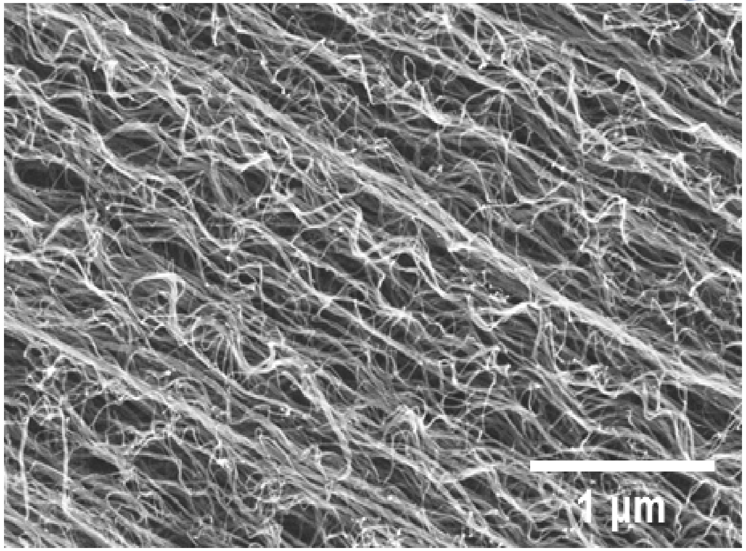
| | $Li_2O_2$ | $Li_2O$ | $O_2$ |
|---|---|---|---|
| Solubility (mM) | 0.414 | 0.044 | 0.003* |
| Diffusivity (cm$^2$/s) | 6.63x10$^{-9}$ | 4.25x10$^{-6}$ | 2.42x10$^{-6}$ |

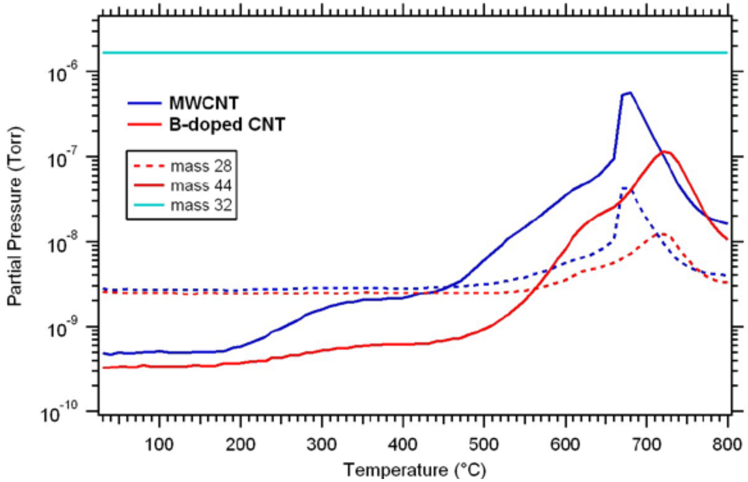
* in (Na,K)$NO_3$

- $Li_2O_2$ and $Li_2O$ salts exhibit enhanced solubility in the molten salt electrolyte compared to organic electrolytes ($10^{-3}$ mM range in DMF, DMSO etc.)
- Very low physical solubility of $O_2$.
- Future topic: Catalytic absorption of $O_2$ in melt

# Technical Accomplishments and Progress
## Milestone D (Synthesize oxidation-resistant carbons)



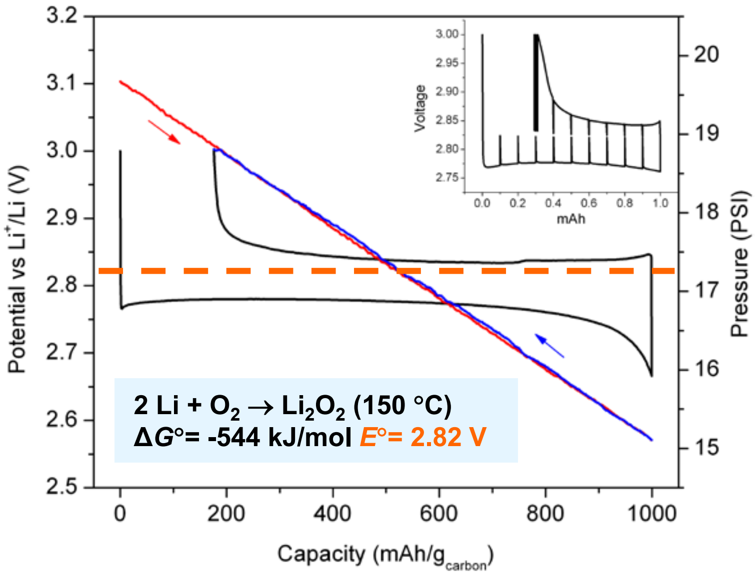



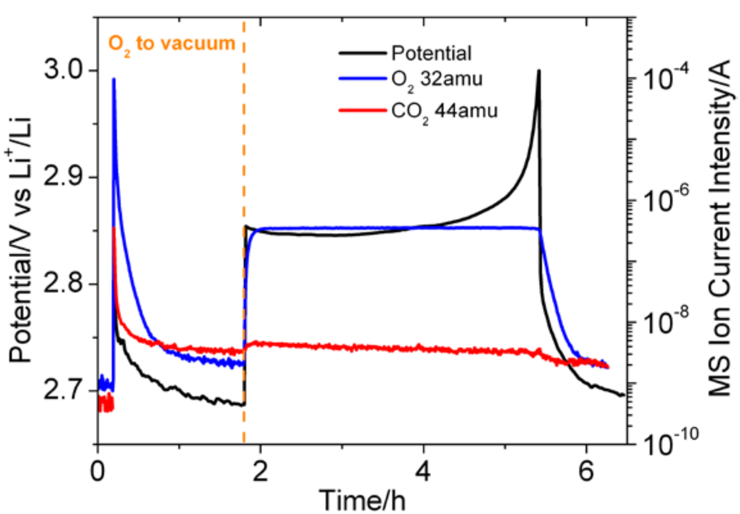




- ➢ CNTs are grown via chemical vapor deposition using the thermal catalytic vapor-liquid-solid method, using Fe nanoparticles as the catalyst
- ➢ Boron-doped CNT samples were produced with flow rates of 1.4 / 1.3 / 0.1 / 2.8 SLPM of Ar / $H_2$ / $C_2H_2$ / 2% $B_2H_6$ respectively
- ➢ TGA/MS analysis under $O_2$ flow demonstrates higher onset temperature for oxidation compared to undoped CNTs

# Technical Accomplishments and Progress

## Milestone E (Quantify $e^-/O_2$ and OER/ORR ratios for baseline carbon air electrodes)




Go/No Go Completed

| Cycle | $(e^-/O_2)_{dis}$ | $(e^-/O_2)_{chg}$ | OER/ORR |
|---|---|---|---|
| 1 | 2.0 | 2.0 | 0.66 |
| 10 | 2.0 | 2.0 | 0.86 |

Test Details

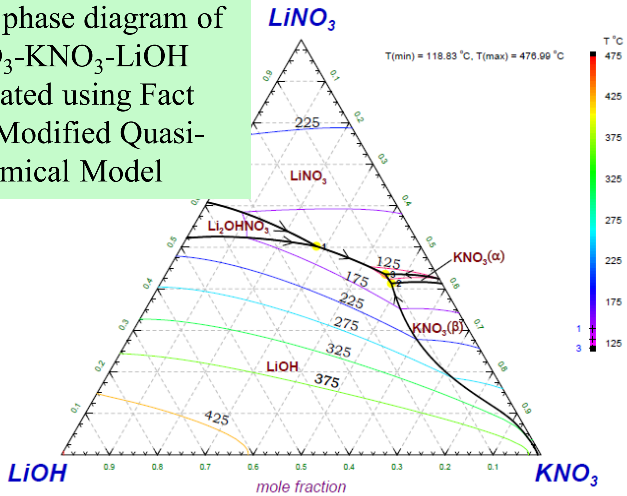
$LiNO_3$-$KNO_3$ dried under vacuum at 200 °C for >48 hrs; 1 cm diameter Super P carbon/PTFE cathode (~5 mg carbon) pressed on stainless steel mesh; Whatman glass fiber separator impregnated with ~100 µL of electrolyte; Li metal anode; Current density = 50 $mA/g_{carbon}$ (0.25 $mA/cm^2$); Cycled in ultra pure $O_2$.

- Extremely low (<50 mV) overpotential is symmetric on discharge and charge
- Pressure curves are symmetric on discharge and charge
- No electrolyte evaporation and no $CO_2$ evolution when cell is charged under vacuum with *in situ* mass spectrometry

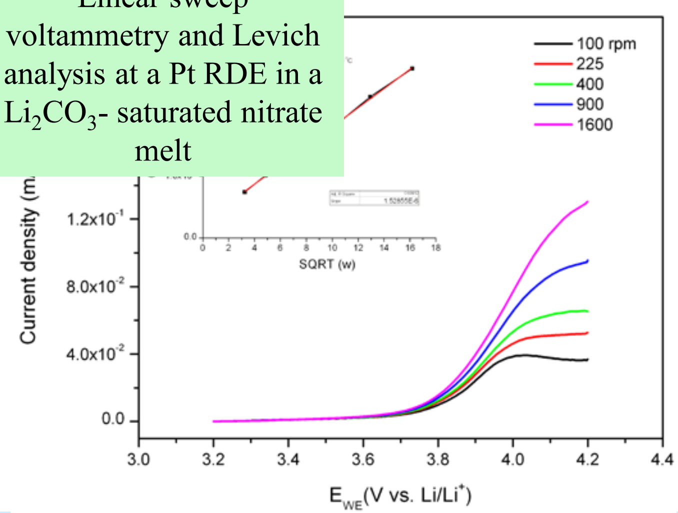
# Technical Accomplishments and Progress

## Milestone G (Ongoing) (Measure diffusion coefficients and solubilities of $H_2O$, $CO_2$, LiOH and $Li_2CO_3$ in (Li,K)$NO_3$ molten salt at 150 °C)

Ternary phase diagram of $LiNO_3$-$KNO_3$-LiOH calculated using Fact Sage, Modified Quasi-chemical Model




Linear sweep voltammetry and Levich analysis at a Pt RDE in a $Li_2CO_3$- saturated nitrate melt




| | LiOH | $Li_2CO_3$ | $H_2O$ | $CO_2$ |
|---|---|---|---|---|
| Solubility (mM) | 4300 | 9.9 | | |
| Diffusivity ($cm^2/s$) | $9x10^{-7}$ | $8.2x10^{-9}$ | | |

- LiOH, $Li_2CO_3$ (expected discharge products under ambient air) can be electrochemically oxidized near equilibrium potentials (3.4 V and 3.6 V, respectively)
- LiOH forms eutectic compositions with alkali metal nitrates. High solubility (4.3 M) may enable high capacity for cells operating in ambient air
- Stable solid electrolyte required for ambient air operation

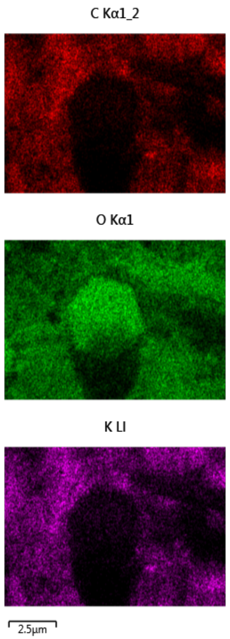
## Collaboration and Coordination with Other Institutions

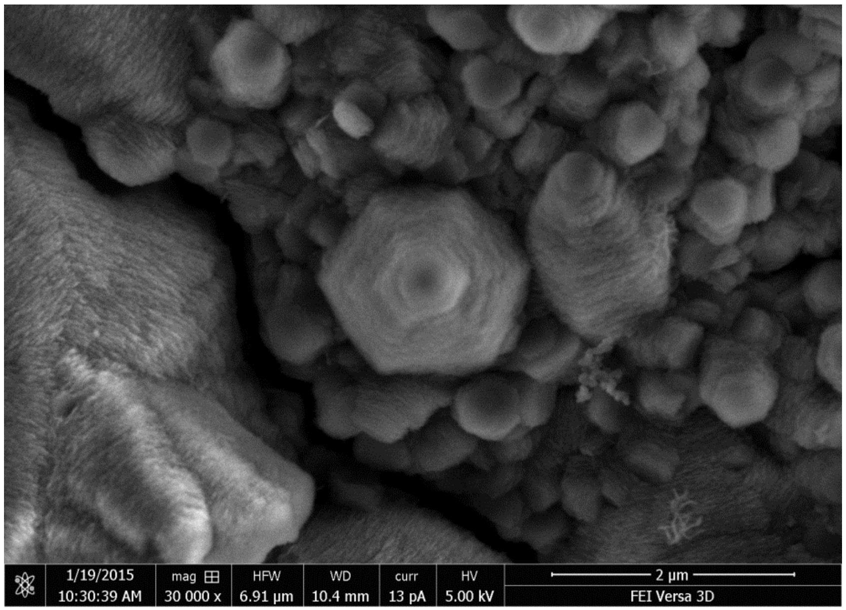
- **Lawrence Berkeley National Laboratory**
  - Prof. Bryan D. McCloskey: $O_2$ electrochemistry in molten salt systems and *in situ* gas analysis

- **California Institute of Technology**
  - Prof. Julia R. Greer: Materials synthesis and characterization (SEM/EDX, XRD, TEM, XPS)

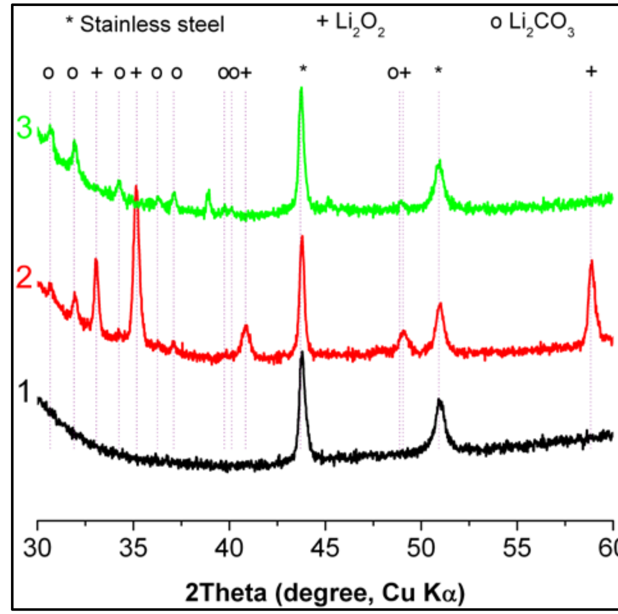
# Collaboration and Coordination with Other Institutions: Examples

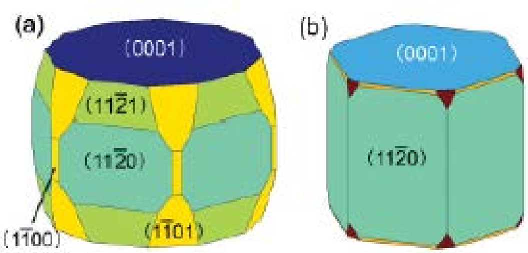
SEM/EDX of discharged $O_2$ cathode




XRD of pristine (1), discharged (2) and fully cycled $O_2$ cathode (3)

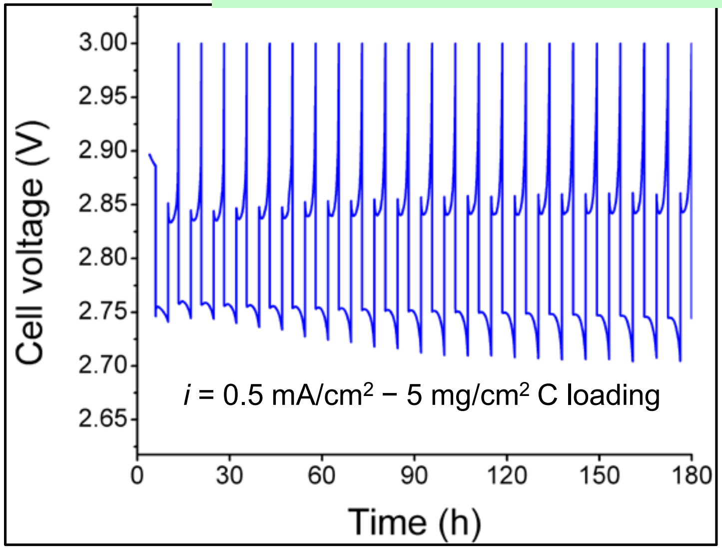


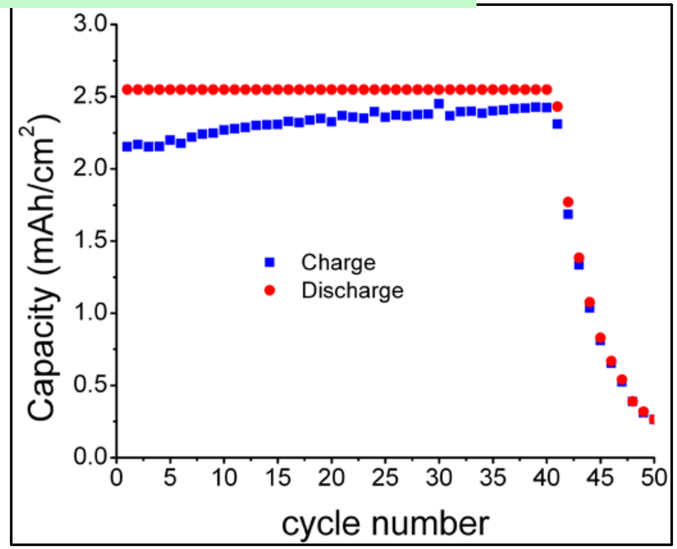




- Equilibrium hexagonal shape of $Li_2O_2$, determined by surface energy calculations and Wulff construction, is observed for the first time in a $Li/O_2$ cell
- XRD shows $Li_2O_2$ and $Li_2CO_3$ after discharge and only $Li_2CO_3$ after full cycle

# Future Work: Identify Non-Carbonaceous Air Electrode Materials

Li/$O_2$ cell cycling in $LiNO_3$-$KNO_3$ melt using an amorphous carbon cathode



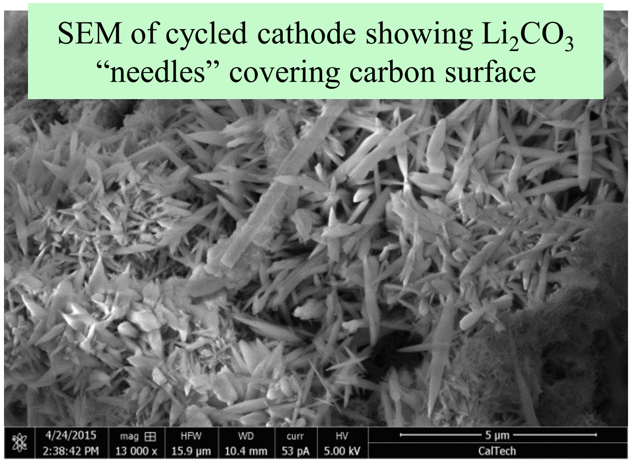




- Decomposition of amorphous carbon electrode causes cell failure, confirmed by post-mortem electrode analysis

- Possible reactions:
  1) $Li_2O_2 + C + ½O_2 \rightarrow Li_2CO_3$
  2) $Li_2O_2 + C + LiNO_3 \rightarrow Li_2CO_3 + LiNO_2$

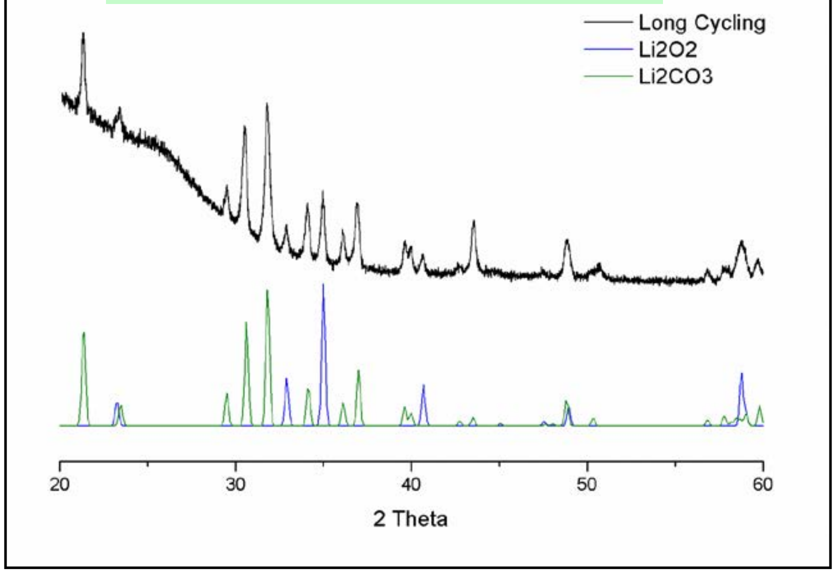
- Alternative electrode materials are needed to improve cycle life

SEM of cycled cathode showing $Li_2CO_3$ "needles" covering carbon surface

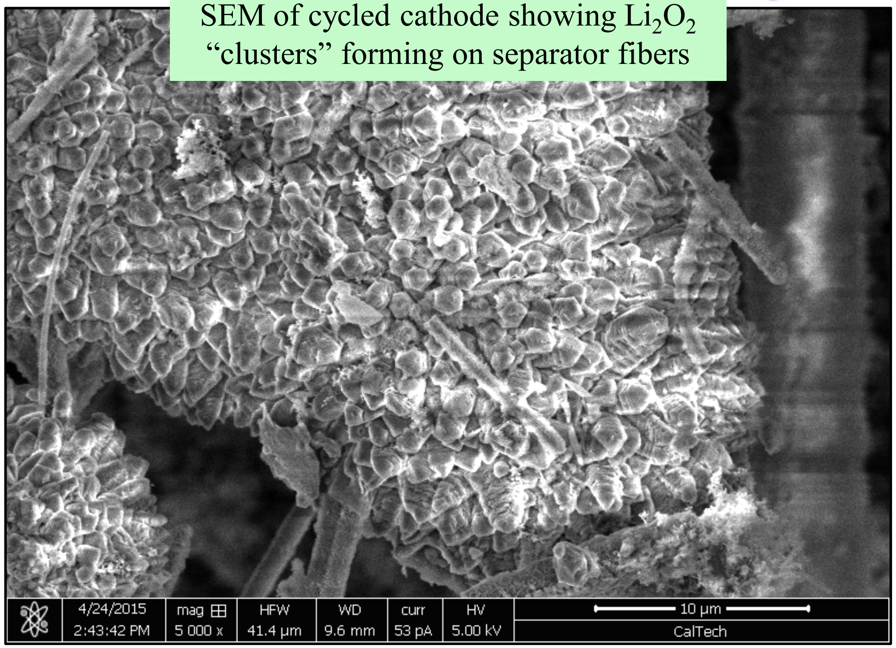


# Future Work: Manage $Li_2O_2$ Dissolution and Precipitation

XRD of cathode following 50 cycles showing $Li_2O_2$ buildup




SEM of cycled cathode showing $Li_2O_2$ "clusters" forming on separator fibers




- XRD analysis of carbon cathode following 50 cycles reveals substantial accumulation of electronically disconnected $Li_2O_2$
- SEM analysis shows large clusters (>10 µm in diameter) of $Li_2O_2$ (hexagonal morphology) deposited within glass fiber separator
- Uncontrolled diffusion and precipitation of soluble $Li_2O_2$ is a major cause of capacity loss.  Proprietary methods to address this issue under development

# Summary

- Project technical approach enables significant improvements in overpotential and stability in Li/air cells and may lessen certain system-level constraints
- All project milestones and go/no-go decision points achieved to-date
- Future, near-term technical objectives include:
  - Identify non-carbonaceous air electrode materials
  - Manage $Li_2O_2$ dissolution and precipitation

Thank you very much to our project team members at Caltech and LBNL and to the DOE Office of Vehicle Technologies for your support!