Efficient Rechargeable Li/O₂ Batteries Utilizing Stable Inorganic Molten Salt Electrolytes

Principal Investigator: Vincent Giordani
Liox Power, Inc.

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

ES233

This presentation does not contain any proprietary, confidential, or otherwise restricted information
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
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 (H₂O, CO₂), necessitating costly and heavy gas handling and O₂ 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/O₂ cells (Li₂O discharge product)
- Demonstrate Li-air battery cycling in ambient air without the need for O₂ purification
**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 (Li₂O₂, Li₂O, LiOH and Li₂CO₃) 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
Stability window of LiNO$_3$-KNO$_3$ eutectic (m.p. 125 °C) on carbon

- Nitrate reduction and SEI formation reaction:
  \[ 2\text{Li}^+ + \text{LiNO}_3 + 2e^- \rightarrow \text{Li}_2\text{O} + \text{LiNO}_2 \]

- \( E = 2.44 \) V vs. \( \text{Li}^+/\text{Li} \) at 150 °C (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$_2$O is sparingly soluble

- Coulombic efficiency for Li plating and stripping on Cu is >95%
## Milestones: FY2014 and 2015

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Demonstrate alkali metal eutectic compositions having eutectic points below 120 °C <strong>Complete</strong></td>
</tr>
<tr>
<td>B</td>
<td>Measure ionic conductivity and Li(^+) transference number in eutectic compositions <strong>Complete</strong></td>
</tr>
<tr>
<td>C</td>
<td>Measure diffusion coefficients and solubilities of O(_2), Li(_2)O(_2) and Li(_2)O <strong>Complete</strong></td>
</tr>
<tr>
<td>D</td>
<td>Synthesize oxidation-resistant carbons <strong>Complete</strong></td>
</tr>
<tr>
<td>E</td>
<td>Go/No-Go: Quantify e(^-)/O(_2) and OER/ORR ratios for baseline carbon air electrodes <strong>Complete</strong></td>
</tr>
<tr>
<td>F</td>
<td>Quantify e(^-)/O(_2) and OER/ORR ratios for oxidation-resistant carbon air electrodes <strong>Ongoing</strong></td>
</tr>
<tr>
<td>G</td>
<td>Measure diffusion coefficients and solubilities of H(_2)O, CO(_2), LiOH and Li(_2)CO(_3) <strong>Ongoing</strong></td>
</tr>
<tr>
<td>H</td>
<td>Synthesize metals and metal alloys of high air electrode stability and/or catalytic activity <strong>Ongoing</strong></td>
</tr>
</tbody>
</table>
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 LiNO₃-KNO₂-CsNO₃ eutectic

Li/O₂ cell cycling at 120°C at 0.25 mA/cm² in LiNO₃-KNO₂-CsNO₃ eutectic

<table>
<thead>
<tr>
<th>Eutectic</th>
<th>M.P. (°C)</th>
<th>t⁺</th>
<th>σ₁₅₀°C (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃-KNO₃</td>
<td>125</td>
<td>0.68</td>
<td>88</td>
</tr>
<tr>
<td>LiNO₃-KNO₂-CsNO₃</td>
<td>90</td>
<td>0.28</td>
<td>115</td>
</tr>
</tbody>
</table>

Very low overpotential and coulombic efficiency improving with increasing cycle number are general characteristics of molten nitrate Li/O₂ cells
Li$_2$O$_2$ and Li$_2$O 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 / H₂ / C₂H₂ / 2% B₂H₆ respectively.

- TGA/MS analysis under O₂ 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)

- 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

\[
2 \text{Li} + O_2 \rightarrow \text{Li}_2\text{O}_2 \text{ (150 °C)}
\]

\[\Delta G^\circ = -544 \text{ kJ/mol} \quad E^\circ = 2.82 \text{ V}\]

<table>
<thead>
<tr>
<th>Cycle</th>
<th>((e^-/O_2)_{dis})</th>
<th>((e^-/O_2)_{chg})</th>
<th>OER/ORR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>2.0</td>
<td>0.66</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>2.0</td>
<td>0.86</td>
</tr>
</tbody>
</table>

**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\text{carbon} (0.25 mA/cm\(^2\)); Cycled in ultra pure O\(_2\).
Technical Accomplishments and Progress
Milestone G (Ongoing) (Measure diffusion coefficients and solubilities of H$_2$O, CO$_2$, LiOH and Li$_2$CO$_3$ in (Li,K)NO$_3$ molten salt at 150 °C)

LiOH, Li$_2$CO$_3$ (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

<table>
<thead>
<tr>
<th></th>
<th>LiOH</th>
<th>Li$_2$CO$_3$</th>
<th>H$_2$O</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (mM)</td>
<td>4300</td>
<td>9.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusivity (cm$^2$/s)</td>
<td>$9 \times 10^{-7}$</td>
<td>$8.2 \times 10^{-9}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Collaboration and Coordination with Other Institutions

- **Lawrence Berkeley National Laboratory**
  - Prof. Bryan D. McCloskey: O₂ 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)
Equilibrium hexagonal shape of Li$_2$O$_2$, determined by surface energy calculations and Wulff construction, is observed for the first time in a Li/O$_2$ cell.

XRD shows Li$_2$O$_2$ and Li$_2$CO$_3$ after discharge and only Li$_2$CO$_3$ after full cycle.
Future Work: Identify Non-Carbonaceous Air Electrode Materials

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

- Possible reactions:
  1) \( \text{Li}_2\text{O}_2 + \text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{Li}_2\text{CO}_3 \)
  2) \( \text{Li}_2\text{O}_2 + \text{C} + \text{LiNO}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{LiNO}_2 \)

- Alternative electrode materials are needed to improve cycle life

Li/O₂ cell cycling in LiNO₃-KNO₃ melt using an amorphous carbon cathode

SEM of cycled cathode showing Li₂CO₃ “needles” covering carbon surface
XRD analysis of carbon cathode following 50 cycles reveals substantial accumulation of electronically disconnected \( \text{Li}_2\text{O}_2 \)

SEM analysis shows large clusters (>10 \( \mu \text{m} \) in diameter) of \( \text{Li}_2\text{O}_2 \) (hexagonal morphology) deposited within glass fiber separator

Uncontrolled diffusion and precipitation of soluble \( \text{Li}_2\text{O}_2 \) 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$_2$O$_2$ 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!