

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

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2016 DOE Vehicle Technologies Program Review

June 6-10, 2016

Project ID: ES233

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Overview



Timeline

- Project start date: Oct 2014
- Project end date: Sept 2017
- Percent complete: 55%

Budget

- Total project funding
 - DOE share: \$1,050K
 - Liox share: \$375K
- Funding received
 - FY15: \$375K DOE, \$130K Liox
 - FY16: \$175K DOE, \$76K Liox

Barriers

- Barriers addressed for Li/air batteries
 - Electrolyte stability
 - Voltage hysteresis
 - Air tolerance

Partners

- > LBNL
 - In situ characterization and mechanistic analysis
- Caltech
 - Nanostructured materials

Project Objective and Relevance

Objective

- To demonstrate the first practically stable electrolyte for Li-air batteries and thus eliminate a barrier to high cycle life
- To solve the problems of high voltage hysteresis, low rate capability and low areal capacity of Li/O₂ cells by operating at elevated temperature and using an inorganic molten salt electrolyte that solubilizes discharge products
 - To provide a cell and system that can operate robustly in ambient air without O₂ purification

Relevance

- All organic electrolytes evaluated to date are insufficiently stable
- High voltage hysteresis, low rate capability and low areal capacity in current Li/O₂ cells arises from low solubility and sluggish charge transport in discharge products
- Intolerance to ambient air necessitates cumbersome and costly air purification



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Comparison of voltage profiles and discharge product morphologies for Li/O₂ cells using molten salt (blue) and DME organic electrolyte (red) (Giordani *et al.* JACS, 2016)



Milestones

FY15

- Q1 Demonstrate eutectic compositions having eutectic points below 120 °C. Measure ionic conductivity and Li⁺ transference number in eutectic compositions. (Dec. 14) Complete
- **Q2** Measure diffusion coefficients and solubilities of O₂, Li₂O₂ and Li₂O. Synthesize oxidation-resistant carbons. (Mar. 15) **Complete**
- **Q3** <u>Go/No-Go</u>: Demonstrate suitability of analytical approach for elevated temperature molten salt metal-O₂ cells. <u>Criteria</u>: Quantify e⁻/O₂ and OER/ORR ratios for baseline carbon air electrodes. Quantify e⁻/O₂ and OER/ORR ratios for oxidation-resistant carbon air electrodes. (Jun. 15) **Complete**
- Q4 Measure diffusion coefficients and solubilities of H₂O, CO₂, LiOH and Li₂CO₃. Synthesize metals and metal alloys of high air electrode stability and/or catalytic activity. (Sept. 15) Complete

FY16

- **Q1** Quantify e^{-}/O_2 and OER/ORR ratio for metals and metal alloys in half cells under pure O_2 . (Dec. 15) **Complete**
- Q2 Determine the kinetics and mechanisms of electrochemical nitrate reduction in the presence of O₂, H₂O and CO₂. Synthesize electronically conductive ceramics and cermets. (Mar. 16) **Complete**
- **Q3** Quantify e^{-}/O_2 and OER/ORR ratio for electronically conductive ceramics and cermets in half cells under pure O_2 . <u>Go/No-Go</u>: Demonstrate $e^{-}/O_2=2$ and OER/ORR ratio=1, +/- 5%. <u>Criteria</u>: Correcting for the effect of Li₂O₂ crossover. (Jun. 16) **Complete**
- Q4 Demonstrate Li₂O yield=1, e⁻/O₂=4 and OER/ORR ratio=1, +/- 5%. Demonstrate solid electrolytes that are stable to molten nitrate electrolytes over a temperature range of 100 °C to 150 °C for 6 months or greater. (Sept. 16) Ongoing

Approach



- Pressure Monitor Mass Spec Valve Reference Electrode
- 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



Accomplishments A reversible Li/O₂ cell with a new morphology for lithium peroxide 3.2 3.00-20 2.95 Extended Cycling and Cell Death 3.1 8, 2.90 2.85 As in literature, observe sudden cell death after about 40 cycles. Ultra low 3.0 2.80 XRD shows Li₂O₂ and Li₂CO₃ despite ending on charge. Potential vs Li^{*}/Li (V) · SEM shows possible electrode passivation and electrically 0.2 0.4 0.6 0.8 18 (ISd) voltage 2.9 mAh disconnected Li₂O₂ (indicative of solution mediated growth). hysteresis Pressul 2.8 17 ong Cycling Li202 Capacity (mAh/cm² and 12003 2.7 16 2 Li + $O_2 \rightarrow Li_2O_2$ (150 °C) 2.6 $e^{-}/O_{2}=2$ (ideal) ΔG°= -544 kJ/mol E°= 2.82 V Dischar 15 2.5 0.5 0 200 400 600 800 1000 20 25 30 35 40 Capacity (mAh/g_{carbon}) cycle number а **Discharge Product Characterization** XRD confirms crystalline Li₂O₂ as discharge product, with Li₂CO₃ side product (likely due to carbon cathode). SEM with EDS shows large crystals reasoned to be Li₂O₂. - Li2O2 - Li2CO3 Capacity with cycle through cell death (a); XRD of cathode after cell death (b); SEM images of accumulated Li_2CO_3 (c) and Li_2O_2 (d) and a cluster of Li_2O_2 growing on a separator fiber (e) Charged Discharged Coulombic inefficiency due to As Built carbon reactivity necessitates Carbon Potassium Oxygen а identification of non-carbon 40 2 Theta XRD through a full cycle (a); SEM/EDS of cathodes discharged cathode (b)



ratio is equal on charge/discharge)

Characterization of battery discharge products c) XRD data d) SEM analysis

Nickel catalyzes the formation of lithium oxide (Li₂O) discharge product



Lithium oxide is observed as discharge product for 1st time
SEM analysis supports formation of Wulff shape lithium oxide crystals

Diffraction of Lithium Oxide

X-ray and electron diffraction are used to confirm that Li_2O is formed on discharge and consumed on charge. Li_2O has an Antifluorite structure.



Selected diffraction with bright and dark field images



Lithium Oxide Morphology

SEM of a discharged cathode reveals an octahedral morphology, which is in agreement with Wulff Constructions of Li₂O from literature



Li-doped NiO promotes reversible nitrate reduction (new rechargeable battery chemistry)



- Both Ni and Li-doped NiO catalyzes reversible nitrate reduction
- High Coulombic and round trip efficiencies achieved



XPS Depth Profile of Nickel

Both the 2⁺ and 3⁺ oxidation states are present on the nickel surface after exposure to the molten salt.

Any catalytic effect comes from the electronic state of this nickel oxide surface, which the depth profile shows to be self-limiting



Design of structured cathode materials with enhanced chemical stability in the air electrode

B-doped carbon nanotubes 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.

Reduced graphene oxide was synthesized from graphene oxide via the reduction of oxidized functional groups using hydrazine hydrate solution. The hydrophobic RGO was precipitated out from the aqueous solution of graphene oxide (4.0 mg/mL) of water.

Nano-architectured nickel truss fabrication begins with writing a polymer template using 3D direct laser writing - the rastering of a two-photon photopolymerization process in 3D space. The resulting polymer template can then be coated in a material of choice (here sputtered nickel) or pyrolyzed into a conductive carbon. The Ni truss is directly written onto a nickel foil current collector.

Nano-structured Li-doped NiO was obtained by mixing LiOH and nanopowder Ni(OH)₂ in H₂O/isopropanol, then dried at 70 °C on a hot plate. The mix was subsequently annealed at 500 °C for 3 h to enhance crystallinity. Li doping level was 10% by stoichiometry, BET surface area (N₂ adsorption) was found to be ~18 m²/g.

LSM-Ni cermet was obtained by ball milling (3 times 10 minutes) lanthanum strontium manganite ceramic material and nickel nanopowder (50/50 wt.%) using a SPEX SamplePrep 8000M mixer. BET surface area of the composite was found to be ~10 m²/g.







Screened numerous alternative cathode materials (Oxidatively stable carbons, Metals, Metals alloys, Conducting ceramics, Cermets)

Nanoporous gold

Molten nitrate Li-O₂ cell characteristics: e⁻/O₂ and OER/ORR ratios

5	201		1190	O ₂ electrode	(e ⁻ /O ₂) _{discharge}	(e ⁻ /O ₂) _{charge}	OER/ORR
E I	Discharge	Charge	1180	(Desired)	2.0	2.0	1.00
ntial vs. Li+/Li	~0.25mA/cm ² 120min (0.5mAh) O ₂ headspace	~0.25mA/cm ² 120min (0.5mAh) O ₂ headspace	ressure (torr)	Super P Carbon	2.0	2.1	0.73
				Boron-doped Carbon Nanotubes	2.0	2.3	0.49
				Reduced Graphene Oxide	1.8	8.8	0.07
Pote 8		and the second	1160	Nickel	2.2	8.0	0.28
	Walking the	and the second s	1100	Gold	3.8	5.7	0.77
		50 100 150 200 250	1150	Palladium	2.5	No OER	N/A
2 0	50 100 15			IrO ₂	2.2	2.2	0.95
Time (min)				RuO ₂	3.0	10.0	0.30
				LSM-Ni	1.2	No OER	N/A
				TiC	No ORR	No OER	N/A

Most other tested materials show poor performance compared to carbon

Understand mechanism of O₂ reduction mediated by nitrate reduction



- Studied the kinetics and reversibility of nitrate reduction reaction at GC planar electrode
- Nitrate reduction in presence of water leads to high currents due to LiOH product solubility



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Lithium metal/ceramic electrolyte interfacial study

Motivation: Protect Li anode to avoid parasitic reactions (nitrate chemical reduction, Li₂O₂ crossover)



Collaboration and Coordination with Other Institutions



- > Lawrence Berkeley National Laboratory
 - Prof. Bryan D. McCloskey: In situ characterization and mechanistic analysis
- California Institute of Technology
 - Prof. Julia R. Greer: Nanostructured materials

Collaboration and Coordination Lion with Other Institutions (LBNL)

Demonstrated the mechanism of Li₂O₂ solubilization in the presence of nitrate anions









- Nitrate anions enhance solubility of LiO₂ and/or Li₂O₂ in both molten salts and organic electrolytes
- Solubilization is due to high electron donating effect of NO₃-
- Effect is demonstrated by increased discharge capacity and morphology of discharge product
- · Consistent with results in molten nitrate

Collaboration and Coordination Liox with Other Institutions (Caltech)

Fabricated Nano-architectured 3D electrode for molten nitrate batteries





Ni truss nanolattice: polymer template coated in nickel



• Ni truss nanolattice used as cathode in molten salt Lithium batteries

EDX analysis reveals growth of lithium oxide within the lattice during battery discharge Ni Lα1_2



Ο Κα1

100µm

100µm



Κ Κα1



100µm

Remaining Challenges and Barriers

- Lithium metal anode protection (Molten nitrate electrolyte slowly consumes metallic lithium)
- Promising results obtained with IrO₂ cathode material however more fundamental work is necessary to understand the discharge and charge mechanisms (Li₂O₂ + Li₂O discharge product?)
- Structured cathode design for improved rate capability
- 4 electron O₂ cycling

Future Work – FY2016/17



• Structurally Designed Air Electrodes for High Capacity and Power

□ Demonstrate discharge specific power and power density ≥800 W/Kg and ≥1600 W/L, respectively, based on air electrode mass and volume (Sep. 2016)

□ Demonstrate discharge specific energy and energy density ≥500 Wh/Kg and ≥800 Wh/L, respectively, based on air electrode mass and volume (Dec. 2016)

Evaluate Protected Li Electrodes for Elevated Temperature Operation

□ Measure interfacial resistance as a function of temperature, current density and cycle number in symmetric Li/Li cells (Dec. 2016)

□ Characterize dendrite growth as a function of temperature, current density and cycle number in symmetric Li/Li cells (Dec. 2016)

Demonstrate Prototype Molten Salt Li-Air Batteries

□ Scale-up downselected cell components for 4 mAh and 10 mAh cells (Mar. 2017)

□ Go/No-Go: Demonstrate ≥10 cycles at ≥90% round-trip energy efficiency in laboratory-scale Li-air cells comprising a molten nitrate electrolyte and protected Li electrode (Jun. 2017)

Summary



- > Investigated the O_2 electrochemistry in several different classes of material
 - Oxidatively stable carbons, precious metals, metal alloys, transition metals and metal oxides, conducting ceramics, cermets
 - IrO₂ identified as promising non-carbonaceous electrode candidate for ORR electrochemistry
- Studied the effect of nitrate anions on ORR mechanisms and solubility of intermediate discharge product LiO₂ to allow solution mediated growth and high reversibility
- Designed new 3D nano-architectured cathodes (Ni and C trusses) for discharge product accommodation
- Identified catalyst for reversible nitrate reduction thus providing novel rechargeable battery chemistry

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