Sandia National Laboratories

SECONDARY TRIVALENT AL-AIR BATTERY DEVELOPMENT UTILIZING EARTH ABUNDANT MATERIALS

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PROJECT PROFILE

Topic: Zinc & Lead Batteries | Vertical: Materials and Systems Innovation

Strategic Pathway: Grow

Project start and finish: FY25-FY26

PROBLEM

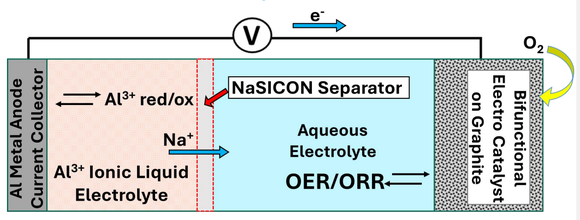
The use of earth abundant materials, with well developed domestic supply chains, can lower costs for grid scale energy storage.

Trivalent materials (e.g. Al^{3+} or Fe^{3+}) are attractive because they have high energy storage capacity. Earth abundant, non-precious metal High Entropy Alloy Nanoparticle (HEA NP) FeNiCoCrMn bifunctional electrocatalysts will increase efficiency and decrease costs.

We demonstrate a secondary Al-air battery consisting of energy dense trivalent Al^{3+} and non-precious metal catalysts.

- **Demonstrate secondary metal-air (Al-air) battery cycling and evaluate efficiency**
- Al-containing Ionic Liquid (Al-IL) electrolyte utilized – Additive effects established last FY
  - Improved Al-IL e-chem has been made
- HEA NP composition optimization for bifunctional catalysis – Stable OER/ORR

Al-Air Battery Schematic



APPROACH

Continued development of the anode electrolyte (AL-IL), membrane separator and cathode HEA NP bifunctional electrocatalysts continued this FY. Full re-design of the test cell was required to facilitate active, functional cycling.

Anode – Al-IL Electrolyte:

- Advancement of the Al-IL (Al-containing ionic liquid) electrolyte was instrumental for the functional Al-air battery – New research enabled Lewis-basic IL electrolyte to protect NaSICON (40mol% $AlCl_3$, 60 mol% NaX)

Membrane/Separator:

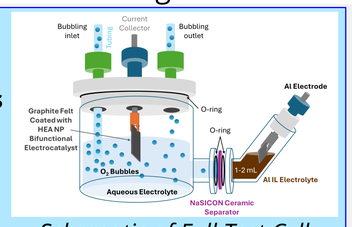
- Polymer membranes failed to prevent electrolyte mixing – Al^{3+} reacted with H_2O
- Na^+ conducting NaSICON separator prevented IL and aqueous electrolyte mixing

Cathode - Equimolar FeNiCoCrMn HEA NP Bifunctional Catalysts:

- HEA NP bifunctional catalysts are highly active for the Oxygen Reduction Reaction (discharge – ORR = $E_{1/2}$) and the Oxygen Evolution Reaction (charge – OER = 10mA/cm^2 potential)
- Stabilizing oxide phase prevents activity loss from sintering

Full Cell Re-Design:

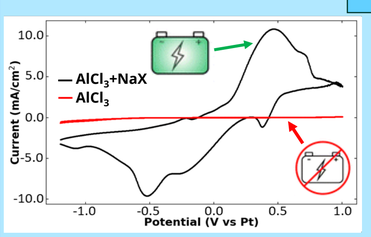
Anode vs Cathode Chambers Current Collectors, Separator Design and Gas Flow Inlets/Outlets



Schematic of Full Test Cell

Al-IL Electrolyte:

Lewis Acid/Base Properties, Composition and Additive Effects, E-chem Stability



Additive Effect on Al-IL E-chem

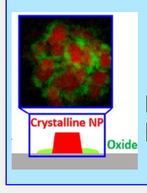
Full Battery Cycling:

Energy Efficiency (EE%), Capacity, SoC

Fully Assembled, ***Secondary Al-air Cell***

HEA NP:

(Composition and OER vs ORR testing)

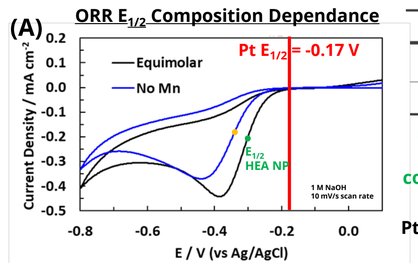


Equimolar FeNiCoCrMn Form FeNiCo Metallic Particles Surrounded by $CrMn_{Ox}$ Stabilizing Phase

RESULTS

HEA NP composition: important for catalytic activity and kinetics

- Taking out Mn from the composition detrimentally affected the catalyst activity (ORR and OER) despite only being part of the oxide stabilizing phase
- Adding in Co ($FeNiCo_2CrMn$) also lead to decreased OER kinetics, but slightly better ORR (as predicted - data not shown) than the equimolar composition



Catalyst Composition	$E_{1/2}$ (V)
Equimolar (FeNiCoCrMn)	-0.262 ± 0.033
No Mn (FeNiCoCr)	-0.297 ± 0.019

ORR $E_{1/2}$ was 35 mV more favorable for Equimolar composition than the no Mn composition

Pt was ~90mV better for ORR

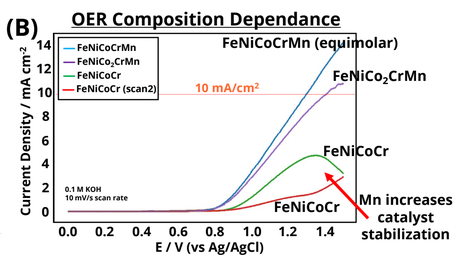
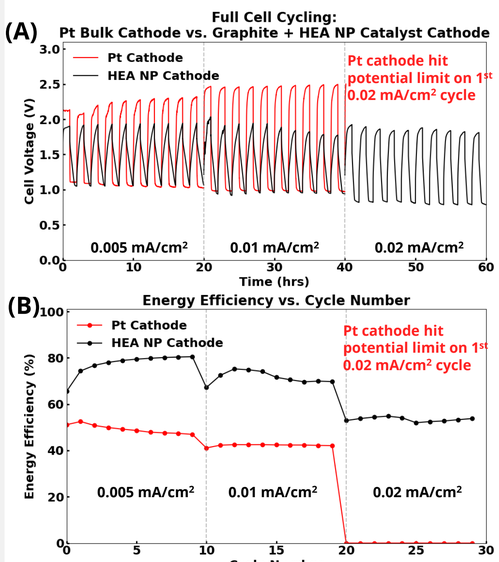


Fig. 3: *HEA NP composition dependance on (A) ORR $E_{1/2}$ and (B) OER onset potential*

Al-Air Full-Cell Cycling Results **Pt cost was >1000x compared to HEA NPs**



Redesigned **secondary Al-air cell** with theoretical capacity of 67 mAh utilizing an Al metal anode, Al-IL electrolyte (Lewis-base additive), and a semi-optimized HEA NP bifunctional OER/ORR catalyst cathode ***reversibly cycled with high energy efficiency (EE%)***.

EE% at 5 μA/cm² over 10 cycles:

Pt Wire: 49.2 ± 1.7% → **28% EE Increase** → **HEA NP Catalyst: 77.4 ± 4.4%**

Fig. 4: *(A) Al-air battery constant current cycling rate test* (0.005 → *0.02* mA/cm^2, 10 cycles each). *(B) Energy efficiency from cycles shown in (A).*

CONCLUSIONS & IMPACT

We have separately demonstrated the various pieces of the Al-air battery and have combined them into a functional secondary Al-air battery system. This will allow room temperature Al-air battery cycling to become and part of the grid as a low-cost energy storage system.

- Newly re-designed test cell allowed full cell cycling experiments
- Al-IL electrolyte paired with Al anode and shown to have high open circuit voltage of ~1.35 V
- Semi-optimized composition HEA NP catalysts performed well compared to a high surface are Pt wire (28% higher EE) and allowed higher current cycling
- Reversible Al-Air full cell cycling demonstrated (>30 cycles)

Impact:

1. Sandia Technical Advance (TA): Percival ,S. J.; Allan-Cole, E.; Blea, M.; "Secondary Aluminum-Ionic-Liquid-Air Battery" SNL TA SD-17369.
2. Paper: Sharma, P.; Chandrasiri, N.; Espano, J. B.; Thapa, A.; Lambert, T.; Percival, S. J.; Wygant, B. R.; Kim, D. Y.; "In situ Raman Spectroscopic Studies of Composition-tuned Nickel Sulfoselenides for the Oxygen Evolution Reaction". *In Review, ACS Catalysis*.
3. Paper: Allan-Cole, E.; Blea, M.; Peretti, A M.; Percival, S. J.; "Novel Secondary Al-air battery with Efficient Recharging utilizing High Entropy Alloy Nanoparticle Bifunctional Electrocatalysts", *In Preparation.*
4. Paper: Richards, D.: Stalcup, M.; Gross, M.; Blea, M.; Valdez, N.; Percival, S. J.; "Electrodeposition of Conformal Aluminum Oxide Precursor Films from a Water In Salt Electrolyte" *In Preparation.*

FUTURE DIRECTIONS

Continued development of this secondary Al-air battery will aim to increase the cycling rates (current density) and access more of the Al-IL capacity in deep charge cycling.

- Understand full cell rate limitations and identify ways to increase current density
- Improve compositions of Al-IL to reduce the interfacial impedance
- Optimize interfacial interactions and mass transport
- Perform long term cycling in full cell (>100 cycles and/or >1000 hours) and evaluate all materials performance over long term cycling
- Increase the capacity utilization of the Al-IL electrolyte

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