Zinc & Lead Batteries*

***(Zn, Pb, Fe, Al multi-valent-based batteries)**

PRESENTED BY

Timothy N. Lambert

DOE-OE Peer Review, Bellevue, Washington, August 7, 2024.

SAND2024-10242C

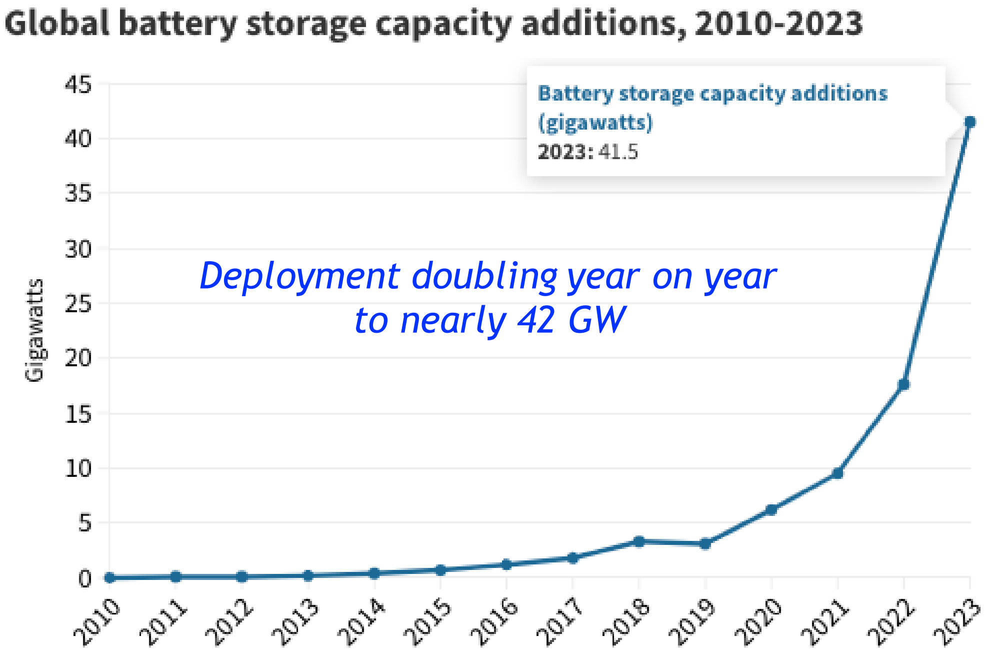
Session OVERVIEW – Zinc & Lead Batteries (Multi-valent)*

OE supports RESEARCH&DEVELOPMENT needs of battery chemistries that can impact Grid Storage: Reliable and resilient electricity system

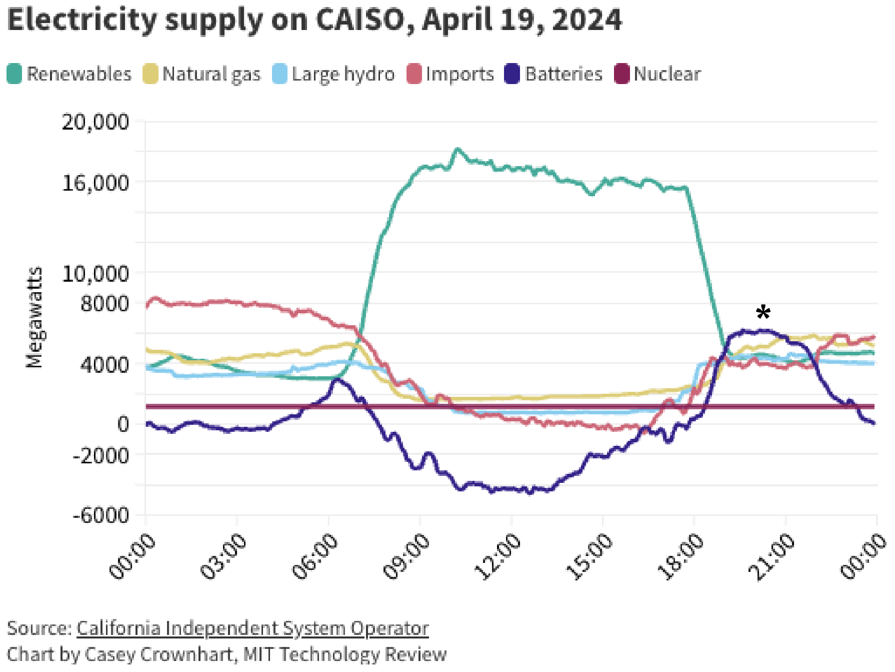
10:05 – 10:20 AM	Program Overview / Zinc & Lead Batteries	Timothy Lambert, *SNL*
10:20 – 10:35 AM	Material Design to Enable Pb Acid Batteries for Long Duration Energy Storage	Tim Fister, *ANL*
10:35 – 10:50 AM	Latest Developments in Mild Acidic Zinc Battery at PNNL	Matt Fayette, *PNNL*
10:50 – 11:05 AM	Earth Abundant Multi-valent Materials for Energy Storage	Stephen Percival, *SNL*
11:05 – 11:20 AM	Molecular Modeling of Gas and Ion Transport in Alkaline Battery Electrolytes	Amalie Frischknecht, *SNL*
11:20 – 11:35 AM	Progress with Manufacturing and Deploying Zn|MnO_2 Batteries for Grid-Scale Applications	Gautam Yadav, *Urban Electric Power*

Battery-based Grid Storage

"Battery storage in the power sector was the fastest-growing commercial energy technology on the planet in 2023"



Deployment doubling year on year to nearly 42 GW



"Batteries are starting to show exactly how they'll play a crucial role on the grid"

* *On April 16, (2024) for the first time, batteries were the single greatest power source on the grid in California during part of the early evening, just as solar fell off for the day.*

10 GW in CA
Playing a part in balancing the grid
(2019 – 1.9 GW on entire grid, ~ 1.1% total)

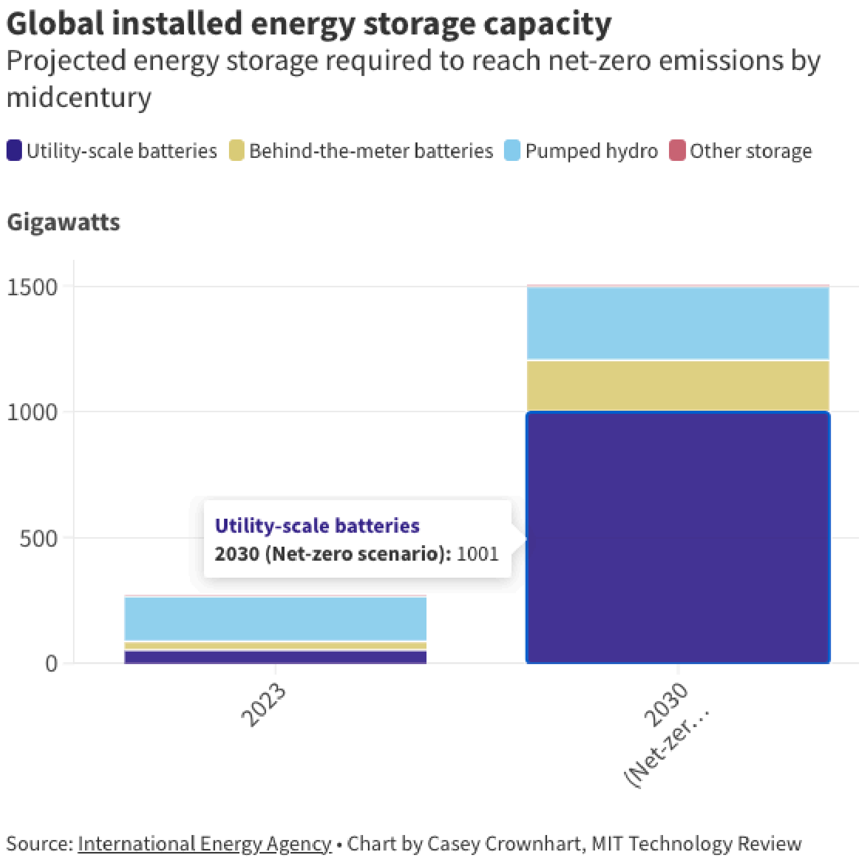
International Energy Agency report calls batteries a "master key"

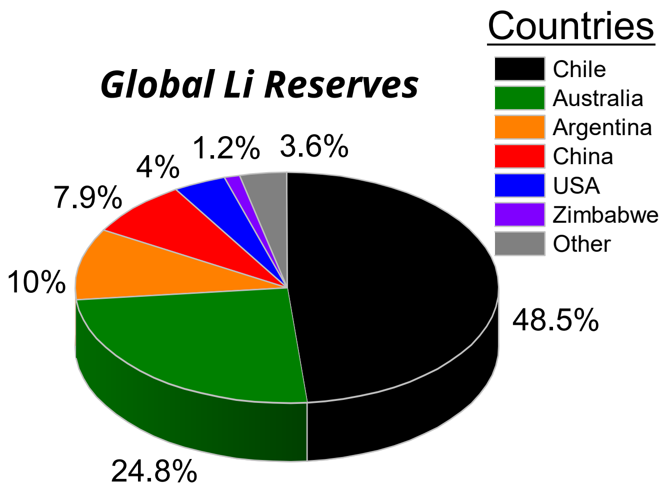
https://www.iea.org/reports/batteries-and-secure-energy-transitions

https://www.technologyreview.com from May 2, 2024

Battery-based Grid Storage

"We need to build a lot more storage"

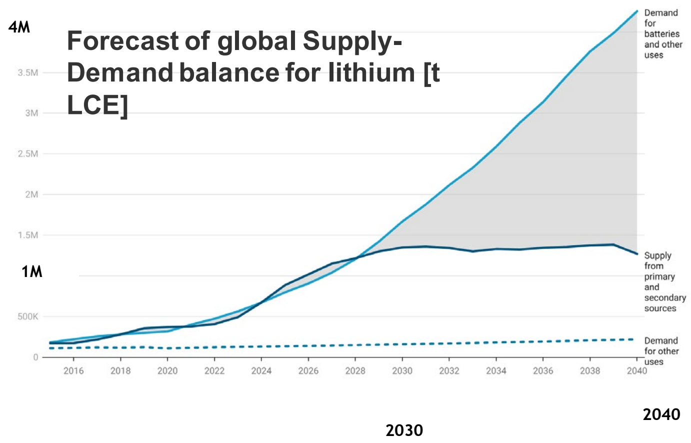


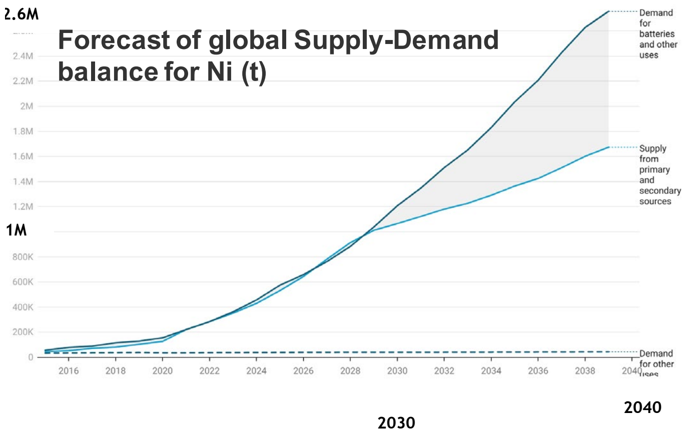


Source: BP Statistical Review of World Energy, 2021

Lithium supply chain issues by ~ 2030 ?

https://rmis.jrc.ec.europa.eu/analysis-of-supply-chain-challenges-49b749





https://www.technologyreview.com from May 2, 2024

https://www.iea.org/reports/batteries-and-secure-energy-transitions

Electrochemical Grid Storage 'Requirements'

- Low cost: < \$100/kWh,
- LDES: Levelized Cost of Storage by 2030: ~ \$0.05/kWh (> 10 h discharge)
- Low-risk components: earth-abundant, minimally processed, available supply chain (in US?)
- Easy to manufacture – roll to roll manufacturing
- Long cycle life: Tens of years of operation
- Safe
- High energy density **

Energy = Voltage (V) x Capacity (mAh/cm^2)

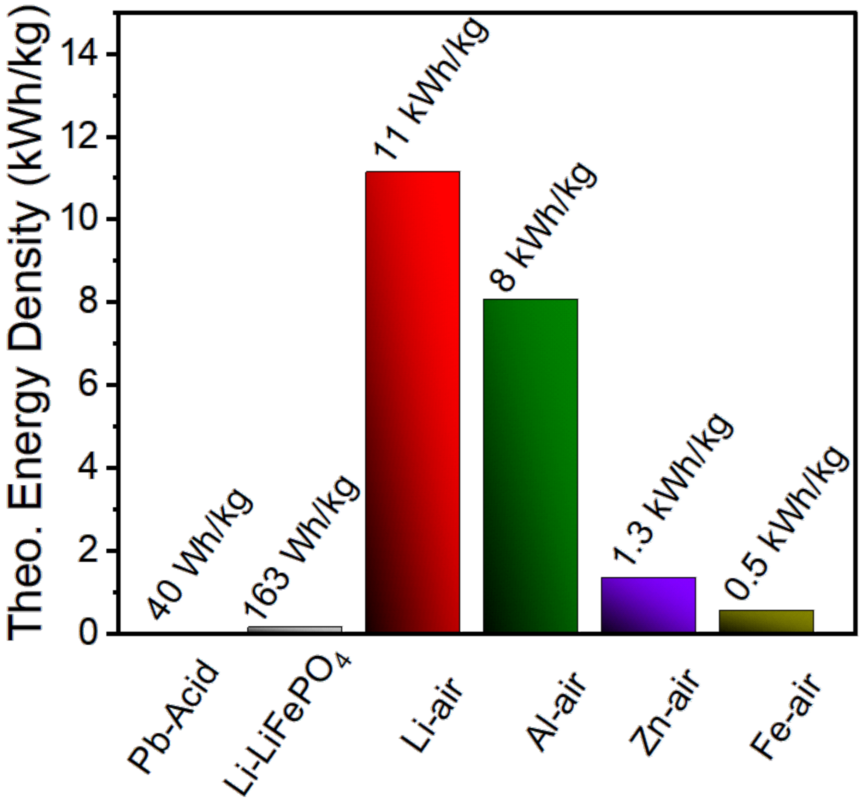
Lower Voltage Systems Require will higher Capacities to be Competitive

Zn/MnO_2 : 15 mAh/cm^2 to achieve similar energy density to a lithium cobalt oxide (LCO) battery with 1-5 mAh/cm^2 active loading

M. B. Lim et al. Rechargeable alkaline zinc-manganese oxide batteries for grid storage: Mechanisms, challenges and developments. doi.org/10.1016/j.mser.2020.100593.

A case for multi-valent Zn, Pb, Fe, Al-based batteries

These Materials have a lot of energy

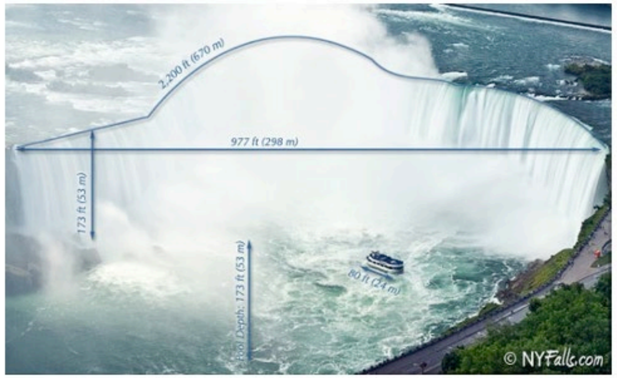


1^0 - Zn/MnO_2

(400 Wh/L ~ \$20/kWh)

Wikipedia, user Aney, 2005

Niagara Falls: 60,000 MWh/day



Anode (*)	**Cost \$M**	GHG Produced ($Mt\ CO_2$)	Volume (m^3)	Mass (tonnes)
Zinc	**93**	1.5	6,200	44,000
Lithium	**370**	6	10,200	5,300
Lead	**230**	4	12,000	120,000

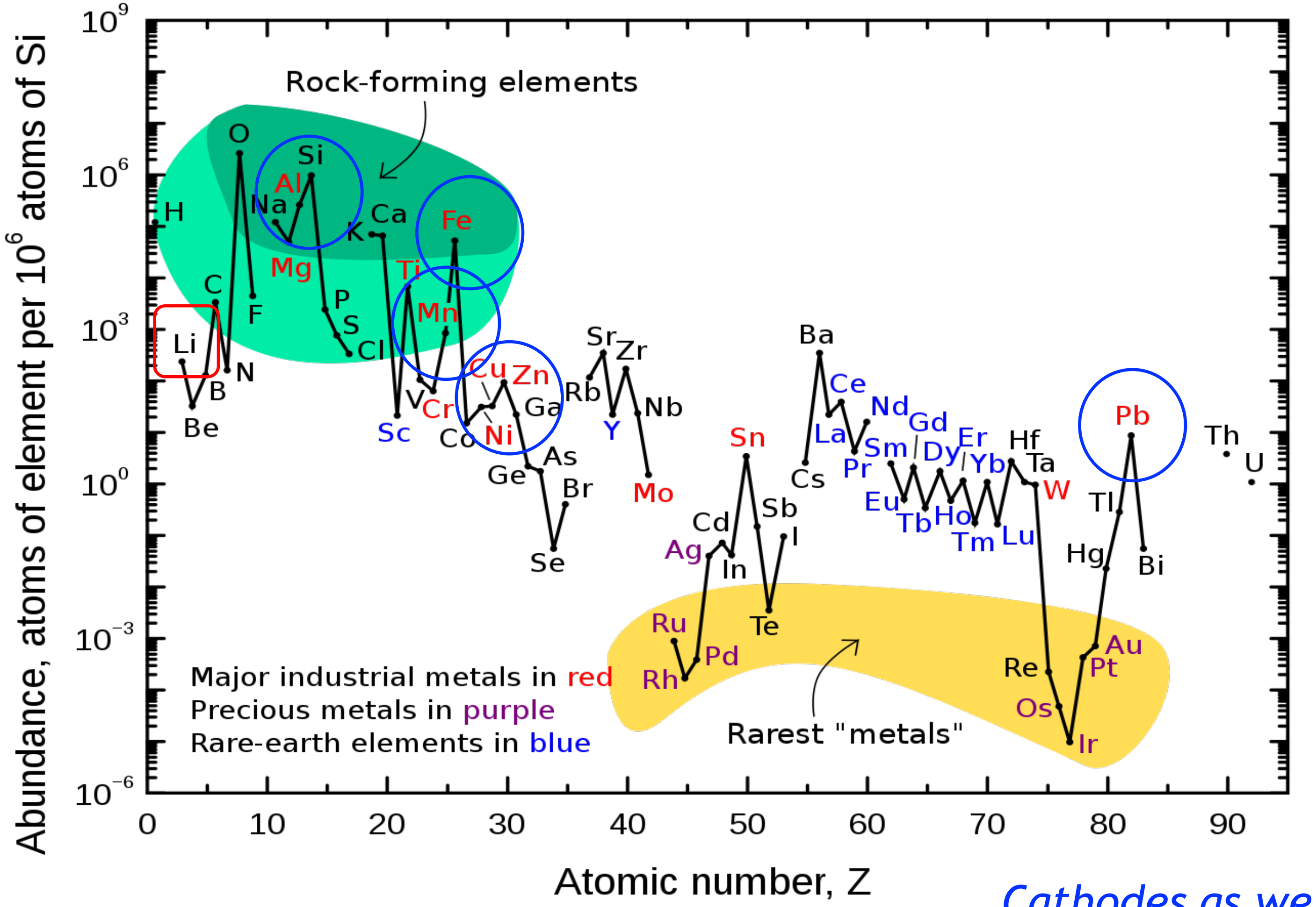
adapted from S. Banerjee et al. DOE-OE Peer Review 2021

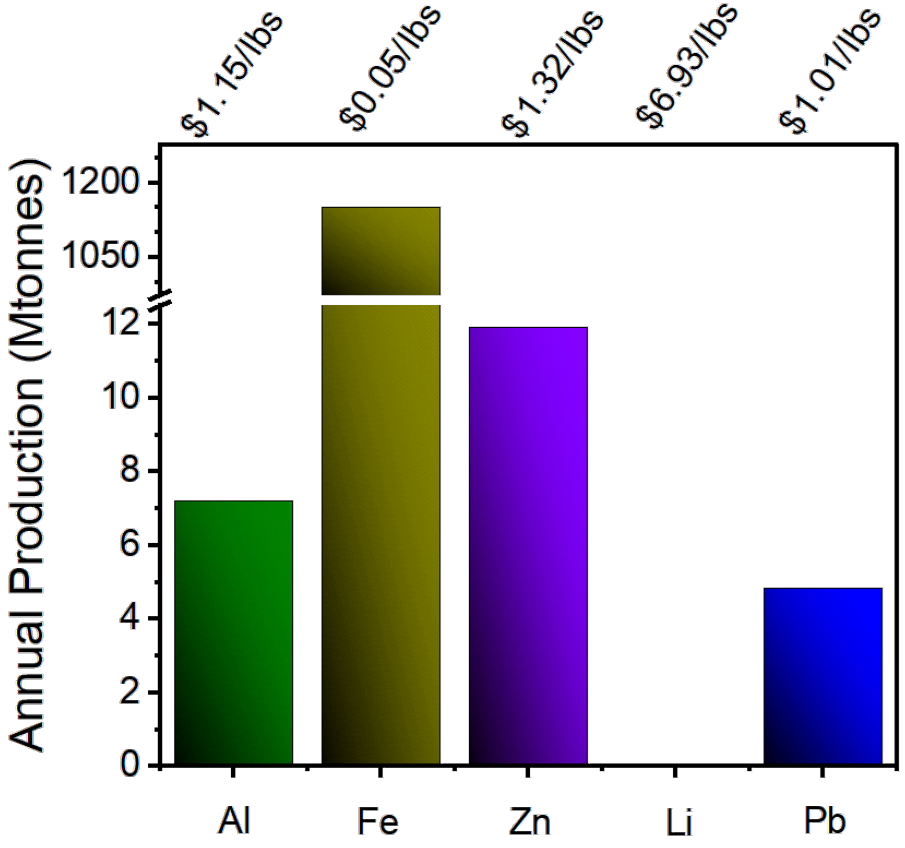
Ahuja *et al.*, *J. Phys.: Conf. Ser*, **2021**, *1913*, 012065

Durmus *et al.*, *Adv. Energy Mater.*, **2020**, *10*, 2000089

A case for multi-valent Zn, Pb, Fe, Al-based batteries

Low Risk Materials that are readily available at low cost





Cathodes as well

https://www.samaterials.com/zinc/1345-zinc-rod-zinc-bar-zn-rodbar.html

Durmus *et al.*, *Adv. Energy Mater.*, **2020**, *10*, 2000089

Rechargeable Zn-based Batteries

- Low-cost, high energy density, safety, and global availability have made Zn-based batteries attractive for more than 220 years!

- *Diverse* Zn-batteries offer a range of properties to meet growing demand across varied applications:

✓ Renewables integration (including microgrids)

✓ Backup power (assurance for data centers, telecom, etc.)

✓ Grid stability and resilience

✓ Behind-the-meter applications for residential and commercial applications (Lower energy cost, power quality, etc.)

Zn-MnO_2

URBAN ELECTRIC POWER

1 MWh UEP alkaline battery backup system for the San Diego Supercomputer Center (CA).

ZĒLOS

Zn-Ni

ZincFive

ZAF Energy Systems

Æsir Technologies, Inc.

ENZINC

Zn-Air

ZINC8

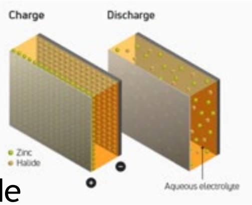
ABOUND an energy solutions company

ZAF Energy Systems

e-zinc

Zn-Br

eos



35 MWh EOS Zn-Br system planned to provide 10 hour storage for solar-plus-storage microgrid with Indian Energy (CA).

redflow

Zn-Br flow battery installation

Zn-ion

SALIENT ENERGY

coulomb TECHNOLOGY

enerpoly

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Zn-MnO_2

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ZĒLOS

$Zn + 2MnO_2 + 2H_2O \rightarrow ZnO + 2MnOOH$
OCV = 1.61 V per cell; Operating V = 1 – 1.5V
Practical Specific Energy Density
~ 90 – 150 Wh/kg
135 – 450 Wh/L

Zn-Ni

ZincFive

ZAF Energy Systems

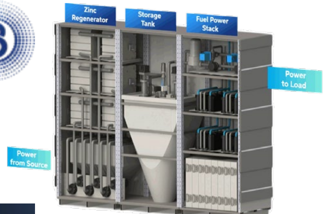
Æsir Technologies, Inc.

ENZINC

$Zn + 2NiOOH + 2H_2O \rightarrow Zn(OH)_2 + Ni(OH)_2$
OCV per cell = 1.73V; Operating V = 1.2-1.6V
Practical Specific Energy Density
~ 70 – 150 Wh/kg
200 – 450 Wh/L

Zn-Air

ZINC8



ZAF Energy Systems

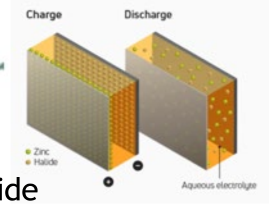
e-zinc

$Zn + 1/2O_2 \rightarrow ZnO$
OCV = 1.65 V per cell; Operating V = 0.9 – 1.4V
Practical Specific Energy Density
~ 100 – 400 Wh/kg
135 – 1000 Wh/L

High utilization of capacity
Bidirectional oxygen electrocatalysis remain challenging

Zn-Br

eos



35 MWh EOS Zn-Br system planned to provide 10 hour storage for solar-plus-storage microgrid with Indian Energy (CA).

redflow

Zn-Br flow battery installation

$Zn + Br_2 \rightarrow ZnBr_2$
OCV = 1.85 V per cell; Operating V = 1 – 1.8V
Practical Specific Energy Density
~ 65 – 75 Wh/kg
60 – 70 Wh/L

Zn-ion

SALIENT ENERGY

coulomb TECHNOLOGY

IMPRINT ENERGY

Printed Energy

enerpoly

$Zn + MO_x \rightarrow ZnMO_x$
OCV = 1.60 V per cell; Operating V = 1 – 1.5V
Practical Specific Energy Density
~ 80 – 150 Wh/kg
200 – 450 Wh/L

Values from: Josef Daniel-Ivad, International Zinc Association, WVU Zinc Battery Supply Chain Workshop Presentation

Rechargeable Zn-based Batteries

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Zn-MnO_2

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ZĒLOS

Zn-Ni

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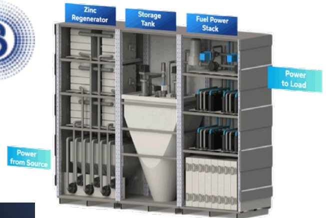
ENZINC

Zn-Air

ZINC8

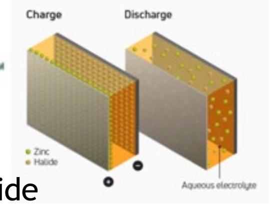


ZAF Energy Systems

e-zinc

Zn-Br

eos



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redflow

Zn-Br flow battery installation

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SALIENT ENERGY

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IMPRINT ENERGY

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enerpoly

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Latest Developments in Mild Acidic Zinc Battery at PNNL

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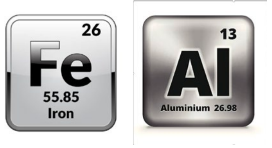
Progress with Manufacturing and Deploying Zn|MnO_2 Batteries for Grid-Scale Applications



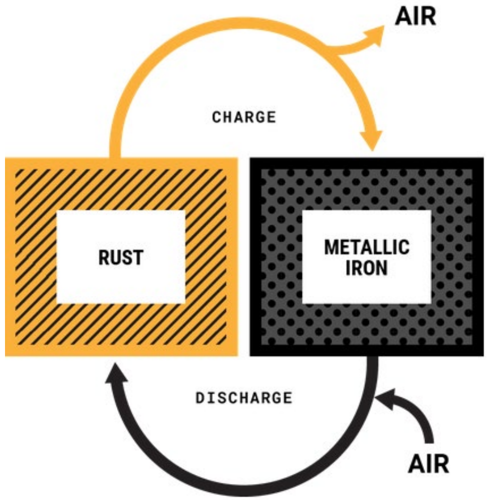
Rechargeable Fe or Al-based Batteries

- Commercialization of Fe and Al batteries
- Long Duration Energy Storage Applications – economical with earth abundant materials

Fe-air

(The 100 h battery)

Form energy



Forms Rust, Electrochemical 'un-rusting' utilizing excess PV/Wind

$3Fe + 2O_2 \rightarrow Fe_3O_4$

Theo V = 1.28 V per cell

Practical Specific Energy Density

~ 50-75 Wh/kg

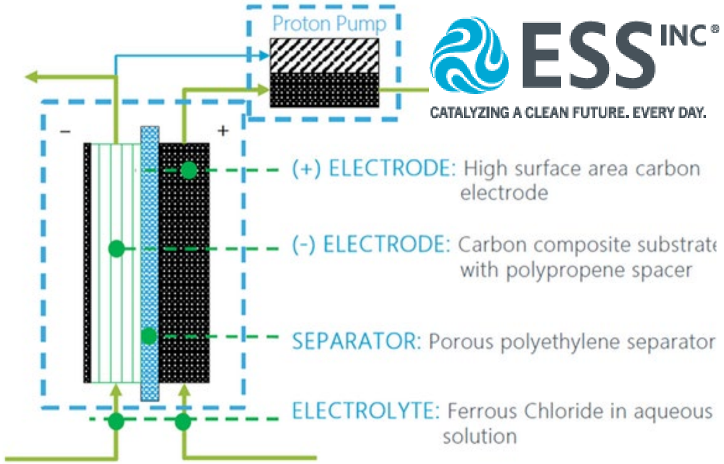
HER upon charge, poor discharge rate due to $Fe(OH)_2$, air cathode ?

https://doi.org/10.1002/cplu.201402238

https://formenergy.com/technology/battery-technology/

Fe Flow

ESS INC® CATALYZING A CLEAN FUTURE. EVERY DAY.



The ESS iron flow battery uses the same electrolyte on both positive and negative sides. And the proton pump maintains the state of charge and battery health.

Based on Ferrous and Ferric chloride

"ESS iron flow chemistry delivers 25 years or more with no capacity fade or degradation."

$3\ Fe^{2+}{}_{(aq)} \rightarrow 2\ Fe^{3+}{}_{(aq)} + Fe0_{(s)}$

Max V = 1.21 V per cell

Practical Specific Energy Density

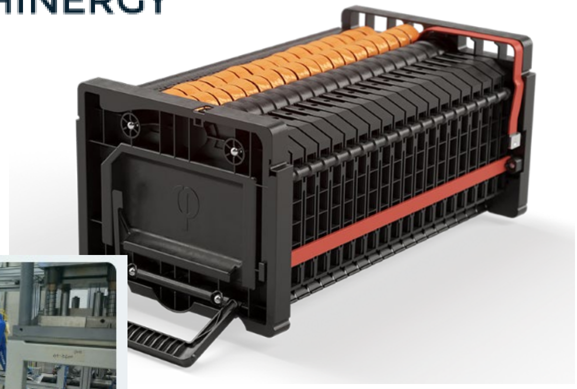
~ 20 Wh/L

Crossover, Air oxidation, pH, plating

https://essinc.com/iron-flow-chemistry/

Al-air (& Zn-air)

PHINERGY



Phinergy launches its new automated production line, capacity will reach up to 10,000 backup systems per year

Pure Al corroded by Electrolyte, $$ catalyst, recharge ?

Forms Alumina Hydroxide , later re-processed

$4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3$

OCV = 1.2 V per cell; ~ 0.7 V in saltwater

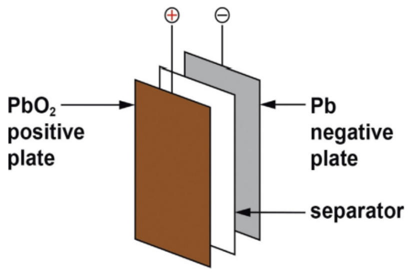
Practical Specific Energy Density

~ 1300 Wh/kg

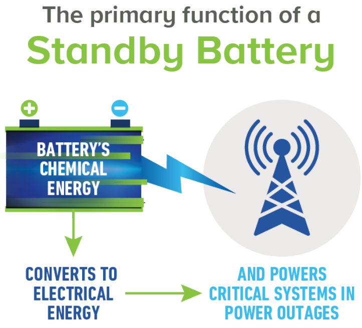
https://phinergy.com/

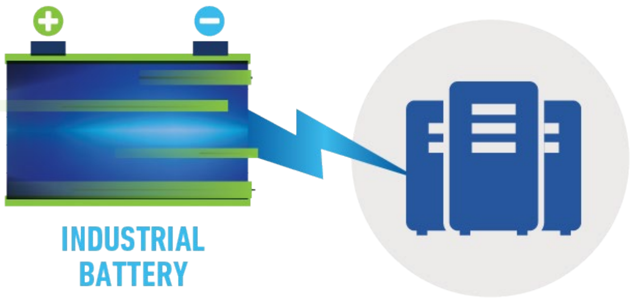
Rechargeable Pb-based Batteries

- First invented in 1859, large industry - (Provide about 45% of the world's rechargeable power)*
  $52.1 billion in 2022
- Large-format lead-acid designs are widely used for storage in backup power supplies in cell phone towers, high-availability emergency power systems like hospitals, and stand-alone power systems



$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$$





*https://batterycouncil.org/

Successful recycling program

Improve energy density, low temperature performance, cycle life, charging efficiency, rates

Installed 2012, Lead-based Ultra-battery used for frequency regulation at Lyon Station, Pennsylvania
3.6 MW power capability

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

OCV = 2.1 V per cell; Operating V = 1.8-2.1 V
Practical Specific Energy Density
~ 35-40 Wh/kg
~ 100 Wh/L

Material Design to Enable Pb Acid Batteries for Long Duration Energy Storage Tim Fister, *ANL*

G. May et al. Lead batteries for utility energy storage: A review. J. Energy Storage 15 (2018), 145-147.
Y. Zhang et al. Advances and challenges in improvement of electrochemical performance for lead-acid batteries: A comprehensive review J. Power Sources (2022) 520, 230800

Storage Innovations 2030 – Technology Strategy Assessments

Storage Innovations 2030 (SI 2030) goal is a program that helps the Department of Energy to meet Long-Duration Storage Shot targets.

These targets are to achieve 90% cost reductions by 2030 for technologies that provide 10 hours or longer of energy storage.

On July 19, 2023, DOE released a series of technical reports summarizing and analyzing the results from the SI 2030 stakeholder engagement process, including SI Flight Paths and SI Framework, as detailed in the Methodology report.

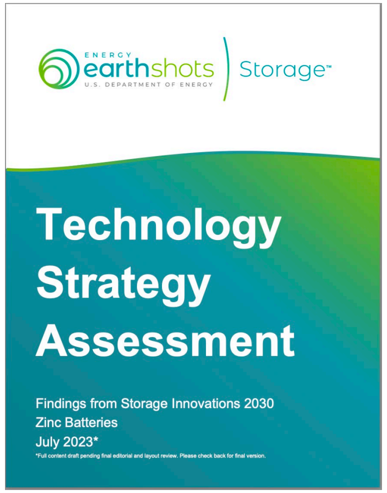
These reports are opportunities to explore promising RD&D pathways to substantially lower the costs of long-duration energy storage.

Precompetitive Energy Storage Technology Liftoff

Energy Storage Demonstration and Validation

Released July 19, 2023, DOE

- Methodology Report
- Lithium-ion Batteries Technology Strategy Assessment
- Lead-acid Batteries Technology Strategy Assessment
- Flow Batteries Technology Strategy Assessment
- Zinc Batteries Technology Strategy Assessment
- Sodium Batteries Technology Strategy Assessment
- Pumped Storage Hydropower Technology Strategy Assessment
- Compressed-Air Energy Storage Technology Strategy Assessment
- Thermal Energy Storage Technology Strategy Assessment
- Supercapacitors Technology Strategy Assessment
- Hydrogen Storage Technology Strategy Assessment

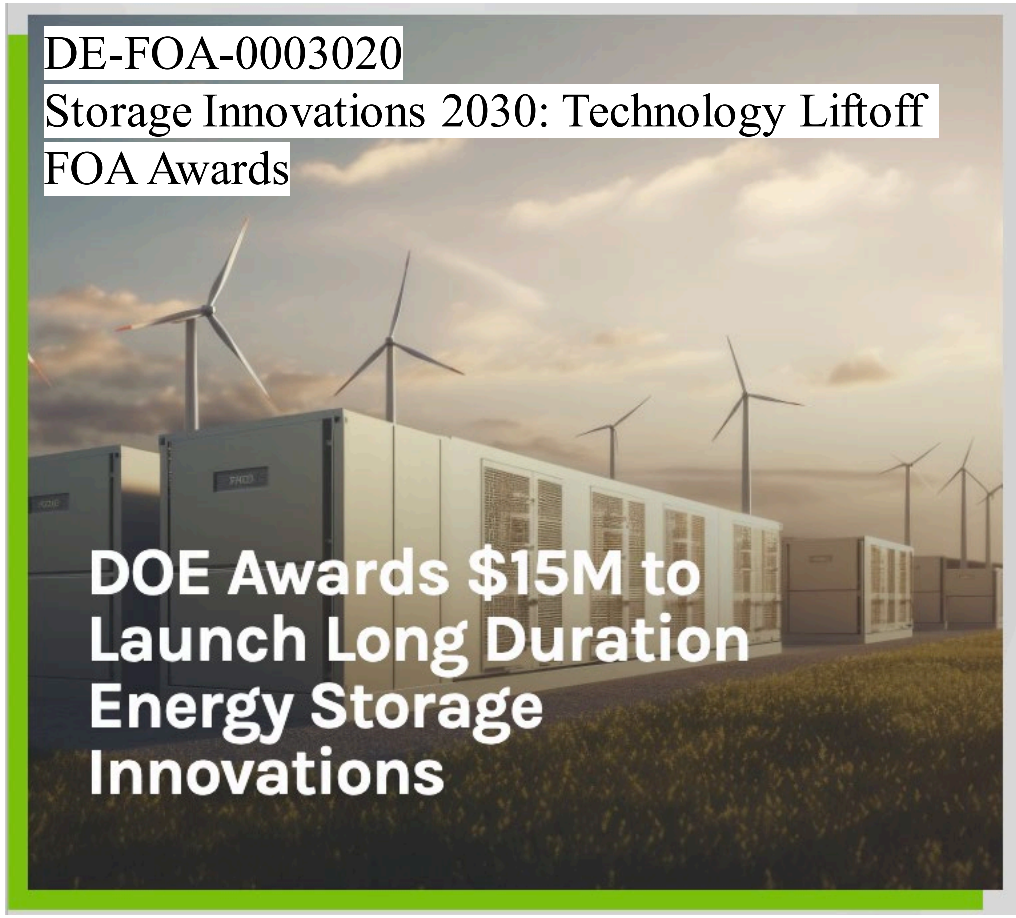


Technology Liftoff: LDES: Pathways to LCOS of $0.05/kWh

ESGC: To enable long-duration energy storage technologies through durable research partnerships

Selections Announced April 8, 2024

"Pre-competitive R&D" includes activities that are of interest to multiple or all entities in the partnership. Such activities should propel an entire technology industry forward, and the outputs of this work should provide value to all participating members of the partnership.



The following projects have been selected:

- **Newlab, LLC**
  - Project Title: *Enabling high-capacity **Zinc** utilization through electrode and electrolyte fundamentals*
  - Federal share: $4,992,570
- **Battery Council International**
  - Project Title: *Consortium for **Lead** Battery Leadership in LDES*
  - Federal share: $4,972,746
- **Clean Tech Strategies LLC**
  - Project title: *Pre-Competitive Research & Development to Accelerate the Maturation of **Flow Battery Technologies** into Cost-Effective Long Duration Energy Storage*
  - Federal share: $5,000,000

https://www.energy.gov/oe/articles/doe-awards-15m-launch-innovations-long-duration-energy-storage-earthshot

POSTERS – Zinc & Lead Batteries

OE supports RESEARCH&DEVELOPMENT needs of battery chemistries that can impact Grid Storage: Reliable and resilient electricity system

Stabilizing Zn Anodes by Molecular Interface Engineering with Amphiphilic Triblock Copolymer	Xingbo Li, *WVU*
Mapping electrode and acid speciation in lead batteries using powder X-ray diffraction	Tiffany Kinnibrugh, *ANL*
Interrogation of Pb-acid battery performance using ultrasonic techniques	Tim Officer, *UC*
Investigation of Calcium Zincate ($Ca[Zn(OH)_3]_2 \cdot 2H_2O$) Cycling Performance for Rechargeable Alkaline Zinc Batteries	Patrick Yang, *CCNY*
Sr-doped barites for enhanced nucleation in lead-acid batteries	Colin Campbell, *PNNL*
Zn-Air Batteries for Long-Duration Energy Storage	Ruhul Amin, *ORNL*
Inhibiting the Formation of Zinc Hydroxy Sulfate for High-Performance Aqueous Zn Batteries by stabilizing the pH of electrolyte	Wonkwang Lim, *PNNL*
Flowing Zinc-Air Batteries Enabled by Nickel Sulfoselenide Oxygen Electrocatalysts	Bryan Wygant, *SNL*
Electrochemical Cycling of Zinc in Mildly Acidic, Acetate-Based Electrolytes for Zinc-ion Batteries	Debayon Dutta, *CCNY*

PROJECT CONTACTS

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David Arnot

Rachel Habing

Ciara Wright

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AND
OUR MANY COLLABORATORS!

This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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OE supports RESEARCH&DEVELOPMENT needs of battery chemistries that can impact Grid Storage: Reliable and resilient electricity system

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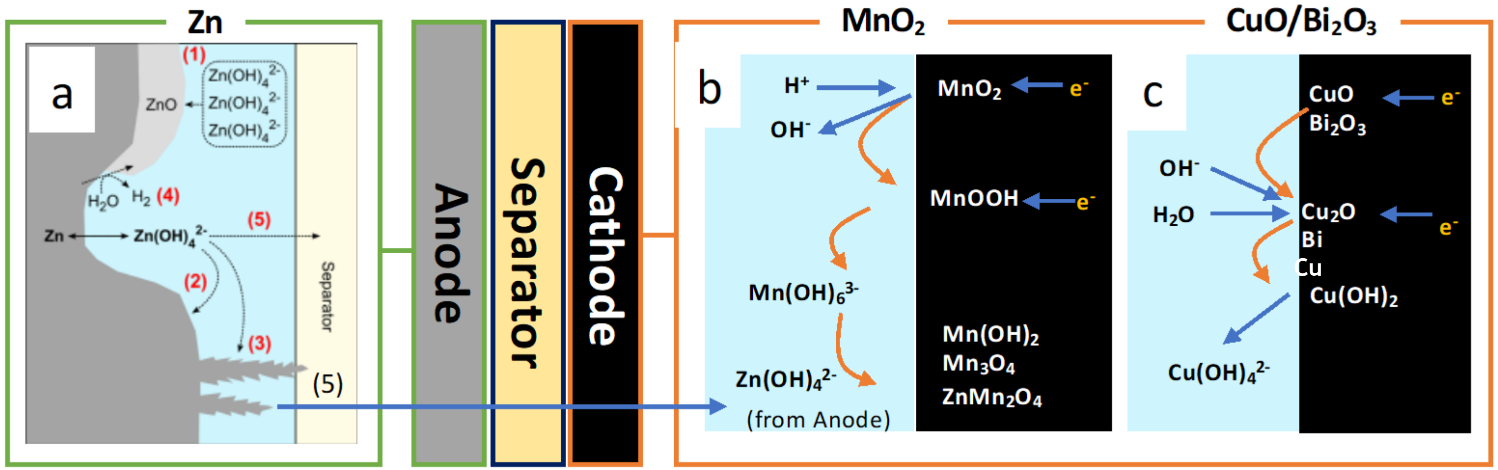
Thank. you

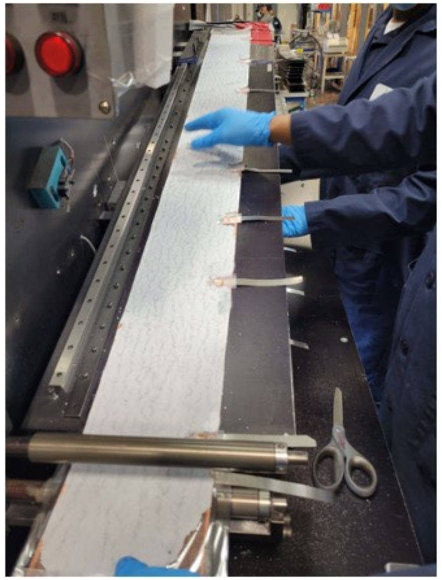
DOE OE: Low Cost Aqueous Batteries based on Zinc

***Program Objective*: Develop the understanding, materials, methods, components & technologies to enable low cost Zn-based batteries for grid and long duration energy storage**

- Zinc-based batteries offer an energy dense, safe and readily manufacturable technology
- OE Funded Project collaboratively investigates new materials and chemistries while supporting technology maturation and US manufacturing
- Zn/(1e-)MnO_2, Zn/(2e-)Bi,Cu-MnO_2, Zn/(2e-)Bi-CuO, Zn/Ni, Zn/air, Zn-ion.



Adapted from *"A Critical Comparison of Mildly Acidic versus Alkaline Zinc Batteries"* *Acc. Mater. Res. 2023 4, 4, 299-306.*



Photos provided by UEP

Sandia National Laboratories; CUNY The City University of New York Energy Institute; NM State University; Lawrence Livermore National Laboratory; URBAN ELECTRIC POWER; U.S. DEPARTMENT OF ENERGY

OE program focuses on increased understanding/performance at lower cost and increased safety

Zn Project Team – Sandia National Laboratories and Collaborators

Sandia National Laboratories

Timothy Lambert

Stephen Budy, Matthew Lim, Igor Kolesnichenko, Noah Schorr, David Arnot, Rachel Habing, Logan Ricketts, Elijah Ruiz, Nelson Bell, Ciara Wright, Bryan Wygant

Alkaline Batteries for Grid Storage

Stony Brook University

Prof. Esther Takeuchi

Amy Marschilok, Ken Takeuchi

Advanced Materials for Next Generation Batteries

CUNY The City University of New York Energy Institute

Prof. Sanjoy Banerjee

Damon Turney, Michael D'Ambrose, Junsang Cho, Brendan Hawkins, Snehal Kolhekar, Michael Nyce, Xia Wei, Prof. Rob Messinger

Stable Zinc Anodes for High-Energy-Density Rechargeable Aqueous Batteries

URBAN ELECTRIC POWER

Gabe Cowles

Gautam Yadav

Gabe Cowles, Gautam Yadav, Jinchao Huang, Aditya Upreti, Meir Weiner, Sanjoy Banerjee

Advanced Manufacturing Research

NM STATE UNIVERSITY

Prof. Igor Vasiliev

Birendra A. Magar, Nirajan Paudel

Theoretical Studies of the Electrochemical Behavior of Solid-State Cathode Materials

Membrane Modeling

Sandia National Laboratories

Amalie Frischknecht

Lawrence Livermore National Laboratory

Cheng Zhu

3D electrodes for rechargeable Zn-MnO_2 batteries

Tony Van Buuren

Prof. Joshua Gallaway

Andrea Bruck, Matthew Kim, Erik Zimmerer, Yogeshwaran Agilan

Understanding Phase Change Processes of Energy Storage Materials

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Ryan Hill, Andrew Meyer

Zn-ion Batteries

Prof. Nian Liu

Collaborative research to advance solid state ion conductors for emerging batteries [w/Erik Spoerke (SNL)]

Zn-air

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