Pacific Northwest
NATIONAL LABORATORY

Advancing Zn- and Pb-based Batteries for a Safe and Reliable Grid

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Presentation 700

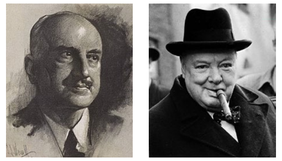
DOE-OE Peer Review
Oct. 25, 2023

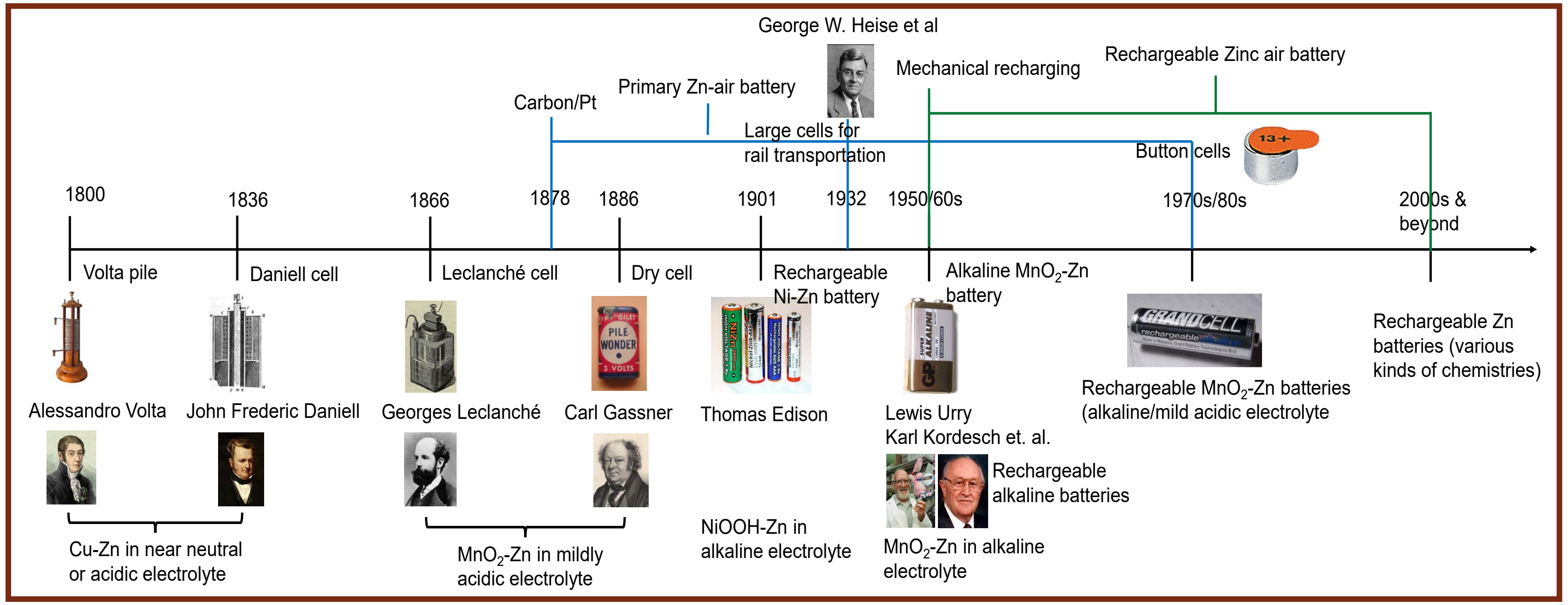
U.S. DEPARTMENT OF ENERGY BATTELLE

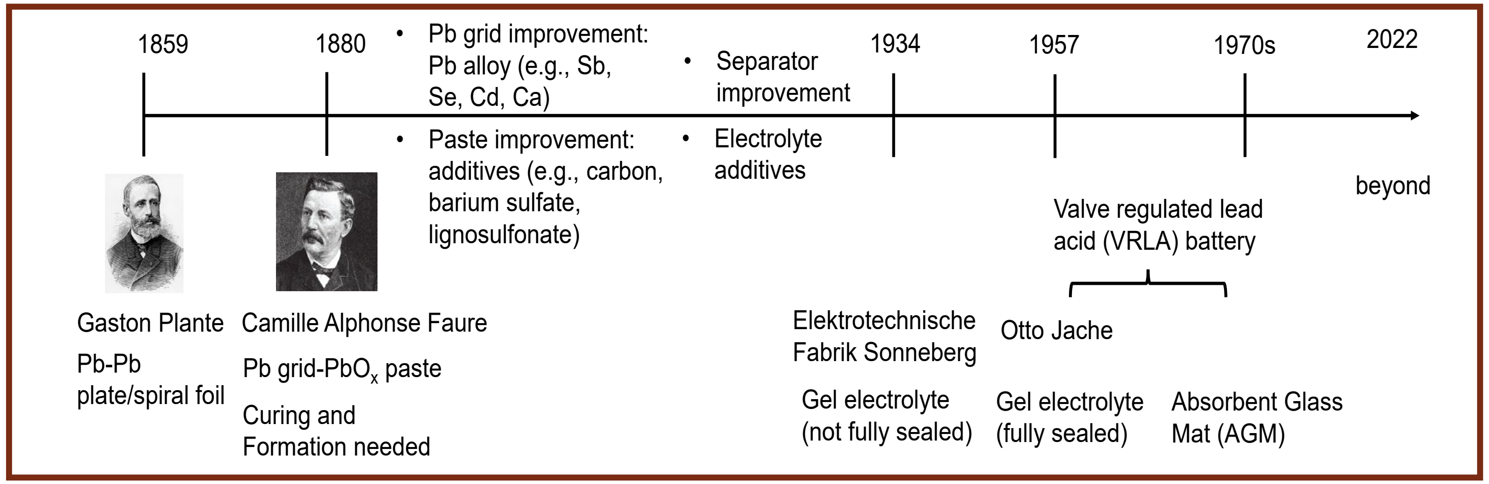
"Learning from history & moving forward"

"Those who cannot remember the past are condemned to repeat it."
George Santayana
The Life of Reason, 1905

"Those that fail to learn from history are doomed to repeat it."
Winston Churchill



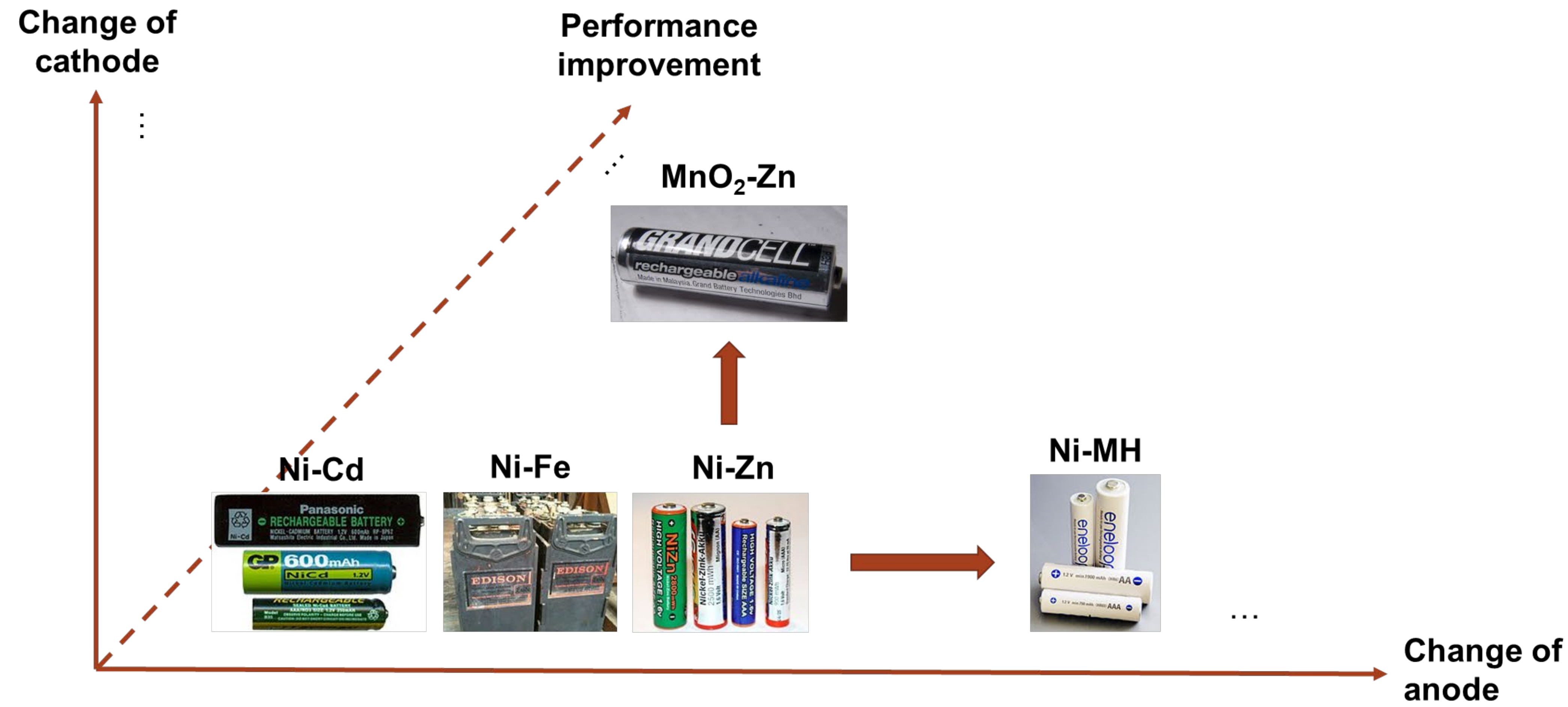




What can we do differently to help move battery technologies forward?

https://www.helios-h2020project.eu/news/batteries-long-history-powerful-future
https://silo.tips/download/a-brief-history-of-batteries-and-stored-energy
Martin Winter, Brian Barnett, Kang Xu, Chem. Rev. 2018, 118, 11433-11456

Rechargeable aqueous batteries: Technology evolution



Lead acid

There isn't a perfect battery.

There are various routes towards "better" batteries.

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Rechargeable aqueous batteries: Technology sheet

Status	Ni-Cd	Ni-Fe	Ni-Zn	Ni-MH	MnO_2-Zn*	Lead acid
Energy density	~40-60 Wh/kg ~50-150 Wh/L	~20-25 Wh/kg ~30 Wh/L	~100 Wh/kg ~280 Wh/L	~60-120 Wh/kg ~140-300 Wh/L	~150 Wh/kg ~400 Wh/L	~35-40 Wh/kg ~80-90 Wh/L
Voltage	~1.2V	~1.2V	~1.6V	~1.2 V	~1.5V	~2.1V
Self-discharge	~10-20%/month, improved to ~1-2%/month	~20-30%/month	Increase after ~50 cycles, ~2-3%/month	~30-50%/month Improved to ~0.1-3%/month	~1%/month	~3-20%/month Improved to ~0.1-3%/month
Lifetime	~2000 cycles	>20 years durability	~800 cycles @80% DOD	~2000 cycles	Tens of cycles (deep), 500+ (shallow)	~800-1000 deep cycle
Material sustainability & environment impact	Relatively expensive Toxic (EU restricted sales in 2006) Recycle (?)	High cost of manufacture Less toxic Recycle (?)	Cost effective Less toxic Recycle (?)	Cost effective Less toxic Recycle (?)	Cost effective, Less toxic Recycle (?)	Cost effective Toxic Recycle

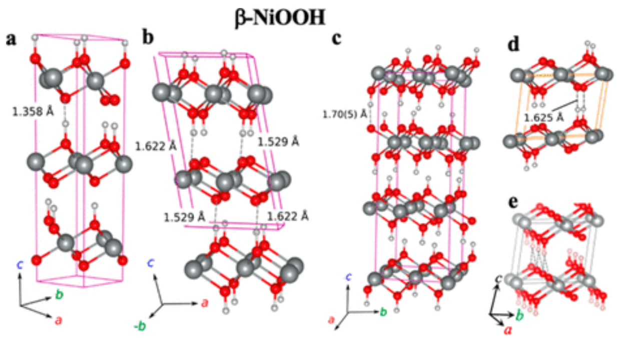
A new battery technology must benchmark against existing technologies (e.g., lead acid, Li-ion)

What are the "primary" features of rechargeable aqueous batteries?

- Cost effective and relatively safe
- Rechargeability at deep cycling
- Self-discharge
- Gassing

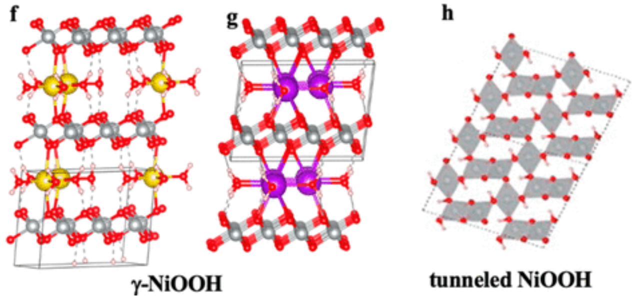
Rechargeable aqueous batteries: Chemistries & electrochemistries

Batteries	Redox reactions: Negative	Redox reactions: Positive	Redox reactions: Total reaction	Parasitic reactions	Rechargeability (Lifetime)
Lead acid	$Pb + HSO^{-}_{4} \rightleftharpoons PbSO_4 + H^+ + 2e^-$	$PbO_2 + HSO^{-}_{4} + 3H^+ + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$	Parasitic reactions: Gassing $M + 2H_2O \rightleftharpoons M(OH)_2 + H_2$ $H_2O \rightleftharpoons H^+ + OH^-$ Electrolyte instability/saturation $Zn(OH)_4^{2-} \rightleftharpoons Zn(OH)_2 + 2OH^-$ $Zn(OH)_2 \rightleftharpoons ZnO + H_2O$ Electrode passivation $PbSO_4$, $Fe(OH)_2$, $Cd(OH)_2$ Electrode dissolution $2MnO(OH) \rightleftharpoons MnO_2 + Mn^{2+} + 2OH^-$	500 deep cycle
Ni-Cd	$Cd + 2OH^- \rightleftharpoons Cd(OH)_2 + 2e^-$	$2NiO(OH) + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^-$	$2NiO(OH) + Cd + 2H_2O \rightleftharpoons 2Ni(OH)_2 + Cd(OH)_2$		~2000 cycles
Ni-Fe	$Fe + 2OH^- \rightleftharpoons Fe(OH)_2 + 2\,e^-$	$2NiO(OH) + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^-$	$2NiO(OH) + Fe + 2H_2O \rightleftharpoons 2Ni(OH)_2 + Fe(OH)_2$		>20 years durability Only slow charge/discharge
Ni-Zn	$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$	$2NiO(OH) + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^-$	$Zn + 2NiO(OH) + H_2O \rightleftharpoons ZnO + 2Ni(OH)_2$		~800 cycles @80% DOD
Ni-MH	$OH^- + MH \rightleftharpoons H_2O + M + e^-$	$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$	$NiO(OH) + MH \rightleftharpoons Ni(OH)_2 + M$		180-2000 cycles
MnO_2-Zn* (alkaline)	$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$	$2MnO_2 + 2H_2O + 2e^- \rightleftharpoons 2MnO(OH) + 2OH^-$	$Zn + 2MnO_2 + H_2O \rightleftharpoons ZnO + 2MnO(OH)$		Tens of cycles (deep), 500+ (shallow)



Limited rechargeability (lifetime) of batteries at high DOD:

- **Proton/H_2O involvement**
- **Electrode phase transition**
- **Passivation/limited solubility of the intermediate/final products**
- **Electrode catalytic effect**

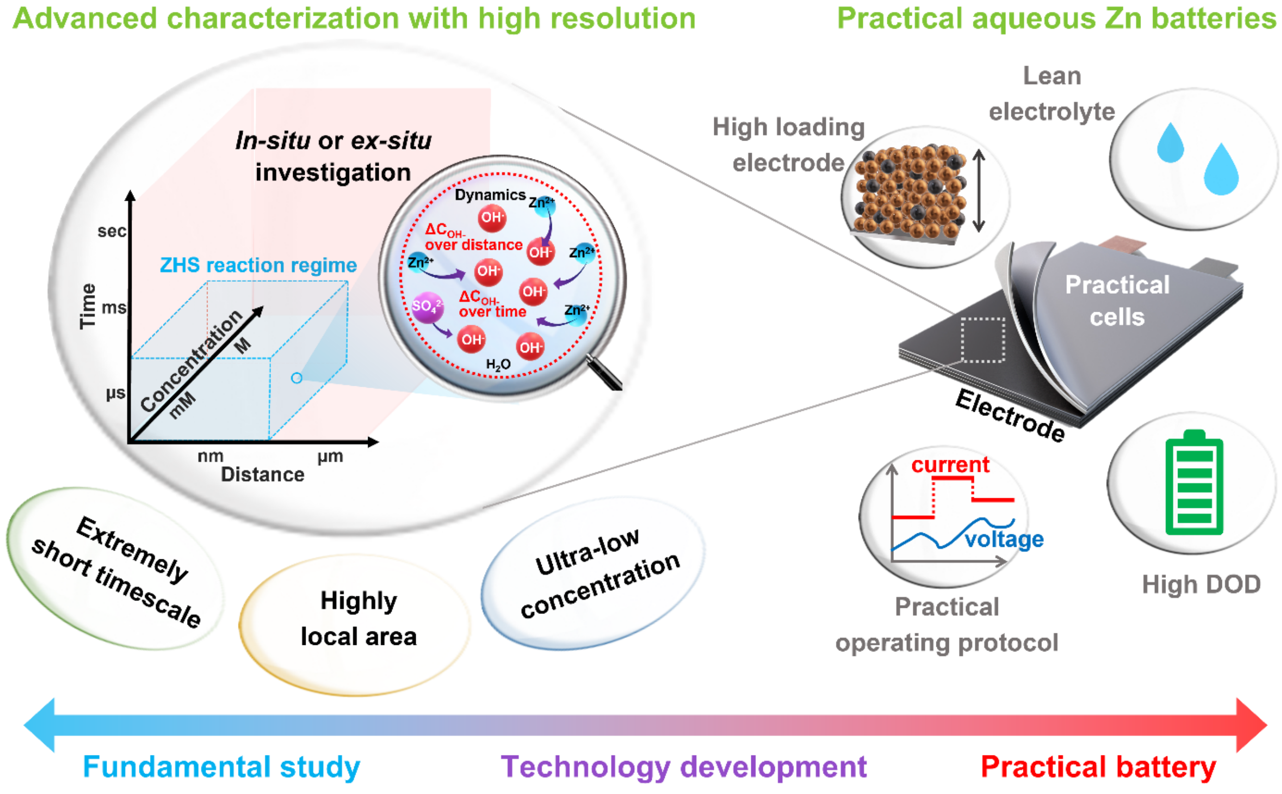


Y.-F. Li, et al. *J. Phys. Chem. C* 2021, 125, 27033.

Next chapter for Pb & Zn batteries

Objectives: Improve the rechargeability of Zn batteries and prolong the cycle life of deep cycle Pb batteries under practical grid duty cycles.

For fundamental study: the knowledge obtained in model systems needs to be transferable to practical batteries.



For technology development: material/manufacturing cost needs to be considered after concept demonstration

Electrolyte

- Electrolyte-electrode interaction

Cathode

- “Intercalation” or “regenerable” cathodes (?)

Anode

- “Intercalation” or “regenerable” anodes (?)

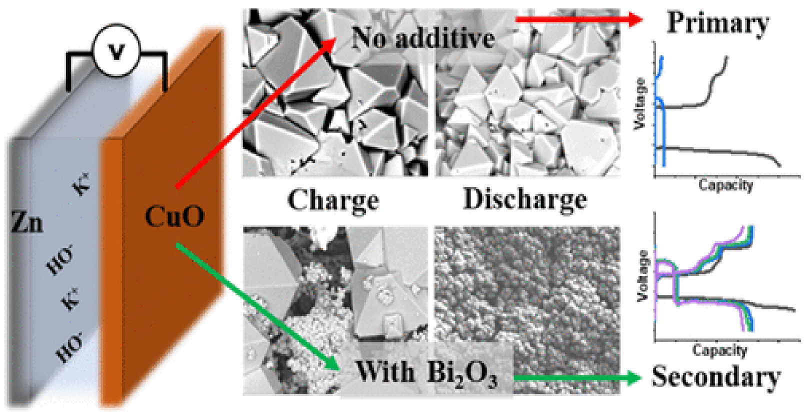
New chemistry/battery design

The leap of technology can be achieved with a thorough understanding of the mechanism & advanced characterization of the key components.

W.-G. Lim, et al. *Small. Methods* 2023, DOI: 10.1002/smtd.202300965

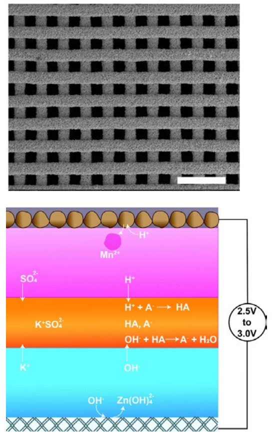
Research status

CuO cathode

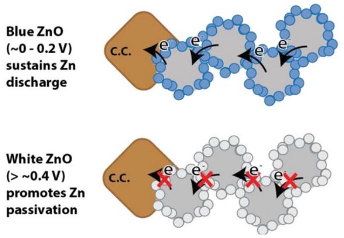


N. B. Schorr, et al. *ACS Appl. Energy Mater.* 2021, 4, 7073

3D Zn



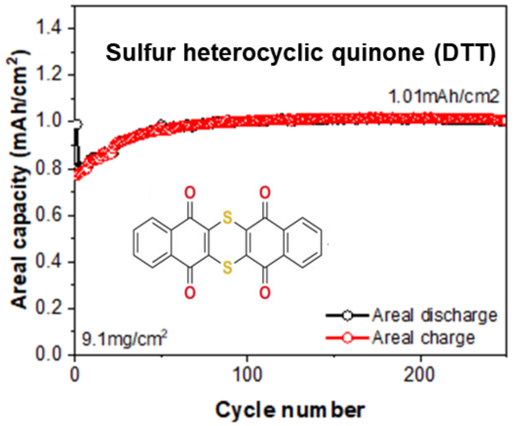
Electroactive ZnO

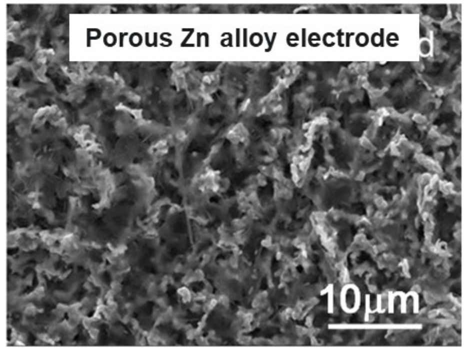


Gelled membrane-less Zn-MnO$_2$ battery

C. Zhu, et al. Small Struct. 2023, 4, 2200323
G. G. Yadav, et al., Mater. Horiz. 2022, 9, 2160
B. E. Hawkins, et al. *Adv. Energy Mater.* 2022, 12, 2103294.

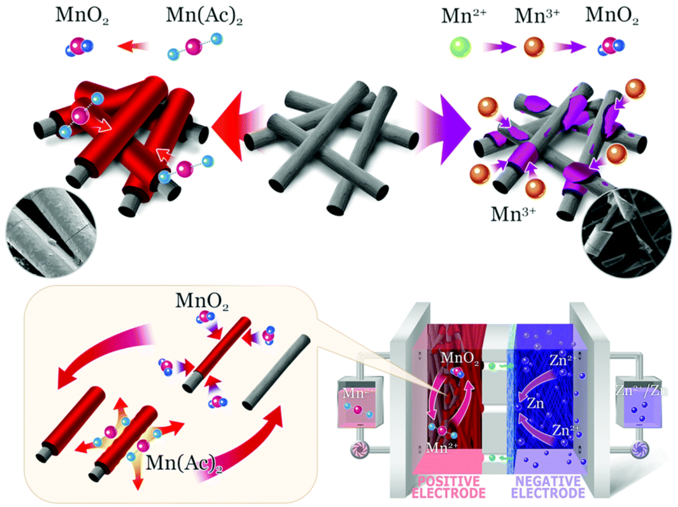
"Intercalation" cathode & alloy anode





M. Fayette, et al. *ACS Energy Lett.* 2022, 7, 1888
H.K. Han, et al. in preparation

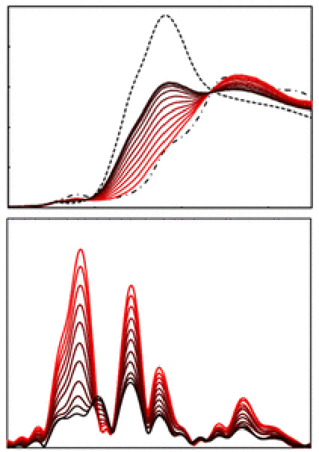
Flow design



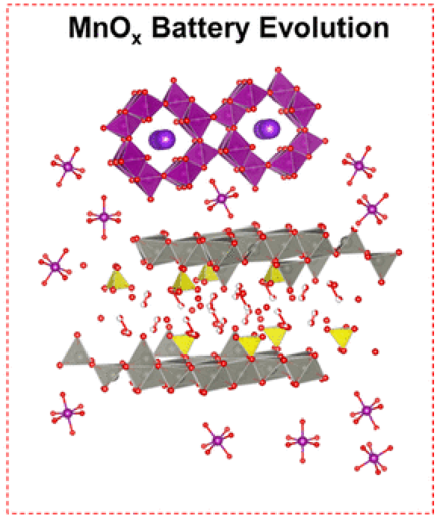
C.X. Xie, et al. *Energy Environ. Sci.* 2020, 13, 135.

Understanding the Mn redox reactions

Operando XAS

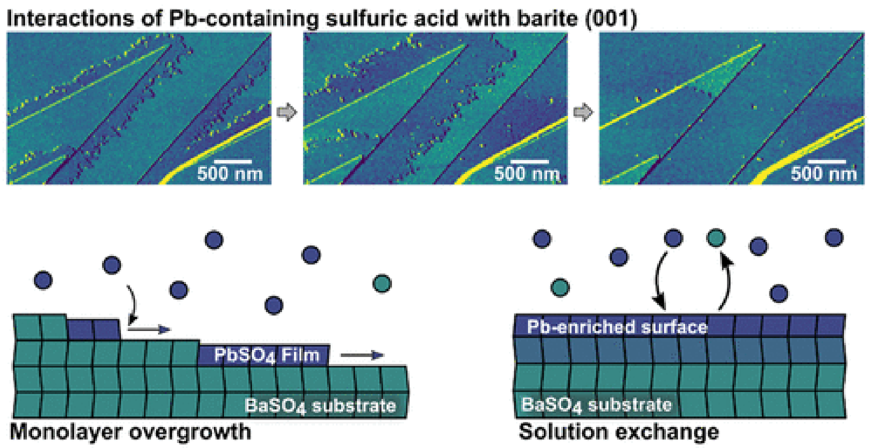


MnO$_x$ Battery Evolution



D. Wu, et al. *J. Am. Chem. Soc.* 2022, 144, 23405.

PbSO$_4$ growth on Barite



B. A. Legg, et al. *ACS Appl. Mater. Interfaces* 2023, 15, 10593.

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Oral presentations in the session

Time	Presenter	Institutions	Title
3:45 - 4:00 pm	Timothy Lambert	Sandia National Laboratories	Progress in Aqueous Zn-based Batteries
4:00 - 4:15 pm	Gautam Yadav	Urban Electric Power (UEP)	Zinc-Manganese Dioxide Batteries for Long Duration Energy Storage Systems
4:15 - 4:30 pm	Sanjoy Banjeree	CUNY-EI/CCNY/UEP	Progress with Manufacturing and Deploying Zn-MnO_2 Batteries
4:30 - 4:45 pm	Matthew Fayette	Pacific Northwest National Laboratory	Zinc Battery Research at PNNL
4:45 - 5:00 pm	Tim Fister	Argonne National Laboratory	X-ray Characterization of Sulfation in Lead Batteries During Cycling
5:00 - 5:15 pm	Vijay Murugesan	Pacific Northwest National Laboratory	Addressing Interfacial Complexities in Pb-acid Batteries to Enable Higher Cycling Life






Posters

Presenter	Institutions	Title
Jungsang Cho	CUNY Energy Institute	Ionic Diffusion in Hydrogel Electrolytes for Two-Electron Zn-MnO2 Batteries
Debayon Dutta	City College of New York	Comparing Hydrogen Evolution Rates in Potassium Acetate and Potassium Hydroxide-based Electrolytes for Zinc Aqueous Batteries
Tim Fister	Argonne National Laboratory	Molecular Mechanisms of Nucleation and Growth on Barite Expanders for Lead Acid Batteries
Amalie Frischknecht	Sandia National Laboratories	Enabling Simulations of Alkaline Electrolytes in Zinc Batteries
Joshua Gallaway	Northeastern University	Spectroscopic Characterization of Rechargeable Alkaline Batteries for the Grid
Tiffany Kinnibrugh	Argonne National Laboratory	Understanding the Structure and Properties of the NonStochiometric Lead Dioxide
Xingbo Liu	West Virginia University	Synergistically Stabilizing Zinc Anodes by Molybdenum Dioxide Coating and Tween 80 Electrolyte Additive for High-Performance Aqueous Zinc-Ion Batteries
Bryan Wygant	Sandia National Laboratories	Improving Alkaline Zinc-Copper Oxide Batteries Through Chemical Modifications
Bryan Wygant	Sandia National Laboratories	Transition Metal Multichalcogenides as Bifunctional Oxygen Electrocatalysts for Zinc-Air Batteries
Patrick Yang	The CUNY Graduate Center and The City College of New York	Understanding the Role of Calcium Zincate (Ca[Zn(OH)3]2·2H2O) in Improving Cycle Life and Performance in Rechargeable Alkaline Zinc Batteries
Cheng Zhu	Lawrence Livermore National Laboratory	Additive Manufacturing of Structured Electrodes for Rechargeable Zinc Batteries

Acknowledgements

We acknowledge the support of Dr. Imre Gyuk and the OE Energy Storage Program for this work.

Thanks for your attention!