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
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U.S. DEPARTMENT OF ENERGY   BATTELLE

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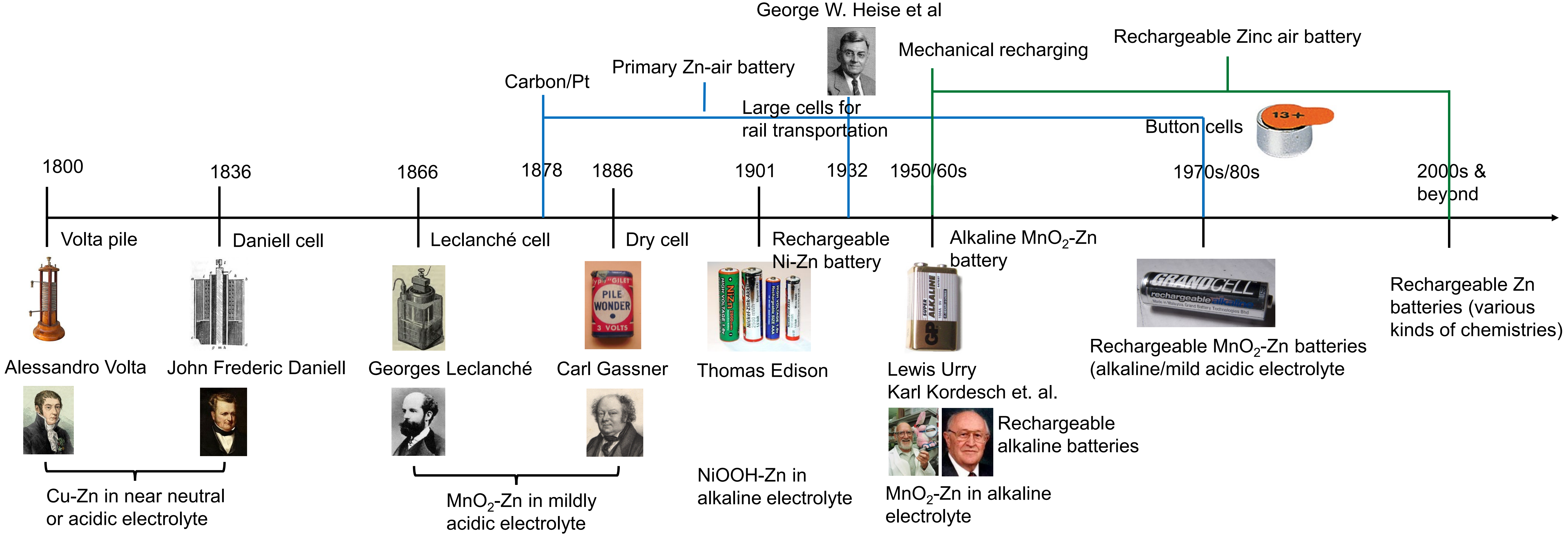
“Look forward & learn from history”

- **Zinc and lead batteries have long histories, mature industries, and sizeable markets**
  - Development history
  - Industry & market
- **Zinc and lead batteries will have a powerful future in grid energy storage**
  - Battery chemistries
  - Objectives & approaches
- **Introduction of oral presentations and posters**

Long history – Zn battery

First battery

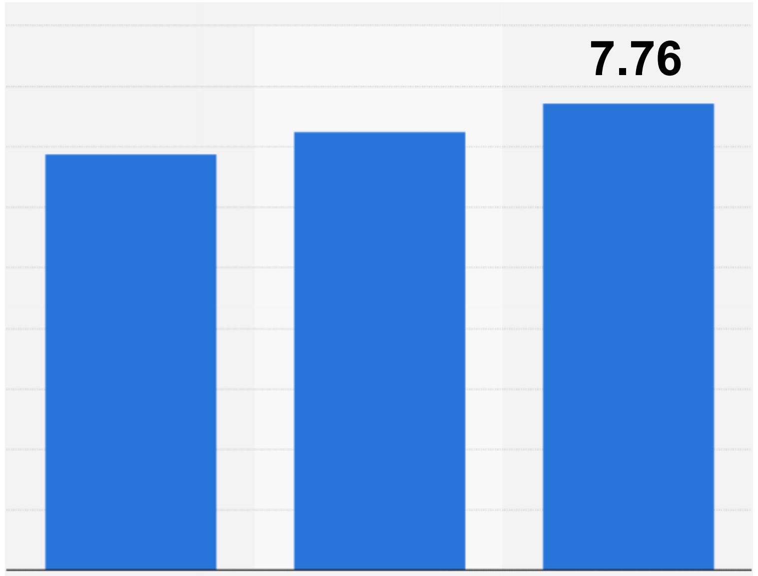


Diverse chemistries; Alkaline or near neutral/acidic electrolyte systems; Earnest battle for rechargeability.

https://silo.tips/download/a-brief-history-of-batteries-and-stored-energy
https://www.helios-h2020project.eu/news/batteries-long-history-powerful-future
Journal of Power Sources, 1984, 12, 177.
https://www.pv-magazine.com/2022/02/09/zinc-batteries-old-technology-brings-new-values/
https://www.electrochem.org/dl/ma/201/pdfs/0257.pdf

Mature technology – primary Zn battery

Alkaline battery industry



Duracell Inc.	Toshiba International Corp
Energizer Holdings	FDK Corporation
Camelion Batterien GmbH	Panasonic Corporation
Gold Peak Industries (Holdings) Limited	Zhejiang Mustang Battery Co., Ltd.
Sanyo	GPB International Limited
Sony	Maxell Holdings, Ltd.

Applications: Primary alkaline batteries for consumer electronics and household use etc.

Huge market: Market is valued at USD 7.76 Billion (Statista & Marketwatch) in 2021 and is expected to have a CAGR of ~4.9% in the next a few years.

https://www.statista.com/statistics/881135/alkaline-battery-market-size-worldwide/
https://www.marketwatch.com/press-release/alkaline-battery-market-size-to-worth-around-usd-1086-billion-grow-at-cagr-49-by-2028-2022-09-23
https://www.bloomberg.com/press-releases/2020-11-04/alkaline-battery-report-world-market-to-grow-by-usd-493-35-million-by-2024

Long history – Pb battery

First rechargeable battery

1859 — 1880 — 1934 — 1957 — 1970s — 2022 beyond

- Pb grid improvement: Pb alloy (e.g., Sb, Se, Cd, Ca)
- Paste improvement: additives (e.g., carbon, barium sulfate, lignosulfonate)

- Separator improvement
- Electrolyte additives

Gaston Plante

Pb-Pb plate/spiral foil

Camille Alphonse Faure

Pb grid-PbO_x paste

Curing and Formation needed

Elektrotechnische Fabrik Sonneberg

Gel electrolyte (not fully sealed)

Valve regulated lead acid (VRLA) battery

Otto Jache

Gel electrolyte (fully sealed)

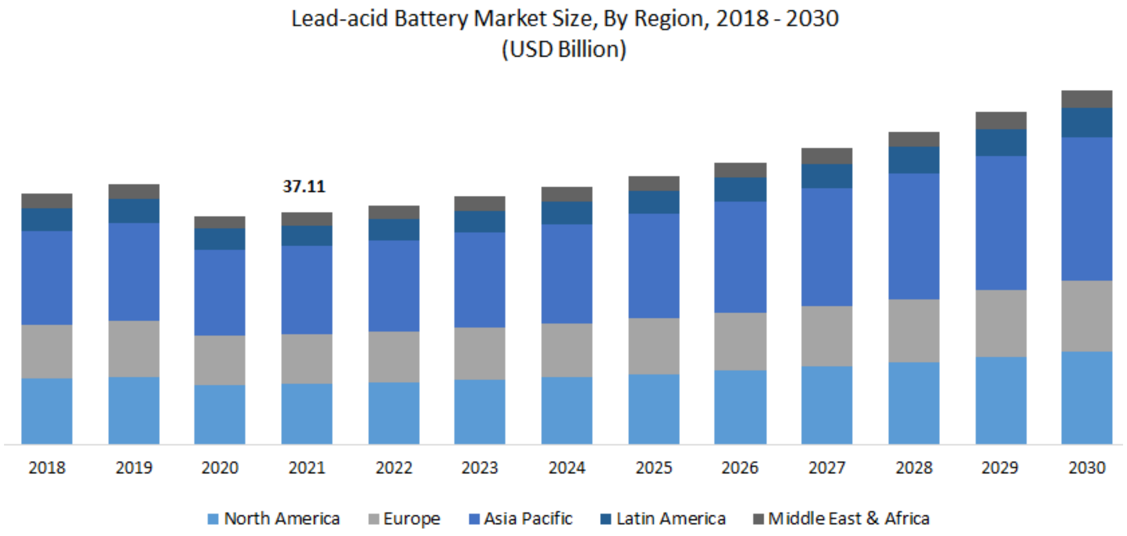
Absorbent Glass Mat (AGM)

Simple chemistry; Acidic electrolyte; Earnest battle for prolonged cycle life and low maintenance.

https://silo.tips/download/a-brief-history-of-batteries-and-stored-energy

Mature technology – Pb battery

Pb battery industry



East Penn Manufacturing Co.	SiteTel Sweden AB (NorthStar)
ATLASBX Co. Ltd.	Yokohama Batteries Sdn. Bhd.
Exide Technologies	Furukawa Electric Co
C&D Technologies, Inc.	Exide Industries Ltd.
Johnson Controls	Chaowei Power Holdings Limited.
Leoch International Technology Ltd and Crown Battery Manufacturing	NorthStar Amara Raja Corporation GS Yuasa Corp.
Narada Power Source Co., Ltd.	Shandong Sacred Sun Power Sources Co

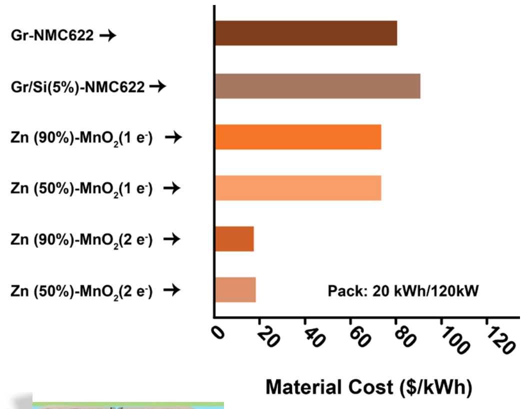
Applications: Starting batteries (majority) & deep cycle batteries

Huge market: Market is valued at USD 37 Billion (Polaris Market Research, USD 42.33 Billion by Bloomberg) in 2021 and is expected to have a CAGR of ~5% in the next a few years.

https://www.polarismarketresearch.com/industry-analysis/global-lead-acid-battery-market
https://www.bloomberg.com/press-releases/2022-07-07/at-5-1-cagr-lead-acid-battery-market-worth-59-97-billion-by-2028-exclusive-report-by-brandessence-market-research

New journey for Pb & Zn batteries

Low-cost alternatives in energy storage space



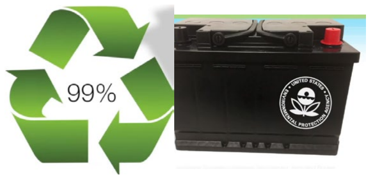
Abundant & cost-effective materials:

Lead is **~$1800/ton** (2022), world resources exceed **2 billion tons**, 2021 global production is **4.7 million tons**.

Zinc is **~$2900/ton** (2022), world resources identified **1.9-2.8 billion tonnes**, 2021 global production is **12.8 million tons**.

Circular life cycle & low risk of battery fire:

Aqueous electrolyte; lead battery is >99% recycled; recycling of alkaline battery is on the way.



Rechargeable Zn industry

AEsir Technologies	Primus Power
Enerpoly	Redflow
Enzinc	Salient Energy
Eos Energy System	Urban Electric Power
EverZinc	ZincFive
E-Zinc	Zinc8 Energy

Deep cycle/Low maintenance Pb acid

East Penn Manufacturing Co.	Amara Raja
Clarios	Leoch
Exide Technologies	Narada
C&D Technologies, Inc.	Enersys

https://www.statista.com/
https://markets.businessinsider.com/commodities/lead-price
Junhua Song et al. Material Today 2021, 45, 191
https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/durable-goods-product-specific-data

Battery chemistries

Reaction mechanisms for Zn batteries (MnO_2-Zn as an example)

	Alkaline system (MnO_2 as the example cathode)	**Mild acid system (MnO_2 as the example cathode)**
Anode reactions	Zn^0 (s) ↔ Zn^{2+} + $2e^-$ - Eq. (1) Zn^{2+} (aq.) + $4OH^-$ (aq.) → $Zn(OH)_4^{2-}$ (aq) - Eq. (2) $Zn(OH)_4^{2-}$(aq.) → ZnO (s) + H_2O (aq.) + $2OH^-$(aq.) - Eq. (3)	Zn^0 (s) ↔ Zn^{2+} (aq.) + $2e^-$ (aq.) - Eq. (7)
Cathode reactions	H_2O (aq.) ↔ H^+ (aq.) + OH^- (aq.) - Eq. (4) MnO_2 (s) + H^+ (aq.) + e^- ↔ MnOOH (s)- Eq. (5) MnOOH (s) + H_2O (aq.) + e^- ↔ $Mn(OH)_2$ (s) + OH^- (aq.) - Eq. (6)	H_2O (aq.) ↔ H^+ (aq.) + OH^- - Eq. (8) MnO_2 (s) + H^+ (aq.) + e^- ↔ MnOOH (s) - Eq. (9) $2MnO_2$ (s) + Zn^{2+} (aq.) + $2e^-$ ↔ $ZnMn_2O_4$ (s) - Eq. (10)

Voltage/Energy density: ~1.5V, ~100-1300 Wh/kg (reactants)

Reaction mechanism for Pb acid battery

Anode oxidization	Pb (s) + SO_4^{2-} (aq)	⟶	$PbSO_4$ (s) + $2e^-$
Cathode reduction	PbO_2 (s) + SO_4^{2-} (aq) + $4H^+$ + $2e^-$	⟶	$PbSO_4$ (s) + $2H_2O$ (l)
Battery reaction	Pb (s) + PbO_2 (s) + H_2SO_4 (aq)	⟶	$2PbSO_4$ (s) + $2H_2O$ (l)

Voltage/Energy density:
~2V, 167 Wh/kg (reactants)

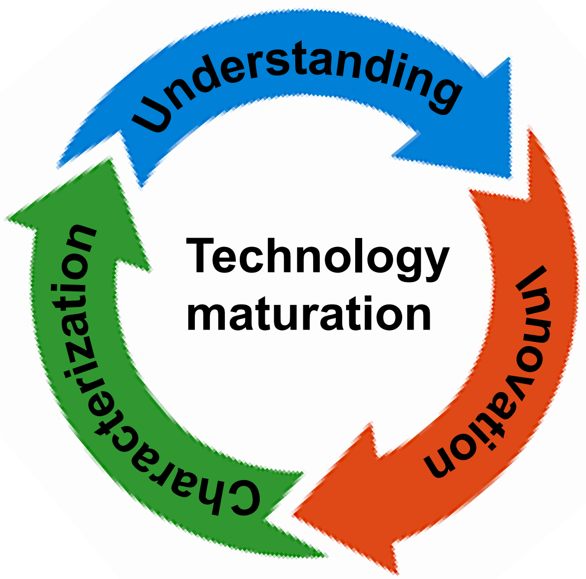
- Electrolyte takes part in redox reactions leading to electrolyte pH/concentration change
- Highly reactive anodes leading to self-discharge and gassing
- Cathode and anode half-cell reactions sometimes are linked through electrolyte reactions
- Reactants/intermediate products have limited stability/solubility in the electrolytes
- Temperature, over charge, potential toxic materials…

Junhua Song et al. Material Today 2021, 45, 191

Objectives & approaches

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

Approaches



Quantum leap through thorough understanding & advanced characterization

Zn battery: Rechargeability

Electrode
- Dendrite formation
- Corrosion & passivation
- Morphology/composition change
- Cathode dissolution
- Irreversible cathode phase transition

Electrolyte
- pH swing
- Dry out
- Salt precipitation
- Gassing

Separator
- Penetration

Pb battery: Prolong cycle life for deep cycle batteries

Electrode
- Corrosion
- Sulfation
- Morphology/composition change

Electrolyte
- Acid stratification
- Dry out
- Gassing

Separator
- Penetration

Junhua Song et al. Material Today 2021, 45, 191
Geoffrey J. May et al. J. Energy Storage 2018, 15, 145

Oral presentations

Time	Presenter	Institutions	Title
3:45 - 4:00 pm	Timothy T. Fister	Argonne National Laboratory	X-ray Analysis of Nonstochiometric Oxides in Lead Acid Batteries
4:00 - 4:15 pm	Timothy Lambert	Sandia National Laboratory	Progress in Aqueous Zn-based Batteries
4:15 - 4:30 pm	Sanjoy Banerjee	The City College of New York/Urban Electric Power	Progress in the Development and Deployment of Zinc Manganese Dioxide Batteries
4:30 - 4:45 pm	Amy Marschilok	Stony Brook University	Mechanistic Studies of Zinc Anode Batteries
4:45 - 5:00 pm	Joshua Gallaway	Northeastern University	Li and Na ion intercalation in layered MnO_2 cathodes enabled by using bismuth as a cation pillar
5:00 - 5:15 pm	Matthew Fayette	Pacific Northwest National Laboratory	Zinc Battery Research at PNNL






Posters

Presenter	Institutions	Title
Amalie Frischknecht	Sandia National Laboratory	Models for Simulations of Alkaline Electrolytes in Zinc Batteries
Xingbo Liu	West Virginia University	Polyvinyl Alcohol Coating Induced Preferred Crystallographic Orientation in Aqueous Zinc Battery Anodes
Noah Schorr	Sandia National Laboratory	Rechargeable Alkaline Zn–Cu Batteries Enabled by Carbon Coated Cu/Bi Particles
Cheng Zhu	Lawrence Livermore National Laboratory	Additive Manufacturing of High-Capacity 3D Zn Anodes for Rechargeable Alkaline Batteries
Krishna Acharya	New Mexico State University	Theoretical Studies of the Discharge Mechanism of CuO Cathodes Modified with Bi2O3 in Rechargeable Zn/CuO Batteries
Jungsang Cho	The City College of New York	Hydrogel Electrolytes Ensuring the Transportability and the 2nd Electron Reaction of Zn-MnO2 Alkaline Batteries
Patrick Yang	The City College of New York	Investigating the Impact of Adding Metallic Zinc to Calcium Zincate Anodes for Improved Performance in Rechargeable Alkaline Zinc Batteries
Patrick Yang	The City College of New York	Investigating Anodes Based on Calcium Zincate (Ca[Zn(OH)3]2·2H2O) for Improved Cycle Life in Rechargeable Alkaline Zinc Batteries
Damon Turney	The City College of New York	Acetate-based water-in-salt electrolytes (WiSE) for improved zinc battery cycling
Gautam Yadav	Urban Electric Power	The Performance of Low Cost and Highly Energy Dense Hybrid Zinc|Manganese Dioxide-Copper Scaled-Cells
Gautam Yadav	Urban Electric Power	Zinc-Manganese Dioxide Battery Development and Commercialization at Urban Electric Power
Bryan Wygant	Sandia National Laboratory	Metal Ion Sensing and Quantification by Anodic Stripping Voltammetry (ASV) for Study of Alkaline Battery Separators