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Technology Strategy Assessment

Findings from Storage Innovations 2030

Zinc Batteries

July 2023

About Storage Innovations 2030

This technology strategy assessment on zinc batteries, released as part of the Long-Duration Storage Shot, contains the findings from the Storage Innovations (SI) 2030 strategic initiative. The objective of SI 2030 is to develop specific and quantifiable research, development, and deployment (RD&D) pathways to achieve the targets identified in the Long-Duration Storage Shot, which seeks to achieve 90% cost reductions for technologies that can provide 10 hours or longer of energy storage within the coming decade. Through SI 2030, the U.S. Department of Energy (DOE) is aiming to understand, analyze, and enable the innovations required to unlock the potential for long-duration applications in the following technologies:

- Lithium-ion Batteries
- Lead-acid Batteries
- Flow Batteries
- Zinc Batteries
- Sodium Batteries
- Pumped Storage Hydropower
- Compressed Air Energy Storage
- Thermal Energy Storage
- Supercapacitors
- Hydrogen Storage

The findings in this report primarily come from two pillars of SI 2030—the SI Framework and the SI Flight Paths. For more information about the methodologies of each pillar, please reference the SI 2030 Methodology Report, released alongside the ten technology reports.

You can read more about SI 2030 at https://www.energy.gov/oe/storage-innovations-2030.

Acknowledgments

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Background

High-Level History

Zinc (Zn) was used as the negative electrode (anode) of batteries dating to the early 1800s, when Alessandro Volta formed early voltaic piles from stacks of alternating copper and Zn. The low-cost, high-energy density, safety, and global availability of Zn have made Zn-based batteries attractive targets for development for more than 220 years. The Zn-carbon battery, originally developed in the later 1800s, was manufactured as a popular primary battery until the 1980s [1]. Although still in limited use today in the United States, Zn-carbon cells were eventually replaced by alkaline Zn-MnO_2 batteries introduced as primary dry cells in 1952 and patented by Paul A. Marsal, Karl Kordesch, and Lewis Urry in 1960 [2-4]. These batteries have become some of the most commercially successful batteries to date, commonly recognized as AA, AAA, C, D, and 9V batteries in everyday use. Initially developed in the 1920s, ZnNi batteries were explored in the 1970s and 1980s as rechargeable batteries capable of hundreds (today ~1,000) of deep discharge cycles, potentially suitable for application in electric vehicles [5-7]. Primary Zn-air batteries, commonly recognized as “button cells” today, were originally patented in 1933 by G. W. Heise [8] and are still in widespread use (e.g., in hearing aids and some film cameras) [5]. Collectively, these historical batteries serve as the inspiration for several of the most commercially advanced batteries for grid-scale storage to date.

Chemistries

Zn-MnO_2 batteries, traditionally primary (not rechargeable) batteries, have been adapted to create low-cost secondary (rechargeable) batteries. These batteries often use an alkaline aqueous electrolyte and are considered more environmentally friendly than other types of batteries as indicated by the U.S. Environmental Protection Agency’s certification of these primary batteries for landfill disposal in the United States. Commercial primary Zn-MnO_2 batteries have an energy density of up to 150 Wh/kg or 400 Wh/L because of the high capacity of the Zn-anode (820 mAh/g) and the MnO_2 cathode (616 mAh/g for “2 electron” or 308 mAh/g for “1 electron” reactions) [4]. As a secondary battery, these systems have been deployed with energy densities on the order of 100 Wh/L and there are anticipated pathways to production at less than $50/kWh [5, 9]. These batteries use a Zn anode and specific forms of manganese dioxide (MnO_2) as the positive electrode (cathode). During electrochemical cycling of the secondary battery, the charge is balanced across the cell by hydroxide ions that move across a porous separator. The expected half-reactions at each electrode and the overall reaction of the cell during discharge are [5]:

Cathode: $MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$ [$E^0 = +0.30V$]

Anode: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ [$E^0 = +1.28V$]

Overall: $Zn + 2MnO_2 + H_2O \rightarrow ZnO + 2MnOOH$ [$E^0_{cell} = +1.58V$]

Zn-Ni batteries have a practical energy density of up to 140 Wh/kg or 300 Wh/L and are capable of approximately 500 charge-discharge cycles [5, 10]. Zn–Ni cells also use an aqueous solution of KOH as the electrolyte and Zn as the anode material, with the same fundamental anode reaction during discharge. In this case, the cathode is nickel oxyhydroxide (NiOOH), which converts to nickel hydroxide [$Ni(OH)_2$] during discharge [5]:

Cathode: $NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ [$E^0 = +0.49V$]

technologies (relative to the $0.17/kWh baseline projected cost), although no subset of the interventions identified result in an LCOS less than the DOE target of $0.05/kWh.

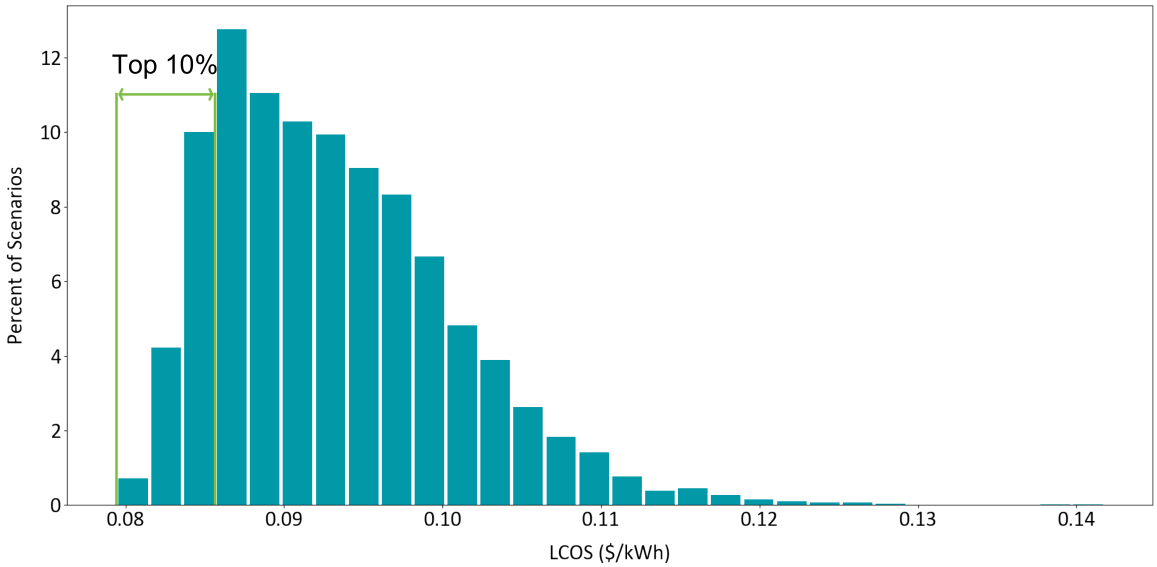

Figure 1. Portfolio frequency distribution across LCOS with the green rectangle indicating the top 10% of the portfolios

The results of the Monte Carlo simulation for the thousands of portfolios that fall *within the top 10% in terms of LCOS impact* are presented in Figure 2. This plot correlates the simulated highest LCOS impact portfolios with the total investment needed to realize that impact. The dots at the top of the chart demonstrate that the top 10% of the portfolios reach their lowest level at an LCOS of roughly $0.08/kWh. The vertical green line demonstrates that the mean investment level required for these portfolios is $155 million. This value represents the marginal investment over currently planned levels required to achieve the corresponding LCOS improvements. The highest density of portfolios in the top 10% are in the $120 million to $150 million range. Not shown on the plot, but indicated in the simulations, is that the estimated timeline required to achieve these LCOS improvements is 5 to 7 years.

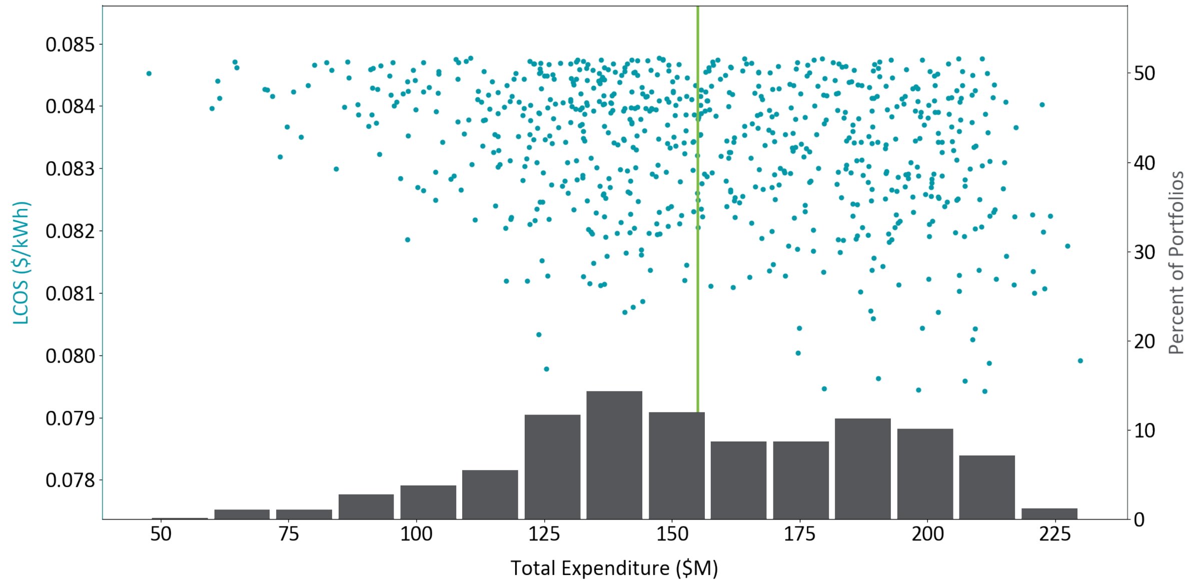

Figure 2. LCOS and estimated industry expenditures for the top 10% of the portfolios. The vertical green line shows the mean portfolio cost.

Note that the impact of each layered innovation is not additive. The impact of each additional innovation is weighted to determine the combined impact. Combinations of investments can be in conflict with or relate to alternative sub-chemistries, thus diminishing their combined impact. Working with SMEs, the research teams established innovation coefficients that are used to measure combined impact.[a] Innovation coefficients for each innovation pairing are presented in Appendix C.

SMEs were also asked for their preferences regarding the investment mechanism, choosing among National Laboratory research, R&D grants, loans, and technical assistance. Table 3 presents the SME preferences for each mechanism. In most cases, a mixture of R&D grants and National Laboratory research were supported, with R&D grants slightly preferred in most cases. There were also indications of support for loans for enhanced domestic recycling, technical assistance funding to support supply chain analytics for sustainable sourcing, and the development of a manufacturing ecosystem and the implementation of manufacturing best practices.

Table 3. SME preferences for investment mechanisms. Cells with asterisks (*) represent more preferred mechanisms. (Technical Assistance includes advice or guidance on issues or goals, tools and maps, and training provided by government agencies or National Laboratories to support industry.)

Innovation	National Laboratory Research	R&D Grants	Loans	Technical Assistance
Mining and metallurgy innovations for battery-grade Zn metal	30%	40% *	10%	20%
Supply chain analytics for sustainable sourcing	20%	30%	10%	40% *
Inactive materials cost reduction	25%	42% *	8%	25%
Separator innovation	29%	50% *	7%	14%
Pack/System-level design	20%	47% *	20%	13%

[a] To demonstrate how innovation coefficients work, the innovation coefficient for the combined investment in mining/metallurgy innovations for battery-grade Zn metal and enhanced domestic recycling is 0.15, which means that the Monte Carlo simulation tool would only include 15% of the defined impact of the second innovation (e.g., enhanced domestic recycling) when added to the first (e.g., mining/metallurgy innovations). The reason for the low coefficient for these innovations is that both affect the raw materials that are used in the manufacturing process (i.e., virgin versus recycled materials). An innovation coefficient of 1.0 indicates that 100% of the impact of the second investment will be added to the impact of the first, while a coefficient of 0 means that the second investment would add no additional value.

Additional Opportunities and Discussion

Beyond the specific technical challenges and opportunities, numerous non-technical challenges concerned the industry team and were raised in both the Framework and Flight Paths engagements. In the Flight Paths listening session, during the initial discussions around significant impediments that are limiting Zn battery deployment, non-technical hurdles, such as funding (particularly around capital investments), were a priority. In fact, this point was reiterated as a major concern because the group identified capital investment at a level of $25 million to $100 million as one of the most significant issues that "keeps the [chief technology officer and chief executive officer] up at night." Notably, these values bridge the large-scale investments from Figure 2 above ($120 million to $150 million) and the activity-specific investments from Table 4 below ($5 million to $20 million). These agreeable values collectively show that large investments (possibly from multiple sources) will be essential for advancing Zn battery commercialization.

Many of the other non-technical issues, such as manufacturing, demonstrations, regulations and safety, supply chain, and end-of-life considerations, have already been called out in the Framework discussion; however, these issues were also raised in the Flight Paths listening session, and there were numerous parallels between the two efforts.

With respect to safety regulations, standards, and policies, many participants noted that these aspects of battery development are disproportionately designed and implemented with a nearly exclusive focus on lithium-ion batteries. Because Zn-based batteries present inherently different chemistries and performance metrics, forcing Zn-based batteries into the Li-ion requirements matrix was seen as limiting, expensive, and ineffective. Some of the key needs identified included a standardized set of cycling protocols, performance requirements, and installation guidelines for different *long-duration storage use cases* (e.g., few versus tens of hours versus 100-hour storage, relevant charge/discharge rates, temperature ranges) rather than imposing short-duration standards and protocols on non-Li-ion, LDES-targeted chemistries. This challenge applied not only to developed batteries but also material supply chain and associated Toxic Substances Control Act (TSCA) requirements. In addition to Li-ion incumbency in the industry, another concern over long interconnect application queues was raised. The current wait time, which is on the order of years, is recognized as a major limiting factor for implementing all emerging technologies.

The discussions about supply chain extended beyond the Li-ion constraints, although there was a mixed response from participants as to whether there was a supply chain concern for Zn batteries. It was recognized that although Zn metal is a globally abundant and inexpensive material, "battery-grade" Zn is not always seen as readily and domestically available, or current supply chains are consumed/dominated by other industries (Zn primary batteries or steel) and many of these supply chains currently are not domestic. There was also some recognition that supply chain and end of life or recycling should be considered as part of a more comprehensive manufacturing ecosystem that remains immature today. There was agreement, however, that as markets grow and the scale of manufacturing increases, this ecosystem is likely to mature. Identifying strategies to repurpose or leverage existing battery manufacturing infrastructure/expertise and to introduce greater automation to manufacturing as that ecosystem matures would help to increase efficiency, limit waste, and reduce timelines to large-scale manufacturing and deployment.

Access to crucial workforce capacity, along with manufacturing, were identified as challenges central to both developed and emerging manufacturing. Many of the workers with expertise in batteries and related technology production are not located in the United States, even if they were trained in the United States (e.g., foreign graduate students). For the remaining domestic workforce, there is competition for workers from both established (Li-ion, Pb-acid) and emerging battery technologies. Prioritizing increased training and education for battery storage (on the whole) would help meet Zn battery workforce needs.

Beyond engaging DOE or National Laboratories with R&D opportunities, there was significant interest in cooperation with DOE to enable demonstration projects and validation/testing sites or to develop cost-modeling tools, analogous to Li-ion resources, such as BatPac. There was additional desire to form Zn-centric consortia or increase engagement with existing consortia like those in development by organizations such as NAATBatt. Public investment in Zn battery science and technology has been modest compared with the scale of the investments in Li-ion batteries. Thus, even modest incremental investments—ranging from fundamental science, as noted above, to tools for those interested in moving technologies to products—would be useful. These activities could be enabled through consortia with multiple companies participating, appropriate academic partners, and taking advantage of DOE and National Laboratory technical and analytics expertise. A small minority of the companies could speak to successful DOE relationships; however, the majority of the respondents were unaware of what DOE resources were available to them, indicating an opportunity to improve community awareness of existing capabilities and expertise available throughout DOE. For those who had tried to work with DOE, there was some concern that the processes for contracting were cumbersome and often prohibitive. Finding pathways to streamline and incentivize collaboration between industry and DOE/National Laboratories would be desirable.

Regarding Zn potential for LDES applications, most participants indicated that a Zn battery technology capable of 10+ hours discharge duration would be produced within 3 years. Moreover, participants indicated that, within the next 3 years, many companies were targeting 4 hours to 12 hours of storage and a few others indicated that they were targeting more than 12 hours of storage. Other participants indicated that they were working toward applications that would compete with other current markets, such as 2 hours to 4 hours of storage, currently dominated by Li-ion. These trends reflected a significant, articulated belief that Zn-based batteries are well suited to LDES, provided they can meet key long-duration performance metrics, such as cycle life on a large scale. The 3-year target for LDES deployment is slightly lower than innovation impact timelines indicated in Table 4. This difference suggests that many of the innovations and improvements proposed may be aimed at later generations or evolving technologies.

Among the significant challenges to realizing the deployment of LDES goals was a poorly defined, immature stationary storage market space that is currently dominated by the Li-ion industry. Some of this market is defined by market policies, which, again, are largely geared toward shorter-duration Li-ion technologies at present. Future revisions to market rules and policies could take full advantage of the capabilities in new technologies. The degree of renewable energy deployment was also identified as an expected market driver for larger-scale, longer-duration storage. Integrating renewables with the storage during this market evolution may help to achieve more efficient and optimal mating of storage capabilities with market needs. Consideration of "the total system" could factor in all of the benefits, challenges, lifecycle, manufacturing, and evolving application needs of a system as priorities and strategies for storage integration are developed. Finally, recognizing that the markets, storage needs, and demands on technology change, it is once again clear that the fundamental R&D underpinning anticipated responsive, adaptive technological solutions must remain a priority.

As presented in Table 4, the Framework Study revealed that separator innovations, cathode materials optimization, improved Zn metal performance, and pack/system-level design for Zn batteries consistently yielded metrics in the top tier, which is designated with asterisks (*). Daggers (†) represent mid-tier metrics and double daggers (‡) represent the lowest tier. Separator innovations were the largest contributor to a reduced LCOS for Zn batteries, and several innovations demonstrate strength in this metric. The Framework Team recognizes that some estimates are

References

[1] K. Kordesch and W. Taucher-Mautner, "Primary Batteries –- Aqueous Systems | Leclanche and Zinc-Carbon," in *Encyclopedia of Electrochemical Power Sources*, 2009, pp. 43-54.

[2] P. A. Marsal, K. Kordesch, and L. F. Urry, "Dry Cell," U.S. Patent 2,960,558, 1960.

[3] W. J. R. Wruck, B, K. R. Bullock, and W. H. Kao, "Rechargeable Zn-MnO2 Alkaline Batteries," *J. Electrochem. Soc.,* vol. 138, no. 12, pp. 3560-3567, 1991.

[4] M. B. Lim, T. N. Lambert, and B. R. Chalamala, "Rechargeable alkaline zinc-manganese oxide batteries for grid stroage: Mechanisms, challenges, and developments," *Mater. Sci. & Eng. R,* vol. 143, 2021, doi: 10.1016/j.mser.2020.100593.

[5] M. B. Lim and T. N. Lambert, *Rechargeable Zinc Batteries for Grid Storage*, 2021. [Online]. Available: https://www.sandia.gov/app/uploads/sites/163/2021/09/ESHB_Ch5_Zinc_Lim.pdf.

[6] F. R. McLarnon and E. J. Cairns, "The Secondary Alkaline Zinc Electrode," *J. Electrochem. Soc.,* vol. 138, no. 2, pp. 645-656, 1991.

[7] W. J. Walsh, "Advanced batteries for electric vehicles - a look at the future," *Physics Today,* vol. 33, no. 6, 1980.

[8] G. W. Heise, "Air-polarized primary battery," Patent 1899615, 1933.

[9] E. D. Spoerke *et al.*, "Driving Zn-MnO2 Gridscale Batteries: A Roadmap to Cost-Effective Storage," *MRD Energy & Sustainability,* vol. 9, pp. 13-18, 2022.

[10] J. F. Parker *et al.*, "Rechargeable nickel–3D zinc batteries: An energy-dense, safer alternative to lithium-ion," *Science,* vol. 356, no. 6336, 2017.

[11] J. Yi *et al.*, "Challenges, mitigation strategies and perspectives in development of zinc-electrode materials and fabrication for rechargeable zinc-air batteries," *Energy & Environ. Sci.,* vol. 11, no. 11, pp. 3075-3095, 2018.

[12] L. Gao *et al.*, "A High-Performance Aqueous Zinc-Bromine Static Battery," *iScience,* vol. 23, 2020.

[13] V. Viswanathan, K. Mongird, R. Franks, X. Li, V. Sprenkle, and R. Baxter, "Grid Energy Storage Technical Cost and Performance Assessment," Pacific Northwest National Laboratory, Richland, WA, and Mustang Prairie Energy, PNNL-33283, 2022.