

3D Zinc Sponge Battery Technology in Mobile and Stationary Energy Storage Applications- It's advantages when compared with lead acid and lithium-ion batteries.

Sauman Das Gupta MIIICHE, Buddha Dev Burman,

INDIAN SCHOOL OF INNOVATION IN SUSTAINABILITY (INSIST)

Abstract—The main purpose of the paper is to highlight the potential of another offshoot of advanced battery technology—3D zinc sponge-based battery technology—that has been overlooked by many during the “Lithium-Ion Decade” of the 2010’s. 3D Zinc Sponge battery technology has come a long way. Originally thought of as a primary (non-rechargeable) battery technology, scientific advances over the last ten years have made possible to make it secondary (rechargeable) 3D zinc-based battery systems that has characteristics which make it cheaper than Lead Acid and equivalent to most existing Lithium Ion. Making it highly attractive for all mobile and stationary energy storage applications. The paper will look primarily at 3D zinc sponge battery Technology developments and advantages when compared with lead acid and lithium-ion batteries.

Present rechargeable battery energy-storage solutions are mainly dominated by lithium-ion batteries and Lead Acid with Nickel Hydride taking a minor share. Lithium-ion batteries are preferred mainly because of their cycle life, energy content, considerable improvement, resourced research, development and deployment programs. There have been reported numerous safety incidents, recycle ability issues, toxicity along with many other obstacles, including logistics restrictions, constrained resource supply (lithium and cobalt), high cost, balance-of-plant requirements, skills availability and cost of setting up manufacturing plants. Even with these disadvantages, Li-ion batteries are widely used. Thus to displace Lithium-Ion batteries the characteristics and it's attributes must be met by any alternative battery system in order to compete for market share.

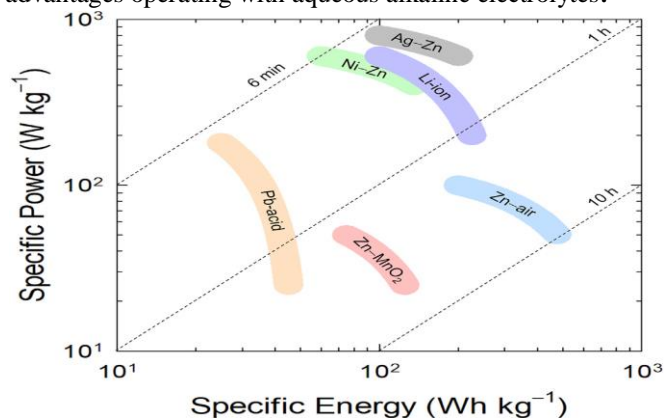
At the research level, many configurations such as Na-ion, Li-S, Li-O₂ and solid Li-Air are being studied and tested, however most of these still incorporate non-aqueous electrolytes that present safety and environmental challenges.

Hence the next generation of high-performance batteries should include alternative safe chemistries making them inherently safer and cheaper to operate than non aqueous lithium-based and toxic lead acid batteries.

Aqueous 3D Sponge Zinc-based batteries can answer that challenge:

A high performance rechargeable zinc based battery has been of interest to battery developers since the time of Thomas Edison. Mr. Edison patented a zinc battery in 1901.

The family of zinc-based batteries—Ni-Zn, Ag-Zn, Zn-MnO₂, and Zn-air—does offer compelling alternatives, having practical specific energies ranging from 80 to 475 Wh kg⁻¹, specific power up to a continuous 800 W kg⁻¹, which has strong validation established over decades in safety advantages operating with aqueous alkaline electrolytes.



Ragone Plot of Zinc-Based Batteries and Their Closest Competitors Ragone plot illustrating the energy and power characteristics of several Zn-based energy-storage systems (Zn-MnO₂, Zn-air, Ni-Zn, and Ag-Zn). Legacy Pb-acid and present Li-ion systems are included for comparison

What eluded Mr. Edison is why his zinc batteries did not last very long - very limited charge/discharge cycle.

Hence, the zinc battery was relegated to a primary or disposable battery. Many people have tried to make zinc commercially rechargeable and the two solutions used are either a flow battery (like a fuel cell) where the “bad” zinc is simply replaced. Or in dendrite suppressing additives added to the electrolyte to slow down but not eliminate dendrite growth. Both of these limited the specific energy of the battery.

The long-standing limitation that has prevented implementing Zn in next-generation batteries lies in its poor rechargeability due to dendrite formation

This problem is bypassed to obtain cycling durability by redesigning the Zn electrode as a monolithic, porous, aperiodic architecture in which an inner core of electron-conductive metallic Zn persists even to deep levels of discharge called 3D Sponge Zinc

The solution like most successful solutions, is elegant in its simplicity. Converting zinc to an open cell sponge(3D Sponge Zinc) form it becomes a continuously wired structure. Unlike the typical powder or slurry forms, the current can flow uninterrupted during charge and discharge. Hot-spots cannot form, dendrites cannot grow, anode cracking does not take place.

The approach 3D Zinc -based alkaline batteries is the first that offers a structural solution to the zinc electrode - a zinc metal micro-sponge. Providing a battery that offers the specific energy of Li-ion batteries but a cost more like lead-acid (zinc is very cheap) and safer (to use as well as for the planet) than both. It also has a simpler supply chain and is not dependent on resource constrained components like Lithium or Cobalt.FIG1A

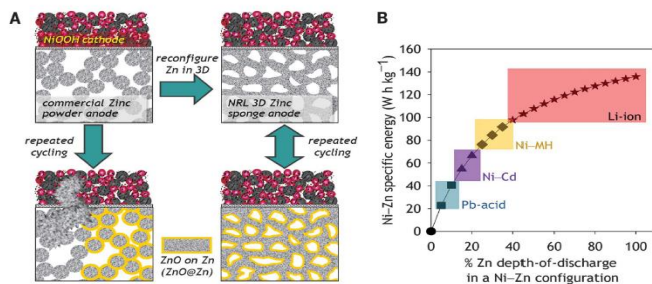


Fig. 1. Possibilities with rechargeable Ni-Zn. (A) Schematic of the effect of recharging Ni-Zn (conventional powder zinc anodes) versus Ni-3D Zn in which the anode is redesigned as a monolithic aperiodic sponge ensuring persistent 3D wiring of the metallic Zn core. Dendrites that form at powder-composite Zn anodes can reach hundreds of micrometers in length (3D, 3I). (B) The calculated specific energy of a fully packaged Ni-Zn cell as a function of increasing Zn depth of discharge versus a capacity-matched NiOOH electrode. The shaded areas highlight the specific energy range of common battery chemistries. For example, at $\geq 40\%$ DOD_{Zn} (percentage of theoretical utilization), Ni-Zn becomes competitive with Li-ion at the single-cell level.

The complete family of 3D zinc-based alkaline batteries (Zn anode versus a silver oxide, nickel oxyhydroxide, or air cathode) is expected to emerge as the frontrunner to replace not only Li-ion but also lead acid and nickel-metal hydride batteries as **Zn is globally available , inexpensive and readily available.Zinc has two-electron redox (Zn^{0/2+}) and low polarizability respectively which delivers high specific capacity and power.**

It has been established Monolithic 3D zinc sponge anodes can be cycled in nickel-zinc alkaline cells hundreds to thousands of times without undergoing passivation or macroscale dendrite formation.

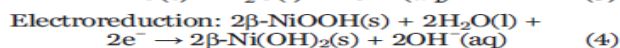
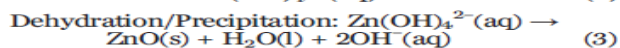
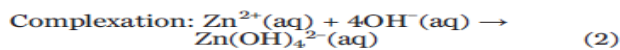
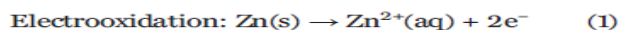
That the 3D zinc sponge anodes can be used to produce secondary batteries that can be cycled thousands of times used with nickel to form primary batteries that allow for deep discharge is based on the results of (3D) zinc form-factor and performance of nickel-zinc alkaline cells in three fields of tests which confirms this:

- (i) **>90% theoretical depth of discharge (DOD_{Zn}) in primary (single-use) cells,**
- (ii) **>100 high-rate cycles at 40% DOD_{Zn} at lithium-ion-commensurate specific energy, and**
- (iii) **Tens of thousands of power-demanding duty cycles required for start-stop microhybrid vehicles.**

In primary 3D Zn-air cells, this “sponge” form factor (3D Zn) discharges >90% of the Zn , translating to a 50% improvement over conventional powder-bed composites When cycling Zn sponges at the demanding current densities that otherwise induce dendrite formation in alkaline electrolyte—typically greater than 10mAcm⁻² We see thee 3DZn restructures uniformly without generating separator-piercing dendrites.

The performance 3D Zn-air cells used to explore the secondary 3D Ni-Zn system in which the battery chemistry used is rechargeable cathode (NiOOH) which is further development of the existing air cathode of rechargeable Zn-air ,also much more economically feasible than Ag(Silver)-Zn.

Nickel-zinc batteries discharge via the oxidation of Zn metal coupled with the reduction of nickel oxyhydroxide according to the anodic (Eqs. 1 to 3; Zn) and cathodic (Eq. 4; NiOOH) reactions.



The theoretical specific energy for Ni-Zn is 372Whkg⁻¹, whereas a practical Ni-Zn battery delivers up to 135 Whkg⁻¹ (~300WhL⁻¹ on a volumetric basis) depending on battery-design considerations and Zn depth of discharge (DOD_{Zn}).

Comparing the specific energy for a fully packaged 3D Ni-Zn cell as a function of increasing DOD_{Zn} versus that for lead-acid, nickel-cadmium, and nickel-metal hydride shows that the performance of Ni-Zn is comparable or superior (Fig. 1B), even at modest utilization of the Zn (10 to 20%DOD_{Zn}). Deeper depths are required ($\geq 40\%$ DOD_{Zn}) to bring Ni-Zn to a specific energy that becomes competitive with common Li-ion batteries at the single-cell level.

The calculations assumed that the Zn and Ni electrodes are present at 39% of the total packaged weight .Which is a conservative assumption because the percentage of packaging weight (casing) is expected to decrease when scaling Ni-3D Zn cells up to vehicle-or user relevant stacks.

It has been reported on electrolyte formulations and electrode additives that minimize shape change of Zn sponge electrodes cycled 20 times to 20% DODZn in a Ni-3D Zn configuration . The proper electrolyte formulation included additives that force dehydration of soluble zincate $[\text{Zn}(\text{OH})_4^{2-}(\text{aq}) \rightarrow \text{ZnO}(\text{s})]$, (Eqs. 2 and 3) at lower concentrations than occur in unadulterated 6 M KOH.

For the deep-discharge and long-term cycling conditions electrolyte formulation of 6 M KOH + 1MLiOH in conjunction with a $\text{Ca}(\text{OH})_2$ -infused Zn sponge electrode was used.

This combination of additives provided superior round-trip cycling efficiency—because

- I. **Li+ augments NiOOH rechargeability by suppressing O₂ evolution ;**
- II. **Ca(OH)₂ induces zincate supersaturation ;**
- III. **300 parts per million (ppm) of In and 300 ppm of Bi predoped into the Zn suppress H₂ evolution.**

The potential application in consumer electronics and wearables, because of the higher cell voltage of 3D Ni-Zn over traditional, single-use alkaline batteries (MnO₂-Zn) is big feature if it can be coupled to use 3D Sponge Zn anode. The ability of 3D Zn sponge anodes to discharge to high- Zn mass-normalized capacity and be recharged without inducing dendritic shorts was probed by exhaustively discharging Ni-3D Zn cells (Fig. 2A)

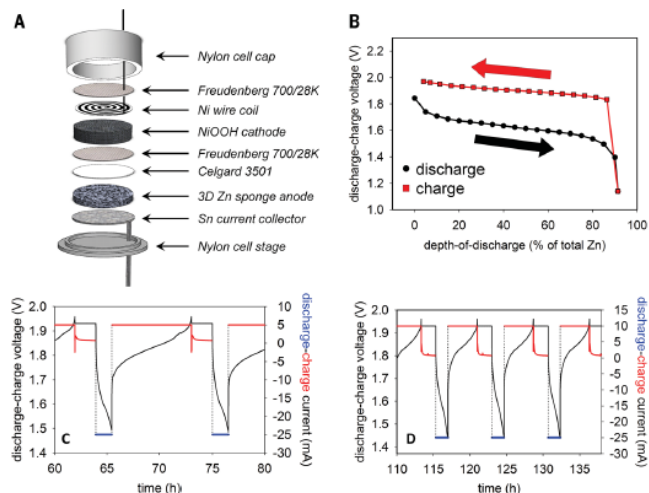


Fig. 2. Cycling performance of nickel-3D zinc cells. (A) Schematic design of the nickel-3D zinc coin cell used in this study. (B) Nickel-3D zinc cells tap >90% of the theoretical Zn capacity upon discharge (black circles, at 10 mA cm^{-2}) and >95% of that discharged capacity can be recovered upon subsequent recharge (red squares, at 10 mA cm^{-2}) with a half-cycle voltage hysteresis of <300 mV. (C and D) The voltage-time curves for cells discharged at 25 mA cm^{-2} to 40% DOD_{Zn}, and recharged at either (C) 5 mA cm^{-2} or (D) 10 mA cm^{-2} . The constant voltage at 1.93 V indicates the potentiostatic region of the charge profile.

at a current density of $\sim 10 \text{ mA cm}^{-2}$ (C/9; i.e., the entire capacity of the battery is discharged in 9 hours) and then recharging at the same rate. These cells reached an average 91% DODZn (743 mAhgZn^{-1} ; 1202 WhkgZn^{-1}) and could be recharged to >95% capacity from these extreme depths (Fig. 2B). Similar Zn depths of discharge were obtained in previous 3D Zn-air studies, but could not probe capacity recovery in this configuration because of the lack of a mature recharge-capable air cathode. Thus the emulsion based route to 3D Zn sponges provides great flexibility in application-

relating to different sizes and form factors as the mold defines the anode size and shape .

To address the feasibility of Ni-3D Zn in fields of use that demand multicell stacks, high cycle life, and power performance, Ni-3D Zn cells were cycled to a DODZn (40%) that translates to a specific energy competitive with Li-ion (Fig. 1B). The long-term experiments were conducted with a 5-mA cm^{-2} break-in cycle consisting of a $\sim 50 \text{ mAh}$ discharge (50% DODZn) and a recharge of $\sim 40 \text{ mAh}$. This first-cycle capacity mismatch was chosen to saturate the electrolyte with zincate and to introduce a buffering amount of ZnO and Ni(OH)₂ into the respective electrodes to minimize gas evolution upon charging . In subsequent cycles, the cells were discharged at 25 mA cm^{-2} (a C/1.5 rate with respect to a nominal capacity of 328 mAhgZn^{-1}) and recharged at either 5 mA cm^{-2} (Fig. 2C) or 10 mA cm^{-2} (Fig. 2D).

A $\sim 3 \text{ mAh}$ potentiostatic hold at 1.93 V was added to the end of each charge to ensure exhaustive oxidation of the NiOOH electrode while avoiding O₂ evolution. The cells ran for 111 and 141 cycles for the 5 mA cm^{-2} and 10 mA cm^{-2} charging cases, respectively, before falling below 50% of nominal cycling capacity.

Upon >20% capacity fade, typically at >80 cycles, injection of electrolyte or water into the cathode compartment revives the non hermetically sealed plastic cells back to nominal capacity, demonstrating that the fade arises from dehydration rather than irreversible passivation of either the cycled 3D Zn or Ni electrodes.

These Ni-3D Zn cells also maintained 100% of the required discharge capacity for 85 and 65 cycles, respectively, with an average energy efficiency of 84% before capacity fading [comparable to the 85% energy efficiency found in Li-ion batteries] .

The cycling stability achieved in electrolyte limited of the surfaces, showed the absence of dendrites, and maintenance of the porosity and interconnectivity of the monolithic sponge; some densification was reported, however, relative to the precycled microstructure, Fig. 3, A to C.

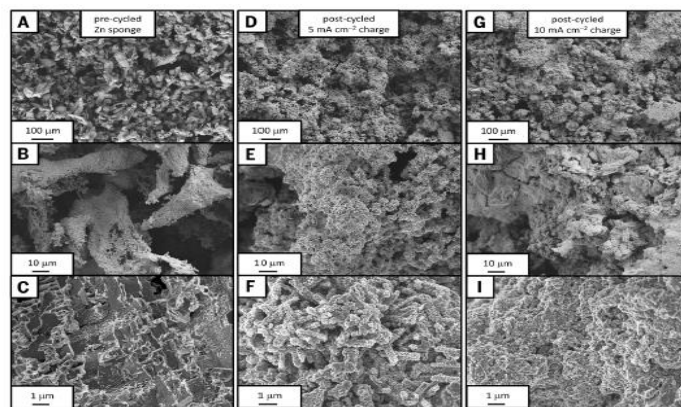


Fig. 3. Postcycling microstructural analysis of 3D Zn sponges. Scanning electron micrographic analysis of (A to C) precycled and (D to I) postcycled Zn sponges after >100 cycles, verifying that minimal shape change occurs and no dendrites are formed when the Ni-3D Zn cell is discharged at 25 mA cm^{-2} to 40% DOD_{Zn}, and recharged at either [(D) to (F)] 5 mA cm^{-2} or [(G) to (I)] 10 mA cm^{-2} .

Ni-3D Zn could compete in a third field of use—replacing lead-acid batteries within microhybrid vehicles.

The duty cycles for a normal “startstop” operation involve pulses for engine start and restart with additional auxiliary constant-use loads such as air conditioning and entertainment systems. Advanced start-stop batteries for microhybrid vehicles currently use lead-acid cells with absorbed glass mat (AGM) technology.

Lead-acid AGM has the advantage of low cost and excellent shelf life in the charged state but suffers from disadvantages as low specific, volumetric energy, life-cycle concerns due to toxic active materials (Pb and PbO₂), electrolyte instability in the discharged state, and poorer cycle life and price point compared with standard SLI (starting-lighting-ignition) lead-acid batteries.

To validate the applicability of Ni-3D Zn as a start-stop battery, approximating the current versus time duty cycle of the BMW microhybrid battery as scaled to a typical single-cell Dimensions (Fig. 4A).

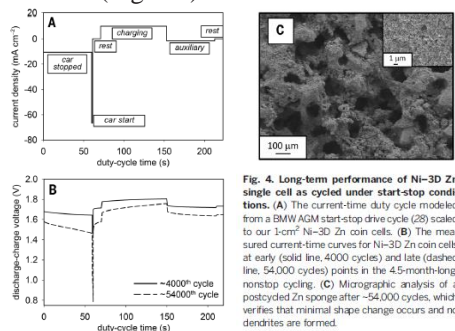


Fig. 4. Long-term performance of Ni-3D Zn single cell as cycled under start-stop conditions. (A) The current-time duty cycle modeled from a BMW AGM start-stop drive cycle (28) scaled to our 1-cm² Ni-3D Zn coin cells. (B) The measured current-time curves for Ni-3D Zn coin cells at early (solid line, 4000 cycles) and late (dashed line, 54,000 cycles) points in the 4.5-month-long, nonstop cycling. (C) Micrographic analysis of a postcycled Zn sponge after ~54,000 cycles, which verifies that minimal shape change occurs and no dendrites are formed.

The following assumptions were used:

- the specific power of individual Ni-3D Zn cells will match that of individual Lead acid cells within the AGM battery commonly used in BMW’s microhybrid systems (e.g., Exide EK900);
- a scaled-up Ni-3D Zn battery requires eight cells to achieve the necessary voltage (~12 V) and would therefore deliver 33% more power than its six-cell Pb-acid counterpart;
- Zn will occupy 19% of the packaged weight.

The through-connected void structure of the sponge serves to improve transport limitations under high-rate demands (fig. S2), as those required during the acceleration phase of a startstop duty cycle.

For start-stop batteries to achieve >104 cycles, it is customary to keep the percentage of capacity used intentionally low. Per 4-min duty cycle, the capacity tapped of the Ni-3D Zn coin cells was kept to <1% DOD_{Zn}. **More than 50,000 cycles (Fig. 4B) were achieved, with cycling stopped only when the high load pulse (~65 mA cm⁻²) reached a preset voltage limit of 0.8 V.** With a nominal 20 start-stop cycles in a round-trip commute, Ni-3D Zn would provide ~2500 days of start-stop performance (>6.8 years of daily use), approaching the average 11.4-year age of U.S. cars. **The cumulative discharge capacity for ~54,000 cycles is ~3**

times that achieved in the 40% DOD_{Zn}/100+ cycles discussed above. Postmortem analysis of the months-long-cycled (still non hermetically sealed) cells revealed a dry cell concomitant with an increased cell resistance. The post cycled 3D Zn sponge remains visibly monolithic; scanning electron microscopy reveals that the pore–solid architecture of the Zn sponge is retained and that no anomalous macroscale dendrites are electrogenerated (Fig. 4C). The effect of a 3D Zn anode based battery on the energy-storage requirements of various electric vehicles (EVs) where assessed. The quantitative assessment fixed the energy capacity for each EV application using the current state of the art for

- an electric bicycle (versus standard lead acid),
- a start-stop microhybrid (versus leadacid AGM),
- an all-electric battery vehicle (versus Li-ion).

Weight and volume savings result for all three applications by using Ni-3D Zn (Table 1).

Table 1. Summary of the projected effect of the nickel-3D zinc-based battery on various weight and normalized capacity metrics of relevance to electric vehicles (EVs). SLA, sealed lead-acid; AGM, absorbed glass mat.

	E-bike		Start-stop microhybrid		Battery electric vehicle	
	SLA	Ni-3D Zn*	AGM	Ni-3D Zn*	Li-ion†	Ni-3D Zn*
Energy capacity (Wh)	540	540	1720	1720	24,000	24,000
Weight (kg)	12.2	5.9	45.0	21.7	339	220
Specific energy (Whkg ⁻¹)	44.3	91.8	38.2	79.2	71	109
Energy density (WhL ⁻¹)	140	225	126	164	96	216

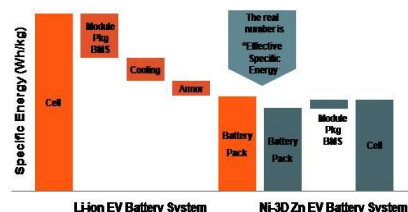
*Calculations for the Ni-3D Zn battery (scaled to match the capacity of a specific application) were made on the basis of a fully packaged battery system. The sensitivity of the energy density of the battery to variations in capacity of the zinc anode and nickel cathode is 20% (fig. S3). †Metrics for the Li-ion stack in the Nissan Leaf were used for comparison.

A projected Ni-3D Zn battery pegged to the specific capacity of the Nissan Leaf (24 kWh) saves 100 kg of weight. Much of the weight and potential cost savings with Ni-3D Zn over Li-based EV batteries come from the reduction or elimination of subsystems that are required for Li-ion battery packs, which include thermal management, sophisticated electronic controls, and structural protection to manage any catastrophic events.

Hence the 3D Zn-based batteries will not require comparably complex subsystems.

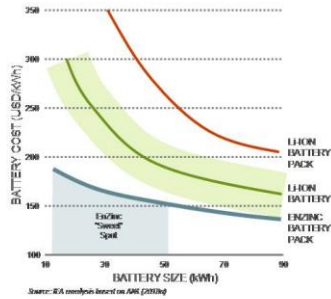
FROM CELL TO BATTERY PACK

LI-ION CELL SPECIFIC ENERGY GETS CUT IN HALF



Lithium Ion Battery costs depends on size

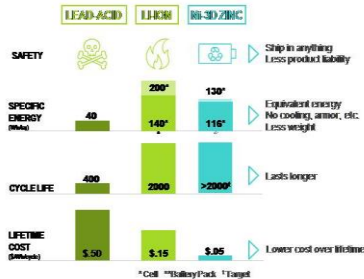
LI-ION BATTERY COSTS DEPENDS ON SIZE



EnZine | 3D ZINC SPONGE BATTERIES

NI-3D ZINC BATTERIES ARE COST EFFECTIVE :

3D ZINC IS THE SAFEST, MOST COST EFFECTIVE SOLUTION



EnZine | 3D ZINC SPONGE BATTERIES

- 3Times Energy of lead acid with 2 to 3 times Cycle life
- 1/3rd The Size ,Weight & Volume of Lead Acid
- Equivalent cost to lead acid to manufacture but 1/10 the per cycle cost to operate
- Half cost of Li-ion with one-third the cost to operate

NI-3D ZINC BATTERY IS FUNDAMENTALLY SAFE

NI-3D ZN IS FUNDAMENTALLY SIMPLE

	Lead-Acid	Li-Ion	Ni-3D Zn
Anode	Lead paste on a lead-selenium grid	Graphite + Binders	3D Zinc
Separator	PVC	Polystyrene	Polystyrene
Cathode	Lead paste on a lead-selenium grid	Cobalt, Nickel, Manganese, Lithium + Binders	Nickel
Electrolyte	Aqueous	Organic Solvents	Aqueous

EnZine | 3D ZINC SPONGE BATTERIES

The advantages of Ni-3D Zn-based batteries is just not just the projected range and cost improvements in EV applications. Eliminating dangers associated with fire risk from incidents of Li-ion thermal runaway, all while using a nonstrategic, globally available, recyclable natural resource.

Possible "INDIA SCENARIO using 3D Ni-Zinc:



India is the world's fourth largest producer of Zinc Ore with abundant reserves. The first documented use and production of pure zinc dates back to 2500 years ago in Jawar in the State of Rajasthan. It is expected that India will produce 6MT of Zinc by 2020 and is capable of producing much more. With the huge increase in EV and electric mobility (two,three wheelers, passenger cars and electric) uptake supported by friendly electric mobility programs that are being facilitated. Aligned with India's focus to reinforce grid capacity, stability and to fast track renewable energy goals is bound to increase the requirements of energy storage systems and subsystems at various levels.3D Zinc based batteries provides a very cost effective minimum carbon footprint solution for self sufficiency to cater to existing and future needs of the country. References

1. C. Davies, "Calls for lithium battery review after Boeing Dreamliner fire at Heathrow," The Guardian (19 August 2015); <https://www.theguardian.com/business/2015/aug/19/lithium-battery-review-boeing-dreamliner-fire-heathrow>.
2. E.-Y. Jong, "Samsung to recall Galaxy Note 7 smartphone over reports of fires," Wall Street Journal (2 September 2016);<https://www.wsj.com/articles/samsung-to-recall-galaxy-note-7-smartphone-1472805076>.
3. "UN bans lithium batteries as cargo on passenger planes," BBC News, Technology (23 February 2016); www.bbc.com/news/technology-35643213.
4. R. O'Brien, R. Nickel, "Battery-hungry world turns to South America's 'lithium triangle'," Reuters (15 March 2016); www.reuters.com/article/us-latam-lithium-idUSKCN0WH1BZ.
5. E. Wesoff, "How soon can Tesla get battery cell costs below \$100 per kilowatt-hour?" Green Tech Media, 15 (March 2016); <https://www.greentechmedia.com/articles/read/How-Soon-Can-Tesla-Get-Battery-Cell-Cost-Below-100-per-Kilowatt-Hour>.
6. P. Bonnick, J. R. Dahn, J. Electrochem. Soc. 159, A981–A989 (2012).
7. A. Sonoc, J. Jeswiet, V. K. Soo, Procedia CIRP 29, 752–757(2015).
8. A. A. Pesaran, G.-H. Kim, J. Neubauer, K. Smith, S. Santhanagopalan, Design and Analysis of Large Lithium-Ion Battery Systems (Artek House, Boston London, 2015).
9. A. M. Zamarayeva et al., Adv. Electronic Mater. 2, 1500296 (2016).
10. J.-S. Lee et al., Adv. Energy Mater. 1, 34–50 (2011).
11. J. McBreen, J. Electroanal. Chem. 168, 415–432 (1984).

12. K. Bass, P. J. Mitchell, G. D. Wilcox, J. Smith, J. Power Sources 35, 333–351 (1991).
13. M. Ma et al., J. Power Sources 179, 395–400 (2008).
14. J. F. Parker, C. N. Chervin, E. S. Nelson, D. R. Rolison, J. W. Long, Energy Environ. Sci. 7, 1117–1124 (2014).
15. D. R. Rolison, J. F. Parker, J. W. Long, U.S. Pat. Appl. No.20140147757.
16. J. F. Parker et al., ACS Appl. Mater. Interfaces 6, 19471–19476 (2014).
17. M. Schmid, M. Willert-Porada, J. Power Sources 351, 115–122 (2017).
18. J. E. Oxley, C. W. Fleischmann, Improvement of zinc electrodes for electrochemical cells, First, second, and third quarterly reports N66-13568, N66-16956, N66-26870 (Leesona Moos Labs, Great Neck NY, 1965–1966).
19. Material Safety Data Sheet, PG-MSDS-0001 (2014); www.jameco.com/Jameco/Products/ProdDS/2115830-MSDS.pdf.
20. J. F. Parker, I. R. Pala, C. N. Chervin, J. W. Long, D. R. Rolison, J. Electrochem. Soc. 163, A351–A355 (2016).
21. E. J. Rubin, R. Baboian, J. Electrochem. Soc. 118, 428–433 (1971).
22. J. X. Yu, H. Yang, X. P. Ai, X. M. Zhu, J. Power Sources 103, 93–97 (2001).
23. Z. Adamedes, Gassing characteristics of high capacity, high energy density rechargeable silver zinc cells, IEEE: Battery Conference on Applications and Advances 41–45 (IEEE, 1998).
24. H. Ali, S. Ali-Oettinger, Advancing Li-ion (2012); https://www.pv-magazine.com/archive/articles/beitrag/advancing-li-ion-_100006681/501/#axzz4QbD0S6qc.
25. M. Chamoun et al., NPG Asia Mater. 7, e178 (2015). <https://doi.org/10.1038/am.2015.32>
26. P. Haeffliger et al., Environ. Health Perspect. 117, 1535–1540 (2009).
27. L. T. Lam, N. P. Haigh, C. G. Phyland, A. J. Urban, J. Power Sources 133, 126–134 (2004).
28. J. Petersen, Micro-hybrids and the multi-billion dollar battery battle, Alt Energy Stocks (2012); www.altenergystocks.com/archives/2012/06/microhybrids_and_the_multibillion_dollar_battery_battle_1.html.
29. United States Department of Transportation, Average Age of Automobiles and Trucks in Operation in the United States (U.S. Department of Transportation, 2014); www.rita.dot.gov/bts/sites/rita.dot.gov/bts/files/publications/national_transportation_statistics/html/table_01_26.html_mfd.
30. A. Gavrilović-Wohlmuther, A. Laskos, C. Zelger, B. Gollas, A. H. Whitehead, J. Power Energy Eng. 9, 1019–1028 (2015).
31. B. Sharifi, M. Mojtahedi, M. Goodarzi, J. V. Khaki, Hydrometallurgy 99, 72–76 (2009).
32. Li, M., Lu, J., Chen, Z.W., and Amine, K. (2018). 30 years of lithium-ion batteries. Adv. Mater. 30, 1800561.
33. Eftekhari, A., and Kim, D.W. (2018). Sodium-ion batteries: new opportunities beyond energy storage by lithium. J. Power Sources 395, 336–348.
34. Fang, R.P., Zhao, S.Y., Sun, Z.H., Wang, W., Cheng, H.M., and Li, F. (2017). More reliable lithium-sulfur batteries: status, solutions and prospects. Adv. Mater. 29, 1606823.
35. Ma, L., Yu, T.W., Tzoganakis, E., Amine, K., Wu, T.P., Chen, Z.W., and Lu, J. (2018). Fundamental understanding and material challenges in rechargeable nonaqueous Li-O₂ batteries: recent progress and perspective. Adv. Energy Mater. 8, 1800348.
36. Balducci, A., Belanger, D., Brousse, T., Long, J.W., and Sugimoto, W. (2017). A guideline for reporting performance metrics with electrochemical capacitors: from electrode materials to full devices. J. Electrochem. Soc. 164, A1487–A1488.
37. Mao, Z., and White, R.E. (1992). Mathematical modeling of a primary zinc/air battery. J. Electrochem. Soc. 139, 1105–1114.
7. Zhang, X.G. (2006). Fibrous zinc anodes for high power batteries. J. Power Sources 163, 591–597.
38. Parker, J.F., Chervin, C.N., Nelson, E.S., Rolison, D.R., and Long, J.W. (2014). Wiring zinc in three dimensions re-writes battery performance—dendrite-free cycling. Energy Environ. Sci. 7, 1117–1124.
39. Parker, J.F., Nelson, E.S., Wattendorf, M.D., Chervin, C.N., Long, J.W., and Rolison, D.R. (2014). Retaining the 3D framework of zinc sponge anodes upon deep discharge in Zn-air cells. ACS Appl. Mater. Interfaces 6, 19471–19476.
40. Parker, J.F., Chervin, C.N., Pala, I.R., Machler, M., Burz, M.F., Long, J.W., and Rolison, D.R. (2017). Rechargeable nickel-3D zinc batteries: an energy-dense, safer alternative to lithiumion. Science 356, 415–418.
41. Energizer. (2016). Product safety data sheet for silver oxide-zinc. http://data.energizer.com/pdfs/silveroxidezinc_psd.pdf.
42. Li, Y., and Dai, H. (2014). Recent advances in zinc-air batteries. Chem. Soc. Rev. 43, 5257–5275.
43. Gu, P., Zheng, M.B., Zhao, Q.X., Xiao, X., Xue, H.G., and Pang, H. (2017). Rechargeable zinc-air batteries: a promising way to green energy. J. Mater. Chem. A 5, 7651–7666.
44. Lai, S.-H., James, M.-I., Wu, X.-C., Dong, Y.-L., Wang, J.-H., Gao, M., Liu, J.-F., and Sun, X.-M. (2017). A promising energy storage system: rechargeable Ni-Zn battery. Rare Met. 36, 381–396.
45. Mainar, A.R., Colmenares, L.C., Blázquez, J.A., and Urdampilleta, I. (2018). A brief overview of secondary zinc anode development: the key of improving zinc-based energy storage systems. Int. J. Energy Res. 42, 903–918.
46. Song, M., Tan, H., Chao, D., and Fan, H.J. (2018). Recent advances in Zn-ion batteries. Adv. Funct. Mater. 28, 1802564.
17. Ko, J.S., Parker, J.F., Vila, M.N., Wolak, M.A.,

- Sassin, M.B., Rolison, D.R., and Long, J.W. (2018). Electrocatalyzed oxygen reduction at manganese oxide nanoarchitectures: from electroanalytical characterization to device-relevant performance in composite electrodes. *J. Electrochem. Soc.* 165, H777–H783.
48. Mainar, A.R., Iruin, E., Colmenares, L.C., Blázquez, J.A., and Grande, H.-J. (2018). Systematic cycle life assessment of a secondary zinc-air battery as a function of the alkaline electrolyte composition. *Energy Sci. Eng.* 6, 174–186.
49. Parker, J.F., Pala, I.R., Chervin, C.N., Long, J.W., and Rolison, D.R. (2016). Minimizing shape change at Zn sponge anodes in rechargeable Ni-Zn cells: impact of electrolyte formulation. *J. Electrochem. Soc.* 163, A351–A355.
50. Zhao, Z., Zhang, Y., Chen, P., Wu, Y., Yang, H., Ding, H., Zhang, Y., Wang, Z., Du, X., and Liu, N. (2018). Graphene oxide-modified zinc anode for rechargeable aqueous batteries. *Chem. Eng. Sci.* <https://doi.org/10.1016/j.ces.2018.06.048>.
51. Chamoun, M., Hertzbert, B.J., Gupta, T., Davies, D., Bhadra, S., Van Tassell, B., Erdonmez, C., and Steingart, D.A. (2015). Hyper-dendritic nanoporous zinc foam anodes. *NPG Asia Mater.* 7, 1–8.
52. Arenas, L.F., Loh, A., Trudgeon, D.P., Li, X., Ponce de León, C., and Walsh, F.C. (2018). The characteristics and performance of hybrid redox flow batteries with zinc negative electrodes for energy storage. *Renew. Sustain. Energy Rev.* 90, 992–1016.
53. Khor, A., Leung, P., Mohamed, M.R., Flox, C., Xy, Q., An, L., Wills, R.G.A., Morante, J.R., and Shah, A.A. (2018). Review of zinc-based hybrid flow batteries: from fundamentals to applications. *Mater. Today Energy* 8, 80–108.
54. Sun, K.E.K., Hoang, T.K.A., Doan, T.N.L., Yu, Y., Zhu, X., Tian, Y., and Chen, P. (2017). Suppression of dendrite formation and corrosion of the zinc anode of secondary aqueous batteries. *ACS Appl. Mater. Interfaces* 9, 9681–9687.
55. Garcia, G., Ventosa, E., and Schuhmann, W. (2017). Complete prevention of dendrite formation in Zn metal anodes by means of pulsed charging protocols. *ACS Appl. Mater. Interfaces* 9, 18691–18698.
56. Higashi, S., Lee, S.W., Lee, J.S., Takechi, K., and Cui, Y. (2015). Avoiding short circuit from zinc metal dendrites in anode by backside-plating configuration. *Nat. Commun.* 7, 11801.
57. Yan, Z., Wang, E., Jiang, L., and Sun, G. (2015). Superior cycling stability and high rate capacity of three-dimensional Zn/Cu foam electrodes for zinc-based alkaline batteries. *RSC Adv.* 5, 83781–83787.
58. Turney, D.E., Gallaway, J.W., Yadav, G.G., Ramirez, R., Nyce, M., Banerjee, S., Chen-Wiegart, Y.-C.K., Wang, J., D'Ambrose, M.J., Kolhekar, S., et al. (2017). Rechargeable zinc alkaline anodes for long-cycle energy storage. *Chem. Mater.* 29, 4819–4832.
59. Li, P.-C., Chien, Y.-J., and Hu, C.-C. (2016). Novel configuration of bifunctional air electrodes for rechargeable zinc-air batteries. *J. Power Sources* 313, 37–45.
60. Guo, Z., Li, C., Li, W., Guo, H., Su, X., He, P., Wang, Y., and Xia, Y. (2016). Ruthenium oxide coated ordered mesoporous carbon nanofiber arrays: a highly bifunctional oxygen electrocatalyst for rechargeable Zn-air batteries. *J. Mater. Chem. A* 4, 6282–6289.
61. Li, B., Ge, X., Goh, F.W.T., Hor, T.S.A., Geng, D., Du, G., Liu, Z., Zhang, J., Liu, X., and Zong, Y. (2015). Co₃O₄ nanoparticles decorated carbon nanofiber mat as a binder-free aircathode for high performance rechargeable zinc-air batteries. *Nanoscale* 7, 1830–1838.
62. Sapunkov, O., Pande, V., Khetan, A., Choomwattana, C., and Viswanathan, V. (2015). Quantifying the promise of ‘beyond’ Li-ion batteries. *Trans. Mater. Res.* 2, 045002.

Joule

ACKNOWLEDGMENTS

The authors wish to acknowledge the efforts of Enzinc Inc team and the U.S. Naval Research Laboratory, the Advanced Research Projects Agency–Energy (ARPA-E) for financial support (award DE-AR-0000391) with the guidance of the ARPA-E staff of the Robust Affordable Next Generation Energy Storage (RANGE) program. Their work was also supported by the U.S. Office of Naval Research. M.F.B. and M.M. thank B. Dussia, R. Tarr, K. Dias, and S. Mohanta for their essential input, as well as the staff of the Venture Greenhouse green technology incubator for helping assess the commercial potential of Zn-based batteries equipped with Zn sponge anodes. I.R.P. was a Naval Research Laboratory–National Research Council Postdoctoral Associate. D.R.R. served as technical lead for the project. J.F.P., J.W.L., and D.R.R. oversaw experimental design. J.F.P. and I.R.P. prepared Zn sponges for use in NiOOH–3D Zn coin cells. C.N.C. harvested the NiOOH cathode and multilayered the charged cathode tape into multi-ply, Ni foam-held NiOOH cathodes. J.F.P. and I.R.P. assembled NiOOH–3D Zn coin cells and ran charge-discharge cycling experiments. J.F.P., C.N.C., and J.W.L. analyzed electrochemical data. J.F.P. and C.N.C. collected electron micrographs of the postcycled Zn sponge anodes. M.F.B. served as project and systems engineering lead for the project. M.M. served as lead for battery design engineering. D.R.R., J.F.P., and J.W.L. are inventors on patent applications US 2014/0147757 and US 2016/0093890, submitted by the U.S. Department of the Navy, which covers the fabrication of 3D interconnected Zn sponges and their use as electrodes in electrochemical cells.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/356/6336/415/suppl/DC1