

Energy Focus

Sponge electrode architecture provides safe, high-performance Ni-3D Zn battery

Current energy-storage technologies rely heavily on lithium-ion batteries. And for good reason: they offer high capacities, relatively long cycle lives, and well-established manufacturing processes. However, Li-ion batteries raise concerns over flammability and require rare and expensive materials. While the storage potential of lithium-ion chemistries is largely tapped out, automobiles and portable electronics will require storage capacities and fire-safety assurances well beyond present-day capabilities. Scientists and engineers are investigating new electrode and electrolyte alternatives in an effort to overcome this challenge. Zinc—an inexpensive and abundant metal—has long been used as an anode in primary alkaline batteries. Unfortunately, zinc permits dendrites to grow on electrode surfaces under typical battery recharging conditions. These tiny needle-like structures may reach $>100\ \mu\text{m}$ in length and short-circuit the battery—but with a whimper (loss of voltage) rather than a bang (flames and sparks).

To address this problem, researchers from the US Naval Research Laboratory (NRL) developed a three-dimensional (3D) Zn sponge electrode architecture and, along with collaborators from start-up company EnZinc, Inc., have incorporated it into a rechargeable battery design. The research effort, led by NRL's Joseph F. Parker, Debra R. Rolison, and Jeffrey W. Long, produced the 3D structure from Zn powder and benign ingredients, and then oxidized the surface to envelop the form factor in a ZnO shell with a fused Zn metal core. The researchers implemented the Zn sponge anode in a nickel-zinc (Ni-3D Zn) system, which uses a rechargeable nickel hydroxide (NiOOH) cathode. This configuration yielded long cycle lifetimes, energy densities that met or exceeded performance levels of lithium-ion batteries, while relying on inexpensive and nonflammable materials. The researchers published their work in a recent issue of *Science* (doi:10.1126/science.aak9991).

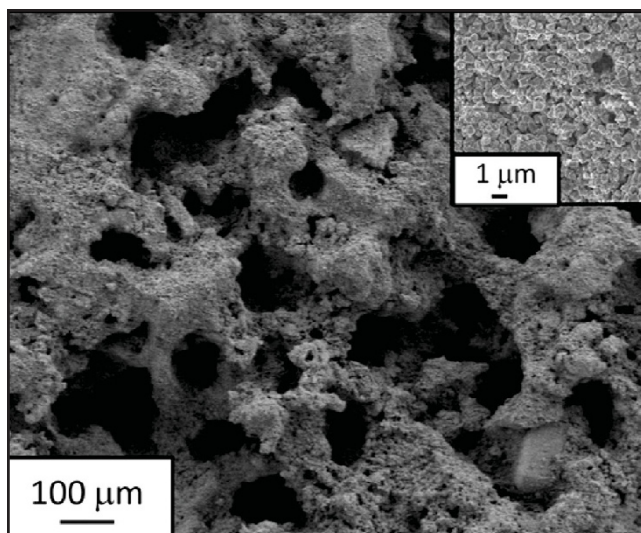
In describing the significance of this research, Rolison says, “In battery research, a common emphasis is on new materials; we instead turned to an old material but brought it into the 3D architectural realm. The aperiodic sponge with its co-continuity of solid

The research team relied on an aqueous mixture of potassium and lithium hydroxides as the electrolyte, along with insoluble calcium hydroxide that was deposited on specific surface locations of the metallic Zn sponge. The Ni-3D Zn cells were cycled in primary (single-use) and secondary (multiple charge/discharge cycles) configurations. A full discharge of the battery allowed 91% of the zinc sponge to oxidize and yielded 1.2 kilowatt-hours of energy per kilogram of the anode material. When the cells cycled repeatedly (reversibly tapping 40% of the total amount of zinc present in the battery), the energy densities reached single-cell Li-ion capacity for over 100 cycles. EnZinc implemented the NRL results into their multicell stack design and found that weight and volumetric advantages accrue for Ni-3D Zn; the new technology minimizes the added weight/volume of system components necessary to manage safety concerns with Li-ion stacks.

The sponge-like structure of the anodes demonstrated a vital microstructural advantage: repeated cycling, including both high and low power loads, did not allow for significant dendrite growth. The anodes endured 54,000 charge/discharge cycles using a duty cycle typical of start–stop batteries, which requires high power pulses, but low utilization of zinc per cycle. The Ni-3D Zn performance demonstrates that it can viably compete against advanced lead-acid batteries in microhybrid electric vehicles.

“By demonstrating extreme capacity in single-use mode, cyclability to high Zn-normalized depths-of-discharge, and tens-of-thousands of short-duration duty cycles,” Parker says, “we can now offer a technologically relevant alternative to fire-prone Li-ion batteries in multiple fields-of-use.”

A novel battery configuration is only as good as its large-scale production viability. To that end, the Ni-3D Zn approach presents important advantages because its raw materials are abundant and its balance of plant requirements (e.g., thermal management, electronic controls, and structural protection) is



Scanning electron microscope image of a Zn anode after 54,000 cycles. The material retained its ordered architecture and shows no dendrites. Credit: *Science Magazine* (AAAS).

zinc to wire electrons and void to plumb electrolyte and dissolved intermediates throughout the entire electrode volume improves electrochemical and chemical reaction uniformity during charge/discharge cycling. The architecture physically suppresses formation of separator-piercing dendrites, which enables unprecedented cycle life and deep utilization of the zinc.”



minimal. Furthermore, the battery can be effectively scaled up from small electronics (<500 Wh) to full electric vehicles (24 kWh). When compared to a lithium-ion battery of a Nissan Leaf automobile, the Ni-3D Zn system is projected to offer similar energy density over a longer lifetime, with greater safety, and at lower cost.

Outside researchers have taken notice. As US Army Research Laboratory (ARL) scientist Oleg Borodin points out, “The 3D sponge architecture enabled a remarkable Ni-3D Zn battery performance at high depth of discharge

and high current densities (high power) without dendrite formation, making it a serious contender to some of the currently used lithium-ion packs due to significantly simplified thermal and electronic management systems.” ARL’s Kang Xu also commented: “For military applications, ‘water’ is really the direction to go. The recent revival of aqueous battery research, including PNNL [Pacific Northwest National Laboratory] and NRL’s Zn chemistries and ARL’s electrolyte, show encouraging results that enable an aqueous battery chemistry with energy densities

and cycle life close to that of Li-ion, but with much higher safety.”

While it is too early to predict the path of this novel battery technology through the energy storage and electric vehicle markets, the Ni-3D Zn breakthrough has already made positive forward progress. The NRL signed a technology licensing deal with co-developer EnZinc, Inc. earlier this year. This agreement paves the way for initial prototyping and eventual market entry, and could mark the emergence of an important new player on the battery scene.

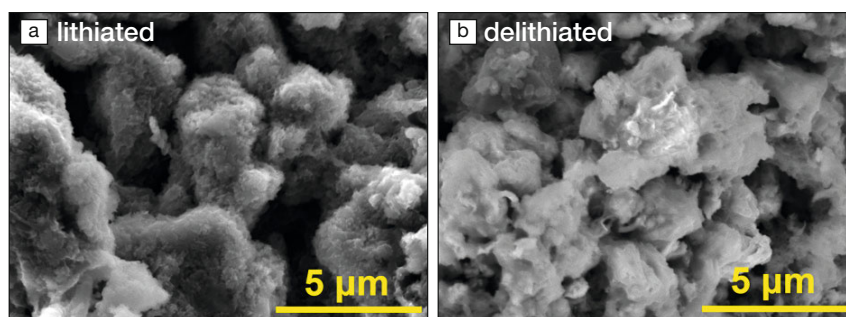
Boris Dyatkin

Energy Focus

Asphalt porous structure enables fast-charging high-capacity Li-metal anode

State-of-the-art lithium-ion batteries (LIBs) employ graphite anodes and transition-metal-oxide cathodes. If in lieu of graphite, Li metal is used as an anode, these batteries can be made more energy dense (increasing both weight-specific and volumetric performance). Unfortunately, Li-metal anodes suffer from nonuniform deposition/dissolution electrochemistry. This leads to needle-like deposits that could cause an internal short circuit in the extreme event and pose a safety risk. This phenomenon is generically referred to as dendrite formation, and is a major challenge for cycle life and commercialization of compact LIBs employing Li-metal anodes. A related aspect of futuristic batteries, especially for automotive applications, is the ability to charge fast. For example, a battery being charged at 6C would recharge in 10 min (1C implies a 60-min charging time). These operational requirements put additional constraints on practical application of Li-metal electrodes.

James M. Tour’s research group at Rice University has come up with an innovative approach to resolving the dendrite problem as well as stable, fast-charging electrodes. The study was recently published in *ACS Nano* (doi:10.1021/acsnano.7b05874).



Porous electrodes made up of asphalt and graphene nanoribbons (GNRs) provide surface for lithium electrodeposition/electrostripping. The lithium deposition at the electrode–electrolyte interface is quite uniform and the dendrite formation is substantially mitigated, as revealed by images of electrode samples (a) with deposited Li and (b) after Li is electrostripped. Credit: James Tour.

Instead of working with bare Li metal electrodes, the researchers developed a porous carbon host for Li electrochemistry using asphalt (Asp). Graphene nanoribbons (GNRs) were added to ensure sufficient electronic conduction. Such a porous Asp-GNR electrode provides better cyclability (hundreds of cycles) and electrode performance (i.e., smaller overpotential), even at higher rates of operation (as high as 10C). Interestingly, the morphology of deposited Li in this host is uniform, rather than the typically observed dendritic features on Li anodes—noting that the term “dendrite” is used here to signify the whole set of nonuniform Li deposition morphologies.

The superior response of these Asp-GNR electrodes is attributed to a complex interplay among interfacial and bulk phenomena. The extremely high surface area

of the Asp-GNR composite (>3000 m²/g) gives rise to more efficient electrochemical reactions at the electrode–electrolyte interface (i.e., lower overpotential), while reasonable conductivity resulting from GNR provides sufficient bulk conduction. Use of asphalt is important as it forms the necessary high-surface-area backbone structure. Additionally, it has very low levels of graphitization, which in turn reduces the propensity for Li intercalation in the host material, and promotes Li deposition at the surface. This intercalation-free approach also favors ultrafast operation, as sluggish solid-state diffusion—which is a characteristic of the intercalation process—is completely bypassed. Thus, the proposed Asp-GNR electrodes exhibit a reasonable balance between different transport processes, which leads to stable and fairly uniform