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.

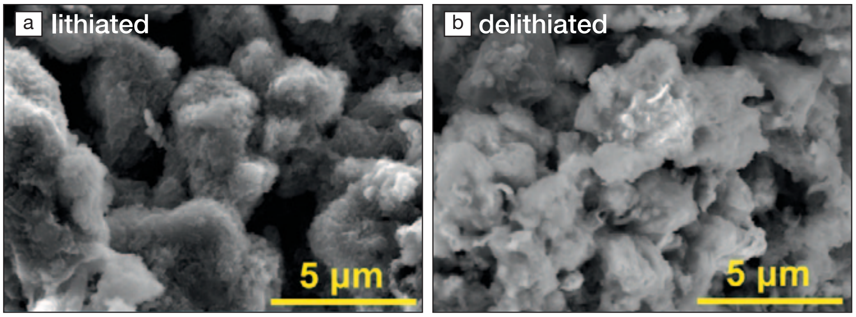
Outside researchers have taken notice. As US Army Research Laboratory (ARL) scientist Oleg Borodin points out, "The 3D sponge architecture enabled a remarkable Ni-3D Zn battery performance at high depth of discharge and high current densities (high power) without dendrite formation, making it a serious 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



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.

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). 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 m^2/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

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cycling. The use of a porous host structure also provides structural rigidity and the space to accommodate volume changes upon Li deposition and dissolution.

While discussing the implications of this work, Martin Bazant from the Massachusetts Institute of Technology (not related to the published work) applauded the improvement in the efficiency of cycling Li-metal anodes in an asphalt-graphene matrix, and felt that it would be interesting to identify the mechanism, either modifying transport or reaction kinetics, in future work.

Thus, the Asp-GNR porous structure offers an interesting solution to the quest for uniform, stable Li-metal electrochemistry. It simultaneously combines augmentative characteristics such as reduced electrode impedance and uniform Li electroplating. Future work relies on further improvement of such electrodes to make them a commercial reality.

Aashutosh Mistry

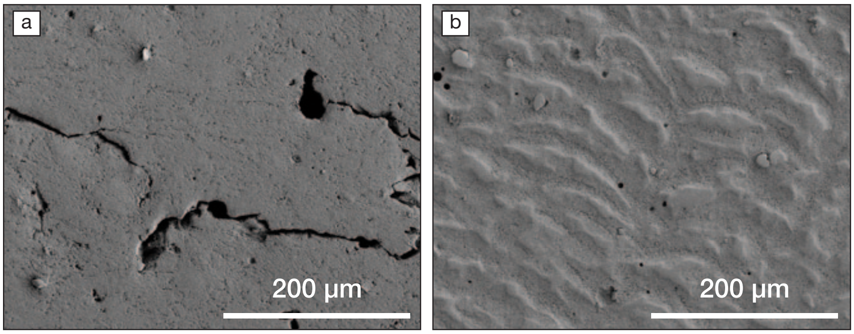
Nano Focus

Solidification technique at the nanoscale expands range of 3D-printable alloys

While three-dimensional (3D) printers have been able to print metal parts for years, the process works only for a few industrially useful alloys. The vast majority of the 5500 alloys currently used cannot be additively manufactured. That could change soon thanks to researchers at HRL Laboratories, LLC in Malibu, Calif., who have developed a way to 3D print high-strength aluminum alloys. The method opens the possibility of 3D printing and welding light, strong alloys that are commonly used to make aircraft frames as well as car and truck parts. It might also lead to 3D printing of any metal. This work is reported in a recent issue of *Nature* (doi:10.1038/nature23894).

Conventional 3D printing of metallic structures involves depositing layers of metal powders and then moving a focused laser or electron beam across the layers one at a time, melting and fusing the material together to form a solid mass.

Because this fusion of metal layers is similar to welding, 3D printing works for alloys that are known to be weldable. In other alloys, such as high-strength aluminum and nickel alloys, it results in cracks that can span multiple layers. The process, called hot tearing, occurs because the grains in these alloys solidify as vertical columns, causing the alloy's residual liquid content to get trapped between them. Later, as the solid material shrinks, the liquid film can rupture.



(a) Microstructure analysis of a 3D-printed component made with the aluminum alloy Al7075 shows large cracks; (b) when the alloy powders are coated with Zr nanoparticles before 3D printing, no cracks are observed. Credit: *Nature.*

Hot tearing would not happen if the alloys solidified as small grains as opposed to large columns. Scientists have tried in the past to disrupt column growth and create a granular microstructure by changing things like the 3D printing speed or the power of the laser. But that does not provide the scientists enough control over the microstructure.

So John H. Martin and his colleagues at HRL Laboratories turned to an old strategy used in metal casting, where additives are commonly mixed into liquid metals to act as seeds for crystals to grow. The researchers coated alloy powders with hydrogen-stabilized zirconium nanoparticles and then used lasers to heat them. As the metal cools and solidifies, it follows the crystalline pattern created by the nanoparticles.

To find a suitable nanoparticle material whose crystal lattice matches that of a specific alloy, the researchers had to analyze over 4500 different alloy and nanoparticle combinations using big data software.

The method works on the two most commonly used high-strength aluminum alloys—Al7075 and Al6061. Microstructure analysis of printed samples showed that while untreated alloy powders gave samples with columnar grains and a high density of cracks, the Zr-coated powders resulted in fine grains without cracks. The mechanical properties of the treated alloys were also better.

"The properties they obtained were very close to those which you'd get from a wrought, or forged, product," says Iain Todd, professor of metallurgy at The University of Sheffield in the UK and director of the UK EPSRC's Future Manufacturing Hub, who was not involved in the work. "An amazing feat."

The approach should be applicable to a wide range of alloys and can be implemented using a range of additive machines, the researchers write in the article. The challenge will be to find the right kind of nanoparticle that works with other material types, Todd says, "nickel superalloys, high strength titanium, intermetallics like titanium aluminides, all of which we use in 3D printing and all of which can display unwanted behaviors in the process."

Prachi Patel

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