New Electrode Structures for Next-Generation Batteries

One of the most promising routes for increasing battery capacity is the geometric optimization of internal electrode structures. In conventional modern battery technology, electrode particles are mixed with binders and sandwiched into laminated structures. Such simple electrodes typically leave about 30–50 percent of the volume unutilized due to limitations in the diffusive process.

A 3D electrode, on the other hand, can permit the facile transport of ions via short diffusion paths and enhanced interfacial area. Furthermore, creating a controlled porosity inside the 3D electrodes allows the electrolyte to deeply penetrate the electrode volume, leading to a very high volume utilization. This, in turn, is expected to eliminate unutilized electrode volume and reduce battery weight. To date, major hurdles in achieving this new concept has been the fact that current 3D printing techniques are mostly limited to extrusion-based methods, which only allow interdigitated geometries [8], sometimes referred to as 2.5D structures (multiple stacked 2D layers). Note that the interdigitated geometries cannot endure load effectively and are not useful as structural materials. Therefore, with conventional 3D extrusion-based printing technology, it is impossible to realize a truly 3D structure with controlled porosity throughout the entire electrode volume.

In this article, we introduce a new concept in 3D printing technology that allows the production of battery electrodes that are lightweight, high-capacity, and display superior mechanical properties. The electrodes have a 3D lattice architecture and a controlled hierarchical porosity distribution over their entire volume. The new printing method leads to a near-full utilization of the electrode material. The technology will lead to a 50 percent (or greater) increase in specific capacity for batteries, effecting a proportional decrease in their weight. In addition, the electrodes can support a significant amount of load while storing the electrochemical energy. This addresses another attribute of batteries with potential implications for military applications: their propensity to integrat- ed into lightweight structural components, such as UAS wings. These superior properties may be achieved by leveraging the expertise from two complementary areas of advanced manufacturing research and development (Carnegie Mellon University and battery design and analysis (Missouri University of Science and Technology).

3D Electrode Fabrication via Novel 3D Printing Technology

The 3D electrodes were fabricated using an aerosol jet-based (AJ) 3D printing method, which allows for the deposition of nanopartic- les dispersed in a solvent (i.e., the nanopar- ticle ink) onto a substrate by creating a mist of particles guided by a carrier gas. The AJ printing system includes two atomizers (ul- trasonic and pneumatic), a programmable XY motion stage, and a deposition head. Figure 2(A) depicts the printing process. The platen on which the electrode was built was heated to 110 degrees Celsius, which helped dry the mass of nanoparticles (diameter of about 20 μm in the present case) by removing the solvents. The next set of droplets was then dispensated at an offset, as shown in Figure 2(A).

In order for these to adhere to the previously formed pillar, we rely on the fact that the surface forces of the droplets scale as r−2, while the inertia forces scale as r3, where r is the radius of the droplet. This allows for strong adhesion forces for the droplet as compared to its inertia forces (i.e., weight) at length scales of 100 μm or less. As a result of this scaling, the printed droplet adhered to the pillar rather than falling off. The platen heat then removed the solvent, so that the pillar is ready to receive the next droplet containing silver nanoparticles.

This process was continued until a full lat- tice was formed. Figure 2(B) presents a schematic of the lithiation for a 5×5×5 lattice and a dense block of equivalent overall size. The charge carrying capacity of the lattice electrodes is significantly higher than that for the block electrode for the same amount of charging time. Figure 2(C) presents representative scanning electron microscope (SEM) images of printed 3D electrodes showing complex lattice geometries and porosities at different length scales. The printing produced controlled porosity at an approxi- mately 100–300 μm length scale, while a smaller porosity at a 1 μm length scale was obtained from sintering of the nanoparticles [9]. The percentage of smaller porosity can be controlled from 1 percent to 20 percent by varying the sintering temperature [10]. The hierarchical porous electrode structures shown in Figure 2(C) are to the best of our knowledge, the first such reported.

3D Electrode Battery Performance

The 3D electrode demonstrates an unprecedented improvement in battery performance, including a 400 percent increase in specific capacity and a 100 percent increase in areal capacity. It also demonstrates a high elec-
shows the comparison of the electrochemical cycling performance for both lattice and block electrodes. Despite some variation among the samples (which might be caused by different material batches), it can be confirmed that the lattice electrode structures significantly enhance the battery performance when compared to the block electrode structures. Further, after 40 electrochemical cycles, the electrode lattice shape was intact upon disassembly of the coin-cell battery during our tests, which implies a robust electrochemical-mechanical property [9].

The mechanical properties of the proposed electrode are also very promising. In order to examine any possibility that the porous electrode structures fabricated using 3D printing could act as structural materials [12], we conducted a mechanical test. The 3D lattice electrodes shown in Figure 2(C) were subjected to compressive loads in an Instron machine with an appropriate load cell, and simulations were carried out to capture their behavior. Figure 4 shows the results of the structure under compression and the corresponding stress-strain diagrams for lattices.

At first, the material acted as a cellular structure (similar to honeycombs), absorbing a large amount of deformation without failure. Strains in excess of 50 percent could be tolerated by the structure. The plateau stress could be increased by 400 percent by coating the electrode structures with a nanometer scale metallic layer. This demonstrates that the 3D printed battery electrodes can be used as structural materials.

### Scalability and Future Work

The 3D nanoparticle printing process is extremely rapid. For example, a droplet of electrode material (20 μm diameter) can be printed in 4–10 milliseconds. Commerically available aerosol jet machines allow up to four printheads to operate in tandem, which further increases printing speed. And heating the platen can quicken the evaporation further increases printing speed. And heating the platen can quicken the evaporation and relieve the intercalation-induced stress. Combined, these advances lead to an extremely potent high-capacity battery system. Future work will involve building 3D-architected electrodes from various anode and cathode materials by considering unique material properties of individual materials. Furthermore, the developed 3D-structured electrode can be integrated with structural components. We will explore building a prototype that demonstrates a hybrid structure (such as UAS wings) that also acts as a battery—leading to versatile transport technologies that allow the structural parts to act as batteries themselves.

We have established that our 3D printing method leads to the production of lattice electrodes with controlled hierarchical porosity present in three dimensions. Such electrodes enhance electrolyte transport through the electrode volume, increase the available surface area for electrochemical reaction, and relieve the intercalation-induced stress. Combined, these advances lead to an extremely potent high-capacity battery system. Future work will involve building 3D-architected electrodes from various anode and cathode materials by considering unique material properties of individual materials. Furthermore, the developed 3D-structured electrode can be integrated with structural components. We will explore building a prototype that demonstrates a hybrid structure (such as UAS wings) that also acts as a battery—leading to versatile transport technologies that allow the structural parts to act as batteries themselves.

### Conclusions and Implications for DoD

In this study, we demonstrate a 3D printing method that can create lattice electrode architectures for robust Li-ion batteries with high capacity. The specific charge capacity and areal capacity of the 3D electrodes are shown to be several times that for comparable solid block electrodes, indicating the effectiveness of electrolyte penetration in the porous structure and improved utilization of electrode active material during the lithiation/delithiation cycles.

These improvements could have significant implications for DoD’s provision of mobile, battery-powered systems. The improved power characteristics of our battery design could allow the structural parts to act as batteries themselves, leading to versatile transport technologies that allow the structural parts to act as batteries themselves.

The authors would like to thank Chunshan Hu and Rit Bezbaruah for several images.