

Rethinking Multifunction in Three Dimensions for Miniaturizing Electrical Energy Storage

by Bruce Dunn, Jeffrey W. Long, and Debra R. Rolison

Electrical energy storage in batteries and electrochemical capacitors (ECs) will be vital for any future success in the global effort to shift energy usage away from fossil fuels. A marked improvement in the performance of these power sources is critical for this effort, yet both are mature technologies with over two centuries worth of chemical energy storage in batteries, while the physical principles underlying storing charge at electrochemical interfaces date to Helmholtz. Improved performance requires redesigning the reaction interphases in which the fundamental processes that store energy in batteries and ECs occur. Energy researchers are now rethinking the requisite multifunction—mass and charge transport, electronic and ionic conductivity, and electron-transfer kinetics—in light of nanoscience and architectural design in three dimensions.¹ We and research groups around the world are in the early stages of demonstrating that the design and fabrication of three-dimensional (3D) multifunctional architectures from the appropriate nanoscale building blocks affords opportunities to improve energy storage for power/size scales that range from micropower upward.

The emergence of microelectromechanical systems (MEMS) as a multi-billion dollar industry for an ever-widening range of electrical, mechanical, and optical products plus the continual downsizing of CMOS (complementary metal oxide semiconductor) electronics will ultimately enable small autonomous devices with sensing and actuation, communication, and rapid chemical/biological analysis or medical functionality. In order to operate independently, these devices must have on-board power from power sources on millimeter (or smaller) scales that deliver milliwatt levels of power for tens of hours. Wireless sensor networks represent an especially appealing opportunity because of the potential use of this technology across a broad range of environments, including urban infrastructure, buildings, and automobiles.² One vision for wireless sensor network applications integrates an energy-harvesting source (solar, thermal, vibrational) with a rechargeable battery to create a completely self-sustaining power source.

The miniaturization of batteries has not kept pace with the size scaling achieved with CMOS electronics. The reduced area available on microscale devices requires that batteries reduce their areal footprint commensurately. For traditional battery designs with two-dimensional (2D) electrode geometries, the areal footprint limitation is problematic as the total amount of stored energy for 2D batteries decreases and the maximum current output falls because of the small electrode area. The 2D battery design inherently imposes a compromise between energy density and power density for footprint-limited applications.

This paper reviews the emerging area of three-dimensional batteries. These architectures represent a new approach for miniaturized power sources that are purposely designed to maintain small footprint areas and yet provide sufficient power and energy density to operate the autonomous devices described above. Although relatively few results have been reported on functional and practical 3D batteries, the active research efforts on designs, fabrication methods, and materials portend a promising future for this field.

What Do We Mean by 3D?

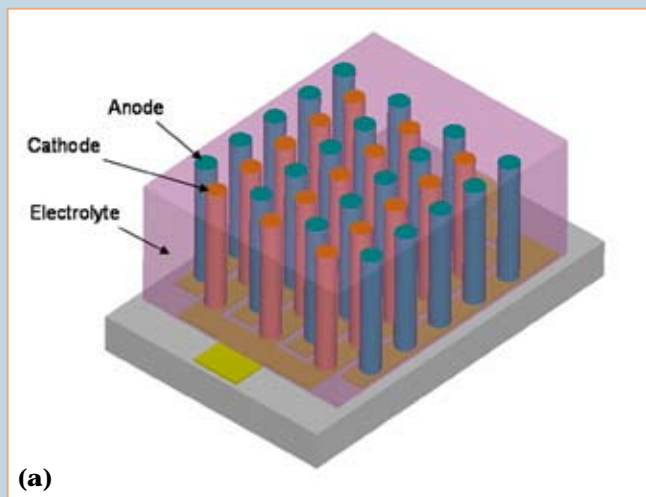
One characteristic that fundamentally defines 3D battery architectures, and is critical for performance, lies in the fact that transport between electrodes remains one-dimensional (or nearly so) at the microscopic level, while the electrodes themselves are configured in nonplanar geometries. In this way it is possible to design electrode architectures that increase the energy density of the battery within the areal footprint by building up (a “skyscraper” metaphor) rather than building out (“ranch house”). Such architectures comprise a 3D matrix of components (cathode, anode, and separator/electrolyte) that, depending upon battery design, are arranged in either a periodic array or an aperiodic ensemble in order to satisfy both the requirements of short transport lengths and large energy capacity.

A number of 3D batteries have either been realized or proposed (Fig. 1). The interdigitated geometry (Fig. 1a), in which anode and cathode arrays are separated by a continuous electrolyte phase, is perhaps the most easily visualized configuration.³ The

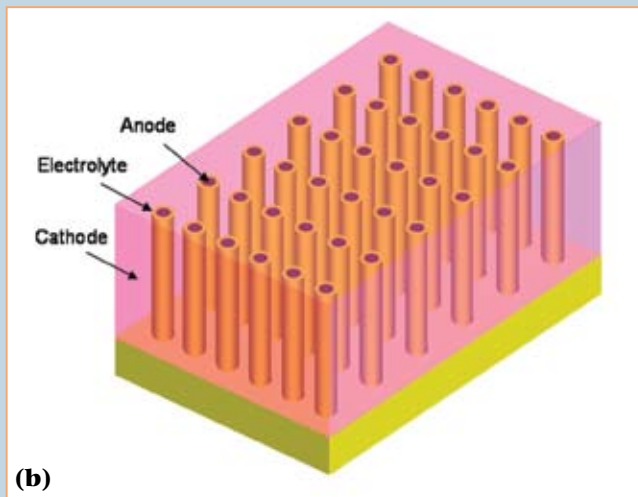
short transport distances between electrodes and the increased interfacial areas lead to a much lower ohmic resistance as compared to traditional 2D battery configurations. The concentric arrangement (Fig. 1b) has a 3D electrode array coated conformally by an electrolyte layer with the remaining free volume filled by the other electrode material. This design, originally proposed by Martin,⁴ not only provides short transport distances between electrodes, it also leads to higher energy densities than those of the interdigitated configuration because of the lower volume fraction occupied by the electrolyte. The use of templating to form inverse opal structures has also served as the basis for fabricating a 3D interpenetrating electrochemical cell.⁵ The templated electrode is coated by an electrolyte and the remaining void space is filled with the other electrode material (Fig. 1c).

In each of these designs, electrode arrays are formed in which the electrode material is configured in a spatially periodic fashion. Relaxing the periodicity condition, however, may be an important consideration for achieving uniform current distribution. One example of an aperiodic 3D configuration is the “sponge” design, proposed by Rolison in 1998, in which the battery is constructed within a mesoporous aerogel nanoarchitecture, in which the electrolyte layer is deposited conformally around the spatially random 3D network of electrode material.⁶ The other electrode material fills the remaining mesoporous and macroporous volume (Fig. 1d). This design ensures that all battery components—anode, cathode, and electrolyte—are co-continuous throughout the sponge structure.

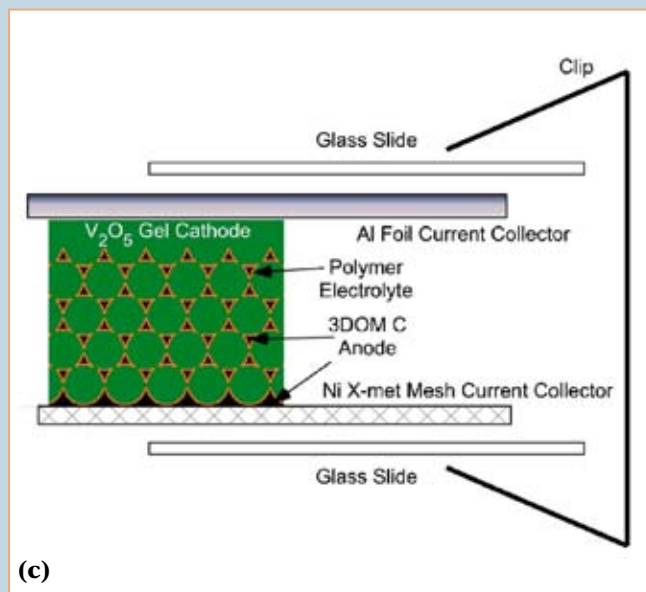
Another type of 3D architecture is based on amplifying the area of a thin film battery, essentially by enhancing the surface area of the substrate upon which the battery is fabricated. One design uses a perforated substrate (glass or silicon microchannel plate) to serve as the fabrication template (Fig. 1e).⁷ The battery is formed by sequential deposition of the current collector, cathode, and electrolyte, followed by filling the anode material into the center hole that remains after the deposition of the other components. Another thin-film approach is based on anisotropic etching of a silicon substrate (Fig. 1f). A solid-state battery has been proposed that consists of a Si thin-film



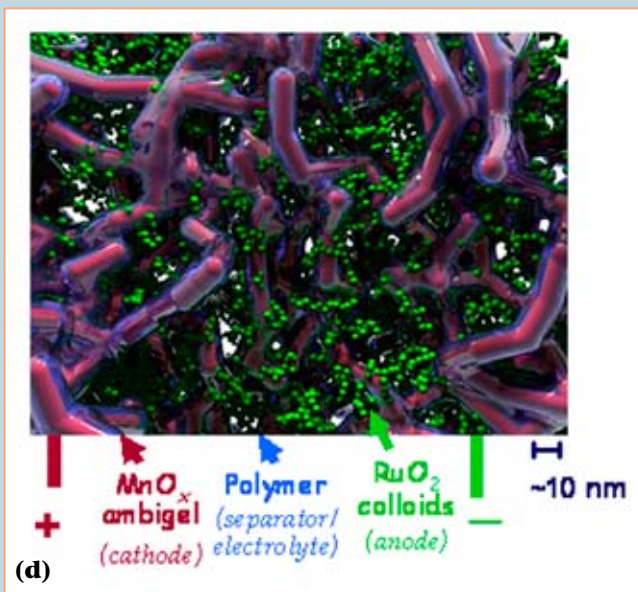
(a)



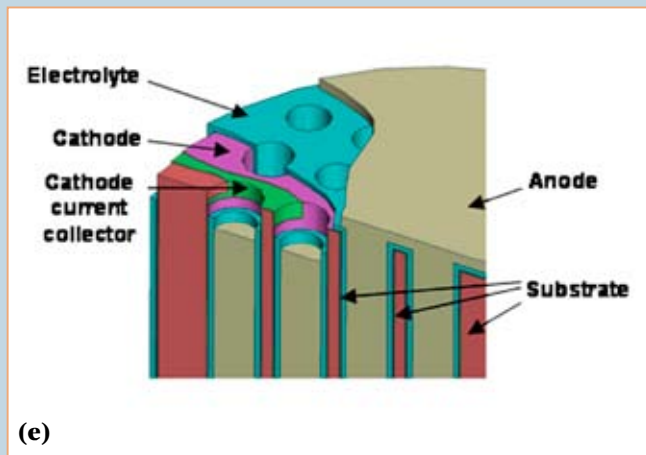
(b)



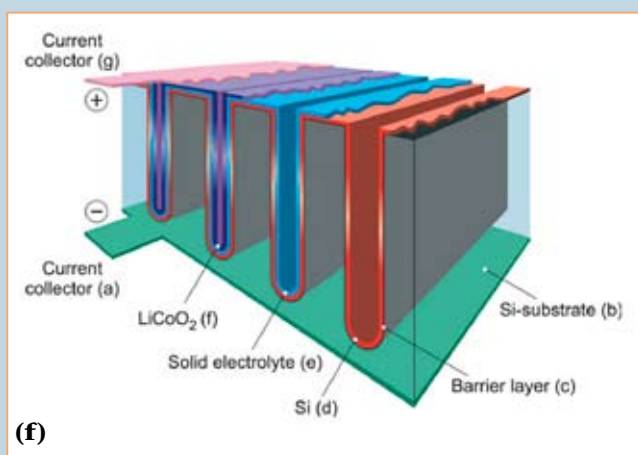
(c)



(d)



(e)



(f)

Fig. 1. 3D battery designs: (a) interdigitated, (b) concentric tube, (c) inverse opal,⁵ (d) "sponge" battery,⁶ (e) perforated substrate,⁷ and (f) micromachined silicon.⁸ Reprinted with permission. (Copyright (2007) American Chemical Society (Fig. 1d), copyright (2005) IEEE (Fig. 1e), copyright (2007) Wiley-VCH (Fig. 1f).)

anode, solid-state electrolyte, and thin-film cathode material.⁸ The prospect of integrating silicon-compatible energy storage with a silicon solar cell is very appealing for autonomous devices.

Can 3D configurations offer a means to keep transport distances short and yet provide enough active material to power MEMS and other small-scale devices for extended periods of time without sacrificing power density or small footprint area? An analysis comparing a conventional 2D geometry with the 3D interdigitated architecture showed that for the same footprint area, 3D capacities can be increased substantially by increasing the length of the electrodes in the array.³ Moreover, as long as the distance between electrodes remains the same, power density is unaffected. The result is that the electrodes incorporated in nearly all of the 3D designs are characterized by high aspect ratios (skyscrapers) so that a small footprint is retained.⁹ A countervailing design consideration for 3D batteries, however, is that the electrode length cannot be increased without limit as ohmic resistance of the electrodes increases progressively.¹ Although this problem has not been treated thoroughly, it is likely that the maximum aspect ratio will depend upon several parameters including the electronic and ionic conductivities of the electrodes, the ionic conductivity of the electrolyte, and the specific electrode geometry.

If 3D batteries are to be integrated into autonomous devices with limited available area for the power source, area-normalized specific capacity (termed "areal capacity") is the more relevant performance metric, rather than traditional gravimetric or volumetric normalization.¹ The importance of using the areal capacity metric is illustrated by the example of MEMS-based sensing, where the area available for the power source is on the order of 1 to 2 mm².¹⁰ In order for the device to operate continuously for one day, the required areal capacity for a lithium-ion battery is estimated to be 5 to 10 mAh/cm² (0.05–0.10 mAh/mm²), a benchmark that highlights the need for 3D batteries. By comparison, a lithium thin-film battery provides substantially less than 1 mAh/cm².⁷

3D Electrodes and Batteries

Although relatively few reports describe operational 3D batteries, a number of studies have been carried out on half cells that possess the 3D electrode architectures incorporated in the different battery designs. These electrochemical half-cell experiments not only establish that electrode materials can be fabricated into the various nonplanar geometries, but also that these 3D electrodes demonstrate the ability to achieve reversible electrochemical behavior in small footprint areas. The comparison shown

in Fig. 2 of lithium-ion insertion in mesocarbon microbeads (MCMB) for both a 3D electrode array (aspect ratio of 3) and a conventional 2D electrode geometry illustrates the significantly higher areal capacity of the 3D electrode.¹¹ Similar results have been shown for other electrode materials and geometries.^{12–14} We note that 3D electrode architectures that are not necessarily associated with a 3D battery design are also generating significant interest because of enhanced kinetics and higher capacity than traditional 2D electrode configurations.^{15,16}

Both lithium-ion secondary and zinc-air primary batteries have been fabricated into 3D configurations. The thin-film approach based on glass microchannel plates (Fig. 1e) uses a nickel cathode current collector, a cathode that is nominally MoS₂, a hybrid polymer electrolyte, and an MCMB anode.⁷ The initial areal capacity, 2 mAh/cm², is 20 to 30 times greater than the corresponding planar (2D) thin film battery (with the same footprint area) and is consistent with the increase in geometrical area associated with the perforated substrate. These microbatteries retained 60% of their capacity after 200 cycles. The 3D-interpenetrating electrochemical cell (Fig. 1c) is based on the use of an ordered macroporous carbon electrode coated with a conformal layer of poly(phenylene oxide) (PPO).⁵ The cathode material that fills the macropores is sol-gel-derived V₂O₅. This work has addressed certain fabrication issues faced by 3D battery designs including pre-lithiation of the carbon electrode and immersion of the complete cell in electrolyte, presumably to improve interfacial contact. Despite these advances, the low electronic conductivity of the V₂O₅ coupled with the narrow interconnection region between 3D macropores limits Li⁺ insertion and V₂O₅ reduction so that reversible cell capacity is well below expected values.

The results with the Zn-air battery demonstrate that 3D configurations can achieve both high energy and power densities within a small footprint area.¹⁷ The anode in this battery consists of an array of high aspect-ratio zinc rods (10-μm diameter, Fig. 3a) across a traditional air cathode with 6 M KOH electrolyte. The operating characteristics of the Zn-air battery (Fig. 3c and 3d) show that high specific capacity is retained even at a discharge rate of 3C. Increasing the rod length increases the specific capacity as expected. One advantage of the array configuration is that the entire rod is accessible to the electrolyte. During discharge, oxidation occurs at the outer surface of the rod while each zinc metal core serves as a current collector. The low resistivity of the metal enables high-aspect ratio structures to be used successfully because ohmic losses are minimized.

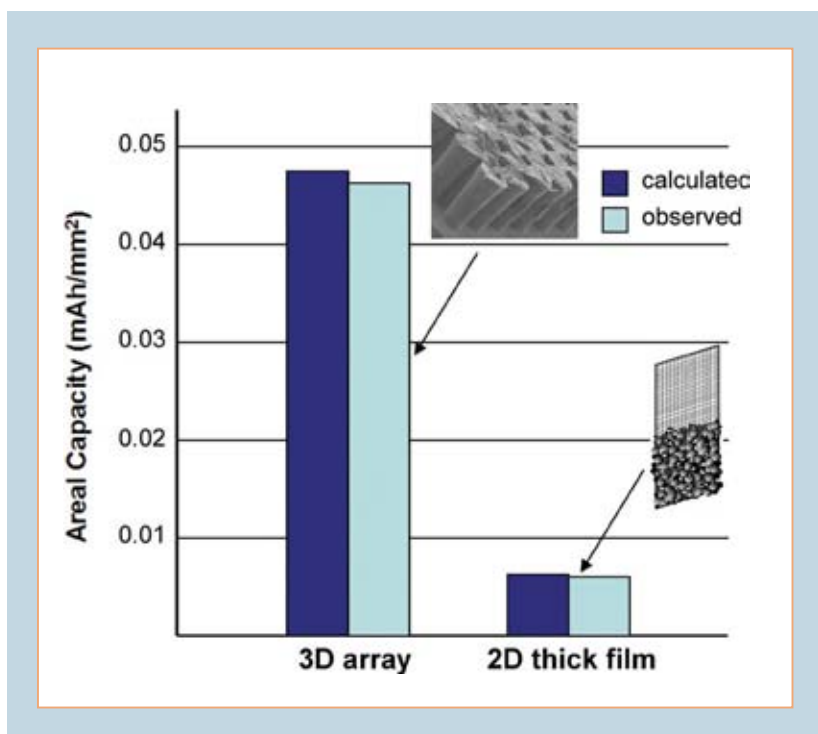


Fig. 2. Comparison of lithium insertion into two different types of MCMB electrodes; (left) 3D array of rods with aspect ratio of 3; (right) 2D electrode prepared on stainless steel mesh. Both electrodes were discharged at 0.1 mA/cm² in an electrolyte of 1 M LiClO₄ in EC/DMC (1:1 vol. ratio). The current density and capacity are normalized to the footprint area of the electrode.¹¹ Reprinted with permission, copyright (2007) IEEE.

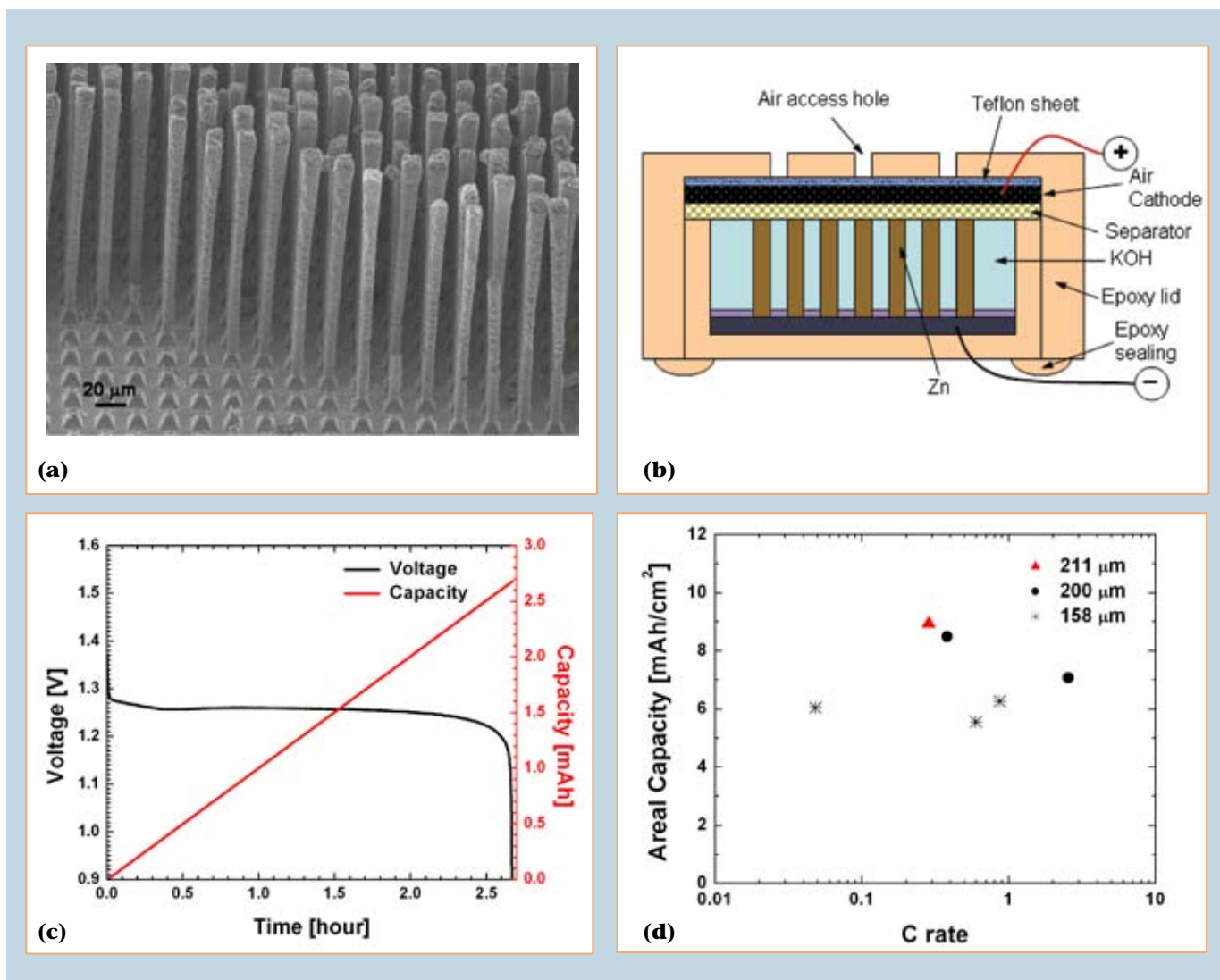


Fig. 3. Components, design, and operation of 3D Zn-air battery; (a) array of Zn rods, 10 μm on each side with a length of 200 μm;¹⁷ (b) schematic of 3D Zn-air battery;¹⁷ (c) discharge characteristics at 1 mA (3.3 mA/cm²) for the 3D Zn-air battery;¹⁷ (d) areal capacity (mAh/cm²) as a function of C-rate for zinc rods of different lengths. Reprinted with permission, copyright (2007) IEEE (Figs. 3a-c).

Future Challenges and Opportunities

The development of 3D battery technology is still in its infancy and although the field still faces certain challenges in developing micropower sources, obvious opportunities exist to apply 3D concepts, materials, and fabrication strategies to realize new directions for miniaturizing electrochemical power. One current challenge is the incorporation of a functional solid-state separator/electrolyte in 3D batteries. The separator/electrolyte of such new battery designs must, of course, provide the same basic functions as in any battery, namely to serve as an effective ionic conductor for the supporting electrolyte of interest (e.g., for Li⁺ salts in the case of a lithium-ion battery) and as an

electronic insulator to prevent shorting between the anode and cathode. The conformal coating of high aspect-ratio 3D architectures that possess curved surfaces is a problem not faced with traditional 2D battery designs. Only a few successful methods have been reported for 3D batteries.

The use of wet chemistry to deposit a hybrid polymer electrolyte was employed for the thin film architecture that uses perforated substrates (Fig. 1e).⁷ Although this processing route is effective for producing the electrolyte tube required with this design, it may not be applicable to more complex electrode geometries. A more general approach, electrodeposition of poly(phenylene oxide), has been successful in forming ultrathin (10 to 80 nm), ionically conducting conformal films on complex 3D aerogel

materials.^{12,18} Recently, this approach was extended to inverse opal architectures⁵ and it should be compatible with other 3D electrode configurations as well. The results for PPO electrodeposition demonstrate the importance of having a non-line-of-sight deposition process to achieve conformal coating of nonplanar geometries. The key to realizing conformal electrolyte coatings in such complex architectures is the use of deposition schemes that are inherently self-limiting. Appropriate modifications to achieve more controlled growth with gas-phase deposition methods such as chemical vapor deposition (CVD) may be difficult, but the self-limiting nature of atomic layer deposition (ALD) may ultimately be beneficial for 3D battery fabrication. Such methods have yet to be demonstrated for the electrolyte compositions required.

Nearly all of the 3D battery research to date has emphasized Li-ion systems. The results with the 3D zinc-standard air primary battery suggest alternative future directions for 3D designs. Integrating 3D electrode designs with traditional battery structures increases electrode surface area accessible to the electrolyte and improves spatial control of electrode reactions and should yield enhanced battery performance in the near term.

A final point to emphasize is how materials and design considerations for 3D batteries resemble those of electrochemical capacitors (ECs). The latter require electrodes with high surface areas because the amount of energy storage at double-layer and pseudocapacitor materials is directly proportional to the area of the electrified interface (which is not necessarily the same as the electrode surface area). The importance of high surface area is analogous to the amplification factors for 3D batteries that use thin films. Deposition of nanoscopic conformal layers of a redox-active oxide on a nanoarchitected current collector lead to ECs with marked improvement in energy and power density.^{19,20} This bilayer architecture also serves as the basis for the sponge geometry (Fig. 1d) as well as other 3D designs.

The 3D battery field is very much an emerging area of research, but the first steps toward realizing new batteries with 3D approaches are now extant. Fabrication methods have been developed for a variety of 3D architectures and the numerous half-cell studies reported to date attest to the feasibility and future promise of these designs. Ultimately, 3D configurations will serve as the basis for microscale batteries that offer high energy and power density within a small footprint area to power the wide range of autonomous microscale devices that are certain to become available in the very near future. ■

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