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### Article

# High Areal Energy Density 3D Lithium-Ion Microbatteries



Miniaturization holds great promise in various fields including healthcare, environmental monitoring, building automation, and robotics. While many electronic components have been successfully miniaturized, small battery technologies continue to underperform larger batteries on volumetric and areanormalized bases. To date, researchers have explored a wide variety of methods for building improved small batteries. In this work a combination of dry etching, photopatterning, and slurry-based processing is shown to be a promising route for the fabrication of powerful and energy-dense small batteries. Janet I. Hur, Leland C. Smith, Bruce Dunn

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### HIGHLIGHTS

Use of semiconductor-based processes to fabricate functional 3D batteries

Photopatterning conformal solid electrolyte around high-aspectratio silicon arrays

Half-cell capacities exhibit highest energy density in mm-scale footprint

Hur et al., Joule 2, 1–15 June 20, 2018 © 2018 Elsevier Inc. https://doi.org/10.1016/j.joule.2018.04.002

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## Article High Areal Energy Density 3D Lithium-Ion Microbatteries

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### **SUMMARY**

Three-dimensional (3D) microbatteries offer an opportunity to provide mobile power at dimensions that are comparable with those of the actuators, sensors, and other internet-connected devices that constitute the internet of things (IoT). To overcome the difficulties of assembling these architectures, we developed an entirely new fabrication route based on semiconductor processing methods. The use of partially lithiated (10% of theoretical capacity) silicon as the negative electrode keeps the volume change suitably controlled so that the Si array registry is maintained during charge and discharge. Photopatterning of SU-8 photoresist creates a conformal solid electrolyte coating around the high-aspect-ratio Si arrays. Rechargeable 3D microbatteries prepared on a 3 mm  $\times$  3 mm footprint have an areal capacity of nearly 2 mAh cm<sup>-2</sup>, operate at current densities up to 0.66 mA cm<sup>-2</sup>, and withstand 100 cycles. The combination of semiconductor-based processing and photopatternable electrolytes holds great promise for the further development of 3D microbatteries for IoT applications.

### INTRODUCTION

A great deal of technological progress over the last 50 years has been driven by miniaturization of electronics. Components such as radios, microphones, logic and memory circuits, and various sensors have all been reduced to drastically smaller dimensions, usually with vastly improved performance.<sup>1</sup> Following the transformative success of mobile devices such as laptop computers and smartphones, there is an extensive effort to deliver even smaller devices including wearable medical devices and wireless sensors that make up the internet of things (IoT).<sup>2</sup> The network of IoT devices created by embedded sensors and actuators is expected to deliver advanced connectivity and automation to systems and environment in nearly all fields. Propelled by the growth of these markets, the number of internet-connected devices worldwide is expected to triple to 60 billion in the next decade.<sup>3</sup> However, the major impediment to the success of these new devices is the availability of matching small batteries and their limited performance.

For example, coin-cell batteries are several times larger than the sensors and actuators they are powering but store less than half the energy density (200 Wh/L) compared with conventional larger lithium-ion batteries used in laptops and electric vehicles (600 Wh/L). This decline in energy density becomes more severe as the battery volume decreases. For the enablement of IoT devices (e.g., sensors for smart grid, field operation devices, and biochip transponders), development of rechargeable lithium-ion batteries (LIBs) with volumes less than 100 mm<sup>3</sup> and energy density exceeding 100 Wh/L remains a major challenge to overcome.<sup>4</sup>

### **Context & Scale**

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Three-dimensional (3D) microbatteries offer a novel design approach for delivering improved areal energy density while maintaining good power and cycling performance. Such architectures are especially promising for miniaturizing mobile power sources that can operate small devices such as wearables, embedded sensors, and actuators that constitute the internet of things (IoT). While a number of 3D electrode geometries have been demonstrated, assembling these electrodes into full 3D batteries has proved difficult. This report presents a scalable, semiconductor-based processing approach adapted to fabricate full 3D batteries. The conformal electrolyte required for this architecture was achieved by photolithographically patterning a photoresist around 3D silicon arrays. The combination of semiconductor-based electrode processing and photopatternable electrolytes holds great promise for the further development of 3D microbatteries for IoT applications.

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In addition to volumetric energy density, areal energy density becomes an important metric in small batteries development given that many applications are constrained by area. As a reference, a 500 Wh/L battery that is 1 mm thick corresponds to 50 mWh cm<sup>-2</sup> or about 12.8 mAh cm<sup>-2</sup> (assuming 3.9 V operating voltage). The low capacity of existing small battery technologies (e.g., thin-film batteries, 0.05–1.0 mAh cm<sup>-2</sup>) is largely a result of increasing packaging overheads and limited active material loading.<sup>5,6</sup> One approach to improving material loading is to fabricate thicker electrodes. Areal capacities up to 6 mAh cm<sup>-2</sup> were demonstrated from thick sintered LiCoO<sub>2</sub> coupled with lithium-metal anodes, but these suffered from poor mechanical integrity, large overpotentials, and limited cycle life.<sup>4</sup>

Three-dimensional (3D) microbatteries were identified as a novel design approach to deliver improved areal energy density while maintaining good power and cycling performance. One strategy for maximizing energy and power density of microbatteries at the full-cell level has been interdigitated anode and cathode configurations.<sup>7–10</sup> The design advantage of interdigitated 3D architectures over thick films is that a short and uniform diffusion path is maintained between the anode and cathode, enabling thick electrodes with high power. Cirigliano et al. demonstrated that a 3D array of graphite posts could deliver up to 5.0 mAh cm<sup>-2</sup>.<sup>11</sup> This corresponds to storing 1–2 orders of magnitude higher areal energy density than thin-film batteries.<sup>6</sup>

The tools and processes used in the development of 3D microbatteries differ a great deal from those used in the manufacture of traditional LIBs. Whereas traditional LIB electrodes are deposited from solvent-based slurries almost exclusively using slotted-die or roll-coating,<sup>12</sup> researchers in the field of 3D microbatteries rely on relatively exotic techniques including photopatterning,<sup>13,14</sup> wet and dry etching,<sup>11,15,16</sup> electroplating,<sup>8,17</sup> sputtering,<sup>18,19</sup> chemical vapor deposition, 3D printing,<sup>9</sup> and combinations thereof. These novel approaches have demonstrated a number of exciting paths forward, but the field is still in its formative stages. As indicated in Figure 1, the areal power and energy performance metrics for recent reports vary over several orders of magnitude.<sup>20,21</sup> About half of the reported full batteries, these approaches do not succeed in packing enough active material to deliver high areal capacity.

While silicon dry etching has been used in 3D architectures, the silicon structure has been seen only as a scaffold upon which active materials are deposited. <sup>16</sup> As a result, the active material consists of a relatively small fraction of the total electrode volume, significantly reducing the energy density. There are few research activities in using dry-etched silicon as an anode itself for 3D batteries.<sup>22</sup> If dry-etched silicon can be effectively utilized as a 3D anode, areal capacities in the range of 10 mAh cm<sup>-2</sup> can be realized.

A major barrier to building practical 3D batteries has been conformally coating the electrolyte/separator material between 3D anode and cathode. Atomic layer deposition has been used with some success to form conformal coatings, but these layers are limited by low ionic conductivity  $(10^{-8} \text{ S cm}^{-1})$  and slow growth rates (1.2 Å per cycle).<sup>23,24</sup> Simply using ultra-thin coatings does not provide a solution to both ionic conductivity and growth rate limitations. Ruzmetov et al. showed how coatings with thickness less than 200 nm are not suitable due to leakage current problems.<sup>19</sup> Alternatively, electropolymerization on negative electrodes has been investigated. However, the self-limiting nature of the electrodeposition process and the presence of

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Figure 1. Full-Cell Performance Data for 3D Microbatteries Reported in the Literature and Compared with Results Reported in this Paper

pinholes are continuing problems.<sup>25–27</sup> A recent report demonstrates that SU-8 photoresist is a promising material for 3D electrolytes, as the SU-8 can be chemically modified to further increase its Li-ion conductivity.<sup>28</sup>

In this report we show that semiconductor-based processing can be successfully adapted to fabricate full 3D batteries (Figure 2). Sturdy 3D anode arrays are made by dry etching crystalline silicon wafers, a method that is reliable and commonplace in semiconductor processing today. For a conformal electrolyte, we photolithographically pattern SU-8 photoresist in micron-thick layers around the 3D electrode arrays and achieve Li-ion conductivity of 5  $\times$  10<sup>-7</sup> S cm<sup>-1</sup>. In this way, energy density is maximized by using silicon as both the scaffold and the negative electrode material instead of just providing the 3D structural template. We show that by cycling silicon at 10% of its theoretical capacity, we retain stable cycling and deliver areal capacity that is at least 20-fold better than state-of-the-art thin-film batteries. We also demonstrate early examples of full 3D batteries built using our approach that deliver up to  $1.8 \text{ mAh cm}^{-2}$  (5.2 mWh cm $^{-2}$ ) in a small-format  $3 \text{ mm} \times 3 \text{ mm}$  footprint, which is among the highest full-cell areal energy densities reported to date (Figure 1). The half-cell capacity for the 3D silicon anode and micro-molded slurry cathode are the highest reported, which points to the enormous potential of this approach (Figure S1).<sup>29-31</sup> To the best of our knowledge, this is the first demonstration of a working full 3D battery using a conformal solid electrolyte, which marks an important step toward the realization of practical power sources with a footprint of less than  $1 \text{ cm}^2$ .

### **RESULTS AND DISCUSSION**

#### **3D Silicon Anode Array**

As a negative electrode material for LIBs, silicon is well known for having high theoretical capacity for lithium storage, up to 4,000 mAh  $g^{-1}$ .<sup>32</sup> A key challenge in realizing such high capacities is the enormous volume expansion (~300%) that silicon undergoes when fully lithiated.<sup>33</sup> In this work silicon was selected not for its high theoretical capacity but for its ease of processing microstructures using dry etching. By utilizing just 10% of the theoretical capacity of silicon, we can obtain a capacity similar to the theoretical capacity of graphite (372 mAh g<sup>-1</sup>). In this regime of cycling, silicon volume expansion should be no more extreme than what is encountered for graphite. From a theoretical perspective, graphite undergoes volume expansion of 74% when fully lithiated to LiC<sub>6</sub>.<sup>34</sup> This is comparable with silicon, which undergoes a volume expansion of 50% to form LiSi,<sup>33</sup> which has a lithium capacity of 954 mAh g<sup>-1</sup>. Of course there are other considerations that will affect cycling, especially phase changes. Lithiation of graphite is a topotactic reaction with lithium

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#### Figure 2. Fabrication Scheme for 3D Battery Based on SU-8-Coated Silicon Arrays

(A) Silicon wafer is coated with oxide and array pattern is etched.

- (B) 3D post array is etched into silicon.
- (C) Scanning electron microscopic image of silicon array.
- (D) SU-8 photoresist is selectively cross-linked around the silicon posts by photolithography.
- (E) Uncross-linked SU-8 is removed in a developer bath and base layer is cross-linked.
- (F) Scanning electron microscopic image of SU-8-coated array.
- (G) Vacuum infiltration of cathode slurry.
- (H) Charging schematic of complete 3D battery.
- (I) Scanning electron microscopic image of full 3D battery.

intercalating in two-dimensional layers between graphite sheets, while lithiation of crystalline silicon involves a crystalline-to-amorphous phase transition with the possibility of forming different and coexisting  $Li_xSi_y$  phases.<sup>33</sup> Our work benefits from ongoing research on crystalline silicon as an anode material.<sup>35,36</sup> Since crystalline silicon is widely used in the semiconductor industry, being able to utilize crystalline silicon as a battery material opens new possibilities for the design and fabrication of on-chip microbatteries for integrated circuits and electronic devices.

The silicon post array used in this work is vertically etched from a whole wafer, giving posts that are 100  $\mu$ m in diameter, 400  $\mu$ m tall, and arranged with a pitch of 200  $\mu$ m (Figures 2A–2C). After etching, there remains a base of silicon to which the posts are attached, and lithium insertion can occur into this base layer in addition to the posts. If we consider the capacity of the posts and ignore the base, the areal capacity that can be stored in the post array is 9.4 mAh cm<sup>-2</sup> (524 Wh/L) when inserting only 9.5% of the theoretical capacity of silicon. The volume occupied by the silicon posts is only 19.6% of the total volume of the battery. This leaves 71.7% reserved for the cathode slurry with the remaining 8.7% occupied by the conformal electrolyte. With the silicon array providing the 3D architecture, it is possible to assemble a 3D cathode around the array using conventional cathode materials. The exact capacity of the cathode depends on factors such as particle packing and the amount of binder, and conductive additives added to the cathode. By assuming that 50% of the cathode material, it is possible to store up to 12 mAh cm<sup>-2</sup>.<sup>37</sup>

The as-prepared silicon posts are heavily doped with boron, giving them high electronic conductivity. For lithium to enter the silicon lattice, it must combine via charge

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#### Figure 3. Results of Silicon Array Half-Cell Cycling

(A) Galvanostatic cycling of bare silicon array with a lithium counter and reference electrode, and  $1 \text{ M LiClO}_4$  in EC/DMC as electrolyte. (B) EIS measurements of the same cell.

transfer with an electron from silicon. As Li ions migrate into the silicon, the diffusivity of Li ions increases and subsequent phase transitions on delithiation leave behind an amorphous silicon.<sup>33</sup>

Evidence for this electrochemically induced phase transition are provided by the galvanostatic cycling data of the bare silicon array shown in Figure 3. In the first lithiation, the electrode potential decreases sharply and then becomes fairly flat, indicating that there is more than one phase present in the electrode. In subsequent lithiation cycles the potential change is more gradual, suggesting that there is a single phase present, which is possibly dependent on kinetics. The first two delithiation cycles show a lower coulombic efficiency (CE) (Figure S2), meaning that some of the lithium is not being removed and either remains in the silicon or at the electrode-electrolyte interface. The phase transition is indirectly evident by the change in appearance of the post array under an optical microscope before and after cycling. The post diameter increase is roughly 2-fold and the appearance changes from smooth and shiny to dark gray and ruffled (Figure S3).

Electrochemical impedance spectroscopy shows the result of the phase transition (Figure 3B). Before lithiation, the Si electrode is essentially a blocking electrode, with ~3 × 10<sup>5</sup>  $\Omega$  measured at low frequencies. After one cycle the impedance drops by ~1,000-fold, forming a semicircular shape representing the Li-Si charge transfer and a low-frequency tail indicating long-range Li motion. After 25 cycles the charge-transfer impedance increases, which could be explained by the pulverization of silicon or growth of interfacial layers. Both of these effects need to be mitigated in a successful battery design.

### **SU-8 Conformal Electrolyte**

3D battery design presents enormous challenges in the manufacture of effective electrolyte/separators. Conventional state-of-the-art battery manufacturing relies on commercially available porous polymer sheets (e.g., Celgard), but this is obviously not adaptable to complex 3D microstructures.<sup>38</sup> For the creation of a uniformly thick coating over 3D structures, processing methods such as atomic layer

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deposition (ALD) and electrodeposition have been explored but present limitations in film thickness and ionic conductivity and uniformity.<sup>23–27</sup> Recent studies reported for 3D batteries have attempted to build batteries without any separator, but in order to prevent electrical shorting these batteries are designed with relatively large interelectrode gaps that decrease the active material available in the battery.<sup>8,9</sup> For a battery with potential consumer applications, it must survive even mild mechanical loading and thus requires an internal separator to prevent electrical contact between electrodes.

SU-8 photoresist has several advantages that make it a promising solid electrolyte for 3D microbatteries. SU-8 has a chemical structure similar to typical polymer electrolytes like poly(ethylene oxide) and poly(methyl methacrylate). Polymers based on this chemistry are well known to give ionic conductivity in the range of  $10^{-5}$  to  $10^{-7}$  S cm<sup>-2</sup>.<sup>39,40</sup> SU-8 has been rigorously engineered to form high-aspect-ratio polymerized structures with resolution down to 1 µm and has been applied widely as a structural and functional material.<sup>41,42</sup> Finally, SU-8 has a large monomer size (molecular weight [MW] ~ 1,300), which is a unique feature compared with other monomers.<sup>43</sup> This provides free volume that can be occupied by traditional liquid electrolytes composed of carbonate liquids and lithium salts. Recent research reported by Choi et al. has shown that chemical modification of SU-8 with a lithium salt produces a lithium-ion conducting solid that retains it photopatterning capability to micronscale resolution.<sup>28</sup> The ionic conductivity of this material can reach  $10^{-5}$  S cm<sup>-1</sup> at room temperature with a wide electrochemical window (>5 V). The electrolyte exhibits excellent mechanical integrity and is thermally stable to at least 250°C.

SU-8 is able to conformally coat the silicon post arrays using photolithography (Figure S4). As a negative tone photoresist, SU-8 covalently crosslinks when exposed to UV light. Using a photomask, we crosslinked SU-8 around silicon post arrays such that the individual coated posts are 20  $\mu$ m larger in diameter than uncoated posts. That is, a uniform 10- $\mu$ m SU-8 coating is applied on the side walls of the silicon posts (Figures 2D–2F). Fully developing the patterned SU-8 will leave the base of the silicon array exposed. Thus, to produce a uniform layer at the base, we limited development time to 5 min so that a 50- $\mu$ m thick coating remained at the base (Figure S16).

SU-8 is a useful conformal electrolyte because, in its crosslinked state, it can swell with liquid electrolyte without dissolving.<sup>28</sup> Therefore, the bonding between neighboring SU-8 monomers is the key property underlying its performance. The bulk of the SU-8 monomer is stable. The only groups that are expected to react are the epoxide rings on the edges of the monomer (Figure S5A). Based on the reaction mechanism in Figure S5B, these epoxide groups are expected to react to form either ether linkages to neighboring monomers or become hydroxyl groups, which are not covalently linked to neighboring monomers.

The ether, epoxide, and hydroxyl groups all have characteristic absorption peaks in the infrared (IR). In Figures 4A and 4B, the IR absorption signals for epoxide (910 cm<sup>-1</sup>), ether (1,070 cm<sup>-1</sup>), and hydroxyl (3,450 cm<sup>-1</sup>) are used to track the degree of reaction.<sup>44</sup>

Across the four UV exposure times, there is a general trend of increasing polymerization as measured by Fourier transform infrared (FTIR) spectroscopy. The epoxide peak decreases and the ether peak increases with increasing exposure time (UV intensity = 8 mW cm<sup>-2</sup>; Figure 4A). The change in the peaks is greatest between 2 and

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Figure 4. Effect of UV Exposure Time on Chemical Structure and Ionic Conductivity of SU-8 (A–D) FTIR spectroscopy shows (A) a decrease in epoxide peaks and increase in ether peaks and (B) an increase in hydroxyl groups with increasing UV exposure. The Nyquist EIS spectra of SU-8 after 24 hr soaking in liquid electrolyte are shown for 10, 40, and 80 s exposure (C). Ionic conductivity is calculated from the sum of R2  $\rightarrow$  R5 using the equivalent circuit in (D) and ranges from 1 to 3 × 10<sup>-7</sup> S cm<sup>-1</sup> with decreasing exposure time.

10 s of exposure. Further increasing exposure time (40 s, 80 s) gives a lesser change, indicating that the number of new ether linkages formed is limited. Interestingly the hydroxyl peak continues to increase steadily for these exposure times (Figure 4B). Taken together, these data suggest that with increasing exposure times relatively fewer ether linkages and more hydroxyl groups are formed.

To confirm the effect of the degree of SU-8 crosslinking, we measured ionic conductivity for each exposure dosage. SU-8 conductivity data were obtained by soaking the SU-8 in liquid electrolyte and measuring electrochemical impedance spectroscopy (EIS) spectra. The first key observation is that the SU-8 exposed for only 2 s dissolved in the electrolyte of 1 M LiCIO<sub>4</sub> in a mixture of ethylene carbonate and dimethyl carbonate (EC/DMC) (1:1 vol%) after 4 hr. This suggests that the limited crosslinking generated from 2 s of UV exposure was not sufficient to adequately crosslink the SU-8 monomers into an interconnected structure.

The Nyquist impedance plots for the 10-, 40-, and 80-s exposed samples after 24 hr of soaking in electrolyte are shown in Figure 4C. All three show very similar semielliptical shapes at high frequencies, which are characteristic of ion conduction through an electrolyte. At lower frequencies the datasets become constant-phase lines that are indicative of long-range ionic diffusion.

An equivalent circuit model was used to fit the data collected at frequencies above 1 Hz. The circuit was based on the standard RC parallel circuit for ion conduction, but in order to account for the flattened semicircular shape a series of RC circuits were fit and the sum of the resistances ( $\sum R2 \rightarrow R5$ ) was used to calculate the ionic resistance

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(Figure 4D).<sup>45</sup> As the exposure time is decreased from 80 to 10 s, the conductivity of the SU-8 increases by more than 2-fold, from 1.2 to  $2.8 \times 10^{-7}$  S cm<sup>-1</sup>. This suggests that the more crosslinked SU-8 decreases the lithium-ion conduction but that the value is still within the range of polymer electrolytes used in LIBs.<sup>40</sup> It is important to find the optimum exposure dose such that the structure is sufficiently robust in the presence of liquid electrolyte and also exhibits high ionic conductivity.

### Vacuum-Infiltrated Cathode

A slurry of a well-known insertion cathode, LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA), with a lithium capacity around 180 mAh g<sup>-1</sup>,<sup>46</sup> was filled between the SU-8-coated silicon posts using vacuum infiltration (Figure 1G). After the slurry was applied around the posts, vacuum was used both to remove air bubbles between the posts and also to speed solvent drying from the slurry. The anode array is 400  $\mu$ m deep and neighboring posts are separated by 100  $\mu$ m, resulting in thick regions of cathode between anode posts. This geometry presents a long ion diffusion path for accessing the entire capacity of the cathode; thus, electronic and ionic conductivity must be maximized.

Flakey graphite was used as the electrically conductive cathode additive. For improved ionic conductivity a supporting gel electrolyte was added. This gel is a 2:1:1 molar mixture of lithium bis(trifluoromethane)sulfonimide salt (LiTFSI), tetraglyme (TG), and poly(ethylene oxide) (MW = 1,450). This system is reported to have ionic conductivity of  $1.1 \times 10^{-3}$  S cm<sup>-1</sup> and stability up to 5 V versus Li  $^{0/+}.^{47,48}$  Long-range ion diffusion in the electrode is facilitated by this liquid electrolyte, as ionic conduction in liquid electrolytes is several orders of magnitude higher than it is in solid transition metal oxides.<sup>49</sup>

With this balance of electronic and ionic conductivity, the 3D cathode is able to support electron and lithium-ion transport through the 400-µm thick interdigitated structure. A test cathode with a total mass of 3.5 mg (39 mg cm<sup>-2</sup>) was prepared by depositing slurry around a bare silicon array and etching away the silicon using XeF<sub>2</sub> gas. When cycled at a current density of 0.22 mA cm<sup>-2</sup>, the 3D cathode achieved 157 mAh g<sup>-1</sup> and 4.4 mAh cm<sup>-2</sup> (Figure 5C). Continued cycling at 0.56 mA cm<sup>-2</sup> gave stable performance with >95% CE (Figures 5A and 5C). At 1.1 mA cm<sup>-2</sup> the initial capacity was lower and the capacity faded quickly (50% over 20 cycles), indicating that the full capacity of the cathode was not accessible at such a high current density (Figure 5C). The capacity fade could also be attributed to crack formation, which was observed after cycling (Figure 5D). Cyclic voltammetry (CV) experiments indicated a subtle change in the performance of the 3D cathode upon cycling, with gravimetric capacity dropping from 132 to 117 mAh g<sup>-1</sup> (Figure 5B). In addition, the peaks in the CV were broader and shifted over a wider potential range, which suggests an increase in the resistance of the cathode.

#### **Full 3D Batteries**

Proof-of-concept full batteries (FB1 and FB2) were tested to establish the power, capacity, CE, and cycle life of this novel battery design. The process flow for building the full batteries is shown in Figure S6. The high-frequency EIS spectra of both batteries are characterized by a semicircular feature representing ion conduction through the SU-8 electrolyte, which is the most resistive component in the full cell. Based on the geometry of the 400-µm tall posts covered with a 10-µm thick electrolyte, the ionic conductivity is calculated to be  $5 \times 10^7$  S cm<sup>-1</sup> for the two batteries. These values are in agreement with the EIS measurement of the coated SU-8 half cell (Figure S7). In the low-frequency regime there is a transition to a constant-phase

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#### Figure 5. Testing of Porous 3D Microstructured Cathode Array

(A) GV cycling curves measured at 0.56 mA cm $^{-2}$ .

(B) CV scans of the 3D cathode before and after GV cycling.

(C) Areal capacity and coulombic efficiency measured during GV cycling at various current densities.

(D) Optical micrographs of 3D microstructured cathode before and after cycling.

element consistent with long-range diffusion of lithium inside the electrodes. FB1 shows a slightly rounded diffusion tail not seen in FB2. This feature is most likely a manifestation of differences in the morphology of the silicon electrodes as a result of amorphization. The difference in the total impedance at 0.1 Hz for the two batteries is less than 30%.

FB1 shows reasonably stable cycling at 0.56 mAh cm<sup>-2</sup> (1.6 mWh cm<sup>-2</sup>; Figure 6B) with CE starting at 98% and decreasing to 92% over 100 cycles (Figure 6C). The noisy and decreasing CE (Figure S13) is evidence of electrochemical irreversibility associated with lithium being retained within the silicon electrode. With FB2 the charge capacity was increased over seven cycles, leading to a maximum discharge capacity of 1.8 mAh cm<sup>-2</sup> (5.2 mWh cm<sup>-2</sup>). The CE for FB2 decreased from above 90% to just over 60% over seven cycles (Figure S14). These and other experiments (not reported here) suggest that cycling the full batteries to achieve higher capacity results in lower CE and faster capacity fade (Figure S15). We attribute the CE decrease to volume expansion of the silicon rods in the electrode array. In the current battery design, the partial lithiation of silicon was based on limiting the silicon capacity to around 400 mAh  $g^{-1}$ . Thus, if the lithium was evenly distributed throughout the rod, an expansion of  $\sim$ 25% would be achieved.<sup>33</sup> However, the 100-µm diameter posts present too long a diffusion path to achieve uniform lithiation throughout the post. Instead, there is a lithiation gradient resulting in much higher volume expansion around the outside of the post. As shown by Sternad et al., working with 50-µm crystalline silicon posts, the outermost region consists of a  $\sim$ 5-µm thick amorphous silicon shell that experienced a greater concentration of lithium during cycling.<sup>22</sup> Lithium insertion into the outer shell becomes less reversible with increasing lithium content, thus leading to a more severe decrease in CE with higher capacity. These

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#### Figure 6. Full Battery Performance

(A) Comparison of Nyquist impedance spectra for two batteries.

(B) GV cycling performance of FB1 at a charge/discharge current 0.66 mA cm<sup>-2</sup>/0.22 mA cm<sup>-2</sup>.
(C) Coulombic efficiency for FB1 over 100 cycles (charge capacity was set at 0.56 mAh cm<sup>-2</sup>).
(D) GV cycling performance of FB2 with a charge/discharge current 0.22 mA cm<sup>-2</sup>/0.11 mA cm<sup>-2</sup>. Charge capacity was increased from 1.1 mAh cm<sup>-2</sup> (cycles 1–4) to 2.2 mAh cm<sup>-2</sup> (cycles 5–6) to 2.8 mAh cm<sup>-2</sup> (cycle 7).

results suggest that an important path forward is to decrease the diameter of the silicon rod in order to provide a shorter diffusion pathway and achieve more uniform lithiation and volume expansion in silicon.

Another feature that likely influenced electrochemical performance is that portions of the battery show significant changes in the silicon structure while other regions show posts that are virtually unaffected. In Figure S8A, the cycled silicon is somewhat pulverized, a result of the volume expansion effect described above. While the SU-8 electrolyte and composite cathode appear relatively unchanged, the disparity in silicon morphology in different regions suggests that electrolyte distribution in the cathode was not uniform and that more conductive regions may have become "hotspots" that delivered a disproportionately large share of the battery's total capacity. A related consideration was the DMC component of the EC/DMC electrolyte whose volatility would occur in unpackaged batteries. It was challenging to keep the electrolyte well contained inside such a small footprint battery without proper packaging.

These small-footprint  $(0.09 \text{ cm}^2)$  3D LIBs demonstrate both high areal energy density and, depending upon the operating conditions, reasonable capacity retention. The discharge capacity corresponds to ~40% of the total capacity available in the full cell. The lost capacity could be from poor ionic or electronic conductivity within certain regions of the cathode. Clearly, the goal of future work is to access the remaining 60% of the capacity and still retain the good cycling performance. These improvements are expected to come from decreasing the diameter (while

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concomitantly increasing the number) of silicon posts to minimize lithiation gradients, improving the uniformity of the cathode, and developing well-packaged full batteries. Another important feature will be to increase the packing density of cathode particles. By further increasing the packing density such that NCA particles occupy 50% of the total cathode volume, our calculations indicate that doubling of the cathode mass and total capacity can be achieved.<sup>37</sup> The realization of these improvements will bring a full-cell areal energy density of 10 mAh cm<sup>-2</sup> within reach.

### Conclusion

In this work we demonstrate a novel method of fabricating and assembling 3D lithium-ion microbatteries with high areal energy density and high capacity retention. The interdigitated 3D architecture-adapted semiconductor processing method known as deep reactive ion etching (DRIE) was combined with a photopatternable polymer electrolyte derived from SU-8 photoresist to obtain a conformally coated silicon electrode array. Tested independently, the 3D anode of an Si post array exhibits a reversible lithium capacity of 14 mAh cm<sup>-2</sup> over 20 cycles, the SU-8 electrolyte gives lithium ionic conductivity of 2.8  $\times$  10<sup>-7</sup> S cm<sup>-1</sup>, and the vacuum-infiltrated 3D cathode delivers 4.4 mAh cm<sup>-2</sup>. Full 3D batteries based on a 3 mm  $\times$  3 mm platform and just 6  $\mu$ L of total volume are, to the best of our knowledge, the first 3D batteries to operate with a conformal solid electrolyte. The full batteries deliver discharge capacities up to  $1.8 \text{ mAh cm}^{-2}$  (5.2 mWh cm $^{-2}$ ), more than twice the highest values reported for thin-film batteries. The batteries operate at currents up to 0.66 mA cm<sup>-2</sup> and survived 100 cycles at 0.5 mAh cm<sup>-2</sup> (1.6 mWh cm<sup>-2</sup>). These results are among the highest energy densities reported in the literature (Figures 1 and S1). The combination of semiconductor-based electrode processing and photopatternable electrolytes holds great promise for the further development of 3D microbatteries for IoT applications.

### **EXPERIMENTAL PROCEDURES**

#### Silicon Dry Etching

Silicon arrays were formed from a highly doped silicon wafer (p-type, Boron doped, 0.001–0.005  $\Omega$  cm). Using plasma-enhanced CVD (STS Multiplex CVD), 5  $\mu$ m of silicon dioxide was deposited. AZ 5214 was spin-coated on the substrate and photo-lithographically patterned. The pattern was transferred to silicon dioxide using dry etching (STS Advanced Oxide Etcher) and the photoresist removed using oxygen plasma for 3 min. The silicon dioxide pattern served as a hard mask during DRIE of silicon posts (Plasma-Therm DSE II). After the desired post height was reached, the wafer was thoroughly cleaned by oxygen plasma to remove polymer residue from DRIE followed by dipping in hydrofluoric acid to remove the remaining silicon oxide mask and native oxide.

The geometry of the anode post array was defined as 100  $\mu$ m in diameter, 200  $\mu$ m in pitch, and 400  $\mu$ m in height. In a 3 mm × 3 mm footprint, the post array was 15 × 15. We used a 10- $\mu$ m thick conformal coating of electrolyte as determined by the photomask used in the photopatterning of the SU-8 electrolyte (Figure S9).

#### **Electrolyte/Separator Fabrication**

SU-8 was filled between the posts and soft-baked at 100°C for 6 hr. The photomask was then aligned over SU-8 filled array followed by UV exposure for 90 s using contact aligner (Karl Suss MA6). The exposed SU-8 was baked at 100°C for 3 min and then developed using SU-8 developer (Microchem) for 20 min. Development was timed to leave 50  $\mu$ m of undeveloped SU-8 on the bottom surface. The

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SU-8-coated array was then soaked in liquid electrolyte for 24 hr before filling the cathode.

#### **Cathode Slurry Preparation and Electrode Fabrication**

The cathode slurry consisted of 75% NCA (5.0- $\mu$ m particles; NEI), 18.3% graphite (Timcal KS6), 1.7% poly(vinylidene fluoride) (PVDF), 2.8% LiTFSI, 1.1% TG, and 1.1% poly(ethylene oxide) (PEO) (MW = 1,450). The slurry was prepared by first mixing LiTFSI, TG, PEO, and PVDF in N-methyl-2-pyrrolidone (NMP) and then adding the appropriate amounts of graphite and NCA with additional NMP. The final solids concentration was 0.6 mg/mL. The ionic conductivity of the gel electrolyte was measured independently by casting it inside a polypropylene tube and pressing in between polished stainless-steel electrodes (6 mm diameter) separated by a 1-mm spacer. The EIS data are shown in Figure S10.

The cathode slurry was applied dropwise over the anode array. The slurry was applied using a micropipette in drops that were  $\sim 3~\mu$ L each. Vacuum was applied using a Buchi V-500 diaphragm pump connected to a sealed jar. Prior to adding any slurry, the array was prewetted with a drop of dimethyl carbonate (Sigma, anhydrous), then a drop of NMP (Sigma, anhydrous) and vacuum was applied for 30 s (Figure S12).

#### **Characterization of SU-8 Photoresist by Infrared Spectroscopy**

SU-8 was spin-coated onto NaCl plates (Edmund Optics, 1 inch diameter, 2 mm thick) in a yellow room to avoid UV exposure. The plates were stored in a vacuum desiccator and dried on 160°C hotplate for 10 min before spin-coating. SU-8 3010 (Microchem) was applied to the plates by spin-coating at 3,000 rpm for 30 s resulting in 10- $\mu$ m coatings. After spin-coating, the samples were heated on a 100°C hot plate for 7 min. The samples were exposed to UV light at 8 mW cm<sup>-2</sup> for varying times (2, 10, 40, and 80 s), after which the samples were again placed on the 100°C hotplate for 7 min. The samples were covered in aluminum foil in the yellow room and transported to a dark room. FTIR (Jasco-670 plus) was performed using 4 cm<sup>-1</sup> resolution and averaged over 100 scans. The background scan was performed on an uncoated NaCl plate that had accompanied the coated samples through all processing steps.

#### **Measurement of SU-8 Photoresist Ionic Conductivity**

SU-8 was spin-coated onto indium-tin oxide (ITO) substrates and exposed to UV light in the same manner described above. After UV exposure and heating, the samples were loaded into an argon-filled glovebox so that atmospheric moisture could not contribute to the ionic conductivity. The samples were soaked in an anhydrous 1:1 mixture of EC/DMC containing 1 M LiClO<sub>4</sub>. EIS spectra were measured after 4, 8, and 24 hr of soaking using a VMP3 potentiostat (300 kHz to 0.1 Hz at 10 mV amplitude). EIS was measured using ITO as the working electrode. The counter electrode was a 0.5-cm<sup>2</sup> piece of stainless steel that was pressed into the SU-8 using a spring clamp.

#### Silicon Anode Half-Cell Testing

Half-cell testing of the silicon array was performed using a 3-electrode flooded cell with lithium foil as both counter and reference electrodes in a 1:1 mixture of EC/DMC containing 1 M LiClO<sub>4</sub>. The silicon array was mounted on a stainless-steel current collector using conductive silver paste (Ted Pella). Galvanostatic measurements at various current densities (0.28 mA cm<sup>-2</sup>, 0.71 mA cm<sup>-2</sup>, 1.42 mA cm<sup>-2</sup>, and 2.84 mA cm<sup>-2</sup>) were made over the potential range 0.01–0.60 V (versus Li<sup>0/+</sup>). ElS

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was carried out using the same conditions as those used in determining the ionic conductivity of SU-8.

#### **Evaluation of Micro-Molded Cathodes**

After vacuum infiltration, the cathodes were either measured electrochemically or mechanically polished to observe the cathode. Those samples that were polished were first potted in Epothin epoxy (Buehler) and cured for 24 hr. Afterward they were cut using a low-speed diamond saw and polished to expose various cross-sections of the infiltrated cathode.

For electrochemical characterization the cathodes were mounted on stainless-steel shim using nickel paste (Pelco). The silicon array was etched away using XeF<sub>2</sub>. The sample was exposed to 60 cycles with 60 s of XeF<sub>2</sub> exposure at 2,500 mTorr followed by a pump-down to 50 mTorr. Samples were heated 4 hr in a 120°C vacuum oven before loading into an argon-filled glovebox. The cathode was tested with galvanostatic measurements (0.22, 0.55, and 1.1 mA cm<sup>-2</sup>) in 3-electrode flooded cells with Li counter, Li reference, and 1 M LiClO<sub>4</sub> in EC/DMC (1:1 mixture) electrolyte. The voltage limits used for both CV and GV were 3.0–4.3 V (versus Li<sup>0/+</sup>).

#### **Full Fabrication and Battery Testing**

Battery construction and assembly involved five processing steps. Initially the SU8coated silicon array was mounted onto a stainless-steel current collector (Figure S6A) using nickel paste. The mounted array was loaded into a 100°C oven and heated on a metal plate. Small pieces of paraffin wax (Sigma) were added (Figure S6B) to fill the volume around the posts. Next, the array was loaded into a small plastic dish. Epoxy (Buehler Epothin) was poured around the wax-coated array (Figure S6C) so that the epoxy came up to the edge of the wax (Figure S11). The anode assembly was then submerged in a bath of n-heptane at 62°C to completely melt the wax (Figure S6D), leaving behind a cavity for cathode filling.

Epoxy-embedded battery assemblies were dried by placing them in the glovebox antechamber (~100 mTorr) overnight. Cathode filling via vacuum infiltration (Figure S6E) was accomplished in an argon glovebox (<10 ppm water and oxygen) equipped with a diaphragm drying pump (Buchi V-500). After filling, the batteries were soaked for 24 hr in PC with 10 Torr vacuum applied using the diaphragm pump once every 6 hr.

A top current collector (1/16-inch Al shim stock) was clamped onto the battery assembly, leaving a small gap from which to apply liquid electrolyte (1 M LiClO<sub>4</sub> in PC) every ~48 hr to counteract evaporation of electrolyte from the cathode. The surface of the cathode was typically smooth and provided a good surface against which to clamp. To promote adequate electrical contact a thin piece of Al mesh can be added between the Al current collector and the cathode. Battery testing was performed using the same electrochemical test equipment described in previous sections.

### SUPPLEMENTAL INFORMATION

Supplemental Information includes 16 figures and can be found with this article online at https://doi.org/10.1016/j.joule.2018.04.002.

### ACKNOWLEDGMENTS

The authors greatly appreciate the support of this research by the Office of Naval Research (N00014-11-1-0673 and N00014-16-1-2164), and gratefully acknowledge

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Dr. Chun-han Lai and Mr. Christopher Choi for their extensive help in scanning electron microscopy imaging.

### **AUTHOR CONTRIBUTIONS**

Conceptualization, J.I.H., L.C.S., and B.D.; Methodology, J.I.H., L.C.S., and B.D.; Investigation, J.I.H. and L.C.S.; Writing – Original Draft, J.I.H. and L.C.S.; Writing – Review & Editing, J.I.H., L.C.S., and B.D.

### **DECLARATION OF INTERESTS**

All of the experiments presented here were completed in the UCLA Materials Science and Engineering Department. The University of California has a patent pending related to this work. After leaving the UCLA Materials Science and Engineering Department, J.I.H. and L.C.S. founded Millibatt, Inc. B.D. is a member of the advisory board.

Received: January 7, 2018 Revised: March 20, 2018 Accepted: April 2, 2018 Published: May 3, 2018

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### **Supplemental Information**

### **High Areal Energy Density**

### **3D Lithium-Ion Microbatteries**

Janet I. Hur, Leland C. Smith, and Bruce Dunn

### **Supplementary Information**



**Capacity (mAh/cm<sup>2</sup>)** Figure S1: comparison of half-cell performance data from the literature with the results reported in this paper (Fig. 3 and Fig. 5).



Figure S2 : Discharge capacity and Coulombic efficiency data corresponding to cycling data for the bare silicon array in Fig. 3a. The drop at cycle 17 follows the increase in testing current from  $1.42 \text{ mA/cm}^2$  to  $2.84 \text{ mA/cm}^2$ .



Figure S3 : Change in appearance of silicon posts (100 µm diameter as prepared) from Fig. 3 before and after cycling.



Figure S4 : Optical image of SU-8 coated half-cell.



Figure S5 : (a) The structure and approximate size of SU-8 monomers. (b) The "zipper" reaction mechanism whereby neighboring epoxide groups on SU-8 form ether bonds in the presence of a photogenerated acid catalyst (HA).



Figure S6 : Schematic of full battery building. (a) The SU-8 coated silicon array is mounted on a stainless steel current collector using Pelco nickel paste (b) Paraffin wax is melted into the array cavity. (c) The wax-filled array is potted in Epothin epoxy. (d) The potted array is soaked in 62°C n-heptane to dissolve away the wax (e) the potted array is filled with cathode slurry by vacuum infiltration.



Figure S7 : (a) Nyquist impedance curve for SU8-coated silicon array (b) A zoom-in around the origin shows a semicircle at high frequencies that is attributed to ionic conduction through the SU-8. Assuming 400  $\mu$ m tall posts coated uniformly with 10  $\mu$ m SU-8, the calculated ionic conductivity is 5.0 x 10<sup>-7</sup> S/cm. This is about 2-3 times higher than the value determined from impedance measurements taken on 2D SU-8. The discrepancy indicates that the exposure of SU-8 to UV, and the cross-linking density may vary along the length of the posts. Some regions may have lower cross-linking density and therefore higher ionic conductivity. In addition, the existence of isolated air bubbles or other defects in the SU-8 coating may increase the conductivity value measured across the array.



Figure S8 : cross-section SEM images of a full 3D battery after 100 cycles at 0.5 mAh/cm<sup>2</sup> (Fig. 6, FB1). (a) Some regions of the silicon look pristine (b) while other regions look pulverized. This suggests that electrolyte percolation through the cathode needs further optimization.



Figure S9 : The geometry of the 3D silicon array is defined by three variables: post diameter (D), post pitch (P), post height (H) and electrolyte thickness (T).



Figure S10 : Ionic conductivity of gel electrolyte. Conductivity of 2:1:1 :: LiTFSI:TG:PEO gel electrolyte  $\sigma$  = 1 x 10<sup>-4</sup> S/cm calculated from the second intercept of the data with the real axis (17,200 ohm).



Figure S11 : Battery processing (a) after wax removal (step Fig. S6d) and (b) after cathode infiltration (step Fig. S6e).



Figure S12 : Prewetting the array with dimethyl carbonate and n-methyl pyrrolidinone prior to cathode infiltration helps to improve cathode density. (a) cathode filled without prewetting step (b) cathode filled with prewetting step.



Figure S13 : Discharge capacity and Coulombic efficiency for FB1 cycling data shown in Fig. 6b. The average decrease in Coulombic efficiency is 0.05% per cycle.



Figure S14 : Discharge capacity and Coulombic efficiency for FB2 cycling data shown in Fig. 6d.



Figure S15 : Discharge capacity and Coulombic efficiency for a 100  $\mu$ m post battery (tested since initially preparing the manuscript) cycled at 5 mAh/cm<sup>2</sup> at a charge discharge current density of 0.04 mA/cm<sup>2</sup>. The capacity fade is more severe than what was seen for FB2.



Figure S16 : SU-8 development was timed (5 mins) to intentionally leave uncrosslinked SU-8 at the base to passivate the silicon base.