# PAPER

# 3D lithium ion battery fabrication via scalable stacked multilayer electrodeposition

To cite this article: Michael J Synodis et al 2019 J. Micromech. Microeng. 29 055006

View the article online for updates and enhancements.



# IOP ebooks<sup>™</sup>

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

J. Micromech. Microeng. 29 (2019) 055006 (9pp)

#### https://doi.org/10.1088/1361-6439/ab0c60

# 3D lithium ion battery fabrication via scalable stacked multilayer electrodeposition

# Michael J Synodis<sup>1</sup><sup>(i)</sup>, Minsoo Kim<sup>2</sup>, Mark G Allen<sup>2</sup> and Sue Ann Bidstrup Allen<sup>1</sup>

 <sup>1</sup> University of Pennsylvania, Chemical and Biomolecular Engineering, Philadelphia, PA, United States of America
<sup>2</sup> University of Pennsylvania, Electrical and Systems Engineering, Philadelphia, PA, United States of America

E-mail: msynodis@seas.upenn.edu

Received 11 October 2018, revised 15 February 2019 Accepted for publication 4 March 2019 Published 25 March 2019

# CrossMark

#### Abstract

This study focuses on the creation of 3D full cell lithium ion batteries via a multilayer stacked electrode approach. The electrodepositon based processes enable individual, deterministic control of all cell dimensions, and thus allow for tunable total energy outputs while maintaining excellent intrinsic performance. Incorporation of electrodeposited nanoporous lithium manganese oxide cathodes and thin film nickel–tin anodes into a vertically interdigitated multilayer cell enables energy densities of up to 193 Wh  $1^{-1}$  and power densities of up to 1233 W  $1^{-1}$ . Additionally, the multilayer fabrication increases device areal and volume scalability over multiple orders of magnitude, resulting in total energy outputs of up to 20 mWh and power outputs of 178 mW.

Keywords: electrodeposition, MEMS, microfabrication, energy storage, lithium-ion batteries

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

### 1. Introduction

In today's complex technological society, power is required over a range of size scales. During the last 15–20 years, there has been substantial growth in sensor, actuator, and other electronic systems across several sectors, including military, industrial, and consumer electronics [1]. Much of this growth has occurred due to advancements in micro- and nano-scale fabrication technologies. Alongside this progress in microelectromechanical systems (MEMS), there has been an increase in device and system connectivity through network and software capabilities. The integration of fabrication advancements and device connectivity has introduced the concept of the internet of things (IoT) [2]. The number and type of devices existing in the expanding IoT universe is continually increasing, but advances in energy storage to power those systems is lagging [1]. Often, the power source for an IoT device is the limiting factor in its introduction to market. Energy harvesting and scavenging devices have seen advancements in recent years, but the capacities needed for many MEMS devices are often greater than harvesting or triboelectric generation can produce [3, 4]. Thus, batteries and supercapacitors are still the dominant sources of energy for microelectronic systems [4]. Due to high energy densities, lithium ion batteries are often the choice of energy storage system, but recent research has focused on improving their power while maintaining that high energy [5, 6]. In order to achieve this goal, the diffusion paths for lithium ions in the system must be minimized, and the electrode surface areas should be maximized. This requires high loading of electrochemically active material into the device, even if individual electrode layers are thin. Nanoparticle and nanorod based approaches [7-13] to building electrodes provide excellent surface area to volume ratio and good power densities, but limits in the height of nanowire growth or the loading of nanoparticles constrains the total energy outputs that are achievable. Additionally, ranges in particle or rod size and diameter during fabrication result in decreased control over the power outputs and limited tunability. Molded or scaffolded structures [14–17] can provide a more controllable process but have lower surface area to volume and can also be limited in height due to maxima in photoresist thickness or self-assembly processes. 3D printing is an emerging option to replace these types of mold-based procedures [18], but the material systems available for printing are still being developed. Thin film and stacking based approaches often seen in commercial systems and macro scale batteries offer fabrication simplicity and scale, but often have lower overall surface areas and incorporate electrochemically inactive materials like polymer binders and conductive additives to achieve mechanical and electrical stability in the devices [19-23]. Thus, a main research need in the energy storage device field is in the fabrication of lithium ion batteries that can be scaled in both the lateral and vertical directions while also incorporating the material advantages that occur on the micro and nano-scale.

To demonstrate progress towards batteries that bridge the gap between the micro and macro scale, the process demonstrated in this work relies on a scalable scaffold approach that generates free-standing, full cell lithium-ion batteries consisting of vertically interdigitated multilayer stacked electrodes. In the fabrication of these structures, individual steps do not constrain any layer dimensions, and as a result the lateral area and volume are decoupled. In turn, the thickness of each material in the electrode is deterministically controlled by the electrodeposition process, and the overall volume can be tuned to provide outputs for specific application needs. The benefits of deterministic engineering of battery electrodes was demonstrated in [24], where precise electrode thickness control and optimized geometries via modeling led to increased power performance. However, the fabrication was limited in vertical scale and to anodes only. The process shown here enables facile assembly of full cells, and thus the fabrication of batteries generated in this study should augment other 3D cells seen commercially and in literature [14, 15, 18, 25, 26].

## 2. Methods

## 2.1. Fabrication Approach

The presented full battery comprises a desired number of vertically-interdigitated electrodeposited anodes and cathodes that are separated by interlayer spacing posts, where each electrode layer footprint area as well as the electrolyte gaps are precisely defined. A schematic of the fabrication process for battery construction, which was extrapolated from our previous work in half cells [27], is provided in figure 1. In the first step (figure 1(a)), a layer of polydimethylglutarimide-based lift-off resist (LOR-3A, Microchem) is spin cast onto a carrier substrate (silicon or glass). This polymer film acts as an adhesion barrier between the carrier substrate and the subsequent metal processing for the electrodes. In the second step



Figure 1. Schematic of the battery fabrication scheme.

(figure 1(b)), a seed layer of metal (i.e. titanium (20nm)/ copper (300 nm-600 nm) is sputtered on the LOR film and thickened with copper (for the anode) or nickel (for the cathode) via electrodeposition. This becomes the basis for the current collector (CC) of each cathode and anode layer in the cell; the fabricated CC's are typically a few microns thick (i.e. 1-3 m). Next, the CC is patterned with interlayer spacing posts via photolithography (figure 1(c)). The pillars are deposited through the mold using the same metal as the CC, also via electrodeposition. Next, the high surface area patterned CC is mechanically detached from the carrier substrate at the interface between the LOR and the seed layer (figure 1(d)). The large difference in adhesion of the polymermetal and the polymer-substrate pairs enables the separation. The CC detachment is initiated by separating the film from the polymer at the corners with a thin needle or blade, and then mechanically peeling until complete separation is achieved. Films should be at least 1  $\mu$ m thick to minimize the risk of tearing during the process. Next, the freestanding patterned CC is covered with a thin film of active material (figure 1(e)), again via electrodeposition. The electrodeposition ensures a conformal deposition of the active material on the both sides of a given CC and enables precise control and scalability of layer thicknesses in an aqueous, room temperature setting. The chosen anode and cathode active materials were nickel-tin (NiSn) alloy and lithium manganese oxide (LMO). Following active material deposition, the patterned layers are diced and assembled into vertically interdigitated electrodes. The assembly is completed with a modified commercial polyethylene separator, laser cut to match the spacing post pattern (figure 1(f)). A heat press process was used to achieve the bonding of the layers. As the patterned separator is heated to just above the glass transition temperature, the layers are pressed down and the material flows just over the top of the spacing posts. After cooling, a mechanical bond has formed



Figure 2. Schematic of the full cell assembled battery.

between the anode/cathode pairs, and the gap between them is equivalent to just above the height of the posts. Crucially, this step also electrically isolates each of the cathode–anode pairs.

In the fully assembled cell schematic shown in figure 2, the tabs extending to the sides indicate the protrusion of the current collector metal to the outside of the patterned area of each layer. These tabs are clamped together to connect each set of anode and cathode layers in parallel to the external load for cycling. The spacing pillars, identified by the white outlined prisms between each anode/cathode pair in the figure, are created during the patterning steps (figure 1(c)) are coated with the separator and bond the layers together in the final step (figure 1(f)). In the schematic only six electrodes (three anode and three cathode) are shown; however, additional electrode pairs can be added through repetition of the process described in figure 1. In this study, batteries of up to 70 pairs were achieved.

The first benefit of fabrication in this way is that the anode and cathode formation occur using the same process, and the assembly into the full cells occurs in a single step. This results in consistent manufacturing of the batteries and has potential to rival the commercial casting processes. In the structure of the cells, the current collector, active material, and electrolyte gap thicknesses are all controlled by electrodeposition time and current density, making them deterministically engineered and reproducible. The use of electrodeposition to deposit the metal layers also provides an advantage in manufacturing expense and complexity. Electroplating can be carried out using room temperature solutions, and there are no vacuum processes needed. Vertically interdigitating the electrode pairs combined with the innate control of all geometrical dimensions also differentiates this process from those described earlier. In nano-rod or micro scaffold approaches, the individual electrodes are often alternatingly patterned horizontally to efficiently use the footprint area. However, in this case a compact cell architecture is still achieved via the laser

cut adhesive separator, but the battery size can be increased in any direction without sacrificing efficient use of the volumetric space. It is important to note that the adhesive separator is patterned to match the spacing pillar orientation. Thus, after the heat press occurs, there is still ample room for the electrolyte to diffuse between the layers. The melted separator provides electrical isolation and mechanical bonding, and the pillars provide the space for the electrolyte and mass transfer of lithium ions between the cathode and anode layers in the cell. Additionally, due to simple and controllable deposition of the layers, thin film and nano-structured materials that exhibit promising results in smaller 3D micro-batteries can be utilized in larger cell volume architectures. Due to high rate capacities and minimized diffusion path lengths of thin film and nano porous NiSn and LMO, intrinsic battery performance can be combined with tunable total outputs via scaling. Lastly, in contrast to typical pouch or cylindrical cell designs seen in consumer electronics [22, 23], the full cell assembly does not require use of electrochemically inert polymer binders or conductive additives to achieve the desired mechanical support and electrical performance. Thus, the dead weight introduced by those materials is eliminated.

#### 2.2. Material synthesis

NiSn and LMO were chosen as anode and cathode active materials, respectively. NiSn has a theoretical capacity of 766 mAhg<sup>-1</sup> [28] and can be conformally deposited via electroplating, which dovetails nicely with the fabrication scheme. LMO has less intrinsic capacity, but it can also be formed via an electrodeposition-based approach. Its lightweight, nanosheet structure increases its rate capabilities. Thus, the thickness of NiSn can be decreased to increase the power capabilities of the anode and still exceed the LMO capacity. Copper and nickel CC's are used for the anode and cathode, respectively, for their high conductivity and stability in the potential regimes of the given electrode.

The characteristics of the materials utilized in the multilayer structure are defined by the electrodeposition solutions and plating conditions. The NiSn and LMO active materials are prepared with aqueous baths, with the NiSn comprised of 0.075 M nickel chloride hexahydrate, 0.175 M tin chloride dihydrate, 0.5 M potassium pyrophosphate, 0.125 M glycine, and 5ml 1<sup>-1</sup> of ammonium hydroxide [28]. The manganese solution consists of 0.1 M manganese acetate and 0.1 M sodium sulfate [29]. Copper is deposited using a commercial mirror copper plating solution (Grobet), and nickel is deposited using a Watts-type sulfate-based solution of 200g 1<sup>-1</sup> nickel sulfate hexahydrate, 5 g 1<sup>-1</sup> nickel chloride hexahydrate, 35 g 1<sup>-1</sup> boric acid, and 3 g 1<sup>-1</sup> saccharin. All materials were purchased from Sigma Aldrich unless otherwise specified.

Each material in the cell is plated cathodically to ensure that the subsequent deposition steps do not corrode the previous layer. Copper, nickel, and NiSn are plated galvano-statically at 10, 5, and 5 mA cm<sup>-2</sup>, respectively, with a tin counter electrode for the NiSn deposition. The LMO material is generated first by electrodeposition of manganese

| <b>Table 1.</b> Battery dimensions for devices built using the demonstrated fabrication scheme. |                                   |                     |                    |                     |                 |                                 |
|---|-----------------------------------|---------------------|--------------------|---------------------|-----------------|---------------------------------|
| Battery   | Footprint area (mm <sup>2</sup> ) | NiSn thickness (µm) | LMO thickness (µm) | Interlayer gap (µm) | Electrode pairs | Total volume (mm <sup>3</sup> ) |
| A   | 25                                | 0.1                 | 0.4                | 10                  | 10              | 4.25                            |
| В   | 56.25                             | 0.2                 | 0.8                | 10                  | 10              | 10.125                          |
| С   | 25                                | 0.2                 | 0.8                | 10                  | 70              | 50                              |
| D   | 225                               | 0.1                 | 0.4                | 10                  | 10              | 38.25                           |
| E   | 225                               | 0.2                 | 0.8                | 10                  | 10              | 40.5                            |
| F   | 225                               | 0.2                 | 0.8                | 10                  | 20              | 81                              |

hydroxide potentiostatically at 1.8 V against a platinum sheet counter electrode. In this process, adopted from [29], water electrolysis occurs at the working electrode (in this case the nickel current collector for the cathode of the battery) during deposition, forming hydrogen gas and hydroxide ions. Positive manganese ions in solution then react with the high concentration of hydroxide ions at the surface to form manganese hydroxide. The chemical steps are summarized in equations (1) and (2).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$Mn^{2+} + 2OH^{-} \rightarrow Mn(OH)_{2}.$$
 (2)

The hydrogen bubbles that are also generated at the surface of the working electrode create a soft mold through which the  $Mn(OH)_2$  is deposited. The resulting film morphology is a series of interconnected nanosheets that combine to form a thin, porous film. The porosity created by the hydrogen evolution allows electrolyte intrusion into the void regions, and thus reduces the distance for solid state lithium ion transport. However, the overall film thickness is still deterministically controlled by the plating potential and time, and thus the multilayer scaffold geometry and device scalability is maintained.

The nanoporous, electrodeposited manganese hydroxide films are converted into the electrochemically active LMO material through submersion in a molten lithium salt. A 3:2 mole ratio of LiNO<sub>3</sub> and LiOH are ground into a fine powder and heated to a temperature of 275 °C. The cathode layers are submerged in the molten salt for 10min, converting the Mn(OH)2 into LiMnO2. Conversion to a lithiated manganese dioxide structure was confirmed by powder x-ray diffraction (Rigaku), shown in S1 (stacks.iop.org/JMM/29/055006/ mmedia). The lithiated and patterned layers were rinsed in DI water, dried, and diced to equal footprint areas with a green laser (IPG Photonics). Bonding and electrical isolation of the individual anode and cathode pairs is achieved with a polyethylene separator (Celgard) that was also cut with the laser to mimic the pillar pattern on each electrode layer. The choice of a commercial polymer separator is important, because it retains all the physical and electrochemical properties required for a battery separator (e.g. electrical insulation, ion transport, and chemical stability in electrolytes), while also having a low melting point to facilitate the adhesive bonding process. Heat pressing at 160 °C and 2 MPa is used to seal the layers together at the intersection of the spacing posts of one later to the bottom of the subsequent layer, in the vertically interdigitated geometry shown in figures 1 and 2.

#### 2.3. Characterization and analysis

The morphologies and structure of the deposited materials and assembled cells were characterized using a scanning electron microscope (Quanta 600F, FEI). Electrochemical tests were carried out using a WaveDriver20 potentiostat (Pine) in two and three electrode setups. For the three electrode tests, lithium foil was used as the reference electrode. The electrolyte for all batteries was a solution of 1 M lithium perchlorate in a 1:1 volume mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). The batteries were cycled between 2 and 4 V versus Li/Li<sup>+</sup>, and data points were taken every second during the discharge. The applied currents for each C rate (where XC rate is defined as the current required to charge and discharge the battery in  $X^{-1}$  h) were determined by the theoretical capacity of the loaded LMO cathode material. The anode layers were purposefully loaded with NiSn in slight excess capacity such that no lithium dendrites would plate on the surface if over charged. The capacity, energy density, and power density were calculated using equations (3)–(5), respectively.

$$Q = I * T \tag{3}$$

$$E = \frac{1}{\nu} * \int_0^T I * V dt \tag{4}$$

$$P = \frac{E}{T}.$$
 (5)

In these equations, v is the volume of the cell, T is the total discharge time, I is the applied current at the given C rate, V is the voltage during discharge, Q is the capacity, E is the volumetric energy density, and P is the volumetric power density. Total power and energy outputs were calculated by multiplying the densities by the cell volume. All electrochemical testing of the fabricated batteries took place inside a glove box (MBraun LabStar Pro) with an argon atmosphere at room temperature.

#### 3. Results and discussion

#### 3.1. Structural characterization

Using the process described above, high surface area 3D lithium ion batteries were built with varying overall volumes, using NiSn anode chemistry and LMO for the cathode. The dimensions of these batteries are summarized in table 1. The controlled electrochemical deposition of thin layers of active materials results in higher power performance by limiting the



**Figure 3.** Optical and SEM images of fabricated 3D batteries: (a) SEM image of a top down view of the LMO cathode layers with spacing pillars; and (b) a magnified SEM image of the nanosheet LMO morphology after deposition and lithiation. (c) An SEM image of a cross section of an assembled three pair full cell battery, where the red arrows identify the NiSn anode layers, the blue arrows identify the LMO cathode layers, and the white arrows identify the separator coated pillars (from the heat press assembly) that provide electrical isolation and form gaps for electrolyte intrusion. The pillars are light in color due to charging of the polymer separator material in the SEM. (d) An optical image of a fully assembled battery, with reference connecting clamps and a penny for size comparison.

solid-state diffusion path lengths of lithium ions. The gaps provided by the interlayer spacing pillars allow for electrolyte intrusion and maximum interfacial contact area between the active material and the electrolyte, where the electrochemical reactions occur. Due to the deterministic and scalable nature of the battery fabrication, the lateral and vertical dimensions of the cells can be changed independently, resulting in cell volumes ranging over two orders of magnitude with varying shapes from thin, wide prisms (e.g. Battery E) to more even, cubic structures (e.g. Battery C).

The current collector and active material volumes within these architectures can be adjusted simply by changing the current densities or deposition times in the electroplating steps. To gain a broad understanding of the mass loading and attempt to optimize the capacities of the anode and cathode, estimates of the material densities were used. In this case, the porosity of the electrodeposited LMO films is estimated to be about 50%, and thus the density is 4.3  $gcm^{-3}$  [29, 30]. For the NiSn films, the density can be estimated by using a weighted average of the Ni and Sn atoms in the films. The tin-nickel atomic ratio in the electrodeposited films was found to be 61%–39% (see figure S3), and thus the density estimation is  $7.95 \,\mathrm{g} \,\mathrm{cm}^{-3}$ , which compares favorably to measurements of electrodeposited NiSn films deposited with similar baths in the literature [28]. Given these density estimates for the active materials in the batteries, the mass ratio of the cathode (LMO) to anode (NiSn) in each cell is about 2:1. The theoretical capacities of NiSn and LMO are 766 m Ahg<sup>-1</sup> and 280 m Ahg<sup>-1</sup>, respectively, so there exists some excess capacity in the anode in each of the batteries A–F described in table 1 [31, 32]. This builds in some safety, as lithium dendrites can form during charging if there is not enough capacity in the anode material [33]. These dendrites have the capability to short the battery, and given the interdigitated structure of the batteries formed from this scalable multilayer process the extra anode mass was deemed acceptable. However, due to the potential error in density estimates and the lack of access to an accurate method of measuring the mass of LMO after the multistep nature of the deposition and lithiation of the films (as well as the porosity generated by the electroplating mechanism), the energy and power density metrics reported below were calculated on a volumetric rather than a gravimetric basis.

SEM images of a sample battery are shown in figure 3. Figure 3(a) shows a top down view of a sample LMO cathode layer with the patterned and deposited spacing pillars coating the surfaces, and figure 3(b) highlights the nanoporous morphology of those films after deposition and lithiation. This morphology is derived from the cathodic electrodeposition of manganese hydroxide and is maintained in the subsequent conversion to LMO. The NiSn layers have the same pillar spacing and height, but no porosity. Figure 3(c) displays an example cross-section of an assembled battery. The cathode and anode layers (consisting of a current collector coated by NiSn or LMO active materials) are bonded together in a vertically interdigitated fashion, which enables device volume scaling in any direction. The interlayer gaps are defined by



Figure 4. 1 C stability data for a sample system, Battery E: (a) charge and discharge curves over time at 0.2 C. (b) Capacity as a function of cycle number at 0.2 C.

the spacing pillars, which have been coated with the separator film during the heat-bonding step in the fabrication process. The polymeric separator gives these pillars a lighter color in the SEM image. The gaps between the layers will ultimately be filled by a liquid electrolyte, which provides the medium for mass transfer of lithium ions between electrodes. In this assembly process, the alignment of the separator/pillars of each electrode layer to the one underneath is not necessary, as long as electrical isolation and mechanical stability are achieved. A sample assembled full cell (Battery B) is shown in figure 3(d), with alligator connecting clamps and a penny included for size comparison.

#### 3.2. Cycling and rate stability

The mechanical and electrical stability of the fabricated cells were characterized by measuring the capacity of the battery over time at low rates of charge and discharge. For demonstration of typical battery performance, data from Battery E is presented here. As seen in figure 4(a), the shape of the charge and discharge curves remain consistent over time, indicating that stable cycling is achieved, and no shorts occur even at the small interlayer spacing. The plateau voltage also remains constant, indicating that the electrochemical reactions occurring during charge and discharge are not deviating over time. The shape of the discharge curves and the similar capacities of the charge and discharge cycles indicate that limited current is being drawn to the side reactions other than SEI formation at the anode during charging. Figure 4(b) displays the battery capacity at 0.2 C cycling and shows that the battery retains over 95% of its original capacity over an extended cycling period. Both plots indicate good mechanical stability of the electrodes.

To determine the rate performance of the cells, the batteries were cycled at varying C rates, from 1 C to 100 C. In each experiment, the charge rate was kept at 0.2 C to keep the input energy constant, and thus directly compare the diffusion limitations and capacity retention at the higher discharge rates. It was found in subsequent experiments that varying the charge rate and discharging at a low, constant rate did not change the trend or the value of the capacity by any significant margin. Figure 5 shows the discharge curves for Battery E at 1, 5, 20, and 40 C. Again, the plateau voltage and curve shape remain constant, even as large current loads are being applied.

The measured voltage at the beginning of discharge drops at higher C rates due to the increased IR drop across the electrodes. The diffusion limitations of the lithium ions through the solid-state active materials result in the lower energy, but the high surface area structure and maintenance of the nanomorphology in the active materials allows a high fraction of the capacity to be retained. This helps increase the power performance and allows more of the loaded LMO to be utilized. In figure 6, the normalized capacity retention is plotted as a function of cycle number at various discharge rates. The measured capacity at 0.2 C was set as the nominal 1.0 value, and subsequently higher rate discharge cycles were compared. At 1 C the capacity was 98% of the low rate value. At 5 C, 86% was retained, at 20 C 71% was retained, and at 40 C just under 50% capacity was achieved. This indicates that the fabrication process is able to generate batteries with good reversibility, rate performance, and electrical and mechanical stability even at high current loads.

#### 3.3. Power and energy performance

While the capacity retention of the active material over cycling at various rates is an important characteristic of the battery electrodes, it is also crucial to determine the efficiency of the batteries on a per volume and total output basis, as this helps determine their utility as power sources for integrated MEMS sensor and actuator systems. The total energy output is a function of the operating voltage, current, and charge/ discharge times for each battery. To compare the intrinsic performance of different types of battery architectures, the power and energy densities are calculated using equations (4) and (5). Figure 7 shows the performance of the electrodes from



**Figure 5.** Discharge curves for Battery E at various C rates, as a function of the accumulated energy density.



**Figure 6.** Capacity retention of Battery E as a function of cycle number, parameterized by C rate. Normalized capacity is determined from the first discharge cycle of the battery at a 0.2 C rate.

this work in comparison to commercial systems and others in the literature. The red circles indicate the performance for batteries A-F. The close clustering of the per volume performance data indicates that the achievable intrinsic power and energy is not impacted by scaling the volume of the cell up or down, either by adjusting the lateral footprint area or the total number of layers. The energy densities of cells A and D are lower than those of B, C, E, and F because the lateral to vertical aspect ratio in the geometry for these cells is high. Thus, reducing the active material thickness has a large impact on energy loading but a relatively low impact on overall cell volume. This can be altered by adjusting the footprint area or changing the interlayer spacing by reducing the height of the spacing pillars, resulting in more cubic or vertically prismatic systems. These changes are well within the range of possible geometries due to the flexibility of the fabrication scheme.

The performance data of the batteries tested in this work are on par with cells built via 3D opal or nanorod approaches or via



**Figure 7.** Ragone plot of power density as a function of energy density for batteries A–F in this work, as compared to full cells reported commercially and in the literature.

solid state thin films [14, 18–25], which indicates that benefits of the thin film electrodeposition and nanoscale morphology of the active materials are not lost when incorporated into the larger structure. While the energy density achieved is lower than macro scale cylindrical or pouch cell batteries due to lower active material loading, the power performance is about a factor of two or three higher. It is promising that competitive per volume performance can still be maintained with batteries sized over two orders of magnitude in size.

The true utility of this fabrication scheme lies in the tunability of the total energy outputs. Figure 8 demonstrates this functionality by plotting total power versus energy for the same batteries shown in figure 7. In this Ragone plot, the red squares for each battery indicate the outputs at various C rates from 1-100. Ideally, as the current load is increased, the power output of the battery will increase with limited sacrifice of energy. The slope of the lines generated by the data points for each battery indicate how well that goal is being achieved. In this case, all the batteries show good rate performance, but the steeper curves are generated by the cells with lower active material thickness. This confirms that managing diffusion limitations of lithium ions within the solid-state active materials is critical to maximizing power. The locations of the data sets for each battery within the overall plot are an indication of total active material loading, which is directly determined by the volume of the cell. Hypothetically, these total power outputs can be shifted anywhere on this plot (indicated by the red arrows) by tuning the fabrication parameters. The other micro-batteries seen in the literature have largely fixed, and usually lower, positions in this plot due to the nature of fabricating nanowire, opal, or 3D printed structures. The larger commercial cells designed for consumer electronics will of course have higher total energy output, but the size and material requirements to achieve that energy is prohibitive for use in smaller IoT applications. The utility of this fabrication approach is that the energy supplied to the application can be deterministically tuned, while the intrinsic performance and efficiency of the system remains the same. The combination



Figure 8. Ragone plot of total power output as a function of total energy for batteries A–F in this work, as compared to full cells reported commercially and in the literature.

of intrinsic performance and scalable total power output seen in the batteries fabricated here could be vital in powering the next wave of MEMS sensors and actuators.

#### 4. Conclusions

Full cell lithium ion batteries were fabricated via a multilayer, vertically interdigitated electrode approach enabled by electrodeposition and lithographic techniques. This process permitted the incorporation of high energy and high rate capable materials into a compact, scalable cell architecture. Utilizing electroplating-based deposition technology for the current collector and active materials allows deterministic control of each dimension of the electrode layers, and the resulting batteries had tunable volumes of over two orders of magnitude. Promising total energy and power outputs of up to 20 mWh and 178 mW, and energy/power densities of 193 Wh l<sup>-1</sup> and 1233 W l<sup>-1</sup> were achieved. The display of high capacity retention at both low and high discharge rates (up to 100 C) demonstrates the utility of this fabrication approach for use in a wide array of energy storage applications. The deterministic fabrication and non-vacuum, room temperature-based synthesis techniques could allow this process to be adapted for different active material chemistries, further increasing the application versatility across the microsystems and IoT device arena.

# Acknowledgments

This work was carried out in part at the Singh Center for Nanotechnology, which is supported by the NSF National Nanotechnology Coordinated Infrastructure Program under grant NNCI-1542153. The authors would also like to thank QNF staff for their technical support and process advice and the University of Pennsylvania for supporting this research.

#### Author contributions

MS designed the fabrication process, conducted the experimental work, and analyzed the electrochemical data. MK helped design the fabrication approach. MS and SA wrote the manuscript. SA and MA supervised the project.

### **Competing financial interests**

The authors declare no competing financial interests.

#### **ORCID iDs**

Michael J Synodis b https://orcid.org/0000-0002-2157-2265

#### References

- [1] Johnson R C EE Times 2015 *MEMS Market: Ups and Upstarts* (http://eetimes.com/document.asp?doc\_id=1328333)
- [2] Atzori L, Iera A and Morabito G 2010 The internet of things: a survey *Comput. Netw.* 54 2787–805
- [3] Steingart D 2009 Power sources for wireless sensor networks *Energy Harvesting Technologies* (Boston, MA: Springer) pp 267–86

- [4] Roco M C, Mirkin C A and Hersam M C 2011 Nanotechnology research directions for societal needs in 2020: summary of international study J. Nanopart. Res. 13 897
- [5] Blomgren G E 2017 The development and future of lithium ion batteries *J. Electrochem. Soc.* 164 A5019–25
- [6] Ferrari S, Loveridge M, Beattie S D, Jahn M, Dashwood R J and Bhagat R 2015 Latest advances in the manufacturing of 3D rechargeable lithium microbatteries *J. Power Sources* 286 25–46
- [7] Yang L, Wang S, Mao J, Deng J, Gao Q, Tang Y and Schmidt O G 2013 Hierarchical MoS<sub>2</sub>/polyaniline nanowires with excellent electrochemical performance for lithium-ion batteries Adv. Mater. 25 1180–4
- [8] Wang C, Wu L, Wang H, Zuo W, Li Y and Liu J 2015 Fabrication and shell optimization of synergistic TiO<sub>2</sub>–MoO<sub>3</sub> core–shell nanowire array anode for high energy and power density lithium-ion batteries *Adv. Funct. Mater.* 25 3524–33
- [9] Wang J, Zhang Q, Li X, Xu D, Wang Z, Guo H and Zhang K 2014 Three-dimensional hierarchical Co<sub>3</sub>O<sub>4</sub>/CuO nanowire heterostructure arrays on nickel foam for high-performance lithium ion batteries *Nano Energy* 6 19–26
- [10] Li X, Xiong S, Li J, Liang X, Wang J, Bai J and Qian Y 2013 MnO@ carbon core-shell nanowires as stable highperformance anodes for lithium-ion batteries *Chemistry* A 19 11310–9
- [11] Li W, Wang F, Feng S, Wang J, Sun Z, Li B and Zhao D 2013 Sol–gel design strategy for ultradispersed TiO<sub>2</sub> nanoparticles on graphene for high-performance lithium ion batteries J. Am. Chem. Soc. **135** 18300–3
- [12] Chen K S *et al* 2017 Comprehensive enhancement of nanostructured lithium-ion battery cathode materials via conformal graphene dispersion *Nano Lett.* 17 2539–46
- [13] Li N, Jin S, Liao Q, Cui H and Wang C X 2014 Encapsulated within graphene shell silicon nanoparticles anchored on vertically aligned graphene trees as lithium ion battery anodes *Nano Energy* 5 105–15
- [14] Pikul J H, Zhang H G, Cho J, Braun P V and King W P 2013 High-power lithium ion microbatteries from interdigitated three-dimensional bicontinuous nanoporous electrodes *Nat. Commun.* 4 1732
- [15] Ning H, Pikul J H, Zhang R, Li X, Xu S, Wang J and Braun P V 2015 Holographic patterning of highperformance on-chip 3D lithium-ion microbatteries *Proc. Natl Acad. Sci.* **112** 6573–8
- [16] Liu D et al 2013 Preparation of 3D nanoporous coppersupported cuprous oxide for high-performance lithium ion battery anodes Nanoscale 5 1917–21
- [17] Armutlulu A, Allen S B and Allen M G 2013 Microfabricated nickel-based electrodes for high-power battery applications *J. Micromech. Microeng.* 23 114008
- [18] Sun K, Wei T S, Ahn B Y, Seo J Y, Dillon S J and Lewis J A 2013 3D printing of interdigitated Li-ion microbattery architectures Adv. Mater. 25 4539–43

- [19] Standard production selection guide 2011 (Infinite power solutions) http://nz.apexelex.com/specs/batteries/ MEC200%20Series%20selector.pdf
- [20] Lai W, Erdonmez C K, Marinis T F, Bjune C K, Dudney N J, Xu F and Chiang Y M 2010 Ultrahigh-energy-density microbatteries enabled by new electrode architecture and micropackaging design Adv. Mater. 22 E139–44
- [21] Specifications for NCR18650BD 2017 (Panasonic) https:// na.industrial.panasonic.com/sites/default/pidsa/files/ panasonic-ncr18650bd-datasheet.pdf/
- [22] SK innovation 2016 http://eng.skinnovation.com/business/ battery.asp
- [23] Choi J W and Aurbach D 2016 Promise and reality of postlithium-ion batteries with high energy densities *Nat. Rev. Mater.* 1 16013
- [24] Huang C, Armutlulu A, Allen M G and Allen S A B 2017 Model-assisted development of microfabricated 3D Ni (OH)<sub>2</sub> electrodes with rapid charging capabilities *J. Power Sources* 358 101–11
- [25] Min H S, Park B Y, Taherabadi L, Wang C, Yeh Y, Zaouk R and Dunn B 2008 Fabrication and properties of a carbon/ polypyrrole three-dimensional microbattery J. Power Sources 178 795–800
- [26] Nathan M, Golodnitsky D, Yufit V, Strauss E, Ripenbein T, Shechtman I and Peled E 2005 Three-dimensional thinfilm Li-ion microbatteries for autonomous MEMS J. *Microelectromech. Syst.* 14 879–85
- [27] Synodis M, Kim M, Allen S A B and Allen M G 2018 MEMS enabled scalable fabrication of high performance lithium ion battery electrodes 2018 IEEE 31st Int. Conf. Micro Electro Mechanical Systems (IEEE) (https://doi. org/10.1109/MEMSYS.2018.8346625)
- [28] Mukaibo H, Momma T, Mohamedi M and Osaka T 2005 Structural and morphological modifications of a nanosized 62 atom percent Sn–Ni thin film anode during reaction with lithium *J. Electrochem. Soc.* 152 A560–5
- [29] Liu D, Zhang Q, Xiao P, Garcia B B, Guo Q, Champion R and Cao G 2008 Hydrous manganese dioxide nanowall arrays growth and their Li<sup>+</sup> ions intercalation electrochemical properties *Chem. Mater.* 20 1376–80
- [30] Fischer J, Chang K, Ye J, Ulrich S, Ziebert C, Music D and Seifert H J 2013 Structural transformation of sputtered o-LiMnO<sub>2</sub> thin-film cathodes induced by electrochemical cycling *Thin Solid Films* 549 263–7
- [31] Hassoun J, Panero S, Simon P, Taberna P L and Scrosati B 2007 High-rate, long-life Ni–Sn nanostructured electrodes for lithium-ion batteries Adv. Mater. 19 1632–5
- [32] Davidson I J, McMillan R S, Murray J J and Greedan J E 1995 Lithium-ion cell based on orthorhombic LiMnO<sub>2</sub> J. Power Sources 54 232–5
- [33] Aurbach D, Zinigrad E, Cohen Y and Teller H 2002 A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions *Solid State Ion.* 148 405–16