

MEMS ENABLED SCALABLE FABRICATION OF HIGH PERFORMANCE LITHIUM ION BATTERY ELECTRODES

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ABSTRACT

This paper reports a fabrication scheme that utilizes MEMS techniques to manufacture high performance lithium ion battery electrodes. The technology enables precise control over all electrode dimensions while maintaining a high surface area geometry that leads to excellent capacity retention and power/energy density performance. Additionally, this scalable scaffold approach allows the same fabrication process to generate electrodes anywhere from $10^{-3} - 1 \text{ cm}^3$ in volume, which gives rise to high total energy output. These scalable, high surface area 3-D constructs could also be applicable in pre-concentrators for chemical sensors as well as in high throughput microfluidic applications.

INTRODUCTION

In today's complex technological society, power is required on a range of size scales. While recent advances have been made in energy harvesting and device integration, the power needs are often greater than harvesting or triboelectric generation can produce [1]. Thus, batteries and supercapacitors are still the dominant sources of energy for the expanding universe of internet-of-things (IoT) sensors, actuators and other MEMS systems, but the fabrication advances for these storage devices have not matched the growing diversity of system sizes and energy needs [2]. Lithium ion batteries are of interest because of their intrinsically high energy densities, and recent work has focused on pushing past the inverse relationship most batteries display between power and energy density. Many of the advances in this area have come due to the incorporation of self-assembled nanostructures [3], nanoparticle deposition [4] or nanowire/rod growth [5], where the high surface area to volume ratio and small lithium ion diffusion path lengths can increase power without sacrificing energy density. However, due to the limited vertical scalability of these types of fabrication procedures, the total power and energy outputs of these devices are low. As a result, an area of need in the portable energy device arena is in the development of fabrication processes that can bridge the gap between nano scale performance advantages and bulk scale device volume.

To address these issues, the process proposed in this work generates free-standing, multilayer electrodes in which the length scales of the lateral and vertical dimensions are decoupled and not limited by any individual fabrication step. As a result, the thickness of each material in the electrode is deterministically controlled, and the overall volume can be tuned to provide outputs for a specific application need. Additionally, the use of aqueous based electrodeposition techniques reduces the need for expensive vacuum processing and enables the same fabrication procedure to be used for both electrodes.

EXPERIMENTAL METHODS

Fabrication of the electrodes

A schematic of the fabrication process for constructing the battery electrodes is provided in Figure 1.

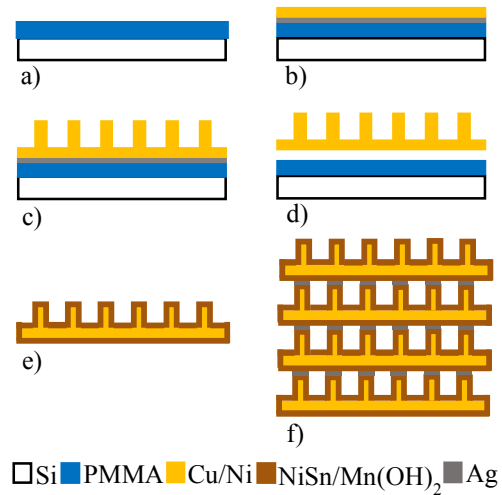


Figure 1: A schematic of the electrode fabrication process

In the first step (Figure 1a), a layer of poly(methyl methacrylate) (PMMA) 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 1b), a seed layer of copper is sputtered on the PMMA film and thickened with copper or nickel via electrodeposition. This becomes the basis for the current collector. Next, the current collector is patterned with interlayer spacing posts using AZ4620 resist (MicroChem) via photolithography (Figure 1c). The pillars are deposited through the mold using the same metal as the current collector, also via electrodeposition. Next, the high surface area patterned current collector is mechanically detached from the carrier substrate at the interface between the PMMA and the seed layer (Figure 1d). The difference in adhesion of the polymer-metal and the polymer-substrate pairs makes this process possible. Next, the free standing patterned current collector is covered with a thin film of active material (Figure 1e). For the anode stacks the nickel-tin alloy is used, and the manganese hydroxide is used for the cathode. Following active material deposition, the patterned layers are diced with a green laser (IPG Photonics) and assembled into multilayer stacks using thin, fast dry silver conductive adhesive (Figure 1f).

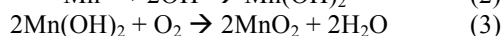
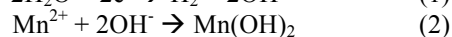
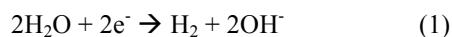
The first advantage of this process is that the current collector thickness, active material thickness, and electrolyte gaps are all explicitly defined by the electrodeposition time and current density, making them deterministically engineered and reproducible. An additional benefit is that the process can be scaled in all

three directions by increasing the area of each electroplated layer as well as the number of stacked layers. The patterning steps only define the interlayer spacing and mechanical support of each layer, and do not constrain the overall volume of the electrode. This scalability combined with the innate control of all geometrical dimensions differentiates this process from those described earlier [3-5]. From a manufacturing perspective, 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. This simplifies the scheme and eliminates the cost of accessing and operating expensive vacuum based equipment.

Material Preparation

The characteristics of the materials utilized in the multilayer structure are defined by the electrodeposition solutions and plating conditions. Copper and nickel current collectors are used for the anode and cathode, respectively. The copper is deposited using a commercial mirror copper plating solution (Grobet), and nickel is deposited using a solution of 200 g/L nickel sulfate hexahydrate, 5 g/L nickel chloride hexahydrate, 35 g/L boric acid, and 3 g/L saccharin. The nickel-tin and manganese hydroxide active materials are also prepared via electrodeposition, with the nickel-tin bath comprised of 0.075M nickel chloride hexahydrate, 0.175M tin chloride dihydrate, 0.5M potassium pyrophosphate, 0.125M glycine, and 5mL/L of ammonium hydroxide [6]. The manganese bath consists of 0.1M manganese acetate and 0.1M sodium sulfate [7]. All materials were purchased from Sigma Aldrich.

Each material in the structure is plated cathodically to ensure that the subsequent deposition steps do not corrode the previous layer. Copper, nickel, and nickel-tin are plated galvanostatically at 10, 5, and 5 mA/cm², respectively, with a tin counter electrode for the nickel-tin deposition. The manganese hydroxide is deposited potentiostatically at 1.8V vs. a platinum sheet counter electrode. The cathodic deposition of the manganese hydroxide material is different from the common metal reduction that occurs in most electroplating. In this process, adopted from [7], water electrolysis occurs at the cathode, 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. Upon drying in the presence of oxygen, the manganese hydroxide is converted into manganese dioxide. This is where the change in oxidation state of the manganese occurs. The chemical steps are summarized in Eqns. 1-3.



The hydrogen gas that is generated at the surface of the working electrode (in this case the nickel current collector) creates a film morphology of interconnected nanosheets. The porosity created by these sheets reduces the distance for lithium ion transport, while the multilayer scaffold geometry maintains scalability and deterministic control over the overall electrode dimensions.

Characterization and Analysis

The morphologies and structure of the electrodes were characterized using a scanning electron microscope (Quanta 600F, FEI). Electrochemical tests were carried out using a WaveDriver20 potentiostat (Pine) in a three electrode setup. Lithium foil was used as the counter and reference electrodes, in an electrolyte of 1M lithium perchlorate in a 1:1 volume mixture of ethylene carbonate and dimethyl carbonate.

RESULTS AND DISCUSSION

Optical and SEM Image Analysis

Using the process described above, high surface area electrodes are built with both cathode and anode chemistries. Figure 2 displays a cross section of a nickel-tin multilayer anode stack, where the interlayer spacing is defined by the lithographically patterned pillars.

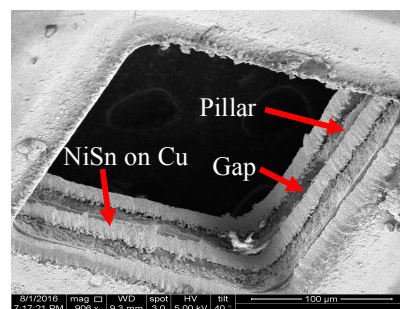


Figure 2: SEM image of a cross section of a multilayer fabricated NiSn anode

The gaps provided by the interlayer spacing pillars allow for electrolyte intrusion and maximum interfacial area between the active material and the electrolyte, where the electrochemical reactions occur. Additionally, the individual layer thickness and footprint area can be defined by the electrodeposition time, current density, and lithographic patterning.

Figure 3 shows an optical microscope image of a top view of fabricated cathode structures, with the spacing pillars showing through from each electrode layer stack.

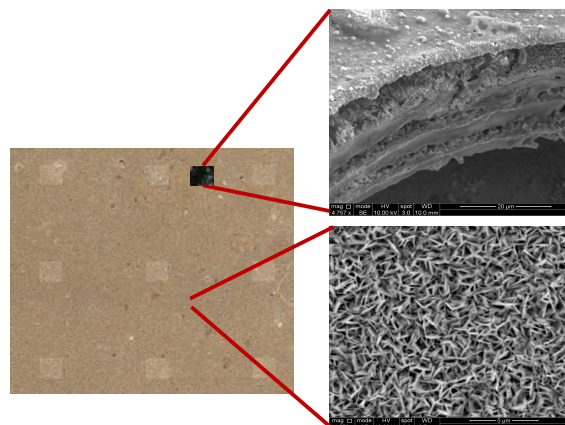


Figure 3: SEM images of a fabricated multilayer MnO₂ cathode. The left image is a top down view of the electrode layers with patterned spacing pillars, the top inset shows a sample cross section, and the bottom inset displays the nano-morphology of the active material.

The insets of the image highlight that the nanosheet morphology of the cathodically electrodeposited manganese hydroxide is maintained even after conversion to MnO_2 and subsequent electrode assembly. While the fabrication process enables the flexibility to build structures in a wide range of sizes, the electrodes built for the demonstration of this work were on the smaller scale. Their dimensions are summarized in Table 1.

Table 1: Anode and cathode dimensions

Parameter	NiSn Anode	MnO_2 Cathode
Footprint area	2.25 cm^2	2.25 cm^2
Current Collector	$1 \mu\text{m}$	$1.5 \mu\text{m}$
Active material	300 nm	350 nm
Interlayer spacing	$5 \mu\text{m}$	$5 \mu\text{m}$
Number of layers	10	10
Total volume	14.8 mm^3	16.2 mm^3

To characterize the performance of the electrodes fabricated using this scalable scaffold process, the structures are cycled against a lithium foil counter electrode of much greater capacity. Cycling occurred in the voltage range of 2 to 0.01 V vs Li/Li^+ at various charge and discharge rates. The specific capacity (capacity per gram of NiSn deposited) is measured for each cycle, and parameterized by the rate of discharge. In this case, $x\text{C}$ rate corresponds to the current needed to discharge the battery in x^{-1} hours. By comparing the specific capacity values at high and low discharge rates, and to those of commercial anodes, insight is gained into how well the nickel-tin material was being utilized throughout the structure, as shown in Figure 4.

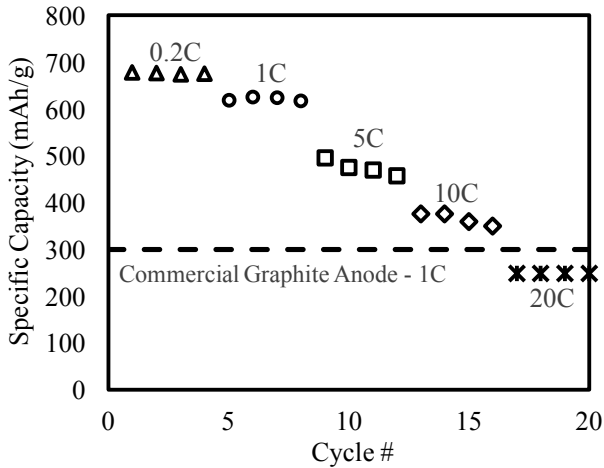


Figure 4: Specific capacity of the NiSn multilayer anodes as a function of cycle number, parameterized by discharge C rate. During each cycle, the anode was charged at a low rate of 0.2C to normalize the capacity retention analysis.

The specific capacity of the electrodes at 0.1C is 685 mAhg^{-1} and is 250 mAhg^{-1} at 20C , or 37% of the low C capacity. This means that at low C rates a large majority of the active material is being utilized, and the structural design enables good retention of that capacity at higher rates when diffusion limitations are critical. The capacity of the fabricated anode when discharged at 10C is still larger than a commercial graphite anode at 1C , which illustrates the promise of these types of structures.

The versatility of the fabrication scheme is also highlighted through the fabrication of cathodes, as described above. The performance results are summarized in Figure 5, where the electrodes were cycled between 2 and 4 V using lithium foil again as a reference and counter electrode.

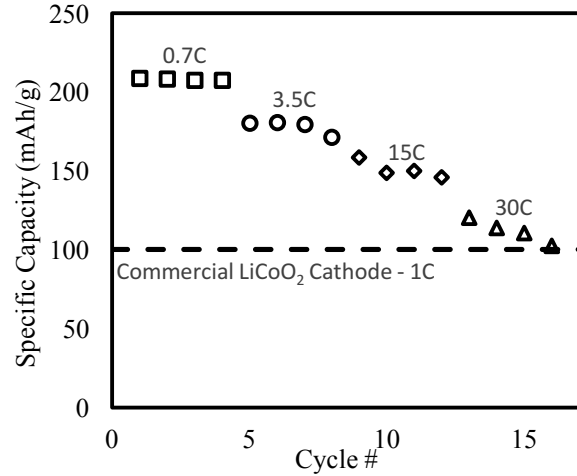


Figure 5: Specific capacity of the MnO_2 multilayer cathodes as a function of cycle number, parameterized by discharge C rate. During each cycle, the cathode was charged at a low rate of 0.2C to normalize the capacity retention analysis.

The specific capacity at a 0.2C discharge rate was 205 mAhg^{-1} , and at 30C it was 120 mAhg^{-1} , which corresponds to a 58% capacity retention with respect to the low rate performance. Thus, while the absolute value of the capacity is not as high as the anode structures due to the difference in material type (insertion vs alloying), the retention is higher. If these materials were incorporated in a full cell, the thickness/mass of the two active materials would be adjusted so that they could each contain the same quantity of lithium ions during charge and discharge transfer. The capacity retention of these multilayer stacked electrodes indicates that this process is adaptable to manufacture both cathode and anode materials, is scalable in three dimensions, and can still provide excellent 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 measure the total power and energy output. This is a function of the operating voltage, current, and discharge rate of the electrodes. To compare the intrinsic performance of different types of batteries, power and energy densities are calculated, in this case on a volumetric basis. Figure 6 shows the performance of the electrodes from this work in comparison to commercial systems and others in the literature. The power and energy density performance of the scalable electrodes tested in this work are on par with those built via self-assembly or nanorod growth methods, which indicates that benefits of the thin film deposition and nanoscale morphology of the active materials are not lost when incorporated into the larger structure. Additionally, as seen in Figure 7, the total possible power and energy output far outweighs those seen in other systems.

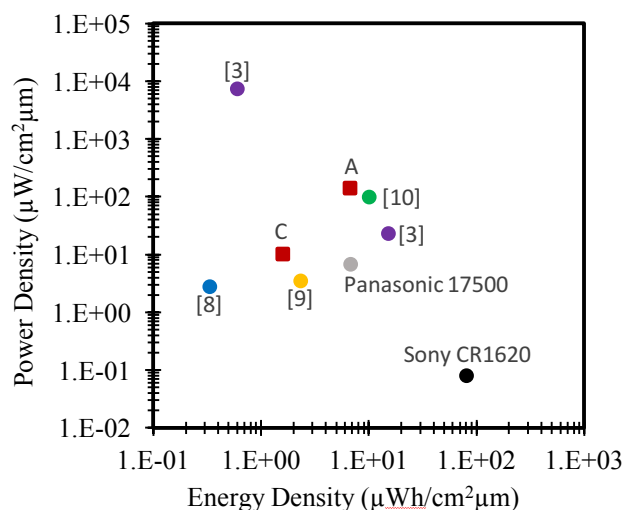


Figure 6: Ragone plot displaying the volumetric power and energy densities for the electrodes fabricated in this work (represented by C and A), compared to those seen in literature [3,8-10] and commercial systems

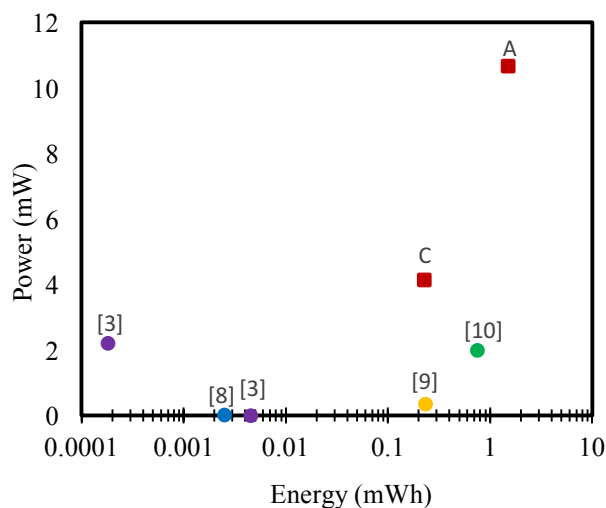


Figure 7: Ragone plot showing total power as a function of total energy output for electrodes fabricated with the process reported here (C and A), compared to those seen in literature [3, 8-10].

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

CONCLUSIONS

A fabrication procedure has been designed to build scalable lithium ion battery electrodes for use in MEMS applications. The use of electrodeposition techniques enables the decoupling of lateral and vertical dimension scaling, and allows the incorporation of a variety of active material chemistries. The anodes and cathodes fabricated here demonstrate excellent capacity retention at low and high discharge rates, and provide high volumetric power and energy densities. Due to the ease and scalability of the fabrication process, the structures can be optimized to provide a wide range of total power outputs, thus increasing

the application versatility for these types of devices. Additionally, the three-dimensional constructs shown in this work could have applications in other MEMS devices such as pre-concentrators for chemical sensors or high throughput microfluidic devices.

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