



Integration of high capacity materials into interdigitated mesostructured electrodes for high energy and high power density primary microbatteries



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HIGHLIGHTS

- Ultra-high power density is achieved in primary microbatteries.
- Integration of high capacity materials enables high energy density.
- Conformal electrodeposition in mesostructured electrodes is demonstrated.
- Dense lithium metal electrodeposition is demonstrated.

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ABSTRACT

Microbatteries are increasingly important for powering electronic systems, however, the volumetric energy density of microbatteries lags behind that of conventional format batteries. This paper reports a primary microbattery with energy density $45.5 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ and peak power $5300 \mu\text{W cm}^{-2} \mu\text{m}^{-1}$, enabled by the integration of large volume fractions of high capacity anode and cathode chemistry into porous micro-architectures. The interdigitated battery electrodes consist of a lithium metal anode and a mesoporous manganese oxide cathode. The key enabler of the high energy and power density is the integration of the high capacity manganese oxide conversion chemistry into a mesostructured high power interdigitated bicontinuous cathode architecture and an electrodeposited dense lithium metal anode. The resultant energy density is greater than previously reported three-dimensional microbatteries and is comparable to commercial conventional format lithium-based batteries.

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1. Introduction

Integration of miniature sensors and radio devices into consumer goods, biomedical devices, and industrial electronics has driven significant interest in microbatteries [1]. Developments in electrode structure engineering have enabled secondary microbatteries with power densities 100 times greater than commercial lithium ion batteries (up to $7.4 \text{ mW cm}^{-2} \mu\text{m}^{-1}$) [2–4]. The high power densities were achieved with interdigitated mesostructured electrode architectures that simultaneously reduced ion and electron transport resistances in the anode, cathode, and electrolyte.

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The electrodes consisted of thin films of electrochemically active materials coated on highly conductive porous metal current collectors, providing good electrical conductivity and reduced solid state ion diffusion distances [2,3]. Electrode interdigitation reduced ion transport lengths across the electrolyte. As is true for all secondary batteries, the energy density was lower than a similarly sized primary battery. Given that for a number of microbattery applications recharging is not possible, the added energy density of a primary system is worth considering. Here we demonstrate how primary microbatteries with both high energy and power density can be realized by integrating large volume fractions of high capacity materials into high power microbattery architectures.

Integration of high capacity primary electrode materials into high power microbattery architectures is challenging. Electrochemically active material must be deposited with nanometer-scale thickness control throughout high surface area porous current

collectors. Because of the interdigitated design, both the anode and cathode materials must be grown on the same substrate. Finally, prevention of electrical shorts between narrowly spaced electrodes is required. Gas-phase deposition methods (e.g. ALD and CVD) provide high quality conformal coatings but require complicated strategies to limit deposition to only the anode or cathode [4–6]. Electrodeposition techniques that take advantage of the electrical separation between anode and cathode have been used to deposit materials into high power secondary electrodes, but the lower capacity and volume fraction of the electrochemically active materials used limited the energy density [2,3]. In a primary system, the materials constraints are reduced, since recharging is not necessary, enabling possible use of high capacity anode materials including silicon, tin [7], lithium [8–12], and conversion reaction based oxides [13–15]. For a primary battery, where dendrite growth and solid electrolyte interphase (SEI) formation during cycling is not important, lithium is perhaps the most promising anode due to its high capacity, low density, and low reference voltage [8–12,16–25]. On the cathode side, maximization of capacity and voltage is important, with the realization that most high capacity cathodes require high processing temperatures for crystallization that are not compatible with other microbattery components [13–15,26]. A notable exception is manganese oxide, which has a high capacity, even in the electroplated version.

Here we integrate large volume fractions of high capacity materials (lithium anode and manganese oxide conversion cathode) into high power interdigitated 3D mesostructured bicontinuous microbattery architectures using near room temperature processing conditions, resulting in the formation of primary microbatteries with impressive energy and power. The primary microbatteries have $5300 \mu\text{W cm}^{-2} \mu\text{m}^{-1}$ peak power density and up to $45.5 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ energy densities. The energy density is greater than previous 3D microbatteries and comparable to commercially available conventional format lithium based batteries [2,27–29].

2. Experimental

2.1. Microbattery fabrication

Fig. 1c outlines the microbattery fabrication, which followed a similar procedure we developed for secondary microbatteries [2]. First, an interdigitated gold pattern that defined the geometry for the microbattery electrodes was fabricated by sputtering 8 nm of chromium followed by 70 nm of gold on a 1 mm thick soda lime glass slide, and then patterned and etched via conventional lithographic processing. The interdigitated gold pattern had 5 mm long and 5 μm wide parallel rectangles, called fingers, connected to two perpendicular 4 mm wide contact pads such that every other finger was electrically connected through a contact pad and neighboring fingers were electrically isolated. The glass slide with gold pattern was then cut into smaller samples, piranha cleaned for ten minutes, immersed in ultrapure water with 3-mercaptopropanesulfonic acid, sodium salt (2.2% by weight) for 3 h and rinsed. Polystyrene (PS) opals were self-assembled onto the gold patterned substrate by first placing the substrate vertically in 1 inch diameter plastic container filled with a colloid solution of 500 nm in diameter PS spheres. The plastic container was then set on a hotplate at 55 °C, covered, and left for 24–30 h until the solution was dry. The substrate was then sintered at 96 °C for 5 h, which increased the contact area between the PS spheres to about 200 nm in diameter. This contact area determines the diameter of the holes, or interconnects, between the 500 nm pores in the inverted nickel current collector. A larger interconnect diameter allows for more active material deposition before the interconnect holes are

pinched closed, which prevents the transport of ions through the porous structure. The PS colloidal solution was made by combining 8 wt% PS sphere solution (1.2 g), purchased from Invitrogen, with ultrapure water (40 g). The porous, bicontinuous nickel current collectors for the cathode electrodes were fabricated by electrodepositing nickel through the PS opal at a constant -1.8 V versus a nickel reference electrode in Technic RTU Mechanical Agitation commercial plating solution. In this step, the anode and cathode current collectors were independently deposited for 2 min and 12 min. The deposition time controlled the anode and cathode current collector sizes. The nickel anode current collector provided a barrier between the gold and lithium that was later deposited, as lithium electrochemically alloys with gold at the lithium deposition voltage. PS was removed by immersing the substrates in a tetrahydrofuran bath for 24 h followed by a tetrahydrofuran and toluene rinse. The resulting nickel current collectors provided the architecture for the microbattery. The cathode current collectors are typically 33 μm wide, 15 μm tall, and 87% porous, separated between 5 μm wide and less than 1 μm tall interdigitated anode current collectors.

2.2. Electrochemically active material electrodeposition

The cathode and anode electrochemically active materials were independently electrodeposited onto the electrically isolated nickel current collectors. The cathode current collector was first primed for manganese deposition by applying 15 cycles of 1.2 and -0.5 V pulsed vs. Ag/AgCl for 0.1 and 3.0 s in ultrapure water with manganese acetate tetrahydrate (0.1 M) and sodium sulfate (0.1 M) titrated to pH 5.5 using sulfuric acid. Manganese oxide was then deposited and partially stripped for 30 cycles by applying 0.6 V vs. Ag/AgCl for 8 s followed by -0.95 and -0.8 V for 2 s each, with a 25 s open circuit rest between each cycle. After deposition, the manganese oxide was electrochemically oxidized by holding the cathode at 1.1 V vs. Ag/AgCl for ten minutes in ultrapure water titrated to pH 3.5 using sulfuric acid.

A 1 mm thick polyethylene gasket with acrylic adhesive and a 0.5 mm² through hole was placed on the microbattery substrate to enable precise measurement of the microbattery area after discharge. Only the electrodes beneath the through hole are exposed to the electrolyte. The substrate was preheated to 110 °C before the mask was added to improve the mask adhesion and prevent electrolyte from leaking to other areas of the electrodes. The microbattery substrate was moved to an argon filled glovebox. Lithium was then deposited onto the anode current collector at 0.75 mA cm⁻² current density with LiClO₄ (1.0 M) and CsPF₆ (0.05 M) in 80% propylene carbonate (PC) solution with 20% vinylene carbonate (VC) based on a recipe from Ding et al. [8]. VC was added to form a thin SEI film and suppress the deleterious reaction between the deposited lithium and the electrolyte [11]. The solution was made by first mixing AgPF₆ (0.05 M) with CsI (0.05 M) in PC (25 ml), and stirring for 12 h in an argon filled glovebox. After mixing, AgI formed a yellow precipitate that was filtered out by running the solution through a 0.45 μm syringe filter. A piece of lithium was then inserted into the solution to react any excess silver ions followed by another filtration step. VC (5 ml) was then added along with LiClO₄ (1 M), after which the solution was filtered and ready for lithium deposition. The cycling efficiencies reported in Table 1 were determined by galvanostatically depositing lithium on a flat nickel substrate for set period of time, typically 1 h, and then galvanostatically de-plating lithium at the same current density until the sample potential reached 0.2 V versus lithium. The cycling efficiency was determined by dividing the coulombs de-plated by the total deposited coulombs. The reported numbers in Table 1 represent the best performance for each

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