Three-Dimensional Thin-Film Li-Ion Microbatteries for Autonomous MEMS

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Abstract—Autonomous MEMS require similarly miniaturized power sources. In this paper, we present the first working three-dimensional (3-D) rechargeable Li-ion thin-film microbattery technology that is compatible with MEMS requirements. The technology has been developed, and full 3-D cells have been manufactured on both glass and silicon substrates. Our 3-D microbatteries have a sandwich-like structure of conformal thin-film electrodes, electrolyte and current collectors. The films are deposited sequentially on all available surfaces of a perforated substrate (e.g., silicon or a glass microchannel plate or “MCP”) using wet chemistry. The substrate has thousands of high-aspect ratio holes per square cm, thereby providing more than an order of magnitude increase in surface area per given footprint (original 2-D substrate area). The full 3-D cell consists of a Ni cathode current collector, a MoO$_3$ S$_2$ cathode, a hybrid polymer electrolyte (HPE) and a lithiated graphite anode that also serves as anode current collector. One 3-D cell with a roughly 1-$\mu$m-thick cathode ran at C/10 to 2C charge/discharge rates and room temperature for 200 cycles with 0.2% per cycle capacity loss and about 100% Faradaic efficiency. The cell exhibited a capacity of 2 mAh/cm$^2$, about 30 times higher than the capacity of a similarly built planar (2-D) cell with the same footprint and same cathode thickness. [1461]

Index Terms—Li-ion 3-D thin-film microbattery, lithium 3-D thin-film microbattery, MEMS, microchannel plate.

I. INTRODUCTION

The miniaturization of electrical, mechanical, and optical systems using MEMS technologies has provided systems and devices with a total volume on the order of at most a few tens of mm$^3$. The recognition that such miniaturized systems and devices need similarly miniaturized power sources has led to a quest for true three-dimensional (3-D) microbatteries (MBs). A recent review of the field [1] presents a wide array of ideas for various architectures and technologies, but states that the construction of an operational, fully 3-D microbattery “has yet to be achieved.” In fact, a realistic technology of such a microbattery based on conformal thin-film structures that follow a 3-D architecture of an operational, fully 3-D microbattery “has yet to be achieved.” In fact, a realistic technology of such a microbattery based on conformal thin-film structures that follow a 3-D architecture of an operational, fully 3-D microbattery “has yet to be achieved.”

Clearly, if one takes advantage of all exposed surfaces in such a structure, the “tiling” of the footprint area with various hole geometries provides distinct advantages over conventional bulk MB’s [9], [10], which essentially miniaturize the geometry of standard batteries. The correct frame of reference for comparison of our 3-D thin-film MB’s are planar (2-D) thin-film batteries, best represented by the Li and Li-ion technology developed at Oak Ridge National Laboratories (ONRL) by Bates and coworkers [11]. 2-D thin-film batteries cannot be considered “microbatteries” since they require relatively large footprints of at least a few cm$^2$ in order to provide reasonable capacity and energy.

The basic proposition behind the architecture of our 3-D microbatteries is that the main disadvantage (i.e., large required footprint) of planar 2-D thin-film batteries can be eliminated. The capacity of such batteries is limited by the active cathode volume, given by the footprint area multiplied by the cathode thickness. In the best case, the cathode may be 5 $\mu$m thick, a more typical maximum thickness being 2 $\mu$m [1]. The maximum expected energy density for a thin-film system is $\sim 2$ J mm$^{-3}$ or 0.56 mWh mm$^{-3}$ (560 mW h/ml) [1]. In terms of capacity, a recent experimental study of commercial thin-film batteries [12] with a footprint of 3 cm$^2$ found that they have a capacity of 0.4 mAh (i.e. 0.133 mAh/cm$^2$). If one could increase the active cathode area for the same substrate footprint, one could increase the energy density and capacity. As disclosed in [2] and shown in Fig. 1(a), a significant gain in geometrical area for film deposition (and therefore cathode volume) can be achieved by having a perforated substrate instead of a flat substrate. The perforations may have any shape. We refer to them as “through-holes.” The area gain (AG) depends on the number of holes or “microchannels” in a MCP, see Fig. 1(b) and on the aspect ratio (height/diameter) of these holes, and, for circular holes, may be estimated from the following equation:

$$AG = \frac{\pi d}{(d+s)^2} \left( t - \frac{d}{2} \right) + 2$$

where $d$ is the microchannel diameter ($\mu$m), $s$ is the interchannel spacing ($\mu$m), and $t$ is the substrate thickness ($\mu$m). Equation (1) reflects the gain in exposed areas due to the added internal cylindrical envelope sidewalls minus the lost top and bottom cylinder “caps,” per footprint unit area. For example, for a substrate with $d = 50\mu$m, $s = 10\mu$m and $t = 500\mu$m, the active surface area gain is about 23. A more exact mathematical model that looks at the “tiling” of the footprint area with various hole geometries predicts a slightly larger value of $AG$ (by about 10%), and indicates that a geometry of hexagonal holes separated by constant thickness walls [as in the MCP shown in Fig. 3(a)] is close to optimal.

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a perforated substrate, one can make a battery with much larger specific performance parameters (e.g., capacity and energy) on the same original substrate footprint.

II. EXPERIMENTAL

We developed and characterized 3-D-MCP-based microbatteries comprising a nickel cathode current collector, a nominally MoS$_2$ cathode, a Hybrid Polymer Electrolyte (HPE) and a lithiated graphite anode that also served as anode current collector. The MCP substrate was a 13 mm diameter, 0.5 mm thick disc, with 50 µm diameter hexagonal microchannels separated by 10-µm walls, and was chosen for the perfection and smoothness of its microchannels. The electrode area of the active cell was 0.2 cm$^2$. Similar microbatteries were made on perforated silicon, with through-holes formed by inductive coupled plasma etching. All layers except the anode were thin conformal films, formed such that they continuously followed the contour of all available surfaces. A schematic isometric view of our MB is shown in Fig. 2(a), and a cross-section through a row of holes is shown in Fig. 2(b). Every layer is continuous and interconnected between all holes through both top and bottom surfaces. The anode fills in the center hole left in each microchannel after the formation of the other layers. Note that the smallest unit that
can in principle serve as an independent MB is 50 μm in diameter and 500 μm long.

The batteries were cycled at room temperature in a Maccor series 2000 battery test system. Scanning electron and optical microscopies were used to characterize the morphology, and various techniques were used to characterize the structure and chemistry of the layers. Following is a short description of each layer, its formation process and its properties.

**A. Ni Current Collector**

An electroless method, which is known to provide conformal coatings, was used to deposit the nickel current collector on all available surfaces of an MCP substrate. The MCP was made of soda-lime glass, with a composition as follows (w/w%): SiO₂ (72.8), Na₂O (13.7), CaO (8.8), MgO (4.0), Fe₂O₃ (0.12), Al₂O₃ (0.1). Prior to Ni plating, the substrate surface was treated using conventional methods [13], [14] by sequential soaking and degreasing in a detergent solution and ethanol, in an ultrasonic bath at room temperature. This was followed by immersion of the MCP in boiling cyclohexane and concentrated (98%) sulfuric acid. The thoroughly degreased surface was etched in the 1:4 mixture of hydrofluoric (40%) and sulfuric (98%) acids. The conventional electroless deposition of nickel involves several sequential stages that include sensitization, activation and nickel reduction [15], [16]. Figs. 3 and 4 show planar (3a), cross-sectional (3b), and tilted (4) SEM views of the MCP with a deposited nickel current collector. The electroless process yields a uniform 2–4 μm-thick nickel layer both inside the microchannels and on the flat areas. We obtained conformal and highly adherent deposits of the nickel current collector with complete coverage of the microchannels. After thorough washing with deionized water, the Ni-plated MCP was subjected to electrochemical cathode deposition.

**B. Cathode**

An inexpensive and relatively simple electrodeposition method was developed for preparation of low-cost and low-toxicity molybdenum sulfide thin cathode layers. Electrodeposition was carried out in the electrolytic bath containing tetrathiomolybdate (MoS₂⁻) anions as the electroactive species. The bath was prepared by mixing of aqueous solutions of Na₂S and Na₂MoO₄ and by adjusting the pH to 7.5–8.0 through addition of HCl or KH₂PO₄. A special flow system was constructed in order to ensure conformal deposition inside the high aspect ratio channels. The Ni-coated perforated sample was placed between two graphite plates acting as counter electrodes. The cell was connected to the reservoir of electrolytic bath via a peristaltic pump that provided a constant flow rate of 0.4 L/min. A thin-film molybdenum sulfide layer was obtained from the electroreduction of tetrathiomolybdate anions by applying a negative constant potential/current to the Ni-coated MCP. The process followed the reaction:

\[
\text{MoS}_2^- + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{MoS}_2 + 2\text{H}_3\text{O}^+ + 2\text{OH}^-.
\]

A highly adherent, homogeneous, compact film about 1 μm thick could be deposited on the nickel-coated glass substrate by pulse current deposition [5]. The structure of the cathode material inside the hole was identical with that on flat areas (Fig. 5). Details on the structure and composition of the cathode film are given elsewhere [3], [5].

As reported in more detail in [3] and [5], an EDS analysis indicated a large atomic surface concentration of oxygen, while powder XRD patterns indicated that the electrodeposited film were mainly amorphous. High-resolution XPS measurements showed that the cathode surface included mainly molybdenum oxides, while its bulk had similar concentrations of Mo-S and Mo-O bond-containing compounds. TOF-SIMS spectra showed the presence of polyion clusters containing both oxygen and sulfur (e.g. MoO₃, MoO₂S and MoS₂O), indicating formation of molybdenum oxy sulfide during electrodeposition. In agreement with the XPS data, the concentration of sulfur containing fragments, calculated from the TOF-SIMS spectra, increased with sputtering time. For example, after 11 minutes of sputtering that penetrated into a depth of close to 100 nm, the predominant species were MoS₂ and MoO₂S [5].

**C. Polymer Electrolyte Membrane**

We chose a commercially available PVDF-2801 copolymer (Kynar) to serve as a hybrid polymer electrolyte (HPE). SiO₂
(Aerosil 130) was added to the polymer matrix to enhance the ionic conductivity and electrolyte uptake. A slurry was made out of these components. The thickness of the membrane and its morphology depended on the percent of solids in the casting slurry, and the type of solvent and pore former. The homogeneous polymer membrane is shown in Fig. 6. A few sequential spin-coating and vacuum pulling steps were employed to insert the membrane slurry into the microchannels. The SEM image in Fig. 7 shows the conformal coating of the microchannels by the polymer electrolyte membrane.

**D. Anode**

We chose MCMB 6–28 (mesocarbon microbeads, Osaka Gas Corporation) as the anode lithium intercalation host material. The MCMB was dried at 200 °C for about 8 h. An anode slurry was prepared by mixing the appropriate amounts of MCMB, polymer binder and a solvent. As with the HPE membrane, consecutive spin-coating and vacuum steps were used to fill the remaining cylindrical cavities of the microchannels with the anode material. Fig. 8 shows a cross-sectional SEM micrograph of the 3-D-MCP cell.

The 3-D-MCP-coated structure was soaked in 1M LiPF₆ 1EC:1DEC or 1M LiBF₄ 1 EC: 9 DEC electrolyte under vacuum to ensure complete wetting of the materials. A lithium foil was placed on the top of the graphite to provide lithium intercalation during the 10 hours rest time of the cell before the first cycle. The final product—a MCP substrate with channels coated by nickel current collector, molybdenum oxysulfide cathode, polymer membrane and anode—was assembled in a 2033 button cell for testing in the Maccor tester. Its ohmic resistance was about 25 Ω.

**III. RESULTS AND DISCUSSION**

**A. Battery Testing**

3-D-MCP microbattery cells were tested at room temperature at 200 to 1000 μA/cm². The voltage cutoff was 1.3 to 2.2 V. Similarly prepared planar (2-D) microbatteries with identical layer structures were tested for comparison under the same operating conditions.

Fig. 9 shows charge/discharge curves of the 3-D-MCP cell. The sloping character of the curves is similar to that of planar cells and typical of lithium insertion/de-insertion into a single-phase host material according to the reaction

$$\text{MoO}_3\text{S}_2 + x\text{Li}^+ + xe^{-} \rightarrow \text{Li}_x\text{MoO}_3\text{S}_2$$

Fig. 10 shows discharge curves after 2 and 19 cycles at 0.2 and 1.0 mA/cm². The discharge profile remained almost unchanged upon prolonged cycling. Fig. 10 shows however that there was a significant discharge overpotential when the rate increased by a factor of 5 (curve 2). The first-cycle utilization of the cathode-active material approached 100%. Fig. 11(a) shows that the Li-ion/HPE/MoO₃S₂ cell ran for about 200 successive cycles with 0.2% per cycle capacity loss and almost 100% Faradaic efficiency. As reported previously [5], the surface of the electrodeposited cathode is highly oxidized. This
Fig. 8. Top view SEM micrograph of the full 3-D-MCP cell filled with the graphite anode. The polishing needed to remove the top surface causes smudging artifacts on the glass inter-cavity walls.

Fig. 9. Typical charge/discharge curves of the 3-D-MCP cell.

Fig. 10. Curves of the 3-D-MCP cell at different current densities. Curve 1: \( i_d = 0.2 \text{ mA/cm}^2 \). Curve 2: \( i_d = 1.0 \text{ mA/cm}^2 \).

results from the high surface area of the nanosize molybdenum oxysulfide and its increased sensitivity to the environment. The surface oxide layer increases the open cell voltage (OCV) of the Li cell and causes some irreversible processes like oxide reduction to occur during the first few charge/discharge cycles. Consequently, the discharge capacity loss is more pronounced in the initial cycling. The surface oxides, however, do not affect the degradation rate of the battery upon prolonged cycling. The cell retained 60% of its capacity after 200 100% DOD cycles. Fig. 12 shows that a discharge current density increase was followed by a capacity drop. The capacity value was restored immediately upon decreasing the discharge rate.

Fig. 11. (a) Cycle life of the 3-D-MCP cell. (b) Comparison of the capacity between the 3-D MB and a 2-D thin-film battery fabricated in parallel.
Li-ion cells were designed and narrow battery capacity seen, vs. a maximum of about attainable in 2-D thin-footprint 3-D microbattery [1] in terms of power, energy and rate of one order of magnitude higher geometric energy density than 3-D microbatteries [1] in terms of power, energy and rate. Our results may also be compared with the reported 80% gain in full-cell 3-D thin-film microbatteries, see Fig. 11(b). The reversible 2.0 mAh/cm$^2$ capacity seen in those batteries is probably greater than 1 mAh/cm$^2$ which means that the factor of 15 is an underestimate of the true 3-D gain. Our results may also be compared with the reported 80% gain in capacity (to 0.125 mA/cm$^2$) provided by carbon micropillar architectures [17], MB’s based on which will bear the closest resemblance to our own.

With a cathode thickness of 3 μm, our microbatteries will have a projected geometrical energy density (per cm$^2$ of substrate footprint) of 10.5 mWh/cm$^2$, vs. a maximum of about 1 mWh/cm$^2$ attainable in 2-D thin-film batteries [18]. In other words, our 3-D thin-film MBs are realistically expected to provide an order of magnitude higher geometric energy density than the best existing 2-D microbatteries. Furthermore, we expect our 3-D thin-film MBs with a modified cathode to outperform all 2-D thin-film MB technologies as well as proposed alternative 3-D microbatteries [1] in terms of power, energy and rate characteristics.

IV. CONCLUSION

The technology described in this paper represents the first working 3-D rechargeable Li-ion thin-film microbattery technology. The development process had to solve complicated technical barriers, such as insertion and deposition of a sandwich of thin-films in long (500 μm) and narrow (<50 μm) channels, as well as on the two remaining flat top and bottom surfaces of the perforated substrate. Full-cell 3-D thin-film microbatteries were fabricated for the first time on multichannel plate substrates.

The capacity gain of the 3-D thin-film microbattery formed on an MCP substrate correlates extremely well with the geometrical area gain provided by the microchannels, which can reach 25–30. The most likely use of these types of batteries will be in autonomous MEMS systems that require a battery footprint of less than 3 × 3 mm$^2$. Based on the results on the first prototype, as well as realistic assumptions of thicker and higher voltage cathodes, we predict that a 10 mm$^2$ footprint 3-D microbattery formed in a 0.5-mm-thick substrate will provide up to 1 mWh, enough for many projected autonomous MEMS uses, for example in smart drug delivery [19] and other miniaturized implantable devices.

REFERENCES

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Her current research focuses on development of thin polymer membranes with good elastic and mechanical properties for lithium ion and lithium 3-D microbatteries.