THREE-DIMENSIONAL NICKEL-ZINC MICROBATTERIES

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ABSTRACT

A silicon-micromachined rechargeable nickel-zinc alkaline microbattery featuring out-of-plane interdigitated electrodes is reported. The three-dimensional (3-D) battery architecture offers a new approach in developing miniaturized power sources to provide enough power and energy density for autonomous MEMS devices and microelectronic circuits on their small foot print. The battery consists of nickel hydroxide cathode and zinc anode post electrodes which are densely packed in an interdigitated manner. The posts are 50 μm in diameter and 400 μm tall, with foot print area of 5x5 mm^2. Initial prototypes demonstrated a functional battery for the first few cycles of operation.

1. INTRODUCTION

Fabricating cubic millimeter size batteries with sufficient active material that can last for extended periods of time is very appealing for standalone MEMS sensors and actuators and can impact where integrated power is required for such applications as communication, sensing and networking.

It has theoretically been shown that improved battery performance can be achieved by configuring the materials currently employed in 2-D thin-film microbatteries into 3-D architectures [1,2]. Different types of 3-D architectures including nano-scale aerogel electrodes and micron size post electrodes have been recently reviewed [2]. 3-D electrodes consisting of micro post arrays have already demonstrated some of these improvements for lithium ion half-cell systems [2-4]. A sandwich-like thin-film battery structure has also been formed in a perforated substrate to demonstrate a 3-D lithium battery [5]. The present work focuses on nickel-zinc batteries, whose key characteristics include the ability to discharge at high rate due to the fast redox reactions [6].

2. DESIGN

Figure 1(a) depicts the schematic of the existing thin-film nickel-zinc microbattery, which is 2-D in nature. The anode and cathode electrodes are separated with electrolyte/separator layer. Figure 1(b) illustrates our 3-D microbattery architecture, consisting of essentially the same materials but configured for much larger electrode surface areas for a given footprint on chip. The electrodes are out-of-plane interdigitated nickel hydroxide (cathode) and zinc (anode) post arrays built on top

of the in-plane interdigitated current collectors. Aqueous KOH serves as the electrolyte.
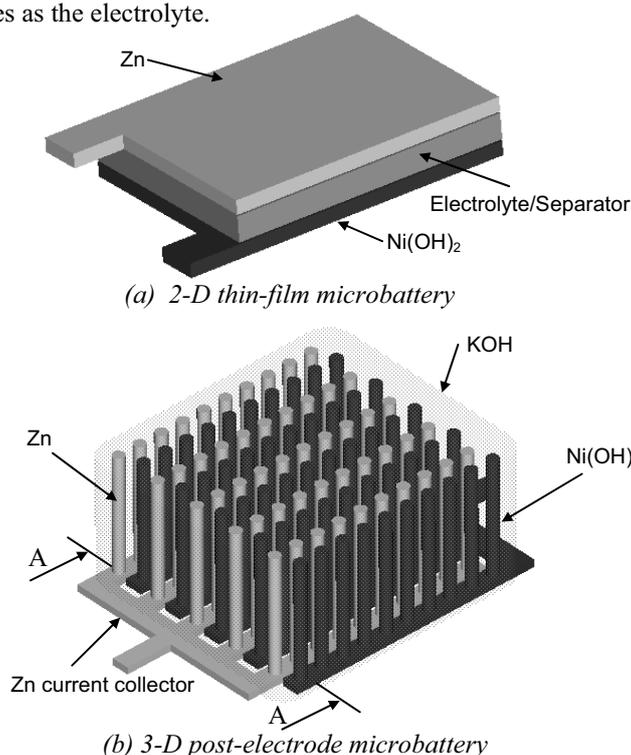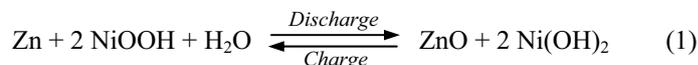

(a) 2-D thin-film microbattery

(b) 3-D post-electrode microbattery

Figure 1: Microbattery architecture

For batteries, larger electrode surfaces (i.e., reaction area) and shorter cathode-anode distances (i.e., diffusion length) lead to higher power density. Energy density, on the other hand, is largely determined by a volume, or the thickness on a given footprint. While high energy density would mean thicker electrolyte and longer diffusion length for the layered 2-D designs, it means longer electrodes and unchanged diffusion length for the 3-D design. By making the electrodes longer rather than thicker, 3-D designs would not trade energy density for power density.

3. CHEMISTRY

Nickel-zinc is an alkaline type, secondary (rechargeable) battery with 1.73 V open circuit voltage. It is an environmentally friendly battery that is currently used in large sizes and mostly in electric bicycles and vehicles. The overall electrochemical reaction is:

$$\text{Zn} + 2\,\text{NiOOH} + \text{H}_2\text{O} \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} \text{ZnO} + 2\,\text{Ni(OH)}_2 \qquad (1)$$

Although this system has less energy density than the competing lithium ion system, it can provide a quick surge of power owing to the fast redox reaction and the resulting high discharge rate. A main drawback of nickel zinc battery is the low cycle life due to corrosion of zinc in the KOH electrolyte. Some efforts have recently been made to increase the cycle life by using alloys of zinc and adding additives to KOH to reduce the zinc dissolution [7].

4. FABRICATION

The fabrication method is based on micro molding the electrode materials on top of current collectors and is described in the following steps with schematic figures at the cross section "AA" of figure 1(b).

A. Current Collectors

Current collectors of the battery are patterned as interdigitated lines on top of the glass substrate. In step 1, after patterning the photoresist, the glass is etched in BOE for 5 minutes to recess the area of the current collector lines. In step 2, 100 Å Ti and 1000 Å Au have been evaporated and patterned by lift-off. The recess brings the metal surface to the same level of glass surface for the subsequent steps.
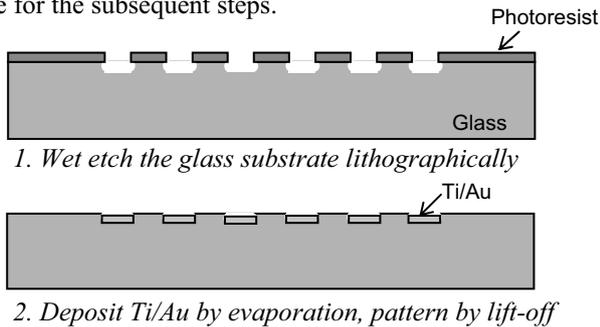
1. Wet etch the glass substrate lithographically

2. Deposit Ti/Au by evaporation, pattern by lift-off

Figure 2: Current collector fabrication

B. Mold

The goal it to provide a mold with high aspect ratio holes, which will be filled in the subsequent electroplating steps, on top of the current collectors. This electroplating template should provide excellent sealing between adjacent current-collecting lines; otherwise the metal is electroplated underneath the mold and shorts between anode and cathode of the final battery. SU-8 as the first candidate did not satisfy this challenge due to poor adhesion to glass, and its removal was hard after molding. Instead, silicon wafer with DRIE-etched holes was used as the mold. It was bonded to the glass using anodic bonding at 450 ºC and 1000 V (figure 3).
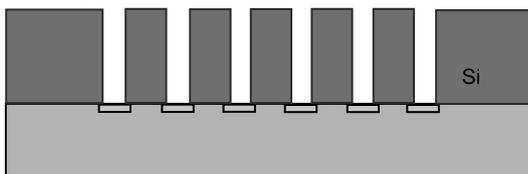
Figure 3: Providing the micro-mold

C. Nickel and Zinc Post Arrays

Nickel and zinc posts are fabricated by filling the mold using electroplating and subsequent removal of the mold (figure 4). The current collectors of the final battery serve as the electroplating seed layers. Step 1 of figure 4 depicts two separate electroplating processes. First, nickel is electroplated using high aspect ratio nickel electroplating solution from Technic Inc. The current density of 20 mA/cm^2 is used and the nickel is deposited at the rate of 18 µm/min. The sample is then rinsed in DI water and electroplated in sulfate-based electroplating solution using the opposite current collector as the seed layer. Current density is adjusted to 30 mA/cm^2 and the zinc is deposited at the rate of 31 µm/min. The silicon mold is then etched away in XeF$_2$ (step 2).
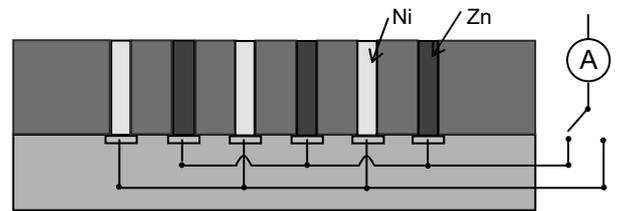
1. Electroplate Ni and Zn successively
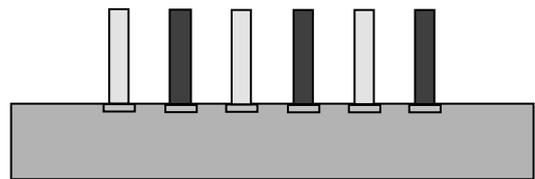
2. Etch the mold away

Figure 4: Fabrication of Ni and Zn post arrays

Figure 5 is an SEM image of nickel and zinc posts prior to the next step of nickel hydroxide deposition. The posts are 50 µm in diameter and 400 µm high. The foot print area covered by electrodes is 5x5 mm^2.
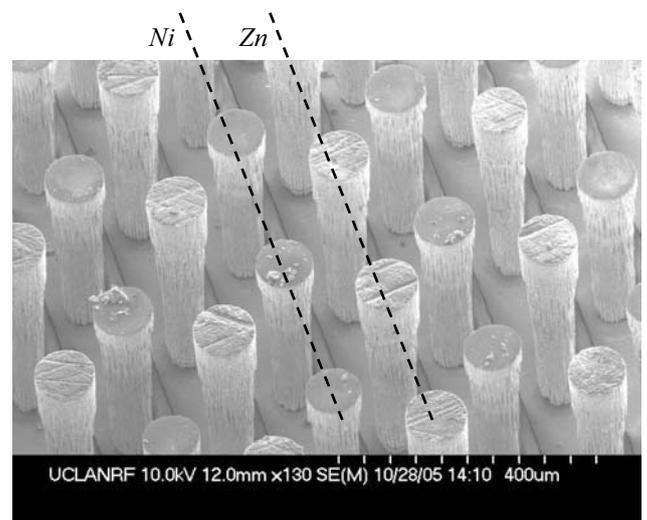
Figure 5: Nickel and zinc post arrays

D. Nickel Hydroxide

Nickel hydroxide is the active material for the cathode. It is deposited on top of the nickel electrode using electrochemical deposition in aqueous nickel nitrate solution. This deposition technique is based on electro-reduction of nickel nitrate on nickel metal [8]. In order to conformally coat the nickel posts, zinc posts were used as the counter electrode during electrochemical deposition (figure 6). In this way, the electric field distribution is uniform around the nickel, and nickel hydroxide can be coated conformally on the post surfaces. The best deposition of nickel hydroxide was observed in 1M $Ni(NO_3)_2$ at 85°C while constant current of 20 mA/cm^2 was applied for 80 seconds.
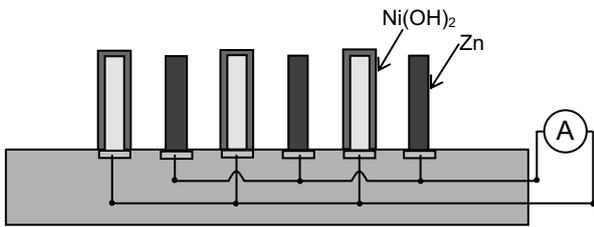

Figure 6: Nickel hydroxide deposition

Figure 7 is an SEM image showing the top of the nickel post covered with nickel hydroxide. A nickel hydroxide of ~5 μm is deposited on the surface of the rod relatively conformally.
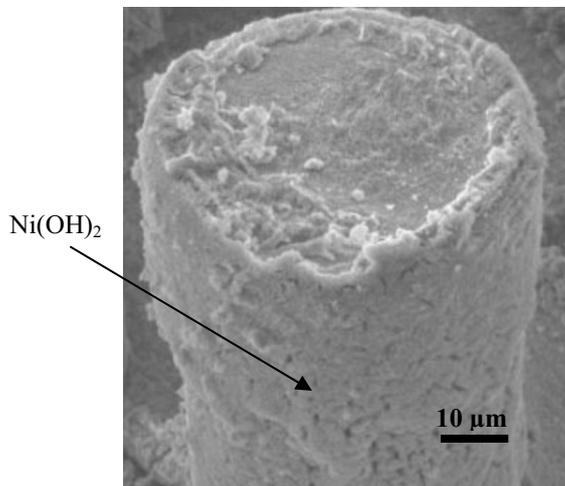

Figure 7: Nickel hydroxide conformal deposition

E. Electrolyte

The device area is defined by epoxy, and 6M KOH is added to serve as the electrolyte and complete the fabrication process (figure 8) except for the final sealing.
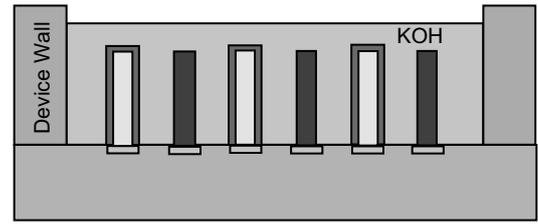

Figure 8: Define device area and fill with the KOH

5. REULTS

Half Cell

To characterize the electrochemical behavior of the deposited nickel hydroxide (cathode), only nickel was electroplated and the holes designated for zinc were left empty. Nickel hydroxide was then electrochemically deposited using a flat platinum counter electrode (unlike Section 4.D). Half cell testing was performed in 6M KOH using zinc sheet as the counter electrode. Proper oxidation/reduction behavior was observed by cyclic voltammetry (figure 9).
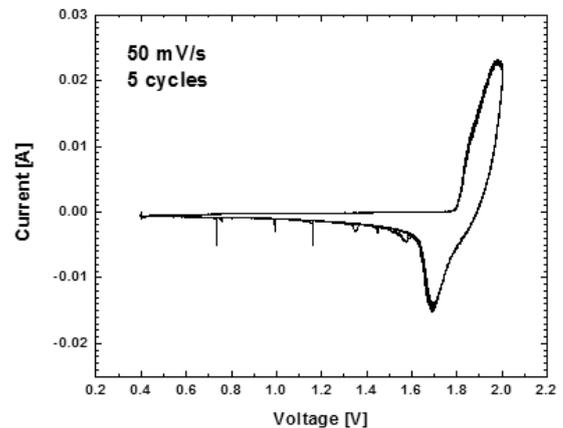

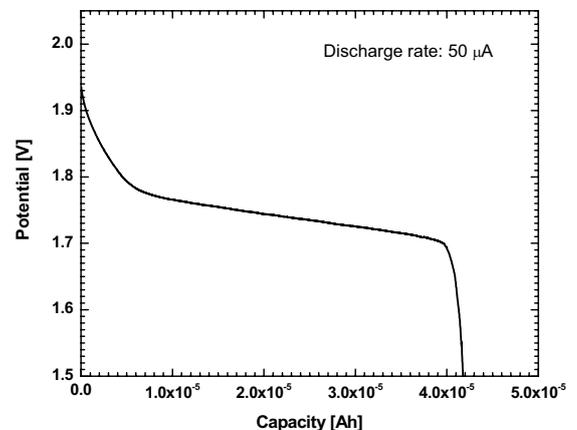*Figure 9: Cyclic voltammetry scan curves of half-cell*

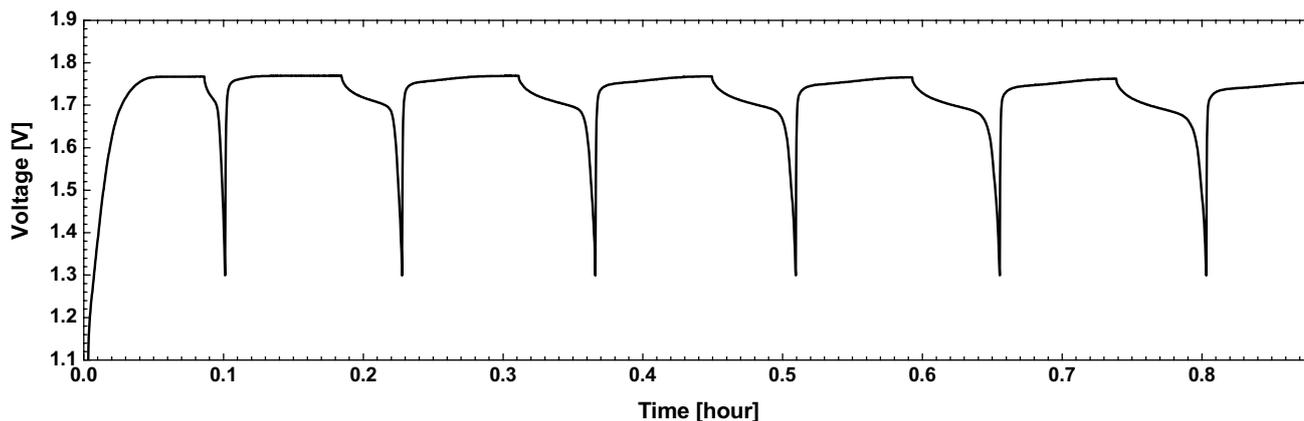*Figure 10: Discharge curve of half-cell*

Figure 11. Charge-discharge curve of the 3-D Ni-Zn microbattery

Due to non-uniform electric field distribution (sharp posts against flat platinum), nickel hydroxide was deposited only on top and edge of the nickel posts, and the majority of the nickel area remained intact. The areal energy density of 0.4 mAh/cm^2 (0.7 mWh/cm^2) was observed during discharge (figure 10).

Full Battery Structure

After observing proper behavior of nickel hydroxide in the half-cell testing, a complete battery structure consisting of zinc anode and nickel hydroxide cathode was tested in 6M KOH electrolyte. Figure 11 shows the proper galvanostatic charge-discharge behavior of the battery during the first 6 cycles. It can be observed that the discharge capacity gradually increases in each cycle. This is due to transformation of nickel hydroxide (Ni(OH)$_2$) to nickel oxyhydroxide (NiOOH) during each discharge period (equation 1). In order to access the capacity of the battery, more cycles are required to transform all the cathode material to NiOOH. After the first 6 cycles, however, zinc was etched in the KOH electrolyte and the cycling test did not proceed further.

6. CONCLUSIONS

A 3-D nickel-zinc microbattery consisting of high aspect ratio electrodes was successfully fabricated. The battery was functional during the first few cycles before the zinc was etched in KOH electrolyte. To achieve the appropriate performance of the battery, zinc needs to survive in the KOH electrolyte for longer periods of time. Our next step is to electroplate zinc alloy instead of pure zinc and also use low-solubility-zinc electrolyte, instead of pure KOH, to reduce the corrosion of zinc anode. The fabrication method introduced here is not limited to nickel-zinc batteries and other types of batteries can be fabricated by molding the electrode materials.

8. REFFERENCES

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