3D MICROSTRUCTURES FOR
FAST CHARGE AND DISCHARGE BATTERIES

A. Armutlulu[1], S.A. Bidstrup Allen[1], M.G. Allen[1,2]
[1]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, USA
[2]School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, USA

Abstract: The present work comprises the design, fabrication, and performance characterization of ordered, high-surface area, three-dimensional (3D) microstructures and their application as current collectors for the electrochemically active material of corresponding energy storage devices. The microstructures are fabricated through sequential electroplating of sacrificial and structural layers in a photoresist mold, followed by selective removal of the sacrificial layers. Nickel oxyhydroxide (NiOOH) was chosen as a secondary battery chemistry and deposited on the MEMS-enabled microstructures, forming functional electrodes for electrochemical energy storage devices. The electrodes are tested by charging and discharging galvanostatically at various rates ranging from 2 C to 120 C where x-C is the rate of complete charge or discharge for 1/x hours. It was shown that the electrode was able to retain 90 % of its capacity at a charge rate of 120 C.

Keywords: 3D electrodes, microbatteries, nickel batteries, sequential electroplating, fast charging

INTRODUCTION

Current energy storage devices, both micro- and macroscale, are expected to have the capability of rapid charge and discharge rates with a minimum loss in energy storage. Conventional batteries possess high energy density enabling them to supply energy to systems for long periods of time, yet often lack similarly high power density resulting in limited energy transfer rates. Supercapacitors, on the other hand, are capable of very fast charge and discharge rates due to their extremely high power density; however, the amount of energy they can store is quite low compared to their battery counterparts. To bridge the application gap between these two energy storage mechanisms, batteries with rapid charge and discharge capabilities are required.

MEMS technologies have been shown to offer the possibility of fabricating high-surface area, 3D structures which can be used in various energy storage systems to potentially improve power density. These 3D structures, in the form of pillar arrays, metal networks, and nanofoams, demonstrated superior performance to their 2D thin-film counterparts in terms of the energy they can store and provide to associated systems [1,2]. Yet they fall short of providing significant improvements in both their energy and power densities.

In this study, a 3D electrode concept consisting of a well-ordered current collector, composed of multiple layers of metal structure and uniformly deposited electrochemically active material, is reported. This concept yields a large surface area enabling greater exposure of the electrochemically active material to the electrolyte, thin and conformal active material coating resulting in short diffusion length for the transport of solid-state ions, as well as high electron conductivity due to metal backbone structure serving as a current collector. In our previous work it was shown that this concept enhances the discharge characteristics of primary Zn-Air batteries [3]. In order to demonstrate both rapid charge and discharge performance, the current study focuses on secondary battery chemistries where NiOOH is selected as the electrochemically active material to be deposited on the high-surface area structures, forming functional electrochemical storage devices.

EXPERIMENTAL
Fabrication of the Current Collector

The fabrication process of the current collector is summarized in Fig. 1. First, a glass substrate is coated with DC sputtered Ti and Cu layers that serve as the seed layer in the electroplating process. Then, a negative tone photoresist, NR21-20000P (Futurrex), with an approximate thickness of 100 μm is spin coated on the substrate and patterned via UV exposure to serve as the mold during the electroplating process. It is followed by the electrodeposition of alternating Cu and Ni layers from their respective electroplating baths. To perform that, a robotic electroplating system, schematically shown in Fig. 2, has been developed that allows the fabrication of 3D structures with microscale features having overall thicknesses of up to several hundreds of microns [3,4]. An aqueous all-sulfate solution and a commercial electroplating solution are utilized for Ni and Cu electroplating

baths, respectively. The substrate is immersed and rinsed in two separate deionized water (DI) baths between the electroplating of two subsequent metal layers to avoid cross-contamination of the electroplating solutions. The electroplating process is conducted at room temperature.
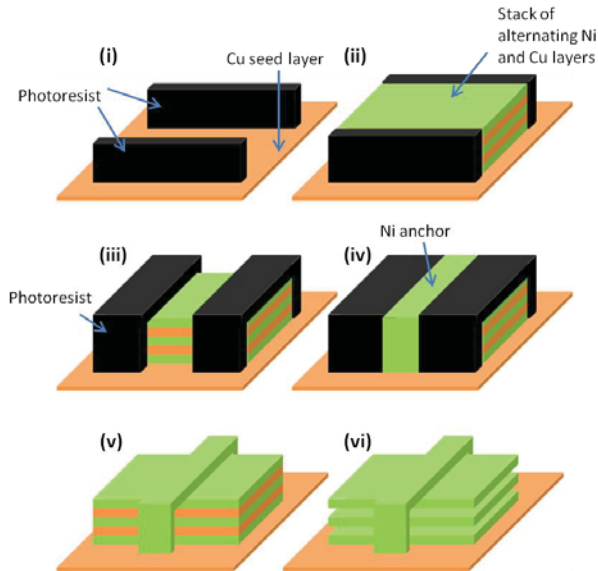

Fig. 1: Fabrication schematic of the current collector demonstrating six major steps: (i) Photoresist mold deposition and patterning, (ii) electroplating of alternating Ni and Cu layers, (iii) second photoresist mold patterning, (iv) electroplating of Ni anchor, (v) removal of photoresist, (vi) selective and complete etching of sacrificial Cu layers.
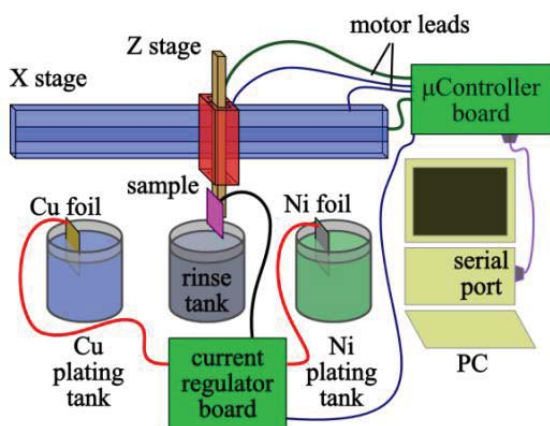

Fig. 2: Conceptual rendering of the robotic electroplating setup

Once the electroplating of the multilayer structure is completed, the photoresist mold is removed using acetone. Following this step, a second photoresist deposition and patterning process is carried out with NR21-20000P photoresist to prepare the mold for the electrodeposition of Ni anchors on specific regions of

the sidewalls of the multilayer structures. These anchors not only provide electrical connection between the Ni layers, but also provide mechanical support to prevent Ni layers from collapsing after the complete removal of the sacrificial Cu layers.

Upon completion of the Ni anchor electrodeposition, the photoresist mold is again removed by acetone. Next, the complete and selective etching of Cu layers is performed. The substrate is exposed to the etchant just long enough to remove all of the electroplated Cu layers while still ensuring that the sputtered Cu seed layer remains intact so that the multilayer structure does not detach from the glass substrate. The fabrication of the high-surface area Ni scaffold, which serves as the current collector for the electrode, concludes upon complete removal of the sacrificial Cu layers. Prior to full drying of the sample in the oven, the structure is immersed first in DI water and then in isopropyl alcohol. This step reduces the risk of potential deformations in the multilayer structure which might stem from the capillary forces applied by the etching solution or DI water, especially in cases where the Ni layers are relatively thin. If necessary, an additional electropolishing step may be carried out for a short period of time to smooth out the rough surfaces and/or to open partially clogged channels on the sidewalls of the structure.

Active Material Deposition

NiOOH is chosen as the active material to be deposited on the multilayer Ni backbone. Various methods exist in the literature illustrating formation of the active material NiOOH, including the electrochemical oxidation of Ni and the electrochemical deposition of $NiOOH/Ni(OH)_2$ from the corresponding solution. The former method enables active material thicknesses within nanoscale ranges, whereas in the latter one, microscale thicknesses can be achieved which enables higher energy capacities for a given surface area. Hence, electrochemical deposition is preferred in this study.

Electrochemical deposition can further be divided in two sub-categories: anodic and cathodic deposition of $NiOOH/Ni(OH)_2$. The latter approach was used in a study that developed a high-efficiency method for active material deposition at room temperature, as well as a formula for predicting the amount of deposited active material [5].

Cathodic deposition of the active material on the highly laminated Ni backbone is carried out in a $Ni(NO_3)_2$ solution at constant current where a Pt mesh is utilized as the counter electrode. To ensure the conformal coating of the Ni backbone, a pulsed current is applied. The substrate is weighed before and

after the deposition process, and the mass of the active material is observed to be in good agreement with the theoretical value. Fig. 3 shows the high-resolution SEM images of the sidewall of the multilayer structure before and after the active material deposition.
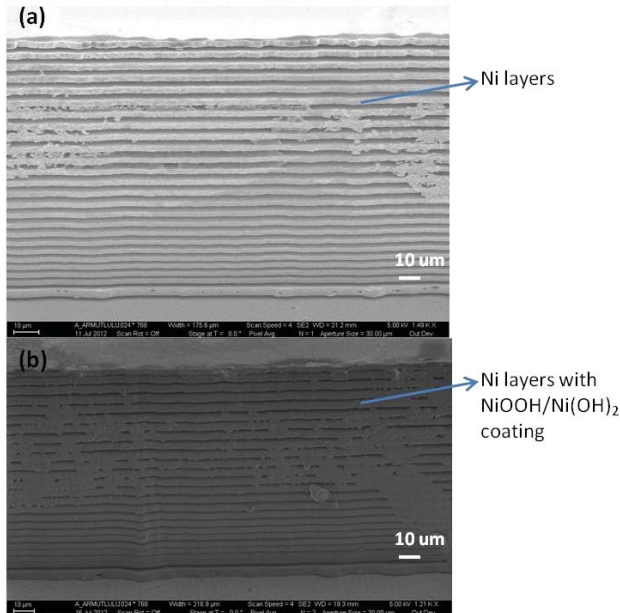

Fig. 3: Close-up SEM images of the sidewall of the multilayer structure: (a) 25-layer Ni current collector immediately after Cu etching, (b) 25-layer Ni electrode after conformal electrodeposition of NiOOH/Ni(OH)$_2$ active material on the current collector.

RESULTS AND DISCUSSION

All electrodes are fabricated on a 1 cm^2 footprint area. Fig. 4 illustrates the optical images of the resulting electrodes. The electrochemical performance of these electrodes during both charging and discharging are galvanostatically examined in a two-electrode system where a large Zn sheet and 6 M KOH solution are utilized as a counter electrode and liquid electrolyte, respectively. The charge rates of the electrodes vary from 2 C to 120 C where the x-C rate refers to the rate at which the electrode is completely charged or discharged in 1/x hours. During the charge and discharge cycles, the potential between the Ni and Zn electrodes is continuously recorded via a potentiostat (PowerLab 2/20 by ADInstruments) at room temperature.

The galvanostatic discharge profile of a system at a discharge current of 2 mA which corresponds to an approximate discharge rate of 2 C, is shown in Fig. 5. In Fig. 5, the inter-electrode potential is plotted with respect to the cell capacity. The discharge profile is observed to be in good agreement with that of other Ni-Zn batteries in the literature [6,7]. A relatively flat discharge profile is followed by a sharp decline near the complete discharge region. The cutoff voltage for the system is determined to be 1.3 V which, once reached, initiates another charge/discharge cycle where the upper limit for charging is 2 V. For the given discharge rate, the areal battery capacity is estimated to be 0.28 mAh/cm^2.
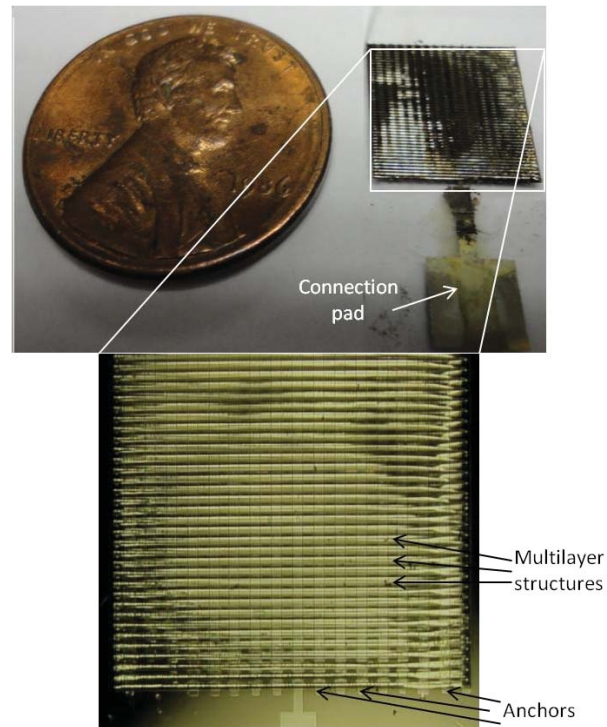

Fig. 4: Optical images of the electrode after charge and discharge tests. Vertical lines in the bottom picture refer to anchors whereas the horizontal ones are multilayer structures.

The relation between the capacity and the charging rate of the system is demonstrated in Fig. 6. The electrode is charged at 6 different rates, ranging from 2 C to 120 C, and discharged at a constant rate of 2 C in each cycle. As expected, a decay is observed in the capacity of the electrode as the charge rate increases. However, the capacity degradation of the electrode is greatly reduced when compared to its commercial counterparts [8]. At charge rates as high as 120 C, which corresponds to a charging time of 30 seconds, the system was able to retain approximately 90 % of its capacity due to the aforementioned morphological features of the electrode and the active material. This high-surface area, multilayer 3D electrode approach can be applied to other battery chemistries, such as Li-ion, as long as the conformal coating of the active material on the metal backbone can be performed.
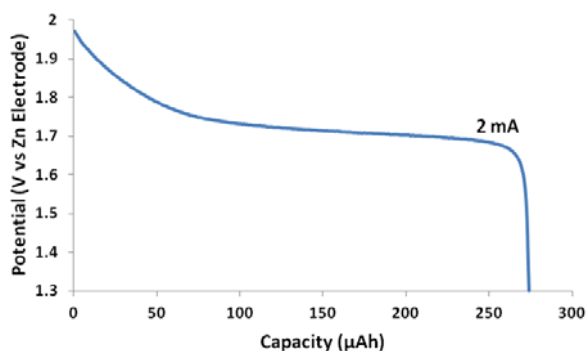
Fig. 5: Galvanostatic discharge profile of the multilayer electrode vs. Zn counter electrode at 2 mA.
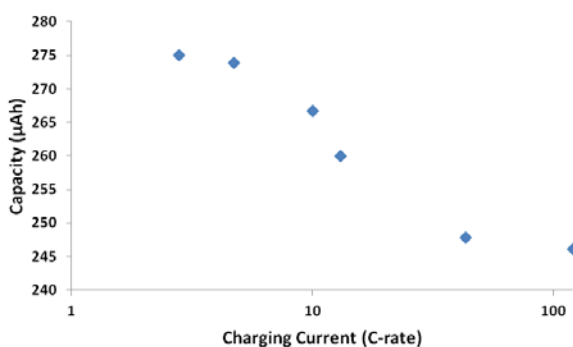

Fig. 6: Capacity of the multilayer electrode at various charge rates.

CONCLUSION

A proof-of-concept, 3D Ni electrode is designed, fabricated, and tested. It is based on a well-ordered, highly-laminated, micromachined metal backbone supporting electrochemically-deposited NiOOH as an active material. A highly conductive metal backbone serving as a current collector enables a reduced resistance for the electron transfer whereas the conformal coating of a thin active material film on the backbone provides shorter transport paths for the diffusion of the solid-state ions. Additionally, the high surface area offers more exposure for the active material to the electrolyte. Combination of all these features results in a low-resistance electrode that is capable of being rapidly charged while retaining most of its capacity, a key step toward improved power density in these secondary battery systems.

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