

NICKEL-OXIDE-BASED SUPERCAPACITORS WITH HIGH ASPECT RATIO CONCENTRIC CYLINDRICAL ELECTRODES

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ABSTRACT

This study reports the fabrication and characterization of a metal-oxide-based supercapacitor with a high surface area 3D microelectrode. This microelectrode is comprised of high aspect ratio SU-8 pillars that are fabricated using backside exposure and coated with alternating Ni and Cu layers via a sequential electrodeposition process. High surface area Ni electrodes are obtained by selective removal of the Cu sacrificial interlayers. Through subsequent electrochemical deposition and heat treatment techniques, these electrodes are conformally coated with nickel oxide. Performance tests are carried out via cyclic voltammetry. Devices were cycled in excess of 400 times with insignificant capacitance degradation. The estimated areal capacitance is found to be 270 mF/cm² which is among the highest areal capacitance values reported for MEMS supercapacitors.

KEYWORDS

Microelectrode, nickel oxide, supercapacitor, electrodeposition, SU-8

INTRODUCTION

Supercapacitors, also known as electrochemical capacitors, are high-power energy storage devices that narrow the application gap between traditional electrostatic capacitors and batteries. Similar to their electrostatic counterparts, they exhibit very rapid charge and discharge capabilities, as well as a high degree of reversibility in repetitive charge/discharge cycles; yet they possess the ability to store substantially more energy per unit mass or volume. These attributes make supercapacitors an attractive candidate for energy storage systems in portable electronic devices.

Energy storage in supercapacitors relies on two mechanisms: (i) energy is electrostatically stored via separated charges in a Helmholtz double-layer that forms at the interface between a conductive electrode surface and an electrolyte; and (ii) energy is electrochemically stored via a phenomenon called pseudocapacitance which involves reversible Faradaic charge transfer between the surface of the electrode and the electrolyte. Capacitance obtained by the latter principle is usually an order of magnitude higher than the former one.

There have been numerous extensive studies on supercapacitors over the past decade [1]. These studies mainly focus on the development of carbon based, metal oxide, and polymeric materials for electrochemical capacitor applications. Supercapacitors based on carbon materials exhibit ultra high surface area where the charge storage is achieved by charge separation inside the double-layer. For supercapacitors involving metal oxide or polymeric materials, on the other hand, the predominant mechanism of charge storage is via

pseudocapacitance.

In this study, we focus on NiO based supercapacitors with high surface area, MEMS-enabled 3D microelectrodes. Apart from NiO being a widely available material and having a relatively high specific capacitance, an electrochemical route to conformal deposition of nickel hydroxide (Ni(OH)₂) on high surface area 3D microelectrodes for fast charging battery applications has been demonstrated [2]. By combining the fabrication techniques for high aspect ratio SU-8 pillars and conformal deposition of nickel hydroxide on high surface area structures, we report a microfabricated NiO based supercapacitor with high areal and specific capacitance.

FABRICATION

Supercapacitor fabrication comprises three major steps: formation of the high aspect ratio SU-8 pillars, preparation of a high surface area electrode made from concentric metal layers deposited on these pillars, and deposition of the active material on the electrode. A schematic describing the last two sections of the fabrication process is shown in Figure 1.

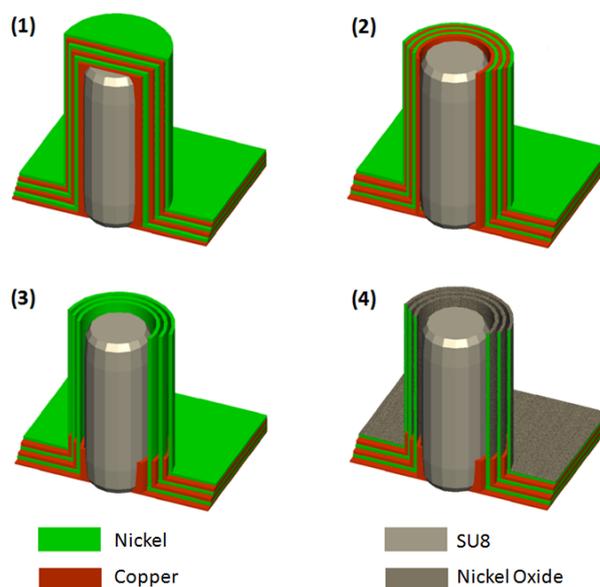


Figure 1: Conceptual rendering of the fabrication process demonstrating the cross-sectional view of the electrodes at each step.

SU-8 Pillars

The first step in the fabrication sequence involves the formation of the SU-8 pillar arrays that will support the electrodes. These pillars are achieved by adopting a thick SU-8 film coating process with an approximate thickness of 1500 μm and an acrylic UV filtering exposure method, coupled with backside exposure [3]. A thick SU-8 photoresist layer (SU-8 2025, MicroChem Inc.) is

dispensed on a Cr-patterned glass substrate and then soft-baked on a hot plate at 95 °C for 15 hours. The SU-8 film is then exposed through the glass and patterned Cr layer using a backside exposure scheme. A 0.22 inch-thick acrylic board (G11, Professional Plastics, Inc.) is used as a UV filter which blocks exposure wavelengths shorter than 400 nm. A UV light intensity of 35 mW/cm² at wavelength of 405 nm was applied with an exposure dose of 18 J. A post-exposure bake is performed at 95 °C for one hour on a hot plate, followed by the development of the photoresist using propylene glycol methyl ether acetate (PGMEA) for nearly 40 minutes. The sample is then carefully rinsed in DI water and dried on a hot plate at 50 °C. Figure 2 demonstrates the SEM image of the resulting SU-8 pillars that have a thickness and diameter of approximately 1000 μm and 100 μm, respectively.

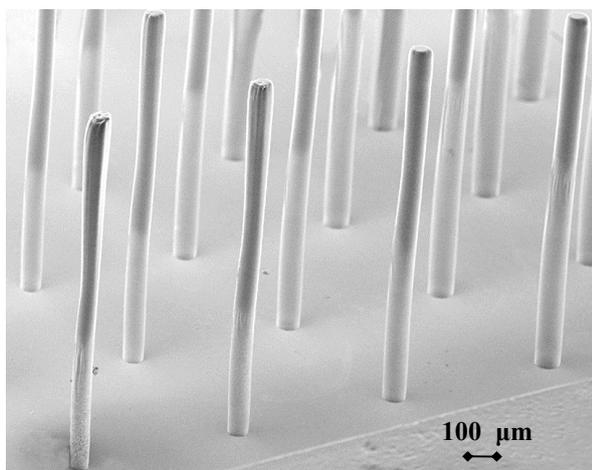


Figure 2: SEM image of the high aspect ratio SU-8 pillar array.

Concentric Metal Pillar Structures

Upon completion of the fabrication process of the SU-8 pillar arrays, Ti (200 nm) and Cu (800 nm) layers are deposited using DC sputtering. Using the sputter-deposited films as a seed layer, alternating Ni and Cu layers are electroplated onto the pillars. A robotic electroplating setup is utilized to deposit 125 pairs of Ni/Cu layers from their respective plating solutions. In this step, the total number of metal layers to be electroplated depends on the spacing between the SU-8 pillars which is subject to further optimization in order to yield as high surface area as possible. This alternating electroplating process has been utilized by our group in earlier studies for various applications where the Ni layers serve as the structural layers while the sacrificial Cu layers are selectively removed [4]. The plating current density is set to 10 mA/cm² and the plating time is adjusted in a way that the thickness of the individual Ni and Cu layers is approximately 1 μm.

To obtain as much surface area as possible, plating would ideally occur exclusively in the radial direction. However, that would require a more complex fabrication process. For simplicity, growth of the layers takes place in both the radial and vertical directions as shown in Figure 1. Once the electroplating of alternating layers is completed, an additional, thick (~15-20 μm) Ni layer is

electroplated in order to enhance the mechanical stability of the pillar array (which is crucial during a subsequent lapping step). Figure 3 demonstrates an SU-8 pillar array on a 1 cm² footprint area immediately after the electroplating process.

Upon completion of the electroplating process, the pillars are mechanically lapped from the top side with emery paper of various grades successively up to 600 grade. Initially, 120 grade emery paper is utilized to remove the majority of the bulk Ni layer on top of the pillars. This mechanical polishing process is performed until all of the electroplated Ni and Cu layers on top of the SU-8 pillars are removed, thereby exposing the interleaved Cu structures, as shown in the second step of the fabrication scheme in Figure 1. To prevent excessive removal during the mechanical polishing process, pillars are periodically observed under an optical microscope. The polishing process concludes once the SU-8 cores in all of the pillars are completely exposed. The pillars are cleaned using a mixture of acetone, methanol, and isopropyl alcohol, and rinsed with DI water. The substrate is then immersed in a concentrated HNO₃ solution for 15 – 20 seconds, and then again thoroughly rinsed in DI water. This step enables the removal of the smeared Ni and Cu layers formed during the mechanical polishing process.

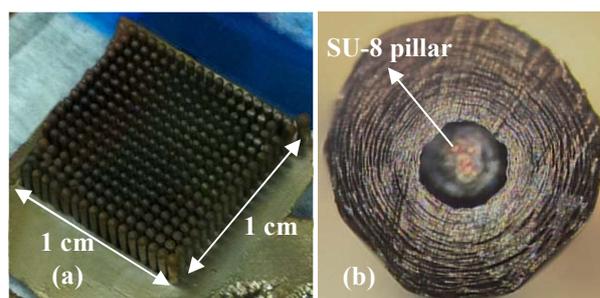


Figure 3: (a) Densely packed pillars after the multilayer electroplating process on a footprint area of 1 cm², (b) optical view of the top surface of a single pillar after heat treatment.

After the mechanical polishing step, the structures are then immersed in a selective Cu etching bath for 12 hours. Based on the experimentally-determined etching rate of ~0.5 μm/min, the solution is expected to etch the Cu layers to a depth of approximately 360 μm from the surface. During the etching process, the etchant was slowly agitated in order to improve the etching rate via addition of convective effects which otherwise would only rely on diffusion and thus, a much lower etching rate would be observed. But care must be taken when adjusting the speed of agitation. Faster agitation would obviously yield higher etching rates but at the same time, would pose the risk of layer deformation which might lead to collapsed layers and clogged channels. The substrate is then placed in DI water for 30 minutes followed by immersion in isopropyl alcohol for another 30 minutes to minimize interlayer surface tension forces. Drying the structure in an oven at 65 °C concludes the fabrication of the current collector. An SEM image of the top view of a single pillar surrounded by the high aspect

ratio concentric hollow cylinders can be seen in Figure 4.

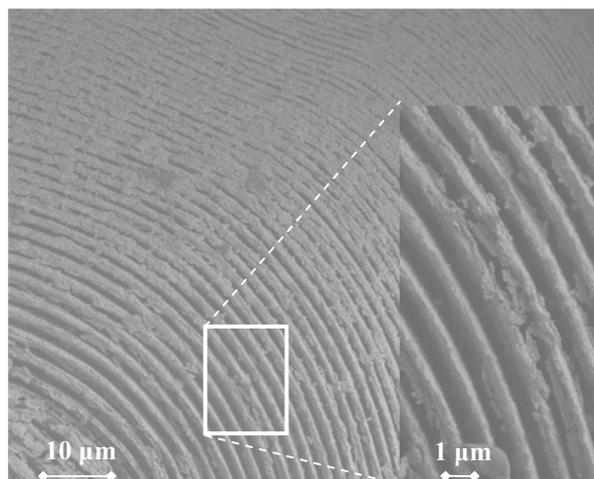


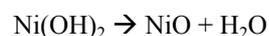
Figure 4: SEM image showing the top view of a single pillar after the selective Cu etching process.

Upon completion of the etching process, the resulting structure is expected to have the form of high aspect ratio (1:360), concentric hollow cylinders providing a dramatically increased surface area. However, mass transport limitations during etching might result in incompletely etched structures and reduced aspect ratio (and surface area). We therefore aim to deduce the effective surface area from the end results of the performance tests, i.e. comparison of the capacitance of the multilayer supercapacitors with another supercapacitor of the same chemistry and a known surface area.

Fabrication of NiO Electrode

The last major step of the fabrication process involves deposition of the active material on the high aspect ratio concentric electrodes. Ni(OH)₂ is chosen as the active material to be deposited. The deposition is carried out cathodically at room temperature in a nickel nitrate (Ni(NO₃)₂) bath with a concentration of 0.2 M and an aqueous solvent of 50 volume percent ethanol. An advantage of this particular deposition technique is that a detailed analysis of this chemistry is available in the literature that provides a theoretical formula predicting the amount of deposited Ni(OH)₂ under certain conditions [5]. Based on this formula, the deposition rate of the active material is a function of current, temperature, Ni(NO₃)₂ concentration, and solvent composition. Before the deposition process, the substrate is immersed in Ni(NO₃)₂ solution and then placed in a vacuum chamber for 15 minutes to ensure that any trapped air between the electrodes is removed. During the deposition process, pulsed currents are applied in an on/off ratio of 1/9 seconds; this ratio was calculated considering the fact that the diffusion time, T , scales with the square of the diffusion length, L^2 , and the reciprocal of the diffusion coefficient, D^{-1} . This pulsed current approach assists conformal deposition of the active material on the high surface area electrode by giving the ions in the bulk solution enough time to diffuse into the deep, high aspect ratio channels. The details of this deposition process can be found in a previous study where NiOOH/Ni(OH)₂

chemistry was utilized as a secondary Ni battery electrode [2]. Upon completion of the active material deposition, the sample is placed in DI water for 15 minutes to remove any residual Ni(NO₃)₂ salts remaining on the surface. Following the rinsing process, the sample is heated in air from room temperature to 300 °C, maintained at that temperature for two hours, and subsequently cooled down to room temperature. This heating process causes the electrochemically deposited Ni(OH)₂ layer to decompose into NiO according to the following reaction:



Various decomposition temperatures were shown to yield different capacitance values; these effects are described in the literature [6]. The optimum temperature for Ni(OH)₂ decomposition resulting in the highest specific capacitance has been found to be 300 °C. It has been also reported that the mass of the electrochemically deposited film reduces to 60% of the initial value when the sample is heated to 300 °C or above which should be taken into account when estimating the specific capacitance of the active material. As confirmed by Figure 3b, the layers surrounding the pillars are still intact after heating the sample to 300 °C. With the thermal treatment of the sample, the fabrication process of the NiO based supercapacitor is concluded.

RESULTS AND DISCUSSION

For the performance tests, samples having pillar arrays with 10x10 evenly spaced pillars on a 1 cm² footprint area are prepared. These tests are performed in a 1M KOH solution. For high power applications, the electrolyte concentration can be increased to achieve higher electrolyte conductivity at the expense of narrowing the functional potential range of the electrode due to the reduced potential at which the oxygen formation occurs. Prior to cyclic voltammetry (CV) experiments, the sample is immersed in the KOH solution, and vacuum is applied as in the case of active material deposition, in order to remove any air trapped inside the high aspect ratio channels.

A three-electrode cell is constructed where Ag/AgCl and a Pt mesh are utilized as the reference electrode and counter electrode, respectively. The potential range is adjusted to -0.2 V to 0.4 V and the scanning rate is set to 20 mV/s. To observe the degree of capacitance improvement provided by the multilayer electrode approach, a planar square Ni electrode with the same footprint area of 1 cm² is also fabricated to be tested along with the multilayer electrodes. This control provides a baseline to assess improvement in the capacitance from 2D geometries to high surface area 3D structures.

Figure 5 shows the CV curve for the Ni(OH)₂ coated sample prior to the heat treatment, where the anodic current values are demonstrated on the positive side. A cathodic peak is observed around 0.3 V which is both shape-wise and potential-wise in agreement with earlier studies in the literature [7]. This result implies that the surface is covered with Ni(OH)₂ layer that undergoes the following redox reactions during the CV tests:

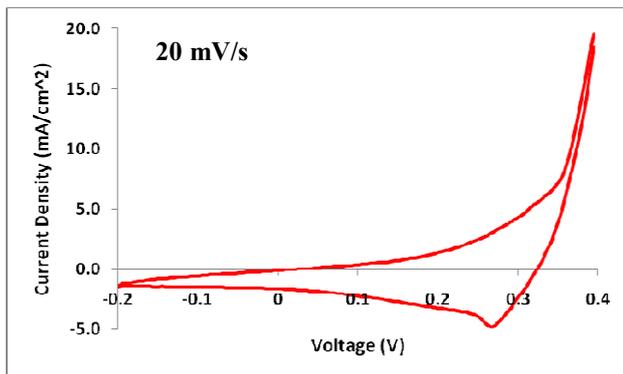
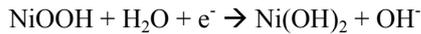


Figure 5: CV curve of the freshly deposited Ni(OH)₂ layer on multilayer pillars.

Figure 6 demonstrates the CV profiles of the plain and multilayer electrode after heating the sample to 300 °C. The areal capacitance, C , of the electrode is calculated from the CV curves according to Equation 1:

$$C = I \cdot \left(\frac{dV}{dt}\right)^{-1} \quad (1)$$

where I is the current density (mA/cm²) and dV/dt is the scan rate (mV/s).

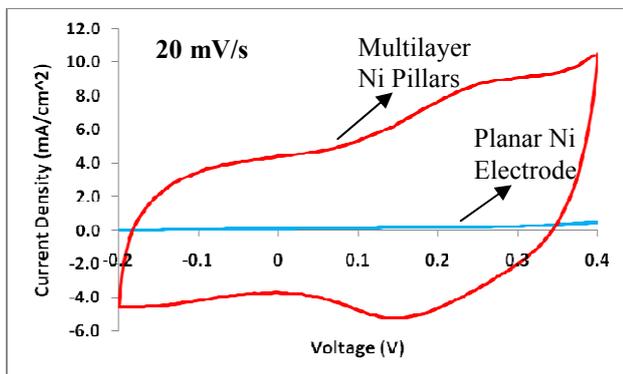


Figure 6: Comparison of CV curves of NiO supercapacitors based on 3D and 2D electrode geometries.

Based on Equation 1, the areal capacitance of the multilayer pillars is estimated to be 270 mF/cm² at a scan rate of 20 mV/s. To estimate the specific capacitance of the active material, this capacitance value is then divided by the mass of the electrodeposited active material and yields 56 F/g, which is very close to a previously reported value [8]. The planar electrode, on the other hand, exhibits an areal capacitance of 11 mF/cm². Considering the fact that the capacitance is linearly related to the surface area, it can be deduced that the multilayer pillar approach results in at least 25-fold increase in the total surface area for a given footprint area. These values are obtained from the CV curves generated after the 50th cycle. Negligible capacitance degradation is observed after performing 300 additional cycles. By adopting more densely packed pillar arrays, building higher aspect ratio

pillars through increased etching times for sacrificial layers, and utilizing alternative metal oxides with higher specific capacitance (e.g. RuO₂), it is possible to increase the capacitance on the same footprint area even further.

CONCLUSION

This work involves design, fabrication, and testing of NiO supercapacitors based on high surface area 3D microelectrodes. Utilizing high aspect ratio SU-8 pillars, sequential electroplating, and conformal Ni(OH)₂ electrodeposition techniques, NiO capacitors are successfully fabricated. These capacitors are shown to be mechanically stable and yield high areal capacitance values of 270 mF/cm² which compare favorably to MEMS-based capacitance values previously reported.

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