A FABRIC-BASED NI/ZN BATTERY USING A MICROFIBER SUBSTRATE AND SEPARATOR

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Abstract: This paper presents a fabrication approach to fiber-based, flexible rechargeable batteries. The approach comprises a microfiber substrate and electrochemical microfabrication technology. A microfiber-based textile sheet is used as the basis for both cathode and anode electrodes. The substrates are metallized throughout their volume using wet strike electroless plating followed by electrodeposition of the appropriate materials (Ni/NiOOH or Zn) to serve as the cathode and anode of the battery, respectively. This approach allows for reasonably uniform coating of the microfibers with electrochemically active material throughout the volume of the substrate, as opposed to sputter deposition of a strike layer, which did not fully penetrate the 200 μm thick microfiber sheet. A unit cell of the battery is formed by a sequential stack of the Ni/NiOOH-bearing fabric, an unmetallized microfiber sheet separator, and the Zn-bearing fabric. Electrical characterization of the fabricated microfiber battery showed an areal energy density of 1.4 μAh/cm^2 after four charge/discharge cycles. The use of microfiber substrates exploits the relatively low cost, physical flexibility, and large surface area of nonwoven fabrics as key functional advantages of MEMS-enabled batteries.

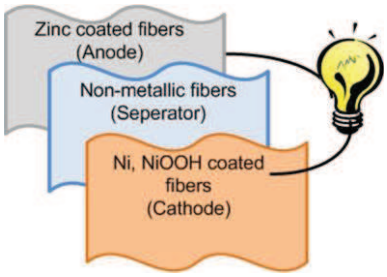
Keywords: Microfiber, Flexible battery, Ni/Zn, Energy storage device.

INTRODUCTION

There is significant interest in fully flexible electronic systems for applications ranging from wearable devices to deformable displays [1-3]. To address the power requirements of such systems, flexibility issues associated with the power source itself should be studied. In addition, as the cost of many electronic components continues to decrease, the cost of the power system must also be considered. Sufficiently inexpensive electronic systems can be used in applications such as disposable electronics; in these applications, environmental considerations associated with the power source must also be taken into account.

Battery electrode materials such as Ni/Zn or Lithium (Li) have shown great promise for power sources due to their reasonably high energy densities [4]. Several fabrication methods for flexible batteries based on these materials have been studied [5-8]. Previous work typically exploits relatively exotic materials (e.g. carbon nanotubes, carbon nanofibers, or graphene) which are dispensed on conventional paper to increase the surface area of the electrode. Electrospun nanofiber sheets are often suggested as battery electrodes due to their large surface area and high porosity [9, 10]. However, the fabrication of these sheets generally requires high voltage sources, and control of the detailed morphology is relatively complex. Nanofiber sheets have typically been used as battery separators rather than as electrodes, since volumetric metallization of hundred-micron-thick nanofiber sheets is challenging.

To circumvent the cost and need for specialized equipment for nanofiber fabrication and metal deposition, low cost materials and simple fabrication processes are greatly needed. In this paper, we propose a simple, accessible method to generate metal coated fabric electrodes for a flexible battery application. As a substrate, polymeric textured sheets from Texwipe® are interesting candidates, as they are commercially available, widely-known, and



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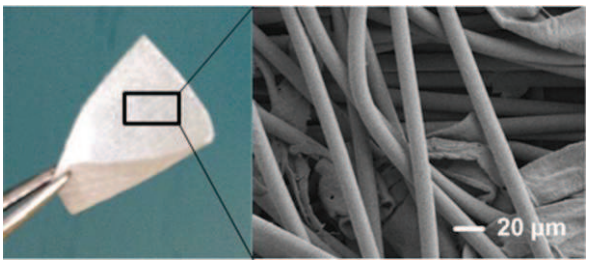

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Fig. 1: Concept of fiber-based Ni/Zn battery: (a) Schematic diagram of fabric Ni/Zn battery, (b) Optical/SEM image of flexible microfiber fabric.

comprised of non-woven microfibers. The average diameter of the fiber is approximately 10 ~ 20 μm. To form the metallized sheets, both sputter deposition of a seed layer as well as wet strike electroless plating are explored, followed by electrodeposition of the electrochemically active materials of interest. The latter approach requires no vacuum-based equipment during the fabrication process, and is therefore of particular interest.

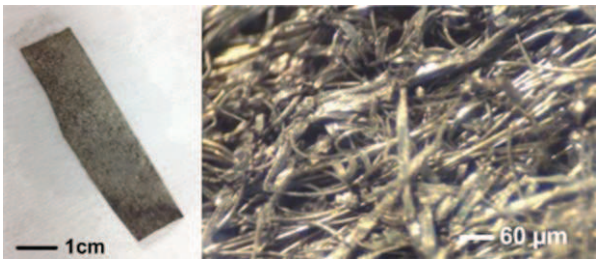
FABRICATION

The flexible, rechargeable, fabric-based battery is comprised of three metal-bearing sheets as described in Figure 1a. The first sheet is metallized with nickel further coated with nickel oxyhydroxide, and acts as the cathode. The second sheet is metallized with zinc and acts as the anode. The third sheet is not metallized and serves as a separator.

Microfiber blended nonwoven sheets from Texwipe® are utilized as the substrate for fabrication. Figure 1b shows an optical and SEM image of a typical TX609 Technicloth nonwoven wiper sheet used in this work. The sheet consists of a hydroentangled blend of cellulose and polyester fibers with no additional chemical binders. The fabrication process proceeds by performing a surface pretreatment on the fiber sheet, followed by deposition of the appropriate electrochemically active material on the pretreated fiber sheet.

Surface Pretreatment on microfiber

In order to deposit metal on the nonconducting fiber sheet, a three step process is employed. First, the surface is sensitized by exploiting the Tollens reaction, in which metallic silver is deposited on surfaces in the presence of certain compounds. To prepare the Tollens reagent, concentrated ammonium hydroxide was added dropwise to a 0.1M silver nitrate solution. Then 0.8 M KOH was added immediately to form a dark precipitate. Additional ammonium hydroxide was added to redissolve the precipitate, resulting in colorless solution. A fiber sheet was taken directly from its clean room packaging and immersed into the Tollens reagent. After immersion, a solution of 0.5 M glucose is added with gentle agitation using a micropipet. In this step, metallic silver is precipitated from the solution and impregnates the porous medium of the fiber substrate. The silver coated fiber sheet was washed thoroughly with de-ionized water. Figure 2a (left) shows the microfiber sheet after the treatment. Uniform coating of microfibers is observed as shown in Figure 2a (right).



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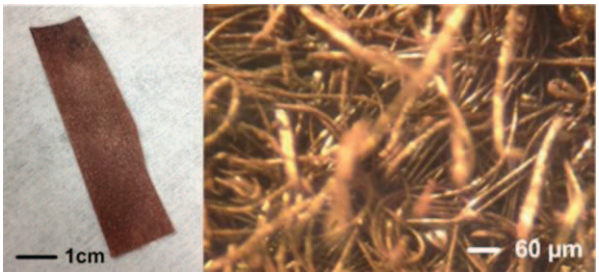


(b)

Fig. 2: Wet chemical metal deposition on microfiber sheet: (a) Silver particles deposited on fiber sheet, (b) Electroless Cu seed layer deposited on the sheet of Figure 2a.

Electroless plating

After the silver surface treatment, the resistivity of the sheet was still relatively high. To reduce this resistivity, the second step in the process, electroless deposition of Cu, is employed. A commercially available electroless deposition kit (Circuposit 3350, Rohm & Haas), which is based on copper chloride and ethylenediaminetetraacetic acid (EDTA), was used in the process. The solution was heated to 42 °C and the silver-bearing fiber sheet was immersed in the solution for 3~5 minutes. The result of electroless copper deposition is shown in Figure 2b (left). The uniform coating of Cu layer is observed based on the color changes of fibers as shown in Figure 2b (right).

Electrodeposition

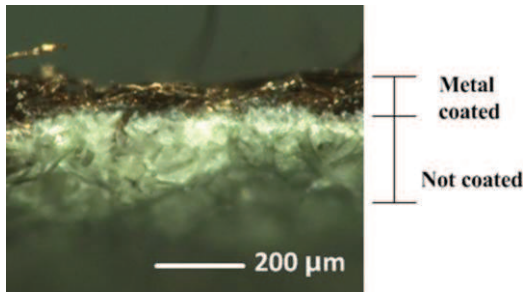
The third step in the process is the electrodeposition of the electrochemically active material of interest, i.e., Zn or Ni, on the treated fiber sheets. On the sheets that will ultimately become anodes, Zn is electroplated at a constant current density of 20 mA/cm^2 (where the area designation refers to the footprint of the sheet) utilizing an acid chloride Zn plating bath. On the sheets that will ultimately become cathodes, Ni is electroplated from a sulfate-based bath at the same current density [11]. The active material for the Ni electrode, i.e. $NiOOH/Ni(OH)_2$, is cathodically electrodeposited

from a $Ni(NO_3)_2$ solution at room temperature using a Pt mesh counter electrode [12]. In order to ensure the conformal deposition of the active material onto Ni-coated fibers, pulse plating techniques are used.

RESULTS AND DISCUSSION

The metallization process described above for fiber sheets is first compared to conventional vacuum-based metal deposition. Figure 3a shows the cross-sectional view of an approximately 200 µm thick microfiber sheet metalized with copper using a DC sputterer for 90 minutes. Metal deposition was observed through approximately the first third of the fiber sheet. Copper deposited using the wet techniques described above resulted in coating of fibers through the entire sheet thickness as shown in Figure 3b.

Two types of cell electrodes were fabricated. The first type consisted of fiber sheets coated using vacuum processes as shown in Figure 3a, which were subsequently electrodeposited with either Ni/NiOOH or Zn to form cell electrodes. The second type consisted of fiber sheets coated using wet processes as shown in Figure 3b, which were subsequently electrodeposited with either Ni/NiOOH or Zn to form cell electrodes. It should be emphasized that both wet-processed and vacuum-processed electrodes were eventually electrodeposited with their respective appropriate electrochemically-active materials prior to testing.



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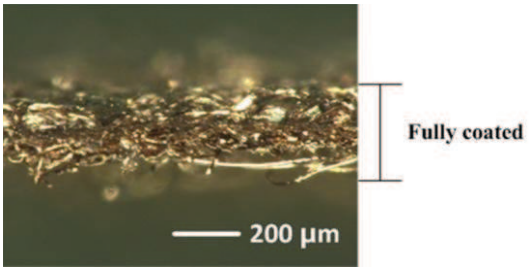

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Fig. 3: Comparison of depth of metal penetration of (a) DC-sputtered copper; and (b) copper deposited by electroless deposition

A battery unit cell is formed by sequentially stacking the Ni/NiOOH coated fabric, a separator, and the Zn coated fabric. Ni/NiOOH and Zn electrodes of 1 cm^2 footprint area were placed on top of each other and tightly pressed between two glass slides. The porous fabric separator prevents electrical contact between the opposite electrodes, while allowing the diffusion of electrolytes. The electrolyte consisted of 3ml of 6 M aqueous KOH solution saturated with ZnO, which was separately prepared and then applied so as to soak into the fabric stack.

Galvanostatic charge and discharge tests are performed to examine the performance of the battery cells, where 100 µA and 10 µA are chosen for the charging and discharging rates, respectively. During these tests, the potential between the Ni and Zn electrodes are continuously recorded by a potentiostat (PowerLab 2/20 - ADInstruments). Figure 4 shows the cell charge/discharge profile. The dashed lines represent the profile of the electrodes formed by vacuum processing, whereas the solid lines represent the profile of the electrodes formed by wet processing. The capacity of the two cells differs significantly as expected, as wet processed electrodes can support significantly more active material.

Wet-processed cells demonstrated an areal energy density (based on footprint) of 1.4 µAh/cm^2, compared to an areal energy density of 0.2 µAh/cm^2 for the vacuum-processed cells. It was also noted that the Zn electrode of the vacuum-processed electrodes was depleted after only the second charge/discharge cycle. A decay of the operating voltage of the cell in the fourth charge/discharge cycle may be related to the dissolution of electrodeposited Zn near the surface of the fiber, which leads to a rise in the internal resistance of the Zn electrode due to the increased diffusion path length of the ions.

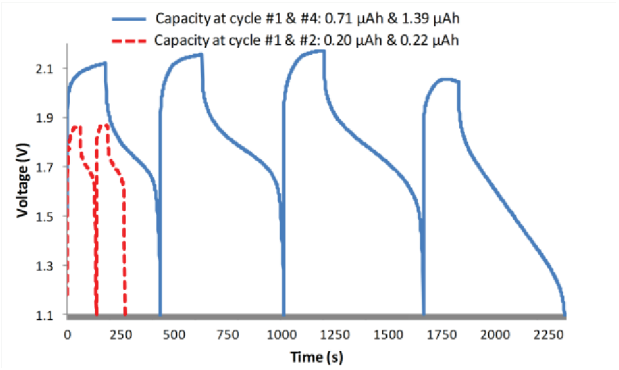

Fig. 4: Galvanostatic charge/discharge profile of vacuum-processed (dashed line) and wet-processed (solid line) Ni/NiOOH-Zn fiber cells.

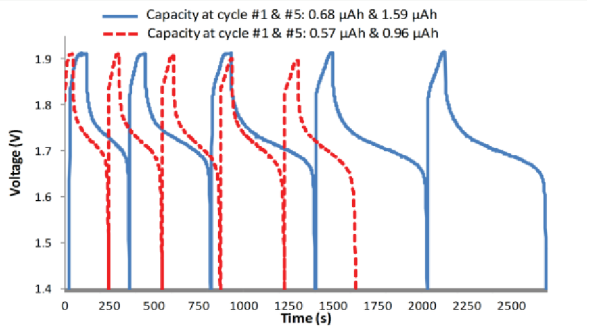

Fig. 5: Galvanostatic charge/discharge profile of cells comprising vacuum-processed (dashed line) and wet-processed (solid line) Ni/NiOOH fiber electrodes vs. Zn sheet.

To isolate the effect of the Zn electrode, an experiment was run in which the Zn-coated fiber substrate was replaced with a Zn sheet. The same cells were then fabricated and the charge/discharge tests repeated. The results are shown in Figure 5. After five cycles, wet processed cells maintained a higher areal energy density (1.6 µAh/cm^2) compared to their vacuum-processed counterparts (1.0 µAh/cm^2) Unlike the flexible Zn electrode case, no decay is observed in the operating voltage of the cell as the number of charge/discharge cycles increases.

CONCLUSION

A fabrication process for microfiber-based flexible batteries with uniform metallic coating through the volume of the fiber sheet has been demonstrated. This process has no vacuum steps and is based on electroless and electroplating of base and electrochemically active materials. Battery cells comprising Ni/NiOOH and Zn microfiber electrodes with a microfiber separator were utilized to demonstrate the applicability of this approach. Electrical characterization of the fabricated microfiber battery showed an areal energy density (based on footprint) of 1.4 µAh/cm^2 at the fourth charge/discharge cycle.

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