Current Applied Physics 14 (2014) 1396–1400

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

# Nickel/nickel oxide coatings for fiber batteries

Daniel Homa [a, *], Qing Zhang [b], Cary Hill [a], Gurbinder Kaur [a], Gary Pickrell [a]

[a] Virginia Polytechnic Institute and State University, 213 Holden Hall, Blacksburg, VA 24060, United States
[b] Stony Brook University, 314 Old Engineering, Stony Brook University, Stony Brook, NY 11790, United States

ARTICLE INFO

*Article history:*
Received 14 April 2014
Received in revised form
25 July 2014
Accepted 14 August 2014
Available online 23 August 2014

*Keywords:*
Micro-battery
Fiber optics
All-fiber optoelectronics

ABSTRACT

A Nickel–Cadmium fiber micro–battery design consisting of a nickel/nickel oxide coated glass capillary tube, cadmium micro–wire, and polyimide micro–tube was evaluated in this paper. The nickel/nickel oxide thin films were deposited via electrolysis and the quality was evaluated via the effect of the sulfate concentration, plating temperature, plating solution pH, and heat treatment. The maximum voltage range of the fiber batteries ranged from 0.68–1.2 V, while the maximum current supplied by battery ranged from 0.6–1.0 mA. The results of this work demonstrate the feasibility of fiber batteries that can be readily adapted to random or ordered hole fibers and readily integrated into all-fiber optoelectronic devices.



## 1. Introduction

The emerging field of crystalline semiconductor core optical fibers has become more prevalent over the past decade with the eventual goal of implementing electronic devices in optical fibers [1]. The successful fabrication of semiconductor core fibers such as Ge, Si and InP in the literature demonstrate the imminent potential of this technology [2–6]. The ability to synthesize devices such as p-i-n junctions [7] and germanium transistors [8] directly in optical fibers demonstrates the feasibility of all-fiber optoelectronics [9]. Unfortunately, powering these devices remains an often overlooked challenge to the direct implementation of stand-alone all-fiber communication [10] and sensing systems [11,12], as well as wearable and implantable optoelectronics [13].

Recently, flexible polymer photovoltaic fibers have shown promise in medical and smart textile applications [14,15], and more traditional optical fibers have been investigated in the field of solar energy [16]. Miniature battery systems have also been developed as a power source within a fiber optic cable [17], but have yet to be explored within a fused silica based fiber. A compatible “fiber optic” battery is essential for independently powering the emerging technology of all-fiber optoelectronics and devices.

Random-hole optical fibers are a new class of optical fibers that employ randomly sized and distributed porosity in the cladding which provides an averaged lower index than the core glass [18,19]. Hence, the waveguide structure and mechanism is analogous to traditional optical fibers, but also provides unique opportunities to exploit the design in sensing and semiconductor applications [20,21]. The high surface area provided by the random porosity is expected to provide a template to optimize the cathode's and anode's power density, allowing for fast charging and current delivery.

In an effort to demonstrate the basic technical feasibility of a fiber battery, we investigated a NiCd battery design. Nickel/nickel oxide coatings were deposited on the surfaces of fused silica and borosilicate capillary tubes via electrolysis. Electrolysis is an established deposition technique employed to fabricate metal oxide coatings on surfaces of various types of materials [22,23], as well as random hole fibers [24]. This process was adapted to synthesize nickel coatings on both sides of borosilicate and fused silica micro-capillary tubes. A basic battery was successfully demonstrated with a nickel coated capillary tube cathode, cadmium wire anode, polyimide microtube separator and a sodium hydroxide solution electrolyte. The successful demonstration of a basic Ni–Cd battery in nickel oxide coated micro capillary tubes is the first step in the evolution of a power source for the emerging all–fiber optoelectronic revolution.

## 2. Experimental details

### 2.1. Materials

The glass capillary tubes (900 × 1100 um, 1500 × 1800 um, 2000 × 2400 um) used as the deposition substrates were obtained

* Corresponding author. Tel.: +1 410 262 4775; fax: +1 540 231 8919.
*E-mail address:* dan24@vt.edu (D. Homa).

http://dx.doi.org/10.1016/j.cap.2014.08.008
1567-1739/

from Fiber Optical Center. The precursor materials for electrolysis, $SnCl_2 \cdot 2H_2O$ (99.0%), $PdCl_2$ (99.0%), $Na_3C_6H_5O_7 \cdot 2H_2O$ (99.0%), $NiSO_4 \cdot 6H_2O$ (99.0%), $NaH_2PO_2 \cdot 10H_2O$ (≥99.0%), $Na_4P_2O_7 \cdot H_2O$ (99.0%), $(CH_2CH_2OH)_3N$ (98%) were obtained from Sigma Aldrich, while the 3-Triethoxysilylpropylamine(KH550) (99%) and cadmium wire (99.999%, metals basis) was obtained from Alfa Aesar. The miniature, translucent amber polyimide tubing, 24 AWG, ID ~ 500 μm, OD ~ 561 μm was obtained from Small Parts, the nickel glue was MG Chemicals 841 Super Shield Nickel Conductive Coating–Pen, and the Arcor bare copper wire was 40 AWG.

### 2.2. Preparation of Ni-coated tubes

Electrolysis nickel plating was carried out by multiple steps: cleaning, surface treatment, sensitization, activation and plating. First, the tubes were ultrasonically cleaned in ethanol for 15 min and ultrasonically cleaned in deionized water for another 15 min, followed by drying for 20 min at 100 °C. The substrates were then immersed in a KH550 ethanol solution for several hours, and subsequently dried for 20 min at 100 °C. Surface sensitization was conducted by immersing the substrates in an aqueous solution containing 10 g/L $SnCl_2$ and 40 mL/L 38% HCl. The substrates were then rinsed with deionized water and activated by immersion in a solution containing 0.5 g/L $PdCl_2$ and 20 mL/L$^-$ 38% HCl. Finally, the substrates were rinsed with deionized water to eliminate the any surface contamination.

The plating process was carried out in a plating bath immediately following activation. The compositions of the plating bath and operation conditions are listed in Table 1. A heat treatment (500 °C, 3 h) was employed to oxidize the Ni coating.

### 2.3. Coating characterization

A field emission scanning electron microscope (FESEM) was utilized to characterize the surface morphology of the Ni-plated tubes. The composition of the coating was determined by energy dispersive X-ray spectroscopy (EDS).

### 2.4. Battery fabrication

A basic battery, as shown in Fig. 1(a), was constructed to demonstrate the feasibility of the concept. Fused silica capillary tubes, ID = 900 μm, OD = 1100 μm, were selected as templates because of their stability and resistance to corrosion. First, a cadmium wire (anode) with a diameter of 300 μm was inserted into a polyimide micro–tube (separator), soaked in a 0.7 M NaOH solution (electrolyte), and inserted into a glass capillary tube with a nickel oxide coated inside diameter (cathode). A copper micro–wire was then coated with an excess of nickel glue and inserted into the glass capillary tube to not only provide a contact with the nickel coating, but also avoid activity between the copper and cadmium wires. Additional electrolyte was injected into the capillary tube and the ends of the glass and polyimide capillary tubes were sealed with cyanoacrylate glue to minimize electrolyte evaporation.

**Table 1**
Chemical composition and plating conditions.

| Chemicals | Composition |
|---|---|
| $NiSO_4 \cdot 6H_2O$ | 20 g/L, 30 g/L,40 g/L |
| $NaH_2PO_2 \cdot 10H_2O$ | 20 g/L |
| $Na_4P_2O_7 \cdot H_2O$ | 80 g/L |
| NaOH | 1–4 mL |
| $(CH_2CH_2OH)_3N$ | 15–25 mL |
| pH | 10, 11, 12 |
| Temperature | 35 °C, 45 °C, 55 °C, 65 °C |
| Plating time | 1 h, 2 h, 3 h, 4 h, 5 h |

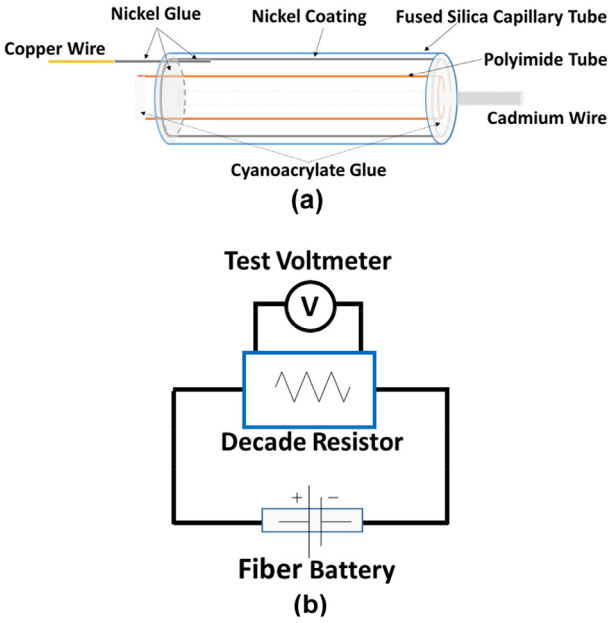


**Fig. 1.** (a) Fiber battery with a nickel coated fused silica capillary tube (cathode), cadmium wire (anode), polyimide tube (separator), and sodium hydroxide solution (electrolyte). (b) Basic test setup for battery discharge testing.

### 2.5. Battery performance testing

The feasibility of the fiber was battery was confirmed via a basic discharge test as shown in Fig. 1(b). The fiber battery was connected to a decade resistor box to simulate a current draw and the voltage was measured continuously with an Agilent 34405A multi–meter across the selected resistor; the data as actively logged with the Agilent BenchVue software. Discharging at a constant resistance simulates operation in many applications, but it must be noted that the current decreases in conjunction with the measured voltage during the test.

## 3. Results and discussion

### 3.1. Coating characterization

Process parameters such as KH550 immersion time, nickel sulfate concentration, pH, plating time and plating temperature were varied in an effort to produce a high quality coatings. In this study, results of the experiments designed to evaluate the effect of KH550 treatment time on the coating thickness and/or quality were inconclusive, and further investigation is required. Qualitatively, as shown in Fig. 2, the nickel sulfate concentration had an effect on the resultant coating quality. A nickel sulfate concentration of approximately 40 g/L produced uniforms coating as shown in Fig. 4(a), while coatings plated with lower sulfate concentrations developed noticeable cracking and delamination, as shown in Fig. 4(a,b). However, the coatings plated with lower nickel sulfate concentrations yielded higher nickel contents and great coating thicknesses. It is suspected that the thicker coating had a tendency to crack due to the increased stress generated at the boundary of the coating and substrate.

A plating solution with a pH of 12 was found to yield a relatively uniform coating as seen in Fig. 3(a). Conversely, a solution pH of 10 yielded a coating with cracks, as shown in Fig. 3(b), while a coating