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Laser Direct-Write Of Alkaline Microbatteries

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ABSTRACT

We are developing a laser engineering approach to fabricate and optimize various types of alkaline microbatteries. Microbattery cells are produced using a laser forward transfer process that is compatible with the materials required to make the anode, cathode, separator and current collectors. The use of an ultraviolet transfer laser (wavelength = 355 nm, 30 ns FWHM) enables other operations such as surface processing, trimming and micromachining of the transferred materials and substrate and is performed in situ. Such multi-capability for adding, removing and processing material is unique to this direct-write technique and provides the ability to laser pattern complicated structures needed for fabricating complete microbattery assemblies. In this paper, we demonstrate the production of planar zinc-silver oxide alkaline cell by laser direct-write under ambient conditions. The microbattery cells exhibit 1.5-1.6 V open circuit potentials, as expected for the battery chemistry and show flat discharge behavior under constant current loads.

INTRODUCTION

Over the last two decades, there has been a continuing trend toward smaller and more autonomous micro-electronic sensing and microelectromechanical devices and systems. As this miniaturization pushes forward, the classical concept of an independent, monolithic power source is no longer sufficient to meet the demands of these advanced devices [1, 2, 3]. In these cases, one of the main concerns is the necessary reduction in both area and thickness of the power source to meet the geometric requirements for integration with the microdevices.

There has been much effort to develop small microbatteries for various primary and secondary chemistries. One successful approach for the lithium based system uses solid state electrolytes in a stacked configuration [4, 5]. In this case, the anode, cathode, and solid-state electrolyte are deposited using standard physical vapor deposition techniques in vacuum with patterning through photolithography. In other experiments, alkaline microbatteries have been produced in a planar configuration where the anode and cathode are located adjacent to each other on the substrate [6, 7]. In this case, materials are deposited through electrochemical and vacuum techniques while the patterning is accomplished through photolithography.

An alternative approach to the production of microbattery cells is through laser engineering [8, 9]. In this technique, we use laser direct-write to directly deposit material where needed [10, 11, 12]. Subsequent laser processing such as annealing or machining is performed *in situ* without the need to remove the substrate. Under this approach, there is no need for expensive vacuum or lithographic processing as all stages of cell construction are performed under atmospheric conditions. Furthermore, our technique does not require re-engineering of fabricated microdevices since we can add material, on location, directly to preexisting circuit boards. We have successfully applied this technique to the production of planar, symmetric hydrous

ruthenium oxide electrochemical capacitors [13, 14] as well as stacked alkaline microbattery structures [15].

In this paper we demonstrate the use of a laser engineering approach to the production of planar alkaline microbattery cells. We use laser direct-write to deposit Zn anodes and Ag_2O cathodes in planar configurations and use laser micromachining to ultimately shape the deposited materials into microbattery cells. Our cells exhibit the appropriate open circuit potential as well as the expected flat discharge behavior under constant current.

EXPERIMENT

Zinc and monovalent silver oxide (Ag_2O) are deposited using a patented laser direct-write technique developed at the Naval Research Laboratory [10, 11, 12]. Figure 1a shows a schematic of the general technique. Commercially available powders are combined with a liquid transfer vehicle to form a suspension or ink. This ink is spread on a borosilicate glass plate using a wire-coater (# 6 Garner) to form a coating approximately 5 μm thick. A frequency-tripled Nd:YVO$_4$ laser (λ=355 nm) irradiates the ink through the back of the glass plate to induce a forward transfer of material to a substrate ~100 μm below the ribbon. The mass of the transferred material is accurately measured using a microbalance (Sartorius M2P) with μg resolution.

The microbattery cell is constructed by first preparing the substrate, then depositing the cathode followed by the anode. We use platinum coated alumina substrates that have been diced into 1 cm x 1 cm squares. The cell geometry is planar (anode adjacent to cathode) with the circular shape of diameter 2500 μm shown in figure 2a. Substrates are prepared by preliminary solvent cleaning using acetone and isopropanol, followed by UV laser micromachining to electrically isolate the anode current collector from the cathode current collector and establish alignment marks (white lines in figure 2a).

In order to improve the conductivity of the Ag_2O cathode material, the powder is mixed with 5 wt.% graphite (Erachem Super P). The powder mixture is combined with a solution of PVDF-HFP binder in propylene carbonate to form the cathode ink. The cathode is deposited in a "C" shape with outer diameter 2500 μm and inner diameter 1250 μm. Following deposition of the cathode, the substrate is baked at 150 °C for 5-10 minutes to remove the propylene carbonate solvent and to bind the cathode to the substrate.

The anode ink used in this experiment is pure Zn mixed with a similar solution of binder and propylene carbonate. This ink is deposited in a circular region of diameter 800 μm and subsequently baked at 150 °C for 5-10 minutes. Finally, after deposition and processing of cathode and anode, the separation gap between them is UV laser micromachined to remove any additional materials that could cause shorting of the cells (figure 1b). The typical weight of transferred material is 200 μg.

Electrochemical evaluation of cell voltage and discharge behavior is carried out using a potentiostat (EG&G PAR Model 263) connected to a probe station. A droplet of 9N KOH is placed on top of both anode and cathode, spanning across the gap to activate the cell. Chronopotentiometry is used to discharge the cells at various currents between the open circuit potential and 0.8 V in a two-electrode configuration.
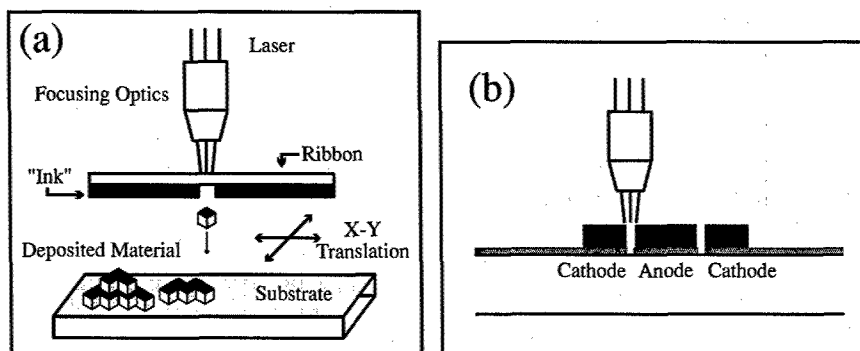
Figure 1. (a) Cartoon of laser direct-write process. (b) Cross sectional view of micromachining between anode and cathode.
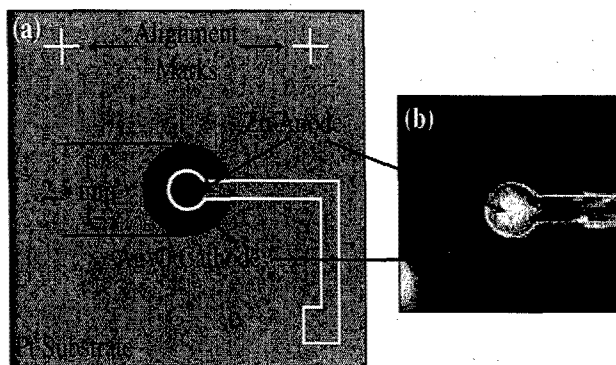

Figure 2. (a) Cartoon of planar battery configuration. (b) Picture of laser deposited planar micro-battery.

RESULTS

Figure 2b shows an optical micrograph of an actual microbattery cell. The separation between the central anode and annular cathode can be clearly seen by the appearance of the white alumina below the substrate surface. The microstructure of the deposited material is shown in figure 3. The cathode shows the appearance of micron sized particles of Ag_2O interspersed in a mesh of threadlike carbon. Such a structure enables good electron conductivity in the cathode through the carbon network, while leaving a relatively large surface area of Ag_2O exposed to the

electrolyte for charge transfer. The anode structure is quite different, exhibiting isolated and clustered particles of Zn approximately 3 μm in diameter. This structure enables a high surface area in contact with the electrolyte.

Upon connecting the microbattery cells to the potentiostat, the open circuit potential is measured for each cell. We find the open circuit potentials range from 1.5-1.6 V as expected for the zinc-Ag_2O chemistry. This suggests that our laser engineering procedure of ink formulation, laser transfer, and subsequent drying does not modify the chemical properties of either anode or cathode material.

A typical constant current discharge curve for a single cell is shown in figure 4 for a current of 10 μA. This particular cell has a cathode mass of 110 μg ($\sim$105 μg Ag_2O) and anode mass of of 80 μg. Based on these masses, the cell is cathode limited with a theoretical capacity of 23.5 μA·Hr. The open circuit potential for this cell is measured to be 1.55 V. Upon discharge, there is an initial drop of $\sim$10 mV to 1.54 V followed by the characteristically flat behavior that is expected for the Zn-Ag_2O system [16]. This initial potential drop is due to internal resistance in the cell which is greater for a planar geometry in comparison to a stacked structure.

After approximately 900 seconds of discharge, the potential in the cell has a sharp drop by 10 mV followed by a flat discharge for a while before exhibiting a second drop of 15 mV and subsequent failure shortly thereafter. Based on optical microscopy of the cell during the experiment, we conclude that sharp decreases in potential are due to partial delamination of the anode with ultimate failure due to complete delamination. Similar failure occurred for all other cells using the same ink formulation and geometry. We have achieved improved adhesion results when using more binder in our formulation, but over time we still have delamination problems. As figure 3b demonstrates, the Zn particles are spherical in shape and large amounts of polymer binder would be necessary to maintain adhesion between them. However, too much binder increases the electron resistance of the anode and therefore increases the loss in the cell and
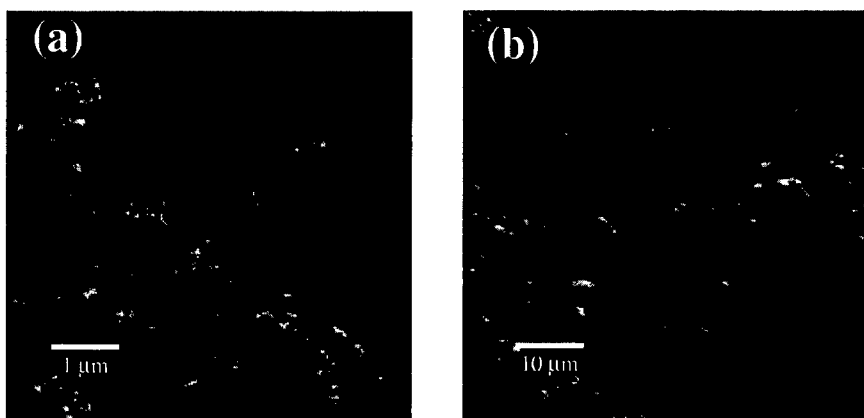

Figure 3. SEM micrographs of (a) cathode and (b) anode. Note different scale bars in the two images.
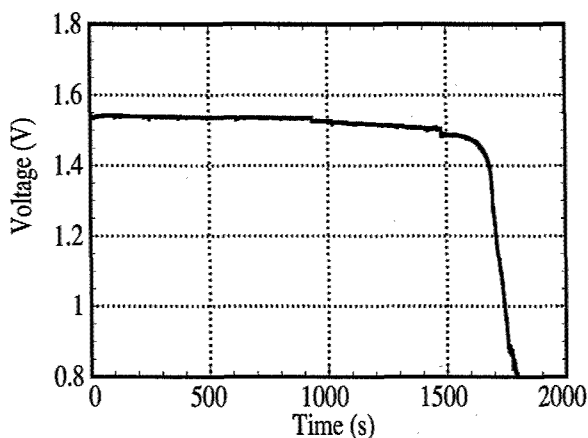
Figure 4. Discharge behavior of alkaline microbattery at 10 μA.

decreases the ability to be discharged at higher currents.

The experimental capacity as well as energy and power of the cell are obtained from the discharge curve of figure 4. The measured capacity of this cell at 10 μA discharge current is 5 μA·Hr, with an energy and power of 7.3 μW·Hr and 14.7 μW respectively. This capacity is less than the theoretical capacity by a factor of approximately 5. As discussed previously, the poor adhesion of the anode is predominantly responsible for the decrease in capacity.

SUMMARY

Laser engineering provides a new approach to making alkaline microbattery cells. We have shown the ability to laser deposit anode and cathode material to construct a working cell in a planar configuration with a total mass of transferred material less than 200 μg. The cell exhibits the expected open circuit potential of the zinc-silver oxide system of 1.5-1.6 V. Under constant current discharge conditions of 10 μA, the cell is able to maintain its potential for almost 30 minutes before cell failure. The open circuit potential and flat discharge behavior observed for our cells indicate that laser engineering is a viable approach for producing alkaline microbatteries in planar geometries. One of the key advantages of this technique is the ability to both deposit and remove material from the substrate *in situ*. The actual capacity and energy of this system are lower than would be expected from theoretical calculation based on the materials used. From visual observations during discharge, it is determined that failure of the cell is not due to complete discharge, but rather due to catastrophic delamination of the Zn anode.

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