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## Laser direct write of planar alkaline microbatteries

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**ABSTRACT** We are developing a laser engineering approach to fabricate and optimize alkaline microbatteries in planar geometries. The laser direct-write technique enables multicapability for adding, removing and processing material and provides the ability to pattern complicated structures needed for fabricating complete microbattery assemblies. In this paper, we demonstrate the production of planar zinc–silver oxide alkaline cells under ambient conditions. The microbattery cells exhibit 1.55-V open-circuit potentials, as expected for the battery chemistry, and show a flat discharge behavior under constant-current loads. High capacities of over  $450 \mu\text{A h cm}^{-2}$  are obtained for 5-mm<sup>2</sup> microbatteries.

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### 1 Introduction

Over the last two decades, there has been a continuing trend toward smaller and more autonomous micro-electronic sensing and micro-electromechanical 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 [1–3]. 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 pho-

tolithography. 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 (LDW) to directly deposit material where needed [10, 11]. 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, directly to pre-existing circuit boards. We have successfully applied this tech-

nique to the production of planar, symmetric hydrous ruthenium oxide electrochemical capacitors [12].

In this paper we demonstrate the production of planar alkaline microbattery cells. We use laser direct-write to deposit Zn anodes and Ag<sub>2</sub>O 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 and the expected flat discharge behavior under constant current with high capacities.

### 2 Experiment

Zinc and monovalent silver oxide (Ag<sub>2</sub>O) are deposited using a patented laser direct-write technique developed at the Naval Research Laboratory [10, 11]. Commercially available powders (Alfa Aesar) 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 5–10- $\mu\text{m}$  thick. A frequency-tripled Nd:YVO<sub>4</sub> laser ( $\lambda = 355 \text{ nm}$ ) irradiates the ink through the back of the glass plate to induce a forward transfer of material to a substrate  $\sim 100 \mu\text{m}$  below the plate. The typical laser energy is 10–11  $\mu\text{J}$  in a 120- $\mu\text{m}$ -diameter spot, corresponding to a fluence for transfer of approximately  $0.1 \text{ J cm}^{-2}$ . The mass of the transferred material is accurately measured using a microbalance (Sartorius M2P) with  $\mu\text{g}$  resolution.

The planar microbattery cell is constructed by first preparing the substrate and then depositing the cathode followed by the anode. The final step

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is to use laser micromachining to remove any deposited material from the gap between the anode and the cathode. We use gold-coated alumina substrates that have been diced into  $1\text{ cm} \times 1\text{ cm}$  squares. 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. The overall footprint of the deposited and micromachined cell is a circular disk of diameter  $2500\text{ }\mu\text{m}$ .

In order to improve the conductivity of the  $\text{Ag}_2\text{O}$  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  $2500\text{ }\mu\text{m}$  and inner diameter  $1250\text{ }\mu\text{m}$ . Following deposition of the cathode, the substrate is baked at  $150\text{ }^\circ\text{C}$  for 5–10 min to remove the propylene carbonate solvent and to bind the cathode to the substrate.

The anode ink used in this experiment is pure Zn flakes mixed with a PVDF-HFP binder solution in dibasic ester. This ink is deposited in a circular region of diameter  $800\text{ }\mu\text{m}$  and subsequently baked at  $150\text{ }^\circ\text{C}$  for 5–10 min. After deposition and processing of the cathode and the anode, the separation gap between them is UV laser micromachined to remove any additional materials that could cause shorting of the electrodes. The typical weight of all transferred material is  $200\text{ }\mu\text{g}$ .

In order to activate the cell, electrolyte is added to the cell by placing a 3-mm-diameter laser micromachined porous membrane (Pall GHP200) soaked in 24 wt.% KOH solution on top of both anode and cathode. This particular base concentration was selected as it optimizes the conductivity at low temperatures [13]. Electrochemical evaluation of cell voltage and discharge behavior is carried out using a potentiostat (EG&G PAR model 263) connected to a probe station. Chronopotentiometry is used to discharge the cells at various currents between the open-circuit potential and  $0.8\text{ V}$  in a two-electrode configuration.

### 3 Results

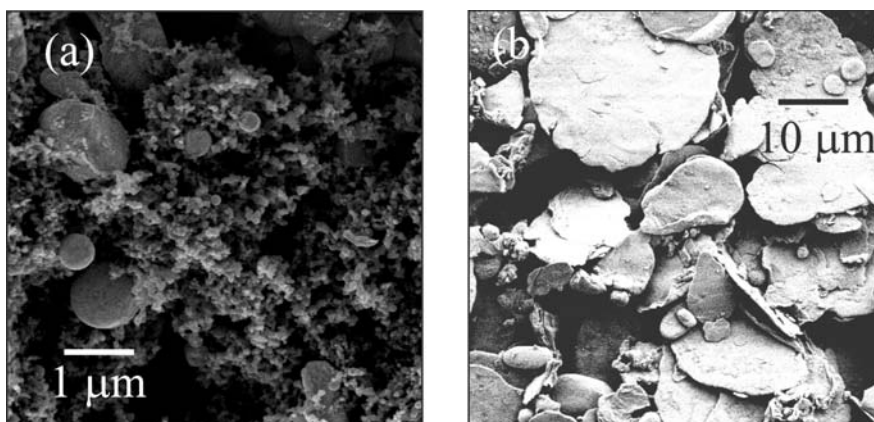
The microstructure of the deposited material is shown in Fig. 1. The cathode shows evidence of micron-sized particles of  $\text{Ag}_2\text{O}$  interspersed in a mesoporous mesh of threadlike carbon. Such a structure enables good electron conductivity in the cathode through the carbon network, while leaving a relatively large surface area of  $\text{Ag}_2\text{O}$  exposed to the electrolyte for charge transfer. The anode structure is quite different, exhibiting a random distribution of large flat flakes. Again, we see large amounts of porosity; however, in this case, the flat surfaces are necessary for improved adhesion of the particles to each other as well as to the substrate. Previous results using spherical zinc particles exhibited delamination of the anode, leading to premature cell failure [14].

Prior to fabrication and testing of the full microbattery cell, we charac-

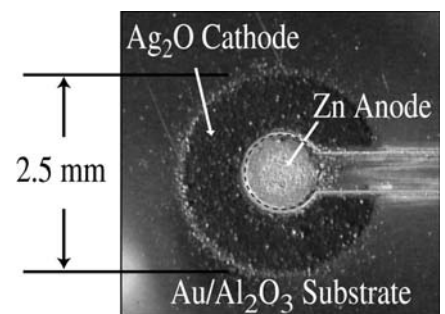
terize the deposited electrode materials through cyclic voltammetry and chronopotentiometry. The LDW electrodes show appropriate open-cell voltages for both cathode ( $0.23\text{ V}$  vs.  $\text{Hg}/\text{HgO}$ ) and anode ( $-1.23\text{ V}$  vs.  $\text{Hg}/\text{HgO}$ ). Further, chronopotentiometry measurements indicate over 90% utilization of the theoretical capacity based on the mass of the deposited electrodes. These results are consistent with the results from other LDW systems, in which it has been shown that the laser transfer process does not harm the physical or electrochemical properties of the electrode materials [15, 16]. It is believed that the primary reason for the preservation of the material properties during the laser process is due to the fact that the laser energy is locally absorbed by the material directly adjacent to the glass plate. The result is that local vaporization takes place, propelling the ink forward while the vast majority of the transferred ink is unaffected by the laser. Such a ‘gentle’ technique has even been shown to successfully transfer living cells to prepared substrates [17].

Figure 2 shows an optical micrograph of an actual microbattery cell. The separation between the central anode and the annular cathode reveals the exposed white alumina below the substrate surface. This circular design enables a relatively large interface length for the given footprint, while keeping the maximum distance between the electrodes small. Stylus profilometry indicates an electrode thickness between 10 and  $20\text{ }\mu\text{m}$ . The electrode thickness is controlled by the number of writing passes over a single location and can be easily varied from one experiment to the next.

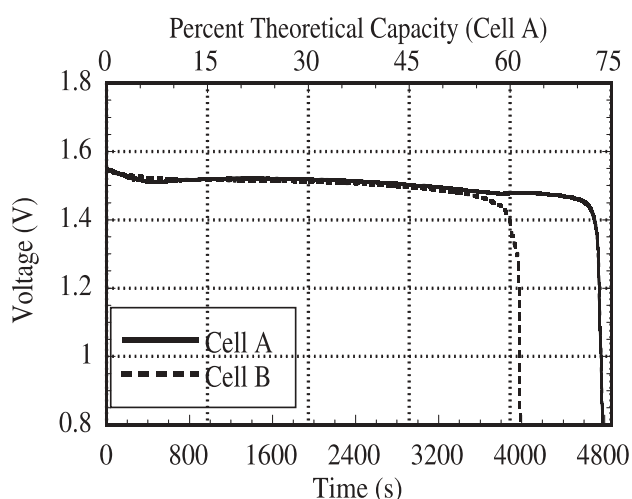
Typical constant-current discharge curves for two individual cells (cell



**FIGURE 1** Scanning electron micrographs of **a** cathode and **b** anode. Note different scale bars in the two images



**FIGURE 2** Picture of a planar microbattery made by laser direct-write



**FIGURE 3** Discharge behavior of alkaline microbattery at 10  $\mu\text{A}$  (cell A) and 20  $\mu\text{A}$  (cell B) as a function of time. Total electrode mass is 116  $\mu\text{g}$  for cell A and 212  $\mu\text{g}$  for cell B. The upper x axis represents the capacity normalized by the theoretical capacity based on the mass of cell A. Multiply by 1.06 to convert the capacity to that of cell B

A and cell B) are shown in Fig. 3 at currents of 10 and 20  $\mu\text{A}$ , respectively. Cell A has a cathode mass of 83  $\mu\text{g}$  ( $\sim 79$   $\mu\text{g}$  active  $\text{Ag}_2\text{O}$ ) and an anode mass of 33  $\mu\text{g}$ , while cell B has the larger masses of 170  $\mu\text{g}$  (cathode) and 41  $\mu\text{g}$  (anode). Based on these masses and the theoretical capacity of silver oxide and zinc, cell A is cathode limited with a theoretical capacity of 18  $\mu\text{A h}$  and cell B is anode limited with a theoretical capacity of 34  $\mu\text{A h}$ .

The open-circuit potential for both cells is measured to be 1.55 V. Upon discharge, there is an initial drop of  $\sim 5$  mV and  $\sim 10$  mV for cells A and B, respectively, followed by the characteristically flat behavior that is expected for the Zn– $\text{Ag}_2\text{O}$  system [18]. This initial potential drop is due to internal resistance in the cell, which tends to be greater for a planar geometry in comparison to a stacked structure and, as expected, scales with the discharge current.

The upper axis in Fig. 3 shows the discharge behavior normalized for the mass of active material in the microbattery. The capacity is calculated by multiplying the discharge current by the time and then normalizing that quantity by the theoretical limiting capacity of the cell. The values represented in the figure are calculated for cell A. However, these values can be converted to cell B by multiplying by 1.06. In both cases, we find that the cells utilize the majority of the active material, reaching greater than 65% of the theoretical limit before

the cell is completely discharged. The actual capacities are 13.3 and 22.1  $\mu\text{A h}$  for cells A and B, respectively. Although the planar geometry is typically considered to have more loss and higher resistance in comparison to stacked configurations [6], our results show that, with the appropriate electrode geometry and microstructure, it is possible to achieve high rates of utilization in the electrode materials.

In order to compare our alkaline microbatteries to others reported in the literature, it is necessary to normalize by the mass and the area of the cells. We calculate the specific capacity by normalizing the capacity by the electrode mass without considering the mass of the electrolyte. The areal density is calculated by normalizing the capacity by the electrode footprint (4.9  $\text{mm}^2$ ). Performing these calculations, we find normalized values of 270 and 450  $\mu\text{A h cm}^{-2}$  and 115  $\text{mA h g}^{-1}$  and 105  $\text{mA h g}^{-1}$  for cells A and B, respectively. These values compare favorably to currently available lithium microbatteries [4, 5] that exhibit densities of only 155  $\mu\text{A h cm}^{-2}$  and nickel–zinc alkaline microbatteries [6] with maximum reported densities of 389  $\mu\text{A h cm}^{-2}$ .

#### 4 Conclusions

Laser engineering provides a viable approach to making alkaline microbattery cells in planar geometries. We have shown the ability to

laser deposit anode and cathode materials to construct working cells with a total mass of transferred material of less than 200  $\mu\text{g}$ . The cells exhibit the expected open-circuit potential of the zinc–silver oxide system of 1.5–1.6 V. Under constant-current discharge conditions of 10 and 20  $\mu\text{A}$ , the cells maintain their potential for over 1 h before the lower-voltage limit is reached. We obtain high capacities of over 450  $\mu\text{A h cm}^{-2}$ , which exceed previously reported results on microbatteries produced by other techniques. The flat discharge behavior and the high capacities observed for our cells indicate outstanding cell performance and potential applications.

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#### REFERENCES

- 1 J.N. Harb, R.M. LaFollette, R.H. Selfridge, L.L. Howell: *J. Power Sources* **104**, 46 (2002)
- 2 P.B. Koeneman, I.J. Busch-Vishniac, K.L. Wood: *J. Microelectromech. Syst.* **6**, 355 (1997)
- 3 M. Balkanski: *Sol. Energy Mater. Sol. Cells* **62**, 21 (2000)
- 4 J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B.S. Kwak, X. Yu, R.A. Zuhur: *J. Power Sources* **54**, 58 (1995)
- 5 J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans: *Solid State Ionics* **135**, 33 (2000)
- 6 P.H. Humble, J.N. Harb, R. LaFollette: *J. Electrochem. Soc.* **148**, A1357 (2001)
- 7 R.M. LaFollette, J.N. Harb, P. Humble: in *Sixteenth Annu. Battery Conf. Applications and Advances*, ed. by R.S.L. Das, H. Frank (IEEE, Piscataway, NJ 2001) pp. 349–354
- 8 K.E. Swider-Lyons, A. Piqué, C.B. Arnold, R.C. Wartena: in *The Encyclopedia of Materials Science and Technology*, ed. by K.H.J. Bushcaw, R.W. Cahn, M.C. Flemings, B. Ilshner, E.J. Kramer, S. Mahajan (Pergamon, New York 2002)
- 9 C.B. Arnold, K.E. Swider-Lyons, A. Piqué: in *Rapid Prototyping Technologies, Vol. 758*, ed. by A. Piqué, A. Holmes, D.B. Dimos (Materials Research Society, Pittsburgh, PA 2003) pp. 101–112
- 10 D.B. Chrisey, R.A. McGill, A. Piqué: US Patent No. 6 177 151 (1999)
- 11 A. Piqué, D.B. Chrisey, J.M. Fitz-Gerald, R.A. McGill, R.C.Y. Auyeung, H.D. Wu, S. Lakeou, V. Nguyen, R. Chung, M. Duignan: *J. Mater. Res.* **15**, 1872 (2000)
- 12 C.B. Arnold, R.C. Wartena, K.E. Swider-Lyons, A. Piqué: *J. Electrochem. Soc.* **150**, A571 (2003)
- 13 V.S. Bagotzky, A.M. Skundin: *Chemical Power Sources* (Academic, New York 1980)
- 14 C.B. Arnold, A. Piqué: in *Rapid Prototyping Technologies, Vol. 758*, ed. by A. Piqué, A. Holmes, D.B. Dimos (Materials Research Society, Pittsburgh, PA 2003) pp. 119–126

- 15 C.B. Arnold, A. Piqué: J. Electrochem. Soc. (2004) in press
- 16 R.C. Wartena, A.E. Curtright, C.B. Arnold, A. Piqué, K.E. Swider-Lyons: J. Power Sources **126**, 193 (2004)
- 17 D.B. Chrissey, A. Piqué, R.A. McGill, J.S. Horwitz, B.R. Ringeisen, D.M. Bubb, P.K. Wu: Chem. Rev. **103**, 553 (2003)
- 18 S.A. Megahed, J. Passaniti, J.C. Springstead: in *Handbook of Batteries*, ed. by D. Linden, T.B. Reddy (McGraw-Hill, New York 2002) Chap. 12, pp. 12.1–12.17