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Rapid prototyping of micropower sources by laser direct-write

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ABSTRACT A laser forward-transfer and micromachining process has been developed to fabricate and optimize mesoscale electrochemical power sources, such as primary Zn–Ag₂O and secondary Li-ion microbatteries. The laser direct-write technique allows for adding, removing and processing the various material systems required for the fabrication of micropower sources on many types of substrates under ambient conditions. In this work, we demonstrate planar zinc–silver oxide alkaline cell configurations with 1.5–1.55 V open-circuit potentials. The 10 mm² samples show a flat discharge behavior under constant-current loads and capacities of $\sim 100 \mu\text{A h cm}^{-2}$. Stacked Li-ion cells with 3.80-V open-circuit potentials have also been fabricated and continue to operate after 50 charge/discharge cycles. The 9 mm² samples exhibit capacities of $110 \mu\text{A h cm}^{-2}$.

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1 Introduction

Current trends for developing advanced electronic systems place emphasis in achieving sizes and weights generally associated with integrated circuits. This requires further miniaturization, while enhancing the functionality and reliability of existing components. 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 how to reduce the volume of the power source without sacrificing its performance in order to meet the requirements for integration with a given microdevice.

There has been significant effort to develop microbatteries for various primary and secondary chemistries. Examples include secondary solid-state lithium-ion cells in a stacked configuration [4, 5] and primary alkaline microbatteries in a planar configuration where the anode and cathode are located adjacent to each other on the substrate [6, 7]. In these cases, materials are deposited through electrochemical and/or vacuum techniques while the patterning is accomplished through photolithography.

Since direct-write techniques do not require photolithographic processing steps, they provide an alternative for the

development and optimization of micropower sources [8]. Among them, laser direct-write is a promising approach for the manufacture of integrated micropower sources since it is compatible with the broad array of materials required for the fabrication of microbatteries. In addition, the laser direct-write system can be used for laser micromachining of the substrate onto which the micropower source is to be deposited or to shape the current collectors, electrodes and interfaces between materials [9]. The combination of additive and subtractive direct-write processes with a single system offers the ability to prototype custom micropower sources with designed power and energy profiles for a particular microelectronic application.

This paper describes the fabrication of two types of microbatteries using laser direct-write processes. The first type comprises primary zinc–silver oxide alkaline cells. Laser direct-write is used for depositing the Zn anodes and the Ag₂O cathodes in a planar configuration. The second type comprises secondary lithium-ion cells. Laser direct-write is used for depositing the carbon anodes and the LiMn₂O₄ cathodes which are then assembled in a stacked configuration. A drop-cast ionic liquid layer is used as the separator. Both systems exhibit the appropriate open-circuit voltages. The primary system is able to operate at relatively high discharge currents, while the secondary system exhibits the ability to be continuously cycled inside an argon-filled glove box.

2 Experimental

For the fabrication of the primary alkaline cells, zinc and monovalent silver oxide (Ag₂O) powders are deposited, while carbon and electrolytic lithium manganese oxide (LiMn₂O₄) powders are deposited for the fabrication of the secondary lithium-ion cells, using a patented laser direct-write technique developed at the Naval Research Laboratory [10, 11]. Each of the commercially available powders (Alfa Aesar or Aldrich) is mixed with an organic vehicle (propylene carbonate or dibasic ester) and a binder (PVDF-HFP) 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 μm thick. A frequency-tripled Nd:YVO₄ 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 100 μm below the glass

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plate. The typical laser fluence for transfers is 0.1 J cm^{-2} . The mass of the transferred material is accurately measured using a microbalance (Sartorius M2P) with μg resolution.

The planar alkaline microbattery cells are constructed by first preparing the substrate and then depositing the cathode followed by the anode. The final step is to use laser micromachining to remove any deposited material from the gap between the anode and the cathode. Gold-coated alumina substrates diced into $1 \text{ cm} \times 1 \text{ cm}$ squares are used for these cells. The substrates are first cleaned 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 fills a $2 \text{ mm} \times 5 \text{ mm}$ rectangle as shown in the micrograph in Fig. 1a. In order to improve the conductivity of the Ag_2O cathode material, the powder is mixed with 5 wt. % graphite (Erachem Super P). Following deposition of the cathode, the substrate is baked at 150°C for 5–10 min to remove the solvent and to bind the cathode to the substrate. Then the Zn ink is deposited to form the anode and subsequently baked at 150°C for 5–10 min. After

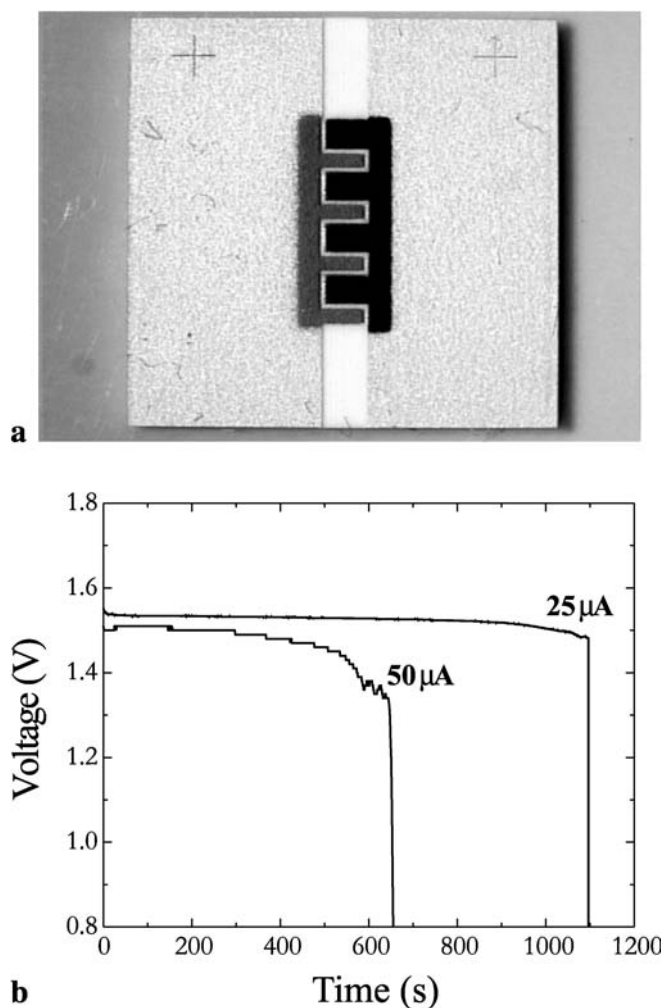


FIGURE 1 a Optical micrograph of a planar $\text{Ag}_2\text{O}/\text{Zn}$ alkaline microbattery made by laser direct-write. b Discharge behavior from two planar alkaline microbatteries at 25 and $50 \mu\text{A}$, respectively, as a function of time. Total electrode mass is $\sim 250 \mu\text{g}$ in both cases

deposition and processing of the cathode and the anode, the separation gap between them is laser micromachined to remove any additional materials that could cause shorting of the electrodes. The typical weight of all transferred material is $250 \mu\text{g}$, while the thickness of the anode and cathode layers is about $10\text{--}20 \mu\text{m}$ as measured by stylus profilometry.

In order to activate the planar cells, a drop of 25 wt. % KOH solution is placed on the electrodes. Electrochemical evaluation of cell voltage and discharge behavior of the alkaline microbattery samples 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 V in a two-electrode configuration.

For the fabrication of the secondary lithium-ion cells, a different type of geometry is used. For these systems, $3 \text{ mm} \times 3 \text{ mm}$ pockets are laser machined into polyimide sheets and backed with Al and Cu foil for the cathodic and anodic electrodes, respectively. Two different types of inks were prepared. For the anode, solid material composed of 90 wt. % high surface area synthetic carbon and 10 wt. % 1–2 micron-sized graphite particles was combined with a PVDF-HFP binder solution in dibasic ester. The cathode ink was prepared from a solid mixture of 85 wt. % LiMn_2O_4 and 15 wt. % 1–2 micron-sized graphite particles. Once spread over the borosilicate-glass plates, these inks are deposited into the 9 mm^2 pockets cut into the polyimide and subsequently baked at 150°C for 5–10 min. The typical weight of all transferred material is $300 \mu\text{g}$, while the thickness of the anode

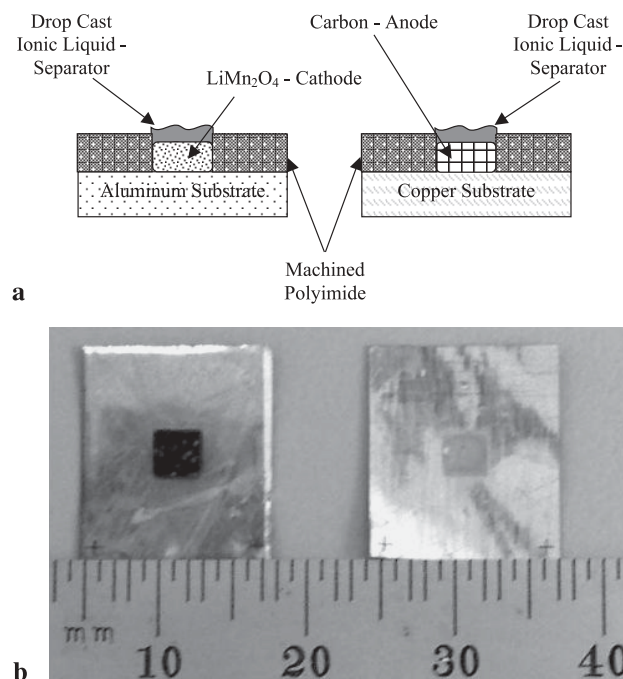


FIGURE 2 a Cross-sectional schematic showing the separate anode and cathode for the Li-ion microbattery made by laser direct-write. The battery is assembled once both electrodes are placed against each other. b Optical micrograph showing the laser-transferred LiMn_2O_4 , prior to drop casting of the separator (left), and the amorphous carbon anode coated with the ionic liquid separator (white in appearance) drop cast over the high surface area carbon (right)

and cathode layers is about 10–20 μm as measured by stylus profilometry.

The separator for these batteries is prepared by drop casting a solid polymer ionic liquid/PVDF-HFP composite material dissolved in acetone [12]. Over each cathode and anode, approximately 0.01 μl of solution is dispensed and the electrodes dried at 100 $^{\circ}\text{C}$ for 5 min. This process is repeated until the well was nearly completely filled with the solid composite. Prior to placing these cathodes and anodes into a dry box for testing, they are dried at 85 $^{\circ}\text{C}$ for 12 h under a dynamic vacuum. Once placed in the dry box, the batteries are assembled by stacking the cathodic pocket over the anodic pocket and clamping each battery together with a tension-adjustable clamp. A schematic showing a cross-sectional view of the individual electrodes for the Li-ion cell is shown in Fig. 2a, while Fig. 2b shows an optical micrograph of the cathode and the anode prior to assembly. Electrochemical evaluation of the material is carried out on an EG&G PAR model 273A using M270 software. Because none of these batteries are sealed or packaged once assembled, all electrochemical experiments are performed in an argon-filled dry box with less than 1 ppm water and oxygen.

3 Results and discussion

Discharge curves for two planar alkaline microbatteries prepared by laser direct-write are shown in Fig. 1b. One cell was discharged at 25 μA while the other was discharged at 50 μA . The open-circuit potential for these samples was between 1.50 and 1.55 V, which is expected for the silver oxide/zinc system. In order to compare these alkaline microbatteries to others reported in the literature, it is necessary to normalize their capacities by the area of the cells, which is given by the electrode footprint (10.0 mm^2). This gives us a specific capacity of $\sim 100 \mu\text{A h cm}^{-2}$ for the cell discharged at 50 μA . For comparison, specific capacities up to 389 $\mu\text{A h cm}^{-2}$ have been reported for a nickel–zinc alkaline microbattery system [6]. The reason why the specific capacity of these samples was lower than expected is due to the delamination of the Zn anode, which caused the cells to fail before they could be fully discharged. Such delamination is responsible for the sudden drop in potential observed in Fig. 1b.

For the Li-ion stacked cells, chronopotentiometry is used for charging and discharging experiments. The open-circuit potential for these samples is measured to be 3.80 V, which is expected for the Li-ion system. After the first several charge–discharge cycles, the charging current was adjusted to the appropriate levels to achieve a complete charge in 1 h. As shown in Fig. 3, the charging plateau is very linear, revealing that the high-conductivity characteristic of the ionic liquid polymer composite gels is maintained during the drop-casting technique [12]. It is worth noting that the upward turning of the charging curve, typical of the Li-ion system, is not observed since the amount of Li removed from the cathodic material was limited to prevent damaging the LiMn_2O_4 layer. This was accomplished by maintaining the measurements at levels below the maximum capacity of the available LiMn_2O_4 . As a result, a constant capacity of 95 mA h/g was observed over the 50 charge–discharge cycles using an absolute current

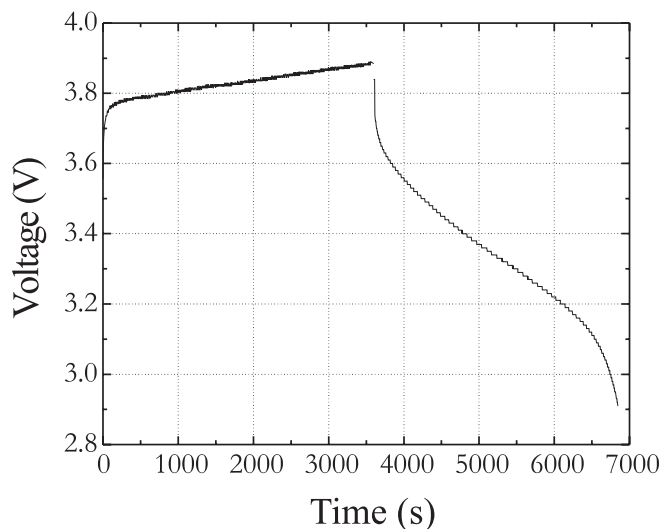


FIGURE 3 Potential vs. time plot corresponding to the 50th charge–discharge cycle for a stacked Li-ion microbattery at 10 μA

of 10 μA . The discharge plateau, while not being completely linear, exhibits only a 0.35 V drop while discharging. This is primarily attributed to the increasing resistance of the anodic material as Li ions are removed. The total battery capacity as assembled is 1.9 mA h, which corresponds to 110 $\mu\text{A h cm}^{-2}$ when normalized by the total area of the cells (9.0 mm^2). For comparison, specific capacities up to 155 $\mu\text{A h cm}^{-2}$ have been reported for lithium microbatteries [4, 5].

4 Summary

This work demonstrates the use of a laser direct-write process for the fabrication of micropower sources such as primary Zn– Ag_2O and secondary Li-ion microbatteries. Planar zinc–silver oxide alkaline cell configurations with 1.55-V open-circuit potentials showing a flat discharge behavior under constant-current loads were demonstrated. The 10- mm^2 samples had specific capacities of $\sim 100 \mu\text{A h cm}^{-2}$. Higher capacities are expected once the planar electrodes can be tested without delaminating from the substrate. Laser direct-write was also used to fabricate stacked Li-ion cells with 3.80 V open-circuit potentials, which continued to operate after 50 charge/discharge cycles. The 9.0 mm^2 samples exhibited capacities of 110 $\mu\text{A h cm}^{-2}$, which compares very well with results obtained from other groups working on lithium-ion microbatteries. The rechargeable Li-ion microcells can provide higher energy and power density than their alkaline counterparts; however, they are highly sensitive to the environment. As a result, appropriate packaging schemes will have to be developed before these Li-ion microbatteries can operate outside the glove box. Ultimately, the goal of this effort is to be able to optimize each of these two battery systems to meet the power-generation requirements of future microelectronic systems.

REFERENCES

- 1 J.N. Harb, R.M. LaFollette, R.H. Selfridge, L.L. Howell: *J. Power Sources* **104**, 46 (2002)
- 2 P.B. Koneman, 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. Zuhr: *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 A. Piqué, D.B. Chrisey (eds.): *Direct-Write Technologies for Rapid Prototyping Applications* (Academic, San Diego, CA 2002)
- 9 C.B. Arnold, R.C. Wartena, K.E. Swider-Lyons, A. Piqué: *J. Electrochem. Soc.* **150**, A571 (2003)
- 10 D.B. Chrisey, R.A. McGill, A. Piqué: US Patent No. 6 177 151 (1999)
- 11 A. Piqué, D.B. Chrisey, R.C.Y. Auyeung, J. Fitz-Gerald, H.D. Wu, R.A. McGill, S. Lakeou, P.K. Wu, V. Nguyen, M. Duignan: *Appl. Phys. A* **69**, 279 (1999)
- 12 T.E. Sutto, P.C. Trulove, H.C. De Long: *Z. Naturforsch. A* **57**, 839 (2002)