Laser Direct Writing of Microbatteries for Integrated Power Electronics

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ABSTRACT

A novel laser-based process developed at the Naval Research Laboratory has been used to fabricate pseudocapacitors and microbatteries with tailored capacities for small electronic devices having size and/or weight restrictions. This process, called MAPLE DW (for matrix-assisted pulsed-laser evaporation direct write) can deposit rugged mesoscale (1 µm to 10 mm) electronic components over any type of substrate. A pulsed laser operating at 355 nm is used to forward transfer material from a tape-cast ribbon to a suitable substrate to form a precision design. With MAPLE DW, customized mesoscale electronic components can be produced, eliminating the need for multiple fabrication techniques and surface-mounted components. Direct write processing is especially attractive for the fabrication of micro-power sources and systems. The versatility of laser processing allows battery designs to be easily modified. Batteries and/or pseudocapacitors can be integrated with power management electronics to deliver a wide range of power outputs. By building power sources directly on electronic components, the weight of the power sources is decreased as the electronic substrate becomes part of the battery packaging and the lengths of interconnects are shortened, reducing conductor losses. RuO_xH_y pseudocapacitors deposited with MAPLE DW show good storage capacities. Pads of hydrous RuO_2 having dimensions of 2.2 mm x 1.0 mm x 30 µm have been deposited in a planar configuration on gold current collectors. Rechargeable Zn/MnO_2 alkaline microbatteries comprising of MnO_2, Zn, an ethyl cellulose separator barrier layer and a KOH electrolyte have also been fabricated by MAPLE DW. The resulting structures with dimensions of 1.5 mm x 1.5 mm x 60 µm represent the first demonstration of a multilayer microbattery made by MAPLE DW. The performance of these prototypes are shown and the potential impact of MAPLE DW for the fabrication of novel microbattery systems for integrated power applications are discussed.

Keywords: MAPLE Direct Write, Laser Transfer, Pseudocapacitors, Microbatteries, Direct Write of Battery Materials.

1. INTRODUCTION

Perhaps the greatest obstacle to increasing the autonomy, portability and functionality of microelectronic and microelectromechanical systems (MEMS) is the availability of suitable power sources. Essentially, the development of miniature power sources such as microbattery systems has not kept pace with the progress achieved towards miniaturization of electronic components. The use of microbatteries offers many inherent advantages for powering microelectronics, microsensors and MEMS devices. By placing the source of power near its load, noise problems due to stray capacitance in the power connections, cross talk between power lines and signal lines, and ohmic losses are reduced. Furthermore, the resulting multiple power sources distributed throughout the entire system would allow each component to be controlled through its own power supply. Such distributed power sources would offer advantages such as reducing control system complexity and noise levels, while increasing power efficiency and speed of operation. Traditional approaches for the manufacture of batteries cannot simply be scaled down in order to achieve the desired reduction in size without sacrificing performance. Novel approaches to the fabrication of microbatteries are required in order to achieve ultimate power and energy levels.

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One of the challenges in developing microbatteries for electronic devices that are still under development is that the power requirements are application specific and often not yet know. For example, different types of MEMS operate at potentials and currents ranging from 10 to 100 V and 1 nA to 1 µA. Some microelectronic devices will be disposable, requiring inexpensive, environmentally friendly primary microbatteries. Others will demand secondary microbatteries with integrated recharging systems to allow years of low- to no-maintenance operation.

What is required are techniques, materials, and tools to build microbatteries on any type of substrate or surface required for the fabrication of self-powered electronic assemblies. Such a capability would create new opportunities in the way electronic systems are currently designed and implemented, because the batteries and the electronics will no longer be developed and manufactured independently. One approach is to utilize rapid prototyping techniques, such as direct write processes for the fabrication of microbatteries. Direct write processes offer the capability to deposit or pattern the different types of materials required to make a battery without the use of masks or patterns. For example, using direct write processes it would be possible to rapidly survey a wide range of battery materials, geometries and configurations, so as to identify those combinations best suited for a particular application. Using this approach it would be possible to fabricate prototype microbattery systems, test and compare their operation with the modeling data and adjust the design or modeling parameters accordingly. These steps could be executed in an iterative fashion for maximum optimization in a fraction of the time required by traditional manufacturing techniques. Direct write processes are the key enabling technology for the above scenario to become a reality.

Over the past decade, various laser-based direct write techniques have been developed for depositing different types of materials such as metals for interconnects and mask repair. More recently, a new laser-based direct write technique, called MAPLE DW, for Matrix-Assisted Pulsed-Laser Evaporation Direct Write, has been used for the direct write of conformal electronic devices[1-4], chemical sensors[5] and even viable biomaterials[6]. In this paper, the use of the MAPLE DW technique for the fabrication of planar RuO_xH_y/Nafion pseudocapacitors and multilayer Zn/MnO_2 alkaline microbatteries is described, together with data showing the performance of the various prototype pseudocapacitors and alkaline microbattery structures made by MAPLE DW.

2. BACKGROUND

MAPLE DW is a laser forward transfer technique similar in experimental approach to LIFT or laser induced forward transfer[7,8]. Unlike LIFT, however, MAPLE DW is a soft laser transfer process, since it does not cause the ablation or vaporization of the transferred material. A schematic diagram of the MAPLE DW system is shown in Figure 1. MAPLE DW is a process that takes place in air and at room temperature in which material is transferred from a support or "ribbon" to a substrate by the irradiation of a laser pulse (λ = 355 nm, 5-10 ns), as shown in the insert in Figure 1.

The "ribbon" is composed of a laser transparent support substrate, such as a quartz disc; and a 1-20 µm thick matrix film, incorporating binders, vehicles and other ingredients, plus the material to be deposited. These various components can either be dissolved or dispersed within the matrix. The matrix material binds the material to be deposited to the support substrate. It also preferentially absorbs the laser radiation and desorbs the material to be deposited from the support, and can assist in the adhesion of the deposited layer. Unlike other laser-based direct write processes, MAPLE DW is a pyrolitic technique with respect to the matrix material, but not with respect to the materials that are to be deposited. This has been confirmed by post-deposition analysis of the transferred materials which have shown no changes in their functionality before and after the transfer process[3]. The material to be deposited can consist of nanophase powders up to micron size particulates, single crystallites, metal-organic or sol-gel precursors and polymer composites. Since the electronic, mechanical, and thermal properties of the materials to be deposited often differ with respect to bulk or single crystals, there is a great deal of complexity in designing the material to be deposited so as to achieve good adherence to the substrate or previous layers and bulk- like properties. The amount of material transferred is a function of the spot size of the laser (5 to 100 µm diameter) and the thickness of the ribbon. MAPLE DW is the equivalent of a "laser typewriter," because the substrate moves on a computer-controlled translation stage underneath the laser and ribbon allowing the fabrication of high-resolution (< 10 µm) intricate designs.

The highly focused laser beam used by MAPLE DW can easily be utilized for micromachining, surface annealing, drilling and trimming applications, by simply removing the ribbon from the laser path. The flexible nature of MAPLE DW allows the fabrication of multi-layered structures in combination with patterning. Thus, MAPLE DW is both an *additive* as well as a *subtractive* direct write process. Once transferred, the material is then usually thermally annealed to remove the residual matrix, sinter the film, and adhere the film to the substrate. MAPLE DW has been used successfully to transfer polymers, ceramics, metals, and biomaterials, and to fabricate metal interconnects, multi-layer capacitors, inductors, resistors, and phosphor displays, examples of which are shown in Figure 2. The performance of the devices is comparable to that of components fabricated with conventional thick-film techniques.

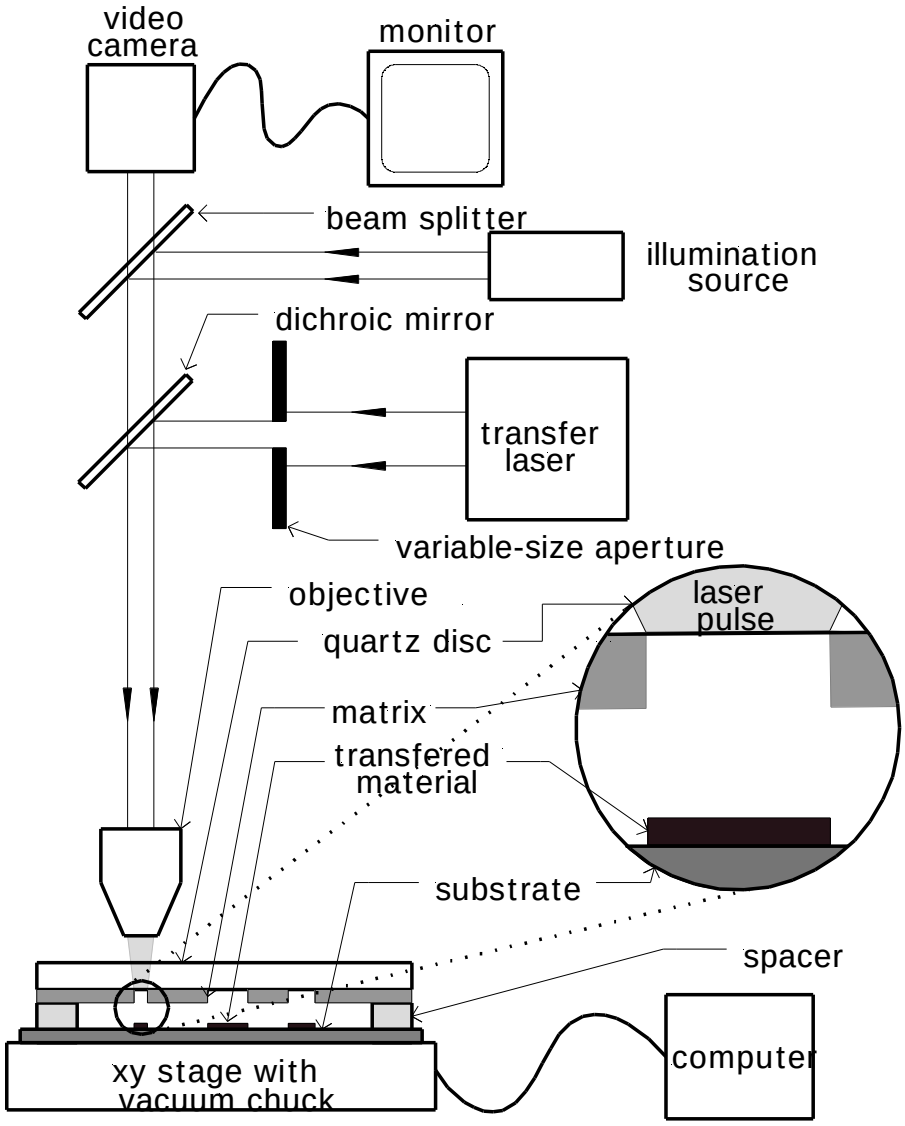

Figure 1. Schematic diagram illustrating the MAPLE DW system basic components. The insert shows a close-up of the region where the material transfer takes place.

MAPLE DW offers many opportunities for microbattery fabrication, because it can be used to nondestructively deposit hydrated and defective powders, as well as to develop a broad platform of battery materials systems (e.g., alkaline, lithium, polymer) that cannot be fabricated using high temperature, lithographic, or vacuum-based processes. The CAD/CAM feature of MAPLE DW can be utilized to rapidly vary and optimize the design of the batteries, plus build series or parallel battery arrays to meet a desired power demand. These DW batteries can also be fabricated directly onto an electronics substrate or solar panel, eliminating some of the packaging weight necessary in a surface-mount battery. MAPLE DW microbatteries may be applied conformally to non-uniform surfaces and/or integrated with other power sources and electronic components to serve systems with size and/or design restrictions.

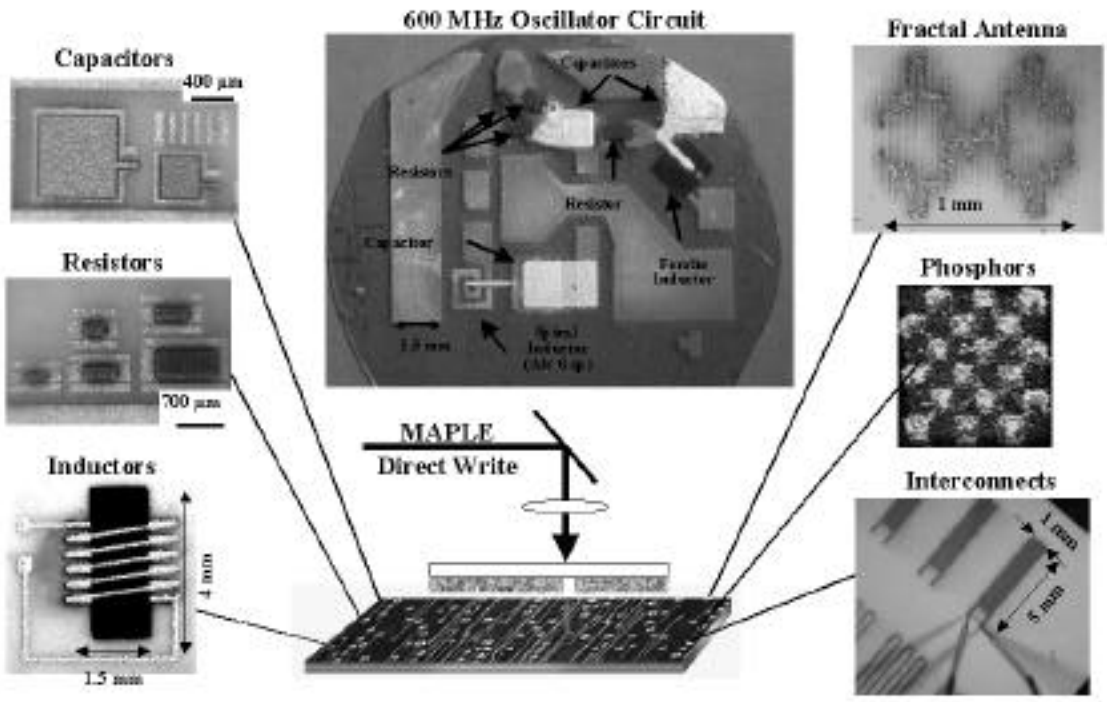

Figure 2. Sample devices fabricated using MAPLE DW.

RuO_xH_y/Nafion pseudocapacitors are an ideal system for initial demonstration of the ability of MAPLE DW to transfer battery materials since these structures are rechargeable and the cathode and anode have identical compositions. Rechargeable Zn/MnO_2 alkaline batteries belong to a class of battery systems which have gained popularity lately due to their high charge retention rate, and to the absence in their manufacture of heavy metals or highly reactive metals like in the cases of nickel-cadmium or lithium batteries. Primary Zn/MnO_2 batteries are also useful for disposable electronic devices.

3. EXPERIMENTAL

Fused silica discs, double side polished, 5.0 cm in diameter and 3mm thick were used as ribbon supports. The coated side of the ribbons was kept at a distance of 50-200 µm from the substrate with a spacer. Both the substrate and the ribbon were held in place using a vacuum chuck over the X-Y substrate translation stage, as shown in Figure 1. The third harmonic emission of a Nd:YAG laser (Quantel) was directed through a square aperture and then through a 10x objective lens, resulting in a 65 µm x 65 µm spot at the ribbon. The laser fluence varied between 0.1 – 1.0 J/cm^2 depending on the material being transferred, and was estimated by averaging the total energy of the incident beam over the irradiated area.

For the MAPLE DW transfers of RuO_xH_y pseudocapacitors, a paste consisting of < 325 mesh commercial RuO_xH_y (Alfa) and ethylene glycol was prepared and applied to the fused silica discs using a wire roller (Sheen No. 1120/18/15) to form the ribbon. The RuO_xH_y matrix was transferred by MAPLE DW onto 1 cm^2 gold-coated glass substrates. The area and number of RuO_xH_y pads were easily modified via computer control. A single pass produced ~ 10-μm thick RuO_xH_y pads, so their thickness was increased to approximately 30 μm by superimposing additional layers (i.e. passes) of RuO_xH_y from fresh areas of the ribbon. The pads were dried at 100 °C on a hot plate to remove excess solvent and then laser micromachined. The pads were then heated to 170 °C in an oven for 1hr to fully remove the ethylene glycol. A drop of 5% Nafion solution (Aldrich) was applied with a pipette on top of the RuO_xH_y pads and dried under ambient conditions to the solid state. Gaps of varying length and width were laser micromachined in order to fabricate cell structures with different interface characteristics.

For the MAPLE DW transfers of Zn/MnO_2 alkaline batteries, powders of Zn (3 μm dia., GoodFellow) and MnO_2 (< 425 mesh, Tekosha) were mixed with α-terpineol (Alfa) to make the pastes. To increase the conductivity of the Zn and MnO_2 layers, 5 to 20 wt% of acetylene carbon black (Alfa) was added to the pastes. A small amount (< 1 wt%) of polyvinylidenefluoride (PVDF, Elf-Atochem) was added as a binder as well. Zn and MnO_2 ribbons were made using the same wire roller as for the RuO_xH_y ribbons. MnO_2 pads 2mm x 2mm in area and 40 μm thick (after four passes) were first transferred by MAPLE DW onto 1 cm^2 gold-coated glass substrates. The pads were heated to 200 °C in an oven for 30 min to remove the α-terpineol. Then a 2 μm thick ethyl cellulose (Aldrich) layer was drop cast over the MnO_2 pads to serve as the separator between the MnO_2 cathode and the Zn anode. A Zn layer was then MAPLE DW onto the ethyl cellulose in the form of a 1.5mm x 1.5 mm x 20 μm pad. The resulting multilayer structure was again heated to 200 °C in an oven for 30 min to remove any α-terpineol residue left in the zinc. A drop of concentrated KOH (Alfa) solution was dropped with a pipette on top of the zinc pads and left for 1 h to soak the whole structure.

The chronopotentiometry of the RuO_xH_y pseudocapacitors and the Zn/MnO_2 alkaline batteries was evaluated using an EG&G PAR 263 potentiostat driven with M270 software. The two-electrode system was operated on a potential scale between 0 and 1 V. The thickness of the RuO_xH_y, MnO_2, and Zn pads was measured using a surface profilometer (Tencor P10) and their morphology surveyed with optical microscopy and scanning electron microscopy (SEM, Leo 1550).

4. RESULTS AND DISCUSSION

Figure 3(a) shows a SEM image from one of the annealed RuO_xH_y pads with a laser micromachined gap on the Au-coated

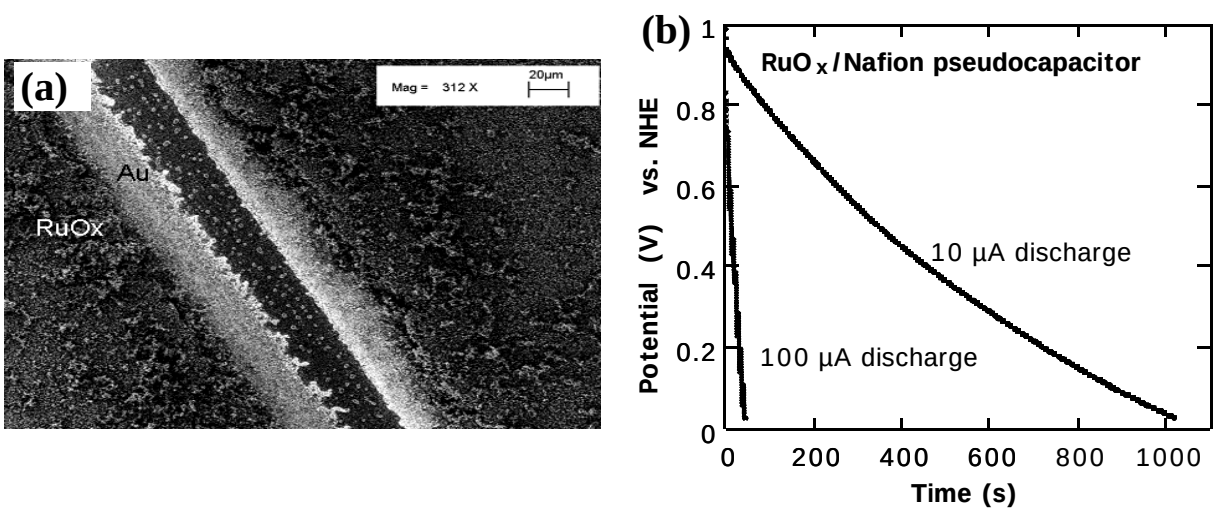

Figure 3. (a) SEM image showing a laser micromachined RuO_xH_y pad. (b) Discharge curves for a pair of 2.2 mm x 1 mm x 30 μm RuO_xH_y pads under two different current drains.

glass substrate. The uniform gap cut between the RuO_xH_y pads is 60 µm and that cut into the Au film is 20 µm. These gaps generated regular interfaces which allowed for uniform discharge of the RuO_xH_y cells. The SEM image from Figure 3(a) also shows the uniform porosity with which the RuO_xH_y pads were deposited, which is ideal for uniform distribution of electrolyte in the electrodes. The cell capacity is modified by varying the length and width of the laser micromachined gap between the pads[9]. Figure 3(b) shows the discharge behavior for a pair of 2.2 mm x 1 mm x 30 µm RuO_xH_y pads and a weight of < 1 mg. As the plot shows, this pads can be discharged uniformly in 1020 sec with a 10 µA drain or in 40 sec with a 100 µA drain. When the cells are linked in parallel, their energy capacity doubles as expected[9]. With further optimization of the cell design, matrix solvents and laser transfer conditions, it is anticipated that the cell performance can be improved by a factor of 5, at which point the RuO_x transferred by MAPLE DW will reach its theoretical levels of power and energy density.

For the MnO_2/Zn batteries, SEM images were taken on individual MnO_2 and Zn pads deposited on Au-coated glass substrates and oven dried, see Figure 4. In order to fabricate a MnO_2/Zn multilayer battery two gold electrodes were made by laser micromachining a trench across the middle of the Au-coated glass substrates. MnO_2 was transferred onto one of the

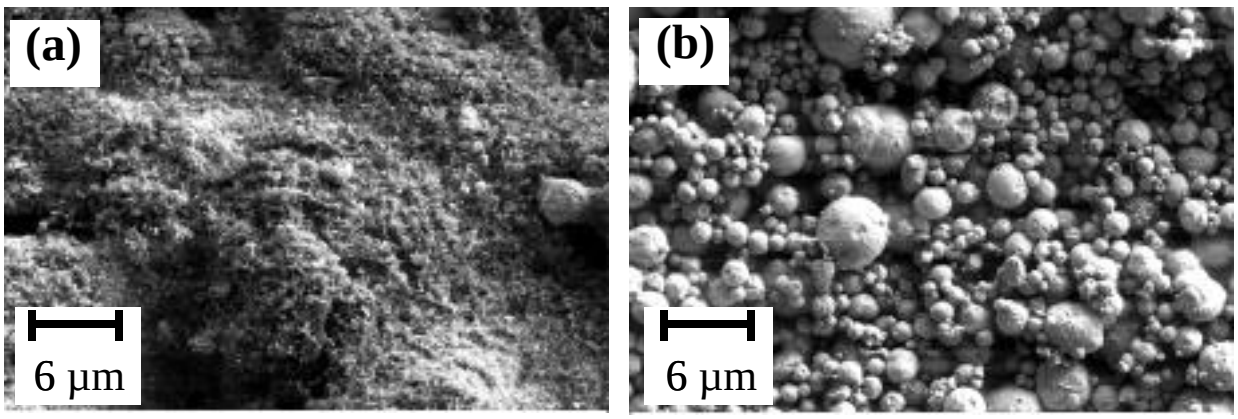

Figure 4. SEM images showing (a) MnO_2 and (b) Zn pads MAPLE DW transferred on a Au-coated glass after oven heating for 30 min. at 200 °C.

electrodes and encapsulated with the ethyl cellulose separator barrier. Then the zinc top electrode was laser transferred across the trench so as to make contact with the surface of the opposite electrode. A schematic diagram showing a side view of the resulting structure is shown on Figure 5(a). Figure 5(b) shows an optical micrograph of the actual structure made by

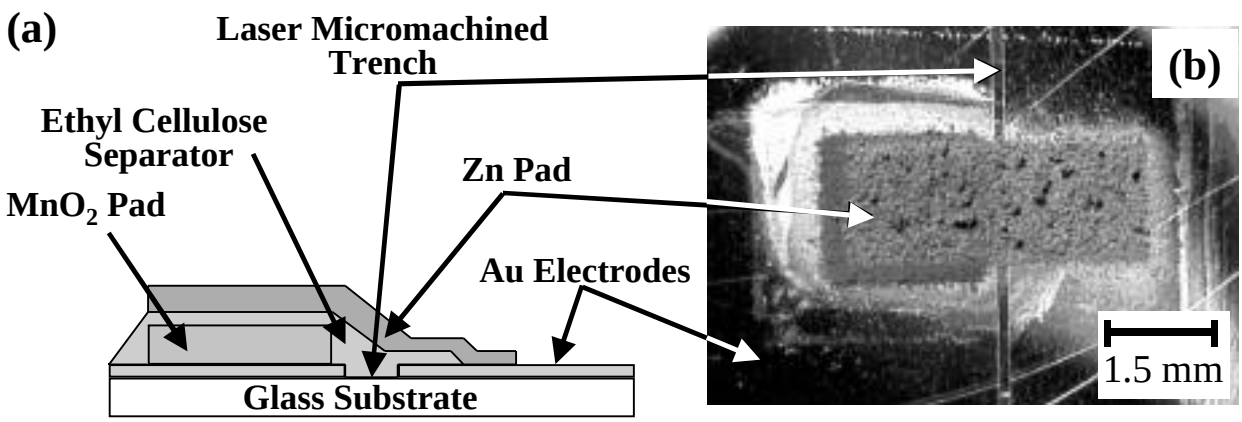

Figure 5. (a) Schematic of a planar MnO_2/Zn alkaline rechargeable battery, showing all its layers. (b) Optical micrograph of a MnO_2/Zn microbattery made by MAPLE DW onto a Au-coated glass substrate.

MAPLE DW. The chronopotentiometry of similar MnO_2/Zn battery was evaluated after being soaked in KOH solution. These measurements prove that the stacked layers in the alkaline batteries are electrically isolated and show that these batteries are energy dense and can be discharged uniformly.

5. SUMMARY

MAPLE DW is an ideal process for the direct write of microbatteries since it operates in air and at low temperatures, conditions which are ideal for the processing of numerous battery materials. MAPLE DW can be used for rapid prototyping of custom-engineered pseudocapacitors and microbatteries in individual or in array type geometries. Cell performance is scaleable and repeatable, and laser micromachined interfaces provide uniform cell discharging. The versatility and CAD/CAM features of the MAPLE DW allow battery systems to be easily reconfigured and integrated with other power sources or electrical components. Many challenges remain, particularly in processing of the materials to optimize cell capacities. Other power sources in development include stacked and planar secondary lithium-ion systems.

6. ACKNOWLEDGEMENTS

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