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Fabrication Of Mesoscale Energy Storage Systems By Laser Direct-Write

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ABSTRACT

Over the last two decades, there has been a trend towards the development of smaller and more autonomous electronic devices, yet the question of how to power these microdevices with correspondingly small power sources remains. To address this problem, we employ a laser forward-transfer process in combination with ultraviolet laser micromachining, to fabricate mesoscale electrochemical power sources, such as microbatteries and micro-ultracapacitors. This direct-write laser-engineering approach enables the deposition of battery materials (hydrous ruthenium oxide, manganese oxide, lithium cobalt oxide, etc.) under ambient temperature and atmospheric conditions, resulting in films with the desired morphological and electrochemical properties. Planar and stacked cell configurations are produced and tested for their energy storage and power delivery capabilities and exhibit favorable performance in comparison to current battery technology.

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. It also requires new strategies to eliminate the long lead times required for the fabrication of prototypes and evaluation of new materials and designs. In particular, for micro-power sources development, the trend is toward the fabrication of sub-millimeter-scale devices which can be incorporated into any type of platform [1,2].

The small size of these power sources introduces new challenges, in particular for the fabrication and packaging of these devices. Traditional approaches for the manufacturing of power sources, such as rolling or pressing powders into metal cans, are not practical when applied to mesoscale systems. Thus, new fabrication techniques are required to develop small power sources that can be integrated with other microelectronic devices.

This paper describes the use of a laser-based direct-write approach, developed at the Naval Research Laboratory, to rapidly deposit and/or process various types of micro-power sources and their associated components. The laser direct-write process has been used successfully for the fabrication of mesoscale energy storage systems, such as micro-ultracapacitors, and microbatteries [3,4].

The first type of micro-power source described in this paper is the hydrous ruthenium oxide micro-ultracapacitor system. This system has a very high specific

capacitance (capacitance per unit mass) and is therefore ideal for small system sizes [5]. These rechargeable devices can be discharged quickly at high power and are thus suitable for circuits with pulsed power requirements, such as for data transmission.

The second system comprises two alkaline chemistry microbatteries, zinc-manganese oxide and zinc-silver oxide. These two common systems are used for numerous applications at the commercial level and have well-established chemistries. They are environmentally friendly and relatively insensitive to ambient conditions. They can be produced in both primary and secondary forms, meaning they can be disposable or rechargeable, although for the purposes of this work, the focus has been on primary cells.

Finally, we have begun work on high-energy, rechargeable lithium-ion microbatteries having lithium cobalt oxide positive electrodes (cathode) and carbon negative electrodes (anode) [6]. These materials have the potential for providing a higher energy and power density than the alkaline system in a rechargeable cell. However, these types of microbatteries are the most challenging since they are sensitive to environmental issues, such as air or water contamination. Ultimately, our goal is to optimize each of these systems to meet the desired power generation requirements for microelectronic applications.

BACKGROUND

Direct-write techniques, which do not require photolithographic processing steps, provide an alternative for the development and fabrication of micro-power sources. Examples of direct-write technologies for fabricating or modifying metallic interconnects and/or other electronic passive elements include ink jet printing [7], direct-write of ceramic slurries (Micropen®) [8], and laser chemical vapor deposition (LCVD) [9]. These techniques excel in certain applications for which lithographic processes are not compatible, i.e., for those applications requiring rapid turnaround and/or pattern iteration, conformal patterning, or patterning onto and over existing components [1]. However, none of the above techniques is capable of operating in air and at room temperature while maintaining near 10- μ m resolution and without requiring *ex-situ* processing. Furthermore, more than one technique must be used to deposit and process the range of materials employed for the fabrication of mesoscopic power sources.

Laser direct-write is a promising approach for the manufacture of integrated micro-power sources since it is compatible with the broad array of materials required to fabricate microbatteries or micro-ultracapacitors. In addition, the laser direct-write system can be used for laser micromachining substrates, current collectors, electrodes and interfaces between materials. This approach offers the ability to prototype custom power sources/systems with optimum power/energy profiles for a particular microelectronic device. Finally the laser direct-write technique allows for the fabrication of micropower sources under ambient conditions, which means that it can accommodate temperature- and vacuum-sensitive battery materials and electrolytes.

The use of laser direct-write to fabricate the next generation of micro-power sources is attractive because it has the potential to satisfy the three requirements of a truly integrated micro-power system. First, it is possible to improve the specific energy and power (energy/power per unit mass) within a system by integrating the power supply directly onto the substrate. This will enable a drastic reduction in the weight of non-

power components in the system. For instance, for a small 5 mm diameter commercial button cell, almost 1/3 of the total mass is due to the stainless steel can used for packaging the active material. If the same battery were to be scaled down to 1mm, the relative mass of the can would now account for over 3/4 of the total mass of the reduced battery.

Second, it is possible to enhance the overall system efficiency by distributing the power to where it is needed. Instead of having one main battery that is fed to multiple devices, a battery at the point of use would eliminate long interconnects and leads from the microsystem. This would reduce ohmic losses, decrease the weight and volume of the total system, plus lower the electromagnetic interference.

Third, and perhaps most important, the power requirements of a micro power source may be met more efficiently if different types of power sources are combined. This is the concept of a hybrid power generating system [2,10]. Such a system may include the ability to deliver energy at various power levels, provide power conditioning and also be capable to harvest energy to enable the energy storage components to be recharged when needed. In this system low power and high energy is delivered by batteries, while high power is supplied by ultracapacitors, and solar cells could be used to harvest energy and recharge the electrochemical power sources.

Batteries

Fundamentally, a mesoscale microbattery is no different from a large scale battery as energy stored as chemical energy is converted to electrical energy through oxidation and reduction reactions. The construction of all electrochemical energy conversion cells consist of 3 major components: anode (negative), cathode (positive), and electrolyte/separator. The electrons for the external load circuit are generated by the oxidation of the active material in the anode. For example, in the case of a Ag_2O -Zn alkaline battery, the Zn metal is oxidized into Zn hydroxide. The resulting electrons go through the load and reduce the active material in the cathode, i.e. the silver oxide is reduced to silver metal. The ions liberated in the process diffuse through the electrolyte/separator towards either the anode or cathode thus completing the circuit. The direction of the ions depend on their charge state. In alkaline cells, negative hydroxide ions move toward the anode while in lithium-ion cells, the positive lithium ions diffuse toward the cathode. The separator prevents the anode and cathode from an electrical short, thereby forcing electrons through the external load. Of course, in order to connect the cell to the outside world, metal current collectors are needed at both the anode and cathode.

To improve battery performance, small amounts of additives are combined with the active material. For instance, since silver oxide is not a very good electron conductor, carbon is added to improve the electronic conductivity. Other additives decrease the formation of gases or self-discharge of the battery. See for example Vincent and Scrosati for an overview of different battery chemistries [11]. Figure 1 shows a simple schematic of a typical battery.

There has been much effort to develop small microbatteries for various primary and secondary chemistries. In one successful approach, the anode, cathode, and solid-state electrolyte are all deposited using standard physical vapor deposition techniques in

vacuum with subsequent patterning through photolithography in order to generate each individual cell [12,13].

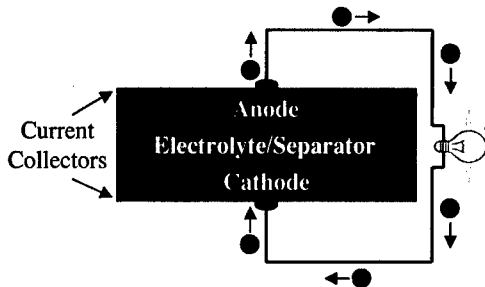


Figure 1. Schematic of a battery cell connected to a load.

Ultracapacitors

An ultracapacitor has properties similar to both batteries and capacitors but lies somewhere in between on the spectrum of energy storage devices. Ultracapacitor cells are constructed by sandwiching an ionically conductive electrolyte between two electrically conductive electrodes. Charge may be stored in a double layer at the interface between the electrodes and electrolyte or in oxidation-reduction reactions at the electrode. There are still an anode and cathode, but in the case of a symmetric device, both of these are the same material.

Like a capacitor, an ultracapacitor has the ability to very rapidly discharge its energy leading to a high power density. However like a battery, it has the ability to store a large amount of energy in the charged state of the active materials. So in the most basic manner, an ultracapacitor can be seen as a battery with a high discharge rate. These devices are typically used for load leveling and applications where short bursts of power are needed. Ultracapacitors go by other aliases such as electrochemical capacitors, supercapacitors, or pseudocapacitors. An excellent discussion on the fundamentals and applications of ultracapacitors is provided by Conway [14].

Laser Direct-Write

Laser direct-write involves the forward transfer of materials from a UV-transparent support to a receiving substrate. The transfers are performed by mixing the active, or sensitive material in a liquid vehicle to form an “ink”, which is applied to the UV-transparent support to form the “ribbon” as shown in Figure 2. The specifics of the laser transfer process have been discussed elsewhere [15,16]. A focused UV laser pulse is directed through the backside of the ribbon so that the laser energy interacts with the ink at the support interface. Because the UV laser pulse is strongly absorbed by the ink, only a very shallow volume of ink at the support interface evaporates due to localized heating from the laser-material interaction. This vaporization forward transfers the

remaining ink by uniformly propelling it away from the support towards the receiving substrate.

By removing the ribbon, the laser pulse can interact directly with the substrate in order to micromachine channels and through vias into polymer, semiconductor, and metal surfaces, as well as trim deposited structures to meet design specifications. All micromachining and material transfer can be controlled by computer (CAD/CAM), which allows the rapid fabrication of complex structures without the aid of masks or moulds. This technique has the potential to generate, by a single tool, complete prototype systems on a substrate including all the components required for a mesoscale energy storage system.

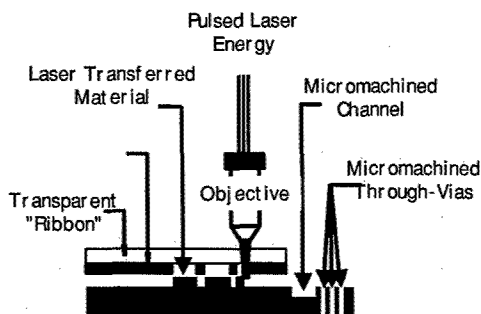


Figure 2. Schematic diagram of the laser direct-write system.

EXPERIMENTAL

Preparation of Ribbons for Laser Direct-Write

Borosilicate glass discs, double side polished, 5.0 cm diameter $\times$ 3mm thick are used as ribbon supports. For the fabrication of the micro-ultracapacitors, commercially available hydrous ruthenium oxide powder (Alfa-Aesar, $\text{RuO}_2 \cdot 2.5\text{H}_2\text{O}$) is oven heated to 150 °C for 18 hours to yield a material with the desired water content of 0.5 mol of H_2O per mol of RuO_2 for optimal charge storage [5]. The dry powder is combined with 5 M sulfuric acid to form a hydrous ruthenium oxide ink. For the fabrication of the alkaline microbattery cathodes, powders of electrolytic MnO_2 (< 425 mesh, JEC) and Ag_2O (< 325 mesh, Alfa) are each mixed with 5–10 wt% graphite (Erachem Super P). The resulting powders are mixed with a solution comprised of PVDF-HFP binder in propylene carbonate until forming a uniform paste to make the MnO_2 and Ag_2O inks respectively. The ink for the anodes is made by mixing, Zn powders (3 μm dia., GoodFellow), in a similar solution of binder in propylene carbonate until forming a uniform paste. Inks for the Li-ion electrodes comprise lithium cobalt oxide, KS6 carbon and an organic binder (PVDF) for the cathode and MCMB 2528 carbon with PVDF for the anode. Both powder mixtures are made into a slurry with 1-methyl-2-

pyrrolidinone(NMP) solvent and mixed until a uniform paste is formed. All the inks are then applied to one side of the borosilicate glass discs using a wire-coater (#6 Gardner) to create a 5 to 10- μm -thick ink layer.

The coated side of the ribbons is kept at a distance of 100–200 μm from the substrate with a spacer. Both the substrate and the ribbon are held in place using a vacuum chuck over the X–Y substrate translation stage. The third harmonic emission of a Nd:YVO₄ laser, $\lambda = 355 \text{ nm}$ (Spectra Physics), is directed through a circular aperture and a 10 $\times$ objective lens, resulting in a 85 μm diameter spot at the ribbon. The laser fluence is varied between 0.1 – 0.5 J/cm² depending on the material being transferred, and is estimated by averaging the total energy of the incident beam over the irradiated area. The mass of the transferred materials is measured using a microbalance (Sartorius M2P).

Fabrication and Testing of Planar Ultracapacitors and Stacked and Planar Microbatteries

RuO_xH_y Ultracapacitors

Planar micro-ultracapacitor electrodes and cells are deposited on 1-cm $\times$ 1-cm gold-coated quartz substrates. Details on the fabrication and testing of these devices are provided elsewhere [3,17]. For the micro-ultracapacitor cells, four current collector pads in the form of a “window pane” are first electrically isolated by UV laser micromachining 20- μm grooves in the surface of the gold-coated substrates. Hydrous ruthenium oxide films, approximately 1-mm $\times$ 2-mm $\times$ 15- μm thick, are then deposited across the machined grooves in the gold-coated quartz and laser micromachined into two identical 0.5-mm $\times$ 2-mm $\times$ 15- μm electrodes. A Nafion film is drop cast on top of the micro-ultracapacitor cell and allowed to air dry to prevent electrode delamination during testing.

The hydrous ruthenium oxide samples are electrochemically evaluated through cyclic voltammetry (CV) and chronopotentiometry (CP) carried out using an EG&G PAR potentiostat (Model 263). For CV, single electrodes deposited on graphite foil are submerged in a solution of 0.5 M H₂SO₄ in a standard 3 electrode configuration using platinum mesh as a counter electrode and a Pd/H reference electrode that is comparable to a normal hydrogen electrode (NHE). For CP, Nafion-coated planar micro-ultracapacitor cells on the gold-coated quartz substrates are submerged under a droplet of 0.5 M H₂SO₄ and the cell is connected to the potentiostat through a probe station. Data is acquired at specified currents for potentials between 0 and 1 V in this two-electrode configuration.

Alkaline Microbatteries

For the stacked alkaline microbatteries, separate MnO₂ and Ag₂O cathode pads, 3 mm $\times$ 3 mm in area and 40- μm thick, are laser transferred onto 1-cm² gold-coated glass substrates. The pads are heated to 150 °C in an oven for 5 to 10 minutes to remove the propylene carbonate solvent and to bind the powders to the substrate. Then a 4-mm $\times$ 4-mm $\times$ 10- μm thick porous insulating layer is laser transferred over each of the MnO₂ and Ag₂O pads to serve as the separator between the metal oxide cathode and the Zn anode. A Zn layer is laser transferred onto the separator in the form of a 2.5-mm $\times$ 2.5-mm $\times$ 20- μm thick pad. At this point, the resulting MnO₂/separator/Zn and Ag₂O/separator/Zn structures are ready for evaluation. For the planar alkaline microbatteries, a four finger

interdigitated structure, 5-mm long by 2-mm wide is formed by depositing interdigitated pads for the Ag_2O cathode and Zn anode onto a laser micromachined Pt-coated alumina substrate, oven drying the pads and then laser micromachining the gap between the pads to remove any debris that could cause a short between the pads.

To characterize the discharge behavior of the zinc/ MnO_2 and zinc/ Ag_2O alkaline microbatteries, a droplet of 9 N KOH is placed on top of the cells. Then, CP measurements are performed using a probe station connected to the potentiostat. Additional information on the characterization and results of alkaline microbattery cells made by laser direct-write appears elsewhere in this proceedings volume [18].

Li-ion microbatteries

The Li-ion electrodes are fabricated onto separate substrates as pads $3\text{-mm} \times 3\text{-mm} \times 40\text{-}\mu\text{m}$ thick. Composites of LiCoO_2 , carbon, and PVDF are transferred onto aluminum foil substrates/current collectors while the carbon/PVDF composite is transferred onto copper foil to serve as the positive and negative electrodes, respectively. After laser transfer, the electrodes are dried in a vacuum oven for 12 hours at 110°C . The electrodes are transferred to an Ar atmosphere and submerged in a 1 M LiClO_4 /propylene carbonate electrolyte solution for at least 12 h prior to electrochemical evaluation.

Single electrodes are evaluated in half-cell measurements by CV at 0.1 mV/sec using the potentiostat and CP using a battery tester (Maccor model 2300). These three-electrode half-cells utilize a Li-foil (Li/Li^+) reference electrode and Li-foil counter electrode that are aligned with 1 cm of the LiClO_4 /propylene carbonate between them [6]. The C negative electrodes are cycled between 1 and 0.05 V vs. Li/Li^+ and the LiCoO_2 positive electrodes are cycled between 3 and 4.2 V vs. Li/Li^+ at various charging and discharging rates. CP is also carried out on full cells where the positive and negative electrodes are also referenced to a (Li/Li^+) reference electrode and aligned with 1 cm of electrolyte between them. There are no rest periods between the multiple charge and discharge cycles.

RESULTS AND DISCUSSION

The layers of the various materials for micro-power sources deposited by the laser direct-write process show similar morphological and electrochemical properties when compared to layers deposited by stenciling. Figure 3 shows scanning electron microscopy (SEM) images of the surfaces of laser transferred films comprising $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$, $\text{Ag}_2\text{O} + \text{C}$ and $\text{LiCoO}_2 + \text{C}$. It is apparent from these images that the laser transfer process does not result in any obvious changes to the morphology of each of these systems, as there are no indications of melted or fractured material on these length scales.

The hydrous ruthenium oxide pad from a laser transferred micro-ultracapacitor has a uniform mesoporous structure that enables the electrolyte to reach all the way into the bulk of the electrode layers, thus allowing a more effective use of the active material (Fig 3a). Figure 3(b) belongs to a silver oxide + carbon layer from one of the alkaline microbatteries. Here again, a porous structure can be observed, together with micron and submicron-sized particles corresponding to the Ag_2O powders. The nanometer scale structures are the porous carbon material, which is evenly distributed through out the pad.

This carbon provides the high electronic conductivity not present in the silver oxide. In addition, it allows electrolyte penetration into the cathode allowing more efficient use of the electrode material. Finally, figure 3(c) shows a LiCoO_2 layer from one of the Li-ion microbatteries. In this case, the high porosity carbon regions can be seen, while the dense material belonging to the LiCoO_2 powders shows a flattened plate structure. This lithium cobalt oxide powder structure facilitates the intercalation of lithium into the lattice leading to higher capacities. These images demonstrate that the laser direct-write

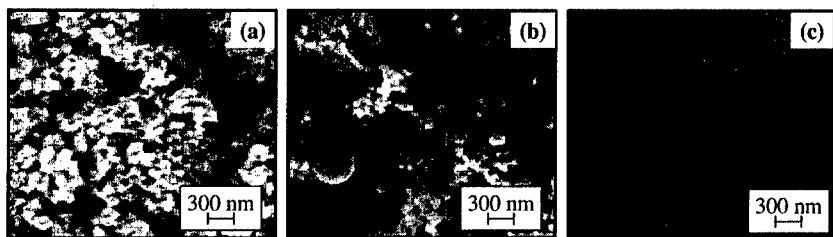


Figure 3. SEM micrographs from the surface of (a) $\text{RuO}_2 \cdot 2.5\text{H}_2\text{O}$, (b) $\text{Ag}_2\text{O} + \text{C}$ and (c) $\text{LiCoO}_2 + \text{C}$ laser transferred films.

technique allows for the deposition of high-surface area, structurally defective and porous materials, which are ideally suited for electrochemical systems.

Planar Micro-Ultracapacitors

Figure 4(a) shows an optical micrograph of a pair of laser transferred planar micro-ultracapacitors. The volume of each cell is 2×10^{-5} ml and the mass is less than 0.1 mg per cell, which is less than the mass of a human hair. The charge and discharge behavior of these micro-ultracapacitors has been evaluated for single cells and for pairs of cell connected in series and in parallel. Figure 4(b) shows the CP plots for charge and discharge at currents of 50 and 10 μA respectively for a single cell, and for series and

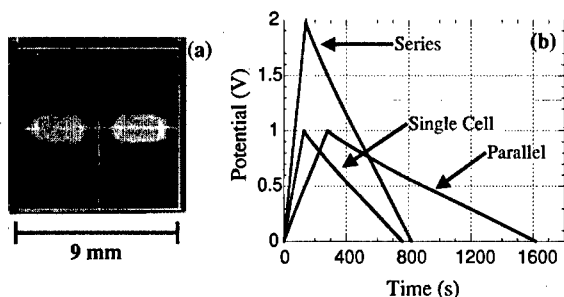


Figure 4. (a) Optical micrograph of a planar micro-ultracapacitor on a gold-coated substrate fabricated by laser direct-write. (b) Chronopotentiometry data from a single cell and from a pair of ultracapacitors connected in series and in parallel, all charged at 50 μA and discharged at 10 μA .

parallel configurations of two cells. The single cell and the pair connected in parallel are charged to 1 volt, while the series configuration is charged to 2 volts. In all cases the discharge behavior remains nearly linear. The discharge times are over 10 minutes at this current. For the single ultracapacitor, the capacitance calculated from this plot, is 6.5 mF. This corresponds to a specific capacitance of ~ 80 F/g when normalized by the measured mass of the laser transferred material (active material plus electrolyte). Furthermore, the capacitance of the series and parallel combinations measured from the plot are in agreement with the appropriate addition of single cell capacitances.

Stacked and Planar Alkaline Microbatteries

Figure 5(a) shows a schematic for the cross-section of a stacked alkaline microbattery cell made by laser direct-write. Figure 5(b), shows a set of optical micrographs illustrating each of the laser transferred layers resulting in a zinc/ MnO_2 alkaline microbattery made on top of a gold-coated glass substrate. After the zinc pad is laser deposited, a graphite foil current collector is placed on top of the zinc and the microbatteries are ready to be tested. The stacked zinc/ MnO_2 alkaline microbatteries all showed open circuit potentials of ~ 1.3 V, which are lower than the expected value of 1.5 V.

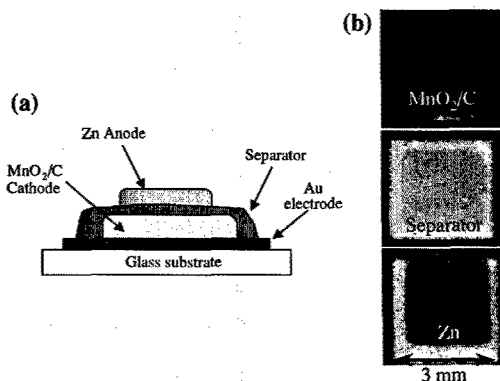


Figure 5. (a) Cross section schematic of a stacked alkaline microbattery made by laser direct-write. (b) Optical micrographs showing each of the layers present in a Zn/ MnO_2 alkaline microbattery.

Figure 6(a) shows an optical micrograph of an interdigitated planar zinc/ Ag_2O microbattery made by laser direct-write. The open circuit potential for the planar cells is 1.55 V, which is to be expected for the silver-oxide/zinc system. Figure 6(b) shows the discharge behavior for the same interdigitated planar cell at a discharge current of 25 μA . The data shows that the planar alkaline microbattery made by laser direct-write has discharge characteristics similar to those from an ideal zinc/ Ag_2O battery. However, the actual capacity for the cell is lower than would be expected from the theoretical capacities of the materials used. After post discharge analysis of the cell, it was

determined that the failure of the cell was due to delamination of the Zn anode. It should be pointed out that none of the alkaline microbattery cells fabricated for this work were packaged and thus the KOH electrolyte solution would evaporate with time. Future work will focus in increasing the specific energy of these alkaline microbatteries, and in developing and testing various packaging approaches.

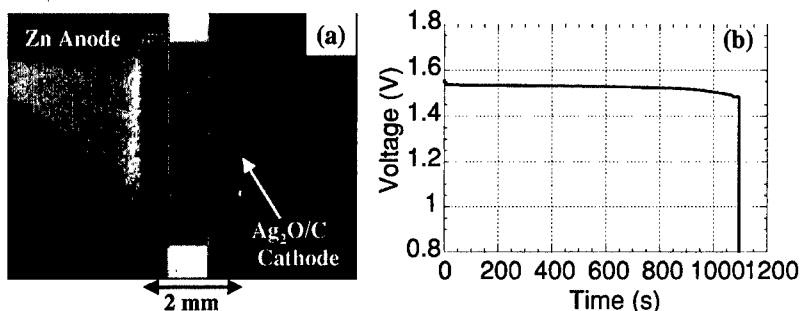


Figure 6. (a) Optical micrograph of a planar interdigitated Zn/Ag₂O microbattery fabricated by laser direct-write on a Pt-coated alumina substrate. (b) Discharge behavior at 25 μ A from this microbattery. The sudden drop at $\sim$ 1100 seconds is due to delamination of the Zn anode.

Li-ion Microbatteries

The electrodes fabricated using the laser direct-write system for a Li-ion microbattery are shown in Figure 7. The Cu and Al foil current collectors are laser micromachined to the required shape, while the carbon anode and LiCoO₂ cathode are laser deposited in 3 mm $\times$ 3 mm pads. Each of these electrodes show excellent capacities in half-cell measurements [6]. Adhesion of the active materials to the current collectors appears to have a large impact on the measured capacities.

Under full cell measurements, a specific discharge capacity of 40 mAh per gram of LiCoO₂ is measured when cycled between 3 and 4.2 V. The capacity continuously increases over the duration of the experiment (after 325 hours of operation and 57 cycles, the capacity is still increasing). The capacity of the cell is lower than the expected 125 mAh/g presumably due to water contamination in the dry box. Future work will focus on eliminating water contamination in the test environment, plus optimizing various packaging schemes.

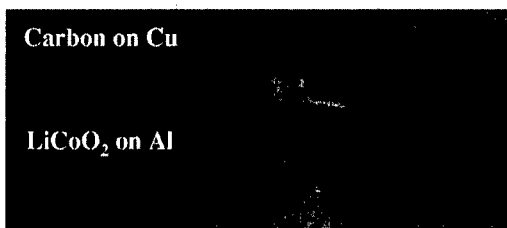


Figure 7. Optical micrograph of a LiCoO₂ cathode pad and a C anode pad laser forward transferred onto Al and Cu current collectors respectively.

SUMMARY AND OUTLOOK

We are applying a direct-write laser engineering technique to the production of integrated and distributed hybrid micropower sources that include planar micro-ultracapacitors, planar and stacked microbatteries and in the future, energy harvesting components. Using laser direct-write in combination with ultraviolet laser micromachining, we have successfully fabricated hydrous ruthenium oxide micro-ultracapacitor cells, primary alkaline manganese-oxide/zinc and silver-oxide/zinc microbatteries in planar and stacked configurations, and secondary Li-ion microbattery electrodes. In most cases, the prototype systems tested for this work showed the expected open circuit potentials and exhibited uniform discharge behavior under constant loads. Several challenges remain such as further increasing the capacity and longevity of these mesoscopic power sources. Future work will focus in addressing these issues plus optimizing the packaging of these devices.

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