

Manufacture of Mesoscale Energy Storage Systems by Laser-Direct Write

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ABSTRACT

The development of micro power systems, on the mm size scale, is necessary for emerging technologies in small, portable micro-electronic device applications. Direct-write processes are used to produce the high-power, low-power, and recharging elements of such mesoscale micro power systems. Successful fabrication of alkaline and lithium based micro-batteries, micro-ultracapacitors, and dye-sensitized micro-solar cells are possible on various low processing temperature and flexible substrates using laser direct-write approaches that are ideally suited for the many different structurally complex electrochemical materials used in these systems. Increased areal energy density is realized by depositing thick layers $> 10 \mu\text{m}$, while maintaining patterns as small as 2mm^2 . Micro-ultracapacitors exhibit high power densities $> 250 \text{mW/cm}^2$, while primary alkaline microbatteries exhibit open circuit potentials of 1.5 V with high capacities and discharge currents up to 1 mA. Secondary LiCoO_2 and LiMn_2O_4 based microbatteries employing a novel nanocomposite solid-state electrolyte exhibit open circuit potentials $> 4 \text{V}$ and have shown multiple recharging cycles without loss of capacity. Results of the different systems will be discussed with particular emphasis on the combination of elements to produce hybrid micro power systems.

Keywords: laser direct write, microbattery, micro power, MEMS, ultracapacitor, photovoltaics

1. INTRODUCTION

Dramatic reductions in the size of microelectronic and microelectromechanical devices has been fueled in recent years by advances in integration and processing techniques [1]. While these new devices have been used as components in larger sensor, actuator, and control systems, the lack of commensurately sized power sources to meet their energy demands has limited their ability to function autonomously. Ambient-condition, laser direct-write processes permit a new solution to this challenge by directly integrating micro electrochemical power sources into the microdevice package, saving valuable weight and space.

Common electrochemical systems for energy storage such as ultracapacitors, batteries, or solar cells are composed of three main internal components: the negative electrode or anode, positive electrode or cathode, and electrolyte/separator. Each of these components is typically constructed of materials with a large degree of structural complexity, such as nanocomposites, solid-state polymers, liquids, or mesoporous mixtures of electrochemically active materials [2]. The unique challenge for mesoscale power sources is to maintain their electrochemical and structural integrity in a confined space subject to the limitations, such as temperature and pressure, imposed by the microdevices, their substrates and packaging. Furthermore, in order to meet the power demands of a given microdevice, combinations of different types of cells, or hybrid power systems, are needed [3]. For instance, an application may require constant low power (lithium or alkaline microbattery), an occasional short burst of energy (ultracapacitor or capacitor), and the ability to be recharged (solar cell).

In this paper, we survey the fabrication and characterization of different mesoscale electrochemical systems including ultracapacitors [4], alkaline microbatteries [5], and lithium microbatteries [6] to meet the demands of microdevices. The detailed electrochemical results for these different systems appear in the literature. Laser direct-write processes provide a general set of processing tools that can rapidly prototype and fabricate these different electrochemical energy storage components. In these cases, the systems obtained exhibit the appropriate voltage characteristics with significant charge storage capabilities.

2. EXPERIMENT

2.1. General Laser Direct-Write

Laser direct-write is a general term that encompasses modification, subtraction and addition processes that can create patterns of materials directly on substrates without the need for lithography or masks [7]. Given a laser source, one can fix the location of the beam and raster the substrate using motion control stages, fix the substrate and raster the beam using mirrors, or a combination of the two. For laser direct-write modification (LDWM) or subtraction (LDW-), one directly irradiates the material of interest and either removes (laser micromachining) or modifies it (melting, sintering, etc.). In both cases, either pulsed or CW lasers may be used effectively.

Our method of laser direct-write addition (LDW+) is shown schematically in figure 1 [8,9]. In this forward-transfer process, we begin with the material of interest for the particular electrochemical system in powder form and combine it with a liquid carrier to form an ink. The ink is spread on a glass plate and fixed approximately $100\ \mu\text{m}$ from the substrate. A pulsed UV laser irradiates the ink from behind the glass plate to propel a mass of material forward to the waiting substrate below [10]. Rastering of either the beam or the substrate produces the desired pattern of material. This ambient process can attain LDW+ resolutions down to $25\ \mu\text{m}$, while LDW- and LDWM resolutions can be as small as $1\text{-}5\ \mu\text{m}$ using appropriate focusing optics. In contrast to many other direct-write deposition techniques available, LDW+ is able to print highly acidic, caustic, or other chemically reactive materials, an important consideration for these electrochemical systems.

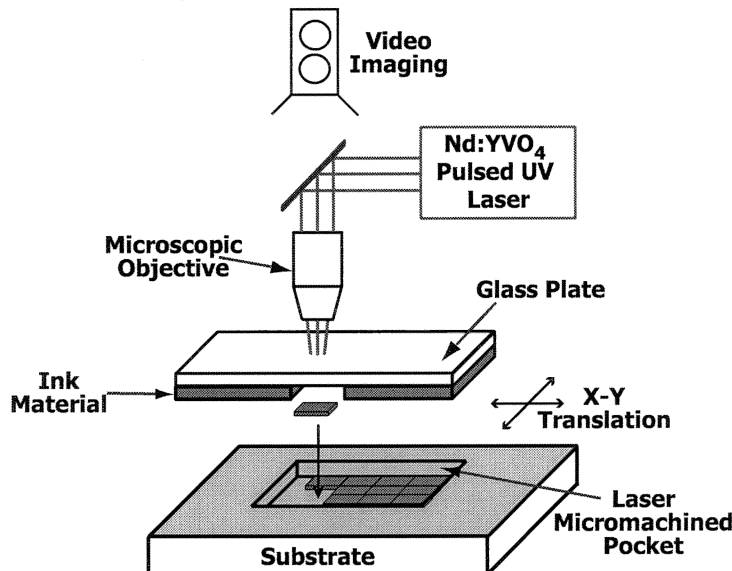


Figure 1. Schematic of LDW+ apparatus. LDW- and LDWM setup is obtained by removing the glass plate and ink.

Originally, LDW+ was developed to deposit “electronic grade” materials such as metals for interconnects, cermets for resistors and dielectrics for capacitors [7], but it quickly became evident that the porous and wet nature of the as-deposited materials were not optimal for these types of systems. Fortunately, the same features of the deposited materials that make laser direct-write less than perfect for electronic grade materials, make it ideally suited for creating mesoscale patterns of the electrochemically active materials for micro power sources.

For this review, representative materials include commercially available $\text{RuO}_2 \cdot 0.5\ \text{H}_2\text{O}$ for ultracapacitors, Zn and Ag_2O for alkaline microbatteries, and C and LiCoO_2 for lithium microbatteries. H_2SO_4 , KOH, and Di-basic ester solutions, respectively are used as the liquid carriers. Binders (Polyvinylidene difluoro-Hexafluoropropylene or PVdF-HFP) and conductivity enhancers (Super P graphite) are added to the powders prior to ink formulation to improve microbattery properties. The subsequent ink is spread on a borosilicate glass plate using a wire-coater to form a $5\text{-}10\ \mu\text{m}$ thick coating. A frequency-tripled Nd:YVO₄ laser ($\lambda=355\ \text{nm}$) with typical laser energies between $10\text{-}25\ \mu\text{J}$ in a $120\ \mu\text{m}$ diameter spot

corresponding to a fluence for transfer approximately $0.1\text{-}0.2\text{ J cm}^{-2}$. The mass of the transferred material is accurately measured using a microbalance with μg resolution.

The laser direct-write processes that we employ should not be confused with typical thin-film material processing such as vacuum deposition or chemical vapor deposition. Films deposited by LDW+ can be made arbitrarily thick by simply adding layers of materials in the same location (typical thin-film processes become difficult above $1\text{-}5\ \mu\text{m}$). This approach can place a larger mass of active material in a fixed footprint, yielding higher energy and power densities than can be made with conventional thin film approaches. Furthermore, the laser direct-write technique is not chemistry specific so that the different materials required for ultracapacitors, microbatteries, or solar cells can all be accommodated in the same "tool" by simply changing the ink.

2.2. Processing and Characterization

Once the inks are transferred, they must be processed to obtain the final structural properties. In some cases, such as the planar geometries, this requires the use of LDW- to shape the material into the desired electrode pattern. In other cases, such as in the microbatteries, the carrier liquid must be removed either locally through LDWM, or globally by gentle heating in an oven ($T < 150\text{ }^\circ\text{C}$).

Electrochemical evaluation of cell voltage and discharge behavior is carried out using a potentiostat (EG&G PAR Model 263) connected to a probe station. Cyclic voltammetry is used to characterize the capacity of the electrode materials while chronopotentiometry is used to determine the energy and power density of the systems.

3. DEVICE FABRICATION

The most important aspect of laser direct-write processes as they are applied to micro power sources is that they do not harm the electrochemical or structural properties of the transferred materials for the laser energies used. Microstructural characterization by SEM and X-ray diffraction shows no significant difference between the starting ink (stenciled) and the laser transferred material. Figure 2 demonstrates this point for the LiCoO_2 microbattery cathode and amorphous $\text{RuO}_2 \cdot 0.5\text{ H}_2\text{O}$ ultracapacitor electrode. The XRD shown in the figure for LDW+ and stenciled material in both cases show the characteristic crystal peaks for the system with no quantifiable difference between them.

The wet, porous structures that are present after LDW+ exhibit extremely high surface areas allowing more complete contact between the electrodes and the electrolyte and therefore enabling better charge transfer and a more complete utilization of the electrode materials. Similar consistencies are observed in the electrochemical behavior (cyclic voltammetry and chronopotentiometry) of the materials between the laser transferred and stenciled samples [11, 12].

We attribute the successful deposition of materials to the proposed underlying mechanism that the laser energy is absorbed in a small region near the ink/glass interface, generating a local vaporization of material. Expansion of this vapor causes the majority of the ink to be propelled forward although it has not directly encountered the incident laser. This same "gentle" mechanism successfully enables living cells to be deposited unharmed to a substrate below [13].

3.1. Planar Structures: Ultracapacitors and Alkaline Microbatteries

Conceptually, the simplest system to construct is one in which the electrodes of the electrochemical cell are arranged adjacent to each other. The first example of this shown in figure 3a is a symmetric hydrous ruthenium oxide micro-ultracapacitor. We use LDW+ to deposit a uniform layer $1000 \times 2000 \times 20\ \mu\text{m}$ of the hydrous ruthenium oxide/sulfuric acid ink. LDW- is used to machine the deposited material in order to isolate two electrode pads as shown in the figure, that are separated by a small ($20\ \mu\text{m}$) gap. Prior to machining, excess water is evaporated from the transferred materials either through conventional oven baking at $150\text{ }^\circ\text{C}$, or LDWM using IR laser irradiation. Overall size and mass of these systems is exceedingly small at $< 100\ \mu\text{g}$. Our recent progress with LDWM has enabled us to devise methods of separating the electrodes and refilling the gap with liquid electrolyte in a single processing step [14].

Planar alkaline microbatteries represent the next level in complexity since they require two different materials for the positive and negative electrodes. In this case, we have developed a standard alkaline chemistry of Zn anode, Ag_2O cathode and KOH electrolyte. By mixing the electrode materials with KOH electrolyte we use LDW+ and LDW- to create planar geometries such as non-compact, interdigitated, or circular structures of varying shapes and sizes (figure 3b and c). As

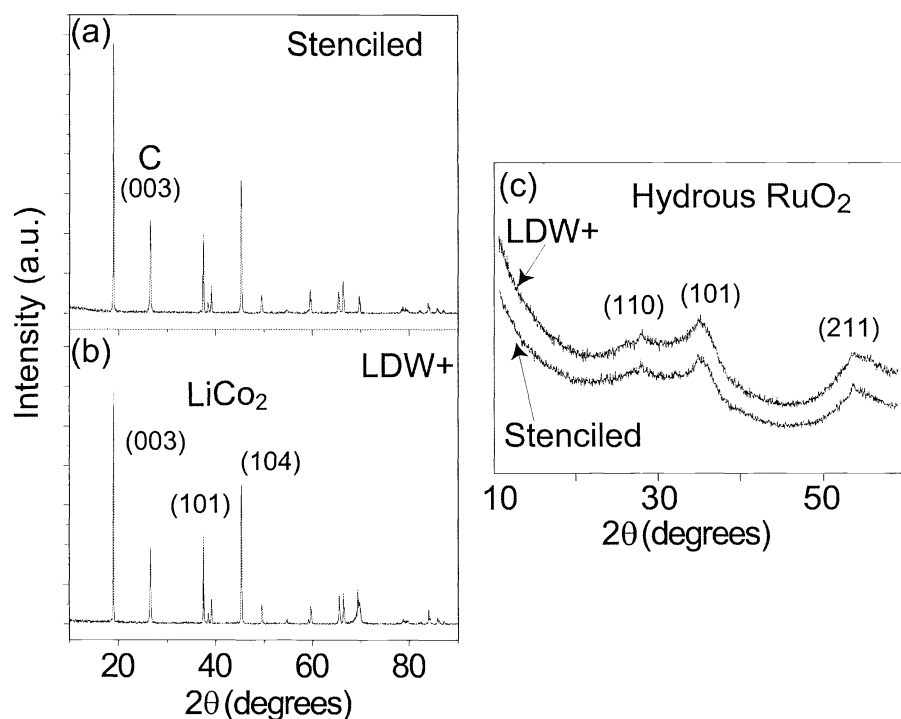


Figure 2. XRD curves for LiCoO₂ cathode and RuO₂ · 0.5 H₂O electrode material. (a) LiCoO₂ material prior to laser transfer and (b) LiCoO₂ after laser transfer. (c) RuO₂ · 0.5 H₂O before and after laser transfer.

in the ultracapacitor case, these materials are processed after deposition in order to use LDW- to completely isolate the electrodes. A droplet of KOH is added to the system after fabrication to fully activate the cell. In these cases, the total mass of both anode and cathode is in the range 200-500 μg , but, the mass is not evenly distributed between the two. Since the capacity of Zn is significantly larger than that of Ag₂O, the mass is scaled proportionately to optimize the active material usage in the battery. Although in theory, the Zn-Ag₂O battery system exhibits the ability to be recharged [2], we have not optimized our system for this feature.

3.2. Stacked Structures: Lithium-ion Microbatteries and Solar Cells

Planar structures are relatively easy to construct, but, stacking the electrodes on top of one another provides more efficient use of limited material and space. These structures require materials that are rigid enough to support the upper layers but ones whose electrochemical properties are not compromised. To this end, we have focused attention on the rechargeable lithium-ion microbattery system, which presents many unique challenges to developing an ambient process that will not harm the sensitive chemistry. For this chemistry, we are using a LiCoO₂ cathode material with a graphite additive to improve electronic conductivity, and a graphite anode material. A key feature of our system is the use of a novel hydrophobic nano-composite solid polymer ionic liquid (c-SPIL) separator material. This material has high ionic conductivity in comparison to other solid state conductors (1-2 mS/cm compared to 0.01 mS/cm) and is chemically and structurally stable [6].

Figure 4 shows the basic geometry where we have used LDW+ to deposit sequential layers of cathode (LiCoO₂ + graphite), c-SPIL, and anode (graphite) into a 3000 x 3000 μm pocket on a thin polyimide substrate machined by LDW- (figure 4b). The cathode, separator, and anode are deposited in order followed by a short oven bake at 75 °C for 10 minutes between layers to remove the excess di-basic ester. The final battery structures are baked at 75 °C for 2 days prior to being placed in a dry Ar atmosphere for testing. This layered structure is significantly thicker (30-50 μm) than a typical thin-film

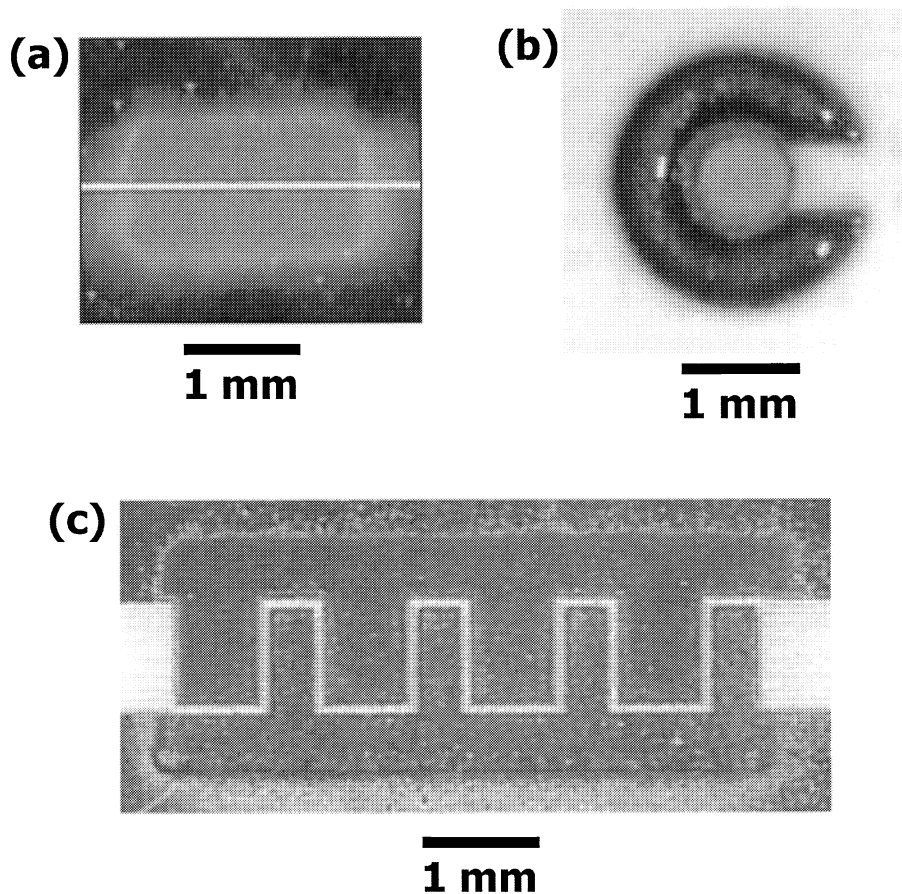


Figure 3. Optical micrographs of functioning planar electrochemical cells by laser direct-write. (a) $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ ultracapacitor structure with symmetric electrodes (total mass < $100 \mu\text{g}$), (b) embedded alkaline microbattery, Zn anode is center gray circle, Ag_2O cathode is outer ring (total mass < $200 \mu\text{g}$), (c) interdigitated alkaline microbattery, Zn anode is lower half, Ag_2O is upper half (total mass < $300 \mu\text{g}$).

microbattery structure ($1\text{-}5 \mu\text{m}$) yet thin enough to remain entirely embedded in the substrate as shown in the figure. The cross-section of the battery shows the distinct layers of the microbattery components.

4. RESULTS SUMMARY

The micro-ultracapacitors are subjected to a constant current charging and discharging to determine the charge storage and power delivery behavior [4]. The constant current discharge on these cells exhibits the expected linear discharge behavior, as shown in figure 5a up to 1 mA discharge with deviations due to ohmic losses at higher currents up to 50 mA . The overall capacitance is calculated from the area under the discharge portion of the curve and is large, $6\text{-}8 \text{ mF}$ corresponding to $300\text{-}400 \text{ mF/cm}^2$ for 20 mm thick electrodes. Output power greater than 2 mW or 100 mW/cm^2 is attainable for a single cells. The parallel and series combinations of cells add appropriately, yielding larger systems with higher voltage or charge storage.

Typical constant current discharge curves for two individual alkaline cells (similar to that of figure 3b with total footprint of 5 mm^2) of different mass are shown in figure 5b at currents of 10 and $20 \mu\text{A}$ [5]. The open circuit potential for both cells is measured to be 1.55 V . Upon discharge, there is a small initial drop in voltage followed by the characteristically

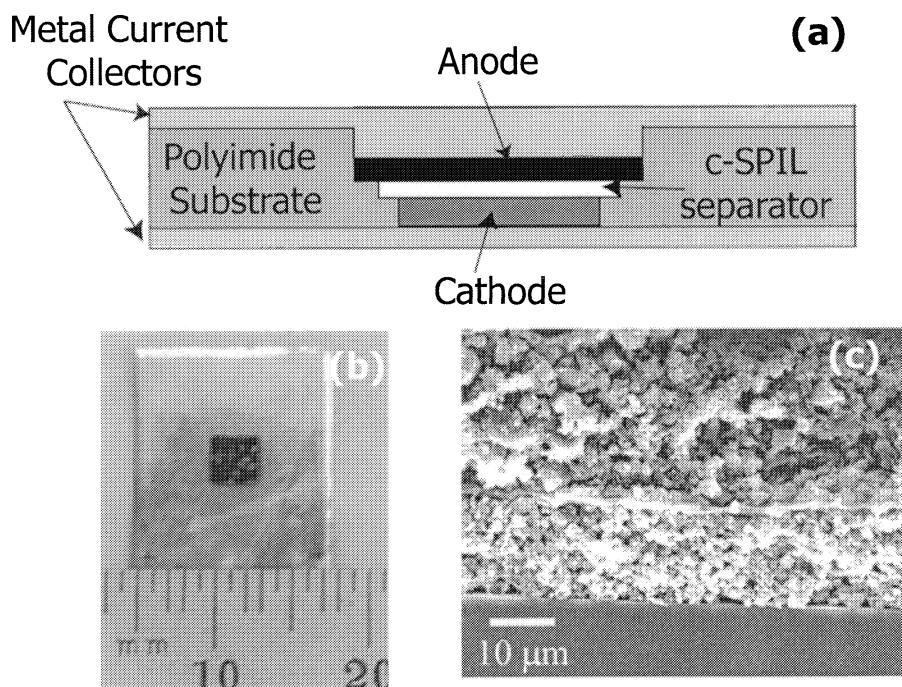


Figure 4. (a) Cartoon of embedded stacked Li-ion microbattery. (b) Plan-view of battery structure. Entire cell fits within 3 x 3 mm. (c) Cross-section SEM micrograph showing the anode (upper region), cathode (lower region), and separator (center) layers. Total mass of microbattery 600-800 μg .

flat behavior that is expected for the $\text{Zn-Ag}_2\text{O}$ system [15]. 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. Discharge times greater than 4000 seconds are easily obtained at both discharge currents for the given electrode masses. These curves demonstrate energy densities greater than 650 mWh/cm^2 from 5 mm^2 cells discharging at $20 \mu\text{A}$.

Figure 5c shows the charging and discharging curve for the 50th cycle of a 9 mm^2 Li-ion microbattery [6]. The duration of the discharge at $9.9 \mu\text{A}$ is 3 hours, over which the average voltage of the cell is 4 V. This results in a high energy density for the system of 1300 mWh/cm^2 . Results on multiple cycles of charging and discharging these cells show the average voltage and capacity exhibit only minor degradation in properties with a decrease of only 4% over 100 cycles.

Figure 6 summarizes the results for the three different systems on a modified Ragone plot. Here we have plotted the energy and power density by the 2-D area on the substrate that is occupied by the microbattery or ultracapacitor. The energy density from both microbattery chemistries is comparable with the maximum values reported in the literature for lithographic and vacuum fabrication techniques [16, 17]. Additional improvement in both power and energy density through optimization of the materials and processing is possible through laser direct-write techniques.

5. CONCLUSIONS

There is currently a demand for small scale power systems that are compatible with present and future advances in microdevice technology. The use of laser direct-write processes to fabricate micro power systems can satisfy this demand. These ambient and low temperature techniques enable mesoscale electrochemical power sources on most types of rigid and flexible substrates and even within the substrate. One of the key aspects of this technique is in the ability to process a wide range of structurally and chemically sensitive materials in complex 2-D and 3-D patterns. Thus a single tool can not only produce a particular type of electrochemical cell, but with only a simple change in the ink, it can also be used to

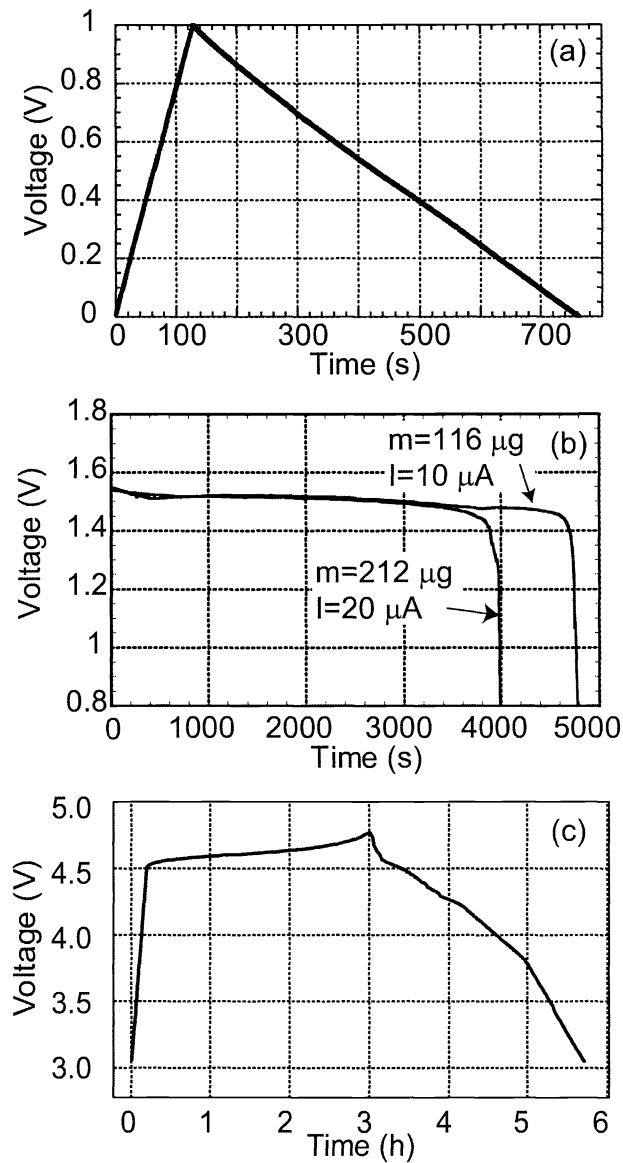


Figure 5. Chronopotentiometry for different electrochemical systems. (a) micro-ultracapacitor system charged at $50 \mu\text{A}$, discharged at $10 \mu\text{A}$, total electrode mass $80 \mu\text{g}$. (b) alkaline microbattery system discharged at 10 and $20 \mu\text{A}$, total electrode mass noted on plot. (c) Li-ion microbattery system charged and discharged at $C/3$, corresponding to $9.9 \mu\text{A}$, on cycle 50. Total mass $800 \mu\text{g}$.

produce other elements of a hybrid system. We have shown the ability to make high power density micro-ultracapacitors as well as high energy density microbatteries in both primary and secondary chemistries on a variety of substrate materials. In all cases, the systems behaved as expected in terms of voltage, and discharge characteristic and demonstrated excellent power delivery and energy storage due to the beneficial structures of the deposited materials. Recent work using the same combination of laser-based processes, have enabled us to develop nanoparticle TiO_2 based solar cells [18] that may be used in a hybrid configuration to recharge an ultracapacitor or microbattery. However, the versatility to deposit and process materials is not limited to micro power sources, but could also significantly benefit applications in catalytic, sensor, or bio

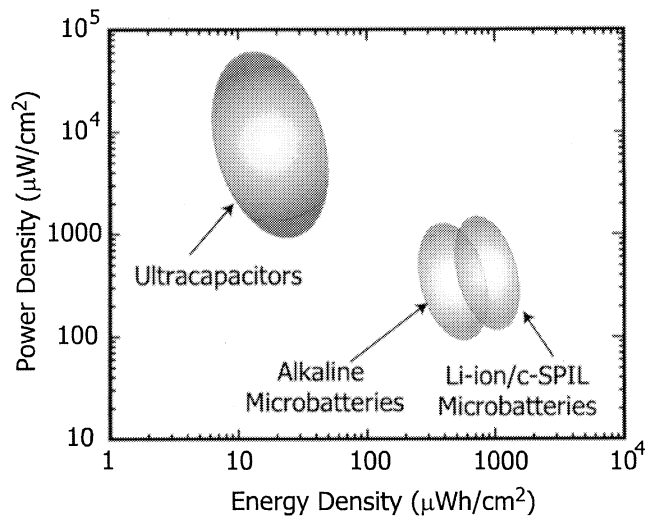


Figure 6. Summary of results for different electrochemical systems on a Ragone plot. Shaded regions correspond to the ranges of values obtained in our system. All values have been normalized by the 2-d area of the mesoscale electrochemical device.

materials. The extension of laser processing to non-traditional areas such as these, opens doors to new possibilities for advanced devices in a wide variety of fields and will have a lasting impact on future technology.

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