

DIRECT-WRITE MICROBATTERIES AS INTEGRATED POWER SOURCES FOR MICROELECTRONIC DEVICES

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We are using a novel laser-based direct-write process to rapidly prototype and fabricate microbattery systems for microelectronics. A range of battery designs and arrays can be fabricated with this low-temperature, ambient-pressure, CAD/CAM process using commercially available materials. The capacity of the batteries can then be tuned to optimize the performance of a specific device. We demonstrate this with the fabrication of planar RuO_xH_y pseudocapacitors. The width and sizes of the cell interfaces are micromachined with the same laser system to change the capacity of the systems. The cell performance is repeatable and can be easily integrated into arrays to modify the capacity of the system.

INTRODUCTION

State-of-the-art portable electronic devices are crippled by inadequate or poorly matched power sources, and this trend is predicted to continue. For the successful implementation of the next-generation of miniaturized electronic devices, a parallel progression in the development of adequate power sources is required. The disadvantage of using batteries as micropower sources is that the power and energy of batteries scale with their size, so small batteries can only deliver low levels of energy. The advantage of pursuing microbattery development is that the manipulation of battery chemical systems and designs are well understood, and microbatteries will not have many of the safety issues (e.g., run-away heat) that trouble large battery systems. Therefore, batteries are likely to be used as either the sole power source or as a component in hybrid power sources for next-generation electronic devices.

One of the challenges in developing power sources for electronic devices that are still under development is that the power requirements are application specific and often not yet known. Different 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 batteries. Others will demand secondary batteries with integrated recharging systems to allow years of low- to no-maintenance operation.

We are exploring a new laser-based process to rapidly design and fabricate prototype batteries with tailored capacities for small electronic devices having size and/or weight restrictions. The MAPLE DW (Matrix-Assisted Pulsed-Laser Evaporation Direct Write) process has been developed at the Naval Research Laboratory to deposit rugged mesoscale (1 μm to 1 mm) electronic components.^{1,2,3} The material for each component is mixed with a viscous vehicle (e.g., a high molecular weight hydrocarbon) to form a matrix which is then tape cast as 1 to 10 μm thick film onto a UV-transparent substrate to create a "ribbon." A pulsed UV-laser operating at 355 nm then forward transfers the component material from the ribbon onto a desired substrate under ambient pressure and temperature conditions. The UV light reacts predominantly with the vehicle, so the

component material is not damaged during the transfer. The amount of material transferred is a function of the spot size of the laser (10 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 (20 μm) intricate designs. Subsequent laser micromachining can also be used to modify the material design or substrate for systems integration. The transferred material is then usually 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. The performance of the devices is comparable to that of components fabricated with conventional thick-film techniques.

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.

In this manuscript, we demonstrate MAPLE DW as a fabrication technique for power sources by creating planar RuO_xH_y /Nafion pseudocapacitors (or ultracapacitors). Like the hydrous metal-oxides used in aqueous batteries, RuO_xH_y stores charge via the “double-injection” of protons and electrons (Eq. [1]).^{4,5}



The rapid discharge rate of RuO_xH_y is due to its high electronic (or metallic) and protonic conductivity. Specific capacitances as high as 720 F/g have been reported for high surface-area materials with the composition of $\text{RuO}_x \cdot 0.5 \text{H}_2\text{O}$.⁶ The capacity of the RuO_xH_y decreases significantly when it is annealed at temperatures > 200 $^\circ\text{C}$ and its proton conductivity is low.^{7,8} RuO_xH_y pseudocapacitors are an ideal demonstration system, because they are rechargeable and the cathode and anode have identical compositions.

EXPERIMENTAL

Commercial RuO_xH_y (Alfa) was annealed in a convection oven at 150 $^\circ\text{C}$ for 12 hours.⁶ The powder was ground and sieved through a 325-mesh sieve and then mixed with a small amount of a high molecular weight organic liquid, such as ethylene glycol or glycerin. The opaque ink was cast as a ~ 10 μm -thick thin film onto a quartz plate using a stainless-steel roller to form the ribbon. The RuO_xH_y ink was then transferred to a 1 cm^2 gold-coated glass slide using MAPLE DW with a 355-nm laser having a spot-size diameter of either 65 μm (Quantel) or 20 μm (Spectra Physics). The area and number of

RuO_xH_y pads were easily modified via computer control. A single pass produced $\sim 10\text{-}\mu\text{m}$ thick RuO_xH_y pads, so their thickness was increased to approximately $30\ \mu\text{m}$ by superimposing additional layers RuO_xH_y from fresh areas of the ribbon. Excess solvent was removed from the ink by heating the deposited RuO_xH_y pads to approximately $100\text{ }^\circ\text{C}$ for several minutes either in a conventional oven or using a hot stage integrated with the MAPLE DW substrate holder. The RuO_xH_y pads were then micromachined with the UV laser to sharpen edges and/or divide large pads, and lines were micromachined in the Au substrate to create separate current collectors for the system. The RuO_xH_y pads were then heated in air at $2\text{ }^\circ\text{C}/\text{min}$ to the boiling point of the ink matrix using a conventional oven, held for 1 h, and cooled. A drop of 5% Nafion solution (Aldrich) was dropped with a pipette on top of the RuO_xH_y pads and dried under ambient conditions to the solid state.

The chronopotentiometry of the RuO_xH_y pseudocapacitors 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 morphology of the RuO_xH_y pads was surveyed with optical microscopy and scanning electron microscopy (SEM, Leo 1550), and the thickness of both the RuO_xH_y ink ribbons and the dried RuO_xH_y pads was determined via stylus profilometry (Tencor P10).

RESULTS

The morphology of the RuO_xH_y pads is highly dependent on the organic vehicle used in the matrix. RuO_xH_y pads deposited from RuO_xH_y /ethylene glycol and heated to $196\text{ }^\circ\text{C}$ are uniformly porous (Figure 1a), while those deposited from a RuO_xH_y /glycerin matrix and heated to $186\text{ }^\circ\text{C}$ show extensive mud cracking (Figure 1b). The pad thickness is approximately $30\ \text{\AA}$ after drying for both systems.

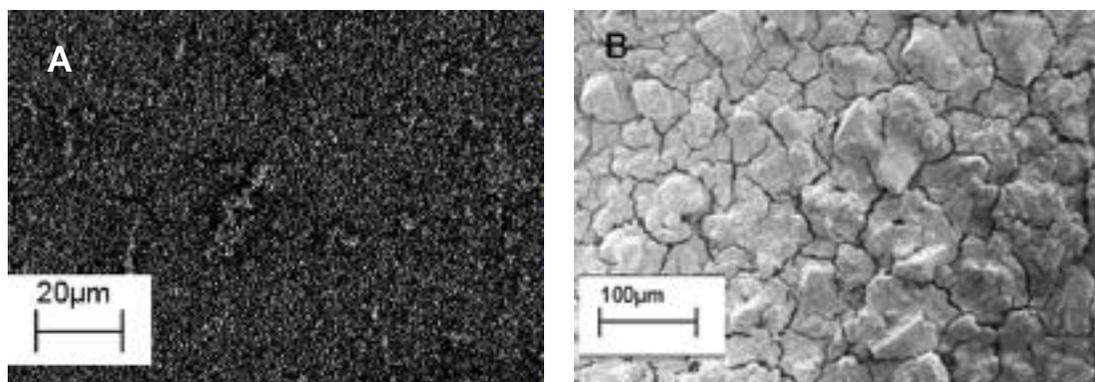


Figure 1. (A) RuO_xH_y deposited from an ethylene glycol matrix is uniformly porous, while (B) that from a glycerin matrix shows extensive mudcracking after annealing.

The chronopotentiometry of a series of four RuO_xH_y pads was evaluated for uniformity. In this experiment, four $1\text{ mm} \times 2\text{ mm} \times 30\ \mu\text{m}$ pads were deposited separately in a quadrant configuration. The space between each pad was $100\ \mu\text{m}$. After deposition, the laser was used to micromachine the edges of the pads to create a 0.32 mm gap across the measurement interface (Figure 2a). The cells were charged to 1 V and then discharged to 0 V. The discharge curves for a single cell and two cells integrated in parallel indicate that the pseudocapacitor energy is scalable (Figure 2b). A single cell

(leads 1 & 2) discharges in 240 sec using a 10 μA drain and 25 s with a 50 μA drain between leads 1 & 2. When the second cell is linked in parallel using leads 3 & 4, the double cell discharges in 500 s and 75 s when drained at 10 and 50 μA , respectively. The cell performance was repeatable with cycling.

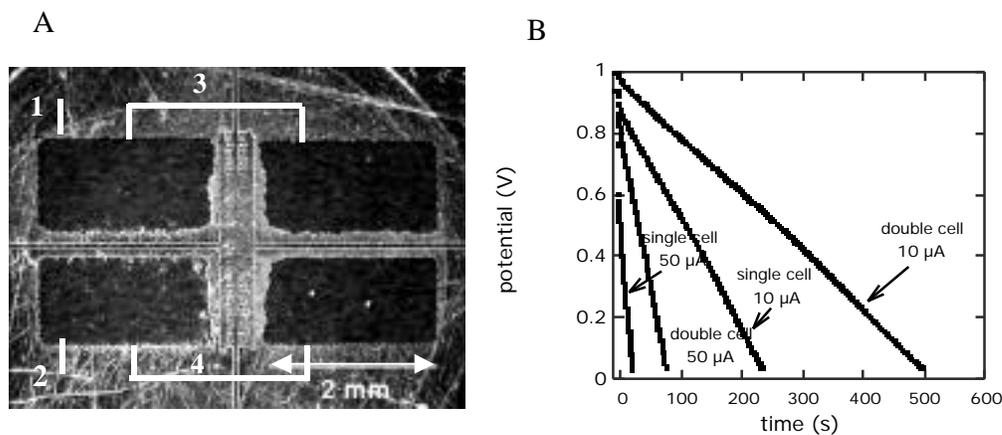


Figure 2. (A) Four 1 mm x 2 mm x 30 μm RuO_xH_y pads deposited on Au and laser micromachined to a 320 μm gap across the measurement interface. (B) The scalable discharge of a single cell (leads 1 & 2) with a double cell (leads 3 & 4) at 10 μA and 50 μA indicates that the cells can be linked in arrays.

The effect of the interface size is demonstrated in Figure 3 for another series of RuO_xH_y pads. In this example, four 2.2 mm x 1 mm x 30 μm RuO_xH_y pads were cut with the laser from a single 4.5 mm x 2.1 mm x 30 μm RuO_xH_y pad with 0.08 mm gaps between each pad (Figure 3a). The cell discharged in 1020 s with a 10- μA drain across the 2-mm interface (leads 5 & 6) and 720 sec across the 1 mm interface (leads 7 & 8).

The cell discharged in 40 s with a 100- μA drain across leads 5 & 6.

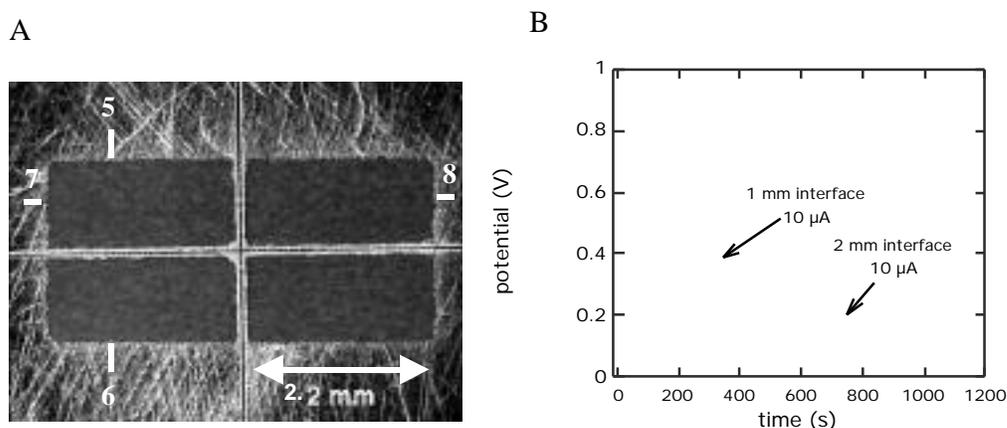


Figure 3. (A) A 4.5 mm x 2.1 mm x 30 μm RuO_xH_y pad deposited on Au and laser micromachined into four 2.2 mm x 1 mm x 30 μm pads with 80- μm gaps between each pad. (B) The cell capacity is greater when it is discharged across the 2-mm wide interface vs the 1-mm wide interface. The cell capacity is also greater than RuO_xH_y pads designed with 320- μm gaps between pads (Figure 2).

DISCUSSION

Using RuO_xH_y/Nafion planar pseudocapacitors, we have demonstrated that MAPLE DW can be successfully used to fabricate a power source. The example given in Figure 2 shows that arrays of batteries can be configured to change the energy of the system. The energy of the system scales to the number of cells in the system, indicating that the cells discharge uniformly across the laser-machined interfaces and do not preferentially short-circuit through one interface. The size and configuration of the interface also correlates to the capacity of the cell. The capacity of the cell is improved by discharging the cell across a wider interface (2 mm vs 1 mm). The cell capacity is also improved by a factor of four in Figure 3 vs Figure 2 (1000 sec vs. 250 sec, respectively, at 10- μ A drain), because the width of the gap between the RuO_xH_y pads is decreased from 320 μ m to 80 μ m, causing a decrease in the thickness and resistance of the Nafion electrolyte. The size and length of the interfaces are easily changed with the MAPLE DW system, so the size and width of the interfaces may be tuned in the future to optimize the cell capacity.

SUMMARY

MAPLE DW can be used for rapid prototyping of custom-engineered microbatteries and microbattery arrays. 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 primary alkaline and secondary lithium-ion systems.

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REFERENCES

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1. 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 and M. Duignan, *Appl. Phys. A*, **69** [Suppl.], S279 (1999).
 2. D.B. Chrisey, A. Piqué, J. Fitz-Gerald, B. Ringeisen and R. Modi, *Laser Focus World*, 113 (2000).
 3. D.B. Chrisey, A. Piqué and R.A. McGill, U.S. Patent approved September 28, 2000.
 4. B.E. Conway, *J. Electrochem. Soc.*, **138**, 1539 (1991).
 5. S. Trasatti, *Electrochim. Acta*, **36**, 225 (1991).
 6. J.P. Zheng, P.J. Cygan and T.R. Jow, *J. Electrochem. Soc.*, **142**, 2699 (1995).
 7. D.A. McKeown, P.L. Hagans, L.P.L. Carette, A.E. Russell, K.E. Swider and D.R. Rolison, *J. Phys. Chem. B*, **103**, 4825 (1999).