

Direct writing of planar ultracapacitors by laser forward transfer processing

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ABSTRACT

We employ a novel laser forward transfer process, Matrix Assisted Pulsed Laser Evaporation Direct Write (MAPLE-DW), in combination with ultraviolet laser micromachining, to fabricate mesoscale ultracapacitors and microbatteries under ambient temperature and atmospheric conditions. Our laser engineering approach enables the deposition of hydrous ruthenium oxide (RuO_xH_y or $\text{RuO}_2 \cdot x \text{H}_2\text{O}$) films with the desired high surface area morphology, without compromising the electrochemical performance of this high specific capacitance material. We compare three different deposition formulations incorporating ethylene glycol, glycerol, or sulfuric acid. The best electrochemical performance is achieved using a mixture of sulfuric acid with $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ electrode material. Our ultracapacitors exhibit the expected linear discharge behavior under a constant current drain, and the electrochemical properties of these cells scale proportionately when combined in parallel and series.

Keywords: laser direct write, laser micromachining, MAPLE-DW, microbattery, electrochemical capacitor, supercapacitor, pseudocapacitor, hydrous ruthenium oxide, RuO_2

1. INTRODUCTION

High capacitance electrochemical capacitors have been studied for more than 40 years, yet it has only been in last decade that they have gained widespread attention.^{1,2} The interest in these systems has arisen mainly from commercial applications, such as electric or hybrid powered vehicles or power backup sources, where there is a need for energy storage systems that can hold relatively large amounts of energy yet deliver it in short pulses leading to high power output.^{3,4} Conventional parallel plate capacitors can deliver high power, but are limited in the amount of energy they can store. Electrochemical capacitors provide an intermediate range of power and energy between parallel plate capacitors and conventional batteries. Hydrous ruthenium oxide ultracapacitors are a type of electrochemical capacitor with a high capacitance due to the rapid double insertion and release of protons and electrons in the active material.^{2,5,6}

The need for high power pulsed energy sources is also important in the development of micro-power sources for microelectronic and microelectronic mechanical systems (MEMS). Although the maximum power requirements for pulsed operations are typically much less than one watt per square centimeter, this low output power is more than can be delivered by a thin-film microbattery.^{7,8} Therefore, the development of hybrid micro-power systems that incorporate a high power ultracapacitor in combination with a microbattery is essential for the future of next generation micro-devices.⁹

The manufacture of thin-film hydrous ruthenium oxide ultracapacitors is difficult due to the complex materials requirements for an effective, high capacitance power source.⁵ The most advantageous morphology for a high capacity ultracapacitor is a permeable, porous structure leading to a large effective surface area.^{1,2} The $\text{RuO}_2 \cdot x \text{H}_2\text{O}$ system has the additional limitation that the capacitance of the material depends on the processing temperature.^{6,10,11} These aspects of morphological constraints and processing temperature limitations, in addition to the presence of water in the oxide structure have made $\text{RuO}_2 \cdot x \text{H}_2\text{O}$ incompatible with standard

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vacuum techniques for thin film growth such as physical vapor deposition. Instead, recent studies of thin film ultracapacitors have focused on the development of anhydrous metal oxide systems deposited by sputtering.¹²

We overcome the difficulties associated with the deposition of hydrous metal oxide films by using a laser direct writing technique, Matrix Assisted Pulsed Laser Evaporation-Direct Write (MAPLE-DW).^{13,14} In this technique, an “ink” composed of a sacrificial liquid matrix (transfer vehicle) and the material to be deposited (passenger material) is laser forward transferred to a substrate below. The presence of a the liquid enable the deposited film to flow and achieve a relatively flat and pinhole-free surface. This technique produces thin-films of the hydrous material with the desired morphological properties without the need for high temperature or lithographic processing following deposition. Ultracapacitor electrodes are shaped from the deposited film using UV laser machining.¹⁵

A distinct advantage of MAPLE-DW is the ability to operate under ambient conditions to deposit a mixture of $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ and a liquid electrolyte. This technique of distributing electrolyte within the electrode is commonly used in the production of larger scale electrochemical power sources, but it is not possible with other thin film techniques such as PVD, CVD, or sol-gel methods. Additionally, the use of liquid sulfuric acid electrolyte, as opposed to solid-state materials, enables higher proton conductivity in the electrolyte and enhances ultracapacitor properties.¹⁶

In this paper, we describe the use of laser processing to deposit functional planar ultracapacitors with energy and power densities commensurate with larger power sources. We capitalize on the advantage of an ambient process to study the influence of different transfer vehicles and find that sulfuric acid vehicles produces ultracapacitors with the best electrochemical properties. Finally, by combining the ultracapacitors in parallel and series, we are able to achieve proportionately larger capacitance and voltage, respectively.

2. EXPERIMENTAL PROCEDURES

Thin film hydrous ruthenium oxide planar ultracapacitors are deposited using the MAPLE-DW technique previously described in detail.^{13,14} Figure 1 shows a schematic of the experimental approach. We transfer a wet ink composed of a liquid vehicle (ethylene glycol, glycerol or sulfuric acid) and the passenger material ($\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$). Commercially available hydrated ruthenium oxide powder is oven heated to 150 °C for 18 hours to yield a material with the desired water content of 0.5 mol H_2O per mol RuO_2 for optimal charge storage.^{6,17} This ink is dispersed on a quartz plate to form the ribbon depicted in figure 1a. A frequency-tripled Nd:YAG laser ($\lambda=355 \text{ nm}$) is used to irradiate the back of the ribbon inducing a forward transfer of material to a substrate 100 μm below the ribbon.

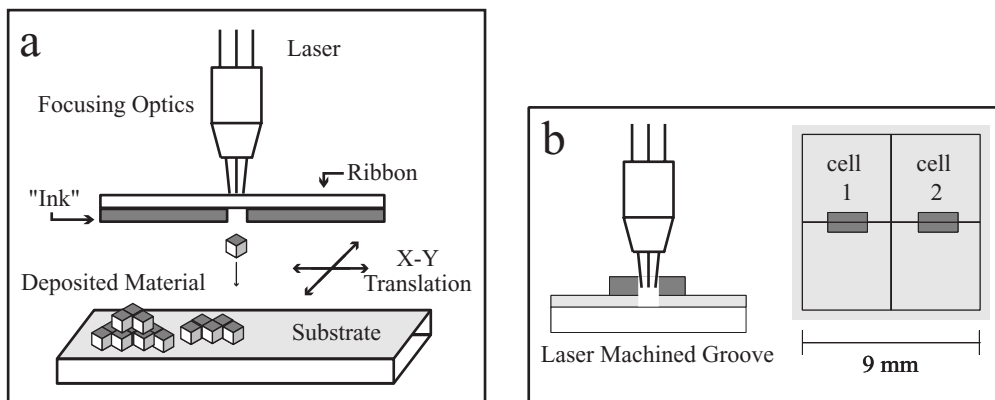


Figure 1. Schematic of MAPLE-DW technique (a)laser forward transfer of a wet “ink” layer for film deposition (b) UV laser machining of film to form isolated electrodes. The two ultracapacitor cells are 1 mm x 2 mm x 10 μm .

The substrate is a 1 cm x 1 cm gold-coated quartz wafer that has been laser machined with a 9 mm “window pane” structure to electrically isolate four current collector pads (figure 1b). Hydrated ruthenium oxide films 1 mm x 2 mm x 10 μm are deposited to span across the machined groove in the gold. A line is then laser machined across the film providing a symmetric planar ultracapacitor with 0.5 mm x 2 mm x 10 μm electrodes. Two such ultracapacitors are deposited on each substrate. The volume of each ultracapacitor is 2×10^{-5} mL and the approximate mass is 50 μg .

The excess vehicle deposited in the $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ film must be removed prior to laser machining in order to obtain sharp interfaces. When we use organic transfer vehicles, the as-deposited films are dried on a hot plate at 100 $^\circ\text{C}$ for 10 minutes prior to laser machining. After the films are machined, the remaining vehicle is removed from the samples by heating in an oven at 5 $^\circ\text{C}/\text{min}$ to 150 $^\circ\text{C}$ and held for 3 hours. For films deposited with sulfuric acid, the excess vehicle is removed by IR laser irradiation ($\lambda=1064\text{nm}$) and the final bake is not used.

Electrochemical evaluation of capacitance and charge-discharge behavior is carried out using a potentiostat (EG&G PAR Model 263) connected to a probe station. The ultracapacitors are encapsulated in Nafion[®] and submerged in 0.5 M H_2SO_4 solution during testing. Multiple chronopotentiometry steps are used to charge and discharge the ultracapacitors between 0 and 1 V in a two-electrode configuration. All cells were charged at a constant current of 50 μA and discharged at 10, 50, or 100 μA .

3. RESULTS AND DISCUSSION

Hydrous ruthenium oxide films deposited and processed by our technique exhibit desirable morphologic qualities of a high capacity ultracapacitor. Figure 2 shows optical and electron micrographs of the deposited material. The optical image (figure 2a) shows we are able to deposit uniform films of $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ which are laser machined with precision ($< 20 \mu\text{m}$ groove). Optical examination indicate that under these processing conditions, there is no large scale collateral damage to the area surrounding the groove.

Under higher magnification with SEM (figure 2b,c), the deposited thin films appear highly porous throughout the active material, regardless of the transfer vehicle used. The porous structure remains undamaged by UV laser machining in the region near the machined groove. This morphology is desirable as it provides a large effective surface area and enables the electrolyte to easily permeate the electrode. This provides high ionic transport to the active material where the balance between protonic and electronic conduction mechanisms within the nanostructured material leads to the high capacitance in the $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ system.¹¹ Since RuO_2 is a metallic conductor, the high level of electrode porosity is not detrimental to the electronic transport.

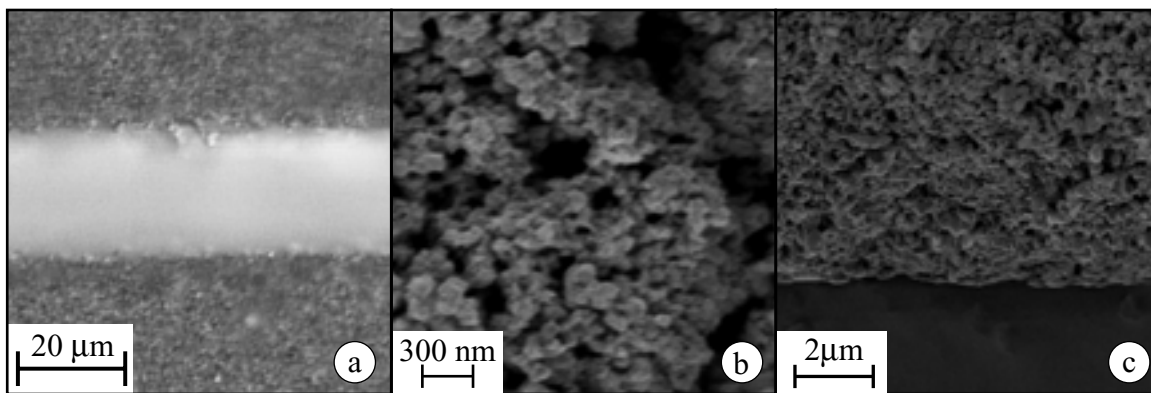


Figure 2. Micrographs of deposited $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ thin-films (a) Optical image at 50x magnification showing the laser machined groove through a $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ film. (b) SEM image of electrode at 20,000x magnification. (c) SEM image of electrode near the laser machined groove (bottom of image) magnified 3000x.

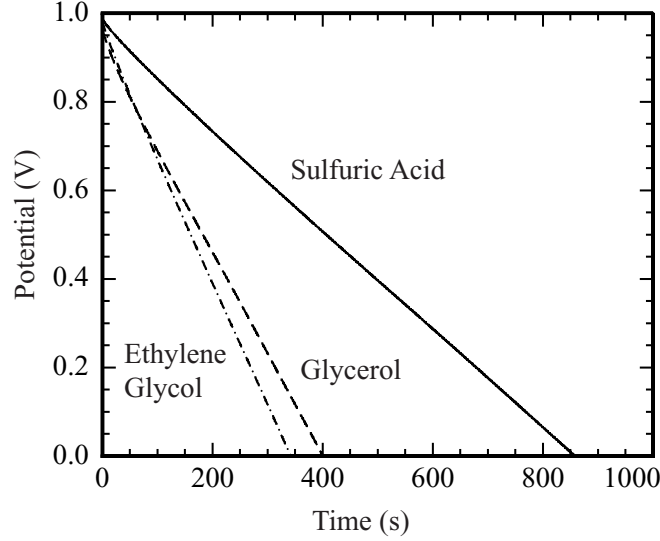


Figure 3. 10 μA discharge profile of $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ ultracapacitors deposited using three different transfer vehicles; ethylene glycol, glycerol and sulfuric acid. Discharge times are 350, 400, and 850 s respectively.

The ultimate test for any of our ultracapacitors is the electrical response of the power source and its ability to store and deliver charge. Figure 3 shows the 10 μA chronopotentiometric discharge profiles for samples transferred with three different vehicles (ethylene glycol, glycerol and sulfuric acid solutions). In all cases, the discharge is linear as expected for an ideal capacitor. Samples deposited from inks containing H_2SO_4 exhibit the longest discharge time, 850 s, as compared to those deposited from glycerol and ethylene glycol based inks that last 400 and 350 s respectively.

A constant capacitance is justified by the linear discharge behavior, so the average specific capacitance of the sample is given by

$$c = \frac{I\Delta t}{m\Delta V}, \quad (1)$$

where I is the constant discharge current, Δt is the total discharge time, ΔV is the maximum potential difference, and m is the mass of the ultracapacitor, including the electrolyte. The specific energy, ϵ , and average specific power, p , are obtained from the area under the curve by

$$\epsilon = \frac{I}{m} \int V dt \quad (2)$$

$$p = \frac{\epsilon}{\Delta t}. \quad (3)$$

Table 1 shows the calculated values of specific capacitance, specific energy and specific power for the data shown in figure 3.

When the discharge current is increased (figure 4), the specific power increases while the specific energy remains unchanged. The discharge time for a ultracapacitor deposited with a sulfuric acid vehicle varies proportionately under 10, 50, and 100 μA discharge currents, and decreases to 80 s at the largest current. This corresponds to a specific power of nearly 1000 mW/g and a specific energy of 21 mW/g. Ultracapacitors prepared using ethylene glycol and glycerol transfer vehicles exhibit a similar scaling behavior with correspondingly lower specific energy.

Table 1. Calculated values of specific capacitance, energy density and average power using equations 1-3 and the data shown in figure 3.

Transfer Vehicle	Specific Capacitance (F/g)	Specific Energy (mWh/g)	Specific Power (mW/g)
H ₂ SO ₄	174	23.0	96.5
Glycerol	83.0	10.4	93.5
Ethylene Glycol	69.5	9.15	96.3

Figure 5 shows a Ragone plot with typical values for different types of energy storage devices.³ The maximum specific power for our RuO₂ · 0.5 H₂O cells deposited with sulfuric acid is represented by a cross on the plot. Our ultracapacitors exhibit behavior in the region of high specific energy and high specific power for an electrochemical capacitor. It should be noted that the main source of uncertainty in our measured values for specific energy and power arises from the mass determination.

Ultracapacitors transferred using a sulfuric acid vehicle exhibit superior electrochemical characteristics in comparison to those deposited using organic transfer vehicles. Typical MAPLE-DW depositions make use of organic vehicles due to their ease in handling and their ability to make stable ink formulations. Sulfuric acid poses additional challenges to the processing and development of a usable formulation due to its high acidity, but the advantages in energy storage outweigh the handling difficulties. We believe the deleterious effects of oxidation and decomposition of residual organics in the presence of the acidic electrolyte may cause contamination to the electrically active hydrous ruthenium oxide. In contrast, the use of a sulfuric acid transfer vehicle precludes the need for complete removal of the transfer vehicle thus decreasing the possibility for contamination of our active material and enabling a better distribution of electrolyte in the electrode.

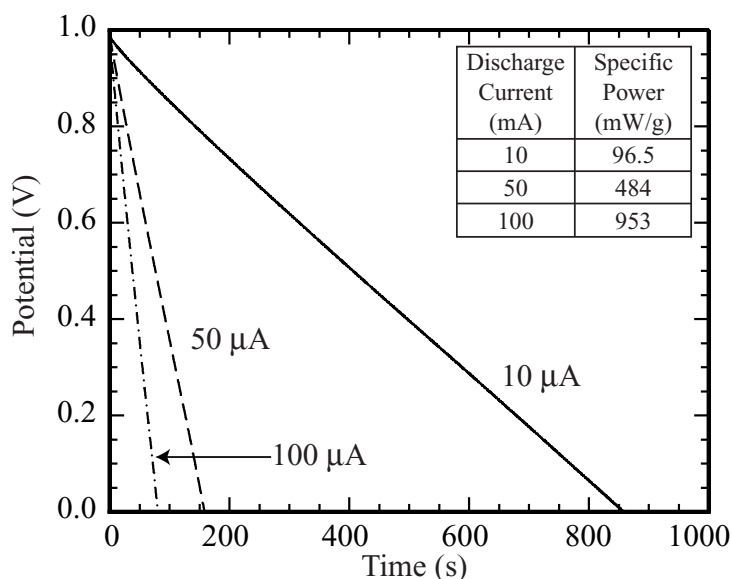


Figure 4. Chronopotentiometry of RuO₂ · 0.5 H₂O ultracapacitors for sulfuric acid transfer vehicle at 10, 50 and 100 μA discharge currents. The discharge times of 80, 160, and 850 s respectively convert to the specific power values through equation 3.

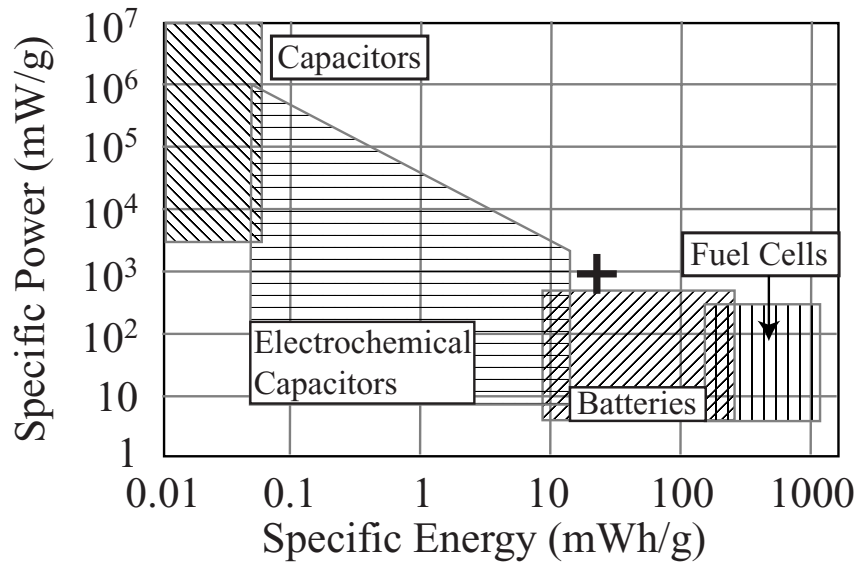


Figure 5. Ragone plot of various energy storage devices.³ The cross represent our data from ultracapacitors deposited with a sulfuric acid transfer vehicle and a discharge current of 100 μA .

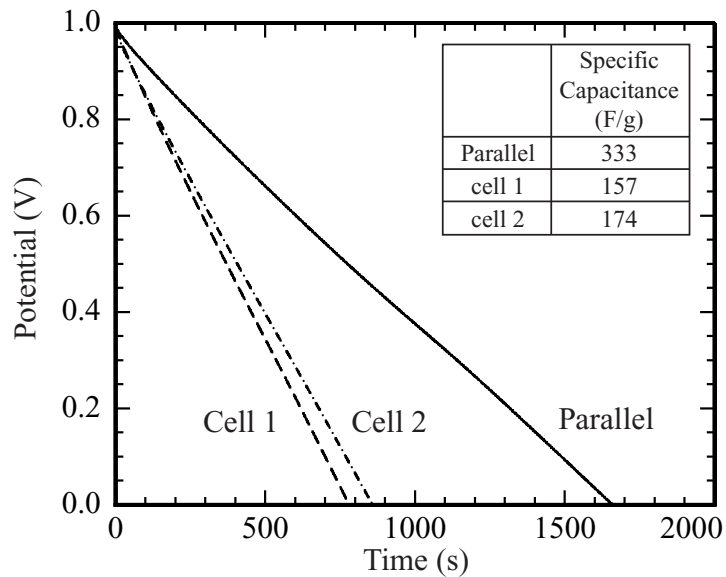


Figure 6. Chronopotentiometry of $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ ultracapacitors for sulfuric acid transfer vehicle at 10 μA discharge currents on two cells and the parallel combination. The values for specific capacitance are given in the table.

Further evidence of process viability is demonstrated when the ultracapacitors are connected in parallel and series. Figure 6 shows 10 μA discharge profiles for two ultracapacitors deposited with sulfuric acid and connected in parallel. Again, the system is charged to 1 V and the discharge curves exhibit linear behavior. However, this parallel configuration has an extended discharge time of 1660 s. Calculations show the specific capacitance of the system is additive, as expected for capacitors in parallel, while the specific energy reflects the average of the two individual cells.

Ultracapacitor cells are also combined in series to increase the voltage of the system. In this case (the data is not shown here), the system is charged to 2 V at 50 μA . Upon discharge at 10 μA to 0 V, we find the specific energy and specific power remain essentially unchanged. The calculation of capacitance from this system exhibits the expected inverse addition rules of series capacitors.

4. SUMMARY

We have demonstrated that a laser engineering approach is a viable method for fabricating mesoscale ultracapacitors. Ultracapacitors of hydrous ruthenium oxide electrodes and sulfuric acid electrolyte are successfully produced using an ambient forward laser transfer technique (MAPLE-DW) in addition to UV laser machining. The evaluation of two different organic transfer vehicles and sulfuric acid transfer vehicle indicates that the choice of sulfuric acid enhances the electrochemical properties of the ultracapacitors. Configurations of $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ ultracapacitors in series and parallel exhibit the expected additive behavior.

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