



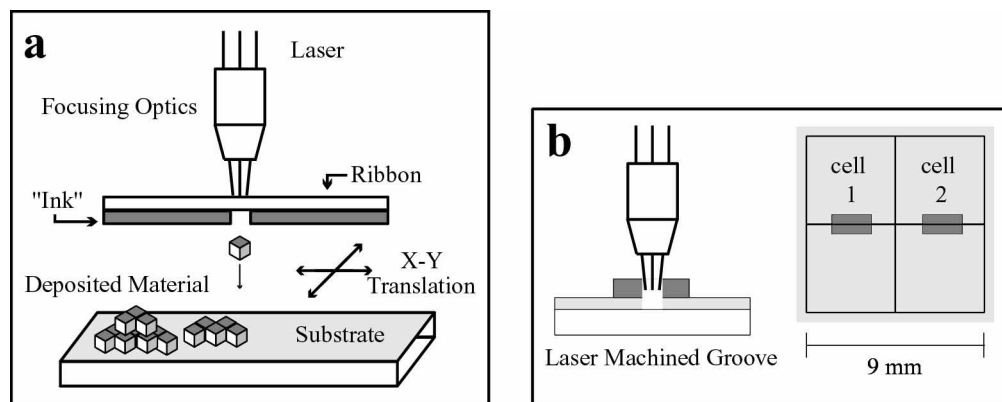
advantage of an ambient process to mix sulfuric acid into the electrode material during laser transfer to improve the energy qualities in comparison to other organic formulations. Finally, by combining our pseudocapacitors in parallel and series, we are able to achieve proportionately larger capacitance and voltage, respectively.

## EXPERIMENT

Thin film hydrous ruthenium dioxide planar pseudocapacitors are deposited using the MAPLE-DW technique that has been previously described in detail [9,10]. Figure 1a shows a schematic of the experimental approach. We use a wet “ink” composed of a liquid vehicle (ethylene glycol, glycerol or sulfuric acid solutions) and the passenger material ( $\text{RuO}_2 \cdot 0.5 \text{H}_2\text{O}$ ). The hydrated ruthenium dioxide powder is commercially purchased (Alfa) and prepared by oven heating to  $150^\circ\text{C}$  for 18 hours prior to ink formulation [12]. This yields a material with the desired water content of  $\sim 0.5$  mol  $\text{H}_2\text{O}$  per mol  $\text{RuO}_2$  [4]. A frequency-tripled Nd:YAG laser ( $\lambda=355$  nm) is used to irradiate the back of the ribbon inducing a forward transfer of material to a substrate below the ribbon.

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 contact pads (figure 1b). Deposited material spans across the machined groove in two 1 mm x 2 mm x  $10 \mu\text{m}$  pads. A line is then laser machined across both pads providing two symmetric planar pseudocapacitors each with 0.5 mm x 2 mm x  $10 \mu\text{m}$  electrodes. The volume of each pseudocapacitor is  $2 \times 10^{-5}$  mL and the approximate mass is 50  $\mu\text{g}$ .

The deposited films retain a significant amount of vehicle following laser transfer, which enables the deposited material to achieve a relatively flat, pinhole-free surface. However, the excess vehicle must be removed prior to laser machining in order to obtain sharp structures. In the case of the organic vehicles, we dry the as-deposited films 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. In the case of sulfuric acid, the final bake is not used.



**Figure 1.** (a) Schematic of MAPLE-DW apparatus showing the method of forward laser transfer of an “ink” layer (b) Sample geometry: the two pseudocapacitors cells are 1 mm x 2 mm x  $10 \mu\text{m}$  prior to laser machining.

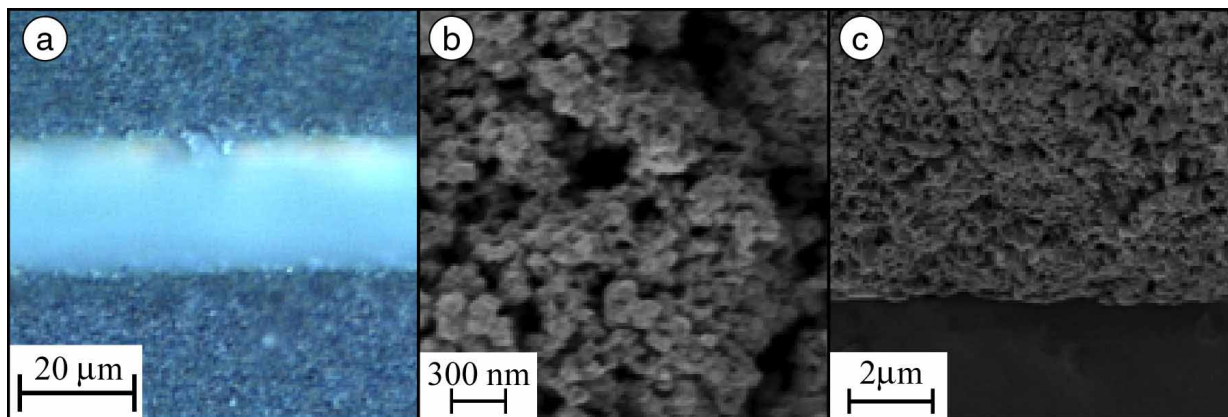
Electrochemical evaluation of capacitance and charge-discharge behavior is carried out using a potentiostat (EG&G PAR Model 263) connected to a probe station. The pseudocapacitors are encapsulated in Nafion<sup>®</sup> to provide structural support and submerged in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution during testing. Multiple chronopotentiometry (CP) steps are used to charge and discharge the pseudocapacitors between 0 and 1 V in a two-electrode configuration. For the results presented here, all samples were charged at a constant current of 50 μA and discharged at either 10 μA or 100 μA.

## RESULTS

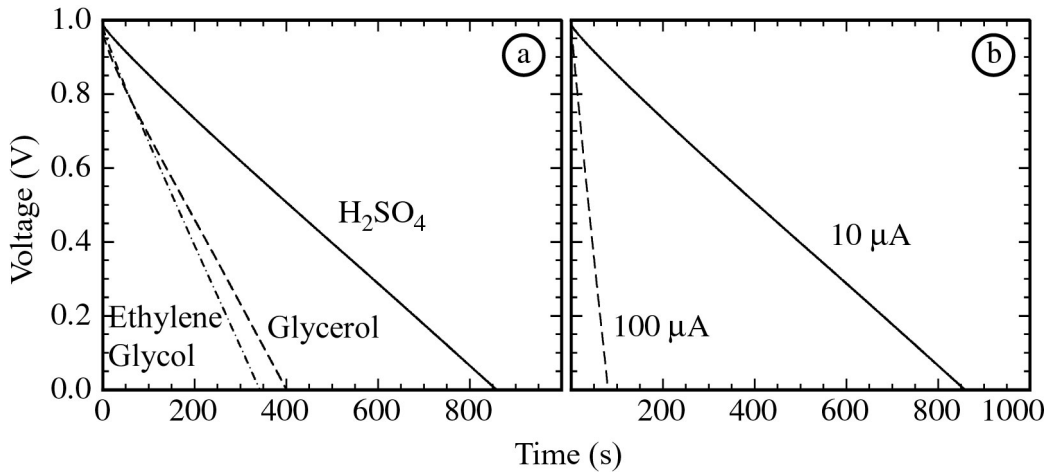
Hydrous ruthenium dioxide films deposited and processed by our technique exhibit desirable morphologic qualities of a pseudocapacitor. Figure 2 shows optical and electron micrographs of the deposited material. The optical image (figure 2a) shows that we are able to deposit flat, uniform pads of RuO<sub>2</sub>·0.5 H<sub>2</sub>O and laser machine them with a large degree of precision (< 20 μm groove). Our studies indicate that under these processing conditions, there is no collateral damage to the area surrounding the groove.

Under high magnification (figure 2b,c), we see the deposited thin film is highly porous throughout the active material. We find this morphology to be independent of the particular transfer vehicle used. Furthermore, the laser machining process does not damage this microstructure in the region near the groove as shown in figure 2c. This morphology is desirable as it provides a large effective surface area and enables the electrolyte to easily permeate the electrode, which provides high ionic transport to the active material. The high level of electrode porosity is not detrimental to the electronic transport since RuO<sub>2</sub>·0.5 H<sub>2</sub>O is a metallic conductor.

The ultimate test for any of our pseudocapacitors is the electrical response of the power source and its ability to store and deliver charge. Figure 3a shows the 10μA discharge profiles for samples transferred with three different vehicles (ethylene glycol, glycerol and sulfuric acid solutions). In all cases, the potential vs. time curve is linear as expected for an ideal capacitor. Samples deposited from inks containing H<sub>2</sub>SO<sub>4</sub> exhibit the longest discharge time, 850 s, as



**Figure 2.** Micrographs of deposited RuO<sub>2</sub>·0.5 H<sub>2</sub>O thin films (a) Optical image at 50x magnification showing laser machined groove (light colored region). Scale bar is 20 μm. (b) SEM image of main pad at 20,000x magnification. Scale bar is 300 nm. (c) SEM image near machined groove (bottom of image) magnified 3000x. Scale bar is 2 μm.



**Figure 3.** (a) Constant current discharge behavior for RuO<sub>2</sub>·0.5 H<sub>2</sub>O pseudocapacitors deposited from different vehicle solutions at 10 μA. (b) Discharge curves for sulfuric acid vehicle samples at 10 and 100 μA. Samples are charged to 1 V at 50 μA prior to discharge.

compared to those deposited from glycerol and ethylene glycol based inks that lasted 400 and 350 s respectively.

If we assume a constant capacitance, which is justified by the linear discharge behavior, then 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,  $\Delta t$  is the total discharge time,  $\Delta V$  is the maximum potential difference, and  $m$  is the mass of the pseudocapacitor including electrolyte.

Furthermore, we can obtain the specific energy,  $\varepsilon$ , and average specific power,  $p$ , from the area under the curve by

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

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

Table I shows the calculated values of specific capacitance, specific energy and specific power for the data shown in figure 3. Pseudocapacitors transferred using a sulfuric acid vehicle exhibit superior electrochemical characteristics in comparison to those deposited using organic transfer vehicles. Although organic vehicles are advantageous for making stable ink formulations, the deleterious effects of oxidation and decomposition of residual organics in the

Transfer Vehicle	Discharge Current (μA)	Specific Capacitance (F/g)	Energy Density (mWh/g)	Average Power Density (mW/g)
H <sub>2</sub> SO <sub>4</sub>	10	174	23.0	96.5
Glycerol	10	83.0	10.4	93.5
Ethylene Glycol	10	69.5	9.15	96.3
H <sub>2</sub> SO <sub>4</sub>	100	163	21.3	953

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

presence of the acidic electrolyte may cause contamination to the electrically active hydrous ruthenium dioxide. Conversely, the sulfuric acid vehicle produces electrodes with the desired electrolyte already present and eliminates the possibility for contamination from the transfer vehicle.

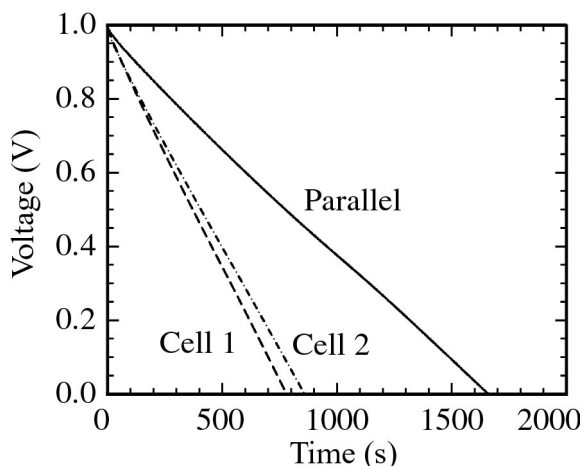
When the discharge current is increased to 100  $\mu\text{A}$  (figure 3b), the specific power increases without significantly affecting the specific energy. The discharge time for a sample deposited with a sulfuric acid vehicle under these conditions is 80 s, which corresponds to a specific power of nearly 1000 W/g and a specific energy of 21 mW/g. These values for specific energy and power compare favorably to literature values for other pseudocapacitor systems [13].

Further evidence of process viability is demonstrated when the pseudocapacitors are connected in parallel and series. Figure 4 shows 10  $\mu\text{A}$  discharge profiles for two pseudocapacitors 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. Further 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.

Pseudocapacitor cells are also combined in series to increase the voltage of the system. In this case (the data is not shown here), we charge the system to 2 V at 50  $\mu\text{A}$ . Upon discharge at 10  $\mu\text{A}$  to 0 V, we do not find significant changes in specific energy or specific power. The calculation of capacitance from this system exhibits the expected inverse addition rules of series capacitors.

## SUMMARY

We have demonstrated that using a laser engineering approach to develop micro-pseudocapacitors is a viable method. Micro-pseudocapacitors of hydrous ruthenium dioxide electrodes and sulfuric acid electrolyte are successfully produced using an ambient forward laser



	Specific Capacitance (F/g)	Specific Energy (mWh/g)
Parallel	333	22.1
Cell 1	157	21.0
Cell 2	174	23.0

**Figure 4.** Constant current discharge curves for two pseudocapacitor cells measured separately and in parallel. The cells are charged to 1 V at 50  $\mu\text{A}$  and discharged at 10  $\mu\text{A}$ . Sulfuric acid is used as the transfer vehicle in these samples. The tabulated values are calculated using equations 1 and 2.

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 pseudocapacitors. Configurations of RuO<sub>2</sub>·0.5 H<sub>2</sub>O pseudocapacitors in series and parallel exhibit the expected additive behavior. To our knowledge, these results represent the first demonstration of high specific energy thin-film hydrous ruthenium dioxide pseudocapacitors incorporating a sulfuric acid electrolyte.

## ACKNOWLEDGEMENTS

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