

# TOWARDS A FLEXIBLE ALL-SOLID-STATE ELECTROCHEMICAL SUPERCAPACITOR USING TOBACCO MOSAIC VIRUS NANOSTRUCTURES AND ALD RUTHENIUM OXIDE

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**Abstract:** A solid-state electrochemical supercapacitor has been developed using a combination of nanostructured nickel and a ruthenium oxide atomic layer deposition (ALD) coating. The electrode morphology is based on a high surface area biotemplate of vertically oriented *Tobacco mosaic virus* (TMV). The biotemplate automatically self-assembles at room temperature in aqueous solution. Nafion® perfluorosulfonate ionomer dispersion is cast on the electrodes and used as a solid proton-conducting electrolyte. The technology presented here will enable thin, solid, flexible high performance supercapacitors that are produced using a combination of bottom-up nanoassembly and top-down microfabrication.

**Keywords:** supercapacitor, ruthenium oxide, Nafion, Tobacco Mosaic Virus

## INTRODUCTION

Supercapacitors store electrical energy as either an electronic double layer (EDL) and/or through a surface redox reaction, where the two types are frequently referred to as EDLC or pseudocapacitors respectively. The charge storage mechanisms are very rapid and highly reversible compared to rechargeable batteries, leading to their use in high power density applications. Current research trends are focused on improving energy density, either by increasing surface area of EDLC or using new nanomaterials. Activated carbon foams are most frequently used due to their high surface area, but further increasing surface area can come at the expense of ionic mobility in the constrained nanogeometries. A library of transition metal oxides are available as redox materials for pseudocapacitors, of which ruthenium oxide ( $\text{RuO}_2$ ) is the leader due to its high gravimetric capacity, intrinsic electronic conductivity, and chemical stability in acidic electrolytes. In the interest of brevity, the reader is referred to a recent review for further information [1].

Two strategies have emerged to minimize the unused volume of  $\text{RuO}_2$  and to increase its energy density: (1) preparation in its hydrated form ( $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ ) so protons can easily penetrate the bulk material, and (2) deposition in a nanostructured state on a high surface area template. Using the later strategy an electrode has been created (Figure 1) from genetically modified *Tobacco mosaic virus* (TMV) which self-assembles onto a prepared substrate at room temperature and is easily metallized for further

processing[2][3]. In its anhydrous form,  $\text{RuO}_2$  has lower capacity than the hydrous form, however, anhydrous  $\text{RuO}_2$  can be deposited by ALD, a technique which is well known for its conformality and monolayer thickness control [4].

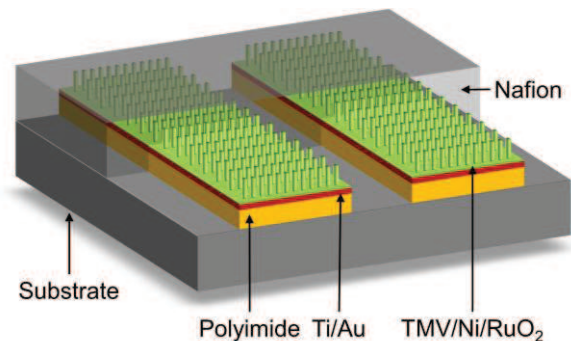


Figure 1. Cross section schematic of the supercapacitor showing silicon substrate, polyimide insulator, gold current collector and  $\text{RuO}_2$  coated TMV. The entire structure is encapsulated in solid Nafion electrolyte.

The energy storage capability of the TMV/Ni/ $\text{RuO}_2$  nanostructure is demonstrated and characterized using DuPont Nafion®, which is a solid sulfonated polymer that can be used as a proton-conducting electrolyte. Previous research has demonstrated  $\text{RuO}_2$  with Nafion used either as a solid electrolyte [5] or a binder [6] with liquid electrolyte.

## METHODS

Fabrication of the biotemplated  $\text{RuO}_2$  electrodes begins with a silicon wafer used as a substrate and

coated with a flexible spin-on polyimide precursor (HD Microsystems HD-4110) that is vacuum baked at 375°C to produce a polyimide insulator. Next the polyimide is roughed in oxygen plasma (Plasma-Therm 790) and coated with a titanium / gold (200 Å / 2000 Å) layer in an e-beam evaporator (CHA Industries). Each wafer was diced into 1 cm by 1 cm chips and the *Tobacco mosaic virus* suspension was prepared as reported previously [2].

Each chip was submerged in a 0.2 g/L suspension of the TMV in phosphate buffer, and the biotemplate was allowed to assemble overnight. The excess TMV solution was removed and a 12:1 solution of phosphate buffer and sodium tetrachloropalladate (NaPdCl<sub>4</sub>) was added to functionalize the TMV surface for electroless metallization. The palladium solution was removed, and an aqueous nickel plating solution of NiCl<sub>2</sub>, glycine, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and dimethylamine borane (DMAB) was added. The nickel plating reaction is autocatalyzed but starts at the palladium functionalized TMV to produce a coating of nickel around the TMV. The reaction stops when the sample is removed from solution and rinsed with water.

RuO<sub>2</sub> was deposited on the TMV biotemplate by a new atomic layer deposition method using repeated cycling of bis(2,2,6 trimethyl cyclohexadienyl)-ruthenium and oxygen in a custom built, cross flow reactor at 225°C. Samples were weighed before and after coating to determine total mass loading.

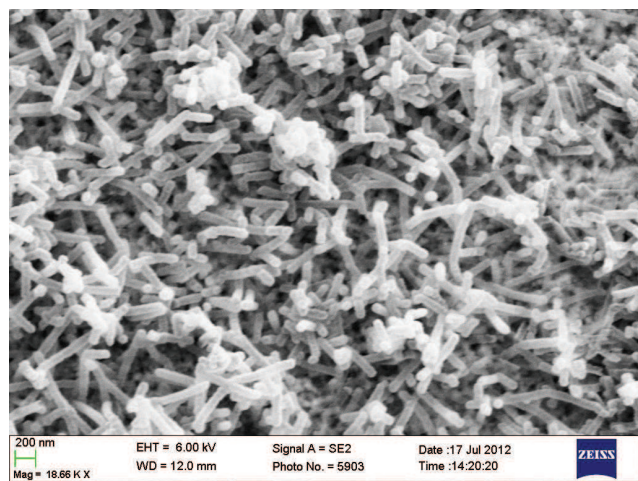


Figure 2. SEM image of RuO<sub>2</sub> deposited by ALD on TMV templated nickel demonstrating that the high surface area is preserved after RuO<sub>2</sub> coating.

The structure of the electrode produced by metalized TMV was evaluated by SEM which shows a high surface area electrode that is ideal for supercapacitors (Figure 2). TEM and EDS (JEOL 2100F) was performed on samples transferred from the electrode surface to a TEM grid. The cross-section

obtained by TEM (Figure 3) demonstrates the layered structure of TMV/Ni/RuO<sub>2</sub>. The composition of the RuO<sub>2</sub> coating was evaluated by powder XRD (Bruker D8 Advance) showing the presence of RuO<sub>2</sub> with broad peaks indicating a nanocrystalline structure (Figure 4).

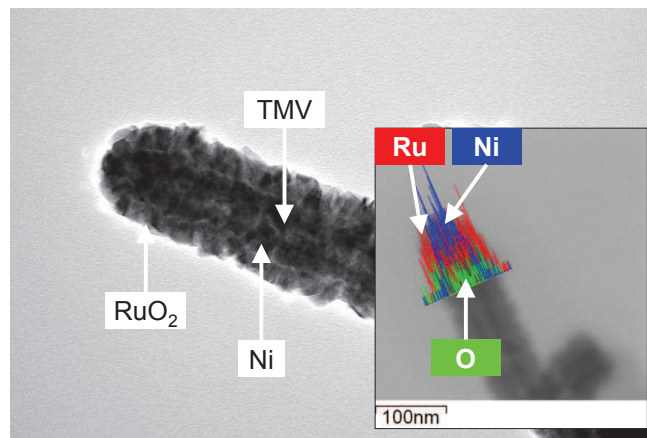


Figure 3. TEM image of a TMV particle showing a uniformly thick, multilayer TMV-Ni-RuO<sub>2</sub> structure (EDS spectrum inset: red is ruthenium, blue is nickel, green is oxygen).

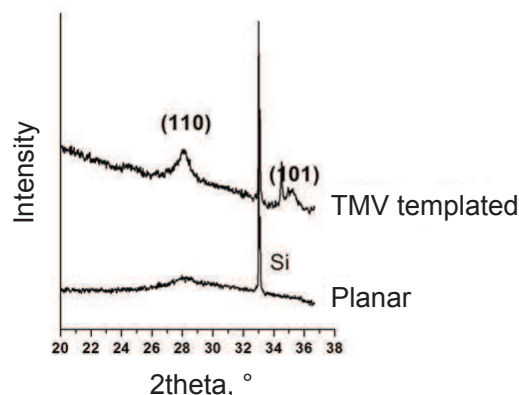


Figure 4. XRD pattern of RuO<sub>2</sub> deposited by ALD on TMV templated Ni on a Si-polyimide-Ti-Au substrate. Broad peaks indicate nanocrystalline RuO<sub>2</sub>.

Supercapacitors were prepared by creating an interdigitated pattern by mechanically scribing through the material stack using a probe station, exposing the underlying silicon substrate and electrically isolating the electrodes. The separation between electrodes was approximately 50 μm, measured during SEM inspection prior to Nafion coating. Nafion dispersion (Ion Power) was spin coated on the chip, solidified at 70°C on a hotplate and annealed for 4 hours at 140°C in a nitrogen purged oven. Nafion was removed from the electrical contact pads by swabbing with isopropyl alcohol resulting in the supercapacitor ships shown in Figure 5. The Nafion thickness was measured to be

approximately 20  $\mu\text{m}$  by a step profilometer (Veeco Dektak 6M) on a sacrificial sample that was scribed through the Nafion to the silicon substrate.

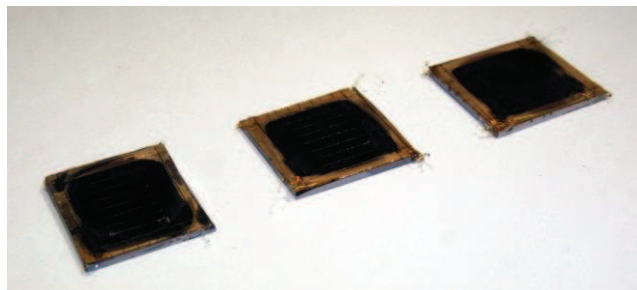


Figure 5. Fabricated supercapacitor chips with electrodes in an interdigitated planar arrangement and coated with Nafion.

Electrochemical tests were performed with the supercapacitor in a symmetrical electrode configuration without a reference electrode. Cyclic voltammetry and chronopotentiometry was used to evaluate supercapacitor performance (CH Instruments 660D potentiostat). The supercapacitor electrodes were suspended in a sealed 50 ml test tube by spring clips that provided electrical contact and mechanical support. The test tube contained a few milliliters of deionized water to make a humidified test chamber since water is required in the Nafion film for proton conduction. Preliminary tests of the capacitance showed the Nafion film is fully hydrated within 10 minutes, and supercapacitor capacitance is negligible when the chamber is purged with dry nitrogen.

## RESULTS AND DISCUSSION

Protonation of the  $\text{RuO}_2$  surface enables energy storage through an oxidation state change that releases electrons – a process that can be reversed with an applied voltage. The devices were tested by cyclic voltammetry at 1 and 100  $\text{mV/s}$  and the capacitance was extracted at the zero voltage crossing. Samples were prepared from the same batch of TMV with and without ALD  $\text{RuO}_2$  (see Figure 6). The addition of  $\text{RuO}_2$  increased the total capacity of the biotemplated nickel electrodes by 9X.

Cyclic voltammetry tests at 1  $\text{mV/s}$  show a capacity of 27  $\text{F/g}$  ( $1.5 \text{ mF/cm}^2$  based on footprint area) and a capacity of 10  $\text{F/g}$  ( $547 \mu\text{F/cm}^2$ ) at 100  $\text{mV/s}$ . The measured gravimetric capacity is lower than reported values for  $\text{RuO}_2$  which range from 125 to 1000  $\text{F/g}$  [7] [8][9]. The capacity of  $\text{RuO}_2$  is highly dependent on the hydration state, the deposition method, the substrate's surface area and particle size. The capacity of solid anhydrous  $\text{RuO}_2$  is less than 1  $\text{F/g}$  and increases to between 19 and 29  $\text{F/g}$  with small amounts of water in the structure ( $\text{RuO}_2 \cdot 0.03\text{H}_2\text{O}$ ) [7].

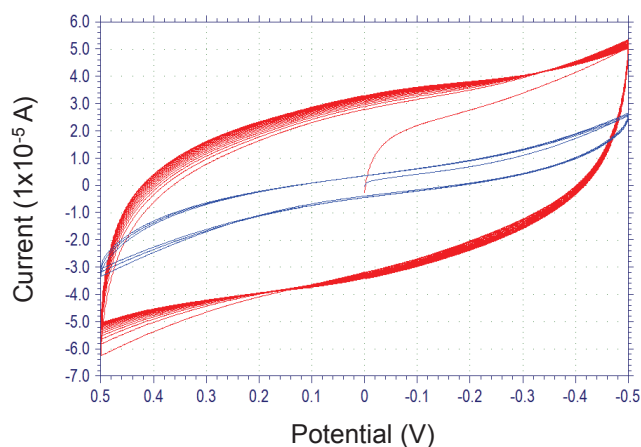


Figure 6. Cyclic voltammogram (100  $\text{mV/s}$ ) of the biotemplated supercapacitor in Nafion electrolyte with (red) and without (blue)  $\text{RuO}_2$  showing 9X increase in capacity.

The measured capacity is likely higher due to the grain structure visible in Figure 3. The grains have a diameter of roughly 10-20  $\text{nm}$ ; water and/or protons may be able to penetrate into the  $\text{RuO}_2$  along these boundaries at low scan rates. A study of gravimetric capacity of  $\text{RuO}_2$  related to particle size rather than water content [9] would predict 30-60  $\text{F/g}$  where the measured capacity is not far from this value at the high scan rate.

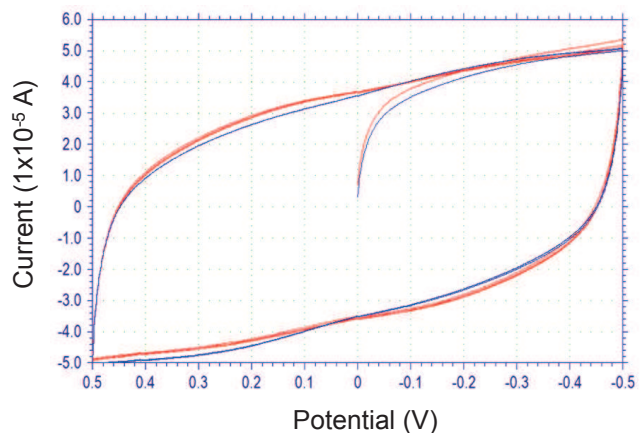


Figure 7. Cyclic voltammogram (100  $\text{mV/s}$ ) of the supercapacitor before and after extended charge/discharge. First (red) and 750th (blue) cycle show no noticeable degradation in performance.

Chronopotentiometry tests at three different current densities were performed. Cyclic voltammetry before and after the tests demonstrate negligible capacity fading after 750 cycles (Figure 7). At  $15.6 \mu\text{A/cm}^2$  (equivalent to 17  $\text{mV/s}$ ) capacity was 17  $\text{F/g}$  ( $938 \mu\text{F/cm}^2$ ), but the behavior at  $1.56 \text{ mA/cm}^2$  shows equivalent series resistance (ESR) limited performance during charge/discharge (Figure 8). Since the current

collector and RuO<sub>2</sub> are both highly conductive, the ESR limitation is likely due to proton diffusion in the Nafion.

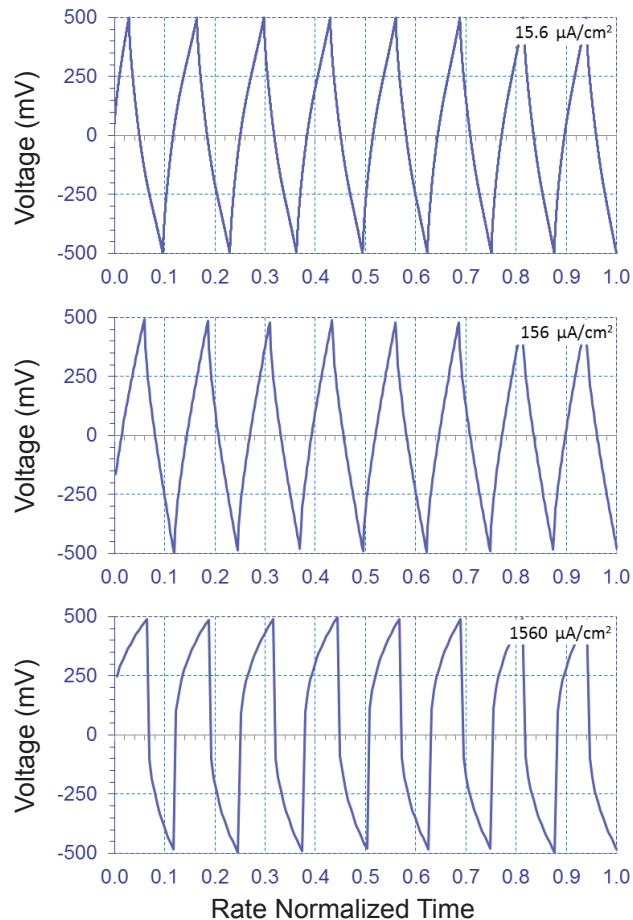


Figure 8. Chronopotentiometry results from the supercapacitor at various current densities. The test at 15.6  $\mu\text{A}/\text{cm}^2$  was extended to 750 cycles and no capacity fading was observed.

During self-discharge tests the voltage dropped to 36.8% of initial voltage in 336 seconds; using the measured capacity of 370  $\mu\text{F}$ , this corresponds to an internal parasitic resistance of 900 k $\Omega$  between the electrodes. Since the current design uses closely spaced interdigitated electrodes and no separator, the internal parasitic resistance may be decreased only by increasing electrode spacing. Future work will focus on optimizing the interdigitated electrode geometry and Nafion coating in order to decrease leakage current while maintaining proton transport.

## CONCLUSION

Nanostructured TMV-nickel combined with ALD provides a new pathway to selectively deposit active supercapacitor materials such as RuO<sub>2</sub> on a high surface area current collector. Using this technique, a

27 F/g RuO<sub>2</sub> gravimetric capacity (1.5 mF/cm<sup>2</sup> based on footprint) was achieved with Nafion electrolyte. The combination of polyimide substrate, TMV-enhanced current collector, RuO<sub>2</sub> and Nafion electrolyte provides a platform to optimize our vision of a high-capacity, thin, solid, flexible supercapacitor.

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