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Solid flexible electrochemical supercapacitor using *Tobacco mosaic* virus nanostructures and ALD ruthenium oxide

M Gnerlich$^{1,2,5}$, E Pomerantseva$^{1,2}$, K Gregorczyk$^{2,3}$, D Ketchum$^4$, G Rubloff$^{2,3}$ and R Ghodssi$^{1,2,3,5}$

$^1$ Department of Electrical and Computer Engineering, University of Maryland, College Park, MD 20742, USA
$^2$ Institute for Systems Research, University of Maryland, College Park, MD 20742, USA
$^3$ Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA
$^4$ Laboratory for Physical Sciences, College Park, MD 20740, USA
E-mail: ghodssi@umd.edu and gnerlich@umd.edu

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Abstract

An all-solid electrochemical supercapacitor has been developed using a nanostructured nickel and titanium nitride template that is coated with ruthenium oxide by atomic layer deposition (ALD). The electrode morphology was based on a high surface area biotemplate of genetically modified *Tobacco mosaic* virus. The biotemplate automatically self-assembles at room temperature in aqueous solution. Nafion® perfluorosulfonate ionomer dispersion was cast on the electrodes and used as a solid proton-conducting electrolyte. A 5.8 F g$^{-1}$ gravimetric capacity (578 μF cm$^{-2}$ based on footprint) was achieved in Nafion electrolyte, and the device retained 80% of its capacity after 25 000 cycles. The technology presented here will enable thin, solid, flexible supercapacitors that are compatible with standard microfabrication techniques.

(Some figures may appear in colour only in the online journal)

1. Introduction

Supercapacitors store electrical energy in an electronic double layer (EDL) and/or through a surface redox reaction, 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 [1, 2]. Current research trends are focused on improving energy density of supercapacitors, either by increasing surface area of EDLC using new nanomaterials or investigating electrolytes with higher voltage windows. Carbons are most frequently used for EDLC electrodes due to their high surface area, low cost and manufacturability [3], 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 (RuO$_2$) is attractive due to its high gravimetric capacity (720 F g$^{-1}$ [4] to 977 F g$^{-1}$ [5]), intrinsic electronic conductivity (37 μΩ·cm [6]), and chemical stability in acidic electrolytes. For more information on RuO$_2$ the following reviews are recommended: [5, 7, 8].

Typically, energy storage in pseudocapacitors involves surface mechanisms, but the capacity can be increased by using redox materials that allow the bulk of the material to participate. The chemical reaction for energy storage in hydrated RuO$_2$ involves protons and electrons, and optimally prepared RuO$_2$·xH$_2$O is able to conduct both. This approach minimizes unused volume and maximizes energy density. An alternative approach to make efficient use of RuO$_2$ is deposition on a nanostructured high surface area template causing a large portion of the RuO$_2$ surface to be in direct contact with the electrolyte, thus allowing for bulk reaction and higher gravimetric and volumetric energy densities. The technology presented here will enable thin, solid, flexible supercapacitors that are compatible with standard microfabrication techniques.
contact with electrolyte. Such an electrode has been created from genetically modified Tobacco mosaic virus (TMV) which self-assembles onto a prepared substrate at room temperature and is easily metalized for further processing [9, 10]. Onto this high surface area biotemplate, RuO₂ thin film was deposited by atomic layer deposition (ALD), a technique well known for its conformality and monolayer thickness control [11]. The drawback of this approach is that ALD methods to deposit hydrated RuO₂ are not available, and the RuO₂ film is anhydrous resulting in reduced gravimetric capacity [12]. Nevertheless, the combination of ALD energy storage materials with TMV has been demonstrated to be a powerful method for producing nanostructured lithium-ion battery electrodes [13, 14] and is expected to be important for new supercapacitor technologies as well.

In this work RuO₂ nanostructures were synthesized through biotemplating and used in a supercapacitor fabricated from solid, flexible materials. DuPont Nafion®—a solid sulfonated polymer—was used as a proton-conducting electrolyte. The combination of a polyimide substrate, TMV-enhanced current collector, RuO₂ and Nafion electrolyte provides a platform to optimize our vision of a thin, solid, flexible supercapacitor.

2. Methods

2.1. Supercapacitor design

The objective of this design is integration of a supercapacitor with a top-down microfabrication process for complex microfabricated systems. The starting substrate is a Si wafer with a flexible, insulating polyimide coating. A metal current collector (Ti/Au) is deposited on the polyimide, and surface area is increased using TMV-1Cys. TMV-1Cys is a genetically modified version of TMV containing a cysteine residue in the coat protein that causes the virus to adhere to surfaces with a preferential vertical orientation. The cysteine residue also provides numerous metal binding sites that allow for the formation of a continuous Ni shell by electroless Ni plating. This procedure rigidly fixes the biotemplate in place and converts the non-conductive TMV-1Cys into a conductive high surface area electrode [9]. A conductive titanium nitride (TiN) layer is then deposited by ALD to protect the Ni from the acidic electrolyte. RuO₂ is also deposited by ALD on the TMV-1Cys/Ni/TiN current collector. A schematic of the design is shown in figure 1. Previous research has demonstrated supercapacitors based on RuO₂ powders with Nafion used either as a solid electrolyte [15] [17] or a binder [16] with liquid electrolyte. In contrast, the RuO₂ thin film in this work is directly deposited on electrodes that have very high surface area. Each electrode is identical and symmetrical in geometry. The silicon substrate may be removed by a silicon etch to release the flexible device.

2.2. Fabrication process

Fabrication of the biotemplated RuO₂ electrode 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. A schematic diagram of the fabrication process is shown in figure 2. Next, the polyimide is roughened in oxygen plasma (Plasma-Therm 790) and coated with a Ti/Au (200 Å/2000 Å) layer in an e-beam evaporator (CHA Industries). Each wafer was diced into 1 cm by 1 cm chips before coating with TMV-1Cys. The TMV-1Cys was prepared as reported previously [9]. Each chip was submerged in a 0.2 g L⁻¹ suspension of the TMV-1Cys in 0.1 M phosphate buffer, and the biotemplate was allowed to assemble overnight. The excess TMV-1Cys solution was removed and a 12:1 solution of phosphate buffer and sodium tetrachloropalladate (NaPdCl₄) was added to functionalize the TMV-1Cys surface for electroless metallization. The palladium solution was removed, and an aqueous nickel plating solution of NiCl₂, glycine, Na₂B₄O₇ and dimethylamine borane (DMAB) was added. The nickel plating reaction is autocatalyzed but starts at the palladium functionalized TMV-1Cys to produce a coating of nickel. The reaction stops when the sample is removed from solution and rinsed with water.

TiN was deposited on the TMV-1Cys/Ni template by 200 cycles of TDMAT and ammonia at 175 °C in a Beneq TFS 500 ALD system. RuO₂ was deposited on the TMV biotemplate by ALD using 2000 cycles of bis(2,2,6 trimethyl cyclohexasadienyl)-ruthenium and oxygen in a custom built, cross flow reactor at 225 °C [18]. Samples were weighed with a microgram-precision analytical balance (Mettler Toledo, XS105) before and after coating to determine total mass loading, which was between 199 and 266 μg cm⁻² for various chips.

Supercapacitors were prepared by creating an interdigitated pattern by mechanically scribing through the material stack using a probe station, exposing the underlying silicon substrate while separating the electrically isolated electrodes. The devices were 8 mm by 8 mm and each electrode is approximately 1 mm wide and 6 mm long. The separation between electrodes was approximately 60 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 h at 140 °C in a nitrogen purged
ramping furnace (Lindberg/Blue M BF51732BC). Nafion was removed from the electrical contact pads by swabbing with isopropyl alcohol. The Nafion thickness was measured to be approximately 20 μm by a step profilometer (Veeco Dektak 6M) on a sacrificial device that was scribed through the Nafion.

2.3. Testing apparatus

Protonation of the RuO₂ surface enables energy storage through an oxidation state change that involves transfer of electrons—a process that can be reversed with an applied voltage. The energy storage capability of the supercapacitor is demonstrated using Nafion. The ionic behavior of Nafion is complex [19], but it generally requires some absorbed water content to maximize ionic conductivity. Electrochemical tests were performed with the supercapacitor in a symmetrical configuration without a reference electrode. To evaluate supercapacitor performance three types of tests using cyclic voltammetry were conducted (BioLogic VSP potentiostat). First, repeated cyclic voltammetry tests were completed with the devices in a controlled temperature/humidity chamber (Espec SH-241). A custom holder was used based on a 50 mL centrifuge tube with spring clips that provided electrical contact and mechanical support. The bottom portion of the tube was removed to expose the chip to the environmental chamber (see figure 3). Second, TMV-templated electrodes without an interdigitated pattern and without Nafion were tested by submerging in 0.5 M H₂SO₄. Third, cycle lifetime tests on interdigitated electrodes with Nafion were completed while the devices were suspended in a sealed 50 mL test tube. The test tube contained either ambient air or a few milliliters of deionized water (DI) to make a humidified test chamber.

3. Results

3.1. Electrode characterization

The structure of the electrode produced by metalized TMV was evaluated by SEM and shows a high surface area electrode ideal for supercapacitors (figure 4). TEM images and EDS spectra (JEOL 2100F) were extracted from nanoparticle samples transferred from the electrode surface to a TEM grid. The cross-section obtained by TEM (figure 5) demonstrates the layered structure of TMV-1Cys/Ni/TiN/RuO₂. The EDS spectrum overlay shows the core from the initial TMV-1Cys particle is 20 nm with a 30 nm nickel coating. The TiN layer is 10–20 nm and the RuO₂ layer is 20–30 nm. It was found that the TiN coating dramatically increased the RuO₂ loading compared to nickel alone, and it also protects the nickel from acidic electrolytes thereby increasing the cycle lifetime. The composition of the RuO₂ coating was evaluated by powder XRD (Brucker D8 Advance) showing the presence of polycrystalline RuO₂ (figure 6(a)).
3.2. Electrode testing

3.2.1. Solid electrolyte. The devices were tested by cyclic voltammetry from 1 to 500 mV s\(^{-1}\) and the capacitance was extracted from current measured at the zero voltage crossing using \(C = i/(dV/dt)\). Since the ionic conduction of Nafion is a strong function of the water content of the polymer, it is expected that capacitance at a particular scan rate would decrease as humidity decreases. The cyclic voltammetry tests in Nafion (figure 7) indicate a maximum capacity of 5.8 F g\(^{-1}\) at 2 mV s\(^{-1}\) where the mass is based on the mass loading and the area of a single electrode. The areal capacity is 578 \(\mu\)F cm\(^{-2}\) based on total footprint area of the device.

Although the gravimetric capacity is low compared to hydrous RuO\(_2\) powders, the stability of the RuO\(_2\)/Nafion supercapacitors is quite good. The devices were tested in either ambient or 100% relative humidity by adding a small amount of DI water to a sealed test tube (the environmental chamber was not used for this test). Cyclic voltammetry at 50 mV s\(^{-1}\) was repeated for up to 25 000 cycles (see figure 8), and the total charge per cycle was evaluated using BioLogic EC-Lab v10.3 software. The capacity of the supercapacitor in high humidity was higher at the very beginning of the test, but the capacity after a few thousand cycles was similar to the device exposed to ambient humidity. The cycle lifetime was poorer in a high humidity environment, and the unusual behavior shown in figure 8 after 15 000 cycles is likely due to interfacial failure and subsequent degradation of the current collector. Possible reasons for this behavior are incomplete coverage of the current collector by TiN, as well as mechanical stress caused by swelling of Nafion at high humidity. At ambient humidity levels the supercapacitor retained 80% of charge/discharge capability after 25 000 cycles.

An estimate of the internal parasitic resistance was made with the potentiostat (input impedance of 10\(^{12}\) \(\Omega\)) from a simple self-discharge test after charging to 0.5 V using 10 \(\mu\)A of current. The time constant indicates this resistance to be 9.4 M\(\Omega\) between the electrodes.

3.2.2. Liquid electrolyte. In addition to tests in Nafion electrolyte, the supercapacitor electrodes were tested in 0.5 M H\(_2\)SO\(_4\) in a symmetrical configuration without a reference electrode (figure 9). A significantly larger capacity of 47 F g\(^{-1}\) at 1 mV s\(^{-1}\) resulted from the test in 0.5 M H\(_2\)SO\(_4\) than resulted from Nafion. It must be noted that the cycle lifetime in aqueous H\(_2\)SO\(_4\) was poor and it appeared that delamination occurred between the Au/Ni interface. This is probably due to dissolution of the Ni in areas that are not completely covered by TiN and RuO\(_2\).

4. Discussion

The Ni-coated self-assembled TMV-1Cys biotemplate enables the production of a stable, nanostructured, high surface area
current collector suitable for microfabricated supercapacitor electrodes, and RuO₂ active material was deposited by ALD. This fabrication approach allows the energy density behavior of this complex system to be studied by electrochemical characterization in liquid and solid electrolytes. A comparison of the specific capacitance as a function of scan rate for these electrolytes is shown in figure 10.

Overall, the measured gravimetric capacities are lower than reported values for hydrated RuO₂, which ranges from 527 to 900 F g⁻¹ [12] depending on the annealing temperature. The capacity of RuO₂ is highly dependent on the hydration state, the deposition method, the substrate’s surface area and particle size. The capacity of solid anhydrous RuO₂ is less than 1 F g⁻¹ and increases to between 19 and 29 F g⁻¹ with small amounts of water in the structure [12]. Although RuO₂ prepared by the ALD method does not contain water, it is a thin film deposited on the nanostructured TMV biotemplate and has significant surface area. Mesoporous anhydrous RuO₂ tested by cyclic voltammetry in H₂SO₄ was found to have a specific capacity between 29–58 F g⁻¹ depending on scan rate [20], and the specific capacity of RuO₂ powders depends strongly on the particle size [21]. Furthermore, the measured capacity of the anhydrous RuO₂ film may be higher than 1 F g⁻¹ due to the grain structure visible in the other RuO₂ layer in figure 5. Such morphology may allow ions to penetrate the surface of the RuO₂ and more material would be electrochemically active compared to a homogeneous film. Pristine chips and chips from the same fabrication run after cyclic voltammetry in 0.5 M H₂SO₄ were compared by XRD (figure 6(b)), showing little change in the structure. A shift in the peak position would be expected if water and/or protons were able to penetrate the surface of RuO₂ during cyclic voltammetry at slow scan rates. Therefore the capacity of the RuO₂ in H₂SO₄ is likely due to the nanostructure of the TMV biotemplate, and the comparatively lower capacity in Nafion is likely due ionic conductivity rate limitations of the polymer electrolyte.

In order to determine whether the measurement from cyclic voltammetry was primarily Faradaic (redox) or non-Faradaic (capacitive), the cyclic voltammetry sweep rate was
Figure 8. Plot of (a) total charge capability (measured by cyclic voltammery at 50 mV s$^{-1}$) and (b) charge retention over 25,000 cycles for RuO$_2$/Nafion supercapacitor with TMV-1Cys/Ni/TiN current collector in ambient humidity and 100% relative humidity.

Figure 9. Cyclic voltammetry curves for RuO$_2$ on TMV-1Cys/Ni/TiN current collector with 0.5 M H$_2$SO$_4$ at scan rates of 1, 10, 100, 500 mV s$^{-1}$. The TMV-templated electrodes are in a symmetrical configuration without a reference electrode.

Figure 10. A comparison of the derived specific capacitances from cyclic voltammetry curves in liquid and solid electrolyte at rates of 1 to 500 mV s$^{-1}$.

for redox current, which in simplified form at 25 °C is given by equation (1) where $n$ is the number of electrons appearing in redox half-reaction, $\frac{dv}{dt}$ is the scan rate, $D$ is the ionic diffusion coefficient, $A$ is the electrode area, $C$ is the ionic concentration:

$$i = 2.687 \times 10^5 n^{1.5} \left( \frac{dv}{dt} \right)^{0.5} D^{0.5} AC.$$  \hspace{1cm} (1)

The current due to the EDLC is purely capacitive in nature and is given by equation (2), where $C$ is the capacitance (F):

$$i = C \frac{dv}{dt}.$$  \hspace{1cm} (2)

If the current is proportional to scan rate to the 0.5 power, the charge storage mechanism is Faradaic, and if it is proportional to the 1.0 power, the charge storage mechanism is non-Faradaic. An intermediate value indicates a combination of both mechanisms. A power law fit to the results in 0.5 M H$_2$SO$_4$ as a function of scan rate was $x^{0.54}$ indicating primarily Faradaic capacity. On the other hand, a power law fit to the capacity in Nafion as a function of scan rate was $x^{0.84}$ indicating a mix of Faradaic and non-Faradaic mechanisms. The overall smaller capacity of the supercapacitor in Nafion may be related to lower ionic transport which would limit the redox reaction with RuO$_2$. Ionic transport limitations due to poor electrolyte contact with RuO$_2$ are unlikely since the Nafion is applied as a liquid dispersion, and it is quite difficult to remove.

Since the present design uses closely spaced interdigitated electrodes and no separator, the leakage current may be decreased only by increasing electrode spacing. However this also increased the distance ions must move through the electrolyte. Future work will focus on optimizing the interdigitated electrode geometry and Nafion coating in order to decrease leakage current and improving proton transport.

varied from 1–500 mV s$^{-1}$. The current due to a Faradaic reaction can be calculated from the Randles–Sevcik equation

$$i = 2.687 \times 10^5 n^{1.5} \left( \frac{dv}{dt} \right)^{0.5} D^{0.5} AC.$$  \hspace{1cm} (1)

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5. Conclusion

A nanostructured supercapacitor electrode was fabricated from TMV-1Cys, Ni and TiN and combined with ALD to provide a new pathway to deposit active supercapacitor materials such as RuO₂ on a high surface area current collector. Using this technique, biotemplated RuO₂ with 5.8 F g⁻¹ gravimetric capacity (578 μF cm⁻² based on footprint) was achieved in Nafion electrolyte. The device retained 80% of its capacity after 25,000 cycles. Future work will include the optimization of electrode geometry, investigation of alternate methods of RuO₂ deposition on TMV-1Cys that allow incorporation of H₂O, and demonstration of a fully flexible supercapacitor after release from the microfabrication substrate.

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