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(54) Title: **RUO₂-COATED FIBROUS INSULATOR**

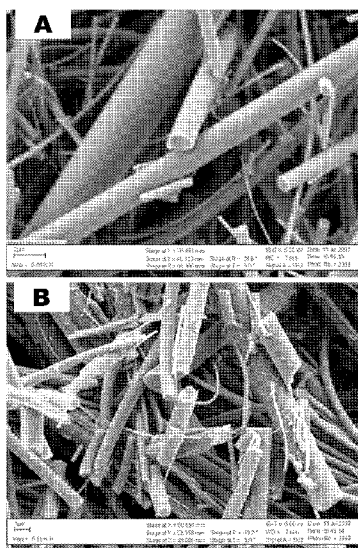


Fig. 1

(57) Abstract: An article having: a nonconductive fiber and a RuO₂ coating. A method of: immersing a nonconductive article in a solution of RuO₄ and a nonpolar solvent at a temperature that is below the temperature at which RuO₄ decomposes to RuO₂ in the nonpolar solvent in the presence of the article; and warming the article and solution to ambient temperature under ambient conditions to cause the formation of a RuO₂ coating on a portion of the article. An article having: a nonconductive fiber and a coating. The coating is made by electroless deposition, sputtering, atomic-layer deposition, chemical vapor deposition, or physical vapor deposition.

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RuO₂-COATED FIBROUS INSULATOR

This application claims the benefit of US Provisional Patent Application No. 60/977,685, filed on 10/05/2007.

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TECHNICAL FIELD

The invention is generally related to RuO₂ and other coatings on fibers.

BACKGROUND ART

10 Ruthenium dioxide (RuO₂), one of the platinum group metal oxides, is an important industrial material due to its metallic electronic conductivity ($\sigma = 10^4 \text{ S cm}^{-1}$ at 25°C), excellent chemical and thermal stability, and diffusion barrier properties (Trasatti, Physical electrochemistry of ceramic oxides. *Electrochim. Acta*, **36**, 225–241 (1991)). The conductivity can depend on the crystalline form (Creutz et al., *J. Phys. Chem. B*, **107**, 6668 (2003)). Hydrous
15 ruthenium oxide (normally designated as RuO_xH_y or RuO₂ • H₂O) is a mixed electron–proton conductor that exhibits large proton capacitances ($\sim 720 \text{ F g}^{-1} \text{ proton}^{-1}$) (Zheng et al., A new charge storage mechanism for electrochemical capacitors. *J. Electrochem. Soc.*, **142**, L6–L8 (1995)). It has recently been recognized that nanoscopic anhydrous RuO₂ exhibits high values of Li-ion uptake ($\sim 260 \text{ mA h g}^{-1}$) as a function of its degree of microstructural disorder (Lytle et al.,
20 The importance of combining disorder with order for Li-ion insertion into cryogenically prepared nanoscopic ruthenia. *J. Mater. Chem.*, **19**, 1292–1299 (2007)). These characteristics have led to the use of ruthenium dioxide in electrodes for such applications as catalysis, electrolysis, photovoltaic devices, capacitors, and thick and thin film resistors.

Many chemical vapor deposition (CVD) techniques have been developed that form
25 dense RuO₂ films on flat substrates, including: sputtering or evaporating ruthenium metal in the presence of oxygen; plasma decomposition of Ru-bearing gases by glow discharge; and thermal or photolytic decomposition of organometallic precursors (Ardizzone et al., Interfacial properties of oxides with technological impact in electrochemistry. *Adv. Colloid Interf. Sci.*, **64**, 173–251 (1996)). Ruthenium dioxide films have been formed by activating oxygen gas and evaporated
30 ruthenium vapor with direct current or radio-frequency radiation (Bunshah et al., U.S. Patent 5,055,319). The deposition of RuO₂ via the reductive decomposition of RuO₄ from aqueous or nonaqueous solutions, pure solid, or vapor creates micrometer-thick RuO₂ films with resistivities of $\sim 10^{-2} \Omega \text{ cm}$ (Yuan et al., Low-temperature chemical-vapor-deposition of ruthenium dioxide from ruthenium tetroxide—a simple approach to high-purity RuO₂ films. *Chem. Mater.*, **5**, 908–

910 (1993))

Because of the high cost of ruthenium precursors, it is desirable to minimize the amount of RuO₂ required for a particular function, for example by preparing RuO₂ in nanoscale, high-surface-area forms to maximize the number of reaction sites for catalytic and sensing applications. Conventionally, micro- and nanostructured RuO₂ electrodes are prepared by modifying the surface of a substrate via dip-coating in or painting on a RuCl₃ solution followed by heating in air to oxidatively decompose the salt to RuO₂. Nanoscopic RuO₂ colloids have also been self-wired onto mesoporous silica aerogel substrates via cryogenic deposition (Ryan et al., US Patent Nos. 6,290,880 and 6,649,091), in which a precursor solution of RuO₄ in a nonpolar solvent (pentane) is equilibrated with a SiO₂ aerogel substrate at dry ice/acetone bath temperatures and allowed to gradually warm to room temperature bringing about the decomposition of RuO₄ to a self-organized, interconnected array of RuO₂ that provides an electronic pathway through the insulating silica aerogel scaffold (Ryan et al., Electronic connection to the interior of a mesoporous insulator with nanowires of crystalline RuO₂. *Nature*, **406**, 169-172 (2000)).

The RuO₂-SiO₂ aerogel composites are high-surface-area electrode materials with weight loadings of RuO₂ >20 wt%, but it is challenging to make quality contacts from the rigid and fragile composites to other solid-state materials. Furthermore, repeated immersion in solvents can cause collapse of the aerogel pore structure (as may occur in applications such as electrochemical production of chlorine (Cl₂) via the chloralkali process), thereby diminishing the surface area. Significant manufacturing costs may be associated with producing the aerogel substrates.

DISCLOSURE OF THE INVENTION

Disclosed herein is an article comprising: a nonconductive fiber; and a RuO₂ coating on a portion of the fiber.

Also disclosed herein is a method comprising: immersing a nonconductive article in a solution of RuO₄ and a nonpolar solvent at a temperature that is below the temperature at which RuO₄ decomposes to RuO₂ in the nonpolar solvent in the presence of the article; and warming the article and solution to ambient temperature under ambient conditions to cause the formation of a RuO₂ coating on a portion of the article.

Also disclosed herein is an article comprising: a nonconductive fiber; and a coating on a portion of the fiber; wherein the coating is made by electroless deposition, sputtering, atomic-layer deposition, chemical vapor deposition, or physical vapor deposition.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention will be readily obtained by reference to the following Description of the Example Embodiments and the accompanying drawings.

Fig. 1 shows scanning electron micrographs of (A) unmodified SiO₂ paper and (B) RuO₂-coated SiO₂ paper (designated herein as RuO₂||SiO₂) after heating in air to 150°C. The RuO₂-modified glass paper had an increased surface roughness and some precipitated nanoparticles of RuO₂ can be observed. Because of the conductive electron contrast between RuO₂ (lighter) and SiO₂ (darker), the nanoscale coating of RuO₂ is apparent even at this magnification on some of the fibers.

Fig. 2 shows a scanning electron micrograph of a RuO₂||SiO₂ fiber calcined in air to 200°C showing a nanoscale coating of RuO₂ on the fiber. The darker region is the SiO₂ fiber and the lighter regions are RuO₂. This image demonstrates that the cryogenically deposited RuO₂ forms a nanoscale coating around the fiber leaving only small portions of SiO₂ exposed.

Fig. 3 shows a bright-field TEM (transmission electron microscopy) image of a RuO₂||SiO₂ fiber calcined to 200°C in which the RuO₂ is observed to form a nanoweb over the surface of the silica fiber. An interfilling of RuO₂ into the crevice formed where two silica fibers overlap on their edge can be observed in the rightmost micrograph.

Fig. 4 shows the effect of calcining on the pseudocapacitance of ruthenia nanoweb supported on glass membranes. Cyclic voltammograms in 0.5 M H₂SO₄ at 2 mVs⁻¹ vs SSCE with a Pt counter electrode of RuO₂||SiO₂ membranes previously calcined in air at: (dashed) 100°C; (dotted) 150°C; (solid) 200°C

Fig. 5 shows conductivity as a function of calcination temperature.

Fig. 6 shows four-point probe conductivity of 200°C-calcined RuO₂||SiO₂ composites.

Fig. 7 shows a typical cyclic voltammogram in sulfuric acid for a 200°C-calcined RuO₂||SiO₂ composite

Fig. 8 shows a typical voltammogram at 200°C-calcined RuO₂||SiO₂ composites in aqueous 5 mM ferricyanide.

MODES FOR CARRYING OUT THE INVENTION

In the following description, for purposes of explanation and not limitation, specific details are set forth in order to provide a thorough understanding of the present invention. However, it will be apparent to one skilled in the art that the present invention may be practiced in other embodiments that depart from these specific details. In other instances, detailed

descriptions of well-known methods and devices are omitted so as to not obscure the description of the present invention with unnecessary detail.

Described herein is a method to fabricate lightweight, flexible, electrically conductive nanocomposites of ruthenium dioxide deposited on a silica fiber membrane. The resulting nanocomposite may have a low weight percentage and volume fraction of RuO₂, but may demonstrate the metallic conductivity and electrocatalytic activity associated with bulk RuO₂ materials.

A multifunctional, flexible electrode may be produced by converting inexpensive silica fiber paper into a conductive platform via cryogenic deposition of nanoscale RuO₂ coatings. The RuO₂-coated filter paper (RuO₂||SiO₂) can exhibit high electronic conductivity and desirable electrochemical properties, but does so at low mass loadings ($\sim 300 \mu\text{g cm}^{-2}$), thereby improving the utilization of this expensive platinum-group metal. The conductive nanoscopic coating can be air- and water-stable and readily functionalized to increase or vary the catalytic activity. The macroscopic properties of the lightweight SiO₂ substrate, *i.e.*, flexibility, compressibility, and robustness, may be retained as the ruthenia-imparted electronic, electrochemical, and electrocatalytic functions are added. This material has potential for use as an electrode platform for important technological applications, including as gas-diffusion electrodes for fuel cells (when modified with an electrocatalyst, such as Pt), conductive membranes, and as multifunctional platforms for electrocatalysis/photocatalysis.

This inexpensive, practical manifestation on the macroscale of a conductor on the nanoscale is an adaptation of a method for wiring the interior of silica aerogels, based on the nonaqueous cryogenic decomposition of RuO₄ to RuO₂ (Ryan, et al., *Nature*, **406**, 169 (2000)). The RuO₂-coated SiO₂ architecture combines the high surface area and mesoporosity of the aerogel with the electronic properties of the self-wired RuO₂ nanoweb, but high weight loadings are necessary to form the conducting network (>20 wt %), and the resultant monolithic objects have relatively low geometric-factor-normalized electrical conductivity ($500 \mu\text{S cm}^{-1}$). Furthermore, the cost of producing aerogel monolithic substrates and their fragile nature present additional challenges to commercialization and application.

To produce a substrate that may be more robust, flexible, and inexpensive, an electrically conductive network of RuO₂ is deposited onto commercially available silica fiber membranes (filter paper) as a fiber scaffold. The membranes may have a thickness of $\sim 200 \mu\text{m}$ and may be composed of submicron-to-micron diameter silica fibers. Macroporous voids, which may be 100s of nanometers to several micrometers, between the fibers offer headspace for the deposition of nanoscopic RuO₂ and for facile infiltration by fluids. In addition to achieving

macroscopic physical properties associated with the SiO₂ substrate, dramatic improvements may be observed in electrical and electrochemical properties and remarkable physical behavior related to the RuO₂ nanoscale coating that forms on the SiO₂ fibers. The electronic conductivity of the RuO₂||SiO₂ composite may be three orders of magnitude higher than that of the RuO₂-nanowired aerogel and is achieved with a significant reduction in the weight loading of RuO₂ (5% vs ~40%). The compressible and flexible nature of the filter paper substrate allows for excellent electrical contact with rough and curved surfaces, a feature not possible with rigid substrates such as an aerogel. The RuO₂||SiO₂ composites are also tolerant to immersion into (and removal from) liquid phases, including water, allowing for solution-based modification and extended operation (and recovery) when used as an electrode structure.

The silica fiber membranes described here have markedly different morphological and physical properties than the silica aerogels described in US Patent Nos. 6,290,880 and 6,649,091. The SiO₂ aerogels had a three-dimensional mesoporous network (pores sized < 50 nm) with a large surface area (~400–500 m² g⁻¹) and a solid phase composed of networked SiO₂ nanoparticles. In contrast, the SiO₂ fiber membranes may be macroporous (pores sized > 50 nm) with a very low surface area (on the order of < 1 m² g⁻¹) and may be composed of submicron-to-micron-sized SiO₂ fibers. The differences in macroscopic physical properties of the two materials are quite significant. The aerogel is rigid and cannot be flexed without shattering, whereas the SiO₂ fiber membranes are flexible and can be easily molded to form quality electronic contacts with uneven surfaces. The SiO₂ fiber paper also has a degree of compressibility (softness) that helps in forming electronic contacts with other materials through pressure. This flexibility and compressibility is not possible with SiO₂ aerogels.

Synthesis of the RuO₂||SiO₂ composite is far simpler than described for aerogel substrates, namely the time for equilibration and RuO₂ deposition may be < 1 day rather than a week and may be carried out in ambient atmosphere rather than on a Schlenk line. The silica filter paper turns black after RuO₂ deposition with a mass uptake typically of 7 wt%. Upon heating the sample in air to 200°C to crystallize the cryogenerated ruthenia (Lytle et al., *J. Mater. Chem.*, **17**, 1292 (2007)), the mass loading drops to 5 wt%, concomitant with removal of organic byproducts, as we previously observed for unsupported cryogenically prepared RuO₂ powder. The weight loading of RuO₂ in the calcined composite was verified by commercial elemental analysis by ICP–AES.

Ruthenia nanowebbs are cryogenically deposited on both SiO₂ aerogel and fiber membrane substrates, but the electronic and physical properties of the resultant materials are significantly different. The RuO₂–SiO₂ aerogels, with RuO₂ weight loadings of ~40 wt%,

display conductivities on the order of 0.5 mS cm^{-1} whereas the $\text{RuO}_2||\text{SiO}_2$ fiber membranes, having RuO_2 weight loading of 5–10 wt%, may display conductance on the order of 500 mS cm^{-1} . Additionally, increasing the calcination temperature of the RuO_2 – SiO_2 aerogel above $\sim 200^\circ\text{C}$ leads to a decrease in electrical conductivity, presumably due to grain-size coarsening.

5 The $\text{RuO}_2||\text{SiO}_2$ fiber membranes may show an optimum in conductivity when calcined to 200 – 250°C , thereby demonstrating higher temperature stability and range of operation. The higher conductance observed for the SiO_2 fiber membrane is remarkable considering the lower weight loading and small volume of RuO_2 . The RuO_2 phase may be constrained to a nanoscale coating yet the material may display high conductivity as if the RuO_2 wires had a geometric factor of
10 micrometers in diameter (as do the silica fibers onto which the cryogenerated ruthenia deposits). Additionally, the $\text{RuO}_2||\text{SiO}_2$ fiber membranes show increased RuO_2 mass-normalized catalytic activity for chloride oxidation over the RuO_2 – SiO_2 aerogels, and it is proposed to use these composites as stand-alone, porous Li-ion insertion electrodes that are moldable for three-dimensional microbatteries, in which the electrode and electrolyte/separator phases are
15 interpenetrated in three dimensions.

The ultrathin RuO_2 shell that coats the fibers comprising the SiO_2 paper closes on itself to create an imperfect, but contiguous electron path around the circumference and along the axis of the curved insulator. The conductive nanoscopic skin of RuO_2 expresses electron transport that mimics the size of the large, insulating object around which it wraps. In this way, electron
20 transport in the $\text{RuO}_2||\text{SiO}_2$ coaxial arrangement appears analogous to the plasmonic character of gold-coated silica spheres. In $\text{Au}||\text{silica}$ core–shell composites, the surface plasmon resonance tracks correlates to the inner and outer diameter of the Au shell, thereby tracking the diameter of the silica spherical core. Unlike metal nanoparticles, the plasmon resonance is not determined solely by the characteristic width of the metal.

25 The prior cryogenic deposition of RuO_2 has been modified to simplify the process. The original synthesis was carried out under vacuum on a Schlenk line and required a purification step for the pentane precursor. It was also necessary to phase-equilibrate the aerogel substrate with pentane in order to prevent damaging the mesoporous structure. The SiO_2 fiber membrane has a macroporous structure that is not sensitive to solvent infiltration or evaporation and the
30 reaction can be run at ambient pressure. Petroleum ether has been substituted as a solvent and it is not necessary to purify the petroleum ether beforehand. These new materials may be easier to process on a larger scale at a greatly reduced cost of fabrication.

The disclosed RuO_2 coating method may be performed on any nonconductive article. By “nonconductive” is meant that the electrical conductivity is low enough that it is considered

in the art to be nonconductive. For example, the material conductivity may be less than about 10^{-9} S/cm and/or the bulk conductivity may be less than about 10^{-12} S/cm. The article may be in the form of a fiber or thread, being an elongated, flexible, and relatively small diameter object. Small diameters include, but are not limited to, submicron size to tens of microns. The article may comprise a plurality of entangled fibers, meaning that the fibers form a cohesive mass. The entangled fibers may be in the form of a woven or non-woven sheet, such as a membrane or fiber-formed paper. Such a membrane or paper may be flexible while retaining its cohesiveness. The entangled fibers may also form a more three-dimensional, non-sheet article.

Any nonconductive fibers may be used including, but are not limited to, polymer, ceramic, and glass. The fibers may comprise or be entirely silica glass (SiO_2), such as in a silica fiber membrane. Such membranes are commercially available and are generally used as filters. The membranes may have fibers up to about 10 microns in diameter. The fibers in the membrane may have a wide range of diameters, or they may be monofilaments, having a range of diameter that deviates from the average by no more than about 5%. The diameter and length of the fibers may be adjusted to tune the electrical properties of the article.

The article has a RuO_2 coating on a portion of the article, which may include the entire article. The RuO_2 coating may be formed by the methods disclosed herein or any other method that produces the coating. The coating need not entirely cover all of the fiber or fibers. However, the coating may cover enough of the fiber or fibers such that the RuO_2 forms an electrically connected network throughout the article. The network has the effect of increasing the bulk electrical conductivity of the article. A bulk conductivity of at least about 500 mS/cm may be achieved when the article contains only up to 10 wt% RuO_2 . The coating may have an average thickness of up to about 10 nm. This average thickness does not include non-coated portions of the fiber or fibers. The thickness and RuO_2 loading may be adjusted to tune the electrical properties of the article.

The article may also have a second material deposited on the RuO_2 coating, such as a metal, metal oxide, polymer, molecular or ionic species or ceramic. The deposited material may be electrophoretically deposited, where the deposited material acts as an oxidant while RuO_2 acts as a reductant. (The phrase "metal, metal oxide, ceramic, or platinum" may refer to the material in pre-deposit or post-deposit form.) One suitable material is platinum.

The same fibrous articles may also be made with other coatings besides RuO_2 . Any coating that may be made by electroless deposition, sputtering, atomic-layer deposition, chemical vapor deposition, physical vapor deposition, atomic layer deposition, or sol-gel methods may be deposited on the fiber or fibers. The morphology and dimensions of the coating and electrical

properties of the article may be the same or different from those of RuO₂ depending on the material used. Suitable coating materials and methods are disclosed in A. Niskanen et al., Radical enhanced atomic layer deposition of titanium dioxide. *Chem. Vap. Dep.*, **13**, 152-157 (2007); J.-H. Luo et al., Atmospheric pressure MOCVD of thin Fe films on carbon fibers. *Chem. Vap. Dep.*, **13**, 574-580 (2007); C.B. Clemons et al., Modeling, simulation, and experiments of coating growth on nanofibers. *J. Appl. Phys.*, **103**, 044304 (2008); R.A. Caruso et al., Titanium dioxide tubes from sol-gel coating of electrospun polymer fibers. *Adv. Mater.*, **13**, 1577-1579 (2001); J-H Ahn et al., Electroless coating of tungsten oxide on the surface of copper powder. *Mater. Res. Bull.*, **43**, 2266-2271 (2008); J. Biener et al., Ruthenium/aerogel nanocomposite via atomic layer deposition. *Nanotechnology*, **18**, 055303 (2007); Dhawan et al., "Thin conducting polypyrrole film on insulating surface and its applications" *Bull. Mater. Sci.*, **16**, 371-380 (1993); Bhat et al., "Development of Conductive Cotton Fabrics for Heating Devices" *J. Appl. Polym. Sci.*, **102**, 4690-4695 (2006); Agarwal et al., "Conductive wood microfibres for smart paper through layer-by-layer nanocoating" *Nanotechnol.*, **17**, 5319-5323 (2006). The thickness of the coating (including a RuO₂ coating), as defined above may be, but is not limited to, up to about 10 nm or 20 nm. The ratio of the diameter of the fiber to the thickness of the coating may be, but is not limited to, at least about 3, 5, 10, or 200 or higher. For example, a 100 nm diameter fiber might have a 20 nm coating.

RuO₂ may be deposited on articles, which may be fibers or non-fibers, by immersing the article in a solution of RuO₄ and a nonpolar solvent. The immersion is done at a temperature that avoids decomposition of RuO₄ in that solvent in the presence of the article. As RuO₄ may decompose at room temperature in solvents, the immersion may be cooled by a dry ice bath (about -78°C) or in an aqueous ice bath (about 0°C). The immersion may continue until the entire surface of the article or a sufficient amount of the surface of the article is wet with the solution.

Before the immersion, it may be desirable to equilibrate the article in the nonpolar solvent without the presence of RuO₄. This is performed at the same temperature as the immersion. By this method, the article is at the same temperature as the RuO₄ solution when it first contacts the article.

Once the immersion is complete, the article and solution are warmed to ambient temperature under ambient conditions. Ambient temperature includes, but is not limited to, room temperature, about 25°C, about 20 to about 30°C, and temperatures typically occurring in laboratory and manufacturing facilities with or without climate control. The warming occurs under ambient conditions, meaning that the warming need not be slowed by maintaining any

cooling of the solution, nor hastened by direct heating of the solution by anything other than ambient air or objects in contact with the solution, article, or vessel containing them.

Suitable nonpolar solvents include, but are not limited to, a hydrocarbon solvent or petroleum ether. The solvent may be resistant to oxidation by RuO_4 and may be free of heteroatoms that may cause nucleation and growth of RuO_2 precipitates instead of coating the article.

The RuO_4 may be obtained in an aqueous solution, where it may be more stable than in a nonpolar solution. In that case, the RuO_4 may be extracted into the nonpolar solvent before immersing the article.

The nanoscale RuO_2 coating deposited throughout the electrode can be electrochemically addressable. It may be electrochemically and selectively modified with metal nanoparticle catalysts creating a composite membrane that can serve as a carbon- and ionomer-free gas diffusion electrode in a fuel cell. These composites may also be used as stand-alone, porous Li-ion insertion electrodes that are moldable for three-dimensional microbatteries, in which the electrode and electrolyte/separator phases are interpenetrated in three dimensions. It is also a practical and inexpensive material that can now attain the vaunted electronic and electrochemical properties of ruthenium oxide—high electronic conductivity, high capacitive charge storage, and fast electron transfer—by distributing the material at modest amounts on inexpensive, insulating substrates.

Having described the invention, the following examples are given to illustrate specific applications of the invention. These specific examples are not intended to limit the scope of the invention described in this application.

Example 1

Strips of ~0.2-cm-thick silica fiber membranes (~3.5 cm × 1 cm in geometric area, total mass ~75 mg) were placed in clean petroleum ether in a flask held in a dry ice/acetone bath at -78°C. An aqueous solution of RuO_4 (10 mL of 0.5 wt% RuO_4) was extracted into ~20 mL of chilled petroleum ether, and then equilibrated with SiO_2 membranes at 78°C for two days. (Hazard warning: RuO_4 is volatile and rapidly oxidizes skin—handle in a fume hood with standard protective gear.) The flask was then removed from the dry ice bath and warmed to room temperature under ambient conditions. On the basis of visible observations, the RuO_4 decomposed to RuO_2 as the flask warmed to room temperature. The flask was held at room temperature for >12 hr, then the petroleum ether was decanted off and the resulting composite

was washed with several 100 mL aliquots of petroleum ether. Approximately 5–20 wt% of the Ru in solution was deposited onto the SiO₂ surfaces of the fibers that comprise the glass membrane, and the remainder of Ru in solution precipitated directly from solution as nanoscopic ruthenium oxide powder. It is possible to recover the precipitated RuO₂ and re-oxidize to RuO₄ with a strong oxidant such as potassium periodate and then extracted into an alkane such as pentane or petroleum ether for future depositions. This synthesis was successful on macroscopic substrates and may be scaled up to much larger substrates if desired.

The resulting composite was electrically conductive throughout based on two-point probe measurements, with a resistance of ~10 kΩ for a 0.2 cm-thick sample. The resistance decreased by four orders of magnitude by heating in flowing oxygen to 200°C. This mild heat treatment increased the area of contact between deposited particles and, based on analysis by TEM, converted the disordered, as-deposited ruthenium oxide into the more conductive, crystalline rutile RuO₂ form. The four-point conductivity of the annealed nanocomposite was on the order of 500 mS cm⁻¹ at room temperature in air.

A weight loading of 5–10% of RuO₂ was typically observed, by measuring the mass of the SiO₂ membrane before and after RuO₂ deposition. Scanning electron microscopy analysis of the SiO₂ membrane before and after deposition showed that the smooth surfaces of the SiO₂ fibers do not show significant morphological change after RuO₂ deposition and calcining to 150°C (Fig. 1). Higher magnification micrographs of RuO₂-coated SiO₂ fibers revealed the presence of nanoscale RuO₂ coatings on the SiO₂ fibers and some RuO₂ precipitates (Fig. 2). The volume fraction of RuO₂ in the product was small, as no agglomerates are observed between the fibers. The TEM analysis confirmed the formation of a nanoscale coating of RuO₂ on the silica fibers and shows that these colloids nucleate into an interconnected nanoweb of RuO₂ (Fig. 3). The thickness of the 200°C-calcined RuO₂ skin that coated the silica fibers was <10 nm as directly observed at higher magnification by taking advantage of the Z-contrast between Ru and Si to identify the RuO₂ phase where small breaks in the coating occurred. Because SEM analyzes only a small portion of the sample, numerous RuO₂||SiO₂ composites prepared under nominally similar conditions were imaged, confirming the reproducibility of the synthesis.

The RuO₂||SiO₂ membranes, after calcining in air or oxygen, displayed pseudocapacitance similar to that of bulk hydrous ruthenium oxide (RuO_xH_y). Fig. 4 compares the cyclic voltammograms in sulfuric acid of composite membranes calcined at 100, 150, and 200°C (in air). The currents are normalized to the mass of the membranes. Assuming a weight loading of 5 wt% RuO₂, the specific capacitance of RuO₂ in the 200°C annealed sample was 650 F g⁻¹, which is on the same order of magnitude as specific capacitances determined for bulk

RuO_xH_y (Zheng et al., Hydrous ruthenium oxide as an electrode material for electrochemical capacitors. *J. Electrochem. Soc.*, **142**, 2699–2703 (1995); Jow et al., Electrochemical capacitors using hydrous ruthenium oxide and hydrogen inserted ruthenium oxide. *J. Electrochem. Soc.*, **145**, 49–52 (1998)). The high pseudocapacitance for RuO₂||SiO₂ membrane composites is attributed to the nanoscopic dimensions and high surface area of RuO₂, even though the bulk membrane structure has a relatively low surface area. Previous studies have shown that crystalline anhydrous RuO₂ powders (prepared by annealing hydrous RuO₂) have lower specific capacitances than hydrated forms (Dmowski et al., Local atomic structure and conduction mechanism of nanocrystalline hydrous RuO₂ from X-ray scattering. *J. Phys. Chem. B*, **106**, 12677–12683 (2002)). Cryogenic or sub-ambiently prepared RuO₂ as bulk, nanoscopic powder or deposited on a silica membrane, is unique because it is both anhydrous and disordered. It crystallizes upon heating, remains anhydrous, and shows increasing specific capacitance with temperature up to 250°C.

Example 2

Lightweight, flexible electrodes were prepared by cryogenic deposition of ruthenia onto silica fiber paper substrates (Pallflex tissuquartz, Pall Life Sciences). The SiO₂-fiber substrate, used commercially as a filter for sampling aerosols and acidic gases, had a thickness of ~0.4 mm and was composed of submicron-to-micron diameter fused SiO₂ fibers. Two 15 mL aliquots of petroleum ether (Fisher Scientific), pre-chilled for 1 min in a dry ice/acetone bath, were used to extract RuO₄ from a 10 mL aqueous solution (0.5 wt% solution, Strem Chemicals). The phase transfer was carried out in ~1 min in order to avoid decomposition of RuO₄ in the petroleum ether phase; the nonaqueous phase was collected in a flask held in a dry ice/acetone bath to allow any transferred water to freeze and settle out of solution. The nonaqueous solution was then decanted into a pre-chilled glass vial containing a rectangular strip of SiO₂ paper (4.5×3 cm, ~70 mg) immersed in ~10 mL of petroleum ether. The capped vial was chilled in the dry ice/acetone bath for 45 min allowing RuO₄ to equilibrate with the SiO₂ fibers, and then removed from the bath and held at room temperature overnight (~15 h). Decomposition of RuO₄ to RuO₂ occurred slowly, beginning within 15 to 20 min upon removal from the bath. The petroleum ether and precipitated RuO₂ were then decanted off, and the resultant RuO₂||SiO₂ composite was washed with copious amounts of petroleum ether, air dried for 1 to 2 h and then dried under vacuum overnight.

Conductivity: The electrical resistance of an as-prepared RuO₂||SiO₂ electrode was measured in-situ in air as a function of temperature from 25 to 300°C in a two-probe cell. A 0.7

$\times 0.7$ cm strip of $\text{RuO}_2||\text{SiO}_x$ paper was sandwiched between two spring-loaded gold foil electrodes inside a quartz tube and heated with resistive tape powered by a Barnet Company temperature controller. Au leads were welded to the Au foil and fed to the instrument leads. A thermocouple placed next to the sample regulated the power supply ensuring accurate temperature control at the sample. Resistance was measured with a voltmeter at 25°C intervals after the sample was held for 15 min at each temperature with the exception of 200°C (2 h) and 300°C (30 min). In one experiment, the sample was cooled to room temperature after measuring the resistance at 200°C to verify that the increased conductivity upon crystallization is maintained upon cooling.

The geometric resistances at room temperature in air of $\text{RuO}_2||\text{SiO}_2$ electrodes heated in air to 200°C for 2 h were determined by the four-point probe method of van der Pauw. The electrodes were cut into strips $\sim 1 \times 0.7$ cm and connected to copper wire leads with silver conductive epoxy (CW2400, Circuit Works). Current was applied with a Solartron SI1286 Electrochemical Interface and potential was measured with a voltmeter.

The as-prepared $\text{RuO}_2||\text{SiO}_2$ composite was electrically conductive throughout with a two-point resistance of ~ 20 k Ω . The conductivity as a function of calcination temperature, measured *in situ* from 25 to 300°C (Fig. 5) increased sharply from 25 to 150°C and plateaued at $\sim 200^\circ\text{C}$. The four orders of magnitude increase in conductivity is consistent with conversion of poorly ordered, as-deposited RuO_2 into the more conductive crystalline rutile form (Ryan et al., *Nature*, **406**, 169 (2000); Lytle et al., *J. Mater. Chem.*, **17**, 1292 (2007)). The 200°C -calcined nanocomposite remained amorphous to X-rays, but exhibited lattice fringing in TEM analysis correlated to 2–3 nm ordered domains. Prolonged heating at 300°C sharply decreased conductivity of the composite, which arose from dewiring of the RuO_2 network as the nanoskin of the RuO_2 coarsened. The conductivity measured at a given calcination temperature was maintained upon cooling to room temperature. In order to minimize coarsening and organic impurities while maintaining high conductivity, the thermal processing was limited to $< 280^\circ\text{C}$.

Despite the low weight loading of RuO_2 on the low surface area, macroporous SiO_2 paper, high macroscopic electronic conductivity was observed. The four-point conductivity of the 200°C -calcined papers measured by four-point probe ranges from $0.3\text{--}0.7$ S cm^{-1} at room temperature in air ($n = 12$, where each of the 12 samples derives from independent synthetic batches). This geometry-normalized conductivity does not completely express the remarkable behavior observed here because the RuO_2 occupies < 0.1 vol.% of the electrode (to determine the volume fraction of RuO_2 the density of the RuO_x phase was assumed to be 7.06 g cm^{-3} (theoretical for RuO_2) and the wt% of RuO_2 in the sample (weight gain after calcination to

200°C) taken to calculate the volume of RuO₂ and divide that by the geometric volume of the RuO₂||SiO₂ paper.) The conductive phase was constrained to a skin of ruthenia that coated an insulating silica fiber, yet the nanoscale conductor mimicked a larger sized object. To highlight the oddity of this form of a well-studied metallic oxide, consider the density-normalized

conductivity of RuO₂ in three forms: 50 S cm² mg⁻¹ (the porous RuO₂||SiO₂ paper described here); 12 S cm² mg⁻¹ (as measured for a pressed pellet of cryogenerated RuO₂ powder calcined to 200°C); and 14 S cm² mg⁻¹ (as calculated for polycrystalline RuO₂). (The nanoscopic 200°C-calcined cryogenerated RuO₂ was pressed into a 1 cm × 0.16 cm × 0.17 cm pellet with a mass of 70.3 mg; the conductivity (four-terminal measurement) was divided by the geometric pellet density to obtain the density-normalized conductivity. For bulk RuO₂, we divide the known intrinsic conductivity of polycrystalline RuO₂ (~100 S cm⁻¹) by the theoretical density. For the RuO₂||SiO₂ composite, we divide the measured conductivity (four-terminal measurement) by the density of RuO₂ in the composite.

To probe the mechanism of conduction, the temperature dependence of the conductivity of 200°C-calcined RuO₂||SiO₂ composites was examined using *in-situ* four-terminal measurements of resistance (Fig. 6). When the data are fit to an Arrhenius model, the electrical transport is consistent with an activated conduction process, although one with very low activation energy: 8 meV from 20 to 260°C. At temperatures below 20°C, the temperature dependence of the conductivity follows a power law, which may arise from the disjointed character of the electron connection between domains in the ruthenia nanoskin and between ruthenia domains across fibers. The growth of the nanoscale RuO₂ phase starts as a filigreed, networked coating on the individual fibers (verified by TEM imaging of the thinner silica fibers in the paper, Fig. 3). The ruthenia then appears to fill in on the wider fibers (Fig. 2), but junctions will still exist between wires and between individual nanocrystallites of RuO₂ that comprise the nanoskin. In keeping with the physically discrete nature of the nanoscopic domains of ruthenia, 200°C-calcined RuO₂||SiO₂ papers exhibit a negative temperature coefficient of resistivity (TCR), unlike the positive TCR expected of a metallic conductor and obtained for compacted RuO₂ powder (R. Sahul et al., *Sensors Actuators A* **125**, 358 (2006)). The change in resistivity with temperature for 200°C-calcined RuO₂||SiO₂ paper is negative over the entire measured range (-160 to 260°C) with a TCR of -0.7 mΩ cm K⁻¹ derived from the linear portion from 20 to 180°C. Negative TCRs from 20 to 150°C were previously observed for cracked, 1–2-μm-thick films of ruthenia and for compact films calcined at temperatures < 500°C with the apparent semiconducting process attributed to activated electron transport at film discontinuities (Lodi et al., *Surf. Technol.*, **14**, 335 (1981)). The coefficients reported for the micrometer-thick

films (on the order of $1 \mu\Omega \text{ cm K}^{-1}$) are much lower than measured for the non-compact RuO_2 nanoskins.

Electrochemistry: All electrochemical measurements were made using a Solartron SI 1286 potentiostat on $\text{RuO}_2||\text{SiO}_2$ composites calcined to 200°C . A gold foil with a gold wire welded to it was used as the electrical contact/support and a Pt mesh was used as the auxiliary electrode. The $\text{RuO}_2||\text{SiO}_2$ composites were attached to the gold foil with an all-plastic paper clip and the gold wire was fed to the measurement lead. Measurements were conducted in a three-neck flask purged with Ar for ~ 30 min before the experiment and with Ar flowing over the solution during measurements. The cyclic voltammetry of $\text{RuO}_2||\text{SiO}_2$ paper was measured at ambient temperature in $0.5\text{M H}_2\text{SO}_4$ at 2 mV s^{-1} with a SSCE reference electrode. The response of an $\text{RuO}_2||\text{SiO}_2$ composite electrode for the ferricyanide redox couple was measured in 1 M KNO_3 with $5 \text{ mmol K}_3\text{FeCN}_6$ at 5 mV s^{-1} with a SCE reference electrode. Measurement of the double layer capacitance was made in acetonitrile with 0.1 M tetrabutylammonium perchlorate using a Ag/AgNO_3 reference electrode at 25 mV s^{-1} . In this case, the $\text{RuO}_2||\text{SiO}_2$ was attached to a Pt wire contact with the all-plastic paper clip.

In addition to its many uses as an electronic material, RuO_2 is noted for its properties as an electrochemical catalyst, energy storage material, and electrode material that exhibits fast electron transfer kinetics (Rolison et al., *J. Electrochem. Soc.*, **126**, 407 (1979)). A typical cyclic voltammogram in sulfuric acid for a 200°C -calcined $\text{RuO}_2||\text{SiO}_2$ composite (Fig.7) exhibits the large proton capacitance (Zheng et al., *J. Electrochem. Soc.*, **142**, L6 (1995)) characteristic of bulk hydrous ruthenium oxide (RuO_xH_y). The large capacitive and featureless constant current response observed over the potential window is due to reversible oxidation/reduction of surface sites with a concurrent exchange of protons and electrons (Zheng et al., *J. Electrochem. Soc.*, **142**, 2699 (1995); Jow et al., *J. Electrochem. Soc.*, **145**, 49 (1998)). The specific capacitance of the $\text{RuO}_2||\text{SiO}_2$ composite, normalized for the mass of RuO_2 was 650 F g^{-1} , which is the same order of magnitude as disordered RuO_xH_y (Zheng et al., *J. Electrochem. Soc.*, **142**, L6 (1995)). The high specific capacitance demonstrates that a large portion of the deposited RuO_2 was electrically addressable and contributes to the observed electrochemical response.

Taking advantage of the effective wiring of the RuO_2 network, the surface area from the double-layer capacitance measured in an aprotic solvent (acetonitrile) with a bulky cation (tetrabutylammonium) can be calculated. The current response was featureless and capacitive in nature and from the capacitive envelope, and assuming a typical double-layer capacitance of $10 \mu\text{F cm}^{-2}$, the surface area was determined to be $\sim 90 \text{ m}^2 \text{ g}^{-1}$. For comparison, the surface area of cryogenically generated RuO_2 powder (calcined at 200°C) is $30 \text{ m}^2 \text{ g}^{-1}$ as measured by N_2 -

sorption. The larger surface area achieved for the nanoscale RuO₂ coating is due to the significantly smaller domain size of RuO₂ on the SiO₂ fibers as compared with the precipitated, agglomerated nanoscopic powder.

The response of the RuO₂||SiO₂ composite as an electrode for the ferricyanide redox couple was also studied. A typical voltammogram in 5 mM ferricyanide shows a reversible oxidation/reduction process with a peak separation of 76 mV (Fig. 8), demonstrating that the oxide captures the fast electron-transfer kinetics typical of this redox couple. These electrochemical results demonstrate that an electrochemically addressable high-surface area RuO₂ phase can be deposited on a very low surface area substrate producing a multifunctional electrode with extremely low weight loadings of RuO₂.

Microscopy: Scanning electron microscopy (SEM; Carl Zeiss Supra 55) was used to characterize the nanoscale RuO₂ coating on SiO₂. For analysis, the specimens were prepared by attaching a small portion of the composite to an aluminum stub with conductive carbon tape. A JEOL 2200FS transmission electron microscopy (TEM) equipped with a Gatan CCD camera and Noran System Six EDS was used to characterize the paper morphologies, confirm particle size and the nature of the coating, image lattice fringes, and elemental identification. For analysis, the specimens were prepared by dry-grinding then brushing the fibers/dust onto holey-carbon support Cu grids.

TEM: Surface area of bulk cryogenerated RuO₂ calcined to 200°C was determined by nitrogen physisorption using a Micromeritics ASAP2010 accelerated surface area and porosimetry analyzer. The sample was degassed at 100°C for 24 h prior to characterization.

In this RuO₂||SiO₂ composite, the nanoscale RuO₂ phase made a networked coating (film) on the individual fibers but was likely to have junctions between wires or between individual nanocrystals of RuO₂. Individual wires of RuO₂ exhibited standard metallic conductivity but when taken as a whole, a very low activated process is observed related to wire-to-wire junctions.

The cost and strategic importance of the platinum group metals have always tempered their practical adoption in the vast array of technologies in which they would otherwise be used. We can now attain the vaunted electronic and electrochemical properties of ruthenium oxide—high electronic conductivity, high capacitive charge storage, and fast electron transfer—by distributing the material at modest amounts on dirt cheap, insulating substrates. The design strategy of forming closed nanoscale shells of charge-transport materials around curved substrates should be applicable as well to other technologically desirable but expensive materials.

Obviously, many modifications and variations of the present invention are possible in

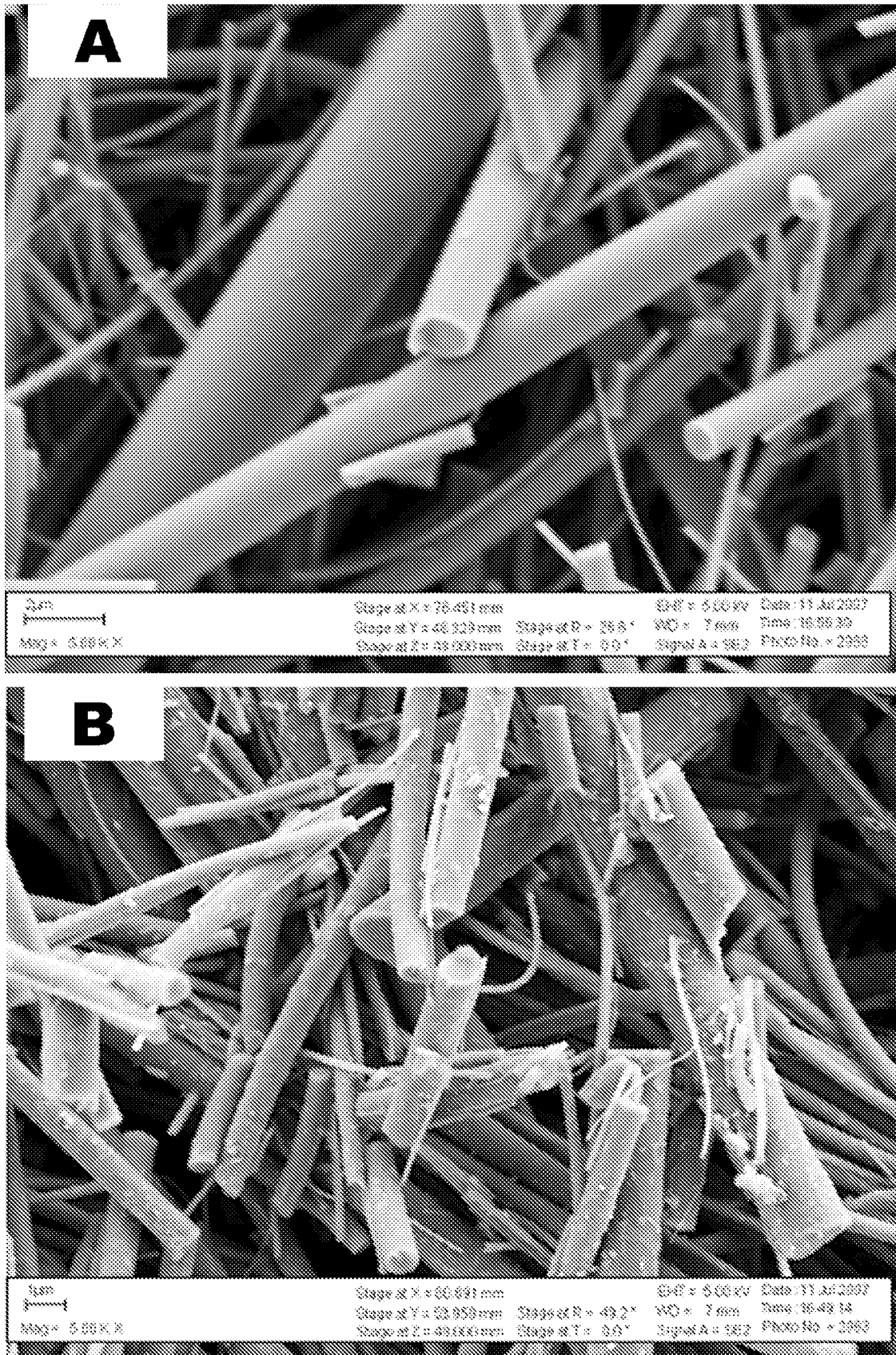
light of the above teachings. It is therefore to be understood that the claimed invention may be practiced otherwise than as specifically described. Any reference to claim elements in the singular, e.g., using the articles “a,” “an,” “the,” or “said” is not construed as limiting the element to the singular.

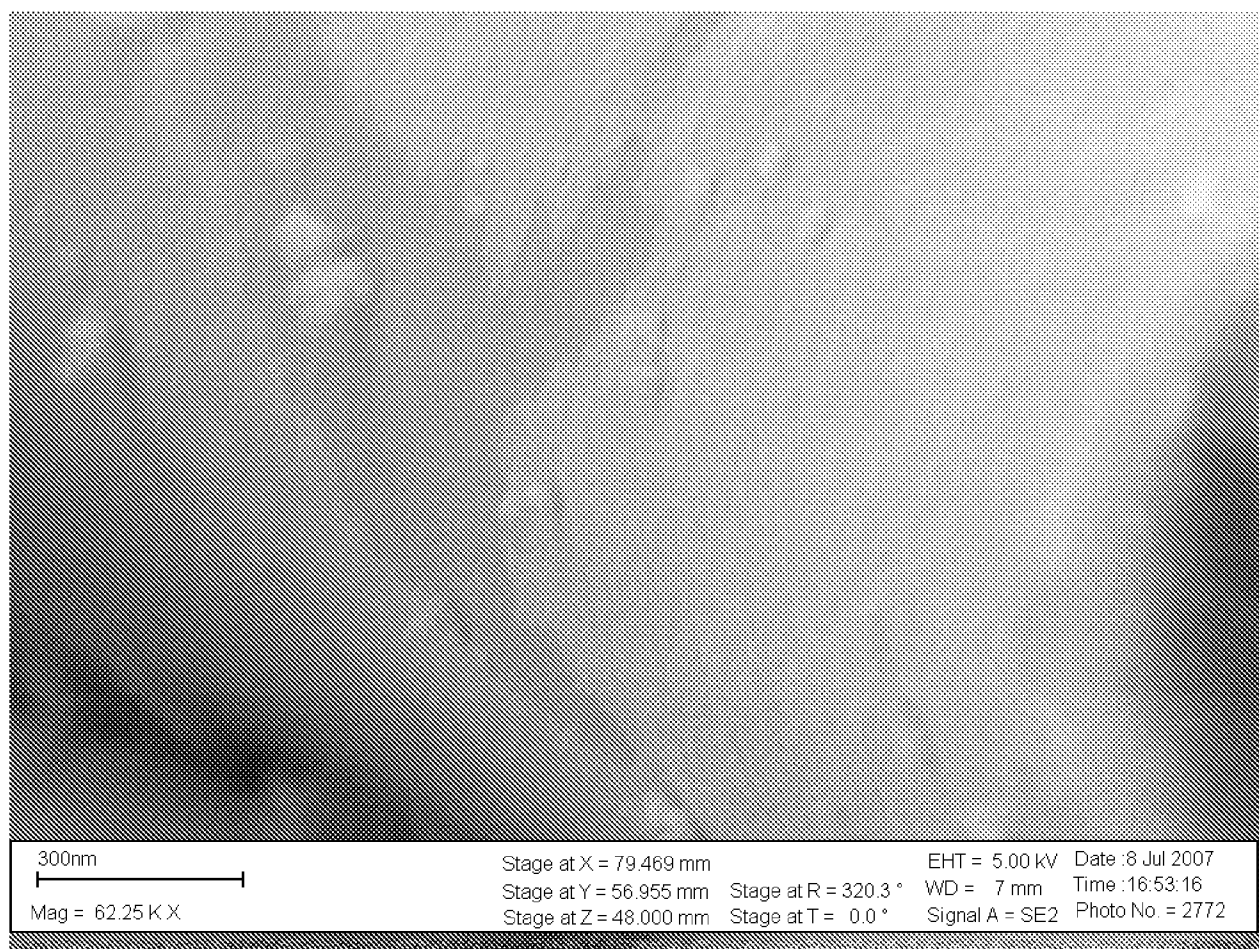
CLAIMS

What is claimed is:

1. An article comprising:
a nonconductive fiber; and
5 a RuO₂ coating on a portion of the fiber.
2. The article of claim 1, wherein the fibers comprise silica.
3. The article of claim 1, wherein the article comprises an entangled plurality of the fibers.
4. The article of claim 3, wherein the plurality of fibers is in the form of a membrane or a
fiber-formed paper.
- 10 5. The article of claim 1, wherein the RuO₂ forms an electrically connected network
throughout the article.
6. The article of claim 1;
wherein the plurality of fibers is a silica fiber membrane; and
wherein the fibers are up to about 10 microns in diameter.
- 15 7. The article of claim 6, wherein the RuO₂ coating has an average thickness of up to about
10 nanometers.
8. The article of claim 6;
wherein the article contains up to about 10 wt% RuO₂; and
wherein the article has a bulk conductivity of at least about 500 mS cm⁻¹.
- 20 9. The article of claim 6, wherein the silica fibers are monofilaments.
10. The article of claim 6, further comprising:
a metal, metal oxide, polymer, molecular or ionic species, ceramic, or platinum deposited
on portions of the RuO₂ coating.

11. A method comprising:
immersing a nonconductive article in a solution of RuO_4 and a nonpolar solvent at a
temperature that is below the temperature at which RuO_4 decomposes to RuO_2 in
the nonpolar solvent in the presence of the article; and
5 warming the article and solution to ambient temperature under ambient conditions to
cause the formation of a RuO_2 coating on a portion of the article.
12. The method of claim 11, wherein the nonconductive article is a fiber.
13. The method of claim 11, wherein the nonconductive article is a silica fiber membrane.
14. The method of claim 11, wherein the nonpolar solvent is a hydrocarbon.
- 10 15. The method of claim 11, wherein the nonpolar solvent is petroleum ether.
16. The method of claim 11, further comprising:
extracting the RuO_4 from an aqueous solution into the nonpolar solvent before immersing
the article in the RuO_4 solution.
17. The method of claim 11, wherein the immersing temperature is maintained by a dry ice
15 bath or aqueous ice bath.
18. The method of claim 11, further comprising:
equilibrating the article in an additional portion of the nonpolar solvent at the temperature
before immersing the article in the RuO_4 solution.
19. The method of claim 11, further comprising:
20 depositing a metal, metal oxide, polymer, molecular or ionic species, ceramic, or
platinum on a portion of the RuO_2 coating.
20. An article comprising:
a nonconductive fiber; and
a coating on a portion of the fiber;
25 wherein the coating is made by electroless deposition, sputtering, atomic-layer
deposition, chemical vapor deposition, or physical vapor deposition.

**Fig. 1**

*Fig. 2*

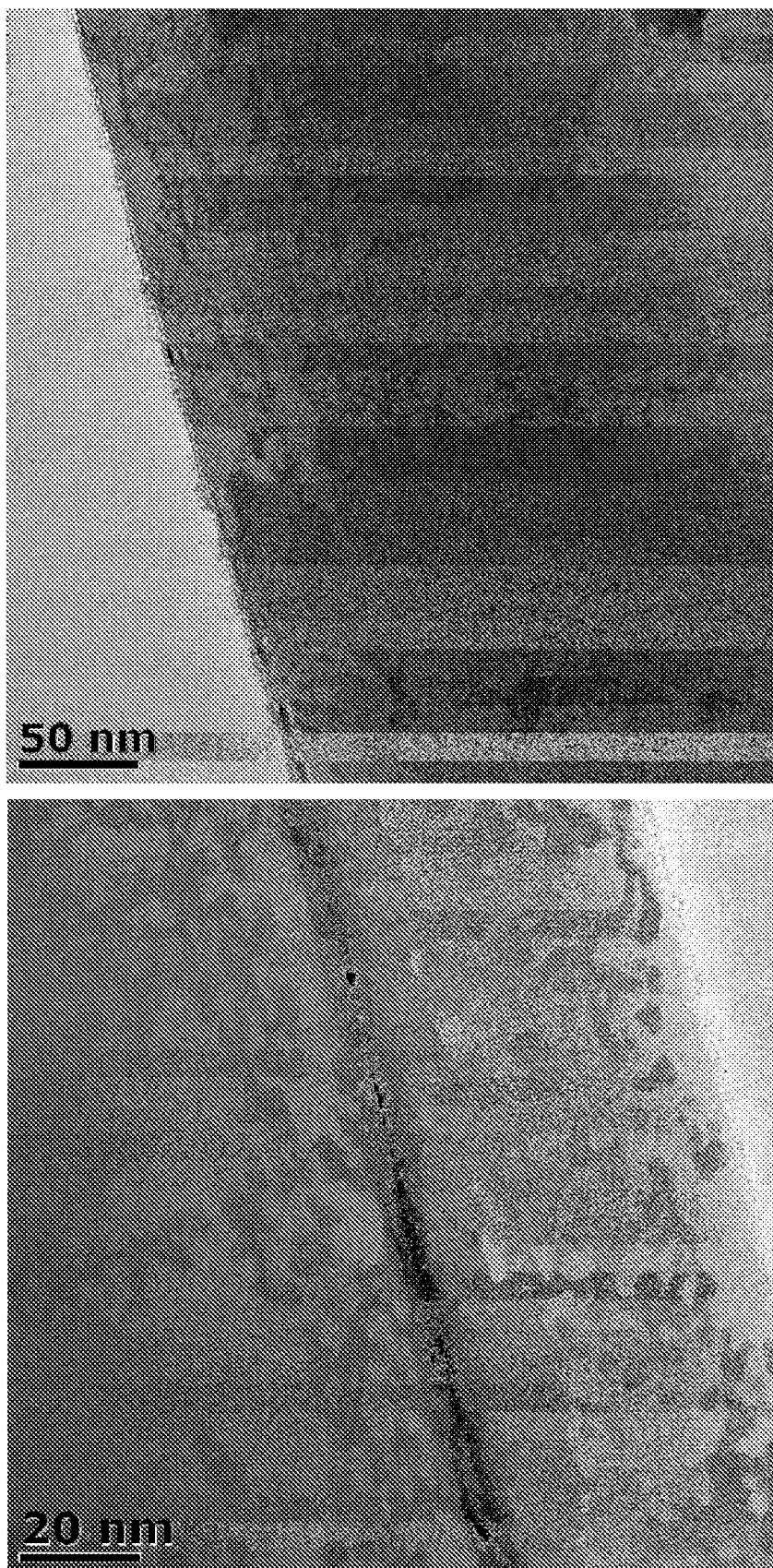
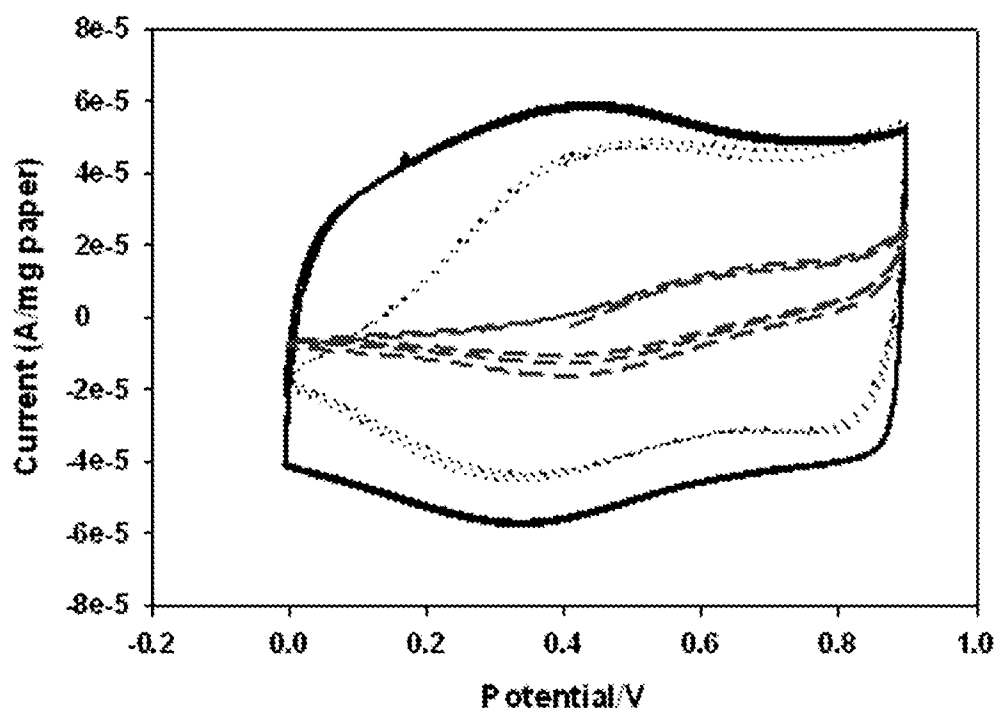
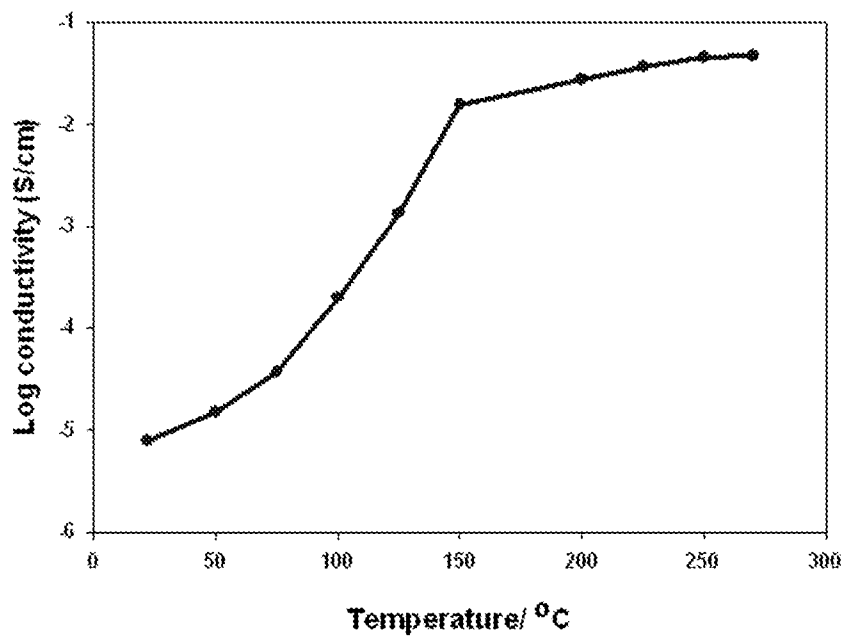
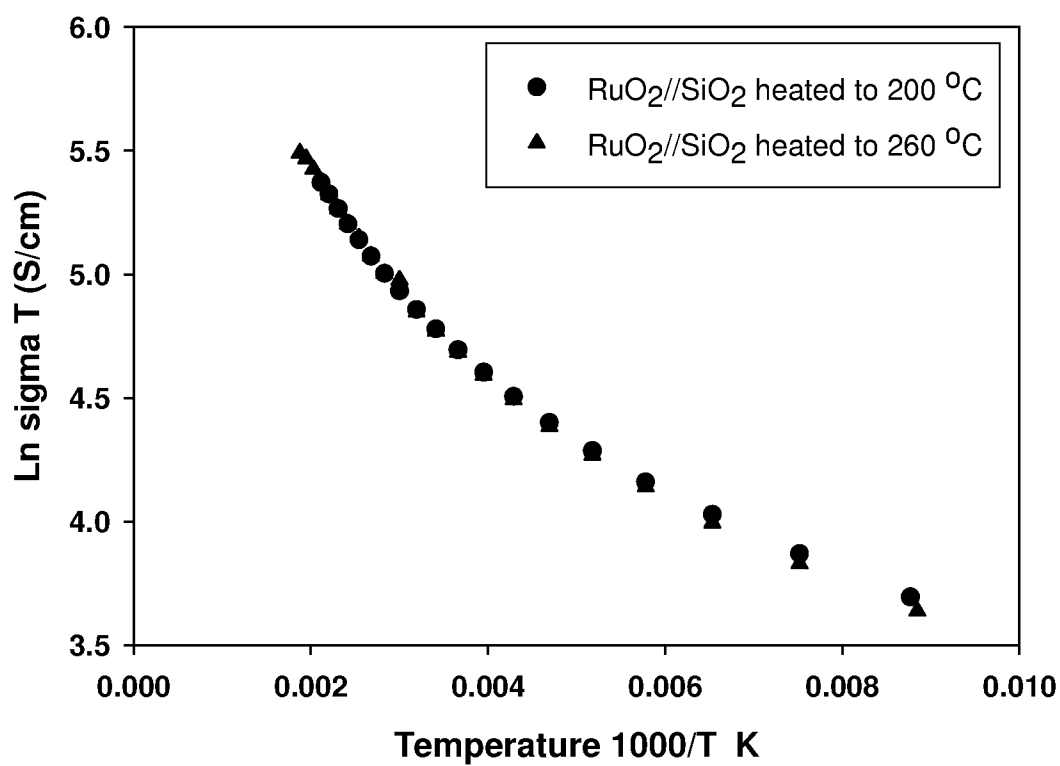
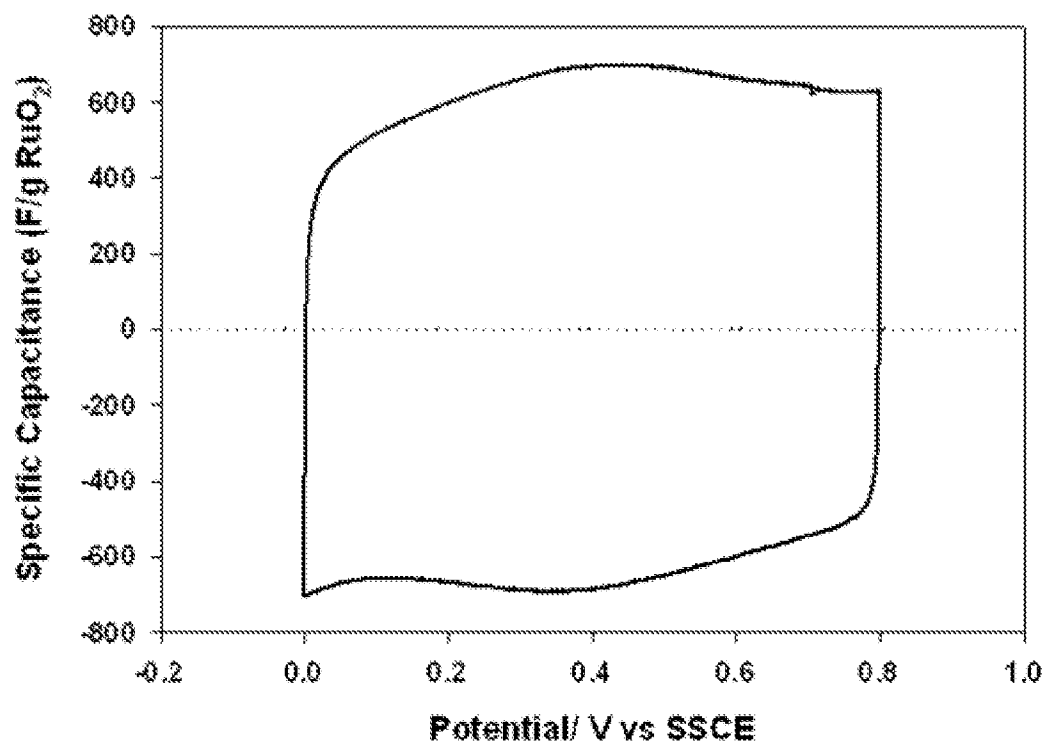
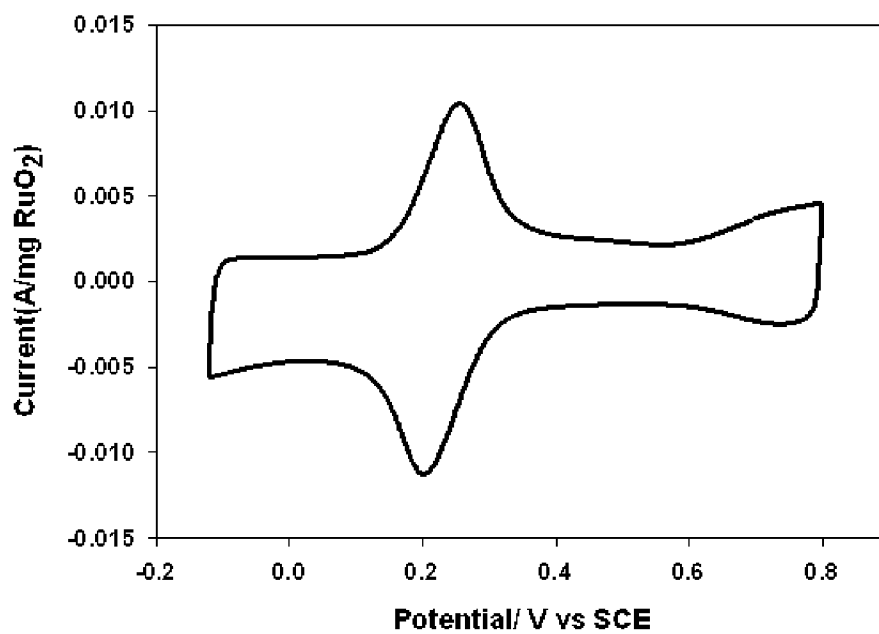


Fig. 3

*Fig. 4**Fig. 5*

*Fig. 6*

*Fig. 7**Fig. 8*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 08/78905

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 37/00 (2008.04)

USPC - 502/103

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8)- B01J 37/00 (2008.04)

USPC- 502/103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and NPL

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Patent, PgPub, OCR: classification), DialogClassic (Derwent, Claims, fulltexts US, EPO, WIPO: keyword), GoogleScholar;
search terms: fibr?, fiber?, coat?, deposit?, ruthenium?, silica?, glass?, paper?, membrane?, web, nonwoven?, filament?, decompos?,
electrode, petroleum ether

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 4,737,257 A (BOULTON) 12 April 1988 (12.04.1988), col 1, ln 20-30; col 1, ln 50-61; col 2, ln 45-52; col 3, ln 3-15; col 5, ln 16-50; col 6, ln 22-68; col 7, ln 48-68; col 8, ln 15-36; col 14, ln 10-29	1-10, 20 ----- 12, 13, 19
X -- Y	US 6,649,091 B2 (RYAN et al.) 18 November 2003 (18.11.2003), col 2, ln 56 to col 3, ln 67; col 4, ln 48-67	11, 14, 16-18 ----- 12, 13, 15, 19
Y	US 5,487,918 A (AKHTAR) 30 January 1996 (30.01.1996), col 1, 54-63; col 6, ln 44-50	15
A	WO 2003/069711 A2 (HENNIGE et al.) 21 August 2003 (21.08.2003)	1-20
A	US 6,099,704 A (BACQUET et al) 08 August 2000 (08.08.2000)	1-20
A	US 3,852,175 A (HOEKJE) 03 December 1974 (03.12.1974)	1-20

☐ Further documents are listed in the continuation of Box C.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

28 November 2008 (28.11.2008)

Date of mailing of the international search report

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