SANDIA REPORT

SAND-2008-3813
Unlimited Release
Printed July 2008

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Metal Oxide Coating of Carbon Supports for Supercapacitor Applications

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Abstract

The global market for wireless sensor networks in 2010 will be valued close to $10 B, or 200 M units. TPL, Inc. is a small Albuquerque based business that has positioned itself to be a leader in providing uninterruptible power supplies in this growing market with projected revenues expected to exceed $26 M in 5 years. This project focused on improving TPL, Inc.'s patent-pending EnerPak™ device which converts small amounts of energy from the environment (e.g., vibrations, light or temperature differences) into electrical energy that can be used to charge small energy storage devices. A critical component of the EnerPak™ is the supercapacitor that handles high power delivery for wireless communications; however, optimization and miniaturization of this critical component is required. This proposal aimed to produce prototype microsupercapacitors through the integration of novel materials and fabrication processes developed at New Mexico Technology Research Collaborative (NMTRC) member institutions. In particular, we focused on developing novel ruthenium oxide nanomaterials and placed them into carbon supports to significantly increase the energy density of the supercapacitor. These improvements were expected to reduce maintenance costs and expand the utility of the TPL, Inc.'s device, enabling New Mexico to become the leader in the growing global wireless power supply market. By dominating this niche, new customers were expected to be attracted to TPL, Inc. yielding new technical opportunities and increased job opportunities for New Mexico.

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Project Overview

The increasing consumer demand for portable devices that require high-energy operation will ultimately lead to small wireless devices. Typically, these devices are powered by batteries; however, replacing these power sources after they are depleted is not always possible or cost-effective for a number of systems. Therefore, alternative devices are needed, such as the EnerPak^{TM} of TPL, Inc., a New Mexico based small business. In order to meet the high power communications loads, the usual approach is to design a power source large enough to handle the highest power load, but again, a large device is not always optimal. In contrast, the EnerPak™ uses low impedance supercapacitors as the primary output device to provide the most efficient delivery of energy to the sensor, and deliver high power bursts for data communication more efficiently than standard batteries. Unlike batteries, supercapacitors can be charged and discharged millions of times without any degradation in their performance. While supercapacitors deliver energy efficiently, they do not store energy efficiently, and so tend to be quite large in comparison to the portable devices needed.

This project focused on testing controlled materials for the microsupercapacitors that possess dramatically improved capacitance and, therefore, higher energy density. The research team that was assembled to attack this problem consisted of two established and productive members of the New Mexico Technology Research Collaborative (NMTRC) from Sandia National Laboratories (SNL) and the University of New Mexico (UNM) along with TPL, Inc. By coupling the synthesis abilities at SNL with the established engineering expertise at UNM for nanoseparations, this complex energy problem was undertaken through the development of monodispersed, charge functionalized, and novel nanomaterials for assembly into improved microsupercapacitors. Through development of novel materials and fabrication/manufacturing processes, UNM and SNL have advanced their technical expertise in the areas of precursor development, nanomaterials, and device integration. Additional benefits of this project were the training of students in the disciplines of chemistry and engineering, which added to the base of technical workers in New Mexico in the field of nanotechnology and further meet the national call for attracting students to these disciplines.

To address the technical issues, the project was broken down into several steps to generate the critical ruthenium oxide (RuO_x)-carbon support interaction necessary for production of supercapacitors: Ru precursor synthesis; RuO_x nanoparticle synthesis; characterization; functionalization of RuO_x; combining RuO_x and carbon support; size selection of RuO_x; supercapacitor fabrication and assembly; and supercapacitor testing. Characterization of the electrical performance of the supercapacitors using measurements of capacitance, equivalent series resistance (ESR), power, and leakage current measured under self-discharge. Sandia and UNM took the technical lead in developing the necessary materials while TPL, Inc. tested these prototypes upon assembly. TPL, Inc. can potentially drive the economic aspects of the development and production of device grade supercapacitors, through coordinated preset meetings and close communication with researchers.

The biggest challenge to commercializing any new technology is cost. As a rule of thumb, for a new technology to be accepted in the market, if the cost increases, it must deliver an order of magnitude increase in performance over existing solutions or it must realize an order of magnitude decrease in cost for the same performance. While a substantial body of work on

RuO_x modified supercapacitor electrodes exists, the microstructured approach that has been employed to date - rather than the nanostructured approach proposed here - limits performance improvements. Nevertheless, these supercapacitors display a two-fold increase in energy storage over conventional electrode materials. The uniform distribution of nanostructured RuO_x within the pore structure of activated carbon electrodes, as was proposed for this project, was expected to deliver at least an order of magnitude higher of improved performance. Furthermore, this effort enabled us the chance to develop a preliminary cost model for the process, providing initial quantitative data to evaluate the potential impact on TPL, Inc.'s EnerPak™ product. In summary, the goal of this project was to position TPL, Inc. as a leader in the portable power market, such that their market base expands, improving the economic viability of New Mexico while increasing the expertise at the NMTRC institutions.

Introduction

The revolution of miniaturizing technologically important devices for portability has been well underway for several decades. However, as devices shrink in size and their number of high energy operations increase, battery technology is nearing its limits in being able to meet the demands alone.[1] Therefore, alternative power sources are required to increase the energy efficiency and energy density available to miniaturized devices. One solution to this problem is to employ supercapacitors. TPL, Inc. has developed an EnerPak^{TM} that employs both microbatteries and microsupercapacitors that harvest energy from the environment (i.e., vibrations, temperature changes) and converts it to electricity. Figure 1 shows the actual EnerPak^{TM} and the schematic of its design. The energy is stored in small, patented microbatteries and microsupercapacitors with an output voltage in these devices that can be configured for 3, 5 or 9V distributions. The microsupercapacitors deliver short, high power pulses with the microbattery used as the backup power.

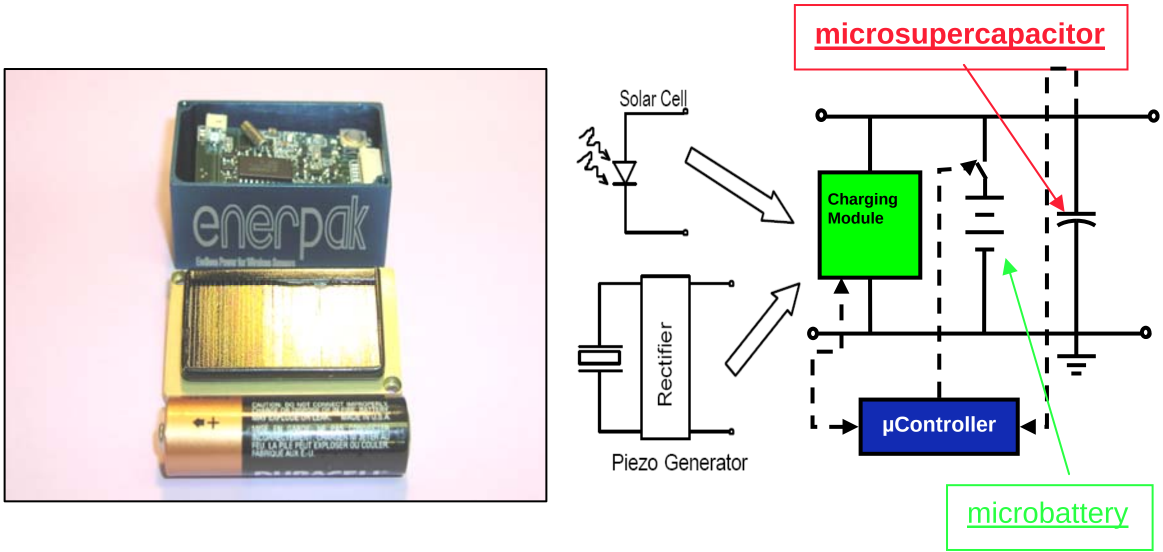

Figure 1. **Picture of the EnerPak^{TM} developed by TPL, Inc. and the schematic of the internal design.**

Unlike batteries, supercapacitors can be charged and discharged millions of times without any degradation in their performance. While supercapacitors deliver energy efficiently, they do not *store* energy efficiently, and so tend to be quite large in comparison to the portable devices needed. The successful development of an improved microsupercapacitor, which possesses increased energy capacitance density on a smaller size scale, will allow further miniaturization and longer battery lifetime. In order to achieve a sufficient microsupercapacitor, new composite materials have to be produced. One material of interest for these applications is ruthenium oxide (RuO_x), which has a high specific capacitance of 720 F/g.[2] The faradic processes RuO_x enables is due to the redox reactions of the oxide atoms at or near the electrode surface.[3] This process gives rise to the so-called "pseudocapacitance," which involves both interfacial reactions and mass transfer of ionic charges across the double layer. This double layer mechanism of energy storage is heavily surface dependant, and thus requires high active surface areas to deliver a high specific capacitance value. However, the capacitance of pure RuO_x decreases rapidly when used alone.[4] This phenomenon has been associated with electrolyte depletion and over-saturation during charge/discharge.[5] It has been reported that the addition of carbon materials increases the capability of RuO_x.[4] Although activated carbons having high surface area and porous structures yield electrodes with high specific energy and power densities, their specific capacitance is at most 40 F/g. By creating a nanocomposite electrode using a redox-reactive material, like RuO_x, within a high surface area of carbon, the resulting small particle size of the RuO_x would increase the redox active surface area of the material giving rise to higher-power devices.

In our present study of generating microsupercapacitors, we have evaluated: several methods of synthesis of RuO_x nanomaterials, integration of RuO_x into a carbon substrate, construction and capacitance testing of resulting materials in a micro-supercapacitor design. In the following sections we will discuss synthesis approaches to RuO_x nanoparticles, characterization of our materials, construction of cells, and testing of our micro-supercapacitor cells. Additionally, the original and quarterly reports are included in the appendices to this report.

Experimental Setup

All chemicals were used as received (Aldrich) and handled under ambient atmospheric conditions in a fume hood, including ruthenium (III) chloride ($RuCl_3$), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), and 1-butyl-3-methylimidazolium hexafluorophosphate (BMeIm-PF_6). Sodium borohydride ($NaBH_4$, Aldrich) was kept under an inert argon atmosphere in a glovebox. De-ionized water (DI water) was produced in house from a Millipore™ filtration system.

Synthesis

Based on literature procedures,[6-8] three synthetic routes to produce RuO_x nanomaterials were undertaken with minor modifications made to ensure high quality RuO_x nanomaterials were made on a scale sufficient enough to allow for evaluation by TPL, Inc

Route 1:[6] In a 500 mL round bottomed flask, BMeIm-PF_6 (29.0 mL, 140 mmol) was added to crushed $RuCl_3$ (6.00 g, 28.9 mmol). The resulting solution was stirred and sonicated at elevated temperatures (~60 °C) until the $RuCl_3$ dissolved. After allowing the solution to cool to room temperature, an excess of $NaBH_4$ (9.64 g, 255 mmol) was added and stirred. After 2 h, the solution was centrifuged and the mother liquor removed. The resulting black powder was washed twice with acetone and then three times with DI water.

Route 2:[7] In a 500 mL round bottomed flask, a 1:1 v/v mixture of MeOH and de-ionized water (318 mL total) was added to $RuCl_3$ (6.60 g, 31.8 mmol) followed by stirring and sonication of the reaction mixture during the entirety of the reaction. After 15 min, a 1.00 M NaOH in MeOH and DI water (1:1, ~ 70.0 mL) was added in 10.0 mL increments until the final pH was adjusted to 7. After 30 min, the solution was centrifuged, mother liquor removed, and the subsequent powder washed three times with DI water.

Route 3:[8] In a 500 mL round bottomed flask, DI water (400 mL) was added to crushed $RuCl_3$ (6.00 g, 28.9 mmol) while simultaneously sonicating and stirring the reaction for a minimum of 20 min. Afterwards the desired amount of carbon substrate was introduced to the $RuCl_3$ solution and allowed to mix for another 20 min. After that time, 30 %wt H_2O_2

(~30 mL) was slowly added to the $RuCl_3$ solution in a fume hood. The reaction mixture was allowed to stir for 1 h and then centrifuged. The resulting black powder was then washed three times with DI water.

Characterization

The resulting RuO_x materials were analyzed by a number of in-house analytical instruments. Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical X'Pert PRO X-ray diffraction unit with Jade6™ XRD pattern processing software version 6.5.1. TEM images were obtained on a JEOL 2010 transmission electron microscope (TEM) equipped with an energy dispersive detector (EDS). FT-IR data were obtained on a Bruker Vector 22 Instrument using KBr pellets under an atmosphere of flowing nitrogen.

Capacitance Testing

Characterization was carried out using the Arbin BT2000 automated testing system. This 24-channel system can automatically charge devices, measure standard parameters such as capacitance, ESR, and open circuit voltage, and discharge under prescribed conditions, as well as enable automated charge-discharge cycling to measure capacitance stability. The constructed device consisted of three active layers: carbon anode, nano-composite cathode, and separator. The electrodes were impregnated with electrolyte solution under vacuum to ensure all porosity was filled. The aqueous electrolyte H_2SO_4 was selected to demonstrate feasibility during testing.

Activated carbon electrodes were made containing 0-50 wt% of RuO_2 powders. The electrodes were fabricated by first mixing the carbon and RuO_2 powder with 4 wt% PTFE binder in a shear mixer. Water was used as the solvent to facilitate mixing which was later removed by evaporation in an oven. The dried electrode mixture was then rolled into a sheet using a rolling mill. The sheet thickness was targeted at 440 microns and is obtained by adjusting the gap in the rolling mill. Electrodes were punched using a round 8.1 mm diameter punch before being infiltrated with electrolyte.

The electrolyte used in these experiments was a 4M H_2SO_4 solution. The electrodes were placed in a vial containing the electrolyte and the vial was placed into the vacuum jar with the lid loosely in place. A vacuum was applied to the vacuum jar and then the isolation valve closed and the electrodes allowed too soak in a static vacuum for several minutes. The vacuum was then slowly released and the process repeated. This cycling was done until the electrodes sank to the bottom of the vial.

The supercapacitor assembly consists of a sandwich consisting of two electrodes on either side of a porous separator membrane. The separator used in this work was selected from the Celgard^{TM} family of poly(propylene) (PP) and poly(ethylene) (PE) separator materials or W.L. Gores's poly(tetrafluoroethylene) separator. The purpose of the separator is to separate the electrodes electronically, while allowing ions to move freely through the pores, transporting charge.

The supercapacitor test structure used in this work was a Tee-Cell (see Figure 2). The components of the Tee-Cell are usually fabricated from stainless steel which is not compatible with the H_2SO_4 electrolyte. Therefore an inert current collector (spacer) made from titanium was placed between the stainless steel components of the Tee-Cell and the electrodes. During assembly a 780 um thick PTFE washer was used to limit the compression applied by the spring in the Tee-Cell. The OD of the washer was the same as that of the current collector so that it would fit inside of the Tee-Cell while the ID was 10.3 mm. This allowed the electrode and separator discs to fit inside the washer. The compression of the 440um thick electrodes (x 2 = 880 um total electrode thickness) was approximately 12.5%.

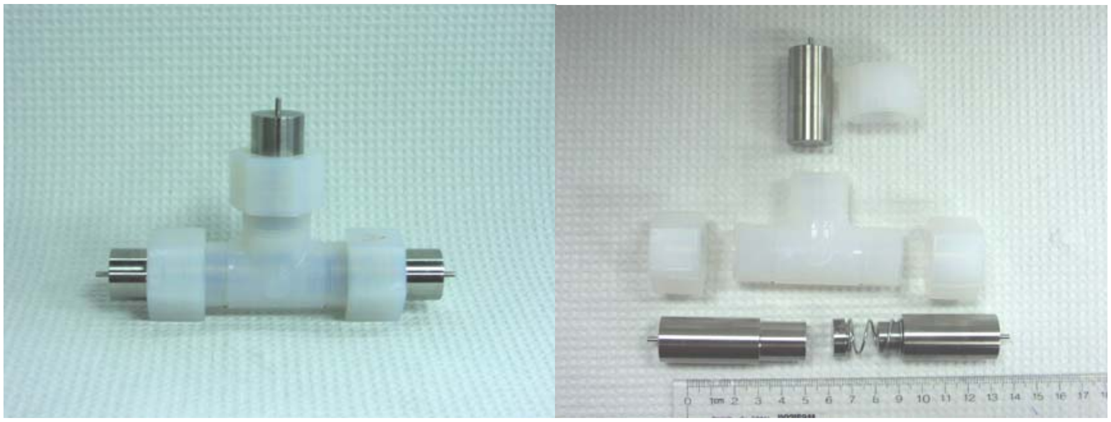

***Figure 2.* Assembled and un-assembled Tee-Cell used for testing supercapacitors.**

Results and Discussion

Our previous research efforts have shown that metal alkoxides ($M(OR)_x$) are excellent precursors to ceramic materials, especially metal oxides.[9-14] By varying the ligand set of the $M(OR)_x$, it has been shown that hydrolysis and condensation rates can be controlled by effectively altering nucleophilic and electrophilic attack on the metal center. [9-14] As a result, metal alkoxides have found wide spread use in chemical solution ("sol-gel"), metal organic chemical vapor deposition (MOCVD), and emerging nanoparticle synthesis.

Therefore, our initial syntheses focused on the methodically controlled decomposition of ruthenium alkoxides ($Ru(OR)_x$) precursors into RuO_x nanoparticles via a solution precipitation route. It is believed that variations in size and morphology may be garnered by changes in one or more key variables: decomposition temperature, solute, time, surfactants, and the precursor used. However, commercial products and literature reports of synthesis routes to $Ru(OR)_x$ or similar species are costly and typically isolated in poor yield.[15] Therefore, we pursued inexpensive synthetic routes using ruthenium precursors from readily available ruthenium(III) chloride ($RuCl_3$). Unfortunately, we were not able to substitute the chlorines with different organic ligands in a cost effective method. Therefore, we decided to undertake literature routes to RuO_x nanomaterials.[6-8] The following discusses the synthetic routes that were investigated to synthesize RuO_x and their intermingling with a carbon substrate (Synthesis), the materials generated (Characterization), and the properties garnered from the addition of these materials (Testing). Details will be discussed below.

Synthesis

As discussed above, our initial attempts focused on direct routes to RuO_x nanomaterials based on $RuCl_3$. This precursor was selected based on several reasons, it was: (i) commercially available, (ii) relatively inexpensive, (iii) relatively air stable, and (iv) used in numerous literature preparatory methods. From the multitude of routes,[2-8] we selected three to generate the RuO_x materials.[6-8]

The first route investigated made use of an ionic liquid (BMeIm-PF_6) as a solvent for $RuCl_3$.[8] It is generally believed that a metathesis reaction permitted the substitution of the chlorines by borohydrides, thus allowing the Ru species to undergo oxidation by the water contained in the ionic liquid, and finally forming RuO_x species. The BMeIm-PF_6 acted not only as a solvent for the poorly soluble $RuCl_3$ salt but also as a coordinating surfactant, thus allowing very small particles of RuO_2 to grow in a controlled fashion. After washing the resulting nanoparticles to remove excess by-products and surfactant, the precipitate was transferred to a TEM grid. The resulting material was found to form 1 - 2 nm RuO_2 crystalline particles, see Figure 3(B). While this route made the materials of interest, the high cost of BMeIM-PF_6 made this route cost prohibitive on the industrial scale. Therefore, other routes that utilized cheaper solvents were investigated.

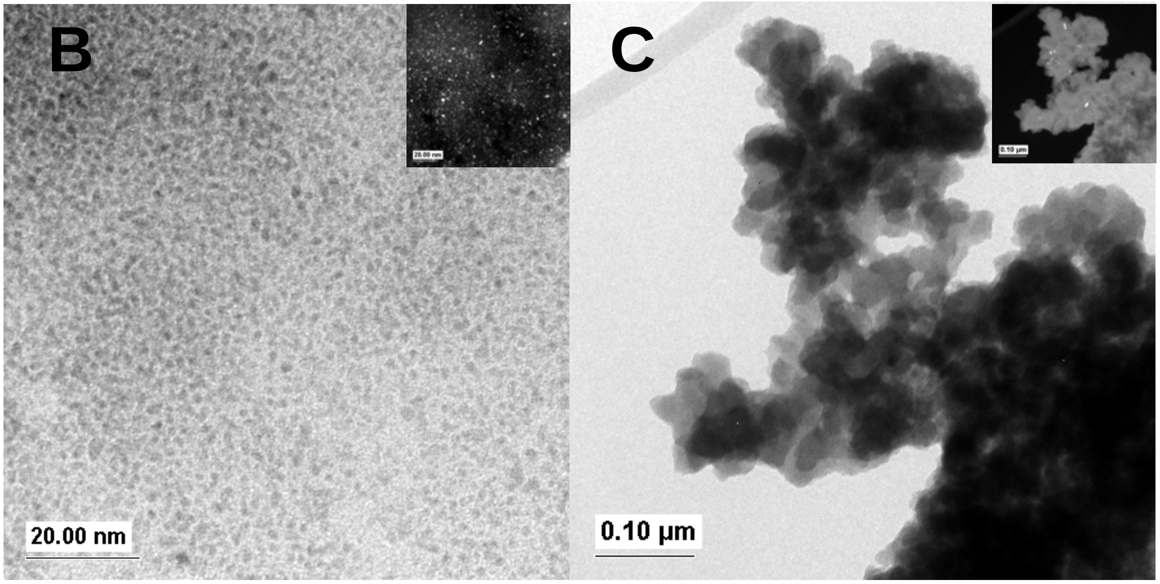

Figure 3. **TEM images of (B) Route 1 and (C) Route 2.**

The second route[6] used a 50/50 mixture of methanol and DI water to dissolve the $RuCl_3$. The addition of the NaOH solution produced RuO_2 nanomaterials that agglomerated to form larger structures, see Figure 3(C). Washing the resulting nanoparticles yielded a blue solution that is believed to contain Na_2O and other by-products. After subsequent washing the solution was colorless and the precipitate was transferred to a TEM grid. Invariably, these larger structures did not fit in the porous carbon substrate, so an *in-situ* approach was considered such that the carbon would be introduced prior to any reactions. The concern with this *in-situ* route is the potential contamination from the secondary production of Na_2O which was found prior to washing by PXRD, see Figure 4. It was decided that a reaction scheme that introduced an organic oxidant could prove to be significantly beneficial in avoiding sodium contamination.

Alternatively, a simpler route was investigated again using $RuCl_3$ dissolved in DI water, mixed with a desired amount of carbon substrate (Route 3)[7]. This route relies on the diffusion of the $RuCl_3$ into the carbon pores where at a later time the Ru would be oxidized by the addition of H_2O_2. Centrifuging of the material and washing several times provided a new material for testing. Unfortunately, Route 3 was started late in the timeframe of this project so quantitative results concerning capacitance were not obtained.

All three routes successfully made RuO_x materials in bulk quantities and were tested by FTIR, PXRD, TEM, and EDS. However, materials generated by Route 1 and 2 were the only two tested for capacitance capabilities.

Surface Functionalization of RuO_x

Our initial plans were to coat the RuO_x nanoparticles with ligands (i.e., carboxylates) that would stabilize the particles as well as impart cationic surface charges (i.e., R_4N^+) that would allow for binding into the anionic pores of the carbon support. It was thought that this would lead to an increased overall capacitance due to the enhanced interactions between the carbon support and the RuO_x NPs. However, based on the structural information, determined by TEM for the carbon support material (described in the following section), the substrate's lack of porosity and cost benefit analysis led to us to abandon this approach.

Characterization

Preliminary characterizations focused on establishing a baseline by determining the properties of the carbon substrate supplied by TPL, Inc. (Norit Supra X). This material was initially thought to contain micron or smaller holes in which RuO_x could intercalate. However, the high resolution TEM picture (Figure 3(A)) shows that this material did not have the expected porosity but actually consisted of a wrinkled surface (more like a sheet of paper that has been crumpled up). Due to the limited time of this project, this material was used as the support; however, other carbon-based materials with controlled porosity are available and should be utilized to realize the initial concept in future attempts.

The RuO_x materials generated from each route were examined via FTIR, PXRD, TEM, and EDS. For each product, the resultant RuO_x materials were dried and then crushed in a crucible, and then dispersed with chloroform ($CHCl_3$) onto the appropriate holder. The various results are discussed below.

FT-IR The preparation of the FT-IR sample followed Route 1 as an indication of the surface chemistry of the RuO_x resulting nanomaterial. The RuO_x was washed as previously discussed, dried, and then mixed with anhydrous KBr. A pellet was formed from the mixed materials and analyzed. Figure 4 shows a sharp peak at 3433 cm^{-1} which correlates to the $RuO_x\text{-}H_y$ stretching vibration. It should also be noted that the surfactant BMeIm-PF_6 is identified as contributing C-CH_3 and CH_2 stretching vibrations in the range of 2923-2854 cm^{-1}, C=C stretching vibration at 1623 cm^{-1}, and CH_2 bending vibration at 1413 cm^{-1}.

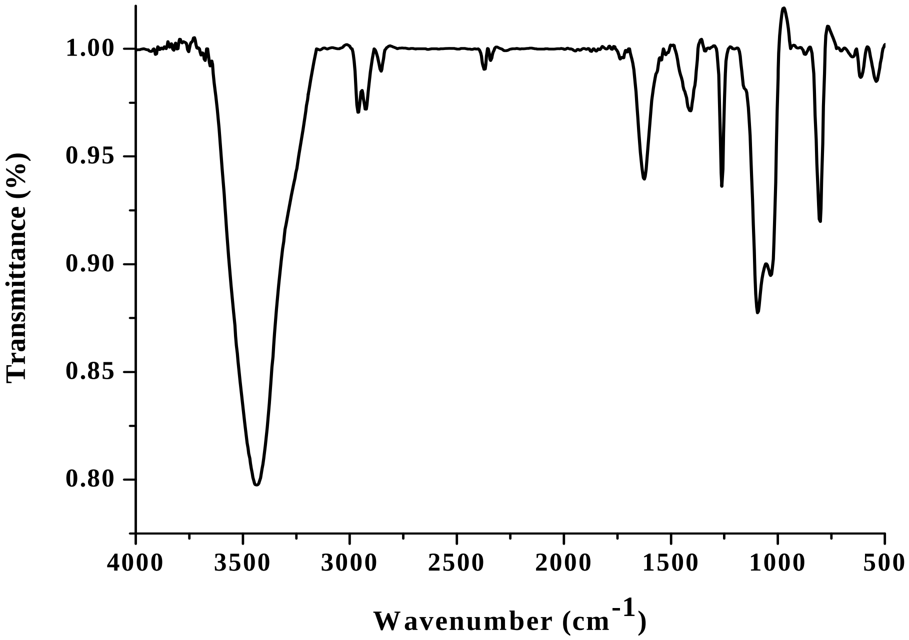

Figure 4. **FT-IR data of RuO_2 generated from Route 1.**

<u>*PXRD*</u> The preparation of PXRD samples followed each route's washing guidelines, and was prepared directly after each synthesis. Figure 5 shows the combined PXRD of Route 1 (green), 2 (blue), and 3 (red). As it can be observed, the patterns are broad and it is difficult to determine the phase of the material. However, comparison to published results shows good correlation between our RuO_x peak positions including similar peak broadening.[5] Jade6™ further identified all three materials as RuO_2 by comparison of the main two-theta peaks residing at 28.0°, 35.1°, and 54.3° to the collected data. The crystal structure is in a tetragonal P42/mnm unit cell configuration. Comparing the materials to one another distinctly shows that Route 1 produced the best bulk crystalline material (Figure 5) while Routes 2 and 3 had more amorphous RuO_2. We suspect this is due to the excess amounts of water that contributes to the uncontrolled nucleation of RuO_2 and subsequently reduced bulk crystallinity. Figure 6 shows the resulting unwashed material from Route 2. It is evident that Na_2O is a significant by-product of Route 2, as determined by Jade6™ reported PXRD peaks at 38.0°, 44.2°, and 64.7°.

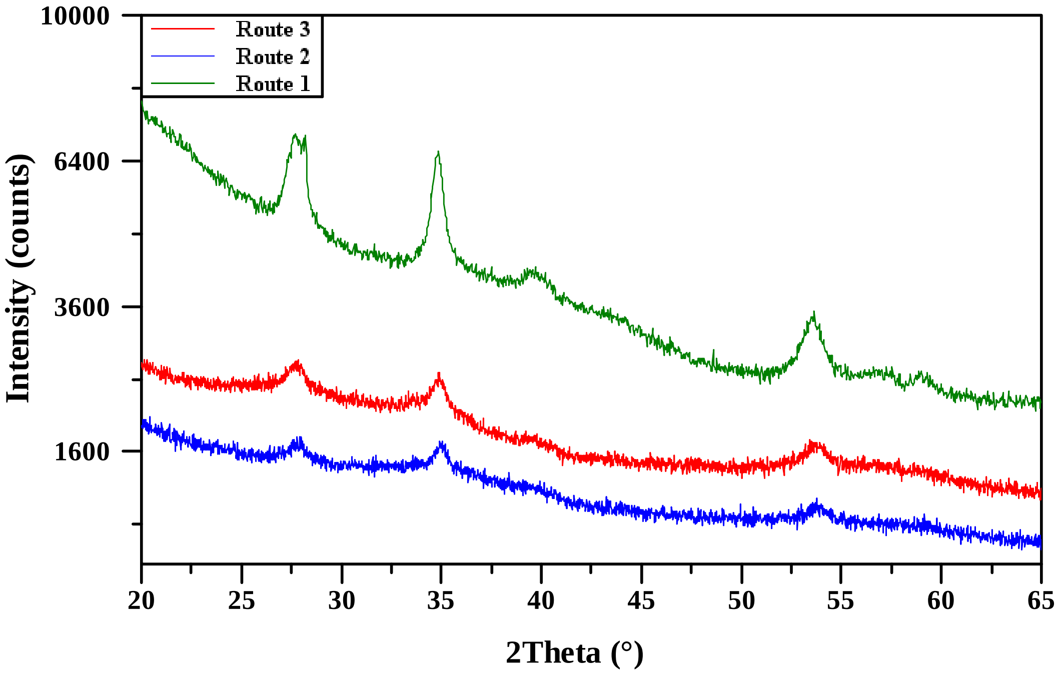

Figure 5. **A PXRD comparison of Routes 1, 2, and 3.**

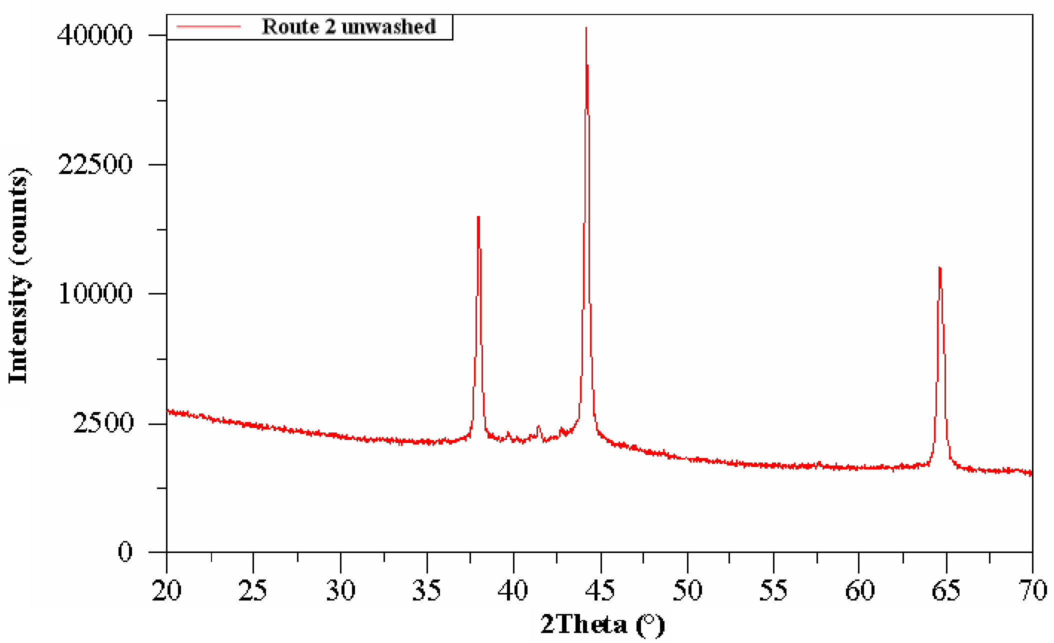

Figure 6. **A PXRD of unwashed material from Route 2. The three large peaks correspond to Na_2O.**

TEM In order to determine some understanding of the size of the materials generated, TEM images were obtained for each route. Figure 7 shows the TEM images of the powder generated by routes 1 – 3. As can be discerned, the dark field results (top right) for Route 1, (B), indicate high crystallinity and the bright field view shows 1-2 nm in diameter particles. For Route 2, (C), the dark field image (top right) indicates the presence of several small well ordered crystalline particles, but the majority of the material particles appear to range from 25 - 100 nm amorphous RuO_x that has agglomerated. The material generated from Route 3 (D), were captured using a scanning TEM (STEM) that allows chemical contrast between materials of heavier atoms to be imaged easier, while lighter atoms appear darker. From the picture it can be seen that the RuO_2 (white) predominantly appears to be amorphous and adheres to the carbon substrate (grey plate-like structure).

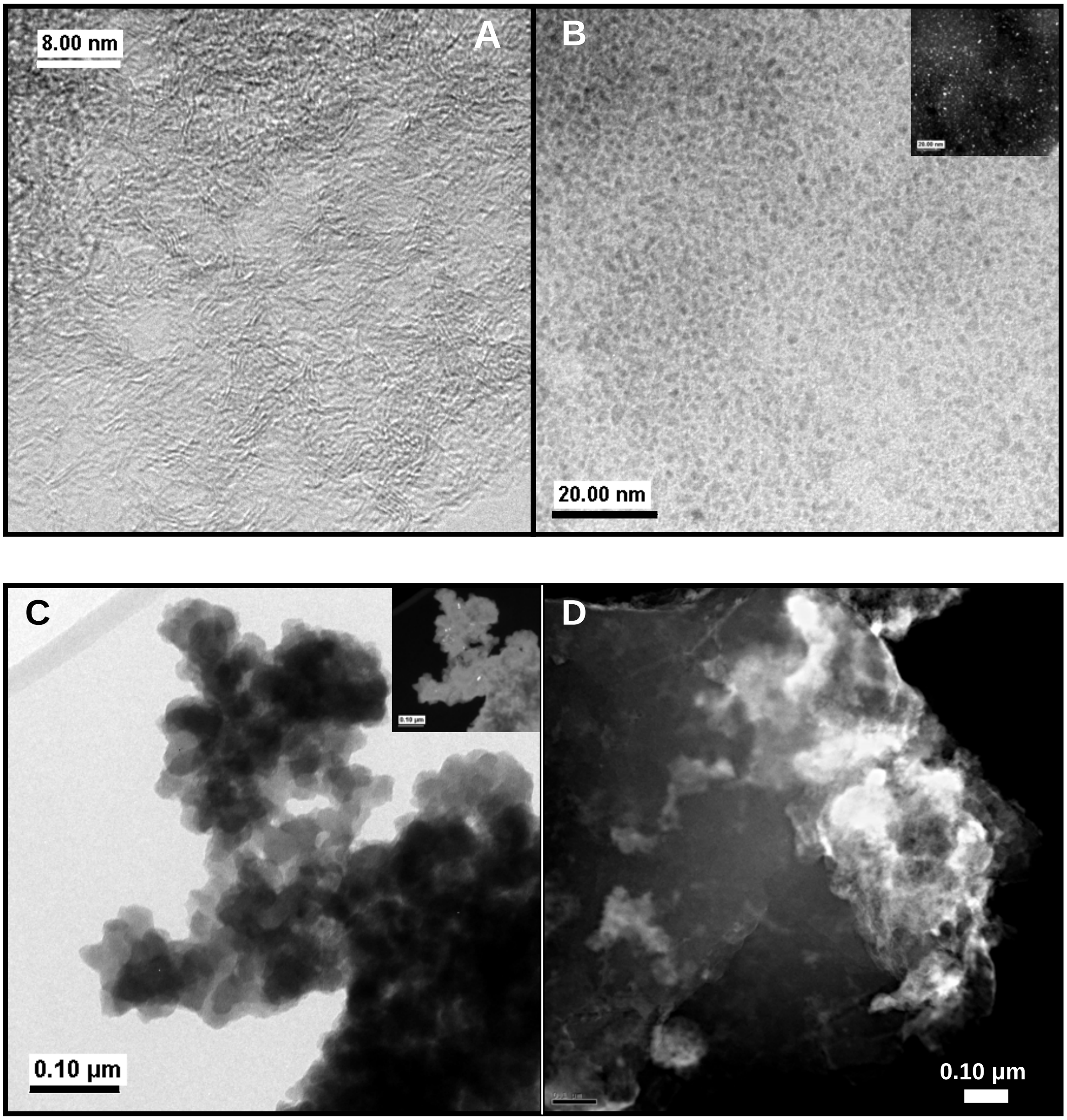

Figure 7. **TEM images with dark field image in upper right corner of: (A) Norit Supra X, (B) RuO_2 from Route 1, and (C) RuO_2 from Route 2. (D) An image from scanning TEM that shows the Norit Supra X coated with RuO_2 (white) from Route 3.**

EDS Since the materials generated proved to be the appropriate sizes, it was necessary to determine the chemical composition of these nanoparticles. Therefore EDS data was obtained on select particles and are shown in Figure 8. The data obtained confirms the majority of the materials contain ruthenium in significant amounts. The copper (Cu) and carbon (C) peaks are both contained in the TEM grid and thus show up in small quantities. However, a notable absence of potential contaminants can be elucidated.

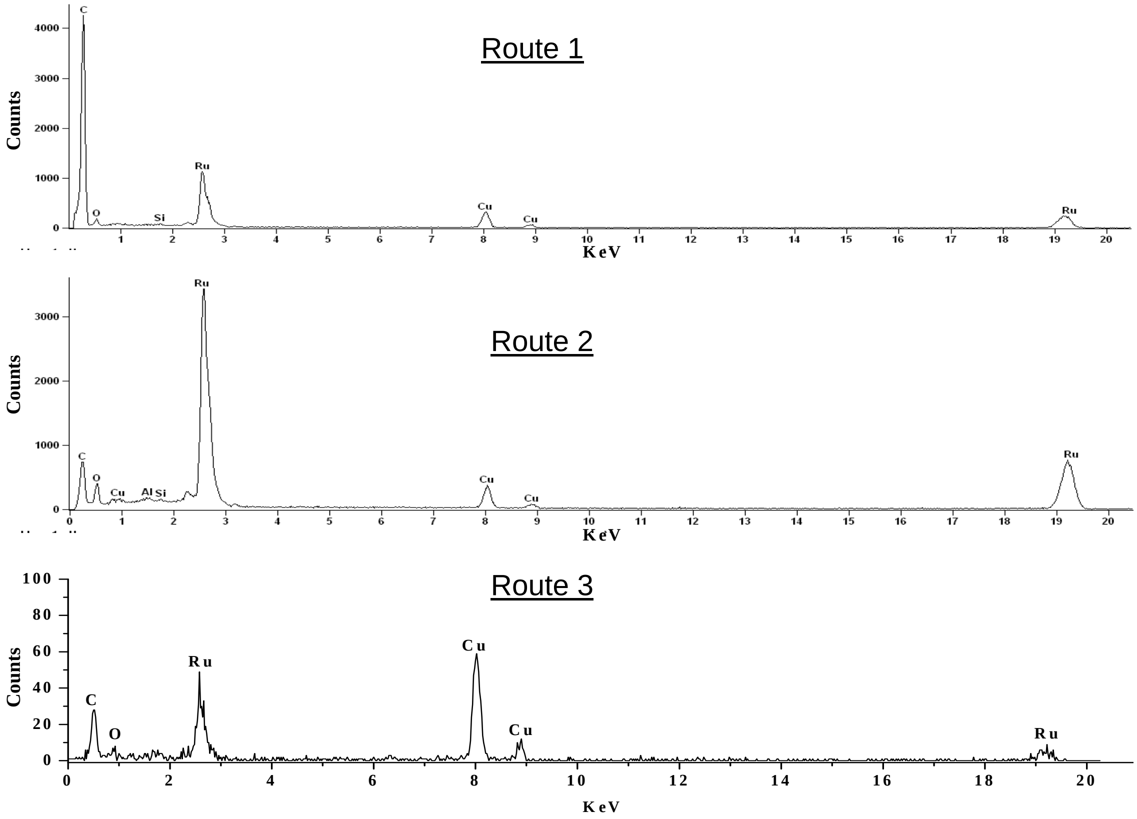

***Figure 8.* EDS data confirming the presence of RuO_x for each sample.**

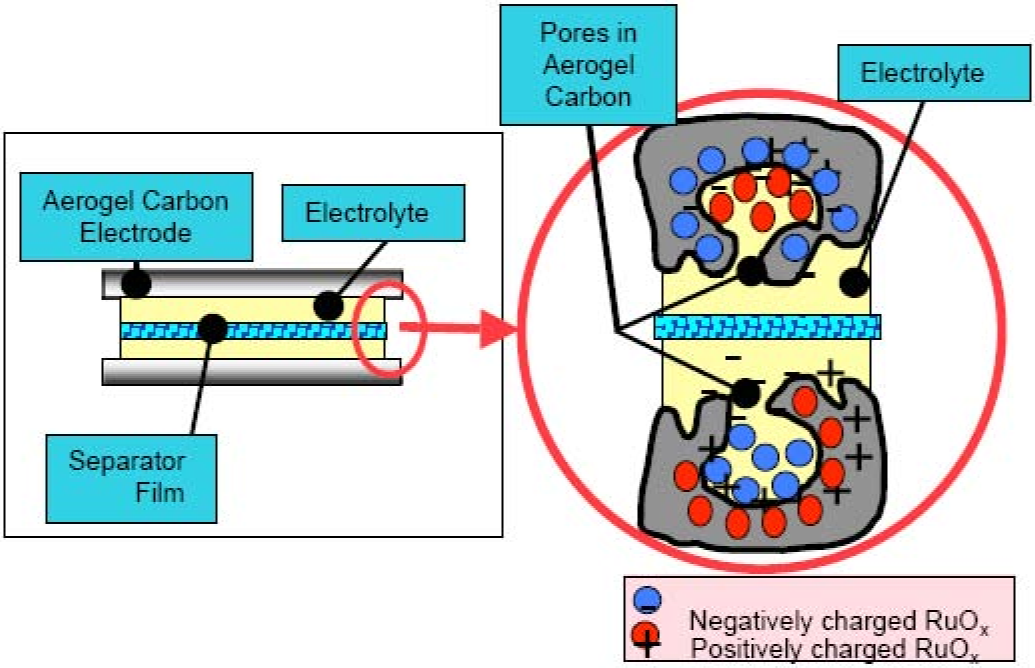

Figure 9. **Schematic of the constructs of the supercapacitor**

Testing

The RuO_x material was then delivered to TPL, Inc. for construction and testing of the microsupercapacitor. A schematic is shown in Figure 9 of the basic constructs of the supercapacitor. As constructed, the micro-supercapacitors were in the discharged state; therefore, the first requirement was to charge them. During charging, positive and negative ionic charges within the electrolyte accumulate at the surface of opposite electrodes compensating for the electronic charge at the electrode surface. A CCCV (Constant Current Constant Voltage) profile was used to charge the micro-supercapacitors. First, a CC charge of one mA was applied to the microsupercapacitor. Once the microsupercapacitor reached its working voltage (1.0 V for aqueous or 2.5 V for organic), a CV charge is performed until the current in the microsupercapacitor drops to nine mA. After charging, the voltage was measured under an open circuit configuration as well as under different loads. These measurements allowed the ESR and capacitance to be evaluated and compared with values for commercial cells.

RuO_2 powders were prepared using Route 1 and Route 2 and evaluated at the beginning of the project. Table 1 contains a description of the samples delivered to TPL by UNM for testing. Upon disassembly of supercapacitors after testing it was noticed that powders prepared from Route 1 discolored the electrolyte. During cycling of supercapacitors made with these powders the ESR increased and the capacitance decreased. Supercapacitors made from Route 2 showed no signs of the problems observed with the powders from Route 1.

Two types of supercapacitors were tested; symmetric and asymmetric. Symmetric supercapacitors utilize two of the same type of electrodes whereas asymmetric supercapacitors utilize two electrodes of different composition. In the testing done here, an asymmetric supercapacitor was made using one electrode with only activated carbon as the active material while the other electrode had some of the carbon replaced with RuO_2. Testing of both configurations showed that asymmetric supercapacitors with the RuO_2 containing electrode used as the cathode gave the best overall performance with respect to ESR and capacitance stability.

Activated carbon electrodes were made containing 0, 5, 15, 25 and 35 wt% un-annealed RuO_2 (Route 2). Electrodes were also made containing 25 and 50 wt% annealed RuO_2 (Route 2) (annealed at 200 ºC). The annealed powders resulted in a higher specific capacitance than the un-annealed powders; summarized in Table 2 and graphically shown in Figures 10 and 11. To begin to understand the behavior of an electrochemical capacitor, it is important to understand that each electrode in the device acts as an individual capacitor, and the total capacitance of the device is modeled as two capacitors in series (i.e., $1/C_T = 1/C_1 + 1/C_2$). In the case of symmetric capacitors with no RuO_x additions, then, the capacitance of each electrode is twice the measured capacitance; however, for asymmetric devices with RuO_x additions in the cathode, one must derive the effective capacitance of the cathode using $1/C_T = 1/C_1 + 1/C_2$. The data is presented in Table 2.

Eliciting further information about the specific contribution from the RuO_x is complicated by the potential dependence of the pseudocapacitance component. Figure 10 represents an electrical equivalent circuit for a cathode containing a double layer component of the capacitance (C_{dl}) and a pseudocapacitance component (C_P). C_P is coupled to the double layer capacitance in a parallel fashion but through a resistance, R_F, related to the Faradaic reaction(s). This resistance is potential dependent and, therefore, the Faradaic component of the total capacitance cannot be easily extracted. Nevertheless, it is apparent that RuO_x additions have delivered an increase in the measured capacitance and a decrease in the measured series resistance.

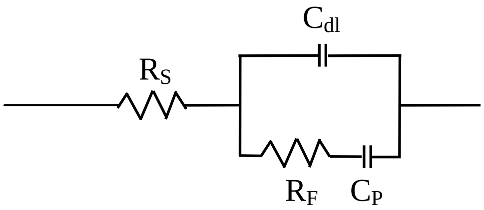

Figure 10. **An equivalent circuit of a composite cathode containing a pseudocapacitive component.**

***Table 1.* Samples Received by TPL from UNM/SNL.**

Sample	Route/Description	Results of Testing
1	1	Observed discoloration of the electrolyte after cycling of supercapacitors using this material. ESR increased and capacitance decreased during cycling.
2	2	No electrolyte discoloration. Improved results when compared to material synthesized using Route 1.
3	2/in-situ RuO_2 + C prepared	Not enough material to mix with binder and fabricate electrodes. Testing could not be pursued.
4	2/Annealed at 200 ºC	Annealed material resulted in higher specific capacitance.
5	2	Used to complete test series with increasing amounts of RuO_2 in electrode.
6	2/Annealed at 200 ºC	Used to complete test series with increasing amounts of RuO_2 in electrode.
7	3	Electrolyte became very discolored during infiltration with electrolyte. Electrochemical testing was not pursued.
8	3/Annealed at 200 ºC/2 hrs	Electrolyte became very discolored during infiltration with electrolyte. Electrochemical testing was not pursued.
9	3/Annealed at 200 ºC/5 hrs	Electrolyte became very discolored during infiltration with electrolyte. Electrochemical testing was not pursued.
10	3/Annealed at 200 ºC/10 hrs	Electrolyte became very discolored during infiltration with electrolyte. Electrochemical testing was not pursued.

***Table 2.* Test results from asymmetric supercapacitors using un-annealed and annealed RuO_2 powder from Route 2.**

Un-annealed[†]

Cathode RuO_2 (wt%)	Capacitance (mF)	ESR (ohm)	Specific Capacitance (F/g)	Capacitance Density (F/cc)
0 *	947	11.9	37.0	418
5	1024	6.24	40.2	452
15	1157	4.10	43.0	511
25	1224	9.15	44.2	540
35	1258	7.25	44.8	555

Annealed (200ºC – 2 hrs)[†]

Cathode RuO_2 (wt%)	Capacitance (mF)	ESR (ohm)	Specific Capacitance (F/g)	Capacitance Density (F/cc)
0 *	947	11.9	37.0	418
25	1317	4.72	45.4	581
50	1676	4.18	51.4	740

† All values are the average of results obtained from four identical supercapacitors.

- Contains only Norit SX Ultra Activated Carbon Powder and 4 wt% PTFE Binder.

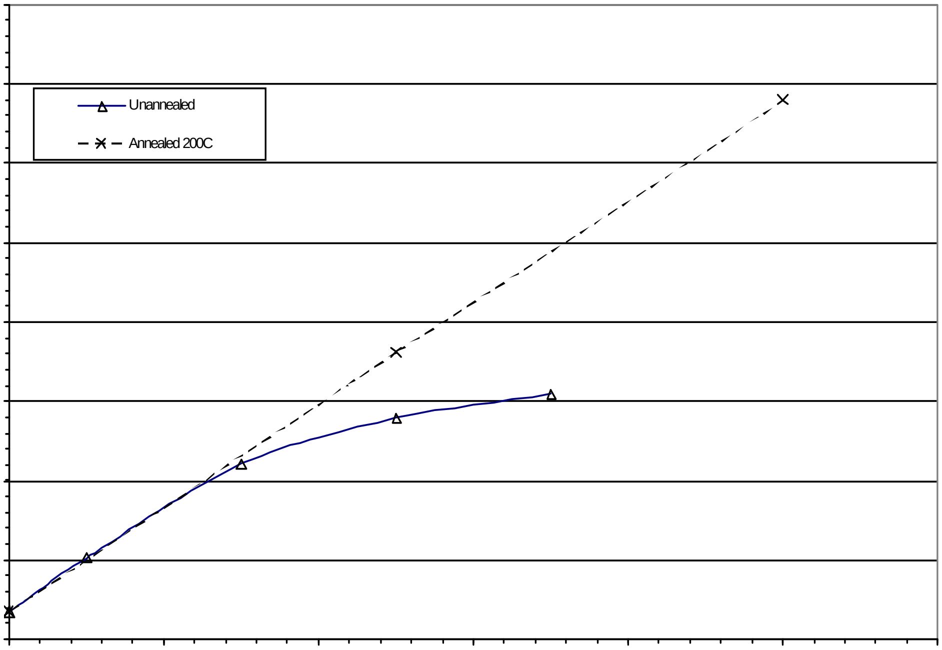

Figure 10. **Capacitance density of asymmetric supercapacitors using annealed and un-annealed RuO_2 powders prepared using Route 2.**

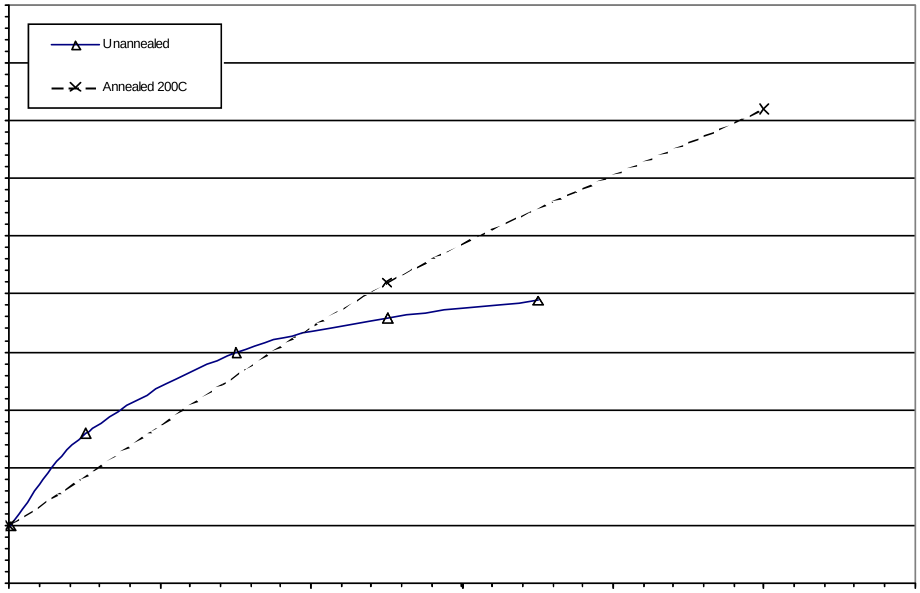

Figure 11. **Specific capacitance of asymmetric supercapacitors using annealed and un-annealed RuO_2 powders prepared using Route 2.**

Conclusion and Summary of Experiment

For this short study on improving the capacitance of microsupercapacitors, we have successfully generated RuO_x nanoparticles, integrated them into a carbon matrix, and successfully tested them. Based on the data collected from the various combinations of materials, it was determined that the RuO_x particles synthesized according to Route 2 produced the highest capacitance when the solution was deposited onto/into the C-substrate. The C-substrate had an appearance more like crumpled paper versus the originally conceived porous matrix. New amorphous C-substrates with controlled porosity were considered as a means to significantly improve this process but due to the limitation in time, this had to be removed from initial investigation. All attempts to generate RuO_x *in-situ* with carbon yielded poor materials that revealed discoloration upon dissolution, and prevented electrochemical testing. It was also found that annealing of the combined materials appears to improve the capacitance of the test device; however, an understanding of why this processing step improves this property is unknown but is assumed to be related to the crystallization and defects generated therefrom. The specific capacitance of 51.4 F/g was achieved using the 50 %wt RuO_2 annealed at 200 ^{o}C for 2 h. which yielded a device capacitance density of 740 F/cc at a scan rate of 1 V/s. Unfortunately, a direct comparison to similar synthesized RuO_2 could not be made because of significantly different testing techniques. Additional work is necessary to fully establish the RuO_x nanoparticle contributions to capacitance in order to determine the improvements to the microsupercapacitor.

Economic Impact

The results of this effort did not show sufficient improvement in supercapacitor electrode materials performance to warrant further investment from TPL. Consequently, there are no plans to create a spin-off company to commercialize this technology.

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Appendices

Appendix A.	Original NMTRC Grant Program Proposal
Appendix B.	First NMTRC Quarterly Report
Appendix C.	Second NMTRC Quarterly Report
Appendix D.	Final NMTRC Report

Grant Overview

This work was funded by a grant from the New Mexico Technology Research Collaborative (NMTRC). The NMTRC is a state-funded program designed to assist in the creation and expansion of a technology-based economy of New Mexico and was established in 2005 by the New Mexico State Legislature to build on the technological successes in New Mexico. The NMTRC works to identify the core technology strengths of New Mexico and facilitates the acceleration and commercialization of these technologies by providing funding, mentoring and business development assistance. The main goal of this organization is to accelerate new technology business formations and expansions that will benefit research programs of the 10 NMTRC members (of which Sandia was one), entrepreneurs, industry, investors and the state of New Mexico. The successful realization of this goal was to improve the overall economy of the state through an increasing number of high-paying jobs, a more diversified economy and the creation of wealth in our state. By promoting interaction between NMTRC members and acting as a resource for both public and private sector entities interested in new job creation in the technology sector, the NMTRC is helping to generate momentum for the burgeoning number of technology-based businesses that reside in New Mexico. Furthermore, NMTRC will become the nation’s premier force in creating economic benefits based on new technology and ensure that these efforts create state-wide economic benefits. For this proposal, the state supplied support of the NMTRC was leveraged with outside investments, including private companies and national laboratories concerning projects with strong commercial potential. A minimum one-to-one match was required for all projects selected and funded by NMTRC.

1. Cover Page

Metal Oxide Coating of Carbon Supports for Supercapacitor Applications

Point of Contact: Timothy J. Boyle
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May 12, 2006

BAA_TRC_06

Volume I - Technical Volume

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2. Application Information Page

This Application Does [X] Does Not [ ] *(Place an "X" between the brackets)*
Include information considered Trade Secret

** Click on the gray portion first, and then type in the request information*

Offeror	Timothy J. Boyle				
Address	Sandia National Laboratories				
	Advanced Materials Laboratory – MS 1349				
	1001 University Blvd SE				
City	Albuquerque	**State**	NM	**Zip Code**	87106
County	USA				

Project Title	**Commercialization of Metal Oxide Coating of Carbon Nanotubes for Supercapacitor Applications**		
TRC Request	$ 198.800	**Cost Share**	$ 225,700
Project Focus *(Place an "X" between the brackets)*	**1 (X) Nanotechnology** **2 ( ) Optics** **3 ( ) Medical Applications** **4 ( ) Digital Media** **5 ( ) Sustainable Natural Resources** **6 ( ) Alternative Energies**		

David Goldheim **Director**
Typed Name and Title of Authorizing Agent **Title**

Signature **Date**

FOR TRC USE ONLY

DATE/TIME RECEIVED	BY:

3. Trade Secret Information.

A. Sandia National Laboratories (SNL)

(1) ID Title: Anhydrous Solution Synthesis of Luminescent Germanium Nanocrystals from Germanium (II) Precursors ID Number: 7744 ID DOE S #: 104451, DOE Waiver Grant Date: 1/27/2005. **ID Originators** Scott D Bunge Org. 01843 / MS - 1349 (505) 272-7623 Timothy J Boyle Org. 01815 / MS - 1349 (505) 272-7625

(2) ID Title: Nanocrystalline Particles for Bio- and Nanotechnology Applications ID Number: 7738 ID DOE S #: 104442 DOE Waiver Grant Date: 7/19/2004 **ID Originators** Timothy J Boyle Org. 01815 / MS - 1349 (505) 272-7625, Timothy N Lambert Org. 01815 / MS - 1349 (505) 272-7633, Hongyou Fan Org. 018151 / MS - 1349 (505) 272-7128

(3) ID Title: Single Source LiCoO2 Precursors Production of Nanoparticles and Thin Films ID Number: 7350 ID DOE S #: 100419 DOE Waiver DOE Waiver Unfiled **ID Originators** Timothy J Boyle Org. 01815 / MS - 1349 (505) 272-7625

(4) ID Title: Cadmium Aryloxides: Alternative Precursors for the Colloidal Synthesis Nanocrystalline CdE (E= S, SE and TE) ID Number:7574 ID DOE S #: 103431 DOE Waiver Unfiled **ID Originators** Scott D Bunge Org. 01843 MS - 1349 (505) 272-7623 Timothy J Boyle Org. 01815 / MS - 1349 (505) 272-7625

(5) ID Title: Synthesis of Metal Nanoparticles ID Number: 7346 ID DOE S #: 100413 DOE Waiver Grant Date:7/17/2003 **ID Originators** Scott D Bunge Org. 01843 / MS - 1349 (505) 272-7623 Timothy J Boyle Org. 01815 / MS - 1349 (505) 272-7625 **Patent Applications** 7346.0 / ORD US Application S #: 100413 Application #: 10/424,231 Filed: 4/24/2003 Patent #:6929675 Issued 8/16/2005

(6) IG Title: Indirect-Bandgap Nanocrystalline Materials as Photo-thermal Devices ID number: SD_10234 ID DOE #: Pending DOE Waiver: Pending Granted? Pending
ID Originators: Timothy N. Lambert Org. 1815 / MS-1349 (505) 272-7633

(7) ID Title: Lead Amide Precursor for the Synthesis of Photonic Nanocrystals SD# 10364 Point of Contact(POC) HERNANDEZ-SANCHEZ,BERNADETTE A., 01815, 505-272-7656 **ID Originators** Bernadette A. Hernandez-Sanchez Org. 01815 / MS – 1349 (505) 272-7656 Timothy J Boyle Org. 01815 / MS - 1349 (505)272-7625

B. UNM

(1) University of New Mexico US Utility Patent Application: Application #: 11/184,540 Filed: 7/19/2005

C. TPL, INC.

TPL Inc.’s preexisting IP relates to and is covered by the following patents and patent applications:

U.S. Patent No. 6,621,687, issued Sep 16, 2003, entitled "Micro-Supercapacitor"
U.S. Patent No. 6,861,170, issued Mar 1, 2005, entitled "Volumetric Micro Batteries"
U.S. Patent Application Serial No. 10/796,329, filed Mar 8, 2004, entitled "Lithium Ion Microbattery"
U.S. Patent Application Serial No. 10/796,532, filed Mar 8, 2004, entitled "MEMS Electrochemical Power System"
U.S. Provisional Patent Application Serial No. 60/756,876, filed Jan 5, 2006, entitled "System for Energy Harvesting and/or Generation, Storage, and Delivery"

Attachment B
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4. Offeror Contact Information

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Authorizing Agent – the individual authorized by the offeror to bind the offeror to the terms and conditions of an award.
Fiscal Agent – the individual authorized by the offeror to sign grant-related financial documents; for example Requests for Payment, Grant Financial Reports, etc.
Grant Administrator – the individual authorized by the offeror for oversight of day-today operations of the award; including preparing progress reports, monitoring project progress, etc.
Project Director - the individual authorized by the offeror to direct the project or program for which the grant has been issued.
The same individual may hold more than one of these positions.

Attachment C

TRC Grant Program
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5. Collaborator Information

Below list each collaborator named in the proposal, a contact name, and contact information for them. Include an e-mail address if available. Attach additional forms as needed.

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6. Abstract

The global market for wireless sensor networks in 2010 will be valued close to $10B, or 200M units. TPL, Inc. is a small local business that has positioned itself to be a leader in providing uninterruptible power supplies in this growing market; however, optimization of a critical component, the supercapcitor, is required. This proposal will aim to produce prototype supercapcitors through the integration of novel materials and fabrication processes developed at NMTRC member institutions. The improved supercapcitor will reduce maintenance costs and expand the utility of the TPL, Inc.'s device, enabling New Mexico to become the leader in the growing global wireless power supply market. By dominating this niche, new customers will be attracted to this Albuquerque based company, yielding new technical opportunities and increased job opportunities for New Mexico.

TPL, Inc.'s patent-pending EnerPak™ product provides the solution to powering wireless devices where it is costly, dangerous or impossible to change batteries on a regular basis. The EnerPak™ converts small amounts of energy from the environment (e.g., vibrations, light or temperature differences) into electrical energy that can be used to charge small energy storage devices. Wireless sensors b that are deployed in difficult-to-access locations, consist of a large number (e.g., several thousand) of sensors, or would require expensive disruption of a process or operation to replace batteries would benefit from this technology. A critical component of the EnerPak™ is the supercapacitor that handles high power delivery for wireless communications. The technical objectives of this proposal will be to provide advanced materials for an improved microsupercapacitors. This will significantly increase TPL, Inc.'s competitive advantage in this growing market. In particular, we will focus on **developing novel ruthenium oxide nanomaterials into carbon supports to significantly increase the energy density of the supercapcitor**. The nanomaterials will be separated by size, through nanometer-scale channels using the surface charges engineered onto the nanoparticles. This charge will also be used to control deposition of the particles, dramatically improving the supercapacitor.

TPL, Inc. is already a leader in design and manufacture of power sources for unattended wireless sensors. To ensure this leadership is enhanced, it is critical that the technical advances described above are evaluated thoroughly. With these modifications, to the existing supercapacitor currently in preparation for commercialization at TPL, Inc. a competitive advantage for this NM-based company along with enhancing research efforts projects at UNM and SNL will occur. Therefore, successful completion of the proposed effort will enable TPL, Inc. to expand its product offerings, delivering enhanced capabilities and opening new market opportunities within New Mexico. TPL, Inc has been selected to participate in the Equity Capital Symposium hosted by Technology Ventures Corporation to secure financing to establish a new business to pursue this market opportunity. This new business will be located in Albuquerque; revenues are projected to exceed $26M in 5 years. Without support of this proposal, the expected technological breakthroughs and economic gains to New Mexico will not be realized.

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7. Table of Contents

8. Project Overview

The increasing consumer demand for portable devices that require high-energy operation will ultimately lead to small wireless devices. Typically, these devices are fueled by batteries; however, replacing these power sources is not always possible or cost-effective for a number of systems. Therefore, alternative devices are needed, such as the EnerPak^{TM} of TPL, Inc., a New Mexico based small business. In order to meet high power communications loads, the usual approach is to design a power source large enough to handle the highest power load. However, the EnerPak™ uses low impedance supercapacitors as the primary output device to provide the most efficient delivery of energy to the sensor, and deliver high power bursts for data communication more efficiently than standard batteries. Unlike batteries, supercapacitors can be charged and discharged millions of times without any degradation in their performance;. While supercapacitors deliver energy efficiently, they do not *store* energy efficiently, and so tend to be quite large in comparison to the portable devices needed. The successful development of an improved supercapacitor that possesses increased energy capacitance densities on a smaller size scale will allow TPL, Inc. to lengthen its lead on the competition and impact a market valued close to $10B, or 200M units. By developing an EnerPak^{TM} with an improved microsupercapacitor, new market opportunities will open up; thereby, yielding an influx of funds to the New Mexico economy necessitating the expansion of new facilities to meet the consumer's demand, leading to spin-off companies creating new jobs, and have numerous other positive impacts on the New Mexico and world markets.

This proposal brings together two established and productive members of the New Mexico Technology Research Collaborative (NMTRC) from Sandia National Laboratories (SNL) and the University of New Mexico (UNM) along with TPL, Inc., an established small business in Albuquerque, New Mexico. SNL participants bring more than 13 years of experience in developing novel precursors that can readily be converted to tailored materials and subsequently modified such that they interact with a variety of surfaces. Coupling the synthesis abilities at SNL with the established engineering expertise at UNM for nanoseparation, a formidable team will exist to attack this complex energy problem through the development of monodispersed, charge functionalized, novel nanomaterials for assembly into improved microsupercapacitors. Since there are a limited number of reports on the formation of ruthenium oxide (RuO_x) nanoparticles, the initial hurdle will be the development of acceptable precursors for the production of the RuO_x nanomaterials which will then be charge functionalized to interact with the carbon (C) supports. Together, this team's unique skills and perspectives ensure a high rate of success for producing novel, previously undeveloped materials that offer orders of magnitude improvement in the performance. This project will focus on generating microsupercapacitors that possess dramatically improved capacitance and, therefore, energy density. In addition to helping TPL, Inc., this project will contribute to existing programs at NMTRC member institutions, including SNL and UNM. Through development of novel materials and fabrication/manufacturing processes, UNM and SNL will have advanced their technical expertise in the areas of precursor development, nanomaterials, and device integration.

This will also enhance the capabilities of an already recognized New Mexico center of excellence for materials synthesis, nanotechnology, and packaging. A further outcome of the success of this project will be enhancement of UNM's capability to attract and train students in the discipline(s) of chemistry and engineering through their ability to provide unique access to technical partnerships with SNL as well as student internships. SNL will have the opportunity to mentor these students in core competency areas and develop a pool of potential future technical employees. This will add to the base of technical workers in New Mexico in the developing field of nanotechnology and meet the national call for attracting students to this discipline.

As mentioned, the increasing use of wireless sensors will impact many markets including border security and building automation with improved safety, increased security, lower heating, ventilation and cooling (HVAC) costs, and increased manufacturing efficiency. Providing comprehensive monitoring capability will require numerous individual devices; moreover, sensors will often be located in inaccessible places and require long intervals between scheduled maintenance. TPL, Inc.'s patent-pending EnerPak™ products provide a long-life solution to powering wireless sensors that eliminates the need to change batteries. The EnerPak™ converts small amounts of energy from the environment (e.g., vibrations, light or temperature differences) into electrical energy to charge very small energy storage devices. A major challenge that faces wireless sensor nodes is the asymmetry of the power demands of sensing, processing, communication, and sleep functions – on the order of four orders of magnitude. Because communication functions draw relatively high power levels (typically from 10s to 100 milliWatts), wireless sensor nodes are designed to communicate infrequently (for example, once a minute to once an hour), reverting to a low-power sleep state to conserve battery life. To address the technical issues, this project has been broken down into several tasks (see Volume II, Table 9) to generate the critical RuO_x-carbon support interaction necessary for production of the supercapacitor. The various tasks include: Ru precursor synthesis; RuO_x nanoparticle synthesis; characterization; functionalization of RuO_x; combining RuO_x and carbon (C) support; size selection of RuO_x; supercapacitor fabrication and assembly; and supercapacitor testing. Characterization of the electrical performance of the supercapacitors using measurements of capacitance, ESR, power, and leakage current measured under self-discharge. Sandia and UNM will take the technical lead developing the necessary materials whereas, TPL, Inc. will test these prototypes upon assembly. TPL, Inc. will drive the economic aspects of the development. This will be coordinated through preset meetings and close communication of these researchers.

The biggest challenge to commercializing any new technology is cost. As a rule of thumb, for a new technology to be accepted in the market, if the cost increases, it must deliver an order of magnitude increase in performance over existing solutions or it must realize an order of magnitude decrease in cost for the same performance. While a substantial body of work on RuO_x modified supercapacitor electrodes exists, the relatively clumsy microstructured approach that has been employed to date - rather than the nanostructured approach proposed here - limits performance improvements. Nevertheless, these supercapacitors display a two-fold increase in energy storage over conventional electrode materials. The uniform distribution of nanostructured RuO_x within the pore structure of activated carbon electrodes, as proposed for this project, is expected to deliver *at least* an order of magnitude higher of improved performance. Furthermore, undertaking this effort will enable us to develop a preliminary cost model for the process, providing initial quantitative data to evaluate the potential impact on TPL, Inc. 's EnerPak™ product.

In summary, the goal of this proposal is to position TPL, Inc. as a leader in the portable power market such that their market base expands, improving the economic viability of New Mexico while increasing the expertise at the NMTRC institutions. In the proposed effort, we will synthesize RuO_x nanoclusters, develop methods to disperse them on carbon substrates for microsupercapacitor electrodes, evaluate the electrochemical properties, and assess the effects on the performance of these supercapacitors. SNL researchers will continue to expand their repertoire of unique nanomaterial synthesis and functionalization while UNM will contribute to the synthesis effort and introduce a novel method for size selection of these functionalized particles. The resulting advanced electrode materials will be delivered to TPL, Inc. to be formed into electrodes, evaluated in standard microsupercapacitor geometries and compared with current state-of-the-art materials. Technically, we will improve the capacitance of the portable power source by introduced charge and size controlled nanoparticles of RuO_x onto carbon surfaces. The novel ability to generate electrochemically active nanoparticles coupled with size separation will strengthen the respective team members' abilities as well as contributing to their leveraged programs. These new products will contribute to the economic viability of an established small New Mexico based business, attracting new customers, as well as potentially creating several spin-off companies.

9. Commercialization, Strategic Value and Economic Development

Wireless devices have many advantages over conventional wired sensors including eliminating heavy, costly and fragile wiring, reducing sensor power requirements, and significant reductions in sensor system size and weight. For example, a wireless sensor promises extended capabilities for government and civilian applications such as homeland security, structural health monitoring, industrial process control, battlefield intelligence and chemical and/or biological (chem./bio) agent detection. This will be accomplished with improved safety, increased security, lower heating, ventilation and cooling (HVAC) costs, and increased manufacturing efficiency. In addition, wireless sensor systems have low maintenance costs, are easy to replace and upgrade, have reduced connector failure compared with hard-wired systems, greater physical mobility and freedom, and faster commissioning. Furthermore, because of their low cost, these devices can be deployed at a small fraction of the cost of hard-wired systems (in which the cost of wiring can reach up to $2000 per foot!). Numerous advances in sensor, communications, and distributed architecture technologies have led to the emergence of first generation devices and several companies now manufacture and sell matchbox-sized devices. Powering wireless sensors presents a challenge because of the asymmetric power demands of different functions of their operation. Wireless sensors have three basic modes of operation: they collect data; they communicate or transmit the data to a remote monitoring system; or they sleep. The power demands of these different functions ranges from microWatts to hundreds of milliWatts. The only way to accommodate these disparate power needs using a battery is to make it big enough to handle the highest power demand. Consequently, it will be oversized for most of the operational lifetime and capabilities of the system. This is clearly an inefficient approach, and there is a need for intelligently designed micropower systems that can extend the life of wireless sensors, and enable them to be deployed where it is impossible to change batteries, while maintaining a small form factor that is commensurate with future miniaturized sensor systems.

TPL, Inc.'s EnerPak™ products provide power for wireless sensors where it is costly, dangerous or impossible to change batteries on a regular basis. Unlike batteries, the EnerPak™ will follow a path of miniaturization delivering integrated products that shrink as customers' sensor products shrink without sacrificing performance. Batteries are self-contained energy sources that convert chemical energy into electrical energy. The EnerPak™, on the other hand, converts small amounts of energy from the environment (e.g., vibrations, light or temperature differences) into electrical energy for use in the wireless sensor. Excess energy is stored in very small energy storage devices – patented microbatteries and supercapacitors. This combination provides the following value features that will drive the market adoption of this enabling technology: long life; efficient pulse power delivery that is necessary for radio frequency communications; back-up power providing redundancy and cold-start ability; and miniaturization and integration. A critical component of the EnerPak™ product is the supercapacitor that handles high power delivery for wireless communications. The proposed effort to develop supercapacitor materials with increased capacitance density will result in supercapacitors that can store more energy within the same volume leading to a significant reduction in the size of the EnerPak™ product. As wireless sensors become smaller, the ability of the EnerPak^{TM} to shrink in the same way while maintaining power delivery capabilities will provide a significant competitive advantage over competing solutions.

Successful completion of the proposed effort will enable TPL, Inc. to expand its product offerings, delivering enhanced capabilities and opening new market opportunities. The wireless sensor market is poised for very rapid growth over the next several years and will need increasingly sophisticated and capable power solutions. The improved performance promised by enhanced supercapacitor materials will be essential if TPL, Inc. is to remain a leader in this exciting market. The global market for wireless sensor networks in 2010 will be valued close to \$10B, or 200M units, up from \$200M or 1.3M units in 2005. The major segments of this market include

- Industrial Process Control (IPC) - process monitoring, machine health and safety;
- Commercial and Residential Building Automation – HVAC, lighting, security, and air quality,
- Automated Meter Reading/Advanced Metering Infrastructure; and
- Niche - agriculture/environment, security, structural health, and government.

The features of our EnerPak™ make it essential for wireless sensor applications that are deployed in difficult or inaccessible locations; consist of a large number (e.g., several thousand) of sensors; or would require expensive disruption of a process or operation to replace batteries. These customer motivating factors leave an addressable market opportunity for our product on the order of 90M units in 2011, largely dominated by the industrial control sector. Therefore, this sector will be our primary target market. The lack of sensor accessibility, and network size in niche market applications are driving the demand for an alternative to batteries. Customers in this sector are highly motivated and will provide useful “beachhead” markets for early demonstration of the technology. End-users in the IPC usually approach a systems integrator to pull together the diverse technologies of sensor hardware, networking technology, and data management. These systems integrators may design their own hardware or may buy it in from specialized wireless sensor manufacturers. TPL, Inc. will target both of these types of customers at the front end of the supply chain. This approach will enable customers to design EnerPak™ products into their products for use in applications either with large numbers of sensors, or with sensors installed in difficult-to-access or dangerous locations. Each of the features that will drive the market adoption of the EnerPak™ also provides a competitive advantage. The long life that is enabled by using energy harvesting technology will significantly reduce maintenance costs. Second, the ability to provide back-up power will enable application in environments with intermittent ambient energy sources (e.g., an aircraft generates no vibrations in the hangar). Third, pulse power capabilities are essential for wireless sensors, and are usually impossible to deliver with small size power sources; the capabilities of our supercapacitors provide this critical feature. Finally, as sensors follow the inevitable path to miniaturization, the EnerPak™ has similar miniaturization potential that conventional batteries can not replicate. For instance, embedded sensors in aircraft, bridges, dams, covert sensors, sensors monitoring an industrial process that cannot be shut down due to cost or safety concerns *can not* use batteries but must use a new technology, such as the EnerPak™. The new materials for the improved supercapacitor proposed here will improve our competitive advantage over batteries because we can make our EnerPak™ even smaller.

Our analysis of the competitive environment firmly established that battery technology is firmly established with the main stream consumer. This new product seeks to replace this older, established technology with a superior product to solve a critical energy and minimize technology problem. This will be accomplished by moving from large, inefficient, low power, short-lived batteries to this exciting new technology. The capabilities of the EnerPak™ outlined above will differentiate it in applications that simply cannot be satisfied with conventional batteries. Initial growth of TPL, Inc.'s business will capitalize on the weaknesses of conventional batteries for these applications and will enable the Company to establish itself in the market. The steps to commercialization will involve the fundamental synthesizing, understanding and development of the components of the supercapcitor. This will be followed by electronic testing of the various components as we ultimately assemble a prototype for the EnerPak^{TM}. Once the prototype is established, field testing, further optimization based on these data, establishing manufacturing protocols, staffing, marketing and additional improvements will follow. This proposal focuses on the initial development and testing of the components of the supercapacitor. TPL, Inc. will undertake the commercialization aspects of this proposal, while UNM and SNL attack the fundamental materials issues.

TPL, Inc. is a New Mexico small business with operations in Albuquerque and at Fort Wingate in Gallup, NM. It also has a wholly owned subsidiary, TPL, Inc. Microelectronics, in San Diego, CA. This organization was acquired in 2004 to provide production and commercialization capabilities for advanced dielectric ceramics manufactured in Albuquerque. With 15 years of business operations in Albuquerque, it is clear that TPL, Inc. is committed to New Mexico. During that period it has built strong ties with local organizations such as Technology Ventures Corporation, UNM, NextGen, SNL, New Mexico Tech., and the local business community. TPL, Inc.'s micropower technologies effort grew out of its Advanced Technologies Division through government Small Business Innovation Research (SBIR) funding that began in 2002. What began at that time as two people working on the project part time has grown into a seven person organization including management, engineering and technician personnel supported by the parent company's business infrastructure. The Micropower Technologies Department of TPL, Inc. was created in June 2004 to focus efforts on the EnerPak™, under the leadership of Dr. Lakeman. Customer interest and market demand dictate transitioning from research and development to a manufacturing organization and the Company is considering equity investment to effectively address the market need. The investment would be used to spin-out the company to focus on commercializing this product. The enhanced performance that successful completion of the proposed effort would deliver would substantially differentiate TPL, Inc.'s EnerPak™ products and greatly increase their competitive advantage.

Since the EnerPak^{TM} is an existing product, the schedule for commercialization would follow: R&D, prototype supercapacitor development, field testing in an EnerPak in an industrial monitoring system, possible redesign based on field data, integrating into our existing manufacturing structure, establishing suppliers, hiring staff, marketing, improvements based on initial feedback. Technical development of the new material and integration into supercapacitor structures will be accomplished using this proposed effort and other government funding sources. As noted elsewhere, TPL has two strategies to finance commercializing its technology depending on how quickly these markets come to fruition. Whether internal or external funding is used, initial financing would allow installation of facilities and equipment to manufacture pilot quantities (10k/week) of new supercapacitor products. Further government contracts, along with commercial partnerships and initial sales revenues may provide resources to expand production capabilities, and finance further development of integrated energy harvesting energy storage systems, including potential technology licensing. Production staff (batching, assembly, test and QC) will be needed, starting in 2008. Initial production quantities, however, will be quite modest (a few 10k batteries/yr.) and can be accommodated hiring 1-3 production workers. As the quantities increase in the 2009 – 2010 timeframe, multiple shift operation will be required to meet maximum capacities. The following provides an estimate of the personnel needed for development, manufacturing and production:

	2008	2009	2010
Management	1	2	2
R&D	6	6	6
Marketing and Sales	0	1	2
Production	2	5	7
Total Staff	**9**	**14**	**17**

TPL, Inc. personnel required to realize development, manufacturing and production objectives

10. Collaboration

In order to meet the goals of this proposal, the development of a microsupercapacitor, two members of the NMTRC (SNL and UNM) have teamed with a New Mexico technology company, TPL, Inc. with offices in Albuquerque and Gallup, NM as well as in San Diego, CA. This collaborative team incorporates a complimentary set of the technical skills, backed by depth of experience, to produce a new microsupercapacitor from novel materials and fabrication processes and involves the following principal investigators Dr. Timothy J. Boyle (SNL), Prof. Sang Han (UNM), and Dr. Charles Lakeman (TPL, Inc.). The new materials generated in this effort will allow for development of a superior micropower source such that it can be successfully commercialize with maximized market acceptance. Collaboration of these research groups with the TPL, Inc. manufacturing experts will result in an iterative process between innovation in materials and processes and practical manufacturing considerations that will optimize the likelihood of success. It is of note that each team member brings their own trade secrets (Section 3 Volume I) to this project and non-disclosure agreements have been signed by all participants.

The Advanced Materials Laboratory (AML) facility of SNL is ideally situated to ensure the maximum interaction between the three institutions. Only 2 miles from UNM and ~ 5 miles from TPL, Inc, with its relatively open access will allow for exchange of ideas and personnel, and meetings to ensure forward progress is being made. Students in the Han group have ready access to the Boyle labs – in fact, Han students attend the weekly Boyle group meetings. Several informal meetings between Dr.'s Lakeman and Boyle have occurred in the past year concerning this research effort. This allowed us to put this enthusiastic team together to answer this BAA, which attests to the close interaction these groups already possess.

The team members from SNL are led by Dr. Boyle, a Principal Member of Technical staff for the past 13 years, in the Ceramic Processing & Inorganic Materials Department in Albuquerque, New Mexico. Over the past 13 years, his work at SNL has focused on developing novel chemistries for the production of tailored materials using sol-gel, metalorganic chemical vapor deposition, and nanomaterials processes. From this work, he has published over 100 refereed papers and obtained more than 10 patents covering various aspects of this research. Further, the chemistry team is enhanced by an organic chemist Dr. Timothy N. Lambert, a Postdoctoral fellow who throughout his research career, has focused on developing novel functional molecules (and more recently, nanomaterials) capable of selective molecular recognition and performing a desired function. These researchers are experts in the development of novel chemistries to produce tailored materials and will use their novel precursor and nanoparticle synthesis skills to attack this problem of creating highly dispersed RuO_x on C-based materials. The work is expected to proceed smoothly since there is a great deal of intellectual property and experience already in place due to other work that the Boyle chemistry research group is already conducting. The synthesis efforts will focus on developing an appropriate Ru-based precursor that successfully makes monodispersed high quality RuO_x nanomaterials. These will subsequently be functionalized to have + or – charges on the terminus of the surfactant in order to assist the separation and binding to the carbon substrate.

The members from UNM are Prof. Han and Louis Tribby, a graduate student from the Chemical and Nuclear Engineering Department with expertise in semiconductor materials. Prof. Sang Han joined the Department of Chemical & Nuclear Engineering at the University of New Mexico in 2000 as an Assistant Professor. His research program encompasses: (1) selective growth of Ge quantum structures/high-quality heteroepitaxial films on Si; (2) scanning tunneling microscopy to fundamentally understand the selective growth process; (3) hybrid micro/nanofluidic systems for advanced bioseparation and analysis; (4) synthetic modification of semiconductor surfaces using self-assembled monolayers of polyfunctional organic molecules; and (5) high-yield Ge^0 nanocrystal (NC) synthesis from novel Ge(II) precursors and NC surface functionalization. The Han group will also use their engineering expertise to assist in development of the nanoparticles, functionalization, and separation. Again, this should proceed smoothly since these two groups have worked informally together for several years. Prof Han's former graduate research assistant (Dr. Henry Gerung) utilized Dr. Boyle's AML facilities to successfully demonstrate Ge(0) NC synthesis from Ge(II) precursors [*J. Am. Chem. Soc.*, **128**, 5244 (2006) and *Chem. Commun.*, **14**, 1914 (2005)]. In Fall 2005, Prof. Han's new PhD student (Mr. Louis J. Tribby) joined the team to continue Dr. Gerung's effort. Mr. Tribby is taking engineering approaches to nanoparticle synthesis and size-selection. He will develop methods of synthesis for RuO_x nanoparticles and implement hybrid micro/nanofluidic separation strategies to size-select them. Should the collaboration be successful, TPL, Inc. will, of course, have the option to employ suitably qualified students engaged in the project to transition technology into products and manufacturing. Especially for Mr. Tribby, a native New Mexican, the TRC support will financially help him to continue his graduate research and education.

The company that will commercialize the resulting technology, TPL, Inc. brings to the team an experienced management staff supporting a technical staff that includes Dr. Charles Lakeman an expert in materials integration. TPL, Inc. employs more than 100 staff members in its NM offices with experience in developing, manufacturing and successfully marketing advanced materials that employs technology similar to that which will be developed by activities under this proposal. Dr. Charles Lakeman has been instrumental in creating and leading TPL, Inc.'s micropower program and developing commercialization efforts for this new technology. He initiated TPL, Inc.'s micropower program in January 2002, building on technology developed under funding from the Air Force Research Laboratory, Kirtland AFB, NM. In June 2004, Dr. Lakeman was appointed Program Manager of the newly formed μ-power Technologies Department. With a total of more than $5M in government contracts, the μ-Power Department currently has an annual budget of ~$1.3M, and a staff of seven. Dr. Lakeman holds three patents including two on microbatteries and microsupercapacitors and the other on his work with Texas Instruments.

The collaborative efforts will be broken down into sub teams to ensure progress is made as follows (i) Nanomaterials Synthesis (NSy), (ii) NanoSeparation (NSp), and (iii) Fabrication and Manufacturing (F/M). The NSy team will lead by Dr. Boyle and consist of SNL employees (Dr. Lambert, Mr. Pratt, Mr. Russell) who will synthesis the RuO_x nanomaterials, functionalize them and intercalate them into the carbon supports. The NSp team will involve the UNM members wherein, Tribby will assist in the development and surface interactions noted above and work with Prof. Han to ensure monodispersed materials as separated by size are available. The F/M team will be lead by Lakeman to build and test the supercapacitor from the materials supplied by the NSy and NSp Team. See Section 9.Volume I for more details and below for a diagram of the technical teams.

Member - Team	Expertise	Role in the Team	Contribution
SNL – NSy			Task 1 – 5
Tim Boyle	Novel chemistries and nanomaterial processes	SNL Principal Investigator	Task 1 – 5
Tim Lambert	Functionalization of nanomaterials	Co-investigator	Task 4 – 5
Harry Pratt Troy Russell	Synthesis	Undergraduate research assistants	Task 1 – 3
UNM - NSp			
Prof. Han	Separation	UNM Principal Investigator	Task 6
Louis Tribby	Synthesis/Separation	Graduate Research assistant	Task 2,4, and 5-6
TPL – F/M			
Charles Lakeman	Guide overall TPL team process	TPL, Inc. Principal Investigator	Task 7-8

As mentioned**, the goal of this proposal will be to provide advanced composite materials with improved performance for supercapacitors that will increase the economic and competitive advantage for this NM-based company.** The members of this team represent a well integrated complementary set of talents. Han group members have regularly been involved in the synthesis aspects of nanomaterials in the Boyle group which lends both groups insights to the other issues and abilities to circumvent problems. This cohesive interaction will allow us to attack the TPL, Inc. supercapcitor issue with a momentum other groups will not possess. Further, the work required by TPL, Inc. easily fits within existing programs in place at both institutions as evidenced by the cost-sharing listing (13. Matching Funds - Volume I) The close involvement of a potential manufacturer and end-user of the advanced materials that will be produced in the proposed effort will ensure that research efforts are directed towards a commercially useful product. This focus will facilitate the transfer of the technology from the lab into a product that enhances the Company's competitive edge, and delivers economic benefits in the form of new businesses and new jobs to the state of New Mexico.

As can be observed from their biographies (Appendix A Volume I), this team is technically proficient to address the issues that arise. However, there are several stages in bringing a new materials technology to commercialization which include: development of materials and processes, engineering development of the product, prototype manufacturing and mass manufacturing. The proposed effort will provide funding for the first stage, development of materials and processes. Data generated in this and any follow-on efforts will be used in SBIR, STTR and other proposals to further the development effort. Engineering development is the maturing of the assembly processes for a particular application so that the devices can be reproducibly manufactured with performance within acceptable tolerances. Follow-on support may be sought from government agencies or private industry end users, to conduct research for these later stages. A similar situation is expected for the product engineering, the results of which will be subjected to alpha testing and beta testing (customers). Prototype and full-scale production may ultimately be undertaken by TPL, Inc. on the basis of signed purchasing contracts, which would provide the collateral for the equipment financing. Depending on how quickly these markets come to fruition, there may be two options to mature and commercialize the technology. If the demand for power systems grows slowly, the maturation of this technology may be financed using continued government contracts and retained earnings. Development of products to meet an opportunity that would require a rapid maturation and increase in manufacturing capability may outpace TPL, Inc.'s ability either to secure government financing (science-for-hire) or to finance the development internally, and other options would be considered including equity financing, strategic partnership or licensing the technology to an established manufacturer.

The synergy of the expert NMTRC member teams with that of a New Mexico based company assembled is expected to maximize the potential for successful commercialization of the resultant improved microsupercapacitor. This will result in expanding the economic impact of this locally based company by increasing its existing market share, providing new markets, increased revenues, increased potential for additional investor funding, increased staffing, and potentially expanded facilities which will result have a large economic impact for New Mexico. In addition, the process will create a technical team and a core competency in nanoscience that will attract other researchers and additional funding to this area of research in the future. We fully expect that a successful outcome of this collaboration will increase our chances for securing other federal research opportunities, while promoting the graduate education of native New Mexicans. The graduate education is one of the vital elements in producing an intellectual pool of technically qualified future workers, who will contribute to the New Mexico economy.

11. Technical Feasibility

A. Personnel. The three teams on this proposal (Sandia, UNM, TPL, Inc) bring critical technical expertise that will ensure the successful development of the microsupercapacitor as well as subsequent commercialization of the product that will enhance the economy of New Mexico through the production of new jobs and businesses. Appendix A lists short biographical sketches for the critical members of this proposal. This proposal will further solidify an informal collaboration that already exists between these three groups (see Sect 10 for more details and Appendix A for biographies of the team members). The Sandia led team will focus on the chemistry aspects of the project, led by Dr. Timothy J. Boyle and Dr. Timothy N. Lambert, who have extensive background in the development of novel precursors, nanomaterial synthesis, and functionalization. Prof. Sang Han has worked the past three years in collaboration with the Sandia group and will assist the chemical development through shared graduate students in an effort to develop separation methods to ensure monodisperse nanoparticles that will assist in the development of the microsupercapacitor. Dr. Charles Lakeman will lead the critical testing of the final materials developed so that figure of merits can be determined to evaluate the newly formed capacitors. Combined, this formidable team presents the necessary expertise to successfully develop the fundamental aspects of the microsupercapacitor. The following describes the background of the capacitor concept, the synthesis of nanoparticles, the subsequent functionalization, the separation of the polydispersed nanoparticles and ultimately the testing of these devices. These devices and the subsequent information learned will ensure TPL, Inc. will be a leader in this highly lucrative niche in the portable power supply market.

B. Background on Supercapacitors. Energy storage devices may be broadly characterized by their energy density (energy stored per unit volume or mass) and by their power (how fast that energy can be delivered from the device). At one end of the scale, conventional capacitors have enormous power but store only tiny amounts of energy. At the other end, batteries can store lots of energy but take a long time to be charged up or discharge. That is they have low power. Relative to these established technologies, supercapacitors (Figure 1) offer a unique combination of high power and high energy performance parameters with commercial relevance. Batteries are 'charged' when they undergo an internal chemical reaction under a potential applied to the terminals. They deliver the absorbed energy, or 'discharge', when they reverse the chemical reaction. In contrast, when a supercapacitor is charged there is no chemical reaction. The energy is stored as a charge or

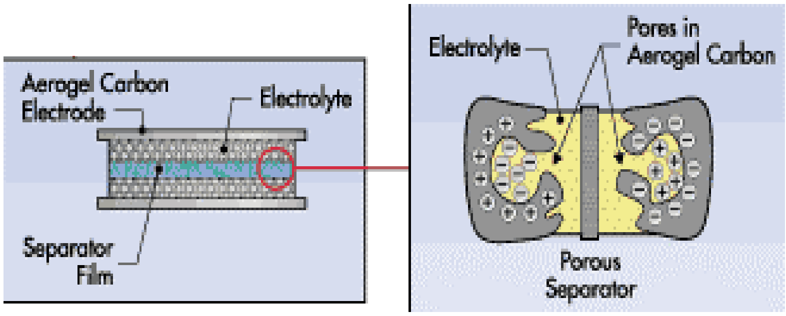

Figure 1. Schematic of the double layer of charge that accumulates on the surface of a supercapacitor.

concentration of electrons on the surface of a material. This difference in principle of operation is the key to the difference in behavior and contrasting benefits of the two broad types of energy storage device.

For many years batteries have been the preferred storage device for most applications because of their superior capability to store energy (i.e. high energy density). The amount of energy, measured in Joules, watt hours or amp hours, that can be stored has been sufficiently high for useful batteries to have been made and sold for all of this century. Where the application has demanded high power, the battery has been over engineered and the lifetime of the battery compromised. New battery technology such as lithium ion has been developed to increase power and energy storage. Fundamentally, however, they are energy storage devices. As such batteries will always be a poor solution where high power is required.

Like batteries, supercapacitors are electrochemical devices; however, rather than generating a voltage from a chemical reaction, supercapacitors store energy electrostatically by polarizing an electrolytic solution [1]. When a potential is applied across the capacitor, the ions in the electrolyte solution are attracted to the oppositely charged electrode. Opposite charges (electrolyte ions and solid state charge carriers) are separated across the electrode-electrolyte interface. Energy is stored across this interface that is defined by the "electrochemical double layer" [2] (Figure 1). The short charge separation, d, and high surface areas, A, of the activated carbons that are used as electrodes in these devices provide very high capacitance ($C=\varepsilon_0 \varepsilon_r A/d$, typically on the order of hundreds of milliFarads, mF) and the stored energy values ($E=½CV^2$, on the order of 1 – 10s of Joules, J). The type of electrolyte determines the working voltage of a supercapacitor. Organic electrolyte systems, like tetraethyl-ammonium tetrafluoroborate in propylene carbonate (TEATFB in PC), can be charged to 2.5-3.0V. Aqueous based electrolyte systems, such as potassium hydroxide and sulfuric acid, can only be charged to 1.0V due to electrolytic decomposition of water at 1.23V. The type of electrolyte also affects the equivalent series resistance (ESR) or internal resistance of supercapacitors. Although supercapacitors with organic electrolytes operate at higher voltages, thus storing more energy ($E=½CV^2$), the ions are larger and less mobile, contributing to a higher ESR and less efficient energy delivery. Capacitors using smaller aqueous ions generally display lower ESR values, and lower concomitant IR energy losses.

Faradaic processes due to redox reactions of oxides, like RuO_x, at or near the electrode surface give rise to so-called "pseudocapacitance" that involves interfacial reaction and mass transfer of ionic charge across the double layer [3]. Pure RuO_x is a mixed electron-proton conductor with a high specific capacitance. RuO_xH_y surface sites are reversibly oxidized and reduced with a simultaneous exchange of protons with the contacting solution producing significant pseudocapacitance. The double layer mechanism of energy storage is strictly a surface phenomenon, requiring high active surface areas to deliver to high specific capacitance values [4]. In contrast, with Faradaic mechanisms (from reduction-oxidation reactions) of energy storage bulk reactions are also possible and can contribute to increased energy storage

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[1] www.maxwell.com/ultracapacitors

[2] Carlen, M. and Kotz, R. "Principles and Applications of Electrochemical Capacitors" *Electrochimica Acta*, **45**(2000) 2483-2498.

[3] Conway, B. E., Electrochemical Supercapacitors, Kluwer Academic/Plenum Publishers, 1999

[4] Lin, C., Ritter, J. A., and Popov, B. N. "Development of Carbon-Metal Oxide Supercapacitors from Sol-Gel Derived Carbon-Ruthenium Xerogels" *Journal of Electrochemical Society* **146** (9) 1999, 3155-3160.

[5]; however the slow kinetics of bulk reactions combined with the high cost of RuO_x make a pure RuO_x microsupercapacitor unsuitable for commercial applications [6]. A device that exploits both double layer capacitance and Faradaic so-called "pseudocapacitance," combines benefits of both approaches, namely high energy density while maintaining high power capabilities.

Studies have shown that electrode materials possessing both double layer and redox processes can enhance the energy density of a device [4]. By creating a nano-composite electrode using a redox-reactive material, like RuO_x, within a high surface area carbon, the resulting small particle size of the RuO_x would increase the redox active surface area of the material giving rise to higher-power devices. By itself, RuO_x has been shown experimentally to have a specific capacitance of 760 F/g [4]. Although activated carbons having high surface area and porous structures yield electrodes with high specific energy and power densities, their specific capacitance is at most 40 F/g. By merging supercapacitor technology with the benefits of nano RuO_x, we will create a low cost, high energy density, high power density, highly specific capacitance device.

Asymmetric supercapacitors have distinct advantages over traditional supercapacitors. Traditional supercapacitors are symmetric in the fact that they have two carbon electrodes that store a double layer of charge. They have a sloping voltage curve and high self-discharge. Asymmetric supercapacitors have one carbon electrode, and one "battery like" electrode that utilizes Faradaic reactions (pseudocapacitance) to provide a flatter voltage curve, higher average energy density, higher average voltage, and low self-discharge. Unlike traditional supercapacitors that store 0.1 electrons of charge per carbon atom, asymmetric supercapacitors can store 1 or 2 electrons, translating into a capacitance that is 10 times greater than traditional supercapacitors. Asymmetric supercapacitors utilize an aqueous electrolyte making them non-flammable, non-hazardous materials. The aqueous electrolyte also allows the supercapacitors perform well at low temperatures.

Like batteries, asymmetric supercapacitors have a low self discharge rate, but unlike batteries they have a long service life, useful for more than 10^5 cycles. This long cycle life eliminates the need to replace worn out batteries making them maintenance free. Supercapacitors also have a higher power density than batteries, requiring a smaller footprint for a given power need.

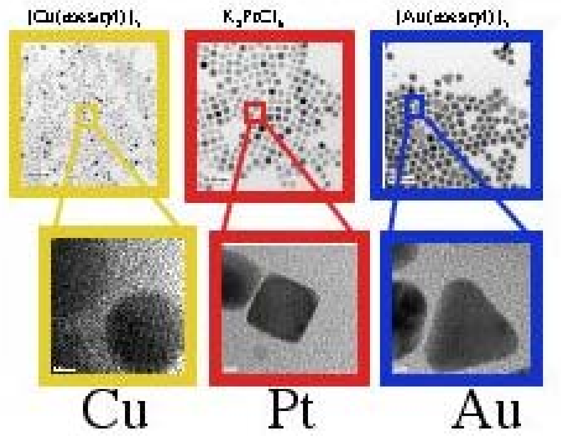

Figure 2. Examples of nanometal particles with varied morphology and composition.

C. Nanoparticles synthesis. The chemistry team is comprised of experienced materials scientists and chemists who have developed many unique and patented routes to complex ceramic materials for solution gelation (sol-gel), metal-organic chemical vapor deposition

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[5] Zheng, J. P., Cygan, P. J., and Jow, T. R. "The Aerocapacitor: An Electrochemical Double-Layer Energy Storage Device" *Journal of Electrochemical Society* **140** (9) 1993, 446-451.

[6] Lin, C., Popov, B. N., and Ploehn, H. J. "Modeling the Effects of Electrode Composition and Pore Structure on the Performance of Electrochemical Capacitors" *Journal of Electrochemical Society* **149** (2) 2002, A167-A175.

(MOCVD), and nanoparticle production. The materials chemistry team members in this application have extensive knowledge in the synthesis and processing of a wide range of tailor-made materials and their subsequent functionalization. Figure 2 shows some of the diversity of unique shapes available for metal nanoparticles isolated in our laboratory from traditional and non-traditional precursors. The basic research efforts of this team have focused on exploring the nature of the precursors' structural and ligand constituency that affect the final morphology of nanoparticles. The chemistry team currently have more than 800 compounds in-house designed for sol-gel and MOCVD processes with 4 to 20 new compounds synthesized and characterized weekly. From this library of compounds, several have been found to be ideal for nanoparticle synthesis with such desired properties as low decomposition temperature, clean (low carbon) conversion pathways, and low crystallization temperatures.

An improved understanding of how to induce some control over the properties of nanoceramic materials has been facilitated by the extensive library of novel precursors and alternative processing routes of complex nanoparticles available at SNL. Synthetic schemes typically involve the dissolution of the desired precursor into a non-coordinating solvent. We favor alkyl (i.e., mesityl), amides (i.e., bis(trimethyl)silylamide), and alcohols (i.e.,neo-pentanol and phenols) as precursors. Each of these compounds has properties that make them attractive for nanoparticle syntheses such as low decomposition temperatures, high solubility, and clean decomposition pathways. Once an appropriate precursor is selected, it is injected into a relatively hot solution of solvent, reductant, and coordinating surfactant (this can be a complex mixture or simplistic one). An example of a standard "simple" synthetic setup is shown in Figure 3. The selection of each component for nanoproduction is critical to the isolation and quality of the nanoparticles as well as to the next step of solubilization and biofunctionalization of the nanoparticles. All of these manipulations are air sensitive and require rigorous inert atmosphere synthetic handling for which we are fully equipped (we have 8 argon glove boxes and 8 Schlenk lines in full operation located in three laboratories, ~2000 sf). It is of note that these activities have led to numerous collaborations with other researchers who have very different application for these materials than their original intended use. For these collaborations with other research institutes, we typically supply expertise, equipment for complicated syntheses, and/or the actual compounds to our collaborators for their investigations. Two independent collaborative efforts have been with the members of the biology team: Profs. San Han (UNM-CHTM) and Dr. Charles Lakeman (TPL, Inc.). The development of the Ru precursors and subsequent RuO_x nanoparticles will combine these efforts and allow for the development of the critical microsupercapacitor needed by TPL, Inc.

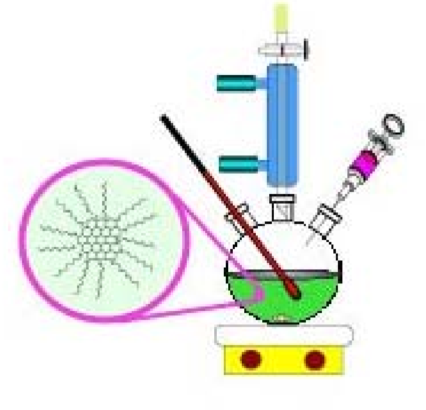

Figure 3. General equipment setup for nanoparticle synthesis (a) three neck round bottom flask, (b) cooling column, (c) nitrogen adaptor, (d) thermometer, and (e) syringe.

Since the synthesis of complex ceramic nanoparticles is in its infancy, the majority of synthetic schemes to the complex ceramics of interest are not known and the numerous synthetic variables must be adjusted to generate high quality materials. A search of the literature reveals there are RuM nanoparticles where M is defined as another metal but no simple routes to RuO_x

are available. This will not prove to be a problem since our synthetic team has a large knowledge base concerning nanoparticle synthesis, substantial synthetic skills, and developed pathways on which to build from in order to synthesize the necessary nanoprobes. For example, we have reported several novel methods for the synthesis of coinage metals, and semi-conductor (CdE) nanoparticles. In addition, the chemistry team has already investigated the production of nanoceramics exploring the variables that control size, morphology, and composition For the first time, we established a direct link between the precursor's molecular structure and the final nanomaterial morphologies obtained for ZnO (Figure 4). Since the nanoregime is relatively new for complex ceramics, full details are not known for the syntheses of the proposed nanoprobes, but numerous investigations from our laboratory and other researchers, suggest that RuO_x based materials can be synthesized.

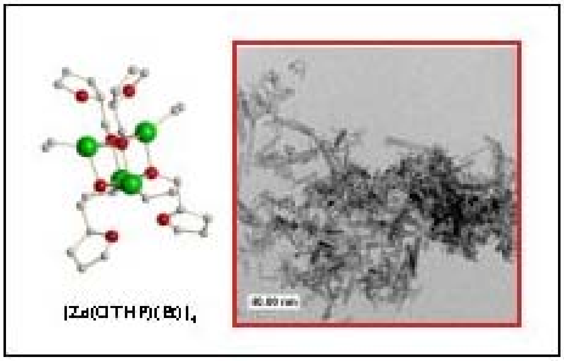

Figure 4. Novel "Zn(OR)(R)(solv)" precursor and the TEM image of the subsequent ZnO nanorods generated using our unique processing route.

In summary, the previous studies the chemistry team has undertaken concerning the synthesis of metals, semi-conductors, and ceramic nanomaterials[4] gives us a substantial knowledge base to build from in order to synthesize these new nanoceramics. The materials chemistry team has: (i) the in depth knowledge of synthesis and subsequent modification to a library of materials precursors, (ii) the understanding of the influence that precursors have on final nanomaterials' morphology and properties, (iii) developed novel processing routes to form tailor-made nanomaterials, (iv) the ability to manipulate all of these conditions to optimize final material properties, and (v) owns or has access to the equipment necessary to fully characterize the properties of the newly developed nanoprobes. Combined, these skill sets will allow the chemistry materials team to address any challenges that occur during this study.

D. Nanoparticle Modification. Dr. Timothy N. Lambert brings expertise in the area of organic synthesis and bio-organic-chemistry to the team effort. The chemistry of metal oxide ceramics lends itself to a variety of functional groups where the terminal moiety can induce different charges. It is anticipated that the RuO_x nanoparticles will have an oxide coating which will either be initially covered with an oxophosphate, phosphate, or amine derivative. These can easily be replaced with bifunctional carboxylic (R-COO-H) acids, phosphates, catechols and other surfactants. That is, the surfactant will have an acetate group that will selectively bind to the surface of the nanoparticle. An undetermined hydrocarbon chain will then be used to separate the carboxylate from the second functional group that may be an amine, thiol, alkyl or other functional group. These terminal functional groups will be used to control the partial charge (δ). This will be used for two aspects of this project, size separation (section E) or for binding to specifically charged walls of the microsupercapacitor. While a number of the surfactants are commercially available, numerous of the specialty species will require synthesis from established or slightly modified protocols available in the literature. Further, interactions with the carbon substrates are going to be another requirement for production of the capacitor. Literature methods for functionalization of carbon surfaces are available in the open literature.

E. Separation. We will separate RuO_x nanoparticles by their size through nanometer scale channels. The nanoscale channels give rise to unique physics that we can exploit to achieve separation of nanoscale objects [US Utility Patent Application No. 11/184,540 filed on July 19, 2005]. In order to monitor effective separation of nanoparticles in nanochannels, we will utilize scanning laser confocal fluorescence microscopy (SL-CFM) and nanomachined waveguide assisted Fourier transform infrared spectroscopy (NWA-FTIRS). When the particles are functionalized with fluorescent labels, the SL-CFM technique helps us visualize the particle flow and measure the advancing speed of nanoparticles in the channels. Figure 5(a) shows our experimental setup, where 100-nm-wide, 1-mm-deep nanochannels are embedded in a multiple internal reflection IR waveguide. The number of channels is on the order of 10^6, and the channel width can be reduced below 50 nm. Due to optical transparency from the top and IR-transparency through the substrate, both SL-CFM and NWA-FTIRS can be applied to interrogate the electrokinetic transport as well as electrostatic response of functionalized RuO_x nanoparticles in nanochannels. We are currently able to monitor both nanoparticle transport as well as characteristic vibrational modes of surface functional groups on nanoparticles. Figure 5(b) simply demonstrates the flow control on charged species (Rhodamine B) in nanochannels, providing a preview of what can be done with RuO_x nanoparticles that possess a net surface charge. We will focus on the pronounced effect of surface charge on nanoparticles as well as z-potential change on separation. Note that the magnitude and sign of z-potential, which is an electric potential near the channel walls, controls the speed and direction of nanoparticle flow.

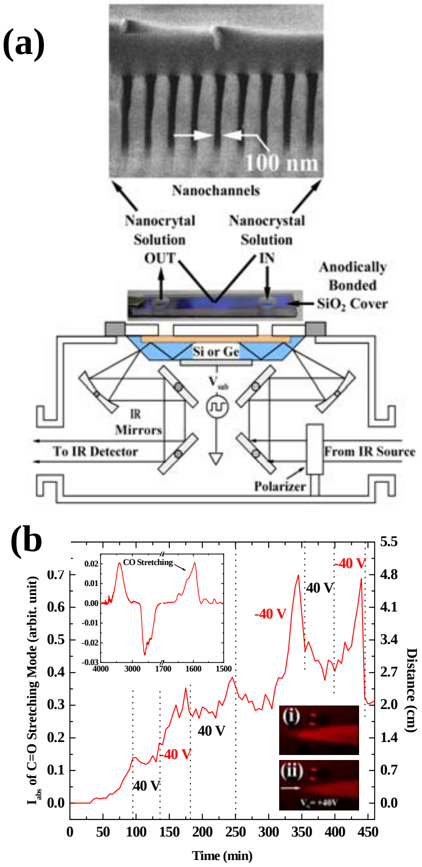

Figure 5. Nanofluidic Information (a) Experimental setup and (b) flow control on charged species.

F. Construction and testing of the microsupercapacitor. TPL, Inc. has extensive experience in the testing of electronic materials. Once the appropriate materials have been generated, the interaction between nanomaterials and carbon support demonstrated, it will be necessary to assemble a microsupercapacitor. The device will consist of four layers: current collector, carbon anode, nano-composite cathode, and separator. The top layer will be a metallic current collector with connections to "I/O" tabs on the top and bottom of the container. The each electrode is vacuum infiltrated with electrolyte. The separator will be a member of the Celgard family of poly(propylene) (PP) and poly(ethylene) (PE) separator materials or W.L. Gores's poly(tetrafluoroethylene) separator. The electrodes will be impregnated with electrolyte solution under vacuum to ensure all porosity is filled. An aqueous or organic electrolyte will be selected to demonstrate feasibility in this Phase I effort depending on the wettability of the electrode. Aqueous electrolytes include lithium perchlorate, potassium hydroxide and sulfuric acid [7].

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[7] US Patent 5,426,561 Yen *et al.*, 1995.

Organic electrolytes include tetra-alkyl-ammonium tetrafluoroborate salts dissolved in propylene carbonate or acetonitrile. All characterization will be carried out using the Arbin BT2000 automated testing system. This 24-channel system can automatically charge devices, measure standard parameters such as capacitance, ESR, and open circuit voltage, and discharge under prescribed conditions, as well as enable automated charge-discharge cycling to measure capacitance stability. Charging and discharging can be carried out at constant current, constant voltage, constant C-rate, constant power, and constant load as well as staircase functions of the current and voltage. As constructed, microsupercapacitors are in the discharged state; therefore, the first requirement will be to charge them. During charging, positive and negative ionic charges within the electrolyte accumulate at the surface of opposite electrodes compensating for the electronic charge at the electrode surface. A CCCV (Constant Current Constant Voltage) profile will be used to charge the microsupercapacitors. First, a constant CC charge of one mA will be applied to the microsupercapacitor. Once the microsupercapacitor has reached its working voltage (1.0 V for aqueous or 2.5 V for organic), a CV charge is performed until the current in the microsupercapacitor drops to nine mA. After charging, the voltage will be measured under an open circuit configuration as well as under different loads. These measurements will allow the ESR and capacitance to be evaluated and compared with values for commercial cells. The ESR value can be used as a preliminary indication of whether the cell design allows the electrochemical processes to proceed efficiently. Factors that would impede these reactions may include low electrolyte conductivity, low permeability of the separator, or high resistance of the carbon electrode. The goal is to obtain values of ESR and capacitance similar to that of commercial cells.

The capacitance is calculated using an embedded routine in the Arbin data acquisition system. During a constant current, I, discharge of the microsupercapacitor, the Arbin measures the change in voltage, DV, specified by the user and multiplies it by the time, Dt, over which the voltage drop takes place to determine the capacitance, C, where

$$C = \frac{I\Delta t}{\Delta V}.$$

Discharge characteristics of as-constructed cells will also be evaluated, as well as self-discharge rate and power density. The effects of varying the discharge rate will be measured to determine the power and rated current. The rated current is the value of the CC discharge that dissipates the working voltage to half its original value in five seconds. Discharge currents from one mA to one A are typically used for COTS microsupercapacitors; for the smaller cells proposed here, currents from one to sixty mA will be used. Lower currents may be required based upon the cell capacitance values achieved. A first order estimation of the cell capacitance will be obtained from the Phase I data. The rated current will be obtained for sample cells by iteratively increasing the current until half of the working voltage is dissipated in five seconds.

Since power is directly proportional to current, (P=VI), the power measured at the rated current will be the standard we use for defining the power of a microsupercapacitor. An embedded routine in the Arbin test system calculates the power dissipated by the device under test (DUT). The system calculates the energy dissipated on discharging a microsupercapacitor with a constant user-defined current between user-set voltage values (V_{low}, V_{high}). The discharge energy, ΔE is:

$$\Delta E = \frac{1}{2} C (V_{high}^2 - V_{low}^2)$$

The power is calculated simply by dividing the discharge energy, ΔE, by the discharge time Δt:

$$P = \frac{\Delta E}{\Delta t}$$

The ESR will be calculated from an embedded routine in the Arbin test system. The routine will apply a nine mA constant current discharge for one ms. The pulse will be repeated ten times and ΔV/I will be calculated for each pulse. The data will be averaged and the resulting ESR will be reported in an Excel file. Self-discharge of a microsupercapacitor gradually reduces the energy stored in the device because there is a decline in open circuit voltage after charging. There are at least four different contributions to the self discharge, or leakage resistance, [8] originating from the: (a) Electrolyte including separator, (b) Current collector, (c) Porous electrode layer including contact to the current collector, and (d) other contact resistances. In order to maintain the full charge, a float current of small magnitude can be applied to balance the self-discharge rate. It is equal to the initial self discharge rate when the charging voltage is removed. This current is called the leakage current. The leakage current will be measured as the voltage drop during a self-discharge of the fully charged microsupercapacitor. The capacitance, C, of the cell has already been determined, therefore the leakage current:

$$I_{leak} = \frac{C \Delta V}{\Delta t}$$

where ΔV is the change in voltage from the working voltage to the end of the instantaneous drop, and Δt is the time over which the voltage drop takes place.

Successful completion of this task will yield data that will be used to determine the performance of the microsupercapacitor. The specific capacitance, ESR, power density and time to self-discharge will be compared with COTS devices and previous iterations of supercapacitors. Differences between the scaled performance of macro-scale supercapacitors and our microsupercapacitors will point out areas that need improvement. Areas that may need to be redesigned, based on experimental data might include volume fraction, composition, and particle size and size distribution of both electrodes as well as the concentration of the electrolyte.

G. Characterization. The materials generated will be completely characterized with a variety of analytical tools available at SNL and UNM. These will include multi-nuclear NMR spectroscopy, Fourier transformed infrared spectroscopy, elemental analysis and/or single crystal X-ray diffraction to understand the structural aspects of the precursors. Further, the subsequent nanomaterials will be imaged using electron microscopy techniques, zeta potential measurements, ultra-violet spectroscopic measurement and photoluminescence measurements available at both TRC institutions. The testing of the device will be performed at TPL, Inc.

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[8]. Kotz, R. and Carlen, M. “Principles and applications of electrochemical capacitors” *Electrochimica Acta* **45** 2000, 2483-2498.

H. Milestones. This project will be broken down into several tasks (see: Table 9,Volume II;12. Management Microsupercapacitor Gantt Chart, Volume I) in an effort to generate the critical component of the supercapcitor. The various tasks are described as: Task 1. Ru Precursor synthesis; Task 2. RuO_x Nanoparticle synthesis; Task 3 Precursor, manoparticle, and interaction characterization; Task 4. Functionalization of RuO_x; Task 5. Size selection of RuO_x; Task 6. Supercapacitor Fabrication and Assembly; Task 7. Microsupercapacitor Testing. Each task is briefly described below. *Task 1. Ru Precursor synthesis (0-12).* Both commercially available precursors and novel compounds developed in the various laboratories will be investigated for the formation of novel RuO_x. *Task 2.* RuO_x *Nanoparticle synthesis (1-12).* Using both literature and unique routes (solution and solvothermal routes) established in our laboratory crystalline nanoparticles of RuO_x will be synthesized. *Task 3. Precursor, manoparticle, and interaction characterization (0 – 12 month).* Single crystal X-ray diffraction, powder XRD, TEM, SEM, FT-IR, UV-vis, and other analytical means will be used to characterize the final materials. *Task 4. Functionalization of* RuO_x (3-12). Using commercially available and in house synthesized ligands when neccessary, we will functionalize the RuO_x nanocrystals with ligands (i.e. carboxylate, phosphate, catechol, etc.) that bind to the nanocrystal surface and display varying charge on the outer surface. *Task 5 Combining* RuO_x *and C support (4 -12).* Combining the two material such that specific charged species go towards specific locations on the support. *Task 6 Size selection of* RuO_x (4 – 12). RuO_x nanoparticles will be separated by their size through nanometer scale channels enhanced by scanning laser confocal fluorescence microscopy and nanomachined waveguide assisted Fourier transform infrared spectroscopy. *Task 7: Microsupercapcitor Fabrication and Assembly (6 -12).* The two halves of the cell will be constructed separately. Each cell half will be infiltrated with electrolyte. A separator will be placed on top of one half of the microsupercapacitor. Both halves of the capacitor will be aligned and sealed. *Task 8: Microsupercapacitor Testing (9-12).* Characterization of the electrical performance of the microsupercapacitors using measurements of capacitance, ESR, power, and leakage current measured under self-discharge.

I. IP Agreements . A cooperative research and development agreement (CRADA) will be put into place which will specifically outline the intellectual property agreements between the institutions prior to initiating the project. These CRADA agreements detail the protection of the intellectual property (IP) as the IP created by the individual institutions is maintained with the institution; whereas, the joint IP is shared by all involved institutions.

J. Rationale of work process. The concept of improving the storage capability of carbon supports through the introduction of ceramic materials is well documented in the literature. The work will follow a logical approach to the formation of the individual parts and subsequent combination to form the necessary supercompacitor device. This will build on established novel methods already available in laboratories for alternative materials but will have applicability to this system. Firstly, the appropriate precursors will be located based on literature and our own knowledge of nanoparticle formation and nanoparticles of high quality RuO_x generated. While underway, the leveraged programs will be on-going that will allow for functionalization of other nanoparticles coupled with size selection based on nanofluidics. Further, testing on the RuO_x materials can be started on the bulk nanomaterial or without ideal nanoparticle RuO_x interactions in place. This will ensure that no member of the team is idol and IP is created for each aspect of the program. Once established, the precursor, RuO_x nanoparticles, surface modification, separation, and interaction will be continually refined and improved, so that when the testing results are obtained, additional improvements can be readily merited out.

K. Challenges. With any endeavor, there are a number of challenges to reaching the technical goal. These are described below, broken down by task: *Task 1.* Ru precursor synthesis: Medium Risk - Several standard precursors are available commercially to intiate the process but novel species will need to be developed to obtain the quality needed for project. Late transition metal are not ameanable to break down that early transition metal species are, therefore, identifying the appropriate ligand set that allows for subsequent decompostion is critical. Metal alkoxides (a standard ceramic precursor) are not available for these species so metal mesityl's (which we have demonstrated are acceptable precursors), amides and even phosphates will be studied. There are no insurmountable technical challenges envisioned here since new precursors can always be synthesized by the NSy Team. *Task 2. RuO_x Nanoparticle synthesis:* Low Risk - Routes are established and minimal risk once the proper precursor is slected. Again, the NSy Team will ensure nanoparticles are formed. It is helpful that specific monodisperse sizes and shapes are not requried for this task. *Task 3 Precursor, manoparticle, and interaction characterization.* No risk – established protocols. *Task 4. Functionalization of RuO_x:* Minimal Risk -f unctionalizing with δ- or δ+ ligands since other funds have established protocols. Again, varying surfactants based on chemical synthesis by the NSy team will ensure this work proceed forward. *Task 5. Combining RuO_x and C support*: High risk but high payoff. The demonstrated control will make for unprecedented charge separation of the microsupercapacitor and other applications. The NSy and NSp team are critical to this aspect that will truly revolutionize the microsupercapacitor. *Task 6. Size selection of RuO_x*: High risk but high payoff - This method is not fully established but with the ability to isoalted controlled nanoparticles thorugh charge may be risky, when successful, this method will apply to numerous other efforts. The NSp team has initiated studies in other systems that will assist this. Again, true monodispersity will help improve the microsupercapcitor but is not critical. *Task 7. Microsupercapcitor Fabrication and Assembly*: Medium risk. – the quality of the materials will establish the assembly process. *Task 8. Microsupercapacitor Testing.* No risk- established protocols.

L. Facilities. Each group has a dedicated laboratory to achieve the above listed tasks. Dr. Boyle and Dr. Han's groups work collaborative in each others laboratory. Dr. Lakeman routinely visits Dr. Boyle's laboratory and has arranged visits for testing visits.

(i) *SNL Facilities.* Dr. Boyle's group is located at the Advanced Materials Laboratory (AML) of SNL. The AML consists of a suite of laboratories and offices occupying approximately 8000 sf in a satellite building located approximately one mile from UNM, 1 mile from the main SNL facilities, and 5 miles from TPL, Inc. The Boyle (SNL) group's three laboratories occupy ~2,000 sf of this building. Each Chemistry team member has a dedicated networked workstation with one or more processors. They have access to numerous networked computers and computer clusters at SNL. Dr. Boyle has a dedicated office of approximately 240 sf. Dr. Lambert also has an office of ~120 sf. The undergraduates have desks located within the laboratory and routine access to their own computers. The AML group makes extensive use of state-of-the-art analytical electron microscopy equipment in the SNL Materials Characterization Department. SNL has an extensive collection of on-line library journals that span numerous research areas of study that is accessible 24/7. Also numerous collaborative interactions with the chemistry, engineering departments give us routine access to the instrumentation present in these divisions. The AML is equipped with all the instrumentation needed to generate and characterize nanoscale materials. Eight gloveboxes for the inert atmospheric synthesis of the necessary precursors along with 10 Schlenk lines are available. Characterization equipment includes a UV-vis spectrometer, a Fluoroscope, XRD powder diffractometer, TGA/DTA, SEM, FTIR spectrometer, CHN/S and O elemental analyzer, AFM, IEC Centra MP4R centrifuge with temperature control, an RE140 Rotary evaporator, and a hotplate with temperature control. The AML has routine access to a JEOL 2010 TEM with 200 kv accelerating voltage, equipped with a Gatan slow scan CCD camera, multinuclear high field NMR spectrometer. The laboratory also possesses in-house facilities for ICP and DCP that will be available on a part-time basis for characterization work if necessary.

(ii) UNM Facilities. Prof. Han has three dedicated laboratories (1500 nsf total) to conduct particle separation, materials characterization, and part of device fabrication. He also shares Keck Foundation Nanofluidics Laboratory, where a ZEISS LSM 510 META Laser Scanning Microscope is housed, and his research group has access to device fabrication facilities at the Center for High Technology Materials (CHTM) where Prof. Han is a member. The major equipment that Prof. Han either owns or has ready access to includes Nicolet 870 IR spectrometer, JEOL 2010 high resolution transmission electron microscope (HRTEM), JEOL 2010F FASTEM, Hitachi S-5200 Nano scanning electron microscope, and Kratos AXIS Ultra x-ray photoelectron spectrometer. The Center occupies a $ 14M, 60,000 sq. ft building provided by the State of New Mexico and University of New Mexico with complete cleanroom and laboratory facilities for advanced research in materials science and engineering.

(iii) TPL, Inc. Facilities. TPL, Inc. occupies 35,000 square feet of office and laboratory space that includes a wide variety of equipment for materials research and development. Electrochemical Characterization: Arbin BT2000 24-channel automated battery microsupercapacitor testing system with auxiliary temperature and voltage monitoring capabilities. Clean Room: 350sq. ft. clean room from class 10 to class 1000; Quintel 2100C contact mask aligner; Specialty Coating Systems 8” spin coater; Veeco FPP-100 four point probe resistivity meter; hot plates, developing and etch stations. Film Laboratory: Specialty Coating Systems 12" spin coater; high-precision dip coater with Compumotor/Daedal motion system in a controlled atmosphere enclosure; Ladd vacuum evaporator; and SPI-Module sputter coater with exchangeable targets. Analytical Facilities: Reichert Epi-Star optical microscope; Brooks digital viscometer; General Laboratory Facilities: Thermolyne 46100 High Temperature Furnace (1700EC); Fisher 999 computer-controlled water bath; various laboratory ovens and vacuum furnaces; balances; fume hoods; chillers; glove boxes; rotary evaporators; BR spinning band distillation system; diamond saw. The facilities and equipment used in this program comply with environmental laws and regulations of the U.S. government and those of the State of New Mexico and local governments for, but not limited to, the following groupings: airborne emissions, waterborne effluents, external radiation levels, outdoor noise, solid and bulk waste disposal practices, and handling and storage of toxic and hazardous materials**.**

M. Unique Capabilities. While the individual groups are recognized as leaders in their respective fields, combined they form a unique group that is sufficiently stronger than the individual components. This allows this team to address larger problems, like the development of the proposed microsupercapacitor.

The wide number and variations of precursors, processing methodologies, and functionalization accessible from the SNL partners allow for optimization that other research efforts cannot address. Further, several patented routes are available to convert these novel precursors into unique materials. Combined this gives the participant unique access to novel routes to these proposed materials.

Synergistically adding to the capabilities at SNL, the UNM group offers micro to nanoscale fabrication capabilities and engineering solutions to separate nanoparticles of desired size and surface functional groups. The nanofluidic separation strategies, in particular, have far-reaching implications for effective nanoparticle separation and detection beyond the scope of this project. Our engineering solutions will prove critical in supplying TPL, Inc. with desired nanoparticles.

TPL, Inc.'s specific experience in the design and fabrication of microsupercapacitors provides unique capabilities that will guide the proposed effort to deliver a useful, commercializable material. There are particular trade-offs in the design of microsupercapacitors for different applications, namely, equivalent series resistance (ESR), capacitance (or energy) density, power capabilities, and duty cycle. TPL, Inc.'s expertise and familiarity with the inter-relationships that exist will be essential for critically evaluating the performance of the materials for use in microsupercapacitors for wireless sensor power supplies.

12. Management

Dr. Lakeman will be the Project manager for the *Metal Oxide Coatings of Carbon Supports for Supercapacitor Applications* project since he will be deciding whether the technology can be successfully commercialized and his company will bear the financial repercussions of the final decisions. He will be advised along the way by a representative from each of the collaborating entities chosen along project team lines (see Section 8 Volume I. Collaborations): Dr. Boyle (NSy), Dr Han (NSp), and Dr. Lakeman (F/M). Subtasks will be assigned to Dr. Boyle concerning the technical lead and Dr. Lakeman concerning commercial aspects, based on their respective talents and expertise (Appendix A. Volume I). Dr. Han will contribute and evaluate both sections equally.

Over the past 13 years at Sandia, Dr. Boyle has lead several large programs that merit his management of the technical side of this project. In particular, he currently is managing a $1.2 M NIH funded program currently (1/4 years) along with a $1.2 M CRADA with Goodyear (1/2 years). Each of these programs is focused on the nanomaterials synthesis and will indirectly contribute to the intellectual property of this proposal (see 13. Matching Funds Volume I). Further, he manages a program with DOE ($312 K 2/3 years) that is used to match the funds for this program. It is focused on understanding and controlling the fundamental aspects of nanomaterials. Dr. Boyle is routinely invited to present his research at national meetings and publishes his work in peer reviewed journals testifying to his ability to manage research projects for successful conclusions that result in high quality products that stand up to rigorous pee review.

Dr. Lakeman has successfully led the growth of the micropower team over the past four years. To do so, he has combined technical development with development of the business opportunity for the technology. This work has been such a success that spin off companies, led by Dr. Lakeman are being pursued for the first time at TPL, Inc. Dr. Lakeman has achieved this success track record by effectively managing the links between technical innovation, successful manufacturing processes and commercialization activities. The work has been funded over this period with more than $5M in SBIR and STTR grants and contracts, both Phase I and Phase II efforts. Dr. Lakeman has served as PI on all but two of those contracts and, in his capacity as Department Manager, has been responsible for financial as well as overall technical operation of all programs. In the small business environment, a manager wears many hats, and Dr. Lakeman's responsibilities have included technical development, financial management, business development, and strategic planning. He is well qualified to lead and focus the commercialization part of this effort.

The other members of the team are experienced researchers and enthusiastically support the project. Dr. Han has experience in working on a number of teams including an NSF

Nanoscale Interdisciplinary Research Team as the lead PI, a UNM team investigating cancer cell signaling pathways with functionalized, fluorescent nanocrystals, and pre-existing collaboration with SNL to investigate selective growth of Ge nanostructures on Si. Prof. Han attracts technically superior graduate students because of his ability to obtain funding, provide the framework for meaningful technical challenges, effectively manage and assess the students work, and support finding practical applications for the resulting technology. The students identified to assist in the synthesis are undergraduate students from UNM working in Dr. Boyle's group (Harry Pratt III and Troy Russell). Dr. Han's group will contribute (Louis Tribby) talent to the team.

The three teams (NSy, NSp, and F/M) have monthly meetings scheduled where the progress will be evaluated by agreement of the three managers of the sub-team. Further, these work meetings will be used to incorporate any changes in direction or initial concept based on latest data. The AML is ideally suited to allow for these interactions. Any contentions that may arise will be decided by Dr. Lakeman, as he is the Project Manager. From these meetings, discussion of the route forward and the go/no-go decisions will be closely monitored. Further, weekly group meetings, which all technical personnel attend from the NSy and NSp are held and the week's technical data results discussed. This information will be sent to all team managers electronically so that an understanding of the progress will had by all. As mentioned, the majority of members have routine contact with Dr. Boyle and tracking of progress will be easily followed. The quality of the final materials will be determined by Dr. Lakeman, since the ultimate utility of these particles will be determined by the properties of the micro nanocapacitor. Ultimate decisions will be made by Dr. Lakeman based on the commercial development perspective. In summary, the project's progress will be monitored by weekly supporting Team reports, monthly Management Team reports, quarterly reports, microsupercapacitor Gantt chart, etc.

The one-year plan will be to generate RuO_x nanoparticles from a rationally generated precursor. These will then be functionalized and introduced to carbon surfaces. The plan shown below details the proposed schedule; however, success in the first year will warrant further research and development to transition the technology to a commercially producible product. The tasks undertaken will include the following: Task 1. Ru precursor synthesis; Task 2.RuO_x nanoparticle synthesis; Task 3 Precursor, manoparticle, and interaction characterization; Task 4. Functionalization of RuO_x; Task 5. Cobination of RuO_x and C support; Task 6. Size selection of RuO_x; Task 7. Microsupercapacitor Fabrication and Assembly; Task 8. Microsupercapacitor Testing. Each task is briefly described below.

Task 1. Ru Precursor synthesis (0-12). Using both commercially available precursors and novel compounds developed in the various laboratories will be investigated for the formation of novel RuO_x. Deliverable soluble precursor that decomposes at appropriate temperatures (200 -300 ^oC). The ability to use both existing and synthesis new precursors ensures this will not be a problem in terms of generating the RuO_x nanoparticles. Deliverable: Ru precursor.

Task 2. RuO_x Nanoparticle synthesis (1-12). Using both literature and unique routes (solution and solvothermal routes) established in our laboratory crystalline nanoparticles of RuO_x will be synthesized. Again, the flexibility due to the NSy teams chemistry will ensure this is not an issue. Further, the requirements for the microsupercapacitor are such that the more problematic issues raise for nanomaterials (i.e, morphological control, monodispersity) are not applicable to this route. Deliverable: nanometer sized RuO_x particles.

Task 3. Precursor, manoparticle, and interaction characterization (0 – 12 month). Single crystal X-ray diffraction, powder XRD, TEM, SEM, FT-IR, UV-vis, and other analytical means will be used to characterize the final materials. Deliverable: Data relating to material characteristics

Task 4. Functionalization of RuO_x (3-12). Molecules with a high affinity for the RuO_x surface will be used to coat the nanocrystals. These molecules will also be terminated with a functional group (acid, amine, alkyl ammonium, etc.) to render the particle charged and/or reactive. The NSy team chemistry variables again plays a major role in ensuring that this route is not going to be a problematic issue. Deliverable: functionalized nanoparticles with positive and negative surface coatings (δ+ and δ-).

Task 5. *Combination of* RuO_x *and C support (4 -12).* Investigating the potential for delivery of charged species to specific locations will be undertaken. This is not critical to the final device operation but will substantially improve the functionality of the device. The properties expected from this capability are highly desired but not necessary to move the process along. Deliverable: charge separated nanoparticles. Deliverable: properly aligned interaction of RuO_x, C-support, and charge distribution.

Task 6. Size selection of RuO_x (4 – 12). RuO_x nanoparticles will be separated by their size through nanometer scale channels enhanced by scanning laser confocal fluorescence microscopy and nanomachined waveguide assisted Fourier transform infrared spectroscopy. This is another desired but not critical step which will have major impact on several nanotechnology issues related and not related to the microsupercapacitor. Deliverable: size specific, monodispersed nanoparticles.

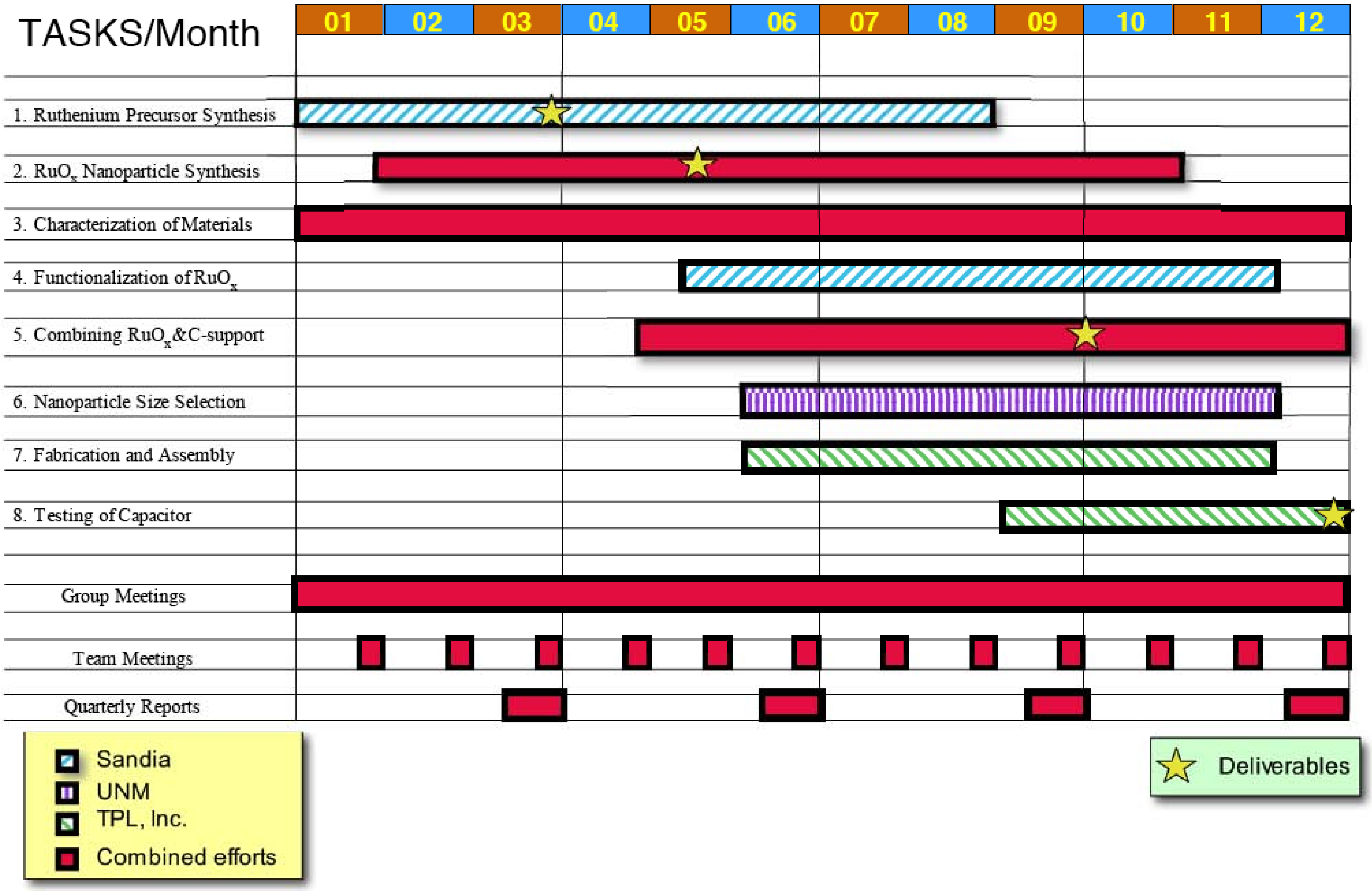
Task 7: Microsupercapcitor Fabrication and Assembly (6 -12). The two halves of the cell will be constructed separately. Each cell half will be infiltrated with electrolyte. A separator will be placed on top of one half of the microsupercapacitor. Both halves of the capacitor will be aligned and sealed. Deliverable: assembled microsupercapacitor

Task 8: Microsupercapacitor Testing (9-12). Characterization of the electrical performance of the microsupercapacitors using measurements of capacitance, ESR, power, and leakage current measured under self-discharge. Deliverable: test results of microsupercapacitor.

With any endeavor, there are a number of challenges to reaching the technical goal. These are described below, broken down by task: *Task 1. Ru Precursor synthesis*: Medium Risk - Several standard precursors are available commercially to intiate the process but novel species will need to be developed to obtain the quality need ed for project. Late transition metal transition metal are not ameanable to break down that early tansition metal species are, therefore, identifying the appropriate ligand set that allows for subsequent decompostion is critical. Metal alkoxides (a standard ceramic precursor) are not available for these species so metal mesityl's (which we have demonstrated are acceptable precursors), amides and even phosphates will be studied. *Task 2.* RuO_x *nanoparticle synthesis:* Low Risk - Routes are established and minimal risk once the proper precursor is slected. *Task .3 Precursor, manoparticle, and interaction characterization.* No risk – established protocols. *Task 4. Functionalization of* RuO_x*:* Minimal Risk -functionalizing with δ- or δ+ ligands since other funds have established protocols. *Task 5; Combination of* RuO_x *and C support.* High Risk - but high payoff – new means of directing nanoparticles will be a major breakthrough for both nanotechnology and device building. *Task 6. Size selection of* RuO_x*:* High risk - but high payoff - This method is not fully established but with the ability to isoalted controlled nanoparticles thorugh charge may be risky, when successful, this method will apply to numerous other efforts. *Task 7. Microsupercapcitor Fabrication and Assembly:* Medium risk. – the quality of the materials will establish the assembly process. *Task 8. Microsupercapacitor Testing.* No risk- established protocols.

The microsupercapacitor Gantt chart that graphically displays the duration of tasks, interactions between the institutions, and the timing of deliverables is displayed below. Included are the tasks associated with the management plan as they appear on the schedule and in the budget. The weekly meetings will focus on the technical aspects of the project while the monthly meetings will cover both technical and commercial issues. As can be seen this is a well-timed and integrated approach. There are no foreseeable roadblocks for all tasks and deliverables should be easily met on time. Parallel synthesis efforts will be underway so if technical problems do arise for a particular route, the other pathway will ensure forward progress is being made. The management meetings will ensure progress is maintained.

Microsupercapacitor Gantt Chart



Metal Oxide Coatings of Carbon Supports for Supercapacitor Applications
Timothy J. Boyle

TRC Grant Program

2006 BAA# TRC_100_06 - Volume I

13. Matching Funds

SNL.

SNL matching funds for Dr. Timothy J. Boyle and other SNL personnel will be associated with the Department of Energy's Office of Basic Energy Sciences entitled "Materials and Engineering Physics; subproject entitled "Fundamentals of Nanoparticle Formation" ($ 140 K; 2/3 years). The basis of this project is to understand how to control and manipulate the fundamental aspects of a variety of nanomaterials including metals, semi-conductors, and ceramics. The development of novel precursors and alternative routes to complex materials is a major aspect of this project. All personnel involved in the NM TRC proposal are also directly involved in the BES project.

Further work conducted in our laboratory also will be leveraged including an internally funded laboratory directed research and development entitled "Alternative Sensors". The fundamental aspects of this project is to develop nanowires of controlled length. Further, we are also involved in Cooperative Research and Development Agreement (CRADA) No. SC01/01640. "Improved Rubber Nanofillers" ($ 600 K) that involved controlled morphological nanoparticle synthesis and functionalization for rubber interaction.

UNM

The Department of Chemical & Nuclear Engineering at the University of New Mexico will provide a release time for Prof. Han to be able to focus on this research effort. The total amount is $10,742.17 for 30 % release time to cover Fall 06 and Spring 07.

TPL, Inc.

TPL, Inc.'s Micropower Department matching funds will come from existing SBIR Phase II contracts. Specifically, two programs will be used: AFRL (Contract No. FA8650-05-C-2613, "Power for Microsystems with Extended Missions") and NASA (Contract No. NNL06AA06C "Power for Vehicle Embedded MEMS Sensors"). Work performed under these contracts is targeted at developing custom EnerPak™ systems for government applications and will provide desired performance parameters for the new devices. This work will serve as in-kind contributions to the proposed TRC effort.

Appendix A. Participant Biographies

Key SNL Personnel

Dr. Timothy J. Boyle

Principal Member of Technical Staff, Sandia National Laboratories (MS 1349),
Processing and Inorganic Chemistry Department 1815, Advanced Materials Laboratory,
1001 University Boulevard, S.E., Albuquerque, NM 87106

a. Education: Postdoctoral Research Assistant, Department of Chemistry, University of California - Irvine (W. J. Evans). Ph.D., Inorganic Chemistry, Kansas University 1990. B.S. Chemistry, George Mason University 1985.

b. Professional Experience: Principal Member of Technical Staff at Sandia National Laboratories (1994-present). Adjunct Professor at The University of Pennsylvania (Department of Materials Science, 2000 - present) Research Advisor for the Center for Micro-Engineered Materials (CMEM) at the University of New Mexico (1998 - present) Adjunct Professor at the New Mexico Institute of Mining and Technology (Department of Chemistry, 1998 - present). Limited Term Ph.D. Appointee at Sandia National Laboratories (1993 -1994). .

c. Publications and Patents: Over 100 refereed publications. 12 granted patents, 4 pending

• *Relevant Patents:*

01. Scott D. Bunge, Timothy J. Boyle, Henry Gerung "Anhydrous Solution Synthesis of Luminescent Germanium Nanocrystals from Germanium (II) Precursors **SNL-TA (7744).**
02. Scott D. Bunge and Timothy J. Boyle "Cadmium Aryloxides: Alternative Precursors for the Colloidal Synthesis Nanocrystalline CdE (E = S, Se and Te)" **SNL-TA filed (7574).**
03. Scott D. Bunge and Timothy J. Boyle "Controlled Construction of Metal Alkoxides using HOR* Ligands" SNL-TA filed **S-100,410/SD-7344**. SNL waived but NNSA/DOE holding for 1 year.

• *Recent Relevant Publications:*

06. Henry Gerung, Timothy J. Boyle, Louis J. Tribby, C. Jeffery Brinker, Scott D. Bunge, Sang M. Han “Solution Synthesis of Germanium Nanowires” *Journal of the American Chemical Society* **2006** (in Press).

05. Timothy J. Boyle*, Harry D. Pratt III, Bernadette A. Hernandez-Sanchez, Timothy N. Lambert, Thomas J. Headley “Synthesis and optical properties of fluorescent ferroan sphalerite inspired (Fe,Zn)S nanoparticles” *Journal of Materials Chemistry* **2006** (in Press).

04. Henry Gerung, Scott D. Bunge, Timothy J. Boyle, C. Jeffrey Brinker, Sang M. Han "Anhydrous Solution Synthesis of Germanium Nanocrystals from the Germanium (II) Precursor $Ge[N(SiMe_3)_2]_2$" *Chemical Communications* **2005** 14, 1914.

03. Timothy J. Boyle, Scott D. Bunge, Todd M. Alam, Gregory P. Holland, Thomas J. Headley, Gabriel Avilucea "Cadmium Amido Alkoxide and Alkoxide Precursors for the Synthesis of Nanocrystalline CdE (E) S, Se, Te)" *Inorganic Chemistry* **2005** 44, 1588.

02. Timothy J. Boyle, Scott D. Bunge, Paul G. Clem, Jacob Richardson, Jeffery M. Dawley, Leighanna M. Ottley, Mark A. Rodriguez, Bruce A. Tuttle, Gabriel R. Avilucea, Ralph G. Tissot "A Novel Family of Structurally Characterized Dysprosium Alkoxides for use as an Amphoteric Dopant for Improved Ferroelectric Characteristics of PDyZT Thin Films" *Inorganic Chemistry* **2005** 44, 1588.

01. Timothy J. Boyle, Scott D. Bunge, Nicholas L. Andrews, Laura E. Matzen, Katherine Sieg, Mark A. Rodriguez, Thomas J. Headley "Precursor structural influences on the final ZnO nanoparticle morphology from a novel family of structurally characterized zinc alkoxy alkyl precursors" *Chemistry of Materials* **2004** 16, 3279.

d. Collaborators and Affiliations.

Nanoparticle collaborations: (i) NIH "Naturally Occuring Fluorescent Materials" – Wilson, Oliver (UNM-SoM); (ii) Goodyear CRADA- Pulford "Improved Rubber Fillers"; (iii) DOE-BES "Controlling Nanomaterial Morphology of Ceramic Materials"; (iv) DOE-EERE "Novel H-Storage Nanomaterials"; (v) External SNL Collaborators Internal LDRD proposal: Hirschfeld (NMTech), Dong (NMTech), Korzeniewski, TTU) Hirschfeld and Dong (NMTech), Datye (UNM), Eden (UI).

Dr. Timothy N. Lambert

Academic History:

- University of Texas – Austin, Chemistry, B.S., 1995
- New Mexico State University – Las Cruces, New Mexico, Chemistry (Organic), Ph.D., 2000
- University of Notre Dame – Notre Dame, Bioorganic/Supramolecular Chemistry, Post-doctoral Fellow/Senior Research Associate, 2001 – 2003
- Sandia National Laboratories, Albuquerque, New Mexico, Chemistry and Nanomaterials, Post-doctoral Fellow, 2003-2005
- Sandia National Laboratories, Albuquerque, New Mexico, Chemistry and Nanomaterials, Research Scientist, Beginning 7/14/2006

Professional History: Beginning 7/2006: Will be promoted to Research Scientist at Sandia National Laboratories; 2003-Present: Postodctoral Fellow, Sandia National Laboratories, Albuquerque, NM (helped lead first successful NIH grant awarded to SNL, Intergrating Complex Ceramics and Nanomaterials into Biological Systems); 2003: Senior Research Associate, University of Notre Dame and Walther Cancer Research Center, Notre Dame, IN (Acting Professor of Chemistry and Head of Research - Sabbatical Leave Replacement for Professor Bradley D. Smith); 2001-2002: Postdoctoral Fellow and Visiting Scientist, University of Notre Dame and Walther Cancer Research Center, Notre Dame, IN (Synthesized Receptors for Phospholipid Complexation and Translocation across membranes)

Selected Honors, Awards, and Professional Societies:

Graduate Student Research Award (1996)
First Place Poster Award at the HSRC/WERC Joint Conference on the Environment, Albuquerque, NM (1998)
Owen B. Weeks Award for Outstanding Graduate Research (1999-2000)
Employee Recognition Award Nominee - Sandia National Labs (2006)
Member of the American Chemical Society, 1995-Present

Selected Publications:

1. Lambert, T. N.; Andrews, N. L.; Gerung, H.; Boyle, T. J.; Oliver J. L.; Wilson, B. W.; Han, S. “Biocompatible Germanium(0) Nanocrystals - Cell Signaling and Photothermal Discovery” J. Am. Chem. Soc. 2006, submitted.
2. Boyle, T. J.; Pratt, H. P.; Hernandez-Sanchez, B. A.; Lambert, T. N.; Headley, T. J. “Synthesis and optical properties of fluorescent sphalerite inspired (Fe,Zn)S nanoparticles” J. Mater. Chem. 2005, in press.
3. Clare, J. P.; Ayling, A. J.;Joos, J.-B.; Sisson, A. L.; Magro, G.; Perez-Payan, M. N.; Lambert, T. N.; Shukla, R. S.; Smith, B. D.; Davis, A. P. "Substrate Discrimination by Cholapod Anion Receptors: Geometric Effects and the Affinity-Selectivity Principle" J. Am. Chem. Soc. 2005, 127, 10739-10746.

4. Hanshaw, R. G.; Lakshmi, C.; Lambert, T. N.; Johnson, J. R.; Smith, B. D. “Fluorescent Detection of Apoptotic Cells using a Family of Zinc Coordination Complexes with a Selective Affinity for Membrane Surfaces that are Enriched with Phosphatidylserine” ChemBioChem. 2005, 6, 2214-2220.
5. DiVittorio, K. M.; Lambert, T. N.; Smith, B. D. “Steroid-derived phospholipids scramblases induce exposure of phosphatidylserine on the surface of red blood cells” BioOrg. Med. Chem. 2005, 13, 4485-4490. Current Research Support: • NIH NCI, Signaling Activity of IgE Receptor Subunits, PI: JM Oliver (UNM); Co-PI: TJ Boyle (SNL) • NIH-NIBIB, Fluorescent Ceramic Naoprobes, PI: TJ Boyle (SNL); Co-PI: JM Oliver (UNM) • GOODYEAR, Improved Rubber Nanofillers, PI: TJ Boyle (SNL); Co-PI: NL Bell (SNL) • DOD, Thermal Battery MgO Separators, PI: D Ingersoll (SNL)

Prof. Sang Han

Academic History:

- University of California – Berkeley, Chemical Engineering, B.S., 1992
- University of California – Santa Barbara, Chemical Engineering, Ph.D., 1998
- University of California – Berkeley, Surface Science, Post-doctoral Research, 1998 – 1999
- Lam Research Corporation, CA, Plasma Diagnostics, Post-doctoral Research, 1999 - 2000

Professional History:

April 2000 – present: Assistant Professor of Department of Chemical and Nuclear Engineering, University of New Mexico, NM; November 1999 – April 2000: Post-doctoral Researcher, Lam Research Corporation, Fremont, CA; November 1998 – October 1999: Post-doctoral Researcher, U. C. Berkeley, CA; September 1993 – October 1998: Graduate Research Assistant, U. C. Santa Barbara, CA; August 1996 – October 1996: Visiting NSF Scholar, Seoul National University, Korea; June 1996 – August 1996: Visiting NSF Scholar, Tokyo Institute of Technology, Japan

Selected Professional Activities:

Chair for Area 8e Electronics and Photonics, AIChE 2006 Annual Meeting. Vice Chair for Area 8e Electronics and Photonics, AIChE 2005 Annual Meeting, Cincinnati, OH. Vice Chair for Area 08e11 Photonics, AIChE 2004 Annual Meeting, Austin, TX.

Selected Honors, Awards, and Society Offices:

Junior Faculty Research Excellence Award, University of New Mexico (2005)
National Science Foundation CAREER Award (2001)
The Electrochemical Society Norman Hackerman Young Author Award (1998)
National Science Foundation Summer Institute in Korea (1996)
National Science Foundation Summer Institute in Japan (1996)

Selected Publications:

1. Henry Gerung, Timothy J. Boyle, Louis J. Tribby, Scott D. Bunge, C. Jeffrey Brinker, and Sang M. Han, "Solution Synthesis of Germanium Nanowires Using a Ge +2 Alkoxide Precursor," J. Am. Chem. Soc., 128(15), 5244-5250 (2006).
2. Henry Gerung, Scott D. Bunge, Timothy J. Boyle, C. Jeffrey Brinker, and Sang M. Han, "Anhydrous Solution Synthesis of High-Quality Ge Nanocrystals from the Germanium (II) Precursor Ge[N(SiMe3)2]2," Chem. Commun., 14, 1914-1916 (2005).
3. Madhava R. Kosuri, Roya Cones, Qiming Li, and Sang M. Han; Bruce C. Bunker, and Thomas M. Mayer, "Adsorption Kinetics of Alkanethiol Self-Assembly on Ge(111)," Langmuir, 20(3), 835 (2004).
4. Sang M. Han, Carlo Carraro, W. Robert Ashurst, and Roya Maboudian, "Formation of Alkanethiol Monolayer on Ge(111)," J. Am. Chem. Soc., 123, 2422 (2001).

5. Qiming Li, Ying-Bing Jiang, Huifang Xu, Steve Hersee, and Sang M. Han "Heteroepitaxy of high quality Ge on Si by nanoscale Ge seeds grown through a thin layer of SiO2," Appl. Phys. Lett., 85(11), 1928 (2004).

Current Research Support:

- NSF CAREER, In Situ Monitoring of Surface Phenomena during Silicon Germanium Deposition and Etching, 05/01/01 – 04/30/06 $ 425,000
- ARO, Growing High-Quality Ge on Si by Nanoscale Heterojunction Engineering, 11/15/04 – 11/14/07, $ 300,000.
- AFRL, Growing High-Quality Ge on Si for Multijunction Solar Cells in Satellites, 8/26/05 – 3/31/07, $247,038.
- NSF NIRT, Fundamental Understanding of Nanofluidics for Advanced Bioseparation and Analysis, 08/01/2004 – 07/31/2008, $ 1,000,000.

Selected Synergistic Activities:

Prof. Han has mentored 10 undergraduate students since Summer 2000 with their summer research: ToniLisa Arviso-Jeans, Dawn Ramirez, Sacha De'Angeli, Angela Zivkovich, Roya Ahmadian, Darin Leonhardt, Christopher Crosher, Ethan Sullivan, Joshua L. Krauss, and Spencer D. Jacob.

Dissertations Directed During Last 5 Years: 2 PhD and 1 MS students graduated and 5 PhD students currently advised Henry Gerung, Germanium Nanomaterials: Synthesis, Characterization, and Applications, PhD (April 6, 2006). Qiming Li, Selective Molecular Beam Epitaxy of Germanium on Oxide-Covered Silicon (June 17, 2005). Madhava Kosuri, Formation of Self-Assembled Monolayers on Semiconductor Surfaces, MS (October 28, 2003).

Key TPL, Inc. Personnel

Dr. Charles D. E. Lakeman

PROFESSIONAL EXPERIENCE

TPL Inc., Albuquerque, NM

June 2004 – Present
Department Manager – Further expanded the MicroPower group to seven full time professionals with >$1.3M in annual revenues (external R&D funding). Developed a strategic plan for commercialization of the EnerPak™ technology.
September 2003 – June 2004
Senior Scientist – Created Micropower program using SBIR and STTR financing; grew the group to 4 professionals generating $750K annually in external R&D revenues; led the development of microbatteries, and microsupercapacitors; invented the "EnerPak" product combining energy harvesting, energy storage and ultra-low power charging circuitry.
March 1998 – September 2003
Advanced Scientist – Developed and implemented a novel microfabrication technology (µCP) for non-silicon materials; co-inventor of novel *volumetric* microbattery and micro-supercapacitor built using µCP.

Texas Instruments Inc., Dallas, TX March 1997 - March 1998
Post Doctoral Researcher
University of California, Santa Barbara October 1994 - March 1997
Post-Doctoral Researcher
Research Center for Advanced Science and Technology, University of Tokyo, Japan
, August 1991 - January 1992 *Visiting Researcher*

EDUCATION

University of Illinois at Urbana-Champaign, USA
Ph.D. Materials Science (August, 1994)
University of Illinois at Urbana-Champaign, USA
M.S. Ceramic Engineering (August, 1991)
University of Leeds, UK
B.Eng (Hons) Ceramic Science and Engineering (July, 1988)

ACADEMIC HONORS

IAESTE Scholarship (1987); American Ceramic Society Annual Meeting, 1990 - 2nd place Graduate Student Poster Competition; BP America Fellowship (1990, 1991); Sigma Xi Scientific Research Honor Society; Keramos Ceramic Engineering Honor Society

SELECTED RELEVANT PUBLICATIONS

C.D.E. Lakeman, T.J. Boyle, J.A. Ruffner, "Process Optimization and Evolution of Stress in $SrBi_2Ta_2O_9$ (SBT) Films Prepared by Chemical Solution Deposition," *J. Sol-Gel Sci.*, **16 (#1-2),** 83, (1999).

C.D.E. Lakeman, T.J. Boyle, "Chemical Solution Deposition of Strontium Bismuth Tantalate Films," Ferroelectric Thin Films VII, *MRS. Symp. Proc.* (1998). *Invited*.

C.D.E. Lakeman, T.J. Boyle, "Substrate Considerations in Chemical Solution Deposition of $SrBi_2Ta_2O_9$ (SBT) Films," *In Preparation,* (1998).

C.D.E. Lakeman, P.F. Fleig, "High Resolution Integrated Passives using Microcontact Printing," *Proc. IMAPS* (2002).

C.D.E. Lakeman, P.F. Fleig, H.R. Perry, "A New High Resolution Process for Passives in Hybrid Packaging," p. 65 in *Proc. 27th Annual Cocoa Beach Conference on Advanced Ceramics and Composites: B*, W.M. Kriven and H-T Lin Editors, The American Ceramic Society, (2003).

C.D.E. Lakeman, P.F. Fleig, J.L. DeGreeff, "MEPS – MEMS Electrochemical Power Supplies: A Solution for Integrated Power for Microsystems," *Proc IMAPS MEMS Workshop*, Boston, Nov. 2003.

C.D.E. Lakeman, P.F. Fleig, J.L. DeGreeff and J. Timothy Trainor "Hybrid Power for Wireless Sensors," accepted for Publication in *Proc. SPIE vol. 6123*, Unattended Ground Sensors (2006).

PATENTS

T.S. Moise, S.R. Gilbert, C.D.E. Lakeman, S.R. Summerfelt, S.A. Yamanaka, "Ferroelectric and Paraelectric Thin Film Devices using Dopants Which Eliminate Ferroelectricity," US Patent No. 6,441,415, August 27, 2002.

D.H. Lewis Jr., J.J. Waypa, E.K. Antonsson, C.D.E. Lakeman, "Micro Supercapacitors," US Patent No. 6,621,687, September 16, 2003.

D.H. Lewis Jr., J.J. Waypa, E.K. Antonsson, C.D.E. Lakeman, "Volumetric microbatteries," US Patent No. 6,861,170, March 1, 2005.

C.D.E. Lakeman, P.F. Fleig, J.L. DeGreeff, T. Chen, "Lithium Ion Microbattery," US Patent Application Serial No. 60/452,974, filed May 23, 2003

C.D.E. Lakeman, P.F. Fleig, J.L. DeGreeff, U.S. Patent Application Serial No. 10/796,532, filed Mar 8, 2004, entitled "MEMS Electrochemical Power System"

C.D.E. Lakeman, P.F. Fleig., J.L. DeGreeff, J.T. Trainor, U.S. Provisional Patent Application Serial No. 60/756,876, filed Jan 5, 2006, entitled "System for Energy Harvesting and/or Generation, Storage, and Delivery"

QUARTERLY REPORT OF PERFORMANCE AND SELF-ASSESSMENT

Metal Oxide Coating of Carbon Supports for Supercapacitor Applications

Covering the Period
July 31 through Sept 30, 2006

TRC Grant Program

Table of Contents

Quarterly Highlights

The proposal entitled "Metal Oxide Coating of Carbon Supports for Supercapacitor Applications" is an effort to synthesize nanoparticles of RuO_x to improve the capacity of a micro-supercapacitor. During the fist quarter of the project, we have successfully generated RuO_x nanomaterials and initiated integration into the C-substrate. The monthly meetings have allowed us to maintain our focus and discuss issues associated with the technical side of the project. Contracts for UNM have been placed with monies awaiting transfer from SNL to UNM. The TPL,Inc contract has been submitted and the buyer is negotiating the final contract. In general, we are on track and making rapid progress. The various tasks are individually discussed below.

Each task's progress is briefly described below.
Task 1. Ru Precursor synthesis. The commercially available precursors Ru acetate has been successfully used to generate RuO_x (Task 2) nanoparticles. Due to the limited decomposition mechanisms, additional precursors based on amide, alkoxide and alkyl derivatives have been synthesized and are currently being characterized. These precursors should make excellent sources for further reaction chemistry with oxygen containing ligands which will be used to synthesize RuO_x nanomaterials.
Task 2. RuOx Nanoparticle synthesis. Synthesis and characterization of RuO_2 nanomaterials, using several literature routes, has been successfully completed. Figure Task 2a, shows a TEM image of the isolated RuO_x materials. Scale-up and subsequent refinement of these processes is well underway. Solvo-thermal attempts at synthesis of RuO_x nanomaterials have led to synthesis of Ru^o nanomaterials (see Figure Task 2b) that may prove useful as an alternative RuO_x nanomaterial synthesis.
Task 3. Precursor, nanoparticle, and interaction characterization. Single crystal X-ray diffraction, powder XRD, TEM, SEM, FTIR, UV-vis, and other analytical means are being used to characterize the precursors and final materials in an on-going process.
Task 4. Functionalization of RuOx (3-12). Using commercially available ligands, and in house synthesized ligands when necessary, for functionalization of the surface of the RuO_x nanocrystals from Task 2 are under development. These ligands bind to the nanocrystal surface and display varying charge on the outer surface. Currently, this step is still under evaluation and is pending Task 5 data.
Task 5 Combining RuOx and C support (4 -12). This marks the next step in currently synthesized RuO_2 nanomaterials. The C-substrate has been supplied and analyzed by TEM analysis. Figure Task 5, shows a TEM image of the C-substrate which requires additional discussion with TPL,Inc. at the monthly meeting. Several varying samples will be provided to create a baseline for subsequent material/process refinements.
Task 6. Size selection of RuOx (4 – 12). RuOx nanoparticles will be separated by their size through nanometer scale channels enhanced by scanning laser confocal fluorescence microscopy and nanomachined waveguide assisted Fourier transform infrared spectroscopy. Initial investigations using CdE materials demonstrate this is a useful method and will be applied to RuO_x nanomaterials. This step is still under evaluation and pending Tasks 5, 8 data.
Task 7. Microsupercapcitor Fabrication and Assembly (6 -12). The two halves of the cell will be constructed separately. Each cell half will be infiltrated with electrolyte. A separator will be placed on top of one half of the microsupercapacitor. Both halves of the capacitor will be aligned and sealed. This step is still pending task 5.
Task 8: Microsupercapacitor Testing (9-12). Characterization of the electrical performance of the microsupercapacitors using measurements of capacitance, ESR, power, and leakage current measured under self-discharge. This step is pending task 7.

As can be seen, we are on task following our timeline established in the original proposal. Funding transfers are underway, but work has continued at a rapid pace in spite of these delays. The project is on time and the various institutions working closely to ensure continued advances.

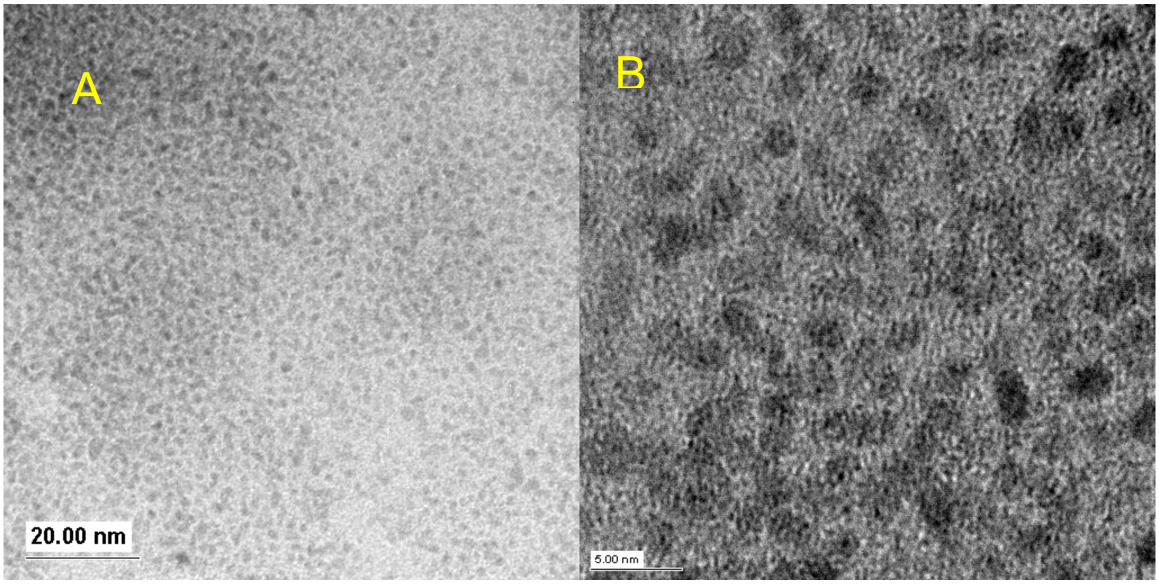


Figure Task 2. A: TEM image of RuO_2 nanoparticles (dark spots). B: HR-TEM image of Ru^o nanoparticles (dark spots).

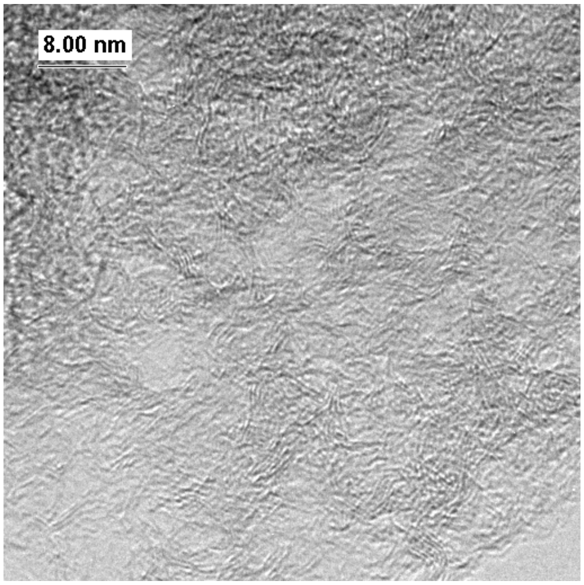


Figure Task 5. HR-TEM Images of carbon substrate.

Financial Status- Expenses and Balance of Funding

Attachment D
Summary Use of Funds Table (Offeror & all Collaborators combined)

Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total		
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	Total
Personnel/Fringe	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Supplies	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Purchased Services	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Subcontracts/ Subgrants	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Travel	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Other (Specify)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Offeror's Use of Funds Table

Name of Offeror:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe	$12,974	$6,715							$12,974	$6,715
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants	$80,000								$80,000	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$92,974	$6,715	$0	$0	$0	$0	$0	$0	$92,974	$6,715
Indirect									$0	$0
Grand Total	**$92,974**	**$6,715**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$92,974**	**$6,715**

Attachment F
Collaborator's Use of Funds Table

Name of Collaborator:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe									$0	$0
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants									$0	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Attachment G
Distribution of TRC Funds by Task
Covering Period: July 31 – September 30, 2006

Use Of Funds	Task 1	Task 2	Task 3	Task 4	Task 5	Task 6
Personnel/Fringe	$2,224	$652	$7,086			
Equipment						
Supplies						
Purchased Services	$80,000					
Subcontracts/ Subgrants						
Travel						
Other (Specify)						
Total Direct	$82,224	$652	$7,086	$0	$0	$0
Indirect						
Grand Total	**$82,224**	**$652**	**$7,086**	**$0**	**$0**	**$0**

Use Of Funds	Task 7	Task 8	Task 9	Task 10	Task 11	Total
Personnel/Fringe						$9,962
Equipment						$0
Supplies						$0
Purchased Services						$80,000
Subcontracts/ Subgrants						$0
Travel						$0
Other (Specify)						$0
Total Direct	$0	$0	$0	$0	$0	$89,962
Indirect						$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$89,962**

Source of Cost Share Table
Covering Period: July 31 – September 30, 2006

Offeror/Collaborator Name	Year 1		Year 2		Total	
	Cash	In-Kind	Cash	In-Kind	Cash	In-Kind
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

short form	*Insert long form*	*short form*	*Insert long form*

C.

QUARTERLY REPORT OF PERFORMANCE AND SELF-ASSESSMENT

Metal Oxide Coating of Carbon Supports for Supercapacitor Applications

Covering the Period
October 1 through December 31, 2006

TRC Grant Program

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Quarterly Highlights

Quarterly Highlights

The proposal entitled “Metal Oxide Coating of Carbon Supports for Supercapacitor Applications” is an effort to synthesize nanoparticles of RuO_x to improve the capacity of a micro-supercapacitor. During the second quarter of the project, we have improved the quality of the RuO_x nanomaterials and initiated integration into the C-substrate. The monthly meetings continue to benefit both sides and facilitate progress forward. Contracts for UNM and TPL,Inc are in place and funds distributed appropriately. In general, we are on track and making rapid progress. The various tasks are individually discussed below.

Each task’s progress is briefly described below.
Task 1. Ru Precursor synthesis. We have switched from the acetate to the chloride derivatives to generate RuO_x (Task 2) nanoparticles with significant ease and cost reduction in the process. Currently, the in-house prepared precursors have not demonstrated a significant improvement in the final nanomaterials generated.
Task 2. RuOx Nanoparticle synthesis. Synthesis and characterization of RuO_2 nanomaterials, using several literature routes on a large scale have been successfully completed. Figure Task 2a, shows a TEM image of the isolated RuO_x materials.

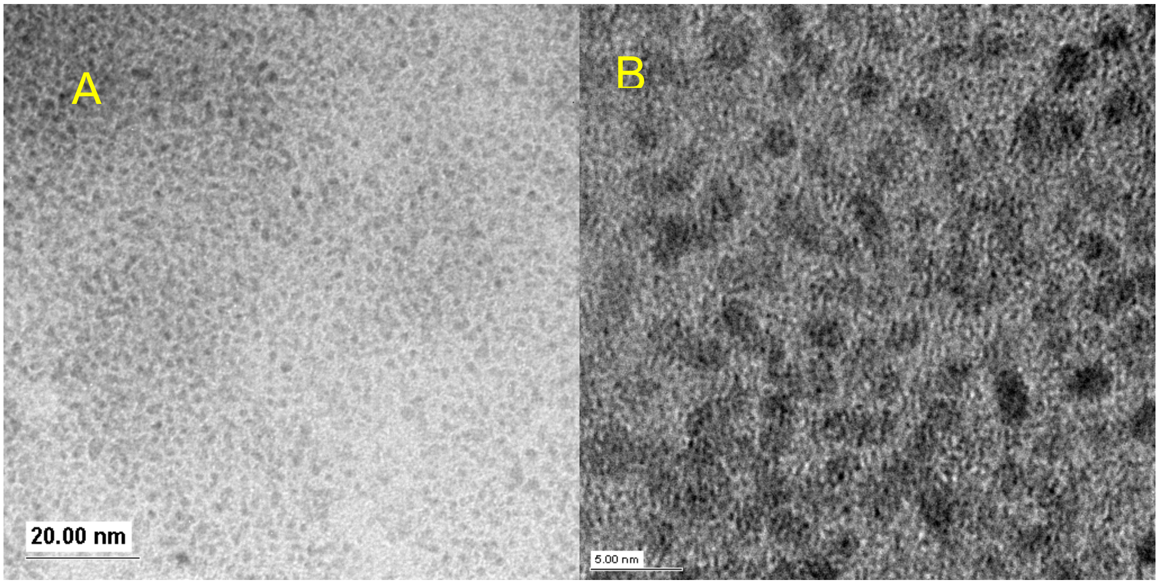

Figure Task 2. A: TEM image of RuO_2 nanoparticles. B: HR-TEM image of Ru^o nanoparticles.

Task 3. Precursor, nanoparticle, and interaction characterization. Single crystal X-ray diffraction, powder XRD, TEM, SEM, FTIR, UV-vis, and other analytical means are being used to characterize the precursors and final materials in an on-going process.

Task 4. Functionalization of RuOx (3-12). Pending results from Task 5 data will determine whether or not functionalization is necessary. The resulting C-substrate are not as initially envisioned and therefore it may not necessitate the previous discussed functionalization.

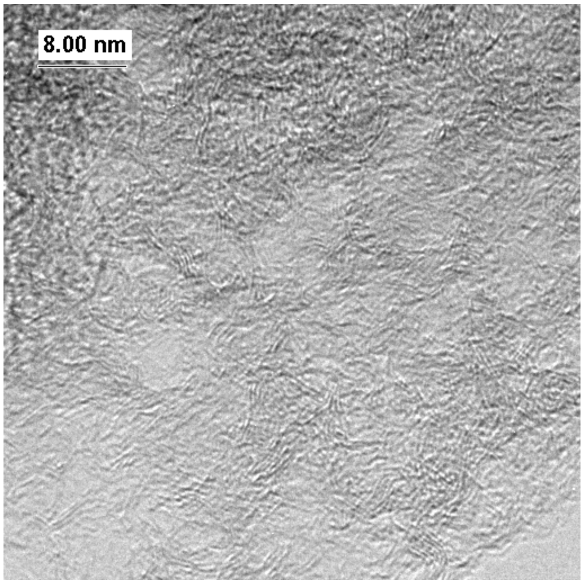

Figure Task 5. HR-TEM Images of carbon substrate.

Task 5 Combining RuOx and C support (4 -12). The first samples of RuO_x nanoparticles have been combined with the activated C-substrate and testing (Task 7 and 8).

Task 6. Size selection of RuOx (4 – 12). Initial investigations using CdE materials demonstrate this is a useful method; however, additional work is needed to apply them to the RuO_x nanomaterials. This step is still under evaluation and pending Tasks 5, 8 data.

Task 7. Microsupercapcitor Fabrication and Assembly (6 -12). The two halves of the cell were constructed separately. Each cell half was infiltrated with electrolyte. The separator was placed on top of one half of the microsupercapacitor. Both halves of the capacitor was aligned and sealed. The RuO_x nanoparticles were incorporated for testing (Task 8).

Task 8: Microsupercapacitor Testing (9-12). Characterization of the electrical performance of the microsupercapacitors using measurements of capacitance, ESR, power, and leakage current measured under self-discharge was initiated. The next set of variables are being explored.

The project is on track with progress being made. The nanoparticles are being incorporated and adjustments based on processing conditions are being made. Redefining of the substrate will simplify the introduction of RuO_x nanomaterials.

Financial Status- Expenses and Balance of Funding

Attachment D
Summary Use of Funds Table (Offeror & all Collaborators combined)

Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total		
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	Total
Personnel/Fringe	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Supplies	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Purchased Services	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Subcontracts/ Subgrants	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Travel	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Other (Specify)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Offeror's Use of Funds Table

Name of Offeror:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Shar
Personnel/Fringe									$0	$
Equipment									$0	$
Supplies									$0	$
Purchased Services									$0	$
Subcontracts/ Subgrants									$0	$
Travel									$0	$
Other (Specify)									$0	$
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$
Indirect									$0	$
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$**

Attachment F
Collaborator's Use of Funds Table

Name of Collaborator:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe									$0	$0
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants									$0	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Attachment F
Collaborator's Use of Funds Table

Name of Collaborator:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe									$0	$0
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants									$0	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Source of Cost Share Table
Covering Period: July 31 – September 30, 2006

Offeror/Collaborator Name	Year 1		Year 2		Total	
	Cash	In-Kind	Cash	In-Kind	Cash	In-Kind
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
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					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Abbreviations

short form	*Insert long form*	*short form*	*Insert long form*

D.

FINAL REPORT OF PERFORMANCE AND SELF-ASSESSMENT

Metal Oxide Coating of Carbon Supports for Supercapacitor Applications

Covering the Period
July 31, 2006 through August 31, 2007

TRC Grant Program

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Final Highlights

The proposal entitled “Metal Oxide Coating of Carbon Supports for Supercapacitor Applications” is an effort to synthesize nanoparticles of RuO_x to improve the capacity of a micro-supercapacitor. In general, we kept on track and made progress to the final goals. In fact, all milestones were met with limited success in terms of achieving the final goal of significantly improving the properties of these supercapacitors. The yearly results are briefly described below.

Introduction

The revolution of miniaturizing highly technological portable devices has been underway for more than a decade. However, as devices shrink in size and their number of high energy operations increase, battery technology is nearing its limits in being able to meet the demands. Therefore, alternative power sources are needed to increase the energy efficiency and energy density available to miniaturized devices. One solution to this problem is to employ supercapacitors. Unlike batteries, supercapacitors can be charged and discharged millions of times without any degradation in their performance. While supercapacitors deliver energy efficiently, they do not *store* energy efficiently, and so tend to be quite large in comparison to the portable devices needed. The successful development of an improved micro-supercapacitor, which possesses increased energy capacitance density on a smaller size scale, will allow further miniaturization and longer battery lifetime.

In order to achieve a sufficient micro-supercapacitor, new composite materials have to be produced. One such material is ruthenium oxide (RuO_x) which has a high specific capacitance of 760 F/g. The faradaic processes RuO_x enables is due to the redox reactions of the oxide atoms at or near the electrode surface. This process gives rise to the so-called “pseudocapacitance,” which involves both interfacial reactions and mass transfer of ionic charges across the double layer. This double layer mechanism of energy storage is heavily surface dependant, and thus requires high active surface areas to deliver a high specific capacitance value. However, the capacitance of pure RuO_x decreases rapidly when used alone. This phenomenon has been associated with electrolyte depletion and over-saturation during charge/discharge. It has been reported that the addition of carbon materials increases the capability of ruthenium oxide. Although activated carbons having high surface area and porous structures yield electrodes with high specific energy and power densities, their specific capacitance is at most 40 F/g. By creating a nanocomposite electrode using a redox-reactive material, like RuO_x, within a high surface area of carbon, the resulting small particle size of the RuO_x would increase the redox active surface area of the material giving rise to higher-power devices.

In our present study of generating micro-supercapacitors, we have evaluated: several methods of synthesis of RuO_x nanomaterials, integration of RuO_x into a carbon substrate, construction and capacitance testing of resulting materials in a micro-supercapacitor design. In the following sections we will discuss synthesis approaches to RuO_x nanoparticles, characterization of our materials, construction of cells, and testing of our micro-supercapacitor cells.

Experimental setup.

All chemicals were used as received (Aldrich) and handled under ambient atmospheric conditions in a fume hood, including ruthenium(III) chloride ($RuCl_3$), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), and 1-Butyl-3-methylimidazolium hexafluorophosphate (BMeIm-PF_6). Sodium borohydride ($NaBH_4$, Aldrich) was kept under an inert argon atmosphere in a glovebox. De-ionized water (DI water) was produced in house from a Millipore™ filtration system.

Synthesis

Based on literature procedures, three synthetic routes to produce RuO_x nanomaterials were undertaken with minor modifications. The routes were increased to allow for gram quantities of RuO_x.

Route 1: In a 500 mL round bottomed flask, BMeIm-PF_6 (29.0 mL, 140 mmol) was added to crushed $RuCl_3$ (6.00 g, 28.9 mmol). The resulting solution was stirred and sonicated at elevated temperatures (~60 °C) until the $RuCl_3$ dissolved. After allowing the solution to cool to room temperature, an excess of $NaBH_4$ (9.64 g, 255 mmol) was added and stirred. After 2 hrs., the solution was centrifuged and the mother liquor removed. The resulting black powder was washed twice with acetone and then three times with DI water.

$$\mathbf{RuCl_3 + BMeIm\text{-}PF_6 \bullet xH_2O + 3NaBH_4 \longrightarrow RuO_2 + 3NaCl + BMeIm\text{-}PF_6 \bullet (x\text{-}2)H_2O + 3BH_4 + 2H_2} \qquad \mathbf{(1)}$$

Route 2: In a 500 mL round bottomed flask, a 1:1 v/v mixture of MeOH and de-ionized water (318 mL total) was added to $RuCl_3$ (6.60 g, 31.8 mmol) followed by stirring and sonication of the reaction mixture during the entirety of the reaction. After 15 min, a 1.00 M NaOH in MeOH and DI water (1:1, ~ 70.0 mL) was added in 10.0 mL increments until the final pH was adjusted to 7. After 30 min, the solution was centrifuged, mother liquor removed, and the subsequent powder washed three times with DI water.

$$\mathbf{RuCl_3 + 3\,NaOH \longrightarrow RuO_2 + 3\,NaCl + H_2O} \qquad \mathbf{(2)}$$

Route 3: In a 500 mL round bottomed flask, DI water (400 mL) was added to crushed $RuCl_3$ (6.00 g, 28.9 mmol) while simultaneously sonicating and stirring the reaction for a minimum of 20 minutes. After 20 minutes, the desired amount of carbon substrate was introduced to the $RuCl_3$ solution and allowed to mix for another 20 minutes. After that time, 30%wt H_2O_2 (~30 mL) was slowly added to the $RuCl_3$ solution in a fume hood. The reaction mixture was allowed to react for 1 hr and then centrifuged. The resulting black powder was then washed three times with DI water.

$$\mathbf{2\,RuCl_2 + 4\,H_2O_2 \longrightarrow 2\,RuO_2 + 4\,H_2O + 3\,Cl_2} \qquad \mathbf{(3)}$$

Characterization

The resulting RuO_x materials were analyzed by a number of in-house analytical instruments. Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical X'Pert PRO X-ray diffraction unit with Jade6™ XRD pattern processing software version 6.5.1. TEM images were obtained on a JEOL 2010 transmission electron microscope (TEM) equipped with an energy dispersive detector (EDS). FT-IR data were obtained on a Bruker Vector 22 Instrument using KBr pellets under an atmosphere of flowing nitrogen.

Capacitance Testing (TPL)

Characterization was carried out using the Arbin BT2000 automated testing system. This 24-channel system can automatically charge devices, measure standard parameters such as capacitance, ESR, and open circuit voltage, and discharge under prescribed conditions, as well as enable automated charge-discharge cycling to measure capacitance stability. The constructed device consisted of four layers: current collector, carbon anode, nano-composite cathode, and separator. The top layer was a metallic current collector with connections to "I/O" tabs on the top and bottom of the container. The separator was selected from the Celgard family of poly(propylene) (PP) and poly(ethylene) (PE) separator materials or W.L. Gores's poly(tetrafluoroethylene) separator. The electrodes were impregnated with electrolyte solution under vacuum to ensure all porosity was filled. The aqueous electrolyte H_2SO_4 was selected to demonstrate feasibility during testing.

Activated carbon electrodes were made containing 0-50wt% of RuO_2 powders. The electrodes were fabricated by first mixing the carbon and RuO_2 powder with 4wt% PTFE binder in a shear mixer. Water was used as the solvent to facilitate mixing which was later removed by evaporation in an oven. The dried electrode mixture was then rolled into a sheet using a rolling mill. The sheet thickness was targeted at 440 microns and is obtained by adjusting the gap in the rolling mill. Electrodes were punched using a round 8.1mm diameter punch.

The electrolyte used in these experiments was a 4M H_2SO_4 solution. Before the supercapacitors were assembled the electrodes were infiltrated with the electrolyte using a vacuum jar. The electrodes were placed in a vial containing the electrolyte and the vial was placed into the vacuum jar with the lid loosely in place. A vacuum was applied to the vacuum jar and then the isolation valve closed and the electrodes allowed too soak in a static vacuum for several minutes. The vacuum was then slowly released and the process repeated. This cycling was done until the electrodes sank to the bottom of the vial.

The electrodes were then assembled into a supercapacitor using a Tee-Cell (see Figure 1). The components of the Tee-Cell are fabricated from stainless steel which is not compatible with the sulfuric acid electrolyte and therefore an inert current collector (spacer) was needed. This current collector/spacer disc was made from titanium metal and was placed between the stainless steel components of the Tee-Cell and the electrodes. During assembly a 780 um thick PTFE washer was used to limit the compression applied by the spring in the Tee-Cell. The OD of the washer was the same as that of the current collector so that it would fit inside of the Tee-Cell while the ID was 10.3mm. This allowed the electrode and separator discs to fit inside the washer. The compression of the 440um thick (x 2 = 880 um total electrode thickness) electrodes was effectively to approximately 12.5%.

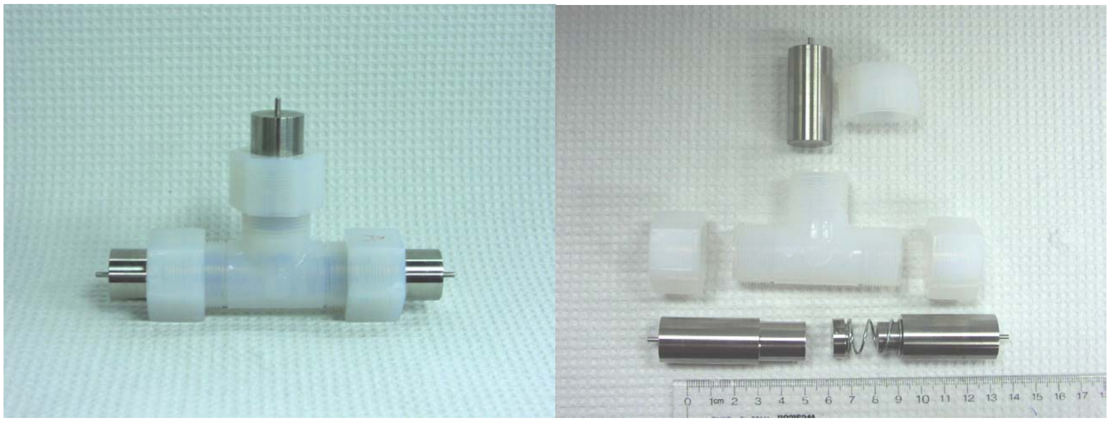

Figure 1. Assembled and un-assembled Tee-Cell used for testing supercapacitors.

Results and Discussion

Our previous research efforts have shown that metal alkoxides ($M(OR)_x$) are excellent precursors to ceramic materials, especially metal oxides. By varying the ligand set of the $M(OR)_x$, it has been shown that hydrolysis and condensation rates can be controlled by effectively altering nucleophilic and electrophilic attack on the metal center. As a result, metal alkoxides have found wide spread use in chemical solution ("sol-gel"), metal organic chemical vapor deposition (MOCVD), and emerging nanoparticle synthesis.

Our initial synthesis attempts were to methodically control the decomposition of $Ru(OR)_x$ precursors into RuO_x nanoparticles via a hot solution precipitation route. Variations in size and morphology may be garnered by changes in one or more key variables: decomposition temperature, solute, time, surfactants, and the precursor used. However, commercial products and literature reports of synthesis routes to ruthenium alkoxides or similar species are costly and typically of poor yield. Therefore, we pursued cheap synthesis routes of ruthenium precursors from readily available ruthenium(III) chloride. Unfortunately, we were not able to substitute the chlorines with different organic ligands in a cost effective method. Thus, we pursued routes that used commercially available ruthenium compounds to synthesize RuO_x nanomaterials.

Therefore, we decided to utilize literature reports to RuO_x materials. The following discusses the synthetic routes that were investigated to synthesize RuO_x and their intermingling with a carbon substrate (Synthesis), the materials generated (Characterization), and the properties garnered from the addition of these materials (Testing). Details will be discussed in detail below.

Synthesis

We decided to investigate direct routes to RuO_x nanomaterials using $RuCl_3$. This precursor was selected based on several reasons; (i) commercially available, (ii) numerous routes utilized this precursor successfully, (iii) relatively air stable, and (iv) provides a cheap source of ruthenium. From the multitude of routes, we selected three to generate the RuO_x materials.

The first route investigated made use of an ionic liquid (BMeIm-PF_6) as a solvent for $RuCl_3$. In general, a metathesis reaction substituted the chlorines for borohydrides, which lead to the Ru being reduced by the water contained in the ionic liquid, thus forming RuO_x species. The BMeIM-PF_6 acted not only as a solvent for the poorly soluble $RuCl_3$ salt but also as a coordinating surfactant, thus allowing very small particles of RuO_2 to grow in a controlled fashion. After washing the resulting nanoparticles to remove excess by-products and surfactant, the precipitate was transferred to a TEM grid. The resulting material was found to form 1-2 nm RuO_2 crystalline particles (Figure 5B). While this route made the materials of interest, the high cost of BMeIM-PF_6 made this route cost prohibitive on the industrial scale. Therefore, other routes that utilized cheaper solvents were investigated.

The second route used a 50/50 mixture of methanol and DI water to dissolve the $RuCl_3$. The addition of the NaOH solution produced RuO_2 nanomaterials that agglomerated to form larger structures, see Figure 5C. Washing the resulting nanoparticles yielded a blue solution that is believed to contain Na_2O and other by-products. After subsequent washing the solution became colorless and the precipitate was transferred to a TEM grid. Invariably, these larger structures did not fit in the porous carbon substrate, so an *in-situ* approach was considered such that the carbon would be introduced prior to any reactions. The concern with this *in-situ* route is the potential contamination from the secondary production of Na_2O which was found prior to washing by PXRD. It was decided that a reaction scheme that introduced an organic oxidant could prove to be significantly beneficial in avoiding sodium contamination.

Alternatively, a more simplistic route was investigated again using $RuCl_3$ dissolved in DI water, mixed with a desired amount of carbon substrate (Route 3). This route relies on the diffusion of the $RuCl_3$ into the carbon pores where at a later time the Ru would be reduced by the addition of H_2O_2. Centrifuging of the material and washing several times provided a new material for testing. Unfortunately, Route 3 was started late in the timeframe of this project so quantitative results concerning capacitance were not obtained. However, materials generated through the various routes were characterized via TEM, PXRD, and EDS with the inclusion of Route 1 and 2's capacitance testing results in the following section.

Characterization

Preliminary investigations focused on understanding the properties of the carbon substrate supplied by TPL, Inc. (Norit Supra X). This material was initially thought to contain micron or smaller holes in which RuO_x could intercalate. However, the high resolution TEM picture shows that this material did not have the expected porosity but actually formed a crumpled carbon surface. Due to limited time, this material was used as the support; however, other carbon-based materials with controlled porosity are available and should be utilized to realize the initial concept in future attempts.

The RuO_x materials generated from each route were examined via PXRD, TEM, and EDS. For each route, the resultant RuO_x materials were dried and then crushed in a crucible, and then dispersed with chloroform ($CHCl_3$) onto the appropriate holder. The various results are discussed below.

FT-IR. The preparation of the FT-IR sample followed Route 1 as an indication of the surface chemistry of the RuO_2 resulting nanomaterial. The RuO_2 washed as previously discussed, dried, and then crushed with KBr. A pellet was formed from the mixed materials and analyzed. Figure 2 shows a sharp peak at 3433 cm^{-1} which correlates to the $Ru\mathit{O}_x\text{-}\mathit{H}_y$ stretching vibration. It should also be noted that the surfactant BMeIm-PF_6 is identified as contributing C-CH_3 and CH_2 stretching vibrations in the range of 2923-2854 cm^{-1}, C=C stretching vibration at 1623 cm^{-1}, and CH_2 bending vibration at 1413 cm^{-1}.

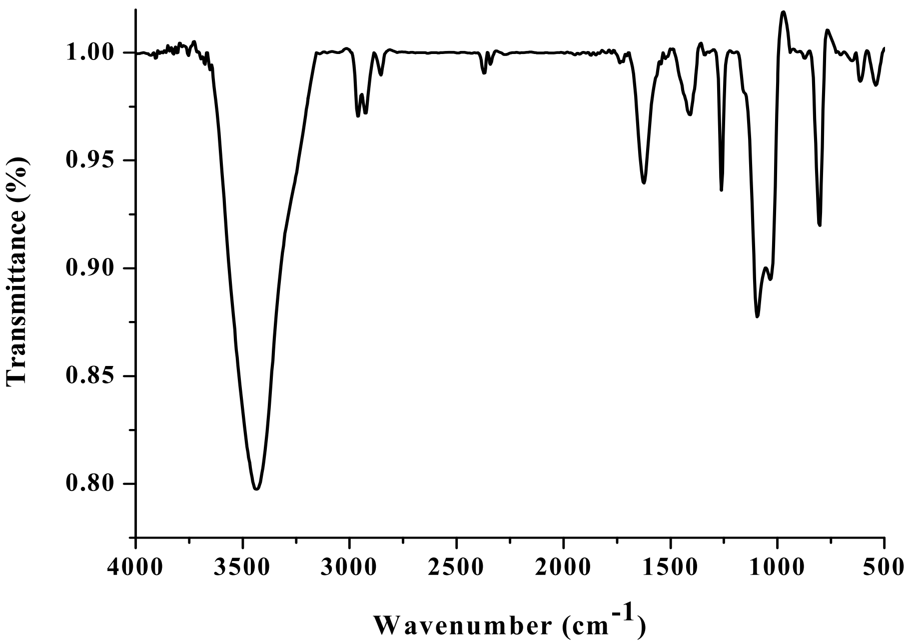

Figure 2. FT-IR data of RuO_2 generated from Route 1.

PXRD. The preparation of PXRD samples followed each routes washing guidelines and were prepared directly after each synthesis. Figure 3 shows the combined PXRD of Route 1 (green), 2 (blue), and 3 (red). As it can be observed, the patterns are broad and it is difficult to determine the phase of the material. However, comparison to published results shows good correlation between our peak positions including similar peak broadening. Jade6™ further identified all three materials as RuO_2 by comparison of the main two-theta peaks residing at 28.0°, 35.1°, and 54.3°. The crystal structure is in a tetragonal P42/mnm unit cell configuration. Comparing the materials to one another distinctly shows that route 1 produced the best bulk crystalline material while routes 2 and 3 had more amorphous RuO_2. We suspect this is due to the excess amounts of water that contributes to the uncontrolled nucleation of RuO_2 and subsequently reduced bulk crystallinity.

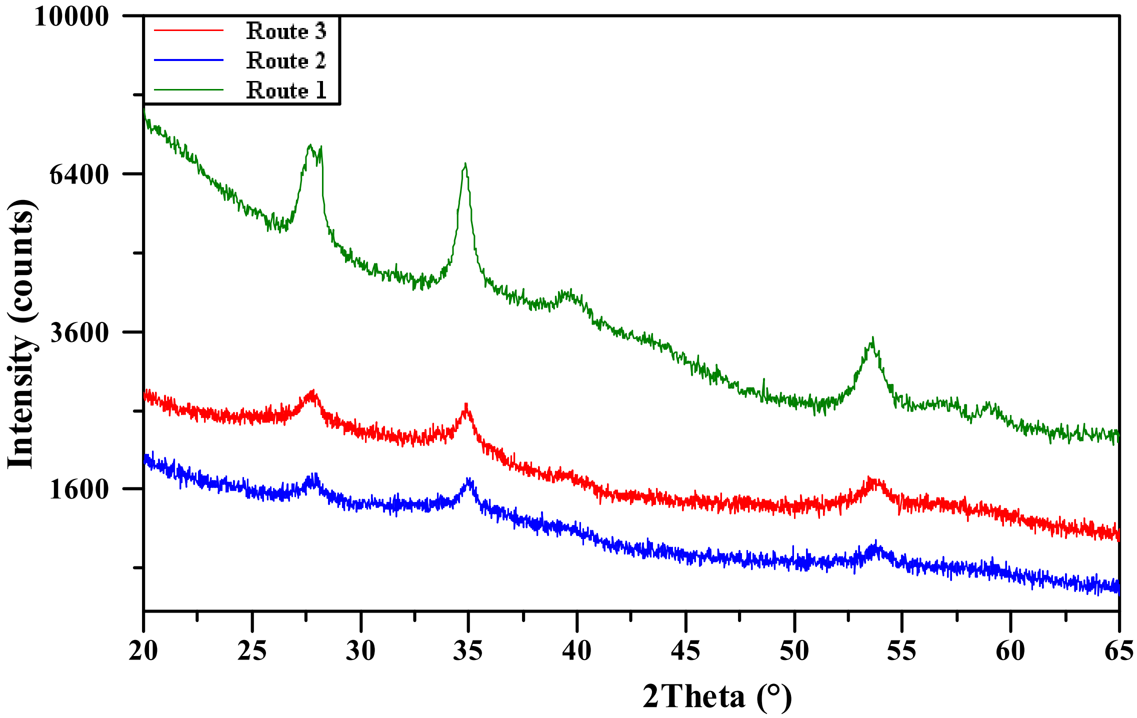

Figure 3. A PXRD comparison of all three routes.

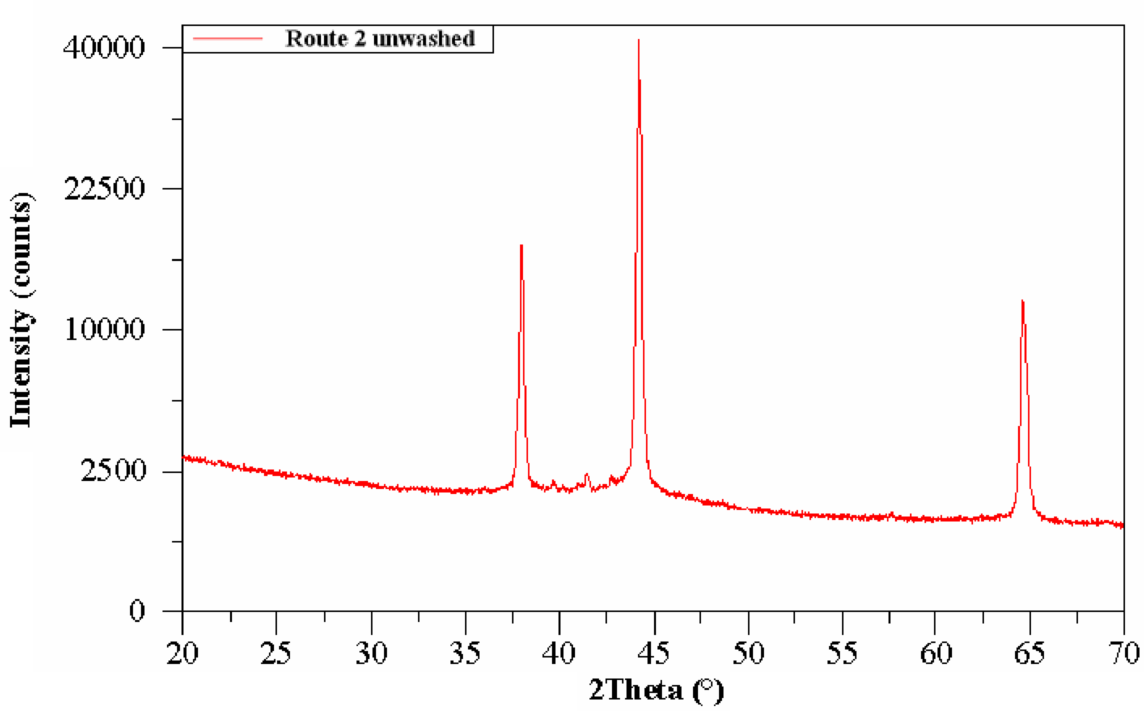

Figure 4. A PXRD of unwashed material from Route 2. The three large peaks correspond to Na_2O.

TEM. In order to determine some understanding of the size of the materials generated, TEM images were obtained for each route. Figure 4 shows the TEM images of the powder generated by routes 1 – 3. As can be discerned, the dark field results (top right) for Route 1 indicate high crystallinity and the bright field view shows 1-2 nm in diameter particles. For Route 2, the dark field image (top right) indicates the presence of several small well ordered crystalline particles, but the majority of the material particles appear to range from 25-100 nm amorphous ruthenium oxide that has agglomerated.

EDS. Since the materials generated proved to be the appropriate sizes, it was necessary to determine the chemical composition of these nanoparticles. Therefore EDS data was obtained on select particles and are shown in Figure 5. The data obtained confirms the majority of the materials contain ruthenium in significant amounts. The copper (Cu) and carbon (C) peaks are both contained in the TEM grid and thus show up in small quantities.

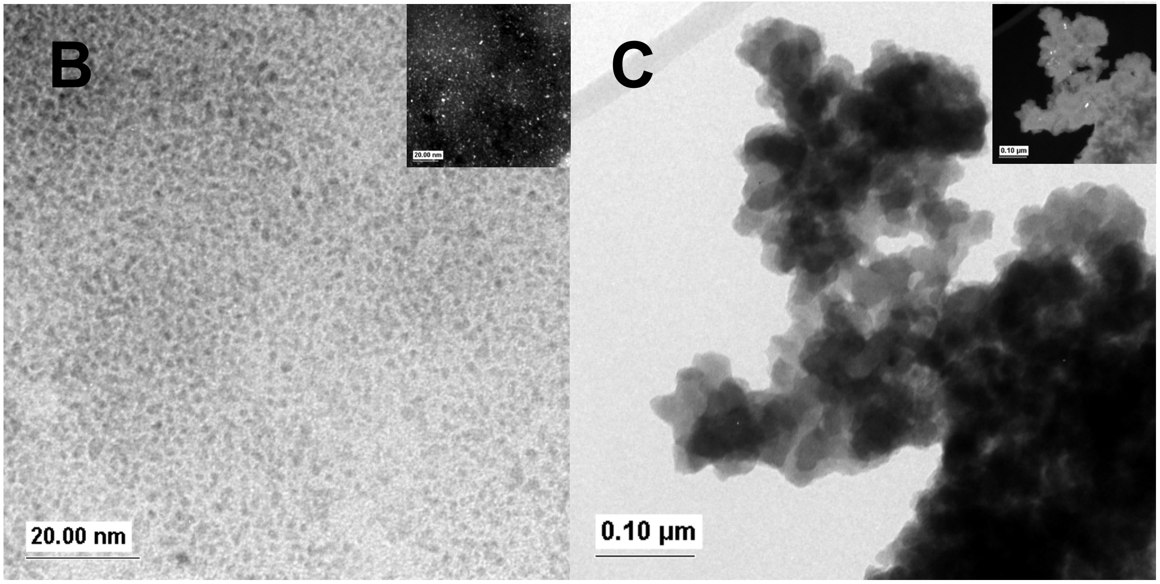

Figure 5. TEM images of: (A) Carbon substrate (Norit supra x), (B) Route 1, (C) Route 2, (D) Route 3.

Testing. The RuO_x material was then delivered to TPL, Inc. for construction and testing of the micro-supercapacitor. A schematic is shown in Figure 6 of the constructs of the supercapacitor. As constructed, the micro-supercapacitors were in the discharged state; therefore, the first requirement was to charge them. During charging, positive and negative ionic charges within the electrolyte accumulate at the surface of opposite electrodes compensating for the electronic charge at the electrode surface. A CCCV (Constant Current Constant Voltage) profile was used to charge the micro-supercapacitors. First, a constant CC charge of one mA will be applied to the micro-supercapacitor. Once the micro-supercapacitor has reached its working voltage (1.0 V for aqueous or 2.5 V for organic), a CV charge is performed until the current in the micro-supercapacitor drops to nine mA. After charging, the voltage will be measured under an open circuit configuration as well as under different loads. These measurements will allow the ESR and capacitance to be evaluated and compared with values for commercial cells.

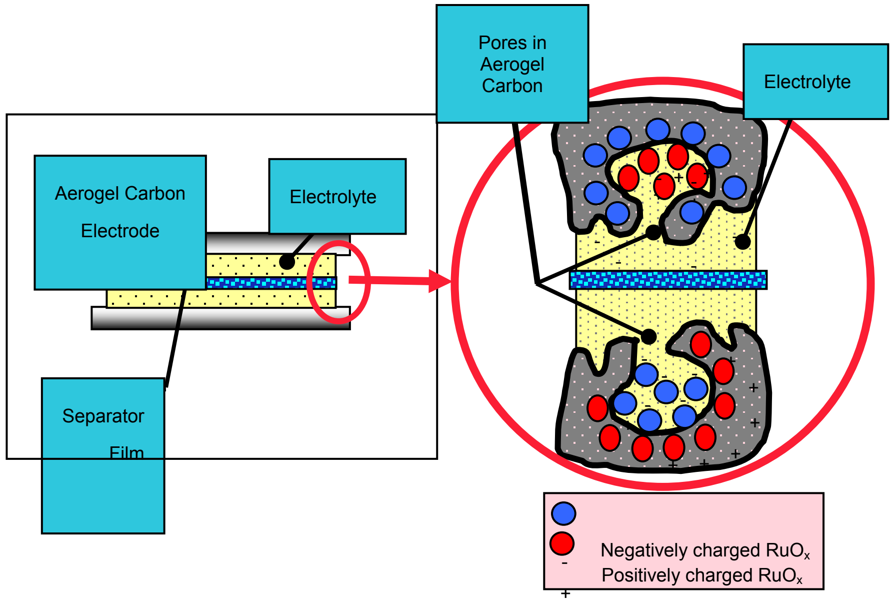

Figure 6. Schematic of the constructs of the microsupercapacitor

RuO_2 powders were prepared using two methods, the Brazilian and NaOH prep, were evaluated at the beginning of the project. Table 1 contains a description of the samples delivered to TPL by UNM for testing. Upon disassembly of supercapacitors after testing it was noticed that powders prepared using the Brazilian prep discolored the electrolyte. During cycling of supercapacitors made with these powders the ESR increased and the capacitance decreased. Supercapacitors made using the NaOH Prep showed no signs of the problems observed with the Brazilian Prep powders.

Two types of supercapacitors were tested; symmetric and asymmetric. Symmetric supercapacitors utilize two of the same type of electrodes were as asymmetric surpcapacitors utilize two electrodes of different composition. In the testing done here an asymmetric supercapacitor is made using one electrode with only activated carbon as the active material while the other electrode has some of the carbon replaced with RuO_2.

Testing of both configurations showed that asymmetric supercapacitors with the RuO_2 containing electrode used as the cathode gave the best overall performance with respect to ESR and capacitance stability.

Activated carbon electrodes were made containing 0, 5, 15, 25 and 35 wt% un-annealed RuO_2 (NaOH Prep). Electrodes were also made containing 25 and 50 wt% annealed RuO_2 (NaOH Prep) (annealed at 200ºC). The annealed powders resulted in a higher specific capacitance than the un-annealed powders (see Figures 7 and 8).

Table 1. Samples Received by TPL from UNM/SNL.

Sample	Description	Results of Testing
1	RuO_2 – Brazilian Prep	Observed discoloration of the electrolyte after cycling of supercapacitors using this material. ESR increased and capacitance decreased during cycling.
2	RuO_2 – NaOH Prep	Improved results when compared to material synthesized using the Brazilian prep. No electrolyte discoloration.
3	RuO_2 + C – NaOH Prep	Did not test. Not enough material to mix with binder and fabricate electrodes.
4	RuO_2 – NaOH Prep Annealed at 200ºC	Annealed material resulted in higher specific capacitance.
5	RuO_2 – NaOH Prep – No Anneal	Used to complete test series with increasing amounts of RuO_2 in electrode.
6	RuO_2 – NaOH Prep – Anneal 200ºC	Used to complete test series with increasing amounts of RuO_2 in electrode.
7	RuO_2 – Peroxide Prep – No Anneal	Did not perform electrochemical tests. Electrolyte became very discolored during infiltration with electrolyte.
8	RuO_2 – Peroxide Prep – Anneal 200ºC/2.5 hrs	Did not perform electrochemical tests. Electrolyte became discolored during infiltration with electrolyte.
9	RuO_2 – Peroxide Prep – Anneal 200ºC/5 hrs	Did not perform electrochemical tests. Electrolyte became discolored during infiltration with electrolyte.
10	RuO_2 – Peroxide Prep – Anneal 200ºC/10hrs	Did not perform electrochemical tests. Electrolyte became discolored during infiltration with electrolyte.

Table 2. Test results from asymmetric supercapacitors using un-annealed and annealed RuO_2 powder.

Un-annealed†				
Wt% RuO_2 in Cathode	Capacitance (mF)	ESR (ohm)	Specific Capacitance (F/g)	Capacitance Density (F/cc)
0 wt%*	947	11.9	37.0	418
5 wt%	1024	6.24	40.2	452
15 wt%	1157	4.10	43.0	511
25 wt%	1224	9.15	44.2	540
35 wt%	1258	7.25	44.8	555

Annealed (200ºC – 2 hrs)†				
Wt% RuO_2 in Cathode	Capacitance (mF)	ESR (ohm)	Specific Capacitance (F/g)	Capacitance Density (F/cc)
0 wt%*	947	11.9	37.0	418
25 wt%	1317	4.72	45.4	581
50 wt%	1676	4.18	51.4	740

† All values are the average of results obtained from four identical supercapacitors.

* Contains only Norit SX Ultra Activated Carbon Powder and 4 wt% PTFE Binder.

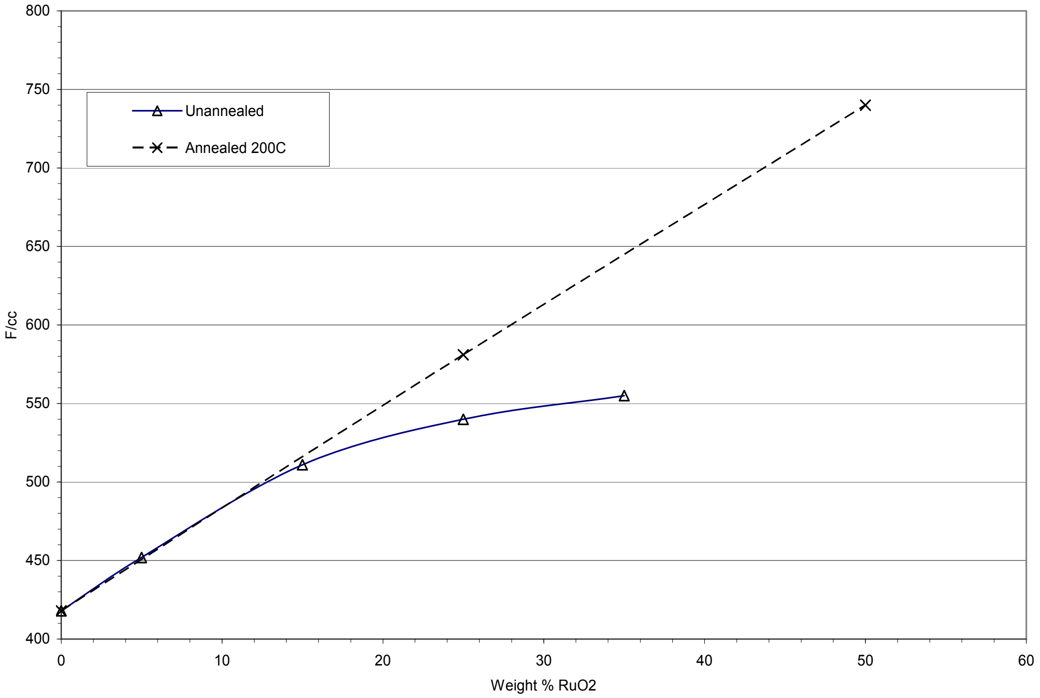

Figure 7. Capacitance density of asymmetric supercapacitors using annealed and un-annealed RuO_2 powders prepared using the NaOH Prep.

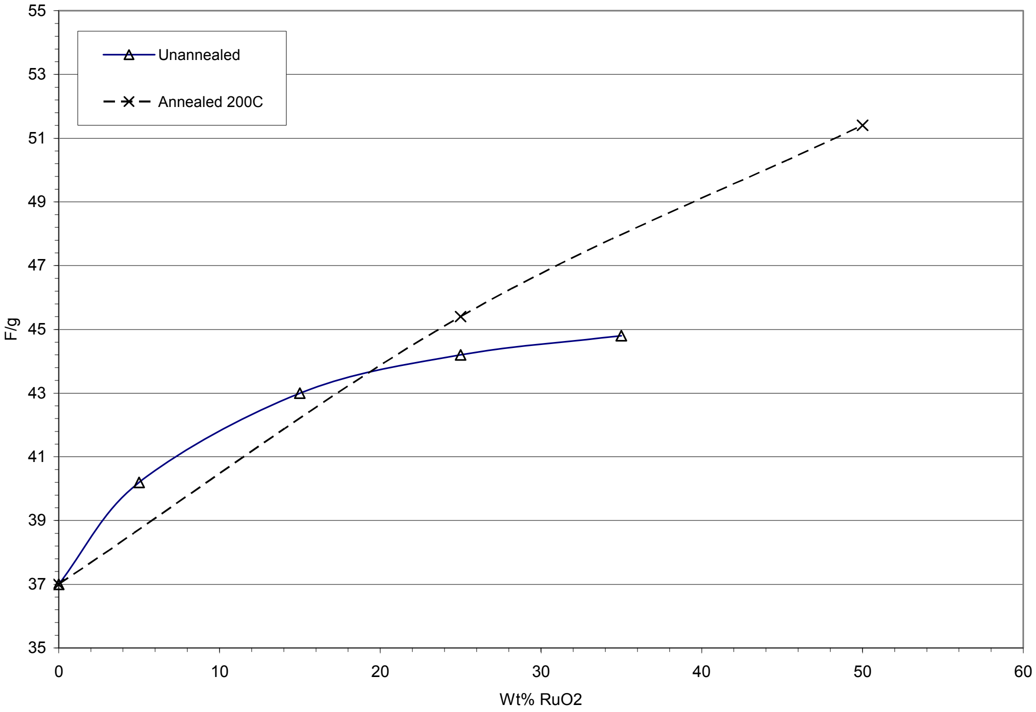

Figure 8. Specific capacitance of asymmetric supercapacitors using annealed and un-annealed RuO_2 powders prepared using the NaOH Prep

Economic Impact

The results of this effort did not show sufficient improvement in supercapacitor electrode materials performance to warrant further investment from TPL. Consequently, there are no plans to create a spin-out company tocommercialize this technology.

Financial Status- Expenses and Balance of Funding

Attachment D
Summary Use of Funds Table (Offeror & all Collaborators combined)

Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total		
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	Total
Personnel/Fringe	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Supplies	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Purchased Services	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Subcontracts/ Subgrants	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Travel	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Other (Specify)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Offeror's Use of Funds Table

Name of Offeror:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe									$0	$0
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants									$0	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Attachment F
Collaborator's Use of Funds Table

Name of Collaborator:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe									$0	$0
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants									$0	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Attachment F
Collaborator's Use of Funds Table

Name of Collaborator:										
Use Of Funds	Quarter 1		Quarter 2		Quarter 3		Quarter 4		Year 1 Total	
	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share	NMTRC	Cost Share
Personnel/Fringe									$0	$0
Equipment									$0	$0
Supplies									$0	$0
Purchased Services									$0	$0
Subcontracts/ Subgrants									$0	$0
Travel									$0	$0
Other (Specify)									$0	$0
Total Direct	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Indirect									$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Source of Cost Share Table
Covering Period: July 31 – September 30, 2006

Offeror/Collaborator Name	Year 1		Year 2		Total	
	Cash	In-Kind	Cash	In-Kind	Cash	In-Kind
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
					$0	$0
Grand Total	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**

Abbreviations

short form	*Insert long form*	*short form*	*Insert long form*

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