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14. ABSTRACT Due to their nanoscale dimensions, nanobattery systems can have many advantages. The electrodes can have higher capacities, lower resistance and faster electron transfer kinetics. In addition we have found that solid electrolytes confined to nanoscale dimensions can have as much as an order of magnitude or greater increase in ion conductivity than the same electrolyte not under those conditions. These factors combine to create the potential for an interesting new power source, both in terms of technological applications and models for nanoscale understanding. This work involved the construction and characterization of nanobattery systems. Also, the nanoelectrochemical techniques necessary to do characterization of these nanopower systems was developed, resulting in new methods for understanding nanodevices.					
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DEVELOPMENT AND CHARACTERIZATION OF NANOBATTERY SYSTEMS

FINAL REPORT

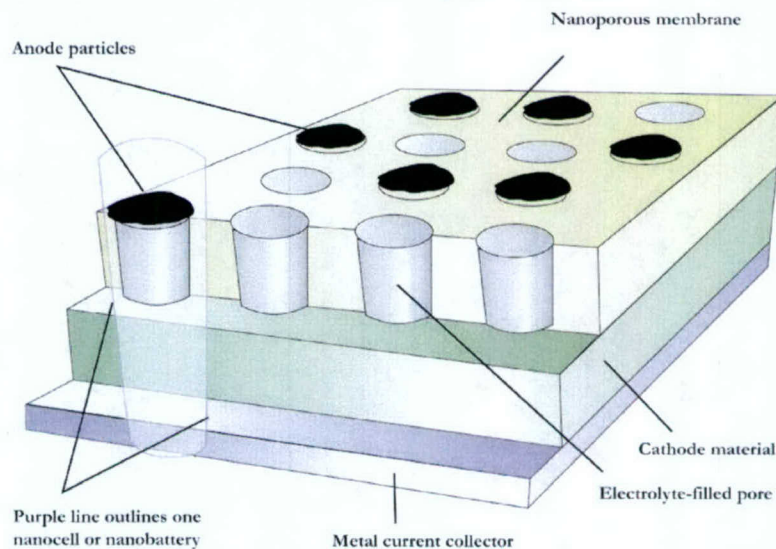
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Technical Section

Technical Objectives

Because of their nanoscale dimensions, nanobattery systems can have many advantages. The electrodes can have higher capacities, lower resistance and faster electron transfer kinetics. In addition, we have found that solid electrolytes confined to nanoscale dimensions can have as much as an order of magnitude or greater increase in ion conductivity than the same electrolyte which is not under those conditions. These factors combine to create the potential for an interesting new power source, both in terms of technological applications and models for nanoscale understanding. The proposed work involves the construction and characterization of nanobattery systems. One configuration of this nanobattery system, using nanosized particles as anodes, is shown to the right. The region highlighted would be a functioning micro or nanobattery. Other configurations exist where nanoparticles can be used for the anode and the cathode. The nanoelectrochemical techniques necessary to do these characterizations will be further developed, resulting in new methods for nanotechnology development.



Specific objectives for this project were:

1. Determine the optimum conditions and methods for the constructing nanobattery systems.

2. Evaluate these systems by using traditional electrochemical techniques. We will also further develop nanoelectrochemical techniques that can be used to study these and other nanopower systems.
3. Gain further information about the anticipated and already observed unique properties of these model nanobattery systems by using FT-IR spectroscopy, Raman spectroscopy, scanning probe microscopy, surface energy studies and the electrochemical techniques mentioned above.
4. Gain a basic understanding of these unusual properties by correlating the data from 2 and 3 in terms of a "free ion" or "continual" model of ion transport, an interface orientation model, or other appropriate models.

Technical Approach

Reported below is work completed since the last reporting period of this grant. Following this discussion is a summary of work completed under the support of this grant.

Microbattery Composite Cathodes Using Carbon Nanotubes

Introduction

The stabilities and efficiencies of cathodes of microbatteries are important for their superior performance. The performance of cathode of microbattery systems can be improved by applying new materials or combining components with unique properties into cathode materials. Individual carbon nanotubes exhibit extraordinary mechanical, thermal and electrical properties. Composite materials using carbon nanotubes as fillers are expected to show similar superior properties. This part of our work reports synthesis of carbon nanotubes by microwave chemical vapor deposition (MACVD) and incorporating them in the cathode of microbatteries to improve battery performance.

In our previous work we have shown that the incorporation of bundles of carbon nanotubes in V_2O_5 sol-gel used in microbattery systems improved battery performance [1]. In this work we describe the synthesis of CNTs. These CNTs were then mixed with the V_2O_5 sol-gel to make a composite cathode for use in micro and nanobatteries. The CNTs were grown on the nanoporous alumina membranes that are typically used to make our micro and nanobatteries and then applying V_2O_5 sol-gel to the membrane to make the cathode. It was hoped that the addition of better dispersed, individual carbon nanotubes in the sol-gel would further improve microbattery performance. In addition to enhanced mechanical properties, interconnected networks of carbon nanotubes are envisioned to provide direct thermal and electrical conductivity paths within the V_2O_5 sol-gel of the composite cathode. Furthermore, the high surface area of carbon nanotubes provides the better access to the electrolyte. Improved capacities and battery response times to charging and discharging are expected. The CNTs were nanocoated with a V_2O_5 sol-gel which, upon curing, formed a xerogel around the carbon nanotubes. This formed a molecular composite cathode. Microbatteries/microcapacitors were made and subjected to charge/discharge cycles with a consistent maximum charge of 4.60 V.

Experimental

Carbon nanotubes were grown by the catalytic decomposition of hydrocarbon precursor gas over metal catalyst nanoparticles that were already deposited on a substrate. In this work a 20 nm layer of nickel was deposited using rf-magnetron sputtering on disk-shaped nanoporous alumina substrates. The alumina disks were 13 mm in diameter and were 60 μm thick and were commercially available (Whatman Anodisc alumina filtration membranes). The pores were either 20 or 200 nm across. The CVD system used in this work was an ASTeX 5010 reactor with a 1.5 kW microwave power generator. The flow rates and ratio of feedstock gases were controlled by a set of mass flow controllers (MFCs) and an MKS Model 247C 4-Channel Readout. An MKS Type 250 Pressure Controller controlled the pressure in the reactor. A type-K thermocouple was used to measure the actual temperature of the substrate stage.

In this work, all the substrates sputtered with nickel thin film were first annealed in a tube furnace at 500°C under hydrogen (H_2) atmosphere for two hours. Then the annealed substrate was transported in air to the microwave-assisted PECVD reactor chamber and placed on a stainless steel substrate stage with the nickel side faced down. The bell jar chamber was pumped down to a base pressure of 3.5×10^{-3} torr using a rotary pump. Then ultrahigh purity H_2 gas was introduced into the chamber to provide a reducing environment for the catalytic metal particles. The flow rate of hydrogen was set at 160 sccm. After the introduction of hydrogen, the microwave plasma was lit inside the reactor for heating the substrate and activating the nickel catalyst nanoparticles. A microwave power of 1 kW and a reactor pressure of 20 torr were maintained for 10 minutes and then 40 sccm of methane (CH_4) gas was introduced into the reactor chamber. Introduction of CH_4 initiated the growth of CNT. Typically, the CNTs were grown for 15 minutes. The substrate temperature was estimated to be in the range of 570-640°C.

As mentioned above, we have developed additional techniques for constructing micro and nanobatteries [1]. Our technique consisted of filling nanoporous alumina membranes with poly (ethylene oxide) (PEO) lithium triflate electrolyte materials. We used micro and nanoparticles of graphite as the anode on one side of the membrane, and used composite materials composed of carbon nanotubes and V_2O_5 sol-gel as the cathode on the other side of the membrane [1]. In effect, a microbattery array of numerous parallel nanocells was made. One of the major tasks of this section of this work was the construction of the cathode for the nanobatteries where individual carbon nanotubes were distributed in V_2O_5 cathode material. This was accomplished by nanocoat with a V_2O_5 sol-gel that upon curing formed a xerogel around the carbon nanotubes. This formed a molecular composite cathode where instead of having bundles of carbon nanotubes as in our previous work [1], we had individual carbon nanotubes in the V_2O_5 , forming the composite cathode. The resulting cathode on the membrane was silver pasted onto a 0.125 mm thick nickel foil, which served as a current collector. The microbatteries were charged and discharged, proving that these small batteries could function. Detailed information about the construction and characterization of the microbattery can be found in our previous work [1].

Results and Discussion

TEM analysis was performed on the carbon nanotubes to determine the wall structure and these studies showed that nanotubes were mostly multi-walled. The outer surface of the nanotube walls were often covered with an amorphous carbon layer. Raman spectroscopy indicated the presence of crystalline graphitic carbon and microcrystalline graphite as well as amorphous carbon in the carbon nanotube layer. The Raman spectrum shows a lower crystalline quality.

Having successfully grown CNTs on porous membranes, we used these CNT covered membranes to make microbatteries which were then characterized. Recently, Bachas and co-workers [2] incorporated carbon nanotubes to enhance electrical properties of sol-gel materials and we incorporated bundles of CNTs in battery cathodes where enhanced performance was observed. The addition of carbon nanotubes in a dispersed state to the V_2O_5 sol-gel studied here should increase the electrical conductivity in the resulting xerogel composites. Similar to our previous experimental technique [1], the charging studies were done under ambient conditions using a Digital Instruments Nanoscope IIIa AFM where the cantilever tip was brought into contact with a selected graphite particle in ~ 100 nm diameter, the anode of the microbatteries. The microbattery was subjected to charge-discharge cycles which consisted of charging at 50 nA to the peak voltage of approximately 4.6 V, then discharging at 50 nA to a potential of 0.5 V. Fig. 5 shows several charge-discharge cycles of the microbatteries with a consistent maximum charge of 4.60 V. This large voltage may be due to overcharging of the system and some capacitance behavior. However, compared to the microbatteries that we previously made without carbon nanotubes in the vanadium xerogel cathode, the addition of the carbon nanotubes to the V_2O_5 sol-gel made a composite cathode with significantly improved battery performance [1]. This can be seen in Fig. 2 where potential versus capacity data for a microbattery fabricated in this work with the individual CNTs at the porous membrane interface is compared with capacity data for a microbattery made in our previous work [1] where CNT bundles are distributed in the bulk composite cathode. It is observed that at any capacity the battery with the individual carbon nanotubes has a voltage that is approximately twice that of the battery made in our previous work. This enhanced performance is most likely due to the superior electrolyte access in the composite cathode through its interconnected networks and a high surface area of the dispersed carbon nanotubes.

Progress Summary for Research Project

The following is a summary of the work that has been conducted during the time period of this grant.

In order to conduct work on the development of nanobatteries, work was done on the development of the advanced techniques necessary to conduct tests on individual micro and nanobatteries such as charge/discharge studies, a.c. impedance spectroscopy, cyclic voltammetry and other electrochemical tests [1, 3-6]. These experiments were done using the tip of an atomic force microscope to make contacts with individual batteries. Being able to investigate electrochemical properties by sampling on the nanometer scale has allowed us to investigate fundamental properties of these electrochemical systems that we would not be able measure otherwise. We believe we have opened new avenues of electrochemical tests on the nanoscale.

Initial work on individual micro and nanobatteries was done with lithium microbatteries made using a nanocomposite $LiMn_2O_4$ cathode, poly(ethylene oxide) electrolyte confined in nanoporous membranes, and micron size graphite particles as anodes. We were able to combine relatively good room temperature ionic conduction, caused by electrolyte confinement in nanopores [7] and potential improved performance by a composite cathode due to the nanoparticle size of the $LiMn_2O_4$, resulting in good microbattery performance, even for our initial studies done under ambient conditions. Charge/discharge tests were done by using an atomic force microscope cantilever tip coated with gold to make contact with individual graphite particles that formed individual microbatteries. The microbatteries were tested under relatively high current densities (1.2 to 1.6 mA/cm²) and were still able to have capacities of 14 – 22 μ A-hr/cm². This is comparable to thin film microbatteries having similar composition reported in the literature [8]. In our initial work, the microbatteries studied had anodes that were 70 – 100 μ m in diameter, which was the realm of interest for new nanotechnology applications.

The work described in the previous paragraph uses nanoconfined electrolyte material and micro sized anode particles. The next step was to use cathode materials on the nanoscale. Initial work in this direction was the characterization of cathode materials confined in nanopores so that the performance of nanobatteries can be better understood and enhanced. V_2O_5 confined in the 200 nm pores of aluminum oxide nanoporous membranes were observed to have two kinds of conductivities. This was observed from a.c. impedance data and was related to the two ways water can be contained in the xerogel matrix of the vanadia: either inside the cavities of the oxide network or intercalated between the nanoscale ribbons found in $V_2O_5 \cdot nH_2O$ xerogels. The conductivities increased when the vanadium pentoxide xerogels were confined in the nanopores, with proton conduction in the oxide network increasing from 10^{-8} to 10^{-7} S/cm and the conduction between the ribbons increasing from 10^{-5} to 10^{-4} S/cm.

This increase in conduction for both types of conduction was attributed to two factors. First, confinement in the nanopores of the alumina membranes forces the ribbon-like structures present in V_2O_5 xerogels to orient parallel to the direction of the pores. This orientation increases both types of proton conduction. Raman spectroscopy showed that the principal structure of the vanadium pentoxide xerogel confined in alumina membranes is of a more amorphous configuration of polyvanadates. Since amorphous structures are known to promote ion conduction over more crystalline matrixes [9], this factor also comes into play in promoting ionic conduction. Once again, the enhanced properties of battery materials, in this case cathode material on the nanoscale, promote nanobattery performance.

Latter in our research a technique was developed for constructing nanobatteries of even smaller electrode dimensions once again exhibiting the enhanced performance described above for V_2O_5 cathode material. An ambigel of V_2O_5 was placed in the 200 nm pores of alumina membrane and cyclic voltammetry data indicated that arrays of these pores filled with V_2O_5 could be analyzed as a nanoelectrode array. The capacity of these nanobatteries was calculated by considering the size of the pores and the depth of penetration of the V_2O_5 gel into the membranes. The capacity of the nanobatteries remained relatively constant for each cycle at a value of approximately 45 mAh/cm²·mm. This performance surpasses our previous studies on microbattery systems, which had volumetric capacities of 5 mAh/m²·mm [1]. The improvement in capacity could be due to several reasons. The SnO_2 anode's ability to store more lithium than graphite [10] could be responsible for higher capacities. In our previous study V_2O_5 xerogels of very low porosity were used as cathodes [1]. The V_2O_5 ambigels used in this study have much higher porosities and surface areas that should improve performance. The improved porosity of the cathode and the utilization of true nanoscale cathodes for charging and discharging together must be important factors. These properties are no doubt beneficial since electrode components of this size and composition result in higher battery capacities, lower resistance, and lower susceptibility to slow electron-transfer kinetics than standard electrode configurations [11-15]. This, the final effort in this research, resulted in functioning nanobatteries with enhanced performance when compared on a specific area or volumetric capacity basis. Such batteries can function as power sources for micro or nanodevices and, when used in a massively parallel format, could be enhanced power supplies for larger scale electronic devices.

In brief, the objectives for this work were:

1. Determine the optimum conditions and methods for the construction of nanobattery systems.
2. Evaluate these systems by using traditional electrochemical techniques and develop nanoelectrochemical techniques that can be used to study these and other nanopower systems.

3. Gain further information about the anticipated and already observed unique properties of these model nanobattery systems.
4. Gain a basic understanding of these unusual properties by correlating the data in terms of a “free ion” or “continual” model of ion transport, an interface orientation model or other appropriate models.

These objectives have basically been achieved.

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Figure 1

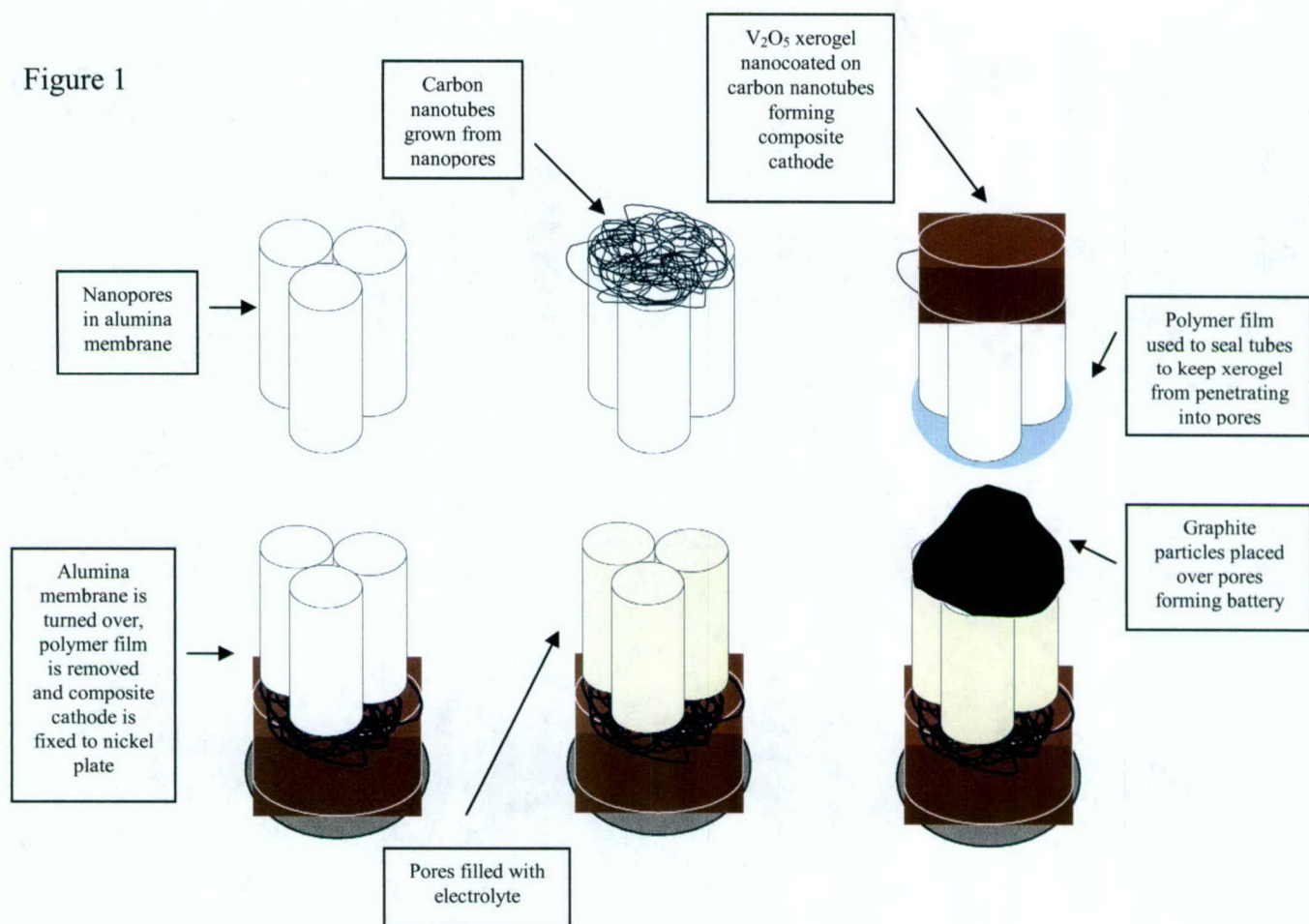


Figure 2

