

Optimization of MnO₂ Electrodeposits using Graphenated Carbon Nanotube Electrodes for Supercapacitors

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PHY 3090U – Material Science

Thursday April 9th 2015

Researchers optimize the performance of graphenated carbon nanotubes (g-CNTs) by manipulating the density of graphene foliates, leading to higher specific capacitance.

The demand for robust and efficient sources for energy and power continually troubles us. Thousands of labs exist today solely for the purpose of discovering a solution, ranging from research in solar powered cells to ocean current turbines. However, researchers in the Nanomaterials and Thin Films Lab of Dr. Jeffrey Glass (Professor, Duke University) believe that the next step in solving the power source problem is through the use of graphenated carbon nanotube (g-CNT) electrodes with electrodeposited (ED) manganese dioxide asymmetric (or hybrid) supercapacitors. These supercapacitors are thought to offer the best trade-off between high energy density batteries and high power density (power per unit volume) supercapacitors.

Supercapacitors are high capacity electrochemical capacitors with capacitance, which is the capacity to store electric energy, of up to 10 000 Farad (at 1.2 volts). They are able to store 10 to almost 100 times the energy per unit mass (or volume) than a simple electrolytic capacitor, and can both deliver and accept charge more efficiently than batteries. Supercapacitors work by having two electrodes separated by a semi-permeable (ion) membrane with an electrolyte, a substance that ionizes when dissolved in solvent, connected to both capacitors. Applying a voltage to the electrodes polarizes them, and so the ions in the electrolyte form an electrical double layer (layer of opposite polarity to the electrode's polarity). These two electrodes form a circuit in series, with two individual capacitors (i.e. C_1 and C_2), so the total capacitance of the system is:

$$C_{total} = \frac{C_1 \cdot C_2}{C_1 + C_2}$$

Next, supercapacitors can be either symmetric or asymmetric. If they are symmetric, then the two electrodes used in the system have the same capacitance value, and the total capacitance of the system is half of the value of each individual electrode. If the supercapacitors are asymmetric, and $C_1 \gg C_2$, then the total capacitance will be approximately equal to that of the electrode with the smaller capacitance.

Electrochemical supercapacitors use a double-layer effect to store electrical energy, and since the dielectric layer is not solid, storage of electrical energy is instead accomplished by two means of storage: double-layer capacitance (electrostatic storage of electrical energy by separation of charge in the double layer) and pseudocapacitance (electrochemical storage of energy from redox reactions with charge-transfer).

Supercapacitors are constructed with two metal foils that collect current and are coated with electrode material (e.g. activated carbon, metal oxide). The foils serve as the power connection between the electrode and the terminals of the capacitor. Then, a semi-permeable membrane for ions insulates the electrodes against short circuits. This is followed by both components being wrapped into a stackable shape like a cylinder or rectangle, stored in a housing unit which is usually an aluminum can, and then finally saturated with organic or aqueous electrolyte. This electrolyte enters the electrode pores and serves as the connection between electrodes through the separator.

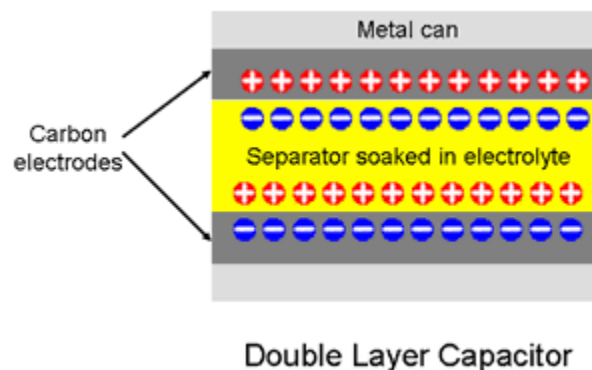


Figure 1: Schematic of asymmetric supercapacitor with composite carbon electrodes

Though several materials can be used to form the supercapacitors internally, carbon nanocomposite cathode systems are being studied very extensively for asymmetric supercapacitors. They offer nearly double the voltage range (2 V) and thus four times the energy density that would normally be achieved with carbon-carbon supercapacitors in aqueous electrolytes. Nanocomposite systems with aqueous supercapacitors have several advantages, such as being non-volatile, having high conductivity electrolytes, are less expensive, safer, and have a higher power density. Nanostructured carbon supports like graphene have only a single atom layer thickness of atoms arranged in a regular hexagonal pattern, allowing a very high surface area availability ($\sim 2600 \text{ m}^2/\text{g}$). This in turn allows specific energy stored to be greater than other materials like activated carbon, while also improving electron and ion transport, mechanic strength, and flexibility. In addition, graphenated carbon nanotubes (g-CNTs) have a hollow walled structure of one-atom-thick graphene sheets, rolled at specific angles to allow for optimal electrical conductivity and access for ions to travel. Though carbon nanotubes can greatly improve capacitor performance, the conductivity and efficiency of these systems can be enhanced even more with the use of nanocomposites made of transition metal oxides like manganese dioxide (MnO_2). Along with strong electron-transferring reactions and low resistance, deposits of manganese dioxide are of low cost, high availability, and have a high capacity (1370 F/g^4). MnO_2 can be deposited with a high surface area morphology, coating the electrodes and increasing the system's charge storage capability.

The results for the tests and subsequent images used to scan the electrode surfaces performed by Glass's group were excellent. SEM measurements of g-CNT films with intermediate foliate (or sheet) density show that they are able to serve as excellent nucleation sites for multiple MnO_2 deposits, specifically along individual g-CNTs. These nucleation sites develop a nanoflower-like morphology with petals of the MnO_2 nanosheets in contrast to previously reported formation of deposits on junctions of overlapping g-CNTs. When asked about the reason for surface area morphology increasing the practical charge storage capability, Dr. Glass said "The amount of charge at a surface is directly proportional to the surface area", saying that "higher density

charge probabilities allow higher charge density” as is the case for carbon edges, thus allowing more charge per unit area than basal carbon planes. Further tests of cyclic voltammetry (CV) and chronopotentiometry, which are the standard test used to measure the activity electrochemical systems, were performed to compare the activity of the g-CNT/MnO₂ electrodes with the standards of CNTs, g-CNTs, and CNT/MnO₂ electrodes. The results from the CV curve show that the g-CNT electrodes with electrodeposited MnO₂ had a quasi-rectangular curve, indicating the desired presence of both electrical double-layer capacitance and pseudocapacitance found in asymmetric supercapacitors. The newly formed g-CNT/MnO₂ electrodes outperformed all previous electrode combinations, with the specific capacitance improving with the decreasing scan rate of the CV. Lowering the scan rate allows electrolyte ions to have more time to access the internal volume of the electrode, optimizing the storage capacity performance. Other tests for important parameters such as charge-discharge efficiency, g-CNT density vs. electrode performance, and specific capacitance for the electrodes all showed noticeable improvement from previously tested CNT/MnO₂ supercapacitor systems.

When asked about expansion of the research done by his group on the composite cathodes for superconductors, Dr. Glass said that the next steps will aim to look at other oxide materials such as vanadium oxide, cadmium sulfide, and titanium oxide. Dr. Glass and many experts in the field of supercapacitors believe that manganese oxide is one of the top materials of interest for supercapacitor research, leading to a high possibility of commercial use in the future. In addition, if the properties of the g-CNT graphene foliate growth (e.g. length, thickness, and volume of layers) can be controlled, then it will allow for better optimization of hybrid structures with metal oxide deposits. Some potential applications for the future use of asymmetric supercapacitors include but are not limited to consumer electronics, electric power tools, and vehicle transport.

Summary for use in RSS Feeds

The need for efficient energy and power sources is in high demand, with many researchers studying asymmetric supercapacitors as a potential solution. Researchers at Duke University's Nanomaterials and Thin Films Lab believe that the use of graphenated carbon nanotubes (g-CNTs) electrodes with electrodeposited (ED) MnO₂ in asymmetric (or hybrid) supercapacitors might be the answer. The study shows that the proposed supercapacitor systems offer the best trade-off between high energy density batteries and high power density, significantly improving in several factors like charge-discharge efficiency and overall electrode performance compared to previous carbon nanotube electrodes.

This paper can be accessed here: <http://pubs.acs.org/doi/abs/10.1021/cm504519m>

Interview Transcript with Dr. Jeffrey Glass

April 9th 2015

1) How does the surface area morphology increase the practical charge storage capability?

The amount of charge at a surface is directly proportional to the surface area. One can imagine that charges of like sign want to repel each other and because of this can only crowd into a particular area at a finite density. Thus more area allows more charge. So per-unit area, the charge will be similar for most conducting surfaces, at least to the first order. So increasing surface area simply means more charge given this phenomenon. A second order affect is the fact that some surfaces can allow more charge per unit area than others. This is a function of many complicated factors but one can think about the band structure of the material or similarly the bonding configuration. Higher density charge probabilities in a given bonding configuration can allow higher charge density when they are the primary bonds terminating the surface. This is the case with carbon edges. They allow more charge per unit area than carbon basal planes.

2) Are galvanostatic charge-discharge curves (chronopotentiometry) usually used to compare electrode performances?

Yes but it can depend some on the application. Also, the specific parameters used in the charge-discharge curves can depend on the application that one is focusing on in the research. So if one has a particular charge storage application in mind, for example charging a cell phone, then this will help determine what type of tests are run on the device. A very different type of application, such as neural probes, will generally dictate a different type of test. For example, cell phones may be charged once a day or so whereas neural probes must charge and discharge many times per second in some cases. However, in general, for early stage research many researchers have decided that the galvanostatic charge-discharge curves are a good way to compare electrodes across multiple laboratories. Thus, when testing new materials for charge storage at the early stages, we often utilize this as one of the tests regardless of the different future applications.

3) Can explain to me microwave plasma enhanced chemical vapor deposition (MPECVD) works?

Just like the microwave oven in your house interacts with a material to heat it up, microwave plasma deposition can be thought of as heating up the gas phase molecules used in CVD. Molecules are excited and put into a metastable state so that they can react more easily with each other and with a substrate. They deposit a material that results from the reaction of the excited gas species onto a substrate. The primary mechanism is the interaction of the electromagnetic radiation of the microwaves with the gas molecules. The "plasma" is a result of this interaction in which an electron is ejected from the gas molecule and creates an ionized species - this is the definition of a plasma. When many ions are formed, the process can be self-sustaining. However, many of the gas phase reactions take place between excited species that are not necessarily ionized but are simply in a metastable excited state. The percentage of ions is actually quite small so to obtain reasonable reaction rates we often want the excited species to participate Rather than just the ions.

4) Is there any reason for the foliate growth to reduce to ~3 – 5 graphene layers at the foliate edge?

Yes, this is a thermodynamic consideration and is simply a result of the fact that the material does not want to have a squared off edge because that would be a high-energy state. Just like water goes into a droplet form rather than a flat square geometry, this g-CNT material approaches a similar configuration. Because it has a structured atomic arrangement, unlike water, it does not get entirely rounded but rather a bit more triangular although the reasoning and mechanism is similar. The surface energy of the atomic planes causes the foliates to move from a 5 to 10 or even 10 to 20 layer base to a 3 to 5 layer so that they gradually become thinner at the edge.

5) Do you have any plans to expand your research to other composite cathodes for superconductor research (i.e. a composite other than MnO_2)?

Yes, there are a number of interesting oxide materials that have been utilized for pseudo-capacitance recently. If we can obtain funding we are thinking about looking at such materials as vanadium oxide, cadmium sulfide and titanium oxide.

6) And continuing from the last point, do you see Manganese dioxide and carbon nanocomposite asymmetric supercapacitors being used in the future to meet wide scale energy demands?

Since this research is very early stage, it's difficult to know right now which material will win in the competition for commercial applications. On the other hand, it does seem like manganese oxide is one of the top materials of interest so it would not surprise me if it does find commercial application. But there will be a lot of engineering work required before this happens so it is just a guess right now.

7) You have a very diverse and extensive academic background. Why did you choose to go into research of nanomaterials and thin films?

It is difficult to say why, but I am passionate about research and materials. It is one of those things that you don't really know how to explain but to be happy in your job and excited about going to work every day, it's imperative to find something you like to do. Research on new materials is simply something I found that I am passionate about. Nanomaterials and thin films are a very interesting area that require a lot of diverse knowledge so that is part of what makes them so interesting to me.