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# Carbon Nanotube Materials for Substrate Enhanced Control of Catalytic Activity

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## Objectives

We are interested in developing the scientific principles to control catalysis and electrocatalysis on the nanoscale. We seek to design interfaces and electrodes using nanoscience to permit; (1) highly efficient and robust catalyst utilization, (2) fundamental investigations of the key reaction steps which are relevant to fuel-forming and fuel-cell reactions, and (3) a route away from precious metal catalysts. We approach this problem using carbon single-walled nanotubes (SWNTs) as tunable supports for catalytic species. Thus, we also seek to understand the materials chemistry issues associated with building functional assemblies with SWNTs.

## Technical Barriers

Current carbon support materials in proton exchange membrane fuel cells (PEMFCs) suffer from poor corrosion resistance and high series resistance such that the activity of the catalyst and its utilization are compromised over time. The physicochemical properties of electrocatalysts supported on carbon nanotubes are strongly influenced by the intrinsic properties of the nanotube support. The tunable control over the nanoscale structure of carbon nanotubes provides a unique perspective for studying, controlling, and enhancing the performance of the catalyst/support interaction. We expect fuel cell electrodes with improved stability, reduced requirements for precious metals, and the potential for fuel cell architectures which may be more readily manufactured.

## Abstract

Carbon SWNTs are attractive materials for supporting electrocatalysts. The properties of SWNTs are highly tunable and controlled by the nanotube's circumferential periodicity<sup>1</sup> and their surface chemistry.<sup>2</sup> These unique characteristics suggest that architectures constructed from these types of carbon support materials would exhibit interesting and useful properties.<sup>3-5</sup> Here, we expect that the structure of the carbon nanotube support will play a major role in stabilizing metal electrocatalysts under extreme operating conditions and suppress both catalyst and support degradation. Furthermore, the chemical modification of the carbon nanotube surfaces can be expected to alter the interface between the catalyst and support, thus, enhancing the activity and utilization of the electrocatalysts. We plan to incorporate discrete reaction sites into the carbon nanotube lattice to create intimate electrical contacts with the catalyst particles to increase the metal catalyst activity and utilization. The work involves materials synthesis, design of electrode architectures on the nanoscale, control of the electronic, ionic, and mass fluxes, and use of advanced optical spectroscopy techniques.

## Progress Report

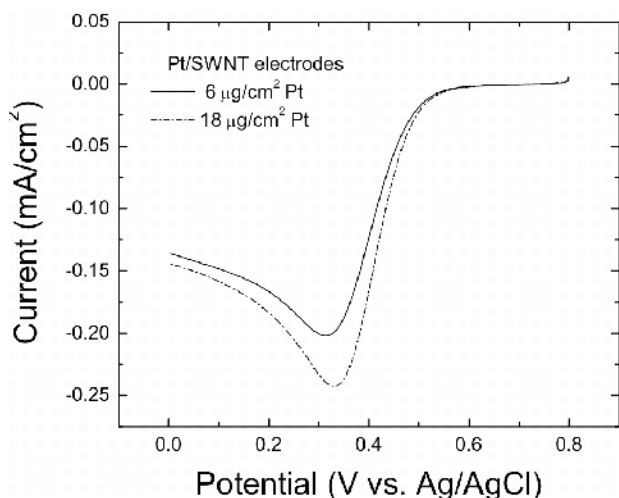
In past years this project has been directed at the growth of nanomaterials for adsorbents and membranes for gas separations and has provided the scientific underpinnings for our EERE-funded work in the area of hydrogen storage. Through these efforts we discovered unique synthetic and purification methods for pure and doped nanotubes, investigated the defect chemistry of nanotubes, studied the interaction between SWNTs and Nafion<sup>®</sup>, and developed methods to disperse catalytic particles onto nanotubes (please see the list of publications and patents which have come from this support). With these advances in-hand we now turn our attention directly to the scientific issues associated with catalysis in fuel-forming and fuel-cell reactions.

An increase in the Pt catalyst utilization efficiency (currently less than 30%)<sup>4</sup> would dramatically decrease the amount of catalyst needed in current PEMFCs. To effectively utilize the Pt catalyst in a PEMFC, the catalyst must have simultaneous access to the gas, the electron conducting medium, and the proton conducting medium. Typically, the catalyst layer for a conventional Pt-catalyzed fuel cell is prepared by an ink-process.<sup>6</sup>

Here, Pt-supported carbon particles are blended with Nafion in order to allow for the simultaneous access of the Pt catalyst to the electron conducting and proton conducting media. A common issue with this conventional blending process has been that the proton transport material, Nafion<sup>®</sup>, tends to isolate the carbon support particles in the catalyst layer, leading to poor electron transport throughout the cell. The use of SWNT-supported electrocatalysts in PEMFCs has the potential to eliminate this problem and improve the utilization efficiency of the electrocatalyst.

Preliminary results (Figure 1) show that the current associated with oxygen reduction on the Pt/SWNT electrodes with 6  $\mu\text{g}/\text{cm}^2$  of Pt is only 20% lower than the current for the Pt/SWNT electrode with 18  $\mu\text{g}/\text{cm}^2$  of Pt. This result suggests that the Pt/SWNT interaction has a pronounced affect on the kinetics of the oxygen reduction reaction. In addition, relatively small amounts of Pt catalyst particles allowed for excellent current densities due to the high surface area and porosity of the SWNT thin films. A variety of Pt particle growth parameters and SWNT thin film processing parameters will be systematically investigated to maximize the Pt utilization efficiency and corrosion resistance with respect to the Pt/SWNT electrodes shown in Figure 1.

The SWNT supports in Figure 1 were synthesized using a thin film preparation method developed in our laboratory. Transparent, optically homogeneous, and electrically conducting films of SWNTs were fabricated using surfactant solubilized SWNT solutions. The solutions were filtered and the films washed with



**FIGURE 1.** Polarization curves for the oxygen reduction reaction at thin film Pt/SWNT electrodes with different Pt loadings (1M sulfuric acid, saturated with oxygen, and sweep rate 5 mV/s). The Pt nanoparticles were directly deposited onto the SWNT thin films using a vacuum sputtering technique. The total amount of Pt was determined from a quartz crystal thickness monitor in the vacuum chamber.

copious amounts of water in order to remove excess surfactant molecules, leaving behind a matrix of high surface area carbon nanotubes. Annealing the films in vacuum at high temperatures in order to induce or drive SWNT recrystallization can subsequently alter the pore size distribution in the matrix. These transparent carbon nanotube films were transferred directly to various substrates. Transmission electron microscopy, Raman spectroscopy, and optical absorption spectroscopy were used to investigate the topology and structure of the SWNT networks and the morphology and size distribution of the catalytic particles. The organization within the SWNT networks was controlled by the surfactant used to solubilize the SWNTs.

## Future Directions

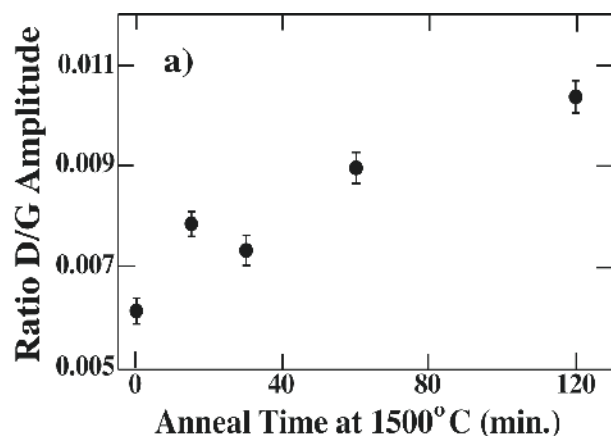
Control over the physical dimensions, location, and intimacy of contact of the catalyst particles will be an important factor in the fabrication of SWNT-supported electrocatalysts with enhanced surface site availability. The chemical and surface properties of carbon nanotubes can be manipulated to affect the extent of the interaction between the catalyst and nanotube surface. We will explore several methods to integrate electrocatalysts onto SWNTs and expect significant advantages over conventional incipient wetness or adsorption techniques.<sup>7</sup>

**Direct Synthesis of Pt/SWNT Materials:** We will explore the *in situ* decoration of Pt nanoparticle catalysts on SWNTs during the high temperature growth of SWNTs by arc-discharge and laser vaporization. The key advantage of our arc-discharge and laser vaporization syntheses over traditional processes for producing fuel cell catalysts is that these methods provide a one-step direct process to produce high surface area catalyst-supported materials of a known composition where the metal catalyst particles and SWNTs are in intimate contact.

**Enhanced Solution Phase Electrodeposition of Catalysts on SWNTs:** Electrochemical techniques are extremely attractive for electrodepositing catalyst nanoparticles onto SWNT supports. Parameters such as deposition potential, time, and solution composition are explored to control growth rate, particle size, and number density. Potential step chronoamperometric measurements coupled with high-resolution microscopy studies will be carried out to provide insights into the nucleation and growth mechanisms of the Pt nanoparticles on SWNTs. Interestingly, the resting potential of the SWNTs is approximately 0.5 V vs. NHE which allows for the spontaneous deposition of certain metals onto the SWNT surfaces. Additionally, we have discovered a novel reductive functionalization reaction which permits the deposition of homogeneous particle sizes as small as 1 nm.

**Stabilization of Catalysts by Dopants in the SWNT Supports:** We have recently discovered new catalysts for the laser synthesis of SWNTs which incorporate boron substitutionally into the lattice.<sup>8</sup> The sp<sup>2</sup>-doped boron atoms are expected to serve as discrete reactive sites for the deposition of atomically disperse metals. In addition, mild surface oxidation processes will be used to improve dispersion and distribution of metal nanoparticles on nanotube surfaces by providing nucleation sites for catalyst growth. The active sites for catalyst adsorption will be controlled during the exposure of the SWNT supports to various purification/oxidation processes. Both the substitutionally doped and oxidized SWNTs will provide trap sites for enhancing electrocatalyst stability.

**Optical Spectroscopy to Determine Electrode Degradation Pathways and Reactive Intermediates:** The degradation of the nanotube support may be simply monitored with *in situ* Raman spectroscopy. We have recently shown that the relative defect densities in SWNTs may be correlated with the Raman intensity of the SWNT D-band.<sup>9</sup> Figure 2 shows the intensity ratio for the SWNT Raman D- and G-bands (D/G) for a purified sample that was annealed to 1,500 °C for varying times in the presence of ~1x10<sup>-5</sup> torr H<sub>2</sub>O. A parallel TEM analysis revealed that this annealing process resulted in the gradual introduction of defects along the edges of the SWNT bundles. The D/G intensity ratio in Figure 2 increases with increasing anneal time, indicating more defects are added during the annealing process. The rising D/G intensity is consistent with the idea that defects not only activate the observation of the SWNT D-band, but also that the intensity may be directly correlated with the number of defects present. This technique is highly sensitive and will allow for various nanotube electrodes to be rapidly evaluated for their stability. By correlating increasing D/G ratios with the Raman SWNT radial breathing



**FIGURE 2.** Raman D/G intensity ratios of a purified SWNT sample that was annealed to 1,500 °C for varying time lengths in the presence of 1 x 10<sup>-5</sup> torr H<sub>2</sub>O.

modes, it will be possible to determine the SWNTs that are the most stable such that optimized electrodes may be fabricated based on the type of SWNT (i.e., semiconducting or metallic).

Infrared spectroscopy is well suited for the study of adsorbed diatomic molecules such as O<sub>2</sub> and H<sub>2</sub> since they are only infrared active in the adsorbed phase. This may be a distinct advantage over Raman spectroscopy for monitoring surface species as both gas-phase and adsorbed molecules are Raman active. Furthermore, reactive intermediates such as hydroxyl or carbonyl groups may easily be monitored with infrared spectroscopy. The formation of hydroxyl groups on catalyst particles will most likely be observed prior to oxidation of the catalyst particle and subsequent degradation. Various particle sizes/positions in the nanotube matrix may be assessed for their relative stabilities. Similarly the formation of either C-OH species or carbonyl species on the nanotube surfaces will most likely precede the formation of defects. By combining *in situ* infrared investigations with Raman analyses an in depth understanding of the degradation processes will be realized. This basic study will not only allow for more durable electrode materials to be nanoengineered, but will also potentially elucidate the scientific underpinnings for degradation in other catalytic processes.

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