Chapter 10: Future Work

The most exciting phrase to hear in science, the one that heralds the most discoveries, is not "Eureka!" (I found it!) but "That's funny..." — Isaac Asimov

Research is the process of going up alleys to see if they are blind. — Marston Bates

10.0. Introduction

I am unsure of the exact details of the work that I will do next, but I have several ideas about what future directions students should take that are along the lines of what I have accomplished so far. If I did have more time, I would evaluate each of these ideas more thoroughly experimentally. It should also be noted that a few of these ideas are topics that I have discussed with others, but at this point have not been implemented and therefore are being recorded in this tome to ensure that they are known. A few of the ideas are currently being pursued.

10.1. Improved Electrospray Apparatus

The first suggestion is for the improvement of the electrospray source being used for the deposition of nano-structured fuel cell material. Currently, the gas flow for the electrospray is introduced into the chamber through two ports located on the external radius and exits through four ports located beneath the substrate holder (see appendix I for more details). The primary responsibility of the gas flow is solvent evaporation with the secondary purpose of ion scavenging. With the gas flow entering and exiting the chamber away from the actual electrospray source, the gas flow may not be utilized as effectively as possible.

To improve the gas introduction method, a minor change in geometry can be made. The gas should be introduced closer to the electrospray source to generate as high of a superficial velocity near the electrospray tip as possible. The construction of a piece so that the gas flow is coaxial with the electrospray capillary should improve the evaporation. An unexpected benefit may be that the resultant electrospray of particles are smaller for a reason unrelated to evaporation. As the gas flow is heated before flowing into the chamber, introducing it closer to the electrospray capillary could convectively warm the capillary that would conductively warm the electrospray solution. Increasing the liquid temperature would decrease the surface tension of the solution. The decreased surface tension has been shown previously to decrease the particle size produced.

This idea is not without a few uncertainties that would need to be solved. Primarily, what should the characteristics of the gas flow be to ensure superior operation. The relevant parameters necessary to evaluate should be gas flow rate and gas temperature. These would have to be optimized to produce the desired structure.

10.2. Conductivity of Nanoscale Solid Acid Fuel Cell

The second suggested project is an alternative method to fabricate nano-structured materials for a more fundamental study of fuel cell conductivity. Currently, the electrospray is being utilized to decrease the feature size of the fuel cell material so that it matches the catalyst size. The electrospray has reduced the electrolyte size to 100 nm, but the effect of reducing the feature size is not clearly demonstrated with this study. The particles agglomerate on the surface, resulting in structures with nanoscale features and larger overall structures.

An alternative approach to fabricate fuel cell material with uniform size is through using a template with uniform pore size. A material such as aluminum oxide can be fabricated so that it has uniform pores with defined sizes. While aluminum oxide is not appropriate due to reactivity with CDP, other materials can be used. The membrane would need to be electronically insulating and semirigid so that it could withstand some mechanical manipulation. The idea would be to fill the pores of the porous membrane with the fuel cell material. A few simple procedures could be successful such as spin coating a saturated solution into the porous material or solvent evaporation from a membrane using the incipient wetness method to fill the pores. Once filled, thin layers of catalytic material could be evaporated or thermally deposited onto the electrode surface. Varying the pore size and the catalytic material would permit study of a few important aspects of fuel cell conductivity. Both fuel cell performance measurements as well as symmetric cell impedance testing could be performed to ascertain these effects.

Beyond examining conductivity mechanism as a function of catalyst material and pore size, the porous membrane could be used as a template for electrode manufacture. Catalytic material could be deposited into the pores first, covering the walls with a thin film. The remaining pore could be filled with fuel cell material. After placing the filled porous material onto a pressed fuel cell pellet, the porous membrane could be removed, exposing the catalytic surface area. The resultant fuel cell electrode triple phase contact area could be maximized with judicious choice of pore size, pore length, and catalyst thickness.

10.3. Tandem Differential Mobility Analyzer Growth of Carbon Nanotubes

While these suggestions have been focused on ideas for fuel cell related applications, my work has been primarily focused on other areas. One of the interesting extensions of the current work would involve the combination of the tandem differential mobility analyzer (TDMA) and carbon nanotube growth experiments. Much work has been completed on *in situ* growth of carbon nanotubes from catalyst particles formed in the microplasma.[*1-3*] In these studies, the measurements had two limitations. First, they were performed using a nano-DMA. While designed to measure particle size in the 3 to 30 nanometer range,[*4*] this instrument does not have a resolution as high as would be desired in the 1–5 nm range to distinguish between agglomeration and monodisperse particle size distributions. The second issue is that the entire particle size distribution is subjected to the carbon nanotube growth conditions. With the high particle concentration and the length inside the growth furnace between microplasma reactor and measurement site, the particles should consist mostly of agglomerates rather than individual particles. The agglomerates would have a complicated surface structure that may allow multiple nanotube growth from a “single” particle.

Using the TDMA configuration with the nano-RDMA would most likely solve these issues.[*5*] The first nano-RDMA would reduce the number concentration so that additional residence time in the nanotube growth section would not lead to particle agglomeration. The first nano-RDMA would significantly narrow the particle size distribution as well, permitting data analysis to determine how a narrower distribution of catalyst size affects nanotube growth rate and type of nanotube produced. Without the initial size selection, the average growth rate is attributed to the average size change of the original distribution.

The reduced particle number concentration will permit the carbon nanotube growth precursor to be varied over a few orders of magnitude. Higher precursor concentration should enable growth kinetics to be measured for nanotubes of substantial length without the complicating effects of agglomeration. The longer nanotubes will have a very large aspect ratio that will be interesting to study from a mobility perspective.[*6*] At some length, the mobility should deviate from the model prolate spheroid that has been previously used to describe the particle.

10.4. Sensitive Faraday Cup Electrometer

One of the biggest limitations in scientific measurements is low signal detection and amplification. For the field of aerosol science, low signals typically imply particle concentration below 10^4 per cubic centimeter. A faraday cup electrometer (FCE) is not appropriate below this concentration range as the noise level of these instruments is ±0.1 fA due to thermal noise in the shunt resistor of the operational amplifier. To measure particle concentrations below this threshold requires usage of a condensation particle counter (CPC) or similar technology. This detector takes submicron particles and condenses vapor on the surface so that the particle size grows substantially, resulting in a particle larger than a micron. The enlarged particle scatters sufficient intensity so as to make low concentrations detectable. Below a critical size ($D_{p,50}$), the efficiency of particle enlargement is less than 50 percent. While improvements are being made on this style of detector, the presently reported size limit for detection is 1.3 nm.[*7*] The reason for this limit is that particles below this size cannot be activated for enlargement to sufficient sizes in order that scattered light can be detected from the enlarged particle. Changing the working fluid improved the detection limit, but the progress has resulted in incremental improvements.

The size detection limit of the CPC is not present in the FCE. Rather than completely discounting the FCE, an alternative circuit design could be used and is being currently pursued. The shunt resistor is responsible for the Johnson noise that limits the lower detection current to greater than 0.1 fA.[*8*] A better strategy is to use a different feedback element: a capacitor with a capacitance on the order of 10 fF. The resulting circuit is an integrating operational amplifier that has a detection limit in the attoAmps range. The major obstacle is designing the circuit so that the integration can be reset, but this has been demonstrated by others.[*9*] The detection capabilities can be further improved through cooling this circuit with a thermoelectric element, to reduce thermal noise. Using this detector could eliminate the need for CPCs and the requisite working fluids that are a considerable hazard when operating in a reduced pressure environment aboard an airplane.

10.5. Nanoparticle Calibration Source for Differential Mobility Analyzers

The calibration of a Differential Mobility Analyzer (DMA) has been performed in two ways. The first method utilized an aerosol source to generate a broad range of diameters and two DMAs. The DMAs are assembled in the Tandem DMA arrangement with the first DMA providing a narrow distribution of the particles to the second DMA that was used to measure the distribution. It is often difficult to obtain broad distributions smaller than 5 nm.

The second method utilized an electrospray source to aerosolize molecular ions or polystyrene beads that are measured in a single DMA. The particles used as the size standard must have well-defined median size and a size distribution that is narrow or monodisperse so that the measured resolution will be that of the DMA. Molecular ions typically have a mobility diameter below 2 nm.[*10*] Larger molecules can have multiple charge states that must be identified using a mass spectroscopy, but do not usually conform to the shape of a spherical particle. Polystyrene spheres are typically used only for diameters larger than 10 nm, as smaller spheres are not well characterized for size, not as narrowly dispersed as would be desired, and not widely available.[*11*]

An interesting calibration standard in the 2–6 nm size range would be quantum dots. Quantum dots are semiconducting nanoparticles comprised of II-VI materials that have photoluminescent properties. The photoluminescence emission wavelength depends on particle size, and could be used to characterize the mean particle diameter and particle size distribution with an independent non-destructive method. These small particles are also spherical in nature and widely available in very narrow size distributions. These particles could be electrosprayed as was attempted with the molecular ions. It will be important to use a radioactive source to reduce the charge state to a single charge. A minor difficulty could be the surfactant layer that caps the particles, but this should lead to an easily correctable diameter offset.

10.6. Nanoparticle Synthesis Using a Water Plasma Electrospray

The primary application of electrospray has been to aerosolize molecules for the purposes of analysis with mass spectroscopy. The electrospray produces highly charged liquid droplets containing the analyte that evaporate until only the analyte remains in the droplet. The parameters of the electrospray will determine the amount of analyte remaining after the droplet has evaporated. Evaporation of low volatility liquids can be expedited through heating the ambient gas.

Recently, the combination of an electrospray and a furnace has been reported to produce nanoparticles.[*12*] The analyte was replaced with a soluble but low volatility organometallic precursor. The droplets produced with the electrospray were passed through a furnace with the assistance of a gas flow.

The furnace is necessary to decompose the precursor to form nanoparticles, but the residence time in the furnace will limit the maximum concentration of monodisperse particles that can be produced. An alternative to the furnace may be capable of producing nanoparticles. It is well-known phenomena that at high applied voltage a plasma will form at the tip of the Taylor cone, as shown in figure 10.1. This phenomena has recently been examined in more detail.[*13*] The electric field at the tip of the Taylor cone is sufficient to cause breakdown, forming a plasma glow. This plasma could produce nanoparticle provided the glow has energetic electrons that can decompose the organo-metallic precursor or creates a reductive environment.

The choice of precursor will be critical to the success of this idea. An initial attempt used auric acid (i.e., $HAuCl_4$) in an attempt to form gold nanoparticles. Nanoparticles did form with the glow, but formed in its absence as well. It was determined that the stainless steel capillary reacted with the acid, reducing the gold salt to its zero-valent state and forming nanoparticles. Selecting an organometallic precursor that will not react with the capillary should permit investigation of whether the plasma can form nanoparticles.

The formation of nanoparticles can be monitored using standard aerosol techniques such as size analysis with a differential mobility analyzer with careful attention being paid to the charge state of the particle. The particles can then be collected electrophoretically for *ex situ* size and composition analysis. Nanoparticles of multiple compositions could be formed through changing the precursor in the solution. In general, the plasma glow of the electrospray could be an ideal source to produce nanoparticles.

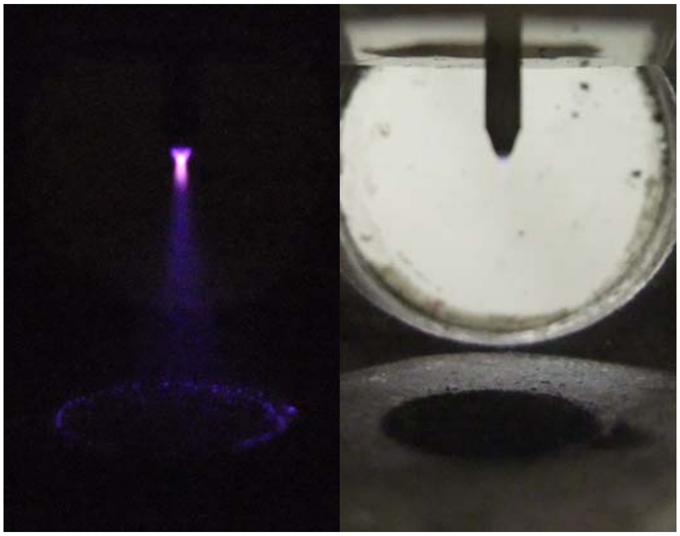

Figure 10.1. Electrospray Plasma

Image of the plasma that develops at the tip of the Taylor cone of an electrospray taken in the dark to highlight the plasma glow that develops. The second image portrays the electrospray apparatus in the light. A faint glow still appears at the tip of the capillary.

References

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