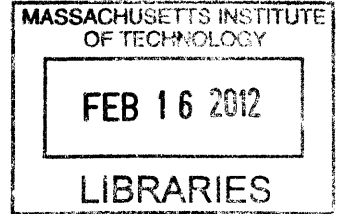


Sonoelectrochemical Synthesis of Submicron Metal Powders

By

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B.S., Mechanical Engineering
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Requirements for the Degree of Master of Science in
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ABSTRACT

Pulsed sonoelectrochemical synthesis is a widely used technique for producing nanoparticles. In this technique, alternating pulses of electric current and power ultrasound are applied to an electrochemical cell to create and suspend particles in the electrolyte. The pulsed technique largely separates the particle morphology defining physical action of electrochemistry and ultrasound. Despite the large body of work characterizing the pulsed method, surprisingly little is written about the behavior of particles in the continuous case, where electric current and ultrasound are simultaneously present. In this thesis, continuous ultrasound assisted electrochemical synthesis of nanoparticles is established. Potentially useful mechanisms for particle size and shape control in continuous reactors are discussed. A continuous sonoelectrochemical reactor was designed and demonstrated to produce submicron copper powders. Improvements to the batch reactor design are proposed to extend the technique to a flow reactor useful for commercial production of submicron metal powders.

Thesis Supervisor: Taofang Zeng
Title: Principal Research Scientist

Table of Contents

1.0 Introduction	6
2.0 Background	9
2.1 Electrochemistry	9
2.2 Electrodeposition of Powders	11
2.3 Ultrasonic Processing	11
2.4 Ultrasonic Electrodeposition	14
3.0 Experimental Apparatus Development	16
3.1 Initial Reactor Design	16
3.2 Improved Reactor Design	19
3.3 Improved Reactor Test	22
4.0 Discussion and Analysis	27
4.1 Continuous versus Pulsed	27
4.2 Particle Behavior in Sonoelectrochemical Reactors	28
4.3 Interactions on Electrode Surfaces	29
4.4 Interactions in Suspension	30
4.5 Suspensive Electrode	33
4.6 Continuous Flow Concept	39
5.0 Conclusions	41
5.1 Potential Applications	41
5.2 Future Development	42
6.0 References	44

Table of Figures

1.1 – Schematic of operating sonoelectrochemical cell _____	7
2.1 – Schematic of acoustic streaming flow lines from an ultrasonic horn _____	13
3.1 – Initial sonoelectrochemical cell design _____	17
3.2 – Improved sonoelectrochemical cell design _____	18
3.3 – Histogram of particle diameters from improved reactor test _____	23
3.4 – TEM micrograph of submicron Cu particles depicting the smallest visible size ____	25
3.5 – TEM micrograph of submicron Cu particles depicting shape uniformity _____	26
4.1 – Schematic of the relative pulse timing for pulsed sonoelectrodeposition _____	28
4.2 – Schematic of cathode surface particle behaviors _____	31
4.3 – Schematic of dependence of particle adhesion with diameter _____	32
4.4 – Schematic of shape dependence of particle durability in ultrasonic fields _____	35
4.5 – Schematic of mechanically driven particle/particle interactions in suspension ____	36
4.6 – Schematic of suspensive electrode concept _____	37
4.7 – Schematic of charge driven agglomeration _____	37
4.8 – Continuous flow sonoelectrochemical reactor concept _____	38

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1.0 Introduction

Nanostructured materials can have unique size and shape dependent properties which can differ greatly from their bulk form [1]. These properties are potentially useful in medicine [2], catalysis [3], electronics [4], and countless other fields. The past several decades have seen the development of a tremendous variety of techniques for the production of nanomaterials, such as evaporation and condensation in low pressure inert gases [5], combustion flame [6], laser ablation [7], chemical vapor deposition [8], electrospray [9], and precipitation [10]. Despite their useful properties, and the myriad production techniques, widespread commercial application of nanostructured materials has been limited [11]. In order to speed adoption of such nanotechnology, even cheaper, more flexible, and more reproducible methods of producing nanomaterials must be developed.

This work concerns the sonoelectrochemical synthesis of submicron sized metal powders. The sonoelectrochemical technique is based on a discovery [12] that electroplating an operating ultrasonic horn, rather than evenly coating the horn's surface, can instead yield a suspension of nanoparticles. Sonoelectrochemical methods promise to be a technique for the low cost bulk production of nanostructured materials.

An example sonoelectrochemical cell is shown in Figure 1.1. At first glance, it appears to be a typical copper plating electrochemical cell. Immersed in a bath of CuSO_4 are two electrodes, the anode and cathode. A power supply drives a current across the cell. At the sacrificial anode, copper atoms are oxidized to Cu^{2+} ions. The ions migrate

through the electrolyte bath and are reduced on the cathode surface. Instead of a typical stationary metal electrode, the cathode is a titanium ultrasonic horn. Before the copper deposit can build up enough to coat the electrode, it is broken up and expelled into suspension in the electrolyte. Understanding the mechanisms by which these deposits grow, disperse, and behave in suspension is necessary to develop the technology for eventual commercial application.

Sonoelectrochemistry is the intersection of several fields: electrochemistry, power ultrasound, and nanotechnology. Understanding how each of these disciplines contributes to the process should enable the adjustment of experimental parameters to tune the properties of the produced particles to suit. What follows is a general overview of each technology, with particular attention paid to aspects important to understanding sonoelectrochemical synthesis.

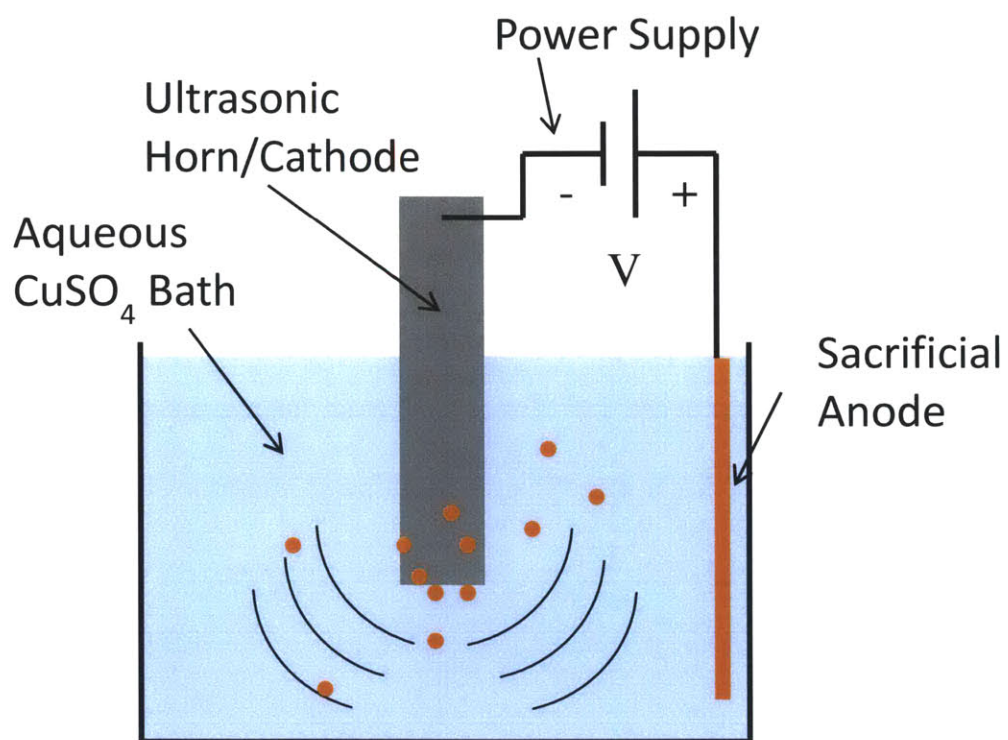


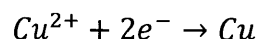
Figure 1.1 – Schematic of operating sonoelectrochemical cell

2.0 Background

2.1 Electrochemistry

Electrodeposition of metals, also known as electrocrystallization or electroplating, is a process where metal ions in solution are driven by an electric field to coat an electrode surface. The morphology of the crystallized metal, known as the electrodeposit, can vary dramatically on the particulars of the electrochemical setup. Electrochemical cells can be designed to cover an electrode in a thin film of material, in a technique known as electroplating. In general, interrelated parameters such as current density, electrode potential difference, bath temperature, metal ion concentration, electrolyte conductivity, bath additives, electrode material and geometry, and bath size all contribute to the character of the deposit. A number of techniques have been developed to produce nanostructured metal products by electrodeposition [13].

Copper was chosen as the product metal for this work because of the large volume of literature concerning the production and characterization of nanostructured copper materials. Typically, the electrodeposition of copper is governed by the following reaction:



Dissolved copper ions are reduced on the cathode of an electrochemical cell to form metallic copper. Though the reaction kinetics of many baths and additives are not fully understood [14], copper electrodeposition is a well characterized industrial process. The

designation of experimental parameters is simplified by the large volume of available trade and scientific literature.

The most widely used copper plating bath is based on an aqueous solution of copper sulfate, CuSO_4 , with copper ion concentrations in the 10-60 g/L range [14]. In solution, the solvated Cu^{2+} atoms are charge carriers, and eventually deposit on the cathode by reduction. Higher metal ion concentrations enable faster mass deposition [14], which can be useful for higher production rates. Addition of sulfuric acid, H_2SO_4 , to the bath increases conductivity by introducing nonreactive charge carriers. Raising the bath temperature tends to increase the conductivity of the electrolyte [15]. Increasing the conductivity of a given bath tends to minimize potential gradients in the electrolyte, which gives more uniform deposits [16].

The morphology of conventionally electrodeposited copper particles is well understood to depend primarily on current density [17]. At all current densities, the deposited particles have some degree of dendritic character. At relatively low current densities, the dendrites are largest, broadest, and most branched. With increased current density, the particles become flatter, with large crystalline surfaces. Even further increased current densities yield different compact dendritic structures. Based on this knowledge, copper appears a good choice for nanostructure production, as the large deposits tend to have dendritic, and therefore generally more fragile structure.

2.2 Electrodeposition of Powders

Conventional electrodeposition has been used to produce metal powders industrially for at least 80 years [18]. Commercially available powders produced by this method have mean diameters in the 10-100 μm range [19]. There are several reported techniques employed to control the size of these conventionally electrodeposited powders. Generally, electrodeposited metals can form powders above the limiting diffusion current [20]. Variations in the limiting current can be achieved by using a bath with lower metal ion concentration, or by adding non reacting conductivity enhancers [19]. Driving the electrochemical cells at over-potentials sufficient to decompose water evolves hydrogen at the cathode, which can help loosen powder and yield dendritic type powders [21]. Organic electrocrystallization inhibitors, such as chelating or complexing agents [22] or surfactants [23], can be added to baths to reduce particle size. Removal of electrodeposited powders can be done actively, by brushing [18] or by shocking the powder off by rapping the cathode [21]. Alternatively, cathodes with low product metal surface adhesion, such as graphite, passively shed powder under gravity [24].

2.3 Ultrasonic Processing

Ultrasound is generally defined as acoustical vibrations of more than 20 kHz. The use of these waves can be divided into two main categories: diagnostic and power ultrasound [25]. Diagnostic ultrasound generally encompasses applications where ultrasonic waves do not dramatically change the sample. Medical ultrasonography concerns the nondestructive transport of ultrasonic waves through tissue, and is an

example of diagnostic ultrasound. Power ultrasound, however, concerns applications where ultrasound has intentional and often dramatic effects on the sample. Ultrasonic welding couples acoustic vibrations to friction between two work pieces to join them. Sonochemistry is another application of power ultrasound, where the application of ultrasonic energy enables high temperature and pressure chemistry to be carried out with great simplicity.

Several technologies have been developed to produce power ultrasound. The two main types used in the laboratory setting are piezoelectric and magnetostriction. Piezoelectric materials deform when electrically polarized. Stacks of piezoelectric material are built and driven at ultrasonic frequencies to generate power ultrasound. Magnetostriction is the tendency of a material to deform when magnetized. This is the effect responsible for the 120 Hz hum of large transformers [26]. Ultrasonic generators based on this principle magnetize and demagnetize material at an ultrasonic frequency. There are several methods to couple the ultrasound to the experiment. Ultrasonic cleaning baths accomplish this by fixing the generator to the floor or wall of the bath. In an ultrasonic horn, the ultrasonic generator is fixed to a quarter or half wave resonator. For strength and chemical stability these resonators are typically constructed from a titanium alloy.

Power ultrasound provides two important effects to electrodeposition; cavitation and acoustic streaming. An ultrasonic wave, like any other acoustic wave, is simply a longitudinal wave that propagates by compression and decompression. When

propagating through a fluid, at high enough amplitude the pressure during the decompression cycle can be lower than the vapor pressure of the fluid or gasses dissolved in it. When this occurs, some of the dissolved gas or fluid vaporizes and forms bubbles, in a process known as cavitation. As the pressure cycle continues, the gas bubble is compressed. Eventually, sometimes after many compression cycles, the bubble will collapse. This is a particularly violent process, as the temperature can routinely reach 5000 K [27]. This collapse generates shocks that can deform and erode nearby materials. As a result, even ultrasonic resonators made of titanium tend to wear.

Acoustic streaming is the steady bulk flow of a liquid driven by the absorption of acoustic waves. In power ultrasound applications, like ultrasonic cleaning baths, the flow can be quite pronounced, amounting to a vigorous mixing action. Just like other mechanical mixing, this bulk flow tends to minimize temperature and concentration gradients [28]. A schematic representation of the acoustic streaming flow lines is included in Figure 2.1.

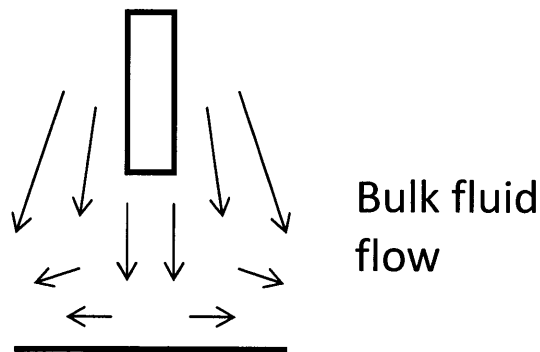


Figure 2.1 – Schematic of acoustic streaming flow lines from an ultrasonic horn

2.4 Ultrasonic Electrodeposition

The application of ultrasound to electrodeposition dates back to at least 1936, with the publication pioneering work on the subject [29]. These researchers found that when a plating bath was subject to ultrasonic waves, a rippling pattern with the same wavelength was formed in the electrodeposit. This basic work proved that ultrasound changes reaction kinetics of electrodeposition. Subsequent studies of the interaction found that the application of ultrasound can improve the industrial electrodeposition process. Several reviews of the topic have been published [30] [31]. Though most of the work concerns topics of utility to industrial users, such as electrode geometry and current densities, there are many results useful to users interested in the production of nanostructured materials.

The effects of cavitation from the application of ultrasound are the most apparent. As described earlier, the formation and implosion of gas bubbles can violent localized shocks, which can dislodge nearby adhered material and gas bubbles. When electrodeposition conditions favor dendrite growth, cavitation is known to break off perpendicular growths and inhibit dendrite formation, instead favoring dense crystal growth [25]. When a cavity moves or collapses near a surface, it displaces fluid and creates rapidly moving streams near the surface [32]. This is important from the perspective of electrodeposition, because the effect causes bulk transport of fluid from outside the conventional double layer. Effectively, this increases the maximum rate at which ions can be transported to the surface for reduction because the process is no

longer diffusion limited [30]. For purposes of calculation, this can be thought of as a decrease in the size of the Nernst diffusion layer.

3.0 Experimental Apparatus Development

3.1 Initial Reactor Design

Initial experiments were run on an electrochemical cell provided by a colleague. The cell was operated in a 500 mL glass beaker. A cylindrical sheet of 18 gauge bare copper was used as an anode. The tip of a ½" diameter solid tip Ti-6Al-4V titanium ultrasonic horn was used as a cathode. Power was supplied to the cell by an Agilent U8002A power supply, which could be operated in both galvanostatic and potentiostatic modes. Stranded copper wire soldered to the anode provided positive electrical connection to the power supply. The titanium cathode was connected to the power supply by twisting a stranded copper wire around the base of the ½" diameter section of the horn. 20 kHz Ultrasonic energy was supplied to the horn by a VCX500 500 watt piezoelectric PZT ultrasonic transducer. The electrochemical cell was temperature controlled by immersing the base in a bath supplied by the external output of a conventional thermostated laboratory water bath. An image of this cell is provided in Figure 3.1. This image was taken after an experimental run, and depicts the cathode after it was removed from the electrolyte.

Preparing and running the electrodeposition experiment was relatively simple. First, the electrolyte bath was prepared by dissolving a quantity of copper sulfate in the required volume of water, typically 250 mL. After transferring this transparent blue electrolyte to the bath, the thermostat was activated and the cell brought to thermal equilibrium. The ultrasonic horn was positioned such that the tip was approximately 1 cm

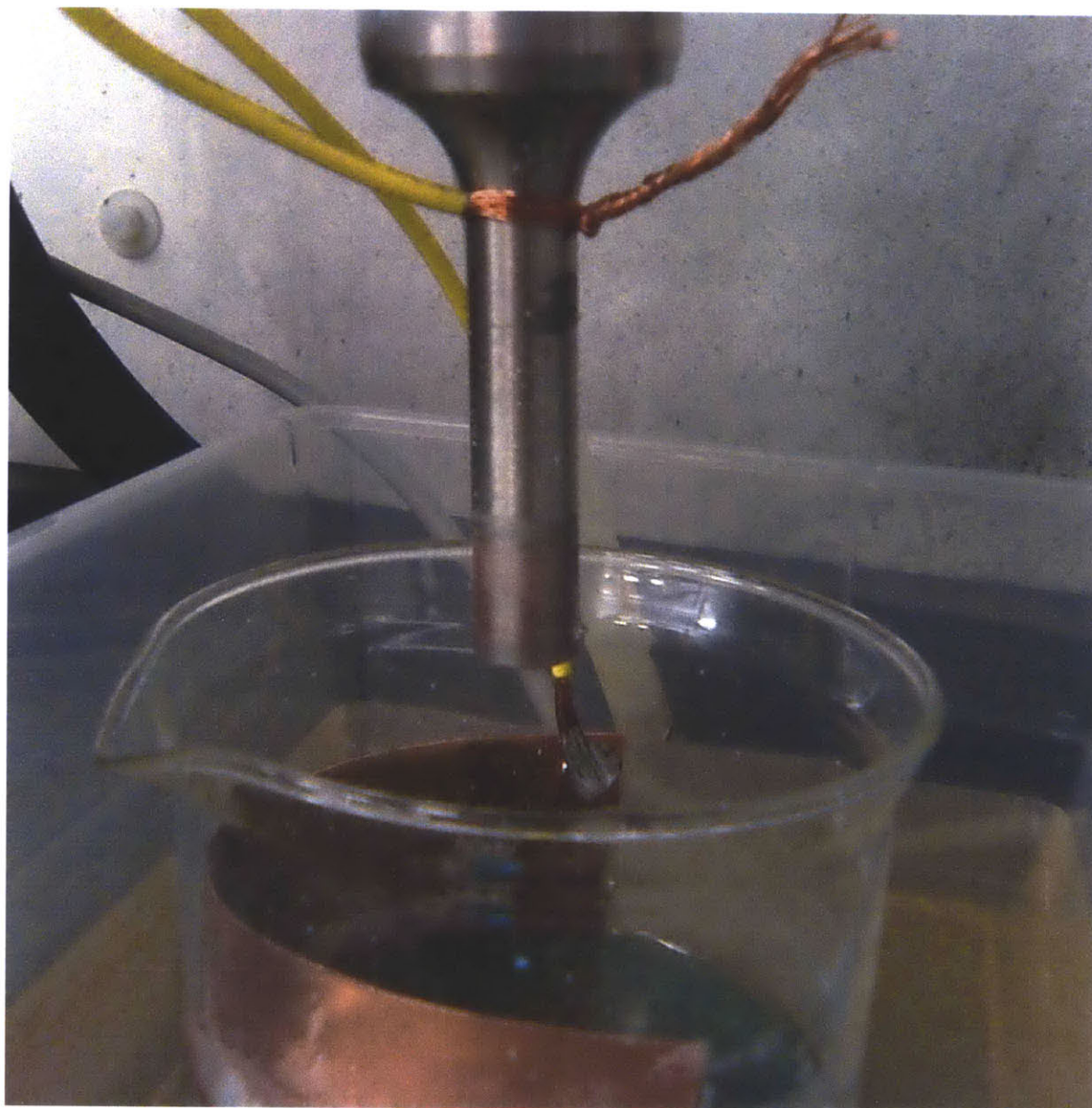


Figure 3.1 – Initial sonoelectrochemical cell design

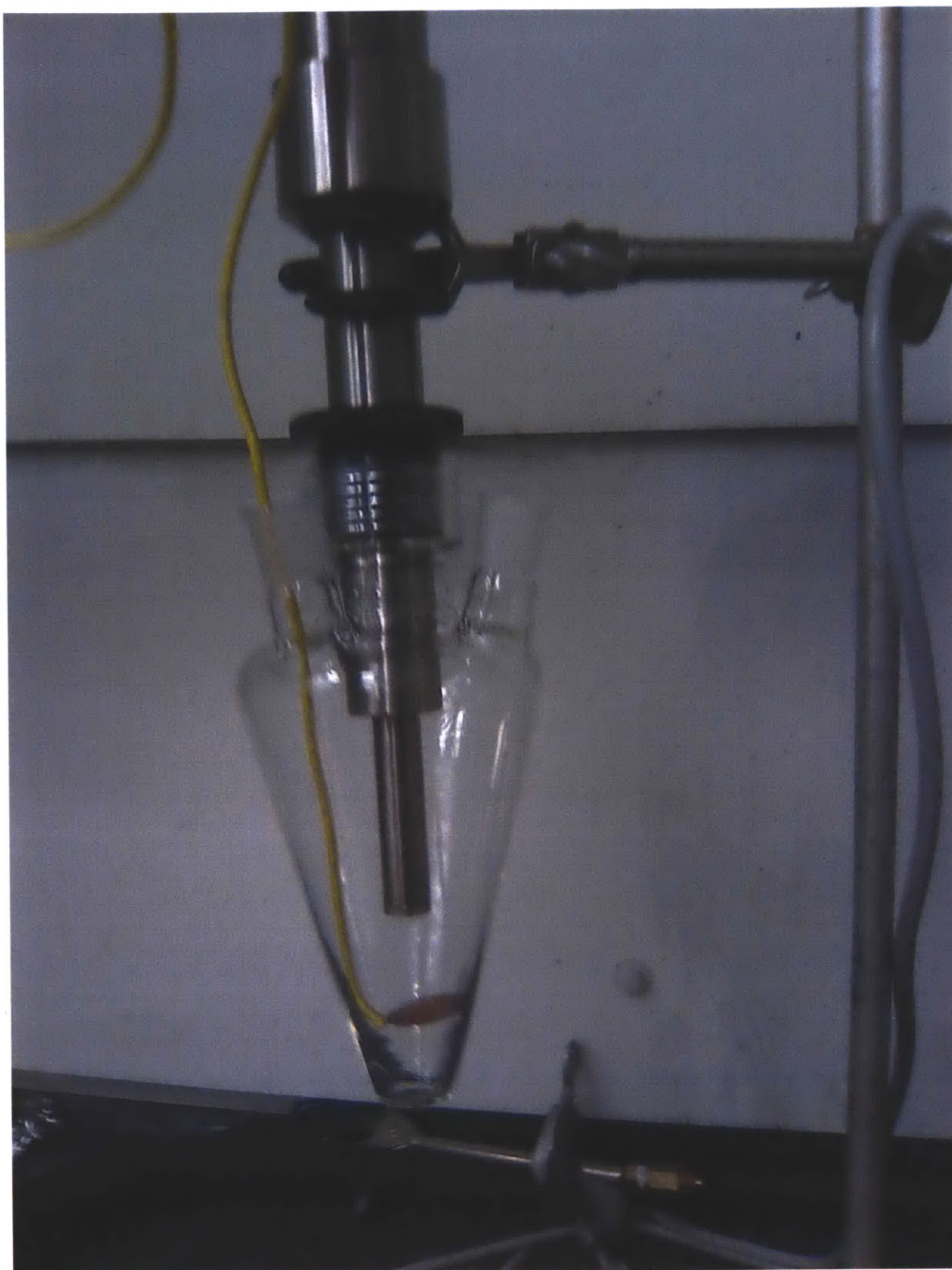


Figure 3.2 – Improved sonoelectrochemical cell design

immersed in the electrolyte, giving an immersed surface area of 1.3 cm^2 . Then, the horn was activated and the output power was adjusted high enough such that cavitation just started to appear. Then, the power supply was activated. After around 20 minutes, the electrolyte would gradually start to turn an opaque green. This color indicated that large quantities of copper particles were in suspension. At this point, the power supply was turned off, then the ultrasonic power.

Samples of the suspended powder were collected using a centrifugation technique. First, the electrolyte solution was decanted from the electrochemical cell to remove the largest copper particles. Then, the solution was poured into 50 mL plastic centrifuge tubes and centrifuged for 10 minutes. After removal from the centrifuge, the now clear blue electrolyte solution was carefully poured out, leaving a thin but visible coating of copper particles on the surface of the centrifuge tube. The tubes were then filled with a convenient fluid, such as water or ethanol, and shaken to return the particles into suspension. TEM samples were prepared by dropping a drop of suspended particles on a carbon coated copper mesh TEM grid from SPI. These samples were then characterized by a DeLong LEVM5 desktop SEM/TEM.

3.2 Improved Reactor Design

The initial reactor had many design flaws. Firstly, the ultrasonic horn, being shared equipment, had a somewhat eroded tip. Tip erosion is an unavoidable process when an ultrasonic horn is used to produce cavitation bubbles. Instead of being an ideal flat surface, the tip of the horn was pitted and rough. This reduces the efficiency of the

ultrasonic horn, as well as promoting fouling, as copper would entrain in the pitted surface and become difficult to remove. The cylindrical portion of the horn tended to entrain copper as well. Figure 3.1, which depicts the initial cell immediately after use, shows the copper fouling of the cylindrical portion of the titanium horn. Additionally, the continuity of the electrical contact for the cathode was suspect, as the hookup wire wasn't securely fixed to the cathode.

Several improvements to the cathode were made. The updated design is pictured in Figure 3.2. First, as the titanium horn was damaged irreparably, a new resonator was purchased. The new horn had a removable and replaceable tip, which means it will be possible to refurbish it in the future when the tip becomes worn. In order to reduce the theoretical problem of deducing the mechanisms of cathode particle formation and separation, as well as to bring the work in line with most of the reported sonoelectrochemical literature, the problem of insulating the cylindrical portion of the cathode was addressed. Though most papers mention that the cylindrical wall of the cathode was insulated [33], the literature is often ambiguous about the precise construction of this insulation. After several attempts it was found that a section of heat shrink tubing, shrunk around the immersed part of the cathode, worked well. It's worth pointing out that placing solid materials in contact with the titanium horn tends to damp the resonator, so it's best to minimize the amount of heat shrink tubing used. The last improvement to the cathode was the electrical connection to the power supply. While it would have been better to have a solid connection, it was discovered that soldering to

titanium is nontrivial. The new ultrasonic horn was purchased with an adaptor for a removable reaction vessel. When the adaptor was installed, it was possible to assemble the instrument with the cathode wire squeezed in place. The connection was robust enough that it didn't require tightening after every run, like the twisted wire did on the initial cathode.

Improvements were made to the anode as well. In the initial design, the anode was constructed from a piece of copper sheet. Chosen for the sake of symmetry, the cylindrical anode was positioned in concentric with the cathode. The anode sat tight against the walls of the glass reaction vessel. The immersed surface area of this electrode was approximately 80 cm^2 , about 60 times larger than the anode area. It was found that during operation, the electrode tended to trap a thin layer of electrolyte between it and the surface of the glass. Layers like decrease the thermal conductivity of the wall, possibly raising the temperature of the electrolyte. As such, a much smaller anode was designed for the improved reactor. This anode, also made of copper, was circular and for the sake of symmetry was placed underneath the cathode. Electrical connection to the power supply was made by soldering a stranded copper wire to the back of the plate. This wire allowed the anode to be easily repositioned. Another consideration for the anode was whether to make it sacrificial or passive. Sacrificial anodes can be useful for maintaining metal ion concentration in the electrolyte, ideally where one atom is ionized for every ion that is passivated. However, attention must be paid to the relative efficiencies of the anode and cathode. At sufficiently large over-potentials, side reactions such as the

decomposition of water can occur. Differences in electrode reaction efficiencies can cause metal ion concentrations to increase [16]. Such imbalances may disturb carefully controlled industrial or laboratory electrodeposition reactions.

The last improvements were made to the cell itself. The initial reaction vessel was an open beaker, which allowed electrolyte to spray out and evaporate freely. Additionally, the reaction vessel wasn't mechanically coupled to the ultrasonic horn assembly, which meant that the relative electrode geometry wasn't set. During operation, the glass beaker would occasionally drift, driven by currents in the cooling bath or the coupled oscillations from the horn. Additionally, the initial reactor vessel was large, given the minute quantity of samples required. Therefore, the new vessel was chosen such that a smaller volume of electrolyte could be easily processed. The new reaction vessel was supplied by the company that produced the ultrasonic horn, Sonics and Materials, Inc. With a supplied adaptor, this vessel attached to the ultrasonic horn, enabling more precise control of the relative electrode positions. The vertical position of the horn was adjustable in the reaction vessel, so the volume of electrolyte to be processed could be adjusted to suit.

3.3 Improved Reactor Test

The following is an example run, which demonstrates the ability of the machine to produce nanoparticles. 250 mL of 0.5 M CuSO_4 was prepared and loaded into the sonoelectrochemical cell. The cell was placed in a water bath and kept temperature stable at 30 C. The ultrasonic horn was activated, and the output was adjusted until

cavitation just started to occur. Then, the power supply was activated in potentiostatic mode at 1.1 V. Over the course of 20 minutes, the current rose from an initial value of 0.21 A to 0.43 A. After 20 minutes, the power supply and the ultrasonic horn were turned off, in that order. The particle suspension was centrifuged and samples prepared for the TEM. Figure 3.4 and Figure 3.5 are TEM images of the particles. The images show a range of particle sizes, with many particles in the sub 100 nm range. Images were processed in ImageJ, and a histogram of particle diameters was prepared, presented here as Figure 3.3. The size distribution of the particles is broad, but weighted heavily towards below 100 nm.

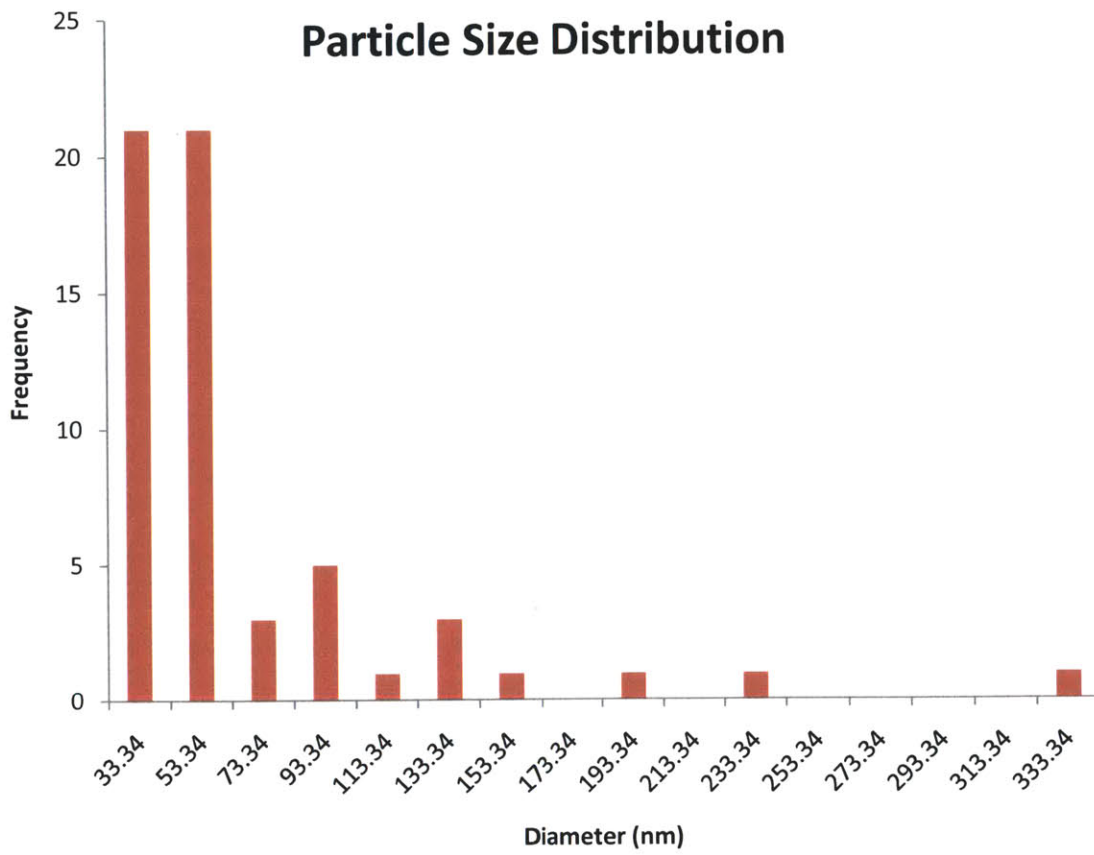


Figure 3.3 – Histogram of particle diameters from improved reactor test

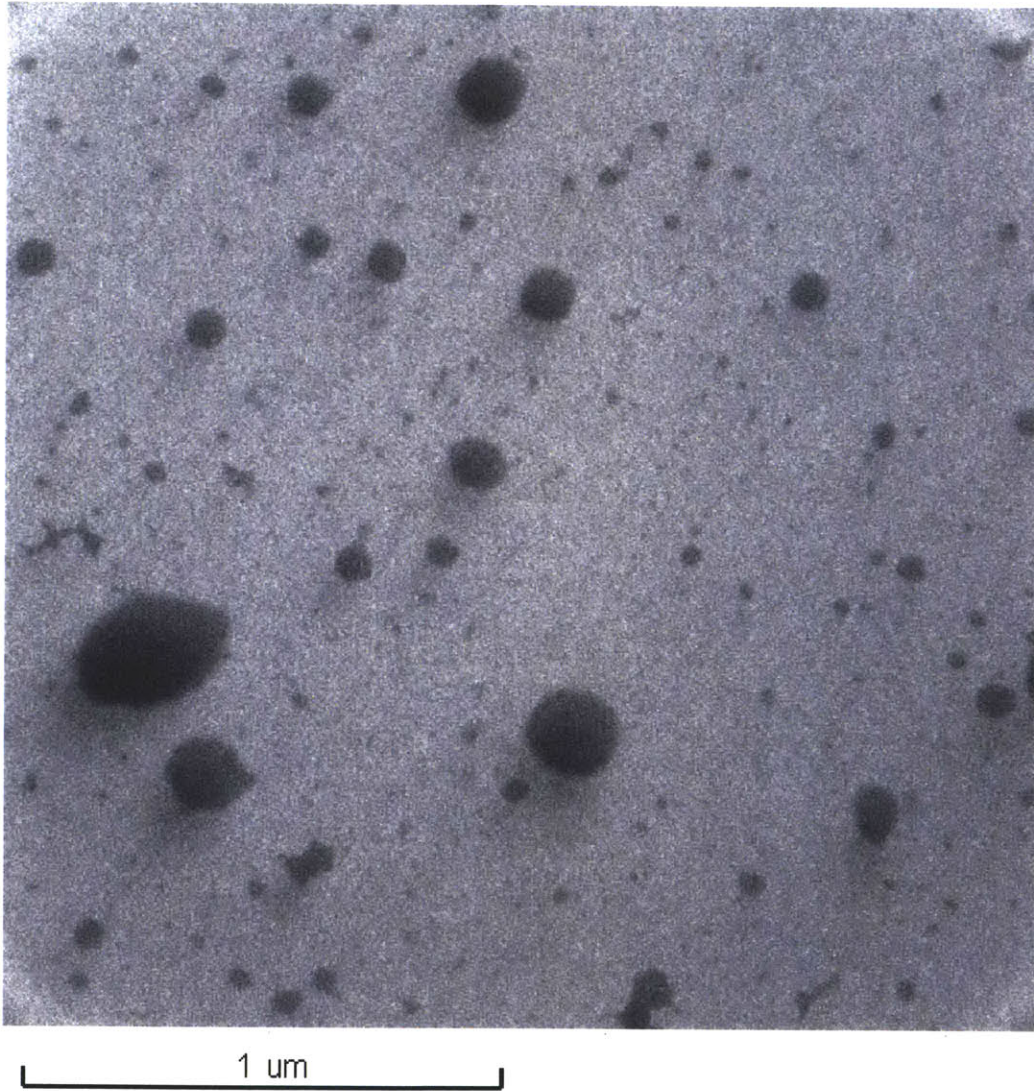


Figure 3.4 – TEM micrograph of submicron Cu particles depicting smallest visible size



Figure 3.5 – TEM micrograph of submicron Cu particles depicting shape uniformity

4.0 Discussion and Analysis

4.1 Continuous versus Pulsed

A review of the sonoelectrochemical literature finds practically all work concerns pulsed sonoelectrodeposition; that is, where the ultrasonic and electroplating processes are both pulsed and out of phase. A schematic representation of the pulsed process is included in Figure 4.1. The typical pulsed sonoelectrodeposition process goes as follows: A cycle starts with a clean electrode. During the electroplating step, an electric current pulse is activated and the surface of the electrode becomes covered in particle nuclei. As the electroplating pulse progresses, the nuclei grow larger. At the end of the electric pulse, the nuclei have grown to their final size. After the electric current is turned off, an ultrasound pulse removes the particles from the electrode and expels them into suspension in the electrolyte. The cycle starts over with the newly cleaned electrode.

The pulsed method has been used to produce highly monodisperse nanoparticles from many metals and semiconductors, including Cu [34], Pt [35], Mg [36], and CdSe [37]. This technique is pleasing from an analytical standpoint. By neatly separating the electrochemical and ultrasonic processes, one can leverage large bodies of previous work which have characterized much of the underlying physics of both processes. The distribution of particle sizes reported in this work is inferior to samples prepared using the pulsed technique [38]. One could argue that this result indicates the continuous method is inferior to the pulsed method. However, the pulsed method precludes capitalizing on unique physics which occur when electrochemistry and ultrasound are

present simultaneously. Improvements to the continuous design might be made with a better physical understanding of the interactions present in both types of reactors. What follows is a discussion of effects which occur in both pulsed and continuous sonoelectrochemical reactors, as well as some that are only present in the continuous case.

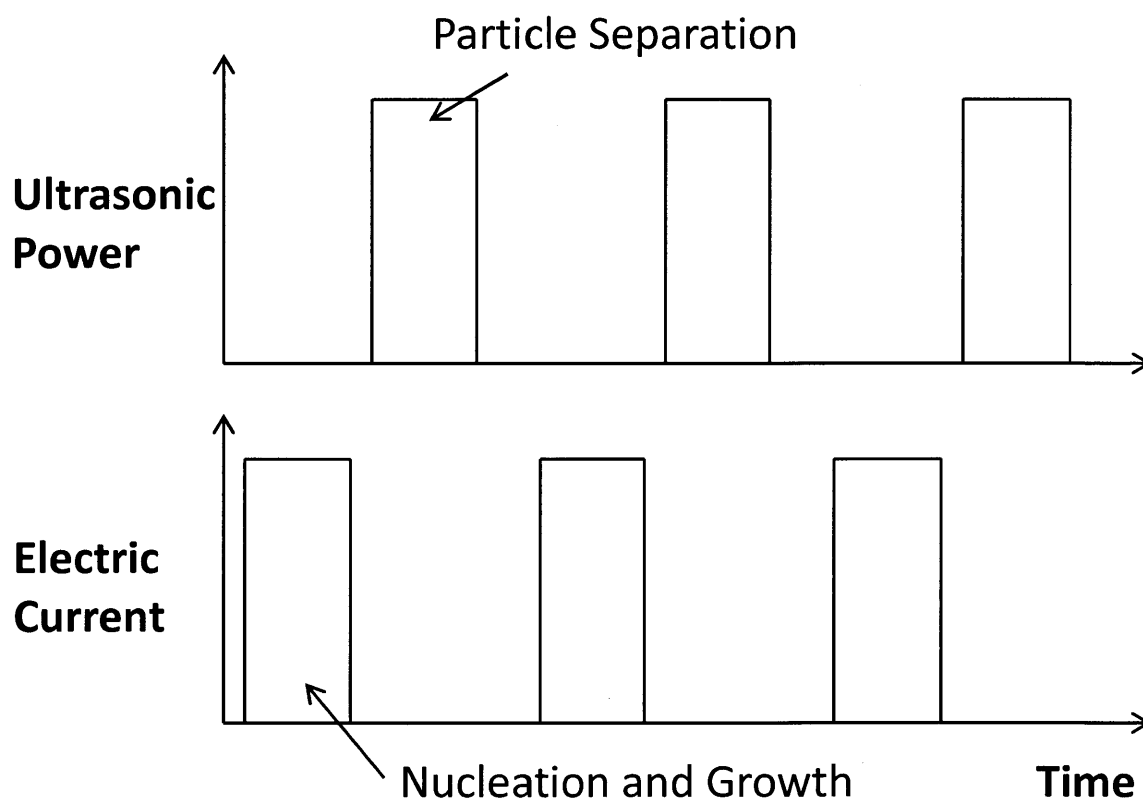


Figure 4.1 – Schematic of the relative pulse timing for pulsed sonoelectrodeposition

4.2 Particle Behavior in Sonoelectrochemical Reactors

In sonoelectrochemical reactors, particle shapes and sizes can be modified by electrochemical or mechanical forces. What follows is a qualitative discussion of some of the mechanisms by which particles in a sonoelectrochemical cell could interact with one another and with the components of the device itself. Methods for minimizing the effects are discussed, with the goal of improving future continuous sonoelectrochemical reactors.

4.3 Interactions on Electrode Surfaces

The behavior of particles on the surface of the cathode is of great interest. Particles form on the surface of the cathode by spontaneous nucleation. In this process, metal ions are reduced on the surface of the cathode. The atoms travel across the surface and coalesce into nuclei, which then grow into larger particles. The particles themselves can coalesce into larger particles on the surface. Schematics of these concepts are depicted in Figure 4.2. As these processes are continuous, in general there is a surface inventory of particles of various sizes. The times particles spend on the cathode determine their size; namely, particles which reside longer grow larger. Application of ultrasound alters the kinetics of these processes [30]. The rate at which these processes occur depends on the electrochemical properties of a given reactor, though they are commonly controlled with additives such as chelating agents or surfactants [14].

The application of ultrasound expels particles from electrodes into suspension in the electrolyte. Identifying general trends in this behavior will be useful for the design of

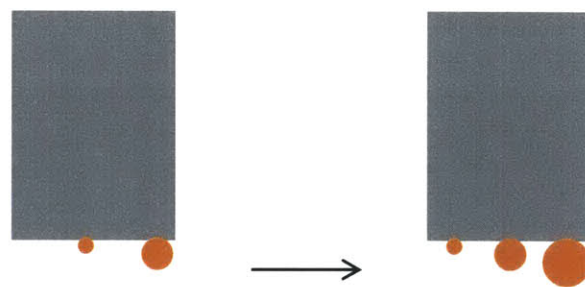
future continuous sonoelectrochemical reactors. One such trend is schematically illustrated in Figure 4.3. There are several possible mechanisms for particle separation, though large local shock from ultrasonic cavity collapse is often regarded as the primary driver [31]. The ability of a particle to adhere to the cathode is likely size dependent. In the minimum dimensional limit, single adsorbed atoms are not dislodged by cavitation shocks. In the large particle limit the particles are subject to bulk fluid motion and inertial effects and are more susceptible to removal by ultrasound. Therefore, there should be some critical size where particles eventually dislodge.

4.4 Interactions in Suspension

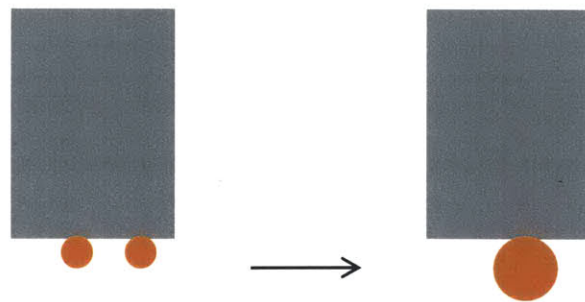
Ultrasonic energy is also coupled to particles which come into the vicinity of the ultrasonic horn tip where cavitation occurs. Just as at the horn surface, cavitation produces highly localized and powerful shocks, which can break particles up. This concept is illustrated in Figure 4.4. The magnitude of this effect depends on the particle shape. Ultrasound tends to break up long dendritic structures, such as whiskers, more effectively than compact crystalline structures, like round particles [25].

Particles can also interact with one another in the bulk electrolyte. Two such situations are depicted in Figure 4.5. In the first case, particles collide in suspension and agglomerate or coalesce into a single larger particle. This process is known as Ostwald Ripening [39], and is often observed as an aging mechanism in stationary suspensions of nanoparticles. The rate at which particles combine by this process decreases with particle radius. The second particle interaction mechanism is collisions which yield additional

smaller particles. Here, particles strike one another with sufficient center of mass energy to disintegrate into additional particles. While this process depends on the particle shape, structure, composition, and various fluid properties, it likely dominates Ostwald ripening for larger particles. This mechanism could be the mechanism for mean particle size reduction observed in an experiment [40] where a nanoparticle suspension was sonicated for 24 hours.



Nucleation and growth



Surface coalescence

Figure 4.2 – Schematic of cathode surface particle behaviors

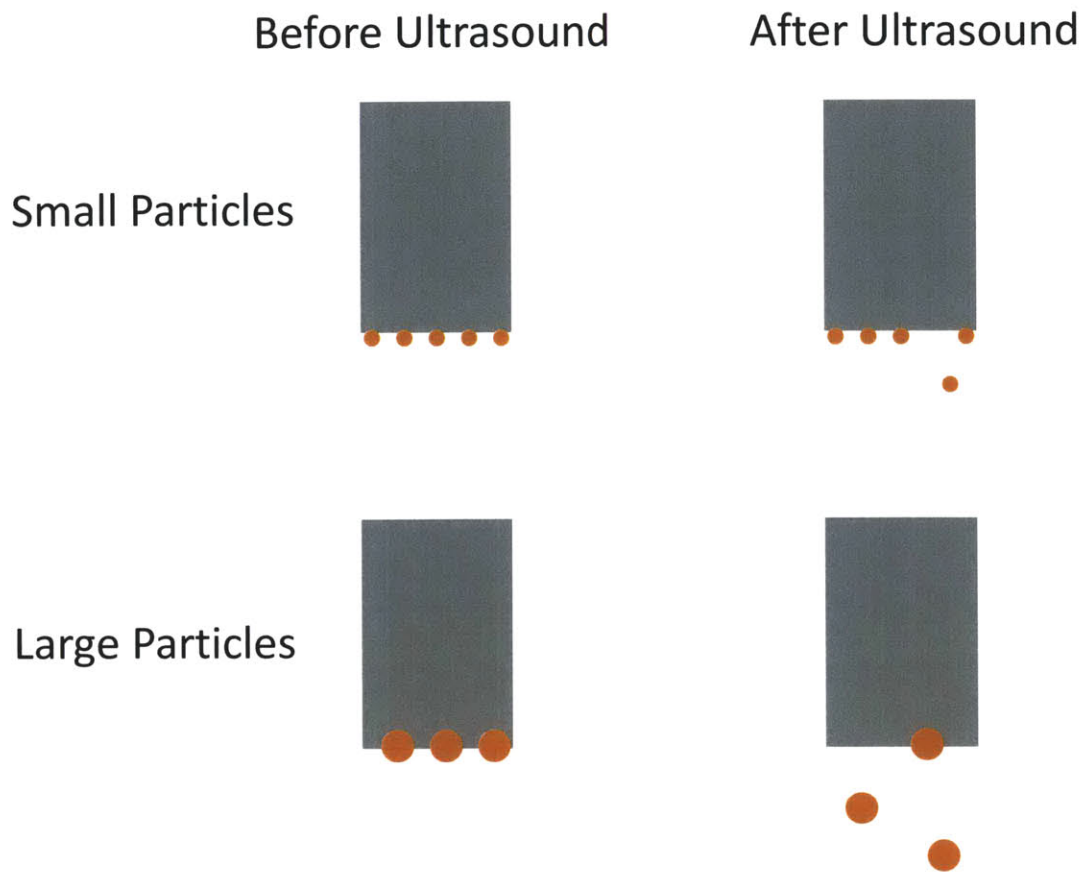


Figure 4.3 – Schematic of dependence of particle adhesion with diameter

4.5 Suspensive Electrode

The suspensive electrode concept [40] is depicted in Figure 4.6. Here, uncharged particles from suspension come into contact with an electrode and pick up a net charge. After returning to solution, the particles behave as the electrode they came into contact with as they return to an uncharged state. For a bath with positive metal ions, particles which come into contact with the cathode acquire net negative charge, and reduce positive metal ions the electrolyte and grow in size. Particles which come into contact with the anode decrease in size as they shed charge by releasing oxidized ions into the electrolyte. In general, the rates of these processes may be asymmetric, depending on the electrochemistry of the particular bath. For example, in a system where the rate reduction of dissolved ions onto a charged particle is greater than the rate of oxidation of copper atoms from a positively charged particle, the system would tend to increase the size of particles over time. Experiments have shown that these highly local electrochemical reactions proceed at a faster rate than other particle growth mechanisms [40].

A corollary to the suspensive electrode theory concerns other behaviors of the suspended charged particles. As the particles carry charge, they carry electric current. Suspended particles have been shown to contribute significantly to the conductivity of an electrochemical cell when ionic charge carriers have been depleted [40]. There is also a particle-particle interaction mechanism. Particles which become charged on one electrode can come into contact with a particle which was charged on the other

electrode. The two particles combine and the new, larger particle has a smaller net charge. A schematic of this process is depicted in Figure 4.7. The rate at which this process occurs relative to others can be understood as follows. The characteristic time which a particle remains charged can be related to the concentration of active ions in the electrolyte, as this is the mechanism for particle charge shedding in the bulk electrolyte. High ion concentration means a particle will react and neutralize faster than a particle in an electrolyte with low ion concentration. The characteristic charge neutralization time can be related to some characteristic particle velocity in the sonoelectrochemical cell. Recall that acoustic streaming tends to increase the average velocity of fluid in the system. If the electrodes are far away, oppositely charged particles will tend to neutralize before coming into contact in suspension.

While these processes appear symmetric, it is important to understand the asymmetries introduced to conventionally designed sonoelectrochemical cells; namely the dual use of the cathode as ultrasonic oscillator. A consequence of this design is the relative intensity of ultrasound on the anode and cathode. Cavitation, and the concomitant dramatic mechanical effects, is typically constrained to the tip of the ultrasonic horn and cathode. The second asymmetry occurs by choice of deposited material. Electrodeposition of cations, like Cu^{2+} , occurs on the cathode. Nucleated particles and cavitation only occur on the cathode in this system.

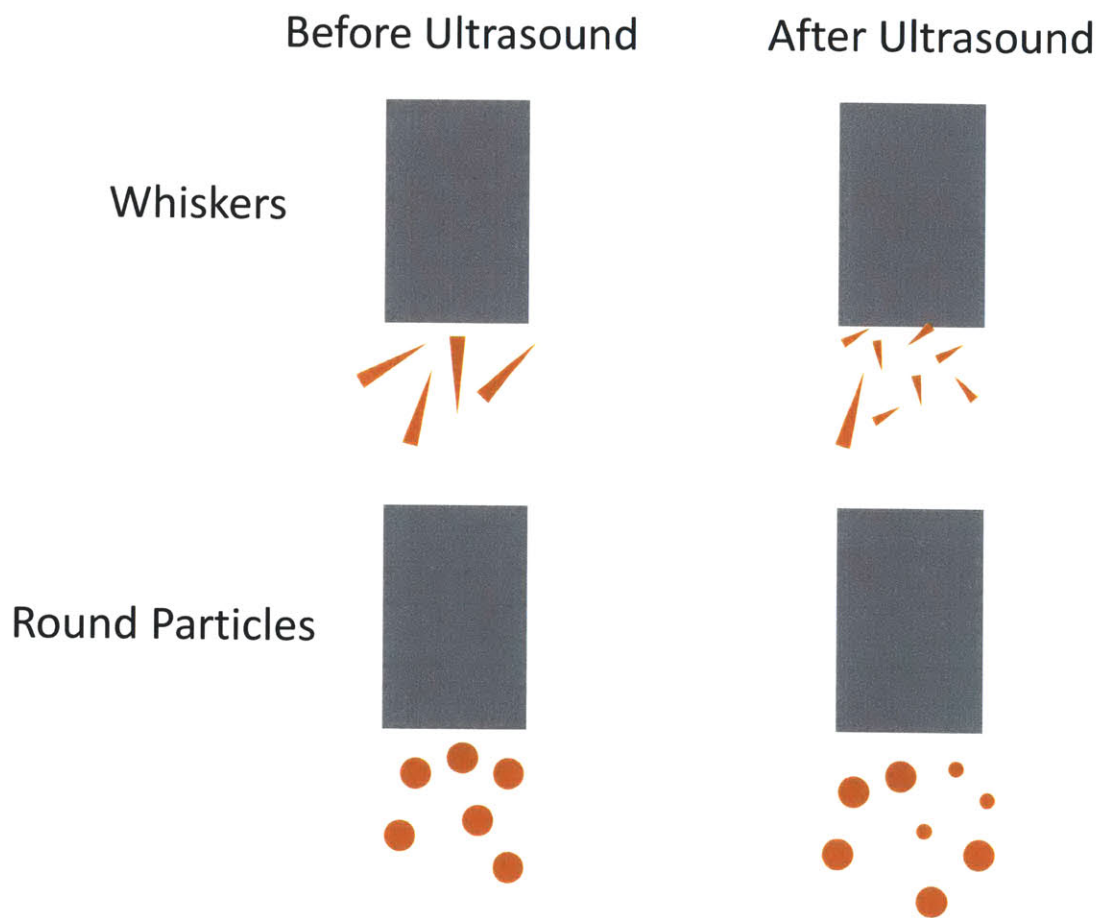
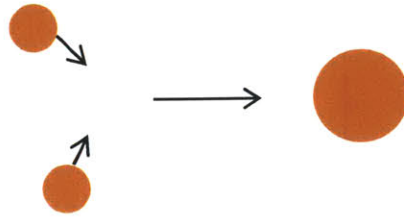
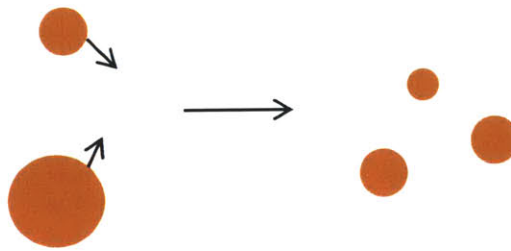


Figure 4.4 – Schematic of shape dependence of particle durability in ultrasonic fields



Kinetic agglomeration or free
coalescence



Kinetic particle breakup

Figure 4.5 – Schematic of mechanically driven particle/particle interactions in suspension

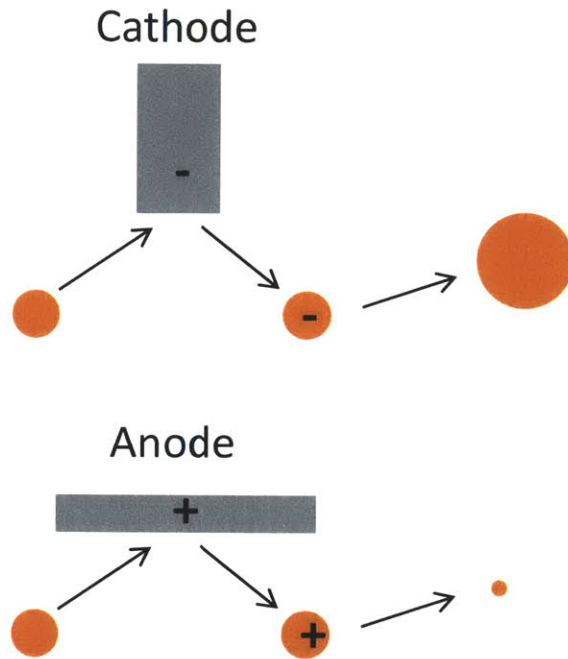


Figure 4.6 – Schematic of suspensive electrode concept

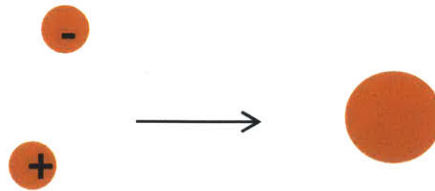


Figure 4.7 – Schematic of charge driven agglomeration

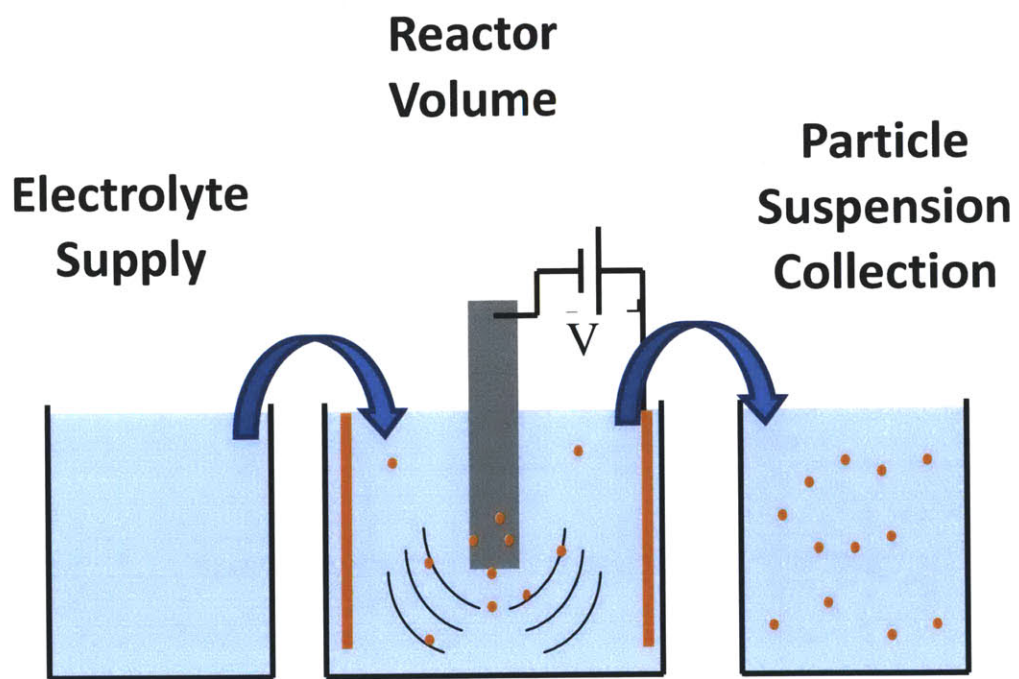


Figure 4.8 – Continuous flow sonoelectrochemical reactor concept

4.6 Continuous Flow Concept

Based on these predictions, continuous sonoelectrochemical reactors should function in the following manner. In operation, the reactor nucleates a large quantity of small particles on the cathode. Once the particles coalesce and grow to a certain critical size, they tend to be ejected into suspension in the electrolyte. The suspensive electrode effect tends to enlarge the particle over time. Ostwald ripening tends to increase the size of the particles, and is a function of time. The longer a batch of electrolyte is run, the larger the first produced particles get relative to later produce particles. This leads to a general broadening the size distribution. Therefore, in order to produce a more uniform nanoparticle product, the effect of these interactions should be minimized.

A continuous reactor concept is proposed to improve the quality of the nanoparticles created by continuous sonoelectrodeposition. A schematic of this concept is depicted in Figure 4.8. To minimize many of the electrochemical and mechanical particle interactions, the particles should be removed from the reactor as quickly as possible after creation. This can be accomplished by using a small sonoelectrochemical reaction volume, with an inlet for fresh electrolyte, and an outlet for product stream. Given a steady flow to and from the reactor, an average residence time can be defined for a fluid volume or a given particle in the reactor. A small residence time minimizes many of the detrimental particle size distribution broadening effects. After removal from the reactor, other stabilization techniques, which may or may not be compatible with the

conditions in the reactor, can be used, such as addition of antioxidants or centrifugation and drying.

5.0 Conclusions

5.1 Potential Applications

The active components in for sonoelectrochemistry are relatively cheap, often priced below \$10,000 for ultrasonic generators which can produce more than 500 watts of radiated ultrasonic power. As such, powders produced by this method would likely be less expensive than those produced by other methods, particularly those that rely on high purity reagents, such as sol-gel or colloidal synthesis, or complex equipment, like chemical vapor deposition or lithographic techniques. While this technique probably won't ever develop highly monodisperse distributions of particles due to the continuous nature of particle formation and growth, there are still potential commercial applications. This technique is potentially useful for the bulk production of submicron metal powders where a wide particle size distribution can be tolerated.

An example of such an application could be a new technique for the low volume production of printed circuit boards (PCBs). Many conventional PCB manufacturing methods rely on masking and chemical etching of copper clad dielectric sheets [14]. Such techniques utilize chemical baths, which are often dangerous and require specialized industrial facilities. As such, low volume multilayer PCBs required for prototyping or laboratory use are often expensive and with long lead times.

An alternative technique which required less complicated equipment would be valuable. One proposed method would be to print silver particle impregnated fluids directly onto dielectric boards using conventional ink-jet printing techniques [4]. High

temperature treatment of these boards would evaporate or react away the carrier fluids, and sinter the silver particles into conductive tracings. In this case, the size distribution of the silver powders is less important than low material cost.

5.2 Future Developments

More advanced electrodeposition techniques, such as two layer baths, haven't been explored as a technique for reducing the reactivity of particles in suspension and as a technique for removing them from the primary reactor bath. Two layer baths often consist of an aqueous layer, where the electrodeposition occurs, and a nonpolar organic or surfactant layer, where particles tend to accumulate [41]. Two layer baths can isolate the electrically active polar layer from the atmosphere, which can lead to higher electrode efficiencies [42].

Commercialization of this technique will require solving several outstanding problems. First there is the problem of removing the product particles from suspension in the electrolyte. This work has relied on centrifugation and washing of small volumes of particle suspensions, which is an inherently batch technique. Alternative methods would need to be developed in order to make this process truly continuous.

Additionally, the long term suitability of these techniques has not been studied. Most studies reported in the literature concern reactors that operate on the scale of hours. In order to scale up these procedures, the long term behavior of components needs to be studied in the context of continuous reactor operations. Problems might arise, for example, from fouling of the electrodes with material created in side reactions.

Another problem might be erosion of the tip of the ultrasonic generator from cavitation. This would lead to minor contamination of the product with titanium, as well as continuous monitoring of the reactor components for wear. While these are potential problems, wear and fouling are common issues with the scale up of laboratory processes.

A complete understanding of the underlying physics of sonoelectrodeposition is still elusive. The combined physical effects of continuous electrodeposition and power ultrasound may still yield new and useful nanostructured products. Further work should be done to interrogate these effects. Advances in understanding of the continuous case will have applications for pulsed sonoelectrodeposition, and vice versa.

6.0 References

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