Construction of a Glow-Discharge Plasma Microelectrode for the Synthesis of Inorganic Solids

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Abstract

This study focuses on the construction of a glow-discharge plasma microelectrode and its potential for usage as a lower-energy synthetic alternative for nano-crystalline multinuclear inorganic solids. Several electrode designs were constructed and assessed, and two different systems showed positive proof of plasma generation. Though a glow-discharge plasma could be generated via both systems, neither produced a reactive plasma plume and thus could not be used as planned for synthesis of inorganic solids.
Background

Motivation for Plasma-Mediated Synthesis

An inorganic chemist has many options for synthesizing new solid-state compounds and materials. Traditional routes typically require extreme reaction conditions (high temperatures and long reaction periods), and yield only somewhat successful results, both in purity and consistency of yield.

The first and most traditional synthetic system for non-molecular inorganic solids begins with inorganic compounds already in the solid state. This strategy, the mechanical mixing approach, mixes related reactant species in appropriate ratios determined by the structure of the target product. The solids are combined into a uniform powder and heated in a furnace. After some significant period of time, sometimes days or weeks, the product powder can be removed and analyzed for product structure. This approach is simple, but not overly efficient: it requires higher temperatures (1000-2000°C) and long periods of time for reaction to occur and when reactions do occur, they do not typically yield homogeneous products.

This synthetic approach relies on solid-state diffusion; unfortunately, the diffusion of unreacted species can be quite difficult in the solid state, and the mechanism of reaction relies heavily on exposure of reactive surface area and proximity of unreacted materials to each other. The Wagner diffusion model predicts an inverse relationship between amount of product formed and rate of reaction: once product begins to form, the process of forming product becomes more difficult. Reactants close in proximity to one another will react quickly, forming product. Remaining unreacted atoms are not in close proximity to other reactants, and must diffuse over a greater distance, often through the forming product, in order to interact with other unreacted atoms (see Figure 1, page 3). Over time, the distance between reactants becomes very large, and
Figure 1. The formation of product (purple) tends to isolate reactants (red and blue) from each other, increasing the necessary distance for diffusion and impeding reaction progress in the solid state. This illustrates the Wagner diffusion model, which predicts an inverse relationship between rate of reaction and amount of product formed.
the reaction process slows and ultimately stops, leaving some amount of unreacted starting material in the reaction vessel. The reaction can continue if the component mixture is removed from the tube furnace, cooled, and again mechanically mixed to produce new reactive surfaces; this process of mixing, heating, cooling, and remixing continues until the analyzed product is of the intended form with little impurity (which could take many cycles, if that point is reached at all).¹

A second traditional approach attempts to overcome the homogeneity difficulties in mechanical mixing by introducing reactants in solution to achieve atomic or near-atomic level mixing. In this approach, a solution of reactants is made in a known molar ratio, based on the target product. In one example of such an approach, the solution is titrated with an excess of the reactive anion of interest and the resultant solid is collected by filtration while stirring the solution to promote homogeneity. The solid is then heated, as before, to promote the decomposition of the precursor in favor of the formation of the target species. Aqueous synthetic approaches are often effective in inorganic chemistry, but these approaches can introduce a different subset of problems than are encountered in the ceramic approach. Solubility of the precursor compounds becomes an issue, as is the precursor structure. When introducing two metal ions in solution with a reactive counter ion, many counter ions are present, and competition between these spectator counter ions and the ions of interest to the final compound can often be difficult to overcome. Based on these difficulties, the precise composition of precursor can be unpredictable, and heating of it can produce an unintended final compound.¹

Based on the significant obstacles faced by these simple synthetic strategies, it is unsurprising that a number of more sophisticated chemical strategies, such as sol-gel processing, cryogenic procedures, and chemical vapor deposition, have been developed in attempt to
circumvent these issues. The objective of this study is to further develop a lower energy, more effective alternative synthetic route to traditional means, via dc glow-discharge plasma. This research effort is not targeting novel compounds: its primary targets are known compounds, synthesized in a novel fashion. Glow-discharge plasmas offer the potential for significant improvement over traditional synthetic methods of solid-state nano-crystalline mixed-metal inorganic compounds.

*Plasma: The Fourth State of Matter*

Plasma, the often times forgotten fourth state of matter, comprises more of the physical universe than do all solids, liquids, and gases combined. Plasmas are found in space, in interstellar material and the solar core and corona, as well as on Earth. Due to their indefinite shape and volume, plasmas have been historically classified as a special-case gaseous phase; however, this thinking has been realigned to reflect the completely different physical properties of this unique phase of matter. In short, plasmas are ionized gases, comprised of different types of charge-carrying species. The presence of these charged particles greatly affects the physical and chemical properties of plasmas: most importantly, these particles cause a response from the plasma to the presence of electromagnetic fields, forming new structures, bonds, and physical arrangements within the plasma when in close proximity to an EM field.

Plasmas are typically formed by a large input of energy, necessary for separating a neutral phase into ions and free electrons. Sometimes this energy stems from increased temperature (thermal energy), an electric current (electrical energy), or a light source. Much attention in recent science has turned to plasmas: their properties, particularly their response to electric and magnetic fields, have given rise to numerous practical applications. Currently, plasmas are revolutionizing industrial, electrical, nuclear, and optical technologies, being used in
engines, transformers, nuclear reactors, electronics, semiconductors, and lasers (to name a few). Scientists are constantly engineering new functions and applications for this interesting phase of matter.

Not surprisingly, plasmas are also used for chemical purposes. Two major categories of plasmas exist in the laboratory setting: high-temperature (fusion) plasmas and low-temperature (glow-discharge) plasmas. Both high and low-temperature plasmas can exist either at a state of complete thermal equilibrium, where all constituents (charged and uncharged particles) exist at the same temperature, or localized thermal equilibrium, where only discrete portions of the plasma exist at the same temperature. This distinction is typically a result of the relative pressures of the plasma systems: at high pressures, plasmas will tend towards thermal equilibrium; at low pressure, thermal equilibrium becomes more difficult to achieve. This study will focus on glow-discharge plasmas: a low-temperature plasma, typically in localized thermal equilibrium.

Glow-Discharge Plasmas and their Applications

A glow-discharge is formed when a flow of gas is subject to a sufficiently high electrical potential difference to make accelerated electrons from an electrode collide with neutral gaseous particles to ionize some of them, forming ions and additional free electrons. The initial excitation of electrons is followed by a subsequent relaxation, causing an emission of radiation. This radiation is often in the visible light region, giving rise to the glow that is characteristic of glow-discharges. Since glow-discharge plasmas are in a state of partial thermal equilibrium, altering several key parameters, such as chemical input, pressure, electromagnetic field structure, or temporal behavior, can greatly change their properties. These slight modifications give rise to
many different varieties of glow-discharge plasmas with a wide range of applications in chemistry.

Glow-discharge plasmas can rely a number of different varieties of electrical current to ionize the discharging gas. First and most predominant in the field are direct current (DC) discharges. These discharges supply the discharging gas with a constant, steady state current over an electrode as the source of electrical energy. This is the simplest form of glow-discharge plasma; however, DC discharges are most effective when the target ionization source is made of a conductive material and do not produce great results in other scenarios. Second, glow-discharges can be obtained from radio frequency sources. Unlike DC discharges, radio frequency (RF) discharges can ionize both conductive and non-conductive materials, a marked improvement over the initially discovered method. The discovery of RF discharges greatly widened the applicability of glow-discharges. A third type of glow-discharge relies on pulsed electric signals to generate a plasma. Pulsed glow-discharges depart from the steady state approach of traditional DC and RF discharges, instead using periodic, high-energy pulsations of electricity to ionize and atomize the target sample. Pulsed discharges, which can operate with either DC or RF pulses, allow for greater control of current and energy flow through the system; additionally, the use of pulsed discharges can aid in ease of measurement for plasmas purposed for analytical or instrumental methods. These three styles comprise all major types of glow-discharge plasmas.

All types of glow-discharge plasmas rely on an electrode system to achieve the electric current necessary to generate the plasma. Depending on the metal chosen as the cathode in glow-discharge electrode systems, metal sputtering (just as occurs in a typical hollow cathode lamp) can occur. This leads to metal atoms and ions from the cathode source mixed in the plasma with
ions and radicals of the input gas. Sometimes, metal sputtering as a result of plasma generation is intentional, as it can help to preserve target samples or provide an additional source of atoms or ions as a means of chemical synthesis; however, metal sputtering can also poison the pure glow-discharge plasma (if plasma purity is the goal for the application at hand). Some glow-discharge experiments have relied extensively on the ability of the cathode to sputter in the discharge process, using the sputtering as an analytical technique to assess the surface coating of particular materials—such experiments were performed by Nathan et. al. and Malherbe et. al.\textsuperscript{4,5} Thus, cathode selection in electrode design becomes of utmost importance as experimental intentions are considered.

Due in part to their high degree of energy and potential reactivity, glow-discharge plasmas have been used as chemical degradation agents. When compared to other forms of plasma, glow-discharges can be generated and are relatively stable in water. For this reason, recent attention has turned towards use of plasmas as agents for wastewater treatment, specifically to treat water with organic contaminants. Glow-discharge, when in contact with water, can dissociate water into its constituent radicals, hydrogen and hydroxide. The hydroxide radical is known to non-selectively oxidize hydrocarbons into carbon dioxide, which can then be boiled out of the water. Given that glow-discharge can fairly easily produce the hydroxyl radical, this application has been studied rather extensively.\textsuperscript{6} In one such study, glow-discharge electrolysis was used to break down aqueous monochlorophenols, a common organic pollutant generated by numerous industrial and agricultural processes.\textsuperscript{7} This experiment relied on an electrode in constant contact with the contaminated water to produce the plasma in a localized zone. As predicted by the glow-discharge model, this procedure successfully reduced the total organic carbon content of the water, giving off carbon dioxide gas throughout the process. This
result is not unusual: many such studies have been carried out using glow-discharge plasmas in this manner using a wide spectrum of organic compounds, showing the versatility of glow-discharges being used in this manner.

Glow-discharge plasmas are a great source of atomization, ionization, and excitation of compounds. Given these properties, glow-discharges can also be used in analytical assessments of unknown compounds, often times in tandem with other instrumental methods. For example, glow-discharges are applied as the precursor ionization source to mass spectrometry; similarly, they can be used as the excitation source for optical emission spectroscopy.\(^3\) Traditionally, use of glow-discharge in instrumental analysis has relied on direct current (DC) or radio frequency (RF) discharge; however, the development of pulsed discharges have allowed for better sample analysis, providing a means of layer-by-layer profile mapping of compounds for mass spectrometry and optical emission spectroscopy. Though other depth-profiling techniques, such as x-ray photoelectron spectroscopy, auger electron spectroscopy, and secondary ion-mass spectrometry, tend to receive more attention than glow-discharge methods, GD-MS and GD-OES offer some distinct advantages over other depth-profiling counterparts.\(^8\) Glow-discharge techniques provide a distinctive blend of high depth resolution, excellent sensitivity, experimental ease, and the ability to determine binding states of atoms; however, these techniques have comparatively limited capabilities of micro-spot analysis (glow-discharges usually have a sampling diameter of about 4 mm, whereas other techniques can work over ranges in the micro or nanometer scale).

**Glow Discharge Plasmas as Synthetic Agents**

Clearly, glow-discharge plasmas have been successfully utilized as both agents of chemical degradation and precursors to known analytical techniques; however, this study will
not focus on either of these applications. Another interesting application of glow-discharge plasmas (and the topic of this study) is their synthetic utility, though considerably less research has been done in this area. Synthesis has been attempted for both organic and inorganic compounds; for nanocrystalline materials and surface crystals; for solid states and aqueous environments. Though relatively little is known about their synthetic capabilities, the possibilities for synthesis by glow-discharge plasmas seem to be nearly endless.

According to a study by Shi et. al., the environment created by glow-discharge plasmas simulates the conditions of a primitive earth environment; their synthetic study attempted to recreate these early planetary conditions in order to study the possible formation mechanisms of common hydrocarbons from elemental carbon and water. This experiment ran a constant DC glow-discharge under an argon atmosphere, utilizing a graphite rod as the anode and a silver thread as the cathode. In theory, the glow-discharge process would create free carbon ions and atoms from the graphite rod as well as radicals of water (similar to the chemical degradation process explored previously), spurring on reactions between these species and creating a variety of hydrocarbons. Through experimental synthesis and analysis, it was determined that this procedure formed an array of organic compounds, many of which were carboxylic acids; however, a concrete mechanism for this process had not been determined at the time of publication.

Other key synthetic work has targeted the production of nanoparticles using glow-discharge plasmas. For such experiments, glow-discharge plasmas provide a safe, ecologically friendly, and economical synthetic route when compared to other methods of nanoparticle assembly. In one example of such work, Liang et. al. evaluated the synthesis of gold nanoparticles under the influence of glow-discharge plasmas. This experiment was carried out
at room temperature with a simple electrode system made up of two stainless steel electrodes in a low-pressure reaction chamber. The argon glow-discharge was developed under a constant DC run between the electrodes through a solution of HAuCl₄. After a five-minute reaction period, well-formed gold nanoparticles were present in the solution, proving the effectiveness of this glow-discharge set-up in synthesizing such particles.¹⁰

Furthermore, glow-discharge plasmas have been employed to synthesize thin films with varying chemical compositions. In similar work by Yu et. al. and Hu et. al.,¹¹,¹² carbon nitride thin films were synthesized on silicon substrates using DC glow-discharge plasma. In the earlier work, by Yu et. al.,¹¹ the plasma generating current was run between a hot filament and the Si substrate platform under an mixed gas environment of H₂, N₂, and CH₄. Through this experiment, it was determined that crystalline carbon nitride thin films could be produced on the silicon substrate; these films were more uniformly deposited and crystallized at higher partial pressures of N₂ gas in the reaction chamber.¹¹ In the research by Hu et. al.,¹² the films were crystallized using a more traditional electrode deposition method, in which the input gas was a varying mixture of N₂ and CH₄. This method produced very uniform carbon nitride thin films on silicon substrates with intermediate cobalt/nickel layers; the films did not deposit as well on the purely silicon substrates. Work in this study showed the importance of the presence of the conductive intermediate layers in the attempted deposition method for thin layer synthesis, as would be anticipated when using a DC glow-discharge.¹²

**Plasma Research at Messiah College**

Glow-discharge plasmas are versatile and lend themselves well to a number of different purposes, applications, and functions. Though much work has been done using glow-discharge plasmas for synthesis, much remains to be investigated. At Messiah College, Dr. Richard W.
Schaeffer and his undergraduate research team have worked on projects dealing with synthesis by glow-discharge plasmas for quite some time. Over the years, he and his team have made progress in solid-state deposition synthesis by DC glow-discharge. This work relies on metal sputtering from the cathode as the source for the secondary ions present for synthesis reactions. All of this previous research was carried out in low-pressure reaction vessels, evacuated to pressures well below normal atmospheric conditions. In this controlled environment, synthesis takes place between the sputtered metal atoms and the input carrier gas-phase ions, radicals, and neutral species without contamination from atmospheric pollutants.

For most of the experiments performed, a copper or silver cathode was utilized and oxygen (O\textsubscript{2}) gas was input into the system. As the metal atoms sputtered off of the cathode and came into contact with the plasma plume created by the increased electrical potential applied to the electrode system, the copper reacted with the oxygen species present to form solid-phase products, typically copper or silver oxide (CuO or Ag\textsubscript{2}O). The reaction products were then deposited on the sample platform or substrate on the bottom of the reaction chamber. Once this outcome was observed, many parameters were altered to determine the effect of each on the purity of the formed oxides as well as the uniformity and thickness of the sample coating. These parameters included plasma power and composition, gas composition and pressure, electrode configuration, and deposition substrate and position.\textsuperscript{13}

Previous work by the Schaeffer group was met with varying levels of success. It was determined that the theoretical synthetic route is viable, and various metal oxides were successfully produced as a result of this work; however, the reproducibility of results in any prior studies was limited at best. Though particle size and morphology was typically consistent for any given synthetic trial, these parameters were not controllable in a predictable manner. It was
difficult for any of the student researchers to produce uniform depositions of the oxide coatings on the target substrates; many of the films created in this manner had a bulls-eye pattern, with a generally circular area of oxide deposition broken by rings with little (if any) deposition. In addition, the group did not find a parameter to alter to improve the thickness of the oxide coating: regardless of the amount of reaction time or the composition of the gas present, the deposition film remained rather thin.\textsuperscript{13}

\textit{Research Objectives}

Continuing on the prior work of the Schaeffer group, the focus of this study will be inorganic synthesis by glow-discharge plasma; however, the methodology will be altered dramatically. Instead of using the low-pressure reaction chambers, a new electrode system will be constructed in hopes that the plasma generated by this new electrode will be stable enough to sustain under atmospheric conditions. Utilizing a self-contained electrode, the input gas will flow directly through a hollow cathode, which will be surrounded by a layer of insulating material and then the anode (see Figure 2, page 14).\textsuperscript{13} The input gas will flow through the base of the cathode and the anode, encountering an electrical potential at the base of the electrode system, becoming ionized into a glow-discharge plasma as it flows through the cell. Theoretically, this set-up should provide a means of stable plasma generation, stable enough to promote either solid-state deposition synthesis (as done by previously by the Schaeffer group) or, possibly, the ability to do solution-state synthesis of inorganic materials. Should this be the case, the plasma generated in this fashion could provide the ability to synthesize any number of inorganic compounds in a wide variety of initial states: whether by metal sputtering from the cathode or by metal ions existing in an aqueous environment, some solid-phase products could, for the first time, be manufactured by glow-discharge synthesis.
Figure 2. A cross-sectional view of the proposed electrode system. Electrode consists of a hollow metal cathode, a layer of insulating material, and a metal anode casing. A current will be run between the anode and the cathode from a high-voltage power source, while a constant flow of gas will be input through the cathode; thus creating a glow discharge plume at the base of the electrode.
Experimental

*Exploration of Traditional Synthetic Routes for CuMgO$_2$*

In order to demonstrate the necessity for novel synthetic pathways, attempts were made to form a simple mixed-metal oxide, MgCuO$_2$, by the two different traditional synthetic routes described in the introduction. For the mechanical mixing (or ceramic) approach, solid CuO and MgO were combined in equal molar ratios to achieve approximately 1.5 total grams of a relatively homogenous powder. The powder was heated to 1000°C in a tube furnace under a flow of oxygen gas over an 18-hour period, cooled, and analyzed by powder x-ray diffraction. The powder x-ray diffraction of the compound showed a very good match for MgCu$_2$O$_3$, and had several strong characteristic peaks for both MgO and CuO in the resultant diffraction pattern. This result communicated that, despite 18 hours of heating at extreme temperatures, a significant amount of starting material was still present in the mixture and the target compound had not been formed. After grinding the solid in a mortar and pestle, the solid was again heated over an 18-hour period at 1000°C. At the conclusion of this cycle, the X-ray diffraction pattern showed no significant change from the originally collected pattern (see Figure 3, page 16), demonstrating the clear pitfalls of this synthetic method.

Alternatively, a solution of 0.10 M Mg(NO$_3$)$_2$ and 0.10 M Cu(NO$_3$)$_2$ was prepared and titrated with an excess of NaOH while stirring, to produce approximately 500 mg of solid product. Half of the gelatinous blue precipitate that formed was suction filtered directly and dried, while the other half was heated to 65°C for an hour, filtered, and dried. Separately, each of these dried solids was heated to 1000°C over a period of 18 hours in a tube furnace and analyzed by powder X-ray diffraction. The directly filtered product, after 18 hours, showed a well-crystallized near-perfect match for MgCu$_2$O$_3$: unfortunately, this was not the stoichiometry of the
Figure 3. Powder x-ray diffraction pattern collected for the first and second mechanical mixing attempts, overlaid. Pattern 1 (bottom) was collected after 18 hours of heating. Pattern 2 (top) was collected after remixing and an additional 18 hours of heating. No detectable change was observed between the two patterns, indicating no further reaction of the solid in the additional heating period. The best matches for the collected pattern, based on the ICPD, were to MgCu$_2$O$_3$ and MgO, so this process failed to react all of the initial MgO.
Figure 4. Powder X-ray Diffraction pattern collected for the co-precipitation synthetic method. The best match to this pattern was MgCu$_2$O, not the intended MgCuO$_2$ phase.
intended compound (see Figure 4, page 17). The sample showed good homogeneity, indicative of a successful tube-furnace reaction; however, the unexpected result implies difficulty in the solution phase of the reaction. Though equal molar amounts of copper and magnesium were available for reaction with the input hydroxide ions in solution, it seems likely that the collected solid was rich in copper with respect to the magnesium. This could be indicative of solubility effects at play in the reaction: since magnesium hydroxide is more soluble than copper hydroxide, more copper hydroxide would be formed in the solid state. Thus, upon heating in the tube furnace, there was more copper available to form the analyzed final product. A similar result was observed for the modified precursor attempt: despite the initial heating of the formed gelatinous solid, the resultant product was MgCu$_2$O$_3$.

These unfavorable outcomes for synthesizing a rather simple compound are not unique: the formation of even trivial mixed-metal systems (this and others like it) can be problematic. Given these difficulties, it is clear that neither route is the optimum synthetic route for compounds of this type. Both routes require significant heating at high temperatures, long reaction periods, and several steps, and even still do not produce phase-pure versions of the intended species (if they produce the intended species at all). Attempting to use either method to produce thin films of mixed-metal systems with consistent particle morphology would be nearly impossible. Enter a number of other synthetic techniques, including glow-discharge plasmas, a low-energy source of reactive species with the ability to control reactive sites and exposure rates. If an effective method could be developed, direct synthesis via DC glow-discharge plasma could circumvent many of the issues that arise from these typical synthetic routes.

*Design of a Plasma-Generating Electrode*
Work on the project first attempted to construct a working plasma microelectrode, the focal point of this study. Based on plasma microelectrodes utilized in previous related studies, the constructed electrode system will follow Figure 2 (page 14). Theoretically, this set-up should provide a means of stable plasma generation, stable enough to promote either solid-state deposition synthesis (as done previously by the Schaeffer group) or, possibly, the ability to do solution-state synthesis of inorganic materials.

Many attempts were made to construct an electrode with resources already in the lab, using various sizes and types of metal tubing, fittings, and insulators. A range of gas flow rates (with argon or oxygen) was utilized for plasma generation. Several of the constructed electrodes are depicted and described in Figure 5 (page 20). First attempts at plasma generation with these electrodes were unsuccessful, despite working at a wide range of voltages and gas flow rates. In each of these attempts, input voltage could be increased to a certain threshold (between 1500-2000 V) with no appreciable or sustainable current (the sign of plasma generation). Past the threshold, the electrode system would spark, sending a surge of current across the barrier and tripping the power source. Thus, no plasma was generated.

Based on the lack of results obtained by the homemade electrode attempts, plans were drawn up for a machined electrode with the specifications from other successful plasma microelectrode work. This new electrode (see Figure 6, page 21) has a stainless steel anode and cathode and uses a thin Teflon tube as the insulating layer. Initial trials with the new electrode showed great promise: using argon as the working gas, the electrode showed high levels of sustained current with even very low input voltage. Since no plasma was visible, it was postulated that this current was too high and resistance on the circuit system would be necessary. With resistance, the system continued to have extremely stable current, yet no visible plasma.
Figure 5. Constructed microelectrodes from in-lab supplies. The mark 1 electrode consists of a glass tube (insulator) encasing a stainless steel tube (cathode), interacting with a copper plate (anode). The mark 2 electrode consists of a small hollow stainless steel tube (cathode) fitted in a short piece of ceramic (insulator) inside a stainless steel fitting (anode). The mark 3 electrode consists of a copper wire (cathode) inside a ceramic tube (insulator), interacting with a copper plate (anode). The mark 2 electrode, the only of these to be entirely self-contained (with no outer counter electrode), was utilized more heavily than the other electrodes shown, given the higher degree of similarity this design shared with the proposed designs in the literature.
**Figure 6.** The machined electrode system, consisting of a stainless steel anode and cathode and a Teflon insulating layer (all self-contained). Top (right) shows the inside of the base of the electrode without the anode cap (inner Teflon disc and hollow cathode). Bottom (right) shows the completely assembled base of the electrode, with anode cap in place. Inside of electrode is similar to cutaway structure shown in Figure 2.
From some investigative work, it seemed to be that the current was due to a shorting of the microelectrode circuit (and the anode and cathode were touching, despite the Teflon disc supposedly separating the two). To resolve this issue, the stainless steel anode cap was removed, sanded flat surrounding the gas flow-through hole, and reinstalled in the microelectrode. Plasma generation attempts with the revised machined electrode were, at first, unsuccessful: as was the case with the previously constructed electrodes, no current could be generated or sustained, despite attempts with different working gases (argon, oxygen, compressed air), gas flow rates, resistances in series with the cathode, and a wide range of voltage. Some additional research and reading revealed a common thread through many of the successful plasma microelectrode attempts: these systems all utilized multiple resistors, most with a resistor in series with the cathode and in series with the anode. When this method was attempted on this system (after several iterations of resistance), a sustained current was observed with gas flow on, and no current was observed with gas flow off. This was positive evidence for the generation of a plasma, though no visible glow-discharge plume could be seen at the base of the electrode.

**Optimization of Conditions – Machined Electrode**

Based on this result, the variables of the system were controlled and altered systematically in order to optimize the electrode and obtain a plasma plume. From these attempts, a set of conditions that would reliably generate a sustainable current of reasonable magnitude (between 8-10 mA) was developed. Using compressed air, argon, or oxygen as the working gas and two 56 kΩ resistors (one in series with the anode and one with the cathode), a sustained current could be sparked at 1400 V and maintained with decreased voltage to approximately 800 V. The current could be sustained through gas flow rates between 40 and 150 mL/min (for representative data from plasma generation trials, see Table 7, page 23). Though no
Anode (Ω) | Cathode (Ω) | Flow Rate (mL/min) | Voltage (V) to obtain plasma | Current (mA) |
---|---|---|---|---|
470k | 470k | 40-110 | 2000 | varied (between 0.30 – 1.5) |

No significant correlation between flow rate and current obtained.

56k | 56k | 45 | 1300-1400 | approx 9 |
Brilliant purple plasma inside reactor, but no plume. Burned through resistors quickly. Can decrease voltage to approximately 800V and maintain a non-zero current.

4.7k | 4.7k | 45-110 | -- | -- |
Resistance too low. Sparked and tripped box at 1100V.

4.7k | 56k | 50 | -- | -- |
No current, tripped box at 1300V.

15k | 15k | 45 | -- | -- |
No current, tripped box at 1300V.

100k | 100k | 45-65 | 1400V | 5-5.5 |
Stable current at 1300V, best at 1400V. Higher flow rate more stable at lower voltage.

**Table 7.** Representative data collected for one plasma generation method. Above trials were conducted at atmospheric pressure using the machined plasma system with 1/2W carbon-fiber resistors and compressed air as the working gas. Other trials (data not included on this table) utilized different working gases (argon and oxygen), pressure conditions, electrode systems, and resistors (wire-wound resistors, 25W).
plume was visible at the bottom of the electrode, a brilliant red-purple plasma could be seen via reflection inside the body of the microelectrode. When a piece of aluminum foil was held in close proximity to the bottom of the flow-through hole, occasional purple sparks would be released from the bottom of the electrode.

Unfortunately, the high voltage coupled with consistently high current quickly overran the low-power resistors (0.5W) originally utilized for experimental control. As the resistors heated and burned in a matter of minutes during plasma generation periods, plasmas could not be sustained over any significant period of time. It became practically necessary to obtain high-power, industrial 100kΩ resistors, rated up to 25W. With these new resistors, plasma generation could continue for extended periods of time without precautionary measures for the resistors. With the new 100kΩ resistors, one in series with the cathode and one with the anode, plasmas could be generated under the same conditions: with compressed air, argon, or oxygen as the working gas at a flow rate between 40-150 mL/min, plasmas consistently ignited between 1100 and 1400 V, at currents in the 6-9 mA range. Even with the adjustments made and the ability to have lengthy plasma generation periods, a glow-discharge plume was still not visible at the base of the electrode.

Despite the ultimate goal to have a plasma generated at atmospheric pressure, the difficulties in obtaining a sustained plume lead to several trials at reduced pressure, in attempts to draw the plasma out of the microelectrode. The first attempt affixed the microelectrode inside a three-necked flask (see Figure 8, page 25). Pressure in the flask was reduced via water aspiration and a plasma was struck in the usual way. Unfortunately, though a current was sustained as before and a visible plasma was struck inside the microelectrode, these attempts were still unsuccessful in generating a visible plume. Another trial at even lower pressure was attempted,
Figure 8. Machined microelectrode system, reduced pressure attempts in 3-neck flasks with water aspiration. Plasma plume did not form.
this time inside the vacuum chamber utilized in previous experiments done by the Schaeffer group (see Figure 9, page 27). The pressure in the reaction vessel was reduced to less than 10 torr, and a plasma was struck inside the microelectrode in the usual way. The current sustained was extremely stable, and the glow-discharge was extremely bright even at lower voltage and currents (500-800 V, 3-5 mA). Unfortunately, there was no visible plume outside of the microelectrode. To determine if the microelectrode emitted an invisible plume, a copper plate was affixed inside the vacuum chamber. If a plasma plume were present (even an invisible one), in theory, it should impinge upon the copper plate and change the surface. After approximately 15 minutes of plasma impingement, the copper surface was unmarked, leaving no evidence for the emission of a plume, undetectable or otherwise.

Redesigning a Plasma Electrode – Back to the Basics

Though a plasma could be struck and maintained with the machined electrode, a plume was not obtained under any tested reaction conditions. Thus, a new microelectrode with variable parameters was designed. Using the same basic design as the original schematics, a stainless steel tube was utilized as the cathode, insulated by a layer of Teflon tape (at first) and then a glass tube, with a stainless steel external anode (see Figure 10, page 28). At the base of the electrode, a thin copper plate was added to the anode with a hand-drilled hole, utilized to restrict gas flow through the bottom of the cell. To prevent short-circuiting, a layer of Teflon was added above the copper plate and an identical hole was drilled into the sheet.

With the new electrode system, a plasma could be struck under similar conditions as before: similar flow rates and voltages were put in, and similar current outputs were obtained. Though a visible plasma could be seen through the base of the electrode, there was no visible plume at the base of the electrode. Many conditions were attempted with this electrode system to
Figure 9. Machined microelectrode system in reduced-pressure attempts, vacuum chamber. Pressures were between 5-10 torr during these attempts. Plasma plume did not form.
**Figure 10.** New microelectrode system with variable parts. Electrode consists of a stainless steel cathode, wrapped in Teflon tape and insulated with a glass rod. Anode is outer stainless steel casing and copper plate at base of casing. Anode and cathode are separated by a thin Teflon disc. Both the Teflon disc and the copper plate have identically drilled holes through them, 1/16” in diameter. Variation in structure at bottom can be made by the addition of Teflon discs and copper plates, to increase thickness of both anode and insulator.
generate a plume without any significant results. To determine whether or not an undetectable plume was generated by this electrode system, a clean copper plate was arranged approximately 1 cm below the bottom of the electrode. At the end of a 3-hour period of supposed plasma impingement upon the copper surface, there was no evidence of etching upon the copper surface and thus, no generation of a plasma plume (visible or otherwise).

**Conclusion**

Motivated by a desire to improve current synthetic methods for solid-state inorganic multinuclear materials, we attempted to form a reactive glow-discharge plasma plume, to be utilized as a low-energy alternative mediator for inorganic synthesis. Several different electrodes were assembled and tested, following the direction of previously successful plasma microelectrodes. For several designs, a plasma could be generated, as attested by the presence of a stable, non-zero current and the characteristic colored glow of a glow-discharge plasma. Despite many attempts to form a reactive plasma plume, none were successful and thus, no attempts could be made to utilize the electrodes in chemically relevant means.

The next steps for this project will need to focus on optimization of electrode design to obtain a reactive plasma plume. When a reactive plume is obtained, chemical syntheses can be attempted. Likely, the first steps will be to impinge the reactive plume onto a copper surface. If the plasma has reactive oxygen carrier species, the expected product of the process would be copper oxide. If that process works in a reproducible fashion, more complicated mixed-metal oxides, like CuMgO₂, will be produced in a similar fashion by plasma impingement upon a mixture of metallic solids.
References


