Appendix I: Electrospray Sources

A1.1 Introduction

Electrospray has been used to aerosolize low volatility materials such as proteins, molecular ions, and inorganic salts. Depending on the nature of the application and the type of the material to be volatilized, the characteristics of the electrospray will be different. Regardless of the actual configuration, the essential element of the electrospray is the formation of a stable Taylor cone. The Taylor cone forms when the surface tension of the liquid, the force due to the applied electric field, and the pressure balance, causing the liquid to form a conical protrusion with a half angle of 45.3° that is typically formed at the end of a capillary. At the tip of the cone, the liquid emits a fine dispersion of charged droplets containing dissolved species. The relatively high volatility liquid will evaporate, resulting in progressively smaller droplets. If the droplet becomes highly charged to the point of the Rayleigh limit, the droplet will emit daughter ions that are significantly smaller to reduce the amount of charge on the droplet. At the daughter ion formation and liquid evaporation process, the insoluble material is the only element remaining. To control the amount of material in the final product, many parameters can be varied including the solvent, the solute concentration, and the evaporation rate (through temperature and gas dilution), among other variables. As the two applications of electrospray described in this work are very different in nature, two very different electrospray units were constructed and are described in the following sections.

A1.2 Electrospray Apparatus: Detailed Assembly

While electrospray sources come in a variety of forms, the electrospray units built for the research described in this report have three basic components: (1) the electrospray unit, (2) the liquid delivery system, and (3) the gas delivery system. While these basic elements are similar for both of the electrospray units constructed, the actual details of the design are different. For instance, the liquid delivery system is identical for the two electrospray sources. A key difference is that the electrospray unit used for thin film deposition requires a holder for the substrate to collect electrosprayed material. To completely describe the two electrospray units, the common liquid delivery system will be described first and the details of the individual electrospray units will follow.

A1.2.1 The Liquid Delivery System

The liquid delivery system selected for both electrospray apparatuses utilizes the gas pressure above the liquid to force the liquid through the electrospray capillary. A regulator is used to reduce the pressure of the compressed air available in the lab to lower pressures. The output of the regulator is attached to a Swagelok "cross" fitting. The first connection of the "cross" has a series of one-way valves (not shown) that will maintain 3 psi of pressure on the regulated line before triggering to release excessive pressure. The second connection is attached to a pressure gauge (range; 0–20 psi). The final connection is attached to a three-way valve (not the common connection of the valve). The common connection of the three way valve is connected with a plastic tube that is inserted through a rubber stopper to the headspace of the liquid reservoir (100 mL round-bottom flask). The third connection of the three way valve is open to ambient pressure. Depending on the direction of the valve, the headspace above the liquid is either pressurized (open to regulator) or not (open to ambient). The rubber stopper has a second piece of plastic tubing protruding through it that is connected to the electrospray capillary. The end of this plastic tube inside the reservoir is immersed in the liquid so that once the reservoir is pressurized the liquid will flow through the tubing. With this configuration, the liquid flow rate can be controlled to a limited extent through adjusting the pressure on the output of the regulator.

To stop the flow of liquid to the electrospray capillary, the three way valve is first opened to the ambient. This will only stop the flow of liquid and the liquid in the immersed plastic tubing will remain stagnant. To empty this liquid back into the reservoir, the drying gas must be flowing through the electrospray chamber and a valve downstream of the electrospray chamber must be closed. Closing this valve will pressure the electrospray system until the gas flows through the capillary, pushing the liquid in the plastic tubing back into the reservoir.

A1.2.2 Electrospray for Volatilization of Molecular Ions

The electrospray unit used to volatilize molecular ions is schematically pictured in figure A1.1. For this system, the electrospray is generated at the tip of stainless steel (SS) capillary (O. D. ≈ 1 mm, I. D. ≈ 130 μm, length 50 mm). The tip of the capillary is carefully machined to a fine point (~200–300 μm) and subsequently sanded (grit 2000) to produce a smooth finish where the tip is perfectly flat.

The capillary is positioned inside an NPT cross (1/4" Stainless Steel) using a custom-machined plastic (Delrin) part with the tip pointing vertically downward. The plastic part is threaded on one end so that it can seal with the NPT fitting. The other end of the plastic part seals against the capillary using an O-ring and a plastic cap to compress the O-ring. This plastic part serves to electrically isolate the capillary from the remaining parts of the electrospray assembly and to hold the capillary so that the sharpened tip is in the center of the cross fitting.

The capillary is biased using a positive high voltage power supply (Acopian 10 kV) while the NPT cross is grounded. The NPT connection opposite the capillary is used for the aerosol outlet. When an NPT to Swagelok fitting was placed on this connection, the gap between the capillary and the grounding point was non-uniform. A piece (I. D. ≈ 1 mm) was machined to fit inside the cross. This piece created a more uniform electric field and decreased the gap between the capillary and the ground, increasing the electric field.

The two remaining connections of the cross adjacent to the capillary are used to introduce the aerosol carrier gas into the electrospray unit and to visualize the Taylor cone of the electrospray. Attached to these connections on both sides is a “tee” fitting where one connection is an NPT type and the other two are Swagelok. The NPT connections are attached to the female NPT connection of the cross in such a manner that an optical path is maintained through the center of the NPT cross. The Swagelok connection not along the optical path is connected to a nitrogen stream that is controlled using a mass flow controller.

To seal the electrospray unit while maintaining the optical path required two identical window assemblies. A small window (5 mm O. D.) is epoxied in place on the inside of a Swagelok nut. Once the epoxy dries, Teflon ferrules are inserted into the nut with the appropriate orientation. A short length (~4 mm; O. D. 6 mm) of stainless steel tubing whose bore has been enlarged is inserted into the ferrules. Without this short section of tubing, the ferrules will not seal and will impede the optical path.

For this assembly using 1-propanol as the electrospray solvent, a positive bias of approximately 3.5 kV is required to maintain the Taylor cone. The Taylor cone could be monitored using a web camera positioned along the optical path. A representative image of the stable Taylor cone is provided in figure A1.2.

A1.2.3 Electrospray for Nano-structured Electrodes

The electrospray unit used to form nano-structured electrodes is schematically pictured in figure A1.3. For this system, the stainless steel capillary (O. D. ≈ 1 mm, I. D. ≈ 130 μm, length 50 mm) used to generate the electrospray was carefully machined to a fine point (~200–300 μm) and subsequently sanded (grit 2000) to produce a smooth finish where the tip is perfectly flat. To generate the electrospray, the capillary is biased using a positive high voltage power supply (Acopian 10 kV) while the aluminum body and the sample holding pedestal are grounded.

The body of the electrospray unit is aluminum (O. D ≈ 50 mm, I. D. ≈ 40 mm, length ≈ 80 mm). On one end, a plastic (Delrin) part is used to position the electrospray capillary so that the tip points vertically upward. The plastic part holds the capillary in place using an O-ring and a plastic cap to compress the O-ring against the capillary. This plastic part serves to electrically isolate the capillary from the remaining parts. An upward geometry was preferable as this prevented any liquid dripping from the capillary onto the substrate holder. Dripping was a major problem as the liquid would re-dissolve the material that had been elecrtrosprayed, resulting in a coarser structure.

On the other end of the aluminum body is a second plastic piece that holds an aluminum pedestal that is used to hold a substrate for material collection. As the sample rests upside down during material collection, a press-fit ring is used to hold the sample on the pedestal. The portion of the pedestal inside the chamber is heated via conduction from the portion outside of the chamber.

In the side of the aluminum body, four ports have been made. Connected to two of the ports are the gas inlet streams on opposing sides of the chamber. The drying gas exits through four holes drilled radially into the side of the pedestal behind the sample. The remaining two ports have windows epoxied into place. One window admits light into the chamber so that observation of the Taylor cones can be made through the other window.

To facilitate drying of the electrosprayed material, the inlet gas lines (T_1), the chamber (T_2), and the pedestal for deposition (T_3) can be heated. Each of these sections is independently heated with heat ropes. The temperature of each section is maintained constant with a temperature controller.

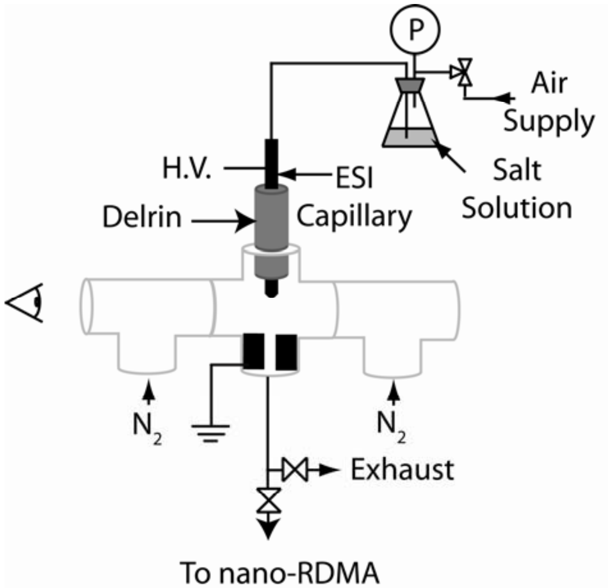

Figure A1.1. Schematic of the Electrospray Source.

Schematic of the electrospray source used to volatilize molecular ions.

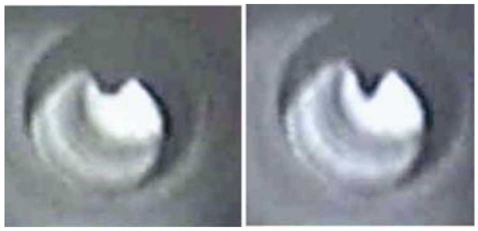

Figure A1.2. Electrospray.

Image captured of the electrospray unit before introducing fluid and after introducing fluid when operating with a Taylor cone.

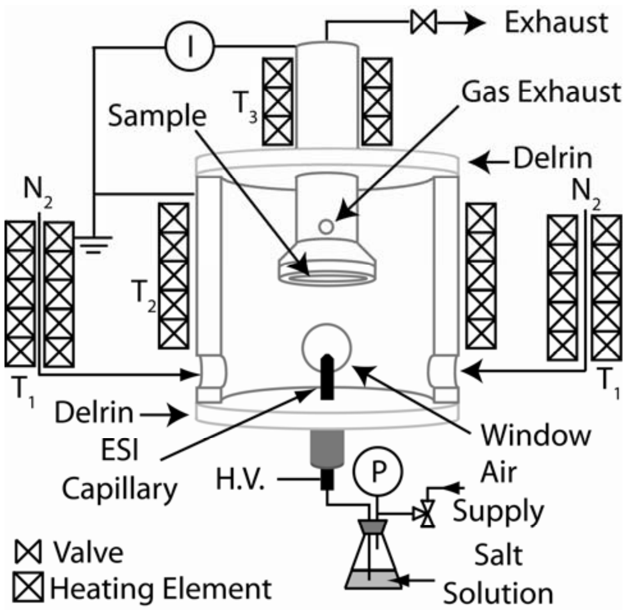

Figure A1.3. Schematic of Electrospray.

Schematic illustration of the electrospray source used to form nano-structured thin films.