Doctoral Thesis

Electrohydrodynamic spraying - Transport, mass and heat transfer of charged droplets and their application to the deposition of thin functional films

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Publication Date:
2004

Permanent Link:
https://doi.org/10.3929/ethz-a-004718257

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Electrohydrodynamic spraying –
Transport, mass and heat transfer of charged droplets and
their application to the deposition of thin functional films

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of

DOCTOR OF SCIENCES

presented by

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Zurich 2004
Acknowledgments

I would like to express my gratitude to Prof. Sotiris E. Pratsinis who supervised my Ph.D. thesis. He was a continuous source of motivation, encouragement, advice and enthusiasm. Many thanks also to my co-examiner Prof. Ludwig J. Gauckler for his interest in my work and the stimulating discussions.

This thesis evolved in close collaboration with Dr. Dainius Perednis and Dr. Lutz Mädler. I would like to thank both of them for many hours of hard laboratory work and intense scientific discussions.

But this work would have not been possible without the contribution of the whole Particle Technology group and the support of the Institute of Process Engineering. I enjoyed and profited very much from an exceptional working atmosphere. Thanks a lot to Roger Müller, Susanne Veith and Karsten Wegner, my long-time companions in the office, further our secretaries Patricia Horn and Illeana Eugster who have been always a source of understanding in “human problems” and a source of help in administrative one’s. Many thanks also to the workshop. They helped a lot with their creativity to find exceptional solutions when I got stuck with a mechanical problem.

Finally I would like to thank my parents, my family and the wonderful Nanette Bauer who were a source of continuous support when times became hard and were always there when I needed them most.

The financial support by the Commission for Technology and Innovation (KTI, Project No. 4810 and 5487), and the Swiss National Science Foundation (SNF, No. 2160 – 064546.01) is kindly acknowledged.
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Zusammenfassung


Elektrosprays eine vielversprechende Möglichkeit für eine schnelle und exakte Prozesskontrolle darstellen, um Zusammensetzung und Morphologie des Produktes zu kontrollieren. Ein weiteres wichtiges Anwendungsgebiet ist die Elektrospray-Ionisation, die die Massenspektrometrie von grossen Molekülen und biologischen Zellen revolutioniert hat.


Kapitel 4 beschreibt die Anwendung eines Conejet und Multijet Elektrosprays auf die Deposition eines dünnen Keramikfilmes. Die Parameter, die das Filmwachstum von Yttria-stabilized Zirconia (YZS) für die Anwendung als Elektrolyt in einer Feststoffbrennstoffzelle beeinflussen, werden untersucht. Die Resultate werden mit den Filmen, die mit einer Zweistoffdüse produziert wurden, verglichen. Es wird gezeigt, dass die anfängliche Tropfengrösse nach dem Tropfenaufbruch und die
Substrattemperatur den grössten Einfluss auf die Filmmorphologie haben. Homogene, nicht gerissene Filme können nur erzeugt werden, wenn die Tropfen nicht verdampfen, bevor sie das Substrat erreichen. Die Substrattemperatur muss oberhalb des Siedepunktes des Lösungsmittels sein, um eine sofortige Verdampfung nach dem Auftreffen zu garantieren, und damit ein Reissen des Films zu vermeiden.
Summary

Electrosprays and their applications are examined in this study. The droplet transport and evaporation of electrohydrodynamic sprays is investigated by modeling and measurement of droplet size and velocity distribution in spray cones. Further, the influence of spray parameters on the deposition of ceramic thin films and their morphology is examined.

The first chapter is reviewing important findings in basic research of charged sprays in general and electrohydrodynamic sprays in detail. Charged droplets appear practically in every droplet production process. Charged droplets become technically interesting when the charge on the droplet is high enough to enable the control of their transport. This leads to investigation of electrohydrodynamic sprays. Electrohydrodynamic sprays generally appear in the capillary-plate configuration where the liquid that shall be atomized is pumped through the capillary that is held at an electrical potential of several kilovolts versus the grounded plate. Different electrospray modes can be distinguished with increasing potential. The modes differ in the way the droplets are produced, droplet size and size distribution, number of charges on the droplet, spray properties (radial droplet distribution and mass flux). The most “popular” electrospray mode is the conejet mode which is well investigated and principally understood concerning cone and jet development and droplet break-up. Other modes are still a mainly unexplored field for research. Further, there is only a minor number of works looking into the droplet history after break-up, although this is a decisive part for the process as for example product quality in deposition processes depends on droplet size, precursor concentration in the droplet, droplet flux distribution, etc. Also most influencing applications which are driving recent research are reviewed. Deposition processes are a main topic as electrosprays have an intrinsic high deposition efficiency due to their guided droplet deposition by the electric field. Especially deposition of ceramic thin films is under investigation recently as electrosprays are a promising technique for a fast and accurate process controlling composition and morphology of the product. Further, electrospray ionization has revolutionized mass spectroscopy of large molecules and biological cells.
The second chapter is focusing on the development of a model describing the droplet transport and evaporation in a conejet electrospray. Therefore a model system is investigated and the important parameters are filtered. The narrow spray after jet break-up is broadening due to mutual electric forces of the droplets, whereas the external electric field is dominating the axial velocity distribution. The mutual repulsion of the droplets is also responsible for the spatial segregation of primary and secondary droplets. The droplet mass transfer is controlled by evaporation and Raleigh breakup into small secondary droplets. But large substrate temperature changes are necessary to accomplish a significant change in deposition droplet diameter.

The third chapter compares two electrospray modes which are significantly different with respect to their spray properties: Firstly, the conejet mode with a controlled break-up and a nearly monodisperse size distribution with a spraying angle smaller than 45°, secondly the intermittent multijet mode with a rather chaotic droplet break-up resulting in a broad droplet size distribution and a spraying angle close to 180°. The model for the conejet introduced in chapter two is compared to droplet size and velocity measurements with a Phase Doppler Anemometer (PDA). Further the model is extended to describe also the behavior of the intermittent multijet and is as well compared to PDA measurements. For the conejet it is found that increasing the substrate temperature leads to an increase of droplet evaporation and thereby to a noticeable increase of the solvent background vapor pressure.

Chapter four describes the application of conejet and multijet electrospray on the deposition of ceramic thin films. The parameters influencing the film growth of yttria-stabilized zirconia (YSZ) films for application in solid oxide fuel cells (SOFC) are investigated. It is shown that the initial droplet size after droplet break-up and substrate temperature appear to have the largest influence on film morphology. Homogeneous, uncracked films only grow if the droplets do not evaporate before reaching the substrate. The substrate temperature has to be above boiling point of the solvent in order to guarantee an instant evaporation after impact in order to avoid cracked surfaces.
1 Electrospraying and its applications

Abstract

Electrosprays are of great interest for technical application as well as tool for scientific research. Here the current state-of-the-art in electrospraying is reviewed. The focus is especially on electrohydrodynamic sprays where the atomization of the bulk liquid is done by electric forces only. The applications of electrosprays are manifold and range from ionization techniques for mass spectrometry of large molecules over crop spraying to spacecraft thrusters. An overview of the different applications is given with a focus on electrospray deposition techniques.

1.1 Introduction

Electrohydrodynamic spraying is already examined for many years since Zeleny’s first systematic investigations (Zeleny, 1917). However, recently it is getting more attention due to a spreading of its applications into diverse scientific and industrial applications. But electrohydrodynamic spraying is only one aspect of phenomena controlled by charged droplets. Practically any droplet production process is also generating charges even without any external electric field applied. The amount of charges produced in a breakup process depends on the concentration and mobility of free ions in the liquid. Smoluchowski (1912) proposed the theory that for natural charging the droplet charge depends on the number of positive and negative ions that happened to be by chance in the liquid volume forming the droplet. On the other hand the production of charged droplets with an external electric field present during the breakup process is more evident and effective than natural charging. This process called induction charging is illustrated by Lord Kelvin’s water dropping machine (Kelvin, 1867). By backcoupling of charges eventually produced by water droplets dripping from two nozzles he was able to establish a mutual potential difference of 10 kV. In 1969 three VLCC’s (very
large crude carriers) exploded during washing operation of the cargo tanks when powerful water jets produced space potentials of several thousand volts in the tanks having a capacity of over 10000 m³ (Bustin and Dudek, 1983). But charged droplets have also an impact on natural phenomena. Salt water droplets emanating from the sea surface (Blanchard, 1958) as well as water fall droplets (Reiter, 1994) are charged due to the natural electric field of the earth (130 V/m). There is a great influence of droplet breakup of seawater bubbles bursting on the surface onto electric charging of the atmosphere (Blanchard, 1958). The droplets are mainly positively charged leaving the earth with a negative potential. Droplet breakup is also one reason for charge separation in clouds which is leading to lightning in thunderstorms. Generally the charged droplet production happens in the form of jet breakup, be it a natural process like a waterfall or a man-made jet for liquid atomization. The charge production by liquid jet breakup is called “Lenard effect” named after the German physicist Phillip von Lenard who discovered the phenomenon by examining the increased electrical charge density near waterfalls (Lenard, 1892).

There is a number of ways to produce sprays for technical application. Most practical atomizers are of the pressure, rotary or twin-fluid type (Lefevbre, 1989). They use mechanical energy to disintegrate the liquid body. It is possible to induce charges into the mechanically atomized sprays by applying a high voltage to the spraying device. A pressure spray with high voltage is for example used for fuel jet production in car engines (Bellan, 1983). In “pure” electrohydrodynamic sprays the liquid is disintegrated by the applied electric potential only. The typical electrospray setup consists of the capillary-plate configuration. The liquid is flowing through the metal capillary exit where the high electric field accelerates the liquid resulting in jets that break up into droplets. Depending on liquid properties, applied potential and setup geometry different electrospray modes appear. They are reviewed in Cloupeau and Prunet-Foch (1990).

The motivation for technical application of charged droplets and electrified sprays can be found in the possibility to control droplet transport, evaporation and life time by applying external electric fields. The advantage for deposition purposes is evident as the droplets can be directed to the wanted location of impact by tailoring the external electric field. Deposition is one of the main applications due to the intrinsic
high deposition efficiency (Siefert, 1984). Since the 40s of the last century there is ongoing development of devices for crop spraying (Bailey, 1988). Electrospray painting is an established process e.g. in automotive industry (Domnick, 2003). But as variable as electrified sprays are their applications. Controlled particle formation (Park and Burlitch, 1996), application in car engines for fuel injection (Kelly, 1999) or medical sprays are under investigation (Ijsebaert et al., 2001).

1.2 Droplet production and charging

1.2.1 Atomization techniques

In order to atomize bulk liquid into droplets, energy has to be brought into the system. Mechanical energy can be added to the liquid by applying high pressure, vibration or kinetic acceleration. Further, electric energy can be added to the system by applying high voltage which is disrupting the liquid body into droplets. Even heating the liquid to boiling point is producing droplets. Air bubbles bursting at the liquid surface lead to the formation of droplets. For the production of charged droplets mostly the “pure” electrospray method of applying a high voltage to a capillary is used. But hybrid electrosprays are applied extensively also, e.g. for production of atomizing charged fuel sprays (Romat and Badri, 2001) where an electric field is applied to a conventional pressure nozzle.

The droplet size that is produced with an atomization device is often essential to the process the spray is applied to. The diameter of droplets which are formed from liquid which is slowly flowing through a thin circular outlet can be calculated from (Lefebvre, 1989):

\[
d = \left( \frac{6d_0 \sigma}{\rho_L g} \right)^{1/3},
\]

where \(d_0\) is the outlet diameter, \(\sigma\) the liquid surface tension, \(\rho_L\) the liquid density and \(g\) the gravity constant. The size of water droplets dripping from an opening with
d_o = 1 mm is therefore d = 3.6 mm. This droplet size and volume feed rate are not suitable for most industrial processes. Therefore the force applied to the droplet has to be increased with respect to the gravitation force in this example. Atomizers applying mechanical energy to the liquid body mostly rely on a high relative velocity of liquid and surrounding gas medium. The influence of the aerodynamic drag force on droplet breakup is investigated already for a long time and can be summarized in the critical Weber number:

\[ \text{We}_{\text{crit}} = \frac{\rho_{\text{air}} U^2 d}{\sigma}, \]

where \( \rho_{\text{air}} \) is the gas density and \( U \) the relative velocity. Hinze (1955) estimated a Weber number of 22 for a free falling drop and 13 if the droplet is suddenly exposed to a high velocity air stream. Taking into account the equation of settling velocity from Hinds (1989) the critical breakup diameter of a free falling water droplet in air is \( d = 5.5 \) mm at its settling velocity of \( v = 15.9 \) m/s. If the droplet would be exposed to a sudden increase of air velocity from zero to 15.9 m/s the droplet size shrinks to 3.25 mm. Assuming a sudden increase from 0 to 100 m/s the critical breakup diameter becomes 78 \( \mu \text{m} \) ! This simple calculation illustrates the principle of most atomizing devices. Rotary, pressure as well as air-assisted atomizers produce a high relative velocity between the liquid that shall be atomized and the gas medium. Pressure atomizers rely on the conversion of pressure into kinetic energy of the liquid. A liquid jet with a high velocity is produced e.g. by forcing the liquid through a plain orifice. The liquid jet is disintegrating into droplets. The air-assisted atomizer is using pressure to produce a gas jet with high velocity which the liquid body is exposed to. Further information about jet breakup, droplet disintegration, details of nozzle design by atomizers using mechanical energy for droplet production can be found in Lefebvre (1989).

The type of atomizer using electric force to overcome the surface tension of the liquid is called electrostatic or electrohydrodynamic. The two terms are used exchangeable in literature. Here the acceleration and droplet breakup is induced by the electric field acting onto the droplet surface. Lord Rayleigh (1879) found that an electrically charged droplet is becoming instable when the outward electrostatic forces
are balancing the surface tension forces. The maximum charge on a droplet with size $d$ can be described according to Rayleigh (1879):

$$q_R = 8\pi(\varepsilon_0 \sigma d^3)^{0.5},$$

where $\varepsilon_0$ is the dielectric constant, $\sigma$ the surface tension and $d$ the droplet diameter.

Lord Rayleigh observed that the instability of a droplet resulted in the emission of a liquid jet. Electrohydrodynamic spraying (EHS) is based on this effect. Duft et. al. (2003) were able to visualize this effect with a high speed camera (Figure 1.1). An ethylene glycol droplet with 58 $\mu$m initial radius was therefore observed. When the droplet reached 24 $\mu$m due to evaporation it become unstable and emitted liquid jets that themselves disintegrated into small droplets.

Typically the setup of EHS consists of an electrically conducting capillary to which a high potential is applied and a grounded counterplate. The liquid is fed through the capillary and is atomized by the electric field at the capillary exit. Cloupeau and Prunet-Foch (1990) describe the different spraying modes that can appear depending on setup geometry (e.g. distance between capillary and plate or capillary radius), volume feed rate, liquid properties (surface tension, electrical conductivity) and applied potential (Figure 1.2). Firstly there is the dripping mode. In the absence of an electric field the liquid flows drop by drop. Increasing the potential from zero increases the

![Figure 1.1: Rayleigh droplet breakup (after Duft et al., 2003).](image)
Figure 1.2: Electrospray modes (after Cloupeau and Prunet-Foch, 1990).

droplet dripping frequency and decreases the droplet size. This behavior has two reasons: The liquid is attracted to the grounded plate due to the action of the external electric field, further the surface tension is reduced due to the accumulation of charges on the surface of the pending droplet. Secondly comes the microdripping mode and later the conejet mode. The liquid droplet at the capillary exit is deformed by the electric field and takes the shape of a cone. A droplet is formed directly at the droplet apex in the microdripping mode. In the conejet mode the cone is extended by a jet which is breaking up into droplets. Clopeau and Prunet-Foch (1989) show that the breakup of the jet is comparable to the uncharged jet-breakup investigated by Lord Rayleigh. Lord Rayleigh’s theory proposes a droplet diameter to jet diameter ratio of 1.89. This ratio is also found for the conejet-breakup for moderately charged jets. The jet-breakup process leads to micrometer sized droplets as even with the capillary outlet being in the order of millimeters the diameter of electrospray jets are in the order of micrometers. Consequently the electrospray mechanism serves as jet miniaturization apparatus. Variations of the conejet appear at the lower and upper potential limit of the stable version. If the potential is slightly under the necessary potential for a permanent jet the intermittent or pulsed conejet is observable. The shape of the liquid at the capillary exit is alternating between the form of a cone (emitting a jet) and a rounded drop. At increased potential the conejet becomes unstable and two or more jets appear. This is the multijet. The number of jets increases with increasing potential. Simple jet, ramified
jet and spindle mode are modes that appear at even higher electric potentials. Here the jets emitted by the capillary are highly charged and unstable. They branch into sub-jets or start wiping. The difference to conejet and multijet mode is mainly the high charge density on the jets. Whereas for conejet and multijet the breakup is still purely of mechanical nature, the charge density for ramified jet is so high that the jet gets torn apart by the mutual repulsion of these charges.

For the electrospray production process Blades et al. (1991) propose the analogy to the physical processes in an electrolysis cell (Figure 1.3). Assuming a positively charged metal capillary the negatively charged ions in the solution are attracted to the metal surface where they become oxidized. The excess of the now positively charged bulk liquid leads to surface instabilities and droplet production. The positively charged droplets transport an electric current towards the grounded electrode where the positive ions are reduced. The electrons required for closing the charge balance are flowing through the external electric circuit

The conejet and intermittent multijet mode shall be introduced more closely in the following.
1.2.2 Conjet mode

The first mentioning of the conejet dates back to 1600. Gilbert (1958) (translation into English) reports in his book “De magnete” that a liquid drop that is subject to strong electric forces adopts a roughly conical shape. But it took still three hundred years until Zeleny (1917) was the first to investigate electrosprays systematically in the capillary-plate configuration. He examined the dripping mode, conejet and multijet of ethanol and glycerine and was the first to take photographic images of the process. Vonnegut and Neubauer (1952) investigated electrosprays with D.C. and A.C. voltage and were also able to see different spraying modes. Among them the dripping mode and the conjet mode. They produced a monodisperse conejet spray with droplet sizes around 1 µm. Like Zeleny (1917) they found that it is hard to establish conejets with undistilled water for its high electrical conductivity. But they were successful with alcohol, lubricating oil and distilled water. There are a number of works dealing with the stability limits of conejets but it is hard to give general rules for boundary values of single parameters like conductivity or surface tension of the liquid as the values are not independently influencing the spray formation process. For the lower limit of the conductivity the estimates range from $10^{-8}$ to $10^{-11}$ S/m (Cloupeau and Prunet-Foch, 1989). The estimates for the upper limit also vary heavily: According to Mutoh et al. (1979) the upper conductivity limit is $10^{-5}$ S/m, but Smith (1986) could establish a conejet at $10^{-1}$ S/m. The situation is similar with the surface tension parameter. Conejets could be established with glycerin ($\gamma = 0.063$ N/m) and even with water ($\gamma = 0.073$ N/m).

Table 1.1 is giving examples of liquids with their properties that were used to establish the conejet mode.

There are efforts to estimate conejet droplet size and electric current ab initio from liquid properties and liquid flow rate. The electric current that is produced by this process and emitted through an electrified jet depending on volume feed rate, liquid properties, setup geometry and electric potential was examined by Fernandez dela Mora and Loscertales (1994). They did not find a relevant influence of the applied voltage and the needle geometry on the electric current if the other parameters (liquid conductivity,
volume feed rate) are kept constant. But they found a relation coupling the electric current \( I \) of the spray with the liquid properties and the volume feed rate \( Q \):

\[
I = f(\varepsilon)\left(\frac{\gamma K}{\varepsilon}ight)^{0.5}.
\]

The function \( f(\varepsilon) \) is determined experimentally. \( K \) is the electric conductivity, \( \varepsilon \) the relative permittivity and \( \gamma \) the surface tension. Gañán-Calvo et al. (1997) derived scaling laws for spray currents and droplet size based on a theoretical model of charge transport. The results compare very well with the experiments. Their description of current and droplet size splits in two domains: high and low conductivity and viscosity liquids. The current in the cone is transported in two ways. There is ion conduction through the liquid due to the electric field and ion transportation due to fluid convection. When applying an electric field to a pending droplet it is deformed to a cone. The cone liquid surface is accelerated towards the apex due to a tangential electric stress on the free ions in the liquid and a jet is formed which is breaking up into droplets. Cone and jet shape, electric current and droplet size therefore depend on viscosity and conductivity of the liquid (Figure 1.4). The domains are separated by a dimensionless variable incorporating the influence of conductivity and viscosity:

\[
G = \left(\frac{\gamma^2 \varepsilon}{\mu K^2 Q}\right)^{\frac{1}{2}},
\]

where \( \mu \) is the liquid viscosity. Gañán-Calvo et al. (1997) found a square root dependence of the current from the liquid feed rate for \( G < 1 \) (high conductivity and viscosity liquids) which is in accordance with Fernandez De la Mora and Loscertales (1994) and a dependence \( I \propto Q^{\frac{1}{3}} \) for \( G > 1 \) (low conductivity and viscosity).

The development of the conejet electrospray can be sliced in three parts that can be examined almost separately. Firstly the development of the cone and its shape, secondly the droplet breakup of the liquid jet that is emitted at the cone apex, and thirdly the transport of the droplets to the counter plate. Consequently, many works are highlighting one of the three aspects:
Theoretical description of the conejet started with Taylor (1964) who was the first to explain the cone shape of the pending droplet at the capillary exit. He calculated the cone angle to be 49.3°. In his honor the conejet is often called Taylor-cone. Joffre et al. (1982) proposed a numerical model for shape calculation of a stable droplet at the capillary exit under the influence of an electric field. Their equations are balancing the inner liquid pressure with the electrical potential distribution between the capillary and a plate. The model results show good agreement with the experimental data and are not restricted to a purely conical shape as Taylor’s analysis. Hayati et al. (1986) were able to visualize the convection patterns inside the cone by adding tracer particles to the liquid. They could show that the liquid is flowing towards the apex at the cone surface.

Figure 1.4: Cone shape, droplet size and electric current depend on the forces acting on liquid and dissolved ions: gravity, electric field, surface tension (from Hartman, 1998)
and flowing back to the base on the middle axis of the cone. They explain the behavior with the semiconductive property of the liquids used for conejet spraying. Due to the low conductivity a potential difference arises between cone base and apex. This induces the above mentioned tangential electric field on the cone surface which is accelerating the liquid. This also explains why undistilled water is not showing a conejet. The high conductivity does not allow a tangential electric field on the surface. Smith (1986) investigated the stability of the cone with respect to the onset potential, capillary radius, liquid conductivity, and viscosity. He also developed a theory for the electric field strength that is necessary to balance surface tension and internal liquid pressure of the cone. Shtern and Barrero (1994) include the electric Marangoni effect as one of the driving forces of the swirling motions in the Taylor-cone. Their equations also describe the vortex generation and breakdown of the cone-liquid flow patterns. Finally, Hartman et al. (1999a) presented a model that is able to calculate the shape of cone and jet. They are also able to give values for the electric field inside and outside the cone and the surface charge density at the cone surface. Further estimations of the liquid velocity at the cone surface are given. From these results even the electric current of the spray system could be calculated.

The breakup of a liquid jet was first calculated by Rayleigh (1878) for inviscid

Figure 1.5: Influence of external electric potential on droplet transport. Conejet picture adopted from Pantano et al. (1996).
jets in vacuum. Schneider et al. (1967) extended the work of Rayleigh by taking the electric charges on the liquid jet surface into account. But they concluded that the importance of jet instability due to charging is negligible in comparison to surface tension. Neukermans (1973) comes to the same conclusion although he states that the growth rate of charged liquid jet by Schneider et al. (1967) was calculated incorrectly. Taylor (1969) investigated experimentally the stability of electrified jets from conejet mode. Also his conclusion is that the breakup mechanism is of mechanical nature. Cloupau and Prunet-Foch (1989) found in their conejet experiments that the ratio of jet diameter to mean volume diameter is not changing with electrification of the jet. As already derived by Rayleigh for uncharged jet the ratio is given as 1.89.

The third part of the EHS system, droplet transport, is only investigated by few authors. The principle of the process is shown in Figure 1.5. The charged droplets follow the external electric field that is applied between the nozzle and the counter-electrode. Gañán-Calvo et al. (1994) developed a Langragian type numerical model for single droplet tracking between the droplet breakup location and the grounded counter-plate. The results are compared to experimental droplet size and velocity values obtained with a Phase Doppler Anemometer (PDA). The axial droplet velocity showed to be very high close to the capillary exit (~10m/s) and decreasing towards the grounded plate following the decreasing electric field gradient. Due to the nature of the breakup the spray is very narrow close to the capillary exit but is spreading towards the plate due to the mutual repulsion of the charged droplets. Further a size segregation could be seen in measurement and calculation. The smaller droplets were pushed towards the spray edges due to their higher mobility. Hartman et al. (1999b) used the model of Gañán-Calvo et. al (1994) but replaced the electric field approximation of Jones and Thong (1971) with their own electric field (Hartman et al., 1999a) which is derived from a numerical calculation including the charge distribution on the cone. The comparison of the model to the experimental data shows similar underprediction of the axial droplet velocity as with Gañán-Calvo’s model. The deficiency was explained by both authors by the entrained air due to momentum transfer from the droplets. Tang and Gomez (1994) examined the conejet spray with a PDA as well. They found that the axial droplet velocity is mainly due to the external field whereas the radial spread of the spray comes from the mutual repulsion of the charged droplets. Their work also includes the
only measurement of entrained air velocity in the conejets. By measuring the velocity of uncharged alumina particles in the air stream they found that the air velocity takes values of about 30 – 40 % of the droplet velocity close to the capillary. The value is approaching zero close to the counter-plate. Up to now there is no existing work including the full process of droplet transport, evaporation, mass and heat transfer, although it is of great importance in most electrospray applications.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( \rho ) [kg/m(^3)]</th>
<th>( \mu ) [Pa s]</th>
<th>( \gamma ) [N/m]</th>
<th>( \varepsilon_r )</th>
<th>( K ) [( \mu S/m )]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>790</td>
<td>0.0032</td>
<td>0.023</td>
<td>20.7</td>
<td>53</td>
<td>Gañán-Calvo et al.(1997)</td>
</tr>
<tr>
<td>n-Butanol 99% pure</td>
<td>810</td>
<td>0.00294</td>
<td>0.0246</td>
<td>17.8</td>
<td>15</td>
<td>Rob Hartman (1998)</td>
</tr>
<tr>
<td>n-Butanol 99% +LiCl</td>
<td>810</td>
<td>0.00276</td>
<td>0.0252</td>
<td>17.3</td>
<td>101/216</td>
<td>Rob Hartman (1998)</td>
</tr>
<tr>
<td>Dioxane + 2/4% formamide</td>
<td>1030</td>
<td>0.00139</td>
<td>0.03</td>
<td>2.3/2.5</td>
<td>0.24/1.1</td>
<td>Gañán-Calvo et al. (1997)</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>1110</td>
<td>0.02</td>
<td>0.046</td>
<td>38.8</td>
<td>1</td>
<td>Jaworek and Krupa (1999)</td>
</tr>
<tr>
<td>Dioxane + 10/25/50/66.7% water</td>
<td>1027/1022/1015/1010</td>
<td>0.00157/0.00205/0.00235/0.00195</td>
<td>0.033/0.037/0.043/0.044</td>
<td>6.25/14.2/34.5/49.1</td>
<td>4.5/170/570/1300</td>
<td>Gañán-Calvo et al. (1997)</td>
</tr>
<tr>
<td>Dodecanol</td>
<td>830</td>
<td>0.012</td>
<td>0.028</td>
<td>6.5</td>
<td>2.85</td>
<td>Gañán-Calvo et al. (1997)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>789</td>
<td>0.00116</td>
<td>0.022</td>
<td>25</td>
<td>30</td>
<td>Rob Hartman (1998)</td>
</tr>
<tr>
<td>Ethylene glycol + LiCl</td>
<td>1109</td>
<td>0.02</td>
<td>0.048</td>
<td>38</td>
<td>21/72/186</td>
<td>Rob Hartman (1998)</td>
</tr>
<tr>
<td>Ethylene glycol + 0.96/0.23/0.042/10/10 M LiCl</td>
<td>1110</td>
<td>0.021</td>
<td>0.048</td>
<td>23.7</td>
<td>240000/62600/16900/500/54</td>
<td>Fernandez De la Mora and Loscertales (1994)</td>
</tr>
<tr>
<td>Formamide</td>
<td>1130</td>
<td>0.0037</td>
<td>0.058</td>
<td>111</td>
<td>28400</td>
<td>Fernandez De la Mora and Loscertales (1994)</td>
</tr>
<tr>
<td>Formamide + 0.147/0.0147/0.00147 M LiCl</td>
<td>1130</td>
<td>0.0037</td>
<td>0.058</td>
<td>111</td>
<td>270000/54900/31600</td>
<td>Fernandez De la Mora and Loscertales (1994)</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1262</td>
<td>0.92(25°C)</td>
<td>0.0063</td>
<td>X</td>
<td>1.57</td>
<td>Ku and Kim (2002)</td>
</tr>
<tr>
<td>Glycerol + 0.191/0.338/0.398/0.863 M NaI</td>
<td>1270/1285/1292/1342/1390</td>
<td>1400(20°C)/1050(25°C)/X/675(30°C)/690(30°C)</td>
<td>0.0063</td>
<td>X</td>
<td>544/1080/1200/1440/1680</td>
<td>Ku and Kim (2002)</td>
</tr>
<tr>
<td>Heptane + 0.1/0.4/1.0% Stadis</td>
<td>684</td>
<td>0.0039</td>
<td>0.021</td>
<td>1.9</td>
<td>0.77/1.9/4.5</td>
<td>Gañán-Calvo et al. (1997)</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>50</td>
<td>Ragucci et al. (2000)</td>
</tr>
<tr>
<td>Methanol</td>
<td>795</td>
<td>0.0059</td>
<td>0.021</td>
<td>33.6</td>
<td>85</td>
<td>Gañán-Calvo et al. (1997)</td>
</tr>
<tr>
<td>Octanol</td>
<td>827</td>
<td>0.0072</td>
<td>0.024</td>
<td>9.93</td>
<td>2.27</td>
<td>Gañán-Calvo et al. (1997)</td>
</tr>
</tbody>
</table>
Table 1.1: Liquids used for conejet electrospraying.

<table>
<thead>
<tr>
<th>Liquid (composition)</th>
<th>Density (g/cm³)</th>
<th>Viscosity (cP)</th>
<th>Surface Tension (mN/m)</th>
<th>Volume Flow Rate (μL/min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octanol + 0.047/0.13/0.38 M H₂SO₄</td>
<td>825.5</td>
<td>0.01064</td>
<td>0.026</td>
<td>10.34</td>
<td>116/567/2300</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>1040</td>
<td>0.0511</td>
<td>0.0344</td>
<td>X</td>
<td>1.22</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>1036</td>
<td>0.03</td>
<td>0.036</td>
<td>31.23</td>
<td>13.3</td>
</tr>
<tr>
<td>Sunflower oil + Stadis</td>
<td>920</td>
<td>0.021</td>
<td>0.029</td>
<td>3.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Water (distilled)</td>
<td>1000</td>
<td>0.001</td>
<td>0.0725</td>
<td>80.4</td>
<td>110</td>
</tr>
<tr>
<td>Water (distilled)</td>
<td>1000</td>
<td>0.00102</td>
<td>0.0740</td>
<td>80.4</td>
<td>140</td>
</tr>
<tr>
<td>Water + 25/50/75% glycol</td>
<td>1040/1080/1100</td>
<td>0.002/0.0042/0.0096</td>
<td>0.071/0.061/0.055</td>
<td>X</td>
<td>45/42/24</td>
</tr>
<tr>
<td>Water + 10⁻⁷/10⁻⁵/10⁻³ LiCl</td>
<td>998</td>
<td>0.01</td>
<td>0.072</td>
<td>80.1</td>
<td>830000/92600/21300/2150</td>
</tr>
</tbody>
</table>

1.2.3. Intermittent multijet mode

The intermittent multijet mode finds hardly any attention in literature. It is a variation of the continuous multijet mode and has the same visual appearance. But the breakup process and droplet size distribution are significantly different. One or several jets are emitted in an intermittent fashion from the capillary rim. In contrast to the cone- and stable multijet it shows a broad polydisperse droplet size distribution. Jaworek and Krupa (1996) investigated the stability regimes of continuous and intermittent multijet mode in the capillary-plate configuration regimes with respect to volume flow rate and electric potential. The continuous multijet showed two to eight stable streams of aerosol in pulsed light shadow graph pictures. Each of the jets had a thickness of a few tenths of a micrometer. On the other hand the intermittent conejet mode showed that small quantities of liquid are ejected in the form of short thick jets alternating at distinct locations of the capillary rim. The intermittent mode could be established from the continuous multijet by increasing external electric field and volume flow rate.

Grace and Dunn (1996) made measurements and calculations on, as they call it, fine sprays which are essentially intermittent multijets. Similar to the conejet also here...
the axial velocity is high close to the capillary compared to near-plate locations which seems evident as the electric field gradient is much higher close to the capillary due to its small dimensions. But this seems to be the only similarity. Near capillary measurements show a broad spray cross section (6 cm diameter at 0.5 cm distance to the capillary). The droplet size measurement with a Phase Doppler Anemometer shows a broad number size distribution for the ethanol spray with diameters between 1 and 30 µm. A size segregation does not appear. The broad size distribution appears in any location of the spray. The transport model of the droplets that was developed by Grace and Dunn (1996) matches qualitatively the measured droplet velocity results in the near capillary region and is able to follow the trends of the axial velocity development in axial and radial direction.

1.3. Electrospray applications

1.3.1 Electrospray deposition (ESD)

Siefert (1984) has shown that the droplet deposition efficiency of charged sprays is at least 80%. Preferential landing of charged droplets is another feature of ESD. Tailored electric fields enable the deposition of charged droplets in desired locations as shown by Kim and Ryu (1994). They used electrified masks to deposit silica nanoparticles in geometric micrometer-sized patterns on GaAs substrates. This makes electrosprays interesting for any kind of layer or film production. Consequently ESD finds application in processes as diverse as pesticide spraying on crops (Law, 2001) and painting of automobiles (Domnick et al., 2003).

There is ongoing research in the field of agricultural sprays for pesticide deposition and product post-treatment since the 1940’s (Bailey, 1988). The excellent deposition efficiency of electrosprays in combination with increasing demand in environmental safety is driving the research in the field of crop spraying. Pesticides have been implicated as being among the top ecological risks worldwide with their 2.25 billion kilograms sprayed annually (Law, 2001). Much inefficiency exists in depositing pesticides onto target-plant surfaces. This can result in 60-70% off target loss. Therefore
the specific problems that have to be addressed in this process are the transport space between spray source and crop surface and the crop shape. The varying transport space influences the droplet evaporation time. The crop shape influences deposition efficiency and possible corona discharges by sharply pointed leaves or hairs (Bailey, 1988). Devices for crop spraying range from small hand-held units like the *Elektrodyn* developed by Coffee (1981) to tractor-mounted systems (Law, 1978).

The challenges facing the automotive finishing industry are to increase the paint transfer efficiency and to reduce volatile emissions without sacrificing the surface quality or line speed (Im et al., 2001). The trend goes therefore from the pneumatic spray guns to rotary cup atomizers with a high voltage applied in order to charge the droplets. The optimal transfer efficiency for this system is higher than 90% under ideal operation conditions (Im et al., 2001). But compared to the pneumatic nozzles the rotary cup gives a darker and duller color appearance which is attributed to the inherent charges. Therefore research is done to investigate the influence of the electric field (e.g. Inkpen and Melcher, 1987), the splashing deformation of the charged droplets upon impact (Fukuta et al., 1993), the concentration of flake content in the droplets (Tachi and Okuda, 1992).

Ink jet printing has been introduced by Sweet (1965) as modern print
technology. His objective was to deflect charged ink jet droplets for oscillographic recordings of waveforms. Therefore a vibrating nozzle produced a droplet chain that was electrostatically charged by a coaxial ring electrode. The charged droplets were deflected by energizing electrodes with potential differences of several kilovolts and deposited on the printing paper which was moved transversely to the jet. Nowadays printers use multiple nozzles in linear arrays. Multicolour ink-jet printers may be used to print coloured patterns even on fabric surfaces (Bailey, 1988).

Numerous works have been published on the production of ceramic particles and films via electrospray pyrolysis deposition. The electrospray pyrolysis deposition setup consist generally of a charged capillary nozzle and a grounded heated substrate (Figure 1.6). A precursor is dissolved in a liquid and sprayed against the substrate. Depending on the process parameters different film morphologies can appear. Table 1.2 is listing ceramic materials produced via electrospraying. A major application of the deposited films can be found e.g. in batteries or fuel cells as electrode (e.g. LiMn$_2$O$_3$) or electrolyte (e.g. YSZ). Chen et al. (1996) list important parameters for the ESD process influencing the product quality: spray production, aerosol transport, solvent evaporation and droplet disruption, preferential landing of droplets on the substrate, discharge and spreading of droplets on the surface, decomposition and reaction of the solute (precursor). The droplet impact is illustrated in Figure 1.7. It shows an isopropanol droplet at $t = 0$, 1 and 6 ms after substrate contact (Sikalo et al., 2002). The droplet Weber number is 287. The droplet is spreading on the smooth substrate and does not show any splashing.

![Figure 1.7: Droplet impact of isopropanol droplet (after Sikalo et al., 2002).](image-url)
All of these processes can considerably influence the morphology and composition of the deposited film. Varying these parameters it was possible to deposit LiCoO$_2$ films with four distinct morphologies and compositions: A dense non-porous layer, a dense layer with incorporated particles, a dense bottom layer with a porous top layer and a fractal-like porous layer.

Further, Choy and Su (2001) propose three different scenarios for the deposition of a CdS film. For substrate temperatures above 450 °C the droplet solvent and precursor evaporated and decomposed before impact on the substrate resulting in the formation of

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Spray</th>
<th>Reference</th>
</tr>
</thead>
</table>
| LiCoO$_2$ | 1. Dense layer  
2. Dense layer with incorporated particles  
3. Porous top layer, dense bottom layer  
4. Fractal porous layer | C-P, Ethanol  
H = 6.0 cm, Φ = 15 kV  
T$_S$ = 200 – 500°C | Chen et al. (1996) |
| NiCoO$_2$ | Uniform porous layers | C-P, Ethanol+Butylcarbitol  
H = 3 cm, 0 - 20kV  
T$_S$ = 350 – 400 °C | Lapham et al. (2001) |
| ZrO$_2$/SiC | Dense ZrO$_2$ particle layer  
Porous SiC particle layer | C-R, Ethanol+Water  
H = 0.8 cm, Φ = 3.5 – 8 kV | Balachandran et al. (2001) |
| LiMn$_2$O$_4$ | Porous layers | C-P, Ethanol+Butylcarbitol  
H = 2–3 cm, Φ = 8–12 kV  
T$_S$ = 250 – 450°C | Chen et al. (1997) |
| YSZ | Dense and porous layers | C-P, Ethanol+Butylcarbitol  
H = 3.0 cm, Φ = 14 – 20 kV  
T$_S$ = 300 – 400°C | Nguyen and Djurado (2001) |
| CdS  
CdSe  
ZnS | Crystalline films | UAG, water  
Φ = 2 – 5 kV  
T$_S$ = 250 – 500°C | Su and Choy (2000) |
| SiO$_2$ | Particle patterns | C-P, Ethanol  
Φ = 15 – 18 kV | Kim and Ryu (1994) |
| SnO$_2$ | Particles | C-R, Ethanol  
H = 2.0 cm, Φ = 5 – 10 kV | Vercoulen et al. (1993) |

Table 1.2: Ceramic materials deposited as films via ESD. (C-P) means capillary-plate configuration, (C-R) means capillary-ring configuration, (UAG) is an ultrasonic aerosol generator, H is the capillary-plate distance, Φ the applied potential and T$_S$ the substrate temperature.
powdery films. For substrate temperatures below 300°C the CdS films were porous resulting from the evaporation of the solvent on the substrate. The films appeared dense and adhesive at intermediate substrate temperatures (300 °C – 450 °C) due to evaporation of the droplets and volatilization of the precursor right above the substrate which leads to a CVD reaction forming the film.

1.3.2 Electrospray ionization

Electrospray ionization has emerged as a powerful tool for mass spectrometry of large and complex molecules. Therefore the molecules are dissolved in liquid that is sprayed via a charged capillary electrode (Fenn et al., 1989). The solvent of the charged solution droplets evaporates and the charge density on the droplet surface increases. Eventually the Rayleigh limit of charge density is reached. The surface becomes unstable and starts emitting charged satellite droplets relaxing the negative pressure produced by the high charge density on the droplet surface. If the droplet radius is small enough the ions in the droplet desorb from the droplet into the ambient gas. Attached to the ions are solvent or solute species that are not ions themselves. This mechanism was proposed by Iribarne and Thomson (1979). The schematic of the process can be seen in Figure 1.8.

![Figure 1.8: Evaporation and desorption process according to Iribarne and Thomson (1979).](image-url)
The molecule-ion system is transported via forced convective gas flow and focused by electrostatic lenses into the mass spectrometer.

Another source of ions is the electrospraying of liquid metal (liquid metal ion sources – LMIS). The very high conductivity of liquid metals (K \(\sim 10^6\) S/m) leads to the formation of exceedingly sharp tips in the conejet mode which may emit predominantly single ions (Prewett and Mair, 1991). But due to the large surface tension LMIS is only applicable in vacuum (Gamero-Castaño et al., 1997).

### 1.3.3 Other Applications

Electrosprays are always an alternative to other spraying techniques. Consequently there is research done on fields of liquid atomization that are traditionally dominated by conventional sprays. The advantages of the different electrospray modes or the implications of charged droplets have to be evaluated against disadvantages of electrospraying, e.g. the potential explosion hazard from the presence of a high electric field.

There is the production of particles often in the nanometer size range. Advantage of the electrospray is the low agglomeration of the particles and the narrow size distribution. Park and Burlitch (1996) produced non-agglomerated titania particles in the size range of 20 nm by spraying an ethanolic solution of titanium alkoxide. Ijsebaert et al. (2001) spray-dried drug solutions for inhalation purposes. By using the conejet mode forming a monodisperse droplet size distribution it was possible to form drug particles in a very narrow size range which is shown to improve inhaling efficiency e.g. for antiasthma drug delivery. The disadvantage of the electrospray process is the low production rate per nozzle which is in the order of g/h or less. Powder production rates of air assisted spray flames are easily in the kg/h range (Müller et al., 2003). Consequently the electrospray particle production is only an alternative for niche products or if direct controlled deposition of the particles on a substrate is of advantage. One of this niches could be the encapsulation of unstable or labile components for example in food processing. Loscertales et al. (2002) developed an encapsulation method by using the conejet electrospray. Two concentric cylinders deliver the
components for encapsulation: the inner cylinder the actual product, the outer the polymer or the polymeric solution that is used to encapsulate the product. The two immiscible liquids form a compound cone and jet when a voltage is applied to the capillary cylinders. The breakup of the jet forms compound droplets with the product solution encapsulated by the polymer.

Due to their aromatic content and high viscosity the so called “logistical fuels” (jet fuel, diesel) are difficult to burn cleanly (Kelly, 1984). But electrosprays are capable to disperse the liquid in a way that combustion proceeds in much the same manner as for a premixed flame with a dispersion energy input of only a few milli watts (Kelly, 1984). Romat and Badri (2001) investigated how the additional charges are influencing the hydrodynamic characteristics (droplet dispersion and size) of a diesel oil injector. The injector is a conventional pressure nozzle atomizing the fuel at 120 bars. The liquid is electrified by adding a needle brought to a high voltage.

Another application of electrosprays can be found in thruster technology. The research of the suitability of electrosprays for space propulsion dates back to the 1960s. The ability to deliver thrust in the range of micro-Newton is needed for controlling small satellites and the execution of space missions in which very accurate positioning of spacecrafts is needed (Gamero-Castaño and Hruby, 2001). The colloid thruster based on conejet electrospraying that was developped for example by Gamero-Castaño and Hruby (2001) is able to deliver a force of 0.3 nN at an acceleration voltage of 1300V.

1.4 Summary

Although electrosprays are known for a long time research has virtually exploded recently due to the new applications found especially in the field of electrospray ion production. But also other applications which are already standard processes in industry like paint spraying are still not completely evaluated. Especially in the field of deposition techniques there is still room for innovation as shown by the establishing of ESD for ceramic thin film production. This requires also further studies to understand the mechanisms of electrospraying in its different forms. Therefore basic research on especially electrohydrodynamic sprays is more active than ever. The more is known
about the conejet mode which is well investigated the more the other electrospray modes come into focus. Further, besides the production process of charged droplets the control of the droplets after production is important in terms of transport, mass and heat transfer but is still only little investigated.

1.5 References


2 Electrospray deposition and evaporation

Abstract

Electrospray transport, evaporation and deposition on a heated substrate is investigated theoretically by Lagrangian tracking of single droplets. The droplet mass and heat transfer are calculated under forced convection and compared to limited cases of electrospray transport only or droplet evaporation only. Segregation of primary and satellite electrospray droplets is observed also, in agreement with data in the literature. The arriving droplet diameter and spatial distribution at the substrate show that evaporation barely affects droplet transport. In contrast, droplet size and salt concentration can be affected significantly by evaporation. It is shown also how process parameters such as substrate temperature, initial droplet diameter and vapor transport may affect the film quality. Accounting for the Rayleigh limit of charged droplets leads to acceleration of their evaporation when high substrate temperatures or small droplet diameters are employed.

2.1 Introduction

Compared to other film deposition techniques, Electrostatic Spray Deposition (ESD) bears the advantage of high deposition efficiency (up to 80%) as the droplets are transported by electrical forces (Siefert, 1984) and do not need a carrier gas as in conventional sprays. The simple setup, the wide choice of precursors and an easy control of product stoichiometry and morphology are additional benefits (Chen et al., 1999). Applications of ESD are found in production of thin LiMn$_2$O$_4$ films for cathode material in rechargeable lithium batteries (Van Zomeren et al., 1994). Chen et al. (1999) used ESD for deposition of ZnO, ZrO$_2$, and Al$_2$O$_3$ from precursor liquid sols. Besides

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functional films, ceramic powders can be synthesized also such as nanocrystalline SnO₂ (Vercoulen et al., 1993).

To improve and control the ESD performance it is important to understand the key parameters of Electro Hydrodynamic Spraying (EHS). Gañán-Calvo et al. (1994), Grace and Dunn (1996) and Hartmann et al. (1999) developed numerical models to describe droplet transport. Their work and that of Tang and Gomez (1994) include experimental investigations. An extensive review on electrosprays and their different modes was written by Clopeau and Prunet-Foch (1994).

The use of hot plates as substrates is common for spray processes for drying and/or pyrolysis of the deposited droplets. Siefert (1984) deposited metal oxides on a glass substrate by corona spray pyrolysis. The deposition efficiency could be increased substantially while the electrical and optical properties of the deposited films could be maintained. The effects of the substrate temperature on CeO₂ film properties was investigated by Konstantinov et al. (2000). They reported cracks in the film for temperatures above 673 K and large crystallites of CeO₂ at low temperatures. The most uniform film was observed at a substrate temperature of 673 K. Also in a study by Nguyen and Djurado (2001) the best zirconia films on stainless steel were deposited at around 673 K. Mahmoud (2001) studied the influence of the substrate temperature on the structural, electrical and optical properties of a polycrystalline Bi₂S₃ film.

Here the process of interest is ESD for production of thin electrolyte films of yttria-stabilized zirconia for fuel cells (Perednis et al., 2001). The general requirements for an electrolyte are good ionic conductivity, negligible electron conductivity and impermeability for the fuel gases. Thus, the quality of the film depends on the ratio of the dissolved precursor salts (yttrium and zirconium salts) to the solvent liquid in the droplet arriving at the substrate. Solvent evaporation during droplet transport is thereby an important parameter and has to be controlled carefully. The temperature of the substrate is varied between 523 K and 723 K to induce the pyrolysis process of endothermic oxidation reactions of the yttria and zirconia salts. Perednis et al. (2001) were able to deposit 5 µm thick crack-free coatings with diameters up to 33 mm. They pointed out that substrate temperature has to be controlled within a narrow range for best film quality. Operating outside this temperature range results in either small grains and crystallites (higher temperatures) or cracks (lower temperatures) in the film leading
to inhomogeneities. Therefore, the quality of the film depends on the interaction between the design (nozzle-substrate distance, nozzle radius and substrate temperature) and spraying parameters (liquid feed rate, electrical potential) as well as material properties (solution viscosity, conductivity, solubility and density).

Therefore a model is developed to calculate the droplet size distribution of an electrospray depositing on a heated substrate. This is accomplished by extending the transport model of Gañán-Calvo et al. (1994) to account for droplet evaporation. That way, the mean droplet size, velocity and concentration and standard deviation at every location in the spray are calculated. The model is based on tracking of each droplet emitted from the electrified nozzle. Droplet mass and heat transfer are calculated for non-isothermal conditions from the nozzle to the heated substrate. In addition the salt concentration of the droplets arriving on the substrate is calculated as this is important for the product film properties.

2.2 Theory

2.2.1 Droplet transport

The migration of droplets emitted from an electrified meniscus towards a grounded counter electrode is quantitatively described using Lagrangian single-droplet tracking of a dilute two-phase flow. Thus a force balance for transport of droplet $i$ is written (Gañán-Calvo et al., 1994):

$$\frac{\pi}{6} d_i^3 \rho_d \frac{d \tilde{v}_i}{dt} = C_D \frac{\pi}{8} \rho_d d_i^2 \tilde{v}_i^2 \tilde{c}_i + q_i \tilde{E}_{\text{ext}} + \frac{1}{4 \pi \varepsilon_0} \sum_{j \neq i} \frac{q_i q_j}{r_{ij}^3}. \quad (1)$$

The first term on the right hand side (RHS) of eq. 1 accounts for the drag force by the surrounding gas. The second RHS term accounts for the force on the droplets by the external electric field $\tilde{E}_{\text{ext}}$ between nozzle and substrate. The third RHS term accounts for the mutual electric forces between the charged droplets and the induced charge on the conductive substrate by the charged droplets (image force). The drag force is the
general form of Newton’s resistance law, where the drag coefficient $C_D$ is (Clift et al., 1978):

$$C_D = \frac{24}{Re} (1 + 0.15 Re^{0.687}), \text{ for } Re < 800.$$  \hfill (2)

The external electric field is calculated as that between a semi-infinite line of charges (representing the needle) and an infinite plane (representing the substrate) separated by distance $H$ (Loeb et al., 1941; Jones and Thong, 1971):

$$E_{ext} = \frac{\Phi}{H} \nabla \Phi^*, \hfill (3)$$

where $\Phi^*$ is a non-dimensional potential:

$$\Phi^*(r^*, z^*) = \frac{K_v}{\log(4H/R)} \log \left( \frac{r^{*2} + (1 - z^*)^2}{r^{*2} + (1 + z^*)^2} \frac{1}{z^* + (1 - z^*)} \right), \hfill (4)$$

with $r^* = \frac{r}{H}$ and $z^* = \frac{z}{H}$.

In general, $K_v$ ranges from 0 to 1 depending on the $H/R$ ratio (Gañán-Calvo et al., 1994). The path of each droplet can be followed through the velocity vector:

$$\frac{d\vec{x}_i}{dt} = \vec{v}_i, \hfill (5)$$

by starting with its formation at the nozzle exit until its deposition to the substrate. It is assumed that the droplets are migrating in still air following Gañán-Calvo et al. (1994) who calculated the ratio of air to droplet velocity to be far smaller than unity. Equation 1 along with eqs. 2 - 5 are integrated in three dimensions even though the spray has a symmetry axis through the center of the spraying cone. By using this symmetry it would have been possible to reduce the necessary spatial dimensions to spare computational time. However, the location of every single droplet, its diameter and velocity have to be
known at each time instant and as such, the spray is not symmetrical. The characteristics of an electrospray are given by the geometry of the ESD setup, the properties of the sprayed liquid, the applied electrical potential and the volume feed rate. For the calculation, additional information is needed for the electrical current between nozzle and spray and the initial mean droplet size. Based on dimensional analysis and experimental results, Gañán-Calvo et al. (1997) derived relations for droplet size and current as a function of liquid properties and flow rate. Two operation regimes can be distinguished by the dimensionless parameter $G$:

For $G = \left(\frac{\gamma \varepsilon_0^2}{\mu^4 \kappa^2 V_1}\right)^{1/3} < 1$:

$$\frac{\bar{d}}{d_0} = 1.6(\varepsilon_r - 1)^{1/6} \left(\frac{\dot{V}_l}{\dot{V}_o}\right)^{1/3} - (\varepsilon_r - 1)^{1/3}$$  \hspace{1cm} (6)

$$\frac{I}{I_o} = \frac{6.2}{(\varepsilon_r - 1)^{1/4}} \left(\frac{\dot{V}_l}{\dot{V}_o}\right)^{1/2} - 2.0$$  \hspace{1cm} (7)

While for $G > 1$:

$$\frac{\bar{d}}{d_0} = 1.2 \left(\frac{\dot{V}_l}{\dot{V}_o}\right)^{1/2} - 0.3$$  \hspace{1cm} (8)

$$\frac{I}{I_o} = 11.0 \left(\frac{\dot{V}_l}{\dot{V}_o}\right)^{1/4} - 5.0$$  \hspace{1cm} (9)

with $I_o = \left(\frac{\varepsilon_0 \gamma^2}{\rho_d}\right)^{1/2}$; $d_0 = \left(\frac{\gamma \varepsilon_0^2}{\rho_d \kappa^2}\right)^{1/3}$; $\dot{V}_o = \frac{\varepsilon_0 \gamma}{\kappa \rho_d}$

### 2.2.2 Droplet evaporation

Droplets undergo evaporation on their way from the nozzle to the heated substrate. This determines their size and salt concentration upon deposition and thereby it affects the quality of the resulting electrolyte film. If low concentrations of the yttrium and zirconium salts are used, the salts have a negligible influence onto solvent evaporation. Frössling (1938) described mass transfer from a droplet in forced convection by:
Table 2.1 shows various correlations for the Sherwood number in the literature. The Kelvin and Fuchs effect are neglected as rather large droplets are employed (Hinds, 1998).

<table>
<thead>
<tr>
<th></th>
<th>( \text{Sh}_0 )</th>
<th>Re validity range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frössling (1938)</td>
<td>( 2 + 0.552 \cdot \text{Re}^{0.5} \text{Sc}^{0.33} )</td>
<td>0 – 1280</td>
</tr>
<tr>
<td>Clift et al. (1978)</td>
<td>( 2 + (1 + \text{ReSc})^{0.33} \text{Re}^{0.077} )</td>
<td>0 – 400</td>
</tr>
<tr>
<td>Beard and Pruppacher (1971)</td>
<td>( 1.56 + 0.616 \cdot \text{Re}^{0.5} \text{Sc}^{0.33} )</td>
<td>2 – 3300</td>
</tr>
<tr>
<td>Ranz and Marshall (1952)</td>
<td>( 2 + 0.6 \cdot \text{Re}^{0.5} \text{Sc}^{0.33} )</td>
<td>0 – 200</td>
</tr>
</tbody>
</table>

Table 2.1: Mass transfer correlations for an evaporating sphere under forced convection.

A comparison of the evaporation time of a butanol droplet with \( d = 20 \mu m \) at a gas temperature of \( T_{g,\infty} = 293 \) K and \( \text{Re} = 10 \), typical for this process, is plotted in Figure 2.1 as predicted using the correlations of Table 2.1 for zero background butanol vapor concentration. As the difference between the correlations is rather small, the one by Ranz and Marshall (1952) is used here.

For a known temperature profile between substrate and nozzle the transient heating of each droplet is calculated. The correlations for heat transfer are analogous to mass transfer, where the Schmidt number is replaced by the Prandtl number in the Sherwood and Nusselt numbers, respectively (Table 2.1):

\[
\dot{Q}_{i,S} = -\pi d_i \cdot \lambda_g (T_{i,\text{ref}}) \cdot \text{Nu}_o \cdot \left[ T_{i,S} - T_{g,\infty} \right] - \Delta H_v \cdot \dot{m}_i. \tag{11}
\]

The second RHS term accounts for droplet evaporation cooling (Frössling, 1938). The relative velocity of the droplets to the surrounding air is equal to the absolute droplet velocity, \( v_i \), as stagnant air is assumed. Here, heat conduction within the droplet is much faster compared to the conduction of the surrounding medium (infinite
conductivity model). So the temperature inside the droplet is uniformly distributed at all times (Sirignano, 1999). Abramzon and Sirignano (1989) extended this model by accounting for Stefan flow:

\[
\dot{m}_i = \pi d_i \cdot \rho_g D \cdot Sh_{\text{eff}} B_{i,m}
\]

(12)

Heat transfer: \( \dot{Q}_{i,S} = \pi d_i \cdot \lambda_g \cdot Nu_{\text{eff}} (T_{i,S} - T_{g,c}) - \Delta H_v \cdot \dot{m}_i \)

(13)

with

\[
Sh_{\text{eff}} = \left[ 2 + \frac{(Sh_u - 2)}{F(B_{i,m})} \right] \ln(1 + B_{i,m}) \;
B_{i,m} = \frac{Y_{i,S} - Y_{c}}{1 - Y_{c}}
\]

and

\[
Nu_{\text{eff}} = \left[ 2 + \frac{(Nu_u - 2)}{F(B_{i,h})} \right] \ln(1 + B_{i,h}) \;
B_{i,h} = \frac{h_{c} - h_{i,S}}{L_{\text{eff}}}
\]

where \( F(B) = (1 + B)^{0.7} \frac{\ln(1 + B)}{B} \); \( Y_{i,S} = \frac{c_{i,S}}{\rho_g + c_{i,S}} \).

At low vapor concentrations this model reduces to eq. 10 and 11 (Frössling, 1938).

The background concentration, \( c_{\infty} \), of the evaporating solvent is an important parameter for droplet evaporation (see eq. 10 and 12) and depends on the transport of the solvent vapor by diffusion and convection, and the source strength determined by the

Figure 2.1: Comparison of various droplet evaporation models (Table 2.1) for the evaporation time of a butanol droplet with initial diameter \( d = 20 \mu m \) at \( T_{g,c} = 293 \) K and zero background concentration of butanol vapor at \( p = 1 \) atm.
evaporation rate of the droplets. Here, the extreme cases for the lowest and the highest possible background concentration are considered and the resulting average droplet diameters are compared for different substrate temperatures. The lowest possible background vapor concentration is \( c_g = 0 \) while the highest is \( c_g(x) = c_g(T_g,x) \) when there is no convection and only diffusion is considered for vapor transport (see Appendix 2 of chapter 2). The average vapor concentration over the spray volume can be calculated from the evaporating droplets and the air exchange rate \( \psi \) of the spray volume induced by convection of the air driven by thermal buoyancy and momentum transfer from the droplets to the air (Appendix 1 and 2 of chapter 2). The spray volume is the geometrical space that contains all droplets of the spraying cone.

All properties of the air-solvent gas mixture in the film boundary layer around the droplet can be assumed constant if they are calculated at reference temperature \( T_{i,ref} \) and at reference composition \( Y_{i,ref} \). The values for \( T_{i,ref} \) and \( Y_{i,ref} \) are evaluated according to the \( 1/3 \) rule of Sparrow and Greg (1958). Non-dimensional versions of equations (1), (12) and (13) can be found in Appendix 2 of this thesis.

2.3 Results

2.3.1 Droplet transport

2.3.1.1 Validation

The droplet transport model (without evaporation) was validated by comparing the numerical solution of eq. 1 – 5 to the droplet spatial and velocity distributions as calculated by Gañán-Calvo et al. (1994). The corresponding computer code is given in Appendix 3 in this thesis. The mean droplet diameter is \( \bar{d} = 38 \mu m \) with a root mean square of 4%. The heptane volume feed rate is \( \dot{V}_l = 8.64 \) ml/h, the electric current is \( I = 45 \) nA, the nozzle-substrate distance is \( H = 30 \) mm and the applied potential is \( \Phi_o = 5.2 \) kV. All these values and the initial droplet velocity and the jet break-up position are taken from Gañán-Calvo et al. (1994). The break-up location of the liquid
jet emitted from the Taylor cone was varied in the radial and transversal directions. Assuming that the number of droplet charges, $q_i$, is proportional to droplet volume (Gañán-Calvo et al., 1994):

$$\alpha_i = \frac{q_i}{q} = \frac{6 \dot{V} q_i}{\pi d^3} = \left(\frac{d_i}{d}\right)^3,$$

(14)

the number of elementary charges on a droplet with $\bar{d} = 38 \, \mu m$ is $3.3 \cdot 10^6$ while the Rayleigh limit for this droplet can be calculated from (Davies and Bridges, 1994):

$$q_R = 8\pi \left(\gamma \varepsilon_0 d^3 / 8\right)^{1/2},$$

(13)

**Figure 2.2**: Spatial (a), axial (b) and radial (c) velocity distributions of electrosprayed heptane droplets ($\bar{d} = 38 \, \mu m$). The distance between the needle and the substrate is $H = 30 \, \text{mm}$ with an applied potential of $\Phi_0 = 5.2 \, \text{kV}$. Each data point is representing a droplet. The solid line represents the present calculation for the average droplet velocity at a given axial position while the broken line that of Gañán-Calvo et al. (1994).
which is for this case $5.5 \cdot 10^6$ elementary charges.

The calculation was performed for $K_V = 0.7$ in eq. 4 following Gañán-Calvo et al. (1994). Figure 2.2a shows a snapshot of the spatial distribution of the electrosprayed droplets. Each point represents an emitted droplet. On the average, there are 552 droplets between nozzle and substrate at these conditions. The spread of the spray increases with increasing distance from the nozzle because of the mutual repulsion of the charged droplets. Figure 2.2b shows the corresponding axial velocity, $v_z$, of these droplets. The thin solid line represents the present calculation at $K_V = 0.7$ for the average droplet velocity as a function of the axial position while the broken line represents the corresponding one by Gañán-Calvo et al. (1994). The predictions of the model by Gañán-Calvo et al. (1994) are matched better if $K_V = 1$ (thick solid line) is used.

Initially the droplet velocity increases as a strong electric field “pulls” the droplets out of the nozzle. However the field intensity decreases away from the nozzle (Figure 2.3) so the droplet velocity exhibits a maximum. After that it decreases

![Figure 2.3: External dimensionless ($\Phi/\Phi_*$) electrical potential of a heptane electrospray: the distance between the needle and the deposition plate is $H = 30$ mm with an applied potential of $\Phi_*$ = 5.2 kV.](image)


monotonically until it almost levels off near the substrate. In fact the velocity starts increasing as droplets approach the substrate and the mirror “image” forces attract them to the substrate. Thus equilibrium between drag and electric forces on the droplet is established resulting in a nearly constant velocity close to the substrate. The results are sensitive to the selected jet break-up position. Given this uncertainty, both calculations are in good agreement. Figure 2.2c illustrates the radial velocity profile of the droplets in the z-direction. Droplets travel faster through the center because of their higher electric field force. The velocity profiles broaden as the spray approaches the substrate. The only significant difference is the strong acceleration of the droplets close to the substrate predicted by Gañán-Calvo et al. (1994) which may be not realistic given the electric potential distribution (Figure 2.3). There it is shown that the electric potential close to the substrate is quite low compared to the region close to the nozzle. The “image” forces of the spray are not compensating for that. The evaporation component of the model is in excellent agreement with Hinds (1998) for the evolution of the diameter of a single evaporating droplet.

2.3.1.2 Segregation

The current electrospray transport model can be used to investigate segregation of droplets according to their size which has been observed experimentally and theoretically during Taylor-cone electrospraying under certain conditions (Nijman, 2002; Gañán-Calvo et al., 1994). In principle the cone-jet mode results in a highly monodisperse droplet size distribution. Increasing the liquid flowrate, however, contributes to the formation of secondary droplets (Camelot, 1999; Nijman, 2002). Nijman (2002), in particular, observed the segregation of primary and secondary droplets into clearly distinguishable regions: The bigger, primary droplets are dominating the inner part of the spraying cone while the secondaries are driven to the outside of the spray. Here, a bimodal initial droplet size distribution was assumed having primary droplet diameter of \( d = 24.3 \, \mu \text{m} \) and satellite droplet diameter of \( 2 \, \mu \text{m} \). Figure 2.4a shows a snapshot of the spatial distribution of this electrospray of a 2 mm thick central slice of the electrospray cone. The separation of primary and satellite
droplets is clearly visible and in excellent agreement with Nijman (2002). It is worth noting that the droplet separation takes place early on in the cone as the satellites have high mobility. Figure 2.4b shows the droplet number flux onto the substrate. It can be seen that the small satellite droplets are confined to the spray edges, whereas the primary droplets are distributed over the whole spray cross section.

2.3.2. Droplet transport and evaporation

Electrospray simulations accounting for droplet transport and evaporation are presented here for a nozzle-substrate distance of \( H = 30 \text{ mm} \) and an applied potential of \( \Phi_e = 5.25 \text{ kV} \) by solving eq. 1 – 13 simultaneously. The liquid properties and setup parameters are chosen as input for the calculation because they are typical for a conejet. The corresponding computer code is given in Appendix 3 of this thesis. The liquid solvent is 2-butanol containing 0.005 mol/l yttrium nitrate and zirconium acetylactetonate. The yttrium and zirconium salts do not affect the evaporation for their
low concentration throughout most of the process so they are neglected. The volume flowrate of this solution is 2.67 ml/h while the substrate temperature ranged between 473 K and 1673 K. Measured axial temperature distributions (thermoelement K-type) within the spray volume are shown in Figure 2.5 for three substrate temperatures. Calculations are performed for the two extreme cases of zero background vapor concentration ($c_\infty = 0$) and for $c_\infty = c_\infty(T_{\text{g,\infty}})$ meaning that there is no convection and only diffusion is considered for vapor transport. More realistic calculations accounting for air entrainment into the spray cone were carried out for the mean background vapor concentration (Appendix 1 of chapter 2).

The initial droplet diameter and the spray electrical current were calculated from eq. 6 – 9 as $d = 19.2 \mu m$ and $I = 39.3 \, nA$, respectively for $G = 7.29 > 1$ using the physical properties of butanol: electrical conductivity, $K = 5 \times 10^5 S/m$, surface tension $\gamma = 0.02254 \, N/m$ and density $\rho = 806 \, kg/m^3$. As electrosprays are rather monodisperse, a narrow droplet size distribution is assumed with root mean square (RMS) of 4% for a Gaussian droplet size distribution resulting in an arithmetic standard deviation of $\sigma = 0.77 \, \mu m$. The initial velocity of the droplet is assumed to be equal to the capillary jet velocity. Using Rayleigh’s criterion for the breakup of liquid jets, the

![Figure 2.5: Normalized gas temperature distribution $\frac{T_{\text{g,\infty}} - 273 \, K}{T_{\text{sub}} - 273 \, K}$ between nozzle and substrate. The measurements were obtained for substrate temperatures of $T_{\text{sub}} = 473$, 573, and 673 K.](image)
breakup wavelength of a jet is $\ell = 4.5 \cdot d_{\text{jet}}$ (Jones and Thong, 1971; Cloupeau and Prunet-Foch, 1989). Using the liquid volume flowrate, the velocity of the emitted droplet by the Taylor-cone can be estimated. As a result, the electrospray jet diameter is $d_{\text{jet}} = 10.1 \, \mu\text{m}$ and the initial velocity of the jet (and droplets) is $v_{\text{jet}} = 9.1 \, \text{m/s}$.

Figure 2.6a shows the spatial distribution of the axial velocity of the droplets as a function of distance from the substrate with each point representing a droplet for a substrate temperature of $T_{\text{sub}} = 673 \, \text{K}$ and no solvent vapor background concentration using the model of Abramzon and Sirignano (1989) and the correlation of Ranz and Marshall (1952). The solid line is the arithmetic average axial velocity of the droplets. The droplets are accelerated close to the nozzle ($z > 27 \, \text{mm}$) by the local high electric field as shown in Figure 2.2b also. Further away, the droplets are slowed down by the aerodynamic drag force and the decrease of the electric field. The acceleration of the droplets that occurs at less than 10 mm from the substrate arises from the forces of the mirror charges induced on the substrate and the decrease in size of the droplets by evaporation.

Figure 2.6b shows a snapshot of the droplet diameter (points) from the nozzle to the substrate as well as the average droplet diameter. Close to the nozzle the air

---

**Figure 2.6:** Snapshot of butanol droplet spatial velocity (a) and diameter (b) distributions for electrospray deposition at a substrate temperature $T_{\text{sub}} = 673 \, \text{K}$ and nozzle-substrate distance $H = 30 \, \text{mm}$, volume flowrate $V_f = 2.67 \, \text{ml/h}$ and electrical current $I = 39.3 \, \text{nA}$. Each point represents a single droplet. The solid line represents the arithmetic average droplet velocity or diameter at a given nozzle-substrate distance.
temperature is low (Figure 2.5) and the droplet velocity is high (Figure 2.6a). Therefore the droplet diameter is hardly decreasing during the first 15 mm. The low velocity of the droplets closer to the substrate and the sharp increase of the gas temperature results in prolonged droplet residence times at high temperatures that reduces sharply the droplet diameter by evaporation.

The evolution of the dimensionless liquid droplet temperature $T^* = T_s / T_o$ ($T_o = 273 K$) is plotted in Figure 2.7. The nozzle and the liquid inside the nozzle have the same temperature as the surrounding air. Therefore the initial droplet temperature is equal to the air temperature at the nozzle tip. Although the surrounding air temperature is increasing towards the substrate, the droplet temperature is decreasing by evaporation cooling (release of heat). But closer to the substrate the air temperature gradient is high and the corresponding wet bulb temperature is considerably higher than the actual droplet temperature at that point. The wet bulb temperature is the equilibrium temperature of the droplet at a given air temperature. Thereby the droplet temperature is increasing again ($z < 15 \text{ mm}$). The mass and heat transfer process is transient so an equilibrium is never reached as has been reported by Sirignano (1983) for droplet heating during spray combustion. Aihara et al. (1972) measured air velocities along the

\[ \text{Figure 2.7: Butanol droplet dimensionless temperature} \ (T^* = T_s / T_o \text{ with } T_o = 273 \text{ K}) \text{ as a function of the distance from the substrate for different substrate temperatures and no background butanol vapor} \ (c_s = 0). \text{ Nozzle-substrate distance } H = 30 \text{ mm, flow rate } \dot{V}_i = 2.67 \text{ ml/h and electrical current } I = 39.3 \text{ nA}. \]
downward facing surface of a heated horizontal plate 250 mm wide for a maximum temperature difference between the plate and the surrounding air of 104°C. The measured air velocities by convection were below 0.1 m/s. Thus the convection velocity is negligible compared to the droplet velocities imposed by the electric field.

Figure 2.8 illustrates the droplet size distribution and the mass at the substrate of a butanol spray depositing on a substrate at $T_{\text{sub}} = 573$ K with $c_v = 0$ accounting for (solid lines) and neglecting (broken lines) evaporation. For the non-evaporating spray the average diameter of arriving droplets at the substrate is rather constant, around 19 $\mu$m, across the substrate with small oscillations arising from the statistics of droplet counting. In contrast, the droplet mass flux decreases by about 30% from the outer region to the center of the substrate. The mutual interaction of the charged droplets results in reduced droplet deposition on the center of the substrate. For a technical application this effect might make it necessary to rotate the substrate off-center in order to obtain uniform films. Accounting for evaporation, the radial distribution of the mass flux hardly changes compared to the non-evaporation case. The

![Figure 2.8: Radial deposition pattern of average droplet diameter and mass flux of a butanol spray depositing on a substrate of $T_{\text{sub}} = 573$ K accounting for (solid lines) and neglecting (broken lines) evaporation. The droplet flux is lower in the center of the spray by the mutual electrostatic repulsion between the droplets. Evaporation does not change the deposition pattern but decreases the overall mass deposited by 37% here.](image-url)
radial droplet size distribution is also constant with a slight decrease in the outer regions of the spray even though the arriving droplets are smaller now, about 16 µm. Similar data are obtained at $T_{\text{sub}} = 473$ K and 673 K. Clearly evaporation does not affect the radial mass flux distribution across the substrate even though it decreased the average deposited mass by 23%, 37%, and 47% for $T_{\text{sub}} = 473$ K, 573 K and 673 K, respectively.

Figure 2.9a shows the average droplet diameter arriving on the substrate at $T_{\text{sub}} = 473$ K – 1673 K, for butanol vapor background conditions of a) zero b) butanol vapor concentration determined by diffusion only and c) the butanol vapor concentration determined by the air exchange rate in the spray volume. As expected, smaller droplets arrive at the substrate with increasing substrate temperatures for a given background vapor concentration condition. The droplet sizes calculated for cases a) and c) are not distinguishable so only one curve is shown (circles). The average air velocity is calculated as 0.4 m/s (Appendix 2 of chapter 2) and contributes to low background vapor concentration along with the low droplet concentrations typically employed with electrosprays. This estimation shows that the convection induced by momentum transfer from the droplets to the air is enough to reduce the background concentration to an

![Figure 2.9: a) Average diameter and b) salt concentration of depositing droplets as a function of substrate temperature for background vapor concentration that either is negligible ($c_\infty = 0$, circles) or at saturation ($c_\infty = c_\infty (T_{\text{sub}})$, squares, diffusion only). Realistic systems perform close to $c_\infty = 0$. Open symbols indicate the droplet diameter when accounting for the Rayleigh limit.](image-url)
extent at which the concentration becomes negligible. At high $T_{\text{sub}}$ there is substantial reduction of the droplet size by evaporation. As a result, evaporating droplets reach the Rayleigh limit for charging (eq. 15) for substrate temperatures above $T_{\text{sub}} = 773$ K which should lead to a disintegration of the droplets. The rate of satellite emission of the overall spray in steady state due to Rayleigh breakup for $T_{\text{sub}} = 873$ K, $1073$ K and $1273$ K is $3200$/s, $4800$/s and $18600$/s, respectively.

Davis and Bridges (1994) showed with dodecanol sprays that the droplets just keep emitting small satellite droplets (with around 2% mass of the “mother” droplet) during the evaporation process when reaching the Rayleigh limit. Using these results, an estimation of the influence of the Rayleigh limit onto the decrease of the droplet size was calculated also in Figure 2.9a for $c_{\infty} = 0$ (open circles). Clearly, accounting for the Rayleigh limit accelerates droplet evaporation. In addition these “emitted” droplets can contribute to the formation of satellite droplets and even submicron or nano dry salt particles upon deposition.

The resulting salt concentration of the deposited droplets can be seen in Figure 2.9b. The measured concentration threshold for precipitation of these salts is $0.03$ mol/l. If the droplets are shrinking down to $9.4$ µm, the precipitation threshold is reached that can result in the formation of hollow particles and particulate deposits as it has been observed experimentally by Perednis et al. (2001). Accounting for the Rayleigh effect hardly alters this picture.

Direct conclusions for film deposition by ESD can be drawn from these simulations. Typically, the substrate temperature is $473 – 773$ K (Perednis et al., 2001). As Figure 2.9a indicates the bulk of the film is made by direct droplet deposition and solvent evaporation from the substrate as long as relatively large droplets, e.g. here larger than $10$ µm, are employed. Smaller droplets evaporate and contribute to the deposition of submicron solid particles that degrade the film quality. These smaller particles can arise from the satellite droplets that appear during electrospraying at high rates or multi-cone electrospraying.
2.4 Summary

A model for transport and evaporation of electrosprayed droplets was developed. The model predicts the droplet salt concentrations of sprayed solution droplets which are used for deposition of electrolyte films for production of solid oxide fuel cells. The model was in reasonably good agreement with a literature model of electrospray transport alone and droplet evaporation alone. It further predicts the size segregation of primary and secondary droplets as found experimentally. The performance of the model was demonstrated for electrospray deposition of a butanol solution containing zirconium and yttrium salts at various substrate temperatures. In addition, the salt concentration in the depositing droplets was estimated from the final droplet size during deposition on the substrate. Evaporation does not dramatically alter electrospray droplet transport but it can drastically reduce droplet size and increase salt concentration affecting, thus, film quality. It was shown also that electrospraying may lead to non-uniform deposits resulting from the mutual repulsion of droplets. Furthermore, accounting for the Rayleigh limit of charging during evaporation may change the final droplet size and even contribute to production of ultrafine satellite droplets and fine nanoparticle deposits that may degrade the film quality.

2.5 References


Notation

A Surface of spray perpendicular to spray axis \( [ \text{m}^2] \)

\( A_{\text{spray}} \) Equivalent area of the spray \( [ \text{m}^2] \)

\( B_{i,h} \) Heat transfer number of droplet \( i \) \([-\text{-}]\)

\( B_{i,m} \) Mass transfer number of droplet \( i \) \([-\text{-}]\)

\( c_{i,S} \) Solvent vapor mass concentration at surface of droplet \( i \) \( [\text{kg/m}^3]\)

\( c_{\infty} \) Solvent vapor mass concentration outside droplet boundary layer \( [\text{kg/m}^3]\)

\( \overline{c} \) Mean solvent vapor concentration \( [\text{kg/m}^3]\)

\( C_D \) Coefficient of drag \([-\text{-}]\)

\( D \) Diffusion coefficient \( [\text{m}^2/\text{s}]\)

\( d_i \) Diameter of droplet \( i \) \( [\text{m}]\)

\( d^* \) Dimensionless droplet diameter \([-\text{-}]\), \( d/\overline{d} \)

\( d_o \) Characteristic diameter of droplet \( [\text{m}]\)

\( d_{\text{jet}} \) Jet diameter \( [\text{m}]\)

\( \overline{d} \) Mean droplet diameter \( [\text{m}]\)

\( \overline{e}_i \) Unity vector of velocity of droplet \( i \) \([-\text{-}]\)

\( E_{\text{ext}} \) External electric field strength \( [\text{N/A}\text{s}]\)

\( F_{\text{el}} \) Electric force acting on a droplet \( [\text{N}]\)

\( G \) Dimensionless parameter for different spray operation regimes \([-\text{-}]\)

\( h_{i,S} \) Enthalpy of solvent vapor at droplet surface \( [\text{J/kg}]\)

\( h_{\infty} \) Enthalpy of solvent vapor outside boundary layer \( [\text{J/kg}]\)

\( H \) Distance between nozzle and substrate \( [\text{m}]\)

\( \Delta H_v \) Latent heat of vaporization \( [\text{J/kg}]\)

\( I \) Electric current \( [\text{A}]\)

\( I_o \) Characteristic electric current \( [\text{A}]\)

\( J \) Momentum of jet integrated over cross section \( [\text{kg m}^3/\text{s}]\)

\( J_d \) Momentum of droplets integrated over spray cross section \( A \) \( [\text{kg m}^3/\text{s}]\)

\( J_{\text{nozzle}} \) Momentum integrated over area at nozzle exit \( [\text{kg m}^3/\text{s}]\)

\( J_{\text{total}} \) Total momentum integrated over spray cross section \( A \) \( [\text{kg m}^3/\text{s}]\)

\( K \) Mass transfer coefficient \( [\text{m/s}]\)

\( K \) Electric conductivity \( [\text{S/m}]\)
K_v Dimensionless value depending on the ratio H / R [ - ]

ℓ Breakup wavelength of jet [ m ]

L_{eff} Effective latent heat of vaporisation [ J/kg ]

m_i Mass of droplet i [ kg ]

m Mean droplet mass [ kg ]

M_i Momentum of droplet i [ kg m / s ]

M_{nozzle} Momentum of spray at nozzle exit [ kg m / s ]

M_{total} Total momentum of spray [ kg m / s ]

N Mean number of droplets in a slice of the spray [ # / m^3 ]

N_{nu} Nusselt number [ - ]

N_{nu,eff} Effective Nusselt number [ - ]

P Air pressure [ atm ]

Pr Prandtl number [ - ]

q_i Charge of droplet i [ A s ]

q_j Charge of droplet j [ A s ]

q̅ Average charge of droplets [ A s ]

q_R Rayleigh charge limit [ As ]

Q_{i,s} Heat transfer rate of droplet i [ J/s ]

r Radial component of position vector x [ m ]

r^* Dimensionless radial component [ - ], r/H

r_{ij} Distance between droplets i and j [ m ]

R Outer radius of the nozzle [ m ]

Re Reynolds number = \frac{\bar{v}_i d_i}{\nu} [ - ]

Sc Schmitt number [ - ]

Sh_0 Sherwood number [ - ]

Sh_{eff} Effective Sherwood number [ - ]

T Time [ s ]

\tau Characteristic time [s], \tau = \frac{\bar{a}^2}{18 \nu \frac{\rho_g}{\rho_d}}

T_{i,ref} Reference temperature of droplet i [ K ]

T_{i,s} Surface temperature of droplet i [ K ]

T_{g,∞} Air temperature outside boundary layer of droplet [ K ]
Characteristic temperature \[ K \]

Surface temperature of droplet \[ K \]

Substrate temperature

Dimensionless temperature \[ - \], \( T / T_o \)

Velocity \[ m/s \]

Velocity of droplet \( i \) \[ m/s \]

Dimensionless velocity \[ - \], \( v / v_o \)

Characterisitic velocity \[ m/s \], \( v_o = H / t_o \)

Jet velocity \[ m/s \]

Air velocity \[ m/s \]

Mean air velocity \[ m/s \]

Mean droplet velocity \[ m/s \]

Axial velocity \[ m/s \]

Volume of grid at location \( \bar{x} \) \[ m^3 \]

Air volume flow rate into and out of the spray volume \[ m^3/s \]

Volume of a slice of the spray with height \( \Delta z \) \[ m^3 \]

Volume of spray \[ m^3 \]

Volume of air which is pushed away by a droplet on its way from nozzle to substrate \[ m^3 \]

Liquid volume feed rate \[ m^3/s \]

Characteristic liquid volume flow rate \[ m^3/s \]

Location of droplet \[ m \]

Reference mass fraction of droplet \( i \) \[ - \]

Mass fraction of solvent vapor at the surface of droplet \( i \) \[ - \]

Mass fraction of solvent vapor out side boundary layer \[ - \]

Axial component of position vector \( \bar{x} \) \[ m \]

Dimensionless axial component \[ - \], \( z / H \)

**Greek symbols**

\( \alpha_i \) Ratio of charge of droplet \( i \) towards mean droplet charge \[ - \]

\( \gamma \) Surface tension \[ N/m \]
\( \varepsilon_0 \) Dielectric constant (\( = 8.854 \cdot 10^{-12} \text{ F/m} \))

\( \varepsilon_r \) Relative dielectric constant [-]

\( \nu \) Air kinematic viscosity [m²/s]

\( \rho \) Density [kg/m³]

\( \rho_d \) Mass density of droplets [kg/m³]

\( \rho_g \) Mass density of air [kg/m³]

\( \sigma \) Width of Gauss distribution [μm]

\( \lambda_g \) Thermal conductivity of air [W/mK]

\( \mu \) Absolute viscosity of liquid [Pa s]

\( \varphi \) Angle of cylindrical coordinates [°]

\( \Phi \) Electrical potential [V]

\( \Phi_o \) Applied electrical potential between nozzle and substrate [V]

\( \Phi^* \) Dimensionless electrical potential [-], \( \Phi / \Phi_o \)

\( \psi \) Air exchange rate [1/s]
Appendix 1: Background vapor concentration

a) Air exchange
The change of the mean vapor concentration is induced by the vapor source through evaporation of droplets and the air exchange rate produced by the air flow in the spray volume:

$$\frac{dc}{dt} = \sum_i \frac{m_i}{V_{spray}} - \psi \cdot c,$$

(16)

The air exchange rate can be estimated from the mean air velocity in the spray volume induced by momentum transfer from the droplets (Appendix 2 of chapter 2). The influence of the mean air velocity on the vapor concentration can be described as:

$$\frac{dc}{dt} = - \frac{V_g}{V_{spray}} c = - \frac{A_{spray}}{V_{spray}} \cdot \frac{V_g}{H} c = - \frac{V_g}{H} c,$$

(17)

where $V_g$ is the air volume flowrate into and out of the spray volume, $H$ is the height of the spraying cone (distance between nozzle and substrate), $V_{spray}$ the volume of the spray, $A_{spray} = \frac{V_{spray}}{H}$ the equivalent area to the mean air velocity and $\nabla_g$ is the mean air velocity. Comparing the second RHS term side of equation (16) with equation (17) the air exchange rate can be written as:

$$\psi = \frac{\nabla_g}{H}.$$

(18)

b) Fickian diffusion only
For the case of diffusion transport only, the butanol vapor background is calculated from the mass loss of the droplets by evaporation and Fick’s second law. The equation for a single droplet is analogous to Cranck (1975):

$$\frac{dc_\infty(\bar{r})}{dt} = -k \cdot \left[ c_\infty(\bar{r}) - c_{i,S}(T_{i,S}) \right] + \nabla^2 c_\infty.$$

(19)
With \( k = \frac{\pi D d_i}{V(\bar{x})} \) a finite volume grid in cylindrical coordinates is chosen for this calculation to cover the space taken by the spray. The height of each grid cell, having volume \( V(\bar{x}) \), in \( z \)-direction is 0.5 mm. The radial distance between each cell is also 0.5 mm. The angle \( \Delta \varphi \) is 6°. The boundary conditions for the vapor concentration are:

\[
\begin{align*}
    c_v(r, z) &= 0 \quad \text{at } r = 3 \text{ cm and } z = 6 \text{ cm} \\
    \nabla c_v(r, z) &= 0 \quad \text{at } z = 0
\end{align*}
\]

for all times. The boundaries were chosen so that they do not affect the calculation. The initial condition for the vapor concentration in all grid volumes at \( t = 0 \) is zero. This leads to a transient calculation. For \( t > 0 \) the vapor concentration is increasing and reaches a steady state after several seconds real time, in which the source for the butanol vapor and the transport by diffusion are in balance at each location leading to a stable size distribution of the droplets arriving at the substrate with respect to time. Figure A1 shows the background concentration at \( T_{\text{sub}} = 573 \text{ K} \) assuming diffusion as transport mechanism for the butanol vapor only. The numerical diffusion calculation was validated by comparing it to the analytical solution (Crank, 1975) of the diffusion from a point source.

\[
\text{Figure A1: Dimensionless butanol vapor concentration of the background at substrate temperature}
\]

\( T_{\text{sub}} = 573 \text{ K} \) assuming vapor transport by diffusion only.
Appendix 2: Estimation of air velocity

The air velocity in the electrospray is estimated analogous to the derivation of the velocity of entrainment by Kanury (1975). He shows that the momentum is conserved over each complete cross-section along the central axis of a gaseous pressurized jet. This principle is also applied here. In the case of a continuous jet the momentum over the cross-section is preserved.

\[ J = \rho \int v^2 dA \]  

(20)

In the case of an electrospray the momentum induced by the force of the net electric field acting on the droplets is increased. The total momentum flux of an electrospray is the momentum flux of the droplets and the momentum flux of the air within the jet area.

\[ J_{\text{total}} = \rho_d \int v_d^2 dA + \rho_g \int v_g^2 dA \]  

(21)

However, the initial momentum of the electrospray at the nozzle exit is inherent only to the droplets, while the air velocity is zero. Further downstream the droplets’ momentum is transferred from the droplets to the air by the air resistance acting onto the droplets. The difference of the total momentum of the spray (air momentum plus droplet momentum) and the momentum of the droplets at position \( z \) is the air momentum. For the calculation of the air momentum the spray between nozzle and substrate is divided into 120 slices of cylindrical form with height \( \Delta z = 2.5 \cdot 10^{-4} \text{ m} \). The area of the slice is given by the outer radius of the spray at position \( z \). The droplet momentum at the nozzle exit is calculated from the mean droplet mass \( M \) of the droplets, the mean droplet velocity \( v_d \) and the mean number of droplets \( N \) in the first slice:

\[ M_{\text{nozzle}} = \overline{N} \cdot \overline{m} \cdot \overline{v}_d. \]  

(22)

The momentum integrated over the area is then given by:
\[ J_{\text{nozzle}} = \frac{M_{\text{nozzle}}}{V_{\text{slic e}}} \cdot V_d \cdot A. \] (23)

The momentum of the droplets in the following slices can be calculated in the same fashion. The total momentum of the spray at each position \( z \) can be calculated from the initial momentum at the nozzle exit and the electric forces \( F_{\text{el}} \) that acted onto the droplets up to the position \( z \).

\[ M_{\text{total}}(z) = M_{\text{nozzle}} + \sum_i \Delta M_i(z) \]

with \( \frac{\Delta M_i(z)}{\Delta t} = F_{\text{el}}(z) \)

\[ \Leftrightarrow \Delta M_i(z) = F_{\text{el}}(z) \cdot \Delta z / \overline{v}_g(z) \] (24)

The total momentum flux then is calculated as in eq. 24.

The difference between total momentum flux and droplet momentum flux is the momentum flux of the air in the slice at position \( z \). The air velocity can then be calculated as:

\[ v_g(z) = \left[ \frac{J_{\text{total}}(z) - J_d(z)}{\rho_g / A(z)} \right]^{0.5}. \] (25)
Abstract

A numerical model for droplet transport and evaporation of electrosprays in a capillary-plate configuration is compared to droplet size and velocity measurements. Two distinct electrospray modes are investigated: the conejet mode with a narrow droplet size distribution and a spraying angle smaller than 45° and the intermittent multijet with a broad size distribution and a spraying angle of approximately 180° at the capillary exit. LiCl/Isopropanol solutions are deposited on a heated plate. The temperature of the plate is adjusted between 20°C and 215°C. The spray droplet transport and evaporation is examined with a Phase Doppler Anemometer (PDA) which is able to track the velocity and size of droplets in the spray. The measurements are compared to the model predictions. For the first time combined droplet transport and evaporation in the multijet electrosprays is calculated. Conejet and multijet calculations are in quantitative match with the measurements. The applicability of the different spraying modes to thin film deposition and particle production is discussed with reference to electrospray transport and evaporation behaviour.

3.1 Introduction

Electrosprays find considerable attention in recent years not only because of the noble prize in chemistry won by John B. Fenn in 2002 for his work on electrospray mass spectrometry of biomolecules (Fenn et al., 1989). Besides the microdispersing of liquids the controlled droplet size and the targeted deposition with high efficiency (Siefert, 1984) led to a manyfold of electrospray applications in industry. Electrospray painting and coating are established processes e.g. in automotive industry (Domnick, 2003).
Electrospraying is also applied in ink-jet printing (Sweet, 1965) and precise deposition of pesticides to crops in order to fulfil environmental regulations (Bailey, 1988).

Electrospray deposition (ESD) is a widely used technique for making thin functional films with applications in batteries, fuel cells, gas sensors, catalysts etc. Depending on the specific application either porous surfaces or smooth dense layers are required. Electrospraying nanoparticle suspensions decreases the particle agglomeration effect and enables the deposition of different materials simultaneously for nano-phase composite materials (Park and Burlitch, 1996). Even quantum dot structures were produced via reactive ion etching using ESD (Kim and Ryu, 1994). Thin dense film formation can also be achieved by ESD from precursor suspensions which pyrolyse when reaching the hot substrate (electrostatic spray pyrolysis). With this method Chen et al. (1995) produced a LiCoO₂ thin film as cathode for rechargeable lithium batteries while a NiCo₂O₄ catalyst film was produced by Lapham et al. (2001). Perednis et al. (2001) deposited thin yttria-stabilized zirconia (YSZ) electrolyte films on porous anode substrates for a Solid Oxide Fuel Cell (SOFC). In general, the final film structure depends on the droplet transport, or precursor concentration in the droplet, solvent evaporation rate, preferential deposition on the substrate, spreading and discharge of the liquid, chemical decomposition and reaction (Chen et al., 1996). A very elegant way to control those properties is the operation in specific electrospray modes. The mode of an electrospray defines droplet size distribution, spray shape, droplet production rate, droplet velocity and droplet charge distribution (Cloupeau and Prunet-Foch, 1990).

Most of the fundamental studies investigated the conejet mode for its interesting feature of having a nearly monodisperse size distribution and for the simplicity of its structure. The control of narrowly distributed droplet size can for example tailor the production of drugs for inhalation purposes (Ijsebaert et al., 2001) where the inhaled drug efficiency depends heavily on the particle size distribution. By adjusting the aerosol size through conejet spraying to 2-3.5 µm the emitted dose could be reduced by 80% compared to conventional inhalers without loosing any clinical effect.

However, the production of larger droplets (several tens of micrometers) in the conejet mode is very difficult. This can be a disadvantage for deposition processes of thin and dense films especially when utilizing high precursor concentrations in order to gain a high deposition rate. In this case small droplets evaporate too fast leading to
precursor precipitation in the droplet and undesired particle production on the substrate. In the case of heated substrates the droplet evaporation is even enhanced as it was shown for the deposition of yttria-stabilized zirconia (YSZ) with a conejet configuration (Perednis, 2003), where even for small precursor concentrations (0.01 M) the droplet sizes of the ethanol/butylcarbitol spray were too small to reach the substrate without evaporating. However, changing the mode of the electrospray to the intermittent multijet electrospray larger droplets can be produced with a broad spectrum. Perednis (2003) succeeded in producing smooth and homogeneous thin YSZ films with the multijet electrospray mode which is fundamentally described here. It will be shown that large droplets reach the substrate surface without significant evaporation. As a consequence the hot surface evaporates the remaining solvent of the deposited droplet and the precipitated precursor reacts on the substrate before the next droplet arrives forming a smooth dense layer. Therefore, the characteristics of the spatial distribution of droplets, their size, velocity and concentration have to be controlled for conejet and multijet electrosprays. It will be shown by theoretical analysis and measurement that the same experimental setup can produce very different sprays just by applying minor changes highlighting the versatility of the electrospray. There exist separate studies for conejet (Gañán-Calvo et al., 1994) and multijet (Grace and Dunn, 1996) examining the transport of the droplets. However, there is still the need for predictive control of the full process including mass and heat transfer of the droplets for film deposition.

3.2 Experiment

The electrostatic spray setup consists of an aluminum plate with distance either \( H = 80 \) mm or 50 mm from the capillary (stainless steel, Hamilton) for the conejet and intermittent multijet mode, respectively. The spray is facing downward. The outer capillary diameter is 2.77 mm in the case of the conejet and 0.72 mm for the intermittent multijet. The aluminum plate can be heated up to 400°C. Isopropanol (Fluka, > 99.5 %) is used throughout the experiments. In the case of the intermittent multijet mode 0.11 mol/l LiCl (Fluka, > 99.0 %) is added to increase conductivity. The conductivities of pure isopropanol and with the addition of LiCl at 20 °C are \( 3 \cdot 10^{-6} \text{S/m} \) and
220 \cdot 10^{-6} \text{ S/m}, respectively. The liquid feed rate through the capillary is 4.95 ml/h for all experiments which is controlled by a syringe pump (Bioblock Scientific, Model A99). A positive potential is applied to the capillary, while the plate is grounded. The potential is obtained by a high voltage supply (Bertan 450, USA). In the case of the conejet spray 7000 V are applied, while the multijet mode is sprayed with a potential of 9000 V.

A 2D – Phase Doppler Anemometer (PDA) (TSI Inc., USA) operated with an Argon Ion Laser (Innova 70) is used for the measurement of the droplet sizes and droplet velocities in the electrospray. The PDA size detection limit is about 1 \mu m. Droplets smaller than 1 \mu m are eliminated from the size and velocity statistic. The mean velocity (or droplet size) over the cross section for a given distance to the substrate is calculated by averaging the values obtained from the measurement at discrete radial distances. If velocity measurements are done at radial positions r = 0, 1, 2, 3, … mm each value is representing the value for a entire ring area as the spray structure is symmetric versus rotation (e.g. the value at r = 1 mm represents the velocities in the ring area between r = 0.5 mm and 1.5 mm). The velocity values are averaged by weighing them with the ring area.

The air temperature distribution between capillary and plate is measured with a K-type thermoelement in the absence of the spray. The spray temperature was varied between 20 °C and 215 °C. Measurement during spraying would cool the element by deposited droplets and the element itself would serve as a grounded electrode. Further, the liquid temperature is measured at capillary exit for each substrate temperature condition.

The images of the droplet production area at the nozzle tip of the intermittent multijet are taken with a Kodak Ektapro HS Motion Analyzer (Model 4540) using a working distance of 2 cm and an exposure time of 0.2 ms.

The DC electric spray current is measured via the voltage drop over a 10 k\Omega resistance between plate and voltage supply.
3.3 Model

Transport, mass and heat transfer of the droplets in conejet and intermittent multijet is described according to Wilhelm et al. (2003). When a droplet reaches the Rayleigh limit (maximum of charges \( q_R \) reached by a droplet)
\[
q_R = 8\pi \left( \frac{\gamma \varepsilon_\infty d^3}{8} \right)^{0.5}
\]
where \( \gamma \) is the surface tension, \( \varepsilon_\infty \) the dielectric constant, and \( d \) the droplet diameter, the droplet emits 2% of its mass as a small droplet which carries the number of charges according to its own Rayleigh limit (Davis and Bridges, 1994; Taflin et al., 1989; Richardson et al., 1989). The measurement of the electric current produced by the charged conejet droplets between capillary and plate enables a calculation of the total amount of charges transported by the spray. Existing studies on the charge distribution of conejet electrospray droplets with respect to droplet size give size-charge relations between \( d \approx q^1 \) (Kelly, 1984) and \( d \approx q^3 \) (Gañán-Calvo et al., 1994). In a later work Gañán-Calvo et al. (1997) reported \( d \approx q^{1.5} \) in accordance with Tang and Gomez (1994) and Hartman (1998) which assumes a higher charge density for smaller droplets. As the value of the power law dependence of 1.5 is postulated by most authors this relation is also used in the model applied in this work in contrast to the earlier work (Wilhelm et al., 2003) where the power law dependence of 3 is used following the work of Gañán-Calvo et al. (1994). As the size distribution of the conejet mode is approximately monodisperse the influence of the size-charge relations on the droplet transport is not significant.

This work compares two alternatives to calculate the conejet spray transport and evaporation. The first method is called “ab initio” since only information on setup geometry, liquid properties (conductivity, viscosity, dielectricity, surface tension), volume feed rate and electric current produced by the charged spray is required. The conditions for droplet velocity after jet breakup is chosen according to Wilhelm et al. (2003) using the Rayleigh’s jet breakup criterion (Cloupeau and Prunet-Foch, 1989). The initial size distribution is assumed monodisperse and the primary droplet size is calculated from the scaling laws of Gañán-Calvo et al. (1997). The ab initio calculation starts right at jet breakup. The second method is called “initial conditions” since the initial droplet size and droplet velocity for the model calculation is taken from PDA
measurements close to the nozzle (for the conejet: z = 70 mm; 10 mm from the nozzle exit). The method used by Gañán-Calvo et al. (1994) to calculate droplet transport is comparable to the one called “initial conditions” here.

For the intermittent multijet location of droplet breakup, initial velocity and size of the droplets are unknown. Several liquid jets can be emitted at the nozzle rim at the same time. Further, these jets develop and vanish in a rather chaotic mode. Figure 3.1 shows two images of the breakup area of the multijet. The liquid encloses the capillary outlet completely and its surface is highly unstable. Waves are running across and liquid jets are emitted from cone shaped raisings where jets are breaking-up into droplets. Similar observations have been made by Jaworek and Krupa (1996). An ab initio calculation of the intermittent multijet mode is not possible today due to its chaotic nature and here the method of “initial conditions” is applied to investigate and predict droplet transport and evaporation. As the electric current transported by the spray cannot be measured due to corona discharge at the capillary rim a different method is applied in order to estimate the droplet charge distribution at the capillary exit. For this estimation it is assumed that the forces of air resistance (term on the right side of eq. 1) and external electric field (term on the left side of eq. 1) acting on a droplet with diameter d at location z_{eq} in the spray are in equilibrium:
where $C_D$ is the drag coefficient, $\rho_g$ the air density, $\rho_d$ the droplet density, $\bar{v}$ the droplet velocity, $\bar{e}$ the velocity direction, $q$ the droplet charge and $E_{\text{ext}}$ the external electric field. Mutual and image droplet forces do not play a significant role for the axial velocity as also shown by Tang and Gomez (1994). In this work their contribution is below 5% for all locations in the spray. With the diameter correlated velocity data from the PDA measurement it is possible to derive the number of charges for each droplet size class. This assumption is valid if the effect of initial breakup velocity has decayed to a velocity value so that the inertia part is negligible at the measurement location $z_{eq}$. For intermittent multijets there is no information available on droplet velocity at the break-up location. But as also the intermittent droplets are a product from jet break-up like the conejet droplets a velocity smaller than 10 m/s is assumed which is a value typical for conejet break-up velocity. The location $z_{eq}$ depends on the droplet size as small droplets have shorter relaxation times and therefore adapt faster to the external electric field conditions compared to larger ones. At larger distances from the capillary the droplets will undergo evaporation resulting in a mass loss keeping, however, number of charges constant. Consequently, the (electric field - air resistance force) equilibrium is applied at locations $z_{eq}$ where the droplet is not influenced by the initial break-up velocity as well as by evaporation. The benchmark value therefore is that at least 90% of the initial velocity value has decayed and less than 10% of the droplet mass has evaporated.

The calculation of the multijet electrospray is split in the transport and evaporation of the smaller droplets (<30 µm) and the larger droplets (>30 µm) in order to save computational time. But, as the large droplets are rare (<2% in number) they do not have significant influence on the inter-droplet forces. This method is validated by comparing the results of the separate calculations with a calculation with both size fractions present shows no significant difference for droplet velocity or evaporation.

Since the PDA instrument has a minimum signal threshold which limits the detection of droplets smaller than 1 µm, the calculation only accounts for droplets larger than 1 µm.
3.4 Results and Discussion

3.4.1 Conejet electrospray

Conejets show generally a monodisperse or a bimodal size distribution (Hartman, 1998) which was observed also for the isopropanol conejets in this work (Figure 3.2). However, the satellite droplets contribute only 18% by number and 2% by volume to the total droplet distribution for $T_p = 20^\circ$C. Figure 3.3 shows the number size distributions of the spray (10 mm from the nozzle, $z = 70$ mm) measured at different radial positions: in the center ($r = 0$ mm), at an intermediate position ($r = 0.44$ mm) and at the spray edge ($r = 1.5$ mm). It can clearly be observed that the satellite droplets are driven to the spray edge due to their high mobility. This droplet size segregation is seen also in a measurement by Hartman (1998) and was theoretically predicted by Wilhelm et al. (2003).

The air temperatures at capillary distance ($z = 80$ mm) are rather low compared to substrate temperatures as shown in Figure 3.4: 20 °C, 39 °C and 50 °C for substrate temperatures 20 °C, 115 °C and 170 °C, respectively. When approaching the substrate
the temperature increases slowly, while only at about 5 mm in front of the heated plate the temperature gradient is very steep.

The ab initio calculated droplet diameter from the scaling laws of Gañán-Calvo

![Diagram](image)

**Figure 3.3**: Conejet droplet number size distribution measured at 10 mm from the nozzle (z = 70 mm) in the center of the spray (r = 0 mm), at an intermediate position (r = 0.44 mm) and at the edge (r = 1.5 mm). Spatial size segregation is observed as predicted by the model due to the higher mobility of smaller droplets.

![Diagram](image)

**Figure 3.4**: Air temperature distribution between nozzle and plate for plate temperatures T_p = 20 °C, 115 °C and 170 °C. Between 20 and 80 mm from the plate a plateau temperature is reached (20 °C, 39 °C and 50°C) for each plate temperature condition (20 °C, 115 °C and 170°C, respectively).
et al. (1997) are validated with the measured diameter of average volume, 
\[ d_{3,0} = \left( \sum d^3 q_d \right)^{1/3}, \]
in the center of the spray \( r = 0 \) mm at nozzle exit (Figure 3.5). 
Good agreement is found with the values obtained by the scaling laws of Gañán-Calvo et al. (1997) for all three plate temperature conditions, and therefore their corresponding liquid temperature which is about 10 % lower than the air temperature at capillary exit for the non-ambient conditions: 36 °C and 47 °C for 115 °C and 170 °C substrate temperature, respectively. Consequently the scaling laws are applied for the ab initio calculation.

The droplet concentration and mass flux illustrates the structure of the spray (Figure 3.6). After breakup of the jet into droplets, the droplet number concentration is higher than 1000 droplets/cm\(^3\). At a position 25 mm from the nozzle \( z = 55 \) mm the radial expansion of the spray is smaller than 7 mm. The concentration is decreasing when approaching the plate mainly because of the spatial spread of the spray. The spatial distribution of the number concentration is more homogeneous close to the plate and in the middle of the spray \( z = 5 \) mm, \( z = 30 \) mm. The width of the spray at \( z = 5 \) mm is about 60 mm in diameter which corresponds very well to the capillary-plate distance of 80 mm which is typical for conejets (Gañán-Calvo et al., 1994). The radial
distribution of the mass flux is comparable to the number concentration distribution as the satellite droplets have hardly an influence. The mass flux at the spray edge still has about 50% of the center value which is important for homogeneous deposition in spray deposition in the conejet mode. The droplet size segregation has no large influence for this configuration due to the negligible volume of the secondary droplets.

Figure 3.7a – c shows the diameter of average volume of the conejet spray measured with the PDA for the three different plate temperature conditions. The evaporation is calculated assuming zero background vapor concentration for plate temperature $T_p = 20 ^\circ C$ (Figure 3.7a). The initial conditions (droplet velocity and size distribution) for the calculation are taken from $z = 70$ mm (10 mm from the nozzle). The calculation shows very good agreement for both methods (ab initio and initial condition). For the conejet spray with a plate temperature $T_p = 115 ^\circ C$ the measured droplet size is underpredicted by the model when assuming zero background vapor concentration. It takes about 60% of relative isopropanol vapor pressure (100% = 15 kPa) at $T_{air} = 39 ^\circ C$ in order to match the measured values throughout the total spray distance (Figure 3.7b). For $T_p = 170 ^\circ C$ the best match with experimental results is obtained at 80% of relative vapor pressure (100% = 25 kPa) at $T_{air} = 50 ^\circ C$ (Figure 3.7c). These calculations show clearly that the background concentration must not be

![Figure 3.6: Measured droplet concentration and volume flux of conejet electrospray for $T_p = 20 ^\circ C$ at distances $z = 5, 30$ and $55$ mm from the plate. Close to the plate the number concentration and mass flux is rather homogeneous.](image-url)
neglected. They further suggest that with increasing air temperature the vapour background concentration is increasing in the spray. In comparison the “ab initio” calculations show a faster evaporation than the calculation using the “initial conditions” method but the resulting droplet diameters on the substrate do not differ significantly for \( T_p = 20 \, ^\circ C \) and \( 115 \, ^\circ C \). For \( T_p = 170 \, ^\circ C \) the droplets even do not reach the substrate (Figure 3.7c). This difference results from the larger droplet spectrum of the measured size distribution which is used in the “initial condition” method. Compared to the monodisperse assumption in the “ab initio” method the larger droplets in the real distribution do not evaporate completely. Consequently the “ab initio” calculation can replace the “initial condition” method if there is no complete evaporation to fear. Measurement and calculation show that it is possible to control closely the breakup and impact droplet diameter of conejet sprays for process optimization. The impact (breakup) diameter is changing here between 24 (26) \( \mu m \) for ambient conditions to 17 (23) \( \mu m \) for \( 170 \, ^\circ C \) plate temperature underlining the ability for precise control of the

*Figure 3.7: Comparison of measured and calculated diameter of average volume for conejet electrosprays at plate temperatures \( 20 \, ^\circ C \) (a), \( 115 \, ^\circ C \) (b) and \( 170 \, ^\circ C \) (c). Calculations with background concentration of isopropanol vapor are also shown.*
process. The mass fraction of the diameter of average volume arriving on the plate for $T_p = 20 \, ^\circ C$ is 68% of the original size whereas the fraction for $T_p = 170 \, ^\circ C$ is 31%. The important controlling parameters are the liquid properties influencing the initial droplet size (scaling laws) and the temperature distribution in the process area influencing the evaporation rate and thereby controlling the final droplet diameter before deposition.

Figure 3.8a - c shows the measured axial velocities averaged over the spray cross-section and the model predictions for plate temperatures $T_p = 20 \, ^\circ C$, 115 $^\circ C$, and 170 $^\circ C$. The residence time in the spray is very similar for all substrate temperature conditions.

process. The mass fraction of the diameter of average volume arriving on the plate for $T_p = 20 \, ^\circ C$ is 68% of the original size whereas the fraction for $T_p = 170 \, ^\circ C$ is 31%. The important controlling parameters are the liquid properties influencing the initial droplet size (scaling laws) and the temperature distribution in the process area influencing the evaporation rate and thereby controlling the final droplet diameter before deposition.

Figure 3.8a - c shows the measured axial velocities averaged over the spray cross-section and the model predictions for plate temperatures $T_p = 20 \, ^\circ C$, 115 $^\circ C$, and 170 $^\circ C$. The droplets have a high velocity after break-up close to the capillary exit compared to droplet velocity closer to the grounded plate. This is attributed to the higher electric field close to the capillary exit. The measurements show a nearly constant droplet velocity close to the plate. Approaching the substrate the match between measured and calculated values is excellent. The difference close to the nozzle can be explained by an induced air flow from the momentum transfer of the droplets to the air. This effect will be largest close to the nozzle where the droplet velocity and concentration is high
The droplet velocity is very high close to the nozzle for the strong electric field which is induced by the small dimensions of the nozzle tip. Close to the plate, the electric field is getting weaker and the droplets attain equilibrium between external electric forces and drag force which leads to a nearly constant velocity. In this region where the initial velocity has only a very minor influence the calculations using “ab initio” and “initial conditions” are in very good agreement. For the ab initio calculation the initial velocity seems to be underestimated due to the slight overestimation of the diameter of average volume by the scaling law at breakup location (see Figure 3.7a, b, c). As the diameter of the jet and consequently also the jet velocity (droplet velocity at breakup) is calculated from the diameter of average volume (Wilhelm et al., 2003) this leads to a lower jet and droplet velocity at the breakup location (Cloupeau and Prunet-Foch, 1989).

The conejet enables excellent control of droplet evaporation by spraying under the moderate temperature conditions. The charged droplets follow the electrical field lines and they are therefore hardly influenced by radial convection leading to a defined residence time in the system. The average (calculated) residence time of a droplet in the
conejet electrospray is nearly equal for different temperature conditions: \( t = 0.031 \) s at \( T_p = 20 \, ^\circ \text{C} \) and \( t = 0.029 \) s for \( T_p = 170 \, ^\circ \text{C} \).

Figure 3.9 shows the axial velocity distribution with the radial distance from the spray axis for the conejet at \( T_p = 20 \, ^\circ \text{C} \). The difference between measured and calculated velocities at \((z = 55 \, \text{mm}, r = 0 \, \text{mm})\) in the order of several meters per second is remarkable. At the edges of the spray the velocity values match. This is another indication for the existence of an induced air flow. Assuming that the difference between calculated and measured droplet velocity can be attributed to air flow the maximum of the air velocity is in the center and approaching zero at the spray edge. Similar findings have been published by Gañán-Calvo et al. (1994) and Hartman (1998). However, as it is evident from this work, the resulting difference in residence time of the droplets does not significantly influence the evaporation as can be seen in Figure 3.6a. A possible underestimation of the electric fields close to the capillary, which could also lead to this underprediction, does not seem realistic as the external electric fields used in this work, by Gañan-Calvo et al. (1994) and by Hartman (1998) are derived from different assumptions.

### 3.4.2 Multijet electrospray

Figure 3.10a shows an averaged droplet size distribution for an intermittent multijet electrospray (here \( T_p = 20 \, ^\circ \text{C} \)) at the nozzle exit. Figures 3.10b and c show the droplet size distributions measured at the center of the spray \((z = 46 \, \text{mm}, r = 0 \, \text{mm})\) and at the spray edge \((z = 46 \, \text{mm}, r = 10 \, \text{mm})\), respectively. The multijet size distribution is polydisperse in contrast to the conejet’s monodispersity. Counting by number 1.3% (10%) of the droplets is larger than 30 \( \mu \text{m} \) (10\( \mu \text{m} \)) and carries 82% (96%) of the liquid volume. The number distribution is completely dominated by the small droplets but the majority of the liquid is transported by the few larger droplets. It is important to note that there is no segregation of small and large droplets as in the case for the conejet mode. This results from the droplet distribution after break-up in the intermittent multijet mode. Droplet producing jets are emitted at the nozzle rim in a random and intermittent fashion in different directions (Figure 3.1). Consequently large and small
droplets are sprayed in a wide spraying angle which leads to a spatial mixing of the droplets of all sizes and mobilities.

Figure 3.11 shows the number of elementary charges for a given droplet size of the multijet at TS = 115 °C. The power law dependence is q ∼ d^{1.82}. For TS = 20 °C and 215°C the exponent is similar: 1.81 and 1.79, respectively. Thereby the charge density is approximately scaling with the droplet surface. It is noteworthy that the proportionality between droplet size and droplet charge for the three sprays is higher than q ∼ d^{1.5} which is the relation that is often found for conejets (see discussion in chapter 3.3). Hendricks (1962) measured a diameter-charge relation between q ∼ d^{1.5} and q ∼ d^{2.3} using an electrospray which is producing a polydisperse droplet size distribution between 0.1 and 10 µm.

The structure of the multijet is different from the conejet. Figure 3.12 shows the measured and calculated droplet concentrations of the multijet spray for Tp = 20 °C at different distances from the plate. Already at 4 mm from the nozzle (z = 46 mm) the
droplet concentration has shrunk to a value of around 1000 droplets/cm$^3$. Grace and Dunn (1996) obtained a similar value when investigating an ethanol multijet electrospray at 5 mm distance from the nozzle. In comparison this concentration decrease was reached by the conejet 25 mm from the nozzle. The spray width of the multijet at that distance is already 10 mm. This large spray angle results from the

Figure 3.11: Charge distribution for multijet electrospray for the condition $T_p = 115 \, \degree C$. The line represents the power law regressed to the droplet size-charge relation. The number of elementray charge per droplet is proportional to $d^{1.82}$.

Figure 3.12: Measured droplet concentration and volume flux of multijet electrospray for $T_p = 20 \, \degree C$ at distances $z = 3, 23, \text{ and } 46 \, \text{mm from the plate. The mass flux is very homogenous close to the plate.}$
The droplet break-up process described above. The droplets are emitted in an angle close to 180°. The concentration is decreasing towards the plate due to increasing spray cross section and evaporation. Close to the plate the droplet concentration is significantly higher in the middle due to the shorter residence time of the droplets compared to the edges of the spray. In contrast to that the mass flux is very homogeneous which is very important for film deposition. It is even more homogeneous than the conejet mass flux close to the substrate. The mass flux at the spray edges at r = 30 mm is still 50 % of the center value.

Figures 3.13a – c show the development of the mean volume diameter with distance to the substrate. The agreement between theoretical prediction and measurement is excellent. All calculations show that the diameter of average volume is increasing with decreasing distance from the plate. Small droplets are evaporating very fast compared to the larger ones and disappear from the statistics. Therefore, the diameter of average volume increases although the droplets are evaporating because the
size distribution narrows. The calculations assume 0% background vapor pressure. Due to the large spraying angle of approximately 180° and the resulting low droplet concentration at the nozzle exit the isopropanol vapor concentration is distributed within a larger volume and has no influence on the droplet evaporation.

Figures 3.14a – c show the velocity distribution of the multijet spray. The data show a good qualitative match between measurement and calculation. Grace and Dunn (1996) who performed their experiments under ambient conditions with pure ethanol as working fluid in the multijet mode reported similar behavior for the velocity distribution along the spray axis. The velocity is around 4 m/s close to the capillary after breakup. Following the central axis towards the plate the velocity is decreasing first to 2.5 m/s and then increases again to 3 m/s at 5 cm from the plate (capillary-plate distance is 20 cm in their work). The calculation of Grace and Dunn (1996) show only a qualitative agreement to the measured velocity close to the capillary. In this work, however, the velocity can be predicted much more accurately. As already observed for the conejet

Figure 3.14: Comparison of measured and calculated axial velocity of droplets averaged over the cross section for multijet electrosprays at (a) \( T_p = 20 \, ^\circ\text{C} \), (b) \( 115 \, ^\circ\text{C} \), (c) \( 215 \, ^\circ\text{C} \). The calculation is qualitatively matching the measurement. The velocities are very much equal for all three plate temperature conditions.
also here the residence time in the system is very similar for the three temperature conditions. Further, the impact diameter of average mass on the plate can be controlled very carefully by adjusting the external temperature conditions. However, the multijet guarantees that the deposition process can be performed without significant droplet evaporation even at extreme temperature conditions (above 200°C) which are often necessary for electrospray pyrolysis.

3.5 Summary

The transport and evaporation of electrically charged droplets in conejet and intermittent multijet in a capillary–plate configuration are investigated by PDA measurement and simulation. The simulations of the conejet electrospray show an excellent agreement with the measured velocity and evaporation data assuming a background concentration of the evaporated solvent. The simulations for the multijet electrospray are in good qualitative agreement with the velocity data and in good quantitative agreement with the diameter development along the spray axis. The nearly monodisperse conejet mode shows excellent control for initial droplet size and evaporation rate. The final droplet diameter can be controlled very precisely to the applied external air temperature. The multijet is characterized by its initial broad droplet size distribution with much larger droplets than in the conejet mode. Also here the evaporation of the droplets can be controlled carefully by heating the surrounding air. Due to the larger droplet sizes in the multijet this mode can be applied for film deposition at more elevated plate temperatures without complete evaporation of the droplets. Further, the mass flux of the multijet is more homogeneous than the conejet which is very important for the deposition of homogeneous films. With the present setup two very distinct sprays that find their applications in many varying production techniques can be established. The developed theoretical model is able to predict spatially detailed droplet size and velocity distributions. This makes it an excellent tool for dimensionalization of ESD setups and helps to evaluate key parameters of the process.
3.6 References


Wilhelm, O., Mädler, L. and Pratsinis, S.E. (2003) Electrospray evaporation and
4 Electrospray vs. Pressurized Spray Deposition of YSZ Films

Abstract

Yttria-stabilized zirconia (YSZ) films (< 1 µm thickness) were deposited on hot substrates by electrostatic and pressurized atomization. Droplet transport and evaporation are examined with a Phase Doppler Anemometer while the film morphology and composition are investigated by SEM and EDX analysis. The effects of spraying configuration, solvent/precursor composition and substrate temperature on the resulting film morphology are examined. Smooth and dense YSZ films can be made at substrate temperatures above the solvent boiling point while precursor influence is negligible. Furthermore, the spray droplet has to reach the substrate without solid precipitation in the droplet or complete evaporation of the solvent. A deposition diagram for film texture was developed as function of droplet size, precursor concentration and substrate temperature using a theoretical model for droplet transport and evaporation.

4.1 Introduction

Spraying precursor droplets on a heated substrate is typically used for thin ceramic film deposition for its simplicity, low equipment cost and a wide choice of precursors (Gurav et al., 1993). Yttria-stabilized zirconia (YSZ) is the most commonly used material for electrolyte films in solid oxide fuel cells (SOFCs) for its chemical and thermal stability even at 1000 °C. In order to improve the performance of the SOFC and simplify its fabrication, a lower operation temperature is desired. This can be achieved by employing new materials that increase the electrolyte ion conductivity or by decreasing the thickness of the YSZ film. An attractive feature of spray pyrolysis is its ability to

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This chapter is partly submitted to *Thin Solid Films*. 
produce YSZ films with a thickness less than a micrometer on substrates with micron-sized pores (Perednis, 2003).

Siefert (1984) deposited metal oxide films on a glass substrate by corona spray pyrolysis. Similarly Konstantinov et al. (2000) made uniform CeO₂ films at 400 °C while cracks or large crystallites were formed at higher or lower temperatures, respectively. Nguyen and Djurado (2001) deposited the best zirconia films on stainless steel at around 400 °C also. Choy (2002) describes the deposition of films and particles composed of a variety of materials by electrospray deposition. Different types of atomization techniques are used for droplet production: ultrasonic, pressurized sprays and electrosprays (Will et al., 2000). Ruiz et al. (1997) used ultrasonic spray to deposit zirconia films and pointed out the importance of droplet size for the deposited film quality. Wang et al. (2000) used a similar setup for deposition of YSZ films but called their process aerosol-assisted chemical vapor deposition as their droplets are evaporated before arriving on the substrate. Chen et al. (1995) investigated thin film deposition (LiCoO₂) by electrospray for production of a cathode for rechargeable lithium batteries. Chen et al. (1998) showed that additives influencing the droplet size in electrosprays resulted in significant changes in the product. Wilhelm et al. (2003) showed that small droplets can fully evaporate during transport and deposition on hot substrates altering, thus, drastically the deposited film quality.

Clearly spray pyrolysis contains several parameters influencing the quality of the product film: substrate temperature, volume flux, droplet size and velocity, temperature field, precursor/solvent composition and setup geometry. Here two common spray pyrolysis techniques are compared and the effect of process parameters on film quality is evaluated. Droplet size, velocity and volume flux is investigated by a Phase Doppler Anemometer (PDA) while the film morphology and composition are analysed by SEM/EDX. Using the model of Wilhelm et al. (2003) the effect of droplet size, substrate temperature and solution concentration on film texture is summarized on a design diagram and compared to the above data.
4.2 Experimental setup

A YSZ film is deposited by spraying precursor solution (Table 4.1) droplets onto a heated substrate. The YSZ precursors are zirconium acetylacetonate (Zr(acac)₄, Fluka), zirconium oxinitrate (ZrO(NO₂)₃, Fluka), and yttrium chloride (YCl₃, Fluka). The solvent is a mixture of 50 vol% ethanol (Fluka) and 50 vol% butylcarbitol (Diethylenglycol monobutylether, Fluka) or a mixture of 50 vol% ethanol (Fluka) and 50 vol% 1-Methoxy-2-Propanol (Fluka) or pure butylcarbitol (Table 4.1). The films are deposited on inconel (Ni-alloy) foil with thickness 0.5 mm and diameter 30 mm. The foil is sucked by a vacuum pump to the surface of a heated aluminum plate.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Solvents, volume ratio</th>
<th>Precursor, molar ratio</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Butylcarbitol/Ethanol (50/50)</td>
<td>Zr(acac)₄/ YCl₃, 84/16</td>
<td>0.1 mol/l</td>
</tr>
<tr>
<td>B</td>
<td>Butylcarbitol/Ethanol (50/50)</td>
<td>Zr(acac)₄/ YCl₃, 84/16</td>
<td>0.01 mol/l</td>
</tr>
<tr>
<td>C</td>
<td>MethoxyPropanol/Ethanol (50/50)</td>
<td>Zr(acac)₄/ YCl₃, 84/16</td>
<td>0.1 mol/l</td>
</tr>
<tr>
<td>D</td>
<td>Butylcarbitol/Ethanol (50/50)</td>
<td>ZrO(NO₂)₃/ YCl₃, 84/16</td>
<td>0.1 mol/l</td>
</tr>
<tr>
<td>E</td>
<td>Butylcarbitol</td>
<td>Zr(acac)₄/ YCl₃, 84/16</td>
<td>0.001 mol/l</td>
</tr>
</tbody>
</table>

*Table 4.1: Composition of the employed sprayed solutions*

The spray droplets containing the precursor are produced either by a downward pressurized nozzle (“P” – pressurized spray deposition) or by two upward electrospray configurations: conejet (C) and multijet (M). The pressurized nozzle (Böllhoff, Compact 2000KM) is located 31 cm above the substrate. An air pressure of p = 0.75 bar is applied to atomize the solution supplied at Q = 30 ml/h by a syringe pump (Bioblock Scientific, A 99). Table 4.2.1 shows all experimental conditions.

The outlet of the electrospray capillary is 6 cm below the substrate. The electrosprays are pointing upward to prevent deposition of millimeter-sized droplets from spraying instability that could destroy the film homogeneity. This is a problem especially for the conejet mode as the high electric conductivity for liquids containing salt precursors prevents a strong tangential electric field component along the cone surface which leads to a low liquid acceleration and consequently to a low volume flux.
through the jet emitted at the cone apex (Hayati et al., 1986). As the volume flux $Q$ is controlled by the syringe pump, more liquid can flow into the cone from the capillary side than drawn by the electric field through the jet. For upward spraying, surplus liquid does not disturb the jet as it is just flowing down the outer capillary surface. During downward spraying, surplus liquid is forming occasionally millimeter-sized droplets dripping onto the substrate. Steel capillaries are used that have outer/inner diameters of $d = 0.6/0.45$ mm (Braun) and $2.7/2.5$ mm (Hamilton), respectively. The smaller one is used for the intermittent multijet mode while the bigger one for the conejet mode of the electrospray. A syringe pump is used to deliver a precursor solution: $Q = 2.8$ ml/h for the multijet (Table 4.2.2: M1 – 4), $Q = 5.7$ and $1.4$ ml/h for the conejet electrospray at the higher and lower precursor concentration, respectively (Table 4.2.3: C1 – 2).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>$T_s$ [°C]</td>
<td>210</td>
<td>250</td>
<td>310</td>
<td>140</td>
<td>180</td>
<td>185</td>
<td>235</td>
</tr>
</tbody>
</table>

*Table 4.2.1: Deposition experiments with the pressurized spray at $p = 0.75$ bar, $H = 31$ cm and $Q = 30$ ml/h.*

<table>
<thead>
<tr>
<th>Experiment</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$ [°C]</td>
<td>196</td>
<td>256</td>
<td>310</td>
<td>365</td>
</tr>
</tbody>
</table>

*Table 4.2.2: Experiments with the multijet electrospray at $\Phi = 10$ kV, $H = 6$ cm and $Q = 2.8$ ml/h with solution A.*

<table>
<thead>
<tr>
<th>Experiment</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>A</td>
<td>B</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>$T_s$ [°C]</td>
<td>260</td>
<td>260</td>
<td>192</td>
<td>260</td>
</tr>
<tr>
<td>$Q$ [ml/h]</td>
<td>5.7</td>
<td>1.4</td>
<td>2.12</td>
<td>2.83</td>
</tr>
<tr>
<td>$\Phi$ [V]</td>
<td>6900</td>
<td>6900</td>
<td>6700</td>
<td>6400</td>
</tr>
<tr>
<td>Spray direction</td>
<td>Up</td>
<td>Up</td>
<td>Down</td>
<td>Down</td>
</tr>
</tbody>
</table>

*Table 4.2.3: Experiments with the conejet electrospray at $H = 6$ cm.*
As the conejet produces considerably smaller droplets than the multijet electrospray for the above setup, conditions were identified that can produce comparable droplet sizes for both electrosprays. So experiments C3 and C4 were carried with a smaller conejet capillary, 1.47/1.07 mm, and lower salt concentration (Table 4.2.3: C3 – 4) to reduce electric conductivity and a downward pointing spray to guarantee that all the liquid is flowing through the jet and droplet size is not decreased by escaping liquid.

The deposited film morphology is investigated by SEM (LEO1530, Field Emission Gun) while homogeneity and chemical composition by EDX (Noran Vintage). A 2D – Phase Doppler Anemometer (PDA) by TSI Inc. with an Argon Ion Laser (Innova 70) is used for measuring spray droplet size (> 1 µm) and velocity at each location. The PDA is measuring single droplets that pass through the volume defined by the crossing of two coherent laser beams.

The air temperature without spraying between nozzle and substrate is measured with a K-type thermoelement. It is not possible to measure temperature during spraying as the droplets cool the element that serves also as a grounded electrode altering the process when electrospraying.

4.3 Results

4.3.1 SEM/EDX analysis of the deposited film

Figures 4.1a - d show SEM pictures of YSZ films deposited by multijet electrospraying of solution A at different substrate temperatures, $T_S$ (Table 4.2.2). At $T_S = 196 °C$ (Figure 4.1a) the film shows severe cracks while for $T_S = 256 °C$ or higher (Figures 4.1b – d) the number of particles deposited on the substrate increases as confirmed by the EDX spectra (Figures 4.1e – h). Cracks are detected (Figure 4.1a and e) as a reduction of the zirconium signal and an increase of the nickel-substrate signal. The enhanced noise-to-signal ratio with increasing substrate temperature indicates increasing number of particles deposited.

Similar results are obtained when depositing YSZ films by pressurized spraying of solution A. Figure 4.2 shows the contrast between $T_S = 210 °C$ (a) and $T_S = 250 °C$
(b). Similar to the multijet electrospray (Figure 4.1a,b), here also the film changes from a cracked to a crack-free one. This transition point is between $T_S = 140 \, ^\circ C$ and $180 \, ^\circ C$ using solution C instead of A (Figure 4.2c,d). Spraying solution D (with a different Zr-precursor compared to solution A) the resulting film is similar to that made with the original Zr-precursor and solution A (Figure 4.2a,b): the transition from cracked to crack-free film (Figure 4.2e,f) is between $185 \, ^\circ C$ and $235 \, ^\circ C$.

When using the upward facing conejet electrospray at $T_S = 260 \, ^\circ C$ (Table 4.2.3: C1), the film is a porous structure made of single particles (Figure 4.3a). The same film texture is obtained when precursor concentration is reduced (Table 4.2.3: C2) though smaller particles are deposited (Figure 4.3b). But for the downward spraying conejet employing lower precursor concentrations, the film morphology (Figure 4.3c,d) again looks similar to that obtained with the multijet electrospray with solution A (Figure 4.1 a,b): At low $T_S$ (192 °C) a cracked film forms (Figure 4.3c) whereas at high $T_S$ (260 °C) a rather homogeneous film is obtained (Figure 4.3d).

Figure 4.1: continues next page.
Figure 4.1: SEM pictures and EDX spectra of the YSZ films on inconel foil sprayed with the multijet electrospray at (a/e) $T_S = 196 \, ^\circ\text{C}$ (M1), (b/f) $T_S = 256 \, ^\circ\text{C}$ (M2), (c/g) $T_S = 310 \, ^\circ\text{C}$ (M3) and at (d/h) $T_S = 365 \, ^\circ\text{C}$ (M4). The Ni line in e–h is for the substrate while the Zr (bold) line refers to the deposit in the EDX spectra.
Figure 4.2: SEM micrographs of YSZ films produced with the pressurized spray at $T_S = 210^\circ C$ (a) and $250^\circ C$ (b) with solution A (Table 2, exp. P1 and P2), at $T_S = 140^\circ C$ (c) and $180^\circ C$ (d) with solution C (exp. P4 and P5), and at $T_S = 185^\circ C$ (e) and $235^\circ C$ (f) with solution D (exp. P6 and P7).
4.3.2 PDA measurements

Figures 4.4a – c show the initial droplet size distributions for the different sprays. The number size distribution of the multijet electrospray shows a strong peak for droplets below 10 µm (Figure 4.4a) but the few big droplets dominate the volume distribution (experiment M1). The nozzle exit distributions of the other multijet
experiments are similar (see mean volume diameter in Figure 4.6). Only 5% of the solution volume is transported by the small droplets (< 10 µm). This is analogous for the pressurized spray (Figure 4.4c) that forms slightly smaller droplets. The number size distribution is different for the conejet electrospray (Figure 4.4b). For both conejet configurations (upward C1/C2 and downward C3/C4) the distribution is very narrow. But the downward conejet in Figure 4.4b (C4) has a significantly larger mean volume size (d = 12 µm) than the corresponding upward (d = 3.4 µm) (C1). The C4 droplet size distribution shows a bimodal number and a unimodal volume distribution. The size distributions of C2 and C3 are similar to C1 and C4, respectively.

Figure 4.5 shows the droplet axial velocity of the a) pressurized spray and b) two electrosprays as a function of the distance to the substrate. The pressurized spray droplet velocity is very high near the nozzle as droplets try to follow the fast dispersion gas
stream. Approaching the substrate, the droplets slow down as the gas velocity decreases roughly proportional to 1/z for a turbulent free jet (Abramovich, 1963). The electrospray droplets owe their high velocity near the nozzle to their charge and local high electric field strength (Wilhelm et al., 2003). Closer to the substrate, the electric field is weaker and the electrospray droplets are decelerated even though they deposit faster than the pressurized spray ones. For the upward facing conejet electrospray (C1,C2 not shown in

\[ \text{Figure 4.5: Mean axial droplet velocity for the pressurized spray (a) and for the multijet and conejet electrosprays (b) at different substrate temperatures.} \]

\[ \text{Figure 4.6: Droplet diameter of average volume for pressurized nozzle (a) and for multijet and conejet electrosprays (b) at different substrate temperatures.} \]

...
Figure 4.5) no droplets could be detected in the middle of the spray at z = 3 cm or closer to the substrate.

Figure 4.6 shows the mean volume droplet diameter along the spray centerline of the pressurized spray (a) and the multijet and downward facing electrospray (b) as a function of the distance from the substrate. The most striking characteristic of the mean volume droplet diameter (for both pressurized spray and multijet electrospray) is its steep increase close (5 mm) to the substrate as small droplets evaporate much faster than bigger ones in the hot zone near the substrate (Wilhelm et al., 2003). As soon as the numerous small droplets cross the detection limit (< 1 µm) of the PDA they are not counted any more disappearing from the statistics so the mean volume droplet diameter increases. Outside this hot zone in front of the substrate, the droplet diameter is rather constant for large distances. The mean volume droplet diameter from the pressurized nozzle shows an increase at the nozzle exit which can be attributed to droplet coagulation. This does not happen with the electrospray as the droplets are charged and mutually repel each other (Wilhelm et al., 2003). The mean volume droplet diameter of the downward facing conejet changes little throughout the transport to the substrate. There are not many small droplets that rapidly evaporate within this spray. In addition butylcarbitol has a rather low equilibrium vapor pressure compared to the mixed solvent droplets employed during pressurized spraying and multijet electrospraying.

4.3.3 Deposition diagram

It was clearly shown that substrate temperature near or below the solvent boiling point leads to cracked films. Too high T_s can lead, however, to grainy films (Figure 4.1c,d) that result from particle formation prior to droplet deposition. In other words, the onset of solid precipitation in the droplet defines the upper limit for deposition of thin films. This takes place when solvent evaporation has increased the solute concentration C above its saturation value, C_s. Mathematical models (Wilhelm et al., 2003) can be used to identify optimal conditions for droplet evaporation during spray deposition that could lead to design and operation diagrams for spray deposition of smooth or grainy films. Using the measured droplet velocity (Figure 4.5a,b) and initial precursor (solute) concentration, C_o, and droplet diameter, d_{p0}, the evolution of droplet
diameter, solute concentration and subsequently the onset of solute precipitation, \( C = C_S \), can be calculated from the nozzle to the substrate at temperature \( T_S \) (Wilhelm et al., 2003).

Figure 4.7a shows the onset of solid precipitation for solution A in electrosprayed initially monodisperse droplets of \( d_{p0} = 5 \) (broken line), 7 (dot line), 9 (solid line) and 13 \( \mu m \) (dot-broken line) for various initial solute concentrations. For each droplet diameter, the corresponding line signifies the onset of precipitation. To the left and below each line, the sprayed droplets have not started precipitating indicating the region for optimal film deposition. In other words these lines indicate the upper limit of \( T_S \) for deposition of smooth films. Given that the boiling point of the heavy solvent (butylcarbitol) 231 °C, one would need a \( T_S \) above 240 °C to avoid cracked films and below 300 °C to avoid grainy films for \( d_{p0} = 9 \) \( \mu m \) and solvent concentrations less than 0.02 mol/l. The upper \( T_S \) can increase to 450 °C when monodisperse droplets of \( d_{p0} = 13 \) \( \mu m \) are used for these concentrations. For faster deposition, the solute concentration can increase nearly up to 0.2 mol/l at these conditions. Figure 4.7a labels also these curves with the geometric standard deviation of the initial spray assuming it is polydisperse with \( d_{p0} = 5 \) \( \mu m \). The broader the spray size distribution, the larger is the upper \( T_S \) for non-grainy films. For the polydisperse spray, the line corresponds to the point where precipitation took place in 80 % of the droplets by number.

The employed size distribution in Figure 4.1 and 4.4a corresponds to the \( d_{p0} = 5 \) \( \mu m \) and \( \sigma_g = 2 \) in Figure 4.7a (solid line) for initial solute concentration of 0.1 mol/l and are shown with square symbols. The data points that are to the left of that line, \( T_S = 196 \) and 256 °C (open squares), do not show precipitation (Figure 4.1a,b) while the ones to the right of it, \( T_S = 300 \) and 350 °C (filled squares), show grainy deposits (Figure 4.2c,d). It is worth pointing out that an increased number of smaller particles are obtained with increasing \( T_S \) as rapid precipitation will take place in more droplets where many small particles will nucleate and deposit on the substrate. Of course the present model cannot predict the formation of cracked films (Figure 4.1a) as this is determined by film drying so droplet evaporation has little, if anything, to do with it.

An analogous calculation can be done for the pressurized spray (Figure 4.7b). The employed size distribution in Figure 4.2a,b and 4.4c corresponds to \( d_{p0} = 5 \) \( \mu m \) and
Figure 7: The precipitation conditions of multijet electrospray (a) and pressurized spray (b) droplets composed of solution A are shown. Each line corresponds to a constant (monodisperse) geometric standard deviation, $\sigma_g$, and variable average droplet diameter or to a constant droplet diameter (5 $\mu$m) and variable $\sigma_g$. To the left and below each line there is no precipitation of precursor material in the droplets by number for the given substrate temperature $T_S$ and initial precursor concentration. Process conditions to the right or above the lines will result in non-uniform, grainy deposits, as solid precipitation has occurred to more than 80 % of the droplets. The M1 – 4 experiments (Table 2.2) correspond to the solid line ($d_{1,0} = 5$ $\mu$m, $\sigma_g = 2$) and are in excellent agreement with this analysis (Wilhelm et al., 2003) for smooth (open squares) and grainy films (filled squares).
$\sigma_g = 2$ in Figure 4.7b. As well here the data points that are to the left of that line, $T_S = 210$ and 250 °C (open squares), do not show precipitation.

4.4 Discussion

YSZ films are deposited with three different sprays on an inconel substrate. The SEM and EDX analysis of the deposited films show that film texture is similar regardless if droplets are deposited with an intermittent multijet electrospray or a pressurized spray (Figure 4.1a,b and 4.2a,b). When spraying butylcarbitol/ethanol as solvent, the film shows a cracked surface for low substrate temperatures between (185 °C, Figure 4.1a/2a) and a crackfree surface for higher temperatures (250 °C, Figure 4.1b/2b). When exchanging the butylcarbitol with methoxy-propanol the transition between cracked and crack-free film is between 140 °C and 180 °C (Figures 4.2c,d). For both solutions this temperature range is close to the boiling point of the less volatile solvent, butylcarbitol ($T_b = 231$ °C) and methoxy-propanol ($T_b = 120$ °C), respectively. This indicates that for crackfree film deposition of YSZ, the substrate temperature should be higher than the boiling point of the solvents in the mixture. Exchanging the zirconium precursor does not alter the result as its concentration is rather small in these solutions (Figure 4.2e,f).

The upward conejet deposited films show a porous structure for both applied precursor concentrations (Figure 4.3a,b). The particle sizes are smaller for lower precursor concentration. The precursor content induces an increased electrical conductivity of the solution which is decreasing the initial droplet size compared to the pure solvent (Gañán-Calvo et al., 1997). The droplets seem to need a minimum initial size to overcome the high temperature area in front of the substrate otherwise the droplets evaporate before their arrival on the substrate. So the solid is precipitating in the droplets during transport and deposits in the form of particles (Figures 4.3a,b). By lowering the precursor concentration and using a low volatility solvent, butylcarbitol, it is possible to obtain a conejet spray whose droplets are able to “survive” during transport through the hot zone in front of the substrate without complete evaporation or solid precipitation. The resulting film morphologies look similar to the ones obtained
with pressurized spray or multijet electrospray deposition. For a substrate temperature around 200 °C the film shows cracks and inhomogeneity. The cracks disappear for a substrate temperature above 250 °C.

The most important parameters for the film morphology are substrate temperature and initial droplet size. Firstly, the substrate temperature has to be above the boiling point of the solvent. This guarantees a fast and effective evaporation of the solvent after droplet deposition. If the temperature is lower, the liquid remains too long on the substrate and a slurry film develops which is drying after the spray deposition process is stopped. The drying of the slurry will result in cracked structures (Figures 4.1a, 4.2a, 4.3c). So it is essential that the substrate is dry at all times during the spraying process. Secondly, the initial droplets have to be large enough so they can reach the substrate without complete evaporation. This is related to setup geometry (transport distance of droplets), droplet velocity and air temperature. For the pressurized spray and intermittent multijet electrospray the initial droplet sizes are sufficiently large (Figure 4.4) as only a small droplet fraction is evaporating that increases by increasing substrate temperature (Figure 4.1e – h). This fraction results in aerosol ceramic particles whose number increases as shown in Figure 4.1c,d. This is undesirable as it ruins the surface smoothness (Figure 4.1f – h).

4.5 Conclusion

YSZ films are deposited by spray pyrolysis with intermittent multijet electrospray and pressurized spray that result in similar droplet size distributions and YSZ film quality. The films become crackfree if the substrate temperature is above the boiling point of the employed solvents. The substrate temperature may not exceed the solvent boiling point by more than 50 °C as with increasing temperature more and more of the smaller droplets are evaporating resulting in the deposition of dry precipitated particles on the substrate that increases film roughness. The importance of the initial droplet size is shown by applying conejets with solutions containing different precursor concentrations. High concentrations induce high electrical conductivity and lead to small droplets (< 10 µm) in conejets. The droplets evaporate during transport and
ceramic aerosol is deposited as porous structure on the substrate. By increasing the initial conejet droplet size by decreasing precursor content similar morphologies as for pressurized spray deposition and multijet electrospray deposition can be obtained. This hypothesis is supported by modelling the onset of solid precipitation conditions in the droplets during evaporation and transport to the film substrate.

4.6 References


5 Research recommendations

A model for droplet transport and evaporation was developed and successfully applied to conejet and intermittent multijet. But there is still the open question if the axial velocity difference between the measured and calculated data close to the capillary exit for electrospraying in the conejet mode is due to air movement induced by momentum transfer from droplets to air. This problem could be modeled by solving Navier-Stokes equations together with the transport and evaporation equations applied here. The measurement of the air velocity by adding tracer particles to the spray as done by Tang and Gomez (1994) does not seem to be a proper way as the particles might get charged somehow which is hard to confute. Further there is the gaseous solvent background concentration that has to be accounted for especially in highly volatile conejet sprays. As the concentration is depending on gaseous sources (evaporating droplets) and gas transport (convection/diffusion) this problem is linked to the previous one. But anyway it would be of great importance to measure the background concentration directly. A feasible way might be to use a mass spectrometer that is fed by air from the spray interior over a ceramic capillary that is not influencing the spray performance.

The conejet spray is well investigated and still nowadays studies are done. As has been shown multijets might be a very versatile tool especially for deposition processes. The practical advantage is, besides the intrinsic features of the multijet, its stability versus external disturbances in contrast to the conejet. An extension of the conejet knowledge in terms of scaling laws, charge distribution etc. to multijet, intermittent multijet and electrosprays at higher potentials is still to come.

The deposition of (uncharged) droplets is extensively studied, as well the decomposition and crystallization of precursors by pyrolysis. But still the complicated mechanism between droplet deposition (how do the charges affect the deposition and spreading of the liquid ?), drying of the solvent and solidification of the precursor (effect of surface tension and surface roughness, diffusion of precursor out of the drying porous precursor material) up to the final pyrolysis (is the precursor precipitated and pyrolised on the substrate or deposited in a CVD process from the drying droplets ?) is predominantly unclear.
Appendix

A1 Electrochemical performance of granulated titania nanoparticles

Abstract

The electrochemical performance of Li-ion insertion into electrodes made of various sizes of anatase titania nanoparticles embedded in larger granulated entities (1 - 10 µm) is investigated. The granules are formed by spray drying of a suspension containing titania nanoparticles made by hydrolyzing titanium tetraisopropoxide. Depending on the three process steps, i.e. hydrolysis-condensation, hydrothermal processing and spray drying, different properties for the electrode made from these granules can be achieved in terms of phase composition, specific surface area (SSA) and specific charge capacity. Hydrothermally processed particles are more resistant to calcination than sol-gel precipitated ones and have a higher SSA which leads to a better performance with respect to specific charge capacity. Electrodes made from granulated nanoparticles have superior specific charge capacity than from non-granulated ones as the former have more inter-particle contacts.

A1.1 Introduction

Titania (TiO₂) electrodes are used in solar cells (Hagdeldt, 1995), electrochromic devices (Granquist et al., 1997) and lithium-ion batteries (Huang et al., 1995). By replacing the carbon at the negative electrode with titanium based oxide materials working at more than 1 Volt, the thermodynamic stability of the electrolyte is guaranteed, which saves 15% energy loss during the first cycles and is expected to improve safety. In order to maintain the cell energy, positive electrode materials with working voltage 1Volt higher than LiCoO₂ can be used. Anatase TiO₂ is a prospective

\[^d\] This chapter will partly be published in the Journal of Power Sources.
interesting negative electrode material for 2V lithium ion batteries due to its convenient formal potential around 1.8 V (vs.Li/Li+). Although there are eight existing polymorphs of titania (Kavan et al., 1996) only the anatase and rutile phase are examined more closely for their electrochemical performance. But rutile shows only a weak intercalation of Li-ions into the titania crystal at room temperature (Kavan et al., 1999). Anatase phase accommodates the charged Li-ions by a first-order phase transformation (Van de Krol, 1999):

\[
\text{TiO}_2 + 0.5 \, \text{e}^- + 0.5 \, \text{Li}^+ \rightarrow \text{Li}_{0.5} \, \text{TiO}_2 .
\]

Many authors report the existence of the orthorombic Li_{0.5} TiO_2 phase (Kavan et al., 2001). Others report maximum electrochemical insertion for Li_x TiO_2 with x = 0.7 – 1 (e.g. Ebina et al., 1999). The ability of the anatase phase to intercalate a large number of Li-ions together with relatively fast kinetics makes it a good candidate for an application in high density lithium-ion batteries (Van de Krol, 1999).

Especially the morphology plays an important role in the kinetics of the charge/discharge process. Several authors report the influence of organised or ordered mesoporous films (Kavan et al., 2001) on the electrochemical performance. Other works mention the importance of the dimension of the crystals in porous electrodes for the intercalation kinetics (Exnar et al., 1997). Supposing that the intercalation time t can be estimated based on the effective diffusion D we get \( t = R^2 / \pi D \) (Exnar et al. 1997). The square root dependence of the intercalation time from the radius R of the crystals makes the use of nanostructured mesoporous electrodes for Li-ion batteries evident.

This is a new approach to organize the electrode in nanoparticles embedded in larger granulated entities in order to increase their interconnectivity. The influence of titania phase, specific surface area and granule morphology on the electrochemical behaviour of the powder is examined. The nanoparticles are derived from a sol-gel process and granulated in a spray drier. The particle size is influenced by hydrothermal treatment and calcination.
A1.2 Experimental procedure

The sol-gel and spray drying processes for production of the colloid suspension and the packaged nanoparticles were described in an earlier paper (Kim et al., 2001) and are only summarized here. A titania suspension is synthesised by hydrolysis and condensation of titanium tetraisopropoxide (TTIP; Ti(OC₃H₇)₄ 97 % Aldrich) in ethanol and water as solvent liquids. In order to form granules out of the sol-gel precipitate (SGP) the suspension is fed into a co-current spray drier. After spray drying, the powders are annealed at 300°C, 450°C, and 600°C, respectively, for 2 hours in an oven.

Figure A1.1: SEM micrographs of spray-dried granules from (a,b) hydrothermally processed (HP) and (c,d) sol-gel precipitated (SGP) granules. The SGP granules consist of numerous hard aggregates whereas the substructure of HP granules appears less compact.
at ambient pressure. Hydrothermally processed (HP) granules are produced by aging the SGP slurry in an autoclave for 12h at 80°C and spray drying the resulting suspension (Kim et al., 2003). As well the HP granules are calcined as well at 300°C, 450°C and 600°C.

The specific surface area (SSA) of the powder is obtained by nitrogen gas adsorption/desorption at 77 K by the multipoint Brunauer-Emmett-Teller (BET) method. X-ray diffraction (XRD, Model D5000, Siemens) was used to evaluate the crystallite structure of the powder samples with Ni-filtered CuKα radiation. The software tool TOPAS was used to evaluate crystallite sizes and crystallite fractions. Scanning electron microscopy is used to get information about the granule morphology (Hitachi, H-900).

The electrochemical analysis is done in a cell with one lithium electrode. For electrochemical measurements, the synthesized samples are mixed with 10% carbon black and 5% PVDF are coated on Al foil using the doctor blade technique. The foils were pressed at 2000 kg/cm² and dried at 150°C for 24h under vacuum. The electrochemical test is performed versus Li-metal in a two electrode cell using EC/DEC 1 M LiPF₆ electrolyte in a Arbin battery test system.

Figure A1.2: XRD spectra at different calcination temperatures of the granulated HP (a) and SGP powder (b): A stands for anatase phase, R for rutile and B for brookite.
A1.3 Results

Figure A1.1 shows SEM micrographs of HP (1a and b) and SGP (1c and d) granules after spray drying. The SGP granules consist of hard agglomerates of nanoparticles which can be seen in Figure A1.1d. This kind of granule substructure cannot be seen for the HP granules. The granule size distribution is between 1 and 10 µm consistent with Kim et al. (2002).

Figure A1.2 shows the XRD patterns of HP a) and SGP b) granules at different calcination temperatures. Most samples show clearly the anatase peak at 20 = 25.3°. Only the sample of SGP granules at 300°C calcination temperature appears to be largely amorphous but it is transformed to anatase at higher calcination temperatures (Song et al., 2000). The HP granules which were calcined at 300°C show already a distinct anatase peak. At 600°C the HP granules contain small fractions of rutile and brookite phase.

Figure A1.3a illustrates the dependence of the specific surface area (SSA) with respect to calcination temperature of SGP (full symbols) and HP (open symbols) titania granules. Increasing the calcination temperature is decreasing the SSA for all investigated powders. The SSA results are within about 10% for the SGP (Kim et al.,

![Figure A1.3](image-url)  
*Figure A1.3: a) Specific surface area (SSA) and b) BET diameter (circles), anatase size (squares) and fraction (triangles) of SGP (filled symbols) and HP (open symbols) granules after calcination at 300°C, 450°C and 600°C for 2 hours. There is no value for the crystallite size of the SGP granule at 300°C because it is mostly amorphous.*
For calcination temperatures above 300°C the SGP powders show a distinctly smaller SSA and bigger particle size than the HP granules. This indicates the higher thermal stability of HP granules. The anatase crystallite size is comparable to the BET primary particle size of the HP granules for calcination temperatures at 300°C, 450°C and 600°C (Figure A1.3b) and in agreement with Kim et al. (2003). The fraction of anatase phase is around 70% for all three calcinations temperatures. The other 30% are brookite phase. The brookite crystals have about the same size (7.8 µm, 10.0 µm, 20.2 µm at 300°C, 450°C and 600°C, respectively) as the anatase crystals. This suggests that the primary particles are single crystals, either anatase or brookite. The sample at 600°C also shows a small rutile peak, 3.7 % by weight. There is no value given for the anatase crystallite size of the SGP granules at 300°C where titania is still largely amorphous. At 450°C and 600°C the anatase phase dominates with 95% by weight. Also here the crystallite size is close to the primary particle size calculated from BET indicating single crystallites.

Figures A1.4a and b show the specific charge capacity of granulated hydrothermally processed and SGP titania electrodes at different C-rates. 1 C corresponds to complete charging of the electrode within 1h. The specific capacity shows good values for charging rates up to C for all electrodes except the SGP which was calcined at 300°C. As a large fraction of this powder is amorphous, it is not active.
for Li-ion intercalation and therefore lost for charging. At low charging rates (C/10 – charging of electrode in 10h) the specific capacity can be up to 140 mAh/g (HP granules at 300°C calcination temperature) which corresponds to \( x = 0.42 \) being close to the value of a completely filled octahedral lattice where \( x = 0.5 \). All powders show good cycling stability. After 20 cycles, the capacity at C/2 (corresponding to charging in 2h) is still more than 90% of the original specific capacity. Higher charge/discharge rates lead to lower specific capacities. The HP granules show in general a better performance compared to the SGP powder at the same charging rate. Only at very low charging rates (C/10) the specific capacity is comparable. The primary particle size of HP primary particles is smaller than the one of SGP primary particles, so a faster Li-exchange is possible between titania lattice and surrounding electrolyte. The best performance is given by the HP granules calcined at 300°C which also have the smallest primary particle size of all powders (\( d_{\text{BET}} = 8 \) nm). Increasing the particle size by calcination lowers the specific charge capacity. Exnar et al. (1997) found that the optimal anatase particle size in practical TiO\(_2\)/LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) button cells is about 10 – 15 nm. Kavan et al. (2003) investigated Li insertion into Li\(_4\)Ti\(_5\)O\(_12\) spinel structures and also saw a decrease of charge capacity with decreasing SSA (meaning increasing particle size). This experiment was performed on thin film electrodes in absence of any supporting additives.

![Figure A1.5: Galvanostatic chronopotentiometry at different calcination temperatures for 2 hours of the granulated HP (a) and SGP (b) electrode.](image)
Figures A1.5a and b show the galvanostatic charge/discharge characteristics of the HP and SGP titania electrodes against lithium metal at 1C rate charge and discharge. The examples were chosen to demonstrate behaviour of electrode with thickness and composition usual in conventional electrodes. Hence, the polarization of electrodes is relatively high and the maximum reversible capacity is in expected range (ca 90 mAh/g) as shown in Fig. A1.4. Despite of high polarization of electrodes due to high ohmic losses can we observe significant difference between HP and SGP electrode.

The performance of an ordered electrode consisting of HP granules concerning the specific capacity is compared to an unstructured (ungranulated) nanoparticle electrode in Figure A1.6. The comparison of SSA of granulated and ungranulated powders show a difference in the range of 10% or less. Figure A1.6 a and b show the specific capacity of granulated and ungranulated electrode for calcination temperature 300°C (a) and 450°C (b) at different charging and discharging rates. The specific capacity is about 20% higher for the granulated nanoparticle electrode at charging rates higher than C for both calcination temperatures. At low charging rate (C/10) the specific capacity has the same value for granulated and ungranulated electrodes. This effect cannot be attributed to the negligible difference in SSA. Presumably it is the increased number of contacts in the granules which facilitates current flow resulting in higher charging capacity. Again at low charging rates the electrode structure has less influence on the intercalation kinetics.

![Figure A1.6: Specific charge capacity at different charging rates of granulated and ungranulated HP powders at calcination temperatures 300°C (a) and 450°C (b).](image)
A1.4 Conclusions

The electrochemical performance of nanosized, granulated anatase titania was investigated. The influence of the primary particle size on the ability of the titania electrode to intercalate Li-ions was clearly shown. With decreasing size of the primary particles down to 8 nm an increase in charge capacity at different charging rate could be found. The maximum charge capacity is 140 mAh/g (at C/10 charging rate) which is close to the value in the orthorombic structure (Kavan et al., 2001). Ordering the primary nanoparticles to larger entities by granulation enhanced the charge capacity of the electrodes as a higher number of bonds or contacts were formed between the nanoparticles during spray drying.

A1.5 References


A2 Dimensionless transport and evaporation equation

All variables that are not defined here can be found in the notation list in chapter 2.

A2.1 Derivation of the dimensionless version of transport equation (eq. 1, chapter 2):

\[
\frac{\pi}{6} \frac{d^3}{r_3^3} \frac{d^3}{dt} = C_d \frac{\pi}{8} \rho_g d_i^3 v_i^2 \varepsilon_i + q_i \vec{E} + \frac{1}{4 \pi \epsilon_0} \sum q_j q_j \varepsilon_{ij}^2 r_{ij}^3
\]

with \( C_d = \frac{24}{Re} (1 + 0.15 Re^{0.687} ) \) and \( \vec{E} = \frac{\Phi_o}{H} \nabla \Phi \).

The derivation is done here for the z-direction. The derivation for other directions is analogous:

\[
\Rightarrow \frac{dv_{iz}}{dt} = \frac{18}{\rho_d} \frac{\rho_g}{Re} \left( 1 + 0.15 Re^{0.687} \right) \frac{v_{iz}^2}{d_i^3} \varepsilon_i + \frac{6}{H \rho_d} \frac{\Phi_o}{\rho_t} \frac{q_i}{\rho_t} \Phi + \frac{3}{2} \frac{\pi^2 \epsilon_0 \rho_d}{\rho_t} \frac{1}{d_i^3} \sum q_j q_j \varepsilon_{ij}^2 r_{ij}^3
\]

with \( t_c = \frac{\bar{d}^2}{18 v \rho_g \rho_d} \), \( T_c = \frac{\bar{d}^2}{18 v \rho_g \rho_d} T_\infty \), \( \bar{q} = \left( \frac{d_i}{d} \right)^3 \); \( \bar{x} = \frac{x}{H} \); \( \bar{t} = \frac{t}{t_c} \); \( \bar{d}_i = \frac{d_i}{d} \); \( \bar{v}_i = \frac{v_i}{v_0} \); \( \bar{v}_o = \frac{H}{t_c} \); \( \bar{T} = \frac{T}{T_\infty} \).

\[
\Rightarrow \frac{H}{t_c^2} \frac{dv_{iz}}{dt^*} = \frac{18}{\rho_t} \frac{v_{t_c}}{d_1^3} \frac{\rho_g}{\rho_d} \left[ 1 + 0.15 \left( \frac{H \bar{d}_i \bar{v}_{iz} d_i^3}{t_c} \right)^{0.687} \right] \frac{H^2}{t_c^2} \frac{v_{iz}^2}{d_i^3} \varepsilon_i + \frac{6}{\rho_t} \frac{\Phi_o}{\rho_t} \frac{\bar{q}}{\rho_t} \Phi
\]

\[
+ \frac{3}{2} \frac{1}{\pi^2 \epsilon_0 \rho_d} \frac{1}{H^2} \frac{d_i^3}{d^3} \sum \frac{d_j^3}{r_{ij}^3}
\]

\[
\Rightarrow \frac{dv_{iz}}{dt^*} = \frac{18}{\rho_t} \frac{v_{t_c}}{d_1^3} \frac{\rho_g}{\rho_d} \left[ 1 + 0.15 \left( \frac{H \bar{d}_i \bar{v}_{iz} d_i^3}{t_c} \right)^{0.687} \right] \frac{\bar{v}_{iz}^2}{d_i^3} \varepsilon_i + \frac{\Phi_o}{\rho_t} \frac{\bar{q}}{\rho_t} \Phi
\]

\[
+ \frac{3}{2} \frac{1}{\pi^2 \epsilon_0 \rho_d} \frac{t_{c_o}^2 \bar{q}^2}{H^3} \sum \frac{d_j^3}{r_{ij}^3}
\]

\[
\Rightarrow \frac{dv_{iz}}{dt^*} = \left[ 1 + 0.15 \left( \frac{18 \rho_g \bar{d}_i \bar{v}_{iz} d_i^3}{d_1^3} \right)^{0.687} \right] \frac{\bar{v}_{iz}^2}{d_i^3} \varepsilon_i + \frac{\Phi_o}{\rho_t} \frac{t_{c_o}^2 \bar{q}}{H^2} \frac{1}{Q} \frac{T_{c_o}^2}{T_{\infty}} \Phi
\]

\[
+ \frac{1}{24} \frac{\epsilon_0 \rho_d}{H^3} \left( \frac{1}{Q} \right)^2 T_{c_o}^2 \sum \frac{d_j^3}{r_{ij}^3}
\]
\[ \Leftrightarrow \frac{dv_{iz}^{*}}{dt^{*}} = \left( 1 + 0.15 \left( \frac{18H}{\rho_d} \frac{pM}{R_m T_o} \frac{v_{iz}^* d_i^*}{T_i^*} \right)^{0.687} \right) \frac{v_{iz}^*}{d_i^*} + \frac{\Phi_{oc} t_{co}^2}{H^2 \rho_d} \frac{1}{Q} T_{iz}^* \nabla z \Phi \]

\[ + \frac{1}{24} \frac{d^3 t_{co}^2}{\varepsilon_o \rho_d H^3} \left( \frac{1}{Q} \right)^2 T_{iz}^* \sum \frac{d_j^*}{r_{ijz}^2} \]

\[ \Leftrightarrow \frac{dv_{iz}^*}{dt^*} = \alpha \cdot \frac{v_{iz}^*}{d_i^*} + \beta \cdot T_{iz}^* \nabla z \Phi + \gamma \cdot T_{iz}^* \sum \frac{d_j^*}{r_{ijz}^2} \]

with \[ \alpha = \left( 1 + 0.15 \left( \frac{18H}{\rho_d} \frac{pM}{R_m T_o} \frac{v_{iz}^* d_i^*}{T_i^*} \right)^{0.687} \right) ; \quad \beta = \frac{\Phi_{oc} t_{co}^2}{H^2 \rho_d} \frac{1}{Q} ; \quad \gamma = \frac{1}{24} \frac{d^3 t_{co}^2}{\varepsilon_o \rho_d H^3} \left( \frac{1}{Q} \right)^2 \]

Interpretation:

\[ \alpha = \left( 1 + 0.15 \left( \frac{18H \rho_{go}}{\varepsilon_o d_i^*} \frac{v_{iz}^* d_i^*}{T_i^*} \right)^{0.687} \right) \quad \text{with} \quad \rho_{go} = \frac{pM}{R_m T_o} \]

\[ \frac{18H \rho_{go}}{d \rho_d} = 27 \frac{V_{cyl} \rho_{go}}{\varepsilon_o d \rho_d} = 27 \frac{m_{go}}{m_d} = 27 \frac{p_{go}}{p_d} \quad \text{with} \quad p \rightarrow \text{momentum} \]

The ratio describes the ratio of momentum transfer from the droplet to the air.

\[ \beta = \frac{\phi_{oc} t_{co}^2}{H^2 \rho_d} \frac{1}{Q} = \frac{1}{\rho_o \phi V} = 2 \frac{W_{el}}{W_{kin}} \]

This is the ratio of the electric energy versus the kinetic energy of a droplet in the spray.

\[ \gamma = \frac{1}{24} \frac{d^3 t_{co}^2}{\varepsilon_o \rho_d H^3} \left( \frac{1}{Q} \right)^2 = \frac{1}{24} \frac{q^2}{4 \pi \varepsilon_o H} \frac{1}{4 \pi} \frac{1}{4 \pi} = \frac{1}{8 \pi^2} \frac{W_{mut}}{W_{kin}} \]

This is the ratio of the mutual droplet force to the kinetic force.
A2.2 Derivation of the dimensionless version of the mass transfer equation (eq. 10, chapter 2):

\[
\frac{dm}{dt} = \pi \frac{d_i}{6} \rho_g D \text{Sh}_{\text{eff}} B_m
\]

with \( \text{Sh}_{\text{eff}} = \left[ 2 + \frac{\text{Sh}_o - 2}{F(B_m)} \right] \ln(1 + B_m) \); \( B_m = \frac{Y_S - Y_\infty}{1 - Y_S} \);

\( F(B) = (1 + B)^{0.7} \frac{\ln(1 + B)}{B} \) and \( Y_S = \frac{c_S}{c_S + c_{\text{gas}}} \) \( c_{\text{gas}} \rightarrow \text{air concentration} \)

\[
\frac{d}{dt} \left( \frac{\pi}{6} \frac{d_i^3}{d_i} \right) = \pi \frac{d_i}{6} \rho_g D \text{Sh}_{\text{eff}} B_m
\]

\[
\rho_d \frac{d^2 d_i}{dt^2} = \pi \frac{d_i}{6} \rho_g D \text{Sh}_{\text{eff}} B_m
\]

\[
\frac{dd_i}{dt} = 6 \frac{\rho_g D_o}{d_i} \frac{T_{\text{ref},1}^{1.5}}{T_o^{1.5}} \left[ 2 + \frac{\text{Sh}_o - 2}{F(B_m)} \right] \ln(1 + B_m) \frac{1}{d_i}
\]

\[
\frac{dd_i}{dt} = 6 \frac{\rho_g D_o}{d_i} \frac{T_{\text{ref},1}^{1.5}}{T_o^{1.5}} \left[ 2 + \frac{\text{Sh}_o - 2}{F(B_m)} \right] \ln(1 + B_m)
\]

\[
\frac{dd_i}{dt} = 6 \frac{\rho_g D_o t_c}{d_i^2} T_{\text{ref},1}^{1.5} \left[ 2 + \frac{\text{Sh}_o - 2}{F(B_m)} \right] \ln(1 + B_m)
\]

\[
\frac{dd_i}{dt} = \frac{1}{3} \frac{D_o}{\nu} T_{\text{ref},1}^{1.5} \left[ 2 + \frac{\text{Sh}_o - 2}{F(B_m)} \right] \ln(1 + B_m)
\]

\[
\frac{dd_i}{dt} = \delta \cdot T_{\text{ref},1}^{1.5} \left[ 2 + \frac{\text{Sh}_o - 2}{F(B_m)} \right] \ln(1 + B_m)
\]

with \( \delta = \frac{1}{3} \frac{D_o}{\nu} \) and \( B_m = \frac{Y_S - Y_\infty}{1 - Y_S} = \frac{c_S(T_S)}{c_S(T_S) + c_{\text{gas}}(T_S)} - \frac{c_{\text{gas}}(T_\infty)}{c_S(T_S) + c_{\text{gas}}(T_\infty)} \frac{1}{1 - Y_S} = \frac{c_S(T_S)}{c_S(T_S) + c_{\text{gas}}(T_S)} + \frac{c_{\text{gas}}(T_\infty)}{c_S(T_S) + c_{\text{gas}}(T_S)} \)

Interpretation:

\[
\delta = \frac{1}{3} \frac{D_o}{\nu} = \frac{1}{3} \frac{1}{\text{Sc}}.
\]

This is the mean droplet size divided by the Schmitt number.
A2.3 Derivation of the dimensionless version of the energy equation (eq. 11, chapter 2):

\[
\frac{dQ}{dt} = \pi d_1 \lambda_g N_u(T_S - T_\infty) - \Delta H \dot{m}
\]

with \(N_u = \left[2 + \frac{\nu_d - 2}{F(B_h)}\right] \ln\left(1 + B_h\right) / B_h\) and \(B_h = C(T_S - T_\infty) / \Delta H\)

\[
\Rightarrow C \cdot m_i \cdot \frac{dT_i}{dt} = \pi d_1 \lambda_g N_u(T_S - T_\infty) - \Delta H \dot{m}
\]

\[
\Rightarrow \rho_d \frac{\pi}{6} d_1^3 \frac{dT_i}{dt} = \pi d_1 \lambda_g N_u(T_S - T_\infty) - \Delta H \frac{\pi}{6} \rho_d d_1^3 \dot{d}_i / dt
\]

\[
\Rightarrow \frac{dT_i}{dt} = 6 \frac{\lambda_g}{\rho_d} N_u(T_S - T_\infty) \frac{1}{d_1^2} - \Delta H \frac{1}{C} \frac{1}{d_i} \dot{d}_i / dt
\]

\[
\Rightarrow \frac{T_o}{t_c} \frac{dT_i}{dt^*} = 6 \frac{\lambda_g}{C^2 \rho_d d^2 T_o} \frac{1}{d_1^2} \frac{1}{\Delta H} \frac{1}{T_o C} \frac{1}{d_i} \dot{d}_i / dt^*
\]

\[
\Rightarrow \frac{dT_i}{dt^*} = 6 \frac{\lambda_g}{C^2 \rho_d d^2 T_o} \frac{1}{d_1^2} \frac{1}{\Delta H} \frac{1}{T_o C} \frac{1}{d_i} \dot{d}_i / dt^*
\]

\[
\Rightarrow \frac{dT_i}{dt^*} = \varepsilon \cdot \left[2 + \frac{\nu_d - 2}{F(B_h)}\right] \ln\left(1 + B_h\right) T_{i_0}^* T_{i_0}^* T_{i_0}^* T_{i_0}^* \frac{1}{d_i^2} - \varphi \frac{1}{d_i} \dot{d}_i / dt^*
\]

\[
\varepsilon = 6 \frac{\lambda_g}{\rho_d d^2 T_o} \Delta H \Delta H \frac{1}{3 \pi C P_{gas} \nu C T_o} \Delta H \frac{1}{3 \pi C T_o}
\]

\[
\varphi = \frac{\Delta H}{T_o C}
\]

Interpretation:

Pr is the Prandtl number. \(\frac{\Delta H}{C T_o}\) is the ratio of the gasous and liquid energy content.
A3 Computer code for conejet electrospray

Line 1 – 34 Definitions
Line 35 – 507 Main programm
Line 36 – 110 Variable definitions and space allocation
Line 112 – 129 Material properties and constants
Line 131 – 147 Input of initial droplet size distribution
Line 149 – 176 Starting values of variables
Line 178 – 595 Iteration over time, Integration of transport and evaporation equations
Line 181 – 197 A droplet that has reached the substrate is erased from the calculation
and reentered at the break up point with the parameter values given here
Line 201 – 231 Initial droplet size, location and velocity of droplet after breakup
Line 239 – 259 Forces of external electric field on droplet
Line 261 – 293 Mutual forces on droplets
Line 300 – 346 Acceleration of droplets
Line 360 – 439 Evaporation and Rayleigh breakup of droplets
Line 441 – 520 Statistical evaluation of droplet size, velocity and concentration
Line 522 – 594 Output of data
Line 599 – 750 Subroutines

1 #include <stdio.h>
#include <stddef.h>
#include <stdlib.h>
#include <string.h>
5 #include <math.h>
#include "NR.H"
#include "NRUTIL.H"

#define NRANSI
10 #define IM1 2147483563
#define IM2 2147483399
#define AM (1.0/IM1)
#define IMM1 (IM1-1)
#define IA1 40014
15 #define IA2 40692
#define IQ1 53668
#define IQ2 52774
#define IR1 12211
#define IR2 3791
20 #define NTAB 32
#define NDIV (1+IMM1/NTAB)
#define EPS 1.2e-7
#define RNMX (1.0-EPS)

25 /***************** Subroutines **** Start **********************/

int dropsize(float *dvert, float *nd, int t);
float ran2(long *idum);
float ran2(long *idum1);
30 float ran2(long *idum2);
35 int main(void) {

/******* Allocation of Vectors and Matrices *** Start ***********/

dr=vector(1,8000);
tempd=vector(1,8000);
ofr=vector(0,200);
d=vector(1,8000);
oz=vector(1,8000); o1=vector(1,8000); o2=vector(1,8000);
uz=vector(1,8000); u1=vector(1,8000); u2=vector(1,8000);
ozz=vector(1,8000); o1z=vector(1,8000); o2z=vector(1,8000);
uzz=vector(1,8000); u1z=vector(1,8000); u2z=vector(1,8000);
fez=vector(1,8000); fer=vector(1,8000);
fe1=vector(1,8000); fe2=vector(1,8000);
fdz=vector(1,8000); fd1=vector(1,8000); fd2=vector(1,8000);
fdz2=vector(1,8000); fd12=vector(1,8000); fd22=vector(1,8000);
fb=vector(1,8000);
duz=vector(1,8000); du1=vector(1,8000); du2=vector(1,8000);
ofz=vector(1,8000); of1=vector(1,8000); of2=vector(1,8000);
d=vector(1,8000);
num=vector(1,8000);
dcol=vector(1,100000);
119

dvert=vector(1,8000);
num=vector(1,8000); num2=vector(1,8000);
ela=vector(1,8000);
nkl=vector(1,8000);
dmz=vector(0,200);
95   dave1g=vector(0,200); dave2g=vector(0,200);
dave3g=vector(0,200);
davc=matrix(0,200,0,200); dav=matrix(0,200,0,200);
dave1=matrix(0,200,0,200); dave2=matrix(0,200,0,200);
dave3=matrix(0,200,0,200); dave4=matrix(0,200,0,200);
100 vavc=matrix(0,200,0,200); vav=matrix(0,200,0,200);
mm=vector(0,200); mmz=vector(0,200); mz=vector(0,200);
vm=vector(0,200);
mtempd=vector(0,200); mtempdz=vector(0,200);
105 vmz=vector(0,200);
fmm=vector(0,200); fmz=vector(0,200);
mzz=vector(0,200);
nd=vector(0,200);
110 /***** Allocation of Vectors and Matrices ***** End *************/

115

120 /***** Material properties and constants ****** Start *************/

pi=3.1415927;

dve=0.00000099;  /*** Diffusioncoefficient ***/
rg=8.31;  /******Gasconstant******/
m=0.06;  /**** molar weight *****/
rog=1.29;  /*** air density *****/
row=780;  /****liquid (solvent) density *****/
125   lam=734000;  /***** latente heat *****/
kd=0.025;     /***** thermal conductivity of air *****/
u=1.5/100000;  /*** viscosity of air ****/
eo=8.854*pow(10,-12); /* dielectric constant */
qo=1.6*pow(10,-19);  /* elementary charge */
130   phio=7025;  /* applied Potential in Volt */
h=0.078; /* Distance between noozle and plate in [m] */
kv=1; /* coefficient for potential equation in GC paper*/
gamm=0.021;  z=0; x=1; rm=1; numb=500;r=0;z=0;d=0;
135 /**** Material properties and constants *** End ***************/

140 /**** Input of droplet size distribution ***** Start *************/

printf("#Bitte geben Sie mir das zu konvertierende File an\n");
scanf("%s",filename);

145 if (NULL!=(infile=fopen(filename,"r"))) {
count=0;
while (((fscanf(infile,"%f",&times))!=EOF)&(count<200)) {
    fscanf(infile,"%f %f",&pe_innen,&pe_out);
    num[count]=times;
    dvert[count]=pe_innen;
    ela[count]=pe_out;
    printf("%f %f %f\n",num[count],dvert[count],ela[count]);
    count++;
}
totalcount=count;
}

150 /**** Input of droplet size distribution **** End ***************/
150 for(x1=0;x1<81;x1=x1+1){
    mm[x1]=0;
    mz[x1]=0;
    vm[x1]=0;
    fmm[x1]=0;
    mzz[x1]=0;
    mtempd[x1]=0;
}

160 for(z1=0;z1<81;z1=z1+1){
    for(r1=0;r1<40;r1=r1+1){
        davc[z1][r1]=0;
        dave1[z1][r1]=0;
        dave2[z1][r1]=1;
        dave3[z1][r1]=0;
        dave4[z1][r1]=0;
        dav[z1][r1]=0;
        vavc[z1][r1]=0;
        vave[z1][r1]=0;
        vav[z1][r1]=0;
    }
}

170 for(z1=0;z1<100;z1=z1+1){nd[z1]=dvert[z1]*1000000;}
for(z1=0;z1<6000;z1=z1+1){tempd[z1]=20;}

175 idum1=5; idum2=9; idum=1;

180 for(t=4;t<50000;t=t+1){
    if(kk>0.1){
        for(xx=0;xx<kk;xx=xx+1){
            gg=nkl[xx];
            minx=numbd-1;
            d[gg]=d[minx];
            mges[gg]=row*pi/6*pow(d[gg],3);
            oz[gg]=oz[minx];
            o1[gg]=o1[minx];
            o2[gg]=o2[minx];
            uz[gg]=uz[minx];
            u1[gg]=u1[minx];
            u2[gg]=u2[minx];
            ela[gg]=ela[minx];
            tempd[gg]=37;
            numbd=numbd-1;
        }
    }
}

190 dt=0.00000267; /** iteration time **/

195 } /********* Starting values of variables ******** Start *************/

200 } /********* Starting values of variables ******** End *************/

205 } /********* Time iteration ******** Start *************/
next=ran2(&idum);
next1=ran2(&idum1);
next2=ran2(&idum2);
minx=numbd;
numbd=numbd+1;
oz[minx]=0.074+(0.00008*next); /* z-location of breakup */
o1[minx]=0.0001*(next1-0.5); /* x-location of breakup */
o2[minx]=0.0001*(next2-0.5); /* y-location of breakup */
if(oz[minx]==0){oz[minx]=0.000001;}
u1[minx]=0.0; /* x-velocity at breakup */
u2[minx]=0.0; /* y-velocity at breakup */
uz[minx]=10.75; /* z-velocity at breakup */
xgreath=dropsize(dvert,nd,t);
d[minx]=num[xgreath]/1000000;
nd[xgreath]=nd[xgreath]+1;
dcol[ttt]=d[minx];
ela[minx]=(-10.297*pow(d[minx]*1000000,3)+
225 +1469.3*pow(d[minx]*1000000,2)
+20942*d[minx]*1000000-28910);
mges[minx]=row*pi/6*pow(d[minx],3);
ttt=ttt+1;
tempd[minx]=37;
}

/******* Initial values of droplet after breakup ** END ****/

/******* Forces acting on droplets*** Start **************/

x=0;kk=0;
for(x=0;x<numbd;x=x+1){
    if(oz[x]<h){

        /************* External Field ***** Start **************/

        z=oz[x]/h;
r=pow(o1[x]*o1[x]+o2[x]*o2[x],0.5)/h;
if(o1[x]==0){o1[x]=o1[x]+0.000001;}
zae=pow(r*r+(1-z)*(1-z),0.5)+(1-z);
245 nen=pow(r*r+(1+z)*(1+z),0.5)+(1+z);
zaez=-pow(r*r+(1-z)*(1-z),-0.5)*(1-z)+1;
nenz=pow(r*r+(1+z)*(1+z),0.5)+(1+z),-2)
    *pow(r*r+(1+z)*(1+z),-0.5)*(1+z)+1);
zaer=pow(r*r+(1-z)*(1-z),-0.5)*r;
nenr=pow(r*r+(1+z)*(1+z),0.5)+(1+z),-2)
    *pow(r*r+(1+z)*(1+z),-0.5)*r;
phiz=kv/5.46*nen/zae*(zaez/nen+zae*nenz);
phir=kv/5.46*nen/zae*(zaer/nen+zae*nenr);

255 fez[x]=phio/h*phiz; /* Feldkraft in z-Richtung **/
fer[x]=phio/h*phir; /* Feldkraft in r-Richtung **/
fe1[x]=fer[x]*o1[x]/r*h; /* Feldkraft in 1-Richtung **/
fe2[x]=fer[x]*o2[x]/r*h; /* Feldkraft in 2-Richtung **/
/******* External Field ***** End **************/

/******* Mutual field ***** Start **************/

f1=1.0*t; ww=1;
if(oz[x]<h-0.01){ww=10;}
f=(f1)/ww; ff=t/ww; f2=f-ff;
if(f2<0.0005){
fdz[x] = 0; fd1[x] = 0; fd2[x] = 0;
fdz2[x] = 0; fd12[x] = 0; fd22[x] = 0;
for(xx = 0; xx < numbD; xx = xx + 1)
{
    if (xx != x)
    {
        rr = pow((oz[x] - oz[xx]) * (oz[x] - oz[xx])
            + (o1[x] - o1[xx]) * (o1[x] - o1[xx])
            + (o2[x] - o2[xx]) * (o2[x] - o2[xx]), 0.5);
        if (rr < 0.01) {
            fdz[x] = fdz[x] + 0.25 / pi / eo * qo * qo
                * ela[xx] * ela[x] / (rr * rr * rr) * (oz[x] - oz[xx]);
            fd1[x] = fd1[x] + 0.25 / pi / eo * qo * qo
                * ela[xx] * ela[x] / (rr * rr * rr) * (o1[x] - o1[xx]);
            fd2[x] = fd2[x] + 0.25 / pi / eo * qo * qo
                * ela[xx] * ela[x] / (rr * rr * rr) * (o2[x] - o2[xx]);
        }
    }
}
/**************** Mutual field ****** End ***********/

/******************** Imageforce **********************/
f[b][x] = 0.25 / pi / eo * qo * qo * ela[x] * ela[x] / (2 * oz[x] * 2 * oz[x]);

/******* Acceleration of droplet *** Start *************/
uges = pow(uz[x] * uz[x] + u1[x] * u1[x] + u2[x] * u2[x], 0.5);
re = uges * d[x] / n u;  /* Reynoldszahl */
rez = uz[x] * d[x] / n u;
re1 = u1[x] * d[x] / n u;
re2 = u2[x] * d[x] / n u;
sc = nu / dve;

cd = 24 / re * (1 + 0.15 * pow(re, 0.687)); /* Widerstandsbeiwert */

if (rez > 0) {cdz = 24 / rez * (1 + 0.15 * pow(rez, 0.687));}
else {cdz = 0;}
if (re1 == 0) {cd1 = 0;}
else {cd1 = fabs(24 / re1 * (1 + 0.15 * pow(fabs(re1), 0.687)))};
if (re2 == 0) {cd2 = 0;}
else {cd2 = fabs(24 / re2 * (1 + 0.15 * pow(fabs(re2), 0.687)))};
if (uz[x] > 0) {nrfz = cdz * pi / 8 * rog * d[x] * d[x] * uz[x] * uz[x];}
else {nrfz = -cdz * pi / 8 * rog * d[x] * d[x] * uz[x] * uz[x];}
if (u1[x] > 0) {nrf1 = cd1 * pi / 8 * rog * d[x] * d[x] * u1[x] * u1[x];}
else {nrf1 = -cd1 * pi / 8 * rog * d[x] * d[x] * u1[x] * u1[x];}
if (u2[x] > 0) {nrf2 = cd2 * pi / 8 * rog * d[x] * d[x] * u2[x] * u2[x];}
else {nrf2 = -cd2 * pi / 8 * rog * d[x] * d[x] * u2[x] * u2[x];}
mp = pi / 6 * d[x] * d[x] * d[x] * row;  /* Masse des Tropfens */

/mp*dt;

\[ du_1[x] = \frac{(fe_1[x] \cdot qo \cdot ela[x] + fd_1[x] \cdot nrf_1)}{mp \cdot dt}; \]
\[ du_2[x] = \frac{(fe_2[x] \cdot qo \cdot ela[x] + fd_2[x] \cdot nrf_2)}{mp \cdot dt}; \]

330

\[ uzh = uz[x] + duz[x]; \]
\[ u1h = u1[x] + du1[x]; \]
\[ u2h = u2[x] + du2[x]; \]

\[ dz = \frac{(uz[x] + uzh)}{2} \cdot dt; \]
\[ d1 = \frac{(u1[x] + u1h)}{2} \cdot dt; \]
\[ d2 = \frac{(u2[x] + u2h)}{2} \cdot dt; \]

335

\[ uzz[x] = uzh; \]
\[ u1z[x] = u1h; \]
\[ u2z[x] = u2h; \]
\[ ozz[x] = oz[x] - dz; \]
\[ o1z[x] = o1[x] + d1; \]
\[ o2z[x] = o2[x] + d2; \]

340

\[ \text{if } (ozz[x] < 0.00001) \{ nkl[kk] = x; kk = kk + 1; \} \]
\[ \text{if } (oz[x] > 0.09) \{ oz[x] = 0.02; \} \]

345

\[ /******** Forces acting on droplets **** END **************/ \]

350

\[ \text{for } (x = 0; x < numb_d; x = x + 1) \{ \]
\[ \quad uz[x] = uzz[x]; \]
\[ \quad u1[x] = u1z[x]; \]
\[ \quad u2[x] = u2z[x]; \]
\[ \quad oz[x] = ozz[x]; \]
\[ \quad o1[x] = o1z[x]; \]
\[ \quad o2[x] = o2z[x]; \]
\[ \} \]

355

\[ /******** Evaporation of droplets ***** Start ***********/ \]

360

\[ \text{for } (x = 0; x < numb_d; x = x + 1) \{ \]
\[ \quad \text{if } (oz[x] < 0.09) \{ \]
\[ \quad \quad \text{if } (oz[x] < 0.003) \{ \text{tempa} = 115 - \frac{(115 - 49) \cdot oz[x]}{0.003}; \}
\[ \quad \quad \text{else} \{ \text{tempa} = 49 - \frac{(49 - 39) \cdot (oz[x] - 0.003)}{0.076}; \} \]
\[ \quad \quad \text{tempref} = \text{tempd}[x] + \frac{(-\text{tempd}[x] + \text{tempa})}{3}; \]
\[ \quad \quad kd = 0.025 / \text{pow}(273, 0.5) * \text{pow}((\text{tempd}[x] + \text{tempa}) / 3 + 273, 0.5); \]
\[ \quad \quad dve = 0.0000099 * \text{pow}((\text{tempa} + \text{tempd}[x]) / 3 + 273, 1.5); \]
\[ \quad \quad \text{temp2} = 1 - \frac{(\text{tempd}[x] + 273)}{508}; \]
\[ \quad \quad pd = \text{exp}(1 / (1 - \text{temp2}) * (-8.16927 * \text{temp2} - 0.09432 * \text{pow}(\text{temp2}, 1.5) \]
\[ \quad \quad \quad - 8.1 * \text{pow}(\text{temp2}, 3) + 7.85 * \text{pow}(\text{temp2}, 6)) \cdot 51.7 * 100000; \]
\[ \quad \quad cde = \frac{m}{rg} / (273 + \text{tempd}[x]) * pd; \]
\[ \quad \quad cu = 0.5 * 15200 * \frac{m}{rg} / (273 + \text{tempa}); \]
\[ \quad \quad cref = cde + (cu - m / rg / (273 + \text{tempa}) * pd) / 3; \]
\[ \quad \quad cgas = 100000 * 28 / 8314 / (\text{tempref} + 273); \]
\[ \quad \quad cet = cde + 0.66666; \]
\[ \quad \quad uges = \text{pow}(uz[x] * uz[x] + u1[x] * u1[x] + u2[x] * u2[x], 0.5); \]
\[ \quad \quad re = uges * d[x] / nu; \]
\[ \quad \} \]
124

\[ sc = \frac{nu}{dve}; \]

\[
cpgas = \left(31.15 - 1.357 \cdot \frac{100}{100000} \cdot \text{tempref} - 1.168 \cdot \text{pow}(10, -8) \cdot \text{pow}(\text{tempref}, 3)\right) / 28 \cdot 1000;
\]

\[
cpet = \left(32.43 + 0.1885 \cdot \text{tempref} + 6.406 / 10000 \cdot \text{tempref} \cdot \text{tempref} - 9.261 \cdot \text{pow}(10, -8) \cdot \text{pow}(\text{tempref}, 3)\right) / 60 \cdot 1000;
\]

\[
cpmix = \frac{cpgas}{cpgas + cpet} \cdot cpgas + \frac{cpet}{cpgas + cpet} \cdot cpet;
\]

\[
cpf = 3016;
\]

\[
cgas = \frac{100000 \cdot 28}{8314} / (\text{tempd}[x] + 273);
\]

\[
yvs = \frac{cdr}{cdr + cgas};
\]

\[
cgas = \frac{100000 \cdot 28}{8314} / (\text{tempa} + 273);
\]

\[
yvu = \frac{cu}{cu + cgas};
\]

\[
\text{bm} = \frac{yvs - yvu}{1 - yvs};
\]

\[
\text{cor} = \frac{\log(1 + \text{bm})}{\text{bm}};
\]

\[
\text{fb1} = \frac{\text{pow}(1 + \text{bm}, 0.7) \cdot \log(1 + \text{bm})}{\text{bm}};
\]

\[
pr = \frac{\text{cpmix} \cdot \text{nu} \cdot 1}{\text{kd}};
\]

\[
\text{sho} = 2 + 0.6 \cdot \text{pow}(\text{re}, 0.5) \cdot \text{pow}(\text{sc}, 0.33);
\]

\[
\text{nuo} = 2 + 0.6 \cdot \text{pow}(\text{re}, 0.5) \cdot \text{pow}(\text{pr}, 0.33);
\]

```plaintext
/*** Rayleigh limit ** Start *****/
```

\[
dr[x] = 2 \cdot \text{pow}(\text{pow(ela[x] + qo/8/\pi, 2) / 0.02/\text{eo}, 0.3333));
\]

\[
\text{if} (\text{dr}[x] > d[x]) {
    \text{mges}[x] = \text{mges}[x] - 0.02 \cdot \text{mges}[x];
    d[x] = \text{pow}(6/\pi \cdot \text{mges}[x] / \text{row}, 0.333333);
    \text{dsec} = \text{pow}(6/\pi \cdot 0.02 \cdot \text{mges}[x] / \text{row}, 0.333333);
    \text{qsec} = 8 \cdot \pi \cdot \text{pow}(\text{gamm} \cdot \text{eo} \cdot \text{dsec} \cdot \text{dsec} \cdot \text{dsec} / 8, 0.5)
    / 1.6 \cdot \text{pow}(10, 19);
    \text{ela}[x] = \text{ela}[x] - \text{qsec};
}
```

```plaintext
/*** Rayleigh limit ** End *****/
```

\[
cgas = \frac{100000 \cdot 28}{8314} / (\text{tempref} + 273);
\]

\[
dm[x] = \pi \cdot dve \cdot d[x] \cdot (\text{cref} + cgas) \cdot (2 + (\text{sho} - 2) / \text{fb1}) \cdot \text{cor} \cdot \text{bm} \cdot \text{dt};
\]

\[
dw = \pi \cdot \text{kd} \cdot d[x] \cdot (\text{tempa} - \text{tempd}[x]) \cdot (2 + (\text{nuo} - 2) / \text{fb1}) \cdot \text{cor} \cdot \text{dt} - \text{lam} \cdot \text{dm}[x];
\]

\[
\text{tempd}[x] = \text{tempd}[x] + \text{dw} / \text{mges}[x] / \text{cpf};
\]

\[
\text{dmh} = \text{dm}[x];
\]

```plaintext
if (d[x] > 0.000001) \{ \text{mges}[x] = \text{mges}[x] - \text{dmh}; \}
```

```plaintext
if (d[x] < 0.000001) \{ \text{nkl}[kk] = x; kk = kk + 1; \}
```

```plaintext
\}
```

```plaintext
/****** Evaporation of droplets *** End ***************************/
```

```plaintext
/****** Statistical evaluation ***** Start ***********/
```

```plaintext
if (t > 15) {
    \text{f1} = 1.0 \cdot \text{t};
    \text{f} = \text{f1} / 10; \quad \text{/** Start an jedem 5ten Zeitschritt */}
    \text{ff} = \text{t} / 10; \quad \text{/** ganze Zahl */}
    \text{f2} = \text{f} - \text{ff};
    \text{if} (\text{f2} < 0.001) \{ \}
```
for (gg=0; gg<numbd; gg=gg+1) {
    i=0;
    for (z1=0; z1<81; z1=z1+1) {
        z11=z1*1.0;
        if (oz[gg]>z11*0.001) {
            if (oz[gg]<(z11*0.001)+0.001) {
                if (t>4) {
                    dmnz[z1]=dmnz[z1]+d[gg]*(dt/(0.001/uz[gg]));
                    cdd1=1000000000000*d[gg]*d[gg]*d[gg];
                    cdd2=1000000000000*d[gg]*d[gg]*d[gg];
                    cdd3=dave1g[z1];
                    cdd4=dave2g[z1];
                    dave1g[z1]=dave1g[z1]+(cdd1/cdd2);
                    dave2g[z1]=dave2g[z1]+(cdd1/cdd2);
                    mm[z1]=mm[z1]+mges[gg]*(dt/(0.001/uz[gg]));
                    mz[z1]=mz[z1]+1*(dt/(0.001/uz[gg]));
                    vm[z1]=vm[z1]+uz[gg]*(dt/(0.001/uz[gg]));
                    fmm[z1]=fmm[z1]-fez[gg]*qo*ela[gg]
                        -fdz[gg]+fdz2[gg]+fb[gg];
                    mtempd[z1]=mtempd[z1]+tempd[gg];
                }
                for (r1=0; r1<40; r1=r1+1) {
                    r11=r1*1.0;
                    r=pow(o1[gg]*o1[gg]+o2[gg]*o2[gg], 0.5);
                    if (r>r11*0.001) {
                        if (r<(r11*0.001)+0.001) {
                            davc[z1][r1]=davc[z1][r1]+1;
                            cdd1=1000000000000*d[gg]*d[gg]*d[gg];
                            cdd2=1000000000000*d[gg]*d[gg]*d[gg];
                            dave1[z1][r1]=dave1[z1][r1]+(cdd1/cdd2);
                            dave2[z1][r1]=dave2[z1][r1]+(cdd1/cdd2);
                            dave4[z1][r1]=dave4[z1][r1]+(cdd1/cdd2);
                            dav[z1][r1]=dav[z1][r1]+(cdd1/cdd2);
                            vava[z1][r1]=vava[z1][r1]+1;
                            vvv1=uz[gg];
                            vvv2=vave[z1][r1];
                            vave[z1][r1]=vvv2+vvv1;
                            dana[z1][r1]=dana[z1][r1]+(cdd1/cdd2);
                        }
                    }
                }
            }
        }
    }
}
for (z1=0; z1<81; z1=z1+1) {
    if (mz[z1]>0) {
        ddz[z1]=dmnz[z1]/mz[z1];
        mmz[z1]=mm[z1]/mz[z1];
    }
}
vmz[z1]=vm[z1]/mz[z1];
fmz[z1]=fmm[z1]/mz[z1];
mtempdz[z1]=mtempd[z1]/mz[z1];
dave3g[z1]=dave1g[z1]/dave2g[z1];
}
}

for(z1=0;z1<81;z1=z1+1)
    for(r1=0;r1<40;r1=r1+1)
        dave3[z1][r1]=dave1[z1][r1]/dave2[z1][r1];

**** Statistical evaluation ******** End ************/

/******* Output to files ******** Start ***************/

f1=1.0*t;
f=(f1)/1000;
ff=t/1000;
f2=f-ff;
if(f2<0.001)
    outfile=fopen("drergebnis_200","w");
    for(x=0;x<numbd;x=x+1)
        fprintf(outfile,%d %f %f %.12f %.12f %.12f %.12f %f %f %f %f %f %f %f %f %f %f %f %f %.12f %x,nd[x],ela[x],d[x],oz[x],o1[x],o2[x],uz[x],u1[x],u2[x],fdz[x],fd1[x],fd2[x],fez[x],fe1[x],fe2[x]);
    fclose(outfile);

outfile=fopen("impuls_200","w");
for(x1=0;x1<81;x1=x1+1)
    fprintf(outfile,"%.10f %.10f %.15f %.10f %.10f %.15f %.15f %.15f ",dave3g[x1],ddz[x1],mmz[x1],vmz[x1],fmz[x1],mz[x1],mm[x1],fmm[x1],mzz[x1]);
    fprintf(outfile,\n"");
    fclose(outfile);

outfile=fopen("drergebnis3_200","w");
    for(x1=0;x1<5000;x1=x1+1)
        fprintf(outfile,"%.20f
 ",dcol[x1]);
    fclose(outfile);

outfile=fopen("drergebnis4_200","w");
    for(x1=0;x1<81;x1=x1+1)
        for(x2=0;x2<40;x2=x2+1)
            fprintf(outfile,"%.20f ",dav[x1][x2]);
    fprintf(outfile,\n"");
    fclose(outfile);

outfile=fopen("drergebnis4_2_200","w");
    for(x1=0;x1<81;x1=x1+1)
        for(x2=0;x2<40;x2=x2+1)
            fprintf(outfile,"%.20f ",dav[x1][x2]);
    }
fprintf(outfile,"\n");
} fclose(outfile);

outfile=fopen("drergebnis5_200","w");
for(x1=0;x1<81;x1=x1+1){
 for(x2=0;x2<40;x2=x2+1){
     fprintf(outfile,"%.20f ",davc[x1][x2]);
 } fprintf(outfile,"\n");
} fclose(outfile);

outfile=fopen("drergebnis6_200","w");
for(x1=0;x1<81;x1=x1+1){
 for(x2=0;x2<40;x2=x2+1){
     fprintf(outfile,"%.20f ",vav[x1][x2]);
 } fprintf(outfile,"\n");
} fclose(outfile);

/******* Output to files ********** End *************/

****** Time iteration ************** End *************/

/******* Main programm ************** End *************/

/******* Subroutines ************** Start *************/

#if defined(__STDC__) || defined(ANSI) || defined(NRANSI) /*ANSI*/
#define NR_END 1
#define FREE_ARG char*

float ran2(long *idum){
    int j;
    long k;
    static long idum2=123456789;
    static long iy=0;
    static long iv[NTAB];
    float temp;
    if (*idum <= 0) {
        if (-(*idum) < 1) *idum=1;
        else *idum = -(*idum);
        idum2=(*idum);
        for (j=NTAB+7;j>=0;j--) {
            k=(*idum)/IQ1;
            *idum=IA1*(idum-k*IQ1)-k*IR1;
            if (*idum < 0) *idum += IM1;
            if (j < NTAB) iv[j] = *idum;
        }
        iy=iv[0];
    }
    k=(*idum)/IQ1;
    *idum=IA1*(idum-k*IQ1)-k*IR1;
    if (*idum < 0) *idum += IM1;
    idum2=(*idum)/IQ2;
    idum2=IA2*(idum2-k*IQ2)-k*IR2;
if (idum2 < 0) idum2 += IM2;
  j=i/NDIV;
  iy=iv[j]-idum2;
  iv[j] = *idum;
  if (iy < 1) iy += IMM1;
if ((temp=AM*iy) > RNMX) return RNMX;
else return temp;
}

int dropsize(float dvert[], float nd[], int t){
  int x,xgreat;
  float great,*dvert1,nextaux1,t1;
  unsigned long int nextaux=1;
  dvert1=vector(1,5000);
  t1=t/2+1;
  for (x=0;x<99;x=x+1){
    dvert1[x]=fabs(((nd[x]+1)/dvert[x]));
  }
  great=dvert1[0];
  xgreat=0;
  for (x=0;x<99;x=x+1){
    if (dvert1[x]<great){
      great=dvert1[x];
      xgreat=x;
    }
  }
  return xgreat;
}

void nrerror(char error_text[])
/* Numerical Recipes standard error handler */
{
  fprintf(stderr,"Numerical Recipes run-time error...\n");
  fprintf(stderr,"%s\n",error_text);
  fprintf(stderr,...now exiting to system...\n");
  exit(1);
}

float *vector(long nl, long nh)
/* allocate a float vector with subscript range v[nl..nh] */
{
  float *v;
  v=(float *)malloc((size_t) ((nh-nl+1+NR_END)*sizeof(float)));
  if (!v) nrerror("allocation failure in vector()");
  return v-nl+NR_END;
}

int *ivector(long nl, long nh)
/* allocate an int vector with subscript range v[nl..nh] */
{
  int *v;
  v=(int *)malloc((size_t) ((nh-nl+1+NR_END)*sizeof(int)));
  if (!v) nrerror("allocation failure in ivector()");
  return v-nl+NR_END;
}
float **matrix(long nrl, long nrh, long ncl, long nch)  
680 /* allocate a float matrix with subscript range  
m[nrl..nrh][ncl..nch] */  
    {  
        long i, nrow=nrh-nrl+1, ncol=nch-ncl+1;  
        float **m;  
685     /* allocate pointers to rows */  
        m=(float **) malloc((size_t)((nrow+NR_END)*sizeof(float*)));  
        if (!m) nrerror("allocation failure 1 in matrix()");  
        m += NR_END;  
690     m -= nrl;  
700     /* allocate rows and set pointers to them */  
        m[nrl]=(float *) malloc((size_t)((nrow*ncol+NR_END)*sizeof(float)));  
        if (!m[nrl]) nrerror("allocation failure 2 in matrix()");  
        m[nrl] += NR_END;  
495     m[nrl] -= ncl;  
700     for(i=nrl+1;i<=nrh;i++) m[i]=m[i-1]+ncol;  
705     /* return pointer to array of pointers to rows */  
    return m;  
}  

void free_vector(float *v, long nl, long nh)  
/* free a float vector allocated with vector() */  
705     {  
710         free((FREE_ARG) (v+nl-NR_END));  
}  

void free_ivector(int *v, long nl, long nh)  
/* free an int vector allocated with ivector() */  
715     {  
720         free((FREE_ARG) (v+nl-NR_END));  
}  

void free_matrix(float **m, long nrl, long nrh, long ncl, long  
nch)  
720     /* free a float matrix allocated by matrix() */  
725     {  
730         free((FREE_ARG) (m[nrl]+ncl-NR_END));  
735         free((FREE_ARG) (m+nl-NR_END));  
}  

#define IM1  
#define IM2  
#define AM  
#define IMM1  
730 #define IA1  
#define IA2  
#define IQ1  
#define IQ2  
#define IR1  
735 #define IR2  
#define NTAB  
#define NDIV  
#define EPS
Line 1 – 7 Include library functions
Line 9 – 23 Definition of variables necessary for subroutines
Line 25 – 30 Definition of Subroutines (Explanation of subroutines see below after main program)
Line 35 Start of main program
Line 39 – 67 Definition of main program variables
Line 70 – 110 Allocation of storage space for vectors and matrices
Line 112 – 129 Definition of constants
Line 131 – 147 Input of initial (discrete) droplet size distribution.
num[count] - mean droplet size of a section, dvert[count] - number fraction of this size section, ela[count] is not used here, totalcount - total number of size sections.
Line 149 – 176 Starting values of time dependent variables.
In order to calculate the average values of droplet mass, droplet velocity and so on, the values are summed in each slice x1 representing a cross-section of the spray. The spray is divided in 80 slices along the spray axis.
mm[x1] - sum of droplet mass in slice z1, mz[x1] – number of droplets, vm[x1] - sum of droplet velocities, fmm[x1] – sum of electrical forces on droplets (external and mutual electric force), mtempd[x1] – sum of droplet temperatures, mzz[x1] – not used here.
A more detailed statistic over the radius is derived as well. The step size of z1 (axial direction) is 1mm. The step size of r1 (radial direction) is 1mm.
nd – dvert * 1000000 (dvert is the number fraction), tempd - initial value of droplet temperature.
Line 178 Start of time iteration
Line 182 – 197 Each droplet has a number. If a droplet reaches the substrate it has to “disappear”. Its number is given to a droplet that is just produced at the nozzle. The new droplet size (d[gg]), velocity (uz[gg] – droplet axial z-velocity, u1 – velocity in x-direction, u2 – velocity in y-direction), charge (ela[gg]) and temperature (tempd[gg]) values have to be “switched” to that number.
Line 199 The iteration time dt.
Line 201 – 231 Initial values of a droplet after breakup. The parameter g2 guarantees that each second time step a droplet is released. The x, y, and z-location of the droplet breakup is chosen as a fixed distance from the substrate +/- a randomized value. The initial velocity in x and y-direction are zero. The axial velocity is calculated from the Rayleigh jet breakup laws (see chapter 2). The charge of a droplet ela is calculated from its size. The procedure how the number of charges per time (which is the electric current) are distributed over the droplet size distribution is described in chapter 2 and 3. The initial temperature tempd is
defined as well. All variables (size, velocity, ...) are attributed to a single droplet until it hits the surface. The values are obviously not constant, they change over time.

Line 233 – 349 Calculation of the total force on one droplet and the resulting acceleration. This procedure is repeated for every droplet $x$. The total number of droplets at the given time instant is $numbd$.

Line 241 – 259 Calculation of the external field on a single droplet. $z$ and $r$ are the dimensionless cylindrical coordinates of the droplet. They are needed to calculate the electrical potential acting on the droplet at its given location. $Phiz$ is the dimensionless external electric force in $z$-direction, $phir$ is the dimensionless form of the force in radial direction. The formula for the external electric potential is given in chapter 2. $fez$ and $fer$ are the dimensional forms of the forces. $fe1$ and $fe2$ are the forces in $x$ and $y$ direction. $h$ is the distance between nozzle exit and substrate.

Line 261 – 294 Calculation of the mutual droplet and mirror force on a single droplet. The forces of the other droplet acting on a certain droplet in $x$, $y$, and $z$-direction are $fd1$, $fd2$ and $fdz$. They are calculated from the droplet-droplet distance $rr$ and the charges $ela$ of the droplets. The same is done for the mirror charges of the droplets. The forces here are called in $x,y$, and $z$-direction: $fdz12$, $fd22$, and $fdz2$.

Line 296 – 300 The image force of the droplet itself is calculated.

Line 300 – 348 The acceleration and the movement of the droplets in time $dt$. The total velocity of a droplet is $uges$. $Re$, $rez$, $re1$, and $re2$ are the total Reynolds number, the Reynolds number in $z$, $x$, and $y$-direction. $sc$ is the Schmitt number. $Cd$ is the total drag. $cd1$, $cd2$, and $cdz$ are the drag in $x$, $y$, and $z$-direction. $nrfz$, $nrf1$, and $nrf2$ are the air forces acting on the droplet in $x$, $y$, and $z$-direction. $mp$ is the droplet mass. $Row$ is the liquid density. $du1$, $du2$ and $duz$ are the velocity increase of the droplet due to the external electric force, the mutual force and the image forces during time $dt$. $d1$, $d2$ and $dz$ are the space steps the droplets made during the time $dt$. In Line 345 it is tested if the droplet has hit the substrate. If yes it is removed in the next time step and reinserted again at the breakup location.

Line 351 – 358 The new droplet velocities and locations are moved from the interim variable to the actual variable. It was necessary to store these values in intermediate variables until the new values are calculated for each droplet.

Line 360 – 439 The droplet evaporation is calculated. Analog to the droplet transport one droplet after the other is calculated.

Line 365 – 366 Definition of the background air temperature $tempa$ at the droplet location.

Line 368 Definition of the reference air temperature $tempref$ as described in chapter 2. This temperature is a kind of a mean value between the background air temperature and the temperature on the droplet surface $tempd$.

Line 370 Temperature dependent heat conductivity of air $kd$ (calculated at reference temperature).

Line 370 – 371 Diffusion coefficient of isopropanol in air calculated at reference temperature.

Line 374 – 376 Isopropanol vapor pressure $pd$ at droplet surface.
Line 377  Isopropanol mass concentration cdr at droplet surface.
Line 378  Isopropanol background mass concentration cu.
Line 379  Isopropanol reference mass concentration cref in the film.
Line 380  Air mass concentration cgas at the droplet surface.
Line 381  Isopropanol reference mass concentration in the film.
Line 383  Absolute droplet velocity uges.
Line 384  Reynolds number for the droplet Re.
Line 385  Schmitt number Sc.
Line 387  Heat capacity of Isopropanol gas.
Line 390  Heat capacity of air.
Line 393  Mixed gas heat capacity cpmix.
Line 394  Heat capacity of fluid.
Line 397  Relative isopropanol mass fraction yvs at droplet surface.
Line 399  Relative isopropanol background mass fraction yvu.
Line 401  Mass transfer number bm.
Line 403  Correction factor fb1.
Line 405  Prandtl number pr.
Line 411  Calculation of Rayleigh diameter dr.
Line 412  – 419 If the actual droplet diameter d[x] is bigger than dr the mass and charge of the secondary droplet and the mass and charge loss of the mother droplet is calculated according to the Davis and Bridges (1994).
Line 423  Mass loss dm of droplet during time step dt. The equation follows the theory of Abramzon and Sirignano and is also described in Chapter 2 of this thesis.
Line 424  Heat energy loss (or gain) dw during time step dt. As well described in Chapter 2.
Line 426  Calculation of droplet temperature tempd[x] change from the heat energy flow calculated in Line 424.
Line 429  If the droplet is bigger than 1 \( \mu \text{m} \) the mass reduction is calculated.
Line 430  If the droplet shrinks below 1 \( \mu \text{m} \) diameter the droplet is taken out of the spray. This border had to be included for technical reasons.
Line 436  – 515 Statistical evaluation of the data.
Line 439  – 443 The evaluation is done every 10th time step.
Line 444  The evaluation is done for every droplet (numbd is number of droplets in spray).
Line 446  – 449 The droplet axial z-location of droplet [gg] is searched.
Line 451  The droplet total size dmz[z1] at position [z1] is calculated (just summing all droplets that are found at that z-location). The droplet size is weighed by (dt/\ldots) with the ratio of time step dt over total expected time of droplet flight through the slice (0.001/uz[gg]), so each droplet is counted only once in the slice z1 and not twice, three times … for slow droplets (which would give them a higher weight).
Line 460  Same as in Line 451, here for the droplet mass mm.
Line 461  Same as before. Here the droplets are counted mz with the weight.
Line 462  Same as before. Here for the velocity.
Line 463  Same as before. Here for electric forces acting on the droplet. But this is
done without weighing here!
Line 465  Same as before. Here for droplet temperature tempd. Again without
weighing.
Line 467 – 470 The droplet radial location is searched. The statistical parameters
evaluated now are taken for a specific location in the spray and not only an
average over the cross-section.
Line 472  Count of droplets davc.
Line 480  Average count diameter dav.
Line 489  Average droplet velocity vav.
Line 501  Average count diameter in a spray cross-section.
Line 502  Average mass in a spray cross-section
Line 503  Average velocity in a spray cross-section.
Line 504  Average electric force in a spray cross-section.
Line 505  Average droplet temperature in a spray cross-section.
Line 506  Diameter of average mass in a spray cross-section.
Line 512  Diameter of average mass at location [z1,r1].
Line 517 – 583 Output of results.
Line 525 – 531 Parameters of each single droplet when the code stops (location,
velocity, …)
Line 534 – 540 Output of mean values (across cross-section): Droplet diameter, velocity,
forces, …
Line 548 – 554 Output of averaged diameters in the given grid.
Line 575 – 582 Output of averaged velocities in the given grid.
Line 690 – 740 Subroutines necessary for matrix definition, …
A4 Computer code for identifying the conditions of precipitation in chapter 4 (Figure 7)

Line 1 – 23   Definitions
Line 25 – 268 Main programm
Line 27 – 55 Variable definitions and space allocation
Line 57 – 78 Material properties and constants
Line 80 – 94 Routine to calculate the droplet diameter which is bigger than 80 % of the droplets (by number)
Line 97 – 266 Routine to calculate the evaporation of the droplet with the above found diameter and identify the temperature and initial precursor concentration conditions for precipitation.

```c
#include <stdio.h>
#include <stddef.h>
#include <stdlib.h>
#include <string.h>
#include <math.h>
#include "NR.H"
#include "NRUTIL.H"
#define NRANSI
#define IM1 2147483563
#define IM2 2147483399
#define AM (1.0/IM1)
#define IMM1 (IM1-1)
#define IA1 40014
#define IA2 40692
#define IQ1 53668
#define IQ2 52774
#define IR1 12211
#define IR2 3791
#define NTAB 32
#define NDIV (1+IMM1/NTAB)
#define EPS 1.2e-7
#define RNMX (1.0-EPS)

int main(void) {

    /*************** definition of variables ***************
    FILE *infile,*outfile;
    long data2pow,i,j,k,x,s;
    float *nkl,xx;
    double dd,zzz;
    float *rm1,tu2,pd,pu,cdr,diff,tempd2,lam,kd,tempdt,*cu1,
          *cdr1,net,rm,ds;
    float sc,cd,re,*dtt,*zzz,tempa,nu,m,rog,row,dp,dx,
         dt,h,pi,hl,d,rg;
    char filename[80];
    float oz,uz,t;
    float omega,z,r,uges,nrfz,nrf1,nrf2,mp,dz,d1,d2,eo,qo,tt,tt1,
         ela,el1,uzh,uhl,u2h,fdz1,rr;
    float gamma,dminz,dmin1,dmin2,diffz,diff1,diff2,dmh,min;
    int gh,ii,x1,x2,x3,minz,min1,min2,minx,numbd,ttt,count,
```
totalcount, xgreat, xgreath;
float *ofz, *of1, *of2, cf[41][41][41][41],
        dm, mges, *dcol, numbdc;
45 float xx, dmo, dml, dmv, dghi, dve, td2, nex1, nex2, pe_innen,
        pe_out, times, *num, *dvert, z11;
float tempref, cgas, cet, cgas, cpmix, cpf, yvs, bm, cor,
        fb1, pr, sho, nuo, dw, cp, tempd, cref;
float dve2, pd2, cdr2, cref2, cpet2, cpmix2, cpf2, yvs2, bm2, bm3,
        cor2, pr2, nuo2, dm2, dw2, dghi2;
50 float mges2, lam2, m2, cet2, cgas2, mges1, verh1, row2, temps;
float sg1, sg2, dg, prop, prop1, prop2, dpm[20][20], tempsm[20][20],
        conc1, massexit, concprep, tempaux, flag;
float fb11, fb12, fb13, sho1, sho2, sc1, sc2, dr, dsec, qsec, gamm;
55 int sg, conc;

/******************************* material properties **********/
pi=3.1415927;
rg=8.31;  //***** gas constant*****
60 m=0.046;  //**** molar weight *****
    m2=0.162;
roq=1.29;  //** density of air *****
row=952;  //****density ethanol*****
row2=997; //****density butylcarbitol *****
65 lam=920000;  ////////// latent heat ethanol*****
    lam2=2515000;  ////////// latent heat butylcarbitol *****
kd=0.025;  ////////// heat conducitvity of air *****
    eo=8.854*pow(10,-12);
60 gamm=0.021;
qo=1.6*pow(10,-19);
z=0;
x=1;
70 rm=1;
r=0;
z=0;
dz=0;
80 for(x=5; x<6; x=x+1){
    dq=x;
    for(sg=2; sg<3; sg=sg+1){
        sg2=sg;
45        sg1=sg2/2+0.5;
        if(sg==1){sg1=1.01;}
        prop2=0;
        dp=0.2;
        for(dp=0.2; dp<50000; dp=dp+0.1){
            prop1=1/(2.5*log(sg1)*dp)*exp(-(pow(log(dp)-
70            log(dq),2))/(2*pow(log(sg1),2)));
            prop2=prop2+prop1*0.1;
        }
        prop=0;
        dp=0.2;
        while(prop<0.8){
            dp=dp+0.1;
30          prop1=1/(2.5*log(sg1)*dp)*exp(-(pow(log(dp)-
            log(dq),2))/(2*pow(log(sg1),2)));
            prop=prop+prop1*0.1/prop2;
        }
    }
}
pm[x][sg]=dp;
printf(" %d %f %f \n",sg,sg1,dpm[x][sg]);
}
}

outfile=fopen("drergebnis_200","w");
for(x=5;x<6;x=x+1){
        for(sg=2;sg<3;sg=sg+1){
                for(conc=0;conc<1;conc=conc+1){
                        for(temps=40;temps<600;temps=temps+1){
                                flag=0;
                                conc1=0.001*pow(2,conc);
                                if(conc==7){conc1=0.1;}
                                tt=0;
                                xx=dpm[x][sg];
                                d=xx/1000000;
                                ela=457.28*pow(dpm[x][sg],2)+23041*dpm[x][sg]
                                        +567.26;
                                mges=row*pi/6*pow(d,3); concprep=1;
                                while(concprep>conc1*(massexit/mges)){
                                        temps=temps+2;
                                        xx=dpm[x][sg];
                                        d=xx/1000000;
                                        mges=row*pi/6*pow(d,3);
                                        mges1=mges*0.1/1949;
                                        mges2=mges*1949/1949;
                                        dm=0;
                                        dm2=0;
                                        tempd=25;
                                        ds=0.0001;
                                        oz=0.06;
                                        while(oz>0.0){
                                                if(mges1/dm<100){if(mges1>mges/1000)
                                                        {ds=ds*0.1;}}
                                                if(mges2/dm2<100){ds=ds*0.1;}
                                                if(ds<0.00000001){ds=0.00000001;}
                                        }
                                        oz=oz-ds;
                                }
                                uz=1.62;
                                if(oz>0.004){uz=(2.03-1.62)*(oz-0.004)/(0.006-
                                        0.004)+1.62;}
                                if(oz>0.006){uz=(2.04-2.03)*(oz-0.006)/(0.008-
                                        0.006)+2.03;}
                                if(oz>0.008){uz=(2.32-2.04)*(oz-0.008)/(0.01-
                                        0.008)+2.04;}
                                if(oz>0.01){uz=(2.57-2.32)*(oz-0.01)/(0.03-
                                        0.01)+2.32;}
                                if(oz>0.03){uz=(3.85-2.57)*(oz-0.03)/(0.05-
                                        0.03)+2.57;}
                                if(oz>0.05){uz=(5-3.85)*(oz-0.05)/(0.06-
                                        0.05)+3.85;}
                                dt=ds/uz;
                                tt=tt+dt;
                                tempa=temps*(0.2-((oz-
if(os<0.014){tempa=temps*(1-(os/0.014)*0.8);}
if(tempa<20){tempa=20;}

/*** reference temperature ***/
tempref=tempp+(-tempp+tempa)/3;

/*** heat conductivity of air ***/
k_d=0.025/pow(273,0.5)*pow(tempref+273,0.5);

/*** diffusion coefficient of solvent in air ***/
dve=0.0000102*pow(tempref+273,1.5)/pow(273,1.5);
dve2=0.00000134*pow(tempref+273,1.5)/pow(273,1.5);

/*** vapor pressure and concentration on droplet surface ***/
t_d2=1-(tempd+273)/513.9;

if(tempd<66.8){pd2=(100-10)*(tempd-37)/(66.8-37)+10;}
if(tempd<37){pd2=(10-1)*(tempd-14)/(37-14)+1;}
if(tempd<14){pd2=1;}

cdr2=m2/rg/(273+tempd)*pd2*mges2/mges;
cref2=cdr2-cdr2/3;

/*** heat capacity of gas and liquid ***/
c_gas=100000*28/8314/(tempref+273);
cpgas=(31.15-1.357/100*tempref+2.68/100000*
tempref-tempref-1.168*pow(10,8)*
pow(tempref,3))/28*1000;
cf=2441.3;
cf2=1732.43;

/*** Vereinfachungen für Diffgleichungen ***/
c_gas=100000*28/8314/(tempref+273);
yvs=cdr/(cdr+c_gas);
yvs2=cdr2/(cdr2+c_gas);

bm=yvs/(1-yvs);
bm2=yvs2/(1-yvs2);
cor=log(1+bm)/bm;
cor2=log(1+bm2)/bm2;

fb11=pow(1+bm,0.7)*log(1+bm)/bm;
f_b12=pow(1+bm2,0.7)*log(1+bm2)/bm2;
\[ fb_{13} = \frac{fb_{11} + fb_{12}}{2}; \]
\[ re = uz*d/nu; \]
\[ pr = cpgas*nu*1/kd; \]
\[ sc1 = nu/dve; \]
\[ sc2 = nu/dve2; \]
\[ sho1 = 2 + 0.6 * pow(re, 0.5) * pow(sc1, 0.33); \]
\[ sho2 = 2 + 0.6 * pow(re, 0.5) * pow(sc2, 0.33); \]
\[ nuo = 2 + 0.6 * pow(re, 0.5) * pow(pr, 0.33); \]

```c
/*** Diffgleichungen für Massen- und Wärmetransport ***/

dr = 2 * pow(pow(ela * qo / 8 / pi, 2) / 0.02 / eo, 0.3333);
    if (dr > d) {
        mges = mges - 0.02 * mges;
        mges1 = mges1 - 0.02 * mges1;
        mges2 = mges2 - 0.02 * mges2;
        d = pow(6 / pi * mges / row, 0.33333);
        dsec = pow(6 / pi * 0.02 * mges / row, 0.33333);
        qsec = 8 * pi * pow(gamm * eo * dsec * dsec * dsec
            / 8, 0.5) / 1.6 * pow(10, 19);
        ela = ela - qsec;
    }
cgas = 100000 * 28 / 8314 / (tempref + 273);
    verh1 = mges1 / mges;
    if (verh1 > 0.00000001) {
        dm = pi * dve * d * (cref + cgas) * (2 + (sho1 - 2) / fb11) * cor * bm * dt;
    } else if (mges1 <= pow(10, -18)) {
        dm = 0;
    } else {
        dm = 0;
    }
dm2 = pi * dve2 * d * (cref2 + cgas) * (2 + (sho2 - 2) / fb12) * cor2 * bm2 * dt;
dw = pi * kd * d * (tempa - tempd) * (2 + (nuo2) / fb13)
        * (mges1 / mges * cor + mges2 / mges * cor2) *
        dt - lam * dm - lam2 * dm2;
    if (fabs(tempa - tempd) < 1) {dw = 0.1 * dw;}
    tempd = tempd + dw / mges / cpf2;
    dnm = dm;
    dnh2 = dm2;
    concprep = (mges1 / mges) * (0.0045 * tempd + 0.169)
        + (mges2 / mges) * (0.0067 * tempd + 0.0254);
    if (mges1 > pow(10, -18)) {mges1 = mges1 - dnh1;
        mges2 = mges2 - dnh2;
    }
d = pow(6 / pi * mges / row, 0.33333);
    massexit = row * pi / 6 * pow(dpm[x][sg] / 1000000, 3);
    if (concprep < conc1 * (massexit / mges)) {oz = 0.0;
        if (oz < 0.000) {oz = 0; flag = 1;}
    }
    printf("%d %f %f %f \n", x, dpm[x][sg], temps, conc1);
    fprintf(outfile, "%d %d %f %f %f %f %f \n",
        x, sg, dpm[x][sg], temps, conc1, concprep, conc1 * (massexit / mges));
}
}
```
Line 80 – 94  Here the droplet diameter which is larger than 80 % of the doplets in a log-normal distribution is calculated. “x” is the mean diameter of the distribution and “sg” the geometric standard deviation. The way to find the 80 % - value is done by integrating the distribution and stopping at 80 %. This calculation can be done for different mean diameters and standard deviations as indicated by the loop.

Line 97 – 100  The identification of the precipitation conditions for a given distribution are done by iterating the temperature (Line 100).

Line 102  The initial precursor concentration is given here (“conc1”)

Line 107  The amount of charges per droplet.

Line 115 – 116  The ratio of Ethanol (mges1) versus Butylcarbitol (mges2).

Line 121  Initial location of droplet “oz”.

Line 131 – 146  Measured droplet velocities.

Line 149  Measured air temperature.

Line 155 – 251  Evaporation routine analogous to A3. Here the calculation is performed for two components (Butylcarbitol and Ethanol).

Line 245  Precipitation ratio of precursor “concprep” at given droplet temperature “tempd”.
Curriculum vitae

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10/1999 – 4/2004  Research and Teaching Associate, Particle Technology Laboratory, Department of Mechanical and Process Engineering, Swiss Federal Institute of Technology (ETH Zurich), Switzerland.
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10/1990 – 5/1997  Studies of Physics at the University of Tübingen, Germany.
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Refereed articles:


