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# Thin Film Deposition by Spray Pyrolysis and the Application in Solid Oxide Fuel Cells

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This thesis is dedicated to my parents <u>Aldona</u> (1952-2003) and Bolius Perednis

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# Summary

Solid oxide fuel cell (SOFC) technology offers efficient power generation with low emission of pollutants because it converts chemical energy directly to electrical energy. However, cost reduction remains the main objective of SOFC development. State of the art high temperature SOFC is based on thick (about 150  $\mu$ m) zirconia electrolyte. Operating temperatures of 900-1000°C are required due to the low specific ionic conductivity of zirconia electrolyte and in order to avoid carbon deposition on the anodes when incomplete reformed fuel is used. This might lead to the interfacial solid state reactions of cell components, and place large demands on the expensive materials chosen as interconnectors (Cr5Fe1Y<sub>2</sub>O<sub>3</sub>). Therefore, reduction of the operating temperature to 700-800°C is strongly desirable in order to reduce system costs and to enhance reliability. Thin film zirconia-based electrolytes contribute to minimizing ohmic losses and therefore to achieving the set goal.

Aim of this study was the development of an inexpensive manufacturing process for thin film oxides suitable as electrolytes for SOFC. The spray pyrolysis method was chosen for deposition of the electrolyte onto porous anode substrates. This is an inexpensive form of coating technology with the potential to produce thin (0.1 to 10  $\mu$ m) and gas tight ceramic films.

In chapter 2 a brief overview of spray pyrolysis is presented with respect to the working principle of this technique and its application to depositing various thin films. In chapter 3 the most important spray pyrolysis parameters are studied. A film growth model is proposed in chapter 4. Chapter 5 focuses on the influence of thermal treatment on the microstructure of the deposited film. Finally, in chapter 6, the application of spray pyrolysis to deposition of thin electrolyte films for SOFC is demonstrated and their performance is reported.

A comparison of two spray pyrolysis techniques, Electrostatic Spray Deposition (ESD) and Pressurized Spray Deposition (PSD), is presented in the chapter 3. For both techniques, the substrate surface temperature is the main parameter that determines the film morphology. Using ESD, the surface morphology is strongly influenced by the composition of the precursor solution and deposition time. When the PSD technique is used for film deposition, the influence of these parameters on film morphology is not pronounced.

Further insight in to the working principle of the spray pyrolysis method is given in chapter 4. Droplet transport and evaporization is investigated using a phase doppler

anemometer. Droplets smaller than 10  $\mu$ m dominated the number distributions and in contrast, the volume distributions were dominated by the droplets larger than 10  $\mu$ m. Significant droplet evaporation is observed at a distance of 1 cm from the substrate. A possible growth mechanism is proposed where the substrate surface temperature and the large droplets (> 10  $\mu$ m) determine the deposition process. Generally, this temperature should be higher than the decomposition temperature of the precursor. Too low deposition temperatures lead to cracks in the films. When the temperature is too high, rough films with particles on the surface are deposited or powder can be produced. In contrast to most authors, the proposed film growth model does not involve a CVD process.

Chapter 5 reports the structural analysis of the films deposited by the spray pyrolysis technique. The influence of thermal treatment on the film microstructure is investigated. Films with a mean grain size of 12 nm have been obtained at an annealing temperature of 700°C. No crack formation is observed during thermal treatment up to 800°C. It was calculated that at 700°C the ohmic losses caused by electrolyte are sufficiently low when the film thickness does not exceed 5.5  $\mu$ m. From the above results it can be concluded that the spray deposited 8 mol% yttria-stabilized-zirconia (YSZ) films would sustain the SOFC operating temperature of up to 800°C.

The application of the spray pyrolysis technique in SOFC technology was demonstrated in chapter 6. Spray pyrolysis allows thin electrolytes to be prepared with low ohmic losses and thereby allows the operating temperature of solid oxide fuel cells to be reduced while maintaining high power output. The bi-layer electrolyte films consisted of a layer of YSZ and a buffer layer of ceria 10 mol% yttria solid solution (CYO). The electrolyte bi-layer was deposited onto porous NiO-YSZ self-supporting anode substrates. The cells were operated using hydrogen as fuel and air as oxidant at temperatures ranging from 600°C to 800°C and exhibited an open circuit voltage of 1.01 V at 720°C indicating a dense and crack-free electrolyte film. A high power density of more than 750 mW/cm<sup>2</sup> was generated by cells with 600 nm thin YSZ/CYO bi-layer electrolyte at 770°C. Cells containing the bi-layer electrolytes were operated for over 450 hours at 720°C with tolerable degradation. Surprisingly, pores with sizes of up to 3  $\mu$ m could be coated by a 500 nm thin electrolyte film

Summarizing, it can be stated that the spray pyrolysis technique is an extremely promising thin film deposition method. The results obtained in this thesis prove that this technique can be successfully used in SOFC technology.

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# Zusammenfassung

Festelektrolyt-Brennstoffzellen (SOFC) ermöglichen eine effiziente Stromerzeugung mit niedriger Emission von Schadstoffen. Sie wandeln direkt chemische in elektrische Energie um und sind nicht dem Carnot Gesetz unterworfen. Derzeit ist die Kostenreduktion das Hauptziel der SOFC Entwicklung. Zirkonoxid, mit einer Dicke von 150 μm, ist heutzutage das meistverwendete Elektrolytmaterial in Hochtemperatur SOFC Systemen. Wegen der niedrigen spezifischen Ionenleitfähigkeit von Zirkonoxid Elektrolyten sind Betriebstemperaturen von 900°C bis 1000°C notwendig. Diese hohen Temperaturen können Festphasen-Grenzflächenreaktion zwischen benachbarten Zellbestandteilen beschleunigen. Hohe Stabilitätsforderungen werden auch an die Interkonnektoren gestellt, so dass nur teure Materialien, wie z.B. Cr5Fe1Y<sub>2</sub>O<sub>3</sub> hierfür verwendet werden kann. Eine Reduktion der Betriebstemperatur von 1000°C zu 700°C ist daher erstrebenswert. Hierdurch können Systemkosten reduziert und die Langzeitstabilität sowie die Zuverlässigkeit verbessert werden. Die Betriebstemperatur kann reduziert werden, indem man Dünnschichtelektrolyten aus Zirkonoxid einsetzt.

Ziel dieser Arbeit war die Entwicklung eines kostengünstigen Prozesses für die Abscheidung von dünnen Schichten von Oxiden, welche als Elektrolyten für SOFC geeignet sind. Für die Abscheidung solcher Elektrolyte auf porösen Anodensubstraten wurde die Sprühpyrolyse gewählt. Sie ist eine kostengünstige Beschichtungstechnologie mit dem Potential 0.1 bis 10 µm dünne und gasdichte Oxidschichten abzuscheiden.

In Kapitel 2 wird ein kurzer Überblick der Sprühpyrolyse in Bezug auf das Funktionsprinzip dieser Technik sowie der Anwendung in Dünnschichtabscheidung präsentiert. Kapitel 3 behandelt die wichtigsten Parameter der Sprühpyrolyse. Ein Modell für das Schichtwachstum wird in Kapitel 4 vorgestellt. Der Einfluss der thermischen Behandlung auf die Mikrostruktur der abgeschiedenen Schicht steht im Fokus von Kapitel 5. Die Anwendung von gesprühten Dünnschichtelektrolyten in einer SOFC Brennstoffzelle wird schliesslich in Kapitel 6 demonstriert.

Ein Vergleich von zwei Sprühpyrolysetechniken, die Elektrostatische Spray-Abscheidung (Electrostatic Spray Deposition (ESD)) und die Druckluft Spray-Abscheidung (Pressurized Spray Deposition (PSD)), wird im Kapitel 3 präsentiert. Die Oberflächentemperatur des Substrates war der wichtigste Prozessparameter für beide

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Techniken, da das Gefüge der Schicht durch diesen Parameter ganz entscheidend bestimmt wird. Bei ESD ist das Gefüge der Oberfläche auch stark von der Abscheidezeit und der Zusammensetzung der gesprühten Precursor-Lösung beeinflusst. Im Gegensatz hierzu sind diese Parameter bei der PSD Technik für die Schichtmorphologie von geringer Bedeutung.

Ein weiterer Einblick in das Funktionsprinzip der Sprühpyrolyse wird in Kapitel 4 gegeben. Der Tröpfchen-Transport von der Düse bis zum Substrat wurde mittels einen Phasen Doppler Annemometer untersucht. Die Tröpfchen die kleiner als 10 µm sind dominieren die statistische-Verteilungen der Anzahl. Im Gegensatz dazu wird die Volumen-Verteilungen von den Tröpfchen grösser 10 µm dominiert. Wesentliche Tröpfchenverdampfung wurde ab einem Abstand von 1 cm zum Substrat beobachtet. Ein möglicher Wachstums-Mechanismus für die Schichten bei dem die Oberflächentemperatur des Substrates und die grossen Tröpfchen (> 10 µm) den Abscheidungsprozess bestimmen wird vorgeschlagen. Ausserdem folgt, dass für die Bildung glatter Oxidschichten die Oberflächentemperatur über der Eine tiefe des gesprühten Precursor liegen soll. zu Zersetzungstemperatur Abscheidungstemperatur führt zu Rissen in der Schicht, wohingegen eine zu hohe Temperatur zu rauen Schichten oder zu Pulver führt. Im Gegensatz zu den meisten Autoren, der vorgeschlagene Wachstums-Model für die Schichten keinen CVD Prozess einschliesst.

Das Kapitel 5 konzentriert sich auf die Gefüge der Schichten. Die abgeschiedenen Schichten sind amorph und kristallisieren während eine Wärmebehandlung ohne Risse zu bilden. Schichten mit einer durchschnittlichen Kristallitgrösse von 12 nm werden nach einer Glühung bei 700°C erhalten.

Die Anwendung der Sprühpyrolyse für die Elektrolyte für die SOFC Technologie wird in Kapitel 6 vorgestellt. Mittels Sprühpyrolyse wurden Dünnschichtelektrolyten mit niederen ohmschen Verlust hergestellt. Hier wird die Betriebstemperatur der Festelektrolyt-Brennstoffzellen von 1000°C auf 700°C reduziert unter Beibehaltung hoher Leistungen. Elektrolytdoppelschichten YSZ und einer 10 mol% Yttriumoxid dotierten Ceroxid Zwischenschicht (CYO) wurden auf poröse NiO-YSZ Anodensubstrate abgeschieden. Die Zellen wurden bei Temperaturen von 600°C bis 800°C mit Wasserstoff als Brennstoff gegen Luft betrieben und erreichten eine Leerlaufspannung von 1.01 V bei 720°C. Dies hat gezeigt, dass eine dichte und rissfreie Elektrolytschicht vorliegt. Hohe Leistungsdichten von mehr als 750 mW/cm<sup>2</sup> bei 770°C wurde von Zellen mit einer 600 nm dünnen YSZ/CYO Elektrolytdoppelschicht erreicht. Diese Zelle wurde bei 720°C über 450 Stunden mit tolerierbarer Degeneration betrieben. Überraschend, Poren mit Größen von bis zu 3 µm wurden mittels die Sprühpyrolyse von einem 500 nm dünner Elektrolytschicht abgedeckt. Zusammenfassend kann man feststellen, dass die Sprühpyrolyse Technik eine vielversprechende Dünnschicht Abscheidungsmethode für die dünne und dichte Metalloxide ist. Die Ergebnisse dieser Arbeit zeigen, dass diese Technik erfolgreich in der SOFC Technologie angewendet werden kann.

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# **1** Introduction

### **1.1** Aim of the study

Ceramic thin film are widely used as protective layers against corrosion, for wear resistance, in optical applications, as sensors and electrical devices as well as thermal barriers. Ceramic thin films may be produced by spray pyrolysis. This method has the potential to produce thin and gas tight ceramic coatings at temperatures as low as 500°C. The spray pyrolysis process is a simple and low cost technique for ceramic thin film deposition and nm-sized powder production. Spray pyrolysis is a coating technique that offers a lot of advantages for the processing of ceramic films. The process equipment is rather simple, the method is robust and when properly controlled, it yields oxide films of high quality at rather low costs. Many coatings have already been prepared by the spray coating process, including Y<sub>2</sub>O<sub>3</sub> stabilized zirconia (YSZ), Al<sub>2</sub>O<sub>3</sub>, and MgO. This process has the potential to produce thin layers on different substrates. As the substrates are heated, the formation of the oxide layers from precursor solutions occurs directly on the substrate surface by pyrolysis and very homogeneous layers with good adhering interfaces on the substrates can be expected. The cation composition of the deposited layers is determined solely by the composition of the precursor solution only.

The aim of this study was the development of an inexpensive manufacturing process for thin film oxides, suitable as electrolytes for Solid Oxide Fuel Cells (SOFC). Solid oxide fuel cells convert chemical energy directly into electrical energy. The state of the art SOFC is based on thick (about 150  $\mu$ m) zirconia electrolytes. Due to the low ionic conductivity of zirconia, operating temperatures of 900-1000°C are required. The high temperatures lead to material problems such as material inter-diffusion and chemical reactions degrading the performance of SOFC. Therefore, reduction of the operating temperature from 1000°C to 700°C is desirable in order to avoid material interdiffusion and to reduce system costs. In order to lower the ohmic losses, one option is to thin down the zirconia electrolyte.

# 1.2 Strategy

In this study we apply the spray pyrolysis technique for the deposition of yttria stabilized zirconia (YSZ) and  $Y_2O_3$  doped CeO<sub>2</sub> films on dense as well as porous substrates. Spray pyrolysis consists of an atomization of a salt-containing liquid, the transport of spray droplets, and pyrolysis of the salt on the substrate to form the ceramic coating. The present study includes the identification of critical spray process parameters, electrical characterization of the coating and characterization of the microstructures of the deposited films.

# **2** State of the art: spray pyrolysis

D. Perednis, L.J. Gauckler (to be submitted to Journal of Electroceramics)

### Abstract

The spray pyrolysis technique has been applied to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, and solid oxide fuel cells. The properties of deposited thin films depend highly on the preparation conditions. An extensive review of the effects of spray parameters on film quality is given to demonstrate the importance of the process parameters. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity, etc. Processes involved in spray pyrolysis technique, such as atomization of the precursor solution, aerosol transport, and decomposition of the precursor are discussed in this review. Only rough models about the mechanism of film formation have been published so far. Many authors have suggested that a modified CVD process occurs close to the substrate. However, many observations contradict the involvement of CVD process during the spray pyrolysis process.

## **2.1** Introduction

The methods employed for thin oxide film deposition can be divided into two groups based on the nature of the deposition process. The physical methods include physical vapour deposition (PVD), laser ablation, molecular beam epitaxy, and sputtering. The chemical methods comprise gas phase deposition methods and solution techniques (Figure 2.1). The gas phase methods are chemical vapour deposition (CVD) [1, 2] and atomic layer epitaxy (ALE) [3], while spray pyrolysis [4], sol-gel [5], spin- [6] and dip-coating [7] methods employ precursor solutions.



Figure 2.1 Chemical thin film deposition methods.

Spray pyrolysis is a processing technique to prepare dense and porous oxide films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective method, especially regarding equipment cost. Spray pyrolysis does not require high quality substrates or chemicals. The method has been employed for the deposition of dense films, porous films, and for powder production. Even multi-layered films can be easily prepared using this versatile technique. Spray pyrolysis has been used for several decades in the glass industry [8] and in solar cell production to deposit electrically conducting electrodes [9].

Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. The following atomizers are usually used in spray pyrolysis technique: air blast (liquid is exposed to a stream of air) [10], ultrasonic (ultrasonic frequencies produce the short wavelengths necessary for fine atomization) [11] and electrostatic (liquid is exposed to a high electric field) [12].

Various reviews concerning spray pyrolysis techniques have been published. Mooney and Radding have reviewed the spray pyrolysis method, properties of the deposited films in relation to the conditions, specific films (particularly CdS), and device application [13]. Tomar and Garcia have discussed the preparation and the properties of sprayed films as well as their application in solar cells, anti-reflection coatings and gas sensors [14]. Albin and Risbud presented a review of the equipment, processing parameters and optoelectronic materials deposited by spray pyrolysis technique [15]. Pamplin has published a review of spraying solar cell materials as well as a bibliography of references on the spray pyrolysis technique [16]. Recently thin metal oxide and chalcogenide films deposited by spray pyrolysis and different atomization techniques were reviewed by Patil [17]. Bohac and Gauckler have discussed the mechanism of chemical spray deposition and presented some examples of sprayed YSZ films [18].

Powder synthesis and film deposition using spray pyrolysis will be discussed in this chapter. The application of these thin films in solar cells, gas sensors, solid oxide fuel cells, and other devices will be described. The models for thin film deposition by spray pyrolysis will also be reviewed.

## 2.2 Powder production

The first patents concerning powder preparation via spray pyrolysis date back to the 1950s [19]. Since then many studies have been conducted on spray pyrolysis processing of fine powders because the method enables high-purity, unagglomerated, nm-sized particles to be produced with homogeneous chemical composition. During synthesis the solution is atomized to droplets which are passed by means of a carrier gas flow through a diffusion dryer, then the thermolysis reactor and finally a calcination furnace. In the diffusion dryer, the droplets undergo solvent evaporation, precursor precipitation, and drying. The dry precipitate particle decomposes in the thermolysis reactor forming a microporous particle. These particles are then sintered in the calcination furnace. The powders from the aerosols can also be obtained by spraying the precursor solution into a flame. This technology was recently reviewed by Pratsinis [20].

Messing et al. have reviewed the spray pyrolysis techniques in terms of process parameters that control the formation of powders [21]. Spray pyrolysis results in particles with morphologies from solid, to hollow and porous, and even fibers can be obtained. It was concluded that the properties of the solution and the precursor can strongly influence the particle morphology.



Figure 2.2 Powder production.

Submicron spherical particles of tetragonal 2 mol% yttria-stabilized zirconia (YSZ) have been synthesized using the spray pyrolysis technique [22]. Yuan et al. have used the flame-assisted ultrasonic spray pyrolysis technique to prepare YSZ powders with a narrow particle-size distribution [23]. Zhang et al. have demonstrated that an important criterion for the synthesis of fine, solid spherical particles is that the precipitated salt does not undergo plastic deformation or melting during heating, because this leads to the formation of shells of

low permeability [24]. Consequently, the residual solvent is entrapped in the core of the drying droplet (see Figure 2.2) resulting in an increase of pressure, because the solvent cannot easily evaporate through the shell. Therefore, the shell cracks producing secondary droplets and broken shell relics which leads to powders of irregular shape. The authors also concluded that high salt solubility is not necessary for the formation of solid and uniform particles as previously stated by others [25].

Using spray pyrolysis at 900°C, Gurav et al. synthesized (Bi, Pb)-Sr-Ca-Cu-O powders which contained a large number of nano-particles (< 30 nm) [26]. Composite powders with 10 wt% Ag which were produced at 700°C consisted of 20-60 nm grains of silver and mixed-oxide phases with a fine dispersion of Ag grains within the particles that was claimed to favourable for processing Bi-cuprate superconducting material.

## 2.3 Thin film deposition and applications

Films prepared by the spray pyrolysis technique have been used in various devices e.g. solar cells, sensors, antireflection coatings, thermal coatings, solid oxide fuel cells, and many others. This section summarizes the performance of the devices and the film deposition using spray pyrolysis.

Thin film deposition using the spray pyrolysis technique involves spraying a metal salt solution onto a heated substrate (Figure 2.3). Droplets impact on the substrate surface, spread into a disk shaped structure, and undergo thermal decomposition. The shape and size of the disk depends on the momentum and volume of the droplet, as well as the substrate temperature. Consequently, the film is usually composed of overlapping disks of metal salt being converted to oxide on the heated substrate.



Figure 2.3 Schematic of spray pyrolysis equipment.

#### **2.3.1** Films for solar cell applications

Transparent and conducting oxide films as windows in solar cells had been prepared by spray pyrolysis. Aranovich prepared highly transparent zinc oxide films on glass substrates [27]. The properties of the deposited films can be varied and controlled by changing the spray parameters, the deposition temperature for instance influences the optical and electrical properties of zinc oxide films [28]. Films with the lowest electrical resistivity were deposited using aqueous solution of zinc acetate at 490°C due to the improvement of crystallinity, while films prepared at 420°C and 490°C showed high transmission (90-95%) in the visible range. This was attributed to the decrease of the film thickness and increase in the structural homogeneity.

The precursor solution is an important process variable. Caillaud et al. investigated the influence of pH of the solution on the thin film deposition and found that the growth rate was dependent on the pH [29]. The rate was only significant if  $3.5 \le pH \le 4.3$ . In this pH range the vaporized precursors are the zinc acetate complexes. Formation of basic salts, adsorption compounds, or precipitates slowed down the growth at higher pH. At low pH, both the amount of zinc acetate and the growth rate decrease until no more deposition occurs.

Transparent SnO<sub>2</sub> electrodes were deposited by spray pyrolysis using tetra-*n*-butyltin (IV) as precursor [30]. The deposition efficiency and crystallinity of the films deposited at 340°C was improved by adding  $H_2O_2$  to the alcoholic precursor solution. The authors proposed two explanations for this effect. One was that  $H_2O_2$  decomposes easily on a substrate to produce an oxygen atmosphere which promotes the oxidation of tetra-*n*-butyltin and reduces residuals within the film. The second was that  $H_2O_2$  and tetra-*n*-butyltin form tin peroxide complexes with direct atomic bondings between tin and oxygen in the precursor solution. This kind of structure is desirable for formation of SnO<sub>2</sub>.

The physical properties of fluorine-doped indium oxide films were investigated with respect to deposition temperature, dopant concentration, air flow rate and film thickness [31]. It was found that the deposition temperature has a remarkable influence on the orientation of the films. The extent of preferential  $(4 \ 0 \ 0)$  orientation increases with increasing film thickness.

#### 2.3.2 Sensors

Gas sensors are based on semiconducting metal oxides that change their electrical conductance in the presence of carbon monoxide and e.g. hydrocarbons. The sensor typically consists of an oxide semiconductor film on an insulating substrate with two metal electrodes attached. Tin oxide is one of the most widely used oxides for this application. Park prepared tin oxide films on glass substrates which were tested as sensors for  $CH_2Cl_2$  in oxygen [32]. SnO<sub>2</sub> thin films with high specific area for NO<sub>2</sub> sensors have been deposited using the spray pyrolysis technique [33]. LaOCI-SnO<sub>2</sub> films produced by electrostatic spray deposition technique have shown promising sensing properties for  $CO_2$  in air [34].

Porous  $\text{SnO}_2$  and  $\text{SnO}_2$ -Mn<sub>2</sub>O<sub>3</sub> films have been prepared using the electrostatic spray deposition technique [35,36]. These films were used in a Taguchi type hydrogen sensors. The grain size of the porous films ranged from 1 µm to 10 µm. It was observed that the grain size increases with a higher concentration of the precursor in the ethanol solvent. The SnO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> (10:1) mixed oxide films showed a sensitivity to hydrogen.

Some metal oxide sensors show a sensitivity to humidity. The influence of process parameters on the sensitivity to humidity of  $SnO_2$ -Fe<sub>2</sub>O<sub>3</sub> films has been investigated [37]. The nature of the iron salt influenced the humidity sensitivity of the samples. The films deposited from an alcohol solution containing Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> exhibit higher sensitivity than a solution containing Fe(NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub>. This fact was explained by the higher porosity of the structure obtained from iron oxalate, because during the oxalate pyrolysis a lot more gaseous decomposition products are released compared to the sulphate precursors.

Thin SnO<sub>2</sub> films for gas sensors have been prepared also by spray pyrolysis using an inorganic as well as an organic precursor solutions [38]. Smooth but not very uniform films were obtained using a solution of  $(NH_4)_2SnCl_6$  in water. On the other hand, very uniform but relatively rough films were deposited using a solution of  $(CH_3COO)_2SnCl_2$  in ethylacetate. Suitable electric properties were measured for films obtained from the organic solution. The deposition temperature was either 60°C with a subsequent treatment at 250°C for one hour or between 150°C and 450°C. The sensitivity and rise time were found to depend on the deposition temperature and the type of precursor solution used. The best results were achieved by spraying an organic precursor solution onto a substrate at about 300°C.

It was observed that the growth rate of  $SnO_2$  films prepared from  $SnCl_4 \cdot 5H_2O$  was higher and their resistance lower in comparison with those of films prepared from anhydrous  $SnCl_4$  [39]. The authors suggested that under identical conditions, the droplets containing  $SnCl_4 \cdot 5H_2O$  require more thermal energy to form  $SnO_2$  than those containing  $SnCl_4$ . Thus the water molecules seemed to influence the reaction kinetics, particularly the growth rate of the films.

#### 2.3.3 Metal oxide coatings

Titania films have been deposited on steel to prevent corrosion using titanium isopropoxide as the precursor [40]. Three different configurations for film deposition were used. In the first configuration, the precursor vapour impinges on the substrate. In the second

configuration, small droplets of the precursor solution impact onto the substrate. In the third configuration the droplets pass through a high temperature region, where solid titania particles are formed and subsequently deposited on the substrate. In all cases the substrate was moved at a velocity of 1 mm/s to 1 cm/s perpendicular to the spray direction. Dense, adherent films were deposited using the first and the second configuration whereas porous films were obtained using the third configuration. The highest deposition rate was achieved when the droplets impact on the substrate surface. 500 nm thin titania films offered protection against corrosion at room temperature.

MgO thin films are commonly used as buffer layers. Thin, uniform, and homogeneous layers of MgO were deposited on Si (100), fused silica and sapphire [41]. These thin films (0.1 to 0.5  $\mu$ m thick) are used as buffer layers for depositing films of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

Kim et al. have studied the influence of additives on the properties of MgO films deposited by electrostatic spray deposition [42]. A large number of separated particles were observed on the surface of MgO films when pure tetrahydrofuran (THF) was used as a solvent. However, smooth and particle free MgO films were deposited when 1-butyl alcohol or 1-octyl alcohol was added to THF. The authors suggest that the alcohols effectively restrain MgO nucleation resulting from the vaporization of droplets. The type of solvent did not influence the crystallinity of the films.

De Sisto et al. deposited 0.2  $\mu$ m thin alumina films by spray pyrolysis using aqueous acetic acid solution of Al acetylacetone [43]. Al<sub>2</sub>O<sub>3</sub> is used in electronic devices as a thin insulating layer. There was no voltage breakdown observed up to 10 V of applied potential. Films obtained by thermal decomposition of aluminium isopropoxide led to voltage breakdowns at 4 V. It was concluded that Al<sub>2</sub>O<sub>3</sub> films deposited using spray pyrolysis exhibit high quality and higher breakdown voltages than those prepared by MOCVD or sol-gel deposition. Even better quality insulating  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> layers with breakdown voltages higher than 20 V were formed on silicon substrates [44].

#### 2.3.4 Solid oxide fuel cells

Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte material in solid oxide fuel cells. Thin YSZ films have already been deposited by spray pyrolysis on the following substrates: glass [45, 46], aluminium [47], steel [48], porous La(Sr)MnO<sub>3</sub> cathode [49, 50], and porous La(Sr)CoO<sub>3</sub> cathode [18]. Setoguchi et al. deposited calcia-stabilized

zirconia (15at% CSZ) onto porous  $La_{0.6}Sr_{0.4}MnO_3$  cathode substrates [51]. Choy et al. were able to deposit the complete cells using spray pyrolysis, however no data on electrochemical performance of the cells were presented [52].

Terbia-doped yttria-stabilized zirconia thin films have been deposited using electrostatic spray deposition [53]. This material exhibits mixed electronic-ionic conductivity at high oxygen partial pressures and therefore, can be used as SOFC electrode. The surface morphology was controlled by changing the deposition parameters and solution compositions. By increasing the deposition temperature, the morphology of the film was shifted from a dense to a highly porous structure.

The electrostatic spray deposition technique has been used to prepare YSZ films on CGO substrate [54]. Most of the thick layers were porous or cracked, but dense thin YSZ layers were found under cracked top layers. Even so, some of the cracked films may also be used as a composite electrolyte, because the cell containing the YSZ-coated ceria electrolyte exhibits a higher open circuit voltage than those with ceria alone [55].

Charpentier et al. deposited porous  $La_{0.7}SrO_{0.3}MnO_3$  films as cathode by spray pyrolysis on YSZ substrates [56]. Porous structures with large pores, having an average diameter of 1  $\mu$ m, and smaller ones with an average pore size of 0.1  $\mu$ m were observed. An electrical conductivity of 10 S/cm was measured at room temperature.

The electrolyte can also be deposited by powder spraying with a high deposition rate [57]. A suspension of YSZ powder with an average grain size of 0.2  $\mu$ m was sprayed onto a pressed Ni/YSZ anode substrate and a layer of 10  $\mu$ m was obtained in 3 minutes. However, a subsequent sintering step at 1400°C was required. In the next step, the La<sub>0.7</sub>SrO<sub>0.3</sub>MnO<sub>3</sub> cathode was prepared similarly. In this case, the La<sub>0.7</sub>SrO<sub>0.3</sub>MnO<sub>3</sub> powder was added to a solution of strontium acetate, lanthanum nitrate and manganese nitrate. A 5  $\mu$ m thin cathode was deposited at 400°C and subsequently annealed at 900°C for 2 hours. This cell was tested at 850°C. The open circuit voltage was lower than the theoretical value due to the presence of pinholes in the thin film electrolyte. Consequently, the maximum power density was only 104 mW/cm<sup>2</sup> at 850°C.

To our knowledge only few reports on fuel cell tests have been presented. A SOFC cell with a Ni-YSZ anode / 15 at% CSZ electrolyte /  $La_{0.6}Sr_{0.4}MnO_3$  cathode arrangement has been tested by Setoguchi et al. [51]. The tests were performed using hydrogen as fuel and oxygen as oxidant. The open circuit voltage (OCV) of the cell with 33 µm thick CSZ film deposited at 100°C was 0.96 V and the maximum power density 500 mW/cm<sup>2</sup> at 1000°C. The cracks in the CSZ film were eliminated by repeated coating (10 times), since the voids of

every coating step are filled by subsequent spraying steps. Also 18  $\mu$ m thick YSZ films have been tested using the same arrangement [50]. In this case a slightly higher OCV of 1.04 V was attained. The cell generated a maximum power density of 490 mW/cm<sup>2</sup> at 1000°C.

#### 2.3.5 Miscellaneous applications

Spray pyrolysis is well suited for producing thin superconducting oxide films of desired stoichiometry on large areas. Langlet deposited YBCO on MgO,  $ZrO_2$  or  $SrTiO_3$  substrates and investigated the influence of experimental conditions on the properties of the films [58, 59]. Hsu et al. deposited 3  $\mu$ m thick Bi-2212 films on MgO substrates with a critical temperature (T<sub>c</sub>) of 81-83 K and critical current density of 4000 A/cm<sup>2</sup> at 78 K [60]. With 1  $\mu$ m thin YBCO films on a MgO substrate much higher critical current densities could be achieved [61]. Films deposited above 600°C exhibited zero resistance at 80 K and critical current of 30 000 A/cm<sup>2</sup> measured using the four probe method.

In [11] the effect of glycerol in aqueous nitrate solutions on the growth of YBCO films was reported. The superconductor films on YSZ substrates prepared from precursor solutions with glycerol showed a sharp superconducting transition, a  $T_c$  as for bulk material (above 90 K), and a strong c-axis-oriented texture. On the other hand, the surface of the film prepared from the aqueous precursor solution was irregular, and had a lower  $T_c$  than the bulk material. Glycerol improves the production of fine droplets, thus improving the surface morphology of the deposited film.

The electrostatic spray deposition (ESD) technique enables porous metal oxide films to be deposited. Chen et al. have deposited porous layers of LiCoO<sub>2</sub> on metal substrates by means of ESD [62, 63]. It was possible to prepare a complete thin film rechargeable lithiumion microbattery by alternating deposition steps of electrode and electrolyte layers [64]. Microbatteries were obtained by depositing two  $Li_{1,2}Mn_2O_4$  films as electrodes and intermediate BPO<sub>4</sub>:0.035Li<sub>2</sub>O film as the electrolyte on an Al substrate. Such batteries exhibited the theoretical OCV, but had high internal resistances which was related to the amorphous structure of the intermediate electrolyte. Van Zomeren et al. deposited LiMn<sub>2</sub>O<sub>4</sub> cathodes suitable for rechargeable lithium batteries [65]. High deposition rates up to 5  $\mu$ m/h were achieved.

Metal films can also be deposited by the spray pyrolysis technique. Aiyer et al. have demonstrated that metallic copper films can be deposited on Si (100) substrates using nebulized spray pyrolysis [66]. Three  $\beta$ -diketonates of copper (bis-acetylacetonato copper

 $(Cu(acac)_2)$ , bis-hexafluroacetonato copper  $(Cu(hfac)_2)$  and bis-dipivaloylmethanato copper  $(Cu(dpm)_2))$  were chosen as precursors. A mixture of ultra pure nitrogen and hydrogen was used as the carrier gas to transport the aerosol. Smooth, dense and uniform films were obtained from  $Cu(acac)_2$  and  $Cu(dpm)_2$ . On the other hand, the film obtained using  $Cu(hfac)_2$  was rough and porous. Good quality films from  $Cu(acac)_2$  precursor were deposited in the temperature range 300°C to 400°C. It was impossible to obtain copper films from  $Cu(dpm)_2$  and  $Cu(dpm)_2$ .

# 2.4 Models for film deposition by spray pyrolysis

Only very crude models about the mechanism of spray deposition and film formation have been developed up to now. There are too many processes that occur either sequentially or simultaneously during film formation by spray pyrolysis for these to be modelled in a straightforward manner. These include precursor solution atomization, droplet transport and evaporation, spreading on the substrate, drying and decomposition of the precursor salt. Understanding these processes will help to improve film quality. Thin film deposition using spray pyrolysis can be divided into three main steps: atomization of the precursor solution, transportation of the resultant aerosol and decomposition of the precursor on the substrate.

#### 2.4.1 Atomization of precursor solution

Air blast, ultrasonic and electrostatic atomizers are normally used in spray pyrolysis techniques. Numerous reports were published on the mechanism of liquid atomization. Rizkalla and Lefebvre examined the influence of liquid properties on air blast atomizer spray characteristics [67]. Lampkin presented results concerning the application of the air blast atomizer in a spray pyrolysis set-up [68]. Recently a theory of ultrasonic atomization was published [69]. Ganan-Calvo et al. have studied the electrostatic atomization of liquids and derived scaling laws for droplet size from a theoretical model of charge transport [70].

Compared with other spray techniques, the electrostatic spray deposition technique has been used only recently for thin film deposition, whereas liquid atomization by means of an electric field has been investigated for many years. Research into electrostatic spray deposition started with Rayleigh's study on the stability of an isolated charged droplet [71]. Electrostatic atomization of liquid was first reported by Zeleny [72]. Grace and Marijnissen have published a review on this type of atomization [73]. Depending on spray parameters, various spraying modes were obtained, resulting in very different droplet size distributions. Cloupeau et al. proposed a classification of these modes [74]. Cone-jet and multi-jet modes are the most important modes for spray deposition. In the cone-jet mode the liquid is distorted at the tip of the tube type nozzle into a conical shape (Taylor cone). This cone is extended at its apex by a permanent jet of very small diameter (see Figure 2.4). The jet usually emits charged mono-dispersed droplets. With increasing electric field, the jet may be split, forming a multi-jet mode where the number of jets increases with applied voltage (see Figure 2.5).



Figure 2.4 Cone-jet spraying of methanol containing a small amount of hydrochloric acid [75].





#### **2.4.2** Aerosol transport

In an aerosol the droplet is transported and eventually evaporates. In case dense films are desired, it is important that during transportation as many droplets as possible fly to the substrate without forming particles before reaching the surface. Sears et al. investigated the mechanism of SnO<sub>2</sub> film growth [76]. The influence of forces which determine both the trajectory of the droplets and evaporation were examined and a film growth model was proposed. Gravitational, electric, thermophoretic and Stokes forces were taken into account. The thermophoretic force pushes the droplets away from a hot surface, because the gas molecules from the hotter side of the droplet rebound with higher kinetic energy than those from the cooler side. For example, at a surface temperature of 350°C and a thermal gradient of 500 °C/cm it was calculated that the thermophoretic force is equal to the gravitational force for a droplet of 2 µm in diameter. Thermophoretic forces keep most droplets away from the surface in non-electrostatic spray process. It was concluded that the film grows from the vapour of droplets passing very close to the hot substrate in a manner of chemical vapour deposition (Figure 2.6). Droplets that strike the substrate form a powdery deposit. The authors suggest that forcing droplets closer to the substrate while avoiding actual contact would improve the efficiency of film growth.



Figure 2.6 Schematic of aerosol transport by Sears et al. [76].

Siefert described the transport processes in corona spray pyrolysis. Here the droplets enter a corona discharge and are transported in an electric field to the substrate [77]. The following forces were taken into account: gravitational, Stokes, thermophoretic, electric, and dielectric forces. The author has calculated that only droplets, with a radius larger than 5  $\mu$ m, will contribute to film formation at a substrate temperature of 430°C. This value depends on the composition of the solution, the applied voltage and the deposition temperature. The solvent is entirely vaporized in the smaller droplets that will consequently lead to powder formation.

The aerosol droplets experience evaporation of the solvent during the transport to the substrate. This leads to a size reduction of the droplet and to the development of a concentration gradient within the droplet. The precursor precipitates on the surface of the droplet, when the surface concentration exceeds the solubility limit. Precipitation occurs due to rapid solvent evaporation and slow solute diffusion. This results in the formation of a porous crust and subsequently hollow particles, which are not desired in film formation because they increase the film roughness.

Yu and Liao developed a model describing the evaporation of solution droplets before the formation of a solid crust [78]. The transfer of mass, momentum, temperature outside and around the droplet as well as effects of precursor precipitation were taken into account. The interactions between droplets were ignored. Rapid increases in droplet temperatures were observed at the beginning of evaporation and at the moment when precursor precipitation on the droplet surface starts. This temperature increase was due to heat evolved as a result of precipitation. At the beginning of this process the evaporation rate very quickly reaches a maximum, then decreases until precipitation takes place. This rate accelerates again simultaneously with droplet temperature when precipitation starts. Increasing the gas temperature caused a steeper concentration gradient inside the droplet. The effects of humidity of the ambient gas were found to be insignificant. Lenggoro et al. investigated powder production by spray pyrolysis using a temperature-graded laminar flow aerosol reactor [79]. They presented results from calculations for the evaporation rate and the change of the precursor concentration within the droplets. The predicted numerical simulation results were in good agreement with the experimental results. The simulations indicated that the solid particles can be formed when the temperature in the reactor is low and constant or distributed inhomogeneously, when the precursor solution concentration is high and when the flow rate of carrier gas is low. Undesired hollow particles are formed when the droplets are large and the droplet number concentration is low. Smaller droplets produce solid particles because the diffusion distance for the solute is shorter, leading to a more uniform concentration distribution within the droplet. Increasing the number of droplets results in a larger solvent vapour concentration in the carrier gas. Consequently, the evaporation rate decreases and precipitation is delayed. Therefore, an increase in the number of droplets decreases the probability of forming hollow particles.

Oh and Kim have studied the behaviour of an evaporating droplet in a non-isothermal field [80]. An alcoholic solution of titanium tetraethoxide was atomized by an ultrasonic nebulizer. Nitrogen was used as carrier gas. The flow and temperature profiles of the carrier gas were calculated and then the motion and evaporation of the droplets simulated numerically. Measurements of deposition efficiency and film thickness distribution were compared with calculated particle trajectories. The comparisons have shown that the deposition efficiency and the area coated increase with the amount of sprayed solution and carrier gas flow rate, but decrease with nozzle-to-substrate distance.

#### 2.4.3 Decomposition of precursor

Many processes occur simultaneously when a droplet hits the surface of the substrate: evaporation of residual solvent, spreading of the droplet, and salt decomposition. Many models exist for the decomposition of a precursor. Most of the authors suggest that only a kind of CVD process gives high quality films by spray pyrolysis.

Viguie and Spitz proposed the following processes that occur with increasing substrate temperature [81]. In the lowest temperature regime (process A in Figure 2.7) the droplet splashes onto the substrate and decomposes. At higher temperatures (process B) the solvent evaporates completely during the flight of the droplet and dry precipitate hits the substrate, where decomposition occurs. At even higher temperatures (process C) the solvent also evaporates before the droplet reaches the substrate. Then the solid precipitate melts and vaporizes without decomposition and the vapour diffuses to the substrate to undergo a CVD process. At the highest temperatures (process D) the precursor vaporizes before it reaches the substrate, and consequently the solid particles are formed after the chemical reaction in the vapour phase. It was speculated that the processes A and D lead to rough or non-adherent films. Adherent films were obtained by CVD at low temperatures (process C).

Choy proposed a deposition model for the so called electrostatic spray-assisted vapour deposition process [82]. This technique is also known as electrostatic spray deposition. The

precursor solution is atomized using an electric field. Porous and amorphous CdS films were obtained below 300°C (process I). At high substrate temperatures (above 450°C) powdery films were produced due to the vaporization and decomposition of the precursor before reaching the substrate (process III). At intermediate temperatures (300-450°C), both processes may occur. The authors suggest that at the optimum temperature the solvent evaporates close to the substrate, and the precursor is volatilized near the vicinity of the substrate and adsorbed onto the surface, followed by decomposition to yield a dense film with good adhesion (process II). This would correspond again to a heterogeneous CVD reaction. It was estimated that the optimum temperature lies between 400°C and 450°C. The presence of large particles on the surface was attributed to very large droplets which might not decompose through the CVD process route when they arrive at the substrate.



Figure 2.7 Description of the deposition processes initiated with increasing substrate temperature by Viguie and Spitz [81].

Chen et al. investigated the correlations between film morphologies and deposition parameters [12]. The films were deposited using the so-called cone-jet mode. It was concluded that the morphology of the film deposited by ESD is determined by the size of the incoming droplets, deposition temperature, the rate of droplets spreading on the substrate, and solution chemistry. The substrate temperature was indicated as the most important parameter. The concentration of the precursor solution had a minor influence on the film morphology. Kosugi et al. has separated the Cu<sub>2</sub>O film deposition process into four steps: 1) arrival of droplets, followed by reduction of the Cu<sup>2+</sup> to elementary copper with glucose; 2) formation and condensation of copper clusters; 3) oxidation of the copper clusters to Cu<sub>2</sub>O clusters; 4) growth and densification of Cu<sub>2</sub>O clusters [83].

The salt decomposition plays an important role in the spray pyrolysis technique. Stryckmans et al. investigated the decomposition of magnesium acetylacetonate (Mg(acac)<sub>2</sub>) and suggested the following model [84]. After melting at 265°C, Mg(acac)<sub>2</sub> is no longer stable. The molecule splits and gives a gaseous organic fragment ( $C_5H_7O_2$ ) and a liquid compound containing magnesium (MgC<sub>5</sub>H<sub>7</sub>O<sub>2</sub>). The gaseous fragment is degraded into smaller molecules. The compound containing the magnesium is slowly degraded to form MgO and organic residues. Higher weight loss than theoretically predicted for the formation of MgO from MgC<sub>5</sub>H<sub>7</sub>O<sub>2</sub> was observed between 290°C and 600°C. It indicates that the MgC<sub>5</sub>H<sub>7</sub>O<sub>2</sub> liquid phase is partially evaporated. Smooth films were deposited in the temperature range 350-420°C. However, some cracks were still observed.

Zirconium acetylacetonate ( $Zr(acac)_4$ ) was often used as precursor in spray deposition of zirconia films. Little information is available in the literature about the decomposition of this salt. Ismail studied the decomposition reactions of  $Zr(acac)_4$  in dry nitrogen [85]. The results showed that the  $Zr(C_5H_7O_2)_4$  had completely decomposed to  $ZrO_2$  at 800°C, through intermediates  $Zr(CH_3COO)_2(C_5H_7O_2)_2$  at 190°C,  $ZrO(CH_3COO)_2$  at 340°C and  $ZrOCO_3$  at 450°C.

Wang et al. investigated the thermal decomposition of  $Zr(acac)_4$  in air using thermogravimetry and infrared spectrometry [86]. Weight loss occurred in three temperature regions: at 110-187°C, 187-245°C and 245-440°C. The IR spectrum of  $Zr(acac)_4$  heated at different temperatures from room temperature to 450°C indicated that all acetylacetone structures decompose completely at 310°C. The above investigations suggest that  $Zr(acac)_4$  does not sublime at atmospheric pressure and the decompositions of precursor compounds are accomplished at 440°C.

It is often assumed that a CVD mechanism is active in the formation of dense films. However, formation of films from non-volatile nitrates, low deposition temperatures, and splats observed on the film surface contradict a CVD process. Matsuzaki et al. prepared YSZ films using volatile zirconium octylate and yttrium octylate as precursors at unusually high substrate temperatures of 600–750°C [87]. Two possible reactions for the film growth were considered, namely the precursors reach the substrate surface in a liquid state and pyrolyze, or the droplets turn into vapors and form the film by the CVD process. In order to choose the growth mechanism, the yttrium content in the film was measured by fluorescent X-ray analysis. The same yttrium content in the precursor solution and in the deposited film was measured. Also no temperature dependence of the yttrium content in the film was observed. These two facts are in contradiction with a CVD mechanism. The vapour pressures of yttrium and zirconium octylates are different, and therefore different yttrium contents are expected in the film and in the solution. Since the vapour pressure changes with temperature, also a temperature dependence of the yttrium content in the film is expected. As this was not the case, they proposed a deposition mechanism without CVD character.
# 2.5 Summary

Spray pyrolysis is a versatile and effective technique to deposit metal oxide films. It is an attractive method to prepare a wide variety of powders and thin film materials for various industrial applications. Metal oxide, chalcogenide and even metal films have been deposited using this technique. Spray pyrolysis opens up the possibility to control the film morphology. The quality and properties of the films depend largely on the process parameters. The most important parameter is the substrate surface temperature. The higher the substrate temperature, the rougher and more porous are the films. If the temperatures are too low the films are cracked. In between, dense smooth films can be obtained. The deposition temperature also influences the crystallinity, texture and other physical properties of the deposited films. The precursor solution is the other important spray parameter which affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be drastically changed by using various additives in the precursor solution.

It is often suggested that a modified CVD process occurs in film formation close to the surface of the substrate. However many observations contradict the involvement of a model with a CVD character. Further efforts are necessary to clarify the model for film deposition in more detail.

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# **3** Morphology and deposition of thin metal oxide films using spray pyrolysis

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#### Abstract

A comparison of two spray pyrolysis techniques, Electrostatic Spray Deposition (ESD) and Pressurized Spray Deposition (PSD), is presented in this chapter. Both techniques have been applied for the deposition of thin yttria-stabilized zirconia (YSZ) films. Thin films with various morphologies have been deposited using the ESD technique. For both techniques, the main parameter that determines the film morphology was the substrate temperature. Using ESD, the surface morphology was strongly influenced by the composition of the precursor solution and deposition time. When the PSD technique was used for film deposition, the influence of these parameters on film morphology was not pronounced.

# **3.1 Introduction**

Spray pyrolysis usually involves atomizing a precursor solution to an aerosol, which is then directed to a heated substrate where a thin film is formed. This thin film deposition method is simple, cost-effective, and a wide choice of precursors can be used. The composition of the film can be easily controlled by the precursor solution. Both, dense and porous structures can be deposited by spray pyrolysis, even on large substrates when scaling up the equipment. Different types of atomizers such as air blast, ultrasonic, or electrostatic can be part of a spray pyrolysis equipment. The technique of atomization determines the droplet size and size distribution, the rate of atomization, and the spray angle.

Air blast atomizers utilize high speed air to produce the aerosol [1]. The liquid is introduced into an air stream and sheared into drops by the energy of the gas stream. Ultrasonic atomizers are electrically driven and operate on an entirely different principle [2]. A titanium nozzle, driven by an electronic power generator, vibrates at ultrasonic frequencies. Higher frequencies produce smaller drops.

An electrostatic atomizer uses the strong, local electric forces appearing at a charged liquid-gas interface to generate extremely fine charged droplets. Various spraying modes can be formed depending on the electric potential applied, the liquid flow rate, the electrical conductivity and the surface tension of the liquid [3]. The most important modes are the cone-jet and the multi-jet modes. The cone-jet mode provides a spray with fine monosized droplets. A broad droplet size distribution can be expected from multi-jet mode operation.

The fraction of material deposited using spray pyrolysis is usually low due to the overspray. Many droplets are deflected or reflected from the substrate surface. The smaller the droplets, the more fogging occurs and the more spray tends to drift. Therefore, a large fraction of droplets is lost. The exception is electrostatic spraying, where this is not the case. However, it is difficult to generate a stable spray of aqueous solution using an electrostatic atomizer.

In the present study, two types of atomizers, an electrostatic and an air blast atomizer were used to generate the aerosol and to deposit smooth and dense metal oxide films. Here we present a spray pyrolysis parameter study.

#### **3.1.1 Spray generation**

Electrostatic atomization of liquids has been investigated since 1914 [4]. However, only recently has it been applied in spray pyrolysis. Electrostatic spray deposition (ESD) was first used for the preparation of thin films of yttria-stabilized zirconia (YSZ) and LiMn<sub>2</sub>O<sub>4</sub> [5, 6]. It was even possible to deposit porous LiCoO<sub>2</sub> films using this technique [7]. The so called corona spray technique is similar to the ESD process [8]. However, the ESD technique generates the aerosol using only high voltage, while the corona spray technique produces droplets using a combination of ultrasound and electric discharge.

Like other spray pyrolysis techniques, the ESD involves spray generation, droplet transport, deposition of droplets, droplet spreading and precursor decomposition. In the ESD technique a high voltage is usually applied to a metal capillary tube through which a precursor solution is fed. The electric field induces the surface charge that causes an outward electrostatic pressure on the solution. This pressure is opposite to the inward directed pressure caused by the surface tension. The precursor solution can be atomized in many different ways, depending on the applied voltage, the flow rate and the physical properties of the liquid. Several attempts have been undertaken to classify the modes of electrostatic spraying [3, 9]. Different droplet sizes are generated in each mode of spraying. Usually the cone jet mode is preferred because it produces monosized droplets in the range of several micrometers. In this mode the liquid surface is distorted into a so called Taylor cone which is extended by a jet. Ganan-Calvo deduced the relation between the droplet size d, the flow rate Q and the physical properties of the solution [10]:

$$d \propto \sqrt{Q} \left(\frac{\rho}{\gamma \cdot K}\right)^{\frac{1}{6}}$$
(3.1)

where  $\gamma$  is the liquid-gas surface tension,  $\rho$  the density, and K the electric conductivity of the liquid. The multi-jet mode can also be used for spraying. This mode develops from the cone jet mode when increasing the applied voltage. For thin film deposition the cone jet mode is used more often than the multi-jet mode.

Liquid atomization by high velocity air has received less attention, in consequence, little is known about the effect of liquid properties on droplet size distribution. In general, the mean droplet size increases with an increase in viscosity, surface tension, and density [1].

#### 3.1.2 Influence of spray parameters on film morphology

Since the dynamics of the evaporation and decomposition reactions are strongly temperature dependent, the substrate temperature plays an important role in spray pyrolysis. Chen et al. [11] observed four types of film morphologies: dense, dense with incorporated particles, porous top layer with dense bottom layer, and fractal-like porous. These four types are schematically shown in Figure 3.1. The authors concluded that the main parameter, which determines the film morphology, is the substrate temperature. The concentration of the precursor solution had a minor effect. At high salt concentrations precipitation became more significant, leading to rough films.



Figure 3.1. Four types of film morphologies obtained by ESD. I, dense film; II, dense film with incorporated particles; III, porous top layer with dense bottom layer; IV, fractal-like porous structure [11].

Ruiz et al. [12] investigated the influence of carrier gas, substrate composition, temperature and time on film morphology. The most important parameters were found to be the deposition temperature and the droplet size, which in turn depends on the carrier gas.

Aranovich et al. [13] observed thinner films at higher temperatures and higher air flows. This was attributed to decreased wetting at higher temperatures which leads to the increase of the droplet splitting, bouncing, and the lateral mobility. Droplets can be swept away by lateral wind. On the contrary, Oh and Kim [14] reported that the deposition rate increases with increasing temperature. However it is difficult to compare these results, because of different experimental conditions. In both cases different types of atomizers were used (air blast and ultrasonic).

The spreading behaviour of droplets is determined by its surface tension and roughness of the coated substrate. It was also reported, that the porosity of a substrate influences the morphology of a film substantially [15].

Films with low porosity were produced when using a solvent with a high boiling point. Then the morphology became more dense compared to a solvent with a lower boiling point [11, 15, 16]. This was attributed to slower evaporation of solvent during the droplet transport and spreading on the substrate that consequently leads to slower precipitation.

It is well known that the physical properties of the liquid influences droplet size distribution in ESD. Therefore, the morphology of a film can be tailored by using additives in the precursor solution. By adding acetic acid to the precursor solution, the morphology of  $TiO_2$  films change from a cracked to a crack-free reticular structure [17]. A large number of particles disappeared from the MgO film surface when 1-butyl alcohol or 1-octyl alcohol was added to the tetrahydrofuran precursor solution [18].

Jergel suggested that metal-organic compounds are more favourable compared to nitrates, due to their volatility and lower decomposition temperatures [19].

Generally, it can be concluded that the film morphology depends mainly on the substrate temperature and the composition of the precursor solution.

# **3.2** Experimental

#### 3.2.1 Set-up

The spray pyrolysis set-up consists mainly of the following parts: a spraying unit, a liquid feeding unit, and a temperature control unit. We have used both electrostatic and air blast atomizers in the spraying unit. The spray pyrolysis technique using the electrostatic atomizer will be called Electrostatic Spray Deposition (ESD), the technique using the air blast atomizer will be called Pressurized Spray Deposition (PSD). These two spray pyrolysis set-ups have different configurations. In case of using the ESD set-up, the solution was sprayed upwards as shown in Figure 3.2. The upward spray direction was chosen to prevent dripping of the non-atomized solution onto the substrate. The solution was sprayed in the opposite direction (i.e. downwards) when the PSD set-up was used (Figure 3.3). The same liquid feeding and temperature control units were employed in the ESD and the PSD set-ups. The equipment utilized in our spray pyrolysis apparatus is listed in Table 3.1.



Figure 3.2. Schematic drawing of the ESD apparatus.

As mentioned before, the ESD set-up utilizes an electrostatic atomizer for the generation of an aerosol. This spraying unit includes a high DC voltage power supply capable of providing voltages of up to 30 kV, a hollow metal needle with an inner diameter of 0.6 mm, and a substrate holder. The liquid feeding unit consists of a syringe pump, a glas syringe, and a flexible tube of Viton material (Ismatec SA, Glattbrugg, CH). A temperature control unit includes a heating plate and either an IR pyrometer or a contact thermoelement. The IR pyrometer was used for contactless temperature measurement of non-metallic substrates. The temperature of the metallic substrates was measured using the contact thermoelement.

Equipment	Model	Manufacturer	Supplier	
Heating plate	CERAN 500, Type 11A	HARRY GESTIGKEIT GmbH, Düsseldorf, Germany	FAUST Laborbedarf AG, Schaffhausen, Switzerland	
Syringe pump	Model A-99	RAZEL SCIENTIFIC INSTRUMENTS, Inc., Stamford, USA	AZEL SCIENTIFIC INSTRUMENTS, Inc., Stamford, USA WINIGER AG, Wohlen, Switzerland	
IR Pyrometer	MODLINE 3	Ircon, Inc., Niles, USA	SIECO AG, Grenchen, Switzerland	
Power supply	Series 225	Bertan High Voltage, Del Power Conversion Group, Valhalla, USA	Altrac AG, Dietikon, Switzerland	
Air blast atomizer	Compact 2000KM	Böllhoff Verfahrenstechnik, Bielefeld, Germany	Dega AG, Sirnach Switzerland	

#### Table 3.1 Equipment used in the spray pyrolysis apparatus



Figure 3.3. Photograph of the PSD set-up.

The temperature between the nozzle and the substrate surface was measured with Ktype thermoelement. The results are shown in Figure 3.4. The air temperature increases steeply in the case of the PSD due to the forced convection cooling effect of the air flow close to the substrate. The temperature begins to increase significantly at a distance of just 5 mm to the substrate. In the case of the electrostatic atomizer (ESD), forced convection is reduced and temperature increases at a distance of 10 mm from the substrate.



Figure 3.4. Comparison of the temperature distribution in the ESD and the PSD set-up.

#### **3.2.2** Chemicals and substrates

A precursor solution based on a mixture of zirconium and yttrium salts was prepared according to the stoichiometry of the required  $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$  films. The salts are listed in Table 3.2. According to eq. (1), physical properties of the solvent influence the droplet size distribution and, as a consequence, the structure of the deposited films. The conductivity and the surface tension of the solution are the most important parameters for stable atomization in the ESD technique. These two parameters should not be too high, otherwise electric disruptive discharges prevent atomization. This is why aqueous solutions are not normally employed in ESD. In contrast to this, the conductivity of the solution has no influence at all on atomization when applying PSD technique. Consequently, an aqueous precursor solution can be used in this technique.

Precursor	Supplier		
Zr acetylacetonate Zr(C5H7O2)4	Fluka Chemie, Buchs, CH No. 96580		
Zr propoxide solution $Zr(C_3H_7O)_4$	Fluka Chemie, Buchs, CH No. 96595		
Zr chloride ZrCl₄	Alfa Aesar Johnson Matthey & Brandenberger AG, Zurich, CH No. 12104		
Zirconyl nitrate hydrate ZrO(NO <sub>3</sub> )2 <sup>.</sup> aq	Fluka Chemie, Buchs, CH No. 96615		
Y chloride YCl3·XH2O	Alfa Aesar Johnson Matthey & Brandenberger AG, Zurich, CH No. 11184		
Y nitrate hexahydrate Y(NO3)3·6H2O	Alfa Aesar Johnson Matthey & Brandenberger AG, Zurich, CH No. 12898		

Table 3.2 Precursors

The solubility of the precursor in the solvent is a very important parameter, since it determines the maximum salt concentration in the solvent. In order to achieve a reasonable deposition rate, the precursor concentration should be as high as possible. On the other hand, it cannot be too close to the solubility limit, because the salt can precipitate in a droplet due to solvent evaporation during aerosol transport, resulting in a hollow particle being formed. Usually ethanol is used to dissolve the precursors. However, ethanol has low boiling point (78°C) and evaporates rapidly. To slow down solvent evaporation, and thereby to hinder particle formation, we mixed ethanol with the solvent butyl carbitol which has a high boiling point (231°C). Usually, the volume ratio of the solvents in the mixture was set at 1:1.The solvents used in our studies are listed in Table 3.3.

Solvent	Boiling point	Supplier
Ethanol C2H5OH	78°C	Fluka Chemie, Buchs, CH No. 32221
Water H <sub>2</sub> O	100°C	
1-Methoxy-2-propanol CH3CH(OH)CH2OCH3	120°C	Fluka Chemie, Buchs, CH No. 65280
Butyl carbitol CH3(CH2)3OCH2CH2OCH2CH2OH	231°C	Fluka Chemie, Buchs, CH No. 62428

Table 3.3 Solvents

Disks of 35 mm in diameter and 75  $\mu$ m in thickness of Inconel 600 (Goodfellow, UK) were used as substrates. This nickel alloy (Ni72/Cr16/Fe8) was chosen as substrate material due to its oxidation resistance. The metal foil has a shiny appearance with a typical surface roughness from rolling operation as shown in Figure 3.5.



Figure 3.5 Surface morphology of the uncoated Inconel 600 substrate.

## 3.2.3 Characterization

The surface morphologies and compositions of the deposited metal oxide films were analysed using a scanning electron microscope (SEM) (LEO 1530) equipped with an energy dispersive X-ray (EDX) detector. The surface microstructure and roughness were analysed using atomic force microscopy (AFM) (TOPOMETRIX Explorer).

# **3.3** Spray parameters

Similar deposition results were obtained using both ESD and PSD. The PSD set-up is preferred for large area coating and for atomisation of an aqueous precursor solution. Unless indicated otherwise, ethanol solutions of Zr acetylacetonate and Y chloride were mixed with butyl carbitol (volume ratio 1:1). To investigate the influence of the solvent, the ethanol was mixed with 1-methoxy-2-propanol. The total salt concentration was normally 0.1 mol/l. The nozzle-to-substrate distance was 6 cm in the ESD set-up and 30 cm in PSD set-up.

The choice of a salt is the most important decision to be made before parameter optimization can be undertaken. The type of salt directly influences three spray parameters: temperature (should be sufficiently high to decompose the salt), salt concentration (limits the maximal concentration in the solution) and type of solvent (restricts the choice of salts due to their insolubility in some solvents). Therefore, the optimal spray parameters usually differ considerably for each type of salt.

#### 3.3.1 Substrate surface temperature

The substrate temperature is the most important spray parameter. Figure 3.6 shows different film morphologies of films deposited using the ESD technique at different temperatures. At temperatures below 200°C the droplets deposited are still rich in solvent. Therefore, a thin, wet layer is present on top of the film during deposition. Too fast drying of this layer results in stresses and subsequent cracking. At too high temperatures (>350°C) the deposited spray droplets are almost dry. Therefore, discrete particles are formed on the surface due to slow spreading. This increases the surface roughness. In this case, a temperature of  $280^{\circ}C \pm 50^{\circ}C$  results in dense films.

The observed dependence on the deposition temperature was also reported by Chen et al. [11]. With increasing temperature the morphology of the film changed from dense (type I), to dense with incorporated particles (type II), then to porous top layer with dense bottom layer(type III), and finally to fractal structures (type IV) (Figure 3.1).

The film morphology was only weakly affected by the substrate surface temperature, in the case of the deposition using the PSD setup with an air blast atomizer. The film was cracked at 200°C and dense (type I) at 250°C as in the case of ESD. However, in contrast to ESD there were hardly any particles on the surface of the film at a deposition temperature of 250°C. The morphology of the film deposited at 350°C could still be classified as type I. It follows that better quality films can be deposited using the PSD setup.







Figure 3.6. Surface morphologies of YSZ films deposited using the ESD technique at different temperatures for 1 hour: (a) 200°C; (b) 250°C; (c) 300°C; (d) 350°C. Precursor solution: 0.085 mol/l  $Zr(C_5H_7O_2)_4 + 0.015$  mol/l  $YCl_3 \cdot XH_2O$  ethanol (50 vol%) + butyl carbitol (50 vol%) solution.

The development of different morphologies can be explained by considering the effect of the electric field and the droplet size. It is well known that electrostatically generated droplets are much smaller than the ones produced using an air blast atomizer. In addition, the droplets generated using high voltage are charged. These small, charged droplets evaporate and shrink, but keep the same total charge. When the so-called Rayleigh limit [20] of a maximum charge density is reached, the droplet will disrupt into a few smaller droplets. This effect increases the number of solid particles on the film surface. Additionally, the strong electrostatic field causes "preferential landing". This action causes agglomeration and attraction of the small charged droplets towards more curved areas on a substrate. On increasing the deposition temperature, more droplets will reach the Rayleigh limit due to the faster evaporation, and consequently more and more nearly dry droplets will impact the substrate. Slow spreading leads to the formation of particles on the surface, and consequently enhances the preferential landing. Therefore, the surface morphology changes from relatively dense (type II) to highly porous (type IV) in the case of the electrostatic atomization. Droplets, generated using the air blast atomizer, are not charged and are not moving in an electric field. So droplet disruption and preferential landing will not occur. Therefore, most of the landing droplets will be still wet and will form a dense layer without particles (type I).

#### **3.3.2** Solution flow rate

Generally the precursor solution flow rate has a minor effect on the film morphology. It may not exceed a certain value, at which film cracking can occur. The maximum value depends on the type of atomizer, deposition temperature, nozzle to substrate distance, etc.

The ESD operates at rather low solution flow rates. The typical range of flow rate is from 1 ml/h to 8 ml/h. These small values are caused mainly by the short nozzle to substrate distance, because the shorter the distance, the larger the spray mass flux will be. Thin wet films are formed during deposition, when the spray mass flow is too large. Stresses and cracks occur due to fast drying. Figure 3.7 shows the surface morphologies of films deposited at 325°C with 1.4 ml/h and 4.2 ml/h flow rates of the precursor solution. Their morphologies both belong to type II. However, the film deposited using the lower flow rate looks slightly denser than that deposited using a higher flow rate. This can be attributed to a larger number of droplets deposited when the solution is fed using a higher flow rate. This results in faster formation of agglomerates. Therefore, films deposited with the low precursor flow rate (Figure 3.7a) contain less agglomerates and look denser than that deposited with the high flow rate (Figure 3.7b).

The PSD setup utilizes another type of atomizer, and consequently the precursor solution is supplied to the atomizer at quite a different flow rate. In the case of the air blast atomizer the flow rate typically ranges from 30 ml/h to 120 ml/h. Within this range of flow rates we have not observed any significant change in the morphology of the layer. The morphologies belong to type I. However, it should be noted that the probability of film cracking is much higher when the precursor solution is supplied at a flow rate of 120 ml/h.



Figure 3.7. Surface morphologies of YSZ films deposited using ESD setup at  $325^{\circ}$ C for 2 h with different flow rates: (a) 1.4 ml/h and (b) 4.2 ml/h. Precursor solution: 0.17 mol/l ZrCl<sub>4</sub> + 0.03 mol/l YCl<sub>3</sub>·XH<sub>2</sub>O ethanol (50 vol%) + butyl carbitol (50 vol%) solution.

Precursor solution flow rate had a smaller influence on the morphology of dense films, when the air blast atomizer was used for aerosol generation. However, this is not the case, when the ESD technique is used for the deposition of porous films. Chen et al. observed that the pore size increases with increasing flow rate of the precursor solution [7].

### 3.3.3 Type of salt

The extremely large choice of precursors is one of the advantages of the spray pyrolysis technique. The main requirements for the precursor salt are: a salt must be soluble in an alcoholic solvent or water, and it must decompose into an oxide at the deposition temperature. We have used chlorides, nitrates and metal-organic salts as precursors.

#### <u>Chlorides</u>

Chlorides have the following advantages: high solubility in ethanol (more than 0.5 mol/l) and low price. Unfortunately they are extremely chemically aggressive (especially zirconium chloride), and cause corrosion of the experimental setup. Also, part of the chlorine ions can remain in the deposited film, causing changes in the material properties. The chlorine impurities also hinder the crystallization of the initially amorphous thin film.



**(a)** 

**(b)** 

Figure 3.8. Surface morphology of YSZ films deposited using ESD setup at 325°C for 2 h with solutions of different chloride concentrations: (a) 0.2 mol/l and (b) 0.1 mol/l. Precursor solution:  $ZrCl_4 + YCl_3 \cdot XH_2O$  ethanol (50 vol%) + butyl carbitol (50 vol%) solution.

Figure 3.8 shows two films deposited with different concentrations of precursor solution. Their morphologies belong to type II. The influence of the concentration on the morphology is not significant. However, more agglomerates and slightly larger particles are present in the film deposited using the 0.2 mol/l solution (Figure 3.8a) compared to the 0.1 mol/l solution (Figure 3.8b). This small difference can be attributed to the spreading of droplets and to the fact that the particle size, after drying, increases with increasing concentration of the precursor solution. The spreading rate of the liquid droplet influences the roughness. Qualitatively, the spreading rate decreases with increasing viscosity. The droplets containing 0.2 mol/l of chlorides are more viscous and consequently spread slower than those containing 0.1 mol/l of chlorides. The spreading may not be completed if the simultaneous drying process proceeds rapidly, and this will result in an increased roughness. It follows that the concentration should not be too high for the deposition of dense, smooth films. On the other hand, a high salt concentration is desired to achieve high deposition rates. However, it is

not always favourable, because the surface roughness of the deposited film increases with increasing salt concentration in the precursor solution, as shown in Figure 3.8.

#### <u>Nitrates</u>

The main drawback of the chloride precursor was its corrosive action. Nitrates appear to be possible substitutes for the chlorides. The solubility of yttrium nitrate in ethanol is adequate. However, the zirconyl nitrate is poorly soluble in ethanol. We have used an ethanol and butyl carbitol (1:1) mixture as solvent. The maximum solubility of yttrium and zirconium nitrates in this solvent mixture is approximately 0.2 mol/l, which is much lower than in the case of chlorides, where solutions of 1 mol/l concentration can be prepared very easily.

The typical morphology of an YSZ film deposited using the ESD setup is shown in Figure 3.9. Obviously, the surface morphology is very different because different precursors are used. The type I morphology was never observed when the YSZ films were deposited with nitrate solutions using ESD technique. The reason is the very low solubility of the zirconium nitrate in the precursor solution, which leads to the precipitation of the solutes in a droplet due to the evaporation of solvent. It seems that landing droplets already contain precipitated particles. This either leads to a porous type III film morphology or a fractal-like type IV morphology.



Figure 3.9. Surface morphology (two magnifications) of an YSZ film deposited using ESD setup at  $325^{\circ}$ C for 2 h and nitrate solution of 0.1 mol/l nitrate. Precursor solution:  $ZrO(NO_3)_2 \cdot aq + Y(NO_3)_3 \cdot 6H_2O$  ethanol (50 vol%) + butyl carbitol (50 vol%) solution.

Surprisingly, quite different film morphologies were obtained using the PSD setup and the same nitrate solution (Figure 3.10). When the deposition temperature was too low, the

film was cracked (Figure 3.10a). At higher deposition temperature the film was crack-free and was of type I morphology. In contrast to the film deposited using the ESD setup (Figure 3.9b), no solid particles are present on the film surface (Figure 3.10b). The absence of particles on the surface can be explained by considering the effect of droplet size on evaporation. The air blast atomizer generates larger droplets than the electrostatic atomizer. Large droplets evaporate slowly, and consequently precipitation of the solute is hindered. It seems that droplets produced using the air blast atomizer were large enough to avoid the precipitation during aerosol transport. Droplets arriving at the substrate did not contain any precipitates. This favoured the formation of the type I morphology.



**(a)** 

**(b)** 

Figure 3.10. Surface morphology of an YSZ film deposited using PSD setup at different temperatures for 1 hour: (a)  $185^{\circ}$ C; and (b)  $265^{\circ}$ C. Precursor solution: 0.085 mol/l ZrO(NO<sub>3</sub>)<sub>2</sub>·aq + 0.015 mol/l Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O ethanol (50 vol%) + butyl carbitol (50 vol%) solution.

#### <u>Metal-organic salts</u>

The other substitutes for zirconium chloride are metal-organic salts. However, the higher cost of metal-organic salts is their main drawback. On the other hand, metal-organic salts have higher solubility in organic solvents. We have investigated the film morphology when using zirconium acetylacetonate, propoxide and butoxide precursors. As yttrium precursor Y chloride was used. The best results were achieved using zirconium acetylacetonate and yttrium chloride precursor solutions, as shown in Figure 3.11. Unfortunately, the maximum concentration of zirconium acetylacetonate in (1:1) ethanol and

butyl carbitol mixture is just 0.15 mol/l, and therefore unfavourable for the increasing of the deposition rate. It should be noted that, in contrast to the other zirconium precursors, zirconium acetylcetonate is also soluble in butyl carbitol. This explains the low number of particles on the film surface when the acetylacetonate precursor is used (Figure 3.11c), because the solute precipitation is very improbable in this case. The surfaces of the films deposited using zirconium propoxide (Figure 3.11a) or zirconium butoxide (Figure 3.12b) always contain a large number of incorporated particles. These particles may be formed on the surface due to solute precipitation and the slow spreading of impacted droplets.



Figure 3.11. Surface morphology of films deposited using different metal-organic precursor solutions: (a) 0.085 mol/l Zr propoxide + 0.015 mol/l YCl<sub>3</sub>·XH<sub>2</sub>O; (b) 0.085 mol/l Zr butoxide + 0.015 mol/l YCl<sub>3</sub>·XH<sub>2</sub>O; (c) 0.085 mol/l Zr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>4</sub> + 0.015 mol/l YCl<sub>3</sub>·XH<sub>2</sub>O; and (d) 0.085 mol/l Zr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>4</sub> + 0.015 mol/l YCl<sub>3</sub>·XH<sub>2</sub>O. ESD setup in (a), (b), (c); PSD setup in (d).

The best film was deposited using the PSD setup with a solution of 0.085 mol/l zirconium acetylacetonate and 0.015 mol/l yttrium chloride (Figure 3.11d). It can be seen that there are hardly any particles on the film surface, and the morphology is of type I. This can be attributed to the optimal droplet size distribution as in the previously discussed case of nitrate precursors. This leads to the conclusion that films of better quality are prepared when using the PSD set-up rather than the ESD set-up. Zirconium acetylacetonate is the best suited precursor for dense film deposition using the ESD technique.

#### 3.3.4 Solvent



Figure 3.12. Surface morphologies of YSZ films deposited using the PSD technique at different temperatures for 1 hour: (a)  $140^{\circ}$ C; (b)  $180^{\circ}$ C; (c)  $235^{\circ}$ C; (d)  $265^{\circ}$ C. Precursor solution: 0.085 mol/l Zr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>4</sub> + 0.015 mol/l YCl<sub>3</sub>·XH<sub>2</sub>O ethanol (50 vol%) + 1-methoxy-2-propanol (50 vol%) solution.

By changing the solvent, physical properties of the solution such as boiling point, solubility of salts, spreading behaviour of droplets on the substrate will change. Therefore, the type of solvent influences not only the maximum salt concentration, but also the deposition temperature, the optimal solution flow rate, and as a consequence the deposition rate. Chen et al. reported that it is necessary to use a solvent with a high boiling point in order to deposit a dense film [11]. However, the results shown in Figure 3.12 contradict the suggestion of Chen et al.. We have deposited dense films using the solvent 1-methoxy-2-propanol with a low boiling point (120°C) using the PSD setup. Using the same setup, but replacing the 1-

methoxy-2-propanol by butyl carbitol that has a boiling point of 230°C, the deposited film was still cracked at 210°C. At temperatures higher than 250° no cracks were observed. It follows that the boiling point of the solvent influences the lowest possible deposition temperature of the dense, crack free films. The lower the boiling point of the solvent, the lower the optimal deposition temperature will be.

#### **3.3.5** Deposition time

The effect of the deposition time on the film morphology deposited at 260°C is shown in Figure 3.13. The film was deposited using the ESD setup in the Taylor cone mode. After 45 minutes the layer looks dense with many particles on the surface, and belongs to the type II morphology. Increasing the deposition time to 300 minutes shifts the morphology of the film to type IV (very porous with agglomerates of small particles). This change of morphology is explained by considering the effect of droplet spreading. Most of the droplets arriving at the substrate are nearly dry. Therefore, they spread slowly and consequently discrete particles are formed on the surface. This leads to an increase in surface roughness, which enhances preferential landing and agglomeration. A charged droplet is more attracted towards more curved areas on the substrate surface, because of the local increase in the electric field. This effect is referred to as preferential landing. The morphology changes from type II to type IV as previously observed [11,21].



**(a)** 

**(b)** 

Figure 3.13. Influence of the deposition time for the Taylor-cone mode spraying using the ESD set-up. Film morphology after 45 min (a) and 300 min (b).

The influence of the deposition time on the film morphology deposited at 250°C using the PSD setup is shown in Figure 3.14. Contrary to the ESD setup, both films belong to the type I morphology indicating that the deposition time does not have a remarkable effect on the film morphology.



Figure 3.14. Influence of the deposition time for the film deposition using the PSD set-up. Film morphology after 60 min (a) and 300 min (b).

#### **3.3.6** Nozzle to substrate distance

Each nozzle has a spraying angle. Therefore, the nozzle to substrate distance determines the area coated and the deposition rate. The smaller distance of the atomizer to the substrate, the higher the deposition rate and the smaller the coated area. However, every experimental spray pyrolysis setup has an upper and lower limit for the distance to the substrate determined mainly by the type of atomizer and the substrate size. In the ESD setup, where a precursor solution is atomized using high voltage, the lower distance limit is determined by the substrate size. The upper limit is influenced mainly by the maximum voltage which is determined by the characteristics of the high voltage power supply unit and by the disruptive discharge voltage. However, electrostatic discharges in the ESD equipment usually occur before the maximum possible voltage is reached. These electric disruptive discharges lead to unstable liquid atomization or even worse, the liquid will not be atomized at all. Therefore, all components of the experimental equipment must be electrically well insulated in order to reduce the probability of discharge. The insulation in our ESD setup is

sufficient for a voltage up to 40 kV. At higher voltages, the atomization becomes inferior or unacceptable. This limits the maximum distance between the nozzle and the substrate to about 20 cm, because at larger distances the electric field strength will not be high enough to atomize the solution properly.

On the other hand, the PSD setup, where the precursor solution is atomized using an air stream, has other kinds of limitations. In this case, the minimal nozzle to substrate distance is limited not by the substrate size, but by the cooling effect of the air flow. At small distances pronounced cooling of the substrate occurs. Simultaneously, more heat is required from the heating plate, because the droplet mass flow density increases with decreasing distance. Consequently, at a critical distance of spray gun to substrate surface it will be impossible to reach the optimal deposition temperature. We have observed that all films were cracked up to the maximum attainable substrate temperature of 240°C, when the spray gun was at 20 cm distance from the substrate surface. After increasing the distance to 30 cm while keeping all other spray parameters constant, we have prepared crack free films already at 180°C. It follows that under these experimental conditions the lower distance limit is 30 cm. The upper limit is determined by the distance at which the spray pattern collapses. Generally, the maximum distance depends on spray gun parameters such as the geometry of atomizer and air pressure.

#### **3.3.7** Additives

It is well known that the morphology of a film can be tailored using additives in the precursor solution [17, 18]. To date little work has been reported on the influence of polymeric additives to the precursor solutions. We have chosen polyethylene glycol (PEG) as additive to modify the properties of the precursor solutions for yttrium-stabilized zirconia (YSZ) thin film deposition.

An aqueous precursor solution based on a mixture of zirconyl and yttrium nitrates was prepared according to the stoichiometry of the desired YSZ films. Solutions containing 1 wt% of polymer additives were also prepared. PEG of 6000 g/mol molecular weight was added to the precursor solution. The effect of polymer additives on the morphology of the YSZ films deposited on sapphire substrates, using water as solvent for 0.1 mol/l precursor solution, is shown in Figure 3.15. The presence of PEG in the precursor solution changed the film morphology from cracked to the crack-free (type I). This can be explained by the binding properties of polymers. A lower surface roughness implies that the polymer improves the spreading behavior of the droplets on the substrate. The results demonstrate a significant role of additives on the microstructure of the films.



Figure 3.15. SEM micrograph of YSZ films deposited using PSD by spraying different precursor solutions at 180°C on a sapphire substrate: A –without polymer additives, B –with PEG.

#### **3.3.8** Deposition rate

Film thickness can be measured using several methods such as spectroscopic ellipsometry, scanning electron microscopy (SEM), step measurement using profilometer, or quartz microbalance technique. Each method has advantages and drawbacks. Spectroscopic ellipsometry is unreliable for rough films. Quartz microbalance is an in-situ film thickness measurement technique. However, it turned out to be unsuitable for spray pyrolysis, because it would be difficult to achieve the same deposition conditions on a substrate and a quartz crystal. Thickness measurement by profilometer requires sharp steps between a film and a substrate - which is very difficult to achieve in the spray pyrolysis process. SEM analysis is the most reliable of all the techniques mentioned, but is time consuming. In this study, we chose the SEM method to measure film thickness, because no suitable and reliable alternative method was found.



Figure 3.16 SEM image of cross-section of an YSZ film deposited on Si wafer in two hours at 280°C by PSD technique. Precursor solution: 0.085 mol/l  $Zr(C_5H_7O_2)_4 + 0.015$  mol/l  $YCl_3 \cdot xH_2O$  ethanol (50 vol%) + butyl carbitol (50 vol%) solution. Nozzle to substrate distance: 44 cm. Air pressure: 0.75 bar. Solution flow rate: 30 ml/h.

Typical cross-section of an YSZ film on Si wafer after two hours of deposition by the PSD technique is shown in Figure 3.16. The thickness of smooth, homogeneous film was 70 nm. The dependence of film thicknesses on the deposition time is shown in the Figure 3.17. The film thickness increases linearly with deposition time. The film deposition rate of 35 nm/h was obtained by the PSD technique. The relatively low deposition rate is attributed to the exhaustion of the precursor solution during aerosol transport. Only a small fraction of the aerosol reaches substrate because many droplets are blown away from the substrate surface by the reflected air flow.



Figure 3.17 Deposition time versus thickness for YSZ film deposited at 280°C by the PSD technique. Precursor solution: 0.085 mol/l  $Zr(C_5H_7O_2)_4 + 0.015 mol/l YCl_3 xH_2O$  ethanol (50 vol%) + butyl carbitol (50 vol%) solution. Nozzle to substrate distance: 44 cm. Air pressure: 0.75 bar. Solution flow rate: 30 ml/h.

# 3.4 Summary

Two types of spray pyrolysis techniques, Electrostatic Spray Deposition (ESD) and Pressurized Spray Deposition (PSD), have been studied and applied to deposit YSZ films. Various film morphologies (from dense to fractal-like) were obtained using the ESD technique. The morphology was influenced by the deposition temperature, the type of precursor salt, the deposition time, and the type of solvent used. The PSD technique is more robust and offers an easier way to deposit dense films compared to the ESD technique. The morphology was influenced by the deposition temperature and the type of solvent as in the case of the ESD technique, but on the other hand the deposition time and the type of precursor salt did not have a significant effect. It was observed that polymer additives to the precursor solution can hinder the cracking of films.

The main parameter that determines the film morphology is the substrate temperature. The higher the temperature, the more particles occur on the surface and the film becomes rough. The film will be very porous at too high a deposition temperature. We have shown that dense films can be deposited using solvents with rather low boiling points at lower temperatures than using the solvent with the higher boiling point. Using ESD, dense films were deposited only by spraying the zirconium acetylacetonate precursor solution. In the case of PSD, dense films were deposited using zirconium acetylacetonate or zirconium nitrate solutions.

# **3.5** References

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# **4** A model for film deposition by spray pyrolysis

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#### Abstract

The process of spray pyrolysis deposition of thin YSZ films using either electrostatic or air blast liquid atomization techniques was investigated. The transport and evaporization of droplet was examined using Phase Doppler Anemometry. Droplets smaller than 10  $\mu$ m dominated the number distribution in both of the techniques. Volume distributions, however, were dominated by droplets larger than 10  $\mu$ m. The droplets size on their flight from the nozzle to the substrate did not change significantly except very near the heated substrate. Significant droplet evaporation started at 1 cm distance in front of the substrate. Combining experimental evidence from spray pyrolysis process with SEM observations, a model for film growth is proposed. The large droplets (> 10  $\mu$ m) control the result of the deposition process. Accordingly, the substrate temperature is a decisive parameter. Too low a temperature leads to cracked films, whereas temperatures above a certain limit, cause rough films with powder particles on the surface to be produced.

# 4.1 Introduction

Due to its chemical and thermal stability and its high oxygen ion conductivity at high temperatures, yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte material in Solid Oxide Fuel Cells (SOFCs) [1]. Various thin film deposition techniques have already been applied to YSZ, including deposition techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD) and spray pyrolysis [2].Spray pyrolysis provides the possibility of producing thin films in the thickness range of 1–10  $\mu$ m at high deposition rates. The simplicity of the process, low cost of the equipment, and a wide choice of precursors are the advantages this technique offers [3].

Little is known about the film growth mechanism during spray pyrolysis. In many studies it was claimed that close to the substrate a CVD-like process would take over and lead to the formation of dense films. This means that the droplets are vaporized in the vicinity of the substrate and the vapour deposits on the substrate [4, 5]. On the other hand, Matsuzaki et al. found experimental evidence incompatible with such a CVD like process [6]. Chen et al. concluded that the morphology of the film deposited by electrostatic spray deposition (ESD) is determined by the size of the incoming droplets, the deposition temperature, the rate of droplets spreading on the substrate, and the solution chemistry [7]. Ruiz et al. stated the importance of the droplet size to the properties of the deposited film [8]. Various film growth models were proposed, and in all of them the deposition temperature and the droplet size plays the dominant role for the film quality. A lack of detailed knowledge regarding the growth of films by spray pyrolysis methods prevails.

Frequently, ultrasonic, air blast, and electrostatic atomizers are used to produce the droplets. In the present study we have compared air blast and electrostatic atomizers. The experimental set-ups were described in the previous paper [9]. The spray pyrolysis set-up utilizing the electrostatic atomizer was called the Electrostatic Spray Deposition (ESD). The set-up with air blast atomizer here will be called the Pressurized Spray Deposition (PSD). The influence of process parameters on the droplet size and velocity distribution were investigated using a Phase Doppler Anemometer (PDA) for both methods. PDA systems can perform non-intrusive measurements of the particle size at any chosen location of a spray cone. Droplet evaporation during the transport to the substrate can thus be investigated.

The morphology and the composition of the deposited films will be analyzed using a scanning electron microscope (SEM) equipped with an energy depressive X-ray (EDX) detector.

# 4.2 Experimental setup

YSZ films were deposited by spraying a solution containing the precursor onto a heated substrate. Yttrium chloride (YCl<sub>3</sub>·6H<sub>2</sub>O) (Aldrich Chemicals, Buchs, Switzerland) and zirconium acetylacetonate ( $Zr(C_6H_7O_2)_4$ ) (Fluka Chemie, Buchs, Switzerland) were dissolved in a 50:50 vol.% mixture of ethanol ( $C_2H_5OH$ ) (Fluka Chemie, Buchs, Switzerland) and diethylene glycol monobutyl ether (butyl carbitol) ( $C_8H_{18}O_3$ ) (Fluka Chemie, Buchs, Switzerland). The precursor solution was prepared according to the stoichiometry of ( $ZrO_2$ )<sub>0.92</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub> films. The total salt concentration in the solvent mixture was either 0.1 or 0.01 mol/1. The films were deposited on substrates of 0.075 mm thick Inconel 600 foil (Goodfellow, UK) with circular samples of 30 mm diameter. The foil was drawn in to the surface of a heated aluminium plate by the means of a vacuum pump.

Film deposition was carried out using either the PSD or the ESD setup. In the PSD setup, the spray gun was located 310 mm above the substrate. The nozzle in the ESD set-up was located 60 mm below the substrate and the spray direction was upwards to avoid instabilities in the electrostatic atomization process, as these could produce large droplets which tend to impair the homogeneity of the film. Two sizes of steel needles were used as nozzles, with inner diameter of 0.6 mm and 2.0 mm respectively. The smaller needle was used for the multi-jet mode, the larger one for the Taylor cone mode of the electrostatic atomization.

The experimental set-up is shown in Figure 4.1. A Phase Doppler Anemometer (TSI, USA) was used to measure droplet sizes and velocities in the spray. The point of measurement is defined by the intersection of laser beams. The optical transmitter and receiver are coupled and traversed together, moving the location of the optical probe for a spatial mapping of the particle size distributions at any chosen location in the spray cone. Data for traverse profile along the long spray cone axis was collected. The size of the smallest particles that can be measured is limited by the amount of light that is scattered by very small particles. Typical limits for conventional PDA configurations are 1  $\mu$ m at the lower end and 1 mm at the upper end.

The temperature distribution between nozzle and substrate is measured by a thermocouple (K-type). The morphology of the deposited films was investigated using SEM (LEO 1530). Information about the homogeneity and chemical composition of the film was obtained by EDX analysis.



Figure 4.1 Schematic drawing of spray characterization using PDA.

# 4.3 Results

#### 4.3.1 Pressurized Spray Deposition

An air blast atomizer is a part of the pressurized spray deposition (PSD) setup. This type of atomizer employs high speed air to produce an aerosol. The air pressure has a significant influence on the droplet size distribution as demonstrated by Figure 4.2. Generally, the higher the air pressure, the smaller the droplets. By increasing the air pressure from 0.75 bar to 1.75 bar, the size of the largest detected droplets was reduced from 50  $\mu$ m to 20  $\mu$ m, simultaneously the size distribution narrows. The spray quality therefore increases with increasing air pressure.



Figure 4.2. Influence of the air pressure on the droplet size distribution. Precursor solution flow rate: 30 ml/h.

However, with increasing air pressure the cooling of the substrate is also increased. In the case of 1.75 bar air pressure, the maximum achievable substrate temperature with the heating system (heating plate CERAN 500) was 180°C. This temperature was certainly too low to obtain crack-free films when spraying the standard ethanol-butyl carbitol precursor solution. We have observed that 250°C is the minimum deposition temperature for crack-free films in the case of this solvent mixture. Therefore, the air pressure of 0.75 bar was chosen for the atomization of the ethanol-butyl carbitol solution, in spite of the spray quality being lower than with an air pressure of 1.75 bar. Increasing the distance between spray gun and substrate reduces the cooling effect. Simultaneously, the deposition rate is also reduced and the area coated is enlarged. The area coated can also be increased by enlarging the spray angle of the atomizer.



Figure 4.3. Mean droplet diameter and droplet number fraction of the pressurized spray with respect to the radial distance. Flow rate: 30 ml/h, distance to substrate: 210 mm.



**Figure 4.4.** Number and volume distribution of droplets in the PSD setup at the centre of the spray cone at 270 mm distance to the substrate. Precursor solution flow rate: a) 30 ml/h and b) 120 ml/h.

The droplet number fraction with respect to the radial distance from spray cone axis is shown in Figure 4.3. The number of droplets decreases in radial direction away from the spray cone axis. Usually, most of the droplets fly along the centre of the spray cone. The droplet diameter hardly changes with the radial position in the spray cone, the droplet number fraction decreases rapidly with the radius. No droplets were detected at distance larger than 70 mm from the central cone axis, thus all droplets were within a 70° spray cone angle. However, half of the droplets are concentrated within the very small angle of 12°. Such a small spray angle is typical for air blast atomizers.

Usually, the solution flow rate has a small influence on spray characteristics in the case of an air blast atomizer. The chosen flow rate of the precursor solution was either 30 ml/h or 120 ml/h. The droplet size distribution on the central axis at 270 mm distance to the substrate for both solution flow rates is shown in Figure 4.4a and 4.4b. Approximately 90% of the droplets are smaller than 10  $\mu$ m in both cases. On the other hand, the small fraction of large droplets dominates the volume size distribution: the droplets larger than 10  $\mu$ m are carrying roughly 80% of the solution volume for both flow rates. It can be concluded that the solution flow rate does not effect significantly the droplet size distribution.



Figure 4.5. Mean velocity of the droplets with respect to the distance from the substrate at various substrate temperatures (PSD setup).

The droplets generated are carried to the heated substrate by the air flow. The droplets have the highest velocity at the outlet of the atomizer, as shown in Figure 4.5. During transportation to a substrate, the mean velocity of droplets decreases due to the retarding Stokes and thermophoretic forces. The thermophoretic force is proportional to the temperature gradient. The air temperature increases steeply due to the forced convection cooling effect of the air flow close to the substrate as shown in Figure 4.6. It follows that the Stokes force has

the main retarding effect far from the substrate and at a distance of 5 mm from substrate the thermophoretic force begins to dominate.



Figure 4.6. Air temperature gradient for substrate temperatures 210°C, 250°C and 310°C (pressurized spray).



Figure 4.7. Mean droplet diameter along the central axis with respect to the distance to the substrate (PSD setup, flow rate 30 ml/h).

The droplet size also changes along the central spray axis due to the increasing air temperature when the droplets are approaching the heated substrate. The mean droplet diameter along the central spray axis at several substrate temperatures is shown in Figure 4.7. The droplet diameter hardly changes with the distance from the nozzle in the range of 70 to

10 mm towards the substrate. Within the last 10 mm, a steep increase in droplet diameter was measured. This increase in droplet size is based on two effects. Close to the substrate the air temperature increases steeply (see Figure 4.6) and in addition the mean velocity of the droplets decreases when they approach the substrate (see Figure 4.5). Both effects lead to higher droplet temperatures and to evaporation of the droplet fraction. A significant evaporation of solvent occurs only in the last centimetre before the droplets hit the substrate. The small droplets (< 10  $\mu$ m) evaporate quickly and eventually vanish from the statistics, because particles smaller than 1  $\mu$ m are no longer detected. In contrast, the large droplets (> 10  $\mu$ m) evaporate slowly and continue to be detected by PDA. Therefore the mean diameter increases and does not decrease as would be expected.

It follows that the small droplets (smaller than 10  $\mu$ m) can be ignored in the film growth model, because they contain only 20% of precursor and evaporate rapidly causing only nm-sized particles on the film surface. Only the large droplets (larger than 10  $\mu$ m) arrive on the substrate surface in a liquid state and can spread on it and consequently form a film.

#### 4.3.2 Multi-jet mode of electrostatic spray deposition

In the ESD set-up a precursor solution is atomized by means of an electric field instead of a pressurized air flow as used in the PSD set-up. Depending on spray parameters, various spraying modes of ESD system are obtained, resulting in very different droplet size distributions. Cloupeau et al. proposed a classification of these modes [10]. The multi-jet mode is among them. In this mode the liquid is distorted at the tip of the tube type nozzle into many jets of very small diameter as shown in Figure 4.8. Every jet emits charged droplets. In the multi-jet mode the number of jets increases with increasing voltage.

The distance between the nozzle and the substrate was kept at 60 mm. Deposition experiments in the multi-jet mode were carried out at a precursor solution flow rate of 2.8 ml/h. A potential of 10 kV was applied between the nozzle and the substrate. The PDA measurement in the centre of spray cone at a distance of 50 mm to the substrate shows a droplet size distribution similar to that for the pressurized spray (Figure 4.9). As in the case of the PSD set-up (Figure 4.4), more than 90% of all droplets are smaller than 10  $\mu$ m. The small fraction of large droplets dominates the volume distribution and carries 85% of sprayed solution.



Figure 4.8. Multi-jet mode of electrostatic spray deposition.



**Figure 4.9.** Number and volume distribution of droplets in the multi-jet mode of ESD at a 50 mm distance to the substrate in the centre of spray cone. Solution flow rate: 2.8 ml/h.

The spray angle is much larger than in the PSD technique when a solution is sprayed using the ESD technique in the multi-jet mode. The radial distribution of the mean droplet diameter at 50 mm distance to the substrate is shown in Figure 4.10. Most of the droplets are within a 45° spray angle, which is much wider than the 12° of the air blast atomizer. Different from the PSD setup, the mean droplet size is lower in the centre of the spray cone than in the peripheral region.



**Figure 4.10.** Mean droplet diameter and droplet number fraction of the multijet mode of ESD with respect to the radial distance. Solution flow rate: 2.8 ml/h, distance to substrate 50 mm.

The mean droplet diameter, along the central spray axis, changes in a manner similar to that in the PSD set-up (Figure 4.11). It is more or less constant up to a distance of 10 mm from the substrate. Then the mean droplet diameter increases steeply which can be explained by the same arguments as in the case of the PSD setup. The air temperature gradient resembles the one for the pressurized spray mode as shown in Figure 4.12. In front of the substrate the temperature rises fast. In the ESD setup the gradient is somewhat less pronounced than in the PSD system, because there is no air flow cooling the plate. The mean droplet velocity of the multi-jet mode of ESD is shown in Figure 4.13. The mean velocity of the droplets along the centre line of the spray also decreases as they approach the substrate, analogous to the case of the PSD setup. However the velocity close to the substrate is higher than the velocity of the pressurized spray (Figure 4.5). This is due to the fact that the droplets are still accelerated by the external electric field between nozzle and the heating plate.



**Figure 4.11.** Mean droplet diameter along the central axis of spray cone for several deposition temperatures (multi-jet mode of ESD).



Figure 4.12. Air temperature distribution for substrate temperatures: 195°C, 255°C, 310°C and 365°C (multi-jet mode of ESD).

It can therefore be concluded that in the case of the ESD multi-jet mode, the generated droplet size distributions are similar to that of the PSD set-up. Compared to the PSD set-up, the spray angle is much larger in the case of ESD and also the velocity of the droplets landing is significantly larger.



**Figure 4.13.** Mean velocity of the droplets along the centre of the spray cone for different substrate temperatures (multi-jet mode of ESD).

#### 4.3.3 Cone-jet mode of ESD

The cone-jet mode is the other important mode of ESD suitable for thin film deposition. In the cone-jet mode the convex shape of the liquid surface at a capillary is normally distorted by the electric field to form a conical shape (Taylor cone). This cone is extended at its apex by a permanent jet of very small diameter (see Figure 4.14). The spray consists of charged mono-dispersed droplets travelling in the electric field from the capillary to the grounded substrate.

The cone-jet mode of the ESD setup allows the generation of nearly mono-sized extremely small droplets. The solution flow rate for the cone-jet mode had to be 5.7 ml/h for the 0.1 mol/l solution and 1.4 ml/h for the 0.01 mol/l solution to obtain a stable spray. The applied potential was 6.9 kV for both concentrations. The distance between the nozzle and the substrate was 60 mm. The conductivities of the 0.1 mol/l and 0.01 mol/l precursor solutions

were 200  $\mu$ S/cm and 60  $\mu$ S/cm respectively. These values are much larger compared to 0.5  $\mu$ S/cm of the pure solvent mixture. Following Ganan-Calvo et al. [11] the droplet size *d* is reciprocally proportional to the electric conductivity of the liquid *K* with an exponent of 1/6 for the cone-jet mode:

$$d = 3.78\pi^{-2/3} \mathbf{Q}^{1/2} \left(\frac{\rho \varepsilon_0}{\gamma \cdot \mathbf{K}}\right)^{\frac{1}{6}} f_b$$
(4.1)

where  $\gamma$  is the liquid-gas surface tension,  $\rho$  the density,  $\varepsilon_0$  the electrical permittivity of vacuum, Q the flow rate, and  $f_b$  the nondimensional radius of the jet at the break-up point. High conductivity leads therefore to very small droplets in this mode.





The droplet size distributions for the two sprayed solutions are shown in Figure 4.15. Measurements were taken 50 mm away from the substrate on the center axis of the spray cone. For both concentrations of precursor solutions very similar droplet size distributions were found. This can be attributed to the close values of solution conductivities. No droplets larger than 7  $\mu$ m were detected. The distribution seems to drop to zero for droplets smaller than 0.5  $\mu$ m but this is due to the limitation of the PDA system as mentioned earlier. In the case of droplet sizes around 1  $\mu$ m and smaller, the amount of light scattered falls below the detection limit, therefore many droplets simply do not appear in the statistics because they are too small to be detected. No droplets can be detected by the PDA at the distance closer than 30 mm to the substrate. Therefore the only plausible conclusion is that the solvent is almost

evaporated on the way to the substrate and the droplets are too small to be detected if they still exist.



**Figure 4.15.** Droplets size distribution in the cone-jet mode of ESD at a 50 mm distance to substrate. Solution flow rate: 1.4 ml/h, precursor concentrations: 0.1 and 0.01 mol/l.



Figure 4.16. SEM images of YSZ films deposited using the cone jet mode of ESD. Precursor concentration: (a) 0.1 mol/l and (b) 0.01 mol/l.

The films deposited using the cone jet mode exhibit many small particles on the surface. Their size ranges from 35 nm to 100 nm. The film deposited by spraying the 0.1 mol/l precursor solution appears porous, as shown in Figure 4.16a. This indicates that the landing droplets were nearly dry and therefore did not spread out on the substrate. In the case of spraying the 0.01 mol/l solution in the cone-jet mode, also many small particles (50 nm to 100 nm in diameter) are observed, as shown in Figure 4.16b. Surprisingly, there is no large

difference in the particle sizes for both precursor solutions. The particle size after drying should increase with the concentration of the precursor solution because the size of initial droplets was similar. This indicates that the droplets of the 0.1 mol/l solution were disrupted and made smaller, otherwise the particles on the film surface would be ten times larger than in the case of spraying the 0.01 mol/l solution. A charged droplet disrupts into smaller droplets when maximum charge density is reached due to solvent evaporation. Therefore it is concluded, that the Taylor cone mode is less suitable than the multi-jet mode for the deposition of dense films.

#### 4.3.4 Comparison of PSD and ESD systems

The characteristics of the spray of the PSD and the ESD multi-jet mode are very similar. The droplet size distribution contains a large number of droplets smaller than 10  $\mu$ m and few larger droplets between 10 and 100  $\mu$ m (Figures 4.4a and 4.9). However, these large droplets dominate the size distribution by volume. Due to the high temperatures close to the substrate most of the small droplets evaporate and are deposited as particles whereas the big droplets arrive as liquid on the substrate. The remaining solvent of the big droplets evaporates after deposition on the substrate forming the YSZ film. The solute in the small droplets can form particles due to precipitation. The experiments consistently show cracks in the film structure for both systems. These can be avoided, only if the substrate temperature is 250°C or higher.

The thermophoretic forces play an important role in droplet transport. These forces retard the droplets during their flight. Droplets are pushed away from a hot surface, because the gas molecules from the hotter side of the droplet rebound with higher kinetic energy than those from the cooler side. The thermophoretic force can be written as:

$$F_{t} = \frac{3\pi \cdot \eta_{a}^{2} r}{\rho_{a}} \cdot \frac{3\kappa_{a}}{2\kappa_{a} + \kappa_{d}} \cdot \frac{\operatorname{grad}(T_{a})}{T_{a}}$$
(4.2)

where  $\kappa_a$  and  $\kappa_d$  are thermal conductivities of the air (about 0.025 Wm<sup>-1</sup>K<sup>-1</sup>) and the droplet (about 0.19 Wm<sup>-1</sup>K<sup>-1</sup> for ethanol) respectively,  $\eta_a$  is the viscosity of air (about 2.2·10<sup>-5</sup> N s m<sup>-2</sup>), r is the droplet diameter,  $\rho_a$  is the density of the air (1.29 kg m<sup>-3</sup>), and  $grad(T_a)$  is the thermal gradient of air. The effect is more pronounced the higher the thermal gradient in front of the substrate is. Obviously, in the case of the PSD setup, the thermophoretic forces close to the substrate are much stronger than for the ESD setup. For example, it can be calculated from Figures 4.6 and 4.12 that at a substrate surface temperature of 250°C and a distance of 2 mm to the substrate the thermal gradient is equal 20 K/mm for the ESD setup and 100 K/mm for the PSD setup. In Figure 4.17 the droplet diameters for both systems versus their velocities are shown as measured with the PDA system. In case of the ESD only positive velocities occur whereas in case of the PSD setup with much higher thermal gradients also negative velocities occur. Therefore, in the case of the PSD setup as shown in Figure 4.17b, many droplets are blown away from the substrate surface because the thermophoretic force is stronger than for the electrostatic setup. No droplets with the negative velocity were detected in case of the electrostatic atomization, because the electric field helps to overcome retarding forces. This explains why in the case of ESD the overspray is much smaller compared to PSD.



Figure 4.17. Thermophoresis effect at 3 mm distance to the substrate. a) ESD setup, b) PSD setup.

# 4.4 Analysis of the deposited films

The films deposited by the ESD and the PSD techniques were examined with a Scanning Electron Microscope (SEM) (LEO 1530) equipped with an EDX detector. The films were deposited on Inconel 600 (Ni72/Cr16/Fe8) substrates. The film deposited using the PSD setup at the lowest substrate temperature of 210°C showed some cracks (Figure 4.18a) whereas the films at a substrate temperature of 250°C and 300°C were very smooth and crack-free (Figure 4.18 b and c).

Although it is difficult to recognize the deposited YSZ film on the SEM images (Figure 4.18 a, b, c), the EDX linescans (Figure 4.18 d, e, f) prove that an YSZ film is present on the substrate surface. In the case of the cracked film, a large variation in the element counts is observed due to the inhomogeneous film morphology, as shown in Figure 4.18d. In every case the substrate exhibited lower counts of zirconium and higher counts of nickel in the crack area. In the case of the crack-free and smooth films, the variation of zirconium counts was much smaller.

The films deposited using the multi-jet mode of ESD were similar in behaviour to those of the PSD set-up. The film deposited at 195°C is cracked (Figure 4.19a). Cracked films occured therefore using two different spray pyrolysis set-ups at the same deposition temperature. The EDX element line scans also look very similar (Figure 4.18d and 4.19e). As can be seen in Figure 4.19b the cracks disappeared when the film was deposited at a substrate temperature of 255°C. This value is very close to the deposition temperature of crack-free films when using the PSD set-up. However, at higher deposition temperature, different film morphologies are obtained when using the ESD set-up. In contrast to the PSD set-up, many particles were observed on the film surface when the film was deposited at 310°C using the ESD set-up (Figure 4.19c). At the deposition temperature of 365°C, the film surface becomes rough and powdery because the evaporation of solvent is too fast. The EDX element line scans prove that the YSZ film is formed in the deposition temperature range 195°C to 365°C, as shown in Figures 4.19e, f, g, h. The smallest number of zirconium counts was obtained at the highest deposition temperature due to the rough and powdery film surface.

It can be concluded that the transition from cracked to crack-free films takes place at the same deposition temperature independently of the spray pyrolysis set-up used. The number of particles on the film surface increases with increasing substrate temperature in the case of the ESD.



Figure 4.18. SEM images and EDX line scans of the YSZ films deposited using PSD setup at a various substrate temperatures: (a/d) 210°C, (b/e) 250°C, (c/f) 300°C. Solution flow rate of 30ml/h.



**Figure 4.19.** SEM images and EDX line scans of the YSZ films deposited using the multi-jet mode of ESD at substrate temperatures of: (a/e) 195°C, (b/f) 255°C, (c/g) 310°C, and (d/h) 365°C.

# 4.5 Decomposition of the salt solutions

After a droplet spreads on the surface of the substrate, the solvent evaporates and the salt precipitates from the solvent. The salt then melts and decomposes. Stryckmans et al. provided a model for magnesium acetylacetonate (Mg(C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>) decomposition [12]. After melting at 265°C, Mg(C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> dissociates in a gaseous organic residue  $\beta$ -diketone (C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>) and a liquid compound containing magnesium (MgC<sub>3</sub>H<sub>7</sub>O<sub>2</sub>):

$$Mg(C_5H_7O_2)_2 \rightarrow MgC_5H_7O_2|_{liquid} + C_5H_7O_2\uparrow$$

It was observed that the dissociation of  $Mg(C_5H_7O_2)_2$  is similar in air and in nitrogen up to 450°C. At higher temperatures different decomposition pathways are followed. The compound containing magnesium slowly degrades to form MgO and organic residues under reducing conditions at 500°C. It was observed that the MgC<sub>5</sub>H<sub>7</sub>O<sub>2</sub> liquid phase in nitrogen atmosphere is partially volatilized between 290°C and 600°C allowing chemical vapour deposition (CVD) of MgO. Under oxidizing atmosphere, the total decomposition to MgO occurred already at 470°C without a CVD process. It follows that the mechanism of salt decomposition depends on the gas atmosphere.

Little information is available in the literature about the decomposition reaction of zirconium acetylacetonate. Wang et al. investigated the decomposition of  $Zr(C_5H_7O_2)_4$  from 40°C to 500°C by infrared (IR) spectrometry and thermogravimetry (TG) [13]. The weight loss of the zirconium acetylacetonate in air was divided into three stages: 110-187°C, 187-245°C and 245-440°C. The results from IR spectrometry suggested that all acetylacetone structures decompose completely at 310°C. Analysis by TG and IR spectrometry revealed that  $Zr(acac)_4$  does not sublime at atmospheric pressure and the decomposition is complete at 440°C.

Dyukov et al. [14] divided the decomposition of  $Zr(C_5H_7O_2)_4$  also into three stages as in the previous study of Wang et al. [13]. In the first stage (100°C-200°C), one ligand of acac was liberated with weight loss of 18.9%. Two subsequent stages (200°C-400°C and 400°C-470°C) are either wider or narrower compared to the Wang et al. study.

We have observed a different  $Zr(C_5H_7O_2)_4$  d decomposition process compared to the Wang and Duykov studies. Figure 4.20 shows the DTA-TG analyses for zirconium acetylacetonate at a heating rate of 10°C/min in air. The TG curve shows that  $Zr(C_5H_7O_2)_4$  is thermally stable up to 170°C. The first mass loss between 170°C and 257°C occurs through a

fast process with a mass loss of 39%. The observed weight loss is attributed to the loss of two  $\beta$ -diketone (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) molecules. The DTA curve in this temperature range reveals the endothermic peak at 215°C due melting of zirconium acetylacetonate. It follows that in the first stage zirconium acetylacetonate dissociates in two gaseous  $\beta$ -diketone (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) molecules and a liquid compound containing zirconium (Zr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>):

$$Zr(C_5H_7O_2)_4 \rightarrow Zr(C_5H_7O_2)_2 \mid_{\text{liquid}} + 2C_5H_7O_2 \uparrow$$

The zirconium acetylacetonate decomposes in the same manner as magnesium acetylacetonate. Further decomposition of the  $Zr(C_5H_7O_2)_2$  liquid involves many processes that occur simultaneously. Several overlapping exothermic peaks between 257°C and 500°C are visible. The strong exothermic peak between 425°C and 450°C accompanied by a fast mass loss refers to formation of  $ZrO_2$ . Simultaneously between 257°C and 500°C the solidification of the  $ZrO_2$  from the  $Zr(C_5H_7O_2)_2$  containing melt due to its decomposition, and crystallization takes place. The data obtained from thermal analysis confirm that the decomposition of the zirconium acetylacetonate is completed at 500°C.



**Figure. 4.20.** Thermal analysis curves of zirconium acetylacetonate  $Zr(C_5H_7O_2)_4$  decomposition in air at a heating rate of 10°C/min.

In nitrogen atmosphere, the zirconium acetylacetonate decomposition involves more stages and is complete at much higher temperature compared to the decomposition under an oxidizing atmosphere [15]. The decomposition starts at 150-200°C with the release of two  $C_{3}H_{4}$  after the reaction:

$$Zr(C_5H_7O_2)_4 \rightarrow Zr(CH_3COO)_2(C_5H_7O_2)_2 + 2C_3H_4$$

The formed complex of zirconium acetate and acetylacetonate formed decomposes to  $ZrO(CH_3COO)_2$  at 340°C. At 450°C,  $ZrOCO_3$  is formed as follows:

$$ZrO(CH_3COO)_2 \rightarrow ZrOCO_3 + CH_3COCH_3$$

Finally, at 800°C the decomposition is completed and ZrO<sub>2</sub> is formed:

$$ZrOCO_3 \rightarrow ZrO_2 + CO_2$$

It follows that, under a nitrogen atmosphere, temperatures approximately 300°C higher are necessary to decompose the zirconium acetylacetonate to zirconium oxide, compared to decomposition in the air.

To estimate the minimum deposition temperature we measured the weight loss of the precursor solution with increasing temperature. Thermogravimetry curves recorded for a pure solvent mixture (ethanol and butyl carbitol) and the solvent mixture with dissolved zirconium acetylacetonate at 10°C/min in air atmosphere are shown in Figure 4.21. The curves indicate that the solvent mixture without dissolved salt evaporates via two weight loss processes peaking at 75°C and 175°C. The first process at 75°C can be attributed to ethanol evaporation. The butyl carbitol has the highest evaporation rate at 175°C and is evaporated completely below 200°C, although the boiling point of the pure butyl carbitol is at 230°C. When zirconium acetylacetonate is added to the solvent mixture, the precursor solution decomposes via three weight loss processes peaking at 58°C, 117°C and 163°C. This means that the solvents start to evaporate at slightly lower temperatures. The process at 117°C can be attributed to the decomposition of  $Zr(C_5H_7O_2)_4$ , which seems to be completed at 200°C.

It can be concluded that acetylacetonates decompose via a melting phase and the further decomposition route depends on the gas atmosphere. When  $Zr(C_5H_7O_2)_4$  is dissolved in ethanol and butyl carbitol mixture, it decomposes to  $ZrO_2$  at a much lower temperature compared to the decomposition of solid  $Zr(C_5H_7O_2)_4$ .



Figure. 4.21. Thermogravimetry (TG) of solvent and precursor solution decomposition in air at a heating rate of 10°C/min.

# 4.6 Film growth model

#### 4.6.1 Summary of the spray parameter study

The spray parameter study was presented earlier in chapter 3. Here a short summary is given in order to derive a model for the film deposition process. It was observed that the influence of a spray parameter on the film morphology depends on the spray pyrolysis setup. In the case of the ESD technique, the film morphology was influenced by the deposition temperature, the type of precursor salt, the deposition time, and the type of solvent. The main parameter that determined the film morphology was the substrate temperature. The number of particles on the surface increased with increasing deposition temperature. Finally, at the highest deposition temperature, the film morphology changed to very porous or fractal like.

The morphology was also influenced by the deposition temperature and the type of solvent in the case of the PSD technique. However, in contrast to the ESD, the deposition time and the type of precursor salt did not have a significant effect. Polymer additives to the precursor solution suppressed somewhat crack formation at low substrate temperatures.

It was demonstrated that cracking of films occurs at lower substrate temperature when solvents with rather low boiling points are used instead of solvents with higher boiling points. Using the ESD setup, the best quality films were prepared only by spraying the zirconium acetylacetonate precursor solution. In the case of the PSD, dense films of good quality were deposited not only using zirconium acetylacetonate precursor, but also by spraying zirconium nitrate solution.

#### 4.6.2 Model for film deposition

Spray pyrolysis involves many processes occurring either simultaneously or sequentially. The most important of these are aerosol generation and transportation, droplet impact with consecutive spreading and precursor decomposition. Based on the above results and observations, a film growth model will be proposed. We will divide the spray pyrolysis process into two stages: before and after droplet impact onto the substrate. In the first stage,

the processes occurring during the droplet transport will be taken into account. In the second stage, film formation on the substrate surface will be considered.

In the first stage, the droplets are transported from the nozzle to the heated substrate. Solvent evaporation is the most important process at this stage. PDA measurements indicated that significant evaporation takes place predominantly in the last 10 mm before the substrate is reached (Figures 4.7 and 4.11). The largest droplets (larger than 10  $\mu$ m) play a more important role than the small ones, because they contain most of the precursor salt (Figures 4.4 and 4.9). Therefore, deposition temperature should be optimized for the large droplets. Additionally, the large droplets evaporate much slower compared to the small ones. Droplets with an initial size larger than 20  $\mu$ m in diameter do not change in size significantly until they impact onto the substrate. Therefore, in the case of large droplets, powder formation or solute precipitation during the droplet transportation is improbable. Droplets with initial size smaller than 3  $\mu$ m in diameter behave differently. Their solvent evaporates completely before reaching the substrate surface. Therefore, they will increase surface roughness and will not make significant contributions to the growth of a dense film as shown in Figure 4.16. The presence of many almost dry droplets in the spray leads to porous and rough films or powder only.



Figure. 4.22. Droplet impact onto a heated substrate.

The first stage ends when a droplet impacts onto the substrate. The five possible results of droplet impact are shown in Figure 4.22. A droplet hitting the surface may stick, rebound, spread or splash on the surface. The spreading of impacted droplets can lead to the formation of a dense film or to rings. The sequence after the droplet has hit the surface depends on its size, viscosity and velocity. If droplets are too small they will rebound due to the retarding thermophoretic forces which are strongest close to the substrate, where the temperature gradient is largest. If they are too viscous or dry, they will stick and if they are too fast, they will splash. If the droplets spread but the velocity is too high, rings are formed.

Consequently, only the spreading of droplets with not too high a velocity will lead to the formation of a dense film.

After droplet impact, the second stage of spray pyrolysis starts. Then the physical and chemical properties of a precursor solution play an important role. In this stage, the spreading of the impacted droplet, the evaporation of residual solvent and precursor decomposition to the oxide take place simultaneously. Fast spreading of droplets leads to the formation of smooth films. The substrate should provide enough heat and temperature for solvent evaporation and salt decomposition. If this is not the case, cracks will develop due to liquid film contraction upon drying. The contraction of a spread droplet on the surface leads to a build-up of stress in the still liquid but viscous film, and when the stress exceeds the local tensile strength, the film fractures (Figures 4.18a and 4.19a). When the impacting droplet contains just sufficient amount of solvent, it spreads over the substrate surface and forms a disk shaped splat. Simultaneously, the zirconium acetylacetonate melts and decomposes to oxide (Figures 4.21 and 4.22). With increasing temperature, the impacting droplets contain less solvent. These nearly dry droplets will stick on the substrate without spreading, and consequently more particles will occur on the film as shown in Figures 4.19b and 4.19c. Finally, at too high deposition temperatures, the solvent of the droplets evaporates before the droplet reached the substrate, and, as result, powder will be obtained.

It can be concluded that the crucial points in our model is to avoid complete solvent evaporation in the droplet during transportation, because this leads either to powder formation or deposition of rough films, and to enhance the spreading of impacted droplets on the substrate. In particular, acetylacetonates which melt during decomposition, improve the spreading behaviour of a droplet on the substrate, and consequently enable the deposition of smooth, dense films.

Chen et al. proposed a model for the formation of a porous film [16]. As in our model, it was considered necessary that the wet droplets reach the substrate surface. In contrast to the model for dense film deposition, slow spreading of droplets on the substrate and a salt concentration gradient within the obtained splat were necessary to obtain porous films. It was suggested that the salt concentration gradient within the spreading droplet is necessary to obtain the ring-shaped splat. These three dimensionally cross-linked rings form a porous structure. The substrate surface temperature, the surface tension of the solution, and the boiling point of the solvent were found to be the most important parameters for the deposition of porous films. The authors also suggested that the type of precursor salt have an influence

on porous film formation, because the porous structure was not obtained using nitrates instead of acetates as precursors.

The film growth models involving the CVD process assume that dense and smooth films are formed, when both the solvent and the precursor salt completely vaporize before a droplet reaches the substrate [4, 5, 17]. However, low deposition temperature and our PDA measurements of droplet evaporation are in contradiction to a CVD process. The PDA measurements indicated that for formation of dense and smooth film it is important that the solvent is not completely evaporated before the spreading of droplets on the surface. The thermal analysis of salt decomposition showed that the CVD model is possible at much higher temperatures and under a nitrogen atmosphere but not in air. In our experiments, we have observed no indication of a CVD process involvement in spray pyrolysis.

## 4.7 Conclusions

Droplet transport and evaporation in spray pyrolysis processes were investigated using PDA. Similar droplet size distributions were obtained for the PSD system and the ESD multijet spraying mode. In both cases, the droplet number distribution was dominated by droplets smaller than 10  $\mu$ m, and on the other hand, the droplet volume distribution was dominated by the droplets larger than 10  $\mu$ m. Significant evaporation of solvent begins only at a distance of 10 mm from the substrate in the case the ESD multijet mode. Due to the larger temperature gradient in the case of the PSD, significant evaporation of solvent starts at even smaller distance, i.e. 5 mm from the substrate.

In the case of spraying in the ESD cone-jet mode, all droplets were smaller than 7  $\mu$ m. These droplets evaporated very rapidly and all of them were smaller than 1  $\mu$ m 30 mm from the substrate. This resulted in films containing many nm sized particles on the surface. It follows that droplets reaching the substrate should be wet to obtain a dense and smooth film. Therefore, the deposition temperature is the most important spray parameter. By increasing the temperature, the film morphology can change from a cracked to a porous microstructure.

Based on the present results, a plausible film growth mechanism was proposed. The large droplets (> 10  $\mu$ m) are more important in film growth than the small droplets. These large droplets contain enough solvent to be spread on the substrate and carry most of the mass of the precursor. The use of acetylacetonates, which melt during decomposition, is beneficial

for the formation of a smooth, dense film. The proposed film growth model does not involve a CVD process.

#### 4.8 References

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# **5** Thermal treatment of metal oxide spray pyrolysis layer

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#### Abstract

The suitability of spray-deposited YSZ films as electrolytes for solid oxide fuel cells (SOFCs) is investigated. The influence of thermal treatment on the film microstructure and electrical conductivity of YSZ thin films is presented. Dense films with grain size in the region of 3-12 nm were obtained on sapphire single crystals and Inconel 600 substrates using the spray pyrolysis technique. No cracks were observed after thermal treatment at 800°C. The electrical conductivity of nanocrystalline thin films were studied at temperatures ranging from 700°C to 1000°C. It was found that at 700°C the ohmic losses caused by the YSZ ionic conductor are sufficiently low for SOFC applications when the films thickness does not exceed 5.5  $\mu$ m.

# 5.1 Introduction

Solid oxide fuel cells (SOFCs) convert the chemical energy of fuel into electrical energy in an efficient manner. However, state of the art SOFCs are limited by high operating temperatures (>800°C). One possibility for lowering the operating temperature is to reduce the electrolyte thickness. Typically, yttria-stabilized zirconia (YSZ) is used as solid electrolyte in SOFC. Thin YSZ films can be prepare by various methods such as spin coating, sol-gel route, chemical vapour deposition (CVD), physical vapor deposition (PVD) and spray pyrolysis. Spray pyrolysis is an alternative to the traditional methods because of its simplicity, low cost and minimal waste production.

Thin YSZ films have already been deposited by spray pyrolysis on the following substrates: glass [1, 2], Si [3], aluminium [4], steel [5], gadolinia-doped ceria [6], porous La(Sr)MnO<sub>3</sub> [7, 8], and La(Sr)CoO<sub>3</sub> cathodes [9]. The deposited films were characterized using x-ray diffraction (XRD) for phase identification and determination of the crystallographic structure. In many cases, wide diffraction peaks indicating nanocrystalline structure were observed. However, the grain size was evaluated very seldom from the XRD pattern. The average grain size for preparation by the Pyrosol process at deposition temperatures of up to 600°C ranged from 20 nm to 30 nm [2]. Choy et al. [7] found that the crystallinity of a film depends on the deposition temperature. The YSZ films deposited below 500°C were amorphous, whereas fully stabilized cubic zirconia was formed when the deposition temperature was above 550°C. Ruiz et al. [5] deposited nanocrystalline zirconia films and observed that the crystallite size increased when the carrier gas was lighter. Nguyen et al. [10] investigated the crystallinity of tetragonal 2 mol.% Y2O3-doped ZrO2 thin films deposited by electrostatic spray deposition. It was found that all films deposited with a low flow rate (2 ml/h) at deposition temperatures of up to 400°C are amorphous. Films deposited at 400°C with a flow rate of 3.9 ml/h were polycrystalline. Generally, films deposited by spray pyrolysis are nanocrystalline under proper deposition conditions. If not, the amorphous structure transforms to nanocrystalline after thermal treatment.

Studies of nanocrystalline materials require accurate determination of the grain size. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) are two major techniques which may be successfully used for structural characterization. We have used these two techniques to study the grain growth in YSZ films deposited by spray pyrolysis. The aim of this work was to study the properties of thin YSZ films as a function of their thermal treatment.

#### 5.2 Experimental

The details of the spray pyrolysis setups used in our studies and the deposition conditions for YSZ thin films have been described previously [11]. YSZ films were deposited on heated sapphire single crystals (Stettler AG) and Inconel 600 foils (Goodfellow) by spraying precursor solutions. A mixture (50:50 vol%) of ethanol (Fluka Chemie, Buchs, Switzerland) and diethylene glycol monobutyl ether (Fluka Chemie, Buchs, Switzerland) was used as solvent for zirconium acetylacetonate (Fluka Chemie, Buchs, Switzerland) and yttrium chloride (Aldrich Chemicals, Buchs, Switzerland). The precursor solution was prepared according to the stoichiometry of the required film  $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ . The total concentration of the salts in the solution was 0.1 mol/l. The precursor solution was atomized to an aerosol by exposing it either to a stream of air or high voltage. The deposition temperature ranged from 250°C to 350°C.

Film topography and surface roughness were analysed using atomic force microscopy (AFM) (TOPOMETRIX Explorer). In this case, the YSZ films deposited on sapphire substrates were heat treated after deposition at 500, 600°C, 700°C, and 800°C for 2 hours in air. The heating and cooling rates were set at 120 K/hour.

The crystallinity of the films was investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). For the TEM studies, disks 100  $\mu$ m thick and 3 mm in diameter were cut from the YSZ coated Inconel 600 foil. The samples were mechanically polished, dimple-grinded and finally ion milled with Ar ions. The TEM studies were performed on a Philips CM30 electron microscope operating at 300 kV. The grain size was determined by dark field imaging.

The in situ X-ray powder diffraction study of the deposited YSZ films was made using a high temperature environmental chamber (G.T.P. Engineering Co.) incorporated in an X-ray powder Scintag diffractometer (Cu-K<sub> $\alpha$ </sub> radiation). In this case, the YSZ film was removed from the Inconel 600 substrate and then analyzed by the X-ray powder diffractometer. The 2 $\Theta$ -scan was performed in steps of 0.02° and count times of 2 s/step at various temperatures from 250 to 700°C. The change of mean grain size was determined by peak broadening measurements.

The surface morphology of the deposited films was characterized using scanning electron microscopy (SEM) (LEO 1530).
The dc conductivity of the films deposited on sapphire single crystals was obtained using 4-point measurement as shown in Figure 5.1. The four parallel electrodes were made by applying platinum paste and platinum wires on the film surface. Measurements were carried out using a Keithley digital multimeter (model 197A) at various temperatures in the range of 700-1000°C in air.



Figure 5.1. Sketch of experimental setup used for four point conductivity measurement.

# 5.3 Results and discussion

### **5.3.1** Structural properties

The crystallization and grain growth in air of the YSZ films were studied using in situ X-ray powder diffraction. For this purpose, the YSZ film deposited on Inconel 600 foil at 275°C was removed from the substrate. The separation of the film from the substrate avoids any influence of the substrate on film crystallization.



Figure 5.2. In situ XRD patterns of the YSZ film as a function of annealing temperature in air. The temperature was kept constant for 60 min at each annealing step.

Figure 5.2 shows the resulting XRD patterns for the YSZ film as deposited and after thermal annealing at various temperatures. The (111) peak begins to increase at 450°C. This change indicates that the as-deposited film is amorphous and significant crystallization of the film begins at about 450°C. Increase of peak intensity and its sharpening indicate that the amount of the crystalline phase increases continuously with increasing temperature from 450°C to 700°C. The width of the (111) peak clearly indicates the presence of fine-grain

polycrystalline YSZ at annealing temperature as low as 450°C. Meanwhile, the narrowing of the width of the diffraction peak with increasing annealing temperatures shows that the mean grain size of the nano-crystals increases with temperature.

With help of the XRD patterns, one can calculate the mean grain size in the films. The full width at half the peak maximum depends on the grain size. If the physical origin of peak broadening is due to the small grain size alone, the mean grain size of the sample can be evaluated by means of the Scherrer equation [12]:

$$D = \frac{0.9\lambda}{B \cdot \cos\Theta} \tag{5.1}$$

where D is the grain size in nm,  $\lambda$  is the wavelength of the x-ray-source in nm (0.154 nm), B is the full width in radian at half of the maximum of the (111) diffraction peak and  $\theta$  is the Bragg diffraction angle.



Figure 5.3. Dependence of the mean grain size on the annealing temperature.

We have used the XRD patterns from Figure 5.2 and the Scherer equation to investigate the influence of annealing temperature on the grain size. As shown in Figure 5.3, the microstructure of YSZ films depends on the annealing temperature, the mean grain size can be varied from 3 nm to 11 nm over the temperature range of 450-700°C. It can be

concluded that rapid grain growth does not occur up to 700°C, because the temperature increase from 450°C to 700°C resulted only in a grain size increase of 8 nm. Rapid grain growth can be expected at higher temperatures as reported previously by Kosacki et al. [13]. The mean grain size of YSZ film prepared by the spin coating method was smaller than 20 nm up to a sintering temperature of 800°C and rapid grain growth started at higher temperatures reaching a mean grain size of 220 nm at 1200°C. Additionally, it was observed that the rapid grain growth on the polycrystalline substrate occurs at lower temperatures than in the case of the single crystal substrate. This was attributed to the faster nucleation mechanism on the polycrystalline substrates.

The crystallite size depends on the deposition temperature i.e. the higher the deposition temperature, the larger the crystallites. Wang et al. [14] calculated from XRD diffraction patterns that crystallite sizes are 18 nm and 27 nm at deposition temperatures of  $550^{\circ}$ C and  $700^{\circ}$ C respectively. It was also observed that the degree of crystallographic orientation increases with increasing deposition temperature. Nguyen et al. [10] deposited crystalline 2 mol.% Y<sub>2</sub>O<sub>3</sub>-doped ZrO<sub>2</sub> thin films by electrostatic spray deposition at a much lower temperature (400°C). Accordingly a smaller mean grain size (7.8 nm) was deduced from the broadening of the (111) XRD peak.



**Figure 5.4**. The evaluation of the YSZ (111) x-ray diffraction peak during thermal treatment at 700°C. The film was deposited at 275°C.

We deposited YSZ films at lower temperature (275°C) compared to other studies [10, 14]. Therefore the YSZ film microstructure obtained is amorphous instead of polycrystalline. Thermal treatment leads to crystalline films with nm-sized grains. The grains grown from the amorphous films after thermal annealing at various temperatures were much smaller than those obtained directly at higher deposition temperatures. For example: the mean grain size of the film deposited at 700°C was 27 nm [14] and 11 nm in the film deposited at 275°C after annealing at 700°C for two hours.

The aim is to use the sprayed YSZ film as the electrolyte in an SOFC that will be operated at 700°C. Therefore, the influence of time on the film microstructure was investigated at an annealing temperature of 700°C. As shown in Figure 5.4, the shape of the (111) x-ray diffraction peak does not change significantly during the 405 minutes at 700°C. Only a small increase in peak intensity was observed. It indicates that very slow grain growth occurs during annealing. The increase of the mean grain size was quantified using the Scherrer equation. As can be seen in Figure 5.5, the largest change in grain size occurs in the first 60 minutes of the annealing at 700°C. Actually, the change from 8.5 nm to 9.5 nm in size can be considered as negligible, because an accuracy of 1 nm is not possible. It can be concluded, therefore, that the film microstructure is stable at an annealing temperature of 700°C at least for 7 hours.



Figure 5.5. Dependence of the mean grain size on annealing time at 700°C.

In some cases, results derived from the XRD pattern analysis can deviate from those obtained using TEM analysis, because the line broadening can be caused by the instrument itself. The maximum grain size that can be measured using XRD is limited. De Keijser et al. [15] applied the Scherrer equation only in the case of grains smaller than 150 nm. Additionally, we have used TEM analysis to check the reliability of the results obtained using the XRD technique. TEM observation, in contrast to the XRD, provides direct imaging of nanocrystalline grains.



**Figure 5.6.** Electron diffraction pattern (a) and TEM dark field image (b) of YSZ film deposited at 375°C on the Inconel 600 substrate. The YSZ film was annealed for two hours at 700°C in air.

The electron diffraction pattern in Figure 5.6a indicates that the film is crystalline after thermal treatment at 700°C. This follows from the sharp rings on the diffraction pattern. The white spots are reflections from the substrate that has a much larger grain size than the film. The grains of the YSZ film were imaged using the dark field mode, where the grains fulfilling the Bragg-condition give a bright contrast and the others are dark. As shown in Figure 5.6b, the grain size is about 10 nm which is very close to the mean grain size of 9.5 nm determined using the XRD method. It can be concluded that we have not observed any discrepancy between the results from TEM and XRD.

## 5.3.2 Influence of thermal treatment on film topography

For optimum fuel cell performance, the YSZ electrolyte film must be free of porosity and cracks to prevent gases to permeate from one side of the electrolyte to the other. Cracks and pores can occur due to crystallization of the amorphous film or during grain growth. Films can also crack due to excessive differences in the thermal expansion coefficients of the film and substrate. Therefore, we investigated the influence of thermal treatment on film topography using various microscopy techniques. Optical microscopy was used for examination of large sample areas. Investigations in  $\mu$ m scale were carried out using SEM. The film surface roughness was measured using atomic force microscopy (AFM). In all cases, our observations were focused on the search for cracks and pores.



Figure 5.7. Optical micrograph of an YSZ film deposited on a sapphire single crystal substrate.

Sapphire single crystals were chosen as substrates due to their low surface roughness. The surface of the YSZ film on sapphire as deposited and thermally annealed at 500°C, 600°C, 700°C and 800°C was observed using optical microscopy after each annealing step. A typical optical micrograph of the YSZ film as-deposited is shown in Figure 5.7. Overlapping splats were observed over the whole film after deposition. The appearance of the film splats

did not change after annealing, i.e. no cracks or any other defects were observed using optical microscopy.

The investigation of the film surface in the  $\mu$ m scale using the SEM confirmed that no cracks occur after thermal treatment below 800°C. It follows that the films can sustain stresses caused by rather large mismatches in thermal expansion coefficients of the YSZ film (~10·10<sup>-6</sup> K<sup>-1</sup>) and sapphire substrate (~8.4·10<sup>-6</sup> K<sup>-1</sup>). In fact, an even larger difference in thermal expansion coefficient, as in the case of Inconel 600 substrate (~11.5-13.3·10<sup>-6</sup> K<sup>-1</sup>), did not lead to crack formation.



Figure 5.8.  $100 \times 100 \ \mu\text{m}^2$  AFM image of a sprayed YSZ film on a sapphire single crystal substrate (deposited at 300°C using zirconium acetylacetonate as precursor and ethanol / butyl carbitol mixture as solvent).

The AFM technique is complementary to the optical microscopy and SEM used previously. It allows a quantitative estimation of film roughness. Figure 5.8 shows a typical AFM scan of the YSZ film deposited on a sapphire substrate. Smooth films can be deposited on flat sapphire substrates with a roughness in the nm range. The film growth mechanism can also be followed using AFM analysis of the sprayed film surface. The droplets hit the substrate surface and spread. The resulting splats have the form of thin disks with diameters up to 100  $\mu$ m and heights of ~20 nm. The surfaces of the films as deposited and thermally annealed at 500°C, 600°C, 700°C and 800°C were observed using AFM. The topography images over an area of 100×100  $\mu$ m<sup>2</sup> were acquired in non-contact AFM mode. No significant change in the surface roughness was observed after the thermal treatment. R<sub>a</sub> values (average deviation in height from a mean line) were about 20 nm for all annealing temperatures up to 800°C (Table 5.1). The differences in these values can be attributed to measuring errors and to the fact that the measurements were not carried out at exactly the same area; consequently, inhomogeneities in the film morphology could play a role. The topography of the YSZ film deposited on sapphire did not change during thermal treatment. In particular it is important that no single crack was found at the observed areas.

Annealing temperature, °C	R <sub>a</sub> , nm
As deposited	25
500	20
600	25
700	45
800	15

Table 5.1 Influence of thermal treatment on film roughness

From the film analyses using various microscopic techniques, it follows that YSZ films deposited using spray pyrolysis can be heated up to at least 800°C without the film cracking or change in film topography. This is very important for the later use of the films as electrolytes in SOFC that must withstand operating temperatures of 700-800°C.

## 5.3.3 Electrical properties of spray deposited films

Fuel cells require electrolytes that, in addition to the gas-tightness discussed above, must develop sufficient oxygen ion conductivity at the operating temperature. Steele assumed that the total internal resistance (electrolyte + electrodes) of a fuel cell will be sufficiently small when the total cell area specific resistivity (ASR) of electrolyte does not exceed 0.15  $\Omega \text{cm}^2$  [16]. The ASR is associated with the specific ionic conductivity and film thickness L as follows: ASR=L/ $\sigma$ , where  $\sigma$  is the specific bulk conductivity of the film material. The use of thinner electrolytes or new materials with high ionic conductivity would decrease the ASR.

In recognition of the influence of the microstructure on the electrical conductivity, we have studied the electrical properties of the nanocrystalline YSZ films. The ionic conductivity of a 160 nm thick YSZ film was measured between 700 and 1000°C in air. The grain size was 10 nm. The measurements were carried out in a four point arrangement with Pt electrodes as

shown in Figure 5.1. The results are shown in Figure 5.9. The electrical conductivity decreases with decreasing temperature. The conductivity remained constant during the measurement. Even at 1000°C it did not change significantly at least for two hours. An activation energy of 1.19 eV was obtained.



Figure 5.9 Arrhenius plot of total conductivity of an YSZ film deposited at 280°C using the spray pyrolysis method.

The calculated activation energy of 1.19 eV is in the range of values reported in other studies [3, 13, 14, 17, 20]. The YSZ conductivity values measured in various studies are listed in Table 5.2. In contrast to the activation energy, the magnitude of the total electrical conductivity at 700°C for YSZ changes by several orders of magnitude. These differences can be attributed to grain boundary and impurity effects, because the microstructure, processing and electrical conductivity of YSZ are strongly related.

It is well known that the electrical properties of nanocrystalline material are not necessarily the same as those of microcrystalline materials. It has been reported that the electrical conductivity at 900°C of spin coated YSZ increases one order of magnitude when the grain size decreases from 2.4  $\mu$ m to 20 nm [17]. The increase in the electrical conductivity was attributed to the grain boundary effect which tends to enhance the electrical conductivity due to a lowering of impurity concentration and higher diffusion in the grain boundary compared to the bulk volume. At 600°C the conductivity of the nanocrystalline film was even orders of magnitude higher compared to the microcrystalline film. This difference in the conductivity results from rather large differences in the activation energies. Nanocrystalline

YSZ films have activation energies of 0.93 eV which is much smaller compared to the 1.23 eV of microcrystalline films.

Activation energy, eV	Conductivity, S/m at 700°C	Preparation method
1.19	0.37	Spray pyrolysis [this study]
1.08	330	Aerosol-assisted CVD [14]
1.12	0.2	Single crystal [20]
_	13	Tape casting [18]
-	0.15	Tape casting [19]
1.15-1.3	-	Spray pyrolysis [3]

Table 5.2 Comparison of YSZ ionic conductivity at 700°C

A wide range of activation energies were reported in other studies. Wang et al. [14] obtained 1.08 eV activation energy for YSZ films deposited by aerosol-assisted CVD. The authors have not observed grain boundary effects. In contrast, Beltran et al. [3] observed that for the YSZ film deposited using the spray pyrolysis technique, both bulk and grain boundary conductivities have higher activation energies of 1.3 eV and 1.15 eV respectively. These activation energies are slightly higher than the values of the YSZ single crystal material (1.12 eV) [20]. The variation of activation energies can be attributed to the different grain sizes and to changes in the oxygen vacancy mobility, which influence the oxygen transport properties.

# 5.4 Summary

Thin films of YSZ were deposited by spray pyrolysis on sapphire single crystal and Inconel 600 substrates. XRD analysis revealed that the as-deposited film is amorphous and significant crystallization of the film begins at about 450°C. The YSZ films deposited using the spray pyrolysis technique were found to contain 10 nm sized grains after annealing at 700°C. No significant influence of annealing time (from 1 hour to 6 hours) on grain growth at 700°C was observed. No cracks in the thin YSZ film were observed after the thermal annealing between 500°C and 800°C. The film showed good electrical conductivity values of 0.37 S/m at 700°C and 1.2 S/m at 800°C with an activation energy of 1.19 eV. These films seem feasible as electrolytes in low to intermediate temperature solid oxide fuel cells up to a thickness of several micrometers.

# **5.5** References

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# 6 Solid oxide fuel cells with electrolytes prepared via spray pyrolysis

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## Abstract

Fuel cells with thin film electrolytes deposited onto a prefabricated anode support using spray pyrolysis were tested. Spray pyrolysis allows thin electrolytes with low ohmic losses to be prepared, thereby enabling the operating temperature of the solid oxide fuel cell to be reduced while maintaining high power output. The electrolyte films consisted of a layer of 8 mol% yttria-stabilized zirconia (YSZ) and a layer of ceria 10 mol% yttria solid solution (CYO). They were both deposited by spray pyrolysis onto NiO-YSZ self supporting anode substrates. The cells were operated using hydrogen as fuel and air as oxidant at temperatures of 600°C to 800°C and exhibited an open circuit voltage of 1.01 V at 720°C indicating a dense and crack-free electrolyte film. High power density in excess of 750 mW/cm<sup>2</sup> was provided by cells with 600 nm thin YSZ/CYO bi-layer electrolytes at 770°C. Cells containing the bi-layer electrolytes were operated for over 450 hours at 720°C with tolerable degradation. Good performance was achieved at 700°C with cells that had more than two layers of different electrolytes, but considerable degradation was observed. Spray parameters, such as deposition temperature showed an effect on the performance of the cells.

## 6.1 Introduction

Solid oxide fuel cell (SOFC) technology offers efficient power generation with low emission of pollutants. However, cost reduction remains the main objective of SOFC development, because in order to be competitive with existing power technologies, fuel cell energy should be as cheap as the energy from state of the art power generators. State of the art high temperature SOFC is based on a 40 to 200 µm thick zirconia electrolyte [1, 2]. Due to the low specific ionic conductivity, high operating temperatures between 900-1000°C are required. High operating temperatures activate the interfacial solid state reactions of cell components, and place large demands on the materials chosen for interconnects. This has led to the application of oxide dispersion stabilized chromium plates as interconnects, with the disadvantage of cost, difficult powder metallurgy for fabrication and the tendency for electrochemical poisoning of the catalytic properties of the electrodes [3]. Therefore, one of the major tasks for the development of SOFC is the reduction of the operating temperature with the objective of using more conventional steel alloys for interconnects at temperatures around 700°C. The operating temperature can be reduced either by reduction of the thickness of the YSZ electrolyte or by application of alternative electrolyte materials such as ceria solid solutions or La(Sr)Ga(Mg)O<sub>3</sub> (LSGM) that have a higher ionic conductivity than YSZ [4]. However, the ionic conductivity regime of ceria solid solutions is rather narrow, and in reducing environments, it is partially reduced to allow electronic conductivity. Therefore too thin ceria electrolytes cause losses [5]. A partial internal short circuit due to the electronic conductivity of thin ceria electrolytes in the fuel cell can significantly reduce their efficiency and performance. The purely ionic conductivity domain of the LSGM is wider, but expensive raw materials are required for their preparation due to the presence of gallium. Moreover, it is difficult to prepare pure single phase LSGM and it is instable at 1000°C [6]. In the absence of new materials which fulfil all the criteria of a suitable fuel cell electrolyte, thin film concepts for electrode supported designs based on the well known YSZ are more promising, although it has a lower ionic conductivity than ceria or LSGM. The YSZ electrolyte should be thin (several µm), so that ohmic losses in a cell can be kept at a tolerable level. Other advantages of fuel cells with thin electrolytes are reduced materials costs and improved fuel cell characteristics [7].

Many methods for depositing thin, dense YSZ films on porous substrates exist. Most of them are either expensive (CVD, PVD, thermal spray) or unsuitable for depositing films thinner than 5  $\mu$ m (tape casting, screen-printing) [8]. Steele and Heinzel claimed that at present the minimum thickness for dense impermeable films which can be reliably mass produced using ceramic fabrication routes is around 10 – 15  $\mu$ m [9].

Spray pyrolysis is an inexpensive form of coating technology with the potential to produce thin (0.1 to 10  $\mu$ m) and gas tight ceramic layers on porous substrates. The ability of the spray deposition technique to produce multiple or even gradient layer designs by changing the spray solution only may lead to further improvements in cell performance. Therefore, the application of thin, spray-coated layers as electrolytes in SOFC was investigated.

Thin YSZ films have already been deposited by spray pyrolysis on dense and porous substrates as buffer layers [10], insulating thin films in electronic devices [11], and electrolytes in fuel cells [12]. The electrostatic spray deposition (ESD) technique is a powerful tool for deposition of porous electrode films [13]. Recently, the preparation of porous LSCF and  $La_{0.8}Sr_{0.2}MnO_3$  cathodes using ESD technique was reported by Taniguchi et al. [14]. Choy et al. demonstrated the capability of spray pyrolysis to deposit all fuel cell components in one production process by switching precursor solutions (porous La(Sr)MnO<sub>3</sub> / dense YSZ / porous NiO-YSZ) [15]. However the authors have not presented any data on electrochemical performance of the cells.

To our knowledge only few reports on fuel cell tests have been presented. Setoguchi et al. measured the current-voltage characteristic of a fuel cell with a sprayed 18  $\mu$ m thin YSZ electrolyte [12]. The cell was tested using air at the cathode side and a hydrogen/water mixture at the anode side. The cell showed 1.04 V open circuit voltage (OCV) and generated a maximum power density of 490 mW/cm<sup>2</sup> at an operating temperature of 1000°C. The small difference in the OCV compared to the theoretical value of 1.1 V results from residual cracks and pores in the electrolyte film. The microstructure of the film was highly dependent on the substrate temperature and the spraying time during preparation. Small cracks were observed when the film was deposited at low temperatures. Fewer cracks were observed after repeated spraying procedures.

The current-voltage (I-V) and current-power (I-P) characteristics of a fuel cell containing a 33  $\mu$ m thick calcia-stabilized zirconia (CSZ) electrolyte were reported [16]. This cell with sprayed CSZ electrolyte attained a slightly lowered open circuit voltage of 0.96 V and a power density of 500 mW/cm<sup>2</sup>. In this case the microstructure of the CSZ film, and consequently the cell performance, was also strongly affected by the substrate temperature during the film deposition process. The OCV of the cell with the CSZ film fabricated at 100°C was higher and the slope of the I-V curve was smaller than with those fabricated at

150°C. From these results one can conclude that thin electrolyte films can be deposited via spray pyrolysis on rough surfaces at rather low preparation temperatures.

Recently, 20  $\mu$ m thick YSZ electrolytes were deposited at 100°C by spraying an aqueous YSZ colloidal suspension and subsequently sintering at 1400°C [17]. In this case a porous NiO-YSZ anode was used as substrate. 5  $\mu$ m thin La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> cathodes were also prepared by spraying a suspension. Current-voltage characteristics of the cells were measured at 850°C with either humidified hydrogen or humidified methane on the anode side and air on the cathode side. The OCV obtained for a single cell was close to 0.9 V. The low OCV value was caused by leaks in the cell sealings and the presence of pinholes in the thin electrolyte. A maximum power density of 120 mW/cm<sup>2</sup> was generated. A degradation of 3.8%/100 h was observed for a cell operating longer than 100 h under hydrogen with a current of 100 mA/cm<sup>2</sup>. The results were promising but improvements in electrolyte deposition have to be made in order to increase cell performance and to reduce aging effects.

So far, various thin film deposition methods have been applied to the fabrication of electrolytes for intermediate temperature SOFC such as electrochemical vapour deposition (EVD) [18], physical vapour deposition (PVD) [19], vacuum plasma spraying [20], tape calendering [21], and screen printing [22]. However, the spray pyrolysis method has very seldom been employed in SOFC technology, although the feasibility to deposit dense electrolyte films for high temperature SOFC has been demonstrated.

In this study electrochemical data of anode-supported fuel cells are reported. The cells containing sprayed, ultra-thin electrolytes were operated at 600°C to 800°C. The effect of process parameters on the cell performances and their aging behaviour are discussed.

# **6.2** Experimental

#### **6.2.1** Anode substrates

Reducing the electrolyte thickness leads to the electrode-supported fuel cell design. The anode as support, compared to the cathode as support, offers the benefits of lower material cost, better strength, and allows the application of more cost efficient conventional ceramic processing steps. Sintered YSZ/NiO-anode substrates (Lot 3205) were obtained from Sulzer Innotec (Winterthur, Switzerland). The anodes were 300  $\mu$ m thick disks containing 8 mol% yttria-stabilized zirconia (YSZ) and nickel oxide (NiO) in the ratio of 30:70 in wt%. The typical microstructure of these substrates is shown in Figure 6.1. For the optimization of deposition parameters, a disk of 35 mm in diameter was chosen as substrate. The substrate structure had a mean pore size of 1.5  $\mu$ m with a mean YSZ grain size of 1  $\mu$ m. The porosity in the sintered state was 26 % measured by Archimedes principle and after reduction of the NiO to Ni the porosity increased to 40 %.



Figure 6.1 SEM images of the anode substrate: (a) fracture cross-section and (b) surface.

### 6.2.2 Electrolyte deposition

Thin film deposition using spray pyrolysis involves the spraying of a metal salt solution onto a heated substrate. We have used the spray pyrolysis technique with two different atomizers for the generation of aerosols, i.e. an electrostatic atomizer and an air blast atomizer. Details about our spray pyrolysis setup were given earlier in Chapter 3. Dense films of YSZ electrolyte were deposited by spraying yttrium chloride (YCl<sub>3</sub>·6H<sub>2</sub>O) (Aldrich Chemicals, Buchs, Switzerland) and zirconium acetylacetonate ( $Zr(C_6H_7O_2)_4$ ) (Fluka Chemie, Buchs, Switzerland) dissolved in an ethanol ( $C_2H_5OH$ ) (Fluka Chemie, Buchs, Switzerland) : diethylene glycol monobutyl ether ( $C_8H_{18}O_3$ ) (Fluka Chemie, Buchs, Switzerland) mixture (50:50 vol.%). The precursor solution was prepared according to the stoichiometry of the required ( $ZrO_2$ )<sub>0.92</sub>( $Y_2O_3$ )<sub>0.08</sub> film. The overall concentration of salts in the solution was 0.1 mol/l. The precursor solution was atomized to an aerosol using either air pressure or high voltage. Typical spray parameters for both types of atomizers are listed in Table 6.1.

Spray Parameter	Electrostatic atomizer	Air blast atomizer
Deposition temperature [°C]	300	280
Solution flow rate [ml/h]	6	30
Distance to substrate [cm]	8	50
Solvent [vol.%]	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>
Salts	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>4</sub> YCl <sub>3</sub> ·6H <sub>2</sub> O	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>4</sub> YCl <sub>3</sub> ·6H <sub>2</sub> O
Concentration [mol/l]	0.1	0.1
Coated area [cm <sup>2</sup> ]	~ 10	~ 100
Deposition rate [nm/h]	300	250
Air pressure [bar]	-	0.75
High voltage [kV]	20	_

Table 6.1 Typical spray parameters

Thin buffer layers of CYO were deposited using identical spray parameters by substituting precursor solutions. The CYO precursor solution was prepared by dissolving yttrium chloride (YCl<sub>3</sub>·6H<sub>2</sub>O) and either cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) (Johnson Matthey & Brandenberger, Zürich, Switzerland) or cerium ammonium nitrate ((NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>) (Fluka Chemie, Buchs, Switzerland) in an ethanol / diethylene glycol monobutyl ether (butyl carbitol) mixture (50:50 vol.%).

The electrolyte film was deposited on the anode substrate by spray pyrolysis. The film as deposited is amorphous. The crystal structure is established during subsequent heating, which may in fact be the first operation of the cell itself. A typical sample was heated after film deposition at a rate of 2 K/min to 700°C, held for 2 hours, and cooled down. Single layer

(YSZ), bi-layer (CYO/YSZ), and multi-layer (CYO/YSZ/CYO) electrolyte films of approximately 1  $\mu$ m thickness were deposited. The deposition parameters for the thin film electrolytes are given in Table 6.2.

### **6.2.3** Cathode preparation

A cathode layer of  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$  (LSCF) of typically 50 µm was finally applied on the electrolyte by screen-printing without subsequent sintering. The slurry was prepared by mixing  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$  powder with terpineol, ethyl cellulose, and beycostat. The composition of the screen-printing slurry is given in Table 6.3. A cross section of a LSCF cathode is shown in Figure 6.2.

Material	Quantity, wt%	Function	Supplier
La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3</sub>	69	Powder	Praxair Speciality Ceramics, USA Lot 03-P2026DM
Terpineol	28	Solvent	Fluka Chemie, Buchs, CH Lot 46480
Beycostat	2.5	Binder	CECA S.A., Paris, France 213
Ethyl cellulose	0.5	Dispersant	Aldrich Chemicals, Buchs, CH 20-064-6

Table 6.3 Recipe for the LSCF paste used for screen-printing



Figure 6.2 Cross sectional view of a screen-printed LSCF cathode.

Table 6.2 Spray parameters for the thin electrolyte film deposition

	P228	P229	GSN71	GSN76	SR2	SR3
Atomizer	Electrostatic	Electrostatic	Air blast	Air blast	Air blast	Air blast
Electrolyte	XSZ	YSZ	XSZ	YSZ/CYO	CYO/YSZ/CYO	CY0/YSZ/CY0
Substrate temperature [°C]	317	335	284	282	282	282
Flow rate [ml/h]	5.7	5.7	70	30	30	30
Distance to substrate [cm]	æ	×	53	53	53	53
Solvent [vol.%]	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>	50 C <sub>2</sub> H <sub>5</sub> OH 50 C <sub>8</sub> H <sub>18</sub> O <sub>3</sub>
Salts	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> )4 YCl <sub>3</sub> ·6H <sub>2</sub> O	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> )4 YCl <sub>3</sub> ·6H <sub>2</sub> O	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> )4 YCl <sub>3</sub> ·6H <sub>2</sub> O	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>4</sub> YCl <sub>3</sub> ·6H <sub>2</sub> O (NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>4</sub> YCl <sub>3</sub> ·6H <sub>2</sub> O Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Zr(C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>4</sub> YCl <sub>3</sub> ·6H <sub>2</sub> O (NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>
Concentration of YSZ solution [mol/l]	0.085 Zr salt 0.015 Y salt	0.085 Zr salt 0.015 Y salt	0.085 Zr salt 0.015 Y salt			
Concentration of CYO solution [mol/l]		1	ſ	0.055 Ce salt 0.017 Y salt	0.34 Ce salt 0.06 Y salt	0.17 Ce salt 0.03 Y salt
Air pressure [bar]	ł	B	0.75	0.75	0.75	0.75
High voltage [kV]	16	16	ł		ſ	
Deposition time [min]	06	06	120	280 (YSZ) 90 (CYO)	60 (CYO) 120 (YSZ) 60 (CYO)	60 (CYO) 120 (YSZ) 60 (CYO)

SOLID OXIDE FUEL CELLS WITH ELECTROLYTES PREPARED VIA SPRAY PYROLYSIS

#### **6.2.4** Fuel cell measurements

Ferritic stainless steel plates with gas channels (1.4509 steel: 18%Cr, Nb, Ti) (Plansee AG, Austria) were used as interconnectors (see Figure 6.3). Thin slurry coatings of LSCF were applied at the airside of the interconnector to enhance the electrical contacts to the cathode. Ni powder slurry consisting of 85 wt% nickel powder (CERAC, Milwaukee, USA, N2003, average grain size 1  $\mu$ m) and 15 wt% terpineol (Fluka Chemie, Buchs, Switzerland) was applied on the interconnector at the fuel side to improve the electrical contacts to the anode. The cell with sprayed electrolyte and screen-printed cathode was then sandwiched between the two interconnects. Platinum wires ( $\emptyset$  0.5 mm) for voltage and current leads were spot welded on each of the interconnects. The cell with interconnectors was mounted into an alumina housing containing the fuel and air supply tubes and placed in a furnace. An external weight of 300 g was loaded on the cell. The test setup is shown in Figure 6.4.



Figure 6.3 Photograph of 3 mm thick interconnector plate (2.4 cm in diameter).

The cell was heated up to the working temperatures of  $600^{\circ}$ C to  $800^{\circ}$ C at a heating rate of 1°/min and operated using hydrogen as fuel and air as oxidant. The hydrogen fuel flow was varied from 0.1 to 1.8 g/h. Due to the unsealed arrangement hydrogen flows higher than 0.5 g/h were necessary to obtain the highest OCV values. The air flow was varied from 10 to 50 g/h.



Figure 6.4 Sketch of experimental setup used for I-V measurements.

# **6.3** Results and Discussion

#### 6.3.1 SOFC with a single-layer YSZ electrolyte film

The microstructures of the fuel cells were examined using scanning electron microscopy (SEM). Figure 6.5 shows the cross-section of a LSCF/YSZ/Ni-YSZ fuel cell (no.P228) structure with a thin YSZ electrolyte prepared by electrostatic spray deposition after operating the cell at 770°C for 115 hours using hydrogen as fuel. It was observed that the electrolyte film was uniform, continuous, and adhered well to the anode and to the cathode but had many small pores. The YSZ film thickness varied from 0.5  $\mu$ m to 1.5  $\mu$ m. Usually, most of the films deposited by ESD were rougher than those deposited using an air blast atomizer.



**Figure 6.5** Cross-section image of a solid oxide fuel cell with a sprayed electrolyte. From the top to the bottom: screen-printed cathode (LSCF), YSZ electrolyte prepared by electrostatic spray deposition (no.P228) and anode substrate (Ni-YSZ cermet).

Figure 6.6 shows an SEM image of a solid oxide fuel cell (no.GSN71) with a sprayed YSZ electrolyte using an air blast atomizer. The cell was operated using hydrogen as fuel at 770°C for 220 hours. The thickness of the electrolyte film was approximately 0.4  $\mu$ m. As can

be seen the film also contained many pores, but in contrast to the one deposited by ESD it was much smoother. The film also appeared to adhere very well to the Ni-YSZ anode. However, this was not the case for the LSCF cathode. The cathode delaminated from the electrolyte because the cell was heated up to the operating temperatures without sintering the cathode.





Figure 6.7 shows the I-V and I-P characteristics of fuel cells, for which the YSZ film was sprayed using either electrostatic (no.P228) or air blast atomizer (no.GSN71). Both cells were operated under similar conditions at 770°C. Air was supplied to the cathode compartment at a flow rate of 25 g/h. Hydrogen gas was supplied to the anode compartment at a flow rate of 0.5 g/h. An open circuit voltage of 880 mV was measured for the cell with the electrolyte deposited using ESD and 970 mV for the cell with the electrolyte sprayed using an air blast atomizer. Due to gas leakage through the YSZ film, open circuit voltages of the cells were lower than the theoretical value of 1.1 V, calculated from the Nernst equation. This leads to the conclusion that open porosity or cracks must exist in the electrolyte films. On the other hand, excellent power densities of 450 mW/cm<sup>2</sup> and 550 mW/cm<sup>2</sup> were generated. The cells generated a power density at 770°C comparable to the one obtained by Setoguchi et al. at 1000°C [12, 16]. It follows that the use of very thin films of YSZ

electrolyte allowed the operating temperature to be decreased by 230°C while at keeping the power output constant.

The performance of the cells with the YSZ films prepared by ESD was strongly dependent on the deposition temperature. The effect of deposition temperature on the I-V characteristics is shown in Figure 6.8. The OCV decreased from 880 mV to 810 mV when the substrate surface temperature during deposition was increased from 317°C to 335°C. This indicates that many open pores were still present after deposition at 335°C. In general, the morphology of the film depends on the rate of spreading, precipitation, decomposition, and reaction of the zirconium acetylacetonate on the substrate. If the spreading of droplets is slow, but the precipitation and the decomposition are fast, the morphology will be granular leading to pores [13]. Qualitatively, the spreading rate decreases with increasing temperature. In addition, dry droplets can be formed when the precipitation and the decomposition of the solute occurs before the droplets reach the substrate. Therefore, fewer pores were closed at higher deposition temperatures. It is extremely important that the droplets arriving at the substrate are still wet, because the droplets may then penetrate pinholes by capillary action. This self-healing process is most important when spraying thin films.



**Figure 6.7** Comparison of fuel cell performances at 770°C. A thin YSZ film was sprayed using either electrostatic ( $\circ \bullet$ ) (no.P228) or air pressure atomizer ( $\Box \blacksquare$ ) (no.GSN71) on a NiO/YSZ anode substrate.

The highest OCV achieved using the ESD method producing films of 1  $\mu$ m thickness was about 0.88 volts. It is more difficult to deposit gas-tight films when the precursor solution is sprayed by an electrostatic atomizer, because the spray consists of many small droplets. These droplets are almost dry when they come into contact with the surface of the substrate because small ones evaporate faster than large ones. Therefore, the open pores of the substrate are covered faster with large droplets. Usually, the droplets generated using air blast atomizers are ten times larger than those obtained using electrostatic atomizers. This explains the higher OCV values of the cells with the electrolyte sprayed using an air blast atomizer.



**Figure 6.8** Effect of deposition temperature on the I-V characteristics of a fuel cell. The cells contain a thin YSZ film deposited using an electrostatic atomizer at  $317^{\circ}C$  ( $\circ$ ) (no.P228) and  $335^{\circ}C$  ( $\bullet$ ) (no.P229) substrate temperature.

Finally, the long term behaviour was investigated for more than 200 hours at 770°C (Figure 6.9). Single layer YSZ electrolyte cell (no.GSN71) showed a continuous degradation over operation time, depending on the current load. The power output decreased rapidly at high current loads, e.g. -1.1 %/h at 480 mA/cm<sup>2</sup> at 770°C. The degradation was slower at low current density, but still intolerable (-0.2 %/h at 120 mA/cm<sup>2</sup>). The degradation of performance was attributed to formation of reaction products between the LSCF cathode and the YSZ electrolyte as already mentioned by Chen et al. [23]. The interfacial reactions can be

suppressed by adding a protective layer of CYO between the YSZ and LSCF [24]. Additionally, Tsai and Barnett observed that the interfacial layers of CYO enhance the electrode performance [25]. Therefore we also deposited a thin CYO/YSZ bi-layer electrolyte using spray pyrolysis onto porous NiO/YSZ substrates.



Figure 6.9 Effect of current density on aging behaviour at 770°C (no.GSN71).

#### 6.3.2 Cell with bi-layer electrolyte film

A sketch of a solid oxide cell with bi-layer electrolyte is shown in Figure 6.10. The CYO/YSZ bi-layer was sprayed using the air blast atomizer. First, the YSZ layer was deposited onto NiO-YSZ anode substrate and then the sample was heated at a rate of 2 K/min up to 700°C and held for 2 hours in order to crystallize the film as well as to complete the decomposition of the Zr and Y compounds. In fact, the additional thermal treatment is not necessary because the crystal structure may be established during be the first operation of the fuel cell at 700°C. Finally, the thin CYO film was deposited on top of the sprayed YSZ electrolyte and then a LSCF cathode by screen printing. The cell was heated up to the working temperatures of 620°C to 770°C during operation.

Figure 6.11 shows a SEM image of the fracture cross-section of a typical solid oxide fuel cell with a sprayed YSZ/CYO bi-layer electrolyte (no.GSN76). The thickness of the electrolyte film varied from 450 nm to 700 nm. The film was sufficiently thick to cover pores

of up to 3  $\mu$ m diameter. The film contained some small pores, which did not effect the gastightness of the film. Delamination of the LSCF cathode during fuel cell operation resulted, because there was no sintering step of the screen-printed cathode.



LSCF (50 µm) Cathode CYO (0.15 µm) Electrolyte YSZ (0.45 µm) Electrolyte NiO-YSZ (300 µm) Anode

Figure 6.10 Sketch of a solid oxide fuel cell consisting of anode (NiO-YSZ), bi-layer electrolyte (YSZ/CYO) and cathode (LSCF).



Figure 6.11 SEM image of the cross-section of a solid oxide fuel cell. From the top to the bottom: screen-printed LSCF cathode, sprayed electrolyte bi-layer (CYO/YSZ) (no.GSN76) and tape-casted anode substrate (Ni-YSZ cermet).

Because of the unsealed test set-up, high hydrogen flows were necessary to flush the anode chamber. Figure 6.12 shows the open circuit voltage of the YSZ/CYO bi-layer electrolyte cell (no.GSN76) as a function of the hydrogen flow rate at 720°C. The OCV increased with increasing fuel flow rate to the maximum OCV of 1010 mV which was measured at a hydrogen flow rate of 1.0 g/h. The theoretical OCV calculated from the Nernst equation at these conditions is 1.1 V. An OCV close to the theoretical value means that the electrolyte is gas-tight. However, this is valid only for a sealed test setup where no mixing of air with the fuel gases can occur. The OCV which was obtained here is close to the theoretical value and indicates that the thin electrolyte film deposited onto the porous anode substrate prevented gas leakage through the electrolyte. The difference between the measured and theoretical OCVs was the result of leakage of gases through the open test set-up.



Figure 6.12 Effect of fuel mass flow rate on OCV at 720°C (no.GSN76).

Figure 6.13 shows the I-V and I-P characteristics for an anode-supported SOFC with sprayed electrolyte bi-layer (no.GSN76) at 770°C. We used hydrogen as fuel (0.5 g/h) and air as oxidant (32 g/h). The maximum power density achieved for this cell was 760 mW/cm<sup>2</sup> at a current density of 1070 mA/cm<sup>2</sup>. The resistance of the load device prevented evaluation of the cell at higher current densities. It is clear from I-P curve, that the peak power density is expected to be higher than the measured value. According to our measurements, the cell with the sprayed YSZ/CYO bi-layer electrolyte (no.GSN76) produced the higher power density

compared to the cell with the sprayed YSZ single layer electrolyte (no.GSN71). For example at 770°C, the cell performance improved from 540 mW/cm<sup>2</sup> to 700 mW/cm<sup>2</sup> at a current density of 950 mA/cm<sup>2</sup> which indicates that the interfacial layer of CYO enhances cell performance.



**Figure 6.13** Current-voltage and current-power characteristics of an anode-supported SOFC with sprayed electrolyte bi-layer (YSZ/CYO) (no.GSN76) and screen-printed LSCF cathode.

Additionally, the protective CYO layer improved long term stability. The cell with the YSZ/CYO bi-layer electrolyte (no.GSN76) was operated at 720°C for over 450 hours (see Figure 6.14). In contrast to the single layer electrolyte cells essentially no degradation of the performance was observed after 70 h of operation at a current load of 240 mA/cm<sup>2</sup>. Under the same current load at 770°C, the power output of the cell without protective CYO layer rapidly decreased at a rate of -0.3 %/h. However, significant degradation occurred at higher current loads, e.g. -0.02 %/h and -0.07 %/h at 360 mA/cm<sup>2</sup> and 600 mA/cm<sup>2</sup> respectively. Suspected reasons for the power output loss are aging of the electrolyte bi-layer and the deactivation of the LSCF cathode due to grain growth. Also the durability of anodes at high current densities (>300 mA/cm<sup>2</sup>) was found to be insufficient [26].

In spite of the decreasing performance at high current loads, the cell (no.GSN76) still generated a reasonable power density after over 450 hours of operation at 720°C (see Figure

6.15). A relatively high power output of 200 mW/cm<sup>2</sup> was obtained even at lower operating temperatures ( $620^{\circ}$ C).



Figure 6.14 Effect of current density on the aging behaviour at 720°C (no.GSN76).



**Figure 6.15** Power output of a single fuel cell with a bi-layer electrolyte after over 450 hours of operation (no.GSN76).

#### 6.3.3 Cells with composite electrolyte films

Although YSZ is the favoured electrolyte material for intermediate temperature SOFC, ceria based electrolytes are attracting much attention due to the high specific conductivity [27]. On the other hand, it is well known that in a reducing atmosphere, ceria develops significant electronic conduction [28]. To overcome this problem, there is the option of employing multilayer electrolytes. The sketch of a solid oxide fuel cell with a multi-layer electrolyte is shown in Figure 6.16. The CYO layer between the NiO-YSZ serves as the electrolyte and the catalytically active layer. The purpose of a YSZ film is to block electronic current. As the electronic transference number of YSZ is much smaller compared to ceria, the electronic current through the multi-layer electrolyte is also expected to be lower compared to the single layer ceria electrolyte. The CYO component between the YSZ and LSCF also serves as a buffer against solid state reactions at the cathode side.



Figure 6.16 Sketch of a solid oxide fuel cell consisting of anode (Ni-YSZ cermet), multilayer electrolyte (CYO/YSZ/CYO) and cathode (LSCF).

The CYO/YSZ/CYO multi-layer electrolyte was sprayed by the use of an air blast atomizer. First, the CYO electrolyte layer was deposited onto a porous NiO-YSZ anode substrate, then the sample was heated at a rate of 2 K/min to 700°C and held for 2 hours at that temperature in order to crystallize the film as well as to complete the decomposition of the Ce and Y compounds. A thin YSZ film was subsequently deposited on top of the sprayed CYO electrolyte. The heat treatment at 700°C was carried out again. Finally, another CYO protective layer was deposited on the previously deposited YSZ film. Without thermally treating the protective CYO film, the LSCF cathode was screen printed onto the multilayer electrolyte. The cell was then heated up to the working temperatures in the range of 700°C to 770°C. As shown in the cross-sectional image (Figure 6.17), the multilayer electrolyte (no.SR3) had many closed pores and some of them were connected to the film surface. The grain size of the electrolyte was 50 to 80 nm. The highest OCV value was 0.85 V at 700°C. This either indicates that the multi-layer electrolyte was not sufficiently dense to prohibit the cross-over of gases through the film or the YSZ component in the multilayer structure did not block the CYO's electronic conduction completely. The thickness of the multi-layer electrolyte film varied from 400 nm to 1200 nm. It is clear that the quality of the multilayer needs to be improved.



**Figure 6.17** Cross-sectional image of a solid oxide fuel cell. From the top to the bottom: screen-printed LSCF cathode, sprayed electrolyte multi-layer (CYO/YSZ/CYO) (no.SR3) and tape-casted anode substrate (Ni-YSZ cermet).

Although relatively low OCV values were measured, high power density could be generated at 700°C. Figure 6.18 shows I-V and I-P curves of two cells with CYO/YSZ/CYO multilayer electrolytes (no.SR2 and no.SR3). The gas flow rates during the measurements were 0.5 g/h of hydrogen and 32 g/h of air. At 700°C the multilayer cell (no.SR3) generated a similar power density of 540 mW/cm<sup>2</sup> at 950 mA/cm<sup>2</sup> current load, as the cells with sprayed single layer electrolyte (no.P228 and no.GSN71) operated at 770°C (see Figure 6.7). The use of the multilayer electrolyte, therefore, makes it possible to reduce operation temperature by 70°C. The performance of the multilayer electrolyte fuel cells was limited by the low OCV.

Further improvements in power density and reductions in operating temperature can be made by assuring a gas-tight CYO/YSZ/CYO electrolyte with a thickness of 1 to  $5 \,\mu$ m.



Figure 6.18 Effect of spray parameters on fuel cell performance. The CYO layers in multilayer electrolyte were sprayed either using  $Ce(NO_3)_3 \cdot 6H_2O$  ( $\Box \blacksquare$ ) (no.SR2) or (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> ( $\circ \bullet$ ) (no.SR3) salt solution.

The long term stability of the cell performance also needs to be enhanced. Multilayer electrolyte cells (no.SR2 and no.SR3) showed significant degradation. The major cause of cell degradation appears to be the existence of many defects in the electrolyte film. The cell materials were damaged in hot spot areas due to gas leakage through these defects. A degradation of -0.38 %/h at a current load of 240 mA/cm<sup>2</sup> was observed at 700°C. Under similar conditions, the cell with a bi-layer electrolyte (no.GSN76) did not exhibit degradation at all.

Film quality can be improved by optimizing the electrolyte deposition parameters. Previously, we showed that the deposition temperature has a strong influence on the gastightness of sprayed YSZ electrolytes (see Figure 6.8). The composition of the precursor solution also plays an important role in the spray pyrolysis process. The effect of the type of salt used is demonstrated in Figure 6.18. Much denser CYO layers were sprayed using cerium ammonium nitrate solutions (no.SR3), in contrast to the films obtained using cerium nitrate solutions (no.SR2). Obviously, cerium ammonium nitrate increases the spreading rate of
droplets on a heated substrate, and consequently enhances the closure of pores in the anode substrate. However, the improvement was insufficient to close all pores. Therefore, further optimisation of spray parameters is required to deposit gas-tight CYO layers.

In spite of the low OCV, a promising cell performance was obtained at 700°C. The CYO/YSZ/CYO multilayer is an attractive electrolyte which offers the possibility of operating a fuel cell at temperatures from 500°C to 700°C.

## **6.4** Conclusions

In the present paper, we presented and discussed results on anode supported SOFCs with approximately 1  $\mu$ m thin electrolytes fabricated by the spray pyrolysis process. Dense and crack-free electrolyte films were prepared on NiO-YSZ anode substrates. This was demonstrated by the open circuit voltage achieved that was close to the theoretical value for cells with bi-layer electrolytes (see Table 6.4).

Cells with a single YSZ electrolyte layer were prepared using an air blast atomizer. They exhibited higher OCV, compared to the electrolytes deposited using an electrostatic atomizer. This indicates that higher quality films are obtained using an air blast atomizer. At 770°C an OCV of 0.97 V and a power density of 550 mW/cm<sup>2</sup> was attained but significant degradation occurred due to the reaction between the LSCF cathode and the YSZ electrolyte. The degradation was reduced by the deposition of a CYO layer on top of the YSZ. The cell with the bi-layer electrolyte achieved a high power density in excess of 750 mW/cm<sup>2</sup> at 770°C.

By depositing a CYO/YSZ/CYO multi-layer electrolyte a further attempt was made to reduce the operating temperature of the SOFC. Good cell performance was demonstrated at 700°C, however the degradation rate was too high. Low OCV values indicated that further improvement of the multi-layer electrolyte film is required. In spite of that the high power outputs are promising for intermediate and low temperature SOFC.

The deposition temperature and the composition of the precursor solution has a strong influence on the OCV of the cells.

We have shown that pores with sizes of up to 3  $\mu$ m can be coated by a 500 nm thin electrolyte film using the spray pyrolysis technique. We have demonstrated that spray pyrolysis can be successfully applied in SOFC technology as a thin film deposition technique.

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Summary
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Table

	P228	P229	GSN71	GSN76	SR2	SR3
Electrolyte	ZSA	ZSY	ZSA	YSZ/CY0	CYO/YSZ/CYO	CYO/YSZ/CYO
Electrolyte thickness [µm]	0.5-1.2	0.7-1.4	0.3-0.5	0.4-0.8	0.3-1.5	0.4-1.2
Anode	NiO-YSZ	NiO-YSZ	NiO-YSZ	NiO-YSZ	NiO-YSZ	NiO-YSZ
Cathode	LSCF	LSCF	LSCF	LSCF	LSCF	LSCF
Operation temperature [°C]	770	770	770	770	100	700
OCV [mV]	810	880	970	1010	740	840
Power at $550 \text{ mA/cm}^2 [\text{mW/cm}^2]$	320	360	400	460	290	380
Max. power density [mW/cm <sup>2</sup> ]	320	450	540	760	540	310

## **6.5** References

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## **7** General conclusions

Electrostatic Spray Deposition (ESD) and Pressurized Spray Deposition (PSD) set-ups have been studied and applied to deposit thin  $O^{2-}$  ion conducting YSZ and CYO films. The PSD technique is more robust and offers an easier way to deposit dense films compared to the ESD technique.

In order to obtain smooth and dense films, the substrate surface temperature was the most important parameter for both spray pyrolysis set-ups. It strongly affects the film morphology and the decomposition of the precursor. The temperature has to be sufficiently high to decompose precursor salts. Too low a deposition temperature leads to film cracking. At too high a temperature powder will be produced as soon as the solvent in droplets evaporate completely during the droplet transport. Crack-free films can be deposited using solvents with low boiling points at lower temperatures than is the case of a solution containing the solvent with the higher boiling point. Films of the best quality were deposited by spraying the zirconium acetylacetonate precursor solution.

The measurements of the droplet sizes indicated that for the PSD set-up and the ESD multi-jet spraying mode the droplet number distribution is dominated by droplets smaller than 10  $\mu$ m. On the other hand, the droplet volume distributions were dominated by droplets larger than 10  $\mu$ m. Notable evaporation of droplets starts at a distance of 5 mm from substrate in the case of the PSD and a distance of 10 mm in the case of the ESD multi-jet mode. This can be attributed to the larger temperature gradient in PSD set-up and/or reflection of the air flow on the substrate.

Due to the higher mass of the larger droplets (>  $10 \mu m$ ) these are more important for film growth than the small droplets. The large droplets carry most of the mass of the precursor, evaporate slowly during transportation and consequently contain enough solvent to spread on the substrate. The smaller droplets are responsible for most of the surface roughness as these are often deposited as powder particles. The zirconium acetylacetonate that melts during the decomposition on the substrate improves the spreading behaviour of the droplet and facilitates the formation of a smooth, dense film.

XRD analysis revealed that the as-deposited films are amorphous and significant crystallization begins upon annealing at about 450°C. Grains of 10 nm in size were observed

after annealing at 700°C. The annealing time (1 to 6 hours) has no significant influence on grain growth at 700°C. No cracks in the thin YSZ film were observed after thermal annealing at 800°C. It follows that the thin electrolyte deposited by spray pyrolysis would sustain the SOFC operation temperature of at least 800°C.

Dense and crack-free electrolyte films were prepared on porous NiO-YSZ anode substrates. Surprisingly, pores with sizes of up to 3 µm were coated by a 500 nm ultra-thin electrolyte film using the spray pyrolysis technique. In SOFC operation mode an open circuit voltage (OCV) close to the theoretical value was achieved. Cells with YSZ electrolyte layer, prepared via the PSD set-up exhibited higher OCV, compared to the electrolytes deposited using the ESD set-up. This indicates that superior electrolyte films can be deposited using the PSD set-up. At 770°C an OCV of 970 mV and a power density of 550 mW/cm<sup>2</sup> was generated but continuous decrease in performance occurred due to the reaction between the LSCF cathode and the YSZ electrolyte. The degradation was considerably reduced after the deposition of a CYO buffer layer on top of the YSZ electrolyte film. This cell with the bilayer electrolyte attained a high power density in excess of 750 mW/cm<sup>2</sup> at 770°C.

The application of a CYO/YSZ/CYO multi-layer electrolyte is very promising for intermediate and low temperature SOFC. One of these cells generated high power density at 700°C, but also showed considerable degradation. The degradation and low OCV values were attributed to defects in the multi-layer electrolyte.

In summary, spray pyrolysis is a coating technique that offers a lot of advantages for the processing of ceramic films. The process equipment is rather simple, the method is robust and when properly controlled it yields nano-structured oxide films of high quality at rather low costs. It can be concluded that spray pyrolysis has been successfully applied in SOFC technology as a thin film deposition technique for ultrathin electrolytes.

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## 8 Outlook

#### General

This thesis was focused on the development of a spray pyrolysis technique that can be applied to an electrolyte for solid oxide fuel cells (SOFCs). Although the spray pyrolysis process was studied for dense films in detail, it needs further investigation in order to improve the competitiveness of this technique over the other thin film processes. Besides the many advantages offered by this thin film deposition method, the low deposition rate remains an important drawback. Therefore, further work is required in the following areas.

#### Film deposition

Electrostatic and the air blast atomizers were installed in our spray pyrolysis set-up. It turned out that films of slightly better quality were deposited and larger areas were coated using the air blast atomizer. However, the deposition efficiency of the air blast atomizer is much lower than that of the electrostatic atomizer. Only 5-10% of sprayed solution reaches the substrate, the rest is blown away by air flow. In contrast, around 90% of spray solution is deposited on the substrate in the case of the electrostatic atomizer. It follows that the electrostatic atomizer is more promising for efficient film deposition at a high rates. The coated area can be increased either by employing an array of nozzles or by moving a single nozzle.

#### **Properties of deposited films**

It is suggested that impedance spectroscopic measurements should be made to study the electrical conductivity of the thin YSZ films. Impedance spectroscopy could make it possible to identify the contributions of bulk and grain boundaries to the total ionic conductivity of the nanocrystalline YSZ film. Long term conductivity measurements are important for application as electrolyte in SOFC. It is possible that the conductivity decreases over a long time period due to grain growth. In this study it was shown that the as-deposited films are amorphous. We also suggest that the influence of deposition temperature on crystallinity and grain size of an YSZ film should be investigated. It is expected that the film deposited above 450°C will already be crystalline. Furthermore, it would be interesting to investigate the influence of a substrate on film microstructure, because different film microstructures can be obtained on single crystal and polycrystalline substrates. Some substrates might be used as templates for preferred texturing of the oxide film.

### Application of spray pyrolysis in SOFC

In the present work we have demonstrated that dense electrolyte films can be deposited by spray pyrolysis. We suppose that porous anode and cathode films can also be deposited. It follows, that spray pyrolysis has a potential to deposit in one production step a complete multilayer fuel cell of porous electrodes and dense electrolyte, but experimental proof is still missing. Further work has to be invested here mainly on the deposition of porous films.

Spray pyrolysis can be used to produce alternative electrolytes such as scandia-doped zirconia, doped lanthanum gallate, or doped ceria. Ceria-based solid solutions are the most promising candidates to replace YSZ electrolyte. Ceria is a mixed ionic-electronic conductor that has a higher ionic conductivity than YSZ. However, a short circuit due to the electronic conductivity of ceria electrolyte can significantly reduce the efficiency and performance of the fuel cell. This problem can be solved by the use of the CYO/YSZ/CYO multilayer electrolyte that was already proposed and tested in the Chapter 6. This multilayer electrolyte requires further investigation. Of primary importance is the improvement of the multilayer electrolyte quality in terms of gas tightness.

#### Miscellaneous applications

The spray pyrolysis technique can be applied also in other non-SOFC technical fields, such as the deposition of tough coatings. A number of natural materials are famous for their strength and toughness. For example, the abalone shell, a composite of calcium carbonate plates sandwiched between protein interlayers, is more fracture resistant than a single crystal of the pure mineral. Toughness in hard biological materials is related to fibrous or lamellar structures that deflect or stop crack propagation. Spray pyrolysis offers a way to fabricate such layered structures with the aim of introducing toughness into brittle materials. A polymer and YSZ multilayer should have higher toughness than a YSZ single crystal.

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## **9** Appendix

### 9.1 Measurement of droplet size distribution using PDA

PDA systems perform non-intrusive measurements of the size and velocity of droplets. The underlying principle of phase Doppler anemometry is based on light-scattering interferometry and therefore requires no calibration. The measurement point is defined by the intersection of laser beams and the measurements are performed on single particles as they move through the sample volume. Particles thereby scatter light from both laser beams, generating an optical interference pattern. Receiving optics placed at an off-axis location projects a portion of the scattered light onto multiple detectors. Each detector converts the optical signal into a Doppler burst with a frequency linearly proportional to the particle velocity. The phase shift between the Doppler signals from different detectors is a direct measure of the particle diameter.

The size of particles that can be measured is limited at the lower end by the amount of light that is scattered by very small particles. Typical limits for common configurations might be 1 or 2  $\mu$ m on the lower end and 500 mm to 1 mm at the upper end.

In this study a system of TSI GmbH company (Aachen, Germany) was used. The main components of the PDA system are listed in the Table 9.1

Component	Model No.
Laser	L70-5E
Fiber optic receiver	RV2070-X-15M
Fiber light multi-colour beam separator	FBL-2
Photodetector module	PDM1000-2P
Multibit digital processor	FSA4000-P
Multibit digital processor	FSA4010
Traversing system	9450-XYZ500

#### Table 9.1 Components of PDA system

### 9.2 Forces acting on droplet

#### **Themophoretic force**

$$F_{i} = \frac{3\pi \cdot \eta_{a}^{2} r}{\rho_{a}} \cdot \frac{3\kappa_{a}}{2\kappa_{a} + \kappa_{d}} \cdot \frac{grad(T_{a})}{T_{a}}$$

where  $\kappa_a$  and  $\kappa_d$  are thermal conductivities of the air (about 0.025 Wm<sup>-1</sup>K<sup>-1</sup>) and the droplet (about 0.19 Wm<sup>-1</sup>K<sup>-1</sup> for ethanol) respectively,  $\eta_a$  is the viscosity of air (about 2.2·10<sup>-5</sup> N s m<sup>-2</sup>), r is the radius of the droplet,  $\rho_a$  is the density of the air (1.29 kg m<sup>-3</sup>),  $T_a$  is the temperature of air (250°C), and grad( $T_a$ ) is the thermal gradient of air (10<sup>5</sup> K/m).

#### **Gravitational force**

where  $\rho_d$  is the density of the droplet (780 kg m<sup>-3</sup>) and g is the acceleration of gravity.

#### Stokes force

where  $v_d$  is the velocity of the droplet (1 m/s).

#### **Electrical force**

 $F_E = qE, \quad q_{\rm max} = 8\pi \sqrt{\gamma \varepsilon_0 r^3}$ 

 $F_g = \frac{4\pi}{3} \cdot \rho_d r^3 g$ 

 $F_s = 6\pi \eta_a v_d r$ 

where  $\gamma$  is the liquid-gas surface tension (0.02 N/m),  $\varepsilon_0$  is the electrical permittivity of vacuum, *E* is the electric field strength (10<sup>5</sup> V/m).

#### Table 9.2 Magnitudes of forces

Radius, µm	Thermophoretic, N	Gravitational, N	Stokes, N	Electrical, N
1	$2.1 \cdot 10^{-13}$	3.2.10-14	4.1·10 <sup>-10</sup>	1.1·10 <sup>-9</sup>
10	2.1.10 <sup>-12</sup>	3.2.10 <sup>-11</sup>	4.1·10 <sup>-9</sup>	3.3·10 <sup>-8</sup>
100	2.1.10 <sup>-11</sup>	3.2.10-8	4.1·10 <sup>-8</sup>	1.1·10 <sup>-6</sup>

# Abbreviations

AFM	Atomic Force Microscopy
ALE	Atomic Layer Epitaxy
ASR	Area Specific Resistivity
Bi-2212	$Bi_2Sr_2CaCu_2O_x$
CGO	$Ce_{0.8}Gd_{0.2}O_{2-x}$
CSZ	15 at% Calcium-Stabilized Zirconia
CVD	Chemical Vapour Deposition
CYO	Ce <sub>0.8</sub> Y <sub>0.2</sub> O <sub>2-x</sub>
DTA	Differential Thermal Analysis
EDS	Energy Dispersive X-Ray Spectroscopy
ESD	Electrostatic Spray Deposition
IR	Infrared
LSCF	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$
MOCVD	Metal-Organic Chemical Vapour Deposition
Ni-YSZ	Mixture of Nickel and YSZ
OCV	Open Circuit Voltage
PDA	Phase Doppler Anemometry
PSD	Pressurized Spray Deposition
PVD	Physical Vapour Deposition
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy
TG	Thermogravimetry
THF	Tetrahydrofuran
XRD	X-Ray Diffraction
YBCO	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>9-x</sub>
YSZ	8 mol% Yttria-Stabilized Zirconia

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# **11** Curriculum vitae

#### PERSONAL

Full Name:	Dainius Perednis
Date and Place of Birth:	August 9, 1973, Kaisiadorys, Lithuania
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### EDUCATION

1998-present	Research associate and Ph.D. Student, Chair of Nonmetallic
	Inorganic Materials, Department of Materials, ETH Zürich,
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1995-1998	Physics studies, Swiss Federal Institute of Technology, ETH,
	Zurich, Switzerland
	Diploma thesis "Imaging of Current Distribution in
	Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>x</sub> Superconducting Films Using Magnetic Force
	Microscopy"
	(Moroscopy
1995	Bachelor in Physics, Vilnius University, Lithuania
	Grading work "Preparation and Properties of MgO-CuO
	Ceramics"
1994-1995	Exchange student at the ETH Zurich, Switzerland
	(The EPS/SOROS mobility grant of the European Physical
	Society)
1001 1005	Diversion studion Vilnius University Lithuania
1991-1992	r nysics succes, v ninus Onversity, Linuania
1991	Matriculation at the secondary school in Kaisiadorys, Lithuania

### LIST OF PUBLICATIONS

Papers:

- J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis and L.J. Gauckler *Fabrication of thin electrolytes for second-generation solid oxide fuel cells Solid State Ionics*, 131(1-2), p. 79, 2000
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  submitted to Solid State Ionics
- (3) D. Perednis, L.J. Gauckler
  *Thermal treatment of metal oxide spray pyrolysis layer* In preparation
- (4) D. Perednis, L.J. Gauckler
  State of the art: spray pyrolysis
  In preparation
- (5) O. Wilhelm, D. Perednis, L.J. Gauckler, S.E. Pratsinis
  Spray pyrolysis deposition of YSZ films by different spraying techniques In preparation
- D. Perednis, O. Wilhelm, S.E. Pratsinis, L.J. Gauckler
  Deposition of thin metal oxide films using spray pyrolysis
  In preparation

#### Proceedings:

- D. Perednis, L.J. Gauckler
  Solid oxide fuel cells with YSZ films prepared using spray pyrolysis
  Proceedings of the 8th International Symposium on SOFCs (2003, Paris, France), vol. 2003-07, p. 970
- D. Perednis, L.J. Gauckler
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- D. Perednis, M.B. Joerger, K. Honegger, L.J. Gauckler
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- O. Wilhelm, L.J. Gauckler, L. M\u00e4dler, D. Perednis, S.E. Pratsinis
  Spray processing in nanoparticle technology
  Proceedings of the 16<sup>th</sup> European Conference on Liquid Atomization and Spray
  Systems (2000, Darmstadt, Germany), p. VIII.7.1

#### Presentations:

- D. Perednis, and L.J. Gauckler
  Solid oxide fuel cells with YSZ films prepared using spray pyrolysis
  8<sup>th</sup> International Symposium on Solid Oxide Fuel Cells, Paris, France, April 27 May
  2, 2003 (talk)
- D. Perednis, and L.J. Gauckler
  Thin metal oxide films for solid oxide fuel cells
  Colloquium of the Department of Materials, ETH Zurich, Switzerland, January 29, 2003 (talk)
- D. Perednis, and L.J. Gauckler
  Solid oxide fuel cells with thin electrolyte films deposited by spray pyrolysis
  5<sup>th</sup> European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, July 1-5, 2002 (poster)
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  Fabrication of thin YSZ electrolyte films using spray pyrolysis technique
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- (6) D. Perednis, M.B. Joerger, K. Honegger, and L.J. Gauckler
  Fabrication of thin YSZ electrolyte films using spray pyrolysis technique
  Laboratory of Electrochemical Energy Conversion, Yamanashi University, Kofu,
  Japan, June 1, 2001 (talk)

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  SOFC Workshop, IEA Program of R&D on Advanced Fuel Cells, Les Diablerets,
  Switzerland, January 16-19, 2001 (talk)
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  4<sup>th</sup> European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, July 10-14, 2000 (poster)
- (10) D. Perednis, and L.J. Gauckler
  *Deposition of thin YSZ films by spray pyrolysis* Colloquium of the Department of Materials, ETH Zurich, Switzerland, April 12, 2000 (talk)
- D. Perednis, and L.J. Gauckler
  Imaging current flow in complex superconducting microstructures by magnetic force microscopy
  8<sup>th</sup> European Conference on Applications of Surface and Interface Analysis, Sevilla, Spain, October 4-8, 1999 (talk)
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  Spain, October 4-8, 1999 (poster)