Electrostatic spray deposition (ESD) technique was applied to deposit thin, dense yttria stabilized zirconia (YSZ) electrolyte films. The YSZ films were deposited on dense substrates (stainless steel, glass and alumina) and porous NiO-YSZ substrates at 400°C. The influence on film morphology of the process parameters such as: salt concentration, polymer additive, deposition time, and substrate nature was studied. A smooth dense film was successfully deposited using the precursor solution based on butyl carbitol and ethanol solvent mixture. A rough porous film was formed when the solvent mixture containing butyl carbitol (40 vol%), water (40 vol%), and ethanol (20 vol%) was sprayed. In this work, we have chosen polyethylene glycol (PEG) polymer as additive to modify the properties of the precursor solutions. The results demonstrated a significant role of the additive on the droplet spreading. The nature of a substrate was not playing a significant role in the film growth.

INTRODUCTION

Electrostatic spray deposition (ESD) is a processing technique to prepare dense or porous ceramic films. In ESD a precursor solution is atomized by electric field to an aerosol, which is then directed to a heated substrate where a thin film is deposited. This thin film deposition method is rather 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.

The ESD technique is a powerful tool for deposition of porous electrodes (1, 2, 3) and dense electrolytes (4, 5, 6). Fuel cells with YSZ electrolyte films prepared by ESD attained a power density of 450 mW/cm² and an open circuit voltage (OCV) of about 0.9 V at 770°C (6). The difference to the theoretical value of 1.1 V was attributed to gas leakage through the YSZ film and unsealed experimental setup.

In order to advance this technology further, a better understanding of the deposition parameters is desirable. Especially the composition of the precursor liquid influences the film growth rate, its thickness and microstructure. Caillaud et al. (7) reported that the ZnO film growth rate is dependent on the pH of the aqueous precursor solution. Acetic
and nitric acids were added to obtain the required pH value. Chen et al. (8) were able to deposit crack-free TiO$_2$ films by adding acetic acid to the precursor solution.

The boiling point of solvent might influence film morphology. Films deposited using a solvent of high boiling point became denser compared to the case when a solvent of lower boiling point was used (4, 9, 10). This was attributed to slower evaporation of solvent during the aerosol transportation and droplet spreading on the substrate that results in slower precipitation. It was observed, that the porosity of a substrate influences the morphology of a film substantially (4).

The present study is focused on the preparation of dense, crack-free YSZ films. The control of the film morphology requires a good understanding of the ESD process, starting with precursor solution atomization and ending with droplet spreading on a substrate. Little work has been previously reported on the influence of polymeric additives to the precursor solutions. In this work, we have chosen polyethylene glycol (PEG) polymer as additive to modify the properties of the precursor solutions for YSZ thin film deposition. Additionally, the influence of the ESD process parameters such as salt concentration, deposition time, solvent mixture and substrate nature will be investigated.

**EXPERIMENTAL**

Zirconia films were prepared using a vertical ESD setup similar to that described in the literature (11, 12).

Porous NiO-YSZ anode substrates and dense stainless steel, glass, alumina pellets were used as substrates. Zirconium acetylacetonate (Zr(C$_5$H$_7$O$_2$)$_2$; Fluka Chemie), zirconyl nitrate hydrate (ZrO(NO$_3$)$_2$·aq; Fluka Chemie) and yttrium chloride hydrate (YCl$_3$·6H$_2$O; Alfa Aesar) have been used as precursors. Two different solvent mixtures were used. Zirconyl nitrate hydrate was dissolved in the solvent mixture consisting of 40 vol% diethylene glycol monobutyl ether commonly known as butyl carbitol (C$_8$H$_{16}$O; Acros Organics), 40 vol% water and 20 vol% ethanol (C$_2$H$_6$O; Prolabo). In the following the solvent mixture will be referred to as BWE 442. 0.04, 0.08 or 0.16 mol/L of zirconyl nitrate hydrate was dissolved in the BWE 442. Additionally, solution containing 0.5 wt% of polyethylene glycol (PEG) (average molar weight of 2000 g/mol) was prepared to investigate the influence of the polymer additive.

The second solvent mixture consisting of butyl carbitol (50 vol%) and ethanol (50 vol%) was used as solvent for zirconium acetylacetonate and yttrium chloride hydrate. The total salt concentration was 0.1 mol/L. The 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$_2$O$_3$)$_{0.08}$ films.

Flow rate of precursor solution was 0.5 mL/h, controlled by a Sage™ M361 syringe pump. The precursor solution was atomized using a positive high voltage from 5 to 10 kV. The nozzle-to-substrate distance was 27 or 47 mm. The deposition time was ranging from 1 minute to 2 hours. The deposition temperature was 400°C, as measured by a thermocouple placed on the heating plate.
The morphology of the films was analyzed using scanning electron microscopy (LEO S440).

RESULTS

In order to study the droplet spreading, 0.08 mol/L of zirconyl nitrate hydrate with small amount of PEG were dissolved in BWE 442 solvent mixture and deposited on glass at 400°C. Significant effect of the polymer additive was observed as shown in Figure 1. It is well known that PEG reduces surface tension and increases the viscosity of an aqueous solution. The influence becomes stronger with increasing polymer concentration and chain length. During an aerosol transportation the polymer concentration in each single droplet is continuously increasing as far as the solvent evaporates. Therefore droplets when they impact the substrate have a lower surface tension and a higher viscosity compared to that of the precursor solution. This further increases the influence of PEG additive. Therefore changes in spreading of droplet, which contains PEG, can be attributed to the effect of reduced surface tension and increased viscosity. The different liquid properties lead to ring-shaped splats in the case of no additive (Fig. 1a) and disk-shaped splats in the case of PEG additive (Fig. 1b). The rings were formed because when evaporation removes solvent at the edge zone of the splat, a flow develops to keep the substrate wet up to the edge of splat. The precursor in droplet is dragged to the outer border of splat by this flow. So, it accumulates to form a ring-shaped splat (Fig 1a) that remains when the solvent evaporates. In the case of adding PEG the droplets are more viscous when they impact substrate. This leads to more homogeneous drying and faster solidification of the splat. Consequently, disk-shaped splats are formed because in this case the precursor does not accumulate at the border of splat.

![Figure 1. The effect of adding PEG 2000 on droplet spreading and drying for the 0.08 mol/L zirconyl nitrate hydrate precursor solution. a) no additive; b) 0.5 wt% of PEG 2000.](image)

In order to study the film growth, zirconyl nitrate hydrate solutions of 0.04 mol/L, 0.08 mol/L and 0.16 mol/L concentration were sprayed for very short time such as 1, 5, and 10 minutes. The film morphology evolution in the case of 0.08 mol/L concentration is shown in Fig. 2. Already after one minute of deposition, a continuous film with many particles on the surface was formed (Fig. 2a). The solid particles are either incorporated in the film or appear on the surface of the film. This indicates that an aerosol consists of a...
mixture of liquid droplets and solid particles. The solid particles result from small
droplets, which have lost all solvent during transportation. The liquid droplets impact
substrate, spread and form the dense layer. As the deposition process continues, the
number of dry particles on the film surface increases. As result small charged droplets
and solid particles preferentially land on the top of already existing solid particles
because they are attracted to the local curvature of surface where a larger electrical field
gradient is present. Chen et al (9) already mentioned the phenomenon of preferential
landing. Preferential landing causes particle agglomeration. Therefore after 5 minutes of
deposition, roughness of the film was increased as shown in Fig. 2b. Later the increased
surface roughness leads to more particle agglomeration. As a result, the film surface
morphology becomes porous as shown in Fig. 2c. Preferential landing causes
simultaneous growing of two layers: bottom-layer formed by the large liquid droplets
spreading on the surface, and the top-layer resulting from the agglomeration of small
solid particles. The porous top-layer grows up faster and becomes the determining factor
for the film microstructure already after 10 minutes of deposition time. It follows that
action of preferential landing and too many small dry particles on film surface can cause
the growth of porous film.

Figure 2. Evolution of zirconia film morphology during the deposition of the 0.08
mol/L precursor solution. a) 1 min, b) 5 min, and c) 10 min.

The tendency to form porous layer was observed for lower (0.04 mol/L) and for higher
(0.16 mol/L) salt concentration as well. Film roughness and porosity were increased
when the concentration of salts was increased to 0.16 mol/L (see Fig. 3b). Already after 5
minutes, a porous coral-like structure was formed. A consequence of an increased
concentration is that droplets get dried faster. This explains why porous morphology was
formed already after 5 minutes in the case of the 0.16 mol/L precursor solution. The
largest particles on film surface were observed, when 0.16 mol/L precursor solution was
deposited because in this case droplets carry the largest amount of precursor. It is obvious
that much smaller particles were formed in the case of 0.04 mol/L precursor solution as
shown in Fig 3a.

Actually, the preferential landing plays an important role only at high deposition
temperatures and in the case of volatile solvents, which are characterized by low boiling
point. In the case of high boiling point precursor solution and optimal experimental
conditions, smooth, dense layers can be deposited independently on deposition time. For
instance, in the case of the precursor solution containing 0.1 mol/L zirconium
acetylacetonate and yttrium chloride hydrate dissolved in butyl carbitol / ethanol mixture
a dense film can be deposited even after 2 h. In this case only few dry particles impact the
film surface leading to dense and smooth morphology. It follows that the precursor
solution containing butyl carbitol / ethanol solvent mixture is better suitable for dense film deposition compared to the butyl carbitol / water / ethanol precursor solution.

Figure 3. Influence of precursor concentration. Zirconia films deposited on glass for 5 minutes using following precursor concentrations: a) 0.04 mol/L; and b) 0.16 mol/L.

In this study different types of substrates such as dense stainless steel, alumina and glass or porous NiO-8YSZ were coated. In all cases the nature of the substrate has not influenced the microstructure of the film. Regardless of metal, ceramics or glass substrate, deposited films were smooth, dense and homogeneous. YSZ films of the same quality were deposited on dense and porous substrates. Micrometer sized pores on NiO-8YSZ anode substrate (Fig. 4b) were completely covered by the YSZ film (Fig. 4a). It can be concluded that the interaction between the substrate and the solution does not play significant role in the film growth.

Figure 4. SEM images of YSZ film deposited on a porous NiO-YSZ anode substrate at 400°C. Deposition conditions: 0.1 mol/L of zirconium acetylacetonate and yttrium chloride dissolved in butyl carbitol – ethanol mixture (1:1 vol%), nozzle to substrate distance: 47 mm, precursor flow rate: 0.5 ml/h. a – YSZ layer, b – uncoated substrate.

CONCLUSIONS

PEG additive significantly improved droplet spreading on a substrate. Action of preferential landing and presence of too many small dry particles on film surface caused
the growth of porous film. The precursor solution containing butyl carbitol / ethanol solvent mixture was better suitable for dense film deposition compared to the butyl carbitol / water / ethanol precursor solution. The interaction between the substrate and the solution does not play significant role in the film growth. Dense and smooth YSZ films have been successfully deposited on porous NiO-YSZ anode substrates.

REFERENCES

1. I. Taniguchi, R. C. van Landschoot, J. Schoonman, Solid State Ionics, 156, 1 (2003).
2. K. L. Choy, W. Bai, S. Charojrochkul, B. C. H. Steele, J. Power Sources, 71, 361 (1998).
3. A. Princivalle, D. Perednis, R. Neagu, E. Djurado, Chem. Mater., 16, 3733 (2004).
4. N. H. J. Stelzer, J. Schoonman, J. Mater. Synthesis and Processing, 4, 429 (1996).
5. T. Nguyen, E. Djurado, Solid State Ionics, 138, 191 (2001).
6. D. Perednis, L. J. Gauckler, Solid State Ionics, 166, 229 (2004).
7. F. Caillaud, A. Smith, J.-F. Baumard, J. Am. Ceram. Soc., 76, 998 (1993).
8. C. H. Chen, E. M. Kelder, J. Schoonman, J. European Ceram. Soc., 18, 1439 (1998).
9. C. H. Chen, E. M. Kelder, P. J. J. M. van der Put, J. Schoonman, J. Mater. Chem., 6, 765 (1996).
10. C. H. Chen, K. Nord-Varhaug, J. Schoonman, J. Mater. Synthesis and Processing, 4, 189 (1996).
11. C. H. Chen, E. M Kelder, M. J. G. Jak, J. Schoonman, Solid State Ionics, 86-88, 1301 (1996).
12. C. H. Chen, E. M Kelder, J. Schoonman, J. Mater. Sci., 31, 5437 (1996).