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Low-temperature synthesis of thin films of YSZ and $BaCeO_3$ using electrostatic spray pyrolysis (ESP)

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Abstract

Electrostatic spray pyrolysis (ESP), or electrospraying, a rather novel technique to generate aerosols, has been used for thin film deposition of oxidic ceramic materials. Yttrium stabilized zirconia (YSZ) and barium cerate ($BaCeO_3$), which are utilized as solid electrolyte materials for solid oxide fuel cells (SOFCs), are synthesized using electrospraying. YSZ can be obtained directly after spraying, whereas $BaCeO_3$ needs to be annealed.

1. Introduction

Recently, a new method was developed to synthesize submicron powders by a modified spray pyrolysis method based on the Delft Aerosol Generator (DAG), called Electrostatic Spray Pyrolysis (ESP) or electrospraying [1–3]. This method comprises of generating an aerosol by applying a high potential (5–25 kV) to a surface of a conducting liquid, which contains desired precursor materials. The method of producing an aerosol of submicron droplets has been described recently in detail in the literature [1–3].

In addition, even more recently, ESP was adapted for depositing thin films of electroceramics and in particular $LiMn_2O_4$ with the spinel structure [4,5].

Besides the simple and cheap deposition of thin films of intercalation electrodes for lithium rechargeable batteries, the low-temperature synthesis of ceramic materials for solid oxide fuel cells (SOFCs) is attracting increased attention [6]. Both physical vapor deposition and solution deposition techniques are currently being developed.

Electrospraying based on the DAG seems a promising route to the simple, cheap, and low-temperature synthesis of ceramic components of SOFCs.

Here we report on the first results of electrospraying of oxide conducting solid electrolyte yttrium stabilized zirconia (YSZ), and the proton conducting solid electrolyte barium cerate ($BaCeO_3$).

The thin layers deposited were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental aspects

As a solvent for both electroceramics absolute ethanol is used in electrospraying. The solutions used for electrospraying contain, 0.002 M YCl_3, 0.025 M $ZrOCl_2$, $\cong$ 1% HCl, and 5% water for the YSZ deposits, and 0.05 M $BaBr_2$, 0.05 M $CeBr_3$, and 10% water for the $BaCeO_3$ deposits, respectively.

The set-up used for the spray pyrolysis deposition is shown in Fig. 1. The equipment consists of a resis-

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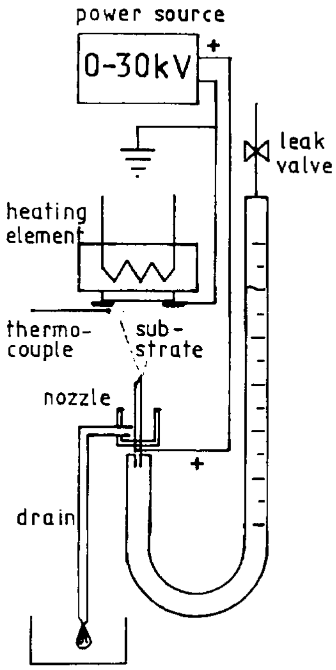

Fig. 1. Set-up for electrostatic spray pyrolysis (ESP).

tively heated substrate holder to which a conductive substrate is mounted underneath. The substrates used were 0.1 cm thick 1.8×2.2 cm×cm aluminium or alumina plates. The alumina substrates were coated with a several nanometers thick film of platinum using an Edwards sputter coater S150B. The description of the set-up has been reported before [5]. In the present study, the nozzle was used as the positive electrode in contrast to that reported in Ref. [5]. For comparison an experiment with a negative nozzle is included in the table.

The present spray parameters are listed in Table 1. The table contains the temperature of the surface before and after deposition (*T*) (the temperature during deposition is 20–50°C lower), the applied voltage between the needle-shaped nozzle reactant supplier and the substrate (*HV*), the average flow rate of the solution (*c*), the used volume of the solution (*V*), and the electrode spacing between the nozzle reactant supplier and the substrate (*d*).

3. Results and discussion

In contrast to the reported polarity of the nozzle in Ref. [5], here a positive voltage was applied to the liquid. The spray obtained for the YSZ deposits does not change significantly by this change of polarity, except a higher value for the potential was needed for spraying with a negative polarity. The aerosol generation of $BaCeO_3$ precursor droplets improved substantially. In fact, we were not able to generate an aerosol from the solution with a negative polarity of the nozzle since a generation of macro droplets occurs. This could probably be due to the larger water content in the latter solution, i.e. 10%.

The growth rate calculated by means of weight increase is 1–5 μm/hour, and depends strongly on the initial concentration of the precursor material.

Thin layers of the YSZ deposits were obtained readily as characterized by XRD (Fig. 2). The deposits, therefore, reveal to be YSZ without any extra annealing step. The remaining peaks observed in the XRD pattern are from the substrate aluminium. SEM study reveals the layers to be slightly porous with a primary particle size of about 0.3 μm, as was also reported for $LiMn_2O_4$ [4,5].

Thin layers of the $BaCeO_3$ deposits initially comprise a mixture of solid barium bromide ($BaBr_2$) and cerium bromide (Ce_2Br_5) (Fig. 3a) as characterized by XRD. The XRD pattern also shows the peaks of the substrate Al_2O_3. After annealing these layers at about 1200°C in air for 15 h the layers were transferred practically into barium cerate as can be seen in the XRD pattern of Fig. 3b, with as impurities Ce_2O_3

Table 1
Experimental results according to the spray pyrolysis process. The symbols are defined in the text.

Sample	*T* (°C)	*HV* (kV)	*c* (μl/min)	*V* (ml)	*d* (mm)
YSZ	400	−14	120	4.0	19
YSZ	400	+8	100	2.0	20
$BaCeO_3$	400	+7	280	7.5	15

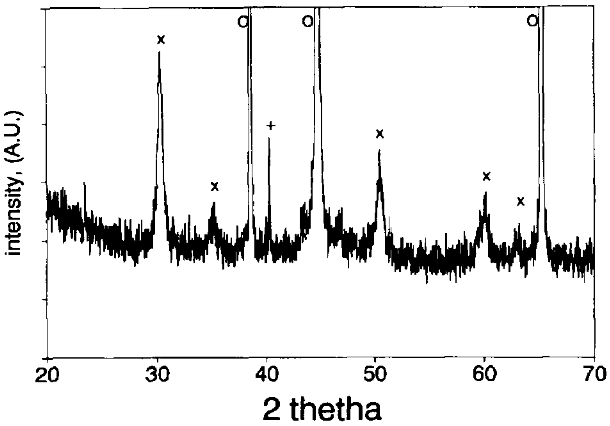

Fig. 2. XRD pattern of a thin film of YSZ deposited by electrospraying at 400°C. The YSZ peaks are indicated by an (×), the remaining peaks are from the substrate aluminium (o), and probably from traces of impurities present in the aluminium substrate (+).

and BaO. BaO reacts with water vapor to form $Ba(OH)_2$, and this is probably present in the layer at room temperature. With regard to the microstructure the SEM study reveals the same results as observed for the YSZ in this work and $LiMn_2O_4$ deposits of Refs. [4,5].

4. Conclusions

Electrostatic spray pyrolysis (ESP) is a novel technique and an excellent tool to generate aerosols. As has recently been shown the aerosols can be used as precursor particles for thin film deposition of oxidic ceramic battery materials. Here it is shown that in particular for YSZ, and $BaCeO_3$ to be used in SOFCs, the ESP technique is very promising to deposit films.

The deposition technique can be used directly, or indirectly to deposit the desired materials in thin layer form. However, further research should be undertaken to control the porosity of the layers. This work is presently in progress in our laboratory.

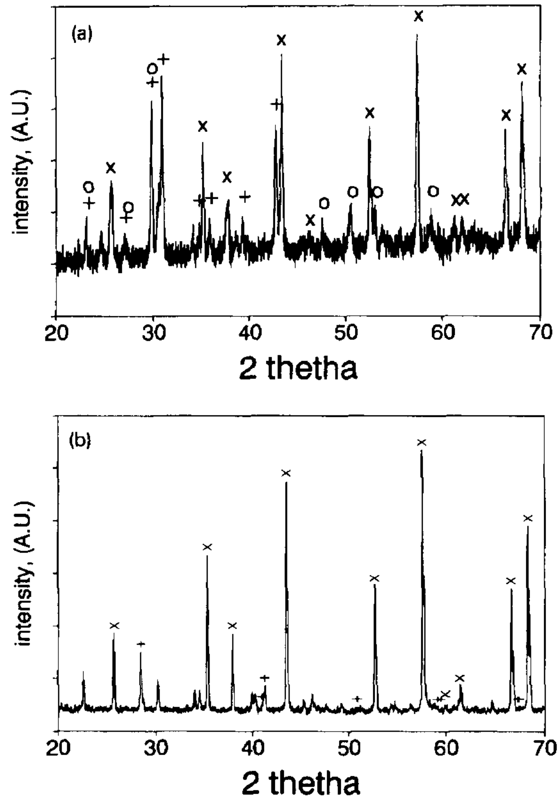

Fig. 3. (a) XRD pattern of a thin film deposited to form $BaCeO_3$ by electrospraying at 400°C. The diffraction peaks reveal the layer to be a mixture of solids of $BaBr_2$ (o) and Ce_2Br_5 (+). The peaks of the substrate Al_2O_3 are indicated by an (×); (b) XRD pattern of a thin film of 3a deposited by electrospraying at 400°C and annealed at 1200°C for 15 h. The peaks of the substrate Al_2O_3 are indicated by an (×); the plus symbols (+) refer to $BaCeO_3$. The remaining peaks are ascribed to Ce_2O_3 and $Ba(OH)_2$.

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