



Applications of spin coating of polymer precursor and slurry suspensions for Solid Oxide Fuel Cell fabrication

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ABSTRACT

In this paper a ceramic deposition method that does not require a high temperature sintering step is presented. The method is used for a fabrication of electrolyte layers for SOFCs and high temperature protective coatings of stainless steel. The preparation of polymeric precursors and ceramic slurries are described and structure evolution of the deposited layers during heat treatment is discussed. Application of described method might help in eliminating problems related to excessive steel corrosion of metal supported SOFCs or reaction between electrolyte and cathode during high temperature sintering process.

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1. Introduction

Ceramic processing methods have evolved greatly in recent years. In the past, methods of simple high temperature sintering were dominating which resulted in excessive grain growth of ceramics. Demand for new thin or/and nanocrystalline layers have lead to the development or adaptation of new techniques. Examples of such technologies are spray coating, plasma spraying, sol–gel and polymer precursors methods [1–3].

Successful development of a method for obtaining fully dense ceramics at low temperatures will offer the possibilities to use new supporting substrates or integration into electroceramic devices. Application of stainless steel as a support of SOFC carries the unavoidable problem of corrosion of the steel at high temperature [3,4]. Using low temperature processing allows fabricating dense functional ceramic layers without excessive damage of the steel. Similarly, high temperature deposition of a dense electrolyte on cathode substrates leads to interdiffusion between materials and formation of a highly resistive interface which lower fuel cell efficiency [5].

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The spin coating process is a deposition method that is well established in the electronics industry. This process is used in microlithography for the manufacture of integrated circuits or in fabrication of antireflective coatings in solar cell applications and many others [6,7]. Recently this technology has gained attention in the SOFC community as a method to produce thin electrolyte layers [8–17]. For example, a slurry spin coating process was used to deposit electrolyte layers on anode supports [8–16]. Such a bi-layer structure is then sintered in a standard ceramic process at high temperature (~1400 °C). Maximum power density using YSZ electrolyte at 800 °C exceeded 1.6 W cm⁻², which can be regarded as a very good result. A low temperature method to form electrolyte on an anode support, which is similar to that used in this study, was evaluated by Pan et al. [17].

In this paper a novel technique for low temperature deposition of ceramic layers on different substrates is presented. The method involves the fabrication of ceramic membranes made of yttria-stabilized zirconia (YSZ) for application in solid oxide fuel cells and high temperature oxidation resistant coatings for stainless steels. The substrates were dense and porous with pore sizes from nano- to micrometer domain. SOFC functional layers served as substrates for deposition of YSZ membranes, i.e. cathode perovskite (La_{0.6} Sr_{0.4} FeO₃) and porous stainless steel (316L). Yttrium oxide for stainless steel protective layers was deposited on a dense Crofer 22 APU substrate. In our previous reports dense ceramic layers were deposited and evaluated on sapphire substrate, platinum foil and anode supports [18–20]. This method was also used

for fabrication of porous functional layers for SOFC applications [21,22].

2. Experimental

2.1. Substrates fabrication and preparation

The thickness of deposited layers as function of spinning speed was determined by comparing the mass change before and after deposition on glass substrates of 25 mm × 25 mm in size (Menzel Glaser, Germany). Before the deposition, substrates were heated to ~380 °C for surface pretreatment, which improves surface wetting.

Cathode perovskite supports of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ were sintered from powders prepared by a modified Pechini process [23,24]. Powders were initially precalcined at 1050 °C for 4 h. Grain size of this powder was less than 200 nm. More details about cathode material preparation are given in [24]. Powders were compacted uniaxially at 100 MPa and sintered at 1150 °C, which resulted in porosity of ~40% of theoretical. After sintering the diameter and thickness of the supports were about 25 and 1 mm, respectively.

A porous 316L stainless steel was obtained from Mott Corporation, USA. It has austenitic (face centered cubic) crystal structure and is composed mainly of Fe (~65 wt.%), Ni (~12 wt.%), Cr (~17 wt.%), Mo (~3 wt.%), Mn (~1 wt.%). The 316L was filter grade of 0.5 μm with porosity of about 25%. Samples of 25 mm × 25 mm × 1.12 mm in size were used for deposition substrates. Before deposition the substrates were washed successively in acetone and ethanol in an ultrasonic bath and dried at 80 °C.

Crofer 22 APU stainless steel was used as substrate material to study the oxidation resistance of polymer precursor produced yttria coatings. The investigated sheets were of 25 mm × 25 mm in size and 2.5 mm thick. They were polished using silicon carbide sandpapers (up to 1200-grit), washed in deionized water and ethanol in an ultrasonic bath and then dried at 80 °C.

2.2. Ceramic slurry and polymer precursor preparation

Slurry of YSZ ($\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-x}$) for the deposition onto substrates was prepared using commercially available YSZ powder (8-HSY, DKKK, Japan) with average particle size of ~100 nm. Suspensions were prepared by ultrasonically dispersing YSZ powders in a water/ethanol/ethylene glycol mixture. A typical composition is 10/20/70 by weight. A composition of 80/20 liquid/YSZ by weight percent was used. Higher solid loadings are difficult to deposit uniformly, because forces obtained by spinning are too low to ensure good uniformity of the film. The obtained slurries are stable (does not undergo visible sedimentation) for at least several hours, what is enough for the deposition process.

Polymer precursors were prepared by dissolving appropriate metal nitrates or chlorides in deionized water (DI) and ethylene glycol (EG) mixture in order to obtain ~0.25 M cation solution. First, metal nitrates for a total of 0.02 mol of resulting composition are dissolved in 20 ml DI and then about 40 ml EG is added. In the second step, water is evaporated by heating this mixture at 80 °C under constant stirring for several hours on a hot plate. After the evaporation, the solvent, typically 2-ethoxyethanol, is added to the mixture in a 1:1 volume ratio. For the preparation of YSZ polymer precursor, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ were used. In case of the deposition of protective coating on stainless steel $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was used to prepare yttria precursors (all chemicals were obtained from Aldrich, USA). The most important factor determining the quality of deposited layers is solution viscosity. It can be controlled either by prolonged heating on a hot plate, causing evaporation of solvents and progressive polymerization reaction to increase viscosity, or dilution by low viscosity liquid, e.g. ethanol, 2-ethoxyethanol. The desired viscosity is from 90 to 190 cP at 25 °C. For many substrates however, the viscosity must be experimentally checked in order to ensure good surface coverage and wetting properties. Using the polymeric precursor with too low viscosity is not practical, because it might require too many impregnations for full skeleton densification or for fabrication of thicker films. On the other hand, too high viscosity of a polymeric precursor leads to relatively thick polymeric film after single spinning that upon drying causes uneven shrinkage and introduces cracks.

2.3. Spin coating deposition procedure

Ceramic layer deposition method used in this study is a two stage spin coating procedure (Fig. 1) developed by Anderson and co-workers [25,26]. In the first stage a ceramic suspension is spin coated onto a substrate. Spin coating spinning rates are usually between 300 and 3000 rpm. After deposition, the substrates are dried at 80 °C for about 30 min and then heated to 380 °C with controlled ramp time of approximately 5 °C min⁻¹ so that the slurry solvents volatilizes and a porous, solid skeleton of loose ceramic particles is built. By controlling both the solid content in the suspension and the spinning rate a skeleton in the range of 400–3000 nm can be formed. The next stage is a multiple deposition of polymer precursor that impregnates the ceramic skeleton to a desired porosity level [18,19]. After every deposition the heating step to 380 °C is performed (heating and cooling rate 5 °C min⁻¹ and 20 min soaking at 380 °C). During heating the polymer precursor decomposes and transforms to nanocrystalline structure with average grain size of ~5 nm. In some cases, e.g. for other polymeric precursors and different compositions or preparation history, this temperature could be too low to crystallize the precursors. After the deposition of all layers, final heat treatment is performed. The temperature and time

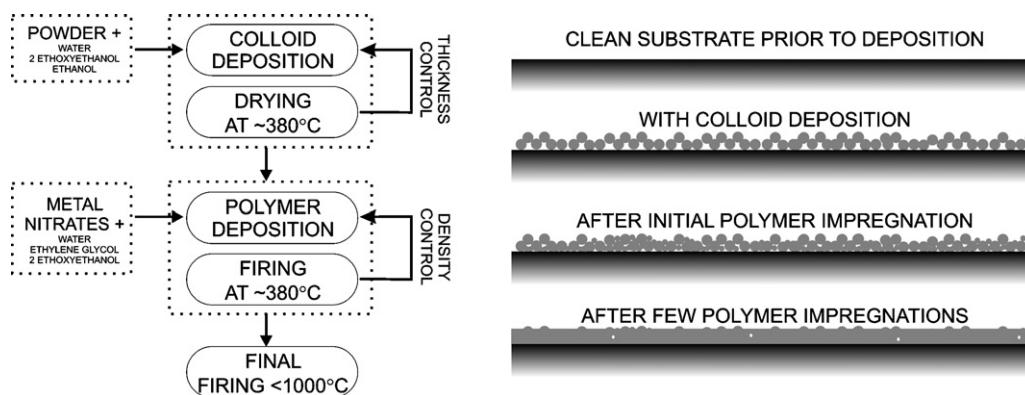


Fig. 1. Combined slurry suspension-polymer precursor deposition procedure using spin coating.

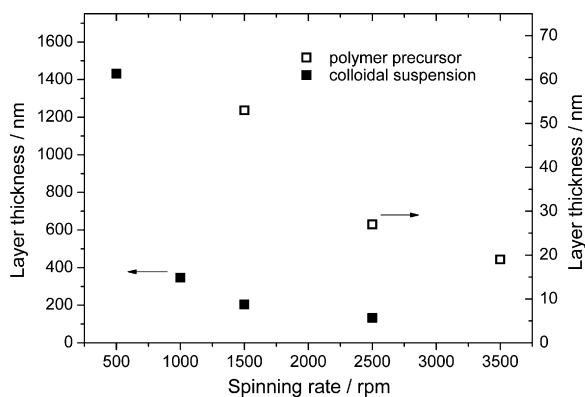


Fig. 2. Thickness of a single deposition of polymer precursor (~ 0.25 M of YSZ) and slurry suspension (20 wt.% of YSZ solid loading) as a function of spin coating spinning rate.

of calcination are dependent on the sample. More details are given in appropriate considerations further in the text. As it was shown previously [18,19], the resulting porosity and microstructure of the sample can be controlled. Optimum layer thickness for one deposition is about ~ 30 nm, which ensures high quality of film that will be described later. When substrates used for deposition are dense and smooth it is possible to spin coat only a polymer precursor. This is the case for steel coatings presented later on in this report.

In both deposition procedures ~ 0.3 ml of precursor or suspension were manually dispensed by a disposable pipette on the substrate which was then placed on a spin coater vacuum chuck (Laurell Technologies WS-400B-6NPP-LITE, USA). For polymer precursor a 30 s spinning time with different speeds was chosen. Slurries were deposited in a two step process. The substrate was first rotated for 10 s at 300 rpm to smoothly distribute the suspension and then the speed was immediately increased to the desired rate so that the excess of the slurry was removed. This procedure provides better uniformity of the film. For these samples maximum processing temperature was 380°C , i.e. samples were not subjected to additional annealing.

2.4. Measurements

The porosity was determined by a fluid displacement method (Archimedes method) using kerosene as the working liquid. XRD patterns were collected from sample surfaces at room temperature using Philips X'Pert Pro with $\text{Cu K}\alpha$ radiation. The Scherrer formula was used for grain size evaluation. The ICDD database was employed for phase matching and description of scans. Scanning electron microscope images were obtained using FEI-Philips XL30-ESEM.

For cyclic thermogravimetry experiments, samples were heated in static air to 800°C (ramp time of 3 h) and held for a desired soaking time. After furnace was cooled, the samples were weighted using a microbalance. This procedure was being repeated several times for the total soaking time of ~ 560 h.

3. Results and discussion

3.1. Spin coating deposition parameters

YSZ polymer precursor and slurry were used to estimate the thicknesses of single deposition for different rotating speeds. As shown in Fig. 2 for both polymeric precursor and slurry, thickness can be well controlled by tailoring the rotating speed. In case of the polymeric precursor deposited at the speeds of about 1500 rpm a resulting thickness is about 50 nm. At speeds higher

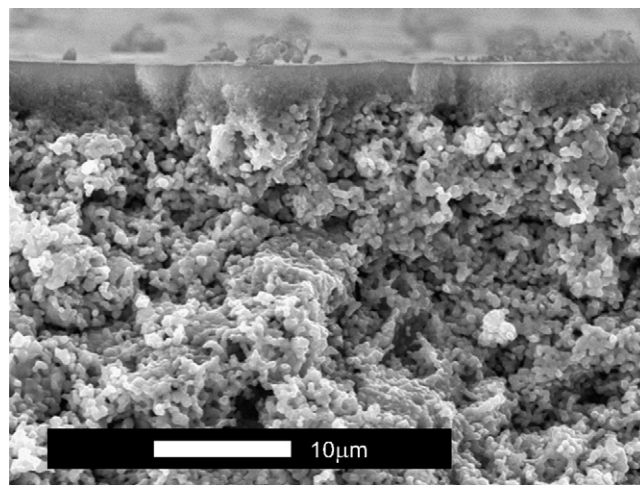


Fig. 3. SEM image of cross-section of YSZ electrolyte deposited on LSF support.

than 2500 rpm thickness is below 30 nm for each deposition, which usually provides the best quality films. In case of the YSZ slurries, the thicknesses in the range from few micrometers to hundreds of nanometers can be obtained and used as a skeleton for soaking by polymeric precursors. It should be stated here, that these results were obtained for the deposition on glass substrates and thus cannot be directly compared to the deposition process on other dense or porous structures. For other types of substrate the thickness may differ, however general relationships and conclusions should remain the same. Special care must be taken when highly porous substrates having irregular surfaces are used. These can provide problems while depositing film by the proposed methods. For the several initial depositions of the polymeric precursor a large deviation from the calculated thickness can be expected. This will be connected to filling of voids on the surface. After initial stage the deposition procedure will be performed on a smoother surface and should be more consistent with results presented here.

3.2. Deposition on cathode ceramic substrates

Fig. 3 shows a porous LSF cathode, which is coated by a thin YSZ electrolyte layer using the proposed method. Substrates with small surface roughness and small pore size result in a very smooth and dense membrane. The deposited layer is ~ 4 μm thick, fully dense and with no observable pinholes or cracks penetrating the film. The coating procedure consisted of one slurry deposition and several polymer precursor depositions. Good bonding on the cathode/electrolyte interface is achieved, which yields good electrical contacts and triple phase boundaries in the interfacial region. The penetration of polymeric precursor helps both electrical contact and adhesion of the coating to the substrate. The low processing temperature decreases the well known and described problem [27,28] of chemical reactions occurring between electrolyte and cathode materials when high processing temperatures are used. High temperature sintering causes reaction of cathode and electrolyte constituents (e.g. Sr and Zr) thus forming new, usually resistive crystalline phases that can be detected by X-ray diffractometry. Other well-suited method for the description of the reaction between those materials can be EDX analysis [28] which would give the information on the local composition. Fig. 4 shows an example of the XRD patterns of the YSZ layer on the LSF sintered at various temperatures for 2 h. These sintering times were chosen similar to the usually used to sinter the cathode on a fuel cell. The expected outcome of these reactions should be proportional to

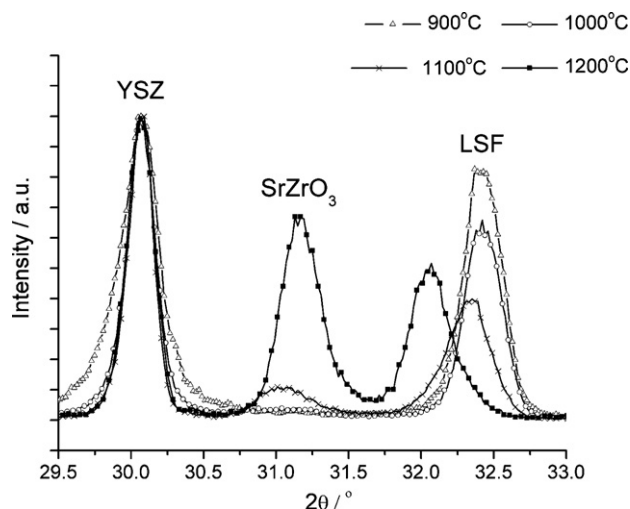


Fig. 4. XRD patterns of the YSZ electrolyte deposited on the porous LSF substrate after heat treatment at different temperatures for 2 h.

the one found in fuel cells [28]. It may be seen that the detrimental reaction between YSZ and LSF does not occur below 1000 °C. Above 900 °C a SrZrO₃ crystallizes on the interface between the support and the electrolyte. Moreover, the volume of the LSF unit cell increases. After processing the YSZ layer on the LSF at 900 °C the electrolyte layer is fully dense and crystalline so no further heat treatment is needed. Moreover the electrolyte is nanocrystalline in nature. The YSZ layer is a composite of suspension and polymer precursor with different initial grain sizes. During sintering the grains of both types grow, but they still may differ in size. Therefore, the XRD reflexes corresponding to the YSZ phase are composed of two components of the same diffraction angle but different widths, which influence the shape of the peak. The deconvolution of the shape of the peak at 2θ of 30.1° allowed estimation of the grain sizes corresponding to the suspension and polymer precursors. The temperature dependence of the size of the YSZ crystallites is shown in Fig. 5. The data obtained for powder which was prepared from polymer precursor by pyrolysis at 600 °C with grain size ~8 nm is shown for comparison. The results show that maintaining final firing temperature below 900 °C provides the electrolyte layer with grain sizes <100 nm both for slurry and polymer precursor derived crystallites.

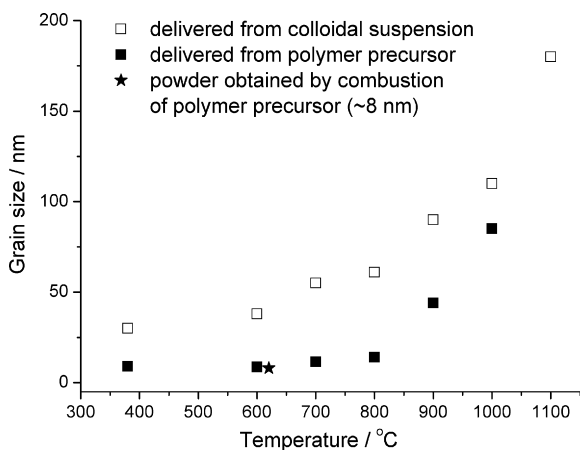


Fig. 5. Polymer precursor and slurry suspension derived grain sizes of the YSZ composite. The arrow indicates the crystallite size of the YSZ powder sintered at 600 °C.

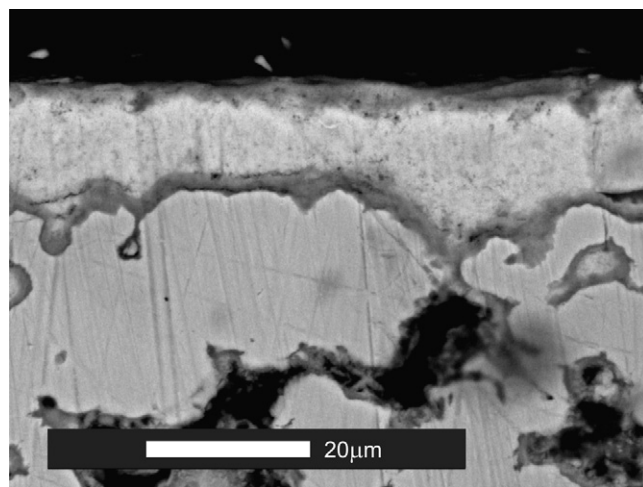


Fig. 6. SEM image of the YSZ electrolyte deposited on the porous 316L stainless steel.

3.3. Deposition on porous stainless steel substrates

Recently, in order to decrease the cost of SOFC, several research groups have been working on development of metal supported SOFC [29–32]. The development requires a stable metal/ceramic structure without extensive metal oxidation which is a crucial task. The proposed technology has potential for the required metal supported SOFC structures.

Thus several experiments were conducted in which YSZ was deposited on stainless steel substrates. The porous steel (316L) used in this study has an average grain size of about 50 μm, pore diameter ~20 μm and surface roughness in the order of 20 μm, which is observed from examination of SEM images of polished cross-sections. Such irregular surface is a demanding structure for film fabrication. In some earlier studies, related to the deposition of ceramic electrolytes on porous steel substrates, first a porous anode layer is deposited on the steel to minimize surface roughness, on which, next, the electrolyte layer is deposited [29,30]. However this procedure requires high temperature sintering step for anode that is detrimental for the cell. In current study the anode is not deposited in between 316L and YSZ to avoid high temperature sintering step. The efficient electrodes (anode and cathode) can be prepared later by low temperature method, for example, by infiltration using appropriate polymer precursors of porous stainless steel [31,32].

Here the aim was to develop a ~10 μm thick, fully dense ceramic membrane directly onto the steel which demands good covering of all surface roughness and surface pore filling in order to avoid cracks and pinholes across the membrane. In this case, one slurry layer of YSZ was first deposited which was then followed by the deposition of YSZ polymer precursor by spin coating. As can be seen in Fig. 6, the layer is dense and smooth with an average thickness ~15 μm. The layer that is seen in between the electrolyte and substrate is an oxide scale that formed during heat treatment (~400 °C) of cell. It is composed mainly of iron and chromium oxides (Fe₂O₃ and Cr₂O₃) what was confirmed by EDX and XRD analysis. The cracks visible in the electrolyte are from polishing of the sample. Even though there is considerable surface roughness on the substrate, the layer is smooth and covers the entire surface filling every pore, with some infiltration into inner pores. This infiltration helps the adhesion of the film to the substrate and increases the region of three phase boundaries when the anode and cathode precursor are used to form electrode layers. Such a process was used by Tucker et al. [31,32], in which the porous steel with deposited electrolyte layer was infiltrated

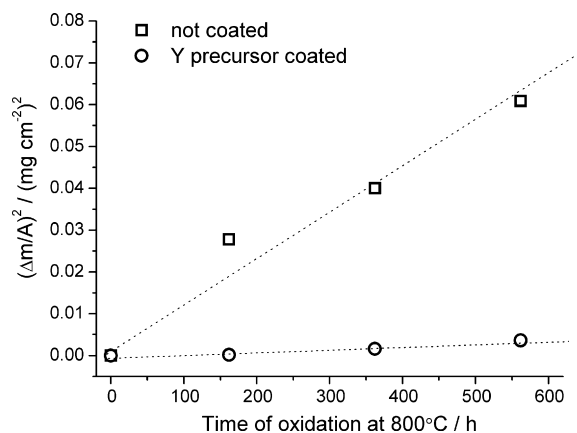


Fig. 7. Cyclic thermogravimetry of the Crofer 22 APU stainless steel for the uncoated and the yttrium precursor coated samples at 800 °C.

by anode or cathode successively on both sides of electrolyte.

3.4. Other applications areas

Polymer precursor methods are well suited for the deposition of dense films on dense substrates. In this manner thin ceria barrier layers can be easily deposited on YSZ electrolytes on the cathode side of the fuel cell in order to minimize reaction between YSZ and perovskite cathode. Also other materials can be deposited on the dense electrolyte layer. Especially promising is the development of thin film cathode layers for micro-SOFC platforms [33]. Materials prepared by this method reveal also nanocrystalline character of grains, which usually possess new and interesting properties [34]. Another possibility is coating of stainless steel substrates by binary or ternary oxides, which can greatly improve high temperature oxidation resistance in SOFC applications [35]. Samples with and without thin film coatings of yttria were prepared and were subjected to cyclic thermogravimetric measurements. The thickness of protective oxide layer was below 500 nm. For those samples only polymer precursor deposition was performed.

During oxidation at elevated temperatures an oxide scale forms on a steel surface resulting in change of sample mass. The mass change can be measured isothermally, by holding sample only at one temperature for all of the measurement time or in a cyclic mode, in which sample is periodically cooled and heated. Cyclic oxidation is a very demanding test for a practical SOFC. During temperature changes on heating or cooling of the cells, the steel substrate, the coating and the oxide scale change dimensions differently due to differences in thermal expansion coefficient of these materials. This can cause stresses, cracking, delamination and other problems. Cyclic oxidation is thus related to a practical oxidation process occurring in a long-term operation of cells. Mass change per unit area in a function of oxidation time is a parameter usually used for comparison of steel degradations. The results of cyclic thermogravimetry of uncoated and yttrium precursor coated Crofer 22 APU stainless steel at 800 °C are presented in Fig. 7. Three oxidation cycles were performed lasting at soaking for 162, 200, and 200 h. The results are plotted in parabolic units on vertical axis, which is connected to the limiting process of the oxidation mechanism. Usually it is related to the diffusion of metal cations from the bulk to the surface exposed to air through formed oxide scale. It can be seen that, in case of the Crofer 22 APU stainless steel coated with yttrium precursor, the mass change is radically decreased in comparison to uncoated Crofer steel plate.

4. Conclusions

A relatively simple method for low temperature ceramic layer deposition is presented. It is shown that this method can be used for fabrication of electroceramic devices. The method is very versatile and a broad range of thickness of nanocrystalline coatings can be obtained. Several examples of applications were shown: i.e. the ~4 μm electrolyte film deposited on a porous cathode, the ~15 μm electrolyte on a porous steel substrate and the thin film of yttria protective layer against high temperature oxidation on stainless steel. The low temperature nature of the process offers the ability to overcome many of the problems that are encountered with high temperature ceramic processing. The substrate interaction with deposited ceramic might be minimized due to low temperature film fabrication. Also the demand for exact thermal expansion coefficient matching can be lowered due to omitting incompatibilities that are more destructive at higher temperatures. However, this technique is still in its development phase and still parameters are needed to be examined in order to fully control the deposition process, e.g. types of solvents, firing temperatures.

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