Synthesis of supported CeO$_2$ nanofibers via electrospinning

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Abstract. Fibrous CeO$_2$ non-woven mats are synthesized via electrospinning. Homogeneous and stable aqueous polymer/cerium acetate blend spinning solutions are used. It is shown how the parameters of the solution, electrospinning, thermal post-processing can be successfully combined thus providing the synthesis of fibrous webs with mean diameters in the nanosized range. The morphologies of the samples are recorded under SEM and HRTEM while SAED is applied for studying their phase composition. The results obtained pave the way for the development of functional immobilized and self-supporting electrospun ceria ceramic materials.

1. Introduction

Cerium oxide could be reasonably classified as a strategic solid state material since it is extensively employed as a catalyst or as a promoter for supported metal or metal-oxide catalysts [1,2]. The so-called structural promotion effect is usually attributed to the ability of the lattice defects of various crystalline cerium oxides to act as catalytically active sites whereas its textural promotion effect relates to excellent CeO$_2$ thermal and mechanical resistance [3]. Besides, non-stoichiometric cerium oxides, CeO$_{2-x}$ exhibit greater catalytic activity than the stoichiometric one [4] the same behavior already been proved for oxygen-deficient crystalline phases of TiO$_2$ [5].

Similarly to all materials of applied interest, the contemporary progress in the field of advanced nanostructured CeO$_2$ ceramics is continuously stimulated by the development of novel synthesis techniques. In the last decade a revived preparation route, the electrospinning, is successfully applied for design of meso- micro- and nanostructured ceramic fibrous materials [6, 7]. The renewed interest to that relatively inexpensive, simple and exceptionally versatile fabrication technique could be primarily attributed to the synthesis of a broad set of low dimensional continuous fibres with high length-to-diameter ratio, specific surface area, and porosity and possibilities for their alignment and spooling [8 - 10]. Moreover, recently the electrospinning is combined with chemical and physical modification techniques, thus remarkably expanding the wealth of engineered fibrous materials over composites and ceramics [11]. Another peculiarity of the electrospun fibres is their relatively easy preparation in the form of supported or free-standing membranes and nonwoven or woven mats. Nowadays, the trend for synthesis of fibrous ceramics via electrospinning having novel chemical and phase composition and amazing morphologies is continuing. The overview of the opened literature shows, however, that the results on CeO$_2$ are on a small scale compared to electrospun nonwoven mats.
of other ceramics. For example using polyvinyl alcohol (PVA) as assisting polymer and Ce(NO$_3$)$_3$ ceramic precursors, CeO$_2$ nonwoven mat comprised of defect free fibres having diameters in the range 50-100 nm is synthesized [12]. The results presented are related, however, to both one and only polymer/ceramic precursor blend solution and electrospinning parameters. Further, an attempt for synthesis of CeO$_2$ is made using polyvinylbutiral (PVB) as assisting polymer [13]. The statement for hybrid mats synthesis built up of fibres of 200 to 500 nm diameters is supported, however, by an electron image of a couple CeO$_2$ fibres of high material density and low porosity. The specific surface area of those samples is 2,4 m$^2$/g is then not a surprising value. Several years later, using the same polymer and cerium precursor, PVB and Ce(NO$_3$)$_3$, hybrid as spun and crystalline CeO$_2$ nanofibers are synthesized [14]. It is established that by increasing the amount of Ce(NO$_3$)$_3$ in the spinning solution the average diameter of CeO$_2$ nanofibres increases while the opposite trend is observed on rising the calcination temperature. Since the micrographs of the final mats display small areas of poor fibre quality, the application of a complete set of imaging and analytical techniques is barely reasonable.

Summarizing the results discussed above it should be concluded, that PVA or PVB and Ce(NO$_3$)$_3$ could be applied as assisting polymers and cerium precursor in a narrow range of weigh ratios for preparation of CeO$_2$ nonwoven mats with low fibre yield and unsatisfactory fibre morphology.

In searching the basic rules governing the preparing of optimal spinning solutions, we continue to check a strategy with proven efficiency for synthesis of fibrous mats of other important nanostructured ceramics [15]. Most generally, the essence of the applied concept consists in using water soluble metal organic ceramic precursors which are able to preserve the viscoelastic properties of the assisting polymer in the blend solution in wide range of polymer/organic precursor weight ratios. On the basis of that concept we used cerium acetate Ce(CH$_3$COO)$_3$ and high molecular polymer. The main goal of the present study is to follow the opportunity for high yield synthesis of fibrous supported and free standing CeO$_2$ membranes via electrospinning for catalytic applications.

2. Experimental
The blend spinning solutions were prepared via gentle mixing aqueous solutions of 8,0 wt% polyethylene oxide (PEO) (M, = 800 000) and saturated concentration of Ce(CH$_3$COO)$_3$ in weight ratios between 3:1 and 1:10. In that interval the blend solutions exhibited viscoelastic properties under electrospinning conditions. The applied field strength (AFS) between the capillary tip and counter electrode was kept 1,0 kV/cm while the flow rates were of the order of 0,02 - 0,1 mL/h. Pieces of soda lime glass and aluminium foil arranged over the collector, served as substrates. PEO free calcinated fibres are obtained via two-step non-isothermal procedure in a quartz tubular furnace under conditions of controlled PEO pyrolysis [16, 17]. Depending on the efficiency of emanating gases removal, self-supporting or immobilized fibrous membranes were obtained. The samples were imaged and recorded under scanning electron microscope Jeol T 200 and HRTEM Jeol 2100. The later was used for verifying the phase composition via SAED. The free-standing and supported membranes display no morphological and phase composition differences.

3. Results and discussions
In the present study a wide scale of PEO/Ce(CH$_3$COO)$_3$ weight combinations were prepared and tested under electrospinning conditions at a constant AFS of 1,0 kV/cm. In all cases dense nonwoven mats were accumulated on the substrate surfaces and the remaining parts of the collector. Further, the as spun samples were subjected to two stage thermal procedure aiming efficient polymer removal and calcination. Thus, supported and self-supported crystalline fibrous CeO$_2$ membranes are prepared.

Figure1 shows low and high magnification scanning electron micrographs of PEO free fibres. These were obtained from aqueous blend solution having PEO to Ce(CH$_3$COO)$_3$ weight ratio 1: 1 (a) and 1:10 (b). A synthesis of continuous defect free fibres in the first case is clearly seen. In addition, a pliability that is typical for pure PEO fibres is preserved thus evidencing polymer memory effect. At tenfold increase of Ce(CH$_3$COO)$_3$ weight concentration in the spinning solution, keeping the same electrospinning and thermal conditions, a dense fibre web is also synthesized as shown by the
Figure 1. Scanning electron micrographs of PEO free calcinated fibres at low and high magnification: PEO / Ce(CH$_3$COO)$_3$ weight ratio 1:1 (a) and 1:10 (b); AFS 1.0 kV/cm

electron micrographs on figure 1b. Obviously, the increase of ceramic precursor weight part within the blend spinning solution is accompanied by a significant decrease of the mean fibre diameter. Thus, the results obtained demonstrate a trend opposite to that already observed earlier using PVB and Ce(NO$_3$)$_3$ based spinning solution [14]. Also, the electron micrographs on figure 1b shows that in addition to fibre mean diameter decrease, the high ceramic precursor concentration favours the formation bead defects. These experimental conditions represent the upper limit for the synthesis of defect free fibres, provided the concentration of PEO in the spinning solution is kept 8.0 wt%.

Figure 2 Transmission electron micrographs and SAED patterns of PEO free calcinated Ce-O fibres; AFS 1.0 kV/cm; PEO/Ce(CH$_3$COO)$_3$ weight ratio: 1:1 (a) and 1:4 (b); (c) magnified single fibre of (a).

Figure 2 presents transmission electron micrographs and corresponding SAED spectra of PEO free, calcinated at 500°C of samples electrospun from spinning solutions differing fourfold in PEO / Ce(CH$_3$COO)$_3$ solution weight ratio. Webs comprised of defect free fibres built up of individual nanosized grains are seen on both micrographs. In those cases the trend of fiber mean diameter reduction from 220 nm to 140 nm with increasing the ceramic precursor concentration in the blend solution is also seen. Further, it was established that CeO$_{2-x}$: Cubic, a = 11.700Å, SG Ia3 [18a], CeO$_2$: Hexagonal, a = 8.360Å, c = 10.420Å, SG P6/mmm [18b], Ce$_2$O$_3$: Rhomboedral (Hexagonal), a = 3.981 Å, c=6.063 Å, SG P321 [18c] and Ce$_2$O$_3$:Rhomboedral (Hexagonal) a = 10.370Å, c = 9.670Å, SG R [18d] are the basic phase constituents of the calcinated fibers as revealed by the diffraction analysis of the recorded polycrystalline SAED patters. Therefore, thermally stimulated either complete or partial reduction of the as spun hybrid mats takes place resulting in the evolution of crystalline grains of CeO$_2$, CeO$_{2-x}$, and traces of cerium oxides with lower oxygen content. Besides,
the electrospun fibers are highly porous (figure 2c) and could supply nucleation sites for further loading of nanoclusters from various catalytically active elements or compounds. On this basis it is hard to avoid the conclusion that self-supporting or immobilized fibrous membranes of cerium oxides synthesized via electrospinning could be successfully used as efficient catalyst supports. Moreover, similarly to the nanoparticles, the opportunity for nucleation and growth of nanosized grains having non-stoichiometric phase composition is a substantial prerequisite for an enhanced catalytic efficiency [4].

4. Conclusions
A simple experimental approach for high yield synthesis of immobilized and self-supporting electrospun cerium oxides based nonwoven mats is proposed. It relays on the preparation of reliable PEO/cerium three acetate blend spinning solutions. It is shown how the latter can be reproducible electrospun within a broad range of polymer/ceramic precursor weight ratios under same electrospinning conditions. The synthesized immobilized and self-supporting electrospun membranes refer to nanostructured crystalline fibrous materials having a significant porosity. These are very promising parameters for their further applications in the field of applied catalysis.

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