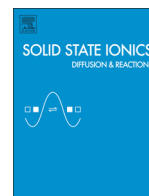




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# Electrophoretic deposition of a self-stabilizing suspension based on a nanosized multi-component electrolyte powder prepared by the laser evaporation method

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## ABSTRACT

This work presents the results of study of non-aqueous suspensions based on a solid state electrolyte Ce<sub>0.8</sub>(Sm<sub>0.75</sub>Sr<sub>0.2</sub>Ba<sub>0.05</sub>)<sub>0.2</sub>O<sub>2-δ</sub> (CSSBO) prepared by the method of high-energy material dispersion–laser evaporation of the ceramic target. The thermal behavior of the powder was studied by thermogravimetric and differential thermal analysis (TG-DTA); the sintering kinetic was investigated by the dilatometric method. Electrokinetic study showed that the powders with nanoparticles that had an average diameter of 15 nm formed a self-stabilizing suspension with a high value of ζ-potential (+31 mV) in the isopropanol/acetylacetone (50/50 vol.%) dispersing medium. The CSSBO thin films (2 μm) that deposited on the dense electrode substrate of La<sub>2</sub>NiO<sub>4+δ</sub> (LNO) after sintering for 6 h at 1400 °C had a uniform microstructure with an average grain size of 4 μm and total conductivity of 0.1 S/cm at 650 °C.

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## 1. Introduction

The recent tendency to lower the solid oxide fuel cell's (SOFC) operating temperature to below 800 °C is motivated by the reduced degradation of the cell components, greater flexibility in cell design and lower manufacturing costs due to a broadening of the electrode and interconnector material choice [1]. However, the electrolyte conductivity decreases significantly when the operating temperature is lowered. This disadvantage can be overcome by decreasing the electrolyte resistance either by developing alternative materials that possess higher ionic conductivity in an intermediate temperature range and/or decreasing the electrolyte thickness.

The investigations of multi-component solid-state electrolytes based on CeO<sub>2</sub> have shown that co-doping with rare earth and alkaline earth elements leads to increased conductivity in comparison with single-doped solid solutions and, in some cases, expands their electrolytic domain which feature is characterized by the critical oxygen partial pressure  $p_{O_2}^*$  below which the electronic conductivity exceeds the ionic conductivity [2–5]. Among the numerous co-doped CeO<sub>2</sub>-based electrolyte systems investigated in our present study [6], the lowest

$p_{O_2}^*$  value of  $3.3 \times 10^{-23}$  atm at 750 °C was observed for Ce<sub>0.8</sub>(Sm<sub>0.75</sub>Sr<sub>0.2</sub>Ba<sub>0.05</sub>)<sub>0.2</sub>O<sub>2-δ</sub>. This electrolyte possessed the highest value for total conductivity in air equal to  $6.3 \times 10^{-2}$  S/cm at 750 °C.

Nowadays, there is an increasing interest in the development of technologies for the production of nanosized powders. The potential of such powders derives from the extremely small dimensions of the particles and thus their unique physical properties. The laser evaporation technique is known to be a highly versatile and potent method for the production of nanopowders across a broad spectrum of applications [7–9]. Recently, this method was adapted by our research group for the production of nanopowders for electrochemical applications [10].

Several methods are currently used for thin film deposition in SOFC technology [11]. Electrophoretic deposition (EPD) is one of the colloidal processes used in ceramic production and has advantages such as a relatively brief formation time, little restriction on the shape of substrate, no requirement for binder burnout as the green coatings contain few or no organics and easy control of the film thickness through simple adjustment of the deposition time and applied voltage [12–14].

The performance of EPD in producing homogeneous films with high green density strongly depends on the particle surface chemistry, the behavior of the surface–liquid interfaces under an electric field, and the development of particle–particle and particle–substrate networks during particle assembly [15]. The investigations concerning stabilization of

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suspensions made of nanosized powders with subsequent EPD of the electrolyte films for SOFC's application are represented mostly by study performed on  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (SDC),  $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (GDC), and yttria-stabilized zirconia (YSZ) nanosized powders produced by the combustion method utilizing various organic fuels under laboratory conditions or commercial powders fabricated by well-known firms such as Tosoh (Japan), Sigma-Adrich (UK), and Fuel Cells Materials (USA) [16–20]. The study of suspensions of commercial GDC powder [20] showed that the isoelectric point in aqueous suspension occurred at neutral pH values in the region of 7. Polyacrilamid (Duramax-D3005) in the amount of 3.0 wt% was used as a deflocculant in an aqueous medium and phosphate ester (Beycostat-C213) in the amount of 2.0 wt%—in ethanol. To achieve sedimentation stability of the suspensions and superior quality of the deposited films, iodine [17], water [18], and hydrochloric acid [19] were used in addition to stabilizers and dispersing additives.

Our earlier studies have shown that the preparation of stable suspensions for EPD can be simplified by using weakly aggregated nanopowders fabricated by the laser evaporation method [21]. Comprehensive investigations into the influence of the dispersion medium, the acidity of the medium, and the presence of a polymer modifier on the formation of a thin YSZ layer have revealed that the suspensions based on such powders tend to be stable without the addition of special stabilizers because of the self-formation of an electrical double layer on the particles' surface [22–24].

The aim of the present work is to develop the optimal rheological parameters for a suspension based on CSSBO powder prepared by the method of laser evaporation of the ceramic target. An electrokinetic study was performed on the suspensions with the isopropanol and isopropanol/acetylacetone dispersing media. The suspension with superior characteristics was used to deposit thin electrolyte films (2  $\mu\text{m}$ ) by the EPD method on a dense cathode substrate made of  $\text{La}_2\text{NiO}_{4+\delta}$  (LNO). LNO possesses a coefficient of thermal expansion (CTE) equal to  $12.9 \times 10^{-6} \text{ K}^{-1}$ , which is close to that of the electrolyte chosen ( $12.5 \times 10^{-6} \text{ K}^{-1}$ ). It also has good chemical stability under cathodic conditions, a proper level of electronic conductivity, and a high level of ionic conductivity ensuring excellent electrochemical performance [25]. The microstructure and electrical properties of the deposited film were investigated and compared with the properties of the compact samples.

## 2. Experimental procedure

### 2.1. Synthesis of the materials

$\text{Ce}_{0.8}(\text{Sm}_{0.75}\text{Sr}_{0.2}\text{Ba}_{0.05})_{0.2}\text{O}_{2-\delta}$  (CSSBO) powder was initially prepared by a solid-state reaction method as described elsewhere [26]. The nanopowder was obtained by the method of laser evaporation of a ceramic target using an LS-06 ytterbium fiber laser with a wavelength of 1.07  $\mu\text{m}$ . For the target preparation, CSSBO microsized powder was dry-pressed into a pellet 80 mm in diameter and 20 mm in height and then sintered at 1300 °C, 3 h. The laser operated in a pulsed regime, which is favorable for the formation of fine uniform nanopowders (NPs) with narrow particle size distribution. The pulse frequency was 5 kHz with pulse duration of 60  $\mu\text{s}$ . The average irradiation power output was approximately 600 W. The working gas (a mixture of  $\text{N}_2$  and  $\text{O}_2$  with a volume ratio of 0.79:0.21) was blown into the evaporation chamber at the rate of 70 l/min. The linear flow rate at the target surface was approximately 15 m/s. The oxide vapors were expelled from the focal spot and condensed as NPs, which were carried by the working gas into the cyclone with the fine filter, where the powder was collected.

A JEOL JEM 2100 transmission electron microscope (TEM) was used to characterize the CSSBO NPs. X-ray phase analysis was carried out on a D8 DISCOVER diffractometer in copper radiation with a graphite monochromator on a diffracted beam. Processing was carried out using Topas-3 software with the Rietveld algorithm of structural parameter

refinement. The specific surface area of the NPs was determined by a volume version of the BET method based on the low-temperature equilibrium sorption of nitrogen vapors by a Micromeritics TriStar 3000 vacuum sorption analyzer. Thermal analysis was performed using a NETZSCH STA-409 analyzer with simultaneous quadrupole mass-spectrometry. CSSBO NPs was densified by magnetic pulse compaction at 300 MPa and pulse duration of 100  $\mu\text{s}$ , and its sintering kinetic was studied using a Dil 402 dilatometer under heating to 1500 °C at the rate of 5 grad/min.

The  $\text{La}_2\text{NiO}_{4+\delta}$  (LNO) powder was synthesized via a two-step ceramic technology (1150 °C for 2 h, 1230 °C for 5 h). XRD analysis on the LNO revealed a  $\text{K}_2\text{NiF}_4$ -like structure (sp. gr. *Fmmm*,  $a = 0.5448(1) \text{ nm}$ ,  $b = 0.5477(1) \text{ nm}$ ,  $c = 1.2667(8) \text{ nm}$ ). After final sintering, the LNO was ball-milled to the state of having a specific surface area equal to 1  $\text{m}^2/\text{g}$  and then dry-pressed into samples of disk and bar shape at 150 MPa and sintered at 1400–1500 °C for 3 h. The LNO supports were polished, cleaned in an ultrasonic bath, and burned out at 900 °C for 1 h and used for carrying out EPD. The relative density of the LNO support was calculated from the XRD data and shown to be 84% of the theoretical density.

### 2.2. Electrophoretic deposition

In order to obtain the suspension of CSSBO NPs, isopropanol and a mixture of isopropanol/acetylacetone (50/50 vol.% ratio) were used as solvent media. BMMA-5 polymer, which is a co-polymer of butyl methacrylate with the addition of 5 mol% of methacrylic acid, was added into the suspension. To ascertain an optimal concentration of the polymeric binder a set of experiments was conducted. The optimal concentration of the binder, when the film was not observed to be cracking during its drying in an air atmosphere, was found to be equal to 2.5–3.0 g/l. At such a level of concentration, the polymeric binder fills the interstices in the nanoparticle packing. At concentrations higher than 3.0 g/l, the rate of the EPD drastically decreases because of the blocking effect of the non-conducting polymeric film adsorbed on the surface of the nanoparticles. Suspensions with the electrolyte concentration of 10 and 20 g/l were treated by a UZV-13/150-TN ultrasonic processor for 5–125 min. Electrokinetic measurements were performed on 120 ml of the suspensions in automatic mode utilizing a DT-300 analyzer. Direct potentiometric titration of CSSBO suspensions was performed with 0.17 N KOH. All measurements of suspensions were carried out under isothermal conditions in air at 25 °C.

The EPD was carried out on computerized equipment of laboratory design which provided constant voltage modes. An LNO substrate 12  $\text{mm}^2$  in area served as a cathode, and a disc (12  $\text{mm}^2$ ) of stainless steel was used as an anode. The distance between the electrodes was 1 cm. Taking into account the regimes of EPD processing developed for thin YSZ electrolyte films [27–29], in the present study, a variety of EPD regimes were tested: at a constant voltage of 40 and 80 V with the time of deposition being varied, the time of deposition remaining constant at 1 min and the applied voltage being varied across the range of 40–100 V. The stable and reproducible results were obtained at 80 V with the deposition current density equal to 1.5  $\text{A}/\text{cm}^2$ . Under this regime, deposition of 1 min duration resulted in a uniform CSSBO green deposit of 2.5  $\text{mg}/\text{cm}^2$  with thickness approximately 2  $\mu\text{m}$ . Densification of the deposited films was performed in a Hermle Labnet Z383 centrifuge with a rotational velocity of 1000 rpm for 2 min.

### 2.3. Electrode support and thin film characterization

Electron microphotographs were obtained using an electron microscope JEOL JSM-6390LA. The conductivity of compact LNO and CSSBO samples was measured by the direct current four-probe method in air in the temperature range of 500–850 °C with steps of 50 °C and isothermal exposure of 1 h within each step. Evaluation of the thin film's conductivity was carried out in the same temperature range during heating

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