



Effect of pore formers on properties of tape cast porous sheets for electrochemical flue gas purification



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ABSTRACT

Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) electrolytes for electrochemical flue gas purification multilayers were fabricated by tape casting and sintering using different types, shapes and sizes of pore formers. The resulting tapes (with thickness of about 400 μm) were characterized by scanning electron microscopy, gas permeability measurements, mercury porosimetry and pore orientation measurements, to investigate the role of the different pore formers on the properties after sintering at a temperature of 1250 °C. Those tapes prepared from different non-spherical pore formers with comparable porosity of about 43%, showed significant differences in gas permeability which could be correlated to an increase in mean pore size and pore connectivity. The degree of pore orientation in the tape casting direction was determined by best-fit ellipse method and a modified linear intercept method and the obtained data were correlated with the corresponding gas permeability.

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1. Introduction

Exhaust gas from diesel engines contains many undesired pollutants such as particulate matter and nitrogen oxides (NO_x), which are formed as a side product from N₂ and O₂ at high temperatures. It is well known, that nitrogen oxides have a negative impact on human health and cause environmental problems such as acid rain and high local ozone concentrations [1,2]; while the particulate matter is carcinogenic [3].

For these reasons great efforts have been made to remove NO_x from the exhaust gases of diesel engines. One approach is to electrochemically reduce the NO_x content by the use of an electrochemical cell, which is composed of a porous solid electrolyte layer between two porous electrodes as represented in Fig. 1. During the catalytic process NO is reduced at the cathode by formation of gaseous nitrogen and oxygen ions (O²⁻), while soot is oxidized to CO₂ on the opposite electrode (anode). The oxygen ions are then transported through the electrolyte to the anode, where they are either oxidized to oxygen or react with the soot [4]. A suitable design for an electrochemical reactor for flue gas purification is a planar arrangement of alternating porous layers of a conductive per-

ovskite (e.g., La_xSr_yMn_zO (LSM)) electrode and an ionic conductor (Ce_{0.9}Gd_{0.1}O_{1.95} (CGO)).

If such an electrochemical flue gas purification reactor is used as a diesel particulate filter, it requires relatively high gas permeability in the order of 10⁻¹¹ to 10⁻¹² m². Such a high gas permeability is required to reduce the pressure drop across the cell and, therefore, the porosity of the different layers of the cell need to be controlled carefully. Ohji et al. described different techniques to obtain porous structures that lead to different level of gas permeability, depending on the processing and type of organic fugitives used [5]. Nevertheless, if the reactor is primarily developed as a unit to remove NO_x to achieve European Union emission regulations for new light duty vehicles (Euro 6 standard for passenger cars and light commercial vehicles) and soot particles are removed beforehand by a separate filter unit, depending on the design of the NO_x removal unit lower gas permeability of 10⁻¹³ to 10⁻¹⁴ m² might be acceptable. It is well known that both gas permeability and electrical conductivity of NO_x electrochemical filters, as well as for SOFC, are strongly dependent on microstructural parameters such as porosity, phase distribution and particle size [6–8].

Tape casting represents a well-established technique to obtain large ceramic sheets with good surface finish and thickness in the range of 0.005–1.5 mm. Hence, tape casting is a cost-effective way to manufacture the above mentioned alternating layers of electrode and ionic conductor in suitable thicknesses. Recently, a few studies

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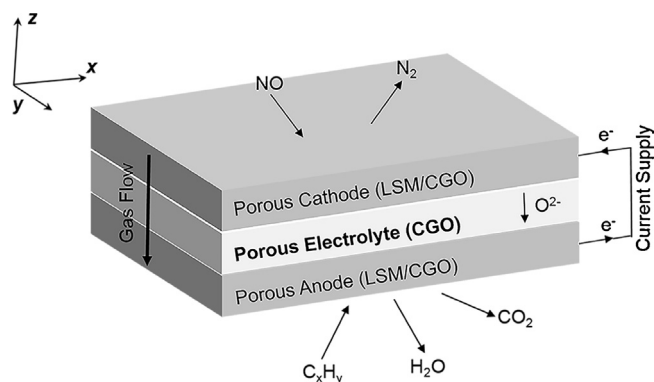


Fig. 1. Schematic representation of an electrochemical flue gas purification cell with porous LSM and CGO layers made by tape casting.

have been undertaken on tape casting of CGO, regarding sintering and densification of porous CGO layers [9–11], the mechanical characterization of thin film porous and dense CGO layers [12,13] and related to gas permeation through porous CGO supports [14]. To obtain porous electrodes and electrolytes by tape casting, pore formers (PF) based on organic fugitives are often added to the slurry. During thermal treatments the PF will be burned out, leaving a porous structure. It is known that during tape casting the non-spherical particles, binder and pore formers are oriented in the tape casting direction due to the shearing forces that occur when the slurry passes below the doctor blades. According to Jeffery's theory [15] bigger particles have the tendency to orient more than smaller particles due to the increased rotation velocity when perpendicular to the tape casting direction. The gas flow in the multilayer structure is perpendicular to the tape casting direction (Fig. 1) of each tape. The pore former particles that orient parallel to the tape casting direction (and perpendicular to the gas flow direction) will contribute to a higher pressure drop than those pore former particles that orient perpendicular to the casting direction. Thus, preferably a control of the microstructure [16,17] with unidirectional pore orientation perpendicular to the casting direction would be desirable. However, for this application, using conventional tape casting process a random orientation of pores would be acceptable.

For the characterization of particle and pore orientation in tape cast products, different methods were used in literature. Fu et al. [18] described a technique based on the linear intercept method to quantify the pore orientation degree by analyzing scanning electron microscopy (SEM) micrographs. Besendörfer and Roosen [19] presented a method to quantify the alignment of the ceramic particles by means of SEM micrograph analysis, and constructing a particle orientation distribution plot with the results obtained from the analysis.

Until now, a detailed analysis of the orientation of pore former particles with different size and shape during tape casting and the influence on microstructure and properties of the resulting thin film layers has not yet been reported, especially not for the application in multilayered porous electrochemical NO_x filters.

Thus, this study focusses on the influence of the use of different pore formers on the microstructure and the gas permeability of thin porous CGO electrolyte layers proposed for electrochemical NO_x filters. For this purpose, it was investigated how pore former particles with different size and shape orient and pack in thin, porous CGO layers during tape casting and how this affects the final microstructure (pore orientation, pore size and shape) and gas permeability after sintering. The porous CGO layer was selected for these studies because it is simple (single phase in contrast to the catalytic LSM/CGO electrode layers) and carries additional main

functionalities of the electrochemical NO_x filter system. Some of these properties of the porous CGO layer system, such as mechanical properties and ionic conductivity, will be reported elsewhere.

2. Experimental

2.1. Raw powders

For tape casting of porous $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) layers the following raw powders were used: an ultra-low surface area CGO powder (ULSA-CGO GDC10-TC, Fuel Cell Materials, Lewis Center, OH, USA, specific surface area of $6\text{ m}^2/\text{g}$, d_{50} : $\sim 0.35\ \mu\text{m}$). Furthermore, 6 different types of pore former were added, each with a different size and shape, acting as sacrificial fugitives to create macro pores in the CGO layer. The poreformers were varying in composition, shape and size: (1) polymethyl methacrylate microparticles (PMMA MR10G, Esprix Technologies, Sarasota, FL, USA, d_{50} : $10\ \mu\text{m}$), (2) spherical graphite (V-UF1 99.9%, Graphit Kropfmühl AG, Hauzenberg, Germany, d_{50} : $3\text{--}5\ \mu\text{m}$), (3) spherical graphite (AF 99.95, Graphit Kropfmühl AG, Hauzenberg, Germany, d_{50} : $10\ \mu\text{m}$), (4) spherical graphite (FormulaBT SLA1518, Superior Graphite, Chicago, IL, USA, d_{50} : $17.7\ \mu\text{m}$), (5) platelet graphite (SGB 10 L/99.9, Graphit Kropfmühl AG, Hauzenberg, Germany, d_{50} : $10\ \mu\text{m}$) and (6) platelet graphite (FormulaBT LBG2025, Superior Graphite, Chicago, IL, USA, d_{50} : $20.9\ \mu\text{m}$). The characteristics of these different pore formers used in this study are summarized in Table 1 (see Section 3.1). Below, the following nomenclature is used to indicate the samples: G = graphite, SPH = spherical, Plate = platelet-shaped and the number at the end denotes the average particle size of the graphite given by the supplier.

2.2. Slurry preparation and tape casting

Six compositions of CGO layers were tape cast by choosing different types of pore former. The concentration of the different pore formers was 23 vol.-% in all tapes (and 31.0 vol.-% of CGO powder, 39 vol.-% of binder and 7 vol.-% of dispersant). One composition without any pore former was also prepared for comparison, which had 54 vol.-% CGO and the same amount of binder and dispersant as the previous ones. The amounts of pore former, CGO powder, binder and dispersant were calculated for the green dried tapes (after removal of solvent).

Tape casting slurries were prepared by dispersing the CGO powder in an azeotropic methylethylketone and ethanol solvent mixture (MEKET) with polyvinylpyrrolidone (PVP) as a dispersant, similar to a procedure described by Lobera et al. [20]. These mixtures were typically ball milled for 72 h at high speed (220 rpm) in PE bottles using zirconia balls. The particle size (d_{50}) after milling was typically around $0.35\ \mu\text{m}$ in the slurry with both particle size distributions (PSD's) exhibiting a bimodal distribution. The pore formers (Graphite and PMMA) were added to the slurries together with additional dispersant. The slurries were ball milled for 5 h at low speed (85 rpm) to allow the pore formers to incorporate to the slurries before the binder addition. The particle size was measured again after milling to ensure that the slurries are well dispersed. A PVB based binder [21] system (mixture of binder, plasticizer and a release agent) is finally added to the slurries and the slurries were then slowly rotated for another 24 h to allow for proper homogenization.

The slurries were finally filtered and de-aired before tape casting onto a polymer film. The suspensions were tape cast, using a doctor blade adjusted to $1.5\ \text{mm}$ for all tapes (corresponding to dried thicknesses ranging from 360 to $450\ \mu\text{m}$, depending on the pore former used) at a casting speed of $20\ \text{cm}/\text{min}$. After sintering porous CGO sheets with a thickness of $310\text{--}430\ \mu\text{m}$ result. It is important

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