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Properties of tape-cast Y-substituted strontium titanate for planar anode substrates in SOFC applications

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Abstract This work evaluates the use of fine-grained yttrium-substituted strontium titanate powders for the preparation of planar anode supported solid oxide fuel cells. Starting from a submicron-sized powder of Y-substituted strontium titanate $Sr_{0.895}Y_{0.07}TiO_3$ (SYT), which was synthesised via spray pyrolysis followed by a grinding process, suspensions of high solid concentration were prepared by steric stabilisation. From these suspensions, tape casting slurries of up to 25 vol% were produced and further processed to ceramic green tapes using the doctor blade technique. The rheological behaviour of the slurries was investigated in dependence on the content of solids and organic additives. Furthermore, the binder burnout and sintering behaviour of the green sheets were characterised. After firing, crack-free substrates of high planarity were obtained. The achieved properties of the sintered tapes such as density, porosity, warping, mechanical strength, and electrical conductivity were determined in dependence on sintering temperature.

Introduction

Tape casting is a well-known process for the manufacture of thin and flat ceramic substrates. This process allows the manufacture of ceramic green tapes with constant thickness on a large scale at low costs. These ceramic green sheets are the basic product for the manufacture of substrates or ceramic multilayer devices, e.g., capacitors, inductors, high integrated circuits, actuators, and gas sensors [1]. In the field of high temperature fuel cells, tape casting is a favoured technique for the manufacture of planar solid oxide fuel cells (SOFCs) [2]. The tape casting process is well described in the literature [3–5]. Typically ceramic powders with an average particle size between 1 and 3 μm, but also submicron and recently nano-sized powders are used for tape casting [6]. Their use also allows the reduction of sintering temperatures [7–9].

Strontium titanate-based powders have promising advantages for SOFCs applications, e.g., a thermal expansion behaviour matching that of the solid electrolyte [10–12], high electrical conductivity after high temperature reduction [11–14] and a low chemical expansion or shrinkage during changes of the gas composition in the case of $Sr_{1-x}Y_xTiO_3$ materials [11, 15]. Especially the latter property is important to guarantee a safe and reliable operation after incidental oxidation of the anode. This has been demonstrated with button cells using $Sr_{0.8}La_{0.2}TiO_3$ [16] and very recently with cells of realistic cell size applying SYT as anode substrate [17]. The SYT-based cells withstand 100 redox cycles without mechanical damage and, depending on the redox cycling conditions, a stable performance.

In addition to the properties listed in [11], a ceramic anode substrate should exhibit a thickness of 0.2–0.8 mm, a porosity of 20–40%, a mean pore diameter of approx. 1 μm and a mechanical strength of about 80–100 MPa comparable with conventional cermet anode substrates [18].

This work describes the preparation of SYT sheets by tape casting for application as SOFC anode substrate. To achieve deagglomerated, stable SYT suspensions of high

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solid loading, it is necessary to adjust solvent and dispersing agent. By adding the proper amount of binder and plasticiser, these suspensions were transferred into tape casting slurries with the desired rheological behaviour and finally cast to form crack-free ceramic green tapes. The properties of the slurries, the casting process, the sintering behaviour as well as the final product properties like porosity, mechanical strength, and electrical conductivity in dependence on sintering temperature are discussed. The sintered specimens are evaluated with regard to porous anode materials in SOFC applications.

Experimental

Materials

A submicron SYT powder, which was synthesised by spray pyrolysis [19] and subsequent milling, was used. The true density of the powder was measured by means of a helium gas pycnometer (AccuPyc 1330, Micromeritics, Norcross, GA, USA); the value was 4.8 g/cm^3. This value is below the theoretical density of fired $Sr_{0.895}Y_{0.07}TiO_3$, which is specified by XRD measurements as 5.06 g/cm^3 [14]. The lower density of the as received powder reflects an intermediate structure caused by a calcination temperature below 1000 °C during powder synthesis. The determination of the specific Brunauer–Emmett–Teller (BET) surface area was carried out using a gas sorption analyser (ASAP 2000, Micromeritics, Norcross, GA, USA). Prior to the measurement, the powder was heated up to 300 °C in vacuum to remove adsorbed molecules. The mass specific surface area was measured using nitrogen as adsorption gas.

From this powder, suspensions were prepared using an azeotropic solvent mixture of ethanol/toluene (analysis purity). The azeotrope combines the dissolving capabilities of both solvents, but evaporates as a single liquid phase retaining its stoichiometry during the drying process. As dispersing agent, a steric stabilising carbonic acid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) was chosen, which is compatible with the binder and plasticiser. For the preparation of the tape casting slurries, the binder polyvinyl butyral (Butvar, Solutia Inc., St. Louis, MO, USA) and alkyl benzyl phthalate as a plasticizer (Santicizer, Ferro Corp., Cleveland, OH, USA) were used.

Slurry preparation and tape casting process

Suspensions were prepared by mixing the as received SYT powder, solvent, and dispersing agent. The solid content as well as the concentration of the dispersing agent was varied. To achieve well dispersed systems, the suspensions were deagglomerated for 24 h by agitating in a shaker-mixer (Turbula, WAB AG, Basel, Switzerland) using yttria-stabilised zirconia (YSZ) grinding balls with diameters of 1.0–1.5 mm. With the addition of binder and plasticiser, the stable suspensions were transferred to tape casting slurries. According to the solid concentration, the amounts of binder and plasticiser were varied. These mixtures were homogenised for another 24 h in the shaker-mixer. Prior to the tape casting process, the slurries were screened (mesh size: 100 μm) to reject large agglomerates and non-dissolved binder. Finally the slurries were degassed under vacuum (230 mbar, 20 min) to eliminate any bubbles.

The viscosities of the casting slurries were determined in dependence on shear rate with a rheometer (Physica UDS 200, A. Paar GmbH, Graz, Austria) using the cone (angle 2°) and plate geometry. The measurements were carried out at a constant temperature of 20 °C. For comparison, the viscosity values at a shear rate of 20 s^{-1} were used. This matches the shear rate, which occurs during the tape casting process under the doctor blade for the chosen gap height and casting velocity. From the rheological point of view, the casting slurries must exhibit a shear thinning (pseudo-plastic) behaviour and viscosities between 4 and 12 Pa s, which are ideal for the doctor blade technique. The degassed slurries were tape cast on a laboratory casting machine of 400 cm length, which is equipped with a moving silicon-coated PET carrier film (Diafoil, Mitsubishi Plastics Inc., Tokyo, Japan) and a static casting head. A casting speed of 700 mm/min was used, the gap height varied from 700 to 1100 μm. The cast slurries were dried at ambient air temperature.

Characterisation of green and sintered tapes

The density of the dried green tapes was determined by the Archimedes method using deionised water as measuring fluid. Previous experiments proved that this fluid does not wet nor infiltrate the green tapes due to their different surface energies. The thermo-gravimetric investigations (STA 409, Netzsch GmbH, Selb, Germany) were performed on green tapes and pure organic additives. Furthermore, the shrinkage behaviour was determined by dilatometry (DIL 402C, Netzsch GmbH, Selb, Germany) on a green tape of 14.52 mm length and a thickness of 285 μm. In the dilatometer the green tape was debinded in air up to 500 °C. After changing the atmosphere to argon, the shrinkage activity was investigated up to a maximum temperature of 1400 °C (heating rate: 5 K/min). From the preceding thermal investigations the following sinter profile was scheduled:

$$\mathrm{RT}^{5\,\mathrm{K/min}}200\,^{\circ}\mathrm{C}^{0.3\,\mathrm{K/min}}500\,^{\circ}\mathrm{C}^{1\,\mathrm{h}}500\,^{\circ}\mathrm{C}^{5\,\mathrm{K/min}}1200\,^{\circ}\mathrm{C}^{2\,\mathrm{h}} \times 1200\,^{\circ}\mathrm{C}^{-5\,\mathrm{K/min}}\mathrm{RT}$$

The sintering process was performed in a tube furnace (CTF 18, Carbolite Ltd., Hope Valley, United Kingdom) on samples of 30 × 30 mm^2 in size. The decomposition of the organic additives occurred in air up to 500 °C including 1 h holding time. After the debinding process, the air atmosphere was changed to a reducing atmosphere of argon/hydrogen (Ar 96%/H_2 4%). Porous, zirconia-coated alumina substrates (Keralpor, Kerafol GmbH, Eschenbach, Germany) were used as sintering support.

The microstructure and physical properties of the substrates were validated in dependence on the sintering temperature to evaluate the development of porosity, mechanical strength, and conductivity. Therefore, the peak temperature with a holding time of 2 h was varied from 1200 to 1340 °C in steps of 20 °C. The density of the sintered substrates was geometrically determined (weight and volume). As theoretical density for fired SYT, 5.06 g/cm^3 was used [14]. The cumulative open pore volume, the average pore diameter and the pore size distribution of the fired samples were measured by means of Hg porosimetry (Pascal 140/Porosimeter 2000, Thermo Electron/Carlo Erba, Rodano/Milan, Italy) under low pressure as well as high pressure conditions. The microstructure of the sintered substrates was investigated by scanning electron microscopy (SEM; Quanta 200, FEI, Prague, Czech Republic). With the laser scanning microscope (UBM ISC 2, UBM Messtechnik GmbH, Ettlingen, Germany) the planarity or warping of the fired samples was detected. The height of the substrate was scanned along a line of 20 mm length taking 500 data points per millimeter. The difference between the maximum and minimum value in micrometer along this 20 mm line scan was used to describe the degree of warpage. This measurement was performed on both sides of the sintered tape, along as well as perpendicular to the casting direction.

To characterise the physical properties of the sintered substrates, the bending strength σ_B was determined using the double ring method (diameters: 6 and 16 mm). For this test, 10 samples of each sintering temperature were measured with a loading rate of 1.0 mm/min (Instron 4204, Instron Ltd., High Wycombe, United Kingdom). The achieved strength data were evaluated via the Weibull statistics. The electrical conductivity was measured with a four-probe DC device using silver wires and paste as contacts. The measurements were performed in Ar/4% H_2 humidified with 3% H_2O between 25 and 910 °C. Each measurement was started at maximum temperature and the temperature was decreased in intervals of 100 K with 5 K/min. After reaching the aimed temperature, the sample was equilibrated for 0.5 h before the conductivity was recorded.

Results and discussion

Materials

The powder exhibits a median particle size d_{50} of 0.79 µm and a specific surface area of 14.97 m^2/g. From the mass specific surface area (BET) the mean primary particle size $d_{1,2}$ of the powder was calculated considering the particle density and assuming monodisperse and spherical particles. The resulting average primary particle size value is 83.5 nm. The SEM micrograph of the powder (Fig. 1) shows that these nano-sized primary particles are strongly agglomerated or partially aggregated by the formation of sintered contacts during calcination of the powder. Tape casting slurries which are made of powders with high specific surface area are generally limited in their accessible solid loading and in the maximum thickness of cast, crack-free green tapes.

Characterisation of the slurries and tape casting process

With the addition of binder and plasticiser the homogenised suspensions were converted to tape casting slurries with a solid concentration of about 64 wt%. The slurries exhibited the required shear thinning behaviour. Table 1 presents the composition and the viscosity of the prepared slurries. Besides the requirement that the slurries are castable, the composition of the slurry has also to be adjusted to avoid crack formation during drying. Crack formation is caused by capillary forces, which occur in porous networks in the presence of liquids and which strongly increase with decreasing particle size [20]. Because submicron or nano-sized particles are used in this study, the content of binder and plasticiser was high and

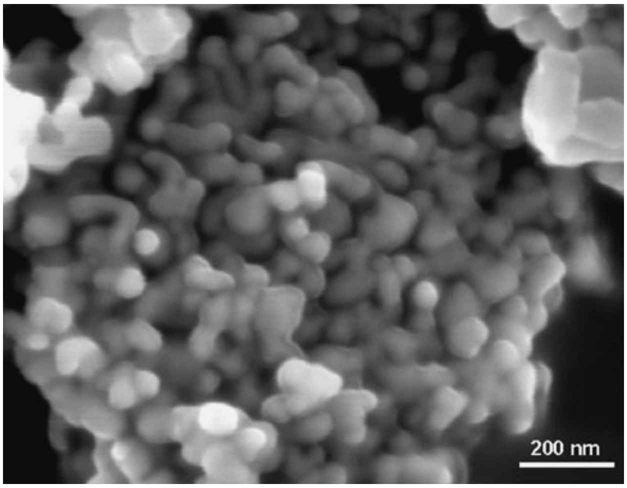

Fig. 1 SEM micrograph of the initial SYT powder

Table 1 Composition and viscosity of the slurries after homogenisation for 24 h

	Solid content (wt%)	Solvent (wt%)	Dispersant (wt%)	Binder (wt%)	Plasticiser (wt%)	Viscosity[a] (Pa s)
YSrTi:1	64.1 (24.9 vol%)	23.3	2.2	5.2	5.2	12.4
YSrTi:2	64.2 (25.0 vol%)	23.6	1.3	5.5	5.5	13.2

4.80 g/cm^3 was used as true density of the as received powder for slurry calculation

[a] Measured at a temperature of 20 °C and a shear rate of 20 s^{-1}

varied between 10.4 and 11.0 wt% to improve stress adsorption. Therefore, the slurry YSrTi:2 showed a slightly higher viscosity value than slurry YSrTi:1. The ideal viscosity values for tape casting slurries are in the range of 4 to 12 Pa s. The investigated slurries showed viscosities up to 13.2 Pa s, which still could be cast without any problem. A skin formation during the degassing and casting process was not observed.

Due to the suitable rheological behaviour and the optimised content of organic additives, all slurries which have been cast with a gap height between 700 to 900 µm could be dried to crack-free and flexible green tapes. Sheets cast with a gap height of 1100 µm showed drying cracks.

Characterisation of green tapes

In dependence on casting height and slurry composition the dried tapes had a thickness between 251 and 332 µm. Due to the large binder and softener content the green densities of the tapes YSrTi:1 and YSrTi:2 had values of only 47.3 and 45.7% of the theoretical density (4.8 g/cm^3), respectively. This is caused by the hindered packing behaviour of the powder, but acceptable for an application as porous anodes. A decreasing amount of organic additives slightly increased the green density. The binder burnout behaviour of the green tapes (Fig. 2) show the typical decomposition of plasticised polyvinyl butyral [21]. The binder burnout starts at a temperature of 190 °C and is completed at 450 °C. In the green tapes, the beginning and the end of the decomposition is shifted to lower temperatures due to catalytic effects of the high specific surface area of the SYT particles.

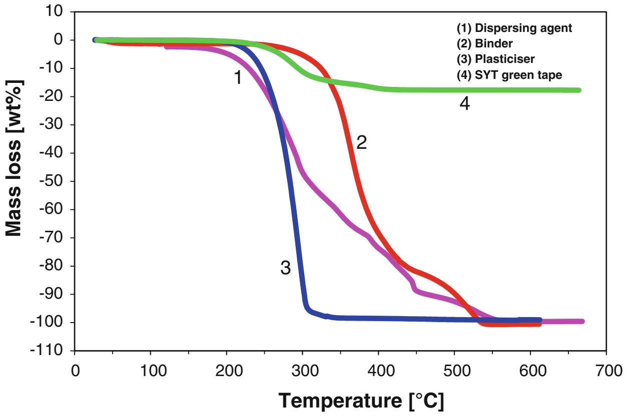

Fig. 2 Decomposition behaviour of the SYT green tape with 17.6 wt% organic additives and the pure organic additives in dependence on temperature (heating rate: 5 K/min in air)

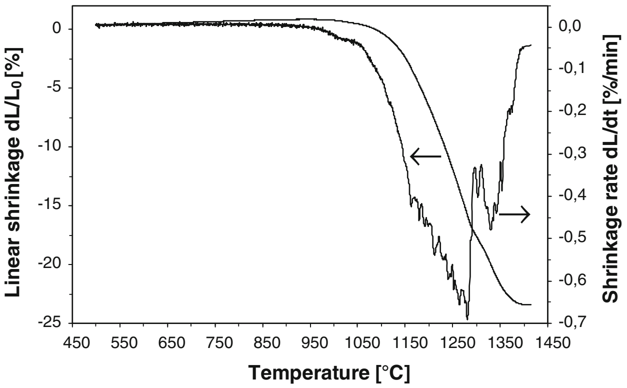

Fig. 3 Linear shrinkage and shrinkage rate of green tape in dependence on temperature (heating rate: 5 K/min)

The dilatometer investigations on the debinded green tape showed an onset of shrinkage at about 1050 °C and a maximum densification rate at 1280 °C (Fig. 3). A total linear shrinkage of 23.4% was observed.

Characterisation of sintered tapes

Depending on the sintering temperature, densities between 51.8 and 95.6% of the theoretical density (5.06 g/cm^3) were obtained. Due to the high polymer content of the green tapes the shrinkage values were relatively high: up to 26% in the X–Y-plane and up to 29% in the Z-direction. Table 2 lists the densification results and the warpage measurements. As expected, the use of higher sintering temperatures resulted in higher sinter densities, as well as in higher shrinkage values. Due to the high sintering activity of the very fine powder, the specimens reached already high density at temperatures of 1320 °C. At temperatures above 1340 °C an interaction between the fired tapes and the support substrates was observed. Due to the homogeneous structure of green sheets and the optimised heating profile, crack-free, non-warped sintered substrates could be obtained (Fig. 4) without applying weight.

Table 2 Densification and warpage behaviour of the fired samples in dependence on sintering temperature

Temperature (°C)	1200	1220	1240	1260	1280	1300	1320	1340
Sintered density[a] (% TD)	51.8	55.4	61.8	74.5	77.8	89.0	95.1	95.6
X–Y-shrinkage (%)	10.0	12.0	15.3	18.1	21.3	24.8	26.0	26.2
Z-shrinkage (%)	13.1	15.4	18.2	21.2	24.6	27.5	28.9	29.1
Average warpage (μm)	26.3	22.3	30.9	32.2	65.9	40.1	67.9	47.6

[a] 5.06 g/cm^3 was used as theoretical density of the fired SYT [14]

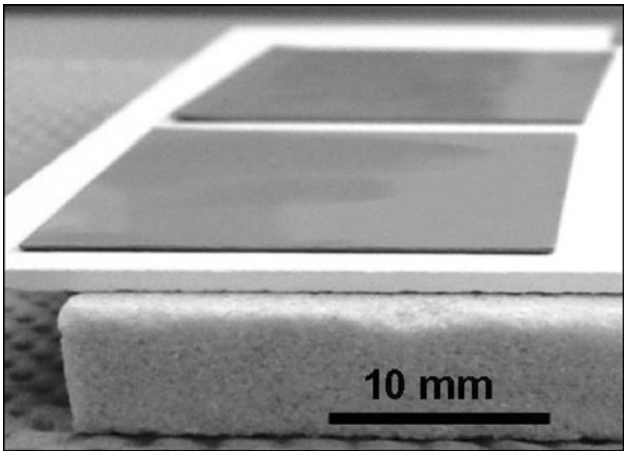

Fig. 4 Flat and crack-free SYT tapes sintered at 1200 °C/2 h (YSrTi:2, thickness: 282 μm)

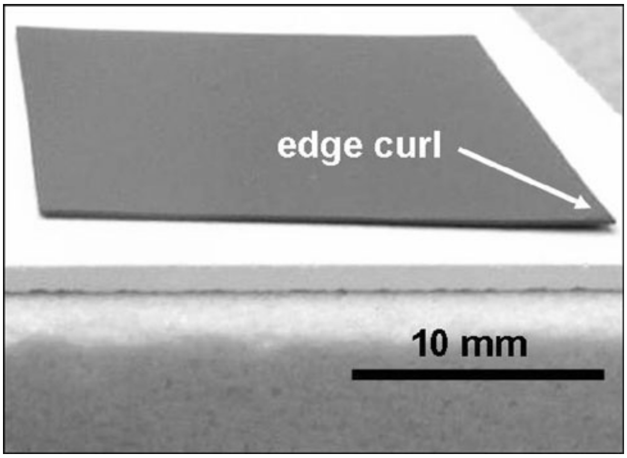

Fig. 5 Edge-curl shown on a SYT tapes sintered at 1280 °C/2 h (YSrTi:2, thickness: 242 μm)

Since the values of warpage differed only slightly between both sides, the average values are listed in Table 2. These values were in the range of 22–68 μm. Higher sintering temperatures showed somewhat elevated warping values, which is the result of an increasing influence of the "edge-curl" effect. This phenomenon is shown in Fig. 5. If the substrates of 30 × 30 mm^2 in size are fired at higher temperature, they exhibit higher densification, and therefore smaller sample sizes down to 22 mm length. Because the scan length is 20 mm, the warpage data are more affected by the "edge-curling" for small samples than for samples which exhibited lower shrinkage. Despite of the "edge-curl" effect the warpage values of the sintered tape are very low (<70 μm height difference on 20.000 μm), which fulfils the requirements for subsequent screen printing steps.

An overview of the Hg porosimetry results provides Table 3. The open porosity decreases with increasing sintering temperature from 47.4 vol% after firing at 1200 °C down to 1.8 vol% at 1320 °C, which corresponds with the density values of 51.8 and 95.1% TD, respectively. These results demonstrate that the required porosity of SYT-anode substrates can be adjusted by choosing an appropriate firing temperature. Since the open porosity of samples fired at 1320 °C was already very low, no porosimetry measurements could be carried out on specimens sintered at 1340 °C. As a result of the use of nano-sized particles, the average pore diameter reached values in the submicron range; it varied between 0.43 and 0.64 μm. A dependence of the pore diameter on sintering temperature could not be detected. The materials fulfil the requirements of pore diameters of around 1 μm and porosities of 20–40 vol%.

Electron microscopic investigations (Fig. 6) demonstrate that the microstructure of these ceramics exhibits grain growth during the sintering process. But due to the small powder particle size and the comparatively low sintering temperature, the fired microstructure still consists of submicron grains. Furthermore, the SEM micrographs show that the desired porosity is homogenously distributed in the microstructure, which is also an evidence for the homogeneity of the cast green tape structures.

The bending strength data of the sintered samples, measured with the double ring method, were derived from the Weibull analysis. Figure 7 shows the characteristic bending strength σ_0 values and the Weibull moduli *m* of the

Table 3 Porosimetry results of the fired samples in dependence on sintering temperature

Temperature (°C)	1200	1220	1240	1260	1280	1300	1320
Open porosity (vol%)	47.4	44.4	38.0	29.4	24.8	13.8	1.8
Cumul. volume (mm^3/g)	183.8	161.3	124.8	84.5	63.8	31.9	3.5
Pore diameter (μm)	0.53	0.56	0.58	0.48	0.49	0.43	0.64

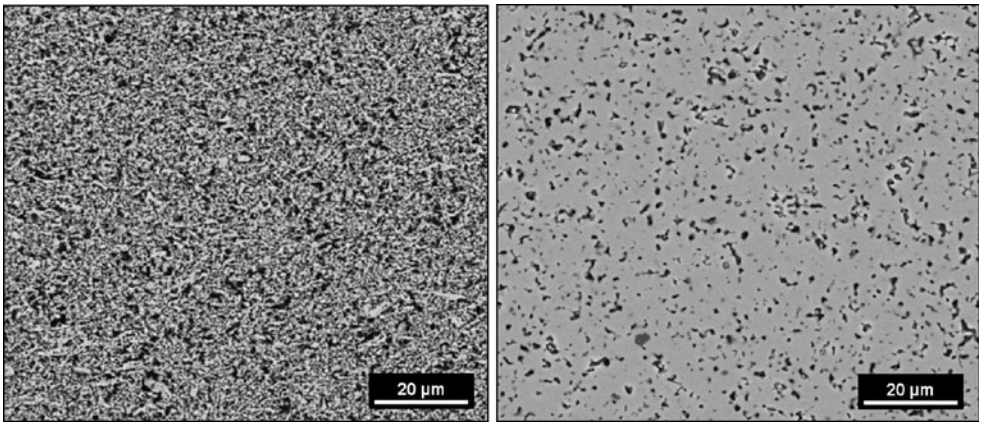

Fig. 6 SEM micrographs of polished cross-sections of SYT tapes (YSrTi:2) sintered at 1200 (*left*) and 1300 °C (*right*)

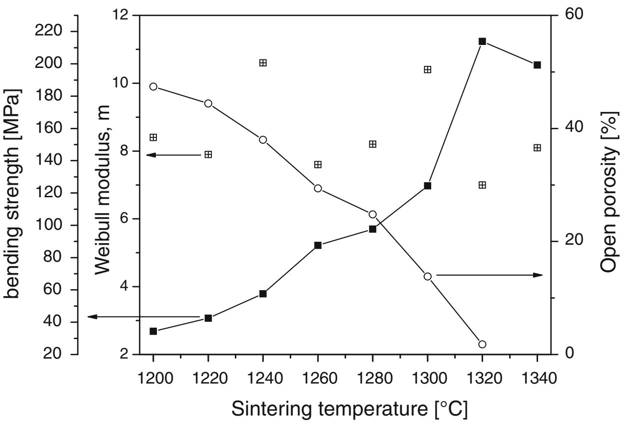

Fig. 7 Bending strength (*closed squares*), Weibull modulus (*crossed squares*), and open porosity (*open circles*) in dependence on sintering temperature

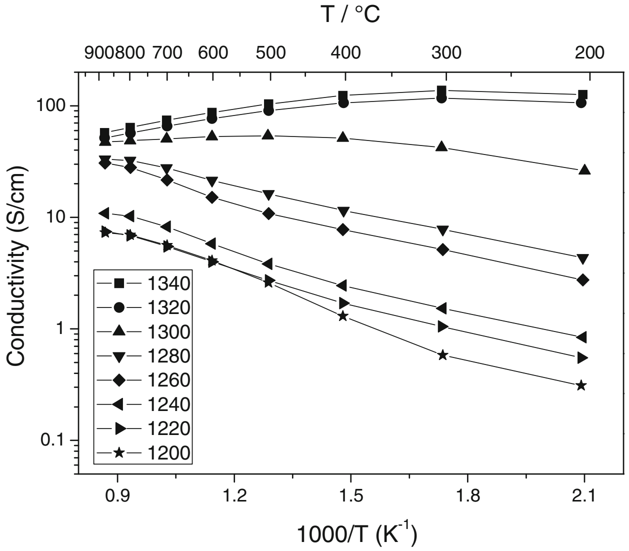

Fig. 8 Electrical conductivity of SYT tapes in dependence on temperature. Specimens sintered in Ar/4% H_2 at various temperatures

sintered SYT substrates in dependence on sintering temperature. The data show the clear correlation between strength and porosity data, whereas the latter is determined by the sintering temperature. The mechanical strength varied between 34.4 MPa for samples sintered at 1200 °C with an open porosity of 47.4% up to 213.9 MPa for samples with an open porosity of only 1.8%, fired at 1320 °C. Tapes sintered at 1340 °C exhibited slightly lower strength values than samples fired at 1320 °C, which is caused by small surface defects resulting from the mentioned partially sticking of the samples on the sintering support at a temperature of 1340 °C. The achieved strength data and the reached Weibull moduli of $7.0 < m < 10.6$ ($m_{\mathrm{mean}} = 8.5 \pm 1.3$; Fig. 7) are very good results for highly porous thin ceramics sheets made in a laboratory scale process. Strength values >80 MPa allow the application of the screen printing process as a coating technology for these porous substrates.

The electrical conductivity of the differently sintered sheets is shown in Fig. 8. The data represent the specific conductivity of the measured material without correction of the porosity. The determination of the specific conductivity of a pore-free material using empirical conductivity–porosity relationships [22] or more sophisticated models [23] could not be determined here, because the different sintering temperatures not only changed the density of the samples but also the number of charge carriers due to the changing fraction of reduced Ti ions. However, the results clearly show that the conductivity increases with increasing temperature and that metallic-like conductivity is obtained at high temperatures for specimens sintered at $T \geq 1300$ °C. The samples sintered at 1260 °C and above also show the necessary conductivity for SOFC application, similar to the reported data in [11, 19]. Since the obtained physical properties of the tape-cast foils are in good agreement with differently processed material, it can be assumed that also the stability towards redox cycling will be comparable to the earlier observed results on the material itself [11], on half cells [19] and tested SOFCs [17]. A further increase of conductivity can be achieved when a powder with lower sintering activity is used. In such a case the desired porosity is shifted to higher sintering temperature at which also more charge carriers are generated [14, 19].

Conclusions

This study presents the complete process cycle for the manufacture of Y-substituted strontium titanate substrates for SOFC applications with adjusted physical properties. Starting from a submicron-sized SYT powder with an average particle size of 0.79 µm consisting of strongly agglomerated nano-sized primary particles ($d_{1,2}$: 83.5 nm), it was possible to produce highly filled suspensions. For preparation of homogenous and stable suspensions the steric stabiliser carbonic acid was used. By adding binder and plasticiser, stable casting slurries could be achieved with the required pseudo-plastic rheological behaviour for the tape casting process. The evaporated slurries with solid contents of up to 64.2 wt% and viscosity values up to 13.2 Pa s were cast and dried to crack-free green tapes of thickness between 250 and 330 µm. The green sheets could be sintered to substrates of high planarity (max. warpage <70 µm). Due to the nano-sized primary particles, dense substrates of 95.1% TD could be already obtained for relatively low sintering temperature of 1320 °C. With different sintering temperatures between 1200 and 1340 °C a wide range of physical properties could be obtained: The porosity values of the sintered substrates varied from 1.8 vol% up to 47.4 vol%, the bending strength reached values between 34.4 and 213.9 MPa and the electrical conductivity increased from 7 to 64 S/cm at 800 °C. These results demonstrate that the relevant properties of tape-cast SYT substrates (porosity, mechanical strength, electrical conductivity, etc.) can be adjusted by specific sintering profiles, which make these SYT tapes suitable for thick film technique and herewith also for the fabrication of anode substrates for SOFC applications. Taking into account the requirements for SOFC anode materials, a mechanical strength of 100 MPa, a porosity of 25 vol% with a medium pore diameter of 0.5 µm and with a conductivity of 32 S/cm can be provided by sintering at a temperature of 1280 °C.

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