

Fabrication of 10%Gd-doped ceria (GDC)/NiO–GDC half cell for low or intermediate temperature solid oxide fuel cells using spray pyrolysis

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Abstract Solid oxide fuel cells (SOFCs) with comparably low operating temperature play a critical role in its commercialization and reliability by allowing low-cost fabrication and a promised longer life. Recently, 10%Gd-doped ceria (GDC) has revealed its importance as solid electrolytes for intermediate temperature SOFCs. Additionally, if GDC is employed in thin film form, rather higher ionic conductivity at further lower temperatures can be obtained and thereby allowing its use in low temperature SOFC. In the present investigation, the preparative parameters of spray pyrolysis technique (SPT) were optimized to deposit dense and adherent films of GDC on ceramic substrate. NiO–GDC was used as ceramic substrate, which also acts as a precursor composite anode for GDC-based SOFCs. Prepared half cells (GDC/NiO–GDC) were characterized using XRD, SEM, and electrochemical impedance spectroscopy. The surface and fractal SEM observations of post heat-treated (at 1,000 °C) GDC/NiO–GDC structure revealed that GDC films were uniform in thickness with improved adherence to substrate. The relative density of post heat-treated films was of the order of 96%, which was attributed to the presence of nano-granules in the thin films. Maximum thickness of the GDC film prepared with

optimized preparative parameters (in single run) was of the order of 13 μm . Fractal SEM of post heat-treated GDC/NiO–GDC system showed homogenous interface, which was further analyzed by electrochemical impedance spectra and found that it does not affect electrical properties of structure significantly.

Keywords Intermediate temperature solid oxide fuel cells · Spray pyrolysis · Ceramic thin films · Gd-doped ceria · Impedance spectroscopy

Introduction

In recent years, to overcome commercialization-related problems of high-temperature solid oxide fuel cells (HT-SOFCs), the research has been diverted to develop the intermediate/low temperature (IT or LT) SOFCs. The IT/LT SOFC has the potential to reduce the cost of cell fabrication, as it would allow the comparatively inferior quality of sealant for sealing, low-cost steel for interconnects, etc. In addition, due to comparatively lower operating temperature, the issues related to thermal aging and thermal mismatch within the cell components would be at its minimum, which indirectly improves the reliability, portability, and operational life of the device. These advantages of IT/LT SOFCs are rather promising for commercialization of SOFCs. However, IT/LT SOFC requires an electrolyte either prepared from alternate material than the conventional (i.e., yttria-stabilized zirconia) or having thickness in the range of 10–20 μm . Recently, despite emergence of electronic conductivity in reducing (anode side) atmosphere at high temperatures (>750 °C), the ceria-based electrolytes (e.g., GDC) have been demonstrated as promising electrolyte for IT-SOFCs (~ 600 °C). The operating temperatures of ceria-based SOFCs can be further

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decreased by implementing it in thin film form [1–7]. Thin film electrolytes will enable device operation at further reduced temperatures by virtue of its comparatively lower active volume (offering low ohmic losses).

The versatility of the spray pyrolysis technique (SPT) and requirement of fabrication of dense, thin solid electrolyte film on functional ceramic substrates (non-conducting at deposition temperatures) makes SPT a most suitable technique for in situ fabrication of electrode/electrolyte structures (half cell). Recently, it has been showed by Choy et al. that SPT can be employed to prepare uniform and dense solid electrolyte films [8–15]. In the present research, the preparative parameters of SPT such as precursor solution concentration and substrate temperature were optimized to deposit dense and adherent films of GDC on the NiO–GDC substrate. The ceramic substrates of NiO–GDC were prepared by conventional ceramic route. The structural characterization and phase confirmation of GDC film on ceramic substrate and that of bare substrate were carried out using XRD. SEM was employed to investigate the surface and fractured morphology of film, substrates, and their interface. Impedance spectroscopy has been implemented to characterize the electrical properties of prepared GDC/NiO–GDC structures.

Experimental

Ceramic substrate preparation

NiO–GDC ceramic substrates were prepared by mixing NiO (extra pure, AR grade), Gd_2O_3 (AR grade, 99.9%), and CeO_2 (AR grade, 99.9%) from HIMEDIA Inc., in a calculated

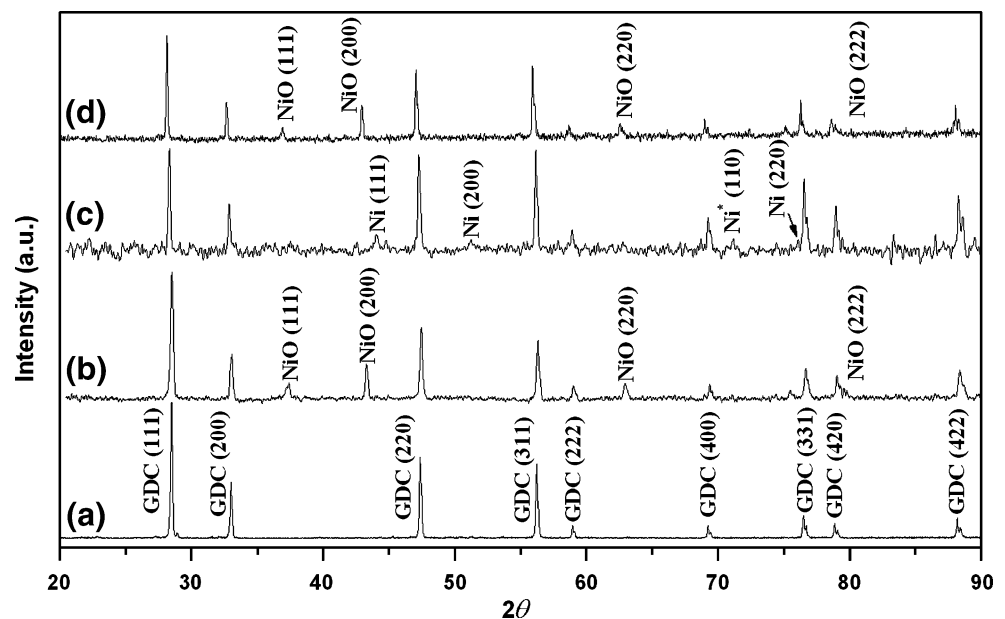
weight proportion to obtain the desired composite phase of $(NiO)_{0.3}-(GDC)_{0.7}$. The mixture were homogenized in agate mortar and sintered at about 1,400 °C for 8 h in air. The NiO–GDC ceramic substrates were prepared with 0.12 cm in thickness and 2.5 cm in diameter. To achieve the total flat surface of pellets, flat neutral alumina sheet was kept above the samples during the sintering. Further, for surface modification, NiO–GDC substrates were heat-treated in reducing atmosphere of 5% H_2 –95%Ar with gas flow rate of 500 ml/min at 900 °C for 8 h. This reduction treatment leads to formation of porous-structured and rough-surfaced Ni–GDC composite (referred as Ni–GDC hereinafter) ceramic substrates.

Thin film synthesis

To deposit GDC, cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.9% pure; ALFA AESAR) and gadolinium nitrate ($Gd(NO_3)_3 \cdot 6H_2O$, 99.9% pure; ALFA AESAR) were dissolved in double distilled water in desired proportion, which was then sprayed by glass nozzle with air as carrier gas. The ceramic substrates were kept on a hot plate with controlled preset temperature. The detailed optimization process of preparative parameters of SPT for deposition GDC thin films on glass substrate has been reported elsewhere [15]. In this study, the optimization was carried out for ceramic substrate.

SPT is a chemical deposition technique and involves the preparative parameters such as, type of salt, solvent, nozzle to substrate distance, substrate temperature, surface and nature of substrate, solution concentration, spray rate, spray quantity, nozzle motion, etc. All these parameters directly/indirectly control the composition, morphology, and electrical properties of deposited thin films. Therefore, one

Fig. 1 XRD patterns of ceramic substrates. (a) GDC, (b) NiO–GDC, (c) Ni–GDC, and (d) NiO–GDC*



could obtain the desired quality of films by optimizing these parameters. However, optimizing the parameters by varying all the preparative parameters simultaneously could not be a good choice. Even keeping one parameter constant and varying the other is still a tough task for the optimization of spray parameters. As these spray parameters are inter-related, one can set the default parameter fixed for a particular setup and vary as few as possible remaining spray parameters.

Here, we have optimized the preparative parameters of SPT incorporating air-blast type of atomizing assembly for the deposition of GDC thin film on NiO–GDC substrate. Initially, we fixed the spray parameters for our systems, for example, atomizing unit (nozzle—air-blast type), nozzle to substrate distance (25 cm), type of salt (metal nitrate), solvent (DD water), nozzle motion/speed (1 cm/s), traversing distance by nozzle (30 cm), etc. The substrate temperature is an important SPT preparative parameter as it plays a key role in pyrolyzing the sprayed droplets and hence the composition and morphology of film. The decomposition of host precursor, i.e., cerium nitrate is determined from its TGA which was about 280 °C [15]. It is obvious that the additives (here, the doping element) in precursor salt of host would change the physical properties of spraying solution and hence further optimizations about the decomposition temperature were necessary. Our attempts of optimization lead us the substrate temperature of 280 °C and solution concentration of 0.04 M for NiO–GDC substrate. However, the films were non-adherent. Further, to improve the adherence and thickness of film, we followed another approach. In this approach, initially the surface of substrate was modified and then the depositions were taken at temperatures less than that of decomposition temperature of precursor. So, prepared films were subsequently heat-treated at temperature above the decomposition temperature. Here, to modify the surface of substrate, we heat-treated the ceramic substrate (NiO–GDC) in reducing atmosphere (5% H_2 –95%Ar) at 900 °C for 5 h. This treatment transformed NiO–GDC composite to the Ni–GDC composite substrate with rough and porous surface. The optimum substrate temperature and solution concentration for these substrates were 250 °C and 0.04 M, respectively. Now, the film formed onto substrate in the “as-deposited” state was the collection of precipitate of Gd and Ce species with entrapped solvent, as the phase formation is possible above 280 °C (from TGA). Thus, for evaporation of entrapped solvent and phase formation, a subsequent heat treatment at 450 °C was employed. Above 450 °C, no weight loss was observed in TGA. Further, to improve the film/substrate interface and grain growth in the films, sintering was carried out at 1,000 °C for 8 h. The sintering resulted in dense films; however, the Ni–GDC phase of substrate was again transformed to NiO–GDC (referred as NiO–GDC* hereinafter).

Characterizations

The phase formation of deposited GDC film, NiO–GDC, NiO–GDC*, and Ni–GDC composite ceramic substrates were studied using PHILIPS X-ray diffractometer (PW-3710) with Cu- $\text{K}\alpha$ radiation source. The surface and cross-

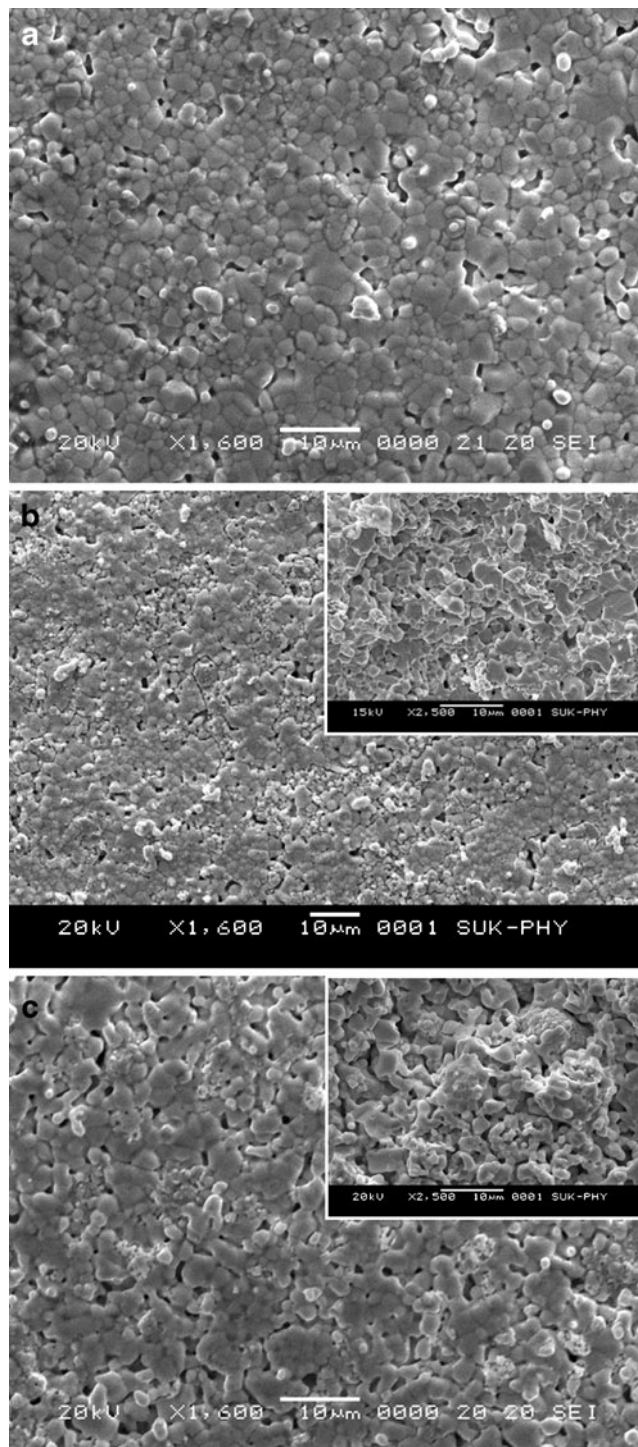


Fig. 2 SEM images of ceramic substrates. **a** NiO–GDC, **b** Ni–GDC, and **c** NiO–GDC*; inset fractured morphology

sectional (fractured) morphologies of the samples were imaged using scanning electron microscope (SEM, JEOL-JSM-6360, Japan). The electrical characterization was carried out by ac impedance measurements using impedance analyzer (SOLARTRON 1260 Impedance Analyzer; 1 mHz–32 MHz). Impedance data were obtained as function of frequency (1 Hz–10 MHz) for various temperatures ranging from 250 to 500 °C. As this particular study is related to fabrication optimization of half cells, attempts to analyze and interpret the impedance data for various electrical processes within the structures were not performed and are out of scope of this paper. Collected impedance data were analyzed by impedance analysis software (ZView Version 2.4a) and used to extract the grain interior (GI) and grain boundary (GB) impedances, which further used to calculate ac conductivities. ac conductivities were then fitted to the Arrhenius relation for thermally activated conduction to determine activation energies.

Results and discussion

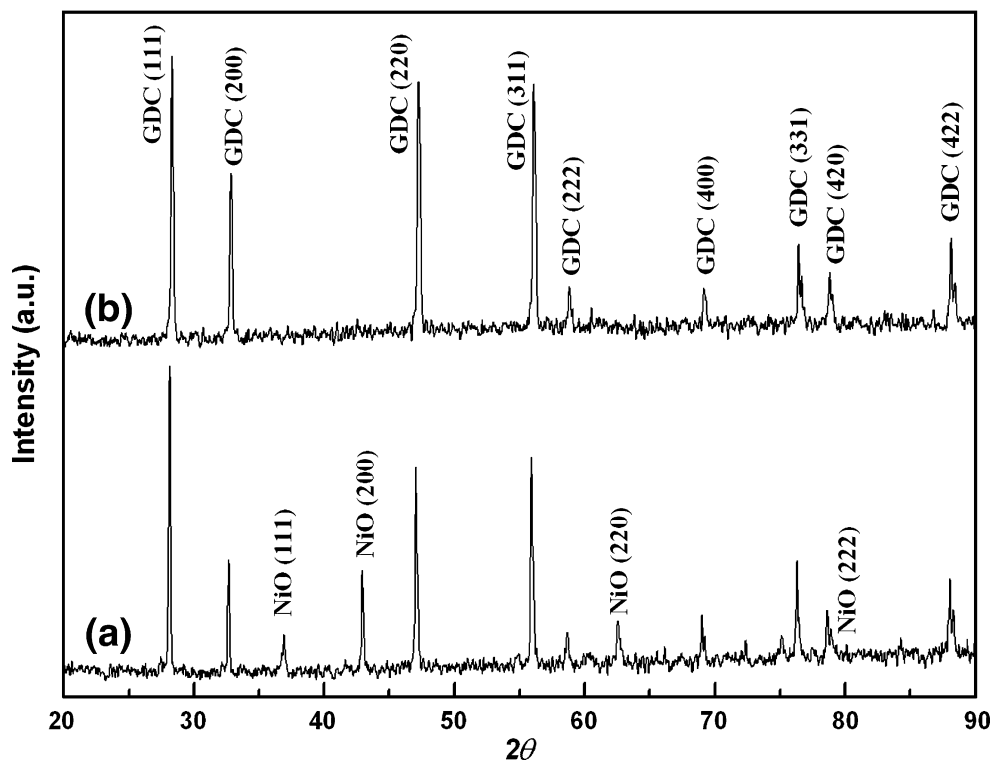
Micro-structural characterizations of bare ceramic substrate

The XRD patterns were compared with JCPDS PDF nos. 75-0161 (10%Gd-doped Ceria), 04-0850 (cubic Ni), and 78-0643 (cubic NiO) to confirm the individual phase peaks and were accordingly indexed in Fig. 1. Indexed patterns confirmed the formation of respective phases in the samples

(Fig. 1a–d). Expansion in lattice parameter of GDC thin film (in excess of lattice parameter of ceria) in addition to absence of respective individual peaks of Gd_2O_3 and CeO_2 confirms their complete dissolution. Presence of peaks corresponding to NiO phase in XRD pattern of NiO–GDC (Fig. 1b) and NiO–GDC* (Fig. 1d) substrates confirms the formation of NiO–GDC composite, while the pattern of Ni–GDC (Fig. 1c) revealed that there were no peaks corresponding to NiO indicating complete reduction of NiO to Ni and confirms the formation of Ni–GDC composite. The average lattice parameters calculated for GDC, NiO, and Ni phases are 5.420 Å, 4.169 Å, and 3.540 Å, respectively, which agrees well with the standard values.

Figure 2 shows the SEM images of the ceramic substrates. The surface morphology of NiO–GDC (Fig. 2a) is porous and upon reduction in H_2 atmosphere at 900 °C, it becomes more porous (Fig. 2b). The increased porosity is attributed to removal of oxygen atom from the NiO during reduction treatment. The uniformity in grain growth pattern has been changed during these thermal treatments, and the NiO–GDC* (Fig. 2c) showed comparatively larger grains than NiO–GDC. Additionally, comparably more porous surface with increased pore size is observed for NiO–GDC* ceramic samples. The average grain size and density of Ni–GDC sample is comparatively lower than that of NiO–GDC and NiO–GDC*, which could be attributed to phase conversion from NiO to Ni phase during reduction treatment and from Ni to NiO during thin film densification treatment, respectively [16, 17].

Fig. 3 The XRD patterns of (a) NiO–GDC* ceramic substrate and (b) GDC film on NiO–GDC* ceramic substrate



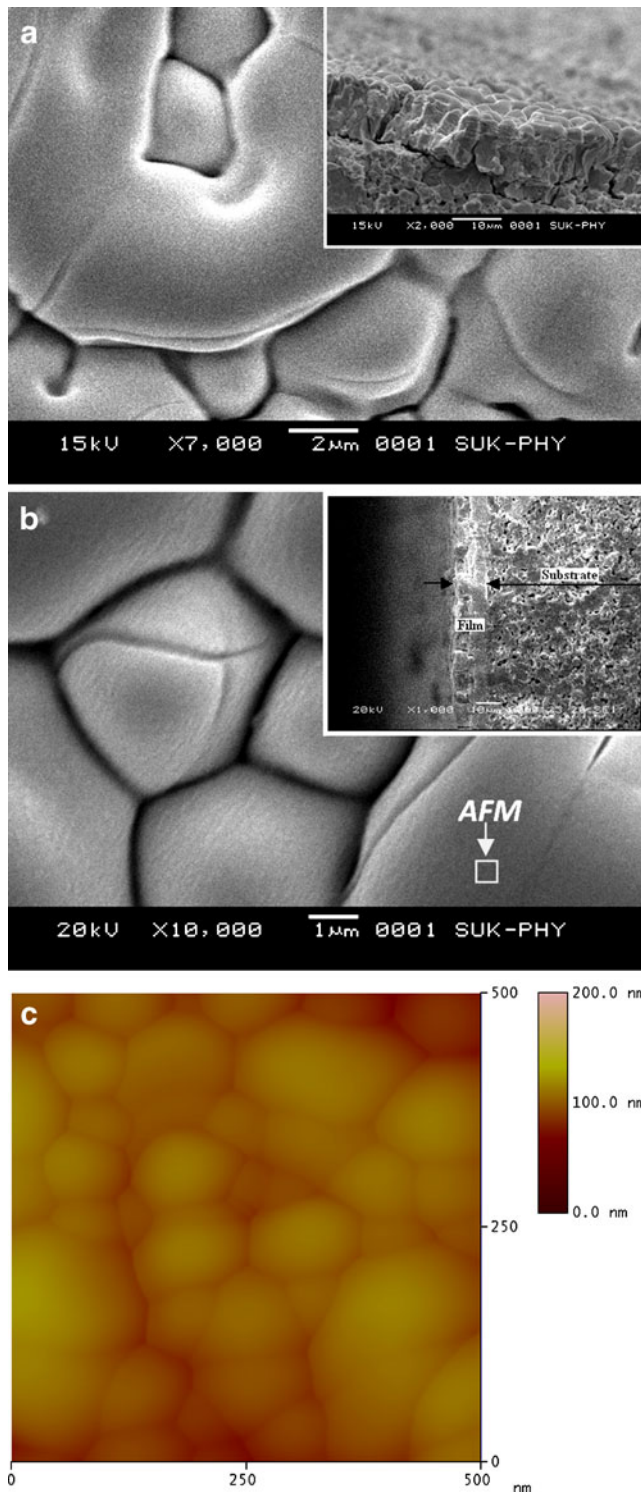


Fig. 4 SEM of GDC films deposited on Ni–GDC substrates annealed **a** at 450 °C for 3 h and **b** at 1,000 °C for 8 h in air. *Insets* fractured morphology showing interface. **c** AFM image of GDC film deposited on NiO–GDC* substrate and annealed at 1,000 °C

Table 1 Analysis of AFM image of sprayed GDC thin film

Surface roughness (nm)	8.86
Min. grain size (nm)	60–70
Avg. grain size (nm)	85
Max. grain size (nm)	150
Grain size distribution	Moderate

Micro-structural characterizations of thin films on ceramic substrates

Figure 3 shows the XRD pattern of GDC film on NiO–GDC* substrate prepared with optimized preparative parameters of SPT. The film thickness was large enough (~13 μm) to screen the peaks originating from substrate (Fig. 3b). Initially, GDC thin films were deposited on Ni–GDC substrates, since our earlier attempts to deposit GDC on NiO–GDC substrate were circumvented on the basis of adherence of films with substrate. Figure 4a shows the SEM of GDC film on Ni–GDC substrate annealed at 450 °C. The fractured SEM (inset of Fig. 4a) indicates that the interface of film and substrate appears physically separate with discontinuous grains in the films. Such interface and grain separation could lead to additional interfacial resistance to the total system. Hence, to avoid these interfacial impedances in the total system and improve the quality of film–substrate interface, the post heat treatment at 1,000 °C in air was carried out. The effect on film/substrate interface and surface morphology of film can be clearly seen in Fig. 4b. The average thickness of the GDC film was measured from fractured SEM of the structures and was of the order of ~13 μm.

Density of the GDC films on NiO–GDC* was of the order of that of GDC bulk samples sintered at 1,500 °C (rel. density >98%). Such higher density in the film was

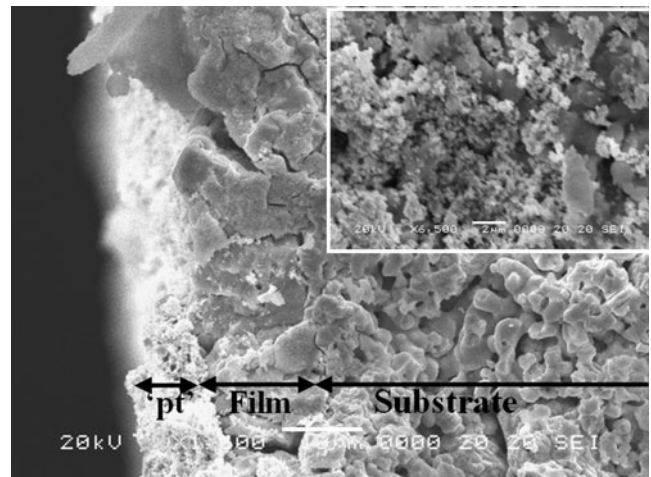
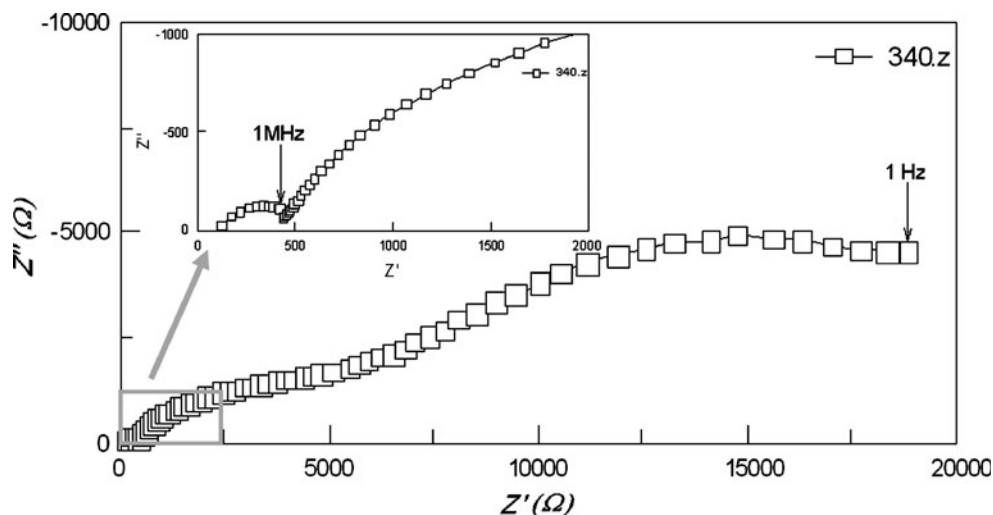


Fig. 5 SEM of tri-layer of ‘pt’ paste/film/substrate; *inset* ‘pt’ paste coated onto surface of substrate

Fig. 6 Typical Nyquist plot of GDC film on NiO–GDC* substrate



achieved only at 1,000 °C. This is attributed to the presence of nano-granules in thin films. Figure 4c shows the AFM image of GDC thin film, which on analysis showed that the average grain size is of the order of 85 nm. Further analysis of surface morphology of films using AFM showed almost smooth surfaces (Table 1). Formation of nano-granules in the film is attributed to ultra-fast pyrolysis reactions occurring at substrates. For the air-blast type of nozzle, it is quite probable that the spray mist consists of fine droplets, which upon pyrolysis leads to precipitates with diameter of the order of few tens of nanometers. These droplets, on decomposition at heated substrate, forms the nucleation center onto substrates, which further undergoes grain growth mechanism to form large grains (few tens of nanometers). Moreover, the post heat treatment assists the grain growth in the film and develops the grains and its intra-grain connectivity.

Impedance measurements of GDC/NiO–GDC* structure

Impedance measurements of bare ceramic substrate were carried out to circumvent the doubt of faulty measurements, which may come from the direct contact of ‘pt’ electrodes (paste) with the substrate from both the sides. However, impedance measurements and cross-sectional SEM image (Fig. 5) have demonstrated that the ‘pt’ paste remains on the surface of the film and does not penetrate the film. Inset of Fig. 5 shows the uniform coating of ‘pt’ paste over the surface of GDC films.

Figure 6 shows impedance spectra (Nyquist plot) of GDC/NiO–GDC* structure, measured at 300 °C. The trend of

spectra matches with that of associated with typical solid electrolytes, where three semicircles corresponding to grain interior, grain boundary, and electrode contributions appear. However, it should be noted here that in principle, one would have different electrical responses due to grains of two kinds (NiO and GDC) and grain contacts of three kinds (GDC–GDC, NiO–NiO, and GDC–NiO). Also, the conductivity across GDC (ionic) and NiO grains (electronic holes) would add different responses to impedance spectra. In addition to that, the situation would be much more difficult for the film/substrate structures (where the contacts should behave most probably differently than into the bulk ceramic). Consequently, to assign the contributions originating from all these sources or to extract all this information from the impedance spectra would require a well-dedicated study (out of scope of present research). Thus, here, we simply assign three semicircles (from right) observed in impedance plots to correspond to slow, intermediate, and fast electrical processes. These designations made here are for the sake of simplicity in comparison of various results. Further, the analysis revealed that the parts of spectra assigned to intermediate and fast electrical processes possess the capacitance values of the order of 10^{-8} and 10^{-11} F/cm², respectively. These typical values of capacitances, in general, originates from GB polarization in a polycrystalline material ($\sim 10^{-8}$ F/cm²) and that of from dielectric relaxation of bulk (grain interior (GI)) material ($\sim 10^{-11}$ F/cm²). Hence, this analogy is further extended and these processes are referred to as GI (fast) and GB (intermediate) processes and the respective conductivities as GI and GB conductivities.

Table 2 GI and GB conductivities at 500 °C and respective values of activation energies determined in temperature range of 200–500 °C

Samples ↓	σ_{GI} (S/cm)	σ_{GB} (S/cm)	E_{aGI} (eV)	E_{aGB} (eV)
NiO–GDC* substrate	0.107	0.0009	0.81	0.90
GDC/NiO–GDC* structure	0.103	0.0005	1.02	0.93

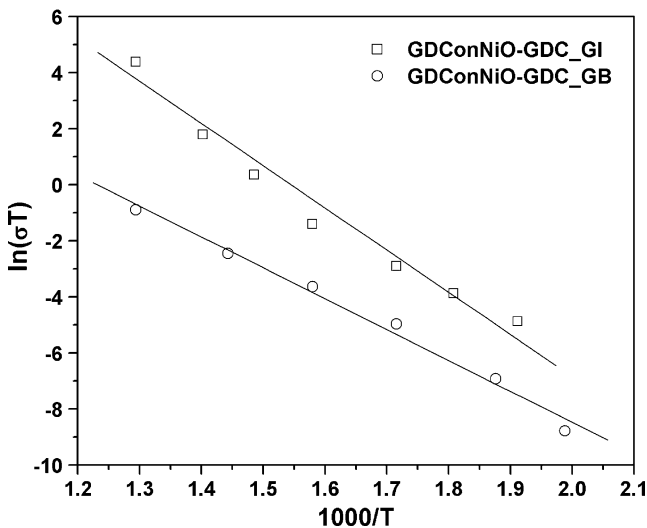


Fig. 7 Variation of $\ln(\sigma T)$ as function of $1,000/T$ for GDC/NiO-GDC*

For higher measuring temperatures, i.e., greater than 440 °C, only two semicircles in the Nyquist plot remains. At higher temperatures, the relaxation time constants associated with impedances due to the fast (GI) and intermediate (GB) processes becomes much lower than those associated with the slow electrical process (capacitance value $\sim 10^{-5}$ F/cm²). As a result, in the Nyquist plot, the semicircle due to GB becomes smaller, while the semicircle due to GI becomes vanishingly small. The values of GI and GB conductivities with respective activation energies are listed in Table 2. GI and GB conductivities of GDC/NiO-GDC* structure has shown the comparatively decreased value than that of bare substrate, which could be attributed to increased overall thickness of sample under investigation and also to the film/substrate interface (Fig. 7).

Here, it was recognized from impedance spectra that the contributions to the overall ionic conductivity from the GI conductivity constantly dominated the GB conductivity for bare as well as coated substrate. The amount of GI dominance in GDC/NiO-GDC* structure was two times than that of bare NiO-GDC* substrate.

Conclusions

The versatility of the SPT for the fabrication of dense, thin solid electrolyte film on functional ceramic substrates has been demonstrated in the paper. The characterization of micro-structural and electrical properties of GDC/NiO-GDC half cell revealed that the SPT could be a low-cost alternative technique for fabrication of a good-quality half cell. GDC/NiO-GDC structure has shown the formation of well-connected, adherent, thick (up to 13 μm), and dense (airtight) layer of GDC film over NiO-GDC substrate. This

type of GDC layer (as solid electrolyte) over a functional ceramic anode support such as Ni-GDC (reduction of NiO-GDC substrate in H₂ atmosphere) finds the promising application in intermediate temperature SOFCs.

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