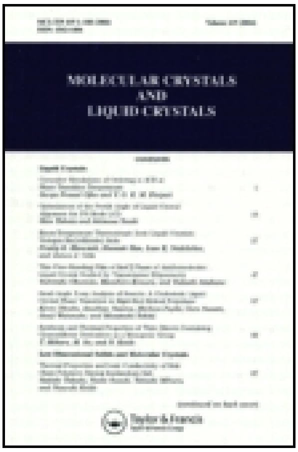

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The Evaluation of Ca Doped GDC Electrolyte Thin Film for Solid Oxide Fuel Cells by Electron Beam Deposition

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Electron beam deposition technique was used for formation of gadolinium Ca doped GDC electrolyte thin films. Ca_GDC electrolyte thin films were grown by evaporating $Gd_{0.1}Ce_{0.9}O_{1.95}$ *ceramic powder. The evaporating Ca_GDC electrolyte powder was synthesized by solid-state reaction method. The GDC thin films were deposited on porous Ni-GDC anode pellet. Operating technical parameters that influence thin film microstructure and crystallite size were studied. It was found that electron gun power (changed in the range of 0.60 to 1.05 kW) has the influence on the crystallite size of GDC thin films and decreased linearly increasing electron beam gun power. The influence of electron gun power and annealing temperature on thin film structure and surface morphology were investigated by X-ray diffraction (XRD) using CuKα-radiation in the range of* $2\theta = 20\sim80^\circ C$*. The XRD peaks was showed formation of single-phase monoclinic structure was confirmed by X-ray diffraction (XRD) for the doped Ca GDC electrolyte. The patterns indicated the intensity of well-cubic fluorite structure phase.The morphology and the size of the prepared particles were investigated with a field-emission scanning electron microscope (FE-SEM). The performance of the cells was evaluated over* $500\sim800^\circ C$ *using humidified hydrogen as fuel and air as oxidant.*

Keywords GDC; Electron beam deposition; Solid oxide fuel cell

Introduction

Solid oxide fuel cells (SOFCs), offering a low-pollution technology to generate electricity chemically with high efficiency, exhibit a great potential in solving the energy crisis and environment pollution [1]. However, long-term stability, cost effective and large scale production and commercialization of thin film electrodes and electrolytes require reducing the operating temperature, whilst maintaining high electrocatalytic activity for the low temperature SOFCs. The research trend aims at lowering the operation temperature, which will allow application of less expensive materials and thus permits faster commercialization of this technology on the mass scale. The typical electrolyte material is cubic ZrO_2 doped with approximately 8 mol% Y_2O_3 (yttria stabilized zirconia-YSZ) [2]. Recent progress in

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*Addressed correspondence to Prof. Hyung Wook Choi, Department of Electrical Engineering, Kyungwon University, San 65 Bokjeong-dong, Sujeong-gu, SeongNam, Gyeonggi-do, 461-701 Korea (ROK). Tel: +8231-750-5562 Fax: +8231-750-5491. E-mail: chw@kyungwon.ac.kr technology allows building anode supported dense electrolytes of only several micrometers thick thus electrolyte resistance can be significantly lowered [3,4]. The application of CeO_2 doped with 10 mol.% Gd_2O_3 (cerium gadolinium oxide $Ce_{0.9}Gd_{0.1}O_{1.95}$-GDC), which exhibits much higher ionic conductivity than YSZ, was proposed in order to further reduce SOFC operating temperature [5]. GDC is considered to be one of the most promising electrolytes for SOFCs to be operated below 700°C, due primarily to its high ionic conductivity at reduced temperatures [6]. There are, however, some reported problems, which obstruct successful application of this material. The main drawback is related to the reduction of GDC at high temperatures in highly reducing atmospheres (e.g. on the anode side of SOFC). As a result an electronic conductivity of GDC is increased, which lowers the open circuit voltage of SOFC due to partial internal short-circuiting [7]. The conductivity of GDC can be affected by several factors such as grain size, which determines the dopants, impurities or even processing routes [8]. One of deleterious conductivity related effects originate from impurities, which residue in the grain boundaries and form highly resistive interfaces [9–10]. Even very small amount of several hundred ppm of siliceous species can drastically increase the grain boundary resistance. However, the production of highly pure powders is economically expensive. Therefore, other ways of obtaining highly conductive GDC powders are sought. One of the ways to mitigate this deleterious effect is to introduce additional phases, e.g. CaO (Calcium oxide) as proposed by Lane et al. [11]. The addition of 2 cation% of CaO improved CGO conductivity. However, the mechanism of GDC conductivity improvement is not completely understood and is still investigated. In addition, decreasing the thickness of the electrolyte further reduces the resistance to ionic transport, resulting in an even lower operating temperature of SOFCs [12]. Doped ceria oxide thin films could be prepared by vapor processing methods (such as chemical vapor deposition (CVD), electrochemical vapor deposition (EVD), metal-organic CVD (MOCVD), sputtering, plasma spray, etc.). Despite these challenges, vacuum methods offer a number of unique advantages. Very thin, fully dense layers can be produced on either porous substrate, which may enable higher power densities to be achieved. In the present work, CaO doped GDC electrolyte thin films were deposited using electron-beam evaporation technique on NiO-GDC substrate. A dense GDC electrolyte, NiO-GDC anode bilayer has been fabricated in this study.

Experimental

Fabrication of NiO-GDC Anode Substrate

Ni-GDC anode powders were synthesized by solid-state reaction method using appropriate oxide materials. The Cerium oxide (CeO_2), Gadolinium oxide (Gd_2O_3) and Nickel oxide (NiO), all with purity above 99% (Aldrich, USA), were used as reagents. Fabrication process is summarized in a flowchart of Fig. 1. The CeO_2 and Gd_2O_3 mixtures starting materials in the compositions $Ce_{0.9}$ $Gd_{0.1}O_{1.9}$ was mixed sufficiently and ball-milled for 24 h with isopropyl alcohol (IPA). After the mixture was dried at 80°C, this powder was calcined in air at 1400°C for 4 h. The selection of ceramic composition of NiO_{60}- GDC_{40} (precursor composite for Ni-GDC anode) substrate was decided on the basis of their viability in prospective use as an anode of half-cell for IT-SOFC [13,14]. The calcined GDC powder was then reground and mixed with NiO in desired proportion to obtain the composite phase of composition of NiO_{60}-GDC_{40} by boll-milled for 24 h. The binder added powder was pelletized with the help of press machine. The green samples then sintered at 1600°C for 4 h

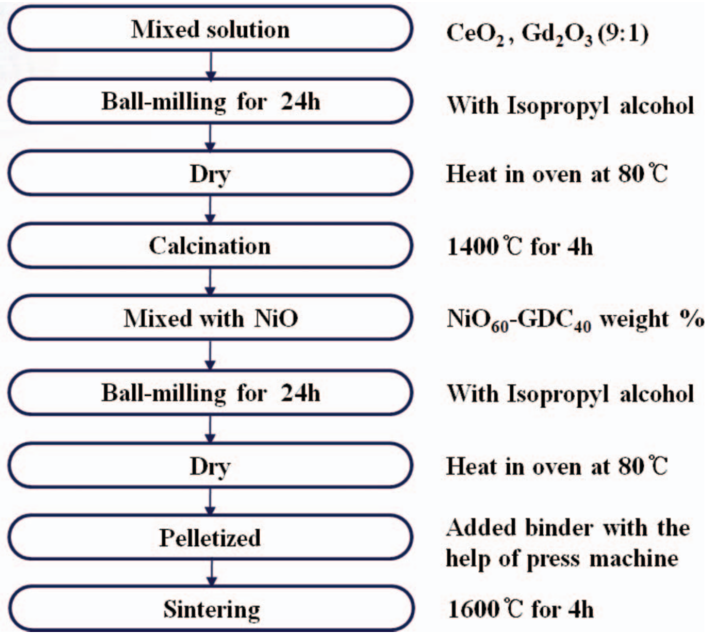


Figure 1. The flowchart for the preparation of Ni-GDC anode substrate.

in air. The pre-sintering (binder removal step) of samples were intentionally excluded, as the high sintering temperature is usually employed to obtain dense ceramic bodies and here we are expecting for porous structured (anode-grade) NiO-GDC substrates. The dimensions of the sintered substrates were 0.15 cm in thickness and 2.0 cm in diameter.

Preparation of GDC (Doped Ca) Thin Film

The Ca doped GDC powders were prepared by mixing GDC powder with 2 mol% of calcium respectively, in the form of an oxide (CaO, 99.99%) in order to introduce Ca into the GDC solid electrolyte, giving the powder. Next, the mixture was ball-milled for 24 h with IPA. Next, the suspension was dried at 80°C and calcined at 1200°C (added CaO mixture) for 4 h in order to decompose incorporated Ca oxides and before used as evaporation materials. The GDC (doped CaO) thin film was deposited on NiO-GDC substrate. It was cleaned in an ultrasonic bath of acetone, ethanol solution, and distilled water for 3 min each before evaporation. The evaporation experiment was performed in a vacuum of 5.8×10^{-7} Torr. The gun power in the e-beam process was in the range of 0.60 to 1.05 kW. The deposition rate was controlled by adjusting the gun power. Substrates were heated at 400°C. The Fig. 2 is a schematic of the half-cell configuration.

Characterization of Thin Films

The crystal structures of the electrolyte thin films were analyzed using X-ray diffraction (XRD) (D/MAX-2200, Rigaku) with the Cu Ka line. The XRD was operated at 40 kV/20 mA in the range of $2\theta = 20$–80 with a scanning speed of 0.02 2θ /min. Surface and cross-sectional morphology were examined with a field emission scanning electron microscopy (FESEM) (Model S-4700, Hitachi). Possible chemical reaction and interdiffusion between

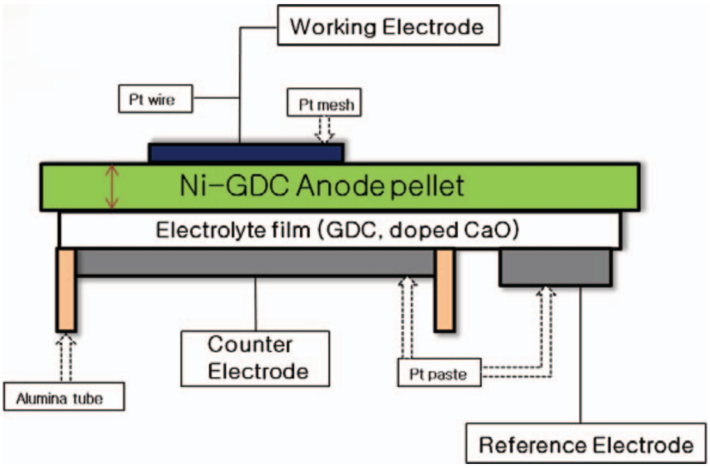


Figure 2. Schematic diagram of half-cell.

the anode and the electrolytes were analysed via energy dispersive X-ray spectroscopy (EDX). The ionic conductivities of the GDC thin films were measured with a 2-probe ac impedance method using an impedance analyzer (Solartron 1255B). The impedance spectra were obtained with the frequency range of 0.1 Hze100 kHz at temperatures from 773 to 1073 K in H_2 and O_2. For the impedance measurement, a Pt electrode was painted by screen printing method on the substrate and then electrolyte film was deposited on the Pt electrode.

Results and Discussion

The electrolyte powders and NiO-GDC anode powder were synthesized by solid state reaction method. Figure 3 the X-ray diffraction (XRD) pattern of electrolyte (GDC, CaO doped GDC) powders represented a typical cubic fluorite structure, and sharp lines repeating

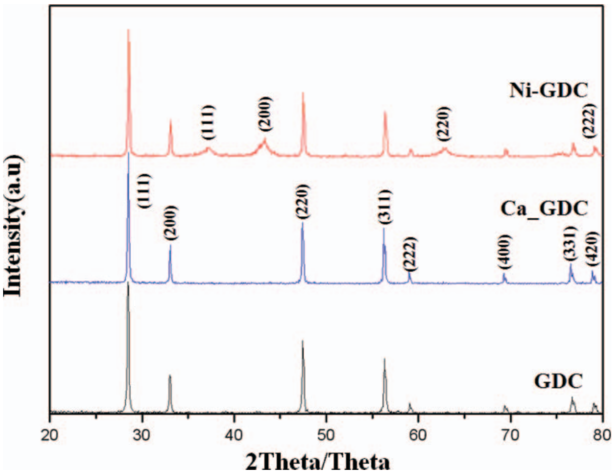
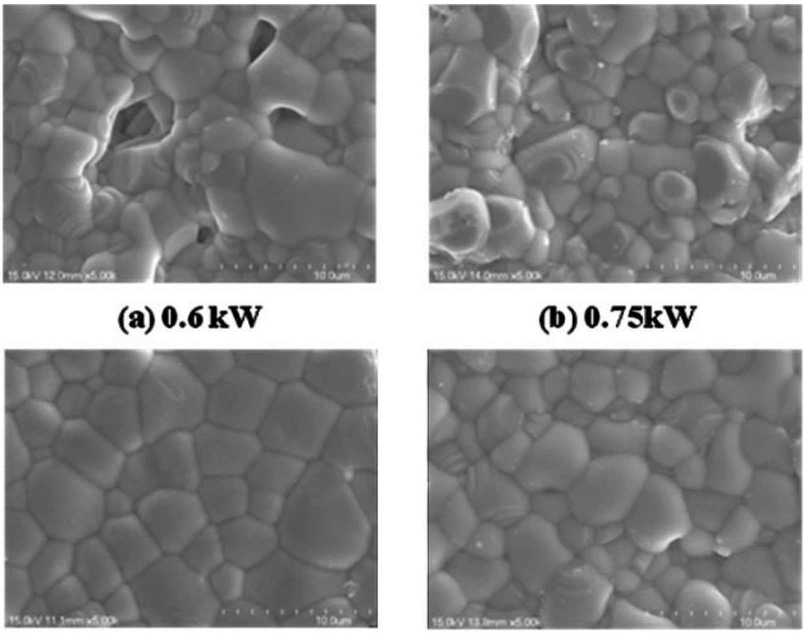


Figure 3. XRD pattern of pure GDC electrolyte (sintering at 1400°C) and CaO-doped GDC electrolytes (sintering at 1400°C).

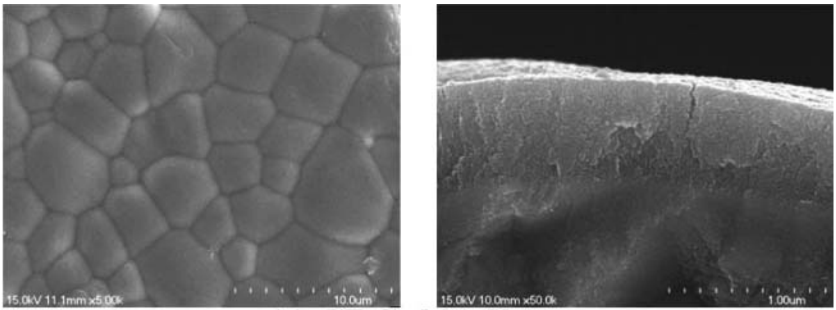


(a) 0.6kW **(b) 0.75kW**

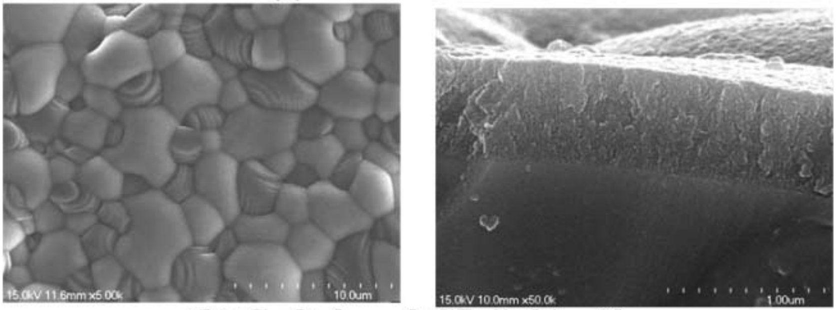
(c) 0.9kW **(d) 1.05kW**

Figure 4. FESEM image of surface view of GDC electrolyte films for various gun power.

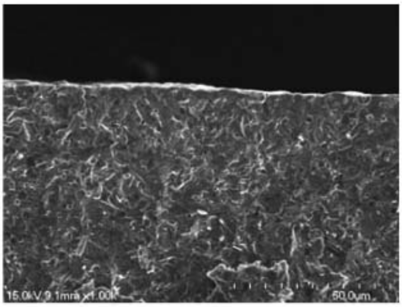
the crystal structure of the evaporating bulk electrolyte powder used in this study, which indicates that a single solid solution of Gd_2O_3-doped CeO_2 is formed after sintering at 1400°C for 4 h and doped CaO GDC is formed after sintering at 1400°C for 4 h. From the figure, it appears that the crystalline structure of GDC material is not altered with the addition of Ca because no reflections corresponding to the new phases are observed. Also, no reflections associated with Ca oxides were observed. This implies that the oxides of Ca are present at concentrations below the XRD detection limit. Figure 4 shows the effect of the microstructure GDC thin film samples the gun power in the e-beam process was in the range of 0.60 to 1.05 kW. Figure 4(a) and (b) shows the surface view of GDC thin films evaporated at the gun power range of 0.60 kW and 0.75 kW. (a) is open pores can be observed from the figure and some closed pores are visible. But, (b) micrograph of the establish existence of a dense structure. No open pores can be observed from the figure although some contamination. The Fig. 4(c) show as the gun power increase, establish existence of a dense film structure. At this point, we estimated that the characteristics of the thin film had been improved dense by increasing the gun power. However, Figure 4(d) show as the not fully dense structure, when gun power of 1.05 kW and over. This is due to that the accelerated evaporation rates by increasing the gun power. Figure 5 shows the surface view and cross-sectional view SEM micrographs of the electrolyte/anode half cell with GDC thin film and CaO added thin film electrolyte. There are some closed pores observed in the cross-section of the electrolyte film, but no connecting pores are found from the GDC film surface to the film/substrate interface indicating that the GDC electrolyte thin-film is gas tight. Additionally, no crack or de-lamination is observed. GDC electrolyte thin-film is uniform in thickness and adheres well to the NiO-GDC anode substrate. The average thickness of the electrolyte thin film is approximately 0.7 μm after deposited temperature at



(a) GDC thin film



(b) CaO doped GDC thin film



(c) NiO-GDC substrate

Figure 5. FESEM image of surface view and cross-sectional view of NiO-GDC substrate/GDC electrolyte layer.

400°C for 2 h. The diffusion of nickel the NiO-GDC composite into the GDC electrolyte was studied by EDX analysis. Nickel distribution across the interface was similar in both pairs, that is, a evaporation temperature (400°C) does not affect significantly nickel diffusion. As shown in Fig. 6, corresponding to the Ni-GDC/GDC interface evaporated at 400°C for 2 h, nickel diffusion was not detected at the electrolyte surface, even in the adjacent to the anode. It is observed that in the electrolyte region (spectrum1) there is no nickel present, whereas in the anode region (spectrum2) nickel and cerium gadolinium oxide phases are present, in accordance with the expected anode composition. The ionic conductivity of the electrolyte films was analyzed by a 2-probe ac impedance method in the operating temperature range from 500°C to 800°C. Table 1 shows resistance for different operating temperatures, decreased resistance with increasing operating temperature. The electrode

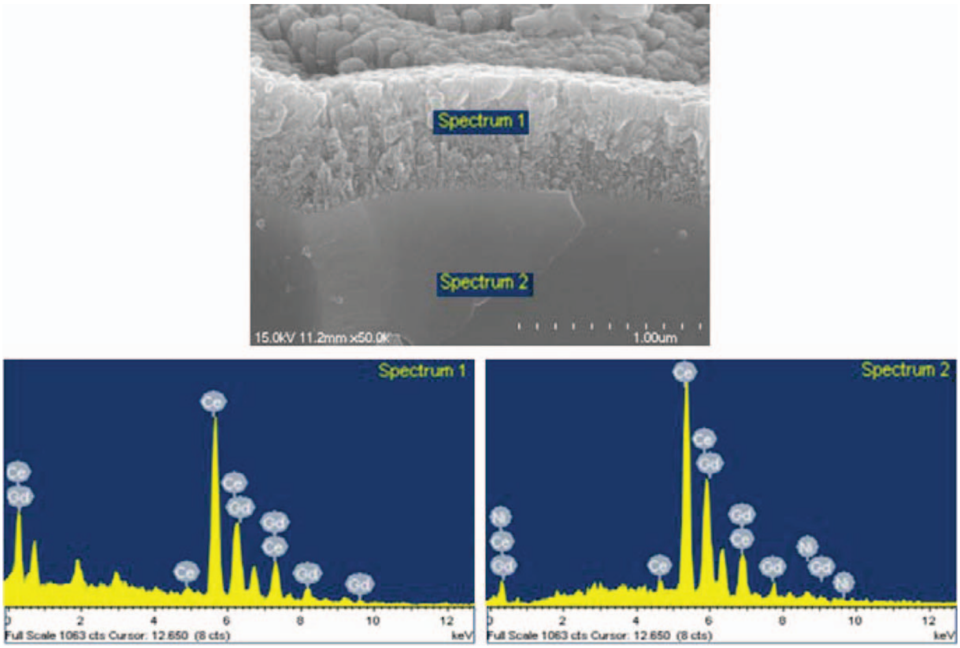


Figure 6. EDX analysis of nickel distribution across the interface of Ni-GDC/GDC evaporated at 0.9 kW gun power.

kinetics is very active at high temperatures due to the increased operating temperature. The ionic conductivity was obtained from the following equation.

$$\text{Ionic conductivity } (\sigma) = \frac{1}{\text{Resistance}} \times \frac{\text{The thickness of the electrolyte}}{\text{The area of the cell}}$$

Figure 7 the present Arrhenius-type plots of the ionic conductivity of the half cells. The effect of GDC and Calcium oxide doped GDC on the ionic conductivity was evaluated. As can be seen in Fig. 7, the ionic conductivity of the sample pure GDC is lower than that of the other samples. At CaO doped GDC electrolytes, no significant increase of the ionic conductivity was observed as compared with that pure GDC electrolyte. CaO doped GDC

Table 1. Resistance of GDC electrolyte half cells for operation temperature

Electrolyte	Operating temperature (K)	R(Ω cm^2)
GDC	1073	2.68
	973	3.62
	873	4.23
	773	6.57
CaO doped GDC	1073	2.19
	973	2.97
	873	3.64
	773	6.01

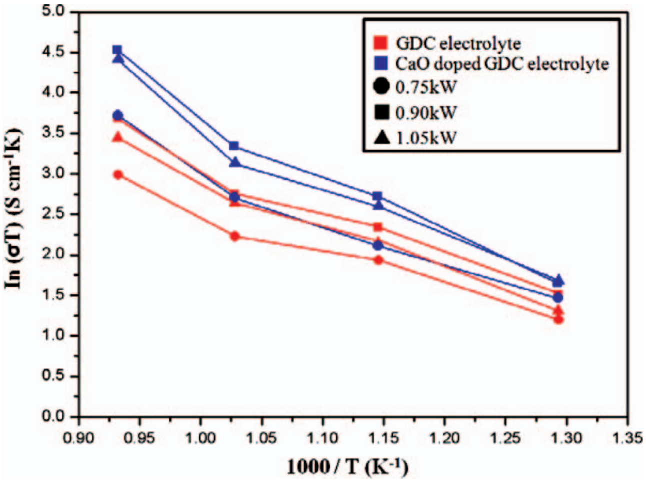


Figure 7. Arrhenius plots of the ionic conductivity of the GDC thin samples.

sample evaporated at 0.9 kW the key functional properties – density and ionic conductivity. The main objective of this work was to prove that the low-temperature processing of the SOFCs is possible.

Conclusions

Anode-supported SOFC was fabricated by the electron-beam evaporation technique to investigate the effects of 2% Cacium oxide cations on the dense of thin-film GDC electrolyte and on the performance of intermediate-temperature SOFC. Thin GDC electrolyte films with a thickness of 0.7μm were successfully prepared by e-beam technique. XRD peaks show that the typical cubic fluorite structure of the CaO doped GDC electrolytes at sintering temperature of 1400°C. A good adhesion to the substrate and dense structure were observed by the fractured surface view and cross-sectional view of the films on NiO-GDC anode substrate temperature of 400°C and gun power of 0.9 kW. Result showed that the improvement of sample conductivity in comparison to both GDC and CaO doped GDC samples. Due to differences in activation energies this positive effect was visible at gun power higher than 0.75 kW. The result of this study indicated that the CaO doped GDC electrolytes by e-beam evaporation technique could be applied for the preparation of thin electrolyte films for intermediate-temperature SOFC after optimizing the film composition and e-beam operating conditions.

Acknowledgment

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