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Synthesis and characterization of nanocrystalline $(\text{Zr}_{0.84}\text{Y}_{0.16})\text{O}_{1.92}-(\text{Ce}_{0.85}\text{Sm}_{0.15})\text{O}_{1.925}$ heterophase thin films

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A new type of nanocrystalline samarium-doped-ceria/yttrium-stabilized-zirconia (SDC/YSZ) heterophase thin film electrolytes was synthesized on MgO and Si substrates by spin coating and thermal treatment of SDC-nanoparticle-incorporated polymeric precursors. In the heterophase films, SDC nanoparticles were uniformly dispersed in a nanocrystalline YSZ matrix. The heterophase structure was stable when fired in air at temperatures up to 850 °C. The nanocrystalline heterophase thin films exhibited electrical conductivities significantly higher than that of the phase-pure YSZ and SDC nanocrystalline thin films at reduced temperatures. The effects of SDC grain size and volume fraction on the electrical conductivity of the heterophase films were also studied.

I. INTRODUCTION

Solid oxide fuel cells (SOFCs) are considered to have great potential for highly efficient stationary power generation. Yttria-stabilized zirconia (YSZ) is the common electrolyte material for SOFCs because of its reasonable electrical conductivity and high ionic transference number in both oxidizing and reducing atmospheres. However, for the traditional SOFC with YSZ electrolytes, the fabrication temperature is usually in the range of 1300 to 1400 °C and the operating temperature is normally 800–1000 °C. This results in an increased cost for expensive thermal-resistant materials and causes problems such as accelerated cell degradation and higher cathodic overpotential. Doped ceria has recently been considered as an alternative electrolyte material to YSZ for reduced-temperature SOFC because of its high conductivity at relatively low temperatures. However, ceria-based electrolytes have low open circuit voltages (OCV) because ceria has a relatively high electronic conductivity, especially in reducing atmospheres.

In the past decade, doped-ceria/YSZ heterophase or

composite electrolytes were used to enhance the electrical conductivity while maintaining a high ionic transference number for reducing the SOFC operating temperature and internal ohmic overpotential.¹ The reported heterophase electrolytes were made by either embedding doped-ceria particles in a continuous YSZ matrix² or constructing YSZ/doped-ceria multilayer structures.^{3,4} In both cases, the highly conductive doped-ceria reduced the effective thickness of the relatively low-conductivity YSZ layer; while the continuous YSZ layer served as a barrier to electronic conduction through the ceria phase. A samarium-doped-ceria (SDC) interlayer between the YSZ electrolyte and cathode can also prevent harmful electrolyte/cathode reactions.^{5,6} The YSZ/SDC heterophase electrolytes improved the open circuit voltage (OCV) compared to the pure SDC electrolyte and provided flatter V-I curves, i.e., less ohmic loss, compared to monophasic YSZ electrolytes.⁷ However, the V-I curve lowered significantly when the YSZ and SDC formed solid solutions at high temperatures because $\text{ZrO}_2\text{-CeO}_2$ solid solutions are mixed conductors^{2,7} and the YSZ-SDC solid solutions are less conductive than either YSZ or SDC.⁸ The grain sizes of SDC and YSZ in the reported heterophase electrolytes were of micron scale to avoid formation of YSZ/SDC solid solution during high temperature fabrication processes.

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Another promising way to lower the SOFC operating temperature is to use nanocrystalline thin-film electrolytes.⁹ Dramatically increased electrical and ionic conductivities have been reported at reduced temperatures in YSZ, CeO_2 , and $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ nanocrystalline thin films with grain sizes less than 30 nm.^{10,11} Enhancement of conductivity in nanostructured materials was attributed to the size-dependent defect properties^{12,13} and increased interface area that facilitated the fast boundary conduction and inhibited formation of segregated impurity layers, commonly SiO_2 , at grain boundaries.¹⁴

More recently, Sata et al.¹⁵ reported an increase of two to three orders of magnitude in ionic conductivity for a heterophase film containing alternating CaF_2 and BaF_2 layers of nanometer thickness compared to bulk CaF_2 and BaF_2 crystals. The enhanced ion conduction was in the direction parallel to the layered interface. The drastically increased ion conduction resulted from a conductivity behavior qualitatively different from the bulk phases of the individual components in the overlapping space-charge regions of the nanostructured two-phase system.^{15–17}

The work of Sata et al.¹⁵ revealed the possibility of developing nanocrystalline heterophase electrolytes for enhanced conductivity at reduced temperatures. However, synthesis of dense, nanocrystalline, heterophase films is difficult by traditional co-firing processes because the nanoparticles of different phases react to form a solid solution at temperatures well below the temperature required for densification.⁸ In this paper, we report a new type of nanocrystalline SDC/YSZ heterophase thin film electrolytes synthesized from SDC-nanoparticle-incorporated polymeric precursors.

II. EXPERIMENTAL

Chemicals used in this study include zirconyl chloride hydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.99%, Aldrich, St. Louis, MO), yttrium nitrate hexahydrate [$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99+%, Aldrich], glycine (99+%, Aldrich), ethylene glycol (99+%, Aldrich), cerium nitrate hexahydrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99+%, Aldrich], and samarium nitrate [$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99+%, Aldrich]. The SDC nanopowders were obtained commercially from NexTech, Lewiscenter, OH. The as-received nano-powders had a composition of $(\text{Ce}_{0.85}\text{Sm}_{0.15})\text{O}_{1.925}$ and grain size of 5–10 nm. The SDC powders underwent pretreatments by firing in air for 10 h at different temperatures. The average SDC crystallite sizes increased to 25, 35, and 45 nm after firing at 800, 1000, and 1200 °C, respectively.

The SDC-nanoparticle-incorporated polymeric precursor was synthesized by the following procedure: (i) The YSZ polymeric precursor, $(\text{Zr}^{4+}, \text{Y}^{3+})$ -chelated poly ethyl glycol, was synthesized by polymerization of an aqueous solution containing ethylene glycol, zirconyl

chloride, yttrium nitrate, and glycine. The precursor had a Y:Zr atomic ratio of 16:84. The detailed polymeric precursor synthesis procedure can be found in the literature.⁶ (ii) A stable SDC colloidal suspension (1 wt% solid content) prepared by ultrasonic dispersion under controlled pH (= 3–4, adjusted by 0.1 N HNO_3) was added to the YSZ polymeric precursor drop-wise under stirring. (iii) The mixture was then heated at 80 °C under stirring for 5 h to remove water and improve the viscosity for film coating. The SDC-nanoparticle-incorporated precursor was then cooled to room temperature under stirring and used to deposit thin films on $\langle 100 \rangle$ magnesium oxide (MgO , $18 \times 18 \times 0.5$ mm) and $\langle 001 \rangle$ silicon wafers.

The typical spin-coating process included a 5-s spinning at 600 rpm followed by a 20-s spinning at 2500 rpm using a two-stage spin-coater (KW-4A, CheMat, Northridge, CA). After coating, the film was dried at 80 °C and fired at 300 °C for 1 min on a hot plate. The film was then fired at 650 °C in air for 4 h. After firing, the films were further annealed at 750 °C for 5 h. The purpose of the 750 °C annealing step was to prevent grain growth during the conductivity measurements in a temperature range of 400–750 °C. It was previously observed on YSZ nanocrystalline films that a thermal treatment at a high temperature could effectively inhibit further grain growth during annealing at relatively lower temperatures.¹⁸ The film coating process was repeated three more times and resulted in a final oxide film thickness of ~140 nm. Thicker films were prepared by additional coatings under identical conditions to obtain strong x-ray diffraction (XRD) peak intensities for examining the crystal phase and grain sizes in the films.

The phase-pure YSZ and SDC nanocrystalline thin films were synthesized using similar procedures as described in the literatures.^{6,18} The atomic ratios of Y:Zr and Sm:Ce in their polymeric precursors were 16:84 and 15:85, respectively. Thus the chemical composition of the phase-pure YSZ and SDC films were $(\text{Zr}_{0.84}\text{Y}_{0.16})\text{O}_{1.92}$ and $(\text{Ce}_{0.85}\text{Sm}_{0.15})\text{O}_{1.925}$, respectively. The YSZ and SDC nanocrystalline films were obtained by the same thermal treatments as those used in the preparation of the heterophase films, namely firing at 650 °C for 4 h followed by annealing at 750 °C for 5 h. Both the pure YSZ and SDC films had a film thickness of ~100 nm using a total of four coating steps. After annealing at 750 °C, the grain sizes of the YSZ and SDC thin films were both ~15 nm. The total electrical conductivities of the thin films were then measured by a four-probe conductivity meter described in a previous paper.⁸

III. RESULTS

The SDC/YSZ heterophase films were first synthesized using SDC nanocrystals fired at different temperatures

with a fixed SDC:YSZ molar ratio of 1:1, which gave a SDC volume fraction of 0.587 (SDC:YSZ volume ratio of 1:0.704), in the final oxide films. The pretreated SDC nano-powders and the as-received powders were used to prepare the SDC nanoparticle-incorporated polymeric precursors. For all these powders, including the untreated one, the SDC crystal structure was not changed in the precursor films after being dried at 80 °C and further heated at 300 °C according to the x-ray diffraction (XRD) tests.

The precursor films containing SDC particles without pretreatment and particles pretreated at 700 °C were found to form YSZ-SDC solid solutions after firing at temperatures as low as 450 °C. Lines d and e in Fig. 1 are XRD patterns of the precursor film containing untreated SDC powders after being fired at 300 °C and the solid solution film after further firing at 450 °C. The precursor film containing SDC powders pretreated at 800 and 1200 °C formed a SDC/YSZ heterophase structure

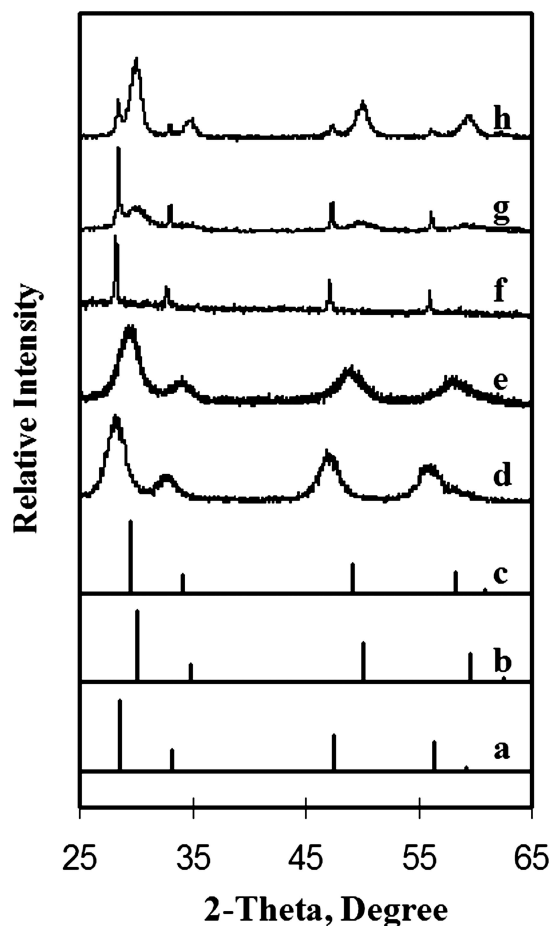


FIG. 1. XRD patterns. Lines a, b, and c are YSZ, SDC, and YSZ/SDC solid solution pellets,⁸ respectively. Lines d and e are films synthesized with untreated SDC; line d was dried at 300 °C and e was fired at 450 °C (solid solution). Lines f, g, and h are films with SDC pretreated at 1200 °C; f was dried at 80 °C, g was fired at 650 °C, and h was fired at 850 °C.

after firing at 650 °C. The heterophase structure of these films was stable during further heat treatment at 850 °C. Lines f, g, and h are XRD patterns of the precursor film containing SDC powders pretreated at 1200 °C after being fired at 300 °C (for 1 min), 650 °C (for 4 h), and 850 °C (for 100 h), respectively.

In the heterophase thin films, the YSZ grain size was ~15 nm after annealing at 750 °C for 5 h. The SDC grain sizes remained unchanged from their values after firing (pretreatment) at 800, 1000, and 1200 °C, which were 25, 35, and 45 nm, respectively. The grain sizes in the films were estimated by XRD.¹⁸ In the following text, SDC800/YSZ, SDC1000/YSZ, and SDC1200/YSZ were used to denote the heterophase films containing SDC particles pretreated at 800, 1000, and 1200 °C, respectively. No intercrystal pores or pinholes were found in the heterophase films by surface examinations using atomic force microscopy as shown in Fig. 2. The four-coat films had a thickness of ~140 nm according to the observation by a field-emission scanning electron microscope (SEM; Hitachi S-5200 Nano-SEM, Japan) for the

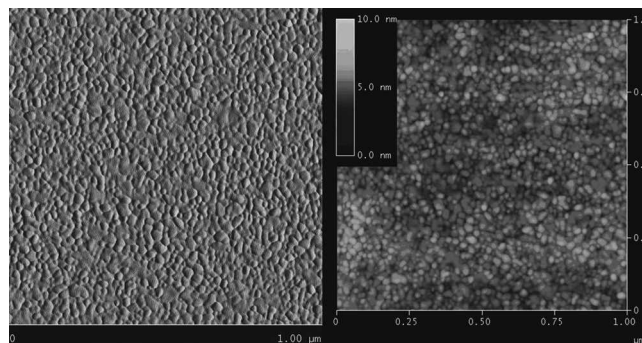


FIG. 2. AFM image of the surface of the YSZ800/SDC heterophase film annealed at 750 °C for 5 h.

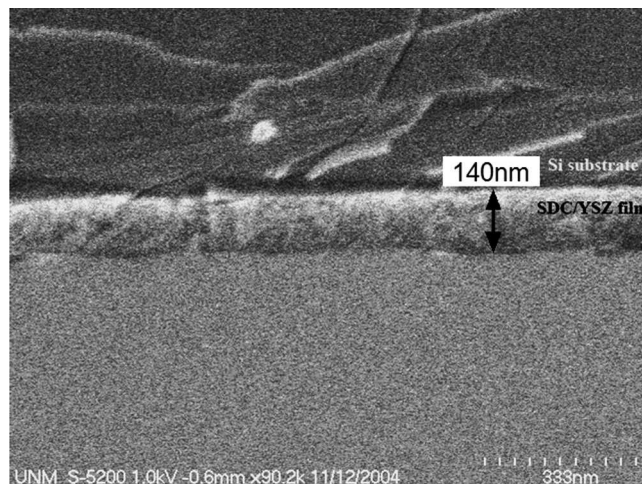
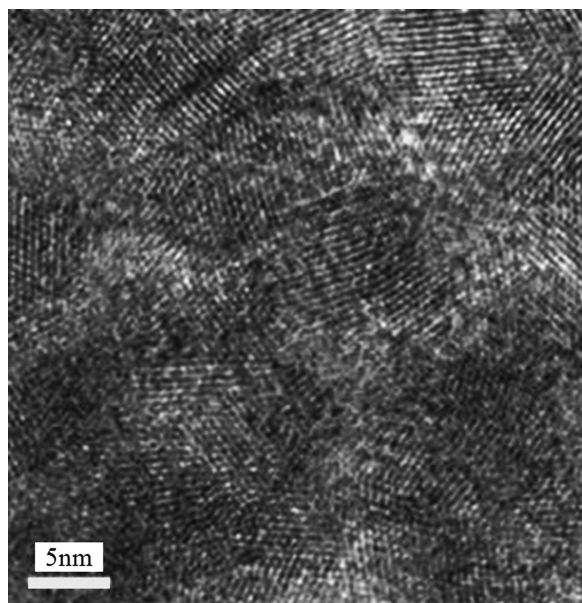


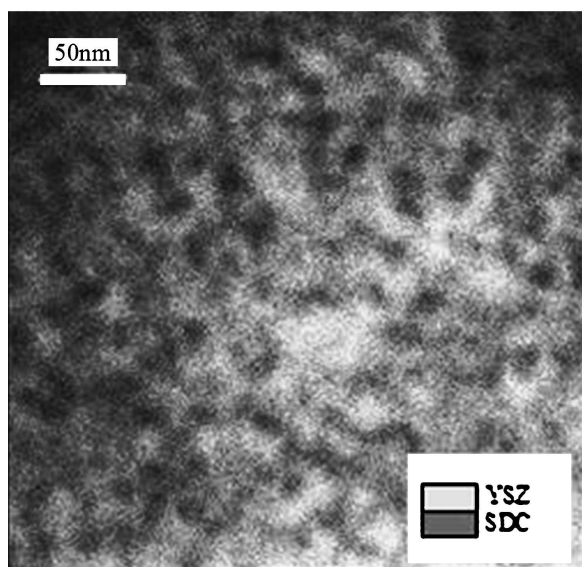
FIG. 3. SEM image of the cross-section of a SDC800/YSZ heterophase film.

cross section of a Si-supported film as shown in Fig. 3. A Si substrate was used here because it provided a better cross section sample for clearer SEM observations compared to the MgO.

The grain size and density of the heterophase thin films were further confirmed by transmission electron microscopy (TEM) as shown in Fig. 4(a) for a film containing SDC nanocrystals pretreated at 800 °C. Figure 4(b) is the image of scanning transmission electron microscopy (STEM) Z-contrast mapping (JEOL 2010 FEG TEM STEM, Oxford EDS, Gatan Imaging Filter, Japan) for the cross section of a SDC800/YSZ heterophase film. The



(a)



(b)

FIG. 4. TEM observations of the SDC800/YSZ heterophase film cross section: (a) TEM image and (b) STEM Z contrast mapping (contrast inverted).

Z-contrast mapping shows that the SDC particles are uniformly dispersed in a matrix of YSZ nanocrystallites.

The total electrical conductivities of the MgO-supported nanocrystalline thin films were measured in air. The results are presented in Fig. 5. The conductivity of the solid solution thin film was not measured because the potentiostat was unable to maintain a stable current under its maximum output voltage (10 V) for the highly resistive thin film. The total conductivity of the nanocrystalline YSZ thin film obtained in this study agreed well with the literature value for a YSZ film synthesized under similar conditions with comparable grain size.¹⁰ With comparable grain sizes, the total electrical conductivity of the SDC800/YSZ heterophase thin film was 3–20 times that of the nanocrystalline SDC film in a temperature range of 450–700 °C and was 2–12 times that of the YSZ nanocrystalline film in a temperature range of 500–700 °C. The extraordinarily high conductivity of the heterophase film at reduced temperatures may be attributed to the fast conduction in both the grain boundaries of homophase regions^{10,13} and the mesoscopic heterojunctions in the nanostructure.¹⁵ Increasing the SDC particle size from 25 to 45 nm caused a moderate decrease in the conductivity because the density of YSZ/SDC heterojunctions is reduced in films with larger SDC nanoparticles.

Because the SDC/YSZ interface density (m^2/m^3) in the heterophase film depends on the SDC:YSZ volume ratio (or SDC volume fraction) and their particle sizes, additional experiments were conducted to study the effect of the SDC volume fraction on the conductivity of the heterophase film. The SDC volume fraction was varied in a range from 0.136 to 0.587 by adjusting the amount of

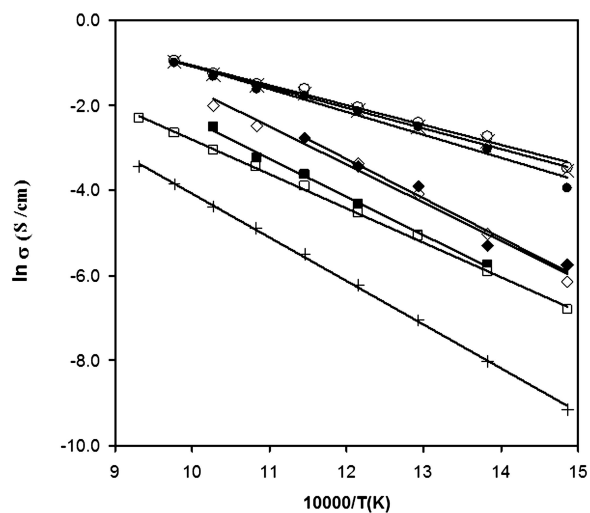


FIG. 5. Electrical conductivities as a function of temperature. (○) SDC800/YSZ heterophase film, (×) SDC1000/YSZ, (●) SDC1200/YSZ heterophase film, (◇) YSZ nanofilm (this work), (◆) YSZ nanofilm (grain size 20 nm),¹⁰ (■) SDC nanofilm, (□) SDC pellet,⁸ (+) YSZ pellet.⁸

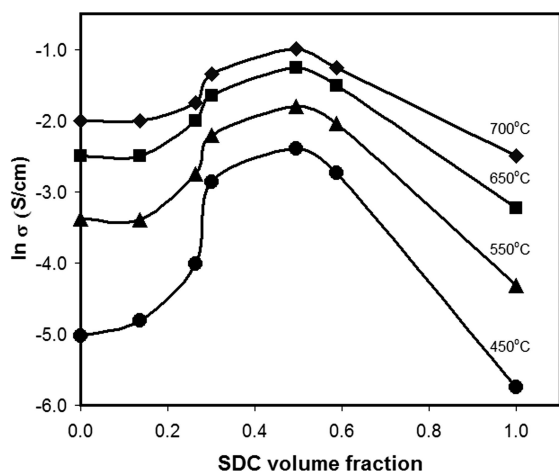


FIG. 6. Electrical conductivity as a function of $V_{\text{SDC}}/V_{\text{YSZ}}$ at different temperatures: (■) 450 °C, (▲) 550 °C, (●) 650 °C, and (◆) 750 °C.

SDC powders added to the polymeric precursors. The SDC powders fired at 800 °C were used for all the films with different SDC volume fractions. The electrical conductivities of the films are presented as a function of SDC volume fraction in Fig. 6, which also includes the data of phase-pure YSZ and SDC films. The highest conductivity was obtained on the film with a SDC volume fraction of 0.495, which possessed the highest interface area among the samples studied. A SDC volume fraction of 0.68 or greater resulted in a porous structure as indicated by the reduced transparency of the film and drastically decreased conductivity.

IV. CONCLUSIONS

Dense, nanocrystalline SDC/YSZ heterophase thin films were successfully synthesized on MgO and silicon wafers from SDC-nanoparticle-incorporated polymeric precursors. At reduced temperatures, the nanostructured YSZ/SDC heterophase film exhibited total electrical conductivity significantly higher than that of the phase-pure YSZ and SDC nanocrystalline thin films with comparable grain sizes. The nanocrystalline SDC/YSZ heterophase thin film may have potential applications in low temperature SOFC, gas separation membranes, and high performance gas sensors. It is also anticipated that the high total conductivity of the heterophase film is due mainly to the enhanced ionic conduction because the SDC nanocrystals are embedded in the ion conducting YSZ matrix.

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REFERENCES

1. T. Hibino, A. Hashimoto, T. Inoue, J. Tokuno, S. Yoshida, and M. Sano: A low-operating-temperature solid oxide fuel cell in hydrocarbon-air mixtures. *Science* **288**, 2031 (2000).
2. Y. Mishima, H. Mitsuyasu, M. Ohtaki, and K. Eguchi: Solid oxide fuel cell with composite electrolyte consisting of samaria-doped ceria and yttria-stabilized zirconia. *J. Electrochem. Soc.* **145**, 1004 (1998).
3. W.S. Jang, S.H. Hyun, and S.G. Kim: Preparation of YSZ/YDC and YSZ/GDC composite electrolytes by the tape casting and sol-gel dip-drawing coating method for low-temperature SOFC. *J. Mater. Sci.* **37**, 2535 (2002).
4. T. Inoue, T. Setoguchi, K. Eguchi, and H. Arai: Study of a solid oxide fuel-cell with a ceria-based solid electrolyte. *Solid State Ionics* **35**, 285 (1989).
5. Y. Matsuzaki and I. Yasuda: Electrochemical properties of reduced-temperature SOFCs with mixed ionic-electronic conductors in electrodes and/or interlayers. *Solid State Ionics* **152/153**, 463 (2002).
6. H.U. Anderson, M.M. Nasrallah, and C. Chan: Method of coating a substrate with a metal oxide film from an aqueous solution comprising a metal cation and a polymerizable organic solvent. U.S. Patent No. 5 494 700 (1996).
7. B. Zhu: Fast ionic conducting film ceramic membranes with advanced applications. *Solid State Ionics* **119**, 305 (1999).
8. M. Price, J. Dong, X. Gu, S.A. Speakman, E.A. Payzant, and T.M. Nenoff: Formation of YSZ-SDC solid solution in a nanocrystalline heterophase system and its effect on the electrical conductivity. *J. Am. Ceram. Soc.* **88**, 1812 (2005).
9. J. Schoonman: Nanoionics. *Solid State Ionics* **157**, 319 (2002).
10. I. Kosacki, T. Suzuki, V. Petrovsky, and H.U. Anderson: Electrical conductivity of nanocrystalline ceria and zirconia thin films. *Solid State Ionics* **136/137**, 1225 (2000).
11. I. Kosacki, C.M. Rouleau, P.F. Becher, J. Bentley, and D.H. Lowndes: Surface/interface-related conductivity in nanometer thick YSZ films. *Electrochem. Solid-State Lett.* **7**, A459 (2004).
12. I. Kosacki, V. Petrovsky, and H.U. Anderson: Band gap energy in nanocrystalline $\text{ZrO}_2:16\%\text{Y}$ thin films. *Appl. Phys. Lett.* **74**, 341 (1999).
13. K. Otsuka, A. Kuwabara, and A. Nakamura: Dislocation-enhanced ionic conductivity of yttria-stabilized zirconia. *Appl. Phys. Lett.* **82**, 877 (2003).
14. C. Tian and S-W. Chan: Ionic conductivities, sintering temperatures and microstructures of bulk ceramic CeO_2 doped with Y_2O_3 . *Solid State Ionics* **134**, 89 (2000).
15. N. Sata, K. Eberman, K. Eberl, and J. Majer: Mesoscopic fast ion conduction in nanometre-scale planar heterostructures. *Nature* **408**, 946 (2000).
16. J. Majer: Space charge regimes in solid two phase systems and their conduction contribution—III: Defect chemistry and ionic conductivity in thin films. *Solid State Ionics* **23**, 59 (1987).
17. J. Majer: Ionic conduction in space charge regions. *Prog. Solid State Chem.* **23**, 171 (1995).
18. J. Dong, M.Z. Hu, E.A. Payzant, T.R. Armstrong, and P.F. Becher: Grain growth in nanocrystalline yttrium-stabilized-zirconia thin films synthesized by spin coating of polymeric precursors. *J. Nanosci. Nanotech.* **2**, 161 (2002).