Nanocomposite Electrodes Fabricated by a Particle-Solution Spraying Process for Low-Temperature SOFCs

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We report a particle-solution spraying process for fabrication of porous electrodes for solid oxide fuel cells (SOFCs). Gd-doped ceria (GDC) particles with composition of $Gd_{0.1}Ce_{0.9}O_2$ were suspended in ethanol containing nitrates of Sm, Sr, and Co in a molar ratio of 1:1:2 to form $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) after combustion in air. The SSC solution carrying GDC particles was pumped through an atomizer and the resulting mist was combusted, depositing a porous composite layer consisting of SSC and GDC on a GDC electrolyte supported by a Ni−GDC anode. Typically, the SSC−GDC composite cathodes consist of large GDC grains (1−2 μm) embedded in nanosized phases of SSC. The highly open porous structure significantly facilitates gas transport while the extremely large surface area dramatically enhances electrode kinetics. As a result, the polarization resistances to oxygen reduction of the GDC−SSC/GDC interface are extremely low, varying from 1.06 Ωcm^2 at 450 °C to 0.45 Ωcm^2 at 500 °C. The activation energy for the electrode reaction was estimated to be about 0.65 eV (62.5 kJ/mol), as determined from impedance spectroscopy performed at different temperatures. For a single cell with a configuration of SSC−GDC/GDC/Ni−GDC, peak power densities of 223 and 385 mW/cm^2 were achieved at 500 and 600 °C, respectively.

Introduction

Solid oxide fuel cells (SOFCs) have a great potential to be the power of the future because of their high energy-conversion efficiency, low pollutant emission, and excellent flexibility with practical fuels (e.g., hydrocarbon fuels with contaminants). Efforts are being made to lower the operating temperature from 800−1000 °C to below 700 °C in order to reduce cost and improve reliability and operational life.[1−8] One of the critical challenges for operation of SOFCs at low temperatures is how to reduce interfacial polarization resistances (R_p). [9] New materials must be identified or developed to improve the intrinsic catalytic properties of the electrode materials. Further, novel fabrication techniques have to be developed in order to create unique microstructures in a cost-effective manner.

It has been generally recognized that composite electrodes offer better performance than single-phase electrodes for SOFCs due to the extension of triple-phase-boundary (TPB) into the porous electrode body away from the traditional electrode−electrolyte interface. As a result, the overpotential at the electrodes can be dramatically reduced. This approach has been very successful for the cathode, which is usually the major factor limiting cell performance. The composite cathodes typically consist of a mixed-conducting material and an ionic conductor such as YSZ[10,11] or GDC.[12−14]

Various fabrication techniques have been studied to optimize the microstructure and distribution of each component. It was demonstrated that cell performance can be improved by sol−gel coating of $La_{0.85}Sr_{0.15}MnO_3$ (LSM) with YSZ or $Sm_{0.2}Ce_{0.8}O_2$ (SDC).[15] Similarly, Jiang et al. modified LSM cathode with $Gd_{0.2}Ce_{0.8}O_2$ (GDC) by an ion impregnation method.[16] The interfacial polarization resistance of the LSM-GDC/YSZ system at 700 °C was reduced to 0.72 Ωcm^2 by multiple coatings to obtain the required thickness and by subsequent firing following each coating to ensure desired crystallographic phases.

Recently, a combustion CVD process was successfully introduced to fabricate components for solid oxide fuel

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cells. Highly porous, nanostructured electrodes with superior electrochemical performances have been prepared using this method.[17,18] In combustion CVD, precursors such as nitrates or organic salts are dissolved in a flammable solvent. The resulting solution is then pumped into a nanomizer, where a combustion flame is created. A film or coating is deposited when a substrate is within or near the tip of the flame. Electrodes of uniform composition, but with vastly different microstructures, have been created under different conditions. In this article, we report a new process for fabrication of SOFC electrodes, a particle-solution spraying process. One component of the composite electrode, $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC), was introduced in the form of nitrates dissolved in a flammable solvent, while the other component of the electrode, GDC, was introduced in the form of solid particles dispersed in the SSC solution. The desired crystalline phase of SSC forms within the flame during deposition. The resulting cathodes have very unique microstructures: each large agglomerate consists of smaller ones, which in turn contains even smaller particles. The smallest feature is within nanoscale. SOFCs with these electrodes have shown very low interfacial polarization resistances and high cell performance at low operating temperatures.

Experimental Section

Anode (65 wt % NiO and 35 wt % GDC) supported GDC substrates were prepared by co-pressing followed by sintering as described elsewhere.[9] Cathodes consisting of SSC and GDC were deposited onto the GDC/NiO−GDC substrates using a particle-solution spraying process. The apparatus for the spraying process is similar to that for combustion CVD as described elsewhere.[19,20] Nitrates of Sm, Sr, and Co in a molar ratio of 1:1:2 (to form $Sm_{0.5}Sr_{0.5}CoO_3$ after combustion) were dissolved into absolute ethanol. GDC particles were prepared by the glycine−nitrate method [21] and were directly dispersed in the SSC ethanol solution. The weight ratio of SSC to GDC was kept at 7:3, corresponding to a volume ratio of 71:29. Before deposition, the solid-solution mixture was ultrasonically dispersed to break apart the large agglomerates. During deposition, a magnetic stirrer was used to prevent particles from settling down. Deposition of cathodes was carried out at 1250 °C for 10 min. Deposition temperature was measured by placing type K thermocouples in the vicinity of substrate surfaces.

The microscopic features of the prepared electrodes were characterized using a scanning electron microscope (SEM, Hitachi S-800) equipped with an energy-dispersive spectroscopy (EDS) attachment. X-ray diffraction analysis was performed on a Phillips PW-1800 diffractometer with a scanning step of 0.005°. Electrochemical performances of the symmetrical cells were measured in ambient air from 450 to 650 °C. Impedances were typically acquired in the frequency range from 0.01 Hz to 100 kHz with an EG&G Potentiostat/Galvanostat (Model 273A) and a Lock-in Amplifier (5210).

Results and Discussion

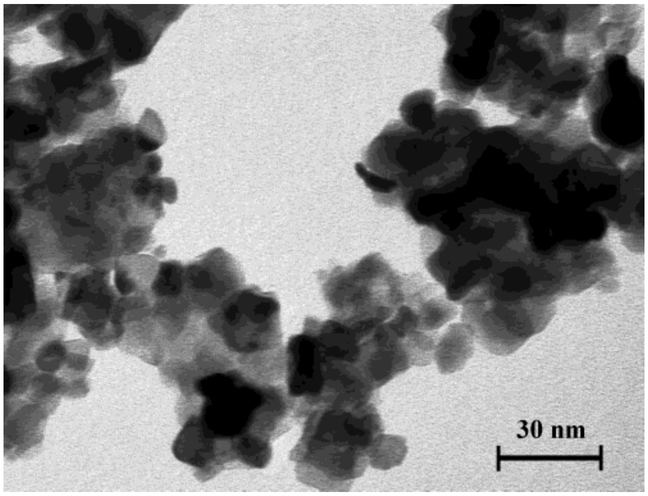

Figure 1. TEM micrograph of the GDC nanoparticles synthesized by a glycine−nitrate method.

Shown in Figure 1 is a typical TEM micrograph of the GDC nanoparticles synthesized by a glycine−nitrate process. The particle size varies from 10 to 30 nm with some agglomeration.

Shown in Figure 2 is a cross-sectional view of an SOFC with the cathode fabricated by a particle-solution spraying process. The dense GDC electrolyte had a thickness of about 20 μm. The cathode is highly porous and is about 30-μm thick. Higher magnification SEM micrographs shown in Figure 2b,c indicate that the large particles (1−2 μm) consist of particles smaller than 50 nm in diameter.

The X-ray diffraction pattern of the cathode shown in Figure 3 indicates that the cathode consists of two highly crystallized phases: SSC and GDC. The GDC peaks came from particles dispersed in solution, while the SSC phase was formed during deposition through chemical vapor reaction. A previous study suggested that highly crystallized SSC phase can be formed at deposition temperatures higher than 1200 °C.[17] In addition, trace of NiO was also observable on the XRD pattern. The NiO signal must be collected from the peripheral surface of the substrate, a NiO−GDC composite anode. It is noted that the baseline of the XRD pattern is not very smooth. A small amount of other phases may be present as implied by the unidentified small peaks. Impedance spectra of a single cell with a configuration of SSC−GDC/GDC/NiO−GDC were measured using a two-electrode configuration in the temperature range of 450−650 °C. Shown in Figure 4a are two typical impedance spectra measured at 500 and 600 °C, respectively. It is noted that each spectrum consists of at least two overlapped semicircles. While it is apparent that multiple processes contributed to the impedance spectra, no attempts were made to separate theses processes. Instead, the impedance data were used only to separate the interfacial polarization resistances (R_p) from other contributions. Clearly, the interfacial polarization resistances (R_p) were much smaller than the bulk resistances of the electrolyte (R_b), even though the electrolyte was only 20-μm thick. For example, interfacial resistances were 0.45 and 0.15 Ωcm^2 at 500 and 600 °C, respectively, while the bulk resistances were 0.58 and 0.38 Ωcm^2 at the two temperatures, respectively. These interfacial polarization resistances (R_p) are compared in Figure 4b with those of the cells having identical materials and configuration but were fabri-

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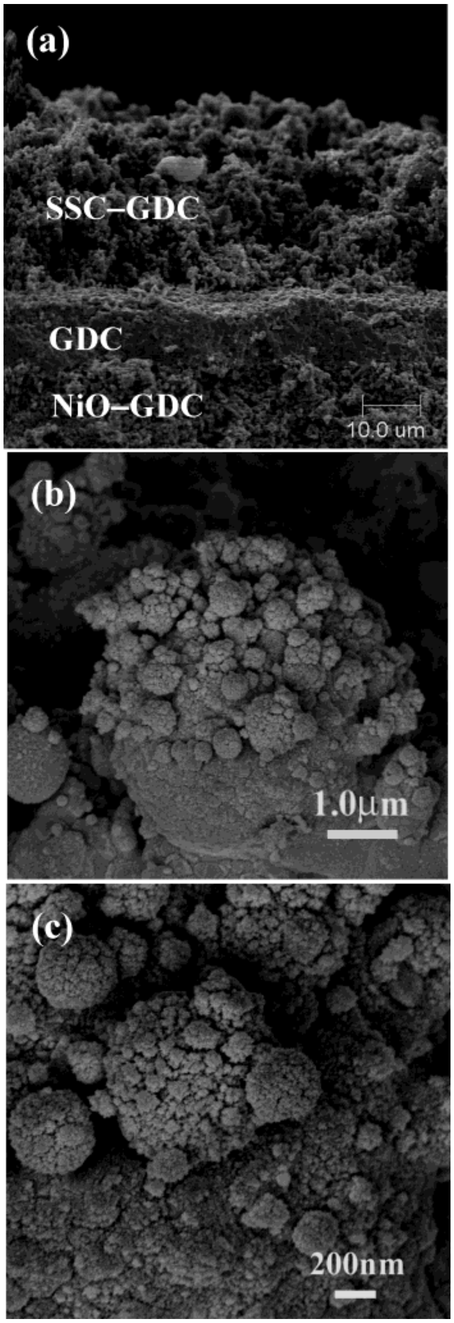

Figure 2. (a) Cross-sectional view of a solid oxide fuel cell with a SSC−GDC cathode fabricated by a particle-solution spraying process. (b) and (c) Higher magnification SEM micrographs of the SSC−GDC cathode showing larger particles surrounded by nanostructured smaller particles.

cated using different processes. Bulk resistances (R_b) and interfacial polarization resistances (R_p) were extracted from the measured impedance spectra and corrected by taking into consideration electronic conduction at the corresponding temperature using the following equation[22]

$$R_p = \frac{R_T - R_b}{\frac{V_{OC}}{E_N}\left[1 - \frac{R_b}{R_T}\left(1 - \frac{V_{OC}}{E_N}\right)\right]} \tag{1}$$

where R_T is the total resistance of the SOFC as

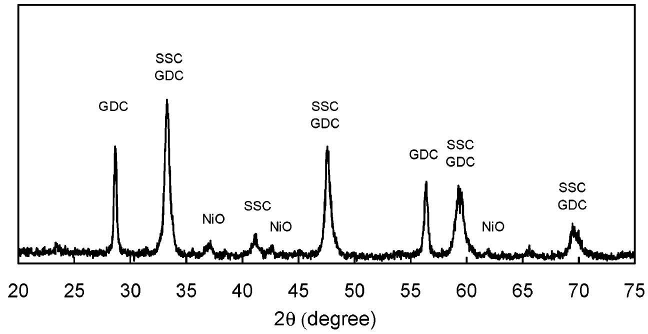

Figure 3. X-ray diffraction pattern of the SSC−GDC cathode (70 wt % SSC and 30 wt % GDC) fabricated by the particle-solution spraying process.

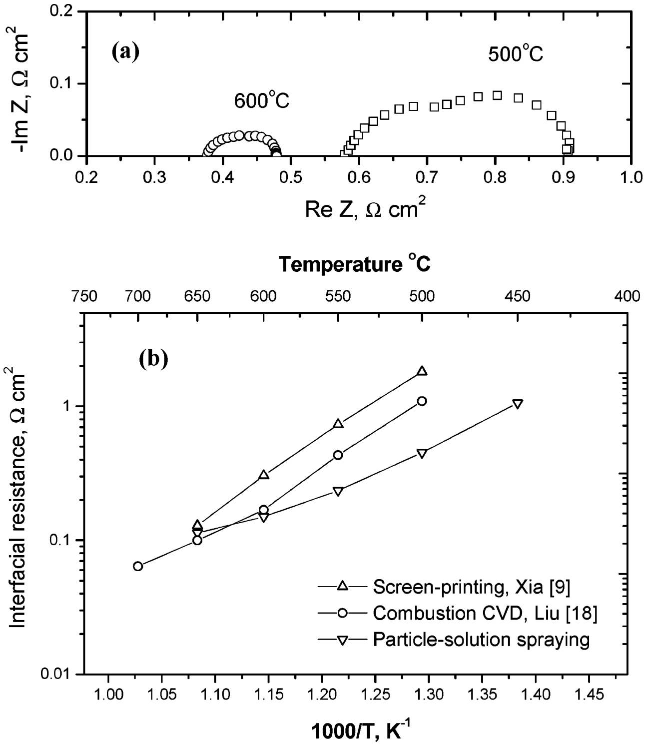

Figure 4. (a) Impedance spectra of a single fuel cell as measured using a two-electrode configuration and (b) comparison of interfacial polarization resistances as determined from impedance spectra for electrodes fabricated using different techniques: screen printing,[9] combustion CVD,[18] and particle-solution spraying.

determined from the intercept of the impedance spectrum with the real axis at low frequencies, R_b is the bulk resistance of the electrolyte as read from the intercept at high frequencies, V_{OC} represents the open cell voltage, and E_N is the Nernst potential across the cell at testing temperatures.

It is evident that fuel cells with cathodes fabricated by the particle-solution spraying process had very low interfacial polarization resistances, especially at low operating temperatures. Typical performances of the SOFC are shown in Figure 5. It is noted that the open circuit voltage (OCV) dropped from 0.9 to 0.8 V as the testing temperature arose from 450 to 650 °C, implying that the mixed-conduction is becoming more significant at higher temperatures and the correction using eq 1 is necessary. The observed peak power densities were about 223, 316, 385, and 411 mW/cm^2 at 500, 550, 600, and 650 °C, respectively.

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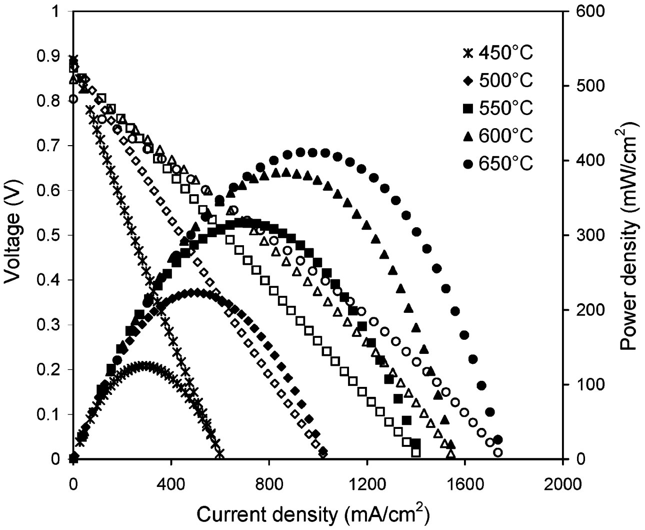

Figure 5. Cell voltages and power densities as a function of current density for fuel cells with SSC−GDC cathode fabricated by the particle-solution spraying process.

The activation energies calculated from the slope of the curves shown in Figure 4b are 1.08 eV (104.4 kJ/mol) for cathodes made by screen printing,[9] 0.90 eV (90.1 kJ/mol) for combustion CVD-derived cathodes,[18] and 0.65 eV (62.5 kJ/mol) for electrodes fabricated using the particle-solution spraying. From the microstructural point of view, the particle-solution spraying process offers the advantages of both conventional ceramic techniques and combustion CVD. Each GDC particle was surrounded by numerous tiny, nanosized SSC particles. Electrochemical kinetics was thus dramatically enhanced.

The particle-solution spraying process combines the merits of combustion and flame spraying. SSC precursors serve as bonding agent for GDC solid particles as well as active composite component. The unique structure created by this process contributes to the superior cell performance. Based on the fundamental principle of the process and the observation of microstructures, the proposed growth mechanism of the nanocomposite cathode is schematically illustrated in Figure 6.

The chemical reaction can be retrieved to the combustion flame. As shown in Figure 6a, microscale liquid droplets containing Sm, Sr, and Co nitrates is sprayed out of orifice of the atomizer together with solid GDC

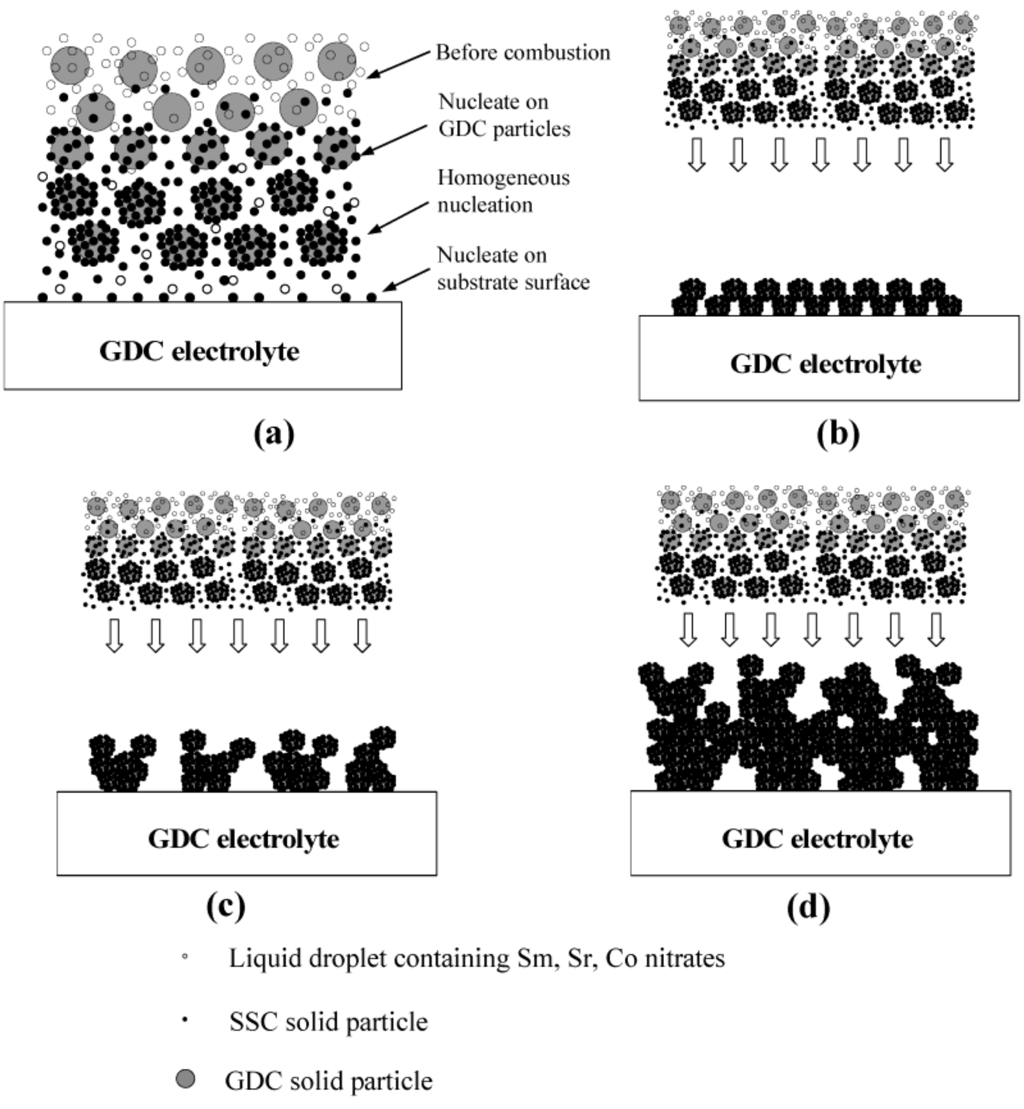

Figure 6. Schematic illustrations of the formation processes of the porous SSC−GDC composite cathodes: (a) three nucleation sites of SSC nanoparticles; (b), (c), and (d) different growth stages of composite grains.

particles. Because these precursor species exist in the gaseous phase throughout the entire combustion flame, nucleation and growth of SSC particles could occur at three locations: on the surface of the GDC substrate, within the combustion flame due to the high precursor concentration, or on the surface of the readily available GDC particles inside the flame. Particle growth, collision, and agglomeration are also expected within the flame during deposition.

At the second stage of growth as shown in Figure 6b, the agglomerates consisting of GDC particles and SSC nanophase are deposited on the surface of GDC electrolyte substrate. The newly nucleated SSC phase on the substrate and the traveling SSC nanoparticles within the flame facilitate formation of good bonding between the large agglomerates and the substrate.

Both sintering and the arrival of new material contribute to the coarsening of the porous film grains as illustrated in Figure 6c,d. This process continues until the deposition is terminated. The final microstructure has fractal features: each large agglomerate consists of smaller ones, which in turn contains even smaller particles. The resulting porous structures have large pores for rapid gas transport and extremely large surface area for fast electrochemical reactions; the porous structures are ideally suited for electrodes in solid-state electrochemical systems.

Conclusions

A particle-solution spraying process has been developed for fabrication of nanostructured, highly porous electrodes for solid oxide fuel cells. GDC particles suspended in an SSC−ethanol solution were burned in a combustion flame, depositing a porous cathode on an anode-supported GDC electrolyte. Extremely small interfacial polarization resistances were obtained, especially at low temperatures such as 450 °C (1.06 Ωcm^2) and 500 °C (0.45 Ωcm^2). A peak power density of 385 mW/cm^2 was achieved at 600 °C.

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