Influence of cathode on electric power of solid oxide fuel cells

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The electric power produced by a Ni/Gd-doped ceria (GDC) anode-supported solid oxide fuel cell with a GDC electrolyte (40 µm thick) and a (La0.8Sr0.2)(Co0.8Fe0.2)O3 (LSCF) cathode using a 3 vol % H2O-containing H2 fuel was measured. The addition of 10 or 50 mass % GDC powder (Ce0.8Gd0.2O1.9) to the LSCF cathode reduced the power density from 320 mW/cm² in the case of no GDC to 137 or 122 mW/cm², respectively. The added GDC particles blocked the conduction path between LSCF particles. The as-prepared LSCF powder was ball-milled using α-Al2O3 balls. The milling decreased the charge transfer resistance at the cathode and increased the power density of the fuel cell.

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Solid oxide fuel cells (SOFCs) are attractive electric power generators because of their high energy conversion efficiency, their ability to utilize a variety of fuels, the possibility of utilizing their high-temperature exhaust gas, and their leakage-proof property because of the use of solid electrolytes. A conventional SOFC with a yttria-stabilized zirconia (YSZ) electrolyte is typically operated at approximately 800°C to enhance the diffusion of oxide ions formed at its cathode. Gd-doped ceria (GDC) and Sm-doped ceria are also candidate electrolytes for SOFCs because they exhibit greater oxide-ion conductivity than YSZ. Decreasing the charge transfer resistance of electrochemical reactions at the electrodes (especially the cathode) is another strategy to increase the electric power generated by SOFCs. At the cathode, the diffusing oxygen molecules adsorb onto the cathode material and dissociate into oxygen atoms. The oxygen atoms react with electrons to form oxide ions at the triple-phase boundary (TPB, the gas–cathode–electrolyte interface). The cathode material is a mixed conductor of electrons and oxide ions.

La2NiO4 and Pr2NiO4, which possess the K2NiF4 structure, have been studied as cathode materials because of their high oxide ion conductivities.1) (Ba0.5Sr0.5)(Co0.8Fe0.2)O3 (BSCF) is also a candidate cathode material for an intermediate-temperature SOFC.2) Other perovskite materials such as (La 1-xSr)xCoO3 (LSM), (La1−xSr)xMnO3 (LSM), and (La1−xSr)xCrO3 (LSC) have been extensively used as cathode materials because of their high electron and oxide-ion conductivities.

A cathode composed of a mixture of GDC and LSCF is expected to exhibit enhanced electrocatalytic activity for the reaction of O2 and electrons. Shah et al.3) measured the performance of a cathode fabricated by impregnating a porous GDC scaffold with a mixed nitrate solution of LSCF precursor. The formed nanometer-scale (50 nm) LSCF network reduced the charge transfer resistance at an operating temperature of 650°C over 300 h. Liu et al.4) prepared an LSCF–GDC composite cathode by impregnating the porous GDC scaffold with a mixed nitrate solution of La, Sr, Co, and Fe and measured the degradation in the composite cathode performance at 750°C in air over 500 h. The GDC scaffold method was effective in expanding the triple-phase boundary (GDC electrolyte–LSCF cathode–O2 gas). However, the charge transfer resistance and ohmic resistance increased because of grain growth of the LSCF nanoparticles. The authors suppressed the grain growth of LSCF by adding MgO and LaNi0.6Fe0.4O3 particles.

In this study, a GDC–LSCF mixed cathode powder was prepared using a dry process and was spread onto a GDC electrolyte to examine the electric power generated by a SOFC fabricated with this electrolyte material. The effect of particle size of the LSCF powder on the electric power of the SOFC was also investigated to increase the length of TPB.

A GDC electrolyte powder with a composition of Ce0.8Gd0.2–O1.9 was prepared by heating a (Ce0.8Gd0.2)(C2O4)3 oxalate solid solution at 600°C for 4 h in air.5) The oxalate solid solution was formed by dripping a 0.2 M Ce–Gd mixed nitrate solution (Ce:Gd = 4:1 molar ratio) into a 0.4 M oxalic acid solution. The obtained GDC powder was milled with α-Al2O3 balls with a diameter of 3 mm for 24 h. The GDC powder was mixed with a 33 vol % toluene–67 vol % isopropanol solution at a concentration of 15 vol % solid. Poly(ethylene glycol) (9 mass %) and polyvinyl butyral (5 mass %) were added as a binder and plasticizer, respectively, into the GDC suspension to prepare a GDC film by the doctor-blade method (DP-100, Tsugawa Seiki Seisakusho, Tokyo).6) A NiO–GDC anode with a Ni/GDC volume ratio of 40/60 was prepared by immersing the milled GDC powder into a 1.4 M Ni(NO3)2 solution. The suspension was freeze-dried and calcined at 600°C for 1 h in air. A (La0.8Sr0.2)(Co0.8Fe0.2)O3 cathode powder was prepared by heating the freeze-dried coprecipitate of La(NO3)3, Sr(NO3)2, Co(NO3)2, and Fe(NO3)3 with (NH4)2CO3 at 900°C for 2 h in air.7,8) The calcined LSCF powder was mixed with the milled GDC powder at a GDC/LSCF weight ratio of 10/90 or 50/50 using a mortar and pestle in a dry process. The GDC electrolyte film was placed on a NiO–GDC powder bed (22 mm diameter, 2 mm thickness) and compressed uniaxially at 50 MPa, followed by isostatic pressing at 294 MPa. The compacts were sintered at 1450°C for 4 h in air. The thickness of the resulting GDC electrolyte film was 40 µm. The
LSFC–GDC mixed powder suspension with 15 vol % solid in a mixed solution of 90 vol % ethanol and 10 vol % ethylene glycol was spread over the GDC electrolyte film on a NiO–GDC anode by screen printing (70 µm mesh, 4 mm diameter) and was subsequently heated at 900°C for 1 h in air. The thickness of the attached cathode layer was 100 µm.

Pt wires were attached to the electrodes of the GDC cell using Pt paste. The GDC electrolyte film containing the cathode and anode was placed on an alumina holder and sealed with a glass O-ring at 870°C. NiO at the anode was reduced to Ni using H2 fuel containing 3 vol % H2O at 800°C. The cell performance was measured at 600–800°C while H2 fuel containing 3 vol % H2O was fed at a flow rate of 100 mL/min into the anode and air was fed at a flow rate of 200 mL/min into the cathode. The direct current–terminal voltage relationship and AC impedance over a frequency range 0.01 Hz–100 kHz were measured at a current density of 80 mA/cm² (As-510, NF Kairosekkei Block Co., Japan).9)

Figure 1 shows the influence of the GDC content in the LSCF cathode on (a) the terminal voltage and (b) the power density on the LSCF cathode cell used in our previous experiments.10) Addition of GDC remarkably reduced the terminal voltage and power density at 800°C and the equivalent circuit for the 0 mass % GDC cathode is shown in Fig. 2. The measured capacitances of 55.1 and 941 µF were larger by factors of 100 and 10, respectively, than that of 0.53 µF calculated for the grain boundary of the dense GDC films with a thickness of 40 µm at 400°C. The calculation is based on a single grain-boundary thickness of 3 nm and a relative dielectric constant of 1.72.14) These results suggest that the arc in the low-frequency range represents the charge transfer characteristics at the electrodes. The ohmic resistance increased from 1.95 Ω in the case of no added GDC to 3.30 Ω in the cases of electrodes with 10 and 50 mass % GDC. The charge transfer resistance also increased from 1.16 Ω in the case of no added GDC to 5.3 Ω in the cases of electrodes with 10 and 50 mass % GDC. These results suggest that the mixing of GDC particles with LSCF particles does not promote the electrochemical reaction at the cathode and increases the resistance of the cathode.

In a previous investigation, the electrical conductivity of a two-component powder compact (alumina–indium tin oxide solid-solution system) formed by colloidal processing was measured to examine the particle connections.13) The formed microstructure was analyzed using the collision theory of particles in a suspension proposed by Smoluchowski.19) We used this theory also in this study to analyze the particle connection of the LSCF–GDC composite cathodes prepared using a dry process. Smoluchowski proposed Eq. (1) for the number of collisions per unit time for any particles dominated by diffusion in a solution:15)
where \( C_i \), \( D_i \), and \( r_i \) are the particle number concentration, diffusion coefficient, and radius, respectively, of particle \( i \). The diffusion coefficient is inversely proportional to the radius of the particle, as indicated by Stokes’ law (\( D = kT/6\pi\eta r_i \), where \( k \) is the Boltzmann constant and \( \eta \) is the viscosity). Collision frequency has a minimum at \( r_i = r_j \) and increases with increasing difference between the particle sizes. The fractional collision frequency between particles \( i \) and \( j \), \( \text{FCF}_{ij} \), is defined as \( b_{ij} / (b_{ii} + 2b_{ij} + b_{jj}) \). Figure 3 shows the fractional collision frequency for the 217 nm LSCF–23 nm GDC system. The particles sizes were calculated from the Brunauer–Emmett–Teller (BET) surface areas of the LSCF and GDC powders. The collision frequency of LSCF–LSCF particles decreased from unity at 0 mass % GDC to 0.115 at 10 mass % GDC; i.e., the conduction paths between LSCF particles was blocked by GDC particles, resulting in the increased resistance. Shah et al.3) also reported that the charge transfer resistance in GDC–LSCF cathodes gradually decreases as the amount of LSCF infiltrated into the GDC scaffold increases (from 0.76 to 12.5 vol %). The conductivity of the composite cathode is more sensitive to the infiltration process than to the dry process. The calculated result in Fig. 3 suggests that the addition of 1 mass % GDC to a LSCF cathode may promote the charge transfer process because of the increased contact between GDC and LSCF particles. As evident in Fig. 2, the charge transfer resistance decreased as the GDC content in the cathode decreased (50 mass % GDC → 10 mass % GDC). However, the ohmic resistances of the cells with 10 mass % GDC and 50 mass % GDC cathodes were similar, indicating that the ohmic resistance was controlled by the contact between GDC particles. An even smaller charge transfer resistance was measured for the 0 mass % GDC cathode, as shown in Fig. 2. This result suggests that LSCF–LSCF contact decreases the charge transfer resistance as well as the ohmic resistance at the cathode. Therefore, the addition of GDC particles larger than the LSCF particles in the cathode, which reduces the contact number of GDC–GDC particles, may decrease the ohmic resistance between GDC–GDC contacts and enhance the charge transfer process between GDC and LSCF particles.

Table 1 summarizes the specific surface area and equivalent diameter of LSCF particles before and after they were milled with \( \alpha \)-Al2O3 balls (3 mm diameter) for 24 h. The specific surface area was increased by ball-milling, and the equivalent diameter decreased from 217 to 141 nm after 24 h. Figure 4 shows the influence of ball-milling of the LSCF powder on the terminal voltage and power density of GDC cells at 600–800°C.
800°C was 135, 324, and 540 mW/cm², respectively, for the milled LSCF cathode. Figure 5 shows the complex impedance plots of GDC cells at a current density of 80 mA/cm², where the GDC cells were fabricated with as-prepared and ball-milled LSCF. The ohmic resistance of cells with ball-milled LSCF slightly decreased from 1.95 to 1.65 Ω. However, the charge transfer resistance decreased from 1.16 Ω for the cell with as-prepared LSCF to 0.14 Ω for the cell with ball-milled LSCF. This result indicates that a decrease in the LSCF particle size increases the length of TPB, where oxygen molecules react with supplied electrons to form oxide ions.

References