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Effect of graphite content on cell performance and microstructure in solid oxide fuel cells

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The presence of graphite materials in the anode composites of high-temperature solid oxide fuel cells exerts a significant effect on the microstructure of the electrodes and electrochemical performance of the cells. Herein, the amount of graphite in the anode materials was intentionally varied during the electrode processing steps. The effect of graphite content on cell performance was evaluated in terms of the resultant microstructure, mechanical strength, and electrochemical performance. A higher quantity of graphite in the anode composite leads to higher porosity, and consequently, to the opposing effects of enhanced electrochemical performance during the initial stages and faster degradation of the current-voltage characteristics. However, among the evaluated graphite-controlled anodes, the one with the lowest graphite content exhibited the slowest degradation rate and a fairly poor electrochemical performance. The balance between the microstructure and the corresponding electrochemical performance is discussed in terms of the optimization of high-performance solid oxide fuel cells.

Key words: Solid oxide fuel cells, Anode-supported cells, Graphite, Microstructure, Electrical properties, Mechanical properties.

Introduction

Solid oxide fuel cells (SOFCs) continue to garner academic and industrial attention as efficient powergenerating systems for operation between 800 and 1000 °C, owing to the resistance of their superior ceramic components to high-temperature loading conditions [1, 2]. In particular, SOFCs exhibit 50-60% higher efficiency than the other competing fuel cells. If the thermal management is taken into account in calculating the ultimate efficiency, SOFCs can be exploited for hydrogen production using the electrochemical reaction of water by application of the electrical potential in the reverse manner [3, 4]. This production concept can be regarded as a direct reverse solid oxide fuel cell system [5-7].

The high-temperature hydrogen production can be applied to a hydrogen reservation system. In terms of power generation, stored hydrogen gas can be consumed by the SOFCs for electrical power generation and vice versa. Depending on the type of materials used in the supporting system in SOFCs, the SOFCs can be categorized as anode-, electrolyte-, or metal-supported SOFCs. Anode-supported SOFCs, in particular, can be constructed onto the anode materials in the form of very thin electrolyte layers with a thickness of 5 to 30 μ m. Compared to the electrolyte-supported SOFCs, anode-supported SOFCs can be operated at temperatures of 700 to 800 °C, i.e., 200 to 300 °C lower than the operating

temperature of the electrolyte-supported SOFCs [8].

In general, the anode materials are fabricated in cermets comprising nickel metal and yttria-stabilized zirconia (YSZ). YSZ acts to suppress the grain growth of nickel materials within the operation temperature and provides a high fraction of triple phase boundaries (TPBs) along with an inherent oxygen-ion conduction path in the anode materials [9, 10]. The TPBs of SOFCs are comprised of a gas phase consisting of oxygen ions and electrons, which is significantly important to the electrodic reactions at both the cathode and anode. The TPBs are inherently dependent on the constituent materials and microstructure of the corresponding electrodes. Therefore, the ultimate cell performance of SOFCs is closely related to the optimization of the microstructure, which includes the composition and distribution of the constituent component materials. In terms of the microstructure, the anodes can be regarded as essential in establishing the electrochemical reactions at TPBs, leading to the effective input of reactant gases and steam, and facilitating the emission of un-reacted water due to enhanced porosity [9, 11]. In general, the porosity can be controlled by judicious selection of pore-forming agents such as graphite or polymer materials, and as is intuitively expected, the higher the content of pore-forming agents, the higher the porosity [9]. However, excessive porosity is linked to the mechanical vulnerability encountered after reaching a certain level of electrical performance, in connection with low mechanical strength in cermet electrodes. The balance between long-term operation performance and mechanical durability must be considered in the

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construction of SOFC stacks.

The current study focuses on the effect of poreforming materials in the anode-supported SOFCs on the anode microstructure, mechanical strength, and electrochemical strength. In particular, the electrochemical performance was monitored herein in terms of the temporal evolution of the microstructure and porosity during cell operation. The practical issues concerning anode materials are discussed with regard to the optimized SOFCs, taking into account the currentvoltage characteristics and the time-dependent degradation rate of the output power.

Experimental Procedures

The present SOFCs were constructed using YSZbased electrolytes with the cathode composites consisting of lanthanum strontium cobaltite ferrite/Smdoped ceria (LSCF/SDC) and anodes comprised of Ni-YSZ cermet. NiO powder (Alfa, 99.9%) was ball-milled for 2 h, followed by drying in an electric oven. The dried NiO powder was mixed with 8 mol% YSZ (Tosoh, TZ-8YSZ) in a 1:1 ratio, and the mixture was subjected to wet ball milling for 24 h. In order to enhance the pressing performance, an organic binder was added to the anode mixture at a concentration of 0.5% PVB (polyvinyl butyral). The ultimate open porosity was controlled by using graphite as a pore-controlling material, where 44 µm graphite materials were added to the main NiO/YSZ mixtures in concentrations of 24, 18, and 12 vol%. After milling, the mixed slurries were dried and crushed into fine powders using a mortar and pestle. The processed powders were then separated using 100-mesh sieves. The prepared powder mixture was pressed into disc-shaped specimens with a thickness of 2 mm and a diameter of 36 mm, and the pressed discs were sintered for 1 hr at 1400 °C.

The fabricated cell was inserted into the measuring apparatus shown in Fig. 1. After installation, the



Fig. 1. Experimental setup employed for testing the electrochemical performance.

measuring system was heated to 750 °C where the cathode side was sparged with gaseous dry air at a flow rate of 50 cc/min, and nitrogen gas was injected to the anode compartment at a flow rate of 100 cc/min. After reaching the operation temperature of 750 °C, hydrogen gas was sparged onto the anode for 30 min at an initial rate of 50 cc/min, after which the hydrogen flow was increased to 100 cc/min, and the air flow was increased to 250 cc/min. The system was stabilized for 1.5 hr. Finally, an electrical loader was employed to transfer the current onto the SOFC unit cell and platinum wires were used for the current-voltage measurements.

In order to measure the mechanical strength of the anode components, the test specimens were intentionally designed so that reliable mechanical information could be acquired. The fabrication procedures were identical to those employed in fabricating the above-mentioned electrochemical cells, except for the size. The cell dimensions were set to $105 \text{ mm} \times 105 \text{ mm} \times 3.3 \text{ mm}$. After sintering the initial pressed specimens, the sintered specimens were machined to $4 \text{ mm} \times 3 \text{ mm} \times$ 33 mm. In order to minimize scattering (uncertainty) in the strength measurements, both surfaces were polished using ultrafine abrasive papers (# 4000); the surfaces were made sufficiently smooth to eliminate the undesired cracks in the anodes. The specimens were further subjected to a reduction process by treatment with hydrogen at a flow rate of 400 sccm, at 750 °C, for 24 hrs. A four-point bending test was performed using an Instron 5583 strength measurement unit where the span was 22 mm in the lower part and 11 mm in the upper region. The strength was measured at a rate of 0.2 mm/min using a crosshead load of 1 kN. In order to obtain the statistical significance in the measurements, strength measurements were repeated seven times before reduction and more than 30 times after reduction.

Results and Discussion

The electron micrograph presented in Fig. 2 shows the variation in the microstructure of specimens with various graphite contents, subsequent to fracture. A higher graphite content (denoted by AP #75) leads to larger grain sizes in the Ni and YSZ materials with consequently high porosity. In the case of lower graphite content, the average grain size decreases and smaller pores with uniform size distribution are observed, as illustrated for 18% graphite (AP #77) and 12% graphite (AP #80). The analyzed porosities of the anodes containing 24, 18, and 12 vol% graphite were 28.4, 22.2, and 14.7%, respectively, based on the Archimedes density measurement. In other words, the porosity decreases consistently with decreasing graphite content, with a proportional increase in the mechanical strength. Electron micrographs acquired after polishing the anode composites show direct evidence of the role of graphite as a pore-forming agent in the SOFC



Fig. 2. Electron micrographs obtained from fractured surfaces of three different anode mixtures: (a) 24 vol%, (b) 18 vol%, and (c) 12 vol%.



Fig. 3. Electron micrographs obtained from polished surfaces of three different anode mixtures: (a) 24 vol%, (b) 18 vol%, and (c) 12 vol% for the initial stages (approximately 0 hr).



Fig. 4. Electron micrographs obtained from polished surfaces of three different anode mixtures: (a) 24 vol%, (b) 18 vol%, and (c) 12 vol% after durability tests performed for approximately 300 hrs.

Table 1. Summary of mechanical strength of the anode composites as a function of graphite content before and after reduction.

Graphite content [vol%]		24	18	12
Porosity (%)		28.4	22.2	14.7
Flexural strength [MPa]	Before reduction	50.9 ± 3.4	95.6 ± 2.4	159.8 ± 5.5
	After reduction	22.8 ± 2.5	60.6 ± 3.0	71.7 ± 5.1

anodes. As shown in Fig. 3, the higher the graphite content, the higher the porosity and the higher the probable grain growth. The microstructural analysis reveals that a high graphite content appears to affect the anode microstructure in an unfavorable manner, i.e., promotes significant grain growth and subsequent disconnection of the three-dimensional networks. As expected from the apparent porosity results, a high graphite content induced a high fraction of large grains along with poor interconnection of the solid phases (see Fig. 4), whereas lower graphite contents led to smaller grains and a more homogeneous microstructure.

Table 1 summarizes the mechanical strength of the anode composites and porosity with special emphasis on

Table 2. Summary of SOFC cell performance as a function of graphite content and operation time.

Contents of graphite [vol%]		24	18	12
$\mathbf{P} = [\mathbf{W}/am^2]$	0 h	1.06	1.04	0.99
	~ 300 h	0.86	0.92	0.89

the graphite contents. As expected from the change in porosity, the mechanical strength decreased significantly after reduction of NiO to Ni. Before reduction, the NiO phases were uniformly mixed in the three-dimensional network, without significant change in the porosity and pore sizes as a function of graphite content. After reduction, however, the NiO was changed into Ni phases, producing a large change in volume, in connection with the formation of large pores. This high fraction of pores leads to a decrease in the mechanical strength of the Ni/YSZ composites. Furthermore, the increase in porosity and pore sizes can result in the disadvantage of degradation of the reliability of the SOFC cells as shown later. Generally, lower porosity is associated with higher mechanical strength. However, the increase in flexural strength with the change in the graphite content from 24% to 18% is much larger than that obtained due to the change from 18% to 12% graphite content. A decrease in the graphite content from 24% to 18% is accompanied by an increase in strength from 22.8 MPa to 60.6 MPa, i.e., by a factor of 2.65. However, the change from 18 to 12% graphite is only accompanied by an increase in strength from 60.6 MPa to 71.7 MPa, although the highest strength was obtained at 12% graphite content. The higher graphite content of 24% can lead to instability in the robust operation of the SOFC due to inferior strength of the reduced anodes.

As summarized in Table 2, at the initial stage of 0 hr, the electrochemical cell performance, particularly the maximum power density, varied in a consistent manner based on the graphite content. Fig. 5 demonstrates the current-voltage characteristics of three different graphite systems. The maximum power density decreased from 1.06, to 1.04 and further to 0.99 W/cm² as the graphite content decreased from 24 to 12%, passing through the intermediate composition of 18% graphite content. In particular, the decrease in maximum power density upon changing the graphite content from 18 to 12% was much larger than that derived from the change from 24% to 18%.

Moreover, in the long-term durability test, the highest graphite content was associated with the greatest change in the electrochemical performance, e.g., 1.06 W/cm^2 at 0 hr to 0.86 W/cm² at 300 hrs with an approximately 18.8% decrease in the maximum power. In the case of 18% graphite content, the maximum power decreased from 1.04 at 0 hr to 0.92 W/cm² at 300 hrs. At the lowest graphite content of 12%, the power decreased from 0.96 to 0.89 W/cm² at the stated times,



Fig. 5. Current-voltage output characteristics of anode-supported SOFC cells with graphite additives of: (a) 24 vol%, (b) 18 vol%, and (c) 12 vol% at 750 °C.



Fig. 6. Time-dependent current-voltage plots of anode-supported SOFC cells with graphite additives of: (a) 24 vol%, (b) 18 vol%, and (c) 12 vol% at 750 °C.

demonstrating that the degradation rate was the slowest for this sample compared to those measured for specimens with 24 and 18% graphite content in the anode Ni/YSZ systems.

From the three long-term performance tests (24, 18, and 12 vol% graphite contents) obtained at the current load of 0.3 A/cm², the 300 h cell voltages were determined to be 0.927 V (at 326.3 h), 0.921 V (at 302.8 h), and 0.915 V (at 328.2 h), respectively, (see Figs. 5 and 6). After extrapolation to 1000 h, the estimated voltage decreases were calculated to be 0.061 V, 0.043 V, and 0.029 V, respectively. The calculated degradation rates (ΔV %/1000 h) are known to be 6.44%/1000 hrs, 4.65%/1000 hrs, and 3.17%/1000 hrs, respectively. The slowest reduction rate was associated with the rather highly tortuous networks of the 12% graphite anode system: the anode with the lowest graphite content exhibits the most stable operation in the solid oxide fuel cells, although the current voltage is inferior to those of the anodes with higher graphite content. A higher graphite content leads to higher porosity along with a faster degradation rate as observed in the long-term durability test, even though the initial current-voltage characteristic is excellent. In contrast, the lowest graphite content was associated with rather poor current-voltage features compared to that obtained at 24% graphite content. Nevertheless, the degradation rate is slowest at the lowest graphite content, thus the cell operation is deemed to be more stable at low graphite content than that achieved at higher graphite contents. The high porosity derived from the higher graphite content is beneficial to the material transport, leading to the lowest polarization loss for these specimens. However, the open porosity is detrimental in terms of the significant grain growth in the metallic nickel grains. The significant grain growth of nickel phases seems to be associated with interparticular densification and large grain growth, ultimately producing the higher tortuosity in the constituent phases (or equivalently, poor interconnection). In contrast, it is concluded that the lower porosity retards the grain growth in electrode materials: significant grain growth breaks down the well-interconnected phases in the nickel and YSZ phases, leading to higher polarization loss in close connection with poor material transport after long-term operation.

This postulate can be confirmed through impedance characterization of the anode composites. In the impedance spectra shown in Fig. 7, the real intercepts on the x-axis reflect the ohmic resistance of the SOFC unit cells, denoted by R_0 . The electrode polarizations are found in the low-frequency regimes after passing the real axis in the complex impedance coordinates, described by the sum of two electrode contributions, i.e., (R_1+R_2) . The respective resistive components were measured as shown in Table 3. The data presented in Fig. 7 and Table 3 indicates that the internal resistance,



Fig. 7. Time-dependent impedance spectra of anode-supported SOFC cells with graphite additives of: (a) 24 vol%, (b) 18 vol%, and (c) 12 vol% at $750 \text{ }^{\circ}\text{C}$.

Table 3. Analyzed bulk and electrode resistances obtained from three different graphite anodes, 24, 18, and 12 vol%.

Contents of graphite [vol%]		24	18	12
Ro/	0 h	0.237 / 0.476	0.222 / 0.925	0.218 / 1.196
	16 h	0.250 / 0.426	0.233 / 0.780	0.231 / 0.814
$[\Omega cm^2]$	$\sim 100 \text{ h}$	0.269 / 0.437	0.248 / 0.770	0.247 / 0.983
	$\sim 300 \text{ h}$	0.290 / 0.532	0.265 / 0.719	0.266 / 0.861

R₀, increases continuously, unlike those due to the electrode polarizations. The anode having the highest graphite content exhibited a high internal resistance of 0.237 cm², and a relatively low polarization of 0.476 cm². The anodes containing 18 and 12% graphite had polarization resistances of 0.925 cm^2 and 1.196 cm^2 , respectively. Interestingly, the subsequent time-dependent polarizations are found to be dissimilar depending on the graphite content. At the highest graphite content of 24%, there was an increase in the polarization after 300 h; however, the lower graphite systems exhibited a reduction in polarization, in contrast with the 24% graphite anodes. Similar trends were observed for the internal resistances, i.e., the internal resistances, R_0 , increased slowly with time. In the case of 24% graphite content, the internal resistance increased with time

from 0.237 to 0.290 cm²; for 18% graphite content, there was an increase from 0.222 to 0.265 cm², and for 12% graphite, from 0.218 to 0.266 cm². The long-term polarization was highly sensitive to the graphite content, i.e., a higher graphite content is detrimental to the electrochemical performance, giving rise to rapid degradation. However, the bulk contribution is not sensitive to the amount of graphite, even though a low graphite content is desirable for minimizing the internal resistance.

In summary, a higher content of graphite in the evaluated anode composites promoted superior cell performance indicated by less polarization during the initial stages of cell operation. However, the time-dependent cell responses demonstrated a dramatic degradation in the electrochemical performance of anodes with a high graphite content compared to the performance of anodes composed of lower-graphite composites. Such phenomena are attributed to the inferior connectivity of nickel phases in relation to the increase in the internal resistance and the resultant decrease in the SOFC cell performance at high graphite content. Taking into account the mechanical brittleness of the 24% graphite content composite, the 18% graphite anode system seems to be optimal in terms of the balance between degradation rate and mechanical strength.

Conclusions

The effect of porosity on the microstructure, strength, and the electrochemical performance of graphitecontaining anode composites was evaluated herein as a function of the graphite content. The change in the graphite content was associated with a consistent change in the microstructure and mechanical strength of the various composites. The relative amount of graphite (or equivalently, pore-forming agent) was inversely proportional to the mechanical strength: less graphite lead to high mechanical strength in conjunction with the lower porosity. Evaluation of the electrochemical cell performance revealed that the maximum power densities decreased with graphite content during the initial stages of cell operation. In the case of high graphite content (24 vol%), the electrochemical polarization was reasonably good, and the internal resistance increased relatively rapidly with time, indicating that the degradation rate was high. Among the anodes with low graphite contents, the 18 vol% graphite materials appear to be optimal based on the maximum power density of 0.92 W/cm^2 achieved after 300 hrs operation in conjunction with the degradation rate of 4.65%/1000 hrs, which is the slowest degradation rate of the anodes evaluated, even though the initial output was relatively inferior to those of materials with higher graphite content.

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