CHARACTERISTICS OF DAMAGE AND FRACTURE PROCESS OF SOLID OXIDE FUEL CELLS UNDER SIMULATED OPERATING CONDITIONS BY USING AE METHOD

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Abstract

The purpose of present research is to estimate the damage of solid oxide fuel cell (SOFC) by using a new factor of acoustic emission (AE) during loading test. Acoustic emission signals and fracture processes were monitored by AE measurement system in real time during the test. In the investigation of fracture process with AE amplitude distributions, high-amplitude, middle-amplitude and low-amplitude signals correspond to vertical cracking, delamination in the cathode, and vertical cracking in the electrolyte, respectively. It was demonstrated that the AE method enabled us to detect these fracture processes and to determine the condition for the onset of the damage in a single cell.

Keywords: Solid oxide fuel cells (SOFCs), Ceria-based single cell, Simulated operating condition, Fracture process

Introduction

Solid oxide fuel cells (SOFCs) have been regarded as a highly efficient power generation system (70\%) for future applications. Since SOFCs convert the chemical energy of the fuel directly to electrical energy without the intermediation of thermal energy, conversion efficiency is not subject to the Carnot limitation. Because of their high temperature of operation (600 ~ 1000°C), natural gas fuel can be re-formed within the cell stack, which eliminates the need for an expensive, external re-former system [1, 2]. Thus, SOFCs are expected to become a major electric power source in the future. In SOFCs, large oxygen potential gradients exist across the two ends of the electrolyte, with the fuel side exposed to highly reducing conditions and the air side to ambient conditions. Under air conditions, electronic charge compensation occurs in ceria-based electrolyte by the formation of \(\text{Ce}^{4+}\). However, when sufficiently reducing conditions prevail, oxygen vacancies form and the \(\text{Ce}^{4+}\) reduces to \(\text{Ce}^{3+}\) in order to maintain electrical neutrality via ionic compensation. The net result is a lattice expansion due to the change in the ionic radii of \(\text{Ce}\) [3, 4]. Thus, when exposed to a reducing environment, the ceria-based electrolyte exhibits lattice expansion, also called chemical expansion, and is therefore subject to differential strain across its thickness that could cause fracture (Fig. 1) [3–6]. In general, electrochemical techniques have been used extensively to determine the electrical performance and electrochemical reliability of SOFCs. In addition to the electrical reliability, it is also important to ensure the mechanical reliability of SOFCs under operating conditions. Thus, the establishment of a suitable
mechanical testing method under the operating conditions is a prerequisite for the development of reliable SOFCs.

This paper presents the experimental results of the investigation of damage on the ceria-based single cells under testing conditions. In this study, a simulated environment testing method combined with acoustic emission (AE) monitoring was developed in order to investigate the fracture processes of SOFCs. It was demonstrated that the AE monitoring conducted in this study was useful to detect and analyze the fracture processes in a single cell.

![Fig. 1 Schematic diagram showing the electrolyte (fully relaxed case) [3].](image)

**Experimental Procedures**

Sintered 20%-samarium-doped ceria, (CeO\(_2\)\(_{0.8}\)(SmO\(_{1.5}\))\(_{0.2}\), or 20SDC, disks were used as the electrolyte. The diameter and thickness of the 20SDC electrolyte were 16 mm and 1 mm, respectively. Cermet of NiO-(CeO\(_2\)\(_{0.8}\)(SmO\(_{1.5}\))\(_{0.2}\) (weight ratio of 60:40) and La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.2}\)-Fe\(_{0.8}\)O\(_3\) were used as the anode and cathode, respectively. The anode and cathode (10 mm diameter) were applied symmetrically on opposite sides of the (CeO\(_2\)\(_{0.8}\)(SmO\(_{1.5}\))\(_{0.2}\) electrolyte by a screen-printing method. The thicknesses of the anode and cathode were 30 µm, and 15 µm, respectively. Figure 2 shows a schematic of the test section of the apparatus used for evaluating the mechanical performance of a single cell under simulated operating conditions. The maximum temperature achievable with the apparatus is 1000°C. The single cell was placed between two concentric Al\(_2\)O\(_3\) tubes. The internal diameters of the outer and inner tubes were 12 mm and 8 mm, respectively. H\(_2\) and O\(_2\) gases were supplied onto the anode and cathode surfaces of the cell through the inner tubes at a flow rate of 100 ml/min and were discharged through the annulus between the tubes. The sealing between the outer Al\(_2\)O\(_3\) tubes and the cell was achieved by melting a soda-glass ring. The thickness of the soda-glass ring was 0.5 mm.

Prior to actual tests, the test section was initially heated to 800°C at a heating rate of 100°C/h and held at this temperature for 1 h in an atmospheric air environment in order to melt the soda-glass ring and form the glass seal. After melting the soda glass, it was then cooled to 550°C at 100°C/h and held at this temperature for 1 h.

Preliminary tests showed that the glass seal failed when the temperature was decreased below 450°C. Thus, the starting temperature was set as 550°C in this study. The temperature range for testing can be adjusted by selecting different types of glass. At this stage, H\(_2\) and O\(_2\) gases were introduced to the test section while the temperature was kept at 550°C. The temperature was then increased monotonically to 800°C and cooled to room temperature at 100°C/h in order to examine the fracture process under a heating cycle. To examine the effect of holding time, the temperature was held at 600°C, 700°C, and 800°C for 1 h during heating. Tests with different specimens were repeated three times to check the reproducibility.

In addition to the simulated operating environment tests, simple uniform heating tests under oxygen environment alone were conducted to examine the effect of the thermal stress on the
fracture processes of a single cell. For this purpose, only O₂ gas was supplied onto both the anode and cathode surfaces of the cell and the same heating experiment was undertaken using the same apparatus shown in Fig. 2. The temperature was raised up to 1000°C for the simple uniform heating tests. Three specimens were used for this series of experiments.

Acoustic emission (AE) signals were detected using a resonant piezoelectric transducer (PAC R15), concurrently with the simulated environment tests and simple uniform heating tests. The AE transducer was attached to the outer Al₂O₃ tube at room temperature away from the heated section. After the electronic signals from the transducer were preamplified (40 dB) and bandpass filtered between 20 kHz and 2 MHz, they were further amplified with a variable broadband amplifier that provided an additional gain of 45 dB. After measurement, in order to observe the fracture behavior of ceria-based single cells, cross sections were observed by scanning electron microscopy (SEM).

Results and Discussion

In the simple uniform heating tests, where both the cathode and anode were subjected to the oxygen environment, no AE signal was detected up to 1000°C. Furthermore, no damage was found by post-test observations using an SEM. The experimental results indicate that the thermal stresses due to the thermal expansion mismatch were insufficient to cause any damage in the single cell.

Next, the results obtained from the simulated environment tests are discussed. Three specimens used in this study produced almost identical results. The energy of the AE signal, E_{AE}, is plotted with the heating temperature in Fig. 3. This result was obtained from one of the three tests. The E_{AE} was determined by mean square amplitude of AE signals. The onset of AE activity occurred when the temperature reached 620°C. The AE activity increased with the increasing
temperature, and eventually ceased at 760°C with no AE activity in the temperature range between 760°C and 800°C. This may indicate that a complete fracture of the single cell had already occurred, approximately at 760°C. It is noticed that no AE activity is observed during the holding time at 600°C and 700°C, suggesting that the heating rate is sufficiently low with respect to the reaction rate responsible for this fracture process. Post-test observation showed that extensive through-thickness cracking took place in the specimens heated to 800°C, and the specimens were completely broken into a number of segmented pieces of several mm. Numerous vertical cracks were generated in the cathode and the crack spacing was typically in the range of 50 ~ 100 µm.

![Acoustic emission behavior under simulated operating condition.](image)

A typical cross-section SEM image of the cathode/electrolyte interface is shown in Fig. 4. The SEM observations identified three types of damage: vertical cracking and delamination in the cathode, and vertical cracking in the electrolyte. Extensive propagation of delaminations was also observed in the cathode film close to the interface, and a limited portion of the cathode film was detached from the electrolyte. No such vertical cracking and delamination were observed in the anode film. The distance between individual vertical cracks was on the order of several mm.

The vertical cracking was observed to initiate from the location of the cathode/electrolyte interface and to frequently terminate inside the electrolyte. As shown in Fig. 4, it was often observed that there was a horizontal gap in the location between vertical cracks in the cathode and electrolyte. This observation suggests that the vertical cracking in the electrolyte was initiated only after the occurrence of the delamination in the cathode.

The salient difference in the damage between the simple uniform heating tests and the simulated environment tests suggests that the above-mentioned damages in the single cell may be primarily due to the chemical expansion in the anode side of the electrolyte and the anode itself. The chemical expansion in the anode side is expected to induce the tensile stress in the cathode side, which may cause the three types of damages. Thus, the vertical cracking in the
Fig. 4 SEM image of a cross section of a single cell after simulated environment test.

cathode and electrolyte is expected to occur in an opening mode, and the delamination growth in the cathode may be brought about by mixed mode cracking, including a shearing mode. Further investigation is needed to examine the contribution from the effect of the thermal expansion mismatch stresses. Figure 5 shows typical waveforms of AE signals. The results showed that AE signals observed during the tests can be classified into three groups, types A, B, and C. This classification is made on the basis of the difference in peak amplitude and wave shape of the AE signal. AE signals of type A have the peak amplitude smaller than 0.1 mV and is burst type. The peak amplitude of the type B signals was typically in the range of 0.1 ~ 0.2 mV and continuous type. Type C signals have the peak amplitude greater than 0.2 mV and burst type.
Figure 6 shows the fracture model of SDC20-based single cell under simulated operating conditions. The correspondence is based on the following observations and discussion. Our preliminary measurements showed that the cathode having a porous microstructure exhibited quasi-brittle fracture behavior with lower fracture energy than the electrolyte. In contrast, the fracture of the dense electrolyte was shown to take place in a catastrophic and brittle fashion. In view of its lower fracture energy and non-catastrophic fracture behavior, the cathode cracking is expected to emit an AE signal of smaller amplitude. In general, inclusion of a mixed mode in the crack propagation tends to increase the fracture energy compared with the crack-opening mode, producing a larger AE energy, and showing continuous-type AE. This suggests that type A may correspond to the vertical cracking and type B to the delamination in the cathode. Type C with larger amplitude and burst-type AE is expected to correspond to the vertical cracking in the electrolyte.

Fig. 6 Fracture process of SDC20-based single cell under simulated operating condition.

The sequence in occurrence of the three types of AE signals appears to correlate well with the fracture processes discussed above. Type A signals start to appear at 620°C, followed by the emission of type B signals. AE signals of types A and B are emitted constantly throughout the ranges of 620°C ~ 760°C and 640°C ~ 700°C, respectively. The first occurrence of type C signals takes place at 660°C. The type C activity increases with increasing temperature and eventually ends at 720°C.

The formation of vertical cracking in the electrolyte must be avoided, since it significantly degrades the electrical performance of the single cell and provides a direct path between the hydrogen and oxygen gases. It seems possible to detect the critical temperature condition of the SOFC by monitoring the AE activity. The present result shows that AE monitoring in the single cell experiment may provide useful information to examine the fracture processes and mechanisms under simulated operating conditions. More quantitative investigation of stress analyses is now underway, and the results will be combined with the present testing method to develop a design methodology for SOFCs.
Conclusions

The main results obtained in this study can be summarized as follow:

(1) A simple testing method was developed which enabled us to examine the fracture processes under the simulated operating environment. Monitoring AE activity was useful to detect and to identify the fracture processes.

(2) The fracture processes of the SOFC involved vertical cracking and delamination in the cathode, and vertical cracking in the electrolyte. The damages were attributable most likely to the stresses induced by chemical expansion.

(3) The AE activities correlated well with the fracture processes observed. The AE results showed that the cathode damage was initiated at 620°C and the first occurrence of the electrolyte cracking took place at 660°C.

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