APPLICATION OF LaNi(Fe)O₃ AS AIR ELECTRODE OF SOLID OXIDE FUEL CELLS

Himeko Orui, Kimitaka Watanabe and Masayasu Arakawa
NTT Energy and Environment Systems Laboratories
3-1, Morinosato-wakamiya, Atsugi-shi, Kanagawa, 243-0198, Japan

ABSTRACT

The relationships between the LaNi(Fe)O₃ (LNF) sintering temperature and the reactivity with scandia- and alumina- stabilized zirconia (SASZ), the contact resistance of the LNF/SASZ interface, and the cell performance were studied to investigate the potential of LNF at low cell operation temperatures. We demonstrate that the constant current operating (CCO) treatment of cells with LNF sintered at 900, 1000 and 1100°C overcomes the trade-off between the adhesion of LNF/SASZ and the interfacial resistance, mainly due to the reaction layer generated in high-temperature sintering, and improves cell performance. The cathodic interfacial resistance becomes one order of magnitude smaller after CCO treatment and that the cell with LNF sintered at 1000°C generates the maximum power density of 1.56 W/cm² at 800°C.

INTRODUCTION

Solid oxide fuel cells (SOFCs) that can be operated at low temperatures have been eagerly studied because they have several advantages in fabrication (1). Especially, the fabrication cost can be reduced by using metal alloy for operation under 800°C. However, under 800°C, SOFCs have relatively low conversion efficiency due to the low ionic conductivity of the electrolytes and the low activity of the electrodes, especially the air electrode.

To reduce the electrolyte resistance, materials having high ionic conductivity, such as the scandia- and alumina-stabilized zirconia (SASZ), have been studied for the electrolyte (2), and anode-supported cells with very thin electrolyte (10-30 µm) have been investigated (3). Several materials having high activity, such as La(Sr)CoO₃, Sm(Sr)CoO₃, and La(Sr)FeO₃, have also been developed for air electrodes to reduce the operating temperature (4-6). Chiba et al. reported that LaNi(Fe)O₃ (LNF) has high activity, high electronic conductivity, and a thermal expansion coefficient that matches that of SASZ (7). However, it is also known that the highly active air electrodes have high reactivity with the doped zirconia electrolyte during sintering at high temperature, resulting in a high ohmic resistance layer at the cathode-electrolyte interface (8). To avoid this problem,
a cell with interlayer between the electrode and electrolyte has been proposed (9, 10). However, this requires an additional complicated fabrication process, which results in higher cost.

In this paper, we study the performance of an anode-supported cell with LNF cathode by investigating the relationship between the LNF sintering temperature and the reactivity with the SASZ electrolyte. We also demonstrate the effect of the constant current operating (CCO) treatment on reducing cell resistance without an interlayer in the LNF/SASZ system.

**EXPERIMENTAL**

Half-cells consisting of anode substrates and electrolytes were fabricated by the co-firing method. Ten mol% Sc2O3- and 1 mol% Al2O3-stabilized ZrO2 (SASZ) was used for the electrolyte. A mixture of 60 wt% NiO and 40 wt% SASZ was used for the anode. The anode and electrolyte green sheets were prepared by doctor blade method. The anode green sheets were laminated until the appropriate thickness was obtained followed by the electrolyte green sheet. The laminated sheets were cut into disks and co-fired at 1300°C to make 35 mm diameter and 1.2 mm thick disks. Figure 1 is a cross sectional scanning electron microscope (SEM) image of the co-fired anode and electrolyte. The electrolyte is about 20 μm thick and dense enough to separate the oxygen and fuel gases. The anode is porous and the adhesion between anode and electrolyte is quite good. The cathode is LaNi0.6Fe0.4O3 (LNF). The cathodes were tape-cast on the electrolyte surface of the half cells and fired at several temperatures between 800 and 1200°C.

The LNF sintering characteristics were measured with a dilatometer (Mac science Co. Dilatometer 5000). In order to estimate the reactivity of the cathode and electrolyte, the mixtures of LNF and SASZ were sintered at several temperatures between 800 and 1100°C and their crystal structure was analyzed by means of the X-ray diffraction (XRD). The microstructures of the cells were observed by SEM.

The setup for the power generation test is schematically shown in Figure 2. The current-voltage characteristics were measured at several operating temperatures using 250 ml/min of air and 100 ml/min of H2 for the oxidant and fuel, respectively. Before measuring the current-voltage characteristics, the constant current operating (CCO) treatment was carried out. We operated the cell at constant current and stepped up the current while keeping the cell voltage at around 0.2 volts. The CCO treatment was carried out for over 48 hours. Electrochemical characteristics were investigated by AC-impedance measurements at around the open circuit voltage (OCV) to obtain more detailed information about the internal resistance of the cells.

**RESULTS AND DISCUSSION**

From the viewpoint of good adhesion (low contact resistance) between cathode and
electrolyte, LNF should be sintered at over 1000°C. However, the XRD analysis revealed a high-resistance La$_2$Zr$_2$O$_7$ phase in the sample sintered at over 1000°C. The intensity of the La$_2$Zr$_2$O$_7$ peak rapidly increased when the sintering temperature exceeded 1000°C. These suggest that both the reaction between LNF and electrolyte and the LNF sintering would progress over 1000°C.

In order to study the influence of the LNF sintering temperature on the internal resistance of the cells, the initial AC-impedance spectra of the cells were measured after sintering LNF at several temperatures. Several AC-impedance spectra are shown in Figure 3. Each consists of mainly two arcs, and the high-frequency arcs are largely influenced by the LNF sintering temperature. From the AC-impedance results for an electrolyte-supported cell with the reference electrode, we confirm that the high-frequency arc diameter corresponds to the cathodic reaction resistance and that low-frequency arc diameter could be anode reaction resistance. We can separate the internal resistance of the cells into three resistance parts from the AC-impedance spectra: $R_0$, which is the intersection point to the real part in the high-frequency range, and $R_1$ and $R_2$, which are obtained from the diameter of the arcs and appear in the high-frequency (several hundreds to 1000 Hz) and low-frequency (around several Hz) range, respectively. Figure 4 shows the sintering temperature dependence of each part of the internal resistance of the cells as evaluated from the AC-impedance spectra. $R_1$ is much larger than $R_0$ and $R_2$ in these sintering temperature range. $R_1$ decreases with increasing sintering temperature until 1000°C. This may be because the adhesion characteristic for the LNF cathode was improved with the increase in sintering temperature. On the other hand, $R_1$ increases with sintering temperature over 1000°C. This can be due to the fact that three-phase-boundary length is shortened by the high resistance layer generated at high sintering temperature over 1000°C.

The typical AC-impedance spectra before and after CCO treatment are shown in Figure 5 (the cell with LNF sintered at 1100°C). The CCO treatment caused a decrease of the total resistance, most of which is due to the decrease of the interfacial resistance of the cathode ($R_1$).

This phenomenon has also been reported for a cell with LSM cathode by Weber et al. (11). They reported cell voltage recovery by decreasing the cathodic reaction resistance with loading of the cell, and claimed that the cathode microstructure at the cathode/electrolyte interface was drastically altered by the cell operation. In their loading, the current was increased to about 0.27 A/cm$^2$ at the cell voltage of 0.7~0.8V. On the other hand, in our CCO treatment, the current was increased as much as possible, with the cell voltage kept at around 0.2 V, which is considerably lower compared to that in usual power generation tests. The degree of cell voltage recovery increased with increasing current, and large currents in the range of 1.5-3 A/cm$^2$ led to an improvement of cell performance. Finally, the power density of cells after CCO treatment was 5-10 times that of the initial one. In addition, SEM images did not reveal any significant change in the cathode/electrolyte interfacial microstructure due to the CCO treatment. Further analysis is needed to clarify the mechanism of cathodic resistance reduction by CCO treatment.
The LNF sintering temperature dependence of $R_0$ and $R_1$ after CCO treatment is shown in Figure 6. $R_0$ decreases with increasing temperature from 800°C to 1000°C, and $R_1$ shows the minimum value in the range of 900 to 1100°C. As shown in Figure 4, the initial $R_1$ of the cells when the LNF was sintered at 900 and 1100°C was larger than when it was sintered at 1000°C, but was decreased to as small as that sintered at 1000°C by the CCO treatment. The CCO treatment would have such effects as improving the adhesion between the cathode and electrolyte and reducing the influence of high-resistance $La_2Zr_2O_7$ phase provided the amount of $La_2Zr_2O_7$ produced is small enough. Figure 7 shows the LNF sintering temperature dependence of power density at 0.7 V when cells were operated at 800°C. The maximum value of 1.33 W/cm² is obtained in the cell with the LNF sintered at 1000°C.

The I-V characteristics of the cell with the LNF sintered at 1000°C are shown in Figure 8. The maximum power densities were 1.56, 0.98, and 0.76 W/cm² at 800, 750, and, 700°C, respectively. The ohmic loss, which is mainly caused by the current collection resistance, becomes large when the operating temperature is decreased from 800°C to 750°C. In spite of the increase in the cell resistance, the maximum power density of this optimized cell was still 0.47 W/cm² at 650°C.

CONCLUSIONS

The relationship between LaNi(Fe)O₃ (LNF) sintering temperature and the reactivity with the scandia- and alumina-stabilized zirconia (SASZ), the contact resistance of the LNF/SASZ interface, and cell performance were studied. We demonstrated that the CCO treatment of cells can reduce the cathodic interfacial resistance. We showed that the cathodic interfacial resistance becomes one order of magnitude smaller after CCO treatment and that the cell with LNF sintered at 1000°C has the maximum power density of 1.56 W/cm² at 800°C. These results suggest that LNF is one of the most promising materials for the SOFC cathode at medium operation temperature.

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Figure 1. Cross-sectional SEM image of the co-fired half cell.

Figure 2. Schematic diagram of the test cell fixed in the apparatus for the power generation test.
Figure 3. The initial AC-impedance spectra of cells with the LNF sintered at various temperatures.

Figure 4. Resistances estimated from the initial AC-impedance spectra.
Figure 5. AC impedance spectra of the cell with the LNF sintered at 1100°C.

Figure 6. Resistances estimated from the AC-impedance spectra after CCO treatment.
Figure 7. Dependence of the power density on LNF sintering temperature.

Figure 8. Relationships between current density and cell voltage (a), and power density (b) when the LNF was sintered at 1000°C, measured as a function of temperature.