Ni-YSZ cermet anode fabricated from NiO-YSZ composite powder for high-performance and durability of solid oxide fuel cells

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Abstract

A functional composite powder, in which nano-sized NiO (40 vol.%) was crystallized on YSZ particles, was synthesized by the Pechini-type polymerizable complex method in an effort to improve the performance and durability of SOFC anodes. The pore-structure (e.g. porosity, pore size) and mechanical properties (e.g. strength, density) of the electrode were optimized by a combination of two different species of YSZ powder (Tosoh 0.3 μm and Millennium 10 μm). A single cell made from the composite powder exhibited high power density of 1.1 W cm^{-2} and high durability under a load of 1.0 A cm^{-2} during 530 h of operating time at 800 °C. It could be concluded that this functional composite would enhance the single cell performance and durability at elevated temperature.
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1. Introduction

Owing to advantages such as high catalytic activity, mechanical/chemical stability, and compatibility with electrolyte and interconnect materials, Ni-YSZ cermet is the most extensively studied material for solid oxide fuel cell (SOFC) anodes [1]. The YSZ phase in the cermet adjusts the thermal expansion coefficient (TEC) mismatch between yttria-stabilized zirconia (YSZ: 11×10^{-6} K^{-1}) and Ni (17×10^{-6} K^{-1}), and inhibits Ni coarsening at elevated temperatures [2,3]. The Ni phase, meanwhile, provides electrical conductivity and catalytic activity for fuel oxidation. In addition, the three phase boundary (TPB) can be extended beyond the electrode/electrolyte interface to the interior of the electrode by introducing the ceramic–metallic composite.

The technical issues addressed by the SOFC anode include long-term stability, thermal/redox cycling stability, and direct utilization of hydrocarbon fuels [4–7]. As nickel is a strong catalyst for hydrocarbon cracking, carbon deposition at a Ni-YSZ cermet occurs readily without complete reformation and/or fuel dilution. Accordingly, many researchers have attempted to find alternative materials with high tolerance to carbon deposition or low catalytic activity for carbon cracking. However, most developers today use a cermet of Ni-YSZ because of its good electro-catalytic property and low price. Its compatibility with the YSZ electrolyte, a state of the art material, also is part of its appeal [8–10]. The main challenge involved with the material is related to the stability of the Ni-YSZ electrode. In this regard, enhanced stability is realized via control of the coarsening of Ni particles and dimensional change in long-term operations (i.e. thermal/redox cycling) at elevated temperatures.

D. Simwonis et al. [11] showed that the poor adhesion of Ni in the SOFC anode leads to agglomeration of Ni and a reduction of TPB. Wilkenhoener et al. [12] meanwhile reported that YSZ particles might effectively inhibit the creep and coarsening of nickel during service. Therefore, reinforcement of the YSZ skeleton, uniform distribution of component phases (i.e. Ni, YSZ, and pore), and increasing the wetting properties between
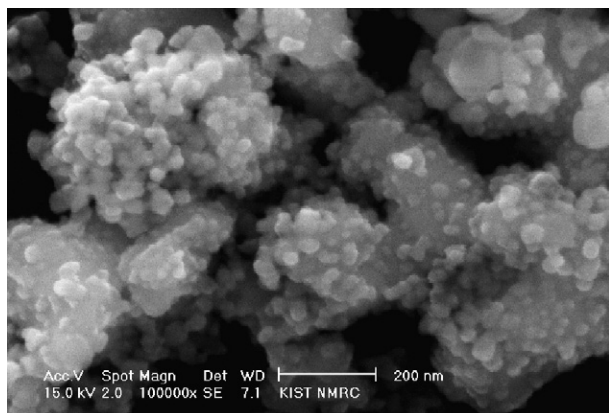

Fig. 1. SEM micrograph of NiO-YSZ composite powder.

Ni and YSZ phases have been presented as possible approaches to the development of high-performance SOFC anodes with extended durability [13–19]. In a previous study, we proposed the use of NiO-YSZ composite powder, which is composed of nano-sized NiO conjugated on YSZ powder [20]. A single cell fabricated from the composite powder exhibited high-performance and excellent tolerance against thermal and redox cycling.

The present paper discusses the development of an anode supported single cell made from NiO-YSZ composite powder as a means to achieve high-performance and durability. Improvement in the performance of a single cell made from the composite powder relative to a commercial cell (InDEC) is demonstrated. Lastly, the durability of the single cell is assessed by long-term testing under high current loading and gas interrupt conditions.

2. Experimental

The method employed for the synthesis of the NiO-YSZ composite powder was reported in a previous work [20]. The microstructure (e.g. porosity, pore size) and mechanical properties (e.g. strength, density, linear shrinkage) of the electrode were optimized by a combination of two different species of YSZ powder (Tosoh 0.3 μm and Millennium 10 μm), hereafter labeled fine and coarse, respectively. $Ni(NO_3)_2 \cdot 6H_2O$ (Junsei Chemical Co.) and citric acid (CA, Junsei Chemical Co.) were dissolved in DI-water at 60 °C. The concentration of the nickel nitrate solution was 0.15 M. YSZ and ethylene glycol (EG, Duksan Chemical Co.) was then added to the Ni nitrate aqueous solution and the mole ratio of citric acid and ethylene glycol was 1:4. The polymeric solution precipitated as viscous resin on the YSZ particles via esterification and condensation under stirring at 180 °C for 4 h. The resin was subsequently dried at 350 °C for 1 h and ash-colored intermediates were thereupon obtained. The resulting polymeric intermediates were calcined at 600 °C and milled in methanol to obtain NiO-YSZ composite powder.

The anode powders were then compacted under uni-axial pressure to form a disc. The thus the obtained green anode discs were 38 mm in diameter and 1.2 mm in thickness. The green

anodes were pre-sintered at 1300 °C for 3 h. YSZ (TZ-8YS, Tosoh, Japan) slurry was then applied onto the anode via dip-coating. The anode supported electrolyte was then sintered at 1400 °C for 3 h to yield a thin (<7 μm), dense YSZ electrolyte film. The method employed for the synthesis of the YSZ electrolyte film has been reported in a previous work by the author [21]. The cathode paste was prepared using $La_{0.8}Sr_{0.2}MnO_3$ (LSM: Praxair, USA) and YSZ (TZ-8YS, Tosoh, Japan) in a weight ratio of 50:50. The cathode layer was screen-printed on the anode-supported electrolyte with an active area of 1.5 cm^2 and a thickness of 30 μm. The cathode layer was sintered at 1150 °C for 3 h.

The morphology of the NiO-YSZ powder was observed via scanning electronic microscopy. Mechanical strengths were measured by three point bending tests with a UTM (H-10K, HOUNSFIELD, U.K.). The single cell performances were evaluated at various temperatures (600–800 °C) in reactive gases of humidified hydrogen (200 cc min^{-1}) with 3% H_2O and air (300 cc min^{-1}). The I–V characterization and durability were measured with a multi-functional electronic load module (3315D, Taiwan). Ac impedance measurements were conducted with a Solatron 1260 frequency analyzer and a Solatron 1287 interface. The ac impedance spectra in a frequency range of
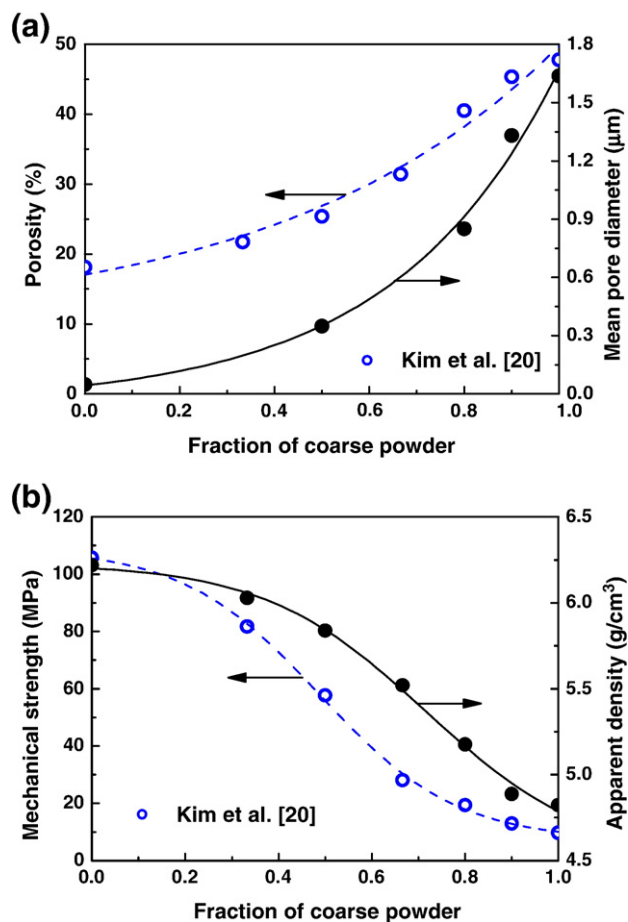

Fig. 2. Characteristics of Ni-YSZ electrode depending on the fraction of coarse powder: (a) porosity and mean pore diameter variations and (b) mechanical strength and apparent density variations (the porosity data and mechanical strength results were taken from ref. [20]).
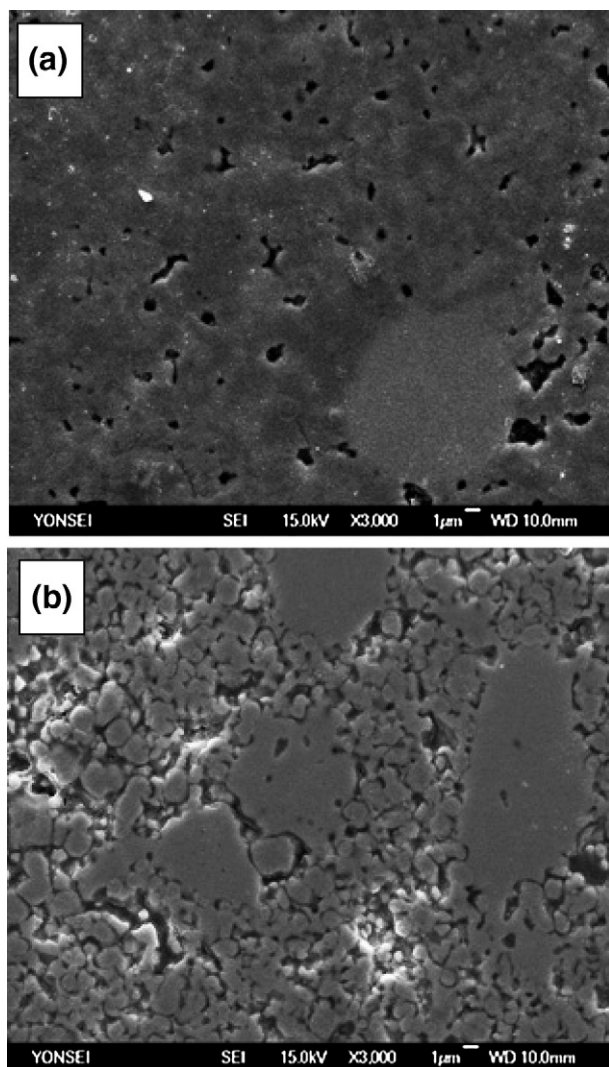
Fig. 3. SEM micrographs of EC: (a) NiO-YSZ electrode and (b) Ni-YSZ electrode.

$0.1–10^5$ Hz with an excitation voltage of 10 mV was taken in order to ensure a linear response.

3. Results and discussion

Shown in Fig. 1 is a SEM micrograph of NiO-YSZ composite powder synthesized by the Pechini-type polymerizable complex method. The core materials are yttria-stabilized zirconia and the conjugated nano-particles are nickel oxide. The composite powder exhibits higher surface area (BET analysis: 14.7 m^2 g^{-1}) than the core YSZ powder (6.2 m^2 g^{-1}) due to the presence of nano-porous composite layers. A composite particle itself offers an abundance of contact sites between Ni and YSZ, which act as active parts in the reaction.

A good cermet anode consists of continuous networks of each phase, including nickel, YSZ, and pores. This indicates that high electrical conductivity, high-mechanical strength, and sufficient gas permeability can be obtained by optimizing the cermet microstructure. Large three phase boundaries (TPBs) are also important for a highly efficient electrode reaction, and the resulting electrical performances. Shown in Fig. 2 are variations of physical characteristics of Ni-YSZ anodes in accordance with the fraction of coarse powder (the porosity data and mechanical strength results were taken from ref. [20]). The porosity and the pore size increase with the fraction of coarse powder. When the fraction of coarse powder was 0.8, the porosity and pore size of the Ni-YSZ anode was 40% and 0.9 μm, respectively (Fig. 2a). The mechanical strength and the apparent density show reverse trends against the pore characteristics. Synthetically, fine powder is beneficial to sintering and high mechanical strength while coarse powder yields desirable pore-structure. Therefore, considering the physical requirements of the anode, the composite powder was optimized at a fraction of 20% fine and 80% coarse powder.

Fig. 3 shows micrographs of electrodes manufactured from the NiO-YSZ composite powder (henceforth referred to as EC). The microstructure of the Ni-based anode changes during reduction due to the difference in specific volume between nickel and nickel oxide. The porosity of the NiO-YSZ (Fig. 3a) and Ni-YSZ (Fig. 3b) electrode was 24.5 and 40.5%, respectively. The pores are uniformly distributed around each grain. The pore networks have direct influence on the performance of the electrode as a concentration polarization, which is the voltage loss associated with the transport of gaseous fuel through the anode. Therefore, the anode must have sufficient porosity to allow enough mass transport and to minimize the loss of useful voltage of a cell performance. Shown in Fig. 4 is the N_2 permeability of the anode substrate depending on the applied pressure. The permeability level increases by nearly one order as a result of the reduction of NiO to Ni. The nitrogen permeability of the Ni-YSZ substrate follows a viscous flow, which demonstrates the availability of an effective pore channel.

The performances of single cells are evaluated with comparative parallel results of a commercial cell and in-house cell. Micrographs of single cells used in the present work are shown in Fig. 5. Each single cell consists of three layers, porous
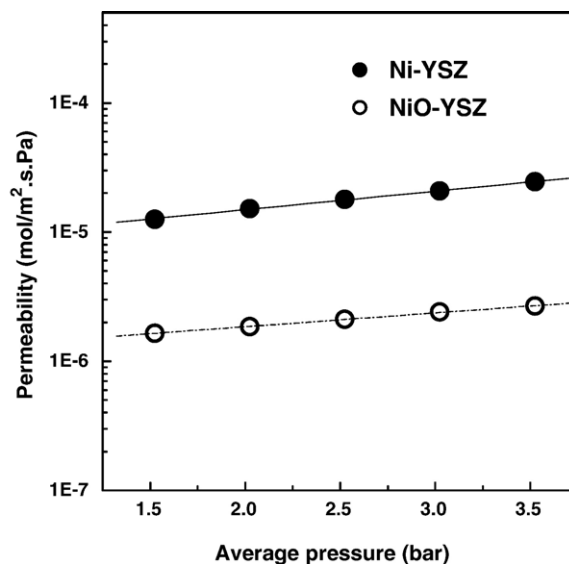

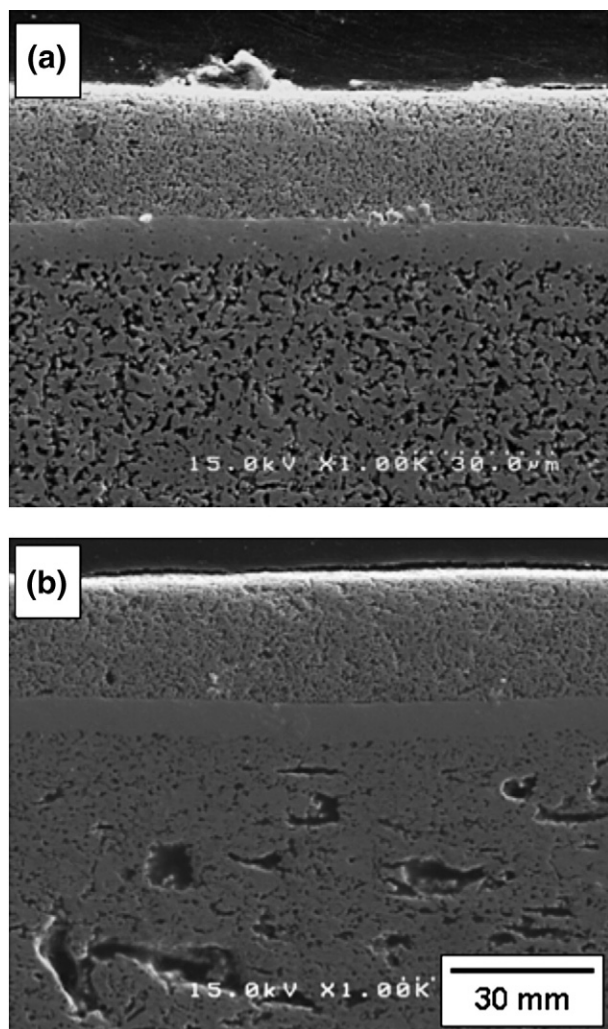Fig. 4. N_2 permeability of EC depending on the applied pressure.

Fig. 5. SEM micrographs (cross section) of anode supported single cell: (a) a single cell made from EC and (b) a single cell made from InDEC anode supported electrolyte.

Although the ohmic resistances are almost the same for each sample, the electrode resistance is remarkably different. The total area specific resistance (ASR) of the EC cell is about 0.42 Ω cm^2, which is a half value of a measured ASR of a single cell composed of the InDEC anode supported electrolyte. The ASR of EC cell is analogous to the literature value of InDEC cell (model ASC 1) at 800 °C (see Fig. 6b). On the whole, the total ASR of the EC cell is lower than that of the InDEC cell, depending on the working temperature, as can be seen in Fig. 6b.

Fig. 7 shows the performances of single cells, in which the only parameter is the Ni-YSZ anode, tested at 800 °C. The maximum power density (MPD) of a single cell composed of the EC is 1.10 W cm^{-2} at 800 °C. The performance of EC shows slightly higher values compared with the literature value of an InDEC cell (model ASC 1), which is the state of the art fuel cell of InDEC. However, the measured performance of a
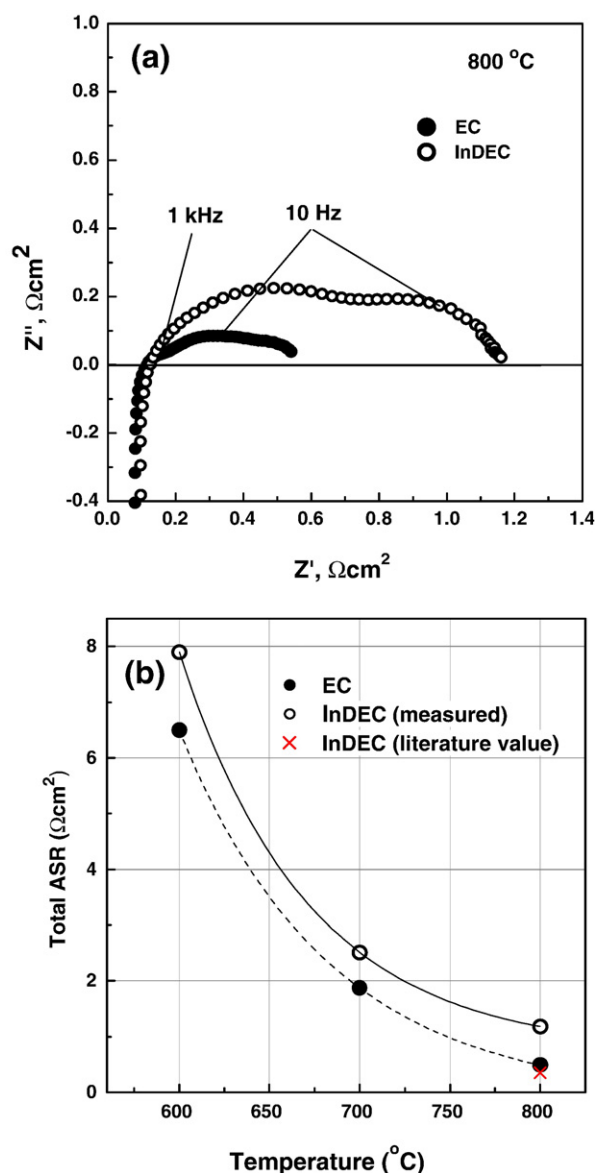
Ni-YSZ anode, dense YSZ electrolyte, and porous LSM + YSZ cathode. In Fig. 5a, the anode is made from the NiO-YSZ composite powder (EC), and a thin (<7 μm) electrolyte layer is synthesized by a dip-coating process. The single cell, shown in Fig. 5b, employs a commercial anode supported electrolyte (InDEC Ltd., Netherlands). Both cathodes are made from the same materials and identical processing. The cells' electrolyte and cathode have similar thickness and microstructure. Conversely, the anode microstructures are very different. The EC (Fig. 5a) exhibits a homogeneous microstructure with uniform size and uniform pore distribution. The InDEC anode (Fig. 5b) has a binary pore distribution of micro-pores and macro-pores. The plate type macro-pores give the impression to be derived from a pore-former such as graphite. In other words, there is a lack in uniformity due to insufficient mixing. Consequently, it is hypothesized that the anode or anode/electrolyte interface accounts for most of the variation in single cell performance.

Shown in Fig. 6 is the total area specific resistance (ASR) of single cells measured by impedance spectroscopy (IS).

Fig. 6. (a) Impedance spectra of single cells measured at 800 °C and (b) total area specific resistance of single cells depending on the working temperature.
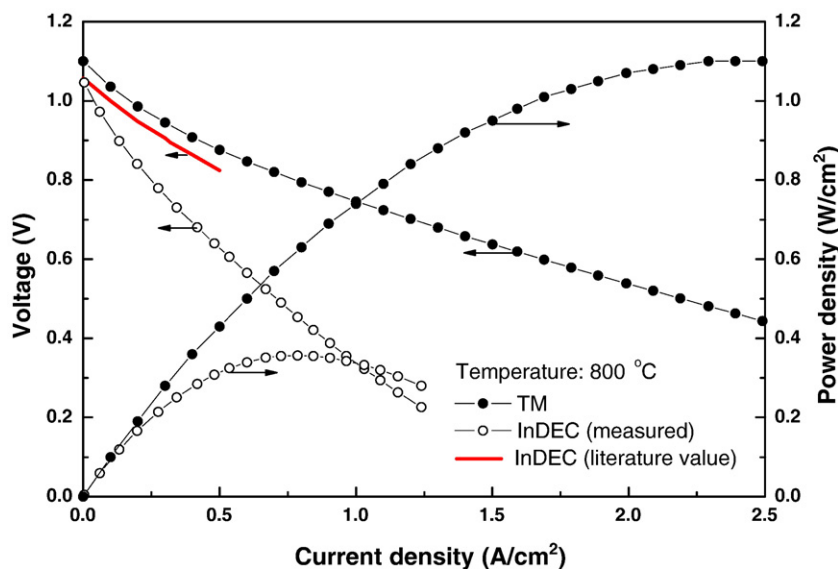
Fig. 7. Voltage and power density vs. current density plots for single cells made from EC and InDEC.

single cell with the InDEC anode supported electrolyte exhibits a reduced cell performance on the whole and shows a MPD of 0.37 W cm^{-2} at 800 °C. This shows the effect of the anode microstructure on the performance of SOFC single cells. The concentration/activation polarization resistance due to the microstructure difference is clearly reflected in the single cell performances.

The performance and durability of the single cell made from NiO-YSZ composite powder is shown in Fig. 8. The open circuit voltage (OCV) of the cell was 1.095 V. The deviation with the theoretical OCV (1.19 V) at 800 °C comes from the water content and purity of gases in each electrode. The durability of the single cell was tested under a load of 1.0 A cm^{-2} and under gas interruption conditions. During the first operation at 1.0 A cm^{-2} between 20 and 220 h, the corresponding cell voltages increased gradually from 0.678 V to 0.812 V. The inclination is due to improvement of the contact resistance between the electrode and the interconnect and/or interfacial resistance between the electrode and the electrolyte by the current flowing during the

initial period of the durability test [22]. During the air interruption test at 110 h for 10 min, the corresponding cell voltage suddenly dropped from 0.812 V to 0.744 V (8.4%). Furthermore, the performance could not be restored to its former level even with an additional 120 h of operation. As a parallel test, hydrogen was interrupted during operation under a load of 1.0 A cm^{-2} at 350 h for 10 min. The cell voltage changed slowly from 0.775 V to 0.749 V (3.0%), and recovered immediately after the gas interruption test. At the open circuit condition, a potential drop was not observed even upon a long period (230–260 h) of air interruption and a low hydrogen flow rate (10 cc min^{-1}). These results show that damage and the reaction velocity of the cathode due to current flow and short-term gas interruption are greater than for the case of the anode. However, it is likely that long-term hydrogen depletion would bring about partial oxidation of the anode and result in catastrophic failure of cell operation. During the whole process of the cell operation, a spontaneous performance decrease could not be observed under conditions of current loading (1.0 A cm^{-2}) and gas interruption. From the results of the durability test, it was demonstrated that the single cell performed well for more than 500 h, even under a severe environment.

4. Conclusions

A SOFC single cell made from NiO-YSZ composite powder exhibits high power densities of 0.12, 0.42, and 1.10 W cm^{-2} at 600, 700, 800 °C, respectively. The single cell shows high durability under a load of 1.0 A cm^{-2} at 800 °C over 530 h of operating time. Notably, Ni-YSZ anode made from the composite powder exhibits high uniformity, high electrical conductivity, high mechanical strength, and high porosity. The results imply that the anode makes a significant contribution to the cell performance. The superior performance and durability demonstrated here is expected to yield increased system reliability and system conciseness.
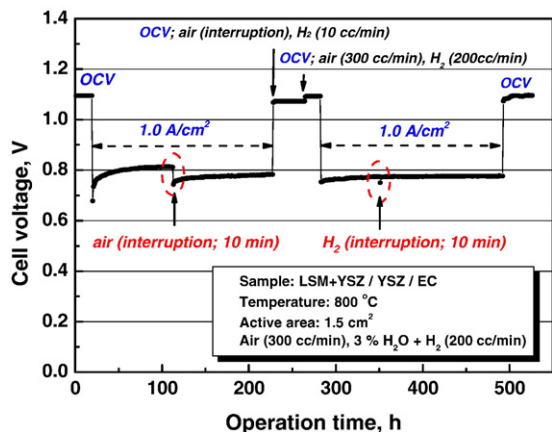

Fig. 8. Long-term stability and gas interruption tests of a single cell made from EC at 800 °C.

Acknowledgements

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