Performance improvement of direct internal reforming solid oxide fuel cell fuelled by H₂S-contaminated biogas with paper-structured catalyst technology

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Abstract

Direct internal reforming (DIR) operation of a solid oxide fuel cell (SOFC) is a very attractive concept for downsizing and cost reduction of SOFC systems. This study aimed to develop stable operation of a DIR-SOFC fuelled by biogas. The current-voltage (I-V) curves of 2 x 2 cm² planar SOFCs (anode- and electrolyte-supported cells, ASC and ESC, respectively.) were measured at 800 °C in the direct feed of a simulated biogas mixture (CH₄/CO₂ = 1), and the flexible structured catalyst material (paper-structured catalyst (PSC)) was applied on the anode material for performance enhancement. By applying a hydrotalcite (HT)-dispersed PSC (HT-PSC), the sulfur tolerance of the SOFC in the DIR operation was remarkably improved. By the effect of the HT-PSC, for both ASC and ESC, a stable cell voltage higher than 800 mV was obtained over 200 h at 0.2 A cm⁻² in the direct feed of simulated biogas under 5 ppm H₂S poisoning.

Keywords: SOFC, direct internal reforming, biogas, H₂S poisoning, paper-structured catalyst, Mg/Al-hydrotalcite

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1. Introduction

Biogas is a mixture of CH_4 (~ 60 %) and CO_2 (~ 40 %) with impurities such as H_2S and NH_3 [1-3], and one of the most attractive **alternative** fuels produced by anaerobic fermentation of low-grade biomass resources (bio-wastes) such as agricultural residues, crop processing residues, livestock waste and garbage. In developing countries, small-sized fermentation reactors are being installed for rural households and farms with international cooperation and support [4,5], and the produced biogas is utilized as an energy source for local consumption (e.g., as a heat source for cooking and a fuel for **decentralized** power generation with gas engine systems).

A solid oxide fuel cell (SOFC), which is a highly efficient energy conversion device, is one of the most promising candidates for use as a distributed power generator. Using SOFCs, the chemical energy of hydrocarbon fuels can be directly converted into electrical energy with an efficiency that is two times higher than that of conventional heat engines [6]. Global dissemination of SOFC systems can contribute to a reduction in greenhouse gas emissions (**More than 30 % reduction of CO_2 emission by the installation of SOFC has been demonstrated in the Demonstrative Research on Solid Oxide Fuel Cells conducted by New Energy Foundation (NEF), Japan [7].**). In particular,

in a region abundant in biomass resources, biogas-fuelled SOFCs are an attractive technology and therefore extensively investigated by several research groups [8-18]. Although hydrocarbon-fuelled SOFC systems are typically equipped with an on-board reformer, which is placed in the front of a cell stack, in principle, reforming within the porous Ni-based anode material (i.e., composite of Ni and stabilized-zirconia, such as yttria-stabilized zirconia (Ni-YSZ) or scandia-stabilized zirconia (Ni-ScSZ), called a “cermet anode”) is possible for high-temperature SOFCs operated above 700 °C due to the catalytic effect of Ni. This unique operation mode is referred to as direct internal reforming (DIR) operation [10-14,19-22].

The DIR-SOFC has the potential to be employed worldwide including in developing countries because complicated fuel processing to obtain pure H₂ is not necessary, leading to downsizing and cost reduction of fuel cell systems. However, to ensure commercial level stability, the structure of the reaction zone for internal reforming must be improved to suppress the thermal stress caused by the strong endothermicity of the reforming reaction [23-28] and the chemical degradation due to coke formation [19,25-27, 29,30] and fuel impurity poisoning [12,31-35].

Continuous electricity generation directly from simulated biogas with the

DIR-operation mode has been demonstrated using lab-scale cells [12-14,36,37]. In this operation mode, electrochemically active H₂ and CO are primarily produced by the dry reforming reaction (1) in the porous cermet anode or anode support.

At the anode/electrolyte interface, the resulting H₂ and CO will be electrochemically oxidized by O²⁻ transported from the cathode side through the dense electrolyte to produce electricity, H₂O and CO₂ (Reactions (2) and (3), respectively).

Because biogas contains 500-4000 ppm H₂S, which is not only harmful to human health but also highly poisonous to catalyst materials for reforming and electrochemical reactions, desulfurization using iron oxides, zinc oxides or activated carbon is an indispensable process [38-40]. Even after the process, if a 1-10 ppm level of H₂S is still remaining in biogas for some reason, sulfur species can easily chemisorb on the surface of a metal catalyst (i.e., Ni) and sometimes form nickel sulfide depending on the temperature [41], resulting in the reduction of the area of the active sites for reforming and blockage of electrochemically active sites (triple phase boundary (TPB)). H₂S

poisoning of the SOFC anode has been thoroughly studied, and Sasaki *et al.* demonstrated the stable operation (for thousands of hours) of an electrolyte-supported cell (Electrolyte: ScSZ, Anode: Ni-ScSZ) at 800 °C under 5 ppm H₂S poisoning in a H₂-rich fuel [32]. For DIR operation, trace H₂S results in fatal damage to the cell performance. Hagen *et al.* reported the strong influence of a 2-10 ppm level of H₂S poisoning on the performance of an anode-supported cell with a Ni/YSZ anode fuelled by CH₄-rich gas at 850 °C [42,43]. Direct use of a hydrocarbon fuel containing H₂S, such as biogas, is challenging because methane reforming on the surface of Ni in the porous anode is highly susceptible to sulfur poisoning, resulting in deactivation of the reforming and electrochemical reactions [12,44]. Therefore, a breakthrough must be found to develop an impurity resistant catalyst material for DIR-SOFC applications.

Recently, we developed a paper-structured catalyst (PSC) whose flexible workability allowed us to easily endow catalytic function to a cell stack without changing the SOFC system configuration [45-47]. The PSC was composed of an inorganic fibre network, which can be prepared by a simple papermaking process during which various types of functional materials can be easily dispersed in the network [48,49]. In our previous study, a considerable improvement in the catalytic performance of the Ni-loaded PSC

was achieved by dispersion of Mg/Al hydrotalcite (HT) in the inorganic fibre network, resulting in the formation of fine Ni particles and suppression of Ni loading on the ceramic fibres that leads to Ni coarsening. This HT-dispersed PSC (HT-PSC) exhibited high sulfur tolerance in the dry reforming of methane at 800 °C [46]. In this study, by the application of the HT-PSC to the conventional anode material, significant improvement in sulfur tolerance in the DIR operation has been demonstrated for the direct feed of simulated biogas ($\text{CH}_4/\text{CO}_2 = 1$), indicating a further increase in the fuel flexibility of SOFCs.

2. Experimental

2.1. Preparation of paper-structured catalyst

Hydrotalcite ($[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3]4\text{H}_2\text{O}$, HT) is an excellent promoter of the reforming reaction [50,51]. Fig. 1 shows the process flow of HT-PSC based on a papermaking technique through a dual polyelectrolyte retention system. The detailed procedure has been previously described [46]. First, 5 g of ceramic fibre (Cf, SiO_2 : 52 wt%, Al_2O_3 : 48 wt%; IBIDEN Ltd., Japan) with an average length and width of 500 and 2 μm , respectively, dispersed in distilled water was crushed using an electric mixer. Then, 2 g of HT was added to the slurry, and the resulting water suspension was mixed

with a designated amount of cationic polyelectrolyte, PDADMAC (Sigma Aldrich LCC, USA), followed by stirring for 3 min. Next, 0.5 g (solid base) of YSZ sol (Zs) (Nissan Chemical Industries Ltd., Japan), which serves as an inorganic binder through a high-temperature heat treatment, and an anionic polyelectrolyte, A-PAM FA-405S (Fujikasui Engineering Co., Ltd., Japan), were added to the slurry followed by stirring for 3 min. Then, 0.25 g (solid base) of an organic pulp fibre suspension were poured into the mixture and solidified by dewatering using 200 mesh. The wet-state paper sheet with a diameter of 16 cm was pressed at 350 kPa for 3 min and dried to form raw paper followed by heat treatment at 800 °C for 5 h to improve the physical strength via binder welding. Pieces of the paper were immersed in a 0.5 M $\text{Ni}(\text{NO}_3)_2$ aqueous solution for Ni loading. After the impregnation process, the samples were heat treated at 800 °C for 5 h.

The microstructure of the prepared HT-PSC (9 wt% Ni loading) is shown in Fig. 2. Cf (Al site ((c))) was welded by Zs (Zr site (d)) to form an inorganic fibre network with an average size of macropores and porosity of 16 μm and 89 %, respectively. Ni ((f)) was loaded selectively on the Mg sites ((e)) corresponding to the HT-derived oxide phase to accommodate very fine Ni particles (less than 10 nm) ((g)). The specific surface area (SSA) and average particle size of Ni, which were measured using CO

pulse measurements, were $21 \text{ m}^2 \text{ g}^{-1}$ and 32 nm , respectively [46]. A small portion of Ni was loaded on Cf, and these Ni can easily agglomerate to form coarse particles with a size of more than 200 nm . Therefore, the average particle size of Ni became larger than that selectively loaded on the HT-derived oxide phase. The geometric parameters of HT-PSC are listed in Table 1.

Fig. 1: Process flow of the HT-dispersed PSC (HT-PSC).

The PSC has the desired geometry to enhance the accessibility of a reactant gas to the surface of the metal catalyst particles. In fact, for the steam reforming of biodiesel fuels with heavy hydrocarbons, the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) was promoted compared to that on a bead catalyst [52], suggesting enhanced mass

transfer due to its unique structure. The PSC can be obtained using a single filtration process, and its **flexible workability** enables cutting, bending and rolling.

Fig. 2: Microstructure of HT-PSC: (a) schematic illustration, (b) FESEM image, (c-f) EDX elemental mapping images and (g) STEM image of Ni particles loaded on the HT-derived oxide [46].

2.2. Preparation of SOFC single cells

The configurations of the anode- and electrolyte-supported cells (ASC and ESC, respectively) are shown in Fig. 3. The thicknesses of the component materials of the

ASC and ESC are summarized in Table 2. These cells were fabricated using the procedures described below.

Fig. 3: SOFC single cells ($2 \times 2 \text{ cm}^2$) prepared in this study. (a) and (b) are schematic illustrations of the ASC and ESC, respectively. (c) and (d) are pictures of the ASC and ESC, respectively. (e) and (f) are cross sectional SEM images of the ASC and ESC, respectively.

To fabricate the ASC, the anode-supported half-cell with an area of $2 \times 2 \text{ cm}^2$ and a thickness of 850 μm was provided by Saga Ceramic Research Laboratory and used in this study. The half-cell was based on the Ni-8YSZ (8 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$) anode-support (NiO:8YSZ = 56 wt%:44 wt%) on which a porous Ni-8YSZ (with the same

composition as anode-support) anode functional layer (AFL) with a 10 μm thickness and a dense 8YSZ electrolyte layer with a 5 μm thickness were formed by screen printing and subsequent sintering at 1050 and 1400 $^{\circ}\text{C}$ for the AFL and electrolyte, respectively. Prior to fabrication of the cathode, pastes of the barrier layer ($\text{Gd}_{0.10}\text{Ce}_{0.90}\text{O}_2$ (GDC)) and anode current collector layer (ACCL) ($\text{NiO}:\text{10ScSZ}$ (10 mol % Sc_2O_3 -1 mol % CeO_2 - ZrO_2) = 80 wt%:20 wt%) were screen printed on the surface of the electrolyte and anode support, respectively, followed by co-sintering at 1200 $^{\circ}\text{C}$ for 5 h. The paste of the cathode functional layer (CFL), which consists of a mixture of $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}(\text{Co}_{0.20}\text{Fe}_{0.80})\text{O}_{3-x}$ and $\text{Gd}_{0.10}\text{Ce}_{0.90}\text{O}_{1.95}$ (LSCF-GDC) (Fuel Cell Materials, USA), was screen printed on the sintered GDC layer. Then, the LSCF paste (Fuel Cell Materials, USA) was printed on the dried LSCF-GDC layer as a cathode current collector layer (CCCL). Finally, the deposited pastes were co-sintered at 900 $^{\circ}\text{C}$ for 5 h to obtain the porous cathode with an area of 1.4 x 1.4 cm^2 .

To fabricate the ESC, a dense 10ScSZ plate with a 160 μm thickness and 2 x 2 cm^2 area was made from a 10ScSZ powder provided by Daiichi Kigenso Kagaku Kogyo, Japan, and selected as the electrolyte. The AFL paste (Ni-10ScSZ ($\text{NiO}:\text{10ScSZ}$ = 56 wt%:44 wt%)) was deposited on the 10ScSZ plate via screen printing following by

sintering at 1300 °C for 3 h to form a porous anode material with an area of 1.4 x 1.4 cm². The ACCL, CFL and CCCL (with 1.4 x 1.4 cm² in area) were prepared using the same procedure as that employed for the ASC. For both ASC and ESC, Pt wires welded with Pt mesh were applied on anode and cathode as voltage and current-collecting probes (Fig. 3-(c, d)). The cross-sectional SEM images of the ASC and ESC focusing on the anode side structure are shown in Fig. 3-(e, f).

2.3. Electrochemical measurement

The test bench for measuring the electrochemical performance of the prepared single cell with PSC (PSC/SOFC stacking) is shown in Fig. 4. First, three pieces of 9 wt% Ni-loaded HT-PSCs with an area of 2 x 2 cm² and a thickness of 1.1 mm were stacked and placed in an alumina cell housing. Then, the SOFC single cell (ASC or ESC) was placed on the “PSC carpet”. For ESC, porous Pt electrode was attached on the electrolyte surface of the cathode side as a reference electrode. Ceramic bond (Aron Ceramic, TOAGOSEI CO., LTD., Japan) was pasted around the outer perimeter of the cell for sealing, followed by heating to 800 °C in 5 h. Then, 50 ml min⁻¹ pure N₂ was fed to the anode side in-plane direction to purge the anode compartment, and after completely purging the compartment, the anode gas was switched from pure N₂ to 50

ml min⁻¹ of pure H₂ (dry). The anode and HT-PSC were subjected to reduction treatment for 15 h.

Fig. 4: Test bench for the electrochemical measurement of the DIR-SOFC fuelled by simulated biogas. A single cell of the ASC or ESC was placed on the HT-PSC embedded in the alumina housing to form the PSC/SOFC stack, and the outer perimeter of the cell was sealed with ceramic bond.

The electrochemical measurements were performed using an automatic SOFC testing system (TOYO Corporation, Japan). Dry H₂ at a rate of 100 ml min⁻¹ was passed through distilled water at 30 °C for humidification, and then, the humidified H₂ (4.2 vol% H₂O-H₂) was supplied to the anode side. For the cathode side, 1 L min⁻¹ of air was supplied. During the measurement of the current-voltage (I-V) curve, **anode overvoltage was measured using the current interruption method, and non-ohmic and ohmic contributions were separately evaluated.** After the measurement with humidified H₂, the fuel flow was switched to **40 ml min⁻¹** of simulated biogas (equimolar mixture of CH₄ and CO₂ (CH₄/CO₂ = 1)) to test the DIR-SOFC.

In this study, the H₂S poisoning test was performed during the DIR operation at

800 °C. In the direct feed with $\text{CH}_4/\text{CO}_2 = 1$ (CH_4 : 20 ml min⁻¹, CO_2 : 20 ml min⁻¹, N_2 : 20 ml min⁻¹), after waiting 2 h to obtain a stable cell voltage under galvanostatic condition of 200 mA cm⁻², 5 ppm H_2S poisoning was started by switching the pure N_2 (20 ml min⁻¹) to a mixture of N_2 (16 ml min⁻¹) and 40 ppm H_2S balanced with N_2 (8 ml min⁻¹). To evaluate the effect of the HT-PSC placed next to the anode on the sulfur tolerance, electrochemical impedance spectroscopy (EIS) was carried out before and during poisoning under the open-circuit condition using a frequency response analyzer (VersaSTAT3, Princeton Applied Research, USA) in a frequency range between 0.1 and 100 kHz with voltage amplitude of 10 mV.

3. Results and discussion

3.1. I-V characteristics of a DIR-SOFC fuelled by simulated biogas

Figs. 5-(a) and (b) show the I-V curves of the ESC (2 x 2 cm² square-shaped) without and with HT-PSC, respectively, with the direct feed of a simulated biogas mixture ($\text{CH}_4/\text{CO}_2 = 1$) measured at 800 °C showing the impact of HT-PSC on the performance of DIR-SOFC. In the absence of the HT-PSC, dummy paper (the heat-treated paper before Ni loading) was placed under the cell rather than HT-PSC. I-V curves for humidified H_2 (4.2 vol% $\text{H}_2\text{O}-\text{H}_2$) were also plotted for comparison. For DIR operation

with $\text{CH}_4/\text{CO}_2 = 1$, the positive impact of the HT-PSC on the cell performance was observed. As shown in Fig. 5-(b), when the HT-PSC was applied, at 0.7 V a considerably high current density close to 1 A cm^{-2} , which is comparable to that of humidified H_2 , was recorded even with the direct feed of $\text{CH}_4/\text{CO}_2 = 1$.

Fig. 5: Performance of ESC ($2 \times 2 \text{ cm}^2$ square-shaped) with the direct feed of a simulated biogas mixture ($\text{CH}_4/\text{CO}_2 = 1$) measured at $800 \text{ }^\circ\text{C}$; (a,b) I-V curves, (c,d) anode overvoltage (non-ohmic) and (e,f) anode overvoltage (ohmic). (a,c,e) and (b,d,f) are the results for without and with HT-PSC, respectively. Results for humidified H_2 (4.2 vol% H_2O) were also plotted (Red).

The electromotive forces (EMFs) at 800 °C that were thermodynamically predicted by HSC 5.1 program (Outokumpu Research Oy, Finland) were 1.086 and 1.111 V for humidified H₂ (4.2 vol % H₂O-H₂) and simulated biogas (CH₄/CO₂ = 1), respectively. As shown in Fig. 5-(a), when HT-PSC was not applied, open circuit voltage (OCV) for the direct feed of simulated biogas was only 1014 mV (97 mV lower than the EMF), whereas OCV close to the EMF was measured for humidified H₂. By applying HT-PSC, OCV for the simulated biogas was boosted up (see Fig. 5-(b)). $\Delta\text{OCV}_{\text{CH}_4/\text{CO}_2}$ (= $\text{OCV}_{\text{CH}_4/\text{CO}_2}$ (with HT-PSC) – $\text{OCV}_{\text{CH}_4/\text{CO}_2}$ (without HT-PSC)) was 73 mV indicating the promotion of reaction (1) by the catalytic effect of HT-PSC, whereas $\Delta\text{OCV}_{\text{H}_2}$ (= OCV_{H_2} (with HT-PSC) – OCV_{H_2} (without HT-PSC)) was zero because reforming reactions are not involved.

Anode overvoltages measured by current interruption method are plotted in Figs. 5-(c)-(f). (c,d) and (e,f) show non-ohmic and ohmic contributions, respectively. In both cases without and with HT-PSC, non-ohmic loss, corresponding to activation overvoltage including mass transfer loss, measured for CH₄/CO₂ = 1 was nearly the same level as that for humidified H₂, indicating electrochemical oxidation of H₂ is predominant even for DIR power generation. When HT-PSC was applied, ohmic loss slightly increased by fuel switching from humidified H₂ to CH₄/CO₂ = 1 (see Fig. 5-(f)),

whereas it remained unaltered in the case without HT-PSC. The slight increase of the ohmic loss may reflect the promotion of endothermic reforming reaction accompanied by cooling effect.

3.2. Improvement of sulfur tolerance by application of HT-PSC

5 ppm H₂S poisoning tests were performed during DIR operation at 800 °C fuelled by simulated biogas. Fig. 6-(a) shows the cell voltages of the ESC and ASC monitored for 200 h during 5 ppm H₂S addition at a constant current density of 0.2 A cm⁻². When the HT-PSC was not applied to the anode material, the cell voltage of the ESC rapidly decreased immediately after starting the 5 ppm H₂S addition, and voltage stabilization was not achieved. This voltage drop is caused by the chemisorption of sulfur species derived from H₂S on the surface of the Ni particles used in the anode material, which block the active sites for methane reforming and electrochemical oxidation causing a large increase in the anode overvoltage [12]. For the ASC, the cell voltage decreased also rapidly by the addition of 5 ppm H₂S but more slowly compared to that observed for ESC. In the current study, the anode functional layers (AFLs) of the ASC and ESC consisted of Ni-8YSZ (10 μm in thickness) and Ni-10ScSZ (20 μm in thickness), respectively. It is reported that Ni-10ScSZ exhibits a considerably higher tolerance to

H₂S poisoning compared to Ni-8YSZ in feeding humidified H₂ [31]. Although the difference in the porous cermet morphology can affect the sulfur tolerance [43], approximately three times higher ionic conductivity of 10ScSZ than that of 8YSZ [53] leading to the extension of TPB would be a main reason of the higher tolerance. Therefore, the present ESC must be electrochemically superior to the ASC especially in the presence of trace H₂S. However, the results of Fig. 6-(a) indicate that for DIR operation of the SOFC, the ASC with Ni-8YSZ is more tolerant to H₂S poisoning than ESC with Ni-10ScSZ. Because the amount of Ni used for the ASC is approximately 80 times larger than that used for the ESC [47], the difference in the poisoning behaviour between the ASC and the ESC may arise from the difference in the extent of the reforming reaction caused by the difference in the Ni content. Therefore, in the DIR operation of the SOFC, promotion of the internal reforming reaction is crucial for enhancing sulfur tolerance.

For the DIR operation fuelled by simulated biogas ($\text{CH}_4/\text{CO}_2 = 1$), unless HT-PSC was applied, long-term operation was impossible in the presence of 5 ppm H₂S regardless of the cell type. In the 3000 h poisoning test with 5 ppm H₂S in the feed containing H₂-rich gas (50% pre-reformed CH₄-based gas ($\text{S/C} = 2.5$): H₂ 37 %, CO 8 %, CH₄ 11 %, CO₂ 3%, H₂O 41 %) as a fuel, after the initial cell voltage drop a

quasi-stable state appeared with a low degradation rate of only 0.68 %/1000 h [32]. Therefore, the rapid voltage drop with 5 ppm H₂S poisoning during the DIR operation was caused by the strong deactivation of the internal reforming reaction to produce H₂ and CO but not by the deactivation of the electrochemical oxidation of H₂ and CO. However, when HT-PSC was applied, the sulfur tolerance of the SOFC was substantially improved. After the initial cell voltage drop, a quasi-stable voltage was obtained even for the ESC. To achieve a DIR-SOFC, a key factor involves maintaining the reforming reaction in the presence of a fuel impurity.

Microstructures of the HT-PSC stacked on the anode of the ESC after the 200 h galvanostatic measurement under 5 ppm H₂S poisoning were shown in Figs. 6-(b) and (c). Carbon deposition slightly occurred mainly on the ceramic fibre (Cf). According to the thermodynamic calculations, the present condition (i.e., CH₄/CO₂ = 1 at 800 °C) is in the carbon formation region, and therefore, carbon deposition inevitably occurs, which was suppressed on the Ni-loaded HT-derived oxide where nanosize Ni particles were still maintained after the 200 h poisoning test. However, as shown in Fig. 6-(c), Ni coarsening up to a maximum of 50 nm did occur. Even if severe coking takes place, blockage of the diffusion pathway can be avoided because the fibre network of PSC has sufficient space for storing the formed carbon.

Fig. 6: Results of H_2S poisoning test with the direct feed of a simulated biogas mixture ($CH_4/CO_2 = 1$) at 800 °C showing enhancement of the sulfur tolerance due to application of the HT-PSC (Blue: without HT-PSC, Green: with HT-PSC): (a) monitoring of cell voltages of the ESC and ASC at a constant current density of 0.2 A cm⁻² after starting 5 ppm H_2S addition, (b) FESEM image of the HT-PSC used for the 200 h poisoning test of ESC, (c) STEM image of Ni particles loaded on the HT-derived oxide in the HT-PSC used for the 200 h poisoning test of ESC, and anode-side EIS spectra measured for ESC (d) without and (e) with HT-PSC.

Anode-side EIS spectra of the ESC with directly feeding simulated biogas mixture were measured under OCV condition, and those before and during H₂S poisoning (5 min after starting H₂S addition) were compared. As shown in Fig. 6-(d), when the HT-PSC was not applied, by the addition of 5 ppm H₂S, polarization resistance was drastically increased. Low frequency region (< 100 Hz) corresponding to mass transfer processes including diffusion of electrochemically active species in the porous anode (100–10 Hz) and gas conversion (< 5 Hz) was strongly affected [44, 54], reflecting strong deactivation of reforming reaction resulting in significant increase of mass transfer resistance even under OCV condition. When the HT-PSC was stacked on the anode material, as shown in Fig. 6-(e), increase of anode-side polarization by sulfur introduction was considerably suppressed. Only charge transfer processes (> 500 Hz) were affected, and mass transfer resistance did not increase by the addition of 5 ppm H₂S, indicating supply of reformat containing H₂ to TPB was uninterrupted in the case with HT-PSC.

The catalytic activities of the HT-PSC and SOFC anode for the dry reforming of methane under 5 ppm H₂S poisoning was monitored using a gas chromatograph. For the test with HT-PSC, 3 pieces of HT-PSCs were mounted in an alumina housing, as shown

in Fig. 4, on which a dense YSZ plate was placed, and ceramic bond was pasted along its outer perimeter for sealing. For the test with the SOFC anode, the half-cell consisting of the ASC without a cathode and a current collector mesh was embedded in the alumina housing and sealed. The production rates of H₂ and CO as well as the CH₄ conversion were measured at 800 °C for a feed containing an equimolar mixture of CH₄ and CO₂ at 40 ml min⁻¹ (same condition as the galvanostatic tests of Fig. 6-(a)), and the results are shown in Fig. 7. In this diagram, the consumption rate of H₂ (or CO) that corresponds to the load current applied in the test shown in Fig. 6-(a) was indicated with a blue arrow. For the HT-PSC, the initial methane conversion prior to the addition of trace amounts of H₂S was 97 % equal to equilibrium, and after initiating the 5 ppm H₂S poisoning, the methane conversion began to decrease at approximately 15 h, suggesting that the surface coverage of Ni metal with chemisorbed sulfur species began to have an influence, and the conversion eventually converged to approximately 87 %, indicating adsorption equilibrium after 20 h [34]. For the HT-PSC with nano-sized fine Ni particles, the dry reforming reaction was sustainable at a high methane conversion that was close to 90 % and produced a sufficient amount of H₂ (approximately 3 times the amount of H₂ consumed by the present load current) even in the presence of 5 ppm H₂S. Therefore, when the HT-PSC was applied to the anode material, after the initial cell voltage drop

within 20 h, a quasi-stable voltage was obtained. The sulfur tolerance strongly depended on the Ni surface area [43,46], and therefore, the catalytic activity of the conventional anode material composed of micron-sized coarse particles significantly decreased within a short period of time due to H₂S poisoning, as shown in Fig. 7. At 4.8 h, the production rate of H₂ decreased down to the level of the estimated electrochemical consumption rate of H₂ (or CO). If H₂ is the predominant reactant in electrochemical oxidation, fuel starvation may occur at around this time, which is consistent with the time when the steep cell voltage drop of the ASC began after starting H₂S addition (see Fig. 6-(a)).

Fig. 7: Monitoring of the production rates of H₂ and CO as well as CH₄ conversion during dry reforming of methane (CH₄/CO₂ = 1: 40 ml min⁻¹) at 800 °C under 5 ppm H₂S poisoning, indicating a higher tolerance of HT-PSC to H₂S poisoning than that of the SOFC anode (Ni-8YSZ anode-support with Ni-8YSZ AFL).

Based on the results from the I-V curve measurements and poisoning tests, the mechanism of the positive effect of the PSC for enhancing sulfur tolerance can be explained. Fig. 8 schematically illustrates the fuel distribution in the anode side of the PSC/SOFC stack to which biogas is directly supplied as a fuel along an in-plane direction from the left side to the right side. Figs. 8-(a) and (b) correspond to the conditions without H₂S poisoning and under H₂S poisoning, respectively. Based on the difference in the porosity of the anode and PSC, as shown in Fig. 8-(a), a larger amount of biogas will pass through the PSC side. Although the reforming reaction (Here, dry reforming of CH₄ is a main reaction.) can occur in both the anode and PSC sides as indicated by orange and pink, respectively, based on the higher porosity and catalytic activity of PSC compared to those of the anode material, the PSC zone may act as a main reaction site to form syngas that is supplied to the electrolyte/anode interface and subsequently consumed to primarily produce electricity via electrochemical oxidation of H₂.

Under H₂S poisoning, as shown in Fig. 8-(b), the biogas distributed to the anode side passes through with low conversion to syngas due to the serious deactivation of the Ni catalyst used in the anode by sulfur (see Fig. 7). Therefore, for conventional SOFCs without HT-PSC, starvation of electrochemically active H₂ can occur in the presence of

trace amounts of H_2S under load condition, resulting in breakdown of power generation within a short period of time, as shown in Fig. 6-(a). However, the HT-PSC maintains a high methane conversion that is close to 90 % even in the presence of trace amounts of H_2S , and therefore, the supply of H_2 in the reformat to the electrochemically active electrolyte/anode interface is uninterrupted, which results in stable cell operation, as shown in Fig. 6-(a). Based on this mechanism, stable operation of the DIR-SOFC under H_2S poisoning, which was previously unattainable, was achieved by the application of a HT-PSC with high porosity and excellent catalytic performance for fuel reforming.

Fig. 8: Schematic illustrations of the fuel distribution for PSC/SOFC stacking with the direct feed of a biogas mixture: (a) without H_2S poisoning and (b) under H_2S poisoning. Red: biogas flow, Orange: syngas produced in anode, Pink: syngas produced in PSC.

Conclusions

Paper-structured catalyst (PSC) was applied for the performance enhancement of direct internal reforming (DIR) SOFC. This study demonstrated that by the application of a hydrotalcite-dispersed PSC (HT-PSC) to a SOFC anode to form a PSC/SOFC stack, stable operation of DIR-SOFC with simulated biogas mixture ($\text{CH}_4/\text{CO}_2 = 1$) containing 5 ppm H_2S was achieved for 200 h at 0.2 A cm^{-2} . HT-PSC contributed to remarkable improvement of sulfur tolerance, because it keeps a high methane conversion in dry reforming reaction that is close to 90 % even in the presence of trace amounts of H_2S , and therefore, the supply of H_2 in the reformat to the electrochemically active electrolyte/anode interface is uninterrupted. The site of the reforming reaction can be allocated to the PSC zone, whose pore size diameter and porosity are approximately 20 μm and 90 %, respectively. This unique geometric structure of the PSC results in higher accessibility of gaseous reactants to the surface of the fine Ni particles compared to that of a pelletized catalyst, such as the anode material of a SOFC composed of coarse Ni particles, leading to enhancement of H_2S tolerance. The notable characteristics of PSC are its easy processing and flexible workability, which enable us to endow any type of cell stack with catalytic function without changing the configurations.

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Tables:

Table 1: Geometric parameters for the HT-PSC prepared in this study.

Ni loading / wt%	BET SSA / m ² g ⁻¹	Ni SSA / m ² g ⁻¹	Average Ni particle size / nm	Porosity / %	Average size of macropores / μm
9	16	21	32	89	16

Table 2: Thicknesses of the ASC and ESC component materials prepared in this study (μm).

	ACCL	Anode-support	AFL	Electrolyte	Barrier layer	CFL	CCCL
ASC	30 (Ni-10ScSZ)	850 (Ni-8YSZ)	10 (Ni-8YSZ)	5 (8YSZ)	3 (GDC)	30 (LSCF-GDC)	35 (LSCF)
ESC	10 (Ni-10ScSZ)	-	20 (Ni-10ScSZ)	160 (10ScSZ)	3 (GDC)	30 (LSCF-GDC)	35 (LSCF)