

Design and Development of Coking Tolerant Paper-Structured Catalyst for Biogas Reforming in SOFC

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**Design and Development of
Coking Tolerant Paper-Structured Catalyst
for Biogas Reforming in SOFC**

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ABSTRACT

Solid oxide fuel cells (SOFCs) are recognized as one of the most effective technologies for the reduction of greenhouse gas emissions due to its remarkably high energy conversion efficiency and fuel flexibility accepting the direct supply of hydrocarbons including renewable biofuels. Among various biofuels, this study focused on biogas, produced by the fermentation of organic waste. When biogas, the mixture of CH_4 and CO_2 , is supplied directly to high temperature SOFC (around 750°C), within the porous anode material including Ni catalyst, CH_4 reforming proceeds to produce syngas, where the main reaction is dry reforming of methane (DRM) ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$) with the contribution of reverse water gas shift reaction ($\text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$). In power generation, although H_2 is predominant reactant ($\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$), the produced steam can convert CO to H_2 via water gas shift reaction ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$), and therefore, CO can indirectly contribute to power generation. This is the power generation process of the direct internal reforming (DIR) SOFC, leading to system downsizing and further enhancement of the electrical efficiency.

The major problem in the DIRSOFC fueled by biogas is the carbon deposition within the anode resulting in the degradation of cell performance. Therefore, improvement of catalytic activity of the anode for the DRM is indispensable. However, the degree of freedom for material selection is not so high, because Ni-yttria stabilized zirconia is typically used in terms of chemical compatibility, chemical and mechanical stabilities and electrochemical activity. Hence, this study adopted the approach to apply a catalyst layer on the anode material. The flexible paper-structured catalyst (PSC) can meet this requirement. PSCs can be prepared by a simple paper-making process using ceramic fibers (Cf) based on filtration. In this study, aiming at the suppression of coking during DRM, oxide particles having oxygen storage capacity (OSC) were tried to be dispersed in the C_f network. Here, ceria-zirconia solid solution, $(\text{Ce,Zr})\text{O}_{2-\delta}$ (CZ), was selected as a oxide support for Ni catalyst.

For the homogeneous dispersion of the CZ in the C_f network, this study adopted co-precipitation method (on-paper synthesis). From the hydroxide precipitate containing cerium, zirconium and nickel ions produced in the aqueous suspension of C_f , CZ phase could be formed by the heat treatment at 600°C after paper-making process. First of all, optimization of the developed process was conducted to maximize the catalytic performance of Ni/CZ-PSC for DRM (Chapter 3). In the on-paper synthesis of Ni/CZ particles, polyvinylpyrrolidone (PVP)

added in the suspension, which can serve as a dispersant to prevent Ni particles from agglomeration, was confirmed to enhance the porosity of the Ni/CZ. NaBH₄ added as a reduction agent to form Ni metal from Ni²⁺ in both the precipitate and the aqueous solution of the suspension at room temperature was confirmed to enhance the Ni retention efficiency during paper-making process. In the DRM test at 750°C, it was demonstrated that co-addition of PVP and NaBH₄ contributed to the improvement of the catalytic performance of the Ni/CZ-PSC.

The effect of CeO₂/ZrO₂ weight ratio on the catalytic performance of Ni/CZ-PSC was investigated (Chapter 4). For the weight ratio of 0.5, 1.0 and 2.0, corresponding to $x = 0.2$, 0.4 and 0.6 in (Ce _{x} Zr_{1- x})O₂, DRM test was carried out at 750°C under the supply of 40 mL min⁻¹ (GHSV = 3800 h⁻¹) of a simulated biogas mixture (CH₄:CO₂ = 20:20 mL min⁻¹). STEM observation revealed that the Ni particles grown on the CZ support became smaller in the order of $x = 0.2$ (29 nm), 0.4 (18 nm) and 0.6 (15 nm). The results of H₂-TPR measurement indicated that at $x = 0.4$ and 0.6 the rate of Ni particles having strong interaction with CZ particles was higher compared to $x = 0.2$. This strong interaction prevents Ni particles from agglomeration and coarsening, contributing to the enhancement of stability during DRM. Moreover, due to the high OSC of CZ, lattice oxygen-mediated surface reaction takes place to consume carbonaceous species deposited on the Ni surface during DRM. This effect was more pronounced for $x = 0.4$ and 0.6, resulting in the excellent coking tolerance of these PSCs.

For DRM, catalytic performance of the Ni/CZ-PSC was compared to the Ni-loaded PSC without the dispersion of promoter oxide particles (Ni-PSC) and the Ni-loaded hydrotalcite (HT)-dispersed PSC (Ni/HT-PSC) (Chapter 5). In the DRM tests performed in the temperature range of 650-800°C, Ni/CZ-PSC exhibited superior catalytic performance to Ni-PSC and Ni/HT-PSC, especially, excellent coking tolerance above 700°C. This superiority of Ni/CZ-PSC came from OSC of CZ and well-dispersion of CZ by the on-paper synthesis. It has been concluded that Ni/CZ-PSC is a promising candidate of the catalyst layer to realize DIRSOFCs.

500 h durability test of DIRSOFC fueled by the simulated biogas was conducted at the constant current density of 100 mA cm⁻² for the PSC/SOFC stacks (Chapter 6). In the case with Ni-PSC, stable power generation could not be achieved because of the rapid degradation in catalytic activity of the Ni-PSC caused by Ni coarsening and severe coking. For Ni/HT-PSC, because the strong interaction between Ni and (Mg,Al)O support derived from HT could lead to form fine Ni particles and prevent Ni agglomeration, high CH₄ conversion could be kept during the durability test. However, also in this case, rapid degradation occurred. In the post-test observation, serious

carbon deposition was observed within the porous anode functional layer, suggesting that incomplete reforming of CH_4 within the Ni/HT-PSC, resulting in the accumulation of intermediate carbonaceous species at the adjacent anode material which brought about coking to hinder the diffusion of reactants and products within the porous anode. In the case with Ni/CZ-PSC, stable cell performance was achieved, demonstrating that Ni/CZ-PSC can function as the catalyst layer to realize DIRSOFC technology.

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Chapter 1: Introduction

1.1 Research background

In order to overcome the present environmental problems and energy security issues, in Dec 2015, the Paris Agreement was adopted to suppress the increase in global mean temperature within 2°C compared to the pre-industrial era. Renewable resources are expected to provide almost 30% of world power demand in 2023 [1]. Photovoltaic and wind power generations are rapidly introduced in environmentally-advanced countries, however, in spite of the most abundant renewable resources in the earth, biomass utilization is not spread widely. Among renewable energies, only biomass has the characteristics of fuel. Therefore, in biomass utilization, generally, it is converted to thermal energy by combustion process to operate heat engine systems. Rather large energy input for the collection of biomass resources and the insufficiency of power generation efficiency of heat engine systems hinder the spread of biomass utilization.

Compared with the conventional power generation systems based on heat engine, fuel cells, electrochemical conversion device, exhibits higher efficiency in the output power range less than several hundred kW level, especially, has double efficiency at the smallest power range less than 5 kW level, because they are free from Carnot limitation and the irreversible losses peculiar to engine systems such as friction and heat transfer losses are minimized. Among various types of fuel cells, solid oxide fuel cells (SOFCs), operated in the temperature range of 600-900°C have the highest power generation efficiency of 50-60% due to the fast reaction kinetics and capability of internal fuel processing (Overall efficiency: 80-90% with the utilization of waste heat as a hot water) [2-4]. In principle, SOFC can accept any hydrocarbon fuels including renewable biofuels without prior fuel processing to produce hydrogen (H_2), whereas other types of fuel cells operated at lower temperature such as polymer electrolyte fuel cell (PEFC) and phosphoric acid fuel cell (PAFC), operated at around 80 and 200°C, respectively, accept only pure hydrogen [5].

Making full use of the fuel flexibility of SOFC, the concept of direct internal reforming (DIR) operation is being investigated by several research groups aiming at system downsizing and further enhancement of the energy conversion efficiency [6]. In operating DIRSOFC, at above 700°C, a hydrocarbon fuel such as CH_4 , C_3H_8 , methanol etc. mixed with reforming agent such as H_2O and CO_2 , is directly supplied to porous anode material containing Ni which can function as a reforming catalyst to produce H_2 -CO mixture (syngas). Then, the produced syngas is electrochemically oxidized to produce electricity.

Among various types of fuel, this study focused on biogas, the near-naturally produced gaseous biofuel via the fermentation of organic waste, typically composed of 60% CH₄ and 40% CO₂ with trace impurities such as H₂S, because the biogas-fueled DIRSOFC, the fusion of renewables and highly-efficient electrochemical conversion technology, has a potential to become an ultimate zero-emission distributed power generator to contribute to the realization of decarbonized society.

1.2 Technical challenges of biogas-fueled DIRSOFC

The major problem in the biogas-fueled DIRSOFC is the deactivation of elementary processes of dry reforming of methane (DRM) ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$) to cause carbon deposition within the porous anode material resulting in the degradation of cell performance. Therefore, improvement of the catalytic activity of the anode for DRM is indispensable. However, the degree of freedom for material selection is not so high, because Ni-yttria stabilized zirconia (YSZ) or Ni-scandia stabilized zirconia (ScSZ) is typically used in terms of chemical compatibility, chemical and mechanical stabilities and electrochemical activity. Hence, this study adopted the approach to apply a catalyst layer on the anode material, which is required to have the properties enabling cartridge-like application. The flexible paper-structured catalyst (PSC) can meet this requirement [7].

1.3 Solid oxide fuel cell (SOFC)

1.3.1 Operating principle

SOFCs have been intensively researched since the 1960s. As shown in Fig. 1.1, an SOFC operated in the temperature range of 600-900°C comprises an oxygen-ion conducting solid electrolyte sandwiched by an anode for electrochemical oxidation of a fuel and a cathode for oxygen reduction.

Oxygen supplied to the cathode is reduced to oxygen ions (O^{2-}) at the interface between cathode and electrolyte (R1). The O^{2-} is transported from cathode to anode sides through electrolyte under the large difference in the oxygen partial pressure between cathode and anode sides as the driving force. At the interface between anode and electrolyte, H₂ supplied to the anode is electrochemically oxidized by the O^{2-} transported from cathode side to produce steam (H₂O) and electron (R2). The generated electrons pass around external circuit toward cathode to be used for the Reaction (R1). This means that electricity can be extracted directly from a fuel,

here H_2 , unlike heat engine generator via conversion of chemical energy of H_2 to thermal energy by combustion process.

In high temperature SOFC, not only pure H_2 but also reformat containing syngas can be supplied as a fuel. In this case, CO can also contribute to electricity generation (R3) [2].

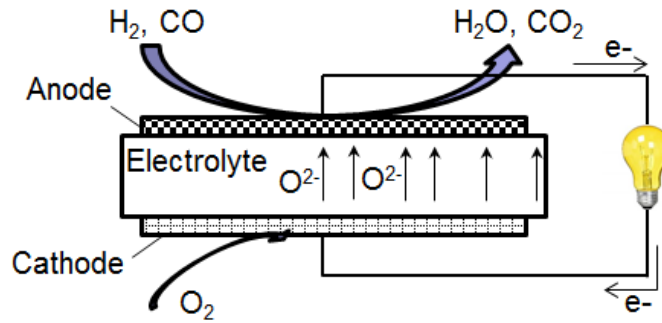
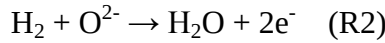
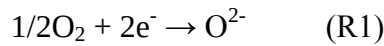


Fig. 1.1: Operating principle of SOFC.



Electromotive force (Emf) of SOFC is given by the Nernst equation (E1) using oxygen partial pressures of cathode and anode sides, $p_{O_2,c}$ and $p_{O_2,a}$, respectively.

$$Emf = \frac{RT}{4F} \ln \frac{p_{O_2,c}}{p_{O_2,a}} \quad (E1)$$

1.3.2 Cell components

1.3.2.1 Electrolyte

Electrolyte must have sufficient oxygen-ion conductivity, and also must act as a separator of fuel and air to avoid direct oxidation of a fuel. Therefore, electrolyte has to be dense and chemically stable in the high oxygen partial pressure gradient. Although there are many types of highly conductive solid oxides, 8 mol% yttria-stabilized zirconia (8YSZ) and 10 mol% scandia-1 mol% ceria-stabilized zirconia (10ScSZ), whose ionic conductivities at 800°C are 0.22 and 0.14 S cm^{-1} , respectively, are commonly used as an electrolyte for SOFC in the viewpoints mentioned above [8,9]. Among the cell components, electrolyte has the highest resistivity, and therefore, ohmic resistance of the electrolyte can become a main factor of the internal resistance of SOFC.

For getting higher electrochemical performance of SOFC, the electrolyte layer should be as thin as possible. In the case of a planar electrolyte-supported cell (ESC), the maximum thickness of 8YSZ should be 100-150 μm level [10].

1.3.2.2 Anode

Ceramic (electrolyte)-metal composite, so-called cermet, is used as an anode material to expand the electrochemical reaction sites, triple-phase boundary (TPB), where reactant gases, electronic conductor and oxygen ion conductor exist together. Smooth gas diffusion to TPB is essential, and therefore, sufficient porosity of around 35% is required for the cermet anode [10,11]. Ni-, Cu- and alloy-based cermets have been widely investigated [12-28]. Among them, Ni is commonly utilized because of high electrochemical activity, high electrical conductivity, reasonable cost and high chemical compatibility (Fig. 1.2) [29]. However, for the typical Ni-YSZ and Ni-ScSZ cermet anodes, Ni coarsening in a reducing atmosphere can become a cause of cell performance degradation [19,30]. When a hydrocarbon fuel is supplied to the anode, because Ni has a high activity for hydrocarbon cracking at high temperature [31,32], carbon formation (coking) will occur to block the TPB as well as the active surface of Ni for fuel reforming, resulting in rapid degradation of cell performance.

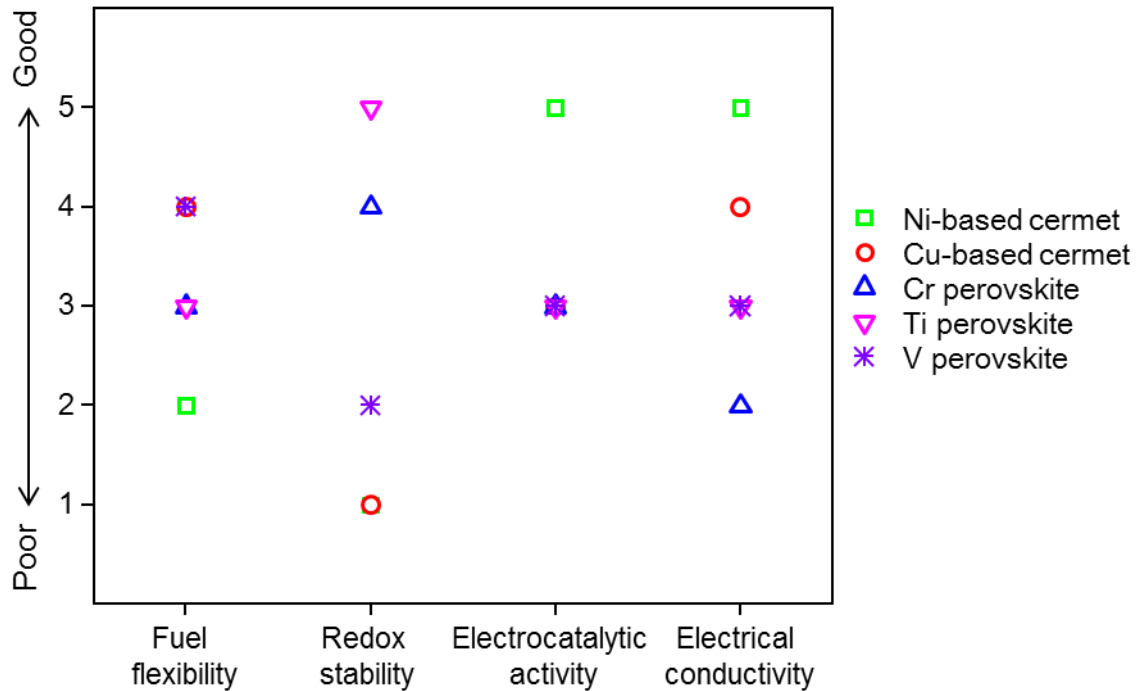


Fig. 1.2: Qualitative indexing of different SOFC anode materials in terms of electrical conductivity, electrochemical activity, redox stability and fuel flexibility [29].

To overcome the coking problem of Ni-based cermet in the direct hydrocarbon utilization, reforming activity of the cermet has to be improved by adding other elements (or components) or replacing a conventional component material with a new material. Oxide materials having the property of mixed ionic and electronic conductor (MIEC), such as fluorite (ceria-based), rutile, perovskite, double perovskite, etc., are promising candidates as a coking tolerant anode material [33-39], however, in the viewpoints of chemical compatibility, thermal expansion matching and electrochemical activity, practically, it is still challenging to replace Ni-YSZ or Ni-ScSZ with these alternative materials.

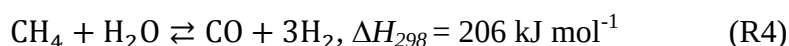
1.3.2.3 Cathode

State-of-the-art SOFC cathode material is an electron conducting oxide. Most common is the perovskite-type lanthanum manganite, LaMnO_3 , in which La is partly replaced by Sr ($(\text{La,Sr})\text{MnO}_3$ (LSM)). A site or B site composition of the perovskite strongly affects the electrical and chemical properties of the cathode. Chemical compatibility of electrode with the electrolyte is especially important to reduce the polarization resistance for SOFC operation. For example, formation of insulating $\text{La}_2\text{Zr}_2\text{O}_7$ at the interface between cathode and electrolyte and segregation of SrO with an excess of Mn (1-10%) at sintering temperature above 1300°C leads to the degradation of the cathode performance [40]. Normally, cathode is composed of two layers. Cathode functional layer (CFL) (LSM/YSZ), the mixture of ionic and electronic conductors, which functions as electrochemical reaction site, is placed on the electrolyte. On the CFL, LSM is placed as a current collector layer. Recently, the mixed ionic-electronic conductor $(\text{La,Sr})(\text{Co,Fe})\text{O}_2$ (LSCF) is a good candidate for SOFC operation at intermedia/low temperatures due to its high electronic and ionic conductivities, and high catalytic activity for oxygen reduction. However, as the rapid drop in ionic conductivity was reported with temperature, the mixtures of LSCF and YSZ (LSCF/YSZ) [41,42] or GDC (LSFC/GDC) [43,44] were commonly used to serve as a CFL for the improving cathode performance [45].

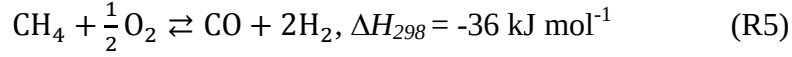
1.4 Dry reforming of methane (DRM)

1.4.1 DRM reaction

Reforming technologies generally rely on steam reforming of methane (SRM) (R4) to produce syngas with H_2/CO ratio of 3.

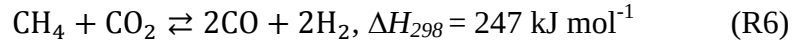


The SRM reaction is a strong endothermic process for which thermal energy must be provided accompanied by additional CO₂ emission [46].

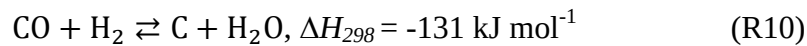
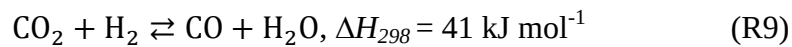
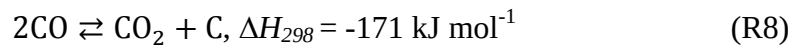
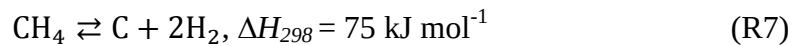


Partial oxidation of methane (POM) (R5) is a mildly exothermic process while conventional SRM process is highly endothermic. Therefore, POM reactor is more economical to heat, on other words, energy saving could be achieved. However, hot-spot is formed during the POM process, especially under high space velocity, which causes the difficulty in process control and greater risks [47].

The DRM reaction (R6), whose endothermicity is comparable to SRM, is an attractive process which offers several advantages: (a) consumption and transformation of CO₂ into valuable syngas, and (b) high availability in some gas fields such as biogas from fermentation of biomass which has the composition of CH₄ and CO₂ relatively comparable with ratio of reactants in R6 [48].



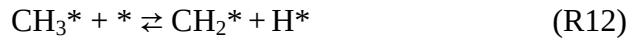
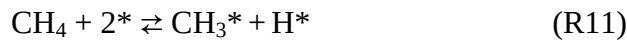
Actually, DRM process includes the following reactions.



CH₄ decomposition (R7) and Boudouard reaction (R8) are the major reactions to produce coke, which can cause rapid deactivation of reforming catalyst. In the thermodynamic point of view, endothermic R7 and exothermic R8 become predominant reactions of coking at higher (above 700°C) and lower temperature (below 650°C), respectively [48]. Kinetically, if the coke produced by R7 is readily consumed by the supplied CO₂ via the reverse Boudouard reaction, coke does not accumulate, and overall reaction can be expressed as R6 (DRM). However, stoichiometric composition for DRM, CH₄/CO₂ = 1, is in the carbon deposition region in the

temperature range of SOFC [49]. Therefore, a support material (promoter) which has ability to remove carbonaceous species from the metal catalyst surface is indispensable [48].

The adsorption and dissociation of CH₄ on nickel related to the direct cracking of a C-H bond. This requires the sufficient energy to against a barrier of about 52 kJ mol⁻¹ and CH₄ hits the free nickel site with free neighbouring sites [50]. The rate of adsorption is an order of magnitude higher on the open (110) plane than on the dense (111) plane of nickel surface [51]. The dissociation of CH₄ and carbon formation on the nickel catalyst is assumed by rate-determining steps (R11-R17) [52].



Where the asterisk (*) is an active site and CH_x* with x = 0, 1, 2, 3 are chemisorbed species. C_{bp} is a carbon atom in the bulk phase of nickel crystal at the subsurface site (ss1) on which cracking reactions take place, and C_{sf} is a carbon atom at the subsurface site (ss2) where is interface of nickel surface and carbon separating out of the nickel particle. C_w is a carbon at the whisker site (ws) under the whisker carbon formation (filamentous carbon).

1.4.2 Catalysts for DRM reaction

Ni, Ru, Rh, Pd, etc, with oxide supports such as SiO₂, Al₂O₃, MgO, TiO₂, CaO, CeO₂, ZrO₂ or La₂O₃ have been reported as the catalysts for promoting DRM process [53]. Although noble metals are active and less sensitive to coking, these applications are restricted by the cost issue [48]. Therefore, at present, Ni-based catalysts are commonly selected, but coking tolerance has to be improved by the introduction of supports or promoters [54].

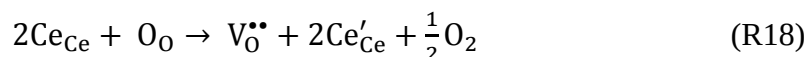
1.4.2.1 Oxide supports

Typical support materials, on which metal catalyst particles are loaded, are oxides such as silica, alumina, zirconia and other mesoporous species [55]. Oxide supports have the functions to enlarge the area of active sites and stabilize metal catalyst particles to suppress agglomeration, even when they are inactive to reforming reaction.

Many oxide supports that can contribute to surface reaction as promoters have been reported so far [56-57]. Because of the high interaction with CO₂, they can promote the dissociative adsorption of CO₂ to form CO and oxygen adatom (O_(ads)), which contributes to the oxidation of CH_{x(ads)}, intermediate species adsorbed on a metal catalyst surface derived from CH₄ decomposition [58]. For example, alkaline and alkaline-earth metal oxides such as K₂O and CaO, respectively, with strong basicity promote the dissociative adsorption of CO₂ on the adjacent Ni surface [59,60]. Especially, MgO, completely miscible with NiO to form stable solid solution (Ni,Mg)O due to the quite similar crystal structure, can retard the reduction process to form Ni metal, resulting in the formation of fine Ni particles [61].

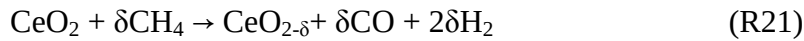
Chen et al. studied the effect of Cu addition for Ni/SiO₂. The results showed that Cu acted as a stabilizer for structure of the active site on Ni surface to create the new active species (Ni-Cu alloy) for CH₄ cracking, preventing the deactivation of Ni catalyst caused by the Ni surface rearrangement due to the absorbed carbon during DRM. The formed Ni-Cu promoted the C-H bond scission reaction to produce CH_x species, which is the main step to activate the DRM process (refer to R11-R17), and prevented the accumulation of fibrous carbon on the Ni particles due to Ni-Cu formation which reduced the Ni atoms for carbon deposition [62].

CeO₂ and CeO₂-based solid solution are well-known promoters for hydrocarbon reforming due to its redox ability (Ce(IV) ↔ Ce(III)), in other words, oxygen storage capacity (OSC). Under the reducing atmosphere, a part of Ce(IV) in CeO₂ is reduced to Ce(III) accompanied by the oxygen release to form CeO_{2-δ} having oxygen vacancies in the crystal structure. The reaction can be expressed by the Kroger-Vink notation (R18).



Oxygen vacancy of the reduced ceria can react with CO₂ to form completely oxidized ceria and CO (R19). On the other hand, lattice oxygen in the CeO₂ can react with carbon chemisorbed on the surface to form reduced ceria and CO (R20). With the same mechanism, lattice oxygen in

the CeO₂ can react with CH₄ to form reduced ceria, CO and hydrogen. (R19) + (R20) is the carbon removal reaction (reverse Boudouard reaction), and (R19) + (R21) is the methane dry reforming reaction. This means that overall reactions are promoted by the lattice-oxygen-mediated cycle originated from OSC nature of CeO₂ [54,63,64].



The fluorite CeO₂ accepts various foreign cations as a dopant to form solid solutions, such as CeO₂-Al₂O₃, CeO₂-Fe₂O₃, CeO₂-MnO₂, CeO₂-SnO₂, CeO₂-Ga₂O₃, CeO₂-RE₂O₃ (RE = La, Sm, Gd, Yb, Y), CeO₂-TiO₂ and CeO₂-ZrO₂ [54]. Among them, CeO₂-ZrO₂ (Ce_xZr_{1-x}O₂) is extensively utilized in many applications due to its considerably high OSC of 456 μmol CO g⁻¹ at the optimum x of 0.5 [54].

1.4.2.2 Bimetallic and perovskite catalysts

The bimetallic catalyst of Ni-Co/Al₂O₃-MgO with the spinel-like framework structure mix of Ni_xMg_{1-x}Al₂O₄ and Co_xMg_{1-x}Al₂O₄ prepared by co-precipitation were reported to have excellent performance for 2000 h DRM. Because of the strong metal-supported interaction from the spinel structure, the small Ni-Co (in general formula of Ni-Co-Al-Mg-O) bimetallic particles (less than 10 nm) were formed, enhancing the contact of carbon species (on metal surface) with the adjacent activated CO₂ (on support oxide), leading to the carbon suppression in comparison with Ni alone [65,66]. Moreover, the combining of Al and Mg oxides provided the high surface area and thermal stability for the catalyst.

Partial substitution of A or B site of perovskite-type oxides (ABO₃, A: lanthanide, B: transition metal) can create defects and promote oxygen mobility within the crystal lattice, and the nonstoichiometric perovskites exhibit excellent properties as functional materials for SOFC application [67,68]. It is reported that the introduction of Sr to Ni-La₂O₃ to form the spinel catalysts of La_{1-x}Sr_xNiO₃ (x = 0-0.1) and La_{2-x}Sr_xNiO₄ (x = 0.0-1.0) produced highly-dispersed Ni particles and enhanced synergetic effect of bimetallic compound, offering the high catalytic activity and stability for DRM [62,69].

1.5 Flexible structured catalyst

1.5.1 Paper-structured catalyst (PSC)

As mentioned in Sec. 1.2, for realizing DIRSOFC, flexible structured-catalyst, which can be applied on an anode material without change in the configuration of a conventional cell stack, is highly desired. Using an inorganic fiber, ceramic ($\text{SiO}_2\text{-Al}_2\text{O}_3$) fiber (Cf) or zirconia fiber (Zf), paper-like framework can be fabricated by the same process as the simple filtration process to make Japanese traditional handmade paper [70-72]. As shown in Fig. 1.3(a), in this inorganic fiber network, metal catalyst particles are dispersed by the impregnation process to have paper-structured catalyst (PSC) [70]. Due to the unique network structure with high porosity over 80%, three-dimensional diffusion of reactant gases readily proceeds to enhance the contact efficiency of the reactants with catalyst particles. 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 as shown in Fig. 1.4 [73].

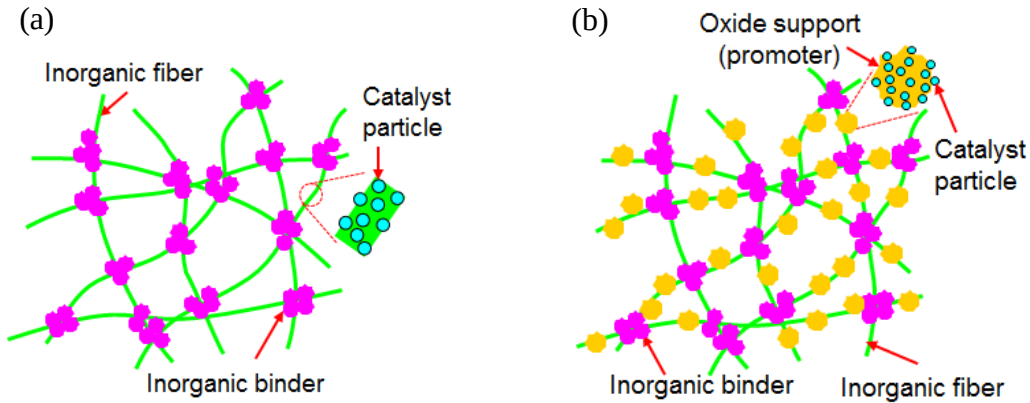


Fig. 1.3: Schematic illustration of inorganic fiber network of PSC (Inorganic fiber: ceramic ($\text{SiO}_2\text{-Al}_2\text{O}_3$) fiber (Cf) or zirconia fiber (Zf)): (a) with the dispersion of metal catalyst particles, (b) with the dispersion of metal catalyst-loaded oxide particles [70].

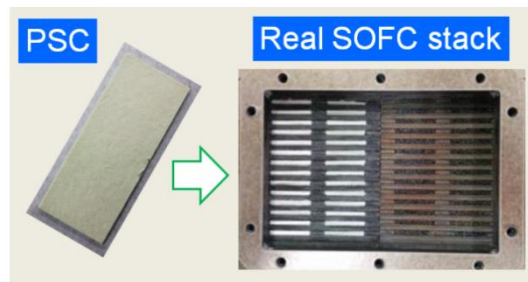


Fig. 1.4: Insertion of PSCs to a real SOFC stack like cartridge [73].

Kitaoka et al. developed metal nanoparticles-loaded PSCs with the dispersion of ZnO, which exhibits the high thermal stability, gas permeability and excellent catalytic performance in a wide range of catalytic applications [72,74-80]. Cu/ZnO for methanol steam reforming (at 200-300°C) [74,75], gold-silver nanoparticles (AuAgNPs) for aqueous reduction of 4-nitrophenol to 4-aminophenol (at 25°C) and CO oxidation [76,77], Pd-based PSC for alcohol oxidation [78,79], and Pt nanoparticles on ZnO paper (PtNPs@ZnO) for NO_x removal (150-350°C) [80], were studied.

Shiratori et al. are trying to apply PSC technology to high temperature energy conversion device, SOFC [70,73,81-87]. For obtaining commercial level stability of DIRSOFC running on biofuels, in addition to the prevention of coking, the suppression of strong temperature gradient generated in SOFC caused by endothermic reforming reactions is one of the most important requirements. Therefore, they designed a functionally-graded catalytic field composed of the array of PSC strips aiming at the homogenization of in-plane temperature distribution during DIR operation. The developed PSC array was attached to SOFC anode and DIRSOFC fueled by simulated biogas was tested at 800°C, resulting in stable electrochemical performance under the current density of 0.2 A cm⁻² with the degradation rate of 1.7%/1000 h [81].

In the paper-making process, any functional materials can be easily dispersed into the inorganic fiber network. Mg-Al layered double hydroxide (Hydrotalcite (HT): [Mg₆Al₂(OH)₁₆CO₃]4H₂O) was selected as a promoter of reforming reaction, and high performance PSC, Ni-loaded HT-dispersed PSC (9 wt% Ni/HT-PSC), was developed [82]. By the application of the Ni/HT-PSC to a SOFC anode, stable operation of DIRSOFC with simulated biogas mixture (CH₄/CO₂ = 1) containing 5 ppm H₂S was achieved at 800°C for 200 h at 0.2 A cm⁻² which was previously unattainable. Ni/HT-PSC contributed to remarkable improvement of sulfur tolerance, because it keeps high methane conversion for DRM close to 90 % even in the presence of trace H₂S, and therefore, the supply of H₂ in the reformat to the electrochemically active electrolyte/anode interface was uninterrupted [83].

1.5.2 Another type of catalytic ceramic-papers

Tuler group developed the catalytic ceramic-papers with Co₃O₄-CeO₂ using at 120°C as NO_x filters employed in diesel engines [71]. Moreover, they also reported the work on Ni-based ceramic paper catalysts for the application to oxidative dehydrogenation of ethane to produce ethylene between 300 and 450°C [88], and that with the ceria promoter was proved to promote ethylene productivity [89]. Binder agent of Ytria-stabilized ZrO₂ (ZrY) can not only improve

the mechanical properties of the papers, but also enhance catalytic performance due to the coverage of Cfs and resulting interaction with the catalytic compounds [89]. For CO oxidation at 150°C, the introduction of Pt-NaY zeolite to the ceramic papers was promising [90].

1.6 DIRSOFC

Mogensen and Kammer defined a DIRSOFC as “conversion in the SOFC without pre-mixing the fuel gas with steam or CO₂, and without processing the fuel before it enters the cell stacks” [91]. This approach can contribute to make SOFC system simple and cheaper. Under practical conditions, nearly half of the heat produced by the exothermic power generation reactions could be absorbed by the internal reforming process. This means that the system efficiency can be enhanced by eliminating the energy penalty associated with heat transfer for external reforming.

1.7 Concept of PSC/SOFC stack for biogas-fueled DIRSOFC

Biogas-fueled DIRSOFC is a promising technology as a compact distributed power generator, especially in developing countries abundant in biomass resources. As mentioned in Sec. 1.2, technical challenge is the creation of a new concept without any change in the established cell components that contribute to commercial level stability of SOFC.

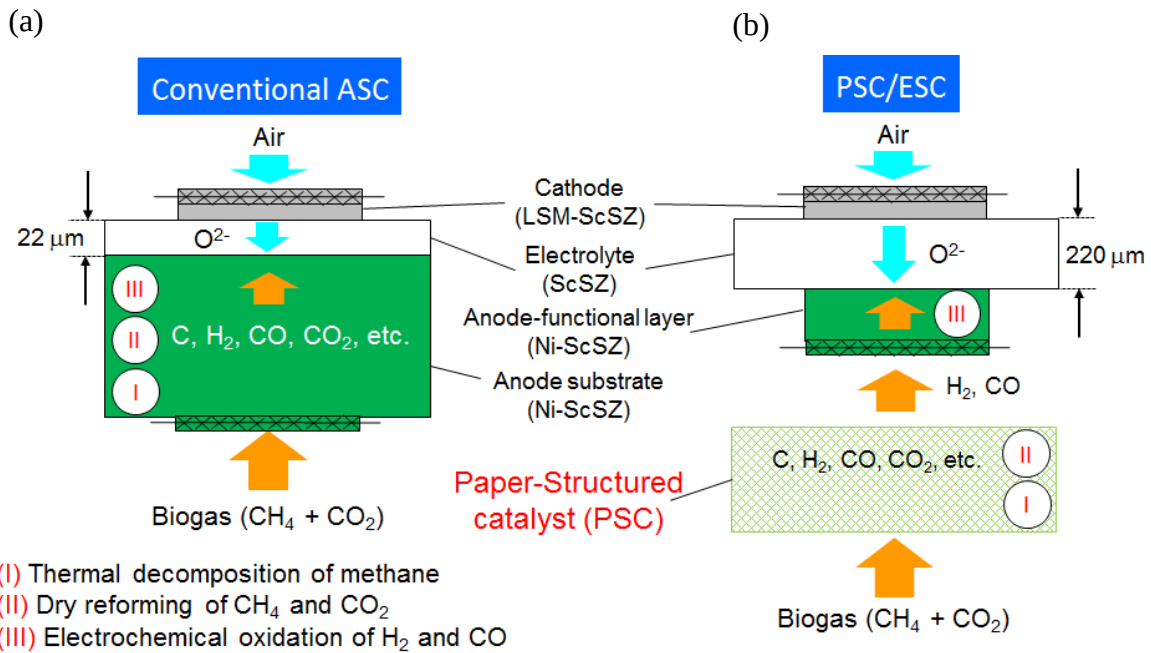


Fig. 1.5: Illustration showing the reactants in the biogas-fueled DIRSOFC for (a) a conventional ASC and (b) the PSC/ESC stack (PSC integration concept).

Reactants in the biogas-fueled DIRSOFC are schematically illustrated in Fig. 1.5. In the case of a conventional anode-supported cell (ASC) (Fig. 1.5(a)), when CH_4 and CO_2 are supplied to the anode, DRM (R6) takes place within the porous domain of the anode to produce H_2 and CO , followed by the electrochemical oxidations to H_2O (R2) and CO_2 (R3), respectively, to generate electricity and heat. In principle, this concept is possible, but actually, impossible due to the insufficient catalytic activity of Ni-YSZ or Ni-ScSZ for DRM to cause coking and rapid fall in the cell temperature attributed to endothermicity of DRM to cause destruction of the cell, especially thin electrolyte. To overcome this issue, the concept of PSC/SOFC stacking has been proposed (Fig. 1.5(b)) [82]. By mounting PSC on the anode side of electrolyte-supported cell (ESC) (to form PSC/ESC stack), functions of reforming and electrochemical reaction sites can be well-separated to eliminate the risks of coking within the anode and rapid cool-down of the cell.

1.8 The need for coking-tolerant PSC

Considering commercial application of PSCs, the catalyst particles dispersed in the Cf network should be composed of non-precious metal and oxide promoters without the choice of precious metal catalyst. As mentioned in Sec. 1.5.1, Ni/HT-PSC exhibits excellent catalytic activity and tolerance to several ppm H_2S poisoning at 800°C . However, even this PSC, coking is still problem especially below 800°C . Because typical operating temperature of state-of-the-art SOFC is in the range of $650\text{--}750^\circ\text{C}$, this study aimed at the development of a PSC tolerant to coking in this temperature range for the feed of $\text{CH}_4\text{--CO}_2$ mixture ($\text{CH}_4/\text{CO}_2 = 1$) simulating biogas.

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Chapter 2: Experimental approach

2.1 Paper-structured catalyst preparation

2.1.1 Raw material

- Ceramic fiber (Cf) (composed of 52 wt% SiO_2 and 48wt% Al_2O_3) with an average length of approximately 500 μm and width of 2 μm (Ibiden Ltd., Japan)
- Cationic polymer poly diallyldimethylammonium chloride (PDADMAC) (Sigma-Aldrich LCC, USA)
- Anionic polymer acrylamide-co-acrylic acid (A-PAM) (Fujikasui Engineering Co., Ltd., Japan)
- Yttria-stabilized zirconia sol (Zs) (20 wt% solid, Nissan Chemical Industries Ltd., Japan)
- Organic pulp fiber as solid base
- Polyvinylpyrrolidone (PVP) (Wako Pure Chemical, Japan)
- NaOH, NaBH_4
- $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2$ (Chameleon Reagent, 98%)
- Hydrotalcite $([\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3] \cdot 4\text{H}_2\text{O})$, Wako Pure Chemical, Japan)

2.1.2 Preparation procedure

In this study, by the paper making process to fabricate the paper-structure fiber network, two procedures for PSC preparation using the impregnation and co-precipitation methods were shown in Fig. 2.1(a) and (b), respectively. The detail description will be expressed in Sec. 3.2.1, 4.2.1, and 5.2.1 of Chapter 3, 4, and 5, respectively.

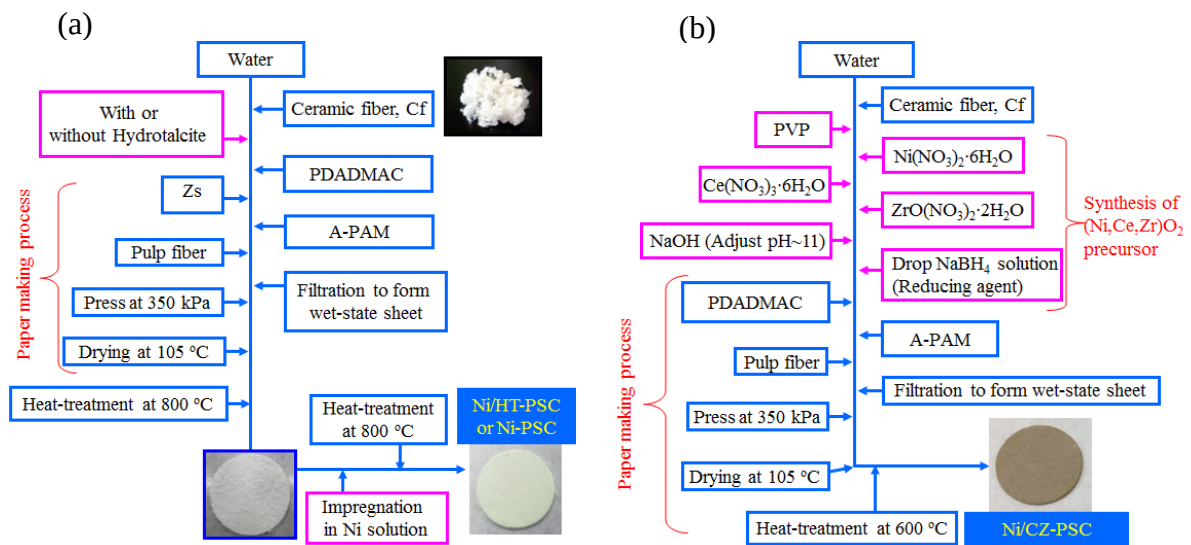


Fig. 2.1: Procedure of PSC preparation by (a) impregnation and (b) co-precipitation.

2.2 SOFC single cell fabrication

The SOFC single cell (electrolyte-supported cell (ESC)) schematically shown in Fig. 2.2 was fabricated by the following procedure. Dense electrolyte plate of 10ScSZ (scandia-stabilized zirconia: 10 mol% Sc_2O_3 – 1 mol% CeO_2 - ZrO_2) with an average thickness of 250 μm and area of $2 \times 2 \text{ cm}^2$ was prepared from 10ScSZ powder (Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan). Inks of 56wt% NiO : 44wt% 10ScSZ and 80wt% NiO : 20 wt% 10ScSZ were screen-printed in that order on the surface of the electrolyte plate as an anode functional layer and an anode current collector layer, respectively, followed by sintering at 1200°C for 5 h to form a porous anode with an area of $1.4 \times 1.4 \text{ cm}^2$. GDC ($\text{Gd}_{0.10}\text{Ce}_{0.90}\text{O}_2$) ink was screen-printed on the opposite side of the anode followed by sintering at 1200°C for 5 h to form a barrier layer with an area of $1.6 \times 1.6 \text{ cm}^2$. Then, inks of $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}(\text{Co}_{0.02}\text{Fe}_{0.80})\text{O}_{3-x}$ (LSCF) – GDC (Fuel Cell Materials, USA) and LSCF (Fuel Cell Materials) were screen-printed in that order on the barrier layer as a cathode functional layer and a cathode current collector layer, respectively, followed by sintering at 900°C for 5 h to form a porous cathode with an area of $1.4 \times 1.4 \text{ cm}^2$. Pt mesh was applied to both the anode and cathode sides as a current collector.

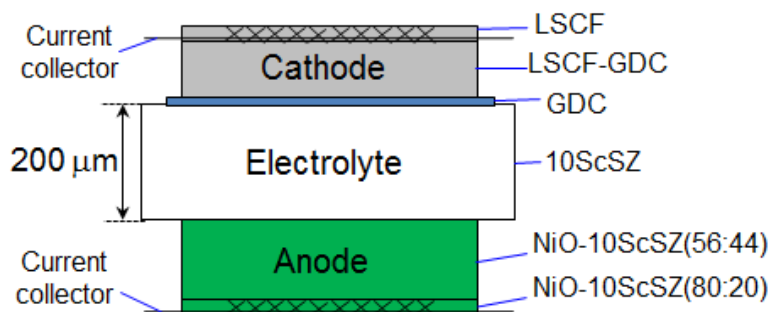


Fig. 2.2: Schematic illustration of the ESC.

2.3 Set-up for testing catalytic performance

2.3.1 Dry reforming test

Using the prepared PSCs, dry reforming of CH_4 was performed in a fixed-bed reactor. For each type of PSC, as shown in Fig. 2.3, two donut-shaped PSCs with an outer diameter of 20 mm, inner diameter of 6 mm, and thickness of 1.1 mm were mounted in an alumina cylinder and heated from room temperature to 750°C under N_2 atmosphere for 4 h.

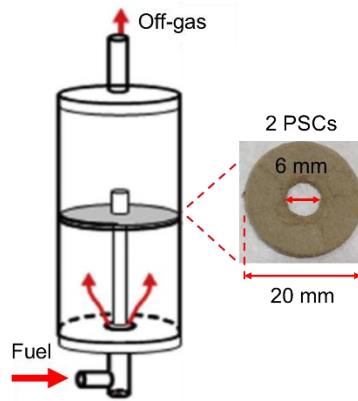


Fig. 2.3: Schematic illustration of the fixed-bed reactor for the dry reforming tests with PSCs.

2.3.2 Electrochemical test

Figure 2.4 shows the experiment of cell operation and electrochemical measurements: (1) A square-shaped alumina holder with a pocket area of $2 \times 2 \text{ cm}^2$ containing the SOFC cell, and the set of electrical wires for connecting the anode, cathode and reference electrodes of cell to the SOFC testing system (3); (2) Horizontal electric furnace for heating the cell; (3) Automatic SOFC testing system (Toyo Corporation, Japan) for gas supply into the cell and the electrochemical measurements of overvoltage and current-voltage (I-V); and (4) Frequency response analyzer (VersaSTAT 3, Princeton Applied Research, USA) for electrochemical impedance spectra (EIS) measurement. The detailed gas supply conditions and electrical parameters for electrochemical measurements will be described in Sec. 6.2.3 (Chapter 6).

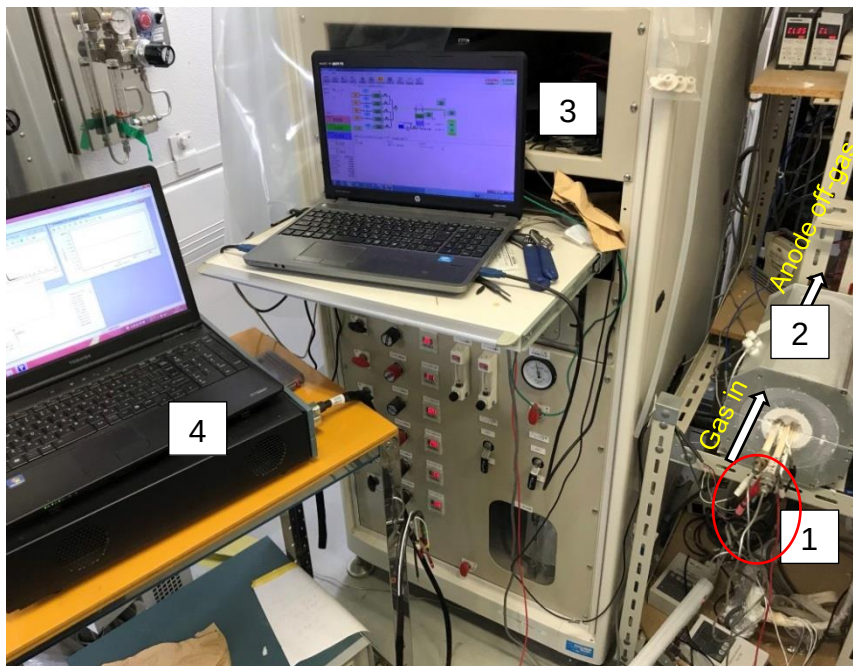


Fig. 2.4: Experiment for cell operation.

2.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) is used to analyze the atomic and molecular structure of a crystal. By measuring the angles and intensities of diffractions, the crystalline structure of material such as phases, lattice parameters, crystallite sizes, so on, is identified. Some equations for the diffraction of X-rays were built but the equation of W. H and W. L Bragg has been considered as more powerful method using monochromatic X-rays. In Bragg's law, atoms are considered in a line and each atom scatters the X-rays in all directions, but constructive interference take place when:

$$n \lambda = 2d_{\text{dhk}} \sin \theta \quad (\text{E1})$$

Where n is the order of diffraction, λ is the wavelength, d is the interatomic distance (spacing between diffracting planes), and θ is the incident angle. The dhk means the three-dimensional atom lattice of a crystal.

In this study, the crystalline structures of the PSCs after reduction treatment at 750°C in 5% H₂ for 5h were analyzed by an X-ray diffractometer (Rint-Ultima III; Rigaku, Japan) with CuK α radiation at 40 kV and 40 mA with 0.02°/step for scanning. The crystallite size of Ni was calculated using Bragg's equation (E1).

2.5 Scanning electron microscopy (SEM) and scanning transmission electron microscope (STEM) with energy-dispersive X-ray spectrometer (EDX)

Microstructure morphology of the PSCs and ESC components were observed by a field emission scanning electron microscope (FE-SEM-S5200; Hitachi High Technologies, Japan) with an energy-dispersive X-ray spectrometer (EDX). EDX which is a chemical microanalysis technique provides the characterization about elemental composition and volume of each element in sample.

For the higher-magnification observation, a scanning transmission electron microscope (STEM-HD2300A; Hitachi High Technology, Japan) with two modes of scanning electron (SE) mode for scanning the surface of sample with a focused beam of electrons, and transmission electron (TE) mode which allows electrons passing through a sufficiently thin specimen to create the image of sample, was used .

2.6 Brunauer, Emmett, and Teller (BET) analysis

The porosity characterizations of the prepared PSCs including specific surface area (S_{BET}), pore size distribution, and pore volume were evaluated by the nitrogen adsorption method using

a Belsorp-mini II analyzer (MicrotracBEL Corp., Japan). About 20~30 mg of the sample was pretreated by drying at 200°C in a vacuum for 2 h. For the measurement, the sample was cooled by nitrogen liquid (-196°C), then a flow of He and N₂ was passed through the sample until the detector reading was constant. The physical adsorption of gas (adsorbate) on the surface of the solid sample (adsorbent) results from the relatively weak forces (van der Waals forces) between adsorbate molecules and adsorbent surface area. By BET theory, the specific surface area of a catalyst powder is calculated by the adsorbate (N₂) amount corresponding to a monomolecular layer on the surface of solid.

2.7 Chemical composition analysis

2.7.1 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry for detecting metals and several non-metals at low concentrations (ppm and lower). 3 mg of the Ni-loaded PSC after reduction treatment at 750°C in 5% H₂ for 5h was dissolved by the mixture of HNO₃ and HCl (volume ratio of 1:3), followed by adding 20 mL of dionized water to obtain the solution of Ni ion. This solution was then used for the ICP measurement. Ni ions in the sample ionized by an inductively coupled plasma are separated and quantified by a mass spectrometer. In this study, the amount of Ni loading in the PSCs was quantified by a Shimadzu ICPE-9000 plasma atomic emission spectrometer (AES).

2.7.2 Gas chromatography (GC)

Gas chromatography is a common type of chromatography used in analytical chemistry to separate and analyze chemical compounds which can be vaporized without decomposition. The automatic gas chromatograph (GC-20B, Shimadzu Corp.) was used for monitoring the reformat compositions from the off-gas in Fig. 2.3 and the reformates of the anode off-gas under OCV condition in Fig. 2.4. The inert gas of He was used as a carrier gas (or mobile phase). The off-gas compounds interacting with the stationary phase of chromatography column have the different retention times: H₂ (1.95 min), N₂ (4.74 min), CH₄ (6.09 min), CO (9.29 min), and CO₂ (9.78 min). The thermal conductivity detectors (TCD) were used to identify each compound and its weight percentage in the off-gas mixture. The working principle of a TCD relies on the difference of thermal conductivity between the analyzed gas/carrier gas mixture (low thermal conductivity) and carrier gas (high thermal conductivity) passing around a tungsten-rhenium filament with a current traveling through it.

2.7.3 Thermal-programmed reduction (TPR)

The reducibility of the prepared PSCs was evaluated by temperature-programmed reduction (H₂-TPR) using a BELCAT-B analyzer (MicrotracBEL Corp.) with a thermal conductivity detector (TCD). The sample of PSC after sintering in air (200 mg) was placed in a glass U-tube and heated from room temperature to 800°C in increments of 2°C min⁻¹ under a 5% H₂/Ar flow (30 mL min⁻¹). At a certain temperature, when the reduction takes place, hydrogen consumed is recorded by TCD.

2.7.4 Thermal-programmed oxidation (TPO)

After the dry reforming test, temperature-programmed oxidation (TPO) was carried out to evaluate the degree of coking in the used PSCs using a BELCAT-A analyzer (MicrotracBEL Corp.). The used PSC sample (100 mg) was placed in a glass U-tube and heated from room temperature to 800°C at a rate of 3°C min⁻¹ under an air flow of 40 mL min⁻¹. With increasing temperature under air flow, the compounds of CO and CO₂ from the oxidation of carbonaceous species in sample were analyzed by a mass spectroscopy.

2.7.5 Raman

Raman spectroscopic analysis was carried out to determine the graphitization degree of carbon formed during dry reforming using a Horiba Jobin Yvon LABRAM 300 (France) Raman microscope with an achromatic flat field monochromator together with mirror-based reflective optics and detector of charge-couple device (CCD). The wavelength region for scanning was 100–3000 cm⁻¹ using a He-Ne laser source (632.8 nm wave-length, 20 mW power).

2.5 Electrochemical measurement

2.5.1 I-V measurement

The correlation of cell voltage of an SOFC and the partial pressures of reactants and products is expressed by Nernst Equation (E2):

$$E = \text{EMF} + \frac{RT}{2F} \ln \left(\frac{P_{\text{H}_2} \cdot P_{\text{O}_2}^{\frac{1}{2}}}{P_{\text{H}_2\text{O}}} \right) \quad (\text{E2})$$

Where, EMF, electromotive force, is obtained when all the energy from the hydrogen fuel (no losses) are assumed to transform into electrical energy. Ideally, open circuit voltage (OCV) under open circuit condition is equal to EMF at standard pressure. However, OCV is normally lower than EMF due to the gas leakage or inevitable errors from experimental set up. When an

SOFC is made and put to use, the cell voltage is less than OCV due to internal losses (expressed by E3) containing activation loss of electrochemical reactions on anode and cathode, Ohmic loss of cell components, mass transport or concentration loss of reactants at the surface of the electrodes, and other problems related to fuel crossover or internal currents, etc.

$$E_{\text{cell}} = \text{OCV} - i(R_a + R_e + R_c) - (\eta_{\text{act},a} + \eta_{\text{act},c}) - (\eta_{\text{conc},a} + \eta_{\text{conc},c}) \quad (\text{E3})$$

Where i is current density; R_a , R_e , and R_c are ohmic resistances of anode, electrolyte and cathode, respectively; $\eta_{\text{act},a}$ and $\eta_{\text{act},c}$ are the activation overvoltages of anode and cathode, respectively; $\eta_{\text{conc},a}$ and $\eta_{\text{conc},c}$ are the concentration overvoltages of anode and cathode, respectively. All internal losses increase with increase of current density, resulting in the drop of cell voltage. Fig. 2.5 is the typical i - V curve of an SOFC.

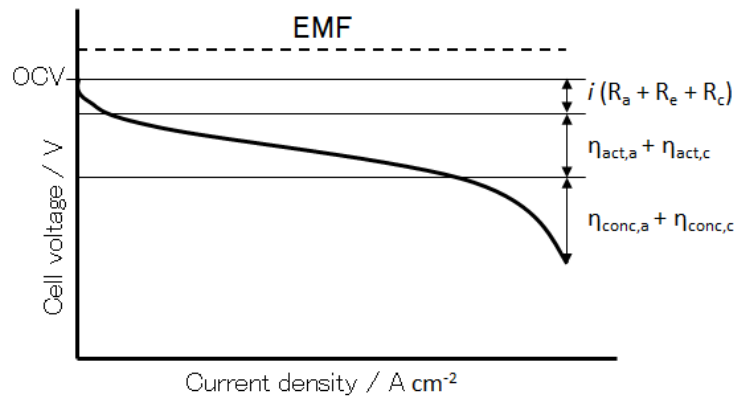


Fig. 2.5: Typical i - V characteristic of an SOFC.

2.5.2 Electrochemical impedance spectroscopy (EIS)

A frequency response analyzer (VersaSTAT 3, Princeton Applied Research, USA), which generates the potential perturbation signal and determines the impedance response, was used for the electrochemical impedance spectroscopy (EIS) measurement of SOFC single cell under open circuit condition in the frequency range of 0.1–100 kHz at a voltage amplitude of 10 mV.

When an electrical current (I) passes through SOFC cell, the cell voltage (U) deviates from its equilibrium value under open circuit condition (U_0). This voltage deviation ($U_{\text{pol}} = U_0 - U$) and the corresponding current can be assigned to polarization resistance (R_{pol}). The electrochemical system of SOFC contains both chemical and physical processes leading to a complicated and non-linear relationship of U and I . Therefore, analysis and evaluation of polarization of electrochemical system by using an alternating current (a.c.) are more sufficient than a direct

current (d.c.). When the system is perturbed by an a.c. input current signal, the a.c. voltage signal observed at terminals of the cell is phase shifted corresponding to the perturbation input and a complex impedance value (Z) expressed into real part and imaginary part in Nyquist theorem.

Fig. 2.6 shows the Nyquist plot of the typical impedance of an SOFC in which real part and imaginary part of impedance are plotted on X-axis and Y-axis, respectively. In the figure, R_0 , R_{pol} , and Z_{pol} are ohmic resistance, total polarization resistance, and frequency-dependent polarization resistance, respectively. Frequency is an implicit variable which is normally expressed by decade values (-2,-1,0,1,2,3,4,5). The blue arrow implies the direction of increasing frequency in Nyquist plot. At low frequencies, impedance is strongly affected by mass transportation or diffusion.

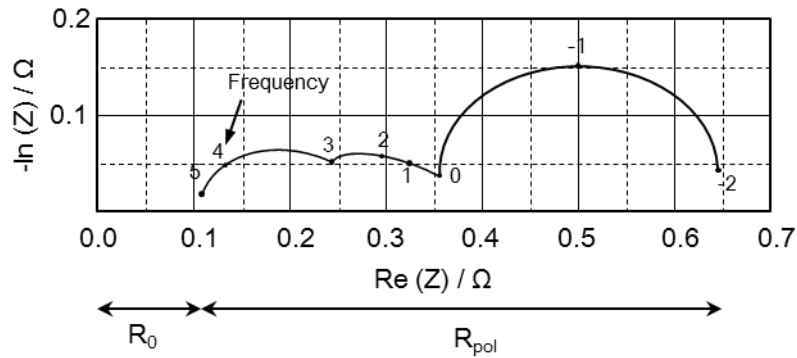


Fig 2.6: Nyquist plot of a typical impedance spectrum of a planar SOFC [1].

Reference

[1] Vielstich, W.; Lamm, A.; Gasteiger, H. A. Handbook of fuel cells: Fundamentals, technology, and application (Volume 2). John Wiley and Sons, Ltd., 111 River St., Hoboken, NJ 07030, vol. 2, Electrocatalysis, 780+pages, ISBN 0-471-49926-9.

Chapter 3: Optimization of preparation process of Ni-loaded (Ce,Zr)O_{2-δ}-dispersed paper-structured catalyst

Modification of process for fabricating Ni-loaded (Ce,Zr)O_{2-δ}-dispersed paper-structured catalyst (Ni/CZ-PSC) was studied for maximizing the catalytic performance for dry reforming of CH₄ (DRM). Co-precipitation process was applied to form a precursor of (Ce,Zr)O_{2-δ} (CZ) during paper-making process (On-paper synthesis). In paper-making process, polyvinylpyrrolidone (PVP) and NaBH₄ were added to the slurry, and these positive impacts on the catalytic activity of Ni/CZ-PSC were clarified.

3.1 Motivation

In order to improve catalytic performance and chemical stability of metal catalysts, particle size, crystal structure, geometry etc. must be adjusted by controlling preparation process [1-3]. The methods such as sol-gel processing and co-precipitation were proven to create high quality catalysts compared to the conventional impregnation [4-6].

For the conventional PSC preparation, metal catalyst particles were loaded in the ceramic fiber (Cf) network by impregnation method [7-12]. Aiming at the performance improvement of Ni/CZ-PSC, in this study, co-precipitation process was applied during paper-making to well disperse the Ni-loaded (Ce,Zr)O_{2-δ} (Ni/CZ) particles in the Cf network. Besides, polyvinylpyrrolidone (PVP) and NaBH₄ were added in the aqueous Cf suspension, and these positive effects on the catalytic performance of Ni/CZ-PSC for DRM were experimentally demonstrated.

3.2 Experimental

3.2.1 Preparation of Ni/CZ-PSC

Fig. 3.1 shows the flow of preparation procedure of Ni/CZ-PSC (refer to Fig. 2.1(b) in Chapter 2). First, 5 g of Cf (SiO₂-Al₂O₃) was mixed with 2.5 g of polyvinylpyrrolidone (PVP) in 250 mL of deionized water, followed by the addition of 1.63 g of Ni(NO₃)₂·6H₂O, 0.42 g of Ce(NO₃)₃·6H₂O, and 0.40 g of ZrO(NO₃)₂ to the suspension. Next, 1 g of NaOH was added and stirred vigorously to form Ni, Ce, and Zr hydroxide precipitates. Subsequently, 40 mL of an aqueous solution containing 2.5 g of NaBH₄ (reducing agent) was added dropwise into the stirred slurry at room temperature for 1 h, followed by the paper-making process using cationic and

anionic polymers. In this process, 15 g of a solution of 0.2 wt% of the cationic polymer (poly diallyldimethylammonium chloride (PDADMAC)), 16.3 g of a solution of 0.2 wt% of the anionic polymer (acrylamide-co-acrylic acid) (A-PAM) and 2.5 g of the organic pulp fiber suspension were poured into the slurry in that order with 3 min stirring for each addition. The resulting slurry was solidified by a filtration process using a 200-mesh filter to form a wet-state paper sheet with a diameter of 16 cm, which was subsequently pressed at 350 kPa for 3 min and dried at 105°C for 5 h to obtain raw paper. Finally, Ni/CZ-PSC was obtained by heat treatment at 600°C (ramp rate of 5°C min⁻¹) in air for 1 h.

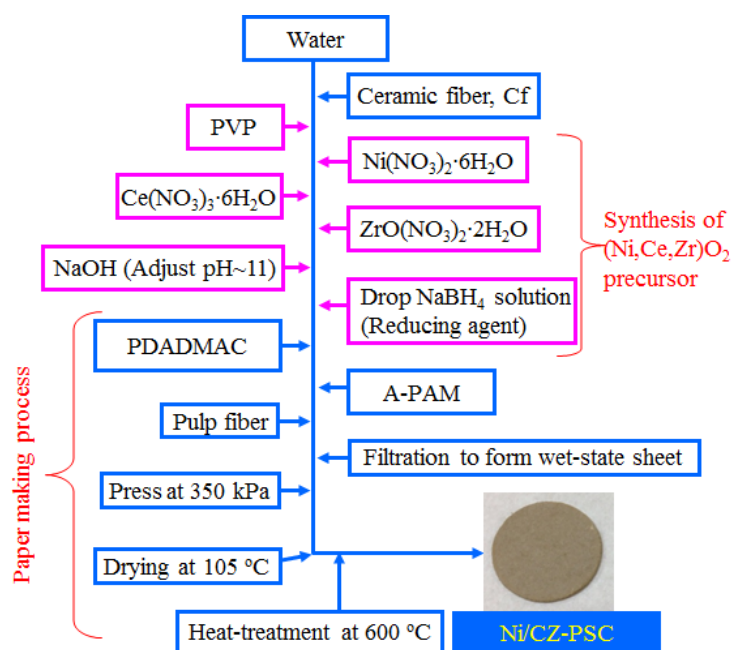


Fig. 3.1: Process flow for the preparation of Ni/CZ-PSC

Table 3.1: Chemicals added for the preparation of four types of Ni/CZ-PSC

Sample	PVP	NaBH ₄
PSC(–,–)	–	–
PSC(P,–)	Added	–
PSC(–,N)	–	Added
PSC(P,N)	Added	Added

Experiments to optimize the preparation process of Ni/CZ-PSC were carried out. For this optimization work, four PSCs, PSC(–,–) (without the addition of both PVP and NaBH₄),

PSC(P,-) (with the addition of PVP), PSC(-,N) (with the addition of NaBH₄) and PSC(P,N) (with the addition of both PVP and NaBH₄) listed in Table 3.1 were prepared. And, the impacts of the additions of PVP and NaBH₄ on the catalytic performance of Ni/CZ-PSC for DRM were evaluated.

3.2.2 Characterizations and analyses

Crystal structures of the prepared PSCs were analyzed by an X-ray diffractometer (Rint-Ultima III; Rigaku, Japan) with CuK α radiation at 40 kV and 40 mA with 0.02°/step for scanning. The crystallite size of Ni was calculated using Scherrer's equation. Microstructures of the PSCs were investigated using a field emission scanning electron microscope (FE-SEM S5200; Hitachi High Technologies, Japan) with an energy-dispersive X-ray spectrometer (EDX). For the observation with higher-magnification, a scanning transmission electron microscope (STEM-HD2300A; Hitachi High Technology, Japan) was used in the two modes, secondary electron (SE) and transmission electron (TE) modes. The specific surface area of the samples, S_{BET} , was measured by the nitrogen adsorption method using a Belsorp-mini II analyzer (MicrotracBEL Corp., Japan). Ni loading in the PSCs was quantified by inductively coupled plasma (ICP) spectrometry (Shimadzu ICPE-9000 plasma atomic emission spectrometer (AES)).

For each type of PSC, two donut-shaped PSCs were mounted in an alumina cylinder and heated from room temperature to 750 °C under N₂ atmosphere for 4 h (see Fig. 2.3 in Chapter 2). To start the 15 h test of DRM, the gas flow was switched from N₂ to a mixture of CH₄, CO₂, and N₂ (molar ratio of CH₄:CO₂:N₂ = 1:1:1) with a total flow rate of 60 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of ~3800 h⁻¹, which was determined as the total reactant flow rate (in mL h⁻¹)/total catalytic volume (in cm³). During the test, reformat compositions were analyzed every 30 min using an automatic gas chromatograph (GC-20B, Shimadzu Corp.). After the dry reforming test, temperature-programmed oxidation (TPO) was carried out to evaluate the degree of coking in the PSCs. The PSC sample (100 mg) used for the 15-h dry reforming test at 750°C was placed in a glass U-tube and heated from room temperature to 800°C at a rate of 3°C min⁻¹ under an air flow of 40 mL min⁻¹.

3.3 Results and discussion

3.3.1 Characterization of the PSCs

Figures 3.2 shows the microstructure of PSC(-,-) after reduction treatment for 5 h. Cf, recognized by Al, entwined together to create the three-dimensional network, where the clusters

of Ni/CZ particles served as the binder of Cfs. Locations of Ni, Zr, and Ce were well overlapped, indicating the formation of (Ce,Zr)O_{2-δ} solid solution (CZ) and its interaction with Ni particles (Fig. 3.2(c-e)).

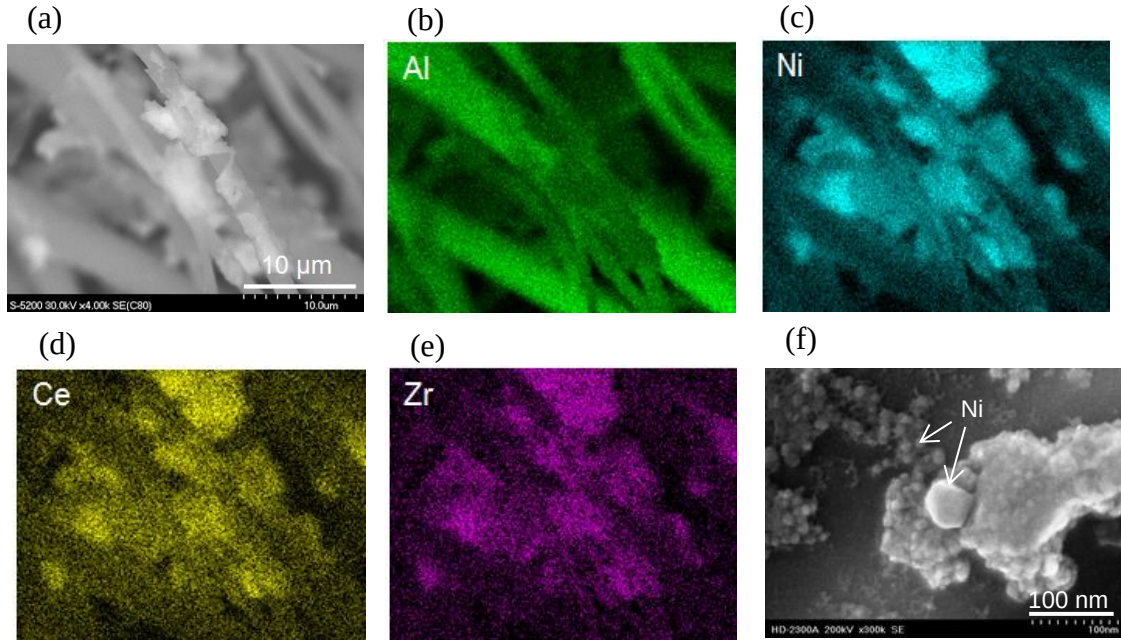


Fig. 3.2: Microstructure of PSC(-,-) without the addition of PVP and NaBH₄ after reduction treatment at 750°C in 5% H₂ for 5 h; (a) FE-SEM image and corresponding EDX mapping images of (b) Al, (c) Ni, (d) Ce, and (e) Zr. (f) is the higher-magnification image focusing on Ni particles by STEM observation

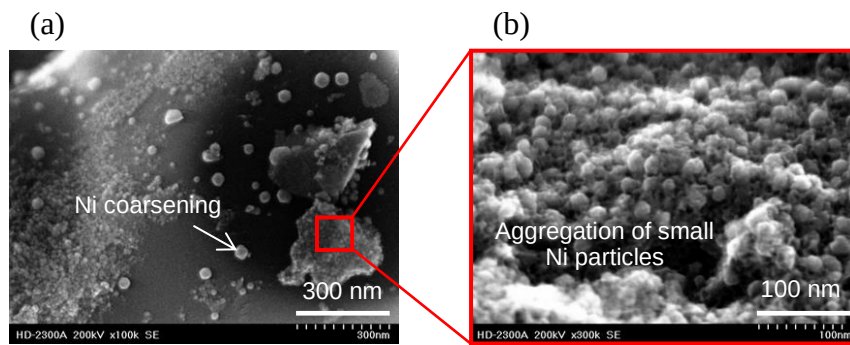


Fig. 3.3: (a) Ni/CZ particles loaded on Cf of PSC(-,-); (b) is the high-magnification image focusing on Ni particles.

The similar solubility product of Ce(OH)₄ (pK_a = 47.7) and Zr(OH)₄ (pK_a = 48.2) for the aqueous solution and the comparable ionic radius of Ce⁴⁺ and Zr⁴⁺ in oxide crystals facilitate the formation of CZ during sintering process [13]. For the PSC(-,-), aggregation of small Ni

particles as well as Ni coarsening on the Cf were significant (Figs. 3.2 (f) and 3.3). Ni particles with the size of 15 nm (average of 20-30 particles observed in SE mode) aggregated to form clusters.

For the PSC(P,-), small Ni particles with the average size of 12.5 nm can be seen in the higher-magnification image (Fig. 3.4(f)). Although the larger particles also existed at other locations (see Fig. 3.5) but their amount were considerably less than those of PSC(-,-), indicating the PVP addition contributed to making the structure of the catalyst particles finer. The specific surface area and pore volume of PSC(P,-) were 17.3 m² g⁻¹ and 25.4 mm³ g⁻¹, respectively, were larger than those of PSC(-,-), may be due to the higher Ni amount (Table 3.2).

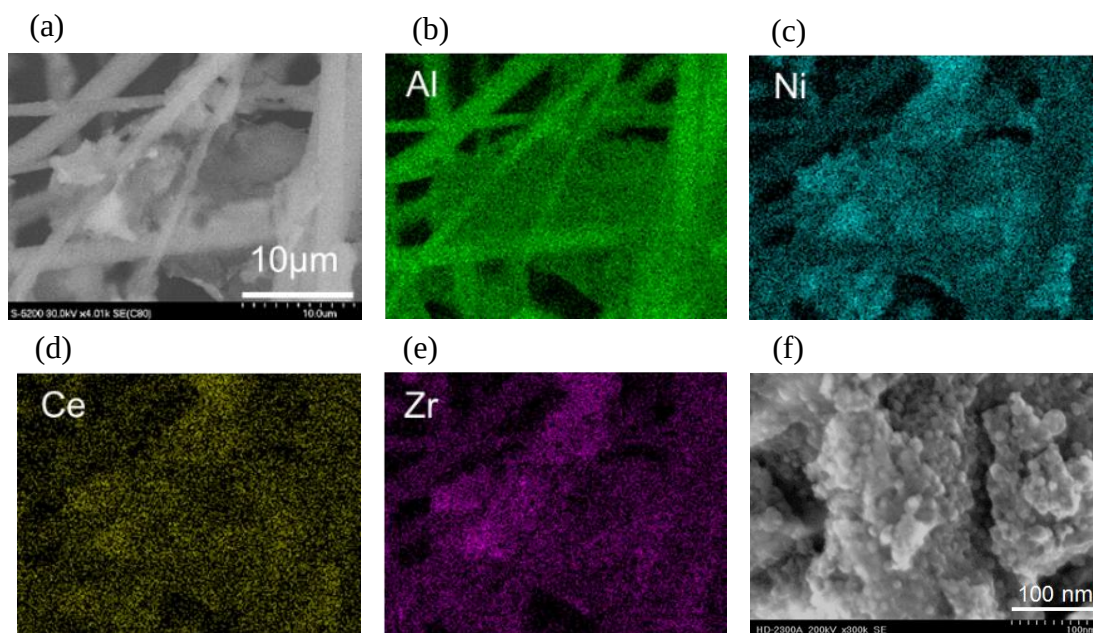


Fig. 3.4: Microstructure of PSC(P,-) after reduction treatment at 750°C in 5% H₂ for 5 h; (a) FE-SEM image and corresponding EDX mapping images of (b) Al, (c) Ni, (d) Ce, and (e) Zr. (f) is the higher-magnification image focusing on Ni particles by STEM observation.

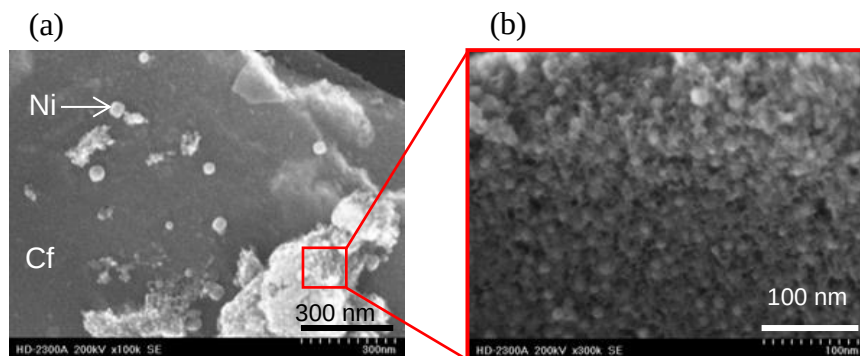


Fig. 3.5: Ni/CZ particles loaded on Cf of PSC(P,-) after reduction treatment at 750°C in 5% H₂ for 5 h: (a) STEM image and (b) is the higher-magnification image of (a).

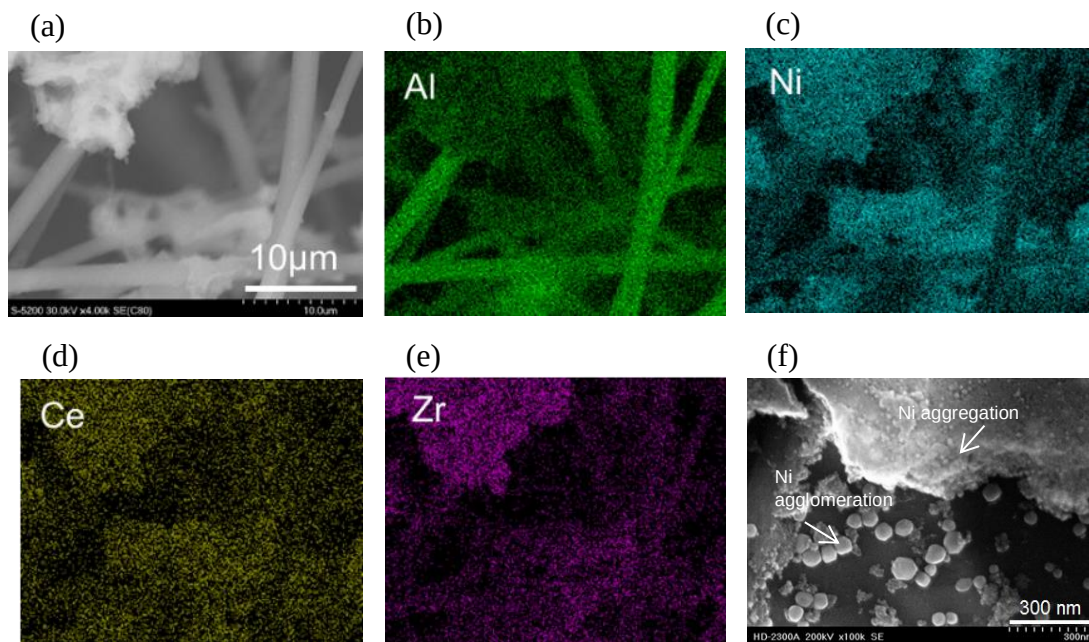


Fig. 3.6: Microstructure of PSC(-,N) after reduction treatment after reduction treatment at 750°C in 5% H₂ for 5 h; (a) FE-SEM image and corresponding EDX mapping images of (b) Al, (c) Ni, (d) Ce, and (e) Zr. (f) is the higher-magnification image focusing on Ni particles by STEM observation.

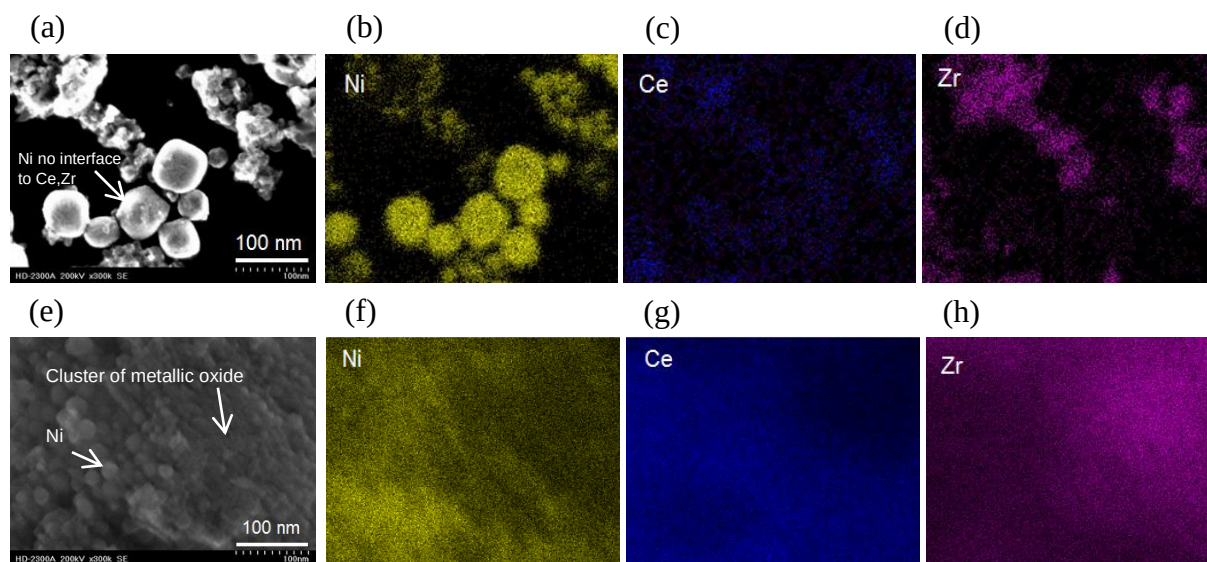


Fig. 3.7: Ni/CZ particles loaded on Cf of PSC(-,N) after reduction treatment at 750°C in 5% H₂ for 5 h: (a) STEM image and (b,c,d) corresponding EDX mapping image of Ni, Ce, and Zr respectively. (e) higher-magnification image at the area of aggregated Ni particles with the surface coverage by very small particles and (f,g,h) corresponding EDX mapping image of Ni, Ce, and Zr, respectively.

For the PSC(–,N), Ni coarsening (average size of the particles over 50 nm (large particles): 58.8 nm) and the aggregation of smaller Ni particles (average size of the particles below 20 nm (small particles): 17.3 nm) were observed in STEM images (Fig. 3.6(f) and Fig. 3.7). As can be seen in Figures 3.7(a-d), at the locations where small Ni particles are formed, Ni, Ce and Zr were overlapped indicating the formation of Ni/CZ, whereas large particles were isolated from CZ, and only have interaction with Cf. The clusters of very small metallic oxide covering the Ni/CZ particles were also observed (Fig. 3.7(e)), which may interfere with gas diffusion to the active sites of catalyst. PSC(–,N) had the relatively small pore volume (21.8 mm³ g^{–1}) and pore diameter (4.99 nm) (Table 3.2). Ni crystallite size of PSC(–,N) (16.3 nm) was considerably larger than that of PSC(–,–) (9.47 nm), indicating that NaBH₄, which serves as a reduction reagent during paper-making process, can promote the enlargement of Ni crystallite.

Table 3.2: Ni loading, BET specific surface area (S_{BET}), pore volume (V_{pore}), average pore size diameter (r_{pore}), crystallite size of Ni (D_{Ni}) and average Ni particle size estimated from STEM observation (d_{Ni}) of the prepared PSCs listed in Table 3.1.

Sample	Ni loading / wt%	S_{BET} / m ² g ^{–1}	V_{pore} / mm ³ g ^{–1}	r_{pore} / nm	D_{Ni}^* / nm	d_{Ni} / nm
PSC(–,–)	3.21	16.0	21.6	5.40	9.7	15
PSC(P,–)	4.86	17.3	25.4	5.86	10.9	12.5
PSC(–,N)	4.65	17.5	21.8	4.99	16.3	58.8**, 17.3***
PSC(P,N)	5.95	24.0	32.8	5.45	12.7	18
* Estimated from XRD patterns with Scherrer equation						
** Average size of large particles (particles over 50 nm)						
*** Average size of small particles (particles below 20 nm)						

For the PSC(P,N), fine Ni particles (average size of 15 nm) were formed on the sponge-like porous CZ (Fig. 3.8(f)), resulting in the highest specific surface area (24.0 m² g^{–1}) among the prepared PSCs (Table 3.2). With the presence of PVP in the suspension, it can capture metallic cations of Ni, Ce, and Zr, promoting the contact of Ni reduced by NaBH₄ with CZ. The surround CZ clusters could protect metallic Ni from agglomeration into large particles during sintering, leading to the finer Ni particle. Therefore, enlargement of Ni crystallite size caused by the addition of NaBH₄ could be suppressed by the addition of PVP.

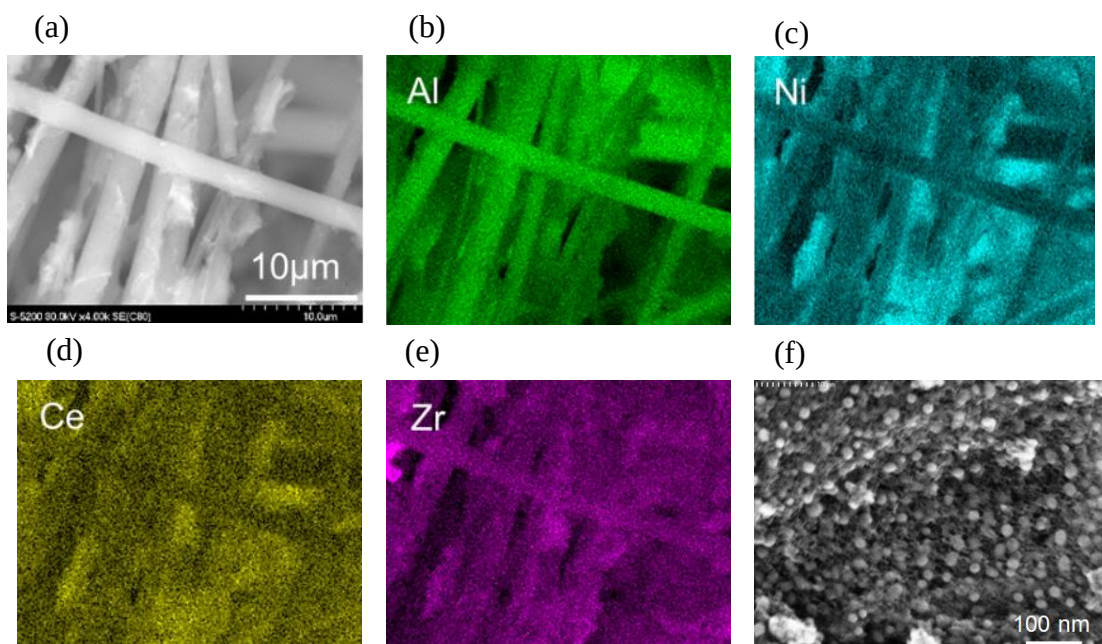


Fig. 3.8: Microstructure of PSC(P,N) after reduction treatment at 750°C in 5% H₂ for 5 h; (a) FE-SEM image and corresponding EDX mapping images of (b) Al, (c) Ni, (d) Ce, and (e) Zr. (f) is the higher-magnification image focusing on Ni particles by STEM observation.

As summarized in Table 3.2, in spite of the same amount of nickel precursor added in the suspension for paper-making, Ni loading was different for each case. From the comparison between PSC(–,–) and PSC(P,–), the PVP addition enhanced Ni loading because the formation of ion-polymer complex in the solution resulted in the aggregation of metal ions in the polymeric chains of PVP. The ion-polymer complex formation is schematically supposed in Fig. 3.9. Since the metallic cations of Ni, Ce, or Zr are trapped with amine group by the ionic dipolar interaction in the polymeric chains of PVP, cations become immobile and crystalize during sintering while PVP is burned out [14]. The cation capture phenomenon and step of PVP removal resulted in the higher Ni efficiency and finer Ni particles in the PSCs with the addition of PVP.

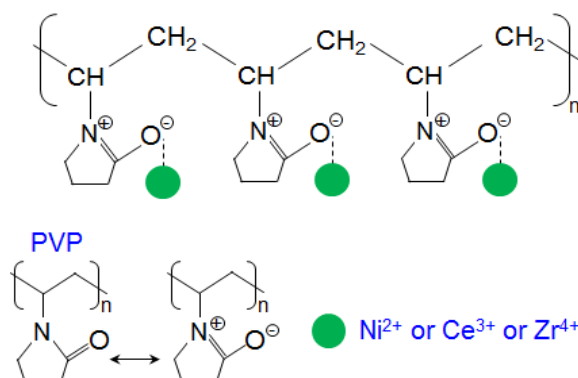


Fig. 3. 9: Schematic description of ion-polymer complex of PVP with metallic cations in the

solution.

From the comparison between PSC(–,–) and PSC(–,N), the NaBH₄ addition enhanced Ni loading, because of the formation of Ni metal particles by which the efflux of Ni²⁺ dissolved in the aqueous Cf suspension can be suppressed during filtration process. However, after adding NaBH₄ to the suspension, it was visually confirmed that a portion of Ni particles reduced by NaBH₄ dropped down to the bottom of beaker, and then the dropped particles were washed out during filtration. Nevertheless, in the presence of PVP in the suspension, the reduced Ni particles existed in (Ce,Zr) hydroxide trapped by polymeric chain, enhancing the Ni retention in solution, therefore, Ni loading was remarkably increased in the case of PSC(P,N).

3.3.2 Effect of PVP on the catalytic performance of Ni/CZ-PSC

The effect of PVP on the catalytic activity of Ni/CZ-PSCs was studied through the comparison of CH₄ conversion for DRM at 750°C between PSC(–,–) and PSC(P,–). The results are shown in Fig. 3.10. The equilibrium conversion at this temperature calculated by HSC Chemistry Ver. 9.0.5 software (94%) was indicated in the diagram. The initial CH₄ conversion for PSC(P,–) (78.3%) was higher than that for PSC(–,–) (66.4%), which is due to the higher Ni loading, the larger specific surface area and the larger pore volume (Table 3.2). Degradation rate of CH₄ conversion within 15 h was 5.4% for PSC(P,–), quarter of PSC(–,–) (21.7%), indicating the improved catalytic performance by the addition of PVP.

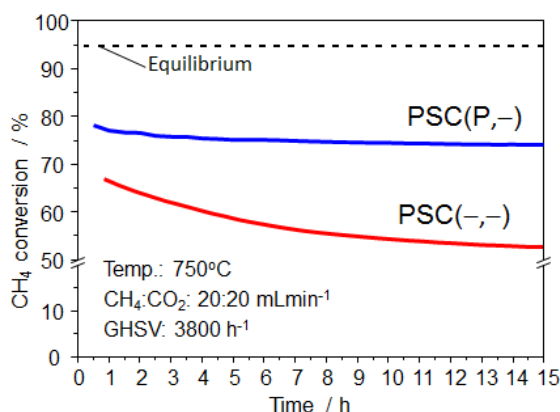


Fig. 3.10: CH₄ conversion in DRM (CH₄: 20 mL min^{–1}, CO₂: 20 mL min^{–1}, GHSV: 3800 h^{–1}) for PSC(–,–) and PSC(P,–) measured at 750°C for 15h. Equilibrium conversion was indicated with the dashed line.

Fig. 3.11 shows the TPO profiles for the PSCs after the 15 h DRM tests. The TPO profile for the Ni-loaded PSC without CZ dispersion (Ni-PSC) was also plotted as a reference. CO₂ mass

signal indicates the oxidation of carbonaceous species, such as amorphous, filamentous, graphitic, etc., deposited in the PSCs, which generally takes place in the range of 300-700°C depending on the degree of graphitization [15,16]. Oxidation peak of more graphitized carbon appears at higher temperature. In both PSCs, coking was considerably suppressed due to the contribution of the lattice oxygen in CZ to carbon removal. Thus, the reason for the higher degradation of PSC(–,–) may be due to the serious Ni agglomeration during DRM test, which was supported by the STEM observation after 15 h DRM test focusing on Ni loaded in PSC(–,–) (see Fig. 3.12). For the PSC(P,–), as can be seen in the TE image (Fig. 3.13(b)), Ni particles were still relatively small and discrete.

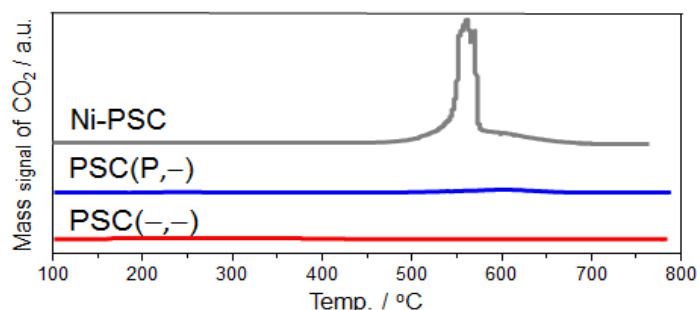


Fig. 3.11: TPO profiles for PSC(–,–) and PSC(P, –), and Ni-PSC after DRM at 750°C for 15h.

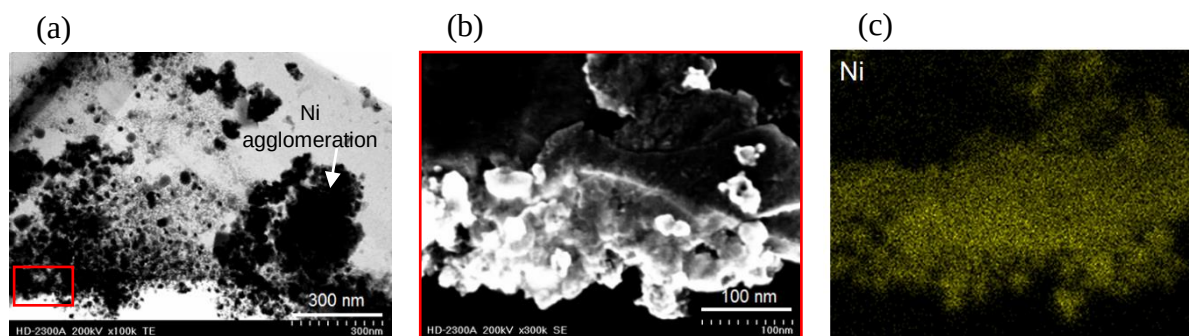


Fig. 3.12: STEM image focusing on Ni loaded in PSC(–,–) after DRM at 750°C for 15h: (a) TE image, (b) high-magnification SE image and (c) corresponding EDX mapping of Ni.

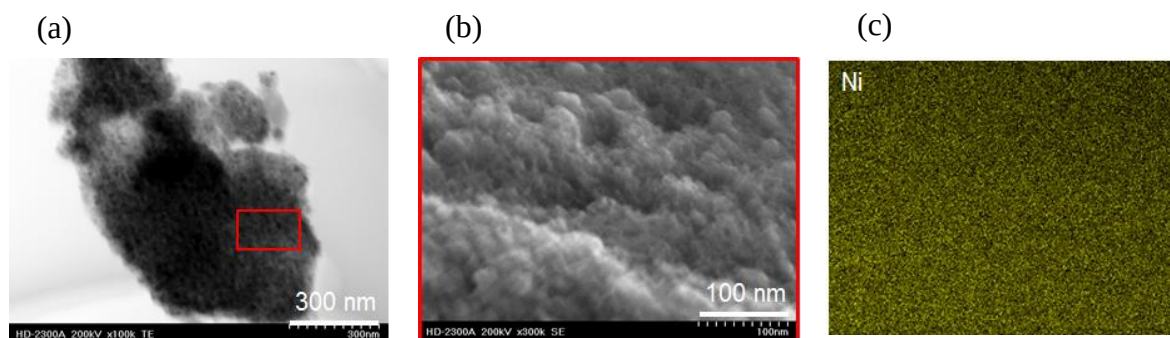


Fig. 3.13: STEM image focusing on Ni loaded in PSC(P,–) after DRM at 750°C for 15h: (a) TE

image, (b) high-magnification SE image and (c) corresponding EDX mapping of Ni.

3.3.3 Effect of NaBH₄ on the catalytic performance of Ni/CZ-PSC

Catalytic performances of PSC(–,–) and PSC(–,N) for DRM were compared to evaluate the impact of the addition of NaBH₄ during paper-making process on the catalytic activity of Ni/CZ-PSC. CH₄ conversion in DRM at 750°C is shown in Fig. 3.14. Initial CH₄ conversions for PSC(–,–) and PSC(–,N) were 66.4 and 79.7%, respectively. Degradation rate of CH₄ conversion within 15 h for PSC(–,–) was 21.7%, higher than that of PSC(–,N) (6.2%), indicating the improved catalytic activity by the addition of NaBH₄.

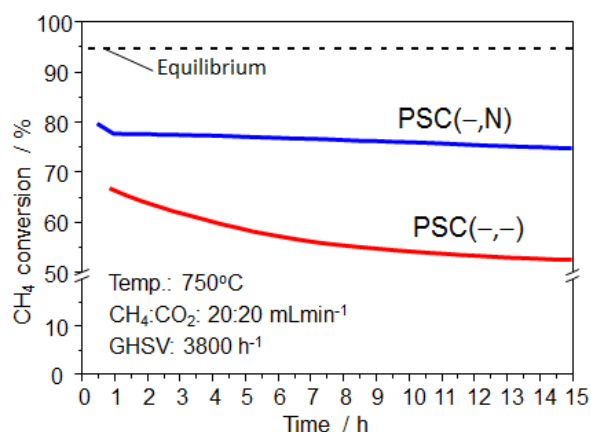


Fig. 3.14: CH₄ conversion in DRM (CH₄: 20 mL min^{–1}, CO₂: 20 mL min^{–1}, GHSV: 3800 h^{–1}) for PSC(–,–) and PSC(–,N) measured at 750°C for 15h. Equilibrium conversion was indicated with the dashed line.

The TPO profiles for PSC(–,–) and PSC(–,N) after 15 h DRM test shown in Fig. 3.15 suggest that coking was more promoted by the addition of NaBH₄ in paper-making process. Fig. 3.16 shows the Ni particles loaded in PSC(–,N) after DRM at 750°C for 15h. Coking occurred mainly on the large Ni particles having weak interaction with the support oxide. Large Ni particle was caught in the clump of carbon fibers, and fine particles were embedded in the carbon fiber with the diameter of about 50 nm. It is also considered that the narrower pores in PSC(–,N) (Table 3.2) can be more easily blocked by the coke formed during DRM, which hinders gas diffusion.

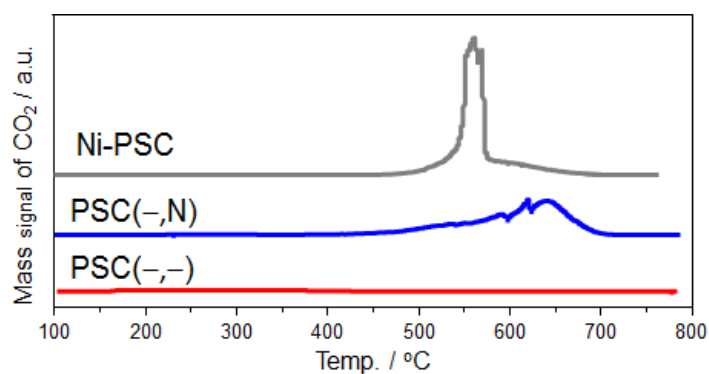


Fig. 3.15: TPO profiles for PSC(-,-), PSC(-,N), and Ni-PSC after DRM at 750°C for 15h.

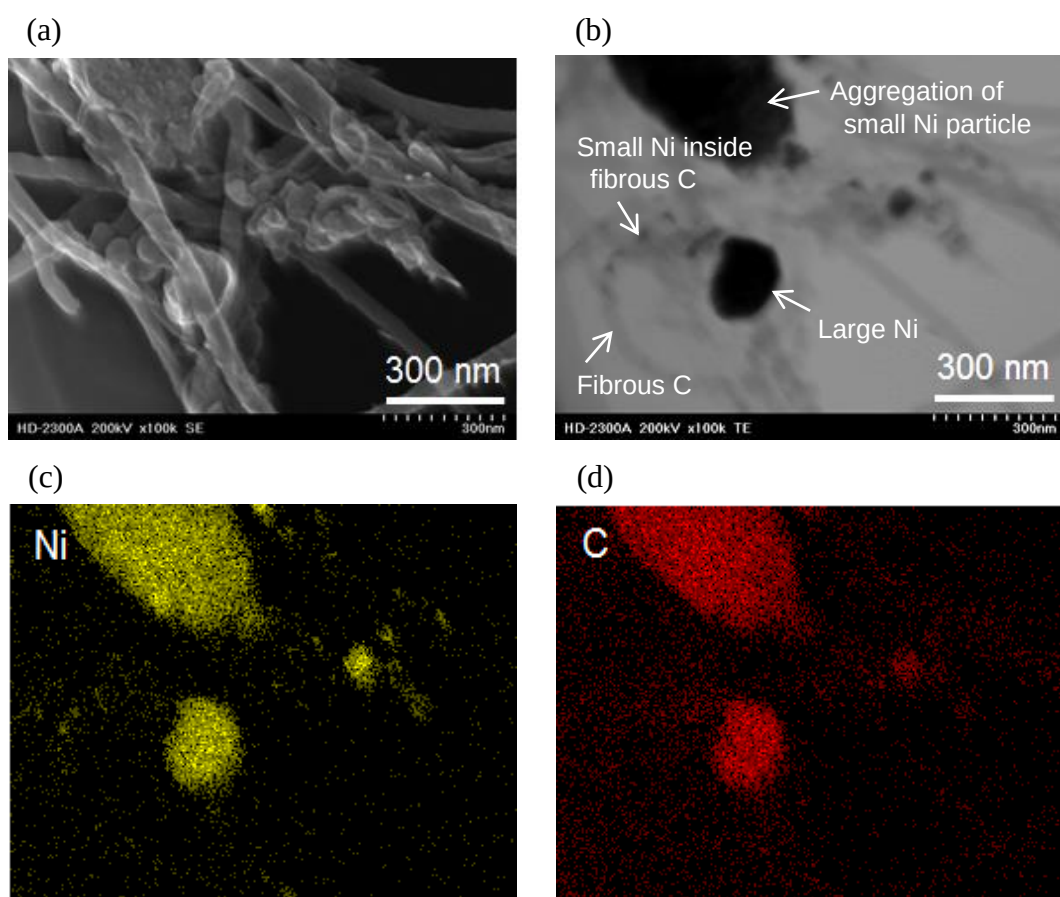


Fig. 3.16: STEM images focusing on Ni loaded in PSC(-,N) after DRM at 750°C for 15h: (a,b) SE and TE images, respectively, and (c,d) corresponding EDX mapping images of Ni and C, respectively.

In the case of PSC(-,-), after the sintering process, in the reducing atmosphere at high temperature, Ni metal is formed from the mixed oxide derived from hydroxide precipitate including Ni, Ce and Zr to form Ni/CZ [17]. However, in the case of PSC(-,N), Ni ions were

reduced to Ni metal in the aqueous Cf suspension for paper-making at room temperature without oxide support, resulting in growth of Ni crystallite and particle (Table 3.2), which may be the cause of coking. Although coking was significant for the PSC(–,N), degradation rate of CH₄ conversion was lower compared to PSC(–,–) in which coke was not formed during DRM. This implies that serious Ni agglomeration is the main factor for the degradation rather than coking.

3.3.4 Effect of co-addition of PVP and NaBH₄ on the catalytic performance of Ni/CZ-PSC

Catalytic activities of the prepared Ni/CZ-PSCs, PSC(–,–), PSC(P,–), PSC(–,N) and PSC(P,N), were compared for DRM. Fig. 3.17 shows the CH₄ conversion in the 15 h DRM test at 750°C.

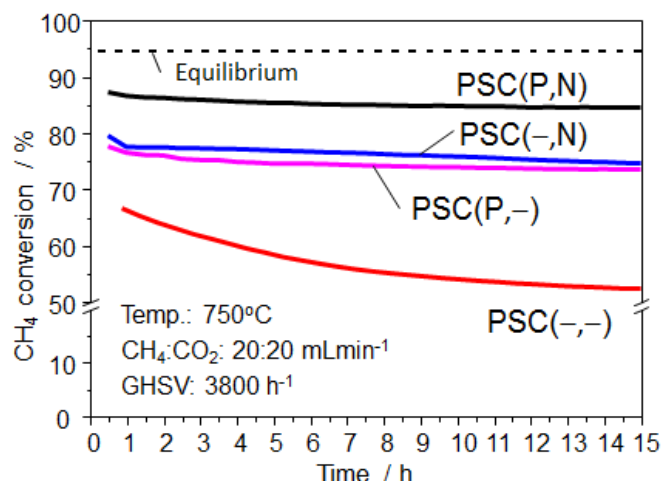


Fig. 3.17: Comparison of CH₄ conversion in DRM (CH₄: 20 mL min^{–1}, CO₂: 20 mL min^{–1}, GHSV: 3800 h^{–1}) for PSC(–,–), PSC(P,–), PSC(–,N), and PSC(P,N) measured at 750°C for 15h. Equilibrium conversion was indicated with the dashed line.

Initial CH₄ conversion and degradation rate for 15 h DRM at 750°C were summarized in Table 3.3. PSC(P,N) exhibited the highest CH₄ conversion (87.5%). In the case of PSC(–,–), CH₄ conversion rapidly decreased, and converged toward 52% within 15 h. On the other hand, performance degradation of PSC(P,–) and PSC(–,N) was more suppressed (CH₄ conversion at 15 h: 74%), and the addition of both PVP and NaBH₄ (PSC(P,N)) resulted in the remarkably higher CH₄ conversion and lowest degradation rate (CH₄ conversion at 15 h: 85%). PSC(P,–) and PSC(–,N) with the same level Ni loading and similar porous structure showed comparable catalytic activity, while serious coking occurred only in the case of NaBH₄ due to the presence of

large Ni particles having weak interaction with oxide support. Ni retention efficiency in the PSC preparation was considerably enhanced by the co-addition of PVP and NaBH₄, and moreover, in spite of the higher Ni loading (Typically, Ni agglomeration is promoted.), fine structure was maintained. These are the reasons for the highest catalytic performance of PSC(P,N). Fig. 3.18 shows the TPO profiles for the PSCs after 15 h DRM test. PVP addition can suppress the drawback of NaBH₄ addition which promotes coking formed from the enlargement of Ni crystallite.

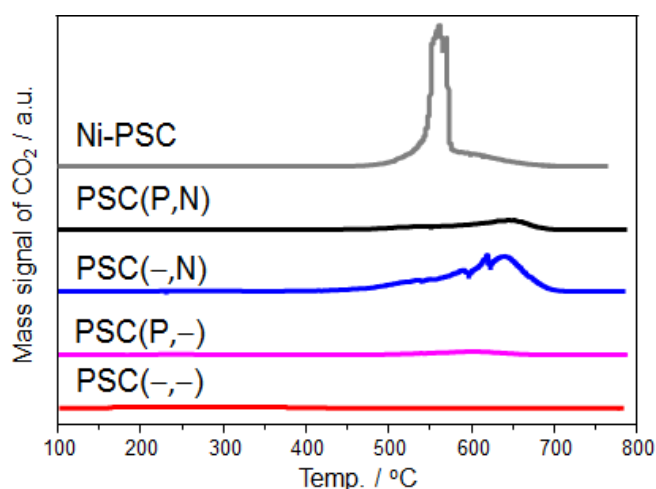


Fig. 3.18: TPO profiles for PSC(–,–), PSC(P,–), PSC(–,N), PSC(P,N), and Ni-PSC after DRM at 750°C for 15h.

Table 3.3: Initial CH₄ conversion and degradation rate in the DRM test at 750°C for the PSCs listed in Table 3.1.

Sample	Initial CH ₄ conversion / %	Degradation rate for 15 h / %
PSC(–,–)	66.4	21.7
PSC(P,–)	78.3	5.4
PSC(–,N)	79.7	6.2
PSC(P,N)	87.5	3.2

Fig. 3.19 shows the nanostructure of Ni/CZ particles loaded in the Cf network of PSC(P,N) after reduction treatment. Boundaries of round-shaped Ni particles were clearly observed (see

Fig. 3.19(c)), while Ce and Zr form the cluster, which is the mixture of ceria and zirconia assigned as CZ solid solution in XRD, and can serve as a support of the Ni particles (Fig. 3.19(d,e)). As shown in Fig. 3.19(f), CZ and Ni particles can be regarded as a shell and a core, respectively.

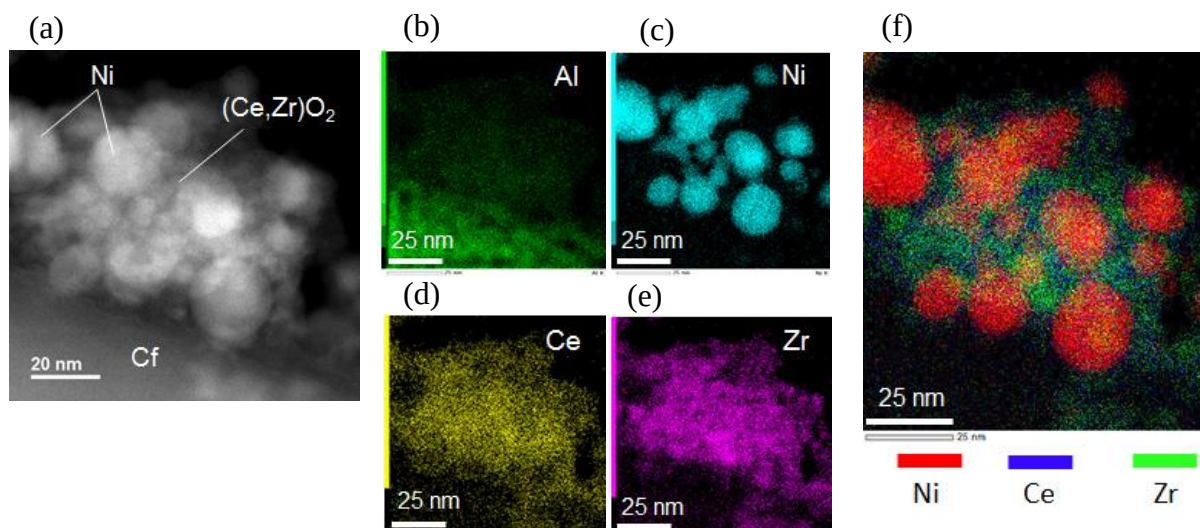


Fig. 3.19: Ni particles formed on the CZ cluster dispersed in the C_f network of PSC(P,N); (a) STEM image, and the corresponding EDX mapping images of (b) Al, (c) Ni, (d) Ce and (e) Zr; (f) is the overlapped image of Ni, Ce and Zr.

The functions of PVP and NaBH₄ were schematically described in Fig. 3.20. PVP serves as a dispersant in the aqueous Cf suspension for paper-making, and therefore it can protect the formation of secondary particles of Ni to create nano-sized particles. When PVP was added, Ni ions were trapped with amine group (PVP-caped Ni), surrounded by PVP-caped Ce and Zr. Thus, the contact between Ni hydroxide and (Ce,Zr) hydroxide was enhanced when pH of solution was adjusted to 11, followed by Ni reduction at room temperature by NaBH₄ with the surrounded ceria and zirconia species. This phenomenon resulted in the interaction between Ni and CZ during sintering at high temperature, leading to the fine and small Ni particle. In addition that, PVP is burned to leave tunnels inside CZ shell after sintering at 600°C to form sponge-like oxide support. This sponge-like shell can also isolate the Ni particles to prevent them from sintering at high temperature [18]. Therefore, the addition of PVP let PSC exert excellent catalytic properties.

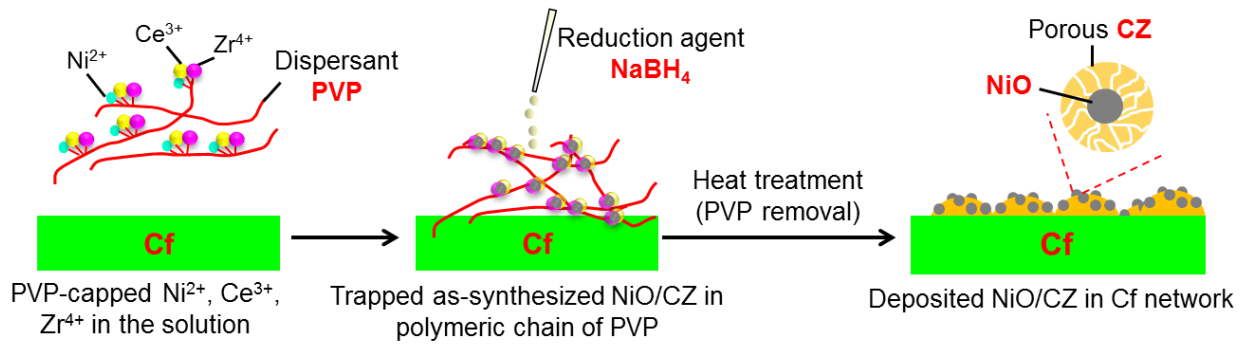


Fig. 3.20: Schematic description of co-addition during on-paper synthesis of Ni/CZ particles.

When NaBH_4 is dropped into the aqueous Cf suspension for paper-making including metal precursors, Ni^{2+} is reduced to Ni^0 . NaBH_4 is decomposed in water to produce BH_4^- , which contributes to the reduction of metal ions (M^{2+}) to produce metal (M: metal surface site) and proton (R1). BH_4^- and OH^- then adsorb onto the metal surface and even metal ions to form M-BH_4 (R2) and M-OH (R3), respectively, which are the most abundant reactive intermediates, subsequently react together to produce metal (R4) and hydrogen (R5) [19].

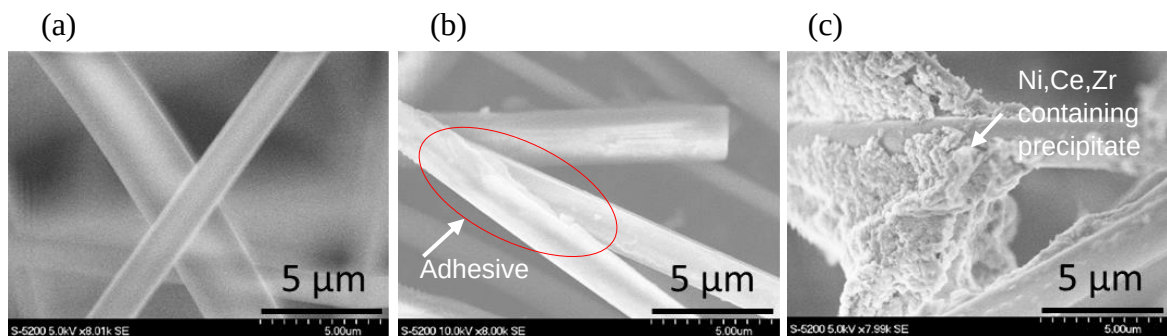
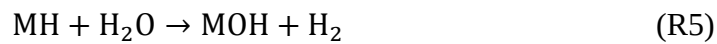
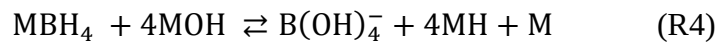
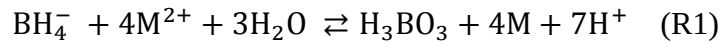


Fig. 3.21: FE-SEM images of (a) raw Cfs, (b) Cfs after steps of adding (Ni,Ce,Zr) precursors and (c) subsequent addition of NaBH_4 into the suspension, respectively.

Fig. 3.21 shows the FE-SEM images of Cfs at each stage of Ni/CZ-PSC preparation (see Fig. 3.1). Surface of the raw Cf (Fig. 3.21(a)) having amorphous structure is flat and smooth. After adding precursors of Ni, Ce, and Zr to deionized water with Cfs, pH of the suspension is down to 2-3. From this suspension, a portion of Cfs was taken out for the FE-SEM observation. Fig. 3.21(b) is the image of the Cfs after drying, showing little adhesives on the Cfs. Before adding NaBH₄, pH of the slurry was controlled at ~11, and the NaBH₄-mediated reduction process was slowly proceeded by dropping NaBH₄ solution with the rate of 0.66 mL min⁻¹ in order to form Ni metal during the formation of hydroxide precipitate containing Ce and Zr, which was confirmed by FE-SEM image (Fig. 3.21(c)). Finally, the Ni/CZ particles can be obtained by the subsequent high temperature heat treatment.

3.4 Conclusions

Optimization of the developed process for the preparation of Ni/CZ-PSC was conducted to maximize the catalytic performance for DRM. In the synthesis of Ni/CZ precursor particles during paper-making process (on-paper synthesis), polyvinylpyrrolidone (PVP) added in the suspension, which can serve as a dispersant to protect Ni particles from agglomeration, was confirmed to make the porous structure of the Ni/CZ particles finer. NaBH₄ added as a reduction agent to form Ni metal from Ni²⁺ in both the hydroxide precipitate and the aqueous solution of the paper-making suspension at room temperature was confirmed to enhance the Ni retention efficiency during paper-making process, but then have negative impact on the catalytic activity. NaBH₄ addition promoted the growth of Ni crystallite or particle, which caused coking during DRM at 750°C. It was demonstrated that co-addition of PVP and NaBH₄ considerably improves the catalytic performance of the Ni/CZ-PSC for DRM. This means the synergetic effect of PVP and NaBH₄. By addition of PVP, Ni reduction by NaBH₄ in the suspension containing hydroxide precipitate and ceramic fiber (Cf) is retarded to form finer structure Ni/CZ in the Cf network.

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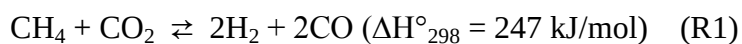
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Chapter 4: Dependence of catalytic performance of Ni-loaded (Ce,Zr)O_{2-δ}-dispersed paper-structured catalyst on chemical composition for dry reforming of methane

Aiming at the improvement of coking tolerance of paper-structured catalyst (PSC) for dry reforming of methane (DRM), Ni-loaded (Ce,Zr)O_{2-δ}-dispersed PSCs (Ni/CZ-PSCs) were prepared. During the paper-making process using ceramic fibers (Cf), Ni-loaded (Ce,Zr)O_{2-δ} particles were synthesized via co-precipitation and subsequent reduction treatment (hereafter called on-paper synthesis). In this chapter, dependence of the catalytic performance of Ni/CZ-PSC on the chemical composition (CeO₂/ZrO₂ weight ratio in paper making process and Ni loading amount) was studied.

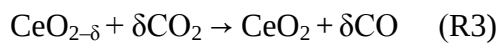
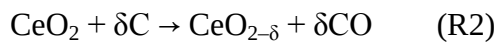
4.1 Motivation

Fuel cell systems for household use have gradually become ubiquitous in Japan because of their high electrical efficiency (39–52%) [1,2]. Among the different types of fuel cells, solid oxide fuel cells (SOFCs) are typically operated at a high temperature (usually between 600 and 900 °C), at which ceramic electrolytes can exert satisfactory ionic conductivity for power generation, have the highest efficiency, and also demonstrate the highest fuel flexibility. This behavior is unlike that of low-temperature fuel cells, which accept only pure H₂ [3–5]. At present, a hydrogen energy-based society may not be the optimum choice, especially in developing countries, because of the associated high cost. However, as these countries have abundant biomass resources, the direct conversion of biofuel such as biogas, which is obtained from the anaerobic fermentation of organic wastes and mainly composed of 50–60% CH₄ and 40–50% CO₂ in volume [6], into electricity using an SOFC system is highly promising in terms of social acceptability as well as reduction of CO₂ emissions. By adopting the direct internal reforming (DIR) operation, system downsizing and enhancement of energy conversion efficiency can be expected [7,8]. When biogas is directly fed to the SOFC anode, dry reforming of CH₄ (R1) takes place within the Ni-based anode material to produce syngas (mixture of H₂ and CO) that is subsequently oxidized to generate electricity [9].



However, inhomogeneous temperature distribution in a cell and carbon deposition within the porous anode are the major problems leading to significant degradation of cell performance [10–14]. To eliminate these problems, the application of additional catalyst layers on the SOFC anode is very effective [15,16]. Recently, Shiratori et al. utilized paper-structured catalysts (PSCs) and considerably improved the electrochemical performance of DIR-SOFCs fueled by biogas [17,18] and biodiesel fuels [19,20]. These authors applied the Ni-loaded hydrotalcite (HT)-dispersed PSC (Ni/HT-PSC) on the Ni-stabilized zirconia cermet anode. The unique structure of the PSC based on the Cf network, in which fine Ni particles and support oxides were well-dispersed, was geometrically suitable for hydrocarbon reforming.

Despite their intolerance to coking, Ni-based catalysts are often used for methane reforming to produce hydrogen because of their lower cost in comparison to noble metal (Ru, Rh, Pd, Ir, Pt) catalysts [21–23]. Promoters with oxygen storage capacity (OSC) such as CeO₂ or CeO₂-based solid solutions with other metal oxides are often utilized to suppress coking on Ni [24–26]. Carbon formed on the CeO₂ surface can react with lattice oxygen to form non-stoichiometric CeO_{2-δ} (R2). Subsequently, CeO₂ can be recovered by interacting with oxygen-containing gas such as CO₂, charging oxygen into the lattice (R3). Through the oxygen exchange, reverse Boudouard reaction (R4) is promoted and carbonaceous species deposited on the Ni surface can be removed [26].



In general, the impregnation method is applied to load metal catalyst particles in the Cf network [15,17]. In this study, Ni-loaded (Ce,Zr)O_{2-δ} (Ni/CZ) particles were synthesized by co-precipitation in the paper-making process and subsequent heat treatment led to the formation of Ni/CZ-dispersed PSCs (Ni/CZ-PSCs). By adopting this process, PSC preparation could be simplified. Catalytic activity of the prepared PSCs for dry reforming of CH₄ was investigated at 750 °C. The effects of the CeO₂/ZrO₂ weight ratio and the Ni loading amount on the catalytic activity are discussed.

4.2 Experimental

4.2.1 Catalyst preparation process

Preparation procedure of Ni/CZ-PSCs was illustrated in Fig. 2.1(b) in Chapter 2. First, 5 g of Cf (Ibiden Ltd., Japan) was mixed with 2.5 g of polyvinylpyrrolidone (PVP) in 250 mL of deionized water (DI). This was followed by the addition of designated amounts of the precursors Ni(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, and ZrO(NO₃)₂ (Chameleon Reagent, 98%) to the suspension. Next, 1 g of NaOH was added and the suspension was stirred vigorously to form Ni, Ce, and Zr hydroxide precipitates. Subsequently, 40 mL of an aqueous solution containing 2.5 g of NaBH₄ (reducing agent) was added dropwise into the stirred slurry at room temperature for 1 h and the paper-making process was initiated by using cationic and anionic polymers to form flocculates including inorganic materials to achieve 100% retention of them [15]. In this process, 15 g of a solution of 0.2 wt% of the cationic polymer poly diallyldimethylammonium chloride (PDADMAC) (Sigma-Aldrich LCC, USA), 16.3 g of a solution of 0.2 wt% of the anionic polymer acrylamide-co-acrylic acid (Fujikasui Engineering Co., Ltd., Japan), and 2.5 g of the organic pulp fiber suspension were poured into the slurry in that order with 3 min stirring for each addition. The resulting slurry was solidified by a filtration process using a 200-mesh filter to form a wet-state paper sheet with a diameter of 16 cm, which was subsequently pressed at 350 kPa for 3 min and dried at 105°C for 5 h to obtain raw paper. Finally, Ni/CZ-PSC was obtained by heat treatment at 600°C (ramp rate of 5°C min⁻¹) in air for 1 h. The average porosity of the prepared PSCs was measured by the mercury intrusion method and found to be 85%. The five types of Ni/CZ-PSCs fabricated with different Ni loading amounts and weight ratios of CeO₂/ZrO₂ and Ni/(Ce,Zr)O_{2-δ} are listed in Table 4.1.

Table 4. 1: Composition, crystallite size of Ni (D_{Ni}), Ni particle size (d_{Ni}), and BET specific surface area (S_{BET}) of the Ni/CZ-PSCs prepared in this study.

Sample	Ni loading / wt%	CeO ₂ :ZrO ₂ / wt ratio	x in (Ce _x Zr _{1-x})O ₂	Ni:(Ce,Zr)O _{2-δ} / wt ratio	D_{Ni}^* / nm	d_{Ni}^{**} / nm	S_{BET} /m ² g ⁻¹
6%Ni/CZ12-PSC	6.4	1:2	0.2	1:1	21	29	23
6%Ni/CZ11-PSC	6.1	1:1	0.4	1:1	13	18	23
6%Ni/CZ21-PSC	6.2	2:1	0.6	1:1	15	15	21
3%Ni/CZ11-PSC	3.5	1:1	0.4	0.5:1	8.6	10	16
9%Ni/CZ11-PSC	9.1	1:1	0.4	1.5:1	19	26	25

*Estimated from XRD patterns with Scherrer equation

**Calculated from STEM images.

For XRD analysis of CeO₂ powder, Ce(NO₃)₃·6H₂O and PVP were mixed in DI water with a weight ratio of Ce³⁺:PVP = 1:1. This suspension was stirred for 2 h on a hot plate at 80 °C and pH 11. The resulting precipitate was dried overnight in the oven, then heat treated at 600 °C in air for 1 h to obtain CeO₂ powder.

4.2.2 Characterizations and analyses

The structures of the prepared PSCs were analyzed by an X-ray diffractometer (Rint-Ultima III; Rigaku, Japan) with CuKα radiation at 40 kV and 40 mA with 0.02°/step for scanning. The crystallite size of Ni was calculated using Scherrer's equation. Microstructures of the PSCs were investigated using a field emission scanning electron microscope (FE-SEM-S5200; Hitachi High Technologies, Japan) with an energy-dispersive X-ray spectrometer (EDX) and a scanning transmission electron microscope (STEM-HD2300A; Hitachi High Technology, Japan). The specific surface area of the samples, S_{BET}, was measured by the nitrogen adsorption method using a Belsorp-mini II analyzer (MicrotracBEL Corp., Japan). Ni loading in the PSCs was quantified by inductively coupled plasma (ICP) spectrometry (Shimadzu ICPE-9000 plasma atomic emission spectrometer (AES)).

The reducibility of the prepared PSCs was evaluated by temperature-programmed reduction (H₂-TPR) using a BELCAT-A analyzer (MicrotracBEL Corp.) with a thermal conductivity detector (TCD). The sample (200 mg) was placed in a glass U-tube and heated from room temperature to 800°C in increments of 2°C min⁻¹ under a 5% H₂/Ar flow (30 mL min⁻¹).

4.2.3 Dry reforming test

For each type of PSC, two donut-shaped PSCs were mounted in an alumina cylinder and heated from room temperature to 750°C under N₂ atmosphere for 4 h (see Fig. 2.3 in Chapter 2). To start the 15-h dry reforming test, the gas flow was switched from N₂ to a mixture of CH₄, CO₂, and N₂ (molar ratio of CH₄:CO₂:N₂ = 1:1:1) with a total flow rate of 60 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of ~3800 h⁻¹, which was determined as the total reactant flow rate (in mL h⁻¹)/total catalytic volume (in cm³). During the test, reformat compositions were analyzed every 30 min using an automatic gas chromatograph.

After the dry reforming test, temperature-programmed oxidation (TPO) was carried out to evaluate the degree of coking of the PSCs. The PSC sample (100 mg) used for the 15-h dry reforming test at 750°C was placed in a glass U-tube and heated from room temperature to

800°C at a rate of 3°C min⁻¹ under an air flow of 40 mL min⁻¹. Raman spectroscopic analysis was carried out to determine the amount of carbon formed during dry reforming by using a Horiba Jobin Yvon LABRAM 300 (France) Raman microscope with an achromatic flat field monochromator together with mirror-based reflective optics and detector of charge-couple device (CCD). The wavelength region for scanning was 100–3000 cm⁻¹ using a He-Ne laser source (632.8 nm wave-length, 20 mW power).

4.3 Result and discussion

4.3.1 Characterization of PSCs

The X-ray diffraction patterns of the prepared PSCs after the reduction treatment at 750°C are shown in Fig. 4.1, and that of the prepared CeO₂ powder is also plotted for reference.

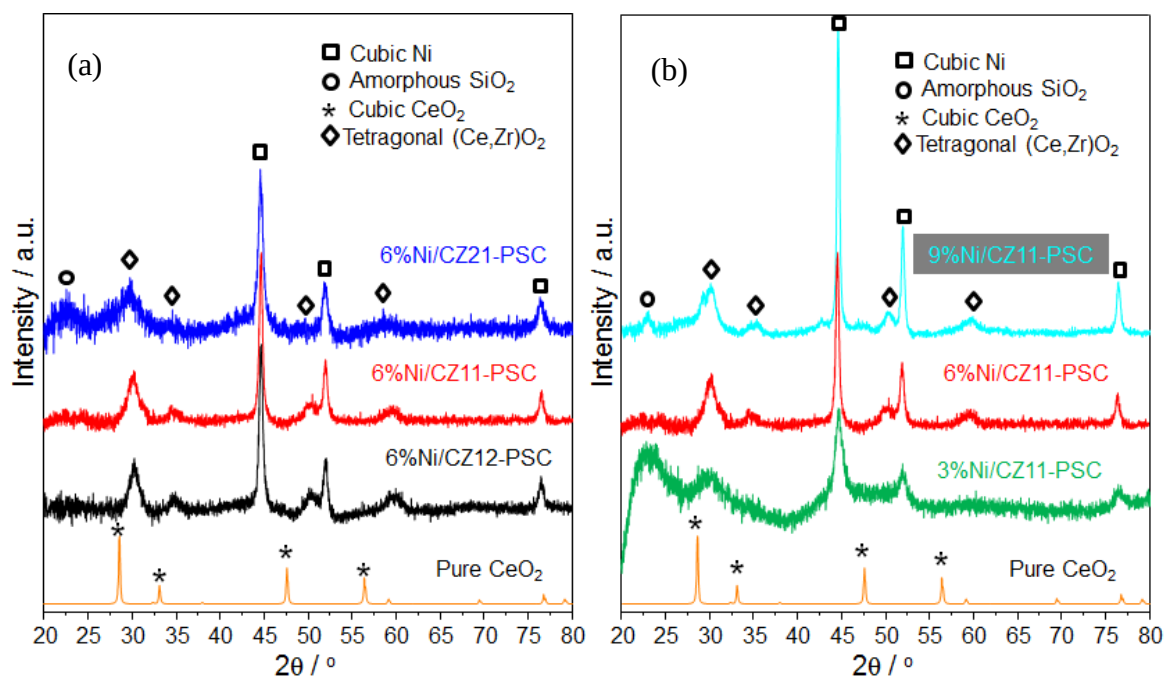


Fig. 4.1: Diffraction patterns of PSCs after reduction treatment at 750°C for 5 h under a 5% H₂-N₂ flow; (a) 6%Ni/CZ12-PSC, 6%Ni/CZ11-PSC, and 6%Ni/CZ21-PSC with different weight ratios of CeO₂/ZrO₂; (b) 3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC, and 9%Ni/CZ11-PSC with different Ni loadings. Diffraction pattern of pure CeO₂ powder is also shown for reference [27].

Figure 4.1(a) and (b) indicate the differences in the patterns for the different weight ratio of CeO₂/ZrO₂ and Ni loading, respectively. Diffraction peaks below 2θ of ~26° correspond to the Cf (SiO₂-Al₂O₃) having an amorphous structure [28]. For all PSCs, the diffraction peaks

reflecting pure CeO₂ were not observed. Peaks appeared at higher angles in comparison to those of cubic CeO₂ (28.5°, 33.1°, 47.5°, and 56.4°) and corresponded to the (111), (200), (220), and (311) faces, respectively (JCPDS Card No. 34-394). Although these peaks were weak because of the rather small amount of the charged oxide source, this reflected the substitution of the smaller Zr⁴⁺ atoms in the CeO₂ crystallite structure, indicating the formation of a tetragonal (Ce,Zr)O_{2-δ} solid solution [29,30]. This (Ce,Zr)O_{2-δ} solid solution could be synthesized in the paper-making process (hereafter called “on-paper synthesis”). As shown in Fig. 4.1(a), the main peak of tetragonal (Ce,Zr)O₂ for the (101) face shifted to a higher angle with the decreasing CeO₂/ZrO₂ ratio, i.e., the (101) peaks for 6%Ni/CZ21-PSC, 6%Ni/CZ11-PSC and 6%Ni/CZ12-PSC were observed at 29.6°, 30.0°, and 30.3°, respectively, indicating the dissolution of smaller Zr⁴⁺ in the crystal lattice of CeO₂.

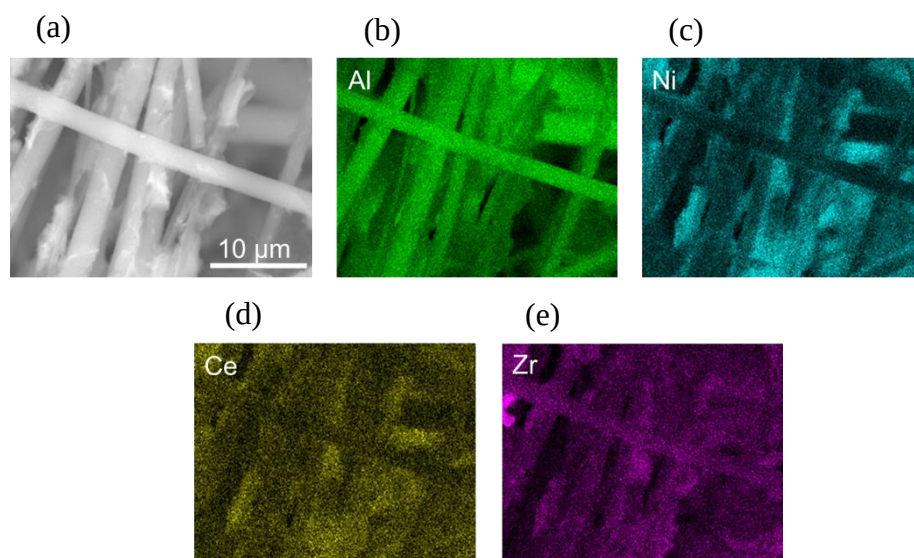


Fig. 4.2: Structure of 6%Ni/CZ11-PSC after reduction treatment at 750°C in 5% H₂ for 5 h; (a) FE-SEM image and corresponding EDX mapping images of (b) Al, (c) Ni, (d) Ce, and (e) Zr [27].

Figure 4.2 shows the microstructure of 6%Ni/CZ11-PSC after reduction treatment. Cf (recognized by Al) were entwined to form a fiber network in which Ni, Zr, and Ce were imaged at the same location and found to be widely dispersed, indicating the on-paper synthesis of (Ce,Zr)O_{2-δ} solid solution. The hydrolyzed metal ions of Ce⁴⁺ and Zr⁴⁺ were precipitated as Ce(OH)₄ and Zr(OH)₄ from their nitrates. Owing to the similar solubility product of Ce(OH)₄ (pK_{sp} = 47.7) and Zr(OH)₄ (pK_{sp} = 48.2), these hydroxides were homogeneously mixed and nanocrystals of (Ce,Zr)O_{2-δ} were formed in the subsequent sintering process [29]. STEM

analysis confirmed the formation of fine Ni particles (about 20 nm in size) on the (Ce,Zr)O_{2-δ} support (Fig. 4.3). The S_{BET} values of 3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC and 9%Ni/CZ11-PSC (see Table 4.1) with different Ni loading and the same CeO₂/ZrO₂ weight ratio (= 1.0) suggest that 9.1 wt% loading is excessive and causes Ni agglomeration.

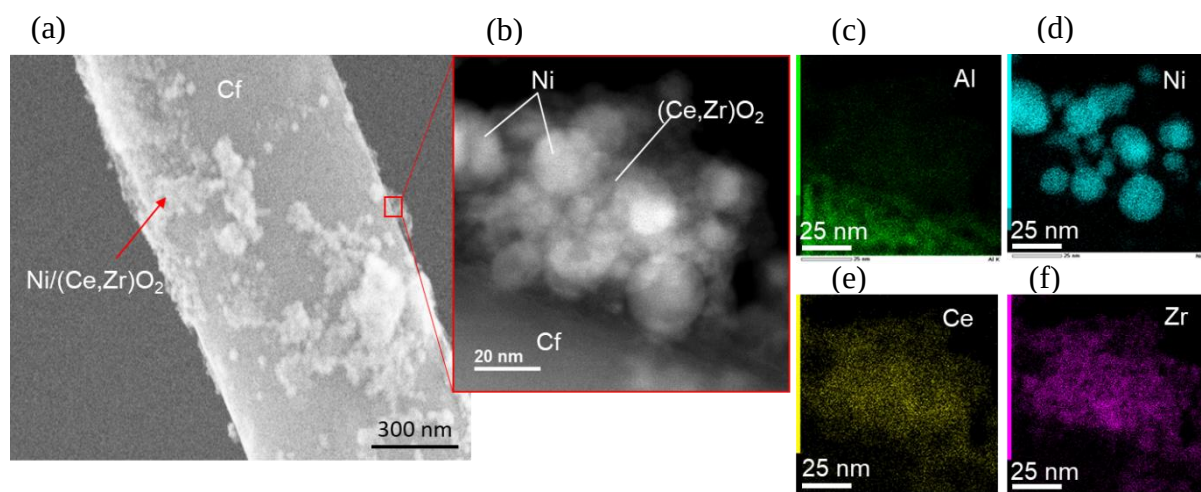


Fig. 4.3: Morphologies of the catalyst particles loaded in 6%Ni/CZ11-PSC after reduction treatment at 750°C in 5% H₂ for 5 h; (a) FE-SEM image, (b) STEM image showing fine Ni particles formed on (Ce,Zr)O_{2-δ}, and the corresponding EDX mapping images of (c) Al, (d) Ni, (e) Ce, and (f) Zr [27].

The different states of Ni dispersion on the (Ce,Zr)O_{2-δ} support are compared in Fig. 4.4. For PSCs with 6 wt% of Ni (6%Ni/CZ12-PSC, 6%Ni/CZ11-PSC, and 6%Ni/CZ21-PSC), the Ni particles grown on the (Ce,Zr)O_{2-δ} support became smaller with increasing CeO₂/ZrO₂ ratio. During on-paper synthesis, the redox cycle ability of Ce³⁺/Ce⁴⁺ could affect the Ni²⁺ ions, and this electron transfer, which enhanced the interactions between Ni and the support oxide [31,32], became more pronounced for higher ceria content and resulted in smaller Ni particles. For the PSCs with the same CeO₂/ZrO₂ ratio of 1 (3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC, and 9%Ni/CZ11-PSC), the Ni particle size increased with increasing Ni loading in the order of 3%Ni/CZ11-PSC < 6%Ni/CZ11-PSC < 9%Ni/CZ11-PSC, as listed in Table 4.1. In the case of 9%Ni/CZ11-PSC, the Ni particle size was not uniform and large particles of size 100 nm were observed (Fig. 4.4(e)). These results suggested that the Ni/(Ce,Zr)O_{2-δ} ratio should be less than 1 for the prevention of Ni agglomeration.

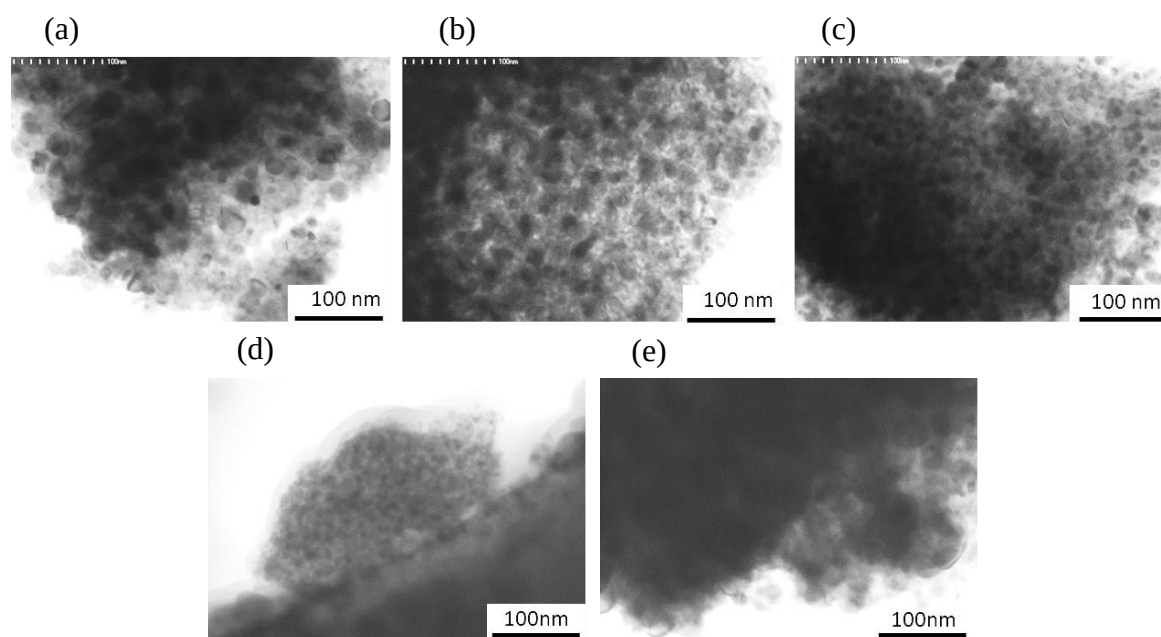


Fig. 4.4: STEM images showing Ni dispersion on (Ce,Zr)O_{2-δ} in (a) 6%Ni/CZ12-PSC, (b) 6%Ni/CZ11-PSC, (c) 6%Ni/CZ21-PSC, (d) 3%Ni/CZ11-PSC, and (e) 9%Ni/CZ11-PSC after reduction treatment at 750 °C under 5% H₂-N₂ flow for 5 h [27].

Figure 4.5 shows the reduction behavior of the prepared PSCs. Figs. 4.5(a) and (b) indicate the dependences on the weight ratio of CeO₂/ZrO₂ and Ni loading, respectively. For the sample without Ni loading, H₂ consumption was observed between 250 and 450°C (Inorganic paper), which corresponds to the reduction of Ce⁴⁺ to Ce³⁺ in the (Ce,Zr)O_{2-δ} support. With Ni loading, this reduction peak shifted to a lower temperature of ~200–250°C (Profile I: Green) [28,33]. The distortion of the (Ce,Zr)O_{2-δ} lattice caused by the incorporation of Ni promoted oxygen mobility, and consequently, lattice oxygen was easily released at a low temperature [34,35]. For the Ni-loaded PSC without the dispersion of any oxide supports such as HT and CZ [36], the reduction peak observed at 265°C indicated the weak interaction of Ni with Cf. In contrast, in the higher temperature region, the main peak at 310°C and the shoulder peak at 384°C likely corresponded to the reductions of surface and bulk NiO, respectively, with stronger interaction [37]. H₂ consumption above 300°C in the profiles of the prepared Ni/CZ-PSCs indicated the reduction of Ni²⁺ to metallic Ni (completed at 660°C) interacting with (Ce,Zr)O_{2-δ}. This was consistent with the STEM/EDX analysis where Ni particles were not observed on Cf of Ni/CZ-PSCs.

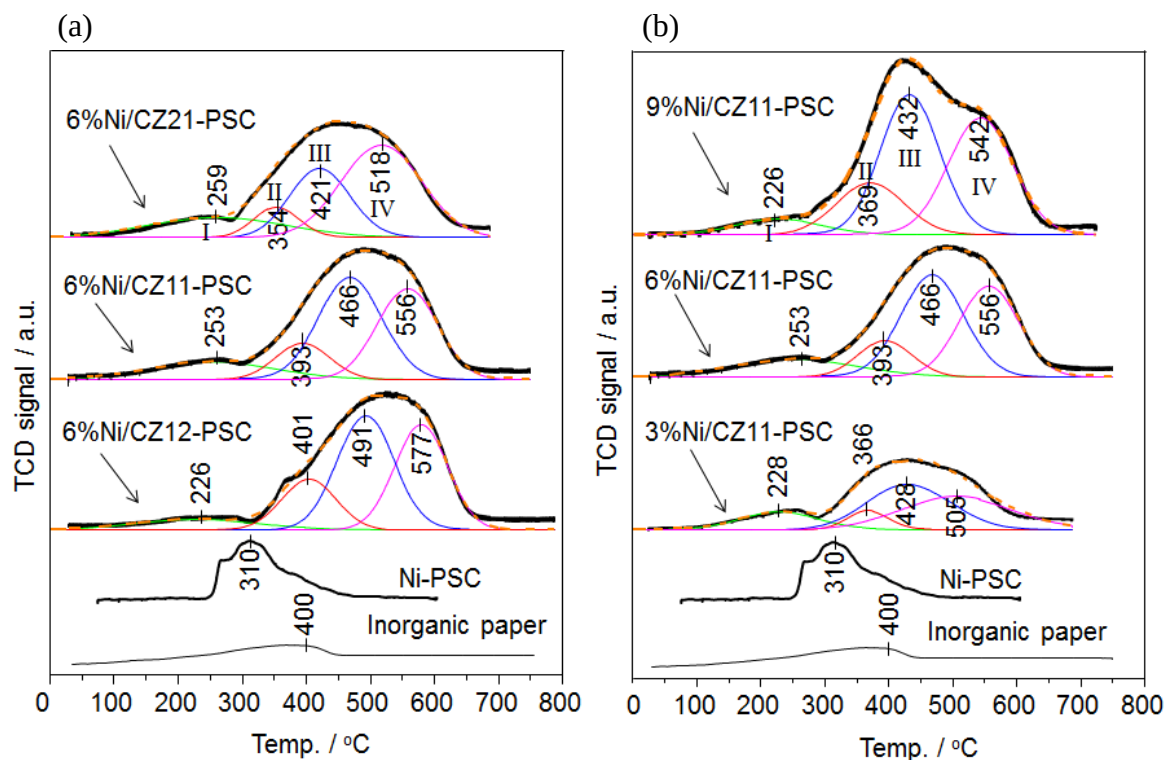


Fig. 4.5: H₂-TPR profiles of the prepared Ni/CZ-PSCs. (a) 6%Ni/CZ12-PSC, 6%Ni/CZ11-PSC, and 6%Ni/CZ21-PSC with different CeO₂/ZrO₂ weight ratios and (b) 3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC, and 9%Ni/CZ11-PSC with different Ni loading amounts. The profiles for the inorganic paper without Ni loading (corresponding to 3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC, and 9%Ni/CZ11-PSC without Ni loading) and Ni-PSC without CZ dispersion are also plotted as references. The results of the deconvolution are indicated with (I) green, (II) red, (III) blue, and (IV) pink profiles [27].

Table 4.2: H₂ consumption estimated from the H₂-TPR profiles

Sample	H ₂ consumption (mmol H ₂ /g _{cat})					Theoretical H ₂ consumption for NiO reduction
	For each component after deconvolution				II + III + IV	
	I	II	III	IV		
6%Ni/CZ12-PSC	0.10	0.23	0.51	0.44	1.18	1.09
6%Ni/CZ11-PSC	0.17	0.16	0.52	0.43	1.11	1.04
6%Ni/CZ21-PSC	0.26	0.13	0.37	0.64	1.14	1.06
3%Ni/CZ11-PSC	0.12	0.07	0.32	0.30	0.68	0.60
9%Ni/CZ11-PSC	0.10	0.28	0.65	0.58	1.51	1.55

In order to further understand the reduction behavior, deconvolution of the TPR profiles was conducted by fitting the experimental TPR curves using Gaussian function. The H₂-TPR profile of the Ni/CZ-PSCs could be separated into four components, from the low temperature region (I) where Ce⁴⁺ was reduced to Ce³⁺ in the (Ce,Zr)O_{2-δ}, to the higher temperature region (II) where NiO was changed to metallic Ni with weak interactions and regions (III,IV) where Ni strongly interacted with (Ce,Zr)O_{2-δ}. (III) and (IV) were associated with the surface and bulk reductions of NiO, respectively. The amounts of H₂ consumed, as estimated from the H₂-TPR measurements, are summarized in Table 4.2.

The sum of H₂ consumption, II + III + IV, was close to the theoretical H₂ consumption for NiO reduction, and had the same tendency with the theoretical value for the change in the material composition. This supports the reliability of the present deconvolution.

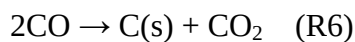
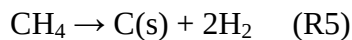
H₂ consumption for I increased with the increasing the weight ratio of CeO₂/ZrO₂ (6%Ni/CZ12-PSC < 6%Ni/CZ11-PSC < 6%Ni/CZ21-PSC), implying OSC increase in this order. The lower OSC might reduce the interaction between Ni and oxide support [34,35], and hence increase the amount of Ni with weak interaction with (Ce,Zr)O_{2-δ}, which was proved by the increase in the H₂ consumption for II in the order of 6%Ni/CZ21-PSC < 6%Ni/CZ11-PSC < 6%Ni/CZ12-PSC, consistent with the order of the Ni particle size observed by STEM.

As shown in Fig. 4.5(b), for 9%Ni/CZ11-PSC with 9.1 wt% Ni loading, corresponding to Ni(wt)/(Ce,Zr)O_{2-δ} (wt) > 1, the contribution of II (Ni with weak interaction with (Ce,Zr)O_{2-δ}) was estimated to be relatively high in comparison to 3%Ni/CZ11-PSC (3.5 wt% Ni) and 6%Ni/CZ11-PSC (6.1 wt% Ni), corresponding to Ni(wt)/(Ce,Zr)O_{2-δ} (wt) ≤ 1, indicating that excessive Ni loading can lead to the increase in the number of weakly-promoted active sites. Moreover, a significantly large H₂ consumption for III indicated the higher density of Ni particles in 9%Ni/CZ11-PSC as compared to 3%Ni/CZ11-PSC and 6%Ni/CZ11-PSC, resulting in the promotion of Ni agglomeration under reducing atmosphere (Fig. 4.4(e)). Thus, the condition of Ni(wt)/(Ce,Zr)O_{2-δ}(wt) ≤ 1 should be satisfied.

4.3.2 Catalytic activity of PSCs for dry reforming of CH₄

Figure 4.6 shows the thermodynamic equilibrium composition of the equimolar mixture of CH₄ and CO₂. The overall reaction of dry reforming of CH₄ (R1) is strongly endothermic, and therefore proceeds forward to give the product with increasing temperature. Carbonaceous species (C(s)) are formed on the catalyst surface mainly via endothermic CH₄ cracking (R5) and

the exothermic Boudouard reaction (R6) [38]. In a wide temperature range below 900 °C, the latter results in H₂/CO > 1 and the lower apparent CO₂ conversion than CH₄ conversion.



The oxide support with OSC, here (Ce,Zr)O_{2-δ}, can promote R4 by the lattice-oxygen-mediated reaction cycle (R2 and R3), accelerating the removal of carbon formed in R5. The formation of carbon mainly occurs in the catalytically active zones having a high CH₄/H₂ molar ratio, for example, in the fuel inlet region, and R6 is more pronounced further downstream in regions with high CO/CO₂ molar ratio [38].

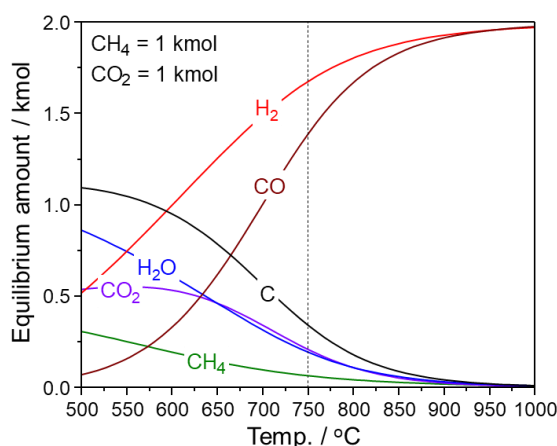


Fig. 4.6: Equilibrium composition for the equimolar mixture of 1 kmol CH₄ and 1 kmol CO₂ calculated by HSC Chemistry Ver. 9.0.5 software.

Figure 4.7 shows the CH₄ conversion and H₂/CO ratio measured in the 15-h dry reforming test at 750°C. The equilibrium conversion of CH₄ at this temperature was 94%. As shown in Fig. 4.7(a), in the case of PSC with 6 wt% Ni, the initial CH₄ conversion increased in the order of 6%Ni/CZ12-PSC (80%) < 6%Ni/CZ21-PSC (85%) < 6%Ni/CZ11-PSC (87%). After ~2 h, the catalytic activity of 6%Ni/CZ12-PSC started to decrease and the CH₄ conversion at 15 h was 71% (11% degradation). On the other hand, both 6%Ni/CZ11-PSC and 6%Ni/CZ21-PSC exhibited a lower degradation rate (3%), indicating that the ratio CeO₂/ZrO₂ ≥ 1 was required for stable catalytic performance. The reason for the low catalytic activity of 6%Ni/CZ12-PSC with CeO₂/ZrO₂ < 1 was the formation of more coarse Ni particles that interacted weakly with the oxide support, as discussed in section 4.3.1.

As shown in Fig. 4.7(b), the H₂/CO ratio was ~0.9 for all cases, which is considerably lower than the equilibrium ratio of 1.2. At temperatures above 700°C, carbonaceous species (C(s)) are formed on the catalyst surface via endothermic CH₄ cracking (R5). Simultaneously, a part of the C(s) is consumed via R4 (also endothermic) because of the presence of CO₂ in the inlet gas. The rather low H₂/CO ratio in the present study can be explained by the strong contribution of the reverse water-gas shift reaction (R7) [39].



For the same ratio of CeO₂/ZrO₂ = 1 (3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC, and 9%Ni/CZ11-PSC), stable CH₄ conversion was achieved in the Ni loading range of 3.5–9.1 wt%. However, under the present conditions, at least 6 wt% of Ni loading was necessary to maximize the conversion.

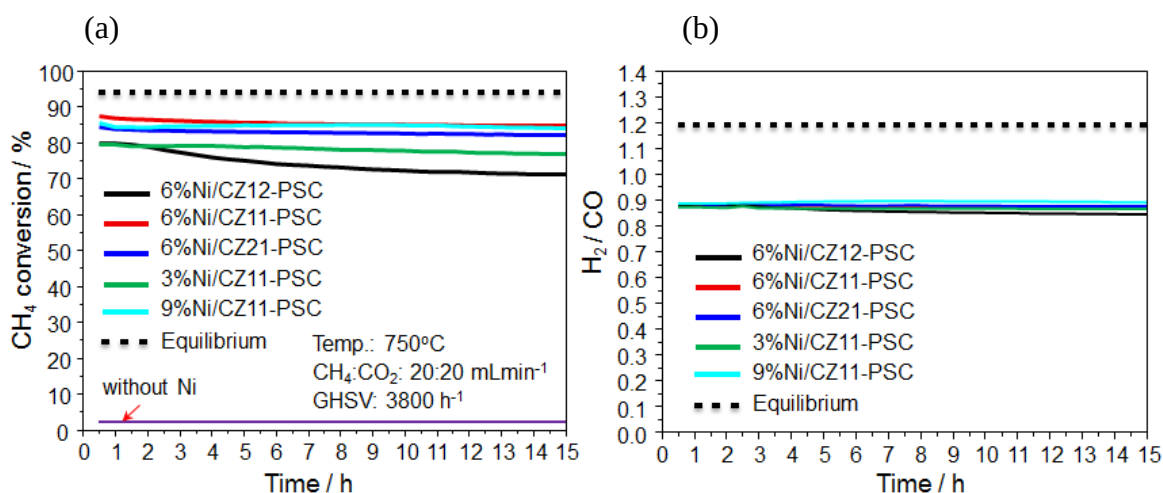


Fig 4.7: Results of dry reforming of CH₄ using PSCs at 750°C; (a) CH₄ conversion and (b) H₂/CO ratio measured for 15 h. Equilibrium conversion is indicated by the dashed line [27].

4.3.3 Characterization of PSCs after 15 h of dry reforming

Figure 4.8 shows the TPO profiles of the PSCs used in the 15 h dry reforming tests at 750°C shown in Fig. 4.7. Detection of CO₂ in the TPO profile implied the oxidation of carbonaceous species deposited in the PSCs. Peaks over 300°C generally indicate the presence of amorphous or graphitic carbon, and those appearing at higher temperatures suggest a greater degree of graphitization [40,41]. The results for the PSCs with 6 wt% of Ni (6%Ni/CZ12-PSC, 6%Ni/CZ11-PSC, and 6%Ni/CZ21-PSC) show that 6%Ni/CZ21-PSC prepared with CeO₂/ZrO₂

= 2 exhibited the highest tolerance to coking. On the other hand, there was significant coking in the case of 6%Ni/CZ12-PSC with CeO₂/ZrO₂ = 0.5.

Carbon accumulation was more pronounced on the Ni particles with weaker interaction with (Ce,Zr)O_{2-δ} [41], because the lattice-oxygen-mediated reaction cycle (as in Reactions R2–R4) did not occur. From the results shown in Fig. 4.5, it was evident that among the PSCs with 6 wt% Ni, the content of weakly interacting Ni particles was the largest in 6%Ni/CZ12-PSC (II in Table 4.2). This negatively affected the catalytic activity of 6%Ni/CZ12-PSC. In the cases of 6%Ni/CZ11-PSC and 6%Ni/CZ21-PSC, the stronger interaction with (Ce,Zr)O_{2-δ} and the higher OSC (I in Table 4.2) may have a positive impact on the catalytic activity. For the PSCs with CeO₂/ZrO₂ = 1 but different Ni loading, the coking tolerance decreased in the order 6%Ni/CZ11-PSC (6.1 wt% Ni) > 3%Ni/CZ11-PSC (3.5 wt% Ni) > 9%Ni/CZ11-PSC (9.1 wt% Ni). Severe coking in the case of 9%Ni/CZ11-PSC was attributed to its high content of Ni particles having weak interactions with (Ce,Zr)O_{2-δ} and agglomeration of Ni during operation.

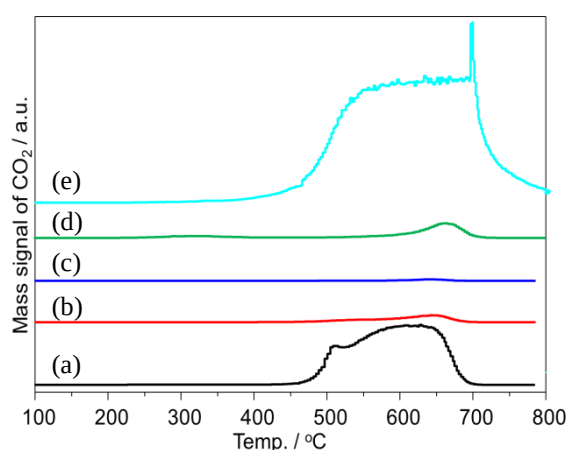


Fig. 4.8: TPO profiles of (a) 6%Ni/CZ12-PSC, (b) 6%Ni/CZ11-PSC, (c) 6%Ni/CZ21-PSC, (d) 3%Ni/CZ11-PSC, and (e) 9%Ni/CZ11-PSC after the dry reforming tests [27].

The morphologies of the Ni/(Ce,Zr)O_{2-δ} particles in the PSCs after the dry reforming test carried out at 750°C for 15 h are shown in Fig. 4.9. In the case of 6%Ni/CZ12-PSC (a), Ni agglomeration and formation of fibrous carbon was confirmed. However, Ni agglomeration was negligible and carbon formation was difficult to observe in 6%Ni/CZ11-PSC (b) and 6%Ni/CZ21-PSC (c) (Fig. 4.4). For the PSCs with CeO₂/ZrO₂ = 1, no change was observed in Ni morphology during dry reforming (3%Ni/CZ11-PSC and 6%Ni/CZ11-PSC), although carbon

agglomerates with some embedded Ni particles were observed in 9%Ni/CZ11-PSC (9.1 wt% Ni) (e).

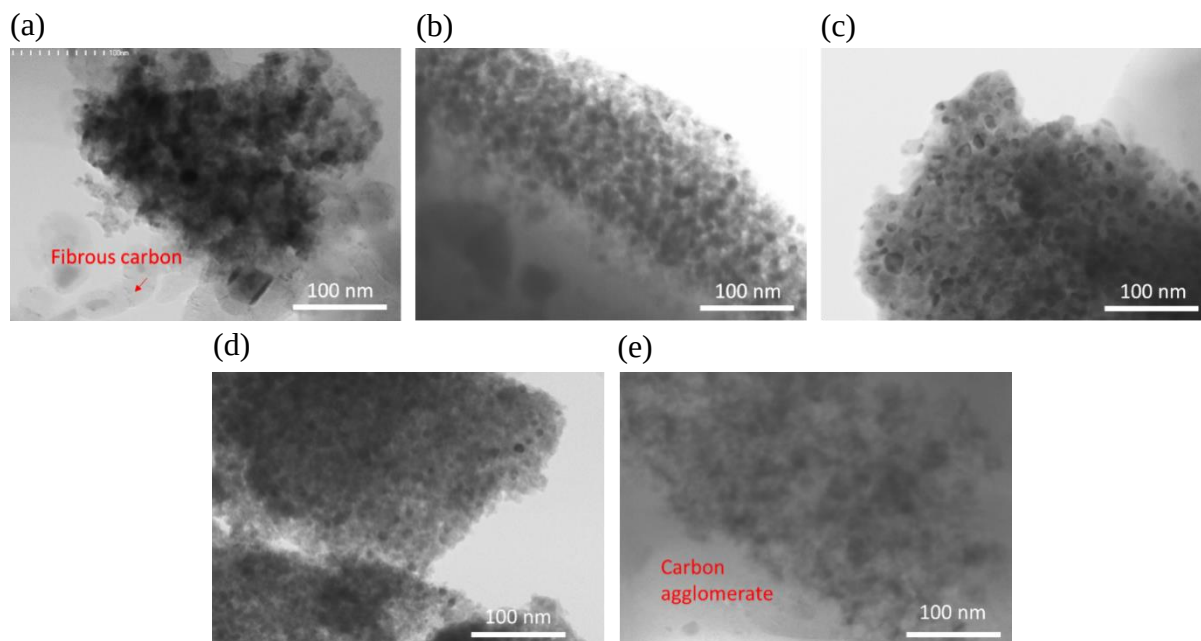


Fig. 4.9: STEM images of Ni/(Ce,Zr)O_{2-δ} particles in (a) 6%Ni/CZ12-PSC, (b) 6%Ni/CZ11-PSC, (c) 6%Ni/CZ21-PSC, (d) 3%Ni/CZ11-PSC, and (e) 9%Ni/CZ11-PSC after the dry reforming test performed at 750 °C for 15 h [27].

Figure 4.10 shows the Raman spectra of Ni/CZ-PSCs after the dry reforming test performed for 15 h. For all samples, three main peaks were observed at 1322, 1569, and 2643 cm⁻¹, corresponding to the D (graphene disorder), G (graphite), and G' (specific to graphene) bands, respectively [42,43]. From the intensity ratio of these bands, formation of multi-wall carbon nanotubes was inferred [35]. The intensities of these bands in the cases of 6%Ni/CZ12-PSC and 9%Ni/CZ11-PSC were higher than those of 6%Ni/CZ11-PSC, 6%Ni/CZ21-PSC, and 3%Ni/CZ11-PSC, indicating a higher intolerance to coking, especially, in the case of 9%Ni/CZ11-PSC, for which the G band peak became the highest instead of the D band.

For the PSCs with CeO₂/ZrO₂ ≥ 1 and Ni/(Ce,Zr)O_{2-δ} ≤ 1 (3%Ni/CZ11-PSC, 6%Ni/CZ11-PSC, and 6%Ni/CZ21-PSC), the lattice-oxygen-mediated reaction cycle (as in R1–R3) is expected to take place easily because of the strong interactions between the small Ni particles and (Ce,Zr)O_{2-δ} oxide support with higher OSC, resulting in the high coking tolerance. In the cases of 6%Ni/CZ12-PSC and 9%Ni/CZ11-PSC, carbon accumulation was promoted on the

coarse Ni particles together with weak interaction with (Ce,Zr)O_{2-δ}, which blocked the active catalytic sites during dry reforming and led to further deactivation of the catalysts.

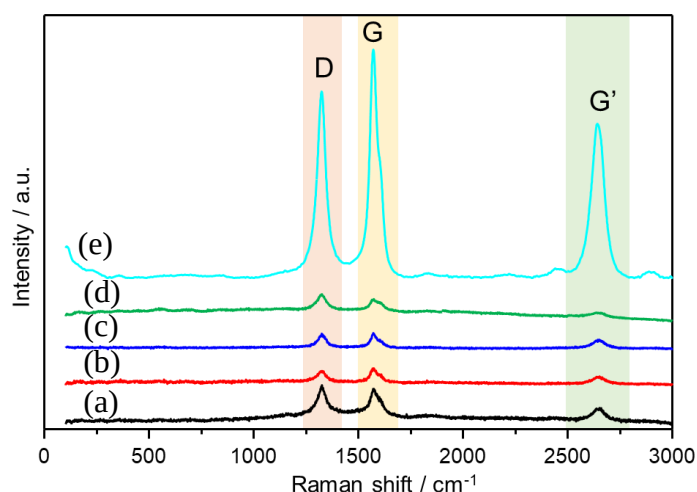


Fig. 4.10: Raman spectra of (a) 6%Ni/CZ12-PSC, (b) 6%Ni/CZ11-PSC, (c) 6%Ni/CZ21-PSC, (d) 3%Ni/CZ11-PSC, and (e) 9%Ni/CZ11-PSC after the dry reforming test performed at 750 °C for 15 h [27].

4.4 Conclusion

In this work, PSCs with Ni particles grown on (Ce,Zr)O_{2-δ} dispersed in a ceramic fiber (SiO₂-Al₂O₃) (Cf) network were prepared via the paper-making process. The (Ce,Zr)O_{2-δ} solid solution could be formed by the developed on-paper synthesis including co-precipitation of cerium and zirconium ions in the Cf suspension, followed by the filtration process for making inorganic paper, and subsequent heat treatment. Catalytic activity of the Ni-loaded (Ce,Zr)O_{2-δ}-dispersed PSCs (Ni/CZ-PSCs) for the dry reforming of CH₄ was evaluated at 750°C with different Ni loading (3.5, 6.1, and 9.1 wt%) and CeO₂/ZrO₂ weight ratios (0.5, 1.0, and 2.0 corresponding to $x = 0.2, 0.4$, and 0.6 in (Ce _{x} Zr _{$1-x$})O₂, respectively). While the loading amount of 3.5 wt% Ni proved to be insufficient for maximizing CH₄ conversion, 9.1 wt% of Ni was excessive because it resulted in agglomeration and the formation of Ni particles that interacted weakly with (Ce,Zr)O_{2-δ}. On the other hand, 6.1 wt% of Ni was found to be close to the optimum load. Among the 6 wt% Ni/CZ-PSCs, the one with the lowest CeO₂/ZrO₂ (= 0.5) resulted in the lowest dry reforming activity and degradation accompanied by coking. The PSCs with CeO₂/ZrO₂ = 1.0 and 2.0 exhibited excellent coking tolerance, which may be a result of the higher OSC as compared to CeO₂/ZrO₂ = 0.5. The 6 wt% Ni/CZ-PSC with CeO₂/ZrO₂ ≥ 1 was

shown to be a promising support catalyst for improving the performance and stability of the DIR-SOFCs fueled by biogas.

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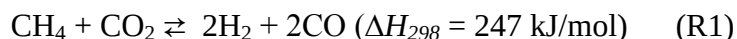
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Chapter 5: Superiority of Ni-loaded (Ce,Zr)O_{2-δ}-dispersed paper-structured catalyst to conventional ones

In this chapter, the catalytic activities of three types of Ni-loaded paper-structured catalysts (PSCs): (a) without the dispersion of support oxide particles in the fiber network (Ni-PSC), (b) with the dispersion of (Mg,Al)O derived from hydrotalcite (HT) (Ni/HT-PSC), and (c) with the dispersion of (Ce,Zr)O_{2-δ} (Ni/CZ-PSC), for dry reforming of CH₄ were compared in the temperature range of 650–800°C to show the superiority of Ni/CZ-PSC to conventional Ni-PSC and Ni/HT-PSC.

5.1 Motivation

Ceramic fibers (Cfs) which are referred to inorganic and non-metallic fibers have a very large aspect ratio and very small cross-sectional area. Among many types of Cfs such as ZrO₂ Cf, SiC Cf, SiO₂-CaO₂, etc., SiO₂-Al₂O₃ Cf has been considered as standard Cf due to its excellent properties such as high thermostability and mechanical flexibility for forming a good textile structure [1]. Thus, flexible PSCs made up of a SiO₂-Al₂O₃ Cf network have been studied for many applications such as energy, chemical processing, removal of poisonous gases, etc., [2-5]. Especially, the application to solid oxide fuel cell (SOFC) is one of the most promising approaches to realize direct internal reforming (DIR) operation of SOFC [6-9], because PSCs can be easily integrated into an SOFC stack to serve as a reforming reaction zone producing syngas (mixture of H₂ and CO) from hydrocarbon fuels. In the case of a biogas mixture of 50%–60% CH₄ and 40%–50% CO₂, syngas production proceeds with the dry reforming reaction (R1) as a major reaction [10-12].



The activity of metal catalysts for dry reforming of CH₄ is reported to increase in the order of Fe < Pt < Os < Co < Ni < Rh < W < Ru [13,14]. Although pure Ni is less active and intolerant to coking compared to pure Ru, it is commonly utilized because of its lower cost. To improve the catalytic properties, a metal catalyst is generally loaded on oxide supports. Mesoporous oxides (Al₂O₃, MgO), basic oxides (CaO, MgO, BaO, BaTiO₃) and oxides with oxygen storage capacity (OSC) (CeO₂-based) are reported as support oxides for Ni [14-16]. Bimetallic (Ni-Co) and Ni-

containing perovskite (LaSrNiO) are also proven to improve catalytic activity [17]. Moreover, the differences in catalytic performance were also reviewed for different catalyst preparation methods [18-20].

In the present study, three types of Ni-loaded PSCs (Fig. 5.1): without the dispersion of promoter oxide particles (Ni-PSC), with the dispersion of (Mg,Al)O derived from hydrotalcite (Ni/HT-PSC) and with the dispersion of (Ce,Zr)O_{2-δ} (Ni/CZ-PSC), were fabricated via impregnation or co-precipitation, and then their catalytic performances in dry reforming of CH₄ in the temperature range of 650–800°C were compared. As a framework for the PSC, Cf can enhance the dispersion of Ni-support oxide particles, and the (Mg,Al)O and (Ce,Zr)O_{2-δ} particles dispersed in the framework serve as a promoter.

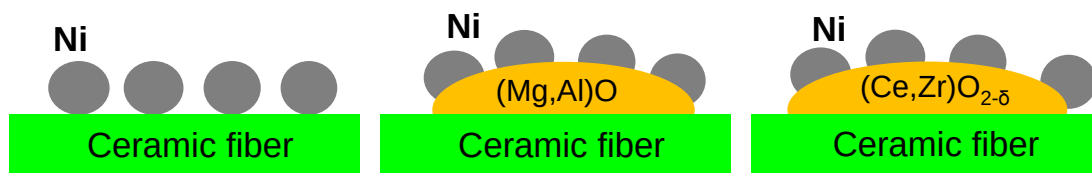


Fig. 5.1: Schematic illustration of three types of Ni-loaded PSCs prepared in this study: (a) without dispersion of promoter oxide particles (Ni-PSC), (b) with dispersion of (Mg,Al)O derived from hydrotalcite (Ni/HT-PSC), and (c) with dispersion of (Ce,Zr)O_{2-δ} (Ni/CZ-PSC).

5.2 Experimental

5.2.1 Preparation of PSCs

Preparation procedure of Ni-loaded PSC (Ni-PSC) and Ni-loaded (Mg,Al)O-dispersed PSC (Ni/HT-PSC) was schematically shown in Fig. 2.1(a) (Chapter 2), and that of Ni-loaded (Ce,Zr)O_{2-δ}-dispersed PSC (Ni/CZ-PSC) was illustrated in Fig. 2.1(b). Details are summarized below.

Ni-PSC

Ni-PSC was prepared by a papermaking process using the dual polymer retention system. First, 6 g of Cf was dispersed in 1 L of deionized water. Then, 15 g of 0.2 wt% solution of cationic polymer (poly diallyldimethylammonium chloride, PDADMAC) was poured into the slurry and stirred for 3 min, after which 2.5 g of yttria-stabilized zirconia sol (20 wt% solid) (Nissan Chemical Industries Ltd., Japan), Zs, was added. Next, 16.3 g of 0.2 wt% solution of anionic polymer (acrylamide-co-acrylic acid, A-PAM) was poured into the slurry and stirred for

3 min. After adding 2.5 g (solid base) of an organic pulp fiber suspension, the slurry was solidified by filtration, and the resulting wet-state paper sheet with a diameter of 16 cm was pressed at 350 kPa for 3 min and dried at 100°C for 2 h to form raw paper. Small pieces of the raw paper with a diameter of 20 mm were heat-treated at 800°C in air for 5 h to form a Cf network by binder (Zs) welding, performed simultaneously to obtain a highly porous structure by removing the organic components. The heat-treated paper was immersed in 0.5 M of Ni(NO₃)₂ aqueous solution for 1 h, and fired at 800°C for 5 h to obtain Ni-PSC.

Ni/HT-PSC

Ni/HT-PSC was prepared by the same procedure as that for Ni-PSC. However, instead of 6 g of Cf, 5 g of Cf plus 2 g of hydrotalcite ([Mg₆Al₂(OH)₁₆CO₃]·4H₂O) was dispersed in the slurry. After the impregnation process for Ni loading, the sample was fired at 800°C in air for 5 h.

Ni/CZ-PSC

A detailed description of the process is given in Sec. 4.2 (Chapter 4). Briefly, 5 g of Cf was mixed with 2.5 g of polyvinylpyrrolidone (PVP) in 250 mL of deionized water. Then, designated amounts of Ni(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O and ZrO(NO₃)₂ corresponding to 0.5 g of Ni/(Ce,Zr)O_{2-δ} with Ni, CeO₂ and ZrO₂ weight ratios of 50%, 33% and 17%, respectively, were dissolved in the suspension. Next, 1 g of NaOH was added and stirred vigorously, after which 40 mL of aqueous solution containing 2.5 g of NaBH₄ was slowly dropped into the stirred slurry for 1 h. Next, 15.0 g of 0.2 wt% cationic and 16.3 g of 0.2 wt% anionic polyelectrolytes and 2.5 g (solid base) of an organic pulp fiber suspension were poured into the slurry and solidified by filtration. The wet-state paper sheet with a diameter of 16 cm was pressed and dried to form raw paper, followed by heat treatment at 600°C in air for 1 h to obtain Ni/CZ-PSC.

The different compositions in the paper-catalyst preparation of three Ni-loaded PSCs are summarized in Table 5.1.

Table 5. 1: Slurry compositions in the papermaking process.

Sample	Cf / wt%	Ni(NO ₃) ₂ ·6H ₂ O / wt%	Precursor of oxide support / wt%	Zs / wt%	Cationic polymer / wt%	Anionic polymer / wt%	Pulp / wt%
Ni-PSC	88	—*	0	4.4	2.6	0.6	4.4
Ni/HT-PSC	65	—*	26 (Hydrotalcite)	3.2	1.9	0.4	3.2
Ni/CZ-PSC	63.6	20.7	7.3 (Ce(NO ₃) ₃ ·6H ₂ O); 2.9 (ZrO(NO ₃) ₂)	0	1.9	0.4	3.2

*For Ni-PSC and Ni/HT-PSC, Ni was loaded by impregnation after the papermaking process.

5.2.2 Characterizations and analyses

Structures of the prepared PSCs were analyzed by X-ray diffractometry (Rint-Ultima III diffractometer, Rigaku, Japan) with CuK α radiation at 40 kV and 40 mA. Crystallite size of Ni was calculated using the Scherrer equation. Microstructures of the PSCs were investigated by field emission scanning electron microscopy (FESEM-S5200, Hitachi High-Technologies Corp., Japan) using an energy-dispersive X-ray spectrometer (EDX) and a scanning transmission electron microscope (STEM-HD2300A, Hitachi High-Technologies). Specific surface area of the samples was measured by the nitrogen adsorption method using a Belsorp-miniII (MicrotracBEL Corp., Japan). Ni loading in the PSCs was quantified by inductively coupled plasma – atomic emission spectrometry (ICPE-9000, Shimadzu Corp., Japan). Reducibility of the prepared PSCs was evaluated by temperature-programmed reduction (H₂-TPR) using a BELCAT-A (MicrotracBEL Corp.) with a thermal conductivity detector (TCD). Here, 200 mg of a sample was placed in a glass U-tube and heated from room temperature to 800°C in increments of 2°C min⁻¹ under 5% H₂/Ar flow (30 mL min⁻¹).

During the 15 h test, the reformat compositions were analyzed every 30 min by an automatic gas chromatograph (GC-20B, Shimadzu Corp.).

For the PSCs after the dry reforming test, temperature-programmed oxidation (TPO) was carried out to evaluate the degree of coking. Here, 100 mg of a PSC sample used for the 15 h dry reforming test at 750°C was placed in a glass U-tube and heated from room temperature to 800°C at 3°C min⁻¹ under 40 mL min⁻¹ air flow.

5.3 Result and discussion

5.3.1 Characterization of PSCs

Figure 5.2(a) shows the X-ray diffraction patterns of Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC after reduction treatment at 750°C for 5 h in the 5% H₂-N₂ stream (50 mL min⁻¹). The diffraction peaks at a 2θ angle of around 22.0° reflect the amorphous structure of SiO₂-Al₂O₃ (Cf) [21]. For Ni-PSC and Ni/HT-PSC, diffraction peaks appeared at the 2θ angles of 30.2°, 35.0°, 50.4° and 60°, corresponding to the (111), (200), (220) and (311) planes of the cubic fluorite phase of ZrO₂, respectively, reflecting the yttria-stabilized zirconia sol (Zs) applied as an inorganic binder. In the case of Ni/CZ-PSC, a tetragonal (Ce,Zr)O_{2-δ} solid solution was formed, as discussed in Sec. 4.3.2 (Chapter 4). It was confirmed in the STEM investigation that fine Ni particles (~13 nm) grew on the (Ce,Zr)O_{2-δ} solid solution dispersed in the Cf network [22]. In the case of (Mg,Al)O dispersion (Ni/HT-PSC), after heat treatment of the raw paper at 800°C (before Ni loading), an (Mg,Al)O solid solution was formed from the hydrotalcite [23]. For the sample after Ni loading and subsequent reduction treatment, as shown in Fig. 5.2(a), the peak of the (200) face of (Mg,Al)O appeared at 43.1°, a lower angle compared to 43.2° of the pure (Mg,Al)O, indicating the incorporation of Ni²⁺, having a larger ionic radius than that of Al³⁺, into the (Mg,Al)O. During the impregnation process for Ni loading, cation exchange between Mg²⁺ in (Mg,Al)O and Ni²⁺ in the nitrate solution took place to form an (Ni,Mg,Al)O solid solution [23,24]. Moreover, the cubic zirconia phase corresponding to Zs was not affected by the (Mg,Al)O dispersion and Ni loading, indicating that Zs was chemically compatible with the other components in Ni/HT-PSC.

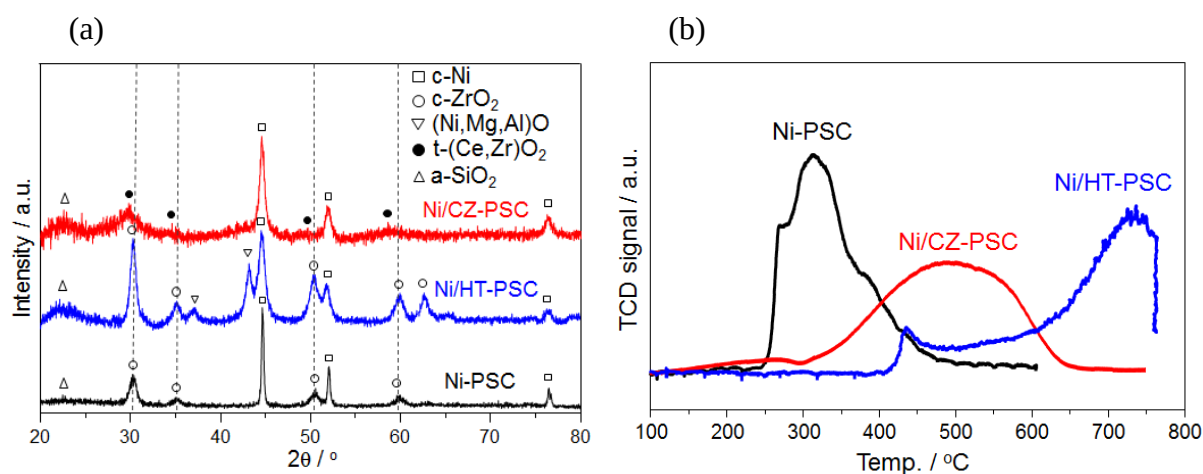


Fig. 5.2: (a) Diffraction patterns of Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC after reduction treatment at 750°C for 5 h under 5% H₂-N₂ flow; c-Ni, c-ZrO₂, (Ni,Mg,Al)O, t-(Ce,Zr)O_{2-δ} and

a-SiO₂ stand for the diffraction peaks of cubic Ni, cubic ZrO₂, cubic (Ni,Mg,Al)O, tetragonal (Ce,Zr)O_{2-δ} and amorphous SiO₂, respectively. (b) H₂-TPR profiles of the as-prepared PSCs.

Figure 5.2(b) shows the H₂-TPR profiles of the as-prepared PSCs. In the cases of Ni/HT-PSC and Ni/CZ-PSC with the particle dispersion of support oxides (Mg,Al)O and (Ce,Zr)O_{2-δ}, respectively, reduction peaks appeared in a higher temperature region compared to Ni-PSC without dispersion of support oxide particles. In the profile of Ni-PSC, three peaks appeared, corresponding to NiO reduction with weak interaction with Cf (265°C), and surface and bulk reductions of NiO with mild interaction at 310°C and 384°C, respectively [25,26]. For Ni/HT-PSC, the small reduction peak at 435°C would reflect the weak interaction of NiO with Zs-derived stabilized zirconia particles. The profile of Ni/CZ-PSC discussed in detail elsewhere [22] includes the reduction peaks of Ce⁴⁺ to Ce³⁺ in the (Ce,Zr)O_{2-δ} support in the range of 200–250°C and NiO interacting with (Ce,Zr)O_{2-δ} above 300°C [25,27]. The broad peak above 300°C is composed of reductions of NiO with weak interaction with (Ce,Zr)O_{2-δ} (peak at 354°C) and surface and bulk NiO (peaks at 421°C and 518°C, respectively), strongly interacted with (Ce,Zr)O_{2-δ} [22].

Reduction temperatures (temperatures of the highest peaks) for Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC were 310°C, 740°C and 490°C, respectively, suggesting that the interaction between Ni and oxide supports increased in the order of Ni-PSC, Ni/CZ-PSC and Ni/HT-PSC. This corresponds to the order of the average particle size of Ni estimated from the STEM images (in Ni/HT-PSC (6 nm) < in Ni/CZ-PSC (15 nm) < in Ni-PSC (larger than 50 nm)). The smallest Ni size of Ni/HT-PSC is attributed to the cation exchange between Ni²⁺ in the nitrate solution and Mg²⁺ in the (Mg,Al)O structure during the impregnation process to form the (Ni,Mg,Al)O solid solution in the subsequent heat treatment whereby the formation of Ni metal particles is retarded [23].

Table 5.2: Ni loading amount, Ni crystallite size (D_{Ni}), reduction temperature of NiO (T_{red}) and BET specific surface area (SSA) of PSCs.

Sample	Ni loading / wt%	D_{Ni} / nm	T_{red} / °C	BET SSA / m ² g ⁻¹
Ni-PSC	12	62	310	5.8
Ni/HT-PSC	8.6	10	740	20
Ni/CZ-PSC	6.1	13	490	24

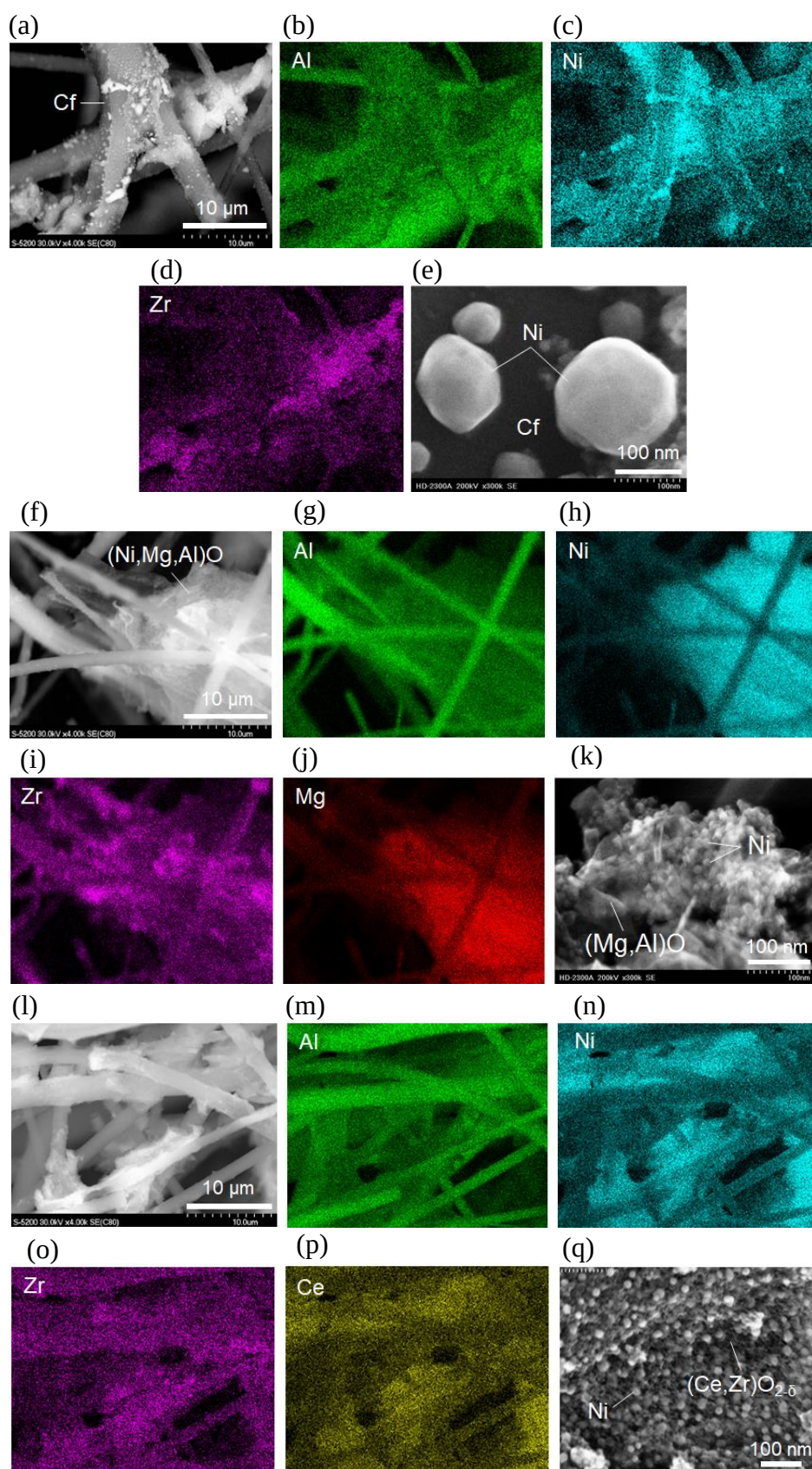


Fig. 5.3: Microstructures of (a-e) Ni-PSC, (f-k) Ni/HT-PSC and (l-q) Ni/CZ-PSC after reduction treatment at 750°C for 5 h under 5% H₂-N₂ flow; (a,f,l) FESEM images and corresponding EDX

mapping images of (b,g,m) Al, (c,h,n) Ni, (d,i,o) Zr, (j) Mg and (p) Ce. (e), (k) and (q) are the higher-magnification images showing Ni metal particles loaded on Cf, fine Ni particles formed on the hydrotalcite-derived (Mg,Al)O and fine Ni particles formed on the (Ce,Zr)O_{2-δ} solid solution for Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC, respectively.

The measured structural parameters and reduction temperature of nickel oxide in the PSCs are summarized in Table 5.2. Crystallite sizes of the Ni measured based on X-ray diffraction line broadening were 62, 10 and 13 nm for Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC, respectively. BET specific surface areas of Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC were 5.8, 20 and 24 m² g⁻¹, respectively.

As shown in Figs. 5.3(a-e), in Ni-PSC, Ni was mainly loaded on the Cf surface, where Ni agglomeration was promoted under the reducing atmosphere with inhomogeneous particle size distribution in the range of 50–100 nm (Fig. 5.3(e)). In Ni/HT-PSC, fine Ni particles (~6 nm) grew on the (Mg,Al)O instead of on the smooth Cf surface (see Figs. 5.3(f-k)), which is attributed to the formation of the (Ni,Mg,Al)O solid solution. Dispersion of (Mg,Al)O in the Cf network was quite effective in providing greater stability against the agglomeration of Ni metal particles [28]. For Ni-PSC and Ni/HT-PSC, Zs acted as a binder connecting the Cfs to form a fiber network.

In the case of Ni/CZ-PSC, as shown in Figs. 5.3(l-q), Ni, Zr and Ce were overlapped and widely dispersed in the fiber network. The better dispersion of (Ce,Zr)O_{2-δ} in the fiber network (Fig. 5.3(p)) compared to (Mg,Al)O in Ni/HT-PSC (Fig. 5.3(j)) is due to the adoption of on-paper synthesis instead of powder dispersion. Good dispersion of Ni/(Ce,Zr)O_{2-δ} may lead to increased contact efficiency with gaseous reactants during dry reforming of CH₄. The average Ni particle size estimated by STEM image was 15 nm (Fig. 5.3(q)). The smaller Ni particle size for Ni/HT-PSC and Ni/CZ-PSC compared to that of Ni-PSC indicates the strong interaction of Ni with oxide supports (Mg,Al)O and (Ce,Zr)O_{2-δ}, respectively.

5.3.2 Catalytic activity of PSCs for the dry reforming of CH₄

Figure 5.4 shows the CH₄ conversion in the dry reforming of CH₄ for the PSCs measured at various temperatures of 650–800°C for 15 h. Equilibrium CH₄ conversions estimated by thermodynamic calculation were 87%, 91%, 94% and 96% at 650°C, 700°C, 750°C and 800°C, respectively (Fig. 4.6). As shown in Figs. 5.4(a-d), Ni/CZ-PSC showed a more stable and higher

catalytic activity for dry reforming of CH₄ compared to Ni-PSC and Ni/HT-PSC despite the lower Ni loading amount (see Table 5.2).

At 800°C, CH₄ conversion was close to equilibrium and independent of the type of PSC (Fig. 5.4(d)), indicating that the reforming reaction may be mainly affected by thermodynamics rather than kinetics. Below 750°C (Figs. 5.4(a-c)), the experimental values are far below the equilibrium, and strongly dependent on the type of PSC. In the case of Ni-PSC, CH₄ conversion was high at the initial stage, but then rapidly decreased with time, while Ni/HT-PSC and Ni/CZ-PSC exhibited higher and more stable catalytic performance. This demonstrates that the catalytic activity of the Ni-based PSC for dry reforming of CH₄ was enhanced by the dispersion of (Mg,Al)O and (Ce,Zr)O_{2-δ}. Compared to Ni/HT-PSC, Ni/CZ-PSC had higher catalytic activity due to the OSC of (Ce,Zr)O_{2-δ} [22] as well as the better dispersion of (Ce,Zr)O_{2-δ} in the fiber network compared to that of (Mg,Al)O.

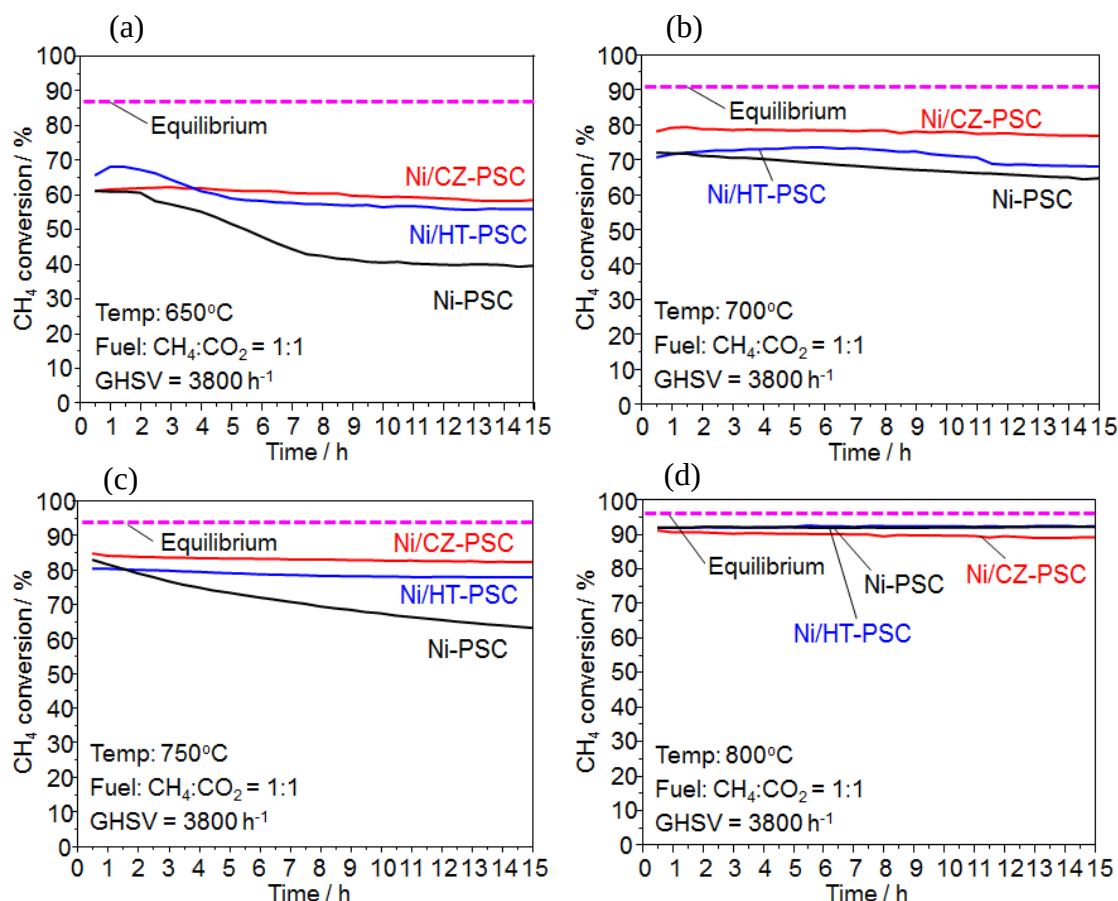


Fig. 5.4: CH₄ conversion in the dry reforming of CH₄ for the PSCs measured at (a) 650°C, (b) 700°C, (c) 750°C and (d) 800°C for 15 h. Equilibrium conversion is also indicated with the dashed line.

Figure 5.5 shows the H₂ selectivity and the ratio of H₂ selectivity/CO selectivity for the PSCs. At 800°C (Fig. 5.5(d)), both H₂ selectivity and H₂ selectivity/CO selectivity are close to unity, indicating that endothermic dry reforming of CH₄ (R1) proceeds close to equilibrium. H₂ selectivity/CO selectivity was lower than unity for all temperatures due to the strong contribution of RWGS reaction (R2) [29]. Because of the contribution of Boudouard reaction (R3), overall reaction can be expressed as reduction reactions of CO and CO₂ to produce carbon (R4 and R5, respectively) [29-31]. These are exothermic, and therefore H₂ selectivity/CO selectivity decreases as temperature decreases.

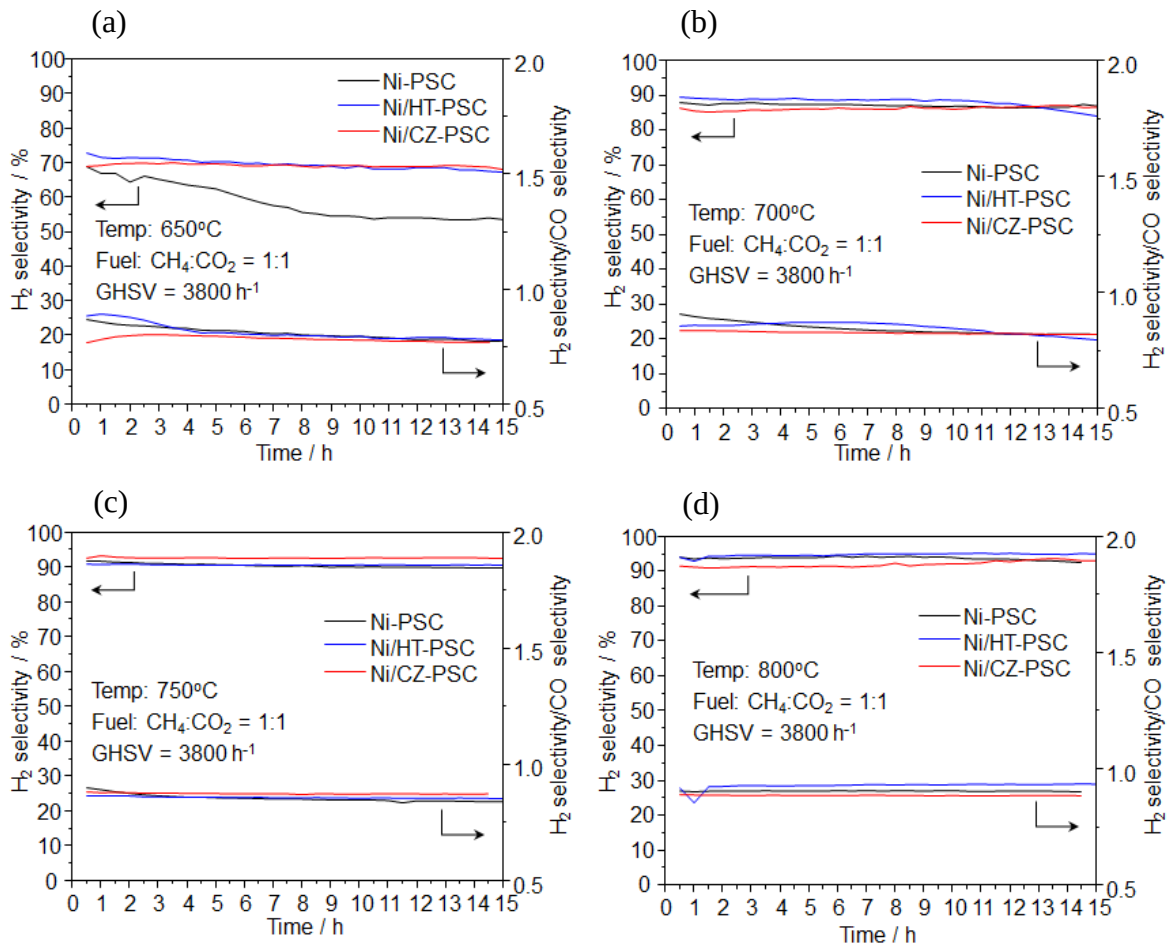
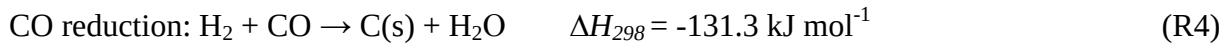
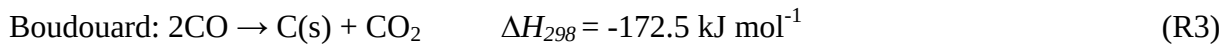
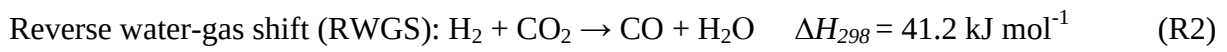


Fig. 5.5: H₂ selectivity and ratio of H₂ selectivity/CO selectivity for the dry reforming of CH₄ measured at (a) 650°C, (b) 700°C, (c) 750°C and (d) 800°C for 15 h.

At 650°C (Fig. 5.5(a)), for Ni-PSC, although initial H₂ selectivity was comparable to those for Ni/HT-PSC and Ni/CZ-PSC, it decreased with time. Initially, Reaction (4) may be predominant, then the contribution of Reaction (5) gradually increased resulting in the decrease in H₂ selectivity to cause serious carbon deposition in Ni-PSC. At 700 and 750°C, as can be seen in Figs. 5.5(b) and (c), respectively, while H₂ selectivity and H₂ selectivity/CO selectivity for Ni-PSC were almost constant and comparable to those for Ni/HT-PSC and Ni/CZ-PSC, CH₄ conversion decreased with time (see Figs. 5.4(b) and (c)), indicating the decrease in catalytically active area for reforming attributed to the carbon deposition to cover active sites and the strong Ni agglomeration [29]. For Ni/HT-PSC and Ni/CZ-PSC, over the tested temperature (650–800°C), CH₄ conversion, H₂ selectivity and H₂ selectivity/CO selectivity were stable. Especially, above 700°C, H₂ selectivity was around 90%, showing the persistence of active sites for reforming.

5.3.3 Characterization of PSCs after dry reforming test

Figure 5.6 shows the TPO profiles for the PSCs after the 15 h dry reforming tests. The appearance of CO₂ mass signals indicates the oxidation of carbonaceous species deposited in the PSCs. Oxidation of carbon at different temperatures refers to various carbon types such as amorphous and graphitic carbon with different degrees of graphitization [32,33]. For all tested temperatures, the TPO profiles show that the use of Ni-PSC caused severe coking, and the coking tolerance increased in the order of Ni-PSC < Ni/HT-PSC < Ni/CZ-PSC. As can be seen in Fig. 5.7(a), fibrous carbon was formed in Ni-PSC during dry reforming at 750°C. Observed in the clump of fibrous carbon were isolated Ni particles, which can be easily coarsened in the reducing atmosphere resulting in rapid degradation of the catalytic performance.

In Ni/HT-PSC, the peak of CO₂ emerged between 450°C and 500°C (Fig. 5.6), corresponding to the formation of fibrous carbon with lower crystallinity compared to Ni-PSC (Fig. 5.7(b)) [32], was small at the reforming temperature of 800°C (Fig. 5.6(d)), and became larger with decreasing reforming temperature. Major carbon formation reactions are R3 and R6, and the above result suggests that carbon formation is governed by R3 with exothermicity. However, CH₄ conversion in the dry reforming was kept constant within the test period, because Ni isolation and coarsening were prevented by the strong interaction with the (Mg,Al)O support, and the deposited fibrous carbon with lower crystallinity did not affect negatively to decrease active sites of Ni [34].

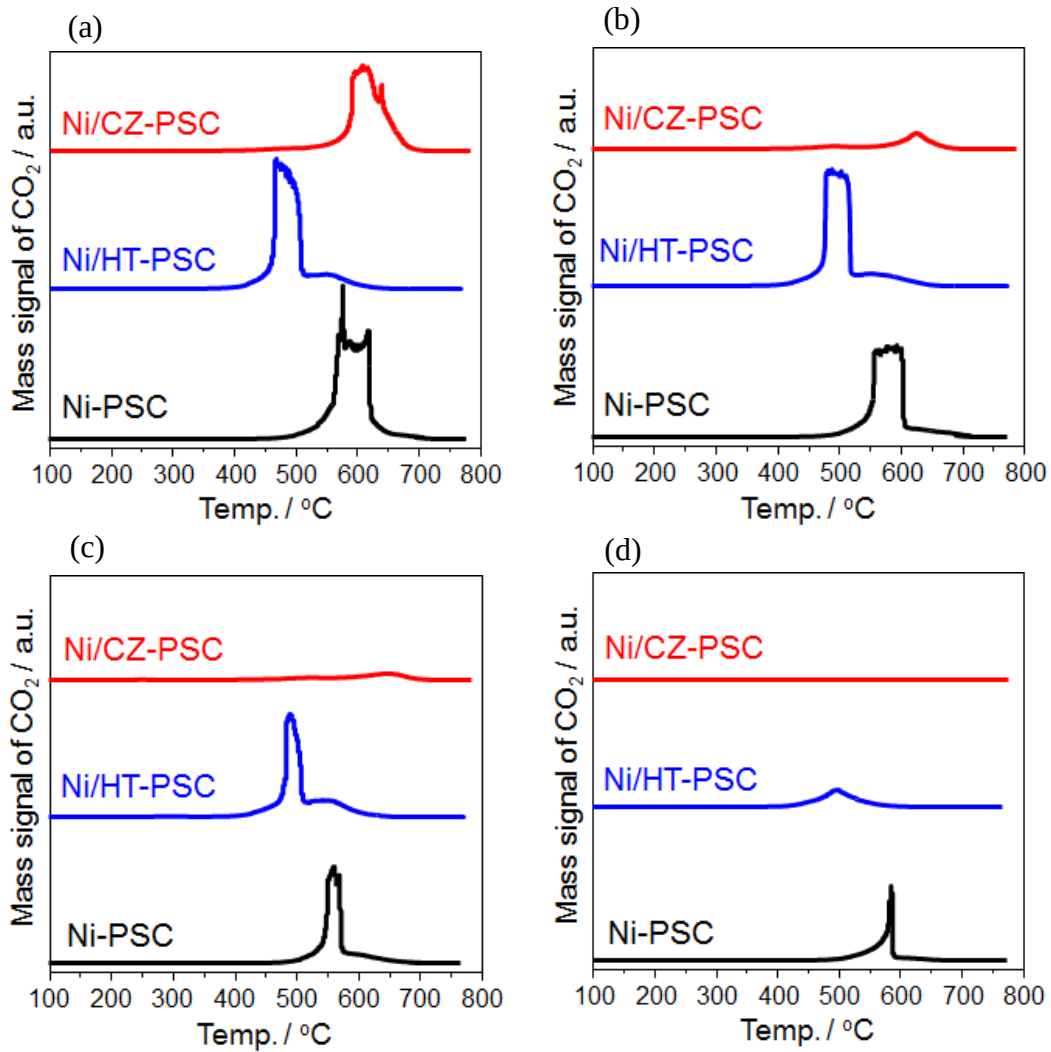
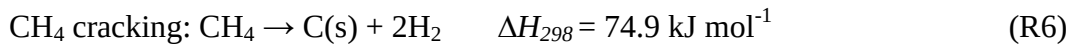


Fig. 5.6: TPO profiles for the PSCs after dry reforming tests at (a) 650°C, (b) 700°C, (c) 750°C and (d) 800°C for 15 h.



It is obvious from Figs. 5.6(b-d) and Fig. 5.7(c) that Ni/CZ-PSC has excellent coking tolerance, suggesting that the lattice oxygen of (Ce,Zr)O_{2-δ} dispersed in the fiber network contributed to the consumption of carbonaceous species deposited on the Ni/(Ce,Zr)O_{2-δ} surface [22]. The overall reaction of carbon removal on (Ce,Zr)O_{2-δ} is a reverse Boudouard reaction (reverse R3) via the mechanism of the lattice-oxygen-mediated cycle (R7) and (R8).



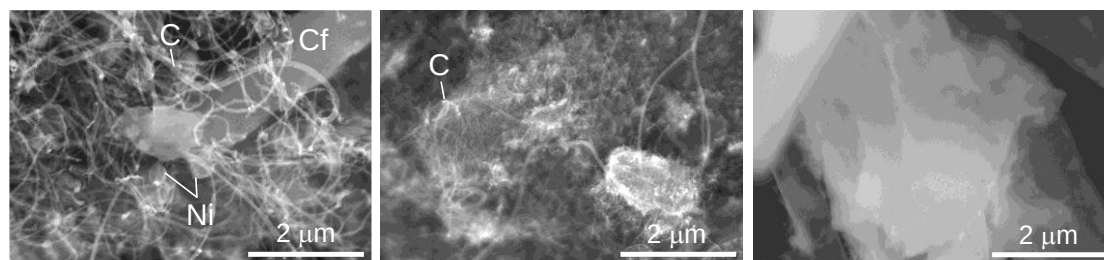


Fig. 5.7: FESEM images of (a) Ni-PSC, (b) Ni/HT-PSC and (c) Ni/CZ-PSC after 15 h dry reforming test at 750°C shown in Fig. 5.4(c).

5.4 Conclusion

Paper-structured catalysts (PSCs) were developed for the dry reforming of biogas. Because the noble characteristics of the PSC with the unique ceramic fiber network structure are easy processing and flexible workability, especially the promotion of gas diffusion, its application to direct internal reforming SOFCs (DIRSOFCs) are greatly promising. This research revealed that Ni-loaded (Ce,Zr)O_{2-δ}-dispersed PSC (Ni/CZ-PSC) exhibited excellent catalytic properties for the dry reforming of CH₄ to fulfill the requirements for application to DIRSOFCs. Coking during dry reforming was significantly inhibited in the temperature range of 700–800°C in comparison with Ni-loaded PSC (Ni-PSC) and Ni-loaded (Mg,Al)O-dispersed PSC (Ni/HT-PSC). This is due to the oxygen storage capacity (OSC) of (Ce,Zr)O_{2-δ} well-dispersed in the Cf network by the on-paper synthesis.

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Chapter 6: Performance improvement of direct internal reforming (DIR) SOFC fueled by biogas by the application of PSC technology

The prepared paper structured catalysts (PSCs) were practically applied to SOFC single cell for the performance improvement of direct internal reforming (DIR) SOFC fueled by biogas. Three types of PSCs characterized in Chapter 5 were integrated into the anode side of an SOFC to investigate their influences on the electrochemical performance of the DIRSOFC.

6.1 Motivation

Fuel cell power generation, which relies on electrochemical reactions to convert the chemical energy of a fuel directly into electricity, is more efficient than that from a heat engine system [1,2]. Among the several types of fuel cells, SOFCs operated at a high temperature (600–900°C) exhibit the highest electrical efficiency (50–60%) due to fast reaction kinetics and the capability of exergy recuperation using exhaust heat with endothermic reforming reactions in a reformer placed adjacent to the SOFC stack or in porous anode material (DIR) [3,4]. DIRSOFC fueled by biogas has been investigated with the motivations of reducing the cost of SOFC systems and carbon-neutral power generation [5-7]. While the chemical energy of biogas composed of CH₄ and CO₂ [8-10] can be directly converted to electricity, this direct conversion can cause carbon deposition within the porous Ni-stabilized zirconia cermet anode, and hence SOFC performance degrades rapidly [11-15]. To solve this issue, studies are underway on a flexible paper-structured catalyst (PSC) made up of an SiO₂-Al₂O₃ ceramic fiber (Cf) network in which metallic catalysts for fuel reforming, such as Ni, Ru, etc., are dispersed [16-18]. PSCs can be easily integrated into an SOFC stack to serve as a reforming reaction zone producing syngas (mixture of H₂ and CO) from hydrocarbon fuels.

Shiratori et al. applied the Ni-loaded (Mg,Al)O-dispersed PSC (Ni/HT-PSC) to SOFC anode (PSC/SOFC stack) and reported outstanding electrochemical performance (1.6 A cm⁻² at 0.7 V) in the direct feed of simulated biogas [19], which is considerably higher than around 0.65 A cm⁻² reported by another group [7].

This PSC also improved the sulfur tolerance of the DIRSOFC fueled by simulated biogas at 800°C [20]. Even under 5 ppm H₂S poisoning, stable performance of DIRSOFC was achieved. Furthermore, the PSC/SOFC concept enabled stable running of DIRSOFC fueled by oleic acid methyl ester (C₁₉H₃₆O₂) at 800°C without coking [21,22]. However, electrochemical performances of PSC/SOFC below 800°C were not yet reported so far.

In this study, three types of Ni-loaded PSCs: without the dispersion of promoter oxide particles (Ni-PSC), with the dispersion of (Mg,Al)O derived from hydrotalcite (Ni/HT-PSC) and with the dispersion of (Ce,Zr)O_{2-δ} (Ni/CZ-PSC) were applied on the anode of an electrolyte-supported cell (ESC) to investigate the impact of PSCs on the performance of DIRSOFC fueled by simulated biogas at 750°C.

6.2 Experimental

6.2.1 Fabrication of electrolyte-supported cell (ESC) and set-up for electrochemical measurement

ESC was fabricated by the procedure described in Sec. 2.2 in Chapter 2. Pictures of the fabricated ESC were shown in Fig. 6.1.

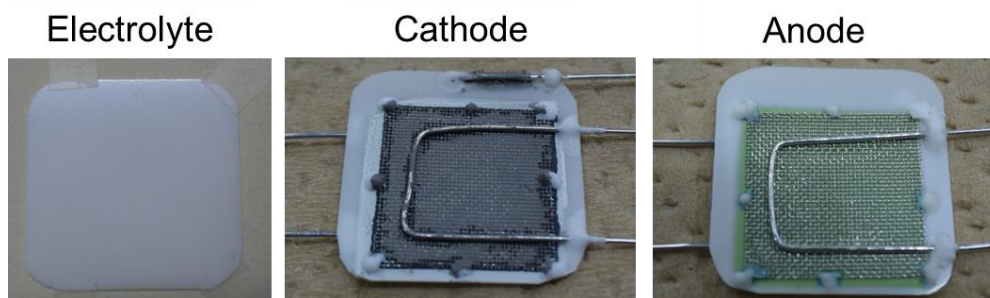


Fig. 6.1: Components of a fabricated ESC consisting of electrolyte, cathode and anode side

Figs. 6.2(a) and (b) schematically depict the ESC without the PSC and PSC/ESC stack, respectively. In the case without PSC (Fig. 6.2(a)), dummy paper (Cf paper without Ni loading) was placed on the anode to match the geometry with PSC (Fig. 6.2(b)). Fig. 6.2(c) shows the set up for the electrochemical experiment. For accurate measurements of overvoltage, a Pt reference electrode was placed on the cathode side of the electrolyte surface at least 2 mm away from the cathode material [23]. The flow of fuel was in the plane direction. On the other hand, the air flow was perpendicular to the cathode surface.

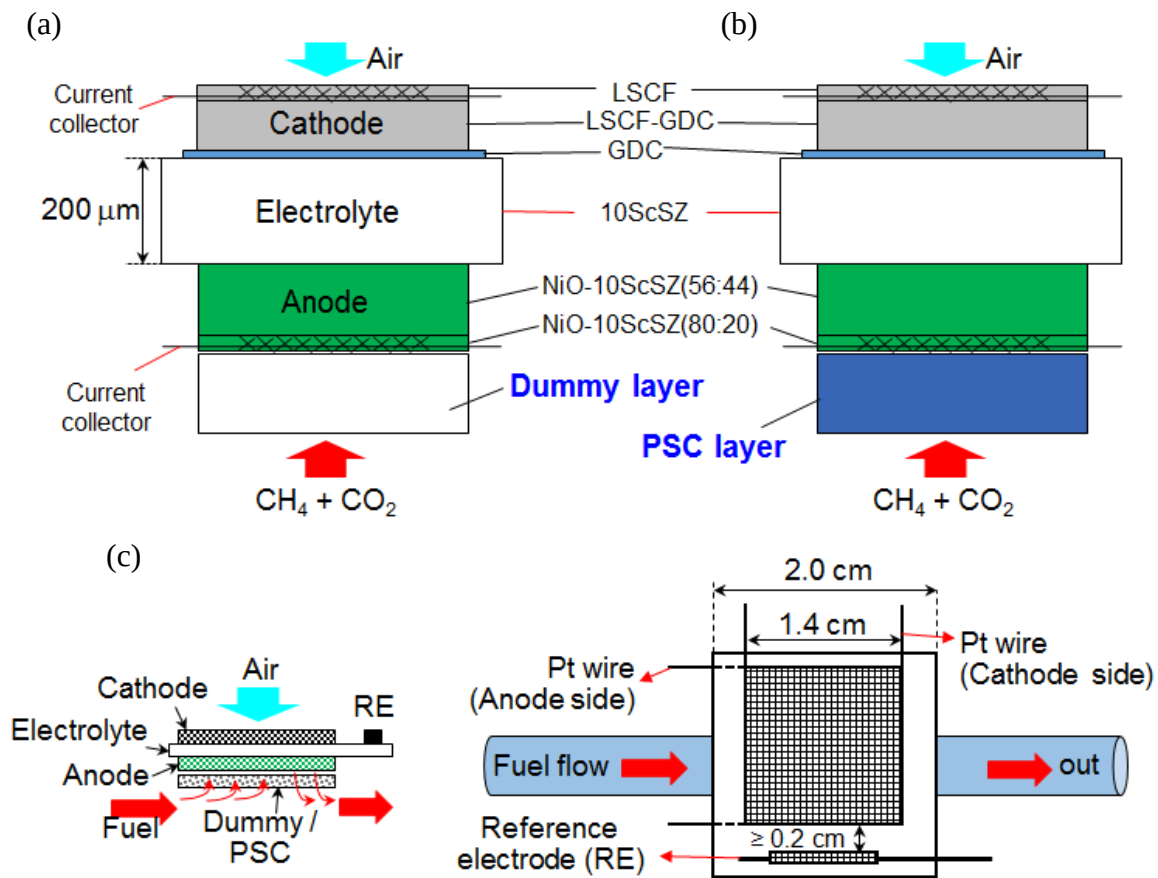


Fig. 6.2: Schematic illustrations of the ESC; (a) ESC without PSC (ESC with Cf paper (dummy paper)), (b) ESC with PSC (PSC/ESC stack), (c) ESC configuration for electrochemical measurements.

Cross-sectional images of the ESC, which indicate the thickness of the anode and cathode, are shown in Fig. 6.3.

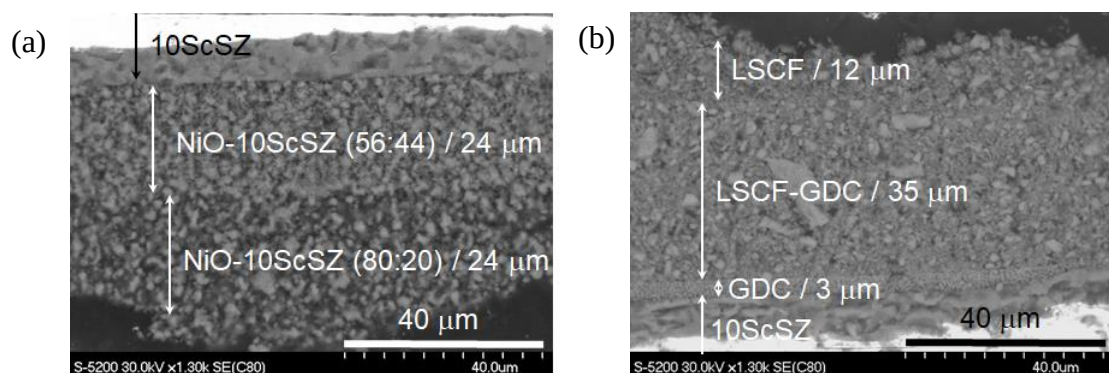


Fig. 6.3: SEM images of the ESC; Cross-sections of (a) the anode after reduction treatment for 5 h under 5% H₂-N₂ flow and (b) the cathode.

6.2.2 Characterization and analysis

Microstructure of ESC was investigated by field emission scanning electron microscopy (FESEM-S5200, Hitachi High-Technologies Corp., Japan).

At 0 and 500 h of the long-term test, the reformate compositions of the anode off-gas were analyzed under OCV condition by an automatic gas chromatograph (GC-20B, Shimadzu Corp.).

For the PSCs after the 500 h PSC/SOFC operation with biogas at 750°C, temperature-programmed oxidation (TPO) was carried out to evaluate the degree of coking. Here, 100 mg of each PSC sample used after cell test was placed in a glass U-tube and heated from room temperature to 800°C at 3°C min⁻¹ under 40 mL min⁻¹ air flow.

6.2.3 Electrochemical measurement

A square-shaped alumina holder with a pocket area of 2×2 cm² was used to mount the PSC and ESC. For the test without PSC, dummy papers (two pieces of Cf paper without Ni loading) were mounted for placement of the ESC. For the test on the PSC/ESC stack, the ESC was placed on two pieces of Ni-PSC, Ni/HT-PSC or Ni/CZ-PSC. Ceramic paste (Aron Ceramic adhesive, Toagosei Co., Ltd., Japan) was applied along the perimeter of the ESC for sealing. Prior to the electrochemical test, the cell temperature was increased from room temperature to 750°C under 40 mL min⁻¹ N₂ flow for 4 h, and then the anode gas was switched to 80 mL min⁻¹ of H₂ for 5 h for the reduction treatment of the anode and PSC. For the cell tests, 1 L min⁻¹ of air was supplied to the cathode side. To the anode side, (I) 80 mL min⁻¹ of humidified H₂ (4.2 vol% H₂O; dry H₂ was passed through distilled water at 30°C), (II) 40 mL min⁻¹ of simulated biogas (equimolar mixture of CH₄ and CO₂ (CH₄:CO₂ = 1:1)) and (III) 80 mL min⁻¹ of diluted biogas (CH₄:CO₂:N₂ = 1:1:6) were supplied.

Electrochemical performance (current-voltage (I-V) curve and overvoltage) was measured by an automatic SOFC testing system (Toyo Corporation, Japan), and electrochemical impedance spectra (EIS) were obtained by a frequency response analyzer (VersaSTAT 3, Princeton Applied Research, USA) under open-circuit conditions in the frequency range of 0.1–100 kHz at a voltage amplitude of 10 mV. In the long-term test, I-V and EIS measurements were carried out at 0 h, 100 h, 300 h and 500 h while 80 mL min⁻¹ of diluted biogas was supplied.

Electromotive forces (EMFs) at 750°C were calculated from the Nernst equation using the oxygen partial pressure of the cathode side, P_{O₂ cathode} (= 0.21 atm), and anode side, P_{O₂ anode}, which was estimated from the equilibrium composition of the input fuel calculated by using the software HSC Chemistry 9.0 [24].

6.3 Result and discussion

6.3.1 Effects of the PSCs on ESC performance

Figure 6.4 shows the electrochemical performances, (a,c) I-V curves and (b,d) anode overvoltage of the ESCs without and with PSC measured at 750°C under the supply of (a,b) simulated biogas and (c,d) diluted biogas. I-V curves and anode overvoltage for humidified H₂ were also measured and plotted in Figs. 6.4(a) and (b), respectively.

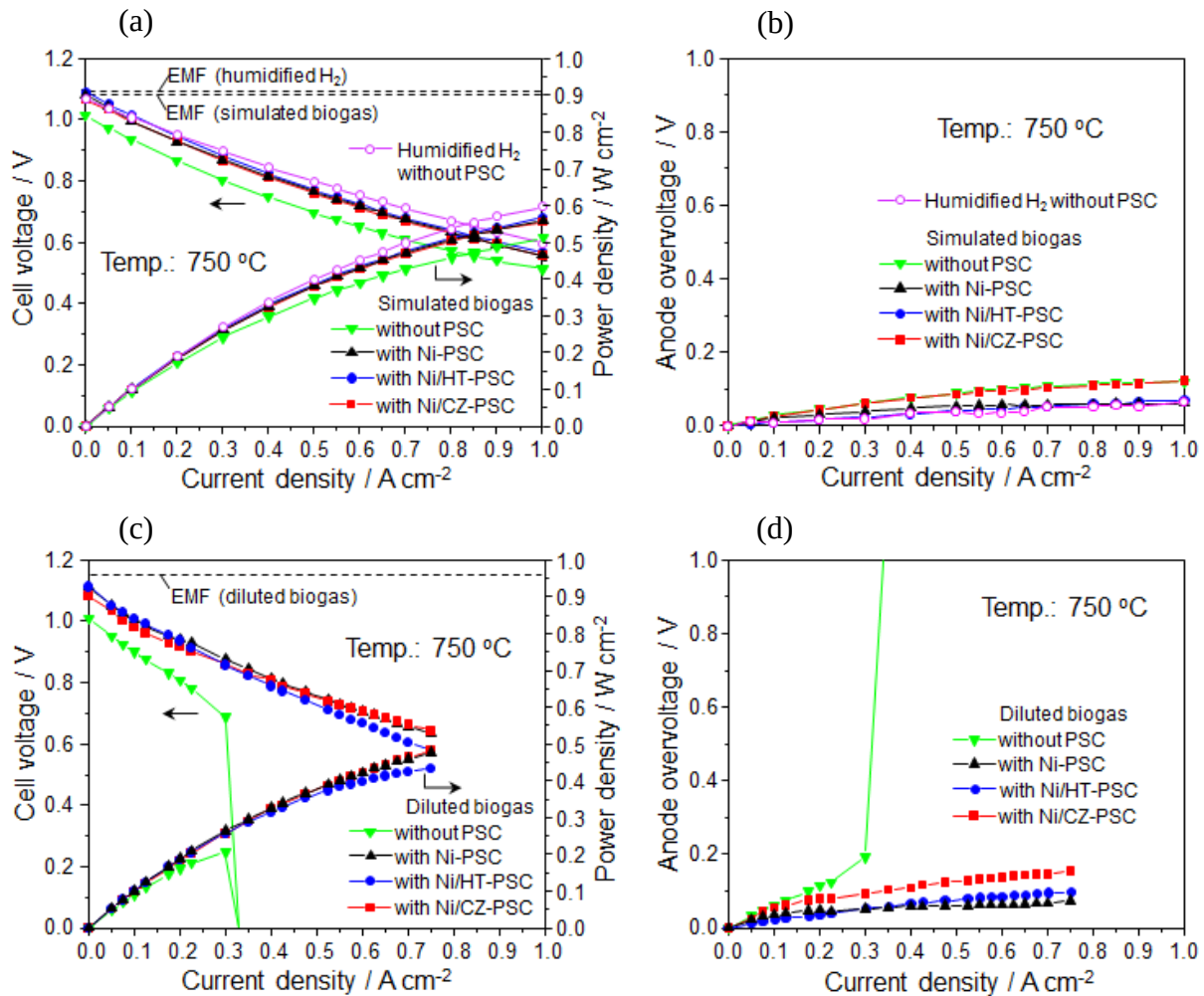


Fig. 6.4: Electrochemical performance of ESCs without and with PSC measured at 750°C: (a,c) I-V curves and (b,d) anode overvoltage under the supply of (a,b) 40 mL min⁻¹ simulated biogas mixture (CH₄:CO₂ = 1:1) and (c,d) 80 mL min⁻¹ diluted biogas (CH₄:CO₂:N₂ = 1:1:6). EMFs calculated from the Nernst equation are also indicated by the dashed lines.

Under the supply of simulated biogas, cell voltages with Ni-PSC, Ni/HT-PSC, and Ni/CZ-PSC under current load were almost the same, and higher than in the case without PSC. Open circuit voltages (OCVs) are summarized in Fig. 6.5. Under the supply of simulated biogas,

OCVs for the cases with Ni-PSC and Ni/HT-PSC were close to the EMF, while that without PSC was significantly lower than the EMF. The OCV difference between with and without PSC was more pronounced for the diluted biogas. The ESC with Ni/CZ-PSC had slightly lower OCVs compared with Ni-PSC and Ni/HT-PSC. This may indicate that the reforming process in Ni/CZ-PSC is somewhat different from that in Ni-PSC and Ni/HT-PSC. The results shown in Fig. 5.4, Chapter 5 suggest that Ni/CZ-PSC tends to promote a low-temperature process (reverse Boudouard reaction), whereas a high-temperature process (CH_4 cracking) was slightly suppressed. At a rather high temperature of 750°C , the degree of CH_4 cracking is considered a key factor for increasing the H_2 concentration in the vicinity of the anode functional layer. This may be the reason why the anode overvoltage for the cases with Ni-PSC and Ni/HT-PSC, promoting CH_4 cracking, was lower than that for Ni/CZ-PSC (Fig. 6.4(b)).

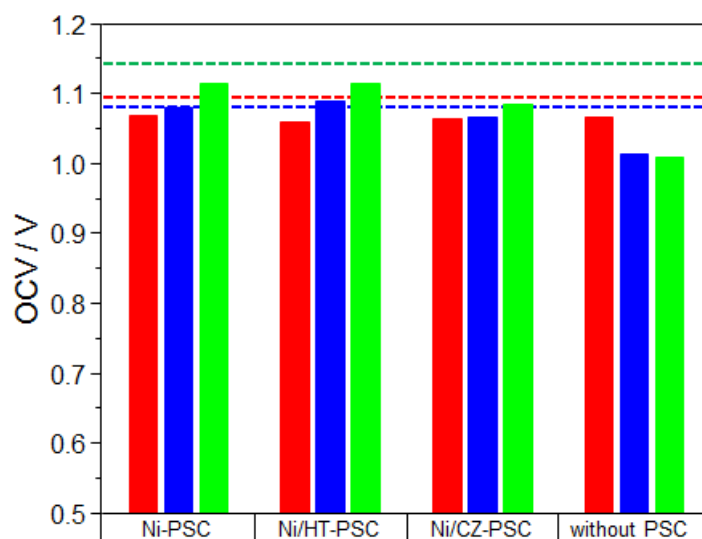


Fig. 6.5: OCVs measured at 750°C for (Red) 80 mL min^{-1} of 4.2 vol% $\text{H}_2\text{O-H}_2$, (Blue) 40 mL min^{-1} simulated biogas ($\text{CH}_4:\text{CO}_2 = 1:1$), and (Green) 80 mL min^{-1} diluted biogas ($\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:6$). EMFs are indicated by the dashed lines.

Under the supply of 40 mL min^{-1} simulated biogas (Fig. 6.4(a)), for all cases, a large voltage drop caused by fuel starvation did not occur up to 1 A cm^{-2} (corresponding to fuel utilization (U_f) of 37%); on the other hand, under the supply of diluted biogas as can be seen in Figs. 6.4(c) and (d), fuel starvation occurred in the ESC without PSC at 0.3 A cm^{-2} ($U_f = 22\%$), whereas in the cases with PSCs, fuel starvation did not take place even at 0.75 A cm^{-2} ($U_f = 55\%$). The results demonstrated that PSCs can contribute to the promotion of mass transfer of

electrochemically active species (H_2) to the anode functional layer in the DIR operation of SOFC [20].

6.3.2 Stability of ESC without and with PSC

Galvanostatic tests at 0.1 A cm^{-2} were carried out for ESCs without and with PSC for 500 h under the supply of 80 mL min^{-1} (GHSV = 6000 h^{-1}) of a simulated biogas mixture ($CH_4:CO_2 = 1:1$).

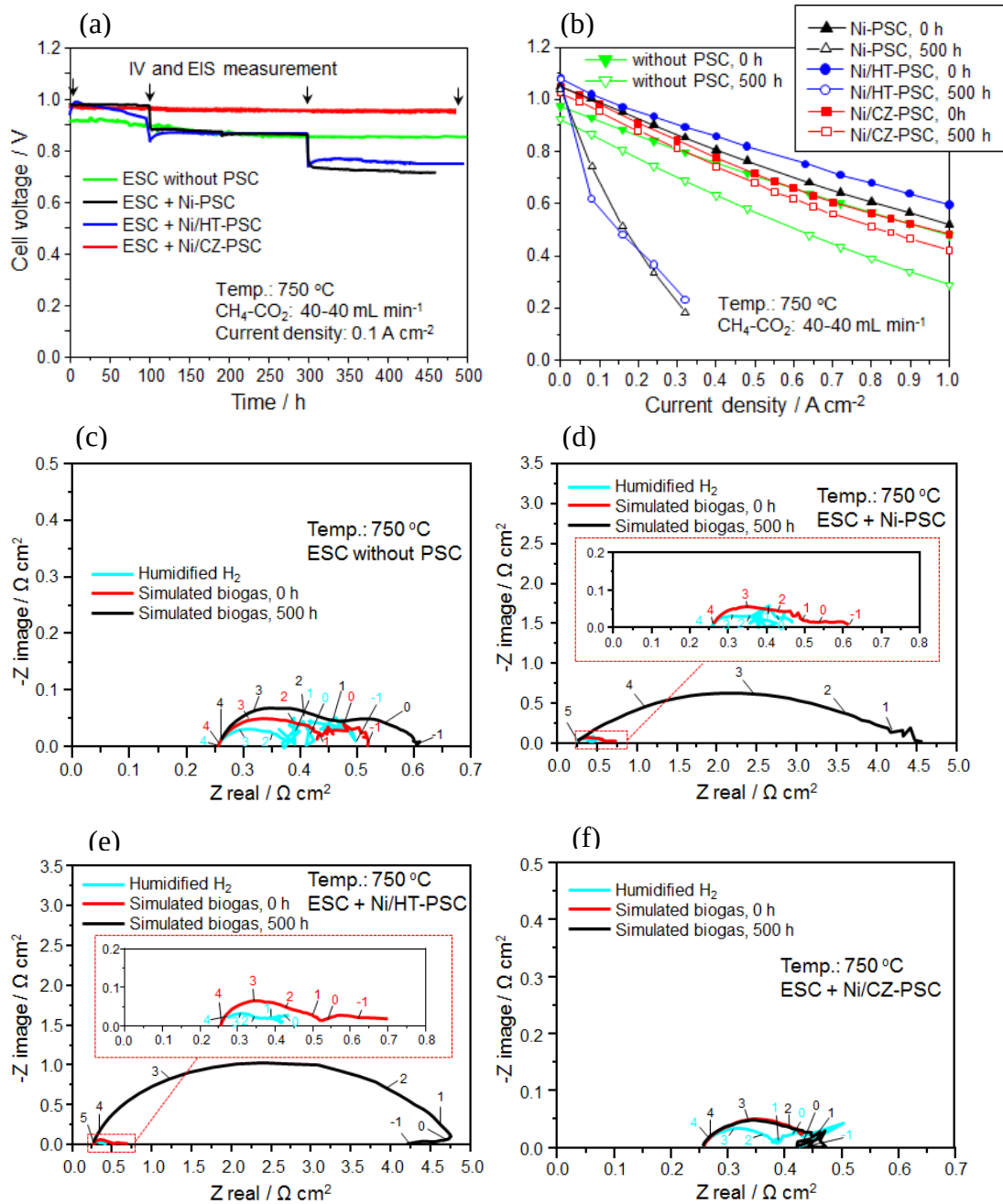


Fig. 6.6: Electrochemical tests on ESCs without and with PSCs under the supply of 80 mL min^{-1} simulated biogas mixture ($CH_4:CO_2 = 1:1$) at 750°C for 500 h: (a) cell voltages at a constant

current density of 0.1 A cm^{-2} , (b) I-V curves at 0 and 500 h, (c-f) anode-side impedance spectra measured under OCV conditions; (c) without PSC, (d) with Ni-PSC, (e) with Ni/HT-PSC, and (f) with Ni/CZ-PSC. The numbers indicated in the figures, -1, 0, 1, 2, 3, 4 and 5, stand for the frequencies of 10^{-1} , 10^0 , 10^1 , 10^2 , 10^3 , 10^4 , and 10^5 Hz, respectively.

Figs. 6.6(a) and (b) show the cell voltages and the I-V curves during the galvanostatic tests, respectively. Degradation rates ($\% \text{ h}^{-1}$) of the cell voltage were 0.015 and 0.005 for the ESC without PSC and with Ni/CZ-PSC, respectively (Table 6.1). Through the application of Ni/CZ-PSC, durability was increased by three times. The degradation rate could not be evaluated for the cases with Ni-PSC and Ni/HT-PSC due to the stepwise voltage drop after each I-V measurement at 100 and 300 h with electrochemical impedance spectroscopy (EIS) under OCV.

Table 6.1: Degradation rates of cell voltages during 500 h galvanostatic tests at 0.1 A cm^{-2} and 750°C under the supply of 80 mL min^{-1} simulated biogas ($\text{CH}_4:\text{CO}_2 = 1:1$) and CH_4 conversions measured under OCV conditions at 0 and 500 h.

Sample	Degradation rate of cell voltage / $\% \text{ h}^{-1}$	CH ₄ conversion under OCV / %	
		Initial	at 500 h
ESC without PSC	0.015	34.3	25.0
ESC with Ni-PSC	–	89.0	56.8
ESC with Ni/HT-PSC	–	91.6	87.6
ESC with Ni/CZ-PSC	0.005	89.5	84.6

Figs. 6.6(c), (d), (e) and (f) show the anode-side impedance of the ESC measured under OCV conditions for the cases without PSC, with Ni-PSC, with Ni/HT-PSC, and with Ni/CZ-PSC, respectively, including the initial impedances for the supply of humidified H_2 and simulated biogas and that for the simulated biogas at 500 h of the galvanostatic test. For all cases, x-intercepts of the high-frequency side corresponding to ohmic resistance were almost the same (about $0.25 \Omega \text{ cm}^2$), which was almost equal to the resistance of the 10ScSZ electrolyte plate calculated from its resistivity. In the case without PSC, by switching from humidified H_2 to simulated biogas, the charge transfer resistance (impedance of high-frequency region) increased,

whereas the mass transfer resistance (impedance of low-frequency region) was insensitive to this fuel switching compared to the charge transfer [25]. During the 500 h galvanostatic test with simulated biogas, both the charge transfer and mass transfer resistances increased. In the cases with Ni-PSC and Ni/HT-PSC, promoting coking, impedance escalation was significant, but with Ni/CZ-PSC, the impedance could be kept constant.

After the 500 h stability test, in the cases with Ni-PSC and Ni/HT-PSC, as shown in Figs. 6.7(a) and (c), respectively, serious carbon deposition was observed in the PSC. However, in Ni/CZ-PSC, coking was not observed (Fig. 6.7(e)), and not detected even in the TPO analysis (see Fig. 6.8). The high initial CH_4 conversion of 90% in the low coking-tolerant Ni-PSC and Ni/HT-PSC would be due to the strong contribution of CH_4 cracking in the PSCs, and then the intermediate carbonaceous species may be easily polymerized to form graphitic carbon within the porous anode functional layer, which can cause carbon accumulation to block the diffusion of reactants and products, leading to an increase in mass transfer losses [26,27]. As shown in Figs. 6.7(b) and (d), serious carbon deposition was observed on the anode in the cases with Ni-PSC and Ni/HT-PSC, respectively. Carbon accumulation is considered to be more greatly promoted under OCV conditions (no oxygen transport from the cathode to anode through electrolyte) set up during I-V and EIS measurements. This can explain the stepwise voltage drops observed at 100 and 300 h for the cases with Ni-PSC and Ni/HT-PSC.

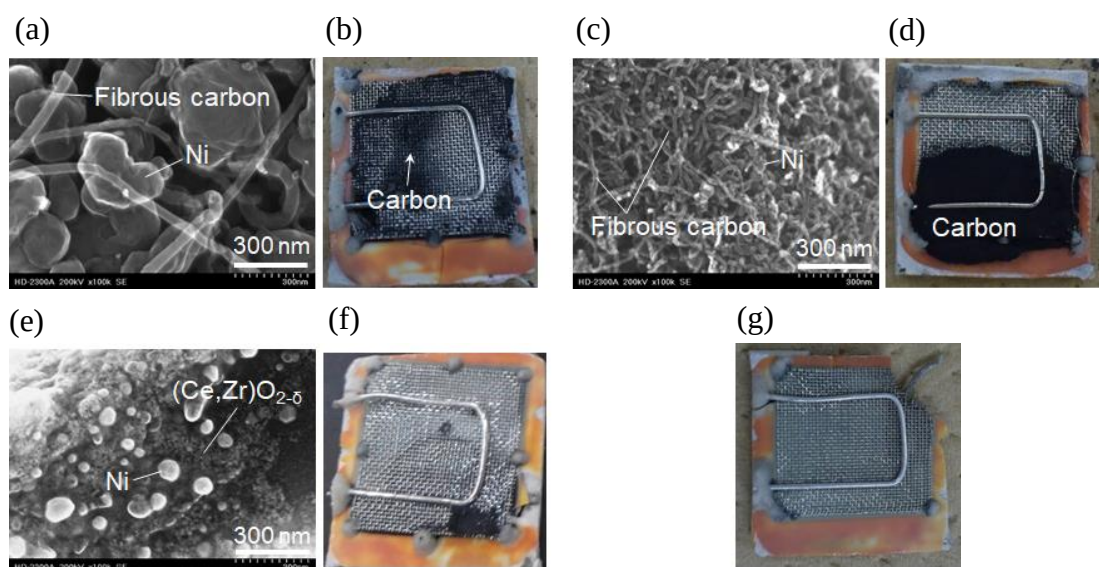


Fig. 6.7: Observations of (a,c,e) PSCs and (b,d,f,g) anode surface after the 500 h galvanostatic test at 750°C for the ESC (a,b) with Ni-PSC, (c,d) with Ni/HT-PSC, (e,f) with Ni/CZ-PSC and (g) without PSC.

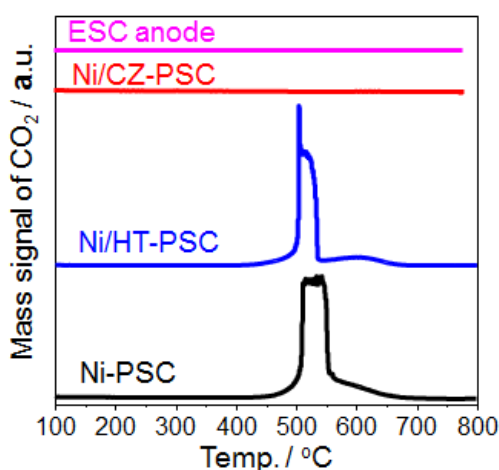


Fig. 6.8: TPO profiles for the samples after 500 h galvanostatic tests shown in Fig 6.6.

As discussed in Sec. 5.3.2 (Chapter 5), promotion of the reverse Boudouard reaction is the reason for the suppression of coking in Ni/CZ-PSC, indicating that the redox cycle of $\text{Ce}^{4+}/\text{Ce}^{3+}$, in other words the lattice-oxygen-mediated cycle, remained during the long-term test [28,29]. In the case without PSC, carbon deposition was not found on the anode (see Fig. 6.7(g)). This is because a large portion of CH_4 just passes through the anode compartment without any reaction (see Table 6.1), and oxidation of carbonaceous species may take place at the triple-phase boundary.

According to STEM investigation, coarsening of Ni particles during the 500 h galvanostatic test was significant in Ni-PSC (from 50–100 to 150–300 nm), reflecting a small active area. In Ni/HT-PSC and Ni/CZ-PSC, Ni particle sizes also increased from 6 and 13 nm to 30 and 30–60 nm, respectively, during the test, but stayed small even after 500 h, resulting in a low degradation rate of the CH_4 conversion; nevertheless, severe coking occurred in Ni/HT-PSC with (Mg,Al)O particles without OSC.

6.4 Conclusion

This study found the following from the performance evaluation of the DIRSOFC with a simulated biogas mixture ($\text{CH}_4:\text{CO}_2 = 1:1$). For the electrolyte-supported cell (ESC) only, in the DIR mode, CH_4 conversion was very low, because a large portion of CH_4 just passed through without H_2 production due to the insufficient catalytic effect of the anode and its geometry, and therefore fuel starvation could easily take place during DIR operation. This result indicates that a support catalyst is indispensable for the stable operation of DIRSOFCs. The flexible paper-

structured catalyst allowed us to easily form a catalyst domain within the cell stack by simply inserting it between the cells.

In the case with Ni-PSC, stable performance of the DIRSOFC fueled by simulated biogas could not be achieved because of the rapid decrease in catalytic activity caused by Ni coarsening and serious coking. Ni/HT-PSC could sustain a high CH₄ conversion during the dry reforming (see Table 6.1) due to the suppression of Ni agglomeration resulting from the strong interaction with (Mg,Al)O support, but the significant formation of fibrous carbon caused the degradation of cell performance. Stable and high performance of DIRSOFC could be achieved by the application of Ni/CZ-PSC, suggesting that this is a promising support catalyst for realizing DIRSOFC technology.

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Chapter 7: Conclusions and future work

7.1 Conclusions

Solid oxide fuel cells (SOFCs) are recognized as one of the most effective technologies for the reduction of greenhouse gas emissions due to its remarkably high energy conversion efficiency and fuel flexibility accepting the direct supply of hydrocarbons including renewable biofuels.

Among various biofuels, this study focused on biogas, the near-naturally produced gaseous fuel via the fermentation of organic waste. When the biogas, the mixture of CH_4 and CO_2 , is supplied directly to high temperature SOFC (around 750°C), within the porous anode material including Ni catalyst, CH_4 reforming proceeds to produce syngas, where the main reaction is dry reforming of methane (DRM) ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$) with the contribution of reverse water gas shift reaction ($\text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$). In power generation based on the electrochemical oxidation, although H_2 is predominant reactant ($\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$), the produced steam can convert CO to H_2 via water gas shift reaction ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$), and therefore, CO can indirectly contribute to power generation. This is the overall reaction process of the direct internal reforming (DIR) operation of SOFC, leading to system downsizing and further enhancement of the energy conversion efficiency.

The major problem in the DIRSOFC fueled by biogas is the deactivation of elementary processes of the DRM to cause carbon deposition within the anode resulting in the degradation of cell performance. Therefore, improvement of catalytic activity of the anode for the DRM is indispensable. However, the degree of freedom for material selection is not so high, because Ni-yttria stabilized zirconia (YSZ) or Ni-scandia stabilized zirconia (ScSZ) is typically used in terms of chemical compatibility, chemical and mechanical stabilities and electrochemical activity. Hence, this study adopted the approach to apply a catalyst layer on the anode material, which is required to have the properties enabling cartridge-like application. The flexible paper-structured catalyst (PSC) can meet this requirement.

PSCs can be prepared by a simple paper-making process using ceramic fibers (C_f) based on filtration. In the C_f network of a PSC, any metal catalysts, such as Ru, Ni, etc., can be dispersed. Furthermore, supported-metal catalyst particles can also be dispersed. In this study, aiming at the suppression of coking during DRM, oxide particles having oxygen storage capacity (OSC) were tried to be dispersed in the C_f network. Here, ceria-zirconia solid solution, $(\text{Ce,Zr})\text{O}_{2-\delta}$ (CZ), with high OSC was selected as an oxide support for Ni catalyst. The lattice oxygen of CZ can

contribute to the promotion of the elementary processes of DRM at the surface. In this study, how the CZ particles can be homogeneously dispersed in the Cf network, how fine Ni metal particles can be formed on the CZ particles (to form Ni/CZ particles) and how the Ni retention efficiency during paper-making process can be increased, were discussed.

In the conventional PSC preparation, after fabricating paper structure using the Cf (SiO₂-Al₂O₃ fiber), metal catalyst loading in the Cf network is performed by the impregnation method. This study adopted the different way, co-precipitation method, so that Ni/CZ particles can be formed in the Cf network with single step (on-paper synthesis). From the precipitate (hydroxide) containing cerium, zirconium and nickel ions produced in the aqueous suspension of Cf, CZ phase could be formed by the heat treatment at 600°C after paper-making process. The co-precipitation-integrated paper-making process to have Ni-loaded CZ-dispersed PSC (Ni/CZ-PSC) developed in this study is now patent-pending.

First of all, optimization of the developed process was conducted to maximize the catalytic performance of Ni/CZ-PSC for DRM (**Chapter 3**). In the on-paper synthesis of Ni/CZ particles, polyvinylpyrrolidone (PVP) added in the suspension, which can serve as a surfactant agent to protect Ni particles from agglomeration, was confirmed to enhance the porosity of the Ni/CZ particles. NaBH₄ added as a reduction agent to form Ni metal from Ni²⁺ in both the precipitate and the aqueous solution of the suspension at room temperature was confirmed to enhance the Ni retention efficiency during paper-making process. In the DRM test using the Ni/CZ-PSC at 750°C, it was demonstrated that both PVP and NaBH₄ additions contributed to the improvement of the catalytic performance of the Ni/CZ-PSC.

The effect of CeO₂/ZrO₂ weight ratio on the catalytic performance of Ni/CZ-PSC was investigated (**Chapter 4**). For the weight ratio of 0.5, 1.0 and 2.0, corresponding to $x = 0.2$, 0.4 and 0.6 in (Ce_xZr_{1-x})O₂, DRM test was carried out at 750°C under the supply of 40 mL min⁻¹ (GHSV = 3800 h⁻¹) of a simulated biogas mixture (CH₄:CO₂ = 20:20 mL min⁻¹). STEM observation revealed that the Ni particles grown on the CZ support became smaller in the order of $x = 0.2$ (29 nm), 0.4 (18 nm) and 0.6 (15 nm). The results of H₂-TPR measurement indicated that at $x = 0.4$ and 0.6 the rate of Ni particles having strong interaction with CZ particles was higher compared to $x = 0.2$. This strong interaction prevents Ni particles from agglomeration and coarsening, contributing to the enhancement of stability during DRM. Moreover, due to the high OSC of CZ, lattice oxygen-mediated surface reaction takes place to consume carbonaceous species deposited on the Ni surface during DRM. This effect was more pronounced for $x = 0.4$

and 0.6, resulting in the excellent coking tolerance of these PSCs. At $x = 0.2$, in addition to the weaker interaction between Ni and CZ, OSC was insufficient, and therefore it showed the lowest catalytic performance accompanied by coking.

The effect of Ni loading amount on the catalytic performance of Ni/CZ-PSC was also studied (**Chapter 4**). Ni particle size increased from 8.6, 18 and 26 nm with increasing the Ni loading amount, 3.5, 6.1 and 9.1 wt%, respectively, and this enlargement caused the increase in the rate of weakly-promoted active sites (Ni having weak interaction with CZ). 9.1 wt% Ni loading was confirmed to be excessive because Ni coarsening in the reducing atmosphere was significant, leading to serious coking during DRM at 750°C. On the other hand, 3.5 wt% Ni loading was insufficient to maximize CH₄ conversion. 6.1 wt% Ni loading was the best in terms of catalytic activity and coking tolerance.

For DRM, catalytic performance of the Ni/CZ-PSC was compared to the Ni-loaded PSC without the dispersion of promoter oxide particles (Ni-PSC) and the Ni-loaded hydrotalcite (HT)-dispersed PSC (Ni/HT-PSC) (**Chapter 5**). For the Ni-PSC and the Ni/HT-PSC, Ni loading was made by impregnation method. X-ray diffraction analyses, STEM observations and H₂-TPR results indicated that in the Ni/HT-PSC and the Ni/CZ-PSC fine Ni particles with the average sizes of 6 and 15 nm, respectively, were formed due to strong interaction of Ni with support oxides, (Mg,Al)O derived from HT and CZ, respectively, whereas Ni particles in the Ni-PSC were larger than 50 nm, significantly larger due to weak interaction between Ni and Cf. In the DRM tests performed in the temperature range of 650-800°C, Ni/CZ-PSC exhibited superior catalytic performance to Ni-PSC and Ni/HT-PSC, especially, excellent coking tolerance above 700°C. This superiority of Ni/CZ-PSC came from OSC of CZ and well-dispersion of CZ by the on-paper synthesis. It has been concluded that Ni/CZ-PSC is a promising candidate of the catalyst layer to realize DIRSOFCs.

Ni-PSC, Ni/HT-PSC and Ni/CZ-PSC were practically applied on the anode of electrolyte-supported cell (ESC) to form PSC/ESC stacks, for which electrochemical performances of DIRSOFC fueled by simulated biogas mixture (CH₄:CO₂ = 1:1) were evaluated at 750°C (**Chapter 6**). In the case of ESC without PSC, during the current-voltage (I-V) curve measurement, steep voltage drop attributed to fuel starvation occurred at fuel utilization (U_f) of 22 %. This phenomenon was caused by the low catalytic activity of porous Ni-ScSZ anode material, which cannot produce sufficient amount of H₂ required for the electrochemical reaction, indicating the indispensability of a support catalyst for the stable operation of DIRSOFCs.

500 h durability test of DIRSOFC fueled by the simulated biogas was conducted at the constant current density of 100 mA cm^{-2} for the PSC/ESC stacks. In the case with Ni-PSC, stable power generation could not be achieved (Stepwise voltage drop occurred) because of the rapid degradation in catalytic activity of the Ni-PSC caused by Ni coarsening and severe coking. For Ni/HT-PSC, because the strong interaction between Ni and (Mg,Al)O support derived from HT could lead to form fine Ni particles and prevent Ni agglomeration, high CH_4 conversion could be kept during the durability test. However, also in this case, stepwise voltage drop occurred. In the post-test observation, serious carbon deposition was observed within the porous anode functional layer, suggesting that incomplete reforming of CH_4 within the Ni/HT-PSC, resulting in the accumulation of intermediate carbonaceous species at the adjacent anode material which brought about coking to hinder the diffusion of reactants and products within the porous anode, leading to the degradation of cell performance. In the case with Ni/CZ-PSC, stable cell performance without stepwise degradation was achieved, demonstrating that Ni/CZ-PSC can function as the catalyst layer to be applied on a SOFC anode to realize DIRSOFC technology.

7.2 Outlook for future work

7.2.1 Further enhancement of catalytic performance of Ni/CZ-PSC

Although Ni/CZ-PSC exhibited the excellent catalytic performance showing coking tolerance for DRM in the temperature range of $700\text{--}800^\circ\text{C}$, it still behaves insufficient coking tolerance at 650°C . Thus, further improvement of catalytic performance is required for the application below 700°C . In this study, preparation procedure of Ni/CZ-PSC based on the integration of co-precipitation process (with PVP and NaBH_4) in the dual-polymer paper-making process has been optimized, and moreover, best CZ composition and Ni loading were determined for the DRM. Remaining approach for further improvement is to control the geometric structure of CZ particles dispersed in the inorganic fiber network of PSC as an oxide support for Ni catalyst. One candidate is the flower-like structure, a mesoporous sphere consisting of nano-sheets look like petals, obtained by hydrothermal synthesis [1]. Fig. 7.1 shows the flower-like CZ (CZ(F)) obtained in the trial preparation. This spongy body is expected to increase the area of reaction site where OSC of CZ can contribute to surface reactions. Actually application of the flower-like Ce-based oxides to the internal catalytic layer for low temperature SOFCs fueled by hydrocarbon to achieve peak power density of 654 mW cm^{-2} at 600°C has been reported [2,3]. Other catalytic applications such as CO oxidation [4,5] and ethanol steam reforming were also reported [6].

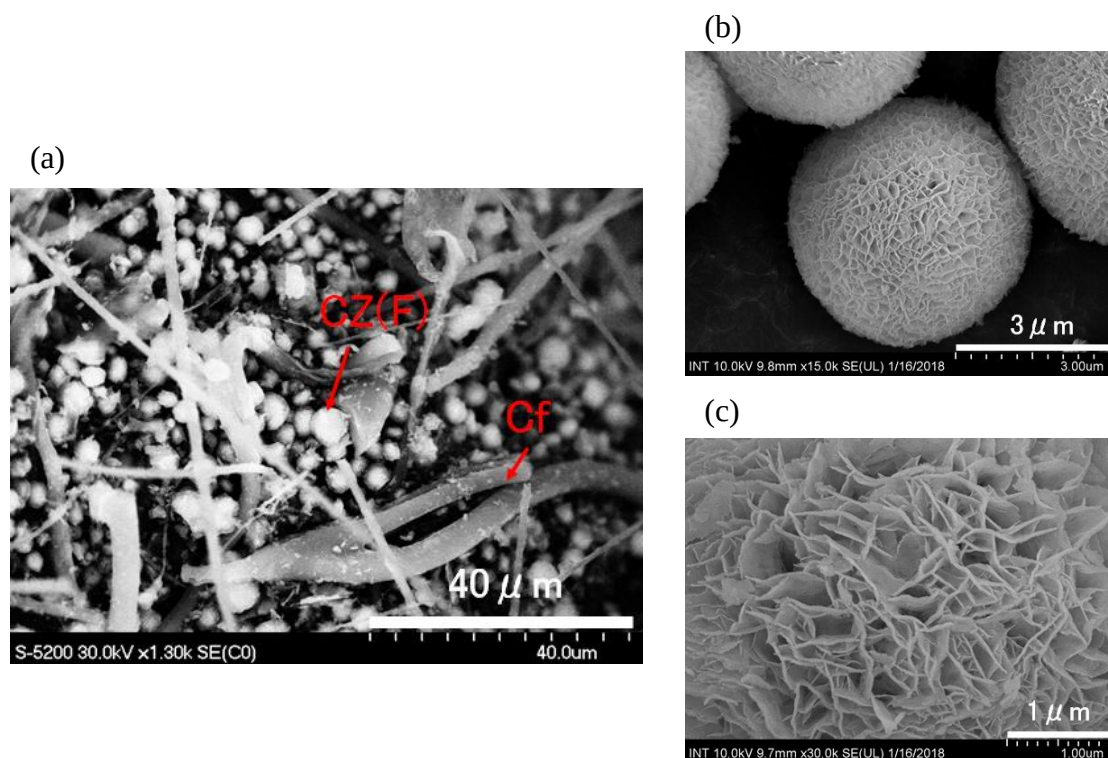


Fig. 7.1: SEM images of the flower-like $(\text{Ce,Zr})\text{O}_{2-\delta}$ (CZ(F)) obtained in the trial preparation; (a) CZ(F) particles dispersed in Cf network, and (b,c) are the higher-magnification images focusing on CZ(F) particle.

Planned procedure to obtain Ni-loaded CZ(F)-dispersed PSC (Ni/CZ(F)-PSC) is as follows. First of all, CZ(F) is prepared. Gelatin of cerium and zirconium precursors with dispersant and reduction agents is formed, subsequently put into an autoclave under 1 MPa at 180°C to synthesize ceria-zirconia mixture. After cooling, the precipitate in the solution is washed and collected by filtration, followed by the sintering at high temperature to remove organic materials and to obtain flower-like ceria-zirconia solid solution (CZ(F)). Here, optimization of the synthesis process considering the amount of dispersant, pH of solution, reaction time, $\text{CeO}_2/\text{ZrO}_2$ weight ratio, etc. has to be carried out to maximize porosity and OSC of CZ(F). Ni will be loaded on the CZ(F) particles by impregnation to obtain Ni/CZ(F) powder, which will be added to the aqueous Cf suspension for paper-making process to have Ni/CZ(F)-PSC. Another possible approach is the on-paper synthesis of Ni/CZ(F). Ni, Ce and Zr precursors are added into the Cf suspension in the presence of dispersant and reduction agent, and then, for this suspension, hydrothermal process is applied, followed by paper-making process to have Ni/CZ(F)-PSC. The on-paper synthesis is expected to strengthen the interaction of Ni with the oxide support (CZ(F)).

to enhance the catalytic performance for DRM below 700°C.

7.2.2. Practical application of Ni/CZ-PSC to real SOFC stack

This study demonstrated that in single cell level electrochemical performance of DIRSOFC fueled by simulated biogas was stabilized by mounting Ni/CZ-PSC on the anode of ESC to achieve 500 h durability (Chapter 6). On the other hand, when this approach is scaled up to stack level test, we have to carefully take the temperature distribution along fuel flow direction into account. Strong endothermicity of DRM can generate steep temperature gradient within the cell. Fig. 7.2 shows the interior temperature distribution along fuel flow direction in the uniform catalyst domain of 0.22 wt% Ni/HT-PSC for the feed of the simulated biogas mixture ($\text{CH}_4/\text{CO}_2 = 1$) [7]. Occurrence of DRM is localized on the fuel inlet side, resulting in strong temperature decrease of this region to cause (A) cell destruction (thermal shock) and (B) coking at the cooled area (predicted by thermochemical calculation). Problem (A) can be avoided by the approach of the PSC array (functionally-graded catalytic field described in Sec. 1.5.1). Even when a uniform catalytic field is applied, if the Ni/CZ-PSC developed in this study is used, risk of problem (B) will be considerably suppressed, because this PSC is coking tolerant over 700°C.

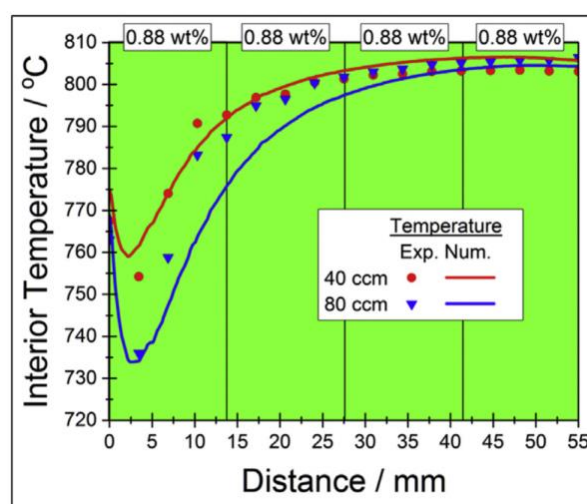


Fig. 7.2: Interior temperature distribution along fuel flow direction in the uniform catalyst domain of 0.22 wt%Ni/HT-PSC for the fuel compositions of $\text{CH}_4/\text{CO}_2/\text{N}_2 = 40/40/100$ and $80/80/20 \text{ mL min}^{-1}$ [7].

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