Comparative study on ammonia oxidation over Ni-based cermet anodes for Solid Oxide Fuel Cells

Ahmed Fathi Salem Molouk ^{a)}, Jun Yang ^{a)}, Takeou Okanishi ^{a)}, Hiroki Muroyama ^{a)}, Toshiaki Matsui ^{a)}, and Koichi Eguchi ^{a)}, *

a) Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

* Correspondence should be addressed to
Koichi Eguchi
Department of Energy and Hydrocarbon Chemistry,
Graduate School of Engineering, Kyoto University,
Nishikyo-ku, Kyoto 615-8510, JAPAN
TEL: +81-75-383-2519, FAX: +81-75-383-2520
E-mail: eguchi@scl.kyoto-u.ac.jp

Abstract

In the current work, we investigate the performance of solid oxide fuel cells (SOFCs) with Ni–yttria-stabilized zirconia (Ni–YSZ) and Ni–gadolinia-doped ceria (Ni–GDC) cermet anodes fueled with H₂ or NH₃ in terms of the catalytic activity of ammonia decomposition. The cermet of Ni–GDC shows higher catalytic activity for ammonia decomposition than Ni–YSZ. In response to this, the performance of direct NH₃–fueled SOFC improved by using Ni–GDC anode. Moreover, we observe further enhancement in the cell performance and the catalytic activity for ammonia decomposition with applying Ni–GDC anode synthesised by the glycine–nitrate combustion process. These results reveal that the high performance of Ni–GDC anode for the direct NH₃–fueled SOFC results from its mixed ionic– electronic conductivity as well as high catalytic activity for ammonia decomposition.

Keywords: Direct NH₃–fueled SOFCs; ammonia decomposition; Ni–GDC; Ni–YSZ.

1. Introduction

Increasing demand in electrical energy inevitably gives rise to the consumption of a large amount of fossil fuels and the emission of greenhouse gases to the environment. Solid oxide fuel cells (SOFCs) are electrochemical generators with high efficiency [1–4]. The performance of SOFC is dependent on the kind of fuel, anode materials, and anodic reactions. High performance can be achieved with hydrogen and hydrocarbon fuels. Hydrogen has been considered as a future clean fuel with the least emission of greenhouse gases [5, 6]. However, the storage and transportation of hydrogen are major obstacles for the large-scale application due to its low volumetric density and boiling point [7, 8].

Recently, ammonia has attracted a great attention as a fuel because of many advantages; carbon free fuel with higher energy density, ease in liquefaction (boiling point: -33.4°C at atmospheric pressure), and narrower flammable range than hydrogen, etc [9-13]. The worldwide distribution system is well established as widely produced commodity chemical and fertilizer. Based on these entire characteristics, ammonia, especially synthesized from the renewable energy, is considered as a future promising fuel and/or hydrogen carrier. Therefore, many studies were conducted in order to improve the performance of direct ammonia-fueled SOFCs using oxide-ion [14-18] or proton [19-23] conducting electrolytes.

Methane or natural gas has been considered as a suitable fuel for SOFCs because of its cleanliness among the fossil fuels and a higher energy density than hydrogen. However, its consumption

inevitably accompanies CO₂ emission. Our previous study indicated that the SOFC consisting of Ni-YSZ|YSZ|(La,Sr)MnO_{3+δ} demonstrated a higher performance with ammonia fuel than that with methane at the same temperature and anodic oxygen potential. The preferable performance of direct NH₃-fueled SOFC resulted from a higher reactivity of NH₃ for decomposition than CH₄ reforming on Ni-YSZ [24].

The Ni-YSZ cermet is the most popular anode material, which achieves most of the requirements for efficient SOFCs [25-27]. However, the activity of Ni-YSZ anode for the electrochemical oxidation of fuels such as hydrocarbon and ammonia is often insufficient [28, 29]. On the other hand, gadolinia-doped ceria (GDC) has several advantages to YSZ as an oxide component for the cermet anode. GDC is a mixed ionic-electronic conductor under reducing atmospheres and its ionic conductivity is higher than that of YSZ [29]. Ceria has been known not only as a mixed conductor but also a catalyst material for oxidation-reduction reactions. Ceria also serves as a support for the Ni catalyst and prevents from sintering to provide a large and active triple-phase boundary (TPB) [30-32].

In this work a comparative study on Ni-YSZ and Ni-GDC cermet anodes for SOFCs using H₂ and NH₃ fuels was conducted. We focused on the evaluation of the catalytic activity of Ni-YSZ and Ni-GDC for NH₃ decomposition and the polarization resistance of each anode. The effect of preparation method of NiO-GDC on NH₃ decomposition reaction was also studied for the development of active anode for direct NH₃-fueled SOFCs.

2. Experimental

Electrolyte supported cells were used for the performance evaluation. Two different Ni-based cermet anodes (Ni-YSZ and Ni-GDC) were prepared. The NiO-YSZ anode powder was prepared by the physical mixing route as described elsewhere [24]. On the other hand, NiO-GDC anode powder was prepared by two methods; i) physical mixing and ii) glycine-nitrate combustion routes. The schematic diagram of the preparation routes is shown in Fig. 1. The physical mixing was carried out by ball-milling of NiO (Wako Pure Chemical Industries), GDC ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$, Shin-Etsu Chemical Co.), and 10 wt.% carbon black as a pore former in ethanol for 24 h. The powder from the physical mixing is denoted as NiO-GDC (PM). For the glycine-nitrate combustion route, stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries), and $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries) were dissolved in water with stirring at room temperature. Glycine (Wako Pure Chemical Industries) was then added to the solution until the molar ratio of total metal ions/glycine reached to 1/2. After complete drying, the self-ignition takes place at *ca.* 350°C. The obtained ash was calcined at 850°C in air for 5 h. The resultant powder was mixed with 10 wt.% carbon black as a pore former and ball-milled in ethanol for 24 h. The powder thus prepared is abbreviated as NiO-GDC (GN). The Ni metal content in the anode was 60 wt.% after reduction treatment at 1000°C for every Ni-oxide cermet. The perovskite type oxide of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.97}\text{MnO}_3$ (LSM) was selected as a cathode and prepared as was reported earlier [33]. The

obtained anode and LSM powders were mixed with polyethyleneglycol (PEG, Wako Pure Chemical Industries) to form slurry.

Cells were fabricated by screen printing the anode slurry on the flat face of YSZ disk electrolyte (8 mol% yttria-stabilized zirconia electrolyte, Tosoh, 500 μm in thickness and 24 mm in diameter) and firing at 1400°C in air for 5 h. Then, the cathode was printed and fired at 1150°C in air for 5 h. The electrode active area was 0.28 cm^2 and the thicknesses were 60 μm and 40 μm for anode and cathode, respectively. A platinum reference electrode was fixed by the platinum paste (Metalor Technologies (Japan) Corp.) around the edge of YSZ disk and fired at 900°C in air for 2 h. Finally, the cell was set between two alumina tubes and sealed by Pyrex glass rings to avoid the gas leakage.

The anode was reduced at 1000°C for 1 h prior to the electrochemical test. The anode gas mixtures were $\text{H}_2\text{--H}_2\text{O--Ar}$ and $\text{NH}_3\text{--H}_2\text{O--Ar}$. The gas composition of $\text{NH}_3\text{--H}_2\text{O--Ar}$ was controlled to achieve the same hydrogen concentration and flow rate of $\text{H}_2\text{--H}_2\text{O--Ar}$ when the complete decomposition of ammonia occurred. The cathode gas was 100% O_2 with a total flow rate of 100 ml min^{-1} . Electrochemical measurements were carried out by the CellTest system (Solartron Analytical, potentiostat/galvanostat 1470E and frequency response analyzer 1455A). After power generation test in hydrogen and ammonia fuels the anode microstructure was observed by a scanning electron microscopy (SEM, Nvision 40, Carl Zeiss-SIINT).

The catalytic activity for NH_3 decomposition over Ni-YSZ, Ni-GDC (PM), Ni-GDC (GN), YSZ, and GDC was studied using a fixed bed reactor. In these measurements, all samples were pre-calcined

at 1400°C for 5 h in air and then ball-milled in ethanol overnight. All powders were pressed into a pellet at 20 MPa and then pulverized to 12 mesh. The sample (0.6 g) was set in a fixed bed reactor and then reduced in H₂-Ar at 700°C for 1 h. After that the temperature was reduced to 350°C within 1 h in hydrogen, and then the reactor was purged with Ar (50 ml min⁻¹ Ar for 30 min). The reactant gas of 66.7% NH₃-33.3% Ar (total flow rate; 60 ml min⁻¹) was supplied to each catalyst with a space velocity of 6000 l kg⁻¹ h⁻¹. The outlet gas was passed through two traps containing 3.5M H₂SO₄ solution (Wako Pure Chemical Industries) to dissolve the unreacted NH₃ and then the flow rate of outlet gas containing H₂-N₂-Ar was measured by using a flow rate meter (VP3, Horiba STEC Co, Ltd.). The percentage of NH₃ decomposition can be calculated using Eq. (1).

$$\text{NH}_3 \text{ decomposition} / \% = \left(\frac{F(\text{NH}_3 \text{ inlet}) - F(\text{NH}_3 \text{ unreacted})}{F(\text{NH}_3 \text{ inlet})} \right) \times 100 \quad (1)$$

where $F(\text{NH}_3 \text{ inlet})$ and $F(\text{NH}_3 \text{ unreacted})$ are the flow rate of ammonia in the inlet gas and unreacted ammonia in the outlet gas, respectively.

The surface basicity of YSZ and GDC was also measured by the temperature-programmed desorption of carbon dioxide (CO₂-TPD) using BELCAT-B (BEL Japan, Inc.). The samples were preheated at 1400°C in air for 5 h and then ball-milled in ethanol overnight. The resultant powder was pressed into a pellet as in the catalyst test. Prior to the TPD experiment, 1 g of the sample was pre-treated in a helium atmosphere at 600°C for 1 h and then cooled to 50°C. Carbon dioxide was

supplied with a flow rate of 30 ml min^{-1} for 1 h. After the sample was purged with helium at 50°C for 0.5 h, the sample was heated to 900°C at a heating rate of $10^\circ\text{C min}^{-1}$ to monitor desorption of CO_2 using an on-line mass spectrometer (Pfeiffer Vacuum, OmniStare GSD320).

The specific surface area was determined by N_2 adsorption-desorption with the BET method at -196°C using BELSORP-miniII (BEL Japan, Inc.) The anode cermets were preheated at 1400°C for 5 h in air and then reduced at 1000°C in hydrogen. Prior to the BET experiment, 0.1 g of the sample was heated at 300°C in vacuum.

3. Results and discussion

3.1 Catalytic activity of Ni-based cermet for ammonia decomposition

In the previous studies, it was suggested that the consumption of ammonia fuel proceeds via the two step reaction over Ni-based electrodes in SOFCs [11, 24, and 34]. Ammonia decomposes over the Ni-based cermet to H_2 and N_2 by the thermal catalytic reaction followed by the electrochemical hydrogen oxidation. Therefore, the catalytic activity of Ni-based cermet for ammonia decomposition is one of the key factors to develop high performance anodes for direct NH_3 -fueled SOFCs. In this study, the catalytic activities for ammonia decomposition over Ni-YSZ, Ni-GDC (PM), YSZ, and GDC were investigated using a fixed bed reactor. The Ni-GDC (PM) cermet demonstrated the highest activity for ammonia decomposition at 600°C among the catalysts tested (see Fig. 2(a)). Though Ni metal was indispensable for sufficient activity, GDC exhibited the catalytic activity to some extent

compared with YSZ which was inactive for the ammonia decomposition. It is expected that activity of Ni metal was further promoted by coexisting GDC because of the chemical interaction between Ni and GDC.

The catalytic decomposition of ammonia is composed of several reaction steps, *i.e.*, *i*) adsorption of ammonia onto catalyst sites, *ii*) cleavage of N-H bond of adsorbed ammonia, and *iii*) desorption of N₂ molecules. Generally, the last two steps control the rate of overall reaction [35-37]. The basic sites on the catalyst surface play an important role for promoting the rate determining step to achieve higher ammonia conversion [38, 39]. Therefore, CO₂-TPD experiment was conducted to YSZ and GDC. In the CO₂-TPD profiles in Fig. 2(b), three peaks of CO₂ desorption were observed for GDC at *ca.* 120°C, 210°C, and 683°C. On the other hand, only two CO₂ desorption peaks were confirmed for YSZ at *ca.* 127°C, and 675°C. These results suggest that both oxides have weak and strong basic sites. The total amount of CO₂ desorbed from YSZ and GDC were 4.5 μmol g⁻¹ and 42.7 μmol g⁻¹, respectively. Thus, it can be considered that the basic sites are abundant on the surface of the Ni-GDC (PM) cermet. Such a surface basicity is expected to be favorable for weakened adsorption of NH₃ and dissociation of N-H bond. On the other hand, it was proven that the hydrogen has a retardant effect for both Ni-YSZ and Ni-GDC anodes blew 800°C [24, 40], and the rate of ammonia decomposition reaction depends on ammonia and hydrogen partial pressure according to the following equation;

$$r_{NH_3} = k P(NH_3)^\alpha P(H_2)^\beta \quad (2)$$

where r_{NH_3} is the rate of ammonia decomposition reaction, $P(NH_3)$ and $P(H_2)$ are the partial pressure of ammonia and hydrogen, respectively, k , α , and β are constants. The values of β at 500°C for Ni-YSZ and Ni-GDC were -0.94 and -0.81, respectively [40]. This indicates that the retardant effect of hydrogen is less significant on the Ni-GDC (PM).

3.2 Electrochemical properties and fuel cell characteristics

Electrochemical impedance spectroscopy was carried out under the open circuit condition for the fuel cells employing the Ni-YSZ and Ni-GDC (PM) anodes with supplying 60% H_2 -0.5% H_2O -39.5% Ar (flow rate; 100 ml min⁻¹) and 66.7% NH_3 -0.8% H_2O -32.5% Ar (flow rate; 60 ml min⁻¹). The impedance spectra of anodes in wet H_2 and NH_3 at 600°C and 1000°C are shown in Fig. 3(a-d). The anodic polarization resistance for Ni-GDC (PM) was smaller than that for Ni-YSZ both in wet H_2 and NH_3 fuels regardless of temperature. The polarization resistances in hydrogen and ammonia were almost the same for the respective anode at 1000°C. On the other hand, the polarization resistance in ammonia was larger than in hydrogen for both anodes at 600°C.

The temperature dependence of the anodic polarization resistance for two anodes in wet H_2 and NH_3 fuels at 600-1000°C was summarised in Fig. 3(e) and (f). The polarization resistance of Ni-YSZ in H_2 was larger than that of Ni-GDC (PM), especially at low operating temperatures. The polarization resistances of Ni-YSZ and Ni-GDC (PM) were almost the same at 900°C and 1000°C in

both H₂ and NH₃ fuels. The difference in anodic polarization resistance for Ni-GDC (PM) and Ni-YSZ is larger in NH₃ fuel than in H₂ fuel at 600–800°C. In the temperature range of 900–1000°C, ammonia completely decomposed to produce H₂ with the similar concentration to that in H₂ fuel gas mixture in the present experimental condition. On the other hand, ammonia decomposed partially at 600–800°C. The deviation of the polarization resistance between NH₃ and H₂ fuels is obviously small for Ni-GDC (PM) even in the low temperature range, whereas the polarization resistance of Ni-YSZ in NH₃ was very large. This tendency indicates that Ni-GDC (PM) is a more appropriate catalyst for NH₃-fueled SOFCs than Ni-YSZ.

It was found that the limiting current was easily observed for a dilute ammonia fuel. This means that hydrogen formed by the partial decomposition of ammonia can be consumed by the electrochemical reaction. Therefore, the effect of ammonia concentration on the limiting current density was investigated to estimate the NH₃ conversion on the cermet. It was assumed that the concentration of hydrogen produced on the cermet corresponds to the limiting current of the cell. A dilute fuel gas mixture of $x\%$ NH₃–0.5% H₂O–(99.5– x)% Ar ($x = 0.3$ – 0.9 , flow rate; 100 ml min^{–1}) was supplied to Ni-YSZ and Ni-GDC anodes at 700–1000°C to estimate the hydrogen concentration produced via ammonia decomposition from the limiting current. The hydrogen concentration was calculated by using following equations;

$$i_{\text{limiting}} = nF \left(\frac{dN}{dt} \right) \quad (3)$$

where i_{limiting} is the limiting current (A), dN/dt is the rate of the electrochemical reaction (mol s^{-1}) which reflects the number of mole of hydrogen produced from ammonia decomposition, n is the number of electrons transferred for the hydrogen oxidation, and F is the Faraday's constant.

$$C(\text{H}_2 \text{ produced}) / \% = \left(\frac{dN/dt}{n_t} \right) \times 100 \quad (4)$$

where $C(\text{H}_2 \text{ produced}) / \%$ is the hydrogen concentration produced by ammonia decomposition reaction calculated from the limiting current, and n_t is the total number of moles of outlet gases (mol s^{-1}) which are unreacted NH_3 , H_2 , N_2 , H_2O , and Ar .

Figure 4 shows current-voltage (I - V) characteristics of single cells employing Ni-YSZ and Ni-GDC (PM) anodes at 700°C and 1000°C with feeding humidified NH_3 . The I - V curves for both cells were almost identical at 1000°C, while at 700°C the cell with Ni-YSZ and Ni-GDC anodes reached to the limiting current of *ca.* 30 and 100 mA cm^{-2} , respectively. The hydrogen concentration produced from ammonia decomposition over anodes estimated from the limiting current is depicted in Fig. 5(a) as a function of temperature. At 1000°C the hydrogen concentration was almost the same for both anodes because ammonia was completely decomposed in this temperature range. Below 800°C, the hydrogen concentration for the Ni-YSZ anode was significantly lowered as compared with that for the Ni-GDC (PM) anode. This tendency corresponds to the fact that Ni-GDC (PM) is more active

for NH_3 decomposition in this temperature region. Thus, the high catalytic activity for ammonia decomposition of Ni-GDC (PM) is favorable. Furthermore, the hydrogen concentration in the vicinity of the anode was highly affected by the ammonia concentration in the fuel gas mixture and the anode material (see Fig. 5(b)); the hydrogen concentration raised by increasing the ammonia concentration, and the conversion level was obviously higher for Ni-GDC (PM) anode.

3.3 Effect of preparation method for Ni-GDC

Further enhancement of anode performance for the direct NH_3 -fueled SOFC was investigated by preparing a fine powder of Ni-GDC with large surface area [41]. It is expected that the activity for ammonia decomposition changes with the microstructure which is affected by the preparation method of the Ni-based cermet. Therefore, the Ni-GDC cermet was prepared through the glycine nitrate combustion route. The catalytic activity of Ni-GDC (GN) for ammonia decomposition was higher than that of Ni-GDC (PM) in the temperature range of 450-600°C as shown in Fig. 6. The anodic overpotential in wet H_2 demonstrated no significant difference between two Ni-GDC cermets from different preparation routes. On the other hand, the anodic overpotential of Ni-GDC (GN) in wet NH_3 was lower than that of Ni-GDC (PM) at 600°C (see Fig. 7(a) and (b)). This led to the performance enhancement of the cell with Ni-GDC (GN) anode due to higher catalytic activity for ammonia decomposition. The anodic polarization resistance for Ni-GDC (GN) was significantly lower in ammonia at 600 and 700°C than that for Ni-GDC (PM), while that in hydrogen was almost

comparable to each other (see Fig. 7(c) and (d)). The high catalytic activity of Ni–GDC (GN) for ammonia decomposition led to an increase in a hydrogen concentration in the vicinity of the anode, resulting in the high cell performance. The BET surface area for Ni–YSZ, Ni–GDC (PM), and Ni–GDC (GN) was 0.6, 0.7, and 1.3 m²g⁻¹, respectively. Every cermet possessed the relatively small surface area after calcination at 1400°C for 5 h and subsequent reduction at 1000°C in hydrogen. However, the surface area of Ni–GDC (GN) was twice as that of Ni–GDC (PM). This indicates that the high activity of Ni–GDC (GN) is ascribed to the large surface area. Therefore, Ni–GDC prepared by the glycine nitrate process is preferable for direct NH₃–fueled SOFCs.

Furthermore, the microstructure of Ni–YSZ, Ni–GDC (PM), and Ni–GDC (GN) was observed by SEM (see Fig. 8). A secondary electron detector and an in–lens detector were effective in observing the topographic image and in distinguishing Ni metal (bright particles) and oxide component (dark particles), respectively. In the case of Ni–YSZ, Ni metal aggregated to form large particles which were not dispersed well as in the case of Ni–GDC (PM) and Ni–GDC (GN). For Ni–GDC cermets, the ceria network prevented aggregation of Ni particles. The small particle size of Ni metal in the Ni–GDC (GN) anode led to the high ammonia decomposition activity, the abundant triple–phase boundary (TPB), and an increase in the rate of electrochemical oxidation of hydrogen produced from ammonia decomposition.

4. Conclusions

In this study the comparison of catalytic activities of Ni-YSZ and Ni-GDC revealed that the Ni-GDC cermet demonstrated higher activity for ammonia decomposition than Ni-YSZ. Doped-ceria possessed a large number of basic sites on its surface which were favourable for ammonia conversion.

The anodic polarization resistance of Ni-GDC anode in NH_3 was smaller than that of Ni-YSZ at 600°C. The hydrogen concentration estimated from the limiting current for ammonia fuel was higher for Ni-GDC than for Ni-YSZ. The results revealed that the SOFC performance was enhanced by using Ni-GDC anode because of the mixed ionic-electronic conductivity of GDC under reducing atmospheres and high catalytic activity for ammonia decomposition. Moreover, the contribution of preparation method of anode material for the ammonia catalytic decomposition and the cell performance was investigated. The cell performance was enhanced by using Ni-GDC prepared through the glycine-nitrate combustion route because of a good distribution of the small Ni particles within anode microstructure which led to the extension of the triple-phase boundary (TPB) and the enhancement of the electrochemical oxidation of hydrogen produced from ammonia decomposition.

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Figure captions

Fig. 1 Schematic diagram of the preparation routes for Ni-YSZ and Ni-GDC cermets.

Fig. 2 (a) Ammonia conversion over Ni-YSZ, Ni-GDC (PM), YSZ, and GDC as a function of catalyst temperature. Reaction condition; 66.7% NH₃-33.3% Ar, gas space velocity = 6000 l kg⁻¹ h⁻¹.

(b) Temperature programmed desorption of CO₂ (CO₂-TPD) for YSZ and GDC.

Fig. 3 Impedance spectra at 600°C and 1000°C in wet H₂ and NH₃ fuel (a-d) and anodic polarization resistance in wet (e) H₂ and (f) NH₃ fuel at 600–1000°C for Ni-YSZ and Ni-GDC (PM) anodes.

Anode gas; 60% H₂-0.5% H₂O-39.5% Ar (flow rate; 100 ml min⁻¹) and 66.7% NH₃-0.8% H₂O-32.5% Ar (flow rate; 60 ml min⁻¹). Cathode gas; O₂ (flow rate; 100 ml min⁻¹).

Fig. 4 *I-V* curves for the cell of Ni-YSZ|YSZ|LSM and Ni-GDC (PM)|YSZ|LSM at (a) 1000°C and (b) 700°C. Anode gas; 0.7% NH₃-0.5% H₂O-98.8% Ar (flow rate; 100 ml min⁻¹). Cathode gas; O₂ (flow rate; 100 ml min⁻¹).

Fig. 5 H₂ concentration produced from ammonia decomposition at the limiting current as a function of (a) temperature and (b) ammonia concentration. Anode gas; *x*% NH₃-0.5% H₂O-(99.5-*x*)% Ar (*x* = 0.3-0.9%, flow rate; 100 ml min⁻¹). Cathode gas; O₂ (flow rate; 100 ml min⁻¹).

Fig. 6 Ammonia conversion over Ni-GDC (PM) and Ni-GDC (GN) as a function of catalyst temperature. Reaction condition; 66.7% NH₃-33.3% Ar, gas space velocity = 6000 l kg⁻¹ h⁻¹.

Fig. 7 Anodic overpotential in wet (a) H₂ and (b) NH₃ fuel at 600°C and anodic polarization resistance in wet (c) H₂ and (d) NH₃ fuel at 600–1000°C for Ni-GDC (PM) and Ni-GDC (GN). Anode gas; 60% H₂-0.5% H₂O-39.5% Ar (flow rate; 100 ml min⁻¹) and 66.7% NH₃-0.8% H₂O-32.5% Ar (flow rate; 60 ml min⁻¹). Cathode gas; O₂ (flow rate; 100 ml min⁻¹).

Fig. 8 Cross-sectional images of (a) Ni-YSZ, (b) Ni-GDC (PM), and (c) Ni-GDC (GN) anode obtained by a secondary electron detector (left images) and an in-lens detector (right images); bright particle Ni; dark phase YSZ or GDC.

Physical Mixing route (PM)

Glycine-nitrate route (GN)

Fig. 1 Schematic diagram of the preparation routes for Ni-YSZ and Ni-GDC.

Fig. 2 (a) Ammonia conversion over Ni-YSZ, Ni-GDC (PM), YSZ, and GDC as a function of catalyst temperature. Reaction condition; 66.7% NH₃-33.3% Ar, gas space velocity = 6000 l kg⁻¹ h⁻¹. (b) Temperature programmed desorption of CO₂ (CO₂-TPD) for YSZ and GDC.

Fig. 3 Impedance spectra at 600°C and 1000°C in wet H₂ and NH₃ fuel (a–d) and anodic polarization resistance in wet (e) H₂ and (f) NH₃ fuel at 600–1000°C for Ni–YSZ and Ni–GDC (PM) anodes. Anode gas; 60% H₂–0.5% H₂O–39.5% Ar (flow rate; 100 ml min^{−1}) and 66.7% NH₃–0.8% H₂O–32.5% Ar (flow rate; 60 ml min^{−1}). Cathode gas; O₂ (flow rate; 100 ml min^{−1}).

Fig. 4 I - V curves for the cell of Ni-YSZ|YSZ|LSM and Ni-GDC (PM)|YSZ|LSM at (a) 1000°C and (b) 700°C . Anode gas; 0.7% NH_3 -0.5% H_2O -98.8% Ar (flow rate; 100 ml min^{-1}). Cathode gas; O_2 (flow rate; 100 ml min^{-1}).

Fig. 5 H₂ concentration produced from ammonia decomposition at the limiting current as a function of (a) temperature and (b) ammonia concentration. Anode gas; $x\%$ NH₃–0.5% H₂O–(99.5– x)% Ar ($x = 0.3$ –0.9%, flow rate; 100 ml min^{–1}). Cathode gas; O₂ (flow rate; 100 ml min^{–1}).

Fig. 6 Ammonia conversion over Ni-GDC (PM) and Ni-GDC (GN) as a function of catalyst temperature. Reaction condition; 66.7% NH_3 -33.3% Ar, gas space velocity = $6000 \text{ l kg}^{-1} \text{ h}^{-1}$.

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Fig. 7 Anodic overpotential in wet (a) H₂ and (b) NH₃ fuel at 600°C and anodic polarization resistance in wet (c) H₂ and (d) NH₃ fuel at 600–1000°C for Ni–GDC (PM) and Ni–GDC (GN). Anode gas; 60% H₂–0.5% H₂O–39.5% Ar (flow rate; 100 ml min⁻¹) and 66.7% NH₃–0.8% H₂O–32.5% Ar (flow rate; 60 ml min⁻¹). Cathode gas; O₂ (flow rate; 100 ml min⁻¹).

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