



## Comparative study on ammonia oxidation over Ni-based cermet anodes for solid oxide fuel cells



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### HIGHLIGHTS

- Ni–GDC shows higher catalytic activity for ammonia decomposition than Ni–YSZ.
- GDC surface demonstrates a higher number of basic sites compared with YSZ.
- Higher production of H<sub>2</sub> from NH<sub>3</sub> decomposition over Ni–GDC anode was confirmed.
- Ni–GDC microstructure dependence of the performance of direct NH<sub>3</sub> SOFCs was proved.

### ARTICLE INFO

#### Article history:

Received 26 September 2015

Received in revised form

20 November 2015

Accepted 21 November 2015

Available online 30 November 2015

#### Keywords:

Direct NH<sub>3</sub>-Fueled SOFCs

Ammonia decomposition

Ni–GDC

Ni–YSZ

### 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 H<sub>2</sub> or NH<sub>3</sub> 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 NH<sub>3</sub>-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 NH<sub>3</sub>-fueled SOFC results from its mixed ionic–electronic conductivity as well as high catalytic activity for ammonia decomposition.

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## 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 CO<sub>2</sub> emission. Our previous study indicated that the SOFC consisting of Ni–YSZ|YSZ|(La,Sr)MnO<sub>3+δ</sub> demonstrated a higher performance with ammonia fuel than that with methane at the same temperature and anodic oxygen potential. The preferable performance of direct NH<sub>3</sub>-fueled SOFC resulted from a higher

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reactivity of  $\text{NH}_3$  for decomposition than  $\text{CH}_4$  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  $\text{H}_2$  and  $\text{NH}_3$  fuels was conducted. We focused on the evaluation of the catalytic activity of Ni–YSZ and Ni–GDC for  $\text{NH}_3$  decomposition and the polarization resistance of each anode. The effect of preparation method of NiO–GDC on  $\text{NH}_3$  decomposition reaction was also studied for the development of active anode for direct  $\text{NH}_3$ –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  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (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  $\mu\text{m}$  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  $\text{cm}^2$  and the thicknesses were 60  $\mu\text{m}$  and 40  $\mu\text{m}$  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

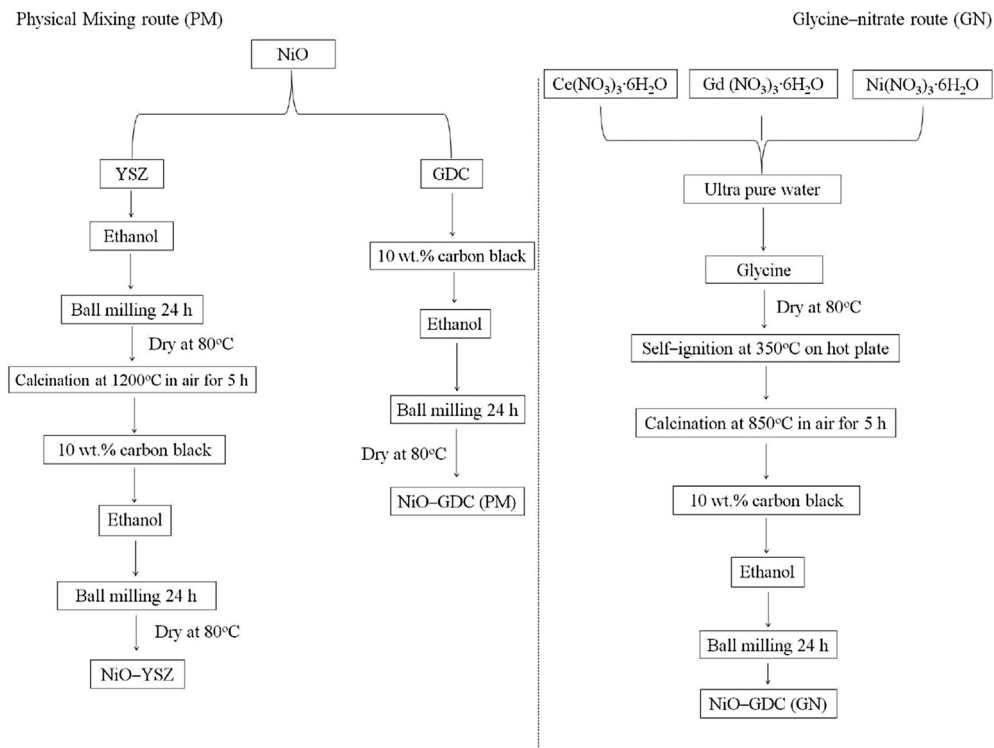


Fig. 1. Schematic diagram of the preparation routes for Ni–YSZ and Ni–GDC cermets.

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