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Development of Ni–Ba(Zr,Y)O_3 cermet anodes for direct ammonia-fueled solid oxide fuel cells

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HIGHLIGHTS

- Ammonia decomposition activity test was performed for various nickel-based catalysts.
- Ni–Ba(Zr,Y)O_3 cermet exhibited the highest catalytic activity.
- Ni–Ba(Zr,Y)O_3 was applied to an anode for ammonia-fueled solid oxide fuel cells.
- The cell performance with ammonia fuel was comparable to that with hydrogen fuel.

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ABSTRACT

In this study, the availability of Ni–Ba(Zr,Y)$O_{3-\delta}$ (BZY) cermet for the anode of direct ammonia-fueled solid oxide fuel cells (SOFCs) is evaluated. In this device, the anodes need to be active for the catalytic ammonia decomposition as well as the electrochemical hydrogen oxidation. In the catalytic activity test, ammonia decomposes completely over Ni–BZY at ca. 600 °C, while higher temperature is required to accomplish the complete decomposition over the conventional SOFC anode of Ni–yttria-stabilized zirconia cermet. The high activity of Ni–BZY is attributed to the high basicity of BZY and the high resistance to hydrogen poisoning effect. The electrochemical property of Ni–BZY anode is also evaluated with the anode-supported cell of Ni–BZY|BZY|Pt at 600–700 °C with feeding ammonia or hydrogen as a fuel. Since the residence time of ammonia fuel in the thick Ni–BZY anode is long, the difference in the cell performance between two fuels is relatively small. Furthermore, it is proved that the steam concentration in the fuel strongly affects the cell performance. We find that this factor is important to satisfy the above mentioned requirements for the anode of direct ammonia-fueled SOFCs. Throughout this study, it is concluded that Ni–BZY cermet will be a promising anode.

1. Introduction

Recently, fuel cells have attracted much attention as a clean power generator with high efficiency. Hydrogen is the best fuel for this electrochemical device, but there are many difficulties in storage and transportation due to its low volumetric density and boiling point (−253 °C). In order to overcome these disadvantages, hydrogen carriers have been proposed as alternative fuels; e.g., methanol, ammonia, methylcyclohexane, and so on.

Among various hydrogen carriers, ammonia is one of the promising candidates because of many advantages, such as ease in liquefaction under mild conditions (−33 °C under ambient pressure or 0.857 MPa at room temperature) and large hydrogen content (17.8 wt.%). Established infrastructures for a fertilizer and commodity chemicals are also available. Although ammonia is well-known as a toxic substance, human nose can detect ammonia odor even below 1 ppm.

Conventionally, ammonia is synthesized from hydrogen and nitrogen through the Haber-Bosch reaction. Since the steam reforming of hydrocarbons is the main route of hydrogen production at the current state, the usage of ammonia is not free from CO_2 emission. However, if hydrogen can be produced from the renewable energy such as solar and wind power generation, the amount of CO_2 emission can be significantly reduced.

The ammonia decomposition reaction will be the effective

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process for on-site hydrogen generation; no CO_2 emission upon decomposition is a great merit.

$$NH_3 \rightarrow 3/2H_2 + 1/2N_2 \; \Delta H^{\circ} = +46 \text{ kJ mol}^{-1} \tag{1}$$

This reaction is an endothermic process and the equilibrium conversion of ammonia is higher than 99% at 400 °C. Hence, it is possible to use ammonia as a fuel for solid oxide fuel cells (SOFCs) without an external reformer. This is because SOFCs are usually operated above 700 °C. In the case of direct ammonia-fueled SOFCs, ammonia is oxidized via the two-step reaction [1]; that is, ammonia decomposes into hydrogen and nitrogen on the anode and subsequently hydrogen is electrochemically oxidized.

Thus, anode materials need to be active for the electrochemical hydrogen oxidation as well as the catalytic ammonia decomposition. Ru-based catalysts are the most active for ammonia decomposition and synthesis [2,3], but their high cost is an obstacle for a wide application. Among non-noble metals, Ni has the highest activity for ammonia decomposition [4]. The catalyst support is also an important component, which alters the catalytic activity significantly. In these respects, the ammonia decomposition activity of Ni catalysts supported on various oxides has been investigated [5–7]. It is reported that rare-earth oxides are effective supports, and Y_2O_3 notably enhances the activity [5].

For SOFC anodes, Ni–ionic conductor cermet is widely used from a point of practical view; 1) an increase in the number of active reaction sites, 2) the suppression of nickel sintering, and 3) the reduction in the mismatch of thermal expansion coefficient with the electrolyte. Thus, the findings for the ammonia decomposition catalysts can be applied in designing SOFC anodes. We recently found that Ni–yttrium-doped barium cerate ($Ba(Ce,Y)O_3$, BCY) cermet showed much higher activity for ammonia decomposition than conventional SOFC anodes, Ni–yttria-stabilized zirconia (Ni–YSZ) and Ni–gadolinium-doped ceria (Ni–GDC) [7]. Rare earth-doped barium cerate ($Ba(Ce,M)O_3$, M: rare earth element) is well known as the proton conductor, and many researchers have been studied its electrochemical properties extensively to apply as an electrolyte of proton-conducting ceramic fuel cells (PCFCs). Since the activation energy of proton migration in these oxides is lower than that of oxide ion, PCFCs can be operated at intermediate temperatures (500–700 °C) [8–14]. As a result, side reactions between component materials will be prevented or suppressed. In addition, unlike SOFCs with oxide ion conductors, the fuel is not diluted because of the production of steam in the cathode side, leading to an improvement in energy conversion efficiency. Although BCY shows high proton conductivity, the chemical stability is low in the presence of CO_2 and H_2O due to the formation of barium carbonate and barium hydroxide [15,16]. These reactions result in the decrease in proton conductivity of the electrolyte [17]. From the standpoint of chemical stability, yttrium-doped barium zirconate ($Ba(Zr,Y)O_3$, BZY) is preferable [16,18]. Furthermore, some authors reported that the bulk conductivity of doped barium zirconate is higher than that of doped barium cerate [19,20].

In this study, thus, we focus on BZY as an alternative ionic conductor in the cermet. The catalytic activity of Ni–BZY for ammonia decomposition was studied in detail. Furthermore, Ni–BZY cermet was applied to the anode of direct ammonia-fueled SOFCs and its performance was evaluated.

2. Experimental

2.1. Sample preparation

Powders of proton conductors, $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY10) and $BaZr_{1-x}Y_xO_{3-\delta}$ (x = 0.10, 0.20), were prepared by the citric acid complex method. $Ba(NO_3)_2$ (Wako Pure Chemical Industries, Ltd.), $Ce(NO_3)_3 \cdot 6H_2O$ (Wako Pure Chemical Industries, Ltd.), $ZrO(NO_3)_2 \cdot 2H_2O$ (Wako Pure Chemical Industries, Ltd.), and $Y(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, Co.) were used as starting materials. Stoichiometric amounts of reactants were dissolved into distilled water, and then citric acid (Wako Pure Chemical Industries, Ltd.) was added at the molar ratio of citric acid/total metal cations of 1.5/1. Finally, the pH value of the solution was adjusted to ca. 8.0 with adding the aqueous ammonia solution (Wako Pure Chemical Industries, Ltd.). The resultant solution was heated on a hot plate until auto-ignition occurred, and then the desired oxide with a perovskite-type structure was obtained after the calcination of the powder at 1100 °C (BCY10) or 1200 °C ($BaZr_{1-x}Y_xO_{3-\delta}$) for 5 h in air.

Ni catalysts supported on oxides were prepared by the impregnation method. The powder of BCY10 or BZY was added into nickel nitrate aqueous solution using $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries, Ltd.). After drying this solution, the resultant powder was calcined at 700 °C for 5 h. The obtained powder was denoted as NiO–BCY or NiO–BZY, which was reduced prior to each characterization to get Ni catalysts supported on proton conductors. For comparison, by using 8 mol.% yttria-stabilized zirconia (YSZ, Tosoh Co.), the conventional SOFC anode of Ni–YSZ catalyst was prepared through the same manner. The loading amount of Ni was 40 wt.% for all catalysts.

X-ray diffraction (XRD) analysis was conducted using Ultima IV X-ray diffractometer (Rigaku) with Cu Kα radiation to identify the phase of the prepared sample. The specific surface area of supports was evaluated by the BET method with N_2 adsorption (Bellsorp-miniII, BEL Japan). For the pretreatment, samples were heated at 300 °C for 30 min in vacuum. The basicity of each support in the catalyst was measured by temperature programmed desorption of CO_2 (CO_2–TPD, BELCAT–A, BEL Japan). Prior to the measurement, oxides were held at 600 °C in a hydrogen atmosphere for 2 h, and then adsorbed hydrogen was flushed for 30 min in He. After cooling to 50 °C in He, samples were exposed to CO_2 for 30 min, followed by the gas replacement with He for 30 min. Subsequently, samples were heated at a rate of 10 °C min^{-1} with a supply of He at a flow rate of 30 mL min^{-1}. The desorption species were monitored by a thermal conductive detector (TCD).

2.2. Catalytic activity test for ammonia decomposition

The ammonia decomposition activity of catalysts was evaluated with a fixed bed reactor at the space velocity of 6000 L kg^{-1} h^{-1}. A 300 mg of catalyst was placed between silica wool layers in a quartz reactor. For the pretreatment, catalysts were reduced at 600 °C for 2 h in 50% H_2–50% Ar at a flow rate of 80 mL min^{-1}. Then, temperature was lowered to 350 °C and the activity test was conducted with the supply of pure ammonia at a flow rate of 30 mL min^{-1} at 350–700 °C. The outlet gas was trapped by diluted sulfuric acid to remove unreacted ammonia and the flow rate of resultant gas was measured with a film flowmeter (HORIBA STEC). By assuming that ammonia decomposed into hydrogen and nitrogen at the ratio of 3:1, the ammonia conversion was calculated as follows;

$$\text{Ammonia conversion (\%)} = (F_{out}/2F_{in}) \times 100 \tag{2}$$

where F_{in} and F_{out} are the flow rate of inlet ammonia gas and outlet H_2–N_2 gas, respectively. In this equation, $2F_{in}$ indicates the flow rate of outlet gas when ammonia is completely decomposed over catalysts. When ammonia decomposes completely, the volume of gas increases twofold (see eq. (1)). This is because F_{in} is multiplied by 2.

In addition, effects of partial pressure of ammonia and hydrogen on the ammonia decomposition were also studied. It is well-known