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Mechanism of Ammonia Oxidation at Ni-Fe/SDC Anode in Ammonia-Fueled SOFCs

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Hydrogen has been regarded as an ideal carrier for energy storage and distribution to support sustainable energy development. However, hydrogen has a difficulty in liquefaction, and thereby has serious problems in storage and transportation. Ammonia is easily liquefied at ambient temperature under a pressure of 10 atm or under ambient pressure at a temperature of about 240 K. In addition, the infrastructure for ammonia technology has been well established. Therefore, ammonia is one of the promising candidates for hydrogen carriers.

Solid oxide fuel cells (SOFCs) are operated at high temperatures; therefore, their electrochemical reactions are facile and internal reforming can be achieved. Hence SOFCs are a promising candidate as power generation systems using ammonia as a fuel in the future. In fact, it has been reported that SOFCs can be operated with ammonia gas as a fuel; however, the performance of ammonia-fueled cells is usually lower than that of hydrogen-fueled cells [1]. In this study, we prepared Ni-Fe/SDC cermets because iron is known as a catalyst for ammonia synthesis and decomposition. Their catalytic activity for ammonia oxidation in SOFCs was investigated.

The performance of Ni-Fe/SDC cermets of different compositions was measured using dry NH_3 as a fuel. From anode polarization curves, the current densities at an overpotential of 0.15 V were estimated and plotted against Ni/(Ni+Fe) atomic ratios are shown in Fig. 1. The addition of Fe in Ni/SDC improved the anode performance up to Ni:Fe = 40:60 (in atomic ratio), at which the cermet showed the best performance. This clearly showed that the presence of Fe enhances the catalytic activity for NH_3 oxidation. However, further addition of Fe decreased the performance. This is partly because iron tends to sinter at high temperatures.

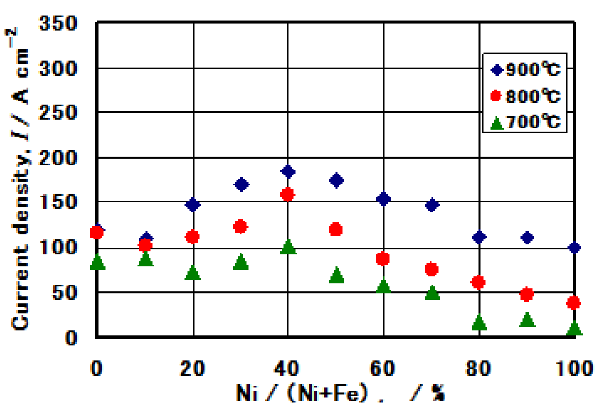

Fig. 1. Variations of current density at an anode overpotential of 0.15 V of Ni-Fe/SDC20 cermet anodes with Ni / (Ni + Fe) ratios at 700, 800, and 900°C. Fuel: dry ammonia, oxidant: air.

It is well known that NH_3 decomposes at temperatures above 400°C ($2NH_3 \rightarrow N_2 + 3H_2$). Therefore it is important to understand whether ammonia is directly oxidized on the Ni-Fe/SDC cermets or not. Theoretical calculation revealed that the OCV increases with temperature when ammonia fuel is direct oxidized ($2NH_{3ad} + 3O^{2-} = 3H_2O + N_2 + 6e^-$), whereas it decreases when hydrogen that is formed by thermal decomposition of NH_3 is oxidized ($2NH_{3\,ad} = N_{2\,ad} + 3H_2$ and $H_{2\,ad} + O^{2-} = H_2O + 2e^-$). The variations of OCV in NH_3 and H_2 fuels are shown in Fig. 2. The OCV in NH_3 increased with temperature, which clearly showed that NH_3 is directly oxidized at the Ni-Fe/SDC cermet.

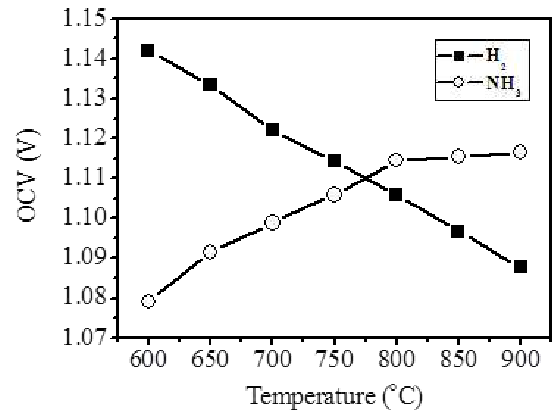

Fig. 2. OCV changes of Ni40-Fe60/SDC cermet in H_2 and NH_3 fuels.

We also found that the Ni-Fe alloy reacts with ammonia to form a nitride (γ-Ni_2Fe_2N), while pure Ni alloy does not. Hence the nitride formation may be related with the high catalytic activity of Ni-Fe/SDC cermet.

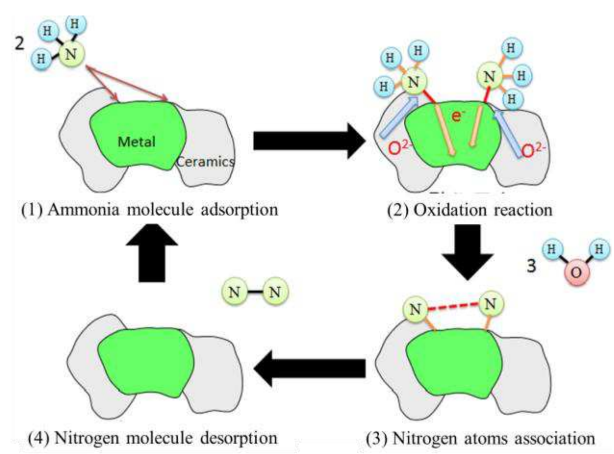

Fig. 3. Schematic images for reaction mechanism for ammonia fuel.

For ammonia decomposition catalyst, it has been reported that Fe has ammonia adsorption ability, while Ni has nitrogen desorption ability [2]. Four elementary steps are involved in NH_3 oxidation at the anode of SOFCs (Fig. 3). Of these, promotion of ammonia molecule adsorption (Step (1)) and nitrogen atoms association (Step (3)) is important in electrode activity. It seems that the activity is determined by a balance between ammonia adsorption and nitrogen desorption. Therefore, the ratio of Ni:Fe = 40:60 (in atomic ratio) was considered to be the most suitable composition for NH_3 oxidation.

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References

[1] Q. Ma, et al., J. Power Sources, 161 (2006) 95.
[2] F. Schůth, et al, Energy Environ. Sci., 5 (2012) 6278.