Development of Ammonia Gas Removal Device

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We have developed a new ammonia gas removal device using fuel cell technology. In this device, yttrium stabilized zirconia (YSZ) is used for the solid electrolyte, lantern strontium manganite (LSM) for the cathode, and Ni/YSZ porous cermet for the anode; and ammonia gas flows through them. The porous Ni (Celmet) is applied to the current collector, which also functions as the gas diffusion layer of the anode. Chained Ni powder made by the titanium-redox method is used for the anode catalyst. This device has achieved a high ammonia detoxification capability and a low pressure drop during exhaust gas flow, which are the key requirements to exhaust gas treatment. Unlike conventional removal methods used in semiconductor manufacturing equipment, this device does not require liquefied natural gas (LNG) or noble metal catalysts, which are used in the burning method and catalytic decomposition method, respectively. The prototype device achieved the detoxifying targets of less than 25 ppm at about 800˚C while emitting no NOx and CO_2. In addition, the NOx concentration at the outlet was less than 0.1 ppm. Thus, the prototype proved that this device is highly effective in detoxification and also environmentally-friendly.

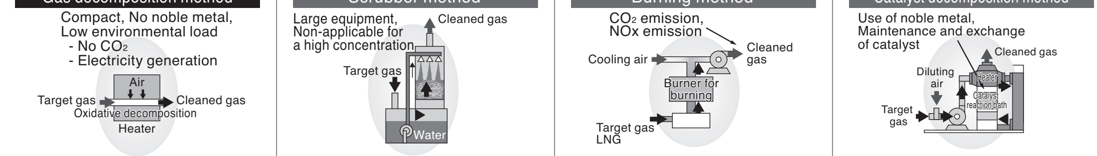
Keywords: ammonia, Celmet, fuel cell, equipment for safety disposal

1. Introduction

High-concentration ammonia is used as a manufacturing process gas for the production of compound semiconductors, such as gallium nitride, but harmful gas emitted from production devices has to be removed to a level lower than the threshold limit value (TLV), the safe level for the human body, in consideration of the work environment. The TLV of ammonia recommended by the Japan Society for Occupational Health and American Conference of Governmental Industrial Hygienist is 25 ppm or lower as a TLV-time weighted average(1).

Table 1 summarizes typical ammonia removal methods. Generally, low-price water scrubbers are frequently used, but a large-scale device is necessary to reduce high-level ammonia gas to below the TLV, and maintenance is also necessary, such as periodic neutralization of ammonia with chemicals. Thus, a compact removal device requiring a lower frequency of maintenance has been investigated, and the catalytic decomposition method, in which ammonia gas is mixed with air and decomposed by heating on a noble metal catalyst, and the burning method, in which ammonia is burned in the burner using liquefied natural gas (LNG), have been practically used. In the catalytic decomposition method, periodic exchange of the noble metal catalyst is necessary, and a large amount of energy is used to mix the gas with a large volume of air. The burning removal device has problems of CO_2 production accompanying LNG combustion and NOx production accompanying high-temperature treatment. In this situation, a compact, environment-friendly removal device requiring a low running cost and lower frequency of maintenance has been increasingly needed.

Table 1. Comparison of ammonia gas removal methods



	Gas decomposition method	Scrubber method	Burning method	Catalyst decomposition method
Processing capacity	Applicable for high-concentration gas	Unsuitable for high-concentration gas	Applicable for high-concentration gas	Applicable for high-concentration gas
Equipment cost	Relatively low	Low	Relatively low	High
Equipment size	Small	Large	Middle	Large
Electricity consumption	Low	Low	Middle	High
Gas emission (CO_2)	0	0	Produced during burning LNG	0
Gas emission (NOx)	0	0	Produced at the combustion temperature	Produced at the processing temperature

To meet these requirements, we have been investigating a gas decomposing element to apply the fuel cell principle using hydrogen-containing gas, such as ammonia, as shown in **Fig. 1**. In this method, ammonia serving as a fuel gas is decomposed to nitrogen and hydrogen by a transitional metal catalyst, such as nickel, without a noble metal catalyst, and finally decomposed to nitrogen and water by electrolyte-derived ions, emitting no CO_2 or NOx, being expected to be an environment-friendly device. In addition, if electricity can be extracted while removing gas, it may be used as power for the device, reducing the running cost. In this study, to efficiently remove relatively high-concentration ammonia gas to a 25-ppm or lower level, we developed an ammonia gas removal device employing the fuel-cell technology. In particular, we focused on the solid oxide fuel cell (SOFC), which is operable at a high temperature and contributes to down-sizing. Herein, we report on the preparation and removal performance of an element using Celmet of our company and chained Ni powder as a Nickel material to efficiently remove ammonia.

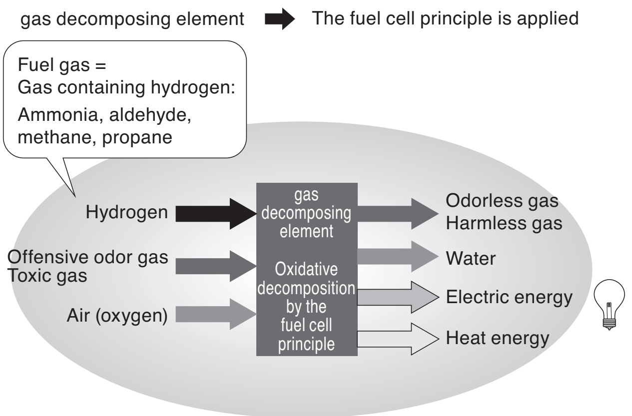


Fig. 1. Schematic illustration of gas decomposing mechanism

2. Methods

2-1 Gas decomposition module

The gas decomposition module is roughly divided into 5 layers: anode current collector, anode catalyst, solid electrolyte, cathode catalyst, and cathode current collector (**Fig. 2**). Porous Ni "Celmet" is used for the anode current collector in which ammonia exhaust gas flows, and chained Ni powder for the anode catalyst. Chained Ni represents the collection of nano-nickel particles prepared employing the titanium-redox process[(2)-(5)]. For the solid electrolyte, yttrium stabilized zirconia (YSZ) ceramics were used. For the cathode catalyst and current collector, lantern strontium manganite (LSM) and Ag-coated porous Ni were used, respectively. For the anode catalyst which markedly influences the removal performance, commercial spherical Ni powder with a mean size of 2 microns was used, and Ni mesh for the anode current collector for comparison.

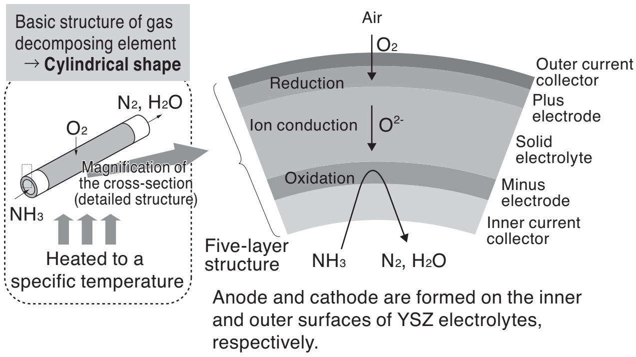


Fig. 2. Basic structure of gas decomposing element

2-2 Ammonia gas removal device and evaluation of ammonia gas decomposition

The prepared ammonia gas decomposition modules were assembled and installed in the ammonia gas removal device. The removal device was aerated with a specific volume of 20% ammonia gas in nitrogen, and the ammonia gas level was measured using an ammonia meter set at the outlet or by sampling a specific volume of the gas into a gas bag and passing it through an ammonia detector tube.

2-3 Analysis of the module

The anode catalyst layer after ammonia removal was analyzed employing scanning electron microscopy (SEM) after processing the cross-section of the gas decomposition module with a cross-section polisher (CP).

3. Results and Discussion

3-1 Basic characteristics of the gas decomposition module

The basic characteristics of the prototype gas decomposition module were evaluated. Ammonia exhaust gas is flowed through the anode current collector. For the gas decomposition and removal device, it is desirable to minimize the pressure drop during exhaust gas flow in the module. **Figure 3** shows the pressure drops when Celmet and Ni mesh are used as the anode current collector. The amount of filled metal was the same, but the pressure drop was small when Celmet was used, resulting in efficient processing of ammonia gas and an increase in the output per module. In a gas flow simulation separately performed, the pressure drop was small when Celmet was used, as its characteristic, suggesting the usefulness of Celmet for the gas diffusion layer in exhaust gas processing, such as this device. **Figure 4** shows the ammonia concentrations measured at the outlet of the gas decomposition modules with the different Ni powder types used as the anode catalyst material. Since reduction is finally applied to form the anode catalyst layer, Ni added as a metal oxide to the anode catalyst layer is reduced and used in many cases. However, we added it as metal powder with a characteristic shape in consideration of the shape of secondary particles. In Ni particles prepared employing the titanium-redox method, primary particles are small, with a size up to 100

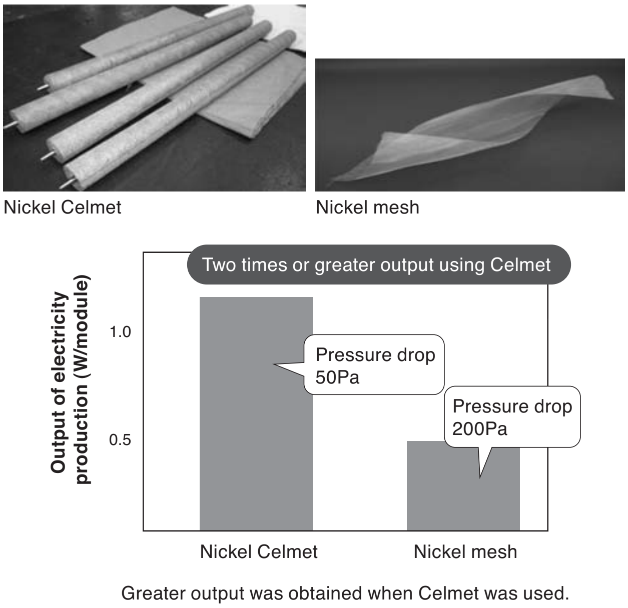


Fig. 3. Comparative evaluation of the anode current collectors

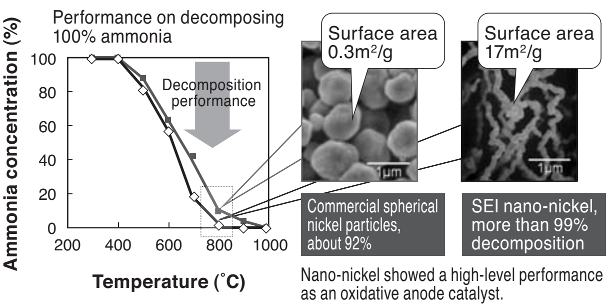


Fig. 4. Comparative evaluation of the anode catalytic performance

microns, and connected like a chain as its characteristic. At the Celmet anode, comprised of a mixture of Ni metal serving as a catalyst and YSZ electrolytes, electrons and oxygen ions conduct through Ni metal and YSZ electrolytes, respectively, for which a structure connecting them may be desirable to enhance electricity. Thus, the anode catalyst layer was prepared as follows: YSZ powder and Ni metal powder were mixed and made into a paste, applied to the solid YSZ electrolyte membrane, and sintered, followed by flowing reducing gas in the early phase to reduce the surface of Ni oxide to form pores. The specific surface areas of the Ni powders measured employing the BET method were: commercial spherical powder (mean particle size: 2 microns), 0.3 m^2/g; chained Ni, 17 m^2/g. On comparison at the same temperature in **Fig. 4**, the ammonia level at the outlet was apparently lower when chained Ni was used. The cross-section of the anode catalyst layer was observed after evaluation. As shown in **Fig. 5**, Ni is minutely and homogenously scattered in the catalyst layer prepared with chained Ni, whereas some gross Ni particles were present and particles were poorly dispersed when the spherical powder was

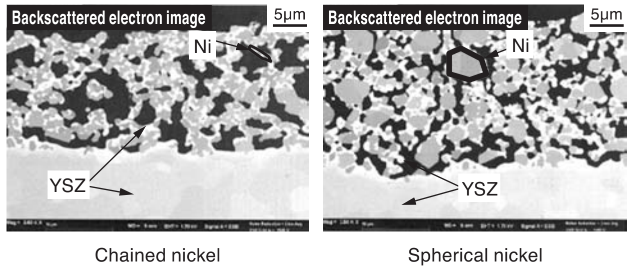


Fig. 5. Cross-section observation of the catalyst layer

used, suggesting that the difference in ammonia decomposition may have been due to the difference in the Ni dispersion pattern.

3-2 Construction of the ammonia gas removal device and evaluation of removal

A specific number of the gas decomposition modules were assembled and arranged in a ceramic heater for heating to construct the ammonia gas removal device shown in **Photo 1**. To evaluate ammonia gas decomposition, 20% ammonia gas was flowed at 100 L/min in the removal device, and, after stabilization, the ammonia and NOx levels

Photo 1. Appearance of the ammonia gas removal device

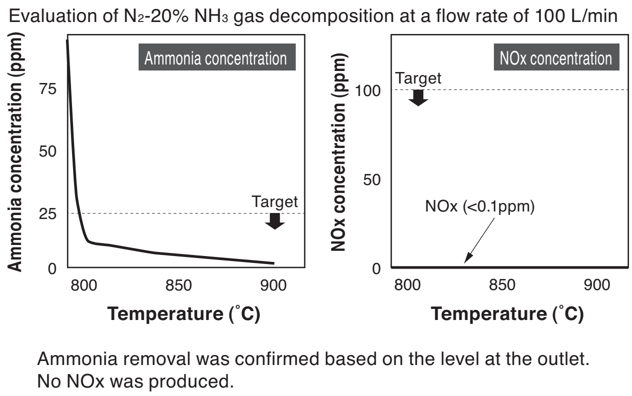


Fig. 6. Gas decomposition results using the ammonia gas removal device

were measured at the outlet. Since electricity production in the module was prioritized during ammonia gas decomposition, the cathode and anode were short-circuited in the test. The results are shown in **Fig. 6**. At the optimum operation temperature for YSZ electrolytes, 800˚C, the gas was removed to below the target level, 25 ppm. In addition, no NOx was produced, although it was a concern, even at a temperature higher than 900˚C, and no CO_2 was produced, demonstrating that this is an environment-friendly removal device. Similar removal performance was also confirmed with actual exhaust gas. An electricity-consuming operation was performed to prioritize ammonia removal in this experiment, but we will promote the development of middle-temperature electrolytes and catalysts to operate the device at a lower temperature and simultaneously achieve high output with decomposition.

4. Conclusion

We have developed a novel ammonia gas removal device applying the fuel cell principle, and demonstrated that it is an environment-friendly removal device emitting no NOx or CO_2.

* CELMET is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.

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