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Nippon Oil's Activities toward Realization of Hydrogen Society

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Abstract

Nippon Oil Corporation, a major Japanese energy distributor, has been devoting extensive efforts toward the establishment of hydrogen supply systems. The Council on Competitiveness-Nippon (COCN), an advisory organization which has influence on Japanese government policy, has announced that the establishment of hydrogen infrastructure should be started in 2015. By that time, we plan to have completed the development of necessary technologies for the infrastructure. It is well recognized that the storage and transportation of hydrogen is the sticking point on the path to realization of a hydrogen economy.

The scope of our research covers key technologies for hydrogen storage and transportation, including carbon fiber reinforced plastic (CFRP) tanks for compressed hydrogen gas, hydrogen storage materials, and hydrogen transportation systems which utilize organic chemical hydride (OCH). This article describes Nippon Oil's strategy for realization of the hydrogen economy.

Keywords: Hydrogen Infrastructure, Hydrogen Storage Materials, CFRP Tank, Organic Chemical Hydride

1 Hydrogen Infrastructure

The time has come to take action to curb global warming. A considerable number of studies have been conducted on ways to limit emissions of greenhouse gases such as carbon dioxide. In particular, it has been recognized that utilization of hydrogen as an energy carrier would improve the efficiency of fossil fuels and contribute to the fight against global warming.

It is very important for energy suppliers to make hydrogen available at reasonable cost at places convenient for the customer. However, at the first stage of a hydrogen economy, sales of hydrogen will not be enough to cover the huge investments required to construct new facilities, so utilization of existing facilities is highly recommended.

Experts have pointed out that oil refineries have considerable capacity for hydrogen production, and currently produce large amounts for use in hydrodesulfurization and other refining processes. However, the facilities are not always operated at full capacity, meaning that refineries have extra capacity to provide hydrogen to the market.

Having extra hydrogen production capacity on hand, oil companies have a clear incentive to study technologies for the transportation and storage of hydrogen, some of which will be mentioned below.

2 High Pressure Hydrogen Storage Tanks

Hydrogen gas has good energy density by weight, but poor energy density by volume when compared with hydrocarbon fuels. Hence, the hydrogen storage pressure in fuel cell vehicles (FCVs) must be set high enough for the vehicles to achieve a good cruising distance. A recent trend has emerged in which the pressure has doubled from 35 MPa to 70 MPa, which has enabled FCVs to drive more than 500 km on one hydrogen charge [1]. Therefore, with hydrogen station applications in mind, we have been developing a large-scale CFRP tank of 80 MPa, capable of hydrogen refilling an FCV equipped with a compressed hydrogen tank at 70MPa.

High-pressure tanks can be classified into four types (Table 1). The most commonly used are CFRP tanks such as the Type III and IV, because they offer many advantages such as high strength/stiffness-to-weight ratio.

Table 1: Types of tank.

Type	Composition
Type I	Metal tank
Type II	Metal liner with hoop lap layer of FRP
Type III	Metal liner with full lap layer of FRP
Type IV	Plastic liner with full lap layer of FRP

The filament winding (FW) fabrication process, which combines the Tow-Prepreg and liner-heating method [2-3], is a method we developed for manufacturing CFRP tanks (Figure 1). Tow-Prepreg is carbon fiber pre-impregnated with thermoset epoxy resin. It is easy to handle and has a long shelf life. One notable feature of Tow-Prepreg is its highly uniform resin content, so the FW method utilizing Tow-Prepreg makes it easy to manufacture tanks of consistent quality.

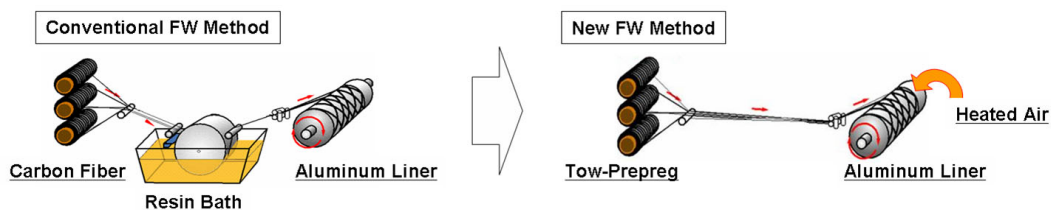


Figure 1: Filament winding fabrication processes.

Generally, the FW fabrication method requires that the dry fiber be passed through a resin bath to impregnate the fiber with resin. In the FW fabrication process utilizing Tow-Prepreg, however, the Tow-Prepreg can be directly wound over the liner. And when the liner-heating method is incorporated, the Tow-Prepreg can cure during the FW fabrication process.

In a cross-section observation of CFRP by optical microscope (Figure 2), we can see that CFRP made using the liner-heating method has fewer voids than that made using the

conventional method. This result indicates that the new liner-heating method can minimize the occurrence of voids, because the epoxy-resin effectively penetrates into the interfiber spaces.

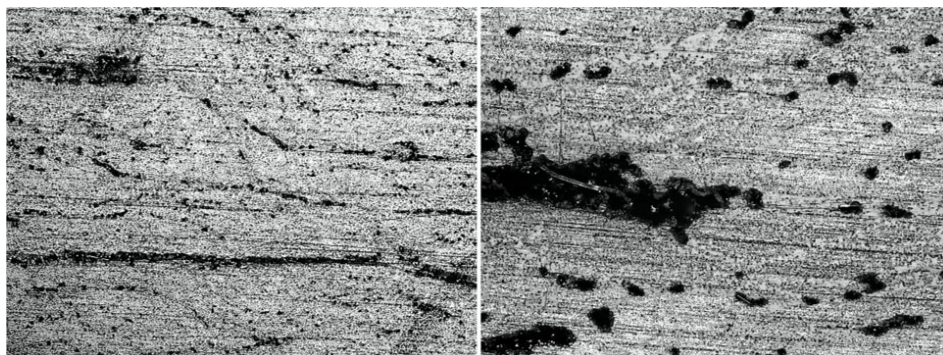


Figure 2: The Photographs of the cross-section observation of CFRP layer by optical microscope at 200-fold magnification. (Right; Conventional method, Left; Liner-heating method)

By using Tow-Prepreg combined with the liner-heating method, manufacturers could expect to achieve cost reductions, increased production efficiency and higher quality CFRP tanks.

3 Hydrogen Storage Materials

We have been developing hydrogen storage materials with the objective of increasing the amount of hydrogen that can be transported with hydrogen trailers. Our target value for hydrogen storage is 5 mass% at 35 MPa, and to achieve this target, we have been focusing on metal-organic frameworks (MOFs) due to their exceptionally high surface areas, high porosity, and chemically-tunable structures. MOFs have attracted much attention due to their potential for various applications, including gas storage materials [4]. For example, MOFs (**3**) can be obtained by synthesis of a combination of metal ions (**1**) and organic ligands (**2**) (Scheme 1).

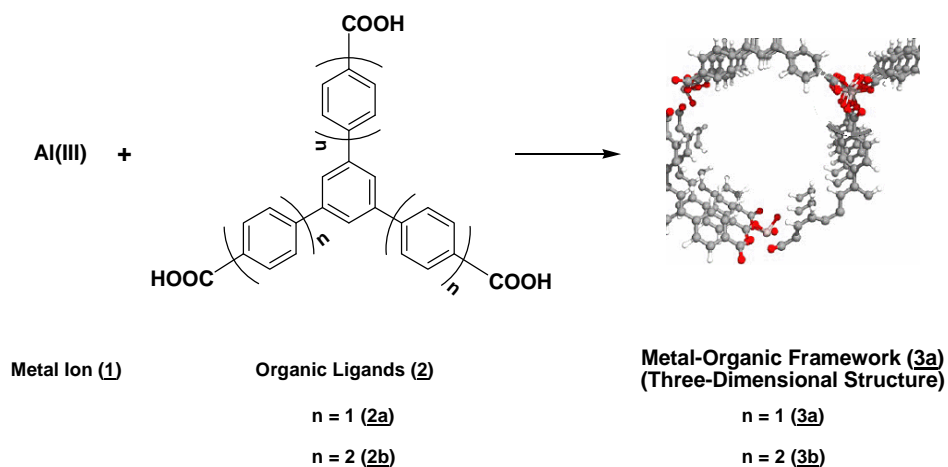


Figure 3: Synthesis of metal-organic frameworks having three-dimensional structure.

Our strategies for improving MOFs are to use light metal ions as the metal source and to enlarge the ligand size to attain a high porosity and large surface area. We were able to obtain an MOF (**3b**) which showed a hydrogen uptake of 0.94 mass% at 35 MPa, by reaction between light metal ions (**1**) and three-dimensional ligands with expanded branches (**2a**) [5].

4 Transporting Hydrogen Using Organic Chemical Hydride

The transportation of hydrogen energy as a liquid fuel is a promising option because it makes effective use of the existing network for liquid fuels. One method for transporting hydrogen energy as liquid fuel is the liquid organic chemical hydride (OCH) system [6]. The OCH system for hydrogen storage and transportation, based on a chemical reaction involving the dehydrogenation of cycloalkanes and hydrogenation of the corresponding aromatics (Scheme 2), is relatively well-established.

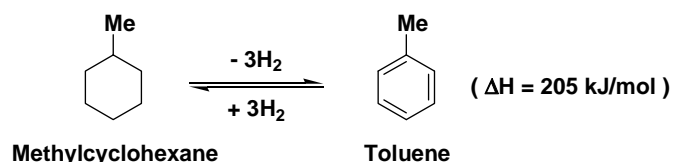


Figure 4: Organic chemical hydride system.

This system has advantages of high gravimetric and volumetric hydrogen density. We have been focusing on developing a compact hydrogen transportation system utilizing the OCH system. We have developed a concept for a hydrogen station which generates hydrogen by the OCH system. With the aim of downsizing the hydrogen feed system, we have developed a micro-channel reactor equipped with a plate-type dehydrogenation catalyst. The micro-channel reactor features a Pd-Ag membrane as the hydrogen separation membrane, which gives it the ability to generate high-purity hydrogen. A picture of the micro-channel reactor, which is a 4-layer design, is indicated in Figure 2. The micro-channel reactor can generate 2.5 L of hydrogen per minute.

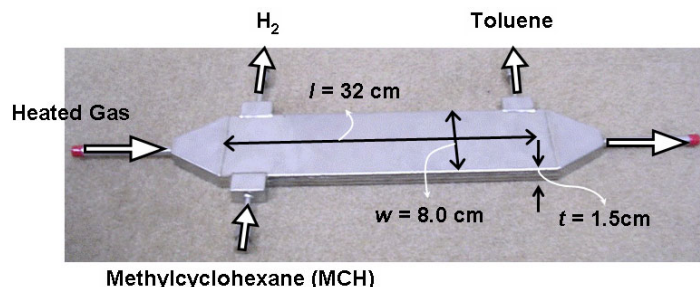


Figure 2: Picture of 4-layer micro-channel reactor.

5 Summary

As described above, we have been developing various technologies for the construction of hydrogen infrastructure, and are confident that our research will contribute to improving the hydrogen infrastructure.

Acknowledgements

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