

● Two of Toagosei's Adhesives Used for New TOYOTA MIRAI

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1. Background

For more than 30 years, research and development have been conducted in many fields toward the so-called hydrogen society, in which hydrogen is produced from water using solar energy (in a form that can be stored and transported as chemical energy) and used as an energy source for industry and daily life.

Fuel cells are well known as systems for efficiently extracting electrical energy from hydrogen, and come in various types. Since 2014, Toyota Motor Corporation (hereafter "Toyota") has been selling the MIRAI fuel cell vehicle (first generation), equipped with a solid polymer electrolyte fuel cell.

In recent years, driven by concerns over global warming and the need to reduce CO₂ emissions, countries around the world have been moving toward regulating gasoline- and diesel-powered vehicles. Under these circumstances, Toyota worked to develop a second-generation fuel cell optimized for mass production performance, with the aim of achieving widespread adoption of fuel cell vehicles. As shown in **Figure 1**, Toyota's second-generation fuel cell consists of hundreds of stacked cells. Hydrogen, air, and cooling water flow through trunk-like channels formed by the pink, green, and blue openings that connect through the entire stack, and are supplied and discharged at the necessary points in each layer (the remaining areas are sealed). Because a large number of cells are required as described above, bonding technology with cycle times on the order of seconds became necessary for the low-cost mass production of fuel cells. The bonding areas needed to offer hydrolysis resistance (since water is generated in fuel cells), durability, and stable quality suitable for automotive applications. There were also challenges specific to this application.

Despite these stringent requirements for adhesives, this represented a unique opportunity for Toagosei to contribute to a promising future application while advancing its specialty short-cycle bonding technologies (such as cyanoacrylate, hot-melt, and UV-curing adhesives), and we took on the development. As a result, a UV-curable adhesive and a hot-melt adhesive were adopted for the two bonding areas, respectively, and are used in the recently launched second-generation MIRAI. This paper highlights an overview of these developments.

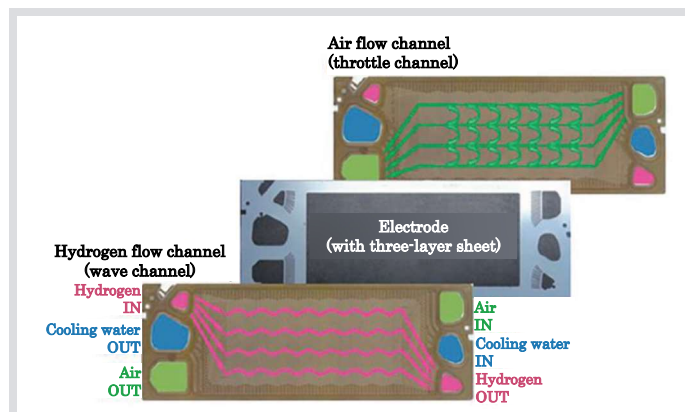


Figure 1: Cell configuration of Toyota's second-generation fuel cell

2. UV-curable adhesive, ARONIX®UVX

UV-curable adhesives are materials that instantly cure the liquid resin when it is irradiated with light (mainly ultraviolet light), and are effective when at least one of the adherends is light-transmitting. Most UV-curable adhesives are liquid resins with a compound containing acrylate groups (which offer excellent radical polymerization) as the main component, combined with a photo-radical polymerization initiator. The adhesive adopted here is also an acrylate-based liquid adhesive. Since these adhesives are in liquid form, they can be applied freely to any shape or area. In addition, since they are solvent-free, no drying process is required, allowing curing and bonding to be completed within seconds after application (sometimes in 1 second or less). Because it forms a three-dimensional chemical cross-linked structure, the cured material offers excellent heat and chemical resistance. Selecting the appropriate chemical structure allows for excellent hydrolysis resistance. Meanwhile, adhesion often needs to be adjusted and improved according to the adherend and application.

In Toyota's fuel cells, as shown in **Figure 2**, the UV-curable adhesive is used to bond the membrane electrode assembly (MEA) to a frame-shaped plastic sheet (a three-layer sheet with hot-melt adhesive on both sides, as described below) that separates the space where hydrogen circulates (the anode side) and air circulates (the cathode side). In other words, it is used to bond the polymer electrolyte membrane at the edge of the MEA to the hot-melt adhesive on the surface of the three-layer sheet.

The first challenge encountered in this application was the adhesion durability to the polymer electrolyte membrane. The polymer electrolyte membrane is a fluorinated polymer with sulfonic acid groups on its side chains, and swells when immersed in hot water. This caused a problem in which the UV-curable adhesive delaminated at the interface with the electrolyte membrane. Subsequent studies have shown that blending certain components maintains adhesion to the electrolyte membrane even after immersion in hot water at 90°C for 3,000 hours. This solved the first challenge.

The next challenge was the screen printability of the adhesive. Toyota selected screen printing as the coating method to apply UV-curable adhesive at high speed in a frame shape, with a controlled film thickness of several tens of micrometers, within seconds. However, when conventional adhesives were applied to screen printing, a large number of air bubbles were generated. One way to eliminate air bubbles is to add defoaming agents, but in this application, such additives had to be avoided as much as possible to prevent impairing the performance and durability of the fuel cell. To address this, a relatively large amount of chemically stable fine particles was blended in to develop thixotropic properties, greatly improving screen printability.

There is an area at the edge of the electrolyte membrane of this fuel cell that is only protected by ARONIX®UVX. Since electrolyte membranes are very thin, ARONIX®UVX also serves to protect them. For this reason as well, it is important that screen printing does not produce bubbles or other defects.

The third challenge was dealing with catalyst poisoning. Because this adhesive is located near the catalyst on the power generation surface, high levels of residual monomer or decomposition products from the photoinitiator after UV curing can poison the catalyst. We solved this problem to a practically usable level by selecting appropriate monomers and photoinitiators.

3. Hot-melt type adhesive, ARON MELT®

As shown in **Figure 3**, the ARON MELT® hot-melt adhesive is applied to both sides of the core material of the three-layer sheet, and is firmly bonded to the metal separator and core material through second-scale heat pressing and cold pressing. This adhesive plays an important role in sealing hydrogen, air, and cooling water over long periods of time and requires excellent adhesive durability.

In the cross-sectional view in **Figure 3**, the left side (the trunk-like channels described in Figure 1) and the power generation area on the right side are sealed off from each other. However, the cell is structured to allow hydrogen and oxygen to flow through at designated locations.

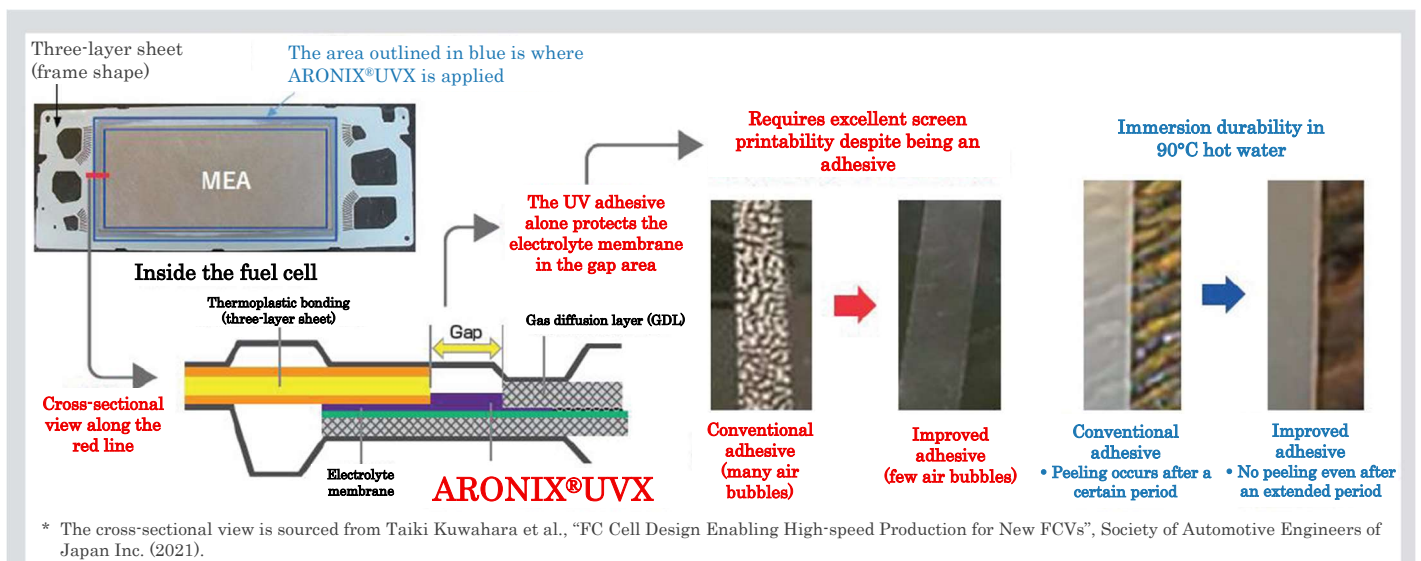
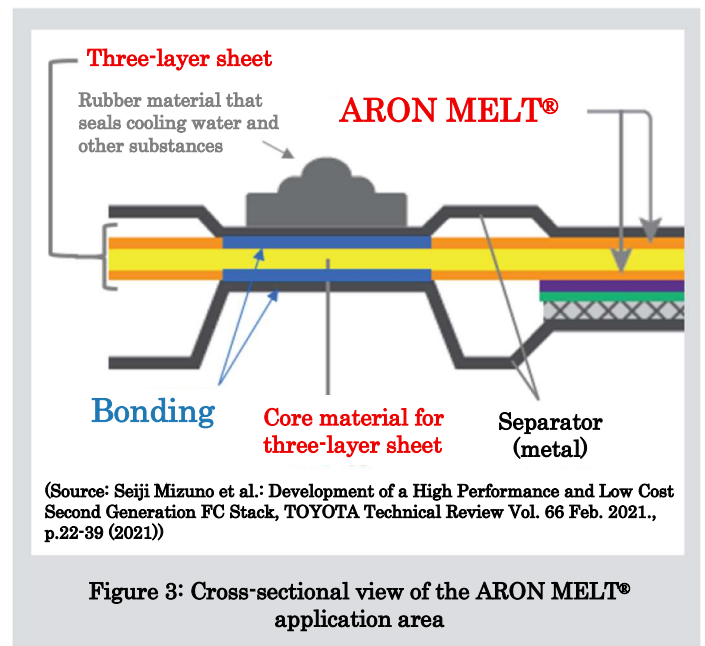


Figure 2: Application areas and characteristics of the UV-curable adhesive ARONIX®UVX

Hot-melt adhesives are materials that are solid at room temperature, but melt and wet the adherend when heated, and become solid and bond when cooled back to room temperature. They offer the advantage of achieving strong adhesion through heat pressing on the order of seconds, and are used in various fields, including food packaging, construction materials, and electronic devices. However, since bonding requires heating and melting, achieving heat resistance above that temperature is usually difficult. Because this application reaches high temperatures during use, we developed a hot-melt adhesive with a melting point above those temperatures while also achieving short-cycle bonding through an increased crystallization rate. The characteristic values are shown in **Table 1**.

Table 1: Characteristic values of hot-melt type adhesive, ARON MELT®

Evaluation item		Physical property values
Melting point	JIS K 7121	142°C
Crystallization temperature	JIS K 7121	109°C
MFR 230°C 2.16 kg	JIS K 7210	15 g/10 min

This application requires strong adhesion to the metal material forming the separator, as well as hydrolysis resistance that does not deteriorate even after long-term exposure to water at high temperatures. These challenges were solved by creating polyolefin compositions containing specially modified polyolefins. In addition, since it is exposed to high-temperature air and water for long periods of time, it must be durable against oxidative degradation. Therefore, the antioxidant content was optimized. Furthermore, since metal ions eluted during use reduce the performance and durability of fuel cells, the adhesive is manufactured under strict control from the raw material control through the manufacturing process, to prevent contamination by metal impurities.

The layers of ARON MELT® are formed on both sides of the core material, as shown in **Figure 3**. The core material offers creep resistance to maintain gas sealing properties over a long period, suppresses thermal expansion and deflection during heat pressing, and ensures the mechanical strength of the final product. These various requirements for sealants are satisfied by using a three-layer sheet that integrates the core material and the adhesive layer. The three-layer sheet adopted here was developed jointly with a film manufacturer.

4. Conclusion

The above studies resulted in adhesives that could meet the performance requirements of the second-generation MIRAI. The final important step was to ensure quality stability sufficient for automotive applications and to establish an inspection system. Through this process, we were able to learn about Toyota's approach to manufacturing and gained valuable experience.

However, this is not the end of the project. Rather, we are only now at the starting line. Toyota is proactively exploring ways to further reduce prices and improve performance. To keep pace with this evolution, we must also improve our technological capabilities in adhesion, manufacturing, and evaluation.