

# Chapter 22

## Polymer Electrolyte Fuel Cells (PEFCs)

Akari Hayashi, Masamichi Nishihara, Junko Matsuda  
and Kazunari Sasaki

**Abstract** This chapter describes operating principles of polymer electrolyte fuel cells. The fundamental components (electrolyte, electrode, and gas diffusion layer) are explained from the viewpoint of material science, followed by a description of cells and stack structures.

**Keywords** PEFC · MEA · Proton conductivity · Nafion · Pt · Carbon · FCV · Hydrogen utilization

### 22.1 Operating Principles of the PEFC [1]

PEFCs are well known for their commercialization for residential and automobile purposes. The fundamental structure of a PEFC is explained in Fig. 22.1. A PEFC is generally composed of a  $H^+$ -conducting electrolyte membrane, electrodes, gas diffusion layers, and separators (bipolar plates). In particular, the electrocatalyst membrane sandwiched by two electrodes, made by highly dispersed precious metal particles on carbon with proton conducting ionomers, is called the membrane electrode assembly (MEA). Hydrogen and air are used as a fuel and an oxidant, respectively. Humidified hydrogen and air (close to relative humidity (RH)) of

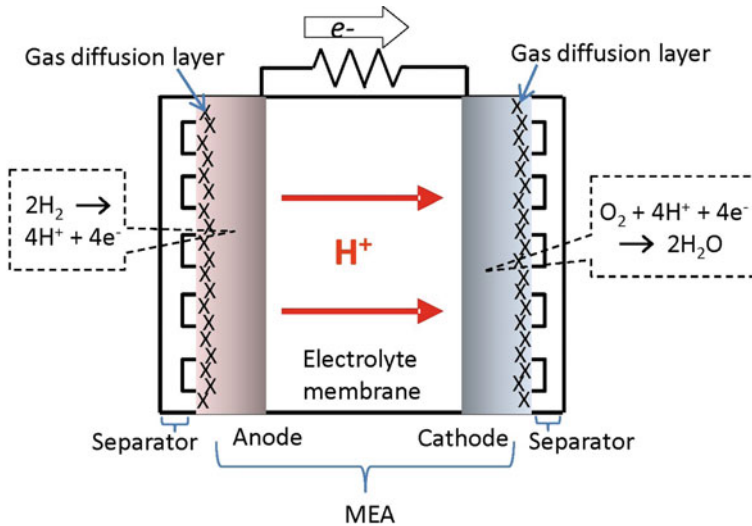
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A. Hayashi (✉) · K. Sasaki  
International Research Center for Hydrogen Energy, Kyushu University,  
Fukuoka 819-0395, Japan  
e-mail: hayashi.akari.500@m.kyushu-u.ac.jp

K. Sasaki  
e-mail: sasaki@mech.kyushu-u.ac.jp

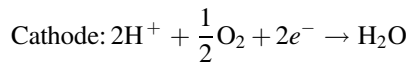
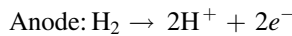
M. Nishihara · J. Matsuda  
International Institute for Carbon-Neutral Energy Research (WPI-I2CNER),  
Kyushu University, Fukuoka 819-0395, Japan  
e-mail: nishihara@i2cner.kyushu-u.ac.jp

J. Matsuda  
e-mail: junko.matsuda@i2cner.kyushu-u.ac.jp



**Fig. 22.1** Fundamental structure of a PEFC

100 %) are supplied, and the PEFC operates under 100 °C. Reactions at the cathode and the anode are given below.



The theoretical open-circuit voltage near room temperature is 1.23 V. The theoretical thermodynamic efficiency derived from the ratio of  $\Delta G/\Delta H$  is about 84 %. At the anode, the overpotential of the reaction is small, and the reaction quickly occurs. On the other hand, at the cathode, the reaction occurs slowly under oxidizing atmosphere, which leads to a major voltage loss in PEFC (see *Electrochemistry and Overpotential* in Sect. 21.1). In reality, the open-circuit potential under atmospheric pressure is about 1 V, which is much lower than theoretical value of 1.23 V. Major reasons for that come from fuel crossover and internal current generation. In the following sections, the fundamental components of a PEFC (electrolyte, electrode, and gas diffusion layer), and cell and stack structures are explained.

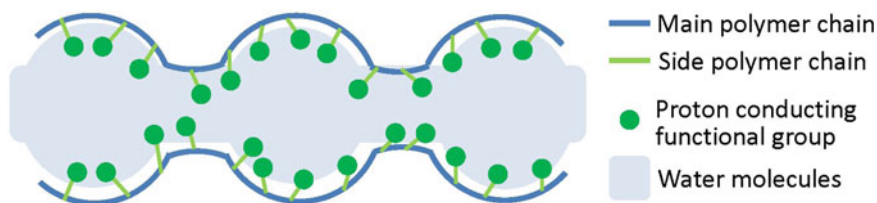


Fig. 22.2 Schematic drawing of hydrophilic channels made by Nafion

## 22.2 Electrolytes

For PEFCs, a polymer electrolyte membrane (PEM) has been used as an electrolyte material. The role of a PEM is to transfer protons. Generally, the thickness of membranes is 20–50  $\mu\text{m}$ . In addition to transferring protons produced at the anode to the cathode, the abilities of preventing electron transfer between the two electrodes as an (electronic) insulator and blocking either hydrogen or air from leaking into the counter side of each electrode are required.

Proton conductivity is derived from functional groups which transfer protons within the PEM; these groups are strong acids like a sulfonic acid. Usually, polymers with many hydrophilic functional groups have high solubility in water and also low mechanical strength, compared to polymers without such functional groups. Therefore, it is necessary to introduce hydrophobic functional groups, while retaining enough proton conductivity. Also, for most PEMs, the proton conducting mechanism is explained by proton transfer through hydrophilic channels made by proton conducting functional groups and water molecules as shown in Fig. 22.2 [2]. Therefore, a certain degree of humidification is essential for proton transfer.

The most typical PEM is a perfluorohydrocarbon electrolyte membrane, called Nafion<sup>®</sup> (Dupont) [3] as shown in Fig. 22.3. Nafion has a framework of polytetrafluoroethylene (PTFE), where the hydrogen of the ethylene part is replaced by fluorine. In addition, the end of the side chains is composed of sulfonic acid ( $\text{HSO}_3$ ) groups. Although the main chain has a hydrophobic character, the side chains

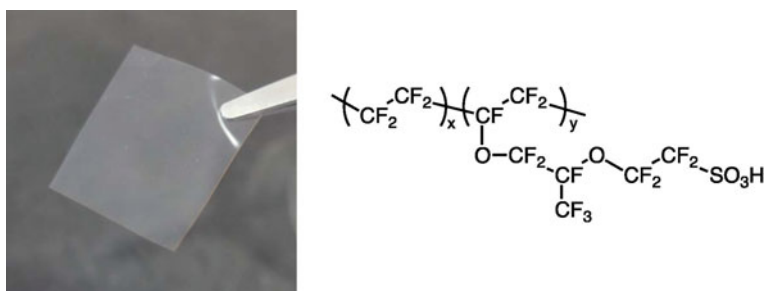
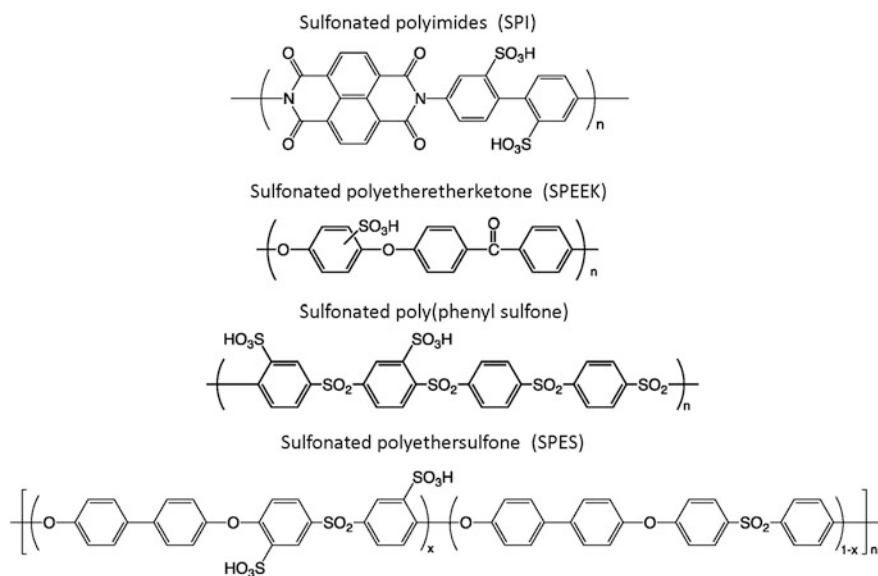


Fig. 22.3 A photograph of Nafion and its chemical structure

reveal hydrophilic regions since the end  $\text{HSO}_3$  group is ionized to  $\text{SO}_3^-$  and  $\text{H}^+$ , attracting water molecules. The presence of  $\text{SO}_3^-$  and  $\text{H}^+$  leads to strong mutual attraction between positive and negative ions from different side chains, and then side chain molecules tend to form clusters within the overall structure. The hydrophilic regions around clusters of sulfonated side chains can adsorb large quantities of water, and then protons can move more efficiently between the two electrodes. Consequently, the power density largely depends on humidity. Since Nafion has high chemical stability and proton conductivity, it is commonly used for PEFC. On the other hand, humidification is essential, and so it is not suitable for operation above  $100^\circ\text{C}$ , which is part of the future directions of PEFC research.

For the next generation electrolyte, the challenge includes the development of new PEMs in place of Nafion. For alternative PEMs, sulfonated aromatic electrolyte membranes are under study for high chemical and thermal stability. For example, sulfonated polyimides (SPI), sulfonated polyetheretherketone (SPEEK), sulfonated poly(phenylsulfone), sulfonated polyethersulfone (SPES), and also the combination of these can be candidates (Fig. 22.4) [4–8]. Even so, since these polymers have high ion exchange capacity (IEC: moles of acid per polymer unit), balancing water solubility and proton conductivity becomes a key issue. For example, increasing the resistance to water solubility by introduction of a monomer unit, which is not much affected by crosslinking and decomposition reactions, is underway [9]. Also, for the purpose of separating hydrophobic and hydrophilic regions at the macroscale and increasing the formation of hydrophilic cluster regions, the use of block polymers or graft polymers is under consideration [10, 11]. Moreover, besides the proton



**Fig. 22.4** Chemical structures of alternative PEMs

conducting process through water clusters, phosphoric acid-doped polybenzimidazole (PBI) membrane [12] or membranes using ionic liquids [13] are also studied.

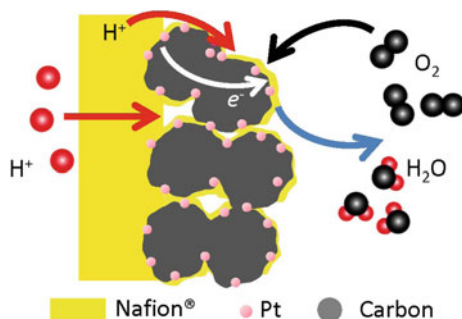
In order to develop practical electrolyte membranes using such new electrolyte materials, high enough proton conductivity, stability, and durability under the real PEFC operating conditions (high temperature, low humidification, or low temperature like under the freezing point) are required. Since there is usually a trade-off between proton conductivity and durability, optimization of the polymer composition is essential.

### 22.3 Electrodes (Electrocatalysts)

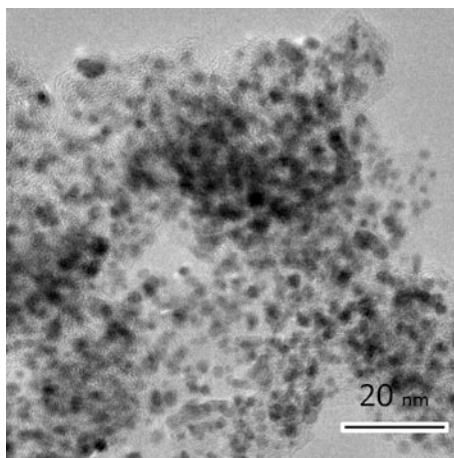
The electrode is composed of a layer of electrocatalysts and ionomers with the thickness of several tens of micrometers. Such a catalyst layer requires high catalytic activity even around room temperature, both electronic conductivity and proton conductivity, and also high mass transfer properties in order to supply reactant gases and remove reaction products. A schematic figure of the electrode (cathode) cross section is shown in Fig. 22.5. In order to utilize all the electrocatalysts along the thickness of the layer, efficient development of a triple phase boundary, formed by the electrocatalyst-electrolyte (ionomer)-reactant gas interface, is essential. Therefore, electrocatalysts are desired to be covered by a thin layer of ionomers with the thickness of a few to several tens of nanometers. In the presence of a triple-phase boundary, hydrogen gas reaches the anode electrocatalyst through the ionomer layer and produces protons at the anode. These protons are allowed to transfer toward the surface of a cathode electrocatalyst first through the ionomer at the anode, then through the electrolyte membrane, and finally through the ionomer layer in the cathode. At the same time, oxygen in the air supplied at the cathode reaches the cathode electrocatalyst through its ionomer layer. Consequently, water is produced as a product.

For electrocatalysts, highly dispersed precious metal catalysts are usually used. Owing to the high acidity of perfluorosulfonic acid, Pt, which is stable in such a severe condition and also able to reduce the overpotential of reactions, is used for

Fig. 22.5 Schematic drawing of cathode cross section

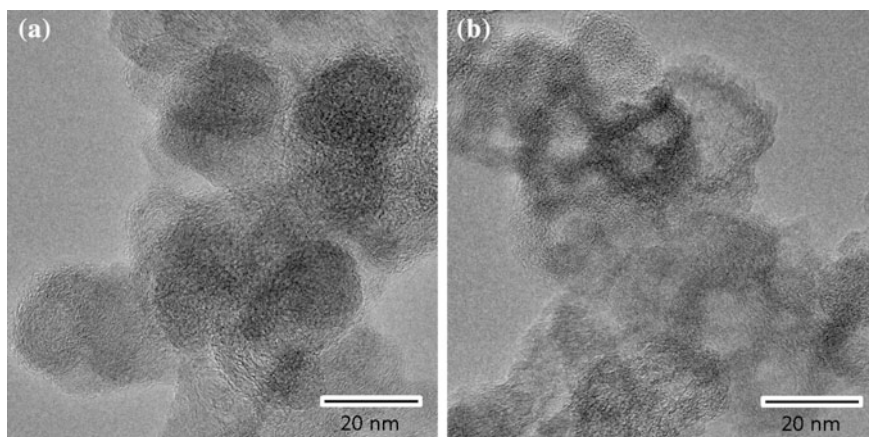


**Fig. 22.6** A TEM image of a typical electrocatalyst, Pt deposited carbon black (Black spots: Pt nanoparticles)



both the anode and the cathode. Since Pt is expensive, it is essential to produce the cell voltage by keeping the amount of Pt as small as possible. Therefore, as shown in Fig. 22.6, Pt nanoparticles are dispersed on carbon black powder with high electronic conductivity. 10–50 wt% of Pt is deposited on the carbon black. The Pt particle size is usually 1–5 nm and its surface area is typically 50–100 m<sup>2</sup>/g. Since Pt nanoparticles have a tendency to grow and form larger particles when the percentage of Pt increases on the carbon support, carbon black with a large surface area is used to effectively disperse the Pt nanoparticles. Commonly, Vulcan (around 250 m<sup>2</sup>/g) and Ketjen Black (800–1300 m<sup>2</sup>/g) are used, and their primary particle size is 10–100 nm (Fig. 22.7).

Recently, in order to further improve the activity and durability of electrocatalysts, and also to reduce the high loading of Pt, thereby lowering the cost, alloys of Pt and other precious metals have been studied. Regarding the anode catalysts,



**Fig. 22.7** TEM images of carbon black, **a** Vulcan and **b** Ketjen black

since hydrogen fuel is often made from reforming hydrocarbon gases like natural gas, a small amount of CO (a few ppm) may be included in the fuel. Such CO adsorbs on the Pt surface and reduces the number of catalytically active sites. To mitigate CO poisoning, a PtRu alloy catalyst is considered as one of the most promising commercially available catalysts. Its CO tolerance characteristics are attributed to a combination of its electronic properties and bifunctional mechanism. In terms of the electronic properties, because of the electron transfer between Pt and added metals, the Pt–CO bond is weakened. In terms of the bifunctional mechanism, oxygen species adsorbed on Ru sites help oxidation of the CO adsorbed on Pt sites. Since there is still room for further improvement, Pt-based binary and ternary electrocatalysts are also being developed [14, 15].

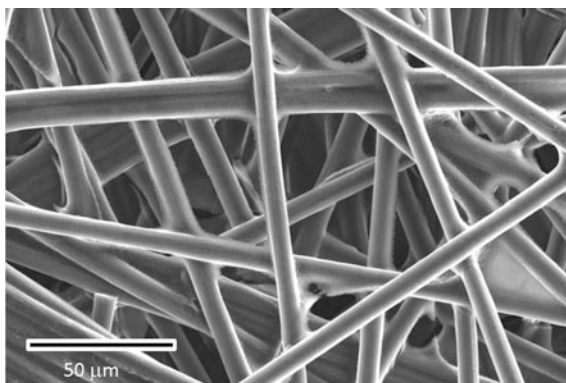
Similarly, for the cathode, in order to reduce the overpotential produced by the slow oxygen reduction reaction, alloying with various metals has been tried [16]. In this case, the surface electronic structure can be controlled to increase the reactivity toward oxygen reduction. Pt–Co- and Pt–Ni-based alloys are known to have high reactivity. Since the surface electronic structure changes, the adsorption of species other than O<sub>2</sub>, such as OH<sup>−</sup>, is reduced, and then more Pt sites remain available for O<sub>2</sub>. This reaction mechanism is believed to be a reason for promotion of the oxygen reduction reaction, resulting in higher reactivity. Recently, Pt monolayer-based catalysts have been under development in order to control the surface electronic structure. The most typical example is a core–shell catalyst, where the shell is made by Pt, but for the core Au or Pd is often used. Usage of nonprecious metals for the core is desired as a topic for further study in terms of cost.

One of the problems for electrocatalysts to overcome is durability. Suppressing the degradation of catalysts is necessary to extend the lifetime of PEFC. During long-term operation, Pt nanoparticles agglomerate and grow. Thermodynamically unstable carbon supports are oxidized, leading to the promotion of Pt agglomeration, dissolution, and detachment. Especially, these phenomena are accelerated under the conditions of high temperature and high voltage. Recently, in order to improve carbon durability, carbon with the surface graphitic structure, showing increased oxidation resistance, has been applied [17, 18]. Even non-carbon materials like metal oxides have been recently introduced as support materials [19–21].

## 22.4 Gas Diffusion Layer [22, 23]

In order to supply reactant gases (hydrogen and air) to the electrode layers homogeneously, a gas diffusion layer is attached at the outer part of each electrode. This gas diffusion layer has a role of current collecting, and is made of carbon with a highly porous structure. Specifically, carbon fibers, whose pore diameter is several micrometers, make a paper-like structure with binder, called carbon paper. Carbon cloth and felts are also often used. Owing to water supplied along with the fuels, and water produced in the cathode reaction, water management is essential. Therefore, the gas diffusion layer has an important role to efficiently remove excess

**Fig. 22.8** A SEM image of carbon paper



water. Hydrophobic PTFE is usually blended with the carbon fibers to form PTFE bridges across the pores of several tens to hundreds of micrometers made by the carbon fiber (Fig. 22.8). Particularly for the cathode side, a microporous layer (MPL) is commonly used as an additional layer on carbon paper. The MPL possesses smaller pores suitable for gas transfer and reducing water retention.

Besides their role of water management, gas diffusion layers need high thermal conductivity to remove the heat produced by reactions, and also high mechanical strength to support electrocatalyst layers that are several tens of micrometers thick.

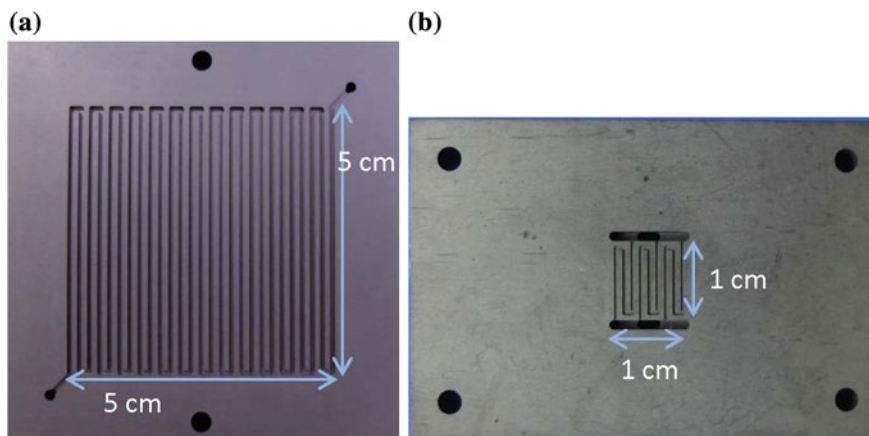
## 22.5 Cell and Stack

A cell voltage commonly used for PEFC is 0.6–0.8 V, and several tens to several hundreds of cells are stacked up for the practical use depending on the required power density. The structure of stacked cells is conveniently called a stack. Usually 700 W or 100 kW are available for residential or automobile uses by stacking.

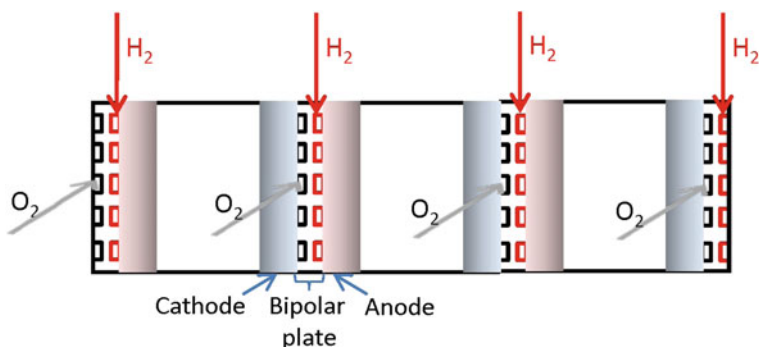
In order to stack cells, separators, where gas flow channels are two dimensionally arranged (Fig. 22.9), are further attached at the outside of the gas diffusion layers, in order to supply hydrogen and air to the MEA through the gas diffusion layers. The separator for PEFC is often called a bipolar plate and has a role to separate the two adjacent reactant gases when cells are stacked up (Fig. 22.10). Furthermore, the separator has the important roles of quickly getting rid of produced water and collecting current. Especially at high power densities, optimization of the channel structure and the thickness of separators become important. Homogenous supply of gases to the cell with high accuracy is required.

In terms of mass production and cost, development of carbon and metal separators is mainly considered [24]. Carbon has high chemical stability, but its electronic conductivity or stability varies depending on its original synthesis processes





**Fig. 22.9** Photographs of separators with **a** 5 cm  $\times$  5 cm flow field of one serpentine pattern developed by JARI and **b** 1 cm  $\times$  1 cm flow field of three serpentine patterns developed in a New Energy and Industrial Technology Development Organization (NEDO) project



**Fig. 22.10** PEFC single cells connected by bipolar plates

or the conditions of its posttreatments. Regarding making gas flow channels, each side of the separator can be patterned individually, leading to the flexibility of patterning.

On the other hand, in the case of metals, they have high electronic conductivity and mechanical strength and thereby an advantage upon thinning. The flow channels are made by pressing a template pattern, and so it takes only several seconds to make the flow channel. Since the patterning at one side is affected by the other side because of the pressing process, the flow channels should be well designed in order not to be affected by the other side of patterning. Since leaching of metal ions may contaminate the electrodes and electrolyte, leading to lowering the power density, careful selection of metal materials and also surface coatings are essential for preventing metal ion leaching. Among various metals, titanium has high corrosion

resistance, and almost no leaching is observed [25]. For this reason, titanium is well used as a material for separators. Since an insulating layer is easily formed on the surface of titanium, coating by Au is used to maintain high electronic conductivity.

## 22.6 Practical Materials and Applications of PEFCs

The latest practical PEFCs developed for automobile application are briefly introduced in this section. Fuel cell vehicles (FVCs) were commercialized in December 2014 after overcoming many problems as explained in Sects. 22.1–22.5. In Chap. 34, the TOYOTA MIRAI will be introduced as an automobile application in detail, but ahead of that the materials used for the PEFC within the MIRAI are focused on here [26]. For the electrolyte membrane, the thickness is reduced to one third of the original, leading to a threefold increase in proton conductivity. For electrocatalysts, Pt/C is still used at the anode, but for the cathode with a slow reaction, a more active PtCo/C is introduced, resulting in 1.8 times higher oxygen reduction activity. The gas diffusion layer is made more porous and thinner in order to increase gas diffusion ability, leading to twice higher gas diffusivity. Regarding the separators, for the cathode side, titanium separators with a 3D fine mesh flow channel are used in order to increase the hydrophobicity and promote oxygen gas diffusion, resulting in homogeneous power generation over the planar direction of the cells. Along with all these improvements to the materials, the power density of MIRAI becomes 2.4 times higher compared to TOYOTA FCHV-adv (2008 model). Please see Chap. 34 for more details.

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