Guest Forum

The Screening Committee Lecture for the First Dr. Masao Horiba's Award

Polymer Electrolyte Fuel Cells (PEFCs)

-State of the Art-

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Fuel cells are electrochemical energy conversion devices and are attracting much attention because of its high-energy conversion efficiency and low environmental impact. Polymer Electrolyte Fuel Cell (PEFC), among them, is expected to be a huge technology in the near future, but there remain some issues to be solved before it finds widespread use. In this paper, while giving an overview PEFC technology, the issues to be solved will be discussed.

Configuration of the Fuel Cell

A fuel cell is a kind of chemical cell, in which oxidation and reduction reactions proceed electrochemically. Electrochemical reactions mean that reduction reaction of the oxidizing reagent (cathode active mass) and oxidation reaction of the reducing reagent are performed separately through mediation by the ions that move in the electrolyte and electrons that move in the external circuit. The released Gibbs Free Energy change ΔG is then converted electric energy, which can do work on load set in the external circuit of the electrons pass. The differences between batteries and fuel cells are summarized as follows: The battery uses only the oxidizing and reducing reagents contained within it. The fuel cell uses the oxygen in air as the oxidizing reagent and the fuel (usually hydrogen) as the reducing reagent, both of which are supplied externally to the fuel cell. In other words, fuel cells can continue generating electricity as long as the oxidizing and reducing reagents are supplied into the device from the outside. Recharge of the secondary cell is to regenerate active materials by reducing oxidized negative active material and by oxidizing reduced positive active materials inside the cell, namely electrolysis to regenerate the starting materials inside the cell.

A diagram of the Polymer Electrolyte Fuel Cell (PEFC) is shown in Figure 1. The reaction is performed by continuous supply of reacting gases that are oxygen in air and hydrogen fuel. One of the key components of the fuel cell is porous electrode that is composed of carbon loaded with platinum-based catalyst. The thin porous anode and cathode are combined to the electrolyte membrane and the formed composites are called membrane electrode assembly, MEA. A gas diffusion layer, GDL, is closely contacting to the porous electrodes of anode and cathode to supply gaseous reactants, oxygen and hydrogen. Separators with slots for supplying the gas to the diffusion layer are located at the back of the GDL.

Sufficient sealing and integrity are required in the separator so that the oxygen and hydrogen will not mix. It is essential that the material is chemically stable under the operating conditions of the fuel cell. The electrolyte must have high proton conductivity and no electronic conductivity. Furthermore, since the generated voltage of this cell is at most 1 V, many single cells are therefore connected in series as a fuel cell stack (with separators serving as bipolar plates) so that it functions efficiently as a power source.

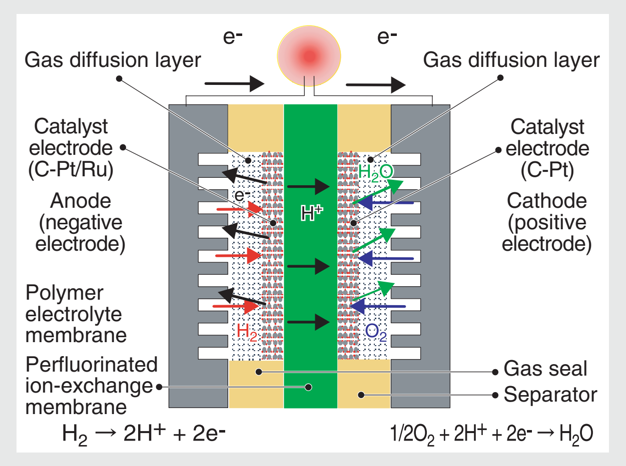

Figure 1 Diagram Figure of a PEFC

Features and Types

Since fuel cells uses oxygen and hydrogen, only water is generated if the reaction proceeds ideally, so the fuel cell is a very clean power generation system. Moreover, the fuel cell is very quiet because theoretically it does not have any moving parts within its main body.

Unlike thermal cycle engines, the electrochemical energy conversion has high conversion efficiency due to no Carnot cycle restriction*1 during conversion, and accordingly 100% of the hydrogen's energy (based on Gibb's free energy) is theoretically converted into the electric power. However, there is little merit in scaling up the size of a fuel cell, and even if its size is increased, there are few advantages to this. Changing our viewpoint, even a small fuel cell can maintain high efficiency. Because of these characteristics, fuel cells are suitable for installation in a location just close to the place where energy is consumed, which leads to the merit that heat produced in the fuel cell can be utilized as a cogeneration system. Thus, not only the efficiency of conversion to electrical energy becomes very high but also the heat wasted in conventional energy conversion devices are utilized. Therefore, very high total energy conversion efficiency is expected for fuel cell systems locating at the consumer sites. The efficiency of a fuel cell using only electric power without utilizing heat (for vehicles etc., included) is not comparatively so high.

Fuel cells are categorized based on the kinds of electrolyte they use. As shown in Table 1, the electrolyte is used at a temperature where it shows sufficient and stable ionic conductivity. The PEFC with its low operating temperature has attracted much attention, allowing application possibilities in domestic electricity generation or in a wide range of vehicles.

Table 1 Various Fuel Cells and their Features

	Low temperature type		High temperature type	
Type	Polymer electrolyte type (PEFC)	Phosphoric acid type (PAFC)	Molten carbonate type (MCFC)	Solid oxide type (SOFC)
Electrolyte	Polymer membrane	Phosphoric acid	Molten carbonate	Stabilized zirconia
Mobile ion	H^+ (water included)	H^+	CO_3^{2-}	O^{2-}
Operating temperature	Normal temperature to approx. 100 °C	Approx. 200 °C	Approx. 650 °C	800 to 1000 °C
Generation efficiency	30 to 60%	36 to 45%	45 to 60%	50 to 60%
Exhaust heat	Warm water	Warm water, Steam	Steam	Steam
Comprehensive energy efficiency (LHV)	70 to 80%	70 to 80%	70 to 80%	70 to 80%
Tolerable CO concentration in fuel	<10ppm	<1%	OK	OK
Features	· Starts/operates at low temperature. · Instantaneous response (H_2) · High current density · Possible to apply to home appliances and electric vehicles	· Exhaust heat can be used for hot-water supply and air conditioning.	· Exhaust heat can be used for combined cycle power generation system. · Internal reforming of fuel is possible.	· High current density · Exhaust heat can be used for combined cycle power generation system. · Internal reforming of fuel is possible.

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[1] Maximum efficiency of heat cycle $\eta = (T_h - T_l)/T_h$ (T_h: Absolute temperature of high temperature heat source, T_l: Absolute temperature of low temperature heat source).

Polymer Electrolyte Fuel Cell (PEFC)

PEFC Single Cell

As shown in Figure 1, the perfluorinated sulfonic acid-based cation exchange membrane (Nafion film, manufactured by E. I. du Pont de Nemours & Co., or equivalent) is used for the electrolyte of PEFC. The thickness of the membrane is 20 to 50 µm. On the fuel side, the porous electrode of carbon powder loaded with catalyst of platinum or platinum-ruthenium was tightly connected to the membrane and on the air side, the porous electrode loaded with platinum catalyst is connected to form MEA. The size of the precious-metals catalyst used for the fuel cell is several nm, and reduction of the amount used has been done so far by increasing the specific surface area. The material, from the point of chemical stability, of the gas diffusion layer and separator is mostly carbon.

Performance of PEFC

One of the reasons that PEFC has attracted much attention in recent years is its high output power density. A voltage of 0.6 V or more can be generated even with a current density of 2 A/cm^2 or more and an output of 1 W/cm^2 or more can be attained. If unit cells are assembled with care, the output power density per volume becomes 1 kW/L or more, and 2 kW/L has been reported already. Gasoline engine would be sufficiently challenged by fuel cells of the output density exceeds 1 kW/L. Therefore, this has resulted in an enthusiasm for fuel cell research and development for vehicles as a high efficiency drive source with low environmental impact. If a high output can be attained, it leads to miniaturization and reduced costs, and expansion of use into domestic electricity etc., with developments for vehicles expected to be added soon. “Well to Wheel” energy efficiencies of various vehicles is shown in Table 2. In the case of the fuel cell vehicle, 58% of the energy efficiency generating hydrogen from oil is multiplied by 50% (38% under the present condition) of the efficiency of the fuel cell to be 29% (22% at the present time). This shows an extreme improvement when compared with the average energy efficiency (approximately 14%) of the present gasoline engine vehicle. In Japan, since one fourth of the oil is consumed by transportation, large scale introduction of fuel cell electric vehicles would lead to a drastic reduction of CO_2 emission from the transportation sector. While its energy efficiency is still lower than that of practical hybrid vehicles, considering the diverse source of fuel resources in near future early introduction of fuel cell vehicles and that proliferation will be essential for sustaining steady progress of the level of our daily life.

Table 2 Comprehensive Energy Efficiency of Vehicles

	Fuel efficiency	Vehicle efficiency	Well to Wheel
Gasoline engine vehicle	88	16	14
HEV (Prius)	88	32	28
HEV (New Prius)	88	37	32
FCHV	58	38 50	22 29
FCHV Prospect	70	60	42

(HEV: Hybrid Vehicle, FCHV: Fuel Cell Vehicle (Hybrid))

PEFC Power Generation System

A PEFC system is composed many parts, as shown in Figure 2. A PEFC stack is the most important part among them. In addition to the stack, a fuel processing system that generates hydrogen from fuel like natural gas, a humidifier of fuel and air, and the air cleaning system because air contains many impurities. Moreover, a heat exchanging system is required in order to keep the temperature of the fuel cell constant and to utilize thermal energy produced in the fuel cell stack. A battery system and its controller would be required to store the generated electricity in addition to a hot water reserver. Probably self-diagnostic electronic equipment is required to control and maintain the whole system in order. The electricity obtained from the fuel cell stack is DC of fairly low voltage, and an inverter is required for its use. These parts themselves further consist of many devices and components. Fuel cell system requires different kinds of, and the synthetic development of wide range of technology is indispensable for achieving pervasive introduction.

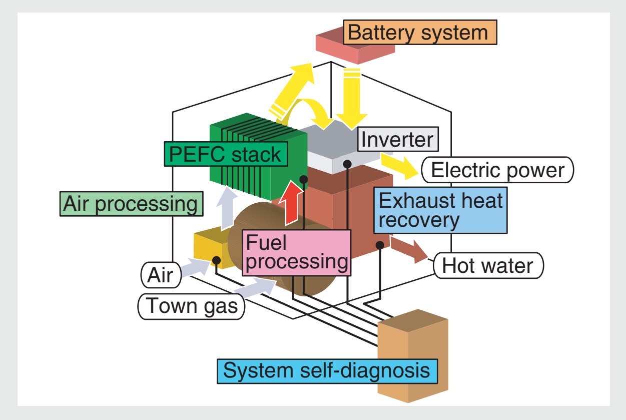

Figure 2 Configuration of PEFC Power Generation System

PEFC Features

Many of features of PEFC shown in Table 3 are originated from the electrolyte. Since the electrolyte membrane is a thin film of the strong acid gel electrolyte, it shows high ion conductivity at near room temperature, and it can tolerate the pressure difference between anode and cathode compartments. Moreover, since a solution of the electrolytic solution is available, the active region, triple phase boundary, where hydrogen and oxygen react can be well designed by impregnating the solution into catalyst electrolyte layer of MEA. This enables an extraordinary high output power of PEFC. However, there is also a disadvantage to this electrolyte membrane. Water is indispensable for the proton conduction through the membrane electrolyte and on the other hand flooding of the porous electrodes cause the shortage of fuel or air, which cause serious deterioration of the fuel cell performance. The water content of fuel and air must be carefully controlled, but it is not easy. The membrane is strongly acidic, and therefore high corrosion resistance is required for all components of PEFC. This limit the choice of materials available and enhances the cost of PEFC. Moreover, since it is a thin film, it is sensitive to contaminants such as very small quantities of metal ions, and heat resistance and mechanical integrity of the membrane are not enough. Furthermore, the chemical stability of the electrolyte membrane itself is not enough, and its degradation is the biggest issues for development of PEFC. The separator and gas diffusion layer contact with strong acid, oxygen, and hydrogen, so the available materials that can be used are limited, and additionally high processing accuracy is required. Since it operates at a low temperature, catalyst poisoning by CO and organic substances contained in fuel and air cause the serious lowering of performance.

Table 3 Features of PEFC

Advantages	Disadvantages
Large output:	Water control: proton conductive mechanism
Controlling triple phase boundary (TPB)	Performance degradation: Change of TPB, Catalyst deterioration
Thin film gel electrolyte	Membrane deterioration: Stability, Small quantity of impurities like metals and organic substances
Perfluoro-acid film	Catalyst: Precious metal (Strong acid electrolyte)
Pressure difference tolerance: Polymer gel	Separator: Corrosion, Thin film, Fine processing
Low temperature operation: Starting at room temperature	Using exhaust heat: Heat exchanger
	Catalyst poisoning: CO, Organic, etc.
Miniaturized	

Nafion

The Nafion used for the electrolyte membrane has a micro phase-separated structure as shown in Figure 3, and it is different from the structure of the hydrocarbon type ion-exchange membranes which are cross-linked. The stability of Nafion against peroxide is not enough although it is said that Nafion has excellent chemical stability. It is know that Nafion is swells heavily with some solvents. This characteristic is utilized to prepare the Nafion solution. This solution is applied to the porous carbon electrode loaded with catalyst and dried then a thin Nafion layer coat the electrode. This thin Nafion layer supports the ion conduction and created a unique structure of triple-phase boundary on the electrode as shown in Figure 4. As a result, the active site on the surface increases largely, and it leads to a reduction of the amount of the expensive precious-metal catalyst.

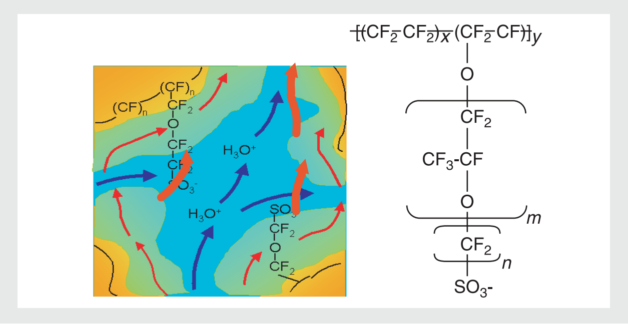

Figure 3 Structure of Nafion

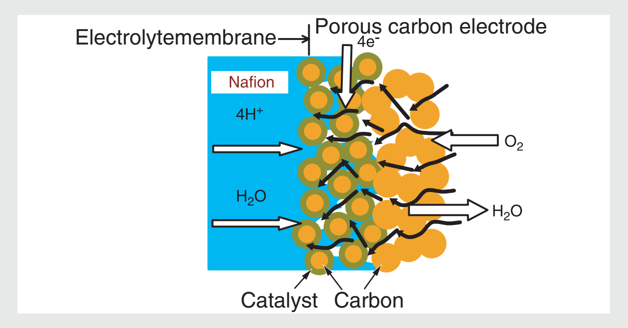

Figure 4 Gas Electrode of PEFC

Technical Problems and PEFC Research

Very long life is required for fuel cells. A lifetime of 50,000 hours or more (possibly 100,000 hours) is required in future for fuel cells of 1 kW-size for domestic stationary use. A lifetime of 5000 hours or more is required for vehicles use, under frequently repeating starting and stopping. It is not easy to satisfy these demands over the fuel cell's lifetime, and has not yet been solved. Even manufacturers of electric appliances, who are the main developers of stationary type systems, have not enough experience to produce such products with a practical operating term of over 50,000 hours. Deterioration of its performance and serious issues are still remaining to be solved for PEFC before large scale practical use. It is necessary to continue steady research on following points:

1. Precise understanding of the reaction in the fuel cell including side reactions.
2. Clarifying of the reaction between materials and side reaction products (especially H_2O_2) etc.
3. Detailed understanding of material characteristics.

The progress in science requires sober recognition of the state of the progress and grasping correctly the issues to be solved. The overcoming of each matter step-by-step leads to the steady advance.

In addition to the lifetime, fuel cells for vehicle use require high operation temperature, over 120 °C, because of heat management. High temperature operation generates exhaust heat of high temperature and enhances the cogeneration efficiency even with stationary use. In order to attain high temperature operation, new electrolyte materials must first be developed. The cost must also be radically cut for large-scale application.

Electrolyte Membrance

Nafion is an outstanding electrolyte membrane with a long history, developed 40 years ago for the fuel cell. However, the membrane does not have enough stability, mechanical strength, and ionic conductivity, and further a sharp reduction of its cost is required. Enough water is essential to sustain proton conductivity. It is difficult to operate at temperature higher than 90 °C under fuel cell conditions. As described later, generation of hydrogen peroxide should be always considered for the electrochemical reduction of oxygen. As for the influence on the membrane material by hydrogen peroxide, fundamental knowledge is still insufficient, including the reaction pathway, and research in this field is expected. Degradation of the electrolyte membrane would give a fatal effect on the fuel cell performance, and therefore the degradation reaction is critical. Hydrocarbon polymers with high thermal stability have attracted attention as base polymer to which ion-exchange group is attached through chemical bond for developing new electrolyte membrane operating at high temperature. Organic and inorganic composite film, glass based electrolyte, etc., are also being developed. However, a remarkable breakthrough has not been attained so far. Clarifying proton conductive mechanism at low water content would help the development of new electrolyte membrane.

Electrode Catalyst

The electromotive force of the hydrogen-oxygen fuel cell is 1.23 V, but the operation voltage in the actual fuel cell is lower than this. As shown in Figure 5, the polarization accompanied with the charge transfer on the anode and cathode and the ohmic drop through the electrolyte is a factor of the cell voltage drop. Mass transfer limitation might arise under the conditions that oxygen and hydrogen are insufficiently supplied, and large voltage drop occurs. Therefore, the gas diffusion layer and MEA structure is important. All voltage loss is converted to generation of heat. Generally the electrochemical oxygen reduction reaction is slow and occupies the principal part of the polarization of the fuel cell. Pt is used for the catalyst of the air electrode of fuel cell in order to enhance the reaction rate. However, even if the Pt catalyst is used, as shown in Figure 6, the oxygen reduction is slow compared with the hydrogen oxidation reaction. Further four-electron path of oxygen reduction proceeds only on very clean Pt, and the reaction route via two-electron reduction leading to hydrogen peroxide formation (equilibrium potential: 0.695 V) could make a major participation. Pt particles show high activity to decomposition of hydrogen peroxide even if hydrogen peroxide is generated. It is considered that hydrogen peroxide concentration does not become remarkably high under high humidification conditions, but its concentration can become high in low humidity operation because the boiling point of hydrogen peroxide is higher than that of water. The transition metal complex of macro-cyclic ligand including Co-porphyrin, oxide bronze compounds, nitride, and others have been extensively investigated to replace the precious metal catalyst. However these catalysts have not overcome the issues of short life.

Pt catalyst of anode decreases its activity largely due to poisoning by carbon monoxide. This poisoning by CO is suppressed by using Pt-Ru alloy catalyst. The method to recover the deteriorated catalyst activity by bleeding oxygen has also been developed. Even using these methods though, the CO concentration is required to keep under 10ppm to suppress the poisoning. Dissolving out of Ru from the alloy catalyst and amount of Ru resources are also large problem. The catalyst other than platinum is difficult to be utilized under PEFC conditions. Generally the precious metal catalyst such as platinum may be considered stable, but it is not always stable at high temperature and in an oxygen atmosphere when the size is reduced down to the 'nano' scale. For future vehicle application, dissolving out of platinum catalyst will be a significant problem.

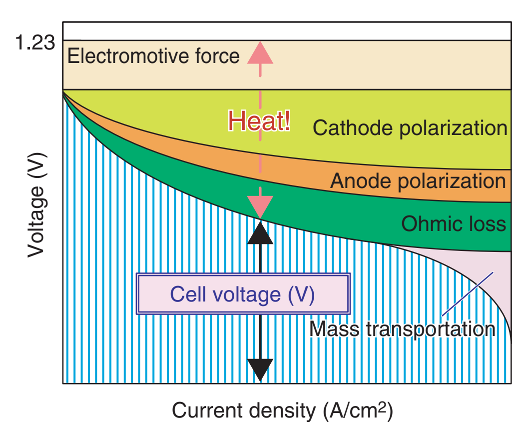

Figure 5 Cell Voltage and Factors Lowering Cell Voltage of PEFC

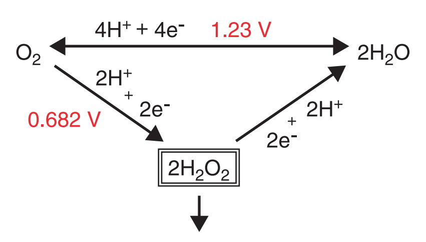

Figure 6 Reduction Reaction Path of Oxygen

Carbon Material

Carbon materials are one of the key materials of PEFC. The nano-size electrode catalyst is supported on the porous carbon electrode with a large specific surface area. The gas diffusion layer that supplies the fuel gas and oxygen to the active part of the electrode and releases the water generated at the cathode is made of a carbon non-woven fabric or carbon fiber textile. Additionally the carbon material is used for the separator that separates hydrogen and oxygen. The carbon material oxidizes as follows:

$$C + H_2O \rightarrow CO + 2H^+ + 2e^- \qquad 0.52\ V$$
$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \qquad 0.21\ V$$

This shows that the cathode is exposed to oxidation conditions continuously. Oxidation of carbon has not been recognized as a large problem in practical fuel cell so far because the reaction speed is so low. It must be considered that the carbon oxidizes when the fuel hydrogen supply is not enough. Oxidation of the carbon support causes the catalyst loss. When the carbon material is oxidized, hydrophilic groups such as carboxyl and hydroxyl are generated on the surface. This enhances wettability of carbon, which may cause flooding of electrode. In order to supply sufficient hydrogen and oxygen smoothly to the active part of the electrode, hydrophobic additives like PTFE are incorporated in the porous electrode and gas diffusion layer. Control of hydrophobicity of the porous electrode and gas diffusion layer is an important obstacle to controlling the degradation of PEFC.

Conclusion

The fuel cells mounted on vehicles have output power of 70 to100 kW. Assuming that the voltage of a single cell is 0.7 V, 100,000 A will pass for a power of 70 kW. This means that 11 liters of hydrogen and 5.5 liters of oxygen react in one second. The fuel cell that precedes this reaction in 1 m^3 or less volume at close to ambient temperature is a supreme reactor when compared with the usual chemistry plant. In order for such technology to become practical use in large-scale, much effort is required. We have to look upon the technological development based on a long-term viewpoint.

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