Progress in Fuel Cell Technologies

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Abstract Progress in fuel cell technologies is reviewed for this special issue. In the diversified society, the fuel cell technology is a significant and most promising field. The fuel cell technologies provide many variations for our uses and possibilities for our lives. Especially, some technological battles in the PEFC, SOFC and DMFC are excitedly interested us.

Keywords: energy conservation, CO_2 exhaust gas reduction, electricity generation, fuel cell, AFC, PAFC, MCFC, SOFC, PEFC, DMFC

1. Introduction

The Kyoto Protocol was adapted at COP3, the Third Conference of Parties to the UN Convention on Climate Change, in Kyoto, Japan, on 11 December, 1997. After the Kyoto Protocol, the complexity of the negotiations has been overcome, and the Kyoto Protocol has been validated on 16 February, 2005. Consequently, for Japan a total cut in greenhouse-gas emissions of at least 6% from 1990 levels should be obligatory in the commitment period 2008-2012.

To overcome this environmental issue, we should make every effort to develop the following items:

(1) To use in higher efficiency of the fossil fuels.

(2) To promote an introduction of petroleum-substitute energies such as natural gasses or coal.

(3) To lower the CO_2 exhaust and environmental pollution matters.

On the other hand, we understand that the electricity is indispensable for our lives and industries. Furthermore, we know an electrify rate of 41 %, which is the electricity energy to the total primary energy, and an electricity generation dependency of the primary energy sources as shown in Figure 1.

As the most promising technology to solve the above mentioned items, we recognize to introduce the fuel cells in the electricity-predominant society, and to be necessary to develop the fuel cell technologies more and more.

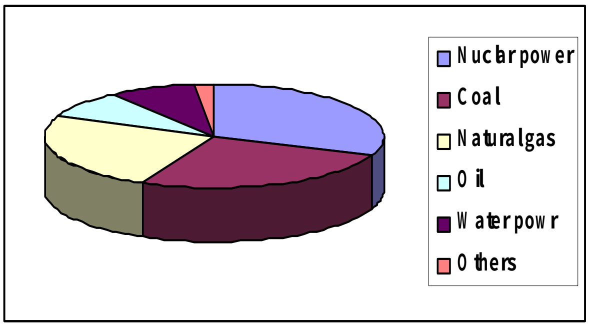


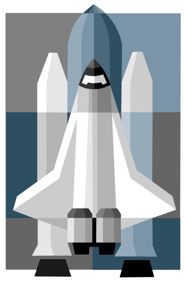
Figure 1 Electricity generation dependency of the primary energy sources in the fiscal year 2005, Japan from the Yomiuri August 10, 2006

2. Generation Changes in Fuel Cell Technology

(1) Creation-generation

The first primitive fuel cell, which converts chemical energy into electrical energy, was successfully demonstrated by Grove in 1839. This fuel cell did not enable commercially to compete with the existing technology because there is the lack of appropriate materials or manufacturing routs.

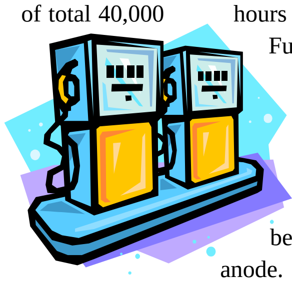
(2) AFC-generation



The alkaline fuel cell, AFC, was practically applied to Apollo Spaceship and Space Shuttle. This fuel cell has many merits of low operation temperature around 80°C, low material cost and high power density at a range of 10 kW. However the fuel cell has some demerits of carbon dioxide poisoning and low life.

(3) First-generation

The phosphoric acid fuel cell, PAFC, has recorded an installation of 142 stacks in 2003 as a MW-class power-generation plant in the ordinary thermal power plant. Furthermore, an advanced type PAFC of 100kW capacity with higher reliability has been installed by 2006. The new one has recorded a long operation of total 40,000 hours for 7 stacks of 20 stacks, reported by Fuji Electric Advanced Technology.



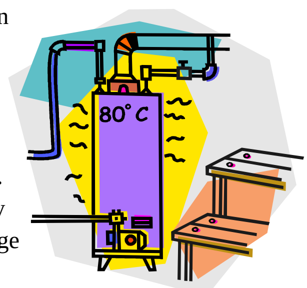
(4) Second-generation

The molten carbonate fuel cell, MCFC, operating at higher temperatures such 650°C has the advantage that both CO and H_2 can be electrochemically oxidized at the anode. So MCFCs have been applied also for the MW-class ordinary thermal power plant, where exhausted heat from the MCFC has been used for the combined generation with a carbon dioxide recycle process.

(5) Third-generation

The solid-oxide fuel cell, SOFC, can in principle, be designed to operate within a wide temperature range of 800-1000°C and to adapt oxide ions or protons as a conduction member. The SOFC is to be useful for an integration system with a gas micro-turbine, a steam reformation of fuel such as diesel, petrol and propane to produce H_2 and CO gases for the anode, and a co-generation system with a small capacity for a residential use.

(6) Residential and Mobile-generation



In our residential use and transportation vehicle use, the diversification in our energy uses, especially electricity and the energy saving efforts move onward steeply. Figure 2 shows an energy consumption rate of an average domestic in 2002 from the Mainichi.

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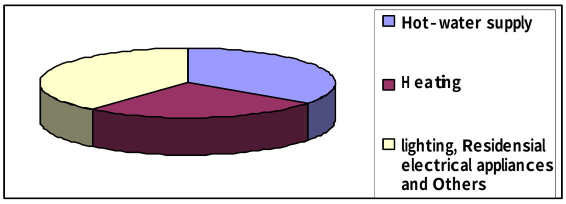
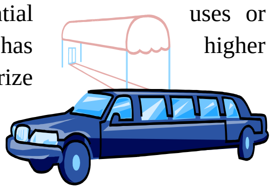


Figure 2 Energy consumption rate of the average residential use

The polymer electrolyte fuel cell, PEFC, has appeared in the late 1980's as a power source for the hybrid-cars or electric motor vehicles. The PEFC for the residential uses or the small dispersed power sources has higher system efficiency, tried to popularize widely.



On the other hand, the direct methanol fuel cell, DMFC, can in principle, design to exclude the reformer from the hydrocarbon to the pure H_2 fuel, and to compact a stack shape and a light weight for mobile or portable uses. Especially, the DMFC will expand for portable electric instruments such the note personal computer, PC, or the mobile phone as a micro-fuel cell. For instance, NEC Corporation has already demonstrated the DMFC with a methanol cartridge for the PC supported by the New Energy and Industrial Technology Development Organization, NEDO.

3. Requirements for Cell Component

Table 1 shows a summary of typical fuel cells. In these cells the most important materials are construction materials for cell frames, electrode plates, catalysts and electrolytes, depending on the fuel gases, the oxygen sources and operating temperatures.

Table 1 Summary of typical fuel cells

Type of fuel cell	PAFC	MCFC	SOFC	PEPC	DMFC
Electrolyte	H_3PO_4 dense solution	Li_2CO_3-K_2CO_3/Na_2CO_3	ZrO_2 (Y_2O_3, CaO)	Ion exchange film	Methanol solution
Conduction ion	H^+	CO_3^{2-}	O^{2-}	H^+	H^+
Electrode substrate	Porous carbon plate	Porous sintered Ni-Cr, porous oxide Ni plate	Ni plate, La-Ni oxide	Porous carbon plate	Carbon nanohorns
Electro-catalyst	Pt based	—	—	Pt based	Pt
Fuel	H_2 including CO_2	H_2, CO	H_2, CO	H_2 including CO_2	Methanol
Operation temperature, °C	150-200	600-700	800-1,000	70-100	70-120
Generation efficiency, %	32-42	-45	40-50	30-40	—
Power density, W/m^2	-2,000	-1,500	-3,500	-5,000	700-1,000

Every fuel cell in the table is developing or demonstrating for the present. To popularize the fuel cells dramatically, it needs to respond the following requirements up the practical demands. Some requirements have been suggested by textbooks such "a big-cyclopedia of the new energies", 2002, edited by the Kogyochosakai Pub. Co., Ltd.

(1)To increase in three-phase interface area

In principle, the electrode reaction of the dissociation reaction, oxidation reaction and reduction reaction on the air electrode and the fuel electrode takes place at the three-phase interface among vapor phase, electrode and electrolyte as shown in Figure 3. Therefore, it is most important factor to increase in the interface area for effective electrode reactions. For the purpose, more efforts of developing fine or porous electrode structures, efficient electro-catalysts and electrolytes with high-ion mobility are carried out steadily.

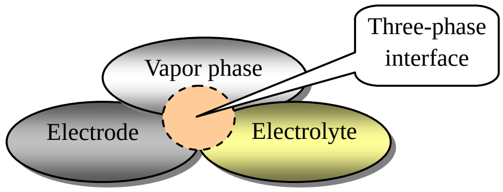


Figure 3 Schematic view of three-phase interface

(2)To reduce the carbon monoxide poisoning

The reformed hydrogen from methanol or natural gas contains generally small amount of carbon monoxide, CO, which is absorbed at below 100°C on the Pt based electro-catalyst to lead the cell voltage drop. In PEFC for the carbon monoxide poisoning, the effort for developing CO-tolerant Pt-alloys such as Pt-Ru against the poisoning, and the installation of CO clean-up unit are inevitable to be below 10ppm of CO content.

(3)To suppress the crossover

In DMFC the fuel gas and the air penetrate through polymer electrolyte to increase in over-voltage level as shown in Figure 4, to drop cell voltage and to decrease in fuel efficiency. These phenomena are called by the crossover. Some schemes of increasing an operation temperature or decreasing the fuel concentration are carried out.

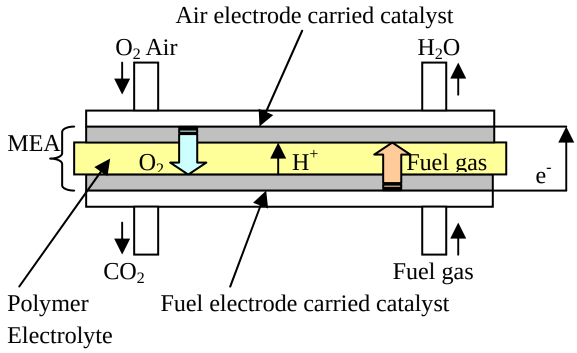


Figure 4 Principle of DMFC with polymer electrolyte

(4)To eliminate the cation impurity

Polymer film has a function of cation exchange in PEFC to introduce some cations such metallic ions into the fuel cell system. It needs to purify using water, to use the filtered air or to clean-up transfer tubes.

(5)To suppress the carbon deposition

Reformed gas used in the fuel cell is called by the water gas consisting hydrogen, carbon monoxide, carbon dioxide and water, and is in the Boudouard equilibrium above 500°C.

$$H_2 + CO_2 \Leftrightarrow H_2O + CO$$

But CO also deposits easily carbon at 500-700^{o}C on a metallic surface.

$$2CO \Leftrightarrow CO_2 + C$$

Since in MCFC and SOFC this carbon deposition phenomenon happen frequently, some amount of water are used to adding to the inlet fuel gas to suppress the carbon deposition.

(6)To prevent the nickel dissolution and deposition

In MCFC the air electrode of NiO contacted with carbonate electrolyte solutes slightly to diffuse in the electrolyte, and the diffused nickel ion reduces on the fuel electrode to deposit a metallic nickel. This phenomenon prevents to keep a desired CO_2 partial pressure during the operation.

(7) To relieve in the thermal stress

It is a significant factor to shorten starting time up by the operation temperature. Therefore, in SOFC, which operates the temperature range of 800-1000^{o}C, the thermal stress due to the thermal expansion differences among constituting materials have to be relieved to keep them safety. Because PEFC, which consists of water or liquid solutions, operates around room temperature, these constituting materials transform into the different phases under atmospheric temperatures below the frozen temperature.

(8) To achieve a quick start

On the other hand, the starting time generally requires for lowering more and more in the practical fuel cell. Because the fuel cell is based on the electrochemical principle, the starting time is considerably long. In the case of SOFC, the starting time up by the operation temperature of 900^{o}C needs about few hours.

In a recent report, a quick start of 30 seconds in a new SOFC has been achieved by the Ritsumeikan Universiry group, announced by the Nikkan Buisiness & Technology, 2006. In this announcement, the SOFC using a gas-transmission type solid electrolyte, some radical oxygen and a flame burning instrument achieved the quick starting time of 30 seconds.

(9) To perform higher power density

The DMFC as the micro fuel cell is developing against the lithium-ion battery for installing it on the PCs or the portable electric instruments. There are significant problems in the DMFC of low power density as shown in Table 1, and large cost share of 25% in the membrane electrode assembly, MEC as shown in Figure 4.

As a solution for the problems, a new type of micro fuel cell has been proposed by NTTDOCOMO group, announced by the Nikkei Business Daily, 2006. The new micro fuel cell can be operated by an aluminum hydride with water, instead of the methanol fuel in the DMFC. The aluminum hydride can produce from some aluminum scraps with a super fine grinding method as shown in Figure 5.

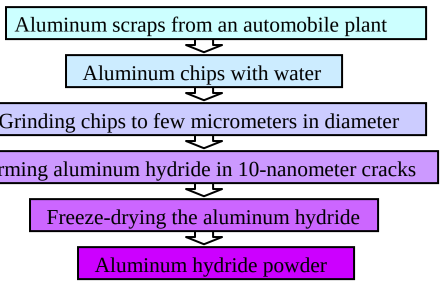


Figure 5 Procedure of the aluminum hydride

4. Prospect of Fuel Cell Market

Today's fuel cell market may divide into three fields of 100 kW or more class for the power generation plant, 1 kW class for residential use or automobile, and the micro-fuel cell for mobile electric instruments.

The 100 kW or more class fuel cells such PAFC or MCFC have a long experience in demonstration, and a steady advancement in their technologies.

The 1 kW class fuel cells such PEFC or SOFC are in a dramatic competition as shown in Table 2, announced by the Nikkei Business Daily. 2006. The PEFC and the SOFC are developing for applying to the residential use and the automobile use.

Table 2 Relative performance in the fuel cell market

Typical fuel cell	PEFC	SOFC	MCFC
Generation efficiency in practical installation, %	33.9	49	<45
Starting time	Short	Long to short	Middle
Compatibility with co-generation	Residential use with hot-water supply	1 kW, residential use for 2,000hrs	-
Cost characteristics	Expensive Pt for electro-catalyst	Using expensive rare earth materials	Low cost in materials
Market targets	Residential use Automobile	Residential use Automobile	Fixed installation in plants

On the other hand, the micro-fuel cells are in creating technologies for practical demands already issued in section 4 (9) against the current advanced battery technologies.

5. Conclusion

As a promising candidate to overcome the environment issues related to the Kyoto Protocol, we propose intensely the fuel cell technologies.

The fuel cell technologies intend to play an important part in total energy conservation and CO_2 exhaust gas reduction. In the diversified society, the fuel cell technologies have many variations and possibilities. In addition of R&D for each fuel cell technologies, many energy systems installed the fuel cells should be significant. Because the generation efficiency of the fuel cell itself may stay around 30-45%, some combinations such micro-turbine or heating instruments increase up to 70% or more in the total generation efficiency.

Finally, we are looking forward to discussing with you in the meeting of the fuel cell promoted by the Metal and Ceramics Technological Committee.

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