論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	EFFECT OF OPERATING CONDITIONS ON THE GAS CROSSOVER IN PEM FUEL CELL
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11411号, 授与年月日:2020年3月26日, 学位の種別:課程博士, 審査員:伏信 一慶,花村 克悟,大河 誠司,齋藤 卓志,笹部 崇
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11411号, Conferred date:2020/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

DISSERTATION OUTLINE

EFFECT OF OPERATING CONDITIONS ON THE GAS CROSSOVER IN PEM FUEL CELL

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Proton exchange membrane (PEM) fuel cell is one of the most promising power generation techniques for automobile and stationary applications due to its prospect for future energy sustainability. However, wide commercialization of PEM fuel cell depends on progress that can be achieved to enhance its reliability and durability along with cost reduction. If the durability of fuel cell is improved, the cost of operation can be dropped due to the replacement frequency of the fuel cell stack is reduced considerably. Although, the fuel cell durability issue has been investigating by many researchers. However, determining the degradation rate as well as improving the durability of fuel cell is still complicated not only because the degradation of a PEMFC can be attributed to degradations of their components, such as membrane, catalyst layers, gas diffusion layers, and bipolar plates, but also because there are many factors could affect the degradation of PEM fuel cell, which including manufacturing/design issues, material characteristics, and operation conditions. These factors result in membrane degradation through physical (including mechanical, thermal degradation) and chemical mechanisms. Therefore, this research work's approach to understanding of the degradation mechanisms of fuel cell components as well as determining the operating conditions that affect the degradation rate of components to define the range of operation which improve durability.

One of the issues affecting the durability of PEM fuel cell is determined by gas crossover phenomenon. Hydrogen and oxygen go through the membrane and to the opposite electrode are reacted to each other to form hydrogen peroxide (H_2O_2) production and subsequently decompose to radical species, such as peroxide ($HO^{\bullet}$) and hydroperoxide ($HOO^{\bullet}$). When H_2O_2 is decomposed to radicals they attack the electrolyte material. Inside the membrane, this decomposition is catalysed by metallic impurities or Pt-particles from the catalyst layers resulting in the accelerated degradation process of the electrolyte material.

Therefore, the overall goal of the present thesis is to conduct both of experimental and numerical analysis, with emphasis on gas crossover through the membrane with different geometric parameters of MEA and operating conditions. Specifically, the main objectives of this dissertation are described as follows:

Chapter 1. Introduction

Transportation is an extremely important element for the day-to-day functioning both of Japan and Vietnam, as well as other country in the world. Without transportation the entire country would, literally, come to a standstill. It is virtually impossible to imagine life without some form of transportation. Privately owned cars, motorcycles, trucks, public buses and subways, trains, planes and boats are all a daily part of our lives. However, the problem is that petroleum-derived liquid fuels are the overwhelming source of energy in the current most commonly used forms of transportation such as automobiles, buses, and trucks. Which are combusted in internal combustion (IC) engine and releases harmful emission to the environment and to our health, the produced harmful emissions include CO_2, the most important greenhouse gas (GHG), as well as criteria-air contaminants (CACs) that cause local pollution like particulate matter (PM), carbon monoxide (CO), sulfur oxides (SO_X), volatile organic compounds, which are unreacted or partially reacted fuel hydrocarbons (HC), and nitrous oxides (NO_X). One of the most important solutions to improve efficiency and reduce emissions of IC engines is to use

alternative fuels. Which not only burn cleaner producing and lower emissions, but also are even renewable, unlike fossil fuels, which means we could develop a continuous supply of them. The alternative fuels in use today include ethanol, biodiesel, methanol, natural gas, liquefied petroleum gas, especially electricity and hydrogen. However, in order to use electricity or hydrogen for vehicels that requires for a new energy technology for energy conversion replacing for IC engines, which is more energy efficient than the IC engines, with minimal or zero pollutant emission.

Implied from the above, battery electric vehicles (EVs) and fuel cell EVs are the latest technologies to meet the transportation in the future due to they use an electric motor, which is higher efficiency and zero tail pipe pollutant emissions than conventional vehicles powered by gasoline or diesel. The pollutant emissions of EVs/fuel cel EVs depend on the energy sources used to generate electricity or produce hydrogen at the plants. Thus, the electric motor only moves the air pollution to the non-urban areas and the pollutant emissions produced by the plants are far easier to manage than in the case of huge amounts of single cars in the daily traffic. Furthermore, the energy sources used to generate electricity or produce hydrogen are diverse, that are fossil energy sources such as coal, oil, and natural gas or renewable energy sources such as biomass, solar, wind, ocean waves, and hydropower. In addition, they can have very low net global warming emissions when renewable sources are used to produce their fuel. Another fact is the reduction of noise caused by the traffic, since the EV's motor running is significantly quieter, thanks to the missing exhaust. Furthermore, the electric motor entirely misses the transmission with the clutch and consists of reduced number of moving particles, unlike the IC engine. Therefore, there is no need for a change of any type of oil, coolant, water or start sparks of the engine. This fact has a consumer-friendly aspect of less wear out of the engine components, going hand in hand with lower maintenance costs, dedicated to the service of the vehicle.

Battery EVs have the most obvious advantage to be the cleanest vehicles on the road today because of their zero tailpipe emissions. While the total global warming emissions of a battery EV depend on the electricity source used to charge its batteries. Therefore, the air polluting process now moves to the non-urban areas where have lower pollutant emissions. Furthermore, the emissions produced by the power plants are far easier management than in the case of huge amounts of single cars in the daily traffic. Simultaneously, with the growing technology and infrastructure in the EVs field today, which brought more convenient to users to can simply recharge the EVs at home or at charging stations installed in workplaces and public parking spots. Especially with a DC fast charger (DCFC) technology, it has significantly reduced the charging duration for electric vehicles. However, currently, battery electric vehicle technology is only most cost-effectively for light and short driving range vehicles such as sedans or hatchbacks. For heavier vehicles such as SUVs, pickup trucks, buses, and light and heavy trucks, the use of battery electric vehicle has become less cost-effectively because of using larger battery capacity with costlier battery packs. In addition, battery recharging time is lengthened to the point that a fully discharged battery would not charge fully overnight.

Similarity to a battery electric vehicle, a hydrogen fuel cell vehicle (FCV) use the propulsive force from electric motor, but electricity energy is produced continuously from the

fuel cell stack instead of using stored energy in batteries such as EV. Therefore, pollutant emissions of FCVs are also much lower than those of ICE vehicles. FCV also has an onboard hydrogen tank such as IC engine vehicle and is refueled directly at hydrogen stations by the driver or staff of the station in a very short time and as convenient as the IC engine vehicle. When a hydrogen tank of FCV is filled up that can operate in the 200 to 300 miles of driving range. Thus, with its large capacity of energy and rapid replenishment is one of biggest advantages to have allowed the fuel cell to apply on larger electric-drive vehicles, such as SUVs, buses and trucks, to be practical.

In brief, EV technologies do not use directly petroleum-derived fuels and thus reduce global warming emissions compared with their gasoline and diesel counterparts. Therefore, battery EVs and hydrogen FCVs can actually both be utilized to address different consumers' needs and provide the greatest opportunity for market penetration. Battery EVs take advantage of the existing electricity infrastructure and are especially efficient and cost-effective for urban environments. Whereas, hydrogen fuel cells are a good option for larger vehicles, longer-distance driving, and drivers lacking a spot at home to recharge.

Since the early days of fuel cell industry, the concept of Hydrogen Economy has evolved significantly. Today, Fuel Cell is not just a fancy terminology for the researchers. It now prepares itself for major contributions in the world which soon face an inevitable shortage on energy resources. Over the past decade, technology advances in this field have offered a wide range of viable alternative energy and transportation options towards a cleaner, more diversified energy and transportation mix. Governments around the globe, including Canada, The United States, Germany and Japan are taking an active role in developing the technology and are making notable investments on near-term products that are meant to bring advantage to their people. Fuel Cell is now out of the labs, but yet needs to address some critical factors before we can find it in our everyday life, in our streets, houses and offices. As an emerging technology, it still needs to prevail over its aged competitors with regard to some key factors as cost, efficiency, durability, reliability and infrastructure availability.

Fuel cells will have to be cost-competitive with the existing conventional alternatives to gain the market share required to have real impact on world scale petroleum use and environmental issues. Fuel cell costs can be included three parts: the material and component costs, labor, and capital cost of the manufacturing equipment. In which labor and capital costs can be reduced by mass-production. Material and component costs, such as catalysts, membrane and bipolar plates, are dependent on technological innovations and the market. Researchers and manufacturers are striving to develop cheaper materials as well as seek cheaper catalyst than Pt. In addition, they also continue to optimize the operating conditions of fuel cell to improve its performance, reliability and durability to meet the ultimate goal of marketability that are the cost reduction for the end-users. So, this will lead to higher costs of research and development of fuel cells. However, the production costs of fuel cell vehicle will drop dramatically when it is mass-produced.

In terms of infrastructure, hydrogen fueling infrastructure has been developed for two last decades. It is expected that there is a strong development of hydrogen production technology as well as a network of hydrogen refueled stations for FCVs, which can meet the growing demand

for the market of hydrogen FCVs in the near future. Unlike fossil fuels, hydrogen fuel does not occur naturally on Earth and thus is not considered an energy source, rather it is an energy carrier. Hydrogen can be produced from diverse resources including fossil fuels, biomass, and water electrolysis with electricity. The environmental impact and energy efficiency of hydrogen depends on how it is produced. There are two pathways most commonly used today to produce hydrogen: reforming and electrolysis method. For reforming method: Synthesis gas (or syngas), a mixture of hydrogen, carbon monoxide, and a small amount of carbon dioxide, is created by reacting coal, oil, natural gas or biomass with high-temperature steam and oxygen in a pressurized gasifier. The subsequently synthesis gas is reacted with steam to separate the hydrogen. This method is the cheapest, most efficient, and most common. For electrolysis method: An electric current is used to split water into hydrogen and oxygen. In this method, the majority of emissions come from producing electricity - not directly from the hydrogen production process.

Along with boosting hydrogen production, the construction of hydrogen fueling stations was also developed in the past several years. By the end of 2016 there were about 4000 fuel cell cars, plus several hundred fuel cell buses were sold to consumers, along with more than 150 hydrogen refueling stations had been built mainly in the United States, Germany, and Japan. With the current development rate of the fuel cell industry, it is estimated that by 2025 there will be about 3000 hydrogen fueling stations to support about 2 million hydrogen fuel cell vehicles. Therefore, the development of hydrogen fueling infrastructure would be meet the requirement of fuel cell vehicle market in the world.

Eventually, in the development of fuel cell, durability of its components has been a vital concern for those involved in this industry. For a PEM fuel cell, durability has been a significant matter when it comes to the membrane electrode assembly. High temperature, highly acidic environment, varying humidity conditions of the MEA along with the presence of highly active reactants would have a significant impact on membrane, catalyst layer and gas diffusion layer lifetimes. Based on the standards of the fuel cell industry, a lifetime of more than 20,000 and 6,000 operating hours would be targeted for buses and cars, respectively, while 40,000 hours of lifetime would be demanded for stationary applications. Although the life targets of automotive industry are considerably lower than the expected lifetime for stationary applications, the fluctuating operating conditions of cars, such as the dynamic load cycling, startup-shutdown and freeze-thaw makes it even more challenging. It has been demonstrated that different degradation routes can lead to failure of various cell components, but considering the expected service times of the fuel cells, membrane shows to be one of the most vulnerable components which predominantly determines the life of a PEMFC. As the main platform of this work and with a specific focus on automotive industry, membrane degradation phenomena in PEMFCs would be on the center of attention throughout this dissertation and would be discussed in details in the upcoming section.

Chapter 2. Single-phase Numerical and Experimental Investigation on the Gas Crossover in PEM Fuel Cell

This chapter details the first phase of the research work, a numerical simulation model has

been built in company with an in-situ microprobe technique has been also applied to determine the properties of the hydrogen and oxygen crossover through the membrane with a range of relevant fuel cell operating conditions. Gas crossover through the membrane is one of the key factors for membrane degradation and performance loss of PEM fuel cell. The permeation of hydrogen and oxygen through the membrane are consumed with the generation of heat and water but without the generating of useful work, leading to a fuel inefficiency. On the other hand, hydrogen peroxide (H_2O_2) is most probably formed by the reaction of crossover hydrogen and oxygen at both the anode and cathode side. After that, the H_2O_2 decomposes to radical species, such as peroxide ($HO^{\bullet}$) and hydroperoxide ($HOO^{\bullet}$) radicals in presence of Fe^{2+}/Fe^{3+} Fenton's cations, which could accelerate the membrane degradation.

In addition, in this chapter, a platinum microprobe technique has been used for quantitatively measuring the amount of gas crossover via diffusion-limited current. A numerical simulation model has been simultaneously built using the partial differential equation solver FreeFem++. This study can help more people in community to access the numerical simulation capability of PEMFC due to FreeFem++'s open source nature, and the FEM based solver facilitates the modeling of possible complex geometry of their target computational domain. A steady-state, two-dimensional, single-phase and non-isothermal model of a single PEMFC has been considered to determine the water content distribution and temperature profile within the MEA, as well as gaseous species transport characteristics in the membrane at low current density (I_{ave} = 0.01 A cm^{-2}). The single-phase model used in this work because at very low current density, liquid water generated in the PEMFC is insignificant and can be neglected. The numerical results are compared to experimental data of the diffusion coefficient of reactant gas in the membrane, in order to gain insight on the gaseous species transport characteristics in the membrane. The results in this chapter showed that:

- The hydrogen and oxygen diffusion coefficient increase as the cell temperature increased. Similarly, increasing relative humidity also make the hydrogen and oxygen diffusion coefficients increased.
- However, the effect of the cell temperature on diffusion coefficient seems more complicated, especially on the oxygen diffusion coefficient, due to the significantly effect of crystalline region at higher temperature in the range of 80-100 °C.
- The relationships between gas diffusion coefficient-temperature and gas diffusion coefficient-relative humidity suggested that both hydrophobic and hydrated cluster regions affected to the gas crossover through the membrane.
- In addition, the hydrogen diffusion coefficient is approximately as twice as that of oxygen one.

Chapter 3. Two-phase Numerical Model to Predict the Gas Crossover in PEM Fuel Cell

As previous chapter, the flexibility of membrane is also related to the amount water in membrane. As the water content is increased, the flexibility of membrane is also increased and then it finally caused more gas crossover rate. This phenomenon, that membrane flexibility is increased by water content, is called membrane swelling. Thus, in this chapter, an attempt is

made in order to describe the extension of the work detailed in **Chapter 2.** The gas crossover through the membrane is investigated by two-phase model under high current density condition with various operating conditions as temperature, relative humidity, outlet pressure, stoichiometric flow rate. In addition, the effects of material physical properties and morphological structure of PEMFC's components on gas crossover through the membrane such as membrane and GDL thickness, GDL porosity, equivalent weight of the membrane, I/C ratio, and Pt loading are also investigated in this chapter. The following conclusions can be made in this chapter:

- A mathematical model using an open source software FreeFem++ that bridges micro-scale heterogeneous surface electrochemical reaction with macro-scale two-phase and non-isothermal transport has been developed and solved in two-dimensions for single PEM fuel cell with various operating conditions, material physical properties and morphological structure of PEMFC's components.
- The predicted results of the diffusion coefficient of gas crossover at high current density also increase as the operating temperature, relative humidity increased.
- Increasing the cell operating pressure improves the cell performance, however the durability of the membrane will be reduced due to an increase in gas crossover through the membrane.
- Due to the accelerated removal rate of liquid water to exhaust channel as increasing stoichiometric flow ratio, thus, resulting into reducing of the water content and local temperature inside the membrane. That impact to reducing the diffusion coefficient of hydrogen crossover. However, for oxygen crossover, due to an increasing in water transport from the cathode side to the anode side by back diffusion result in the amount of oxygen dissolved in the water being diffused through the membrane to the anode side will be also increased.
- The results also show that the diffusion coefficient of gas crossover decrease with increasing membrane thickness or equivalent weight due to reducing water content of the membrane.
- The diffusion coefficient of gas crossover increases as increasing I/C ratio due to a high ionomer causes an increase in the proton conduction to cathode side to electrochemically react with oxygen and generate water, after that water will be dissolved into the membrane and make it to become flexible and swelling. Similarly, the diffusion coefficient of gas crossover also increases as increasing Pt loading due to the total oxygen transport resistance in CL decreased with higher Pt loading, results in an increase in the oxygen consumption at catalyst surface. As a result, the cell performance also improved and more water product generated, that make the membrane becomes more flexible, which enhance gas crossover through the membrane.
- In addition, the liquid water saturation increases significantly as increasing GDL thickness due to accumulate liquid water in the cathode side, result in preventing oxygen diffuse to the CL and reducing the diffusion coefficient of oxygen crossover. Similarly, the diffusion coefficient of gas crossover decreases as increasing GDL

porosity due to the produced water easily passes out of the PEMFC leading to a decrease in the water content in the membrane.

Chapter 4. Conclusions and Recommendations

This dissertation was carried out in an effort to contribute to the improvement of PEMFC durability, a barrier to the commercial success of fuel cell vehicles. It is known that lifetime of a PEMFC depends largely on durability of its polymer electrolyte membrane (PEM), which indeed is the heart of this system. The main objective of this work was to define the diffusion coefficient of gas crossover through the membrane by in-situ experiment and numerical model. Gas crossover was detected by experiment via measuring diffusion-limited current at microprobe positions installed inside the membrane. At the same time, two mathematical models were developed to describe the complex physical phenomena occurring inside the PEM fuel cells. The numerical tool used the partial differential equation solver FreeFem++ to solve the proposed model and to study the effect of the various operating and structure parameters on the gas crossover through the membrane of the cell. The numerical solution obtained shed light on the interaction of the operating conditions and gas crossover phenomena of the PEMFC and lead to more in-depth understanding of the interrelations of the different cell parameters. The code in FreeFem++ has been validated against existing experimental work, the results of the present numerical solution agreed qualitatively with all of the existing experimental work. Few suggestions come to mind for building up on the existing dissertation work towards more in-depth understanding of the physics of the PEFMC and more elaborate quantification of the gas crossover through the membrane of the cell under different operating conditions.

In addition, the aim of the following recommendations is to improve the model presented in this dissertation work so as to gain a more thorough understanding of the physics underlying the operation of the polymer membrane fuel cells:

On Model Work

- Modifying the model to take into account transient effects, in this dissertation work we solved a steady-state model and thus our model is not capable of prediction of the fuel cell response to varying load conditions.
- Studying the different types of flow field design (serpentine, parallel flow, interdigitated ...etc) and its effect on the cell gas crossover regarding pressure drop and uniformity of reactants at the gas channel/porous media interface. Such a simulation would involve more detailed three-dimensional model of the fuel cell.

On Experimental Work

- An enhancement solution of manufacturing CCM with the Pt probes to reduce the possibility of the broken probes during fabrication and measurement.
- In this dissertation work, the diffusion-limited current is measured under steady state operating conditions. So, a new method needs to be devised to define the diffusion-limited current at transient operating conditions.