



## Special Review

Review

### Fuel Cell Research at Toyota Central R&D Labs., Inc.

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■**ABSTRACT**|| Toyota Central R&D Labs., Inc. has engaged in battery research since 1960. Much R&D effort has been placed on several types of batteries; however, these have proven to be insufficient for electric vehicle (EV) applications, because the energy density was too low for desirable EV range and the charging time was too long for convenient operation. We have considered that fuel cells (FCs) would be a good solution for the power source of future vehicles in a clean and energy saving-society, and started our fundamental research work in 1989. A polymer electrolyte fuel cell (PEFC) was selected as the research target.

Here we present some of our research results on the membrane electrode assembly (MEA) and its components (membrane, ionomer, and electrodes) with an aim for high power, high efficiency, and high durability. Some results on hydrogen storage materials and fuel processing methods are also introduced. All research results have been transferred to Toyota Motor Corporation (TMC) prior to starting an FC program at TMC and thereafter we have successively supported TMC for the development of a fuel cell (FC) vehicle called “MIRAI” which was brought to market in December 2014.

A hydrogen infrastructure is currently under construction with hydrogen produced mainly from natural gas due to cost reasons, which means there is still a dependence on fossil fuel resources. A gradual global shift to a renewable energy society is expected; however this may take long time. In the future, FCs are expected to continue playing an important role, and thus our results are expected to contribute to the further development of FC systems.

■**KEYWORDS**|| Polymer Electrolyte Fuel Cell (PEFC), Membrane Electrode Assembly (MEA), Membrane, Catalyst, Hydrogen Storage, Reformer

#### 1. Preface

Fossil fuels have contributed to the development and prosperity of humankind; however, they have also caused environment pollution and now a serious concern with respect to global warming. We have experienced energy crises such as the so-called “Oil Shock” several times in Japan due to various causes. Every time it has occurred, electric vehicles (EVs) have received significant attention, and accordingly high performance batteries for EVs have been strongly demanded.

Toyota Central R&D Labs., Inc. has engaged in battery research since 1960. Much R&D effort has been placed on several types of batteries; however, these have proven to be insufficient for EV applications, because the energy density was too low for desirable EV range and the charging time was too

long for convenient operation. Because of the poor performance of batteries, EVs were already considered as a secondary use car with limited range, but the battery performance at that time was still insufficient even for the criteria. R&D on Li batteries has made much progress recently and they are expected for EV applications again. However, current EVs using state-of-the-art Li batteries still don’t satisfy adequate range and acceptable charging time requirements, especially when compared to internal combustion engine vehicles. Fuel cells (FCs) have been considered to be a good solution, therefore we started our FC research work for transportation applications in 1989.

#### 2. Selection of FC Type

FCs are classified by their electrolytes as shown in **Table 1**,<sup>(1)</sup> because the electrolytes determine

**Table 1** Summary of Major Differences of the Fuel Cell Types.<sup>(1)</sup>

	PEFC	AFC	PAFC	MCFC	ITSOFC	TSOFC
Electrolyte	Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic	Ceramic
Operating Temperature	80°C	65°C~220°C	205°C	650°C	600~800°C	800~1000°C
Charge Carrier	H <sup>+</sup>	OH <sup>-</sup>	H <sup>+</sup>	CO <sub>3</sub> <sup>=</sup>	O <sup>=</sup>	O <sup>=</sup>
External Reformer for CH <sub>4</sub> (below)	Yes	Yes	Yes	No	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites	Perovskites
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Independent Cooling Medium	Process Gas + Electrolyte Calculation	Process Gas + Independent Cooling Medium	Internal Reforming + Process Gas	Internal Reforming + Process Gas	Internal Reforming + Process Gas

PEFC: Polymer Electrolyte Fuel Cell

AFC: Alkaline Fuel Cell

PAFC: Phosphoric Acid Fuel Cell

MCFC: Molten Carbonate Fuel Cell

ITSOFC: Intermediate Temperature Solid Oxide Fuel Cell

TSOFC: Tubular Solid Oxide Fuel Cell

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the major features of FCs, such as the operating temperature, usable fuel (pure hydrogen, reformed or direct methane), the prime cell component, and so on. Considering transportation applications, the FC system must be compact with high power and high efficiency, and have ease of start-up at ambient temperature. The polymer electrolyte fuel cell (PEFC) and alkaline fuel cell (AFC) appeared to be viable candidates based on the above criteria. AFCs were already developed for space applications and some trials for vehicle applications were performed. However, carbon dioxide in the air deteriorates the alkaline electrolyte, which won't occur in space applications where pure oxygen is used as the oxidant.<sup>(1)</sup> Therefore, the PEFC was selected as the research target.

### 3. PEFC

Schematic diagrams of a membrane electrode assembly (MEA) and a PEFC stack are shown in **Figs. 1** (a) and (b) respectively.<sup>(2)</sup> The MEA is comprised of an ion exchange membrane, which acts as an electrolyte, and two electrodes, a cathode and an anode, where electrochemical reactions take place. The MEAs are sandwiched by separators to form a stack. The role of the separator is to make an electrical contact and provide appropriate supplies of air and fuel (hydrogen) to each electrode without mixing. In the primary stage of R&D, it was considered that only carbon materials could be used as the separator because no other materials can endure in the acidic

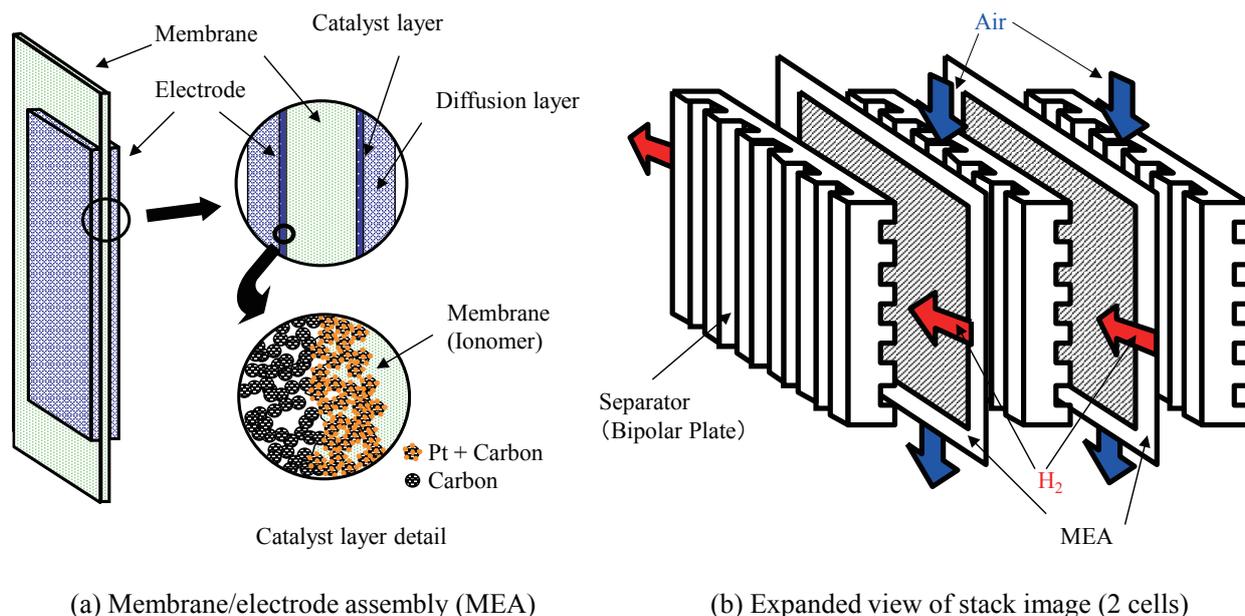


Fig. 1 Schematic image of membrane electrode assembly and stack of PEFC.<sup>(2)</sup>

environment and maintain good electrical conductivity without the formation of insulation layers based on the analogy of phosphoric acid fuel cells (PAFCs). In order to obtain a compact FC stack, thinner separators are required because the MEAs are already sufficiently thin. However, it is difficult to produce thin carbon separators at low cost; therefore metal separators with surface coatings have been investigated and promising technologies have been developed. The details of the separator will be reported elsewhere near future.

### 3.1 MEA

Figure 2 shows an image of cell voltage-current characteristics with the various polarization components. The internal resistance (IR) polarization is dominated by the ionic resistance of the membrane and the electric resistances of the electrodes. Each activation polarization is controlled by the catalyst activity and the effective surface area of the catalyst, which is expressed as the electrochemical surface area (ESA). The diffusion polarization is related to mass transfer, i.e., how fast each reactant can be supplied to the catalyst surface and how fast the reaction product (water) can be removed away from the reaction zone mainly in the cathode. Higher cell voltage is required for higher efficiency and higher current density for higher power.

#### 3.1.1 Membrane and Ionomer

A proton exchange membrane is used as the membrane, which functions as both a proton conductor and a gas barrier. The proton exchange membrane must be hydrated to exhibit proton conductivity by the release of protons from its functional moieties, which are typically sulfonic acid groups. The water uptake of the membrane is important to maintain high conductivity and to reduce IR polarization due to the membrane.<sup>(3)</sup> The molar density of sulfonic acid in the membrane is an important factor to control its proton conductivity. This property is generally expressed by equivalent weight (EW), which represents the molecular weight per one sulfonic acid moiety, so that a lower EW would result in higher conductivity. Therefore, low EW membranes have been investigated and higher proton conductive membranes than conventional Nafion with EW of 1100 have been obtained.<sup>(3,4)</sup> However, it is difficult to reduce the EW value to lower than around 700-800 in the case of a perfluoro membrane, which is typically used in PEFCs, because the perfluoro membrane keeps its shape by Van der Waals' force between main chains without mutual crosslinking<sup>(2)</sup> but the Van der Waals' force is not strong, so quite a little portion of main chain is required

There are two mechanisms for proton conduction

in the membrane: the Grotthuss mechanism and the vehicular mechanism, where the former provides better proton conduction. The protons travel through ion channels in the former mechanism; therefore, the formation and continuity of the ion channels are important. The ion channels are organized well when the membrane is adequately hydrated at middle to high relative humidity (RH), but are not when poorly hydrated at low RH. A membrane with low EW can easily form continuous ion channels; therefore, membranes that are usable at low RH were considered to be realized by this concept. A high acid-density model electrolyte with EW of 175 was synthesized and exhibited high proton conductivity ( $> 0.01$  S/cm) at low humidity ( $120^{\circ}\text{C}$ ,  $< 0.01\%$  RH), however, this was only a model and the membrane is very brittle and not practical.<sup>(4)</sup>

Adequate water is required for the membrane to exhibit good proton conductivity, however, excess water causes blocking of the electrodes, which hinders reactant supply to the electrodes and limits current density, i.e., the diffusion polarization increases. Water generation at the cathode by electrochemical reaction and electroosmotic flow induce larger water uptake at the cathode side than that at the anode side, so that the excess water problem is typically observed at the cathode side, especially at higher current density, although back diffusion of water relieves the uneven water uptake distribution when thinner membranes are used.<sup>(5)</sup> This uneven water uptake distribution in the membrane would also occur along with flow

channel, because water generation rate (current density) is not uniform throughout the flow channel; the concentration of reactants (fuel and oxidant) is high at inlet portion of flow channel but it decreases gradually along with flow channel due to consumption of reactants by the electrochemical reaction, which induces increase in the polarization resistance and thus reduces water generation rate (current density). Therefore, water management is very important, not only vertically to the membrane but also horizontally to the membrane.<sup>(6,7)</sup>

The first PEFC utilized a hydrocarbon membrane but had a severe durability problem.<sup>(1)</sup> The perfluoro membrane has subsequently become the main material, although hydrocarbon membranes are still investigated for cost reasons. The gas barrier properties of hydrocarbon membranes are superior to those of perfluoro membranes; therefore, when the gas barrier properties are critically important, such as with direct methanol fuel cells where chemical shorting by methanol crossover is serious, hydrocarbon membrane would be a better choice.<sup>(8)</sup>

Another issue for the membrane is its mechanical strength because it suffers from repeated tension during wet and dry cycles under FC operation. Perfluoro membranes are not usually crosslinked and they are prone to creep and tear under a worst case scenario, and thus some reinforcement is required. A crosslinked perfluoro membrane has been investigated and bis(sulfonyl)imide crosslinked membrane have improved mechanical properties at high temperature

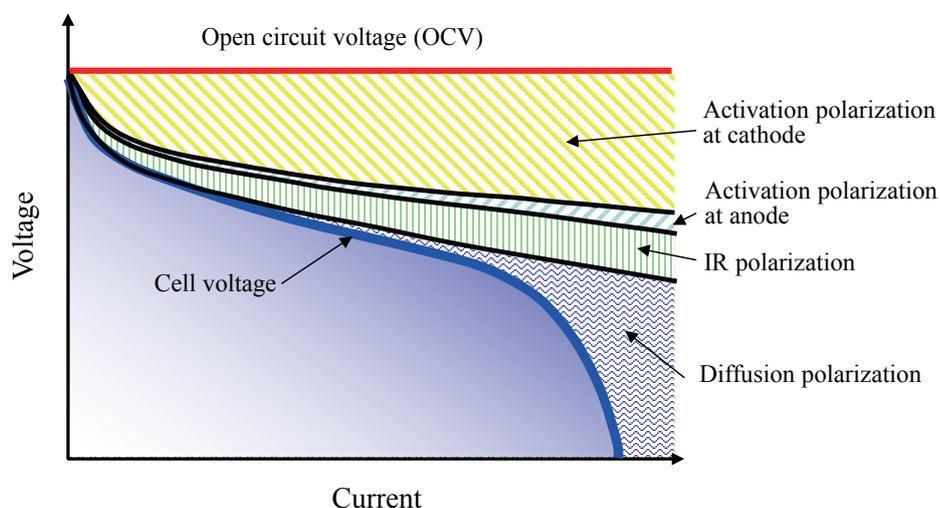


Fig. 2 Cell voltage and polarizations.

with a relatively small sacrifice of the proton conductivity.<sup>(9,10)</sup>

In the three phase interface region of the MEA, where an electrochemical reaction occurs, the catalyst, membrane (electrolyte), and gas phase must contact each other. The membrane material in this region, which is referred to as ionomer, requires a different property than the membranes mentioned the above. The ionomer requires high proton conductivity, which is the same as the membrane, but high gas permeability, which is opposite to the membrane to reduce the diffusion polarization. A dispersion of membrane materials was typically used as a source of the ionomer, but to enhance MEA performance, an improved ionomer with a high gas permeability structure is required.<sup>(11)</sup> Another aspect of ionomer is its acid function moiety. It is well known that anions adsorb to platinum (Pt) electrode surface, which hinders oxygen reduction reaction (ORR) in liquid electrolyte, i.e., it induces activation polarization. The sulfonic acid moiety was not considered to adsorb to Pt surface because it is bonded to a main chain, but it turned out that it adsorbs and affects the ORR; therefore, a more inert acid moiety ionomer is desired.<sup>(12)</sup> Water uptake also influences anion adsorption: sulfonic acid adsorption becomes stronger at lower water uptake.<sup>(13)</sup> Thus, water management is again note to be an important factor.

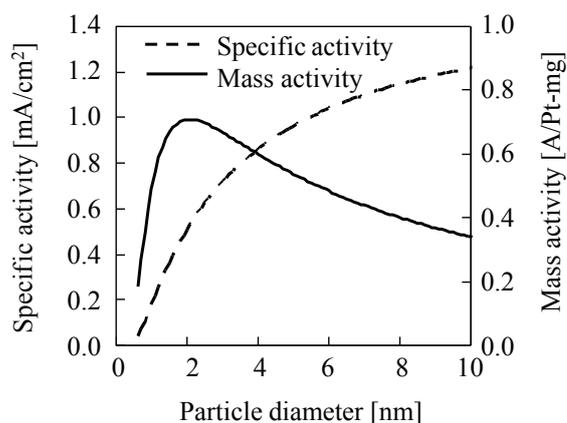
### 3. 1. 2 Electrode

The ORR occurs at the cathode and the hydrogen oxidation reaction (HOR) occurs at the anode. A catalyst for both electrodes is generally platinum (Pt). The activation polarization at the cathode is much larger than at the anode when pure hydrogen is provided, although carbon monoxide poisoning is a serious issue in the case of reformat fuels.<sup>(14,15)</sup> Therefore, much effort has been done on the cathode improvement. Non-Pt catalysts are desirable to reduce cost and have been investigated world wide. A heat-treated cobalt tetraphenylporphyrin supported on active carbon, which retains the Co-N4 structure, has exhibited good activity for the ORR<sup>(16)</sup> but still has inadequate performance by some orders of magnitude compared to Pt. Thus, Pt and Pt-based catalysts are still predominately employed as electrocatalysts for PEFCs. The use of Pt alloys is one approach to improve activity, although they require heat treatment. The surface activity of the alloy catalysts has been

generally improved; however, the particle size has become larger and the mass activity is limited. The use of a chelating agent to Pt-Fe alloy suppresses particle size growth and a higher mass activity than pure Pt has been obtained.<sup>(17)</sup> Other methods to improve the activity of the cathode are under investigation.

Considering the Pt catalyst, a reduction in the amount of Pt is important for cost reasons. The electrochemical reaction takes place on the surface of the catalyst, so smaller particles are preferable to obtain high ESA with a limited amount of Pt. Thus Pt has been supported on a carbon (Pt/C). The size of supported Pt particles is varied with the supporting methods and the carbon materials used as supports. It was well known that there was the particle size effect of the ORR on Pt catalysts; however, the reasons for this were yet to be clarified. The reason became clear by a first principles-based mean-field model calculation. The specific activity decreases with decrease in the particle size because increased Pt-O surface coverage hinders the ORR.<sup>(18,19)</sup> As shown in **Fig. 3**,<sup>(20)</sup> the mass activity becomes maximal at a diameter of 2 nm, which is consistent to experimental studies.<sup>(20)</sup>

Even if a sufficient Pt surface area is provided in the catalyst layer, the entire surface cannot be necessarily utilized for the reaction. The electrochemical reaction takes place only at the three phase interface, where oxygen, protons and electrons can access. Therefore, it is important to know the utilization of the Pt and

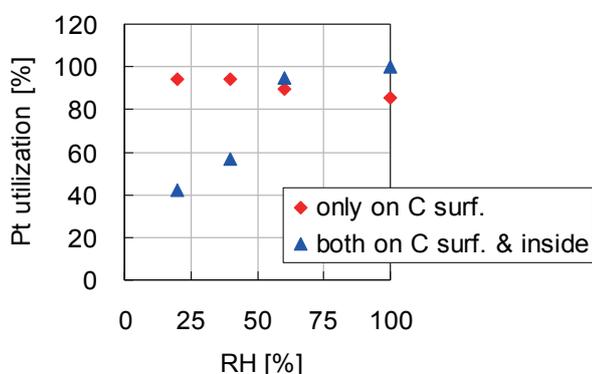


**Fig. 3** Dependences of the specific activity (mA/cm<sup>2</sup>) and mass activity (A/Pt-mg) on the diameter of the nano-particle at 0.9 V (RHE).<sup>(20)</sup>

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increase it to its maximum. A precise method to measure Pt utilization using CO was established and applied to Pt/C catalysts with different types of carbon under various humidity conditions. The Pt utilizations with a porous carbon and a solid carbon are shown as a function of RH in Fig. 4.<sup>(21)</sup> Pt particles are supported on the outer surface and inside of the pore of the former carbon but only the outer surface for the latter carbon. The Pt utilization of the former increases with increase in RH, while that of latter is constant. This indicates that Pt on the outer surface is covered with ionomer and is kept in a proton channel regardless of the RH conditions, while Pt inside the pore is not covered with ionomer but is connected to a proton channel when water permeates into the pore at high RH. The value of Pt utilization currently attained is ca 90%, so there remains little room for improvement in this area.<sup>(21-24)</sup>

Comprehensive techniques have been developed for diagnosis of the cathode catalyst layers of the MEA that involve evaluation of the electronic conductivity, protonic conductivity and gas diffusivity.<sup>(25)</sup> The results indicated that gas diffusion in the catalyst layer limits cell performance the most. Thus, the porosity in the catalyst layer is important, which is affected by support materials, the composition of the layer, and the fabrication methods.<sup>(26-28)</sup> Oxygen is supplied through the pores but at the last stage it must go through the ionomer to reach the catalyst surface, so the oxygen permeability in the ionomer is important. The oxygen diffusion rates in cast Nafion films with different thickness were evaluated and the reciprocal of diffusion-limited current density values are plotted



**Fig. 4** The RH dependence of Pt utilization at 80°C: different Pt-supported sight.<sup>(21)</sup>

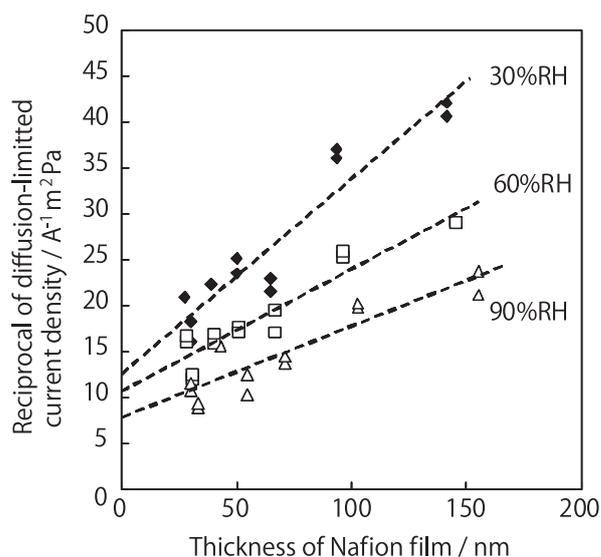
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against thickness as shown in Fig. 5.<sup>(29)</sup> The reciprocal of diffusion-limited current density decreases linearly with decrease in film thickness under all three RH conditions examined, but it does not become zero at zero thickness. This indicates that there is another resistance for oxygen permeation through the ionomer other than diffusion, which is considered to be dissolving resistance or other interfacial barriers.<sup>(29-31)</sup>

### 3. 1. 3 Durability of MEA

Once advancement of the R&D focus on the initial performance was attained, durability issues arose.<sup>(32)</sup> A gradual decline in cell voltage and an abrupt increase in gas crossover rate were observed in durability test of the MEA. The former is related to the deterioration of the cathode and the latter to membrane degradation, and those two are intimately related.

Pt in the cathode catalyst layers is subject to oxidation and reduction during cell operation (potential cycling) and some portion of the Pt dissolves and precipitates somewhere. The situation between Pt particles near membrane side and near gas diffusion layer (GDL) side is different. The number of Pt particles for all sizes decreases with time at the position near the membrane, which means Pt dissolving is dominant in this region and dissolved



**Fig. 5** Relationship between reciprocal of diffusion-limited current density and Nafion thickness at 80°C.<sup>(29)</sup>

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Pt diffuses into the membrane and precipitates in the membrane near the cathode to form a Pt-band. On the other hand, the number of large Pt particles increases at the position near the GDL, which means dissolved Pt deposits on larger Pt particles. These phenomena were confirmed TEM observation and simulations. The mechanisms are different in the different positions of the catalyst layers, although both phenomena contribute to a reduction in the ESA and induce the gradual decline in the voltage.<sup>(33-36)</sup> The use of larger Pt particles and the use of modified Pt are possible options to mitigate this, because the corner of the Pt particles is the most unstable position; the ratio of Pt atoms at corner decreases with increase in particle size, thus, the unstable portion ratio in Pt particle decreases in larger particles, and it would be effective to protect the corner Pt with some materials (modified Pt).<sup>(37,38)</sup>

The perfluoro membrane materials are not hard, therefore there is some possibility that something hard could penetrate into the membrane and make holes, which could be induced by carbon fibers used in GDL and reproduced by a model experiment.<sup>(39)</sup> However, the most serious degradation mode is not mechanical one but chemical.<sup>(39-45)</sup> Fluoride ions were detected in durability test due to attack of the membrane by hydrogen peroxide radicals generated at the electrodes. The membrane was the component that most suffered from deterioration problems at the beginning of the PEFC research when hydrocarbon membranes were used and then replaced by perfluoro membranes. The perfluoro membrane had been widely used in the soda industry for ion exchange membrane electrolysis. Therefore, the perfluoro membrane was at first considered to be chemically stable, although this was not the case. Pt in both electrodes and the Pt-band acts as a creator of hydrogen peroxide radicals and/or a terminator of them depending on the neighboring concentration of hydrogen, oxygen, and hydrogen peroxide radicals, which makes the phenomenon complicated. Thus, variety of additives to mitigate the membrane degradation have been examined and an effective one has been developed.

### 3.2 Fuel

Activation polarization at the anode is at a minimum when pure hydrogen is used; therefore, hydrogen is the best fuel for PEFCs. However, it requires a lot of volume or weight to store adequate amount

of hydrogen in a vehicle. On the other hand a liquid fuel can be refilled quickly and stored compactly in a vehicle, but requires reforming to hydrogen with a CO content of less than 50 ppm.<sup>(1)</sup> In addition, the start up time and thermal managements are important issues for reformer systems. **Table 2**<sup>(2)</sup> shows a comparison of hydrogen storage systems for PEFCs. This comparison was made over 20 years ago; however, the situation has not changed significantly.

#### 3.2.1 Hydrogen Storage

Hydrogen storage options are pressure vessels, liquid hydrogen, metal hydride (MH), absorbent and chemical materials. A pressure vessel is the simplest way to store hydrogen but is bulky and heavy. Liquid hydrogen has a severe problem of boil off, so the other options have been investigated mainly.

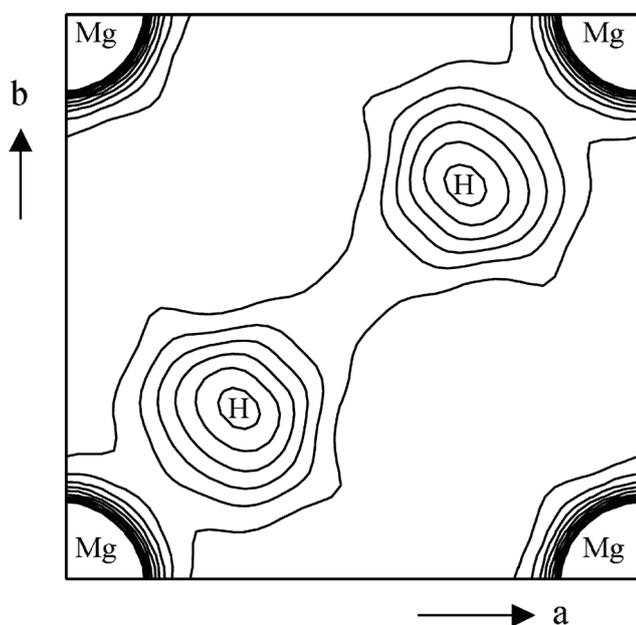
MHs can store hydrogen compactly, which are more compact than liquid hydrogen as a material, and they absorb heat when they release hydrogen, which is advantageous to utilize for cooling the FC system, although this also means a heat exchanger is required for quick charge and discharge of hydrogen. The MH system is heavy, so hydrogen content by weight is quite low.

To search for a good MH candidate, precise structure analyses, first principles calculations and material syntheses were done for various MHs including complex metal hydride.<sup>(46-100)</sup> The bonding nature of hydrogen in the materials was fully uncovered by the maximum entropy method (MEM) from X-ray powder diffraction data using synchrotron radiation, which provided a good guide for further investigations. One of the examples is shown in **Fig. 6**.<sup>(56)</sup> The standard heat of formation of the material ( $\Delta H$ ) represents the stability, which is the temperature of hydrogen release. First principles calculations showed a good correlation between the calculated  $\Delta H$  value and the electronegativity, which is useful to search for potential candidates from literatures. **Figure 7**<sup>(68)</sup> shows the example for borohydrides and the same correlations were obtained in other MH systems. However, appropriate temperature materials have low hydrogen content, while high hydrogen content materials have higher temperature. No good MH materials have been found for passenger FC car applications, however, some materials can be used for FC forklifts where heavy weight is acceptable.

**Table 2** Comparison of hydrogen storage system for PEFC.<sup>(2)</sup> (Requirements for 400km driving)

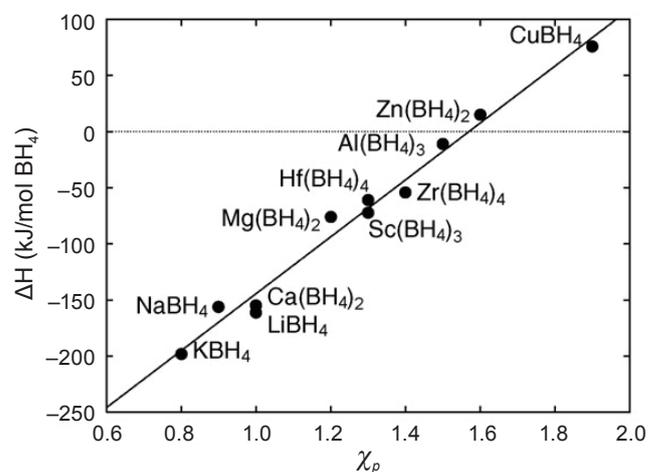
Hydrogen storage system	Hydrogen density Kg-H <sub>2</sub> /L	Working Temp. °C	Fuel properties (Equal to gasoline 15 km/L)			System total weight kg	Hydrogen weight ratio (H <sub>2</sub> /system)		Safety & oper.	Start & stop	System design	Overall evaluation
			Weight kg	Hydrogen Wt%	Volume L		Gravimetric Wt%	Volumetric kg-H <sub>2</sub> /m <sup>3</sup>				
Methanol reforming CH <sub>3</sub> OH + H <sub>2</sub> O →3H <sub>2</sub> +CO <sub>2</sub>	0.103 contains H <sub>2</sub> O	200~300	59.7 contains H <sub>2</sub> O	12.1	70	110	○ 6.6	○ 6.3	○	△	△	○
Pressure vessel (Steel) 15MPa	0.0135	-	7.2	100	535	622	× 1.16	× 9	△	⊙	⊙	×
Pressure vessel (Kevlar) 20MPa	0.018	-	7.2	100	401	233	△ 3.1	△ 11	△	⊙	⊙	△
Metal hydrides (Low temp. type): LaNi <sub>5</sub> H <sub>6</sub>	6.69	20~80	527	1.37	80	880	× 0.82	△ 28	○	○	○	△
Metal hydride (High temp. type): Mg <sub>2</sub> NiH <sub>4</sub>	2.56	250~300	201	3.59	79	390	× - △ 1.85	△ 36	○	△	△	△
Activated carbon, FRP vessel: 6MPa, 87K	0.0291	-186~	80.2	9.0	248	160	△ 4.2	× - △ 20	△	○	△	△
Liquid hydrogen 20K	0.0715	-253~	7.2	100	101	80	⊙ 9.0	△ 36	×	○	○	×

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**Fig. 6** The charge density distribution map in (001) plane of MgH<sub>2</sub> at room temperature by MEM. The contour lines are drawn from 0.0 to 1.5 at 0.15 e/Å<sup>3</sup> intervals.<sup>(56)</sup>

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**Fig. 7** Relation between the heat of formation  $\Delta H$  and the Pauling electronegativity of the cations. The straight line indicates the result of the least square fitting. The zero-point energy contribution to  $\Delta H$  is approximately taken into consideration.<sup>(68)</sup>

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Absorbents such as activated carbons have also been investigated but the hydrogen content is quite low at room temperature, at less than 2% as a material. An increased value of 5% as a materials can be obtained at liquid nitrogen temperature but is still low and unacceptable.<sup>(55,101,102)</sup>

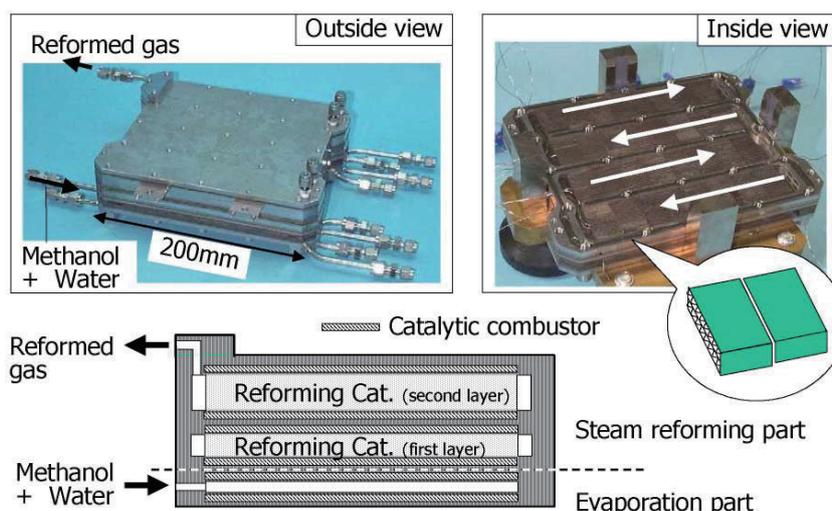
Sodium borohydride is a chemical material that releases hydrogen by hydrolysis and the hydrogen content is high at nearly 10% by weight including the required water weight. However, one problem is that the hydrogen release reaction is exothermic, so that extra cooling energy is required. Another problem is that this material has to be chemically synthesized and much energy is required for recycle of the material; therefore this is not viable for energy storage and would be limited only for emergency purposes.<sup>(103-109)</sup>

### 3.2.2 Liquid Fuel

Methanol was the first prime candidate as a liquid fuel for PEFCs, because it can be reformed at 200 to 300°C, which is not so far from the FC operating temperature of approximately 80°C and thus allows minimum thermal loss. **Figure 8**<sup>(110)</sup> shows a plate type methanol steam reformer developed by us, which has a laminated structure with an evaporator zone, two reforming zones, and plate catalytic combustors, and was demonstrated to have a sufficient hydrogen output with good thermal efficiency.<sup>(110-114)</sup>

However, methanol was not accepted as general fuel,

because no methanol infrastructure existed at that time and methanol is both toxic and miscible with water, which could prove hazardous for the public in the case of spills. Then, there was an increasing expectation that gasoline or gasoline like fuels could be used because of the existing infrastructure. Reforming fuels with C-C bonds requires over 500°C and practically 800°C. **Table 3**<sup>(115)</sup> shows three types of reformer systems. In a 2nd generation reformer, a conventional reformer component in the 1st generation reformer is substituted by a microchannel reactor (MCR) and a CO removal component is eliminated by introducing hydrogen permeator, which results in a compact reformer system applicable to PEFCs (**Fig. 9 (a)**).<sup>(115)</sup> The MCR is a laminated product of metal foils and reforming gas flow passages, and combustion gas flow passages are reciprocally constructed. The thermal capacity of the MCR is very small, hence it can start up quickly. In the 3rd generation reformer, a new concept with a new type of FC, a hydrogen membrane Fuel Cell (HMFC), was introduced (**Fig. 9 (b)**).<sup>(115)</sup> This new FC has an ultra thin proton conductor electrolyte supported on a solid hydrogen membrane (permeator) that can directly accept reformat without removal of CO. The HMFC can operate at the same temperature as the reformer, so a highly compact system with excellent thermal management can be expected. This new FC is still under development and there are some issues to be addressed prior to practical development.<sup>(115-117)</sup>



**Fig. 8** Plate type methanol steam reformer.<sup>(110)</sup>

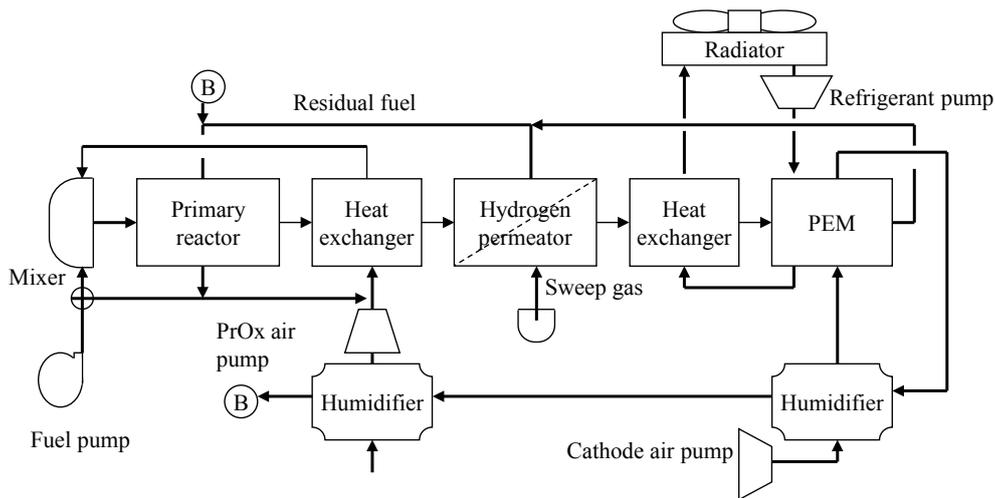
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**Table 3** Evolution of the fuel cell system with reformer.<sup>(115)</sup>

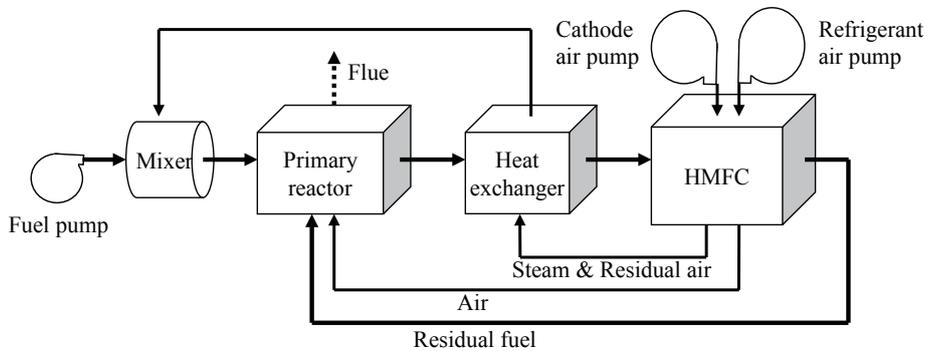
Component	1st Generation	2nd Generation	3rd Generation
Reformer	Monolith Substrate Filter	MCR	MCR
WGS Reactor	HTS & LTS	HTS	-----
CO Removal	PrOx	Hydrogen Permeator	HMFC
Fuel Cell	PEM	PEM	
Heat Exchanger	Evaporator & Recuperator	Recuperator & Humidifier	Recuperator

MCR: Micro Channel Reactor  
 HTS: High Temperature Shift Reactor  
 LTS: Low Temperature Shift Reactor  
 PrOx: Preferential Oxidation Reactor  
 PEM: Proton Exchange Membrane Fuel Cell (Polymer Electrolyte Fuel Cell)

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(a) 2nd generation fuel cell system with fuel reformer



(b) 3rd generation fuel cell system with fuel reformer

**Fig. 9** 2nd generation and 3rd generation fuel cell system with fuel reformer.<sup>(115)</sup>

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#### 4. Summary

We have considered that FCs would be a good solution for the power source of future vehicles in a clean and energy-saving society, and started our fundamental research work in 1989. The PEFC was selected as the research target. All research results, not only those presented here but also those not given in this article, have been transferred to TMC and we have successively supported TMC for development of an FC vehicle called "MIRAI" that was brought to market in December 2014.<sup>(118)</sup>

A hydrogen infrastructure is currently under construction with hydrogen produced mainly from natural gas due to cost reasons, which means there is still a dependence on fossil fuel resources. A gradual global shift to a renewable energy society is expected; however, this may take long time. In the future, FCs are expected to continue playing an important role, and thus our results are expected to contribute to the further development of FC systems.

#### References

- (1) EG&G Services, Parsons, Inc. and Science Applic. Int. Corp., *Fuel Cell Handbook 5th Edition*, p. 1-5 (2000), the U.S. Department of Energy, (CD-ROM).
- (2) Kawahara, K. and Nagano, S., "Polymer Electrolyte Fuel Cell" (in Japanese), *R&D Review of Toyota CRDL*, Vol. 29, No. 4 (1994), pp. 13-22.
- (3) Asaoka, T., Haga, T., Suzuki, T., Kawahara, K. and Abe, K., "Water Uptake and Properties of Electrolytes for PEFCs" (in Japanese), *35th Battery Symp. Jpn.*, 3D18 (1994), pp. 297-298, The Electrochemical Society of Japan.
- (4) Hase, K., Nakano, T. and Koiwai, A., "Performance of High-density of Acid Electrolyte and Analysis of Proton Conduction Mechanism", *ECS Trans.*, Vol. 11, No. 1 (2007), pp. 159-164.
- (5) Kawahara, K., Asaoka, T., Haga, T. and Suzuki, T., "Membrane Electrode Assemblies for Polymer Electrolyte Fuel Cells" (in Japanese), *Battery Technology*, Vol. 10 (1998), pp. 154-159.
- (6) Yamada, H. and Morimoto, Y., "Practical Approach to Polymer Electrolyte Fuel Cell Modeling", *R&D Review of Toyota CRDL*, Vol. 39, No. 3 (2004), pp. 39-45.
- (7) Yamada, H., Hatanaka, T., Murata, H. and Morimoto, Y., "Measurement of Flooding in Gas Diffusion Layers of Polymer Electrolyte Fuel Cells with Conventional Flow Field", *J. Electrochem. Soc.*, Vol. 153, No. 9 (2006), pp. A1748-A1754.
- (8) Hatanaka, T., Morimoto, Y., Hasegawa, N., Kamiya, A., Kawasumi, M. and Kawahara, K., "Direct Methanol Fuel Cells – Current and Future" (in Japanese), *Battery Technology*, Vol. 14 (2002), pp. 117-126.
- (9) Kawasumi, M., Hasegawa, N., Tanaka, H., Nakano, M., Yamamoto, T., Tsusaka, K., Kamiya, A., Muto, A., Asano, T., Morimoto, Y. and Kawahara, K., "Crosslinked Perfluorinated Proton Exchange Membranes for Elevated Temperature PEFC Operation", *208th ECS Meeting* (2005), Abstract No. 927, The Electrochemical Society.
- (10) Tsusaka, K., Asano, T., Kadoura, H., Nakai, K., Hasegawa, N., Kawasumi, M. and Morimoto, Y., "Development of Imide Crosslinked Perfluorosulfonic Acid Membranes by Gas Phase Treatments" (in Japanese), *49th Battery Symp. Jpn.*, 1D07 (2008), p. 194, The Electrochemical Society of Japan.
- (11) Shinohara, A., Kudo, K., Kawasumi, M., Morimoto, Y. and Hasegawa, N., "Non-crosslinked Perfluoro-polymer Electrolytes with Two Acid Groups and Their Properties", *ECS Trans.*, Vol. 58, No. 1 (2013), pp. 253-259.
- (12) Kodama, K., Shinohara, A., Hasegawa, N., Shinozaki, K., Jinnouchi, R., Suzuki, T., Hatanaka, T. and Morimoto, Y., "Catalyst Poisoning Property of Sulfonimide Acid Ionomer on Pt(111) Surface", *J. Electrochem. Soc.*, Vol. 161, No. 5 (2014), pp. F649-F652.
- (13) Kodama, K., Jinnouchi, R., Suzuki, T., Murata, H., Hatanaka, T. and Morimoto, Y., "Increase in Adsorptivity of Sulfonate Anions on Pt(111) Surface with Drying of Ionomer", *Electrochem. Commun.*, Vol. 36 (2013), pp. 26-28.
- (14) Haga, T., Asaoka, T. and Kawahara, K., "Anode Half-reaction Studies in Polymer Electrolyte Fuel Cell (PEFC)" (in Japanese), *39th Battery Symp. Jpn.*, 2B20 (1998), pp.165-166, The Electrochemical Society of Japan.
- (15) Murata, H., Hatanaka, T., Morimoto, Y. and Kawahara, K., "Influences of Fuel Composition on the Anode Electrode Performance for a Polymer Electrolyte Fuel Cell" (in Japanese), *43rd Battery Symp. Jpn.*, 2D08 (2002), pp. 540-541, The Electrochemical Society of Japan.
- (16) Hiroshima, K., Nonaka, T., Asaoka, T. and Morimoto, Y., "XAFS Study of Heat-treated Cobalt Tetraphenylporphyrin Supported on Active Carbon", *ECS Transactions*, Vol. 3, No. 1 (2006), pp. 249-254.
- (17) Asaoka, T., Hiroshima, K. and Morimoto, Y., "Pt Alloy Catalysts for Use with PEFC Cathodes", *R&D Review of Toyota CRDL*, Vol. 40, No. 4 (2005), pp. 33-39.
- (18) Jinnouchi, R., Kodama, K., Hatanaka, T. and Morimoto, Y., "Intermediate Coverage in Oxygen Reduction Reaction by First Principles-based Mean Field Model", *220th ECS Meeting*, Abstract No. 854 (2011), The Electrochemical Society.
- (19) Toyoda, E., Jinnouchi, R., Hatanaka, T., Morimoto, Y.,

- Mitsuhara K., Visikovskiy, A. and Kido, Y., "The d-band Structure of Pt Nanoclusters Correlated with the Catalytic Activity for an Oxygen Reduction Reaction", *J. Phys. Chem. C*, Vol. 115 (2011), pp. 21236-21240.
- (20) Kawamura, Y. and Jinnouchi, R., "Theoretical Study of Particle Size Effect on Oxygen Reduction Reaction on Pt Catalyst", *ECS Trans.*, Vol. 50, No. 2 (2012), pp. 1321-1331.
- (21) Shinozaki, K., Yamada, H. and Morimoto, Y., "Pt Utilization Analysis at Low RH Condition", *ECS Transactions*, Vol. 33, No. 1 (2010), pp. 1217-1227.
- (22) Shinozaki, K., Yamada, H. and Morimoto, Y., "Pt Utilization Analysis Using CO Adsorption", *ECS Transactions*, Vol. 11, No. 1 (2007), pp. 497-507.
- (23) Shinozaki, K., Saeki, T., Hatanaka, T., Yamada, H. and Morimoto, Y., "Pt Utilization Analysis at Low RH Condition" (in Japanese), *50th Battery Symp. Jpn.*, 2E16 (2009), p. 349, The Electrochemical Society of Japan.
- (24) Shinozaki, K., Yamada, H. and Morimoto, Y., "Relative Humidity Dependence of Pt Utilization in Polymer Electrolyte Fuel Cell Electrodes: Effects of Electrode Thickness, Ionomer-to-carbon Ratio, Ionomer Equivalent Weight, and Carbon Support", *J. Electrochem. Soc.*, Vol. 158, No. 5 (2011), pp. B467-B475.
- (25) Suzuki, T., Murata, H., Hatanaka, T. and Morimoto, Y., "Analysis of the Catalyst Layer of Polymer Electrolyte Fuel Cells", *R&D Review of Toyota CRDL*, Vol. 39, No. 3 (2004), pp. 33-38.
- (26) Munekata, T., Tomiyasu, J., Suzuki, T., Ida, A., Yamakawa, S., Asahi, R., Fujiuchi, M. and Morimoto, Y., "Simulation of Catalyst Layer Formation", *224th ECS Meeting*, Abstract No. 1253 (2001), The Electrochemical Society.
- (27) Haga, T., Asaoka, T., Kawahara, K. and Abe, K., "Influence of Electrode Structure on the Performance of PEFC" (in Japanese), *35th Battery Symp. Jpn.*, 3D17 (1994), pp. 295-296, The Electrochemical Society of Japan.
- (28) Hatanaka, T., Nakanishi, H., Mastumoto, S. and Morimoto, Y., "PEFC Electrodes Based on Vertically Oriented Carbon Nanotubes", *ECS Trans.*, Vol. 3, No. 1 (2006), pp. 277-284.
- (29) Kudo, K. and Morimoto, Y., "Analysis of Oxygen Transport Resistance of Nafion Thin Film on Pt Electrode", *ECS Trans.*, Vol. 50, No. 2 (2012), pp. 1487-1494.
- (30) Kudo, K., Suzuki, T. and Morimoto, Y., "Analysis of Oxygen Dissolution Rate from Gas Phase into Nafion Surface and Development of an Agglomerate Model", *ECS Trans.*, Vol. 33, No. 1 (2010), pp. 1495-1502.
- (31) Suzuki, T., Kudo, K. and Morimoto, Y., "Model for Investigation of Oxygen Transport Limitation in a Polymer Electrolyte Fuel Cell", *J. of Power Sources*, Vol. 222 (2013), pp. 379-389.
- (32) Nagai, T., Murata, H. and Morimoto, Y., "Analysis of the Relation between Oxidation State and ORR Activity of Pt by Linear Sweep Voltammetry", *ECS Trans.*, Vol. 33, No. 1 (2010), pp. 125-130.
- (33) Takeshita, T., Murata, H., Hatanaka, T. and Morimoto, Y., "Analysis of Pt Catalyst Degradation of a PEFC Cathode by TEM Observation and Macro Model Simulation", *ECS Trans.*, Vol. 16, No. 2 (2008), pp. 367-373.
- (34) Nagai, T., Murata, H. and Morimoto, Y., "Influence of Experimental Conditions on the Catalyst Degradation in the Durability Test", *J. Electrochem. Soc.*, Vol. 161, No. 6 (2014), pp. F789-F794.
- (35) Yamakawa, S., Murata, H., Takeshita, T., Hatanaka, T., Morimoto, Y. and Hyodo, S., "Numerical Simulation of Pt Surface Area Loss in PEFC Cathode" (in Japanese), *50th Battery Symp. Jpn.*, 2F01 (2009), p. 412, The Electrochemical Society of Japan.
- (36) Takeshita, T., Murata, H., Hatanaka, T. and Morimoto, Y., "Analysis of Pt Catalyst Degradation of a PEFC Cathode by TEM Observation and 1D Macro Model Simulation" (in Japanese), *49th Battery Symp. Jpn.*, 1A09 (2008), p. 6, The Electrochemical Society of Japan.
- (37) Jinnouchi, J., Kodama, K., Hatanaka, T. and Morimoto, Y., "Surface Oxide and Its Effects on Oxygen Reduction Reaction on Pt Nano-particle" (in Japanese), *53rd Battery Symp. Jpn.*, 1F09 (2012), p. 359, The Electrochemical Society of Japan.
- (38) Jinnouchi, R., Toyoda, E., Hatanaka, T. and Morimoto, Y., "First Principles Calculations on Site-dependent Dissolution Potentials of Supported and Unsupported Pt Particles", *J. Phys. Chem. C*, Vol. 114 (2010), pp. 17557-17568.
- (39) Takeshita, T., Miura, F. and Morimoto, Y., "Analysis of Degradation Mechanisms of PEFCs", *207th ECS Meeting*, Abstract No. 1511 (2005), The Electrochemical Society.
- (40) Hatanaka, T., Takeshita, T., Murata, H., Hasegawa, N., Asano, T., Kawasumi, M. and Morimoto, Y., "Electrode and Membrane Durability Issues of PEFCs", *ECS Transactions*, Vol. 16, No. 2 (2008), pp. 1961-1965.
- (41) Takeshita, T., Miura, F. and Morimoto, Y., "Analysis of Degradation Mechanisms of Fuel Cells" (in Japanese), *45th Battery Symp. Jpn.*, 1A03 (2004), pp. 4-5, The Electrochemical Society of Japan.
- (42) Kamiya, A., Hasegawa, N., Taniguchi, T., Morimoto, Y., Kawasumi, M. and Kawahara, K., "Improvement Durability of PEM for Fuel Cell by Introducing Phosphonic Acid Group" (in Japanese), *45th Battery Symp. Jpn.*, 3E15 (2004), pp. 680-681, The Electrochemical Society of Japan.
- (43) Kodama, K., Miura, F., Hasegawa, N., Kawasumi, M. and Morimoto, Y., "Degradation of Nafion Membranes in Hydrogen Peroxide", *208th ECS Meeting*, Abstract

- No. 1185 (2005), The Electrochemical Society.
- (44) Hasegawa, N., Asano, T., Hatanaka, T., Kawasumi, M. and Morimoto, Y., "Degradation of Perfluorinated Membranes Having Intentionally Formed Pt-band", *ECS Trans.*, Vol. 16, No. 2 (2008), pp. 1712-1716.
- (45) Tada, M., Murata, S., Asaoka, T., Hiroshima, K., Okumura, K., Tanida, H., Uruga, T., Nakanishi, H., Matsumoto, S., Inada, Y., Nomura, M. and Iwasawa, Y., "In Situ Time-resolved Dynamic Surface Events on the Pt/C Cathode in a Fuel Cell under Operando Conditions", *Angewandte Chemie Int. Ed.*, Vol. 46 (2007), pp. 4310-4315.
- (46) Miwa, K., Takagi, S., Matsuo, M. and Orimo, S., "Thermodynamical Stability of Complex Transition Metal Hydrides  $M_2FeH_6$ ", *J. Phys. Chem. C*, Vol. 117 (2013), pp. 8014-8019.
- (47) Aoki, M., Saito, K. and Towata, S., "Hydrogen Absorption Kinetics and Structural Properties of  $Mg_{85}Ni_{10}Ca_5$  and  $Mg_{90}Ni_{10}$ ", *J. Alloys and Compd.*, Vol. 386 (2005), pp. 217-221.
- (48) Towata, S., Noritake, T., Itoh, A., Aoki, M. and Miwa, K., "Cycle Durability of Ti-Cr-V Alloys Partially Substituted by Nb or Fe", *J. Alloys and Compd.*, Vol. 580 (2013), pp. S226-S228.
- (49) Towata, S., Noritake, T., Itoh, A., Aoki, M. and Miwa, K., "Effect of Partial Niobium and Iron Substitution on Short-term Cycle Durability of Hydrogen Storage Ti-Cr-V Alloys", *Int. J. Hydrogen Energy*, Vol. 38 (2013) pp. 3024-3029.
- (50) Aoki, M., Noritake, T., Itoh, A., Ishikiriyama, M. and Towata, S., "Improvement of Cyclic Durability of Ti-Cr-V Alloy by Fe Substitution", *Int. J. Hydrogen Energy*, Vol. 36 (2011), pp. 12329-12332.
- (51) Miwa, K., Noritake, T., Towata, S. and Aoki, M., "Evaluation of Stability of Hydrogen in Alloys Using Energy Density Formalism", *J. Alloys and Compd.*, Vol. 580 (2013), pp. S125-S126.
- (52) Kamazawa, K., Aoki, M., Noritake, T., Miwa, K., Sugiyama, J., Towata, S., Ishikiriyama, M., Callear, S., Jones, M. and David, W., "In-operando Neutron Diffraction Studies of Transition Metal Hydrogen Storage Materials", *Adv. Energy Mater.*, Vol. 3 (2013), pp. 39-42.
- (53) Noritake, T., Aoki, M., Towata, S., Seno, Y., Hirose, Y., Nishibori, E., Takata, M. and Sakata, M., "Chemical Bonding of Hydrogen in  $MgH_2$ ", *Appl. Phys. Lett.*, Vol. 81, No. 11 (2002), pp. 2008-2010.
- (54) Isoub, V., Matsunaga, T., Tange, K., Ishikiriyama, M. and Miwa, K., "Synthesis of the Hydride Mixtures  $(1-x)AlH_3/xMgH_2$  ( $0 \leq x \leq 0.3$ ) by Ball Milling and Their Hydrogen Storage Properties", *J. Alloys and Compd.*, Vol. 484 (2009), pp. 426-430.
- (55) Kojima, Y., "Nano-composite Materials for Hydrogen Storage", *R&D Review of Toyota CRDL*, Vol. 41, No. 1 (2006), pp. 44-50.
- (56) Noritake, T., Towata, S., Aoki, M., Seno, Y., Hirose, Y., Nishibori, E., Tanaka, M. and Sakata, M., "Charge Density Measurement in  $MgH_2$  by Synchrotron X-ray Diffraction", *J. Alloys and Compd.*, Vol. 356-357 (2003), pp. 84-86.
- (57) Noritake, T., Aoki, M., Towata, S., Seno, Y. and Hirose, Y., "Charge Density Analysis in Magnesium Hydride", *R&D Review of Toyota CRDL*, Vol. 38, No. 2 (2003), pp. 15-21.
- (58) Kojima, Y., Kawai, Y. and Haga, T., "Magnesium-based Nano-composite Materials for Hydrogen Storage", *J. Alloys and Compd.*, Vol. 424 (2006), pp.294-298.
- (59) Aoki, M., Ohba, N., Noritake, T. and Towata, S., "Reversible Hydriding and Dehydriding Properties of CaSi: Potential of Metal Silicides for Hydrogen Storage", *Appl. Phys. Lett.*, Vol. 85, No. 3 (2004), pp. 387-388.
- (60) Ohba, N., Aoki, M., Noritake, T., Miwa, K. and Towata, S., "Development of New Hydrogen Storage Material CaSi: Theoretical Prediction and Experiment", *R&D Review of Toyota CRDL*, Vol. 39, No. 4 (2004), pp. 40-45.
- (61) Ohba, N., Aoki, M., Noritake, T., Miwa, K. and Towata, S., "First-principles Study of a Hydrogen Storage Material CaSi", *Phys. Rev. B*, Vol. 72, No. 075104 (2005), pp. 1-6.
- (62) Aoki, M., Ohba, N., Noritake, T. and Towata, S., "Hydriding and Dehydriding Properties of CaSi", *J. Alloys and Compd.*, Vol. 404-406 (2005), pp. 402-404.
- (63) Miyoshi, M., Kinoshita, K., Tanaka, K., Aoki, M., Ohba, N., Miwa, K., Noritake, T. and Towata, S., "Hydriding and Dehydriding Properties of Ca-Si-X" (in Japanese), *Toyota Ind. Tech. Rev.*, No. 53 (2007), pp. 42-45.
- (64) Miyoshi, M., Kinoshita, K., Aoki, M., Ohba, N., Miwa, K., Noritake, T. and Towata, S., "Hydriding and Dehydriding Properties of Ca-Si-X", *J. Alloys and Compd.*, Vol. 446-447 (2007), pp. 15-18.
- (65) Li, H.-W., Orimo, S., Nakamori, Y., Miwa, K., Ohba, N., Towata, S. and Züttel, A., "Materials Designing of Metal Borohydrides: Viewpoints from Thermodynamical Stabilities", *J. Alloys and Compd.*, Vol. 446-447 (2007), pp. 315-318.
- (66) Nakamori, Y., Li, H.-W., Kikuchi, K., Aoki, M., Miwa, K., Towata, S. and Orimo, S., "Thermodynamical Stabilities of Metal-borohydrides", *J. Alloys and Compd.*, Vol. 446-447 (2007), pp. 296-300.
- (67) Towata, S., Li, H.-W. and Orimo, S., "Hydrogen Storage Using Borohydrides" (in Japanese), *Bull. of Ceram. Soc. Jpn.*, Vol. 46, No. 3 (2011), pp.183-186.
- (68) Miwa, K., Ohba, N., Towata, S., Nakamori, Y., Züttel, A. and Orimo, S., "First-principles Study on Thermodynamical Stability of Metal Borohydrides: Aluminum Borohydride  $Al(BH_4)_3$ ", *J. Alloys and Compd.*, Vol. 446-447 (2007), pp. 310-314.
- (69) Noritake, T., Aoki, M., Matsumoto, M., Miwa, K., Towata, S., Li, H.-W. and Orimo, S., "Crystal Structure and Charge Density Analysis of  $Ca(BH_4)_2$ ",

- J. Alloys and Compd.*, Vol. 491 (2010), pp. 57-62.
- (70) Miwa, K., Ohba, N., Towata, S., Nakamori, Y. and Orimo, S., "First-principles Study on Copper-substituted Lithium Borohydride,  $(\text{Li}_{1-x}\text{Cu}_x)\text{BH}_4$ ", *J. Alloys and Compd.*, Vol. 404-406 (2005), pp. 140-143
- (71) Aoki, M., Miwa, K., Noritake, T., Ohba, N., Matsumoto, M., Li, H.-W., Nakamori, Y., Towata, S. and Orimo, S., "Structural and Dehydrogenation Properties of  $\text{Ca}(\text{BH}_4)_2$ ", *Appl. Phys. A*, Vol. 92 (2008), pp. 601-605.
- (72) Aoki, M., Miwa, K., Noritake, T., Li, H.-W. and Orimo, S., "Thermodynamical Stability and Dehydrogenation Property of Calcium Borohydride  $\text{Ca}(\text{BH}_4)_2$ ", *R&D Review of Toyota CRDL*, Vol. 44, No. 4 (2013), pp. 43-51.
- (73) Orimo, S., Nakamori, Y., Kitahara, G., Miwa, K., Ohba, N., Towata, S. and Züttel, A., "Dehydrogenation and Rehydrogenation Reactions of  $\text{LiBH}_4$ ", *J. Alloys and Compd.*, No. 404-406 (2005), pp. 427-430.
- (74) Orimo, S., Nakamori, Y., Ohba, N., Miwa, K., Aoki, M., Towata, S. and Züttel, A., "Experimental Studies on Intermediate Compound of  $\text{LiBH}_4$ ", *Appl. Phys. Lett.*, Vol. 89 (2006), 021920.
- (75) Li, H.-W., Kikuchi, K., Nakamori, Y., Ohba, N., Miwa, K., Towata, S. and Orimo, S., "Dehydrogenation and Rehydrogenation Processes of Well-crystallized  $\text{Mg}(\text{BH}_4)_2$  Accompanying with Formation of Intermediate Compounds", *Acta Materialia*, Vol. 56 (2008), pp. 1342-1347.
- (76) Li, H.-W., Miwa, K., Ohba, N., Fujita, T., Sato, T., Yan, Y., Towata, S., Chen, M. W. and Orimo, S., "Formation of an Intermediate Compound with a  $\text{B}_{12}\text{H}_{12}$  Cluster: Experimental and Theoretical Studies on Magnesium Borohydride  $\text{Mg}(\text{BH}_4)_2$ ", *Nanotechnology*, Vol. 20 (2009), 204013.
- (77) Li, H.-W., Kikuchi, K., Nakamori, Y., Miwa, K., Towata, S. and Orimo, S., "Effects of Ball Milling and Additives on Dehydrogenation Behaviors of Well-crystallized  $\text{Mg}(\text{BH}_4)_2$ ", *Scripta Materialia*, Vol. 57 (2007), pp. 679-682.
- (78) Matsunaga, T., Buchter, F., Mauron, P., Bielman, M., Nakamori, Y., Orimo, S., Ohba, N., Miwa, K., Towata, S. and Züttel, A., "Hydrogen Storage Properties of  $\text{Mg}(\text{BH}_4)_2$ ", *J. Alloys and Compd.*, Vol. 459 (2008), pp. 583-588.
- (79) Miwa, K., Ohba, N. and Towata, S., "First-principles Study on Lithium Amide for Hydrogen Storage", *Phys. Rev. B*, Vol. 71 (2005), 195109.
- (80) Nakamori, Y., Ninomiya, A., Kitahara, G., Aoki, M., Noritake, T., Miwa, K., Kojima, Y. and Orimo, S., "Dehydrogenation Reactions of Mixed Complex Hydrides", *J. Power Sources*, Vol. 155 (2006), pp. 447-455.
- (81) Nakamori, Y., Kitahara, G., Miwa, K., Ohba, N., Noritake, T., Towata, S. and Orimo, S., "Hydrogen Storage Properties of Li-Mg-N-H Systems", *J. Alloys and Compd.*, Vol. 404-406 (2005), pp. 396-398.
- (82) Noritake, T., Miwa, K., Aoki, M., Matsumoto, M., Towata, S., Li, H.-W. and Orimo, S., "Synthesis and Crystal Structure Analysis of Complex Hydride  $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ ", *Int. J. Hydrogen Energy*, Vol. 38 (2013), pp. 6730-6735.
- (83) Noritake, T., Aoki, M., Towata, S., Ninomiya, A., Nakamori, Y. and Orimo, S., "Crystal Structure Analysis of Novel Complex Hydrides Formed by the Combination of  $\text{LiBH}_4$  and  $\text{LiNH}_2$ ", *Appl. Phys. A*, Vol. 83 (2006), pp. 277-279.
- (84) Noritake, T., Aoki, M., Matsumoto, M., Miwa, K., Towata, S., Li, H.-W. and Orimo, S., "Crystal Structure Change in the Dehydrogenation Process of the Li-Mg-N-H System", *J. Alloys and Compd.*, Vol. 509 (2011), pp. 7553-7558.
- (85) Noritake, T., Nozaki, H., Aoki, M., Towata, S., Kitahara, G., Nakamori, Y. and Orimo, S., "Crystal Structure and Charge Density Analysis of  $\text{Li}_2\text{NH}$  by Synchrotron X-ray Diffraction", *J. Alloys and Compd.*, Vol. 393 (2005), pp. 264-268.
- (86) Kojima, Y. and Kawai, Y., "IR Characterization of Lithium Imide and Amide", *J. Alloys and Compd.*, Vol. 395 (2005), pp. 236-239.
- (87) Nakamori, Y., Kitahara, G., Miwa, K., Towata, S. and Orimo, S., "Reversible Hydrogen-storage Functions for Mixtures of  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$ ", *Appl. Phys. A*, Vol. 80 (2005), pp. 1-3.
- (88) Noritake, T., Miwa, K., Aoki, M., Matsumoto, M., Towata, S., Li, H.-W. and Orimo, S., "Dehydrogenation Properties and Crystal Structure Analysis of  $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ ", *J. Alloys and Compd.*, Vol. 580 (2013), pp. 585-589.
- (89) Aoki, M., Noritake, T., Kitahara, G., Nakamori, Y., Towata, S. and Orimo, S., "Dehydrogenation Reaction of  $\text{Mg}(\text{NH}_2)_2$ -LiH System under Hydrogen Pressure", *J. Alloys and Compd.*, Vol. 428 (2007), pp. 307-311.
- (90) Kojima, Y., Kawai, Y., Haga, T., Matsumoto, M. and Koiwai, A., "Direct Formation of  $\text{LiAlH}_4$  by a Mechanochemical Reaction", *J. Alloys and Compd.*, Vol. 441 (2007), pp. 189-191.
- (91) Kojima, Y., Kawai, Y., Matsumoto, M. and Haga, T., "Hydrogen Release of Catalyzed Lithium Aluminum Hydride by a Mechanochemical Reaction", *J. Alloys and Compd.*, Vol. 462 (2008), pp. 275-278.
- (92) Orimo, S., Nakamori, Y., Kitahara, G., Miwa, K., Ohba, N., Noritake, T. and Towata, S., "Destabilization and Enhanced Dehydrogenation Reaction of  $\text{LiNH}_2$ : an Electronic Structure Viewpoint", *Appl. Phys. A*, Vol. 79 (2004), pp. 1765-1767.
- (93) Matsumoto, M., Haga, T., Kawai, Y. and Kojima, Y., "Hydrogen Desorption Reactions of Li-N-H Hydrogen Storage System: Estimation of Activation Free Energy", *J. Alloys and Compd.*, Vol. 439 (2007), pp. 358-362.
- (94) Kojima, Y., Kawai, Y. and Ohba, N., "Hydrogen Storage of Metal Nitride by a Mechanochemical Reaction", *J. Power Sources*, Vol. 159 (2006), pp. 81-87.

- (95) Aoki, M., Miwa, K., Noritake, T., Kitahara, G., Nakamori, Y., Orinmo, S. and Towata, S., "Destabilization of  $\text{LiBH}_4$  by Mixing with  $\text{LiNH}_2$ ", *Appl. Phys. A*, Vol. 80 (2005), pp. 1409-1412.
- (96) Kojima, Y., Kawai, Y., Towata, S., Matsunaga, T., Shinozawa, T. and Kimbara, M., "Development of Metal Hydride with High Dissociation Pressure", *J. Alloys and Compd.*, Vol. 419 (2006), pp. 256-261.
- (97) Mori, D., Kobayashi, N., Matsunaga, T., Toh, K. and Kojima, Y., "High-pressure MH Tank" (in Japanese), *Materia Jpn.*, Vol. 46, No. 3 (2005), pp. 257-259.
- (98) Miwa, K. and Ohba, N., "First-principles Study on Hydrogen Storage Materials" (in Japanese), *Materia Jpn.*, Vol. 46, No. 8 (2007), pp. 515-521.
- (99) Tanaka, H., Tokoyoda, K., Matsumoto, M., Suzuki, Y., Kiyobayashi, T. and Kuriyama, N., "Hazard Assessment of Complex Hydrides as Hydrogen Storage Materials", *Int. J. Hydrogen Energy*, Vol. 34 (2009), pp. 3210-3218.
- (100) Tanaka, H., Tokoyoda, K., Matsumoto, M., Kiyobayashi, T. and Kuriyama, N., "Biological Impact Tests on Complex Hydrides Used as Hydrogen Storage Materials", *Int. J. Hydrogen Energy*, Vol. 35 (2010), pp. 11009-11015.
- (101) Kojima, Y., Kawai, Y., Koiwai, A., Suzuki, N., Haga, T., Hioki, T. and Tange, K., "Hydrogen Adsorption and Desorption by Carbon Materials", *J. Alloys and Compd.*, Vol. 421 (2006), pp. 204-208.
- (102) Kojima, Y. and Suzuki, N., "Hydrogen Adsorption and Desorption by Potassium-doped Superactivated Carbon", *Appl. Phys. Lett.*, Vol. 84, No. 20 (2004), pp. 4113-4115.
- (103) Kojima, Y., Kawai, Y., Nakanishi, H. and Matsumoto, S., "Compressed Hydrogen Generation Using Chemical Hydride", *J. Power Sources*, Vol. 135 (2004), pp. 36-41.
- (104) Kojima, K., Suzuki, K., Fukumoto, K., Kawai, Y., Kimbara, M., Nakanishi, H. and Matsumoto, S., "Development of 10kW-scale Hydrogen Generator Using Chemical Hydride", *J. Power Sources*, Vol. 125 (2004), pp. 22-26.
- (105) Kojima, Y., Suzuki, K., Fukumoto, K., Sasaki, M., Yamamoto, T., Kawai, Y. and Hayashi, H., "Hydrogen Generation Using Sodium Borohydride Solution and Metal Catalyst Coated on Metal Oxide", *Int. J. Hydrogen Energy*, Vol. 27 (2002), pp. 1029-1034.
- (106) Kojima, Y., "Hydrogen Storage and Generation Using Sodium Borohydride", *R&D Review of Toyota CRDL*, Vol. 40, No. 2 (2005), pp. 31-36.
- (107) Kojima, Y. and Haga, T., "Recycling Process of Sodium Metaborate to Sodium Borohydride", *Int. J. Hydrogen Energy*, Vol. 28 (2003), pp. 989-993.
- (108) Kojima, Y., Kawai, Y., Kimbara, M., Nakanishi, H. and Matsumoto, S., "Hydrogen Generation by Hydrolysis Reaction of Lithium Borohydride", *Int. J. Hydrogen Energy*, Vol. 29 (2004), pp. 1213-1217.
- (109) Kojima, Y., Suzuki, K. and Kawai, Y., "Hydrogen Generation from Lithium Borohydride Solution over Nano-sized Platinum Dispersed on  $\text{LiCoO}_2$ ", *J. Power Sources*, Vol. 155 (2006), pp. 325-328.
- (110) Nagano, S., Yamamoto, S., Asano, T., Ohsawa, K. and Ogino, S., "Plate Type Methanol Steam Reformer Using New Catalytic Combustion for a Fuel Cell", *SAE Tech. Paper Ser.*, No. 2002-01-0406 (2002).
- (111) Nagano, S. and Ohsawa, K., "A Study of Plate Type Catalytic Combustor for Hydrogen/Carbon-dioxide Mixture Gas" (in Japanese), *Trans. of Jpn. Soc. Mech. Eng. B*, Vol. 76, No. 766 (2010), pp. 983-989.
- (112) Yamamoto, S., Nagano, S., Asano, T. and Ohsawa, K., "Numerical Study on Honeycomb Type Methanol Steam Reformer", *J. of Environ. and Eng.*, Vol. 3, No. 2 (2008), pp. 397-409.
- (113) Nagano, S., Miyagawa, H., Azegami, O. and Ohsawa, K., "Heat Transfer Enhancement in Methanol Steam Reforming for a Fuel Cell", *Energy Conversion and Management*, Vol. 42 (2001), pp. 1817-1829.
- (114) Shou, M., Tanaka, K., Yoshioka, K., Moro-oka, Y. and Nagano, S., "New Catalyst for Selective Oxidation of CO in Excess  $\text{H}_2$  Designing of the Active Catalyst Having Different Optimum Temperature", *Catalysis Today*, Vol. 90 (2004), pp. 255-261.
- (115) Aoki, H., Mitsui, H., Shimazu, T., Kimura, K. and Masui, T., "A Numerical Study on Thermal Efficiency of Fuel Cell System Combined with Fuel Reformer", *Proc. of 16th World Hydrogen Energy Conf.*, Vol. 2 (2006), pp. 1390-1399.
- (116) Shimazu, T., Aoki, H., Wakasugi, T., Kimura, K. and Masui, T., "Highly Energy Efficiency Micro Channel Reactor for Intermediate Temperature Fuel Cell Systems", *Proc. of 16th World Hydrogen Energy Conf.*, Vol. 2 (2006), pp. 1219-1226.
- (117) Rabe, S., Vogel, F., Truog, T.-B., Shimazu, T., Wakasugi, T., Aoki, H. and Sobukawa, H., "Catalytic Reforming of Gasoline to Hydrogen: Kinetic Investigation of Deactivation Processes", *Int. J. of Hydrogen Energy*, Vol. 34 (2009), pp. 8023-8033.
- (118) TMC, "TOYOTA Global Newsroom", <<http://newsroom.toyota.co.jp/en/detail/4197769>>, (accessed 2015-07-15).

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Research Fields:

- Battery
- Fuel Cell
- Electrochemistry

