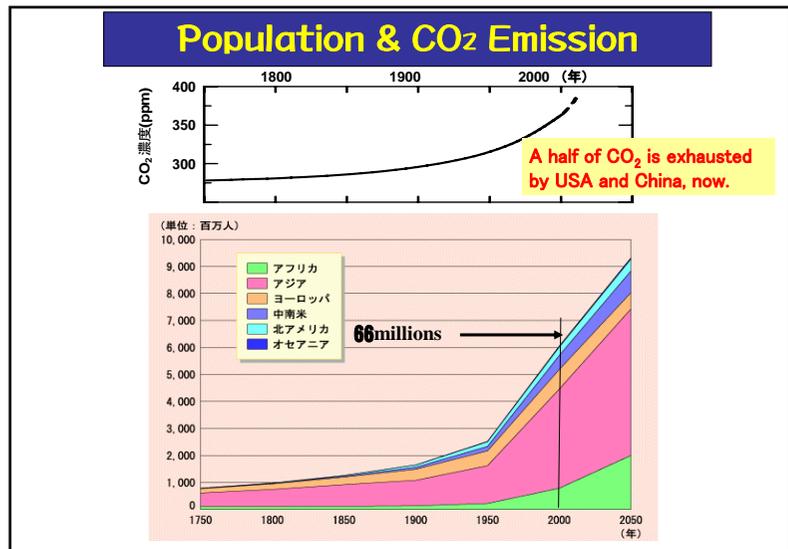
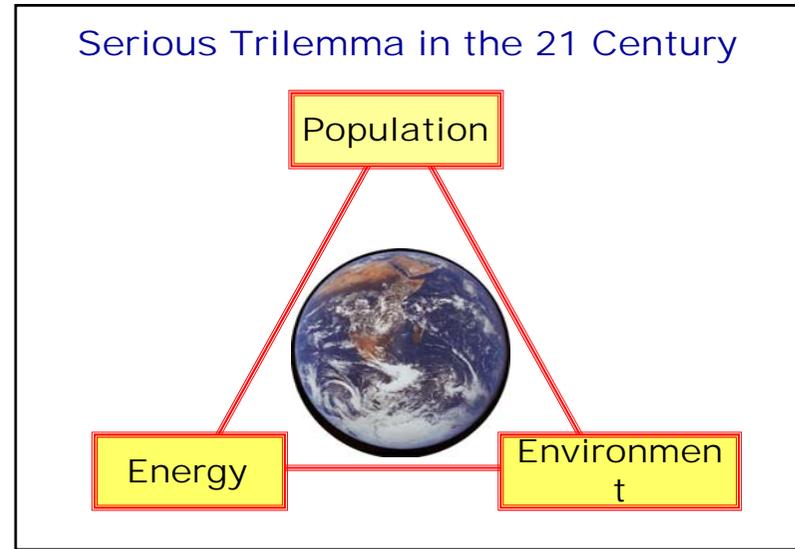


Seminar Lecture at DGIST
January 20th, 2011

Challenge to the Next Generation Fuel Cells For Low-Carbon Emission Society



Masahiro Watanabe
Fuel Cell Nanomaterials Center,
University of Yamanashi



How much amounts of pollutants are exhausted when you forget to turn-off 1kw electric system for 1h?

Air pollutants (grams/h)

CO ₂ (as Carbon)	200
NO _x	4.6
SO _x	3.0
Particulates	0.5

(Based on the electricity from the typical fire power-plant)

How do we meet to the shortage of resources and energy?

○ Saving.....be patient

Be unbearable copes;

- limit the use of electricity
- "Fan yourself" in summer
- "Put many clothes" in winter
- Inhibition of my car
- Inhibition of cell-phone

Be bearable copes;

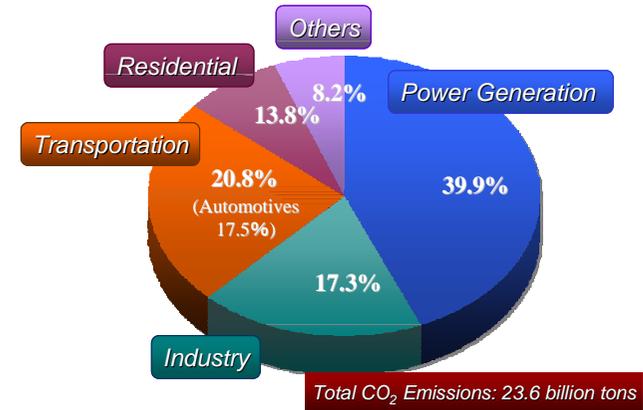
- turn off it frequently
- reasonable aircon-temp.
- walk for a short distance
- Efficient use of battery

Self-control up to some level is valuable, but impossible to come back to such an ancient life-style!

○ Some solution can be found in the scientific technology improving energy conversion efficiency, e.g., electric devices, motor vehicles, *fuel cells* and batteries

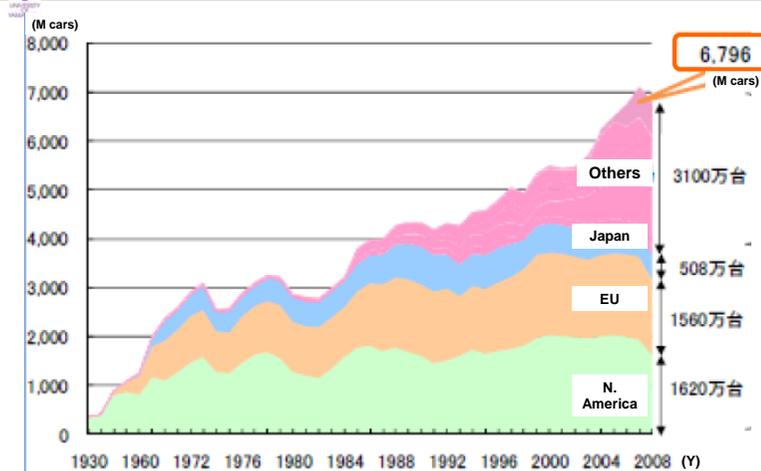
Establish the ways of energy saving & environmental protection!

Origins of the CO₂ Exhaustion



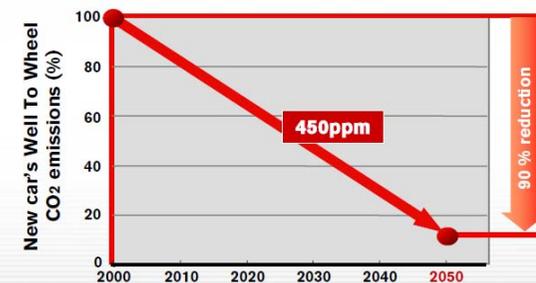
Source; IEA CO₂ EMISSIONS FROM FUEL COMBUSTION, 2004 ed. 6

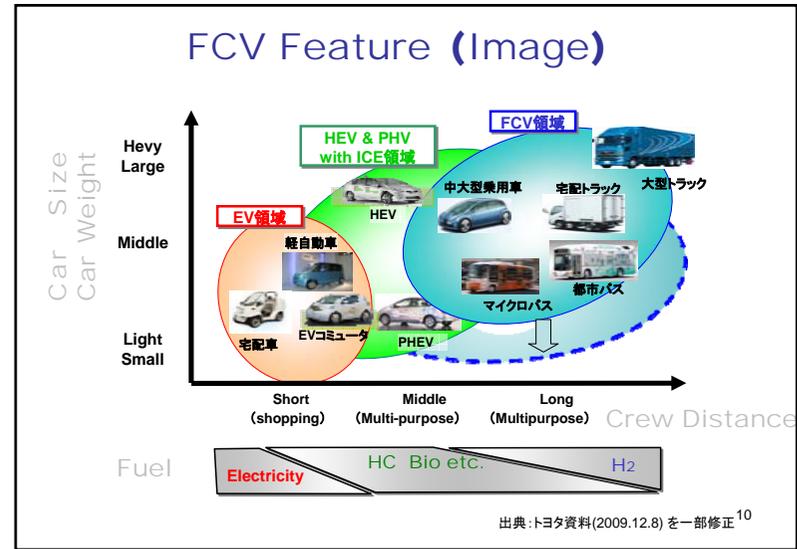
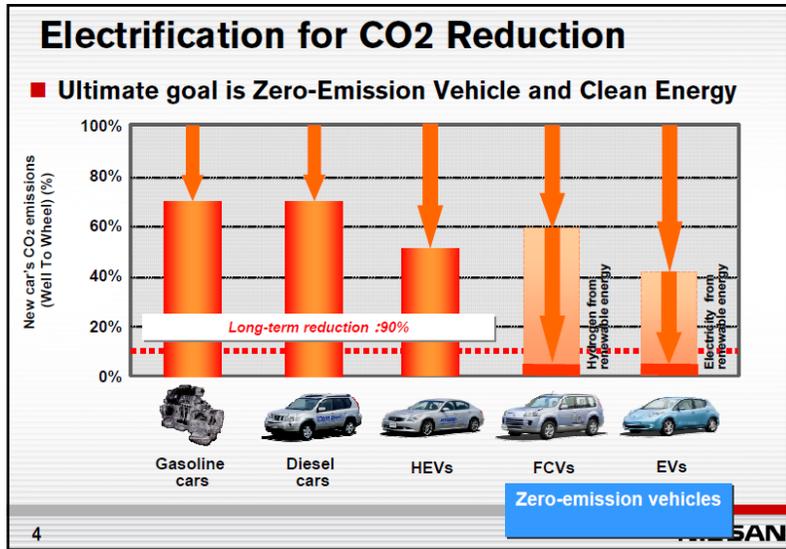
Number of ICE Cars in the world



Long term CO₂ Reduction Scenario

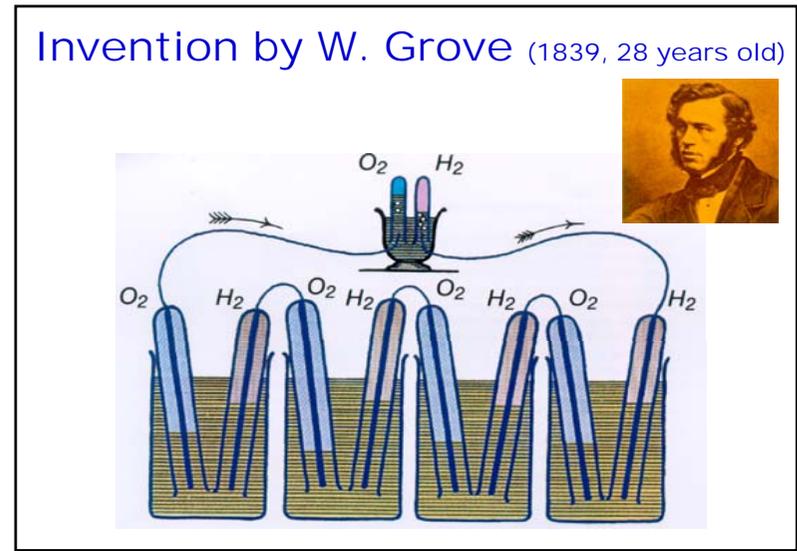
- CO₂ concentration level 450ppm (IPCC report)
- ⇒ CO₂ reduction at 90% (vs 2000) from all new vehicles

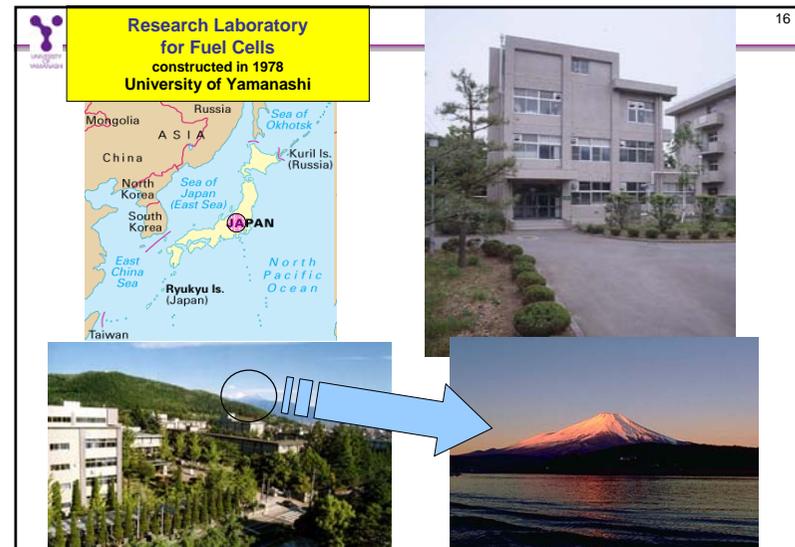
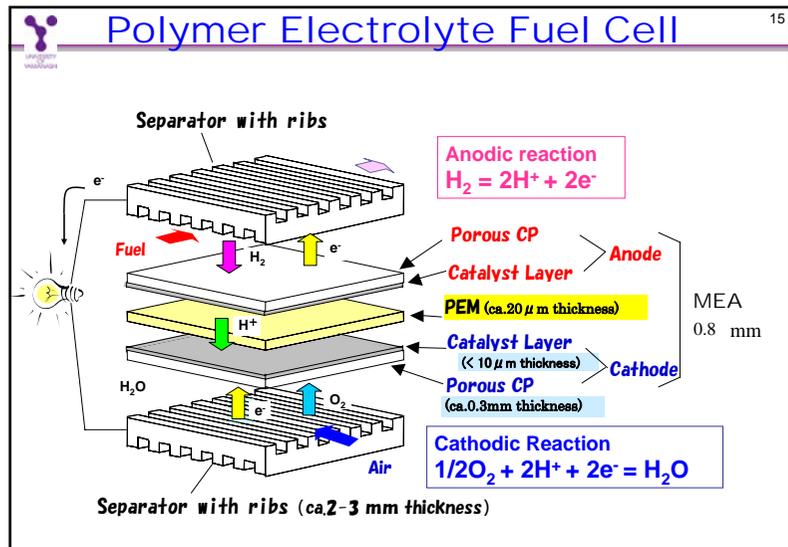
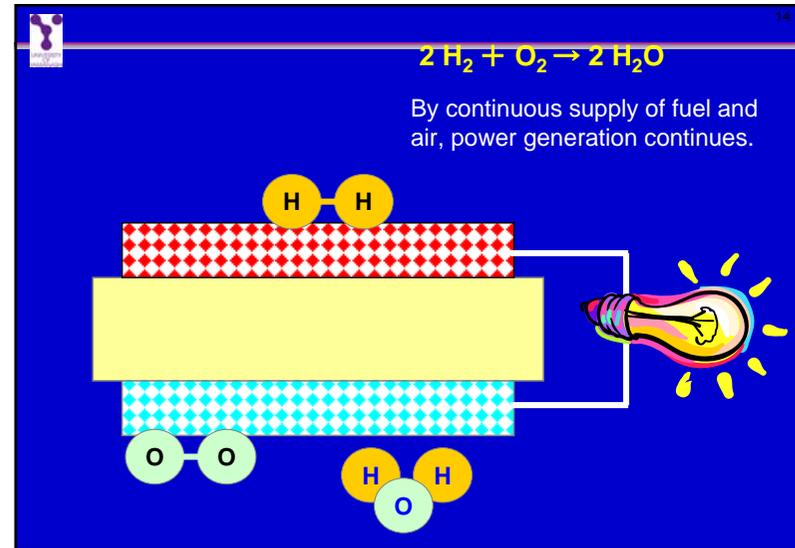
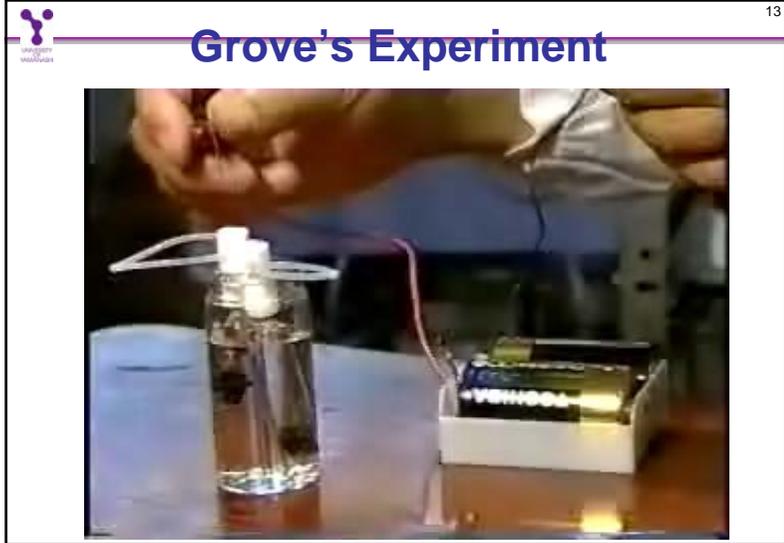




11

What is the Fuel Cells?





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Members in FC Team (April, 2010)

Position	Clean Energy Research Center	Fuel Cell Nanomaterials Center
Profs.	2	8
Associate Profs	1	4
Full Time Guest Profs	—	4
Assistant Profs	—	5
Post-Doc Researches	2	1
PhD course Students	14 (Inc. 2 engs. from FC companies)	
Mr. course Students	16	
B. Students (4 th year)	12	—
Administrative Staffs	4	10
Total	83	



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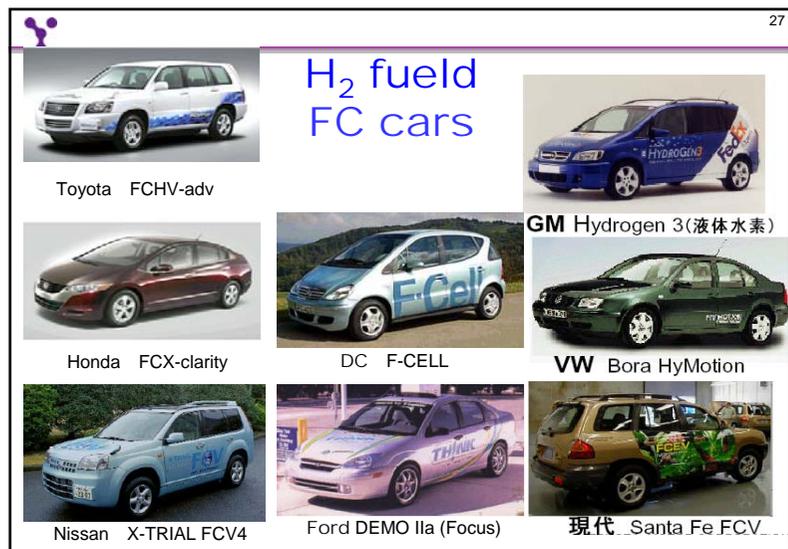
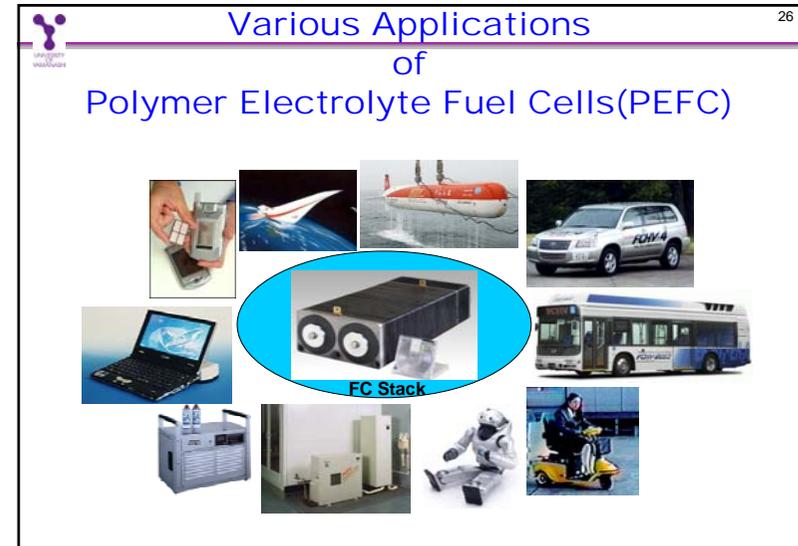
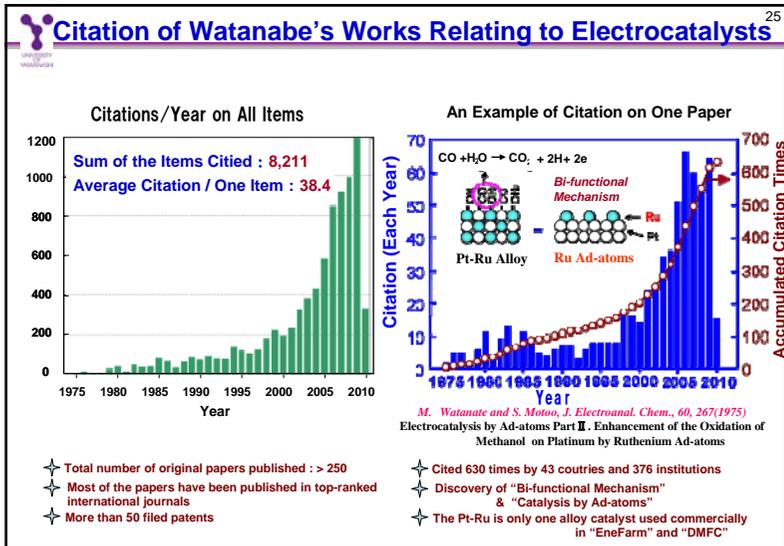
High Performance Fuel Cells

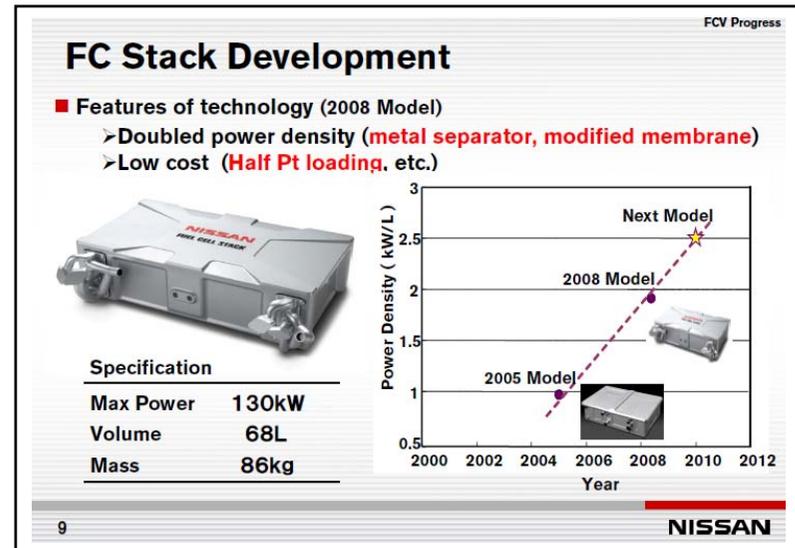
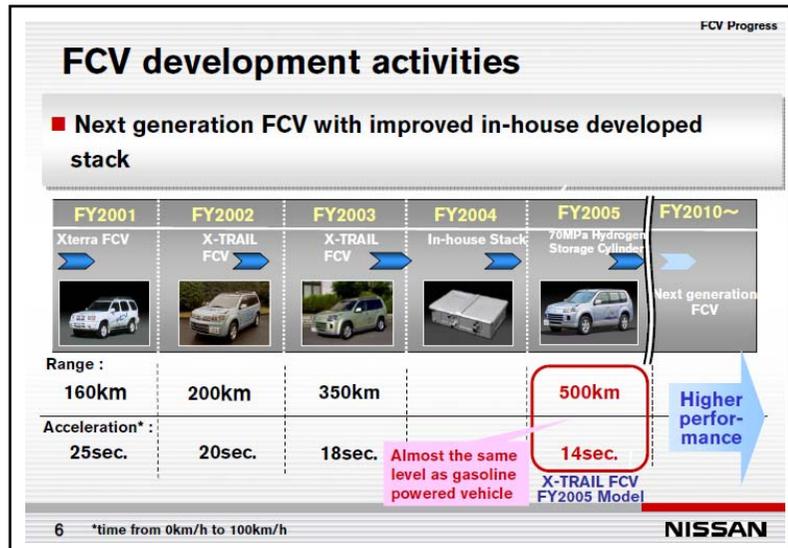
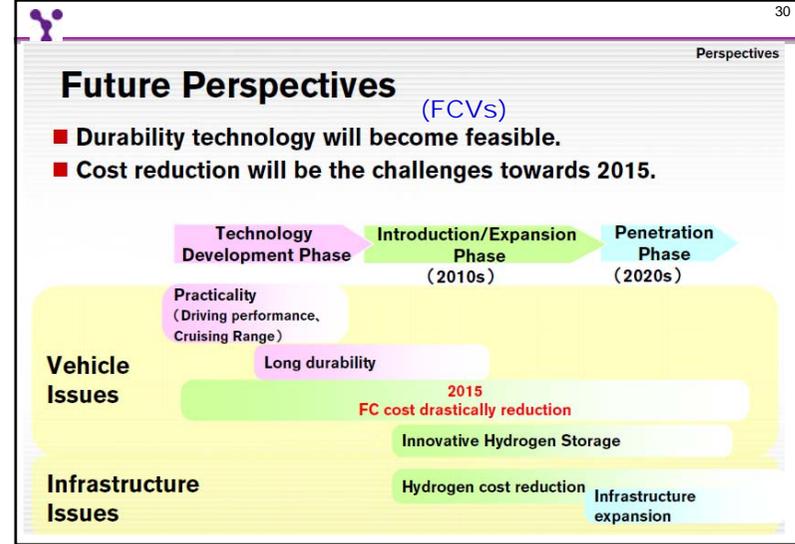
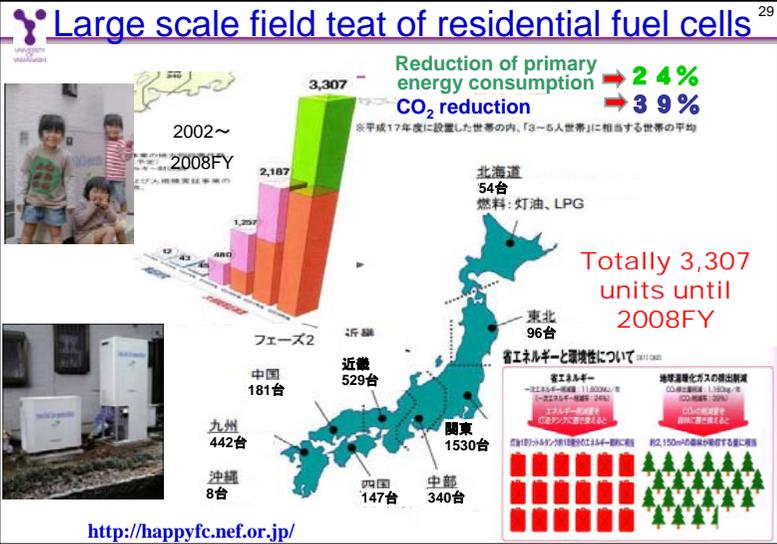
High Voltage (Efficiency)
High Current Density (Power)
Long Life

Controlling Factors

Reactants & Products	=	Boll
Electrocatalysts	=	Players
Electrode Structures	=	Formations
Electrolyte	=	Field
	&	
Promoters	=	Supporters

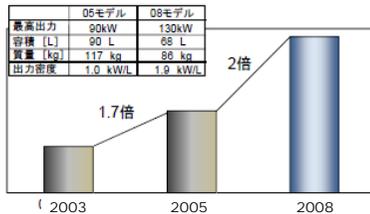
- 24
- ## Research Areas of Prof. Watanabe
- (Starting from 1969 to now)
- Total number of original papers relating to all types of **Fuel Cells** > ca. 250 papers
- A. Establishment of Ad-atom method for Electrocatalyst Design
 - B. Design, Preparation and Evaluation of Highly Dispersed Electrocatalysts
 - C. Design of New High-Performance Electrocatalysts and Their Electrocatalyses
 - D. Design of Gas-Diffusion Eelectrodes and the Applications
 - E. Design of Polymer Electrolytes for PEFCs
 - F. Design of Zeolite Supported Catalysts for H₂ Fuel Purification
 - G. Design of Solid Oxide Fuel Cells for medium Temperature Operation
 - H. Design of Electrocatalysts for CO₂ Reduction
 - I. Others



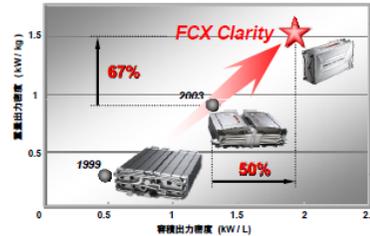


Advances in FC Technologies(1)

Noticeable improvements of the stack size & power density



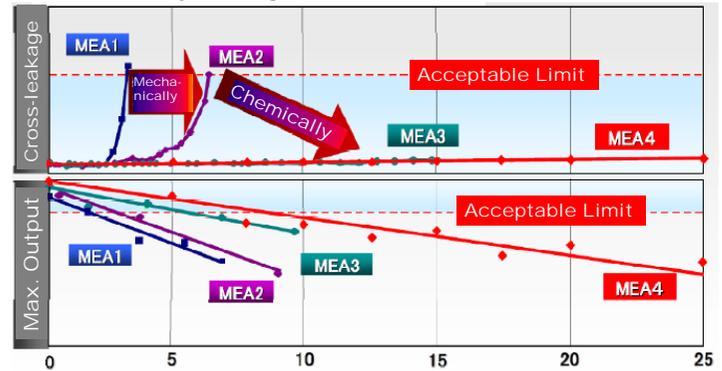
Power Density of Nissan stack
(出典:OHM 2009.1 日産における燃料電池車開発の現状)



Power Density of Honda stack
(ホンダ提供)

Advances in FC Technologies (2)

- Durability changes of MEAs



- Equivalent durable years

2009.2.26 FC-EXPO専門技術セミナー FC-7トヨタ講演資料より

FCVs tested at JHFC Program

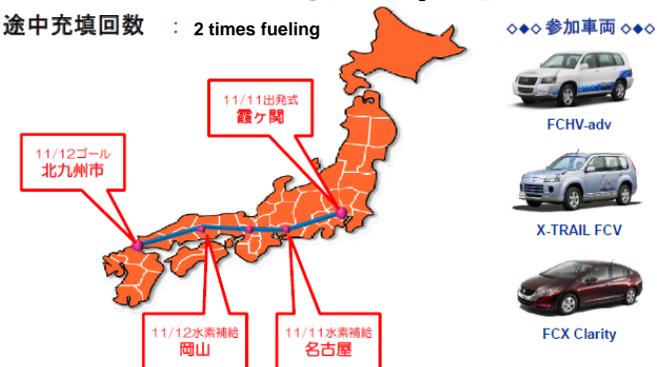
(2010年3月現在)



Long Distance Driving Test

2009.11.11~11.12

走行距離 : 1,137km
 所要時間 : 19 hs
 3車の平均燃費 : 118.4km / kg (714km / H₂ fueling)
 途中充填回数 : 2 times fueling

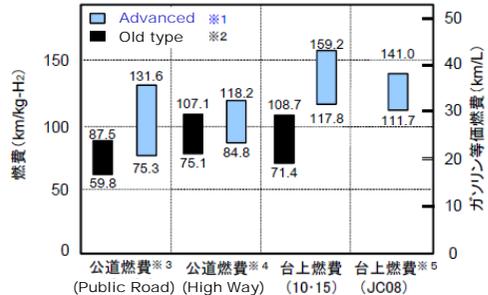


◆◆参加車両◆◆



Fuel expenses of Japanese three FCVs (On board test)

- 実証最新登録車両は一般道路、高速道路ともに燃費が着実に向上している。

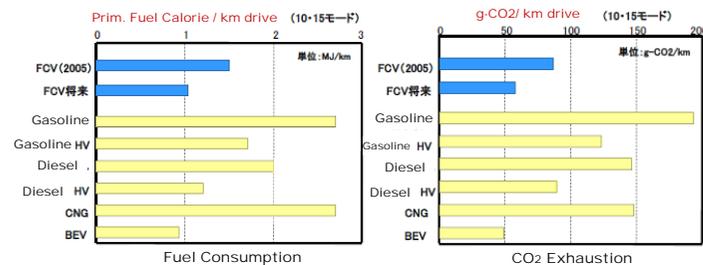


※1 実証最新登録車両: FCHV-adv, X-TRAIL FCV(2005), FCX Clarity
比較FCVの()の数字はモデルイヤー。実証初期登録車両から更新のない車種は含まない。
※2 実証初期登録車両: FCHV(2002), X-TRAIL FCV(2003), FCX(2002), A-Class F-Cell, HydroGen3, ワゴンR-FCV
※3 ※1および※2の車両の公道燃費試験における一般道路コースの区間燃費の平均値を各車種で算出し、分布を示したもの。
※4 ※1および※2の車両の公道燃費試験における高速道路コースの区間燃費の平均値を各車種で算出し、分布を示したもの。
※5 JC08による台上燃費試験は2007年からの実施のため、実証初期登録車両※2の内2車種しか実施していない。
そのため、実証初期登録車両のJC08台上燃費値はデータ不足であり表示していない。

出典:2009年度JHFCセミナー資料

Well to Wheel Based Energy Consumption & CO2 Exhaustion

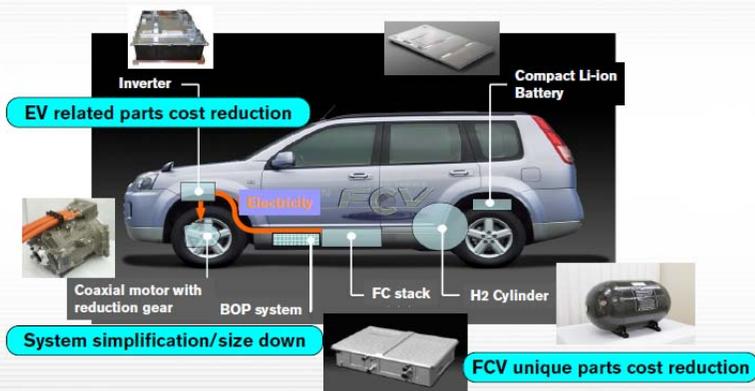
Well to Wheel分析を行なうことにより、初めて車種間のエネルギー効率やCO2排出量の比較を行うことができる。



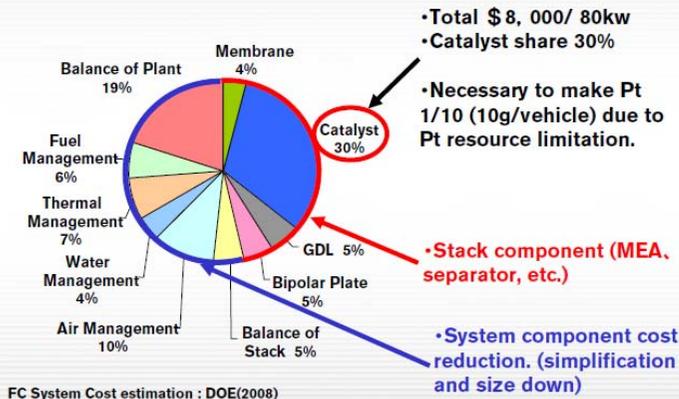
FCV(2005): JHFC1での実証トップ値を使用。水素インフラは実証トップ値(2005年段階)を使用
FCV将来: FCシステム効率を60%とし、その他は文献トップ値を使用 (FCシステム効率は車両効率とは異なる)
FCV以外の車両: 2005年の検討時のデータを使用
水素製造方法: 塩電解副生水素 (現在実現できるCO2排出が最も低いケースを採用)
電力: 日本の電源構成を使用

出典:2008年度JHFCセミナー資料

FCV cost reduction



FC system cost reduction



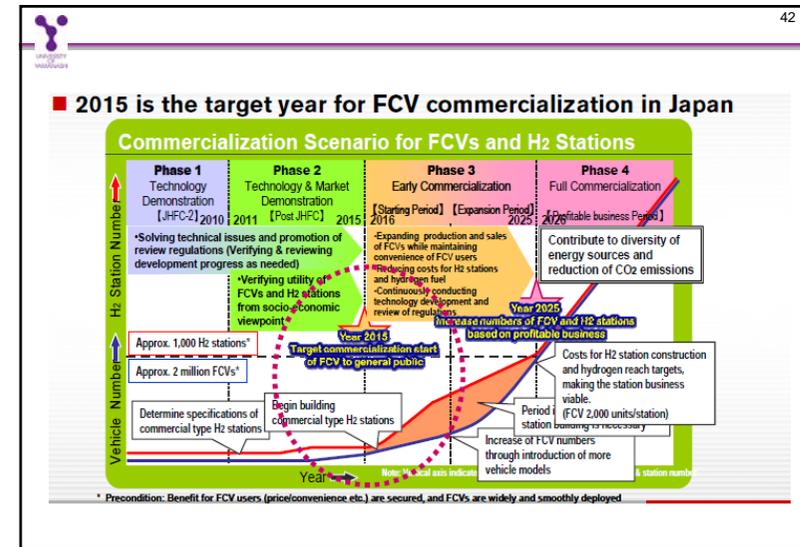
FC System Cost estimation : DOE(2008)

Cost Reduction

Stack and System cost down

MEA is the key : High power density under low Pt loading and low humidity

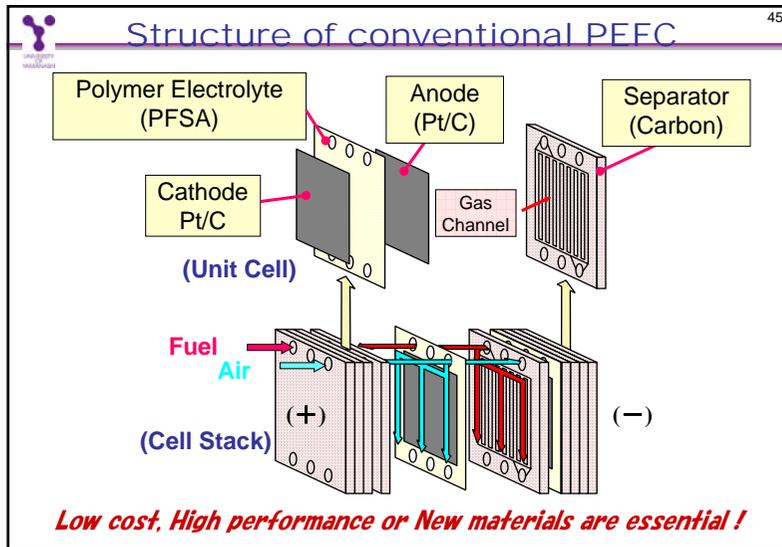
- **Enhance Catalyst activity and utilization**
 - ⇒ Specific activities
 - ⇒ Oxygen and Proton conductivity in catalyst layer
- **Higher temperature & Low/No humidification**
 - ⇒ Water management
- **Contact resistance**
 - ⇒ Separator/GDL/Catalyst layer contact resistance reduction



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Essential Problems Against the wide Application of PEFCs

- 1. Cost Reduction by**
 - Reduction of Pt loading to ca. 1/10 ←
 - Improving MEA performance with lowered Pt loading
 - Reduction of PEM cost to ca. 1/20
 - Reduction of separator cost to ca. 1/20
- 2. Reliability Improvement by**
 - Clarification of the phenomena & technical polishing relating to the degradation
- 3. Infrastructure Construction by**
 - New processes for the production of clean H₂ as well as that for clean gasoline and GTL
 - Easing official controls



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HiPer-FC Project

- Research on Nanomaterials for High Performance Fuel Cells -

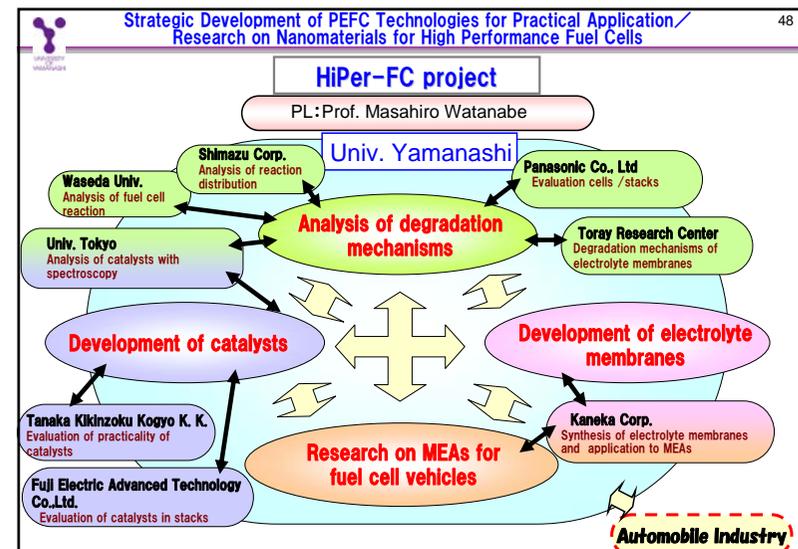
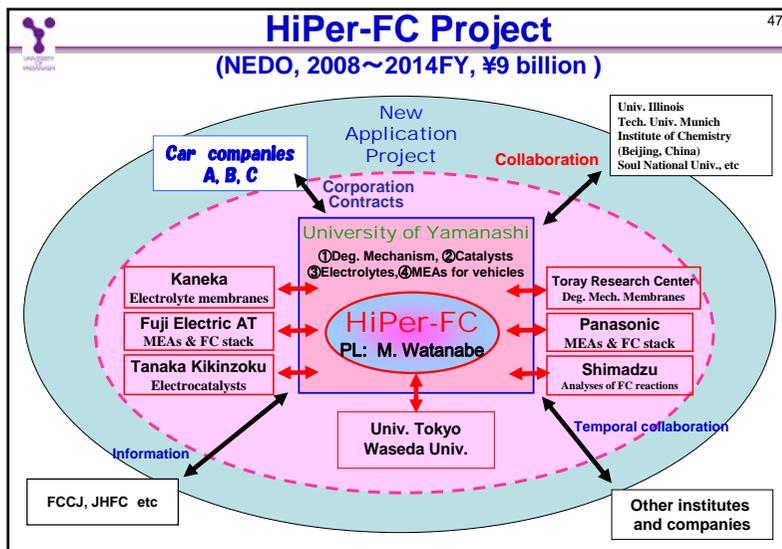
The **Fuel Cell Nanomaterials Center** was established in April, 2008. The University of Yamanashi was adopted as the lead organization for a **7-year project** by the New Energy and Industrial Technology Development Organization (NEDO) in 2008. The Center is the core institution of this huge project, and the total budget of the project is **more than US\$ 80 M.**

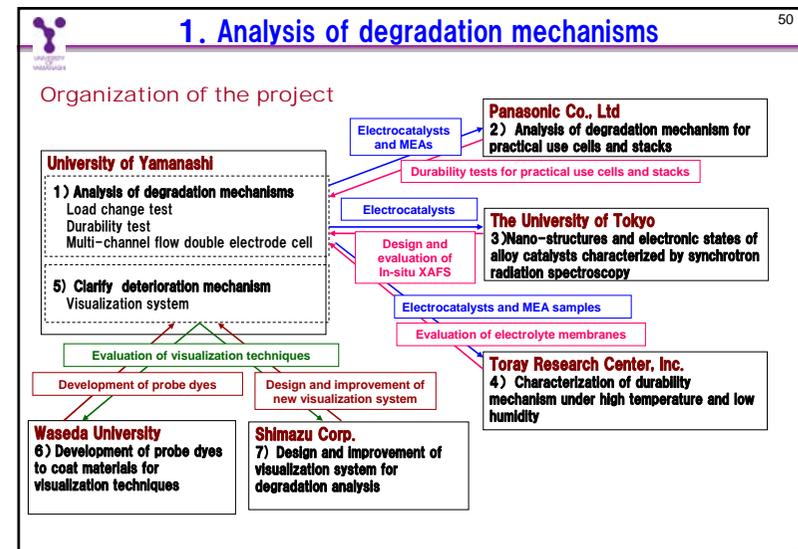
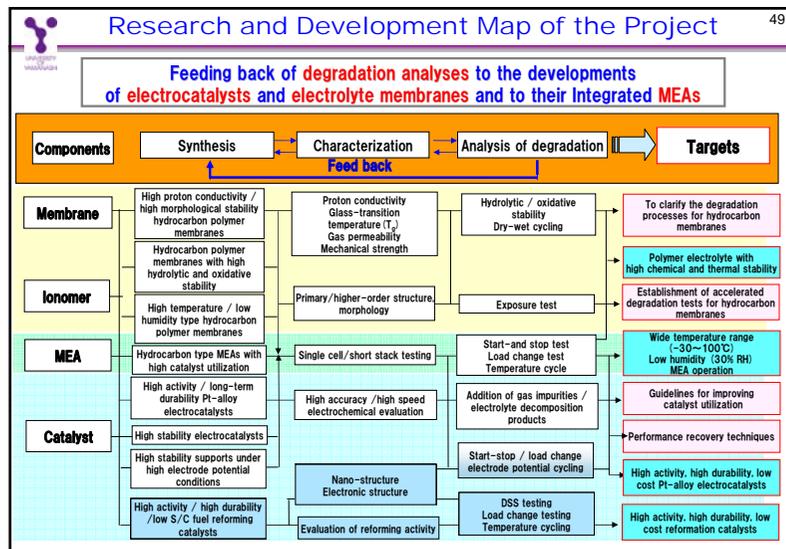
Research Items

1. Analysis of degradation mechanisms
2. Research and development of catalysts with high activity and high durability
3. Development of electrolyte membranes for operation over a wide temperature range and low humidity conditions
4. Research for high performance, high reliability MEAs for automobile use

Final Targets of the Project (FY2008~FY2014)

1. To develop MEAs that can start at -30°C and operate at temperatures up to 100 °C and a relative humidity (RH) of 30%.
2. The catalyst should be decreased to 1/10 of the conventionally used amount.
3. These materials installed in fuel cells are expected to demonstrate prospective performances, e.g. cell efficiencies up to 64% LHV (lower heating value) at 25% of the rated load and durability of 5,000 operating hours and a couple of 10,000 on-off operations.



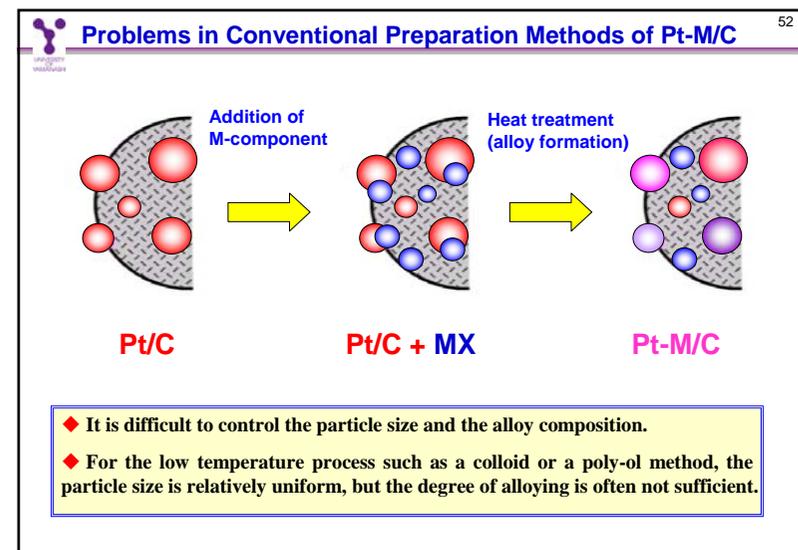


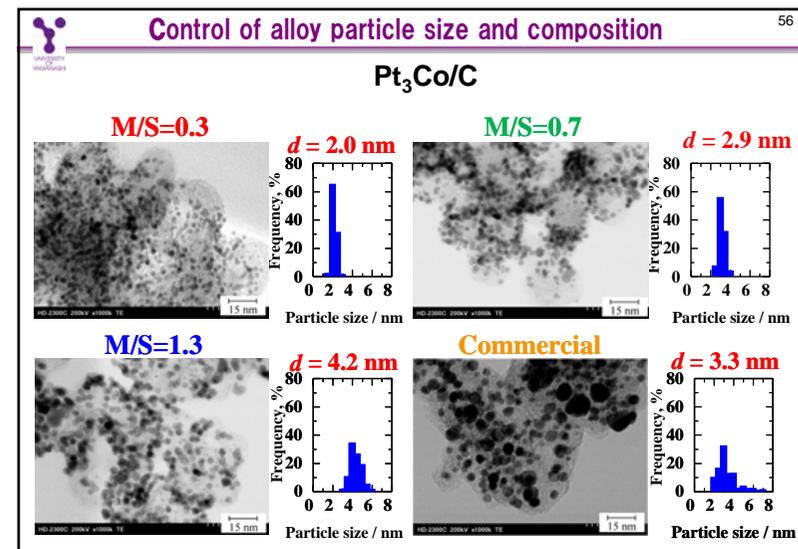
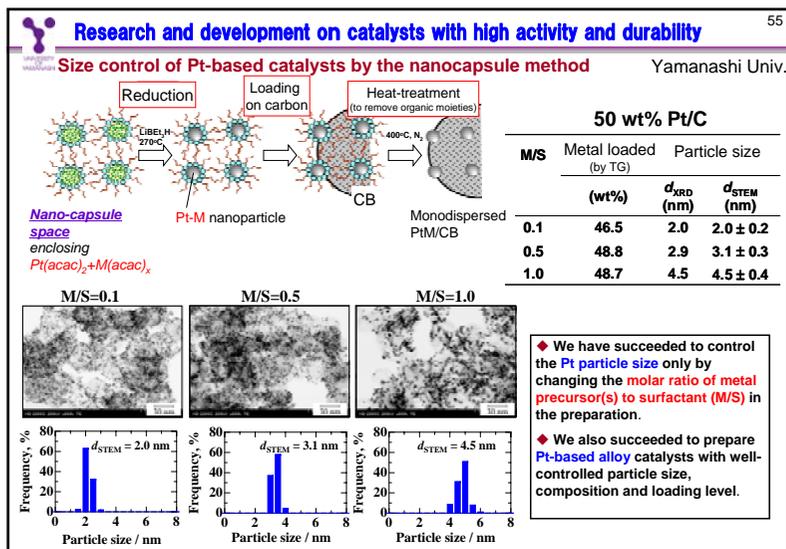
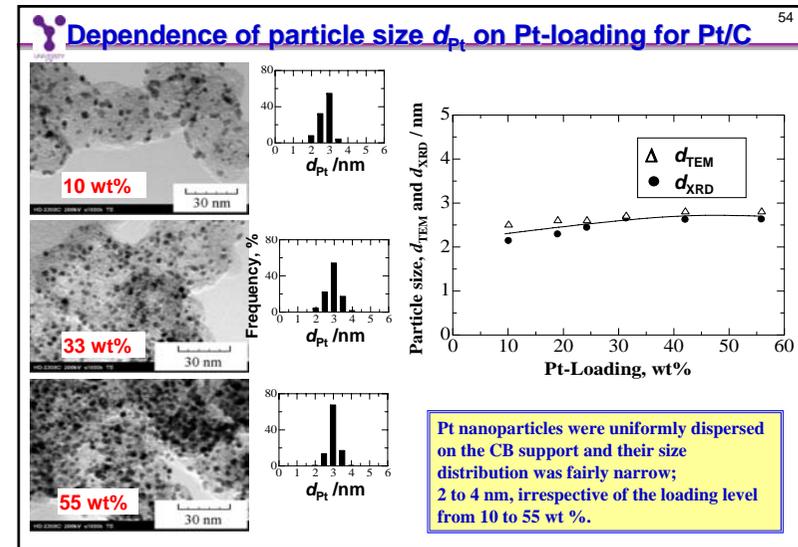
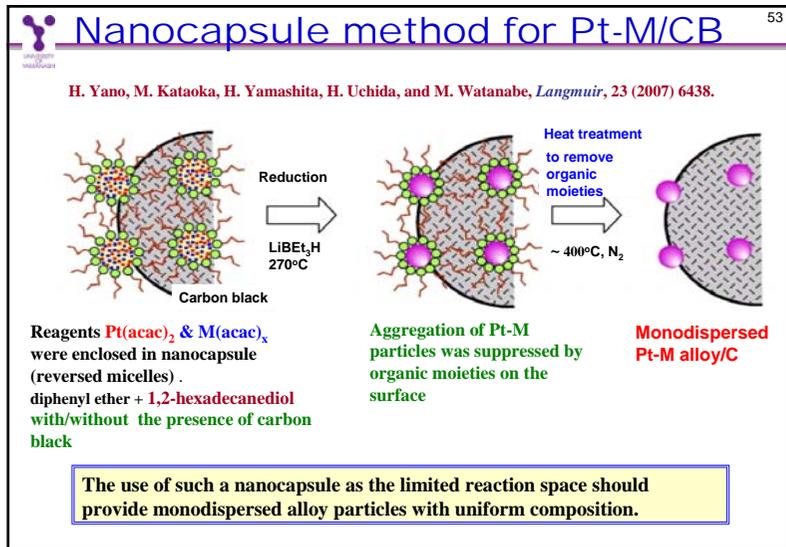
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Preparation of Highly Dispersed Catalysts by Nanocapsule Method

$$J \text{ (A} \cdot \text{g}^{-1}) = S \text{ (cm}^2 \cdot \text{g}^{-1}) \times I \text{ (A} \cdot \text{cm}^{-2})$$

Size & composition controlled catalysts





Pt₃Co/CB prepared by nanocapsule method 57

M/S ^a	Loading (TG analysis) ^b	Composition ^c		Particle size
	(wt%)	Pt (atom.%)	Co (atom.%)	<i>d</i> _{STEM} (nm)
0.3	46.0	74.2 ± 1.4	25.8 ± 1.4	2.0 ± 0.2
0.7	48.1	76.0 ± 1.3	24.0 ± 1.3	2.9 ± 0.3
1.3	50.8	76.6 ± 1.2	23.4 ± 1.2	4.2 ± 0.6
Commercial	47.7	75.7 ± 8.2	24.3 ± 8.2	3.3 ± 1.3

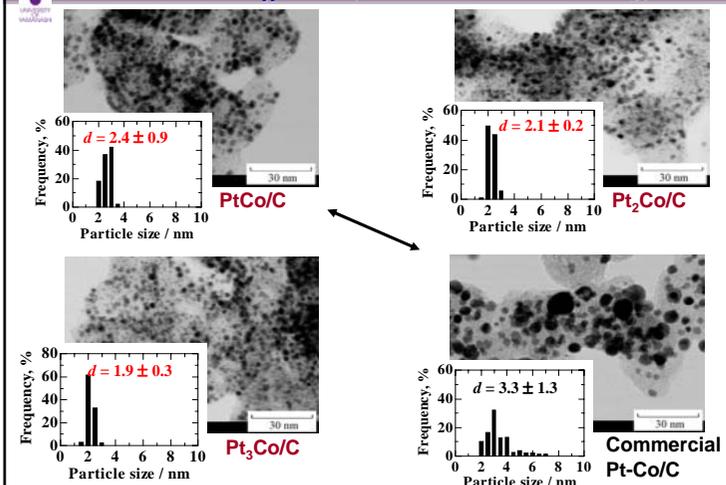
a: Mole ratio of metal salt/surfactant, Pt : Co = 3 : 1 = 75% : 25%

b: TG analysis after 600°C calcination in air; intended metallic composition was 50 wt%

c: Average composition determined by EDX for 20 particles

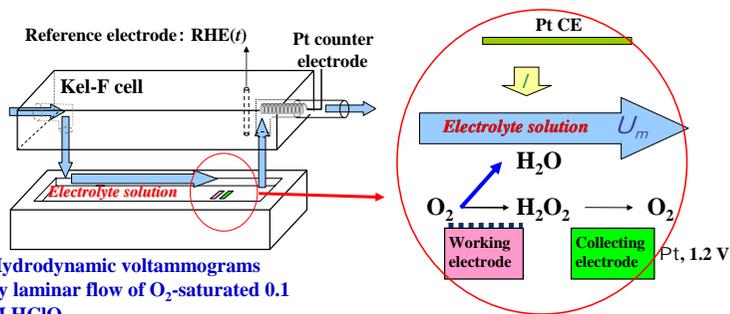
Simultaneous control of particle size, composition and loading amount.

TEM of Pt_xCo/C (50 wt% metal loading) 58



Channel flow double electrode (CFDE) method 59

j_K & P(H₂O₂), Wide temperature range (r.t. to 110°C), Closed system, Low noise



Hydrodynamic voltammograms by laminar flow of O₂-saturated 0.1 M HClO₄

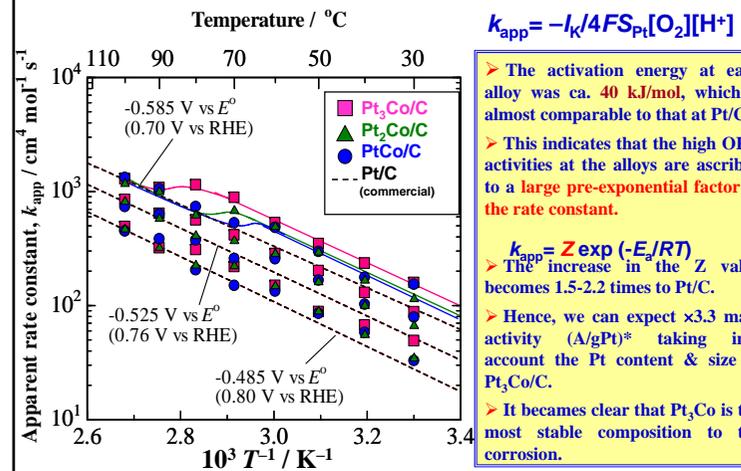
Mean flow rate *U_m* = 10 ~ 50 cm/s
Temperature = 20 ~ 110°C

J. Electroanal. Chem., 574 (2005) 339.
J. Phys. Chem. B, 109 (2005) 5836.
J. Phys. Chem. B, 110 (2006) 16544.

Working electrodes
Nafion-Pt_xCo/C on Au(subs)

$$\frac{1}{I} = \frac{1}{I_k} + \frac{U_m^{-1/3}}{1.165nF[O_2]_w(D^2x_1^2/h)^{1/3}}$$

Arrhenius Plots of ORR Rate Constants 60



$$k_{app} = -I_k / 4FS_{Pt}[O_2][H^+]$$

➤ The activation energy at each alloy was ca. 40 kJ/mol, which is almost comparable to that at Pt/C.
➤ This indicates that the high ORR activities at the alloys are ascribed to a large pre-exponential factor in the rate constant.

$$k_{app} = Z \exp(-E_a/RT)$$

➤ The increase in the Z value becomes 1.5-2.2 times to Pt/C.

➤ Hence, we can expect x3.3 mass activity (A/gPt)* taking into account the Pt content & size at Pt₃Co/C.

➤ It becomes clear that Pt₃Co is the most stable composition to the corrosion.

61

Highly Durable Pt/Graphitized Carbon Catalysts Prepared by Nanocapsule Method

62

Carbon Corrosion at Pt/C Cathode Catalyst

Conventional Pt/CB catalysts [Pt dispersed on high-surface-area carbon black (CB)] are severely degraded by the carbon corrosion at high potentials caused by start-stop cycles.

High Potential Start & Stop Fuel Starvation

$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E = 0.207 \text{ V}_{SHE}$

Agglomeration and detachment of Pt reduce the electro-chemical active surface area (ECA).

We performed the durability tests of three kinds of catalysts by a standard potential-step protocol recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ).

CV (ECA) N_2 -0.1 M $HClO_4$

RRDE (i_{L, O_2} , $P(H_2O_2)$) O_2 -0.1 M $HClO_4$

Potential-step cycles (N) N_2 -0.1 M $HClO_4$
Temperature : 25°C

FCCJ Potential-step cycles for MEA

63

Dependence of MA and ECA on log N

MA at 0.8 V

Catalyst	Cycle Life
n-Pt/GC (nanocapsule)	51900
c-Pt/GC (commercial)	1600
c-Pt/CB (commercial)	700

ECA

Catalyst	Cycle Life
n-Pt/GC (nanocapsule)	11100
c-Pt/GC (commercial)	1200
c-Pt/CB (commercial)	640

The cycle life for MA_{1/2} at n-Pt/GC was **30 times longer** than that of c-Pt/GC.

The cycle life for ECA_{1/2} at n-Pt/GC was **10 times longer** than that of c-Pt/GC.

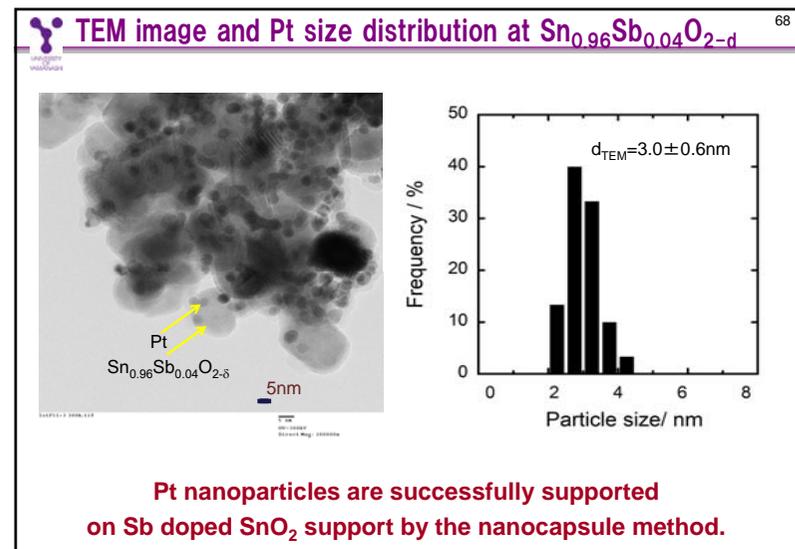
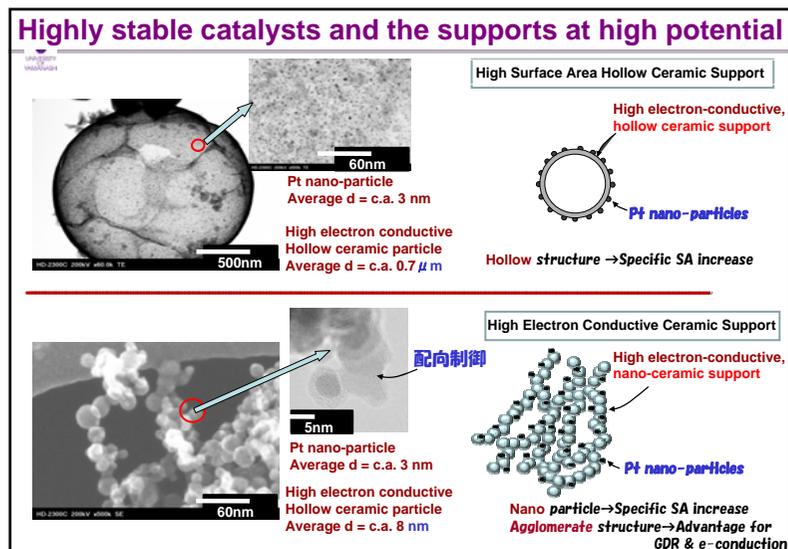
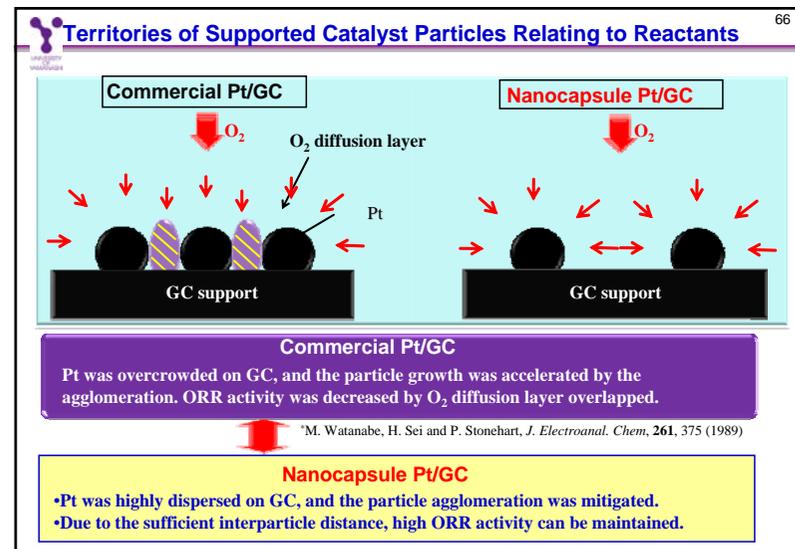
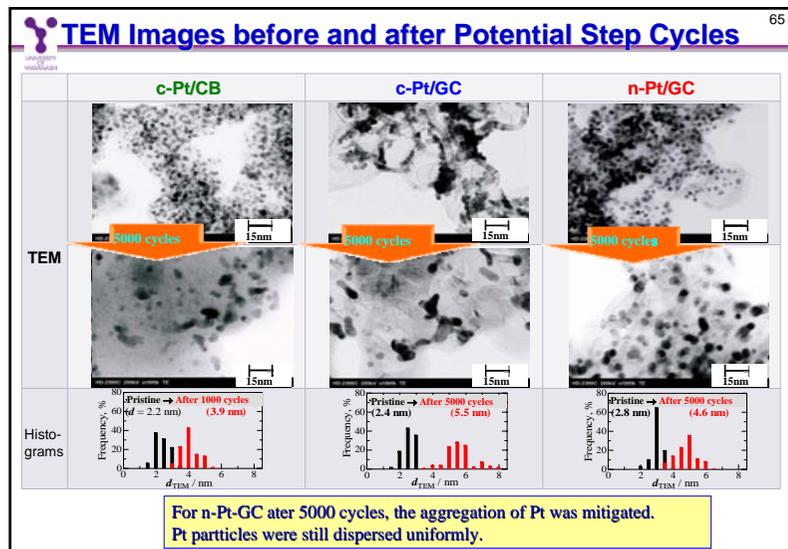
The high durability at n-Pt/GC cannot be explained simply by change in ECA.

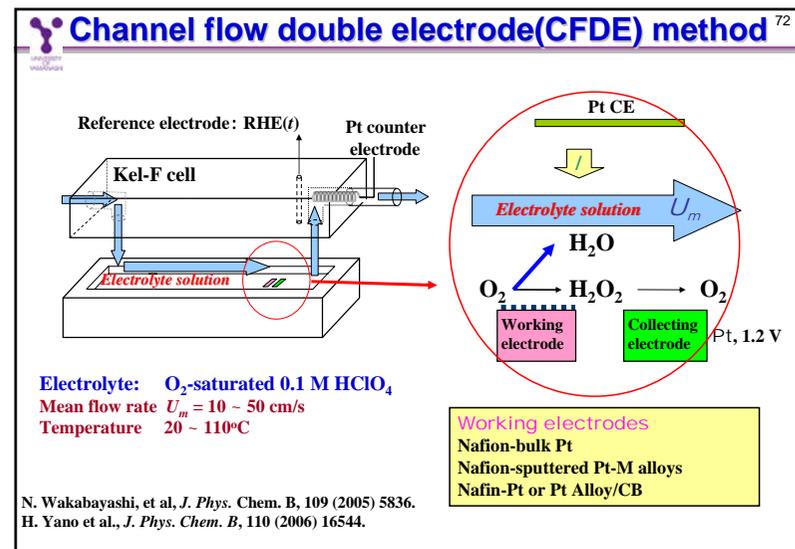
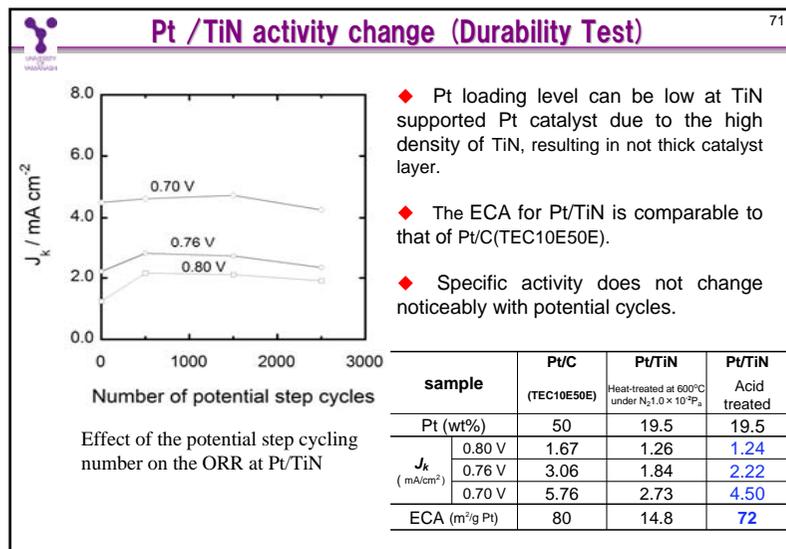
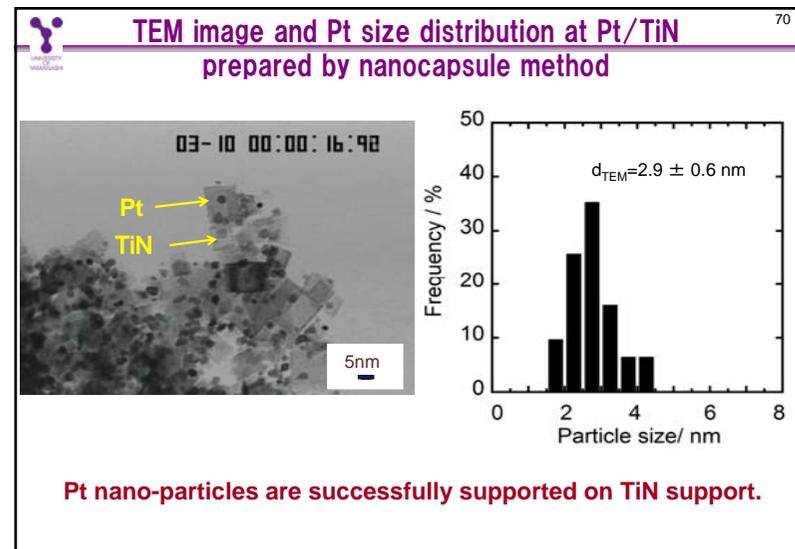
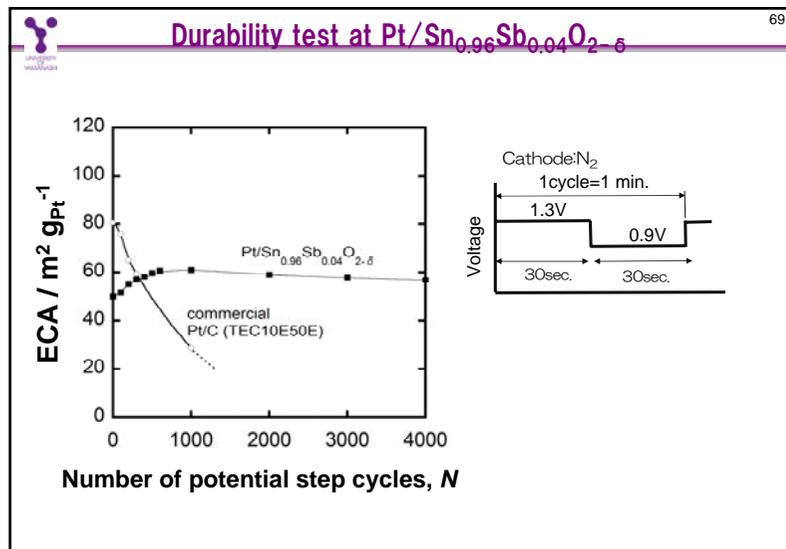
64

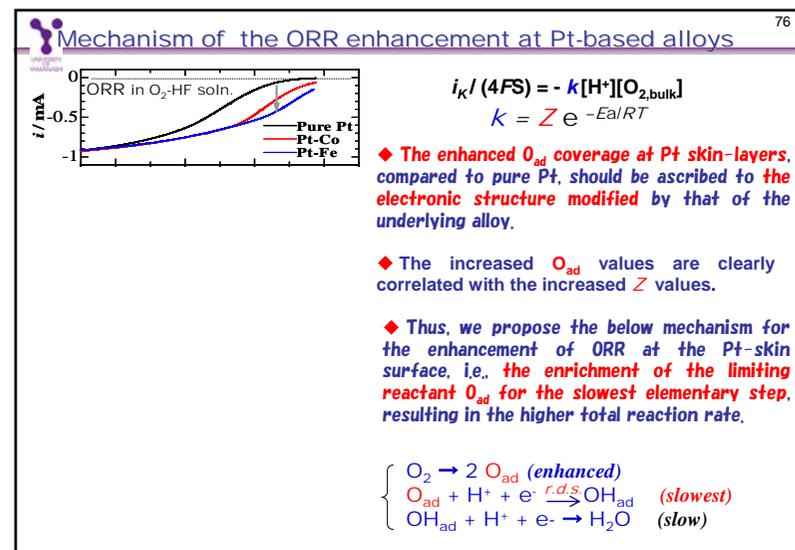
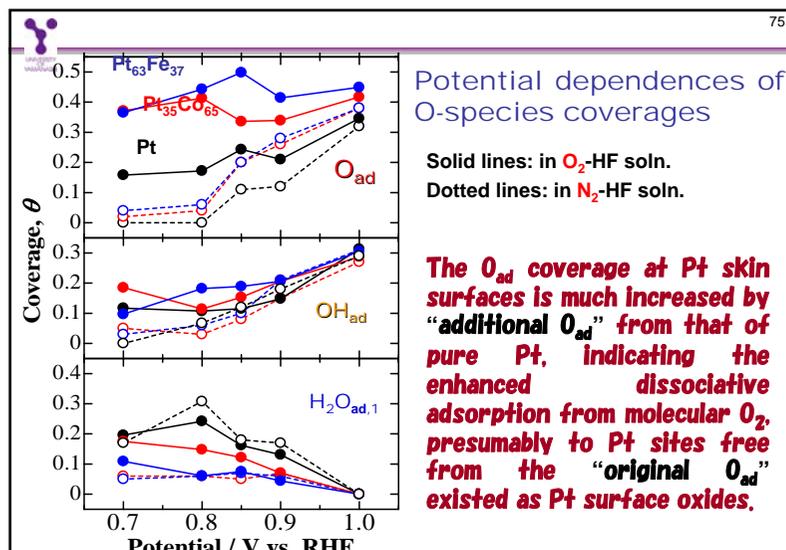
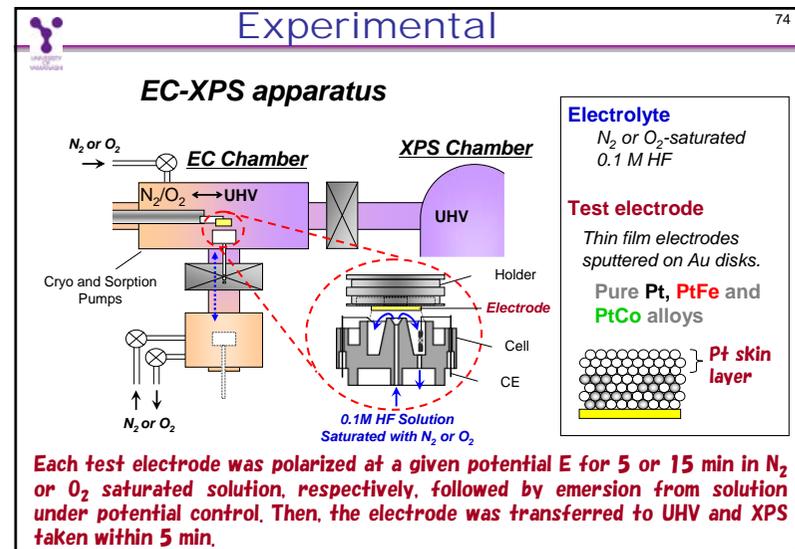
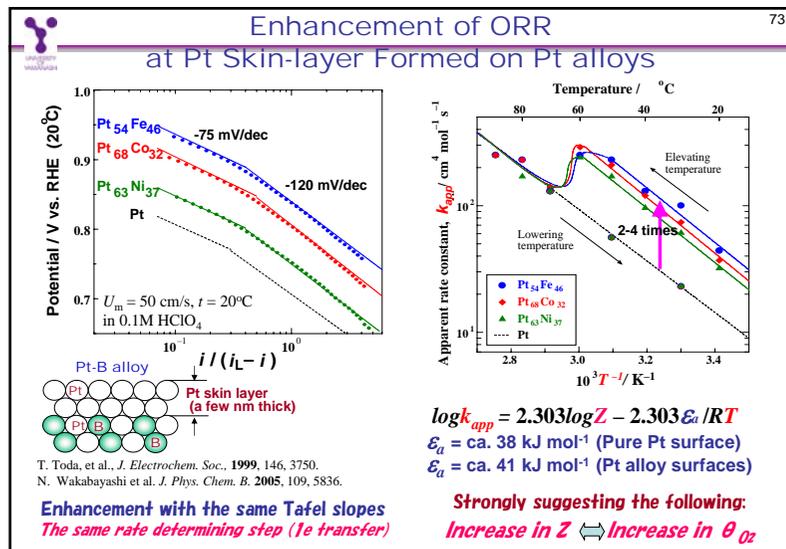
TEM Images before and after Potential Step Cycles

	c-Pt/CB	c-Pt/GC	n-Pt/GC
TEM			
Histograms			

For n-Pt-GC after 5000 cycles, the aggregation of Pt was mitigated. Pt particles were still dispersed uniformly.







SPI membranes containing mobile hydrogen atoms 77
Univ. of Yamanashi

Effect of mobile hydrogen atoms on the properties of SPIs was investigated.

$-(CH_2)_{16}-$
SPI-5

A

SPI-8-m, SPI-9, SPI-10, SPI-11, SPI-12, SPI-13, SPI-14

Synthesis of SPI membranes in large scale 78
Kaneka

SPI-8(80)

Lot number	IEC (meq/g)
1	2.3
2	2.1
3	2.3
4	2.0
5	2.1
6	2.3
7	2.1

- ◆ SPIs were synthesized on a 10 times larger scale.
- ◆ Membranes were cast on a 6 times larger scale.
- ◆ There were only minor differences in molecular weight, IEC and membrane thickness among the different batches.

New SPE block copolymers 79
Univ. of Yamanashi

Conventional block copolymers: sulfonic acid group, Hydrophilic

Our new block copolymers: Very hydrophilic

Increased local concentration of sulfonic acid groups

Hydrophobic, Hydrophilic

Water uptake and proton conductivity 80
Univ. of Yamanashi

- ◆ Block SPEs showed much higher conductivity than the random SPEs.
- ◆ The conductivity of block SPEs was comparable to that of Nafion at >40%RH.

Proton conductivity (S/cm) vs λ

Water uptake (%) and Proton conductivity (S/cm) vs Relative Humidity (%)

A Strategy of the Cost Reduction of Catalysts 81
for Large PEFC Markets

**“ Through the Reduction of Pt Catalysts Used ”
That is the Shortest, the Best and the Most Practical Approach !**

How the 1/10~1/20 reduction could be realized ?



“ Ippon ” with “ Awase-waza ”

Pt-skin on the alloy of Pt & non-precious metal(s) × a few times

Nano-sized catalyst × a few times

Effectiveness of MEA × a few times

High temperature operation × a few times

Synergy effect of catalysts with the supports × a few times

Optimization of operation mode × a few times

26~36 times

1st Fuel Cell Young Summer Seminar 2010 83

[Organizer] FC Nanomaterials Center & Clean Energy Research Center, Univ. of Yamanashi
[Co-organizer] NEDO, Yamanashi Prefecture, ECSJ, Chem. Soc. Japan, etc.

Aug. 17~20, 2010 at Kawaguchi-ko Hotel

90 young scientists & engineers from 9 countries attended.

山梨大は20日まで、富士河口湖畔の河口湖パークホテルで第1回国際燃料電池サマーマナーセミナーを開いている。日本、米国、中国、韓国など9カ国の若手研究者ら約90人が合宿形式で参加。同大は、最先端技術を発信することで燃料電池研究を担う次世代を育成し、同大燃料電池ナノ材料研究センターを世界的な研究拠点にすることを目指している。

山梨大からは大学院生とスタッフ計28人が参加している。第一線で活躍する国内外の研究者が、水素と酸素を化学反応させて電気を発生させる燃料電池の、システムやメカニズムに関する最新の研究成果を発表。研究者同士で交流を深める。

基調講演が始まった18日は、中国・武漢大のシェンリー・チェン教授と信州大の杉本浩教授が、燃料電池の製造コスト削減に向けた新たな電極触媒を解説。トヨタ自動車の広瀬雄彦さんは燃料電池車の開発状況を説明した。

セミナーでは講演のほか、若手研究者によるグループディスカッションや燃料電池車の試乗会も開かれる。

燃料電池ナノ材料研究センターは、燃料電池車の普及に向け、製造コストの削減や耐久性の確保を目指し材料の開発を進めている。同センターの柿沼克良准教授は「セミナーを通じて優秀な人材と情報がセンターに集まることを期待したい」と話している。



Invited Speaker: Japan(3), USA(1), Denmark(1), China(1) and Korea(1)

International Fuel Cell Workshop 2009 82
(Organized every 3 years in Kofu)



海外から、米国、英国、ドイツ、デンマーク、韓国、中国、香港、シンガポール、パキスタン、ベトナム 84



Vehicle trial ride sponsored by Yamanashi Prefecture



Get-together



Group discussion

