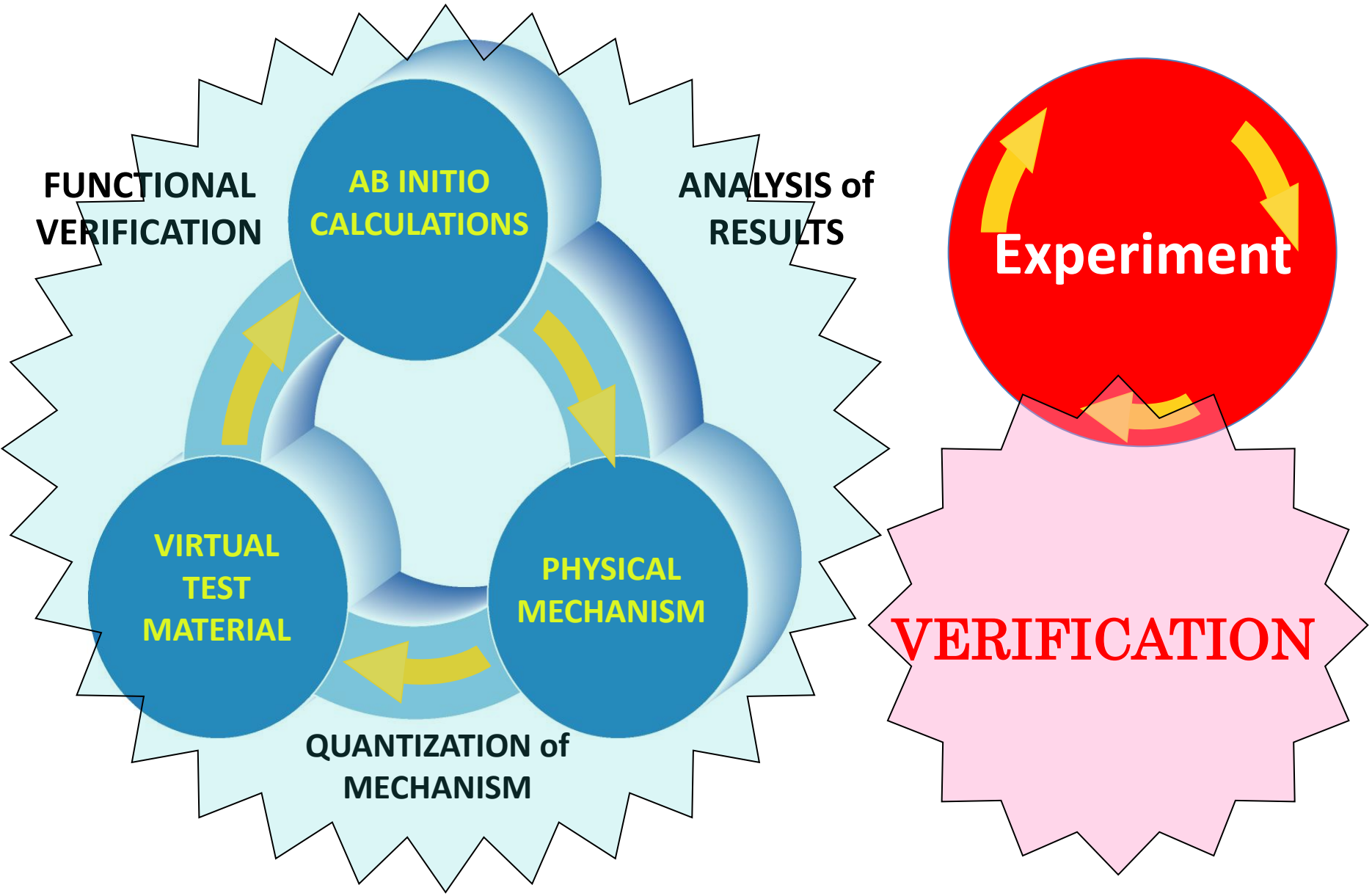
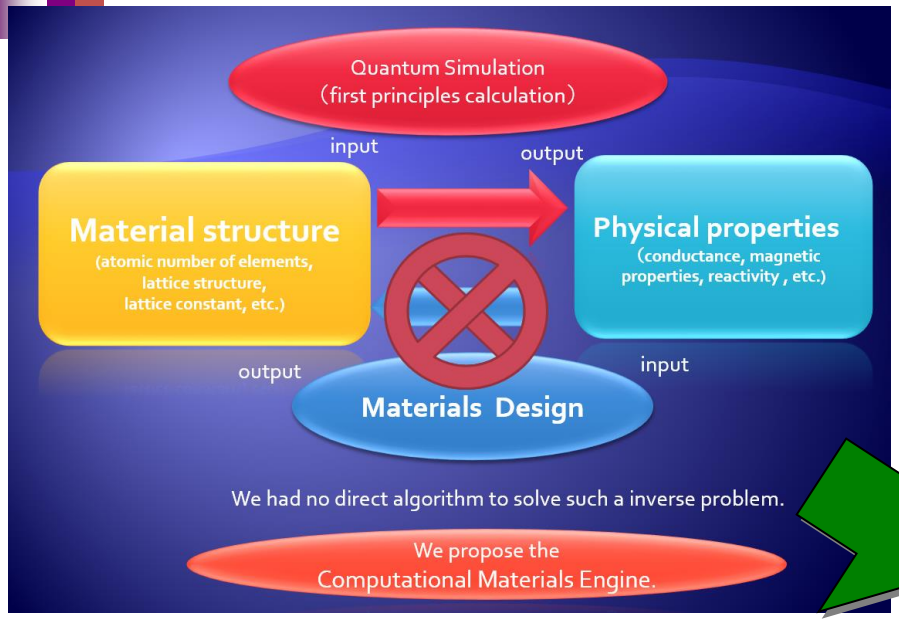
Computational Materials Design® (CMD®)



Computational Materials Design (CMD) Workshop 47
1-5 September 2025

Naniwa Series

CMD (Computational Materials Design)

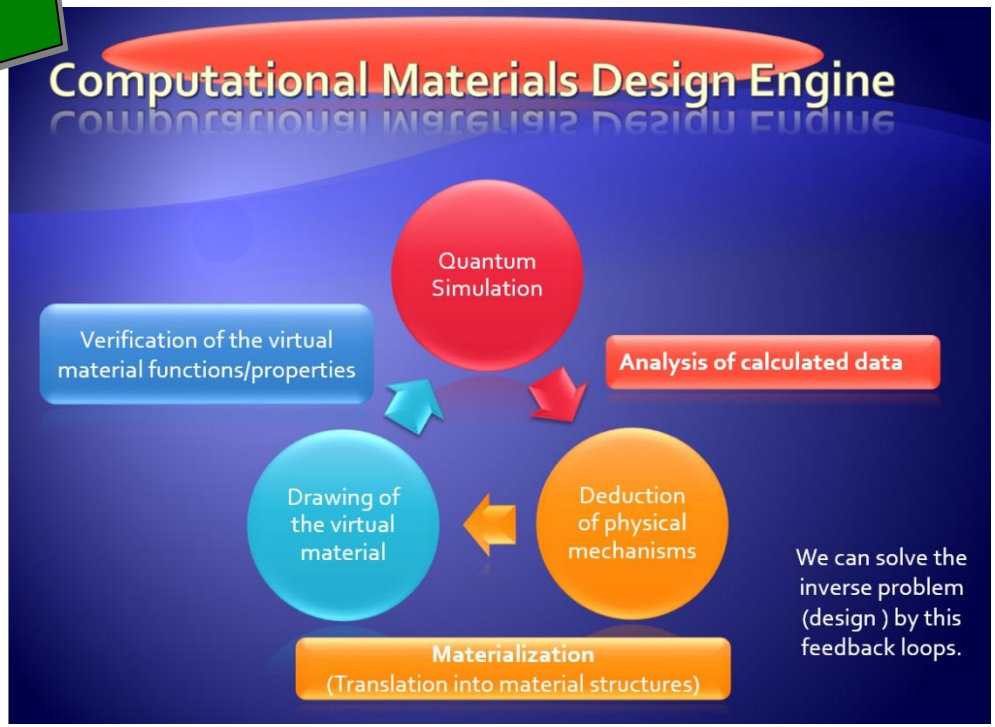


① Kasai group began to develop the 1st generation of CMD about 20 years ago, in order to beyond the conventional first-principle calculations.

H. Kasai, et al., Computational Materials Design from Basics to Actual Applications, Osaka University Press (2005).

② CMD-Naniwa:
the first-principles Quantum simulator for both electrons & nuclei in materials

Since 1998年、
Japanese Patent, 8th July 2011
US patent, 4th Jan. 2012

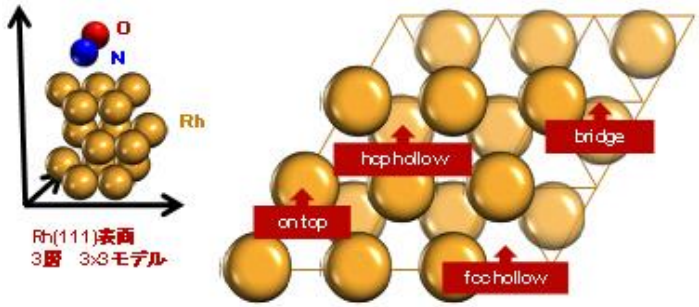


Actual achievements of our R&D

Case 1 : catalysts

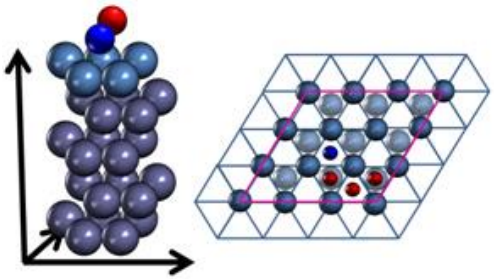
Catalysts for vehicle emissions control

Understanding about the conventional catalysts of noble metals.



CMD-Naniwa

High-performance new catalysis design

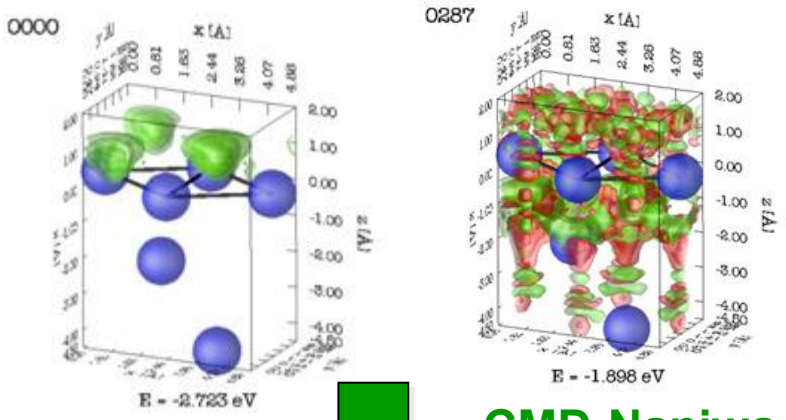


Ex. NOx reduction catalyst →designed new NO dissociative adsorption surface

JP Patent No. 5002761, 15 other patents and more than 20 academic papers..

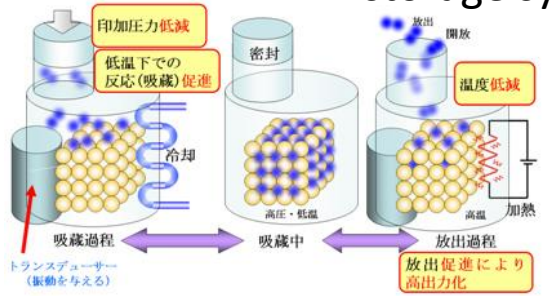
Case 2 : hydrogen storage

Understanding about Quantum states of hydrogen in materials



CMD-Naniwa

New invention for Hydrogen storage system



JP Patent No. 4222932, 7 other patents and more than 20 academic papers.

Actual achievements of our R&D

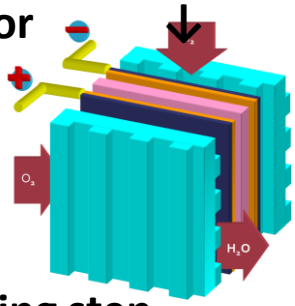
Case3 : Fuel Cell

Understanding about the various elementary reactions in Fuel Cell by CMD-Naniwa

- **Analyze obstructive factor**

↓

How to reduce disincentive



- **Finding the rate-controlling step**

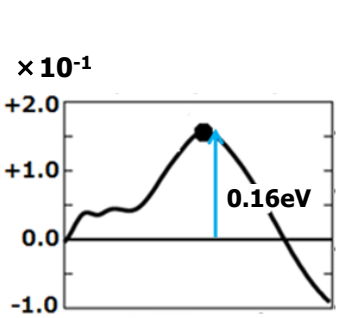
→ **design alternative reactions**

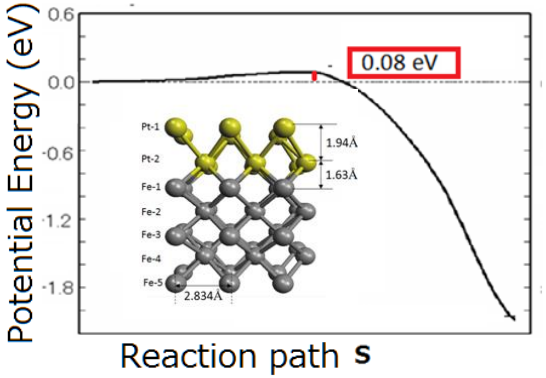
Higher-active catalysis

CMD-Naniwa

Ex. Disociative adsorption of oxygen molecule

Pt surafce → New designed surface





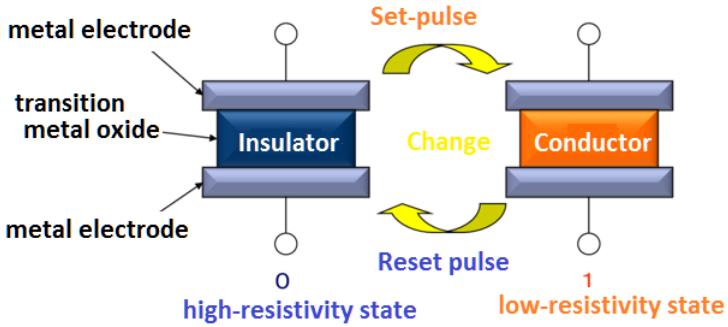
JP Patent No 3765050, 12 other patents and more than 30 academic

Case4 : Resistive random-access memory

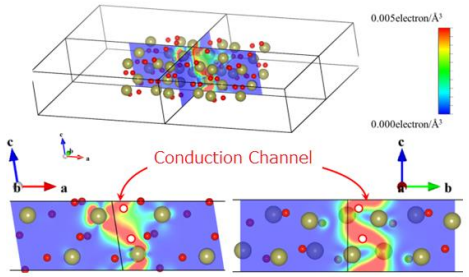
Development of the next generation non-volatile RAM

CMD

- **Voltage pulses can induce the transition between high- and low- resistivity states**



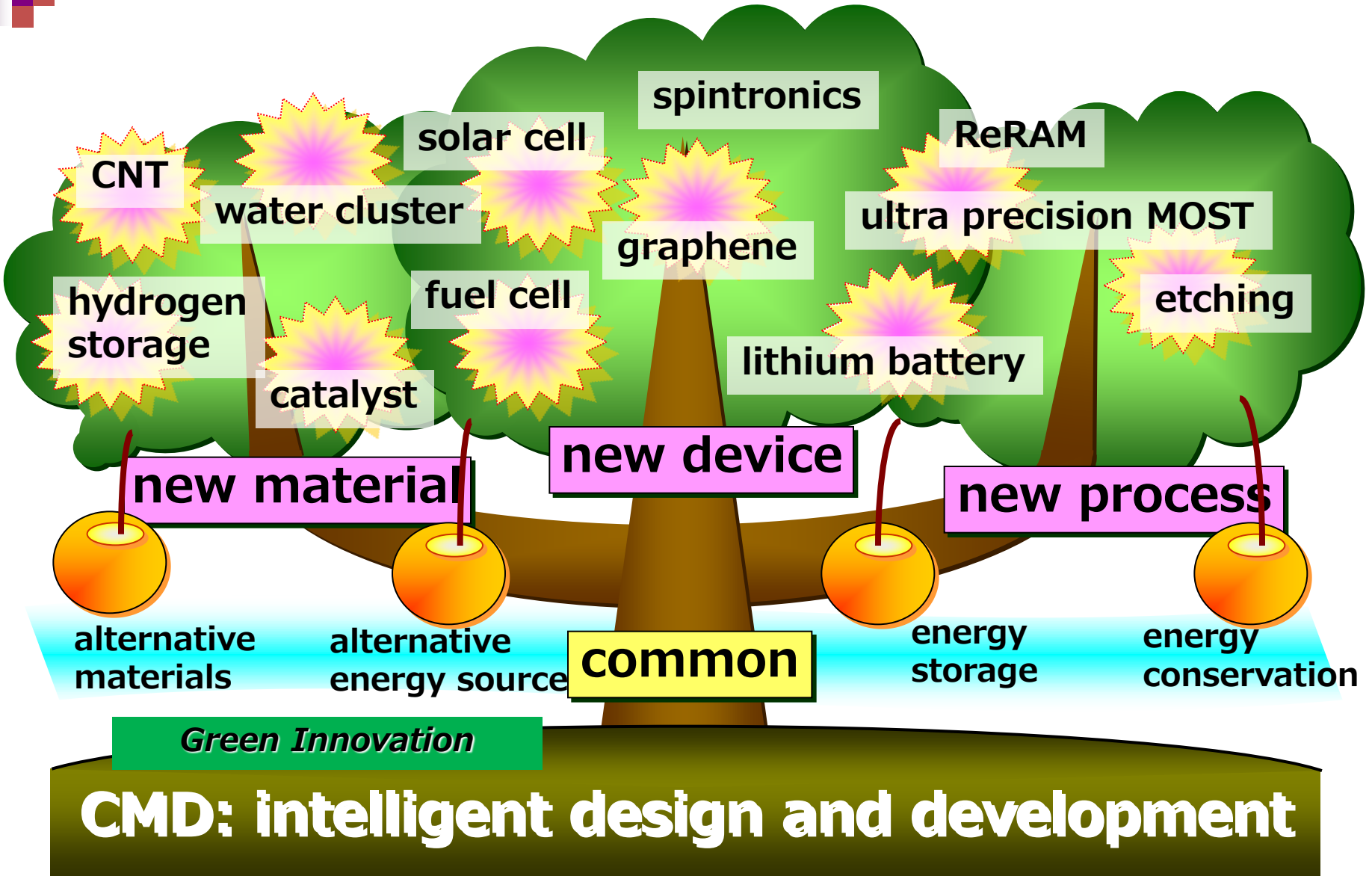
- clear-up the expression mechanism of conduction channel



Press release : **Sep. 2011**

JP Patent application No. 2006-257970/355977, 3 others and more than 10 academic papers.

Our Big Data: CMD-driven Creation of new technology and next generation industries



計算機ナノマテリアルデザイン先端研究事例
ー持続可能な水素経済を目指してー
Computational NanoMaterials Design
Case Study Towards Sustainable Hydrogen Economy

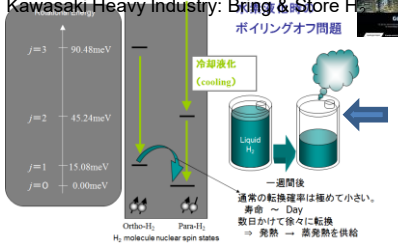
笠井秀明 (Hideaki Kasai)　ジェフリ タヌジ (Jeffrey Tanudji)
大阪大学 (Osaka University), 明石高専 (NIT Akashi)

JVSS
VACUUM2022
真空展

持続可能な水素経済を目指して
Towards a Sustainable Hydrogen Econon

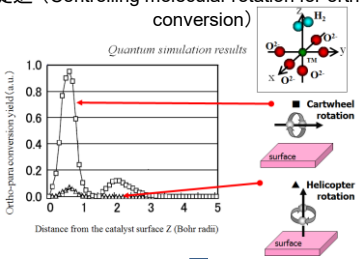
液体水素運搬船
(Liquid Hydrogen Tanker)

液化天然ガスタンカーから液体水素タンカーへ
From LNG Tanker to LH_2 Tanker
Kawasaki Heavy Industry: Bring & Store H2



Hydrogen boil-off problem during storage

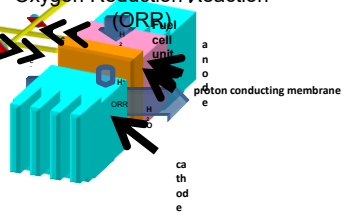
水素分子の回転状態の制御によるオルトパラ転換の促進（Controlling molecular rotation for ortho-para conversion）



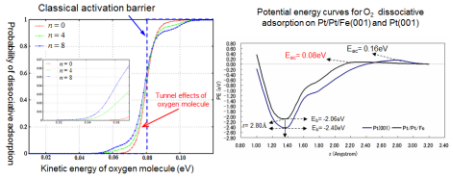
Launching & Naming Ceremony of Liquid Hydrogen Tanker “SUISO FRONTIER”
11 December 2019, Kobe, Japan

固体高分子形燃料電池
(Proton Exchange Membrane Fuel Cell)

Oxygen Reduction Reaction (ORR)



Dissociative adsorption of oxygen



Based on classical mechanics, it is calculated that the operating temperature is higher than 1000℃ for conventional Pt catalyst and 500℃ even for the newly designed Pt(2ML)/Fe catalyst surface.

1. The dissociative adsorption reaction of oxygen molecule on cathode catalyst surface is rate limiting reaction.
2. Quantum tunneling effects lower the operating temperature (~ room temperature)

量子トンネル効果によって動作温度が低下する

Designed surface: Pt-coating Fe (Co) surface (Core-Shell) can enhance the dissociative adsorption reaction of oxygen molecule
コアシェル構造（白金・コバルト）鉄

➢PATENT NUMBER 7063376 (JAPAN 25 April 2022) PtCoMn(白金・コバルト・マンガン 最強の触媒！

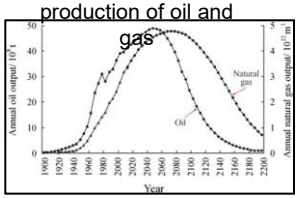
計算機ナノマテリアルデザイン先端研究事例
―持続可能な水素経済を目指して II―

Computational NanoMaterials Design
Case Study Towards Sustainable Hydrogen Economy-2

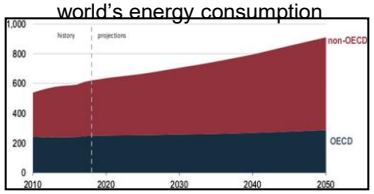
JVSS
VACUUM2023
真空展

笠井秀明 (H. Kasai), ジェフリ タヌジ (J. Tanudji),岡田美智雄 (M. Okada), A. A. Padama, W. T. Cahyanto, S. Zulaehah, W. Widnarto, F. Abdullatif, M. Effendi, 中西 寛 (H. Nakanishi)

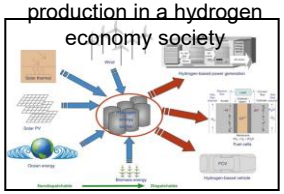
Trends in the global production of oil and gas



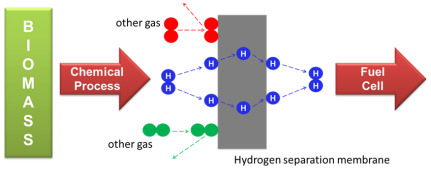
History and projection of world's energy consumption

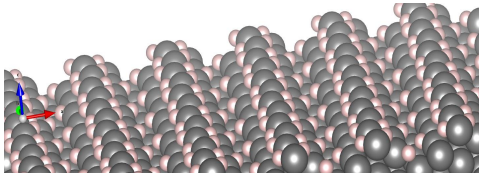


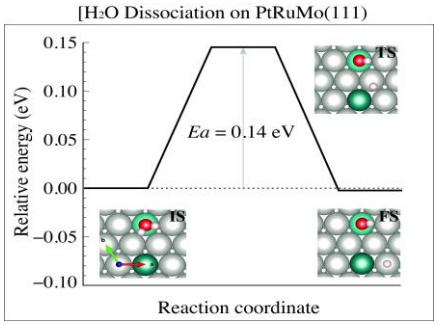
Vision for hydrogen production in a hydrogen economy society

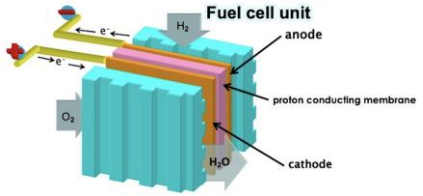


持続可能な水素経済を目指して
Towards a Sustainable Hydrogen Economy



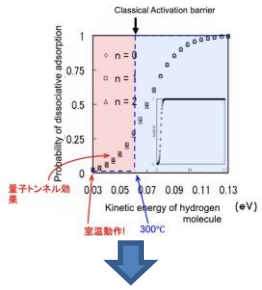






Proton Exchange Membrane Fuel Cell (PEMFC)

Quantum dynamics of dissociative adsorption of Hydrogen molecule



The dissociative adsorption reaction of hydrogen molecule on anode catalyst surface has been shown

Quantum tunneling effects lower the operating temperature (~ room temperature)
量子トンネル効果によって動作温度が低下する!

2
0

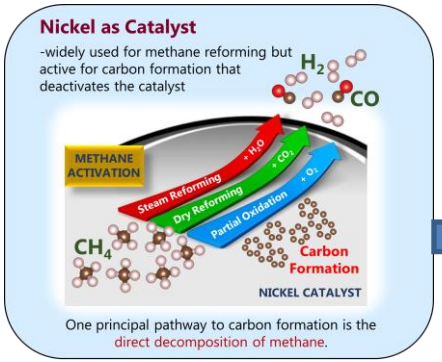
計算機ナノマテリアルデザイン先端研究事例
ー持続可能な水素経済を目指してIII ー

Computational NanoMaterials Design
Case Study Towards Sustainable Hydrogen Economy

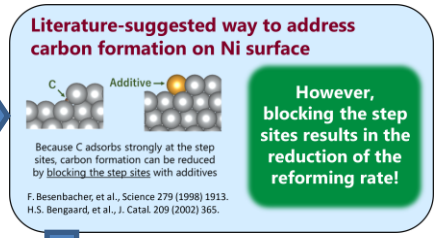
JVSS
VACUUM2024
真空展

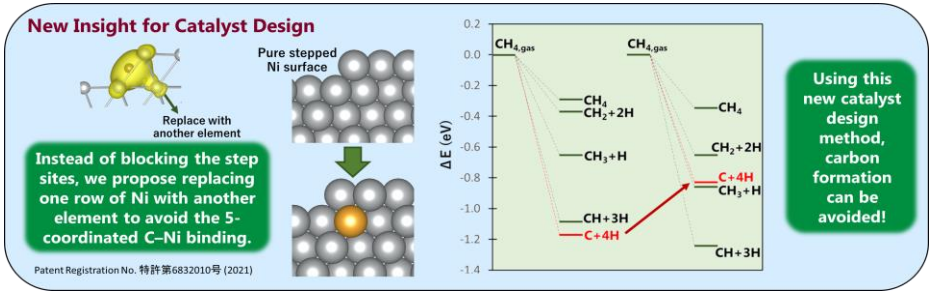
笠井秀明 (H. Kasai),[1] R.L. Arevalo,[2] S.M. Aspera,[3] M.C.S. Escano,[4] A.A. Padama,[5] 岡田美智雄 (M. Okada),[1] 中西寛 (H. Nakanishi)[6]
[1]大阪大学 (Osaka University), [2]明石高専 (National Institute of Technology, Akashi College), [3]信州大学 (Shinshu University)
[4]福井大学 (University of Fukui), [5]University of the Philippines

メタンから水素を製造するNi触媒のデザイン



Hydrogen gas can be produced from methane using methods such as dry reforming, steam reforming, and partial oxidation. One important issue is the design of efficient and stable catalysts for these reactions.





炭素原子はステップサイトに強く吸着し、5配位C—N結合ができます。そのため改質率が低下します。
5配位C—N結合を避けるために、Niの1つの列をを別の元素に置き換えることを提案します。
詳細は特許第6832010号をご覧ください。

Summary

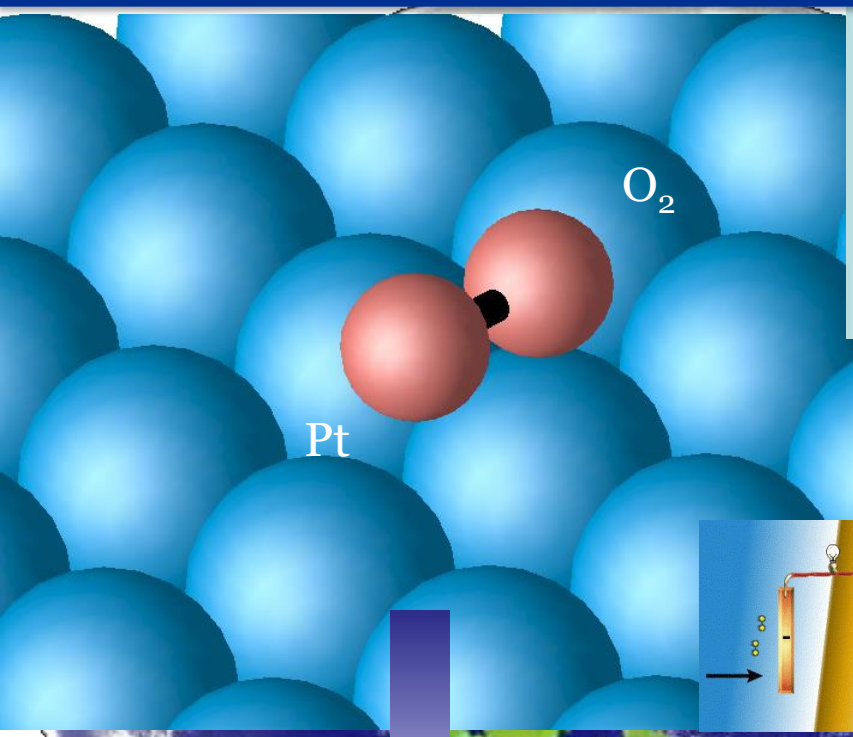
- The high stability of carbon on stepped Ni surface is characterized by a unique 5 coordinated C–Ni bonding between atomic carbon at the fivefold site and Ni atoms from both the surface and subsurface layers.
- We proposed replacing specific subsurface Ni atoms of stepped Ni surface with another element, as new approach to catalyst design aimed at improving the resistance of Ni surface to coke formation in hydrocarbon reforming processes.

Reference:

R.L. Arevalo, S.M. Aspera, M.C.S. Escaño, H. Nakanishi, H. Kasai, *Tuning methane decomposition on stepped Ni surface: Role of subsurface atoms in catalyst design*, Scientific Reports 7 (2017) 13963.

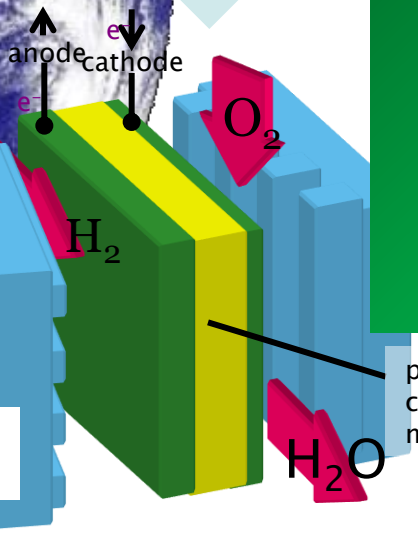
Towards Hydrogen-based Society

Why Hydrogen FUEL CELL?



Fuel cell offers an efficient power generation over combustion systems. Low emission is also guaranteed.

Pt reactivity towards O2 in the cathode can be tuned.



Polymer Electrolyte Fuel Cell (PEFC)

1. Low-temperature operation
2. Favorable power-to-weight ratio
3. Efficient chemical to electrical energy conversion with low emission

Anodic reaction:

$$H_2 \rightarrow 2(H^+ + e^-)$$

Cathodic reaction: $\frac{1}{2}O_2 + 2(H^+ + e^-) \rightarrow H_2O$

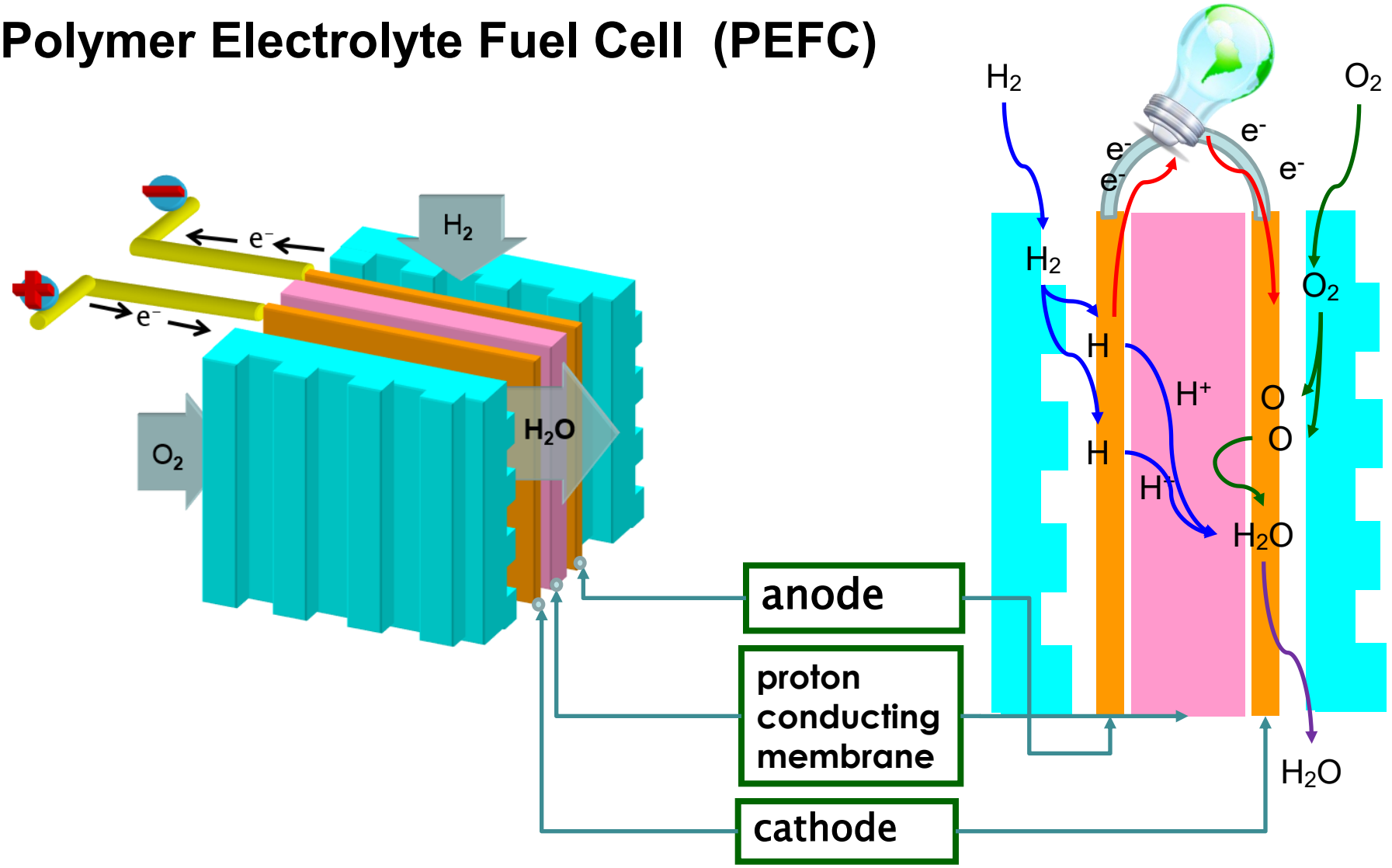
燃料電池は、すべてが量子反応のデバイスと考えられる！

―究極のエコ電池開発への大きな一歩―

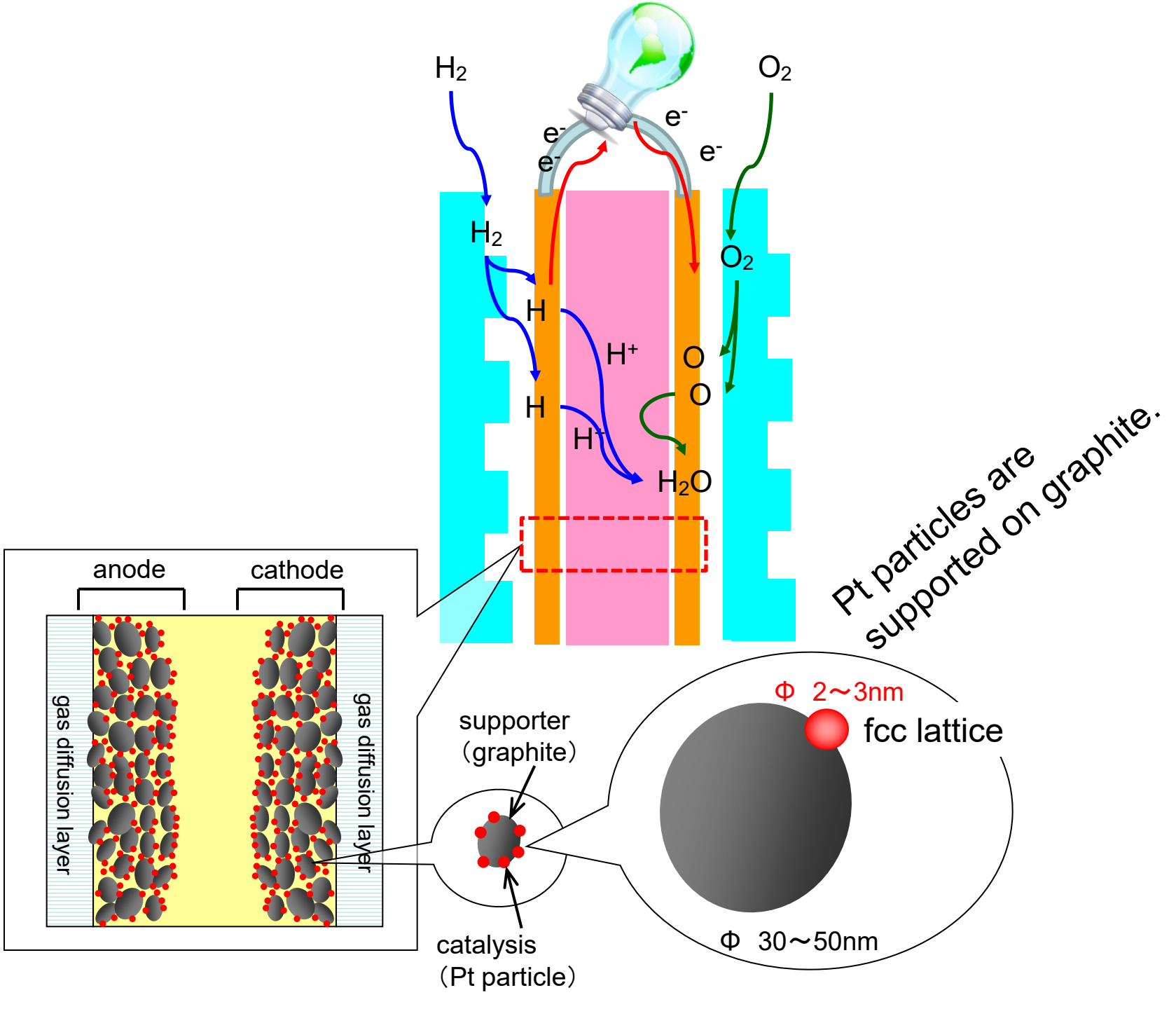
Hydrogen Fuel Cell should be considered as the quantum mechanical device!

― giant step toward ultimate energy devices for avoiding their ecological footprint ―

Polymer Electrolyte Fuel Cell (PEFC)



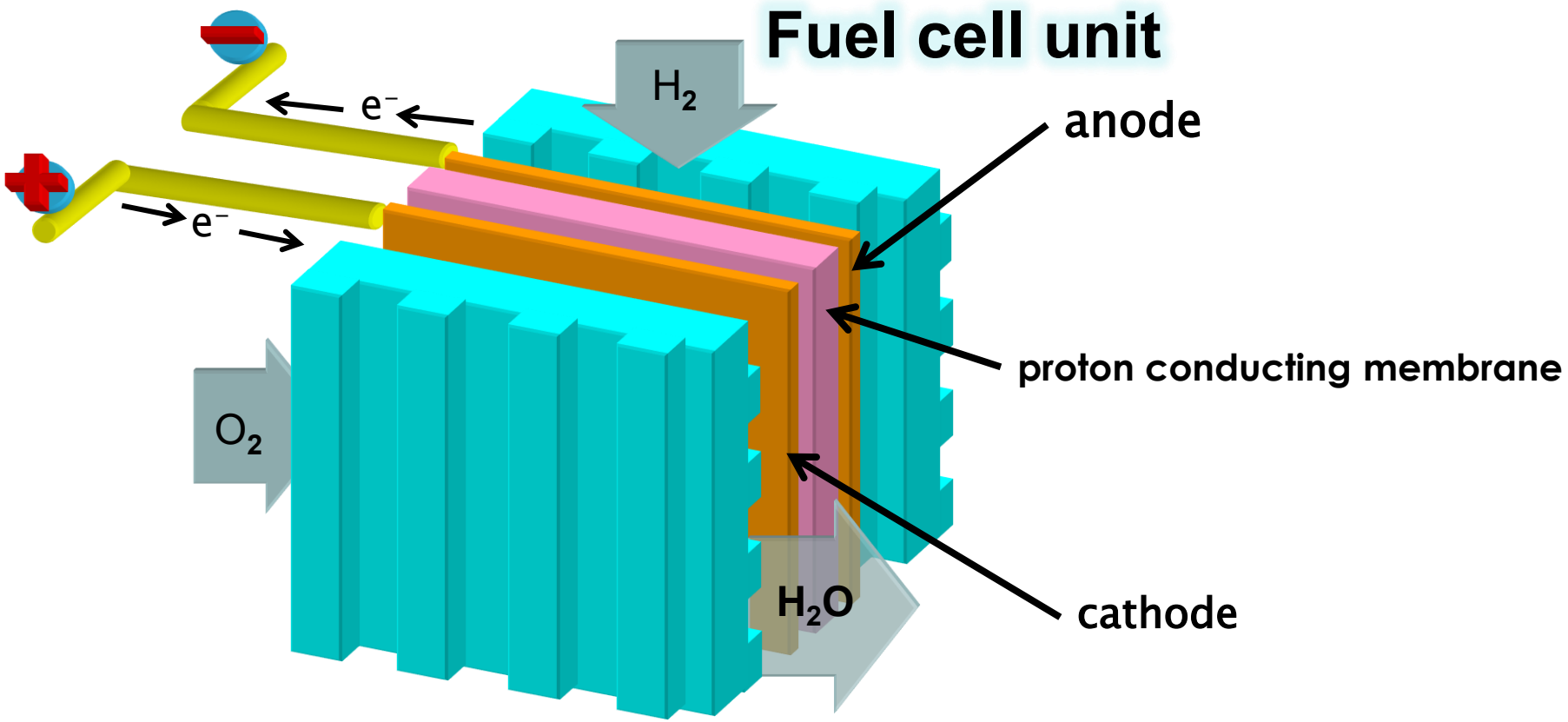
PEFC transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy with only exhaust of water


H2
O2
e-
e-
e-
e-
H2
O2
H
H+
O
O
H
H+
H2O
anode
cathode
gas diffusion layer
gas diffusion layer
supporter
(graphite)
catalysis
(Pt particle)
Pt particles are
supported on graphite.
Φ 2～3nm
fcc lattice
Φ 30～50nm

Result 1 : Anode reaction properties and CMD

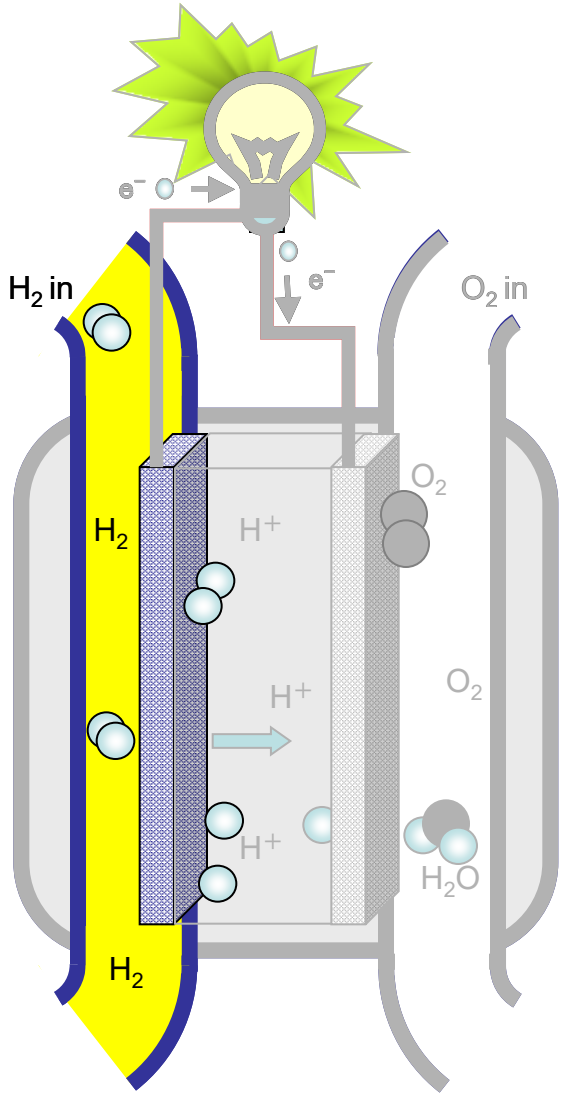
- The dissociative adsorption reaction of hydrogen molecule and diffusion of adsorbed hydrogen atom on anode catalyst surface proceed by the quantum tunnel effect even at room temperature.

Hydrogen Reactions on Fuel cell anode



Polymer Electrolyte Fuel Cell (PEFC)

Elementary reactions in the fuel cell electrode

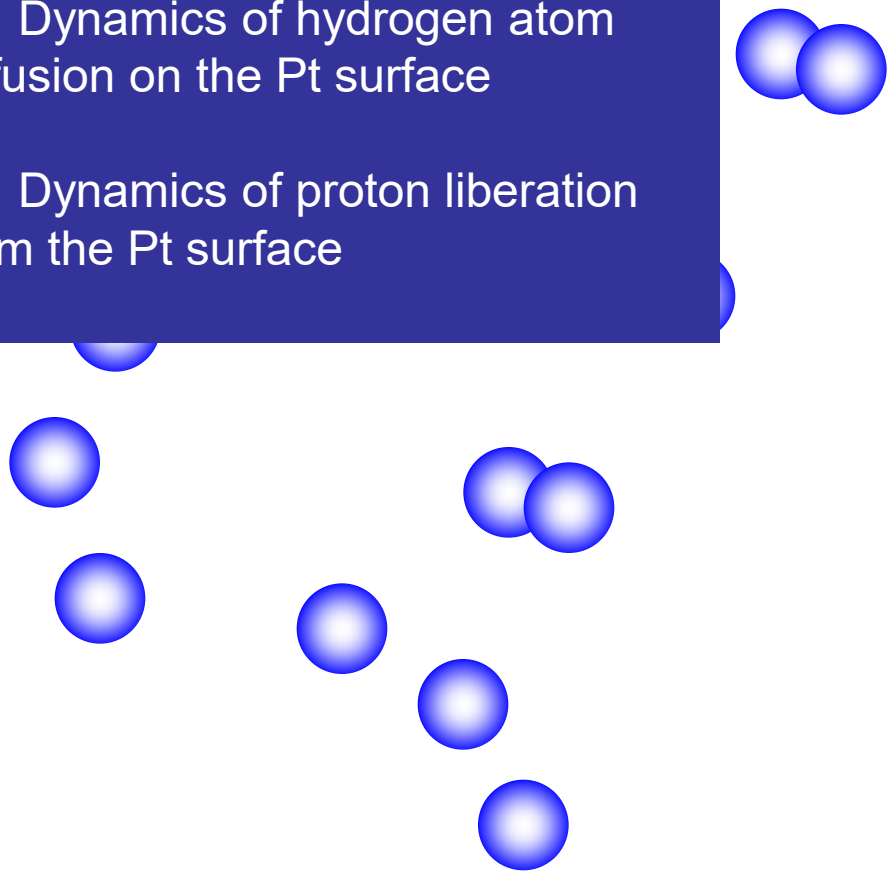


Atomic scale description

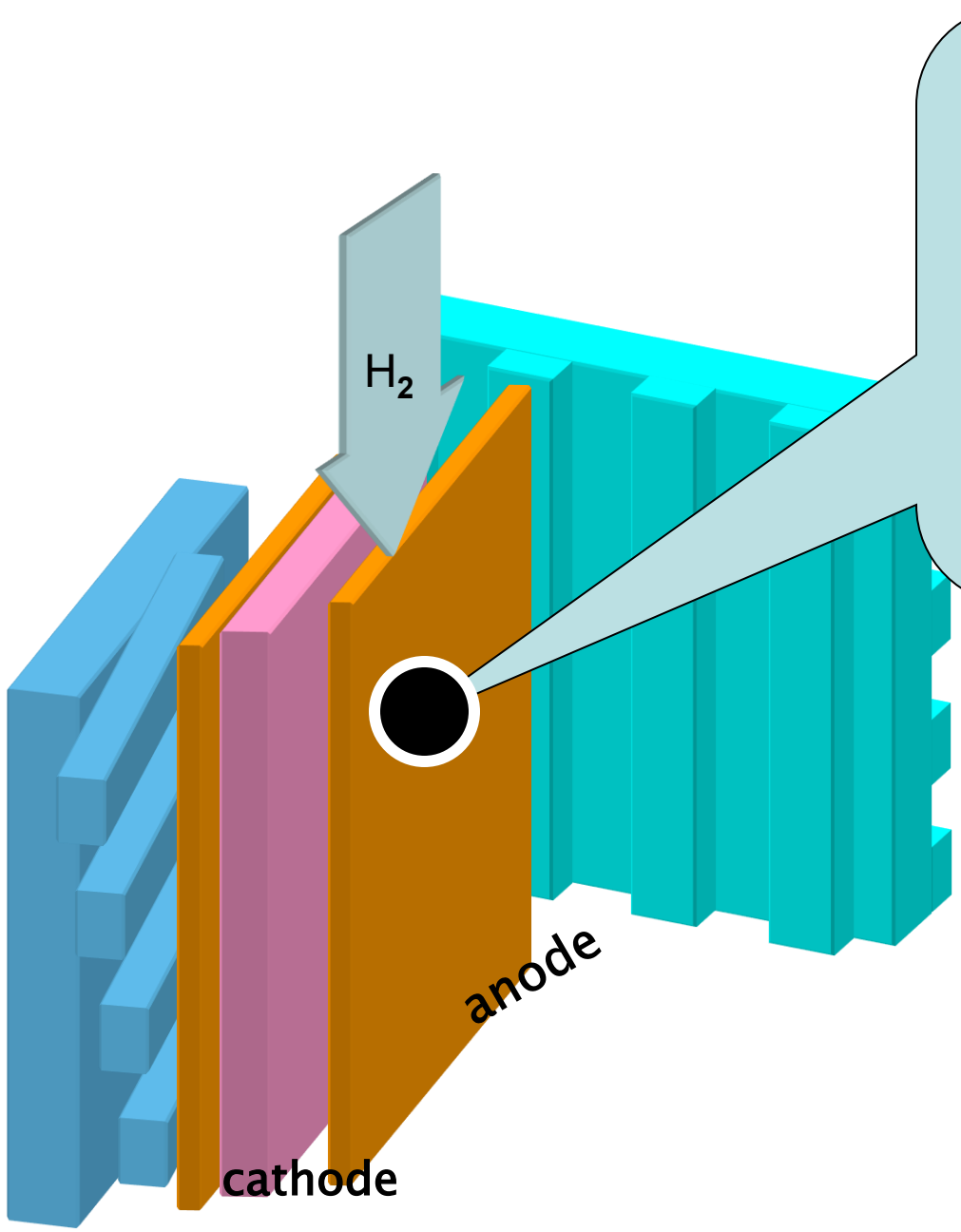
① Dissociative adsorption of hydrogen molecules on the Pt surface: reaction dynamics

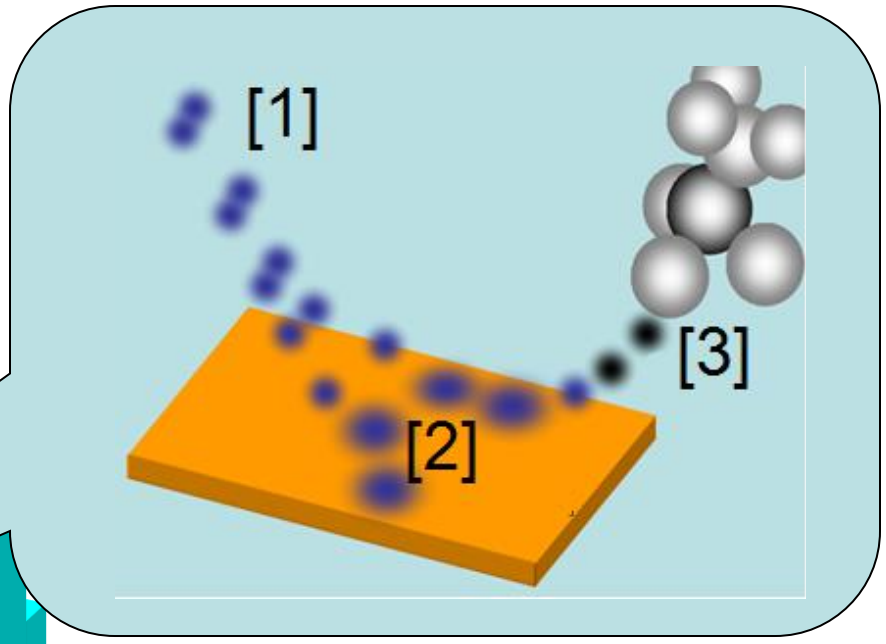
② Dynamics of hydrogen atom diffusion on the Pt surface

③ Dynamics of proton liberation from the Pt surface



- Three elementary processes on anode



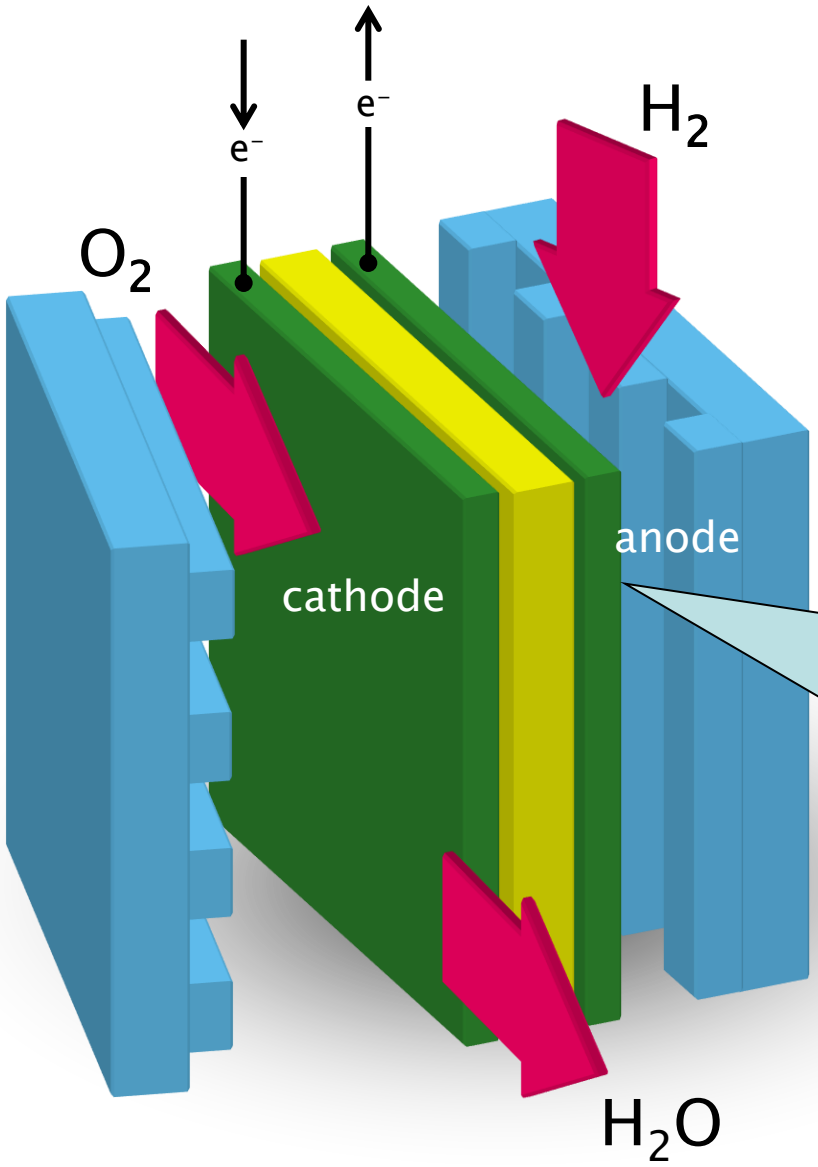


[1] Dissociative adsorption of H_2 molecule on the electrode surface

[2] Adsorption/migration of H atom on the electrode surface

[3] H^+ transmission from the electrode to the proton conducting membrane

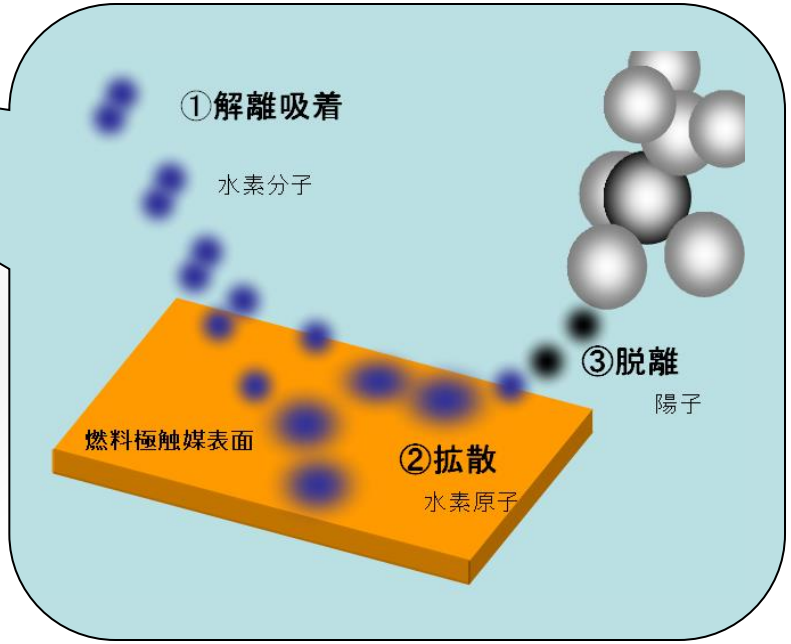
Dissociative adsorption of hydrogen molecule on anode catalyst surface



① Dissociative adsorption of H_2 on the electrode surface (Pt)

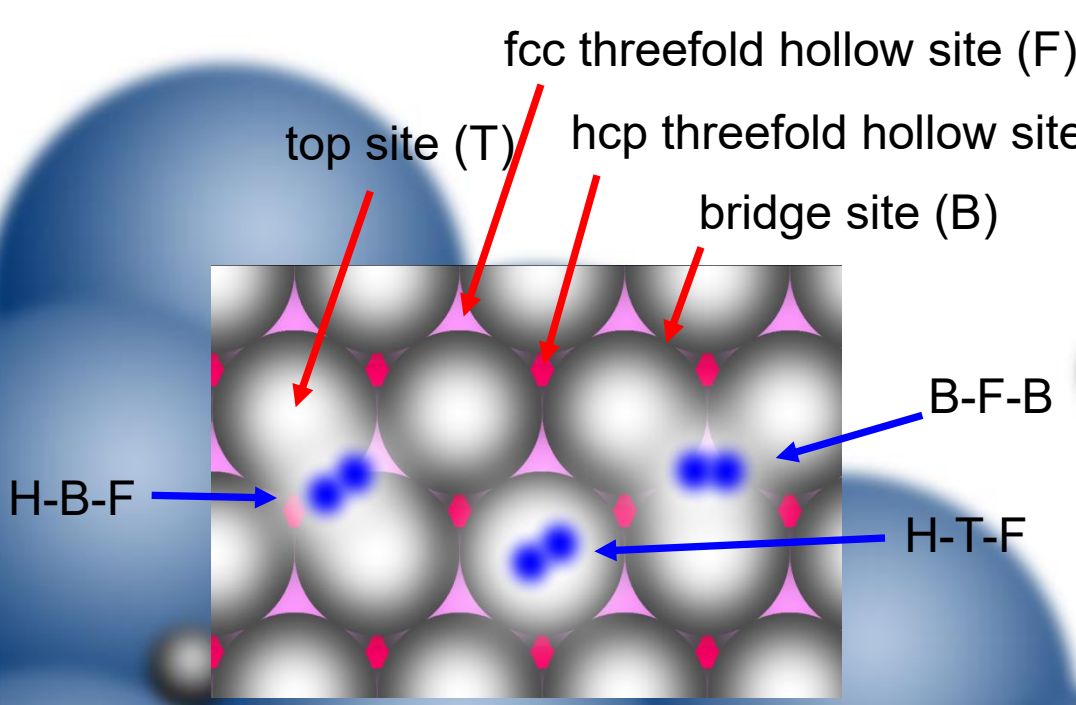
② Adsorption/migration of H (atoms) on the electrode surface

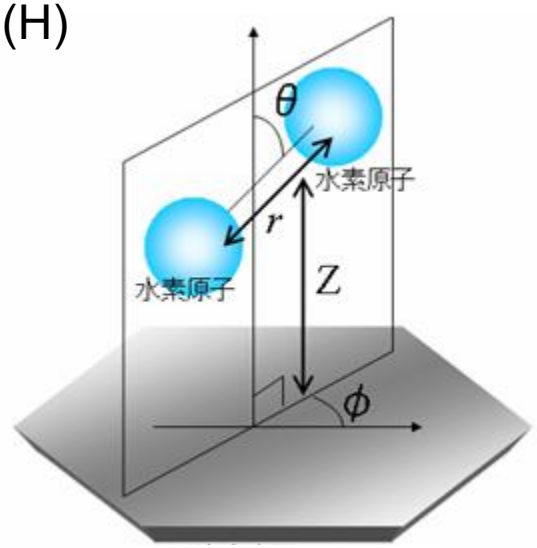
③ H^+ transmission from the electrode to the proton conducting membrane



Dissociative adsorption of Hydrogen molecule

The Pt(111) surface and the orientations of H_2 relative to the surface during dissociative adsorption.



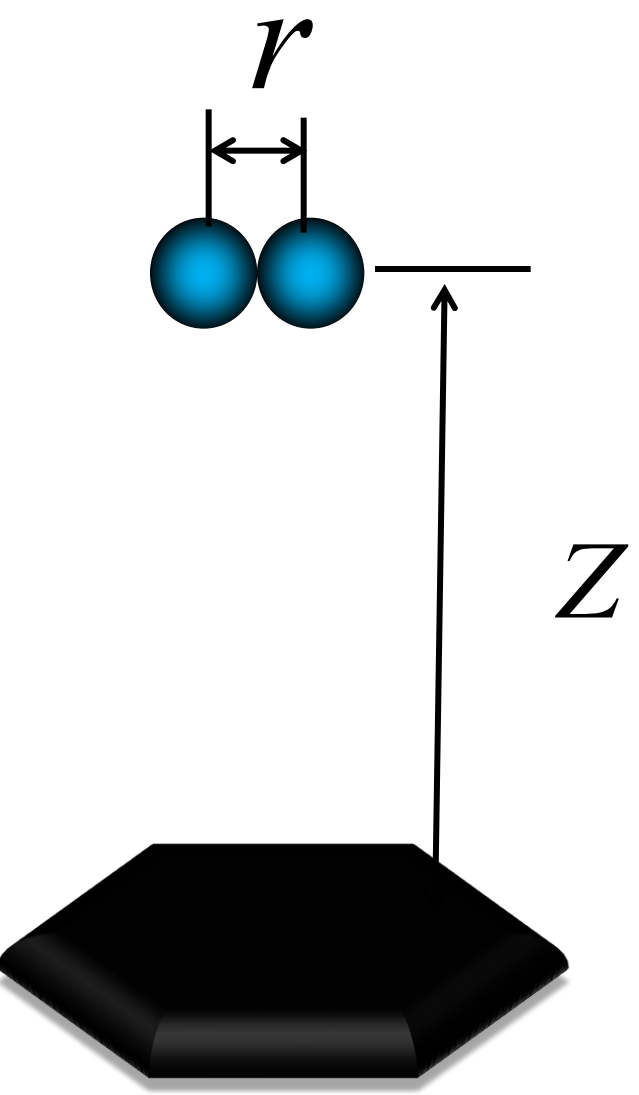


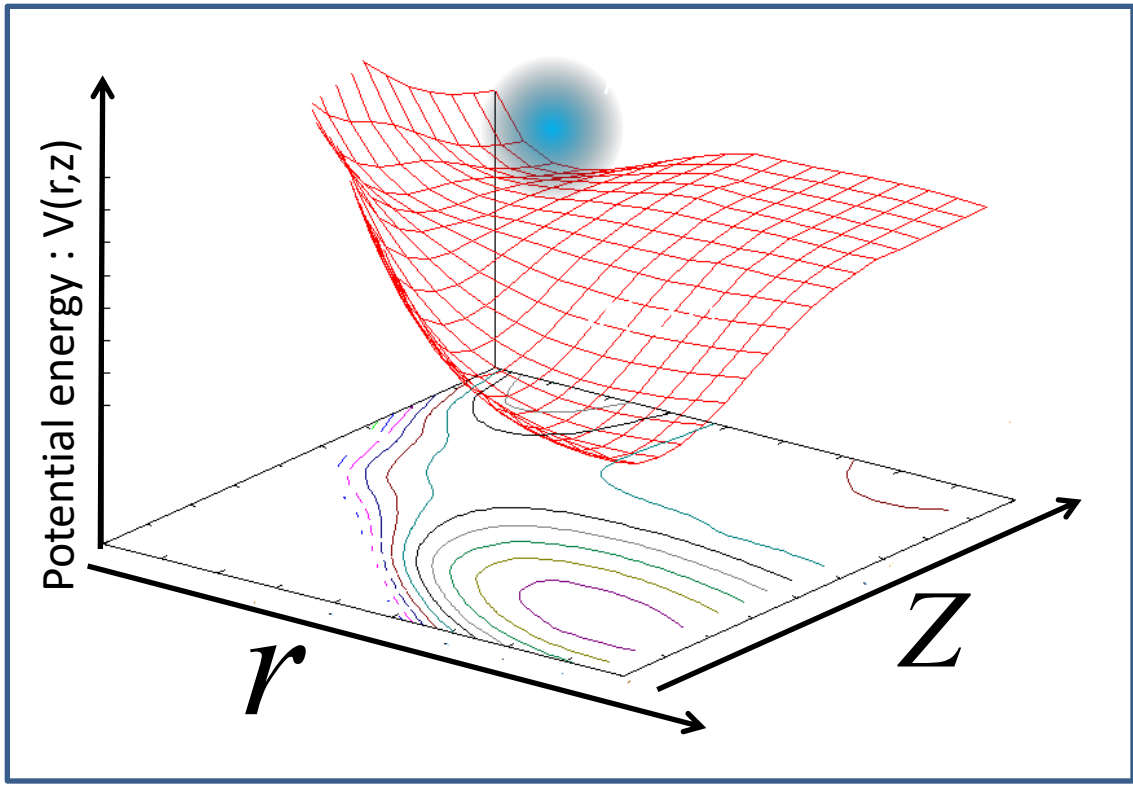
Pt surface

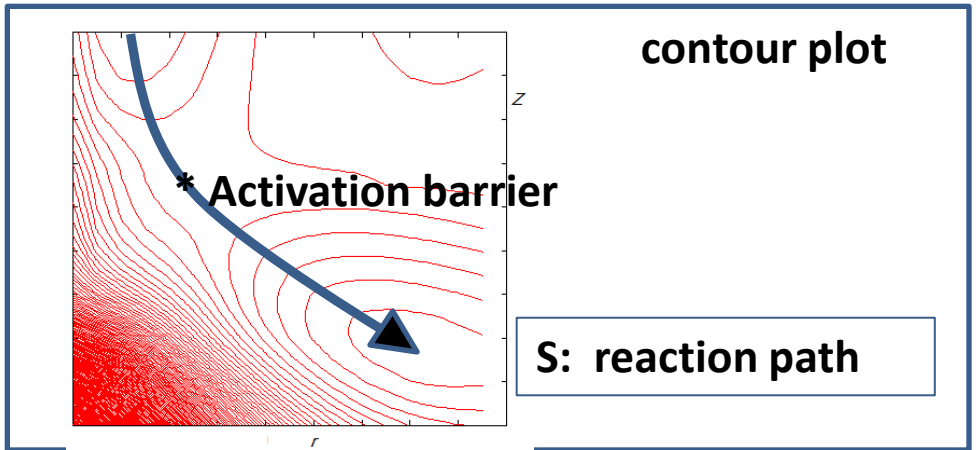
Example:
H-B-F : center of mass of H_2 is above a bridge site; the H atoms dissociate towards the hcp and fcc hollow sites

r : H-H distance
Z : height of H_2 (H_2 center of mass) from the surface
Φ (phi) : azimuthal axis
θ (theta) : polar axis

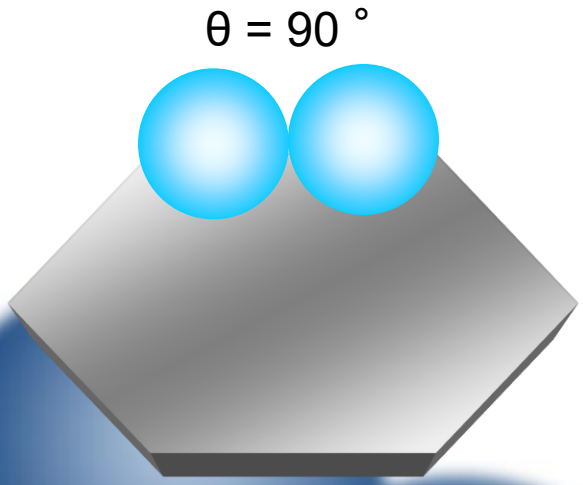
Typical potential energy surface for the molecular dissociative adsorption reaction

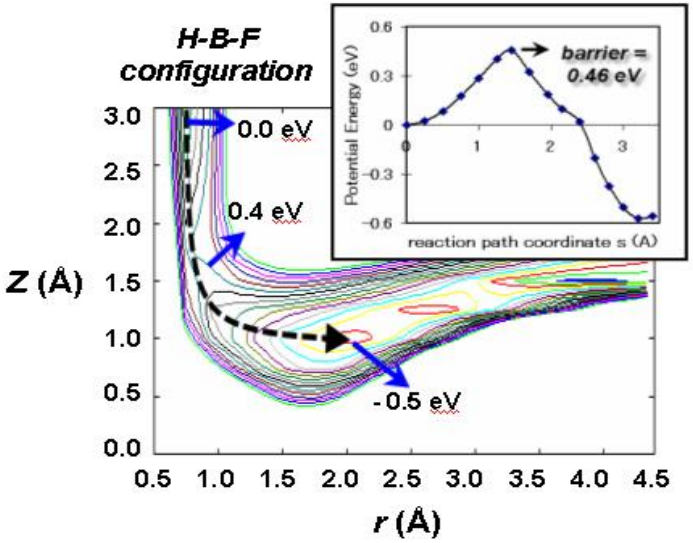


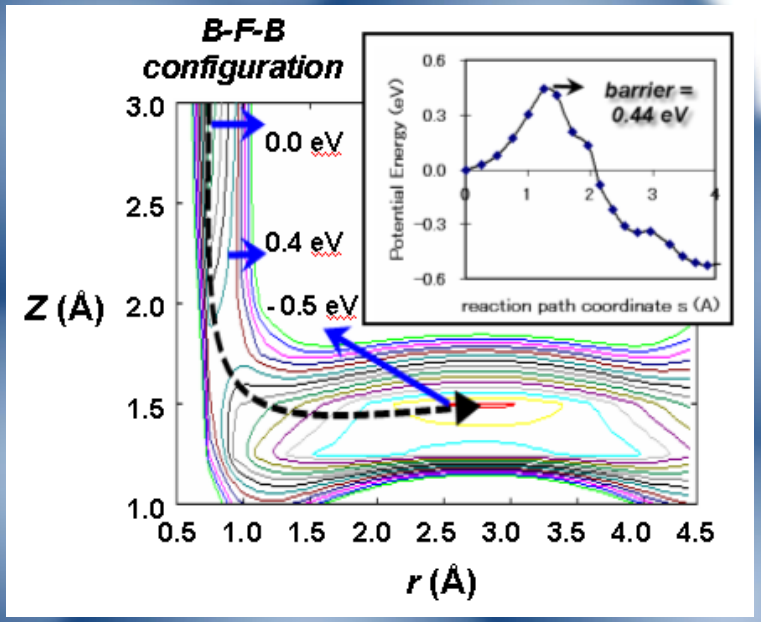


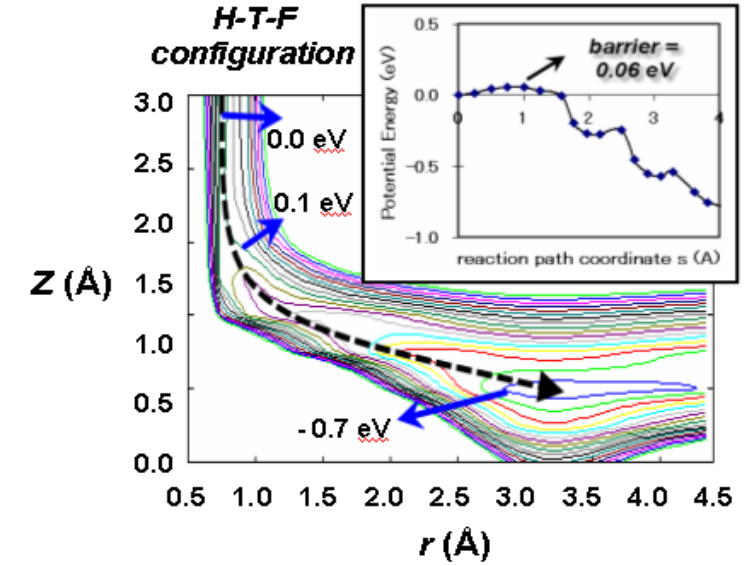


Dissociative adsorption of H_2 on Pt









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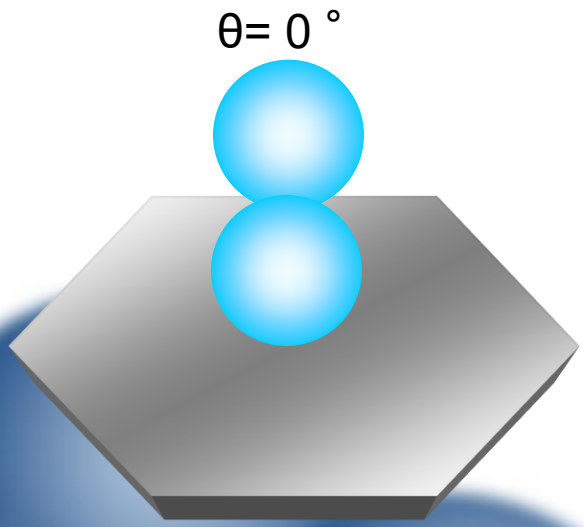
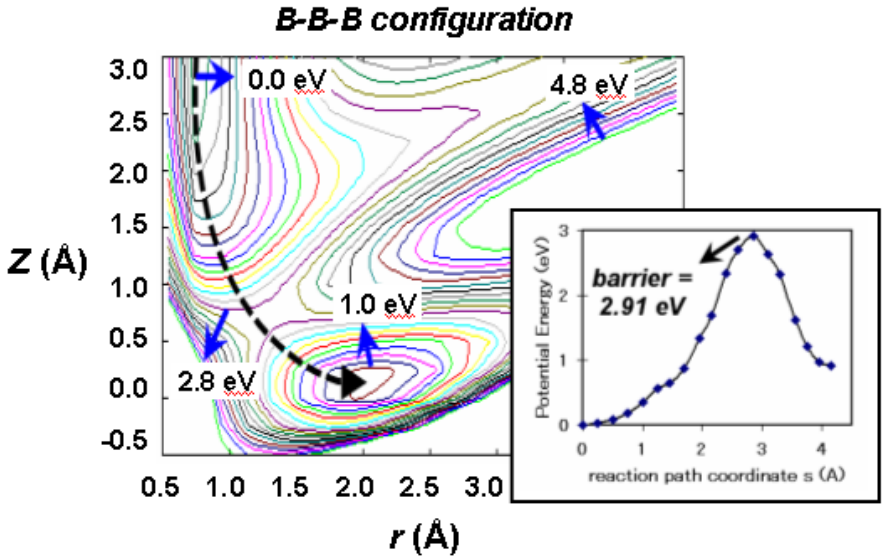
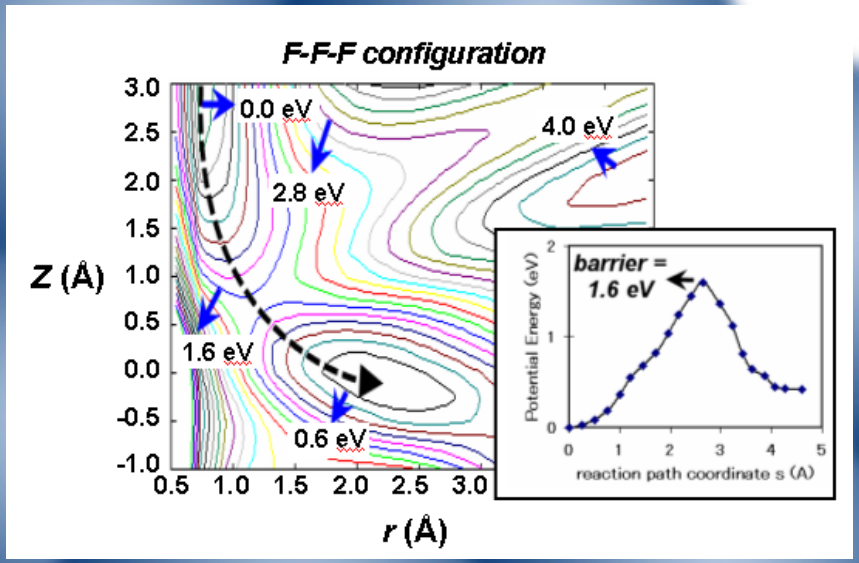
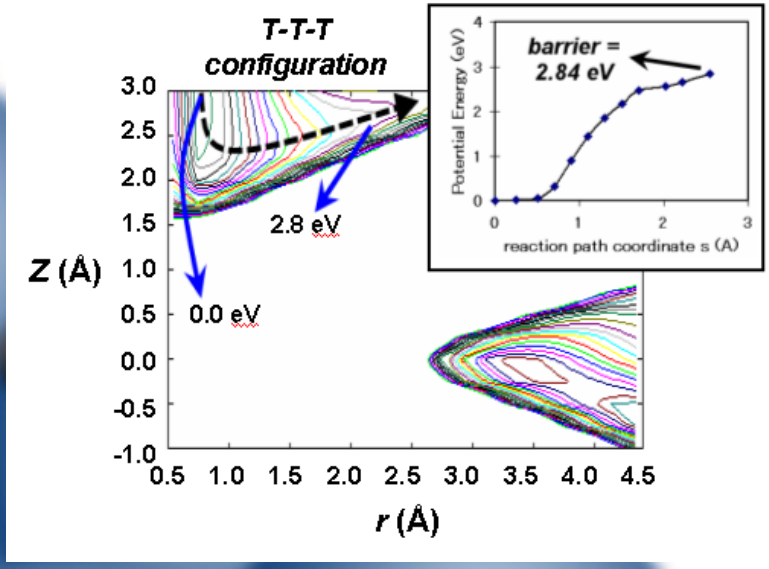
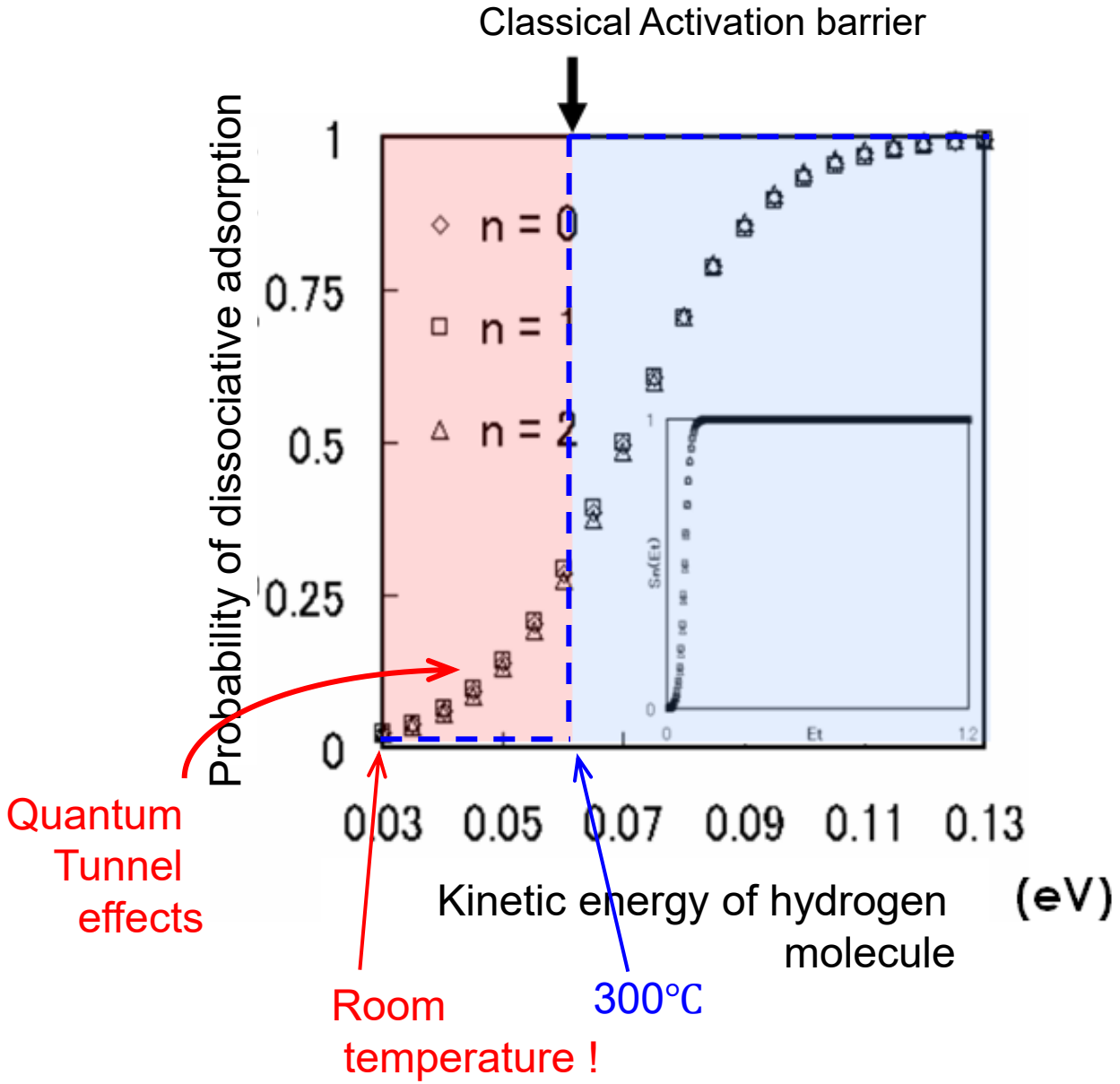




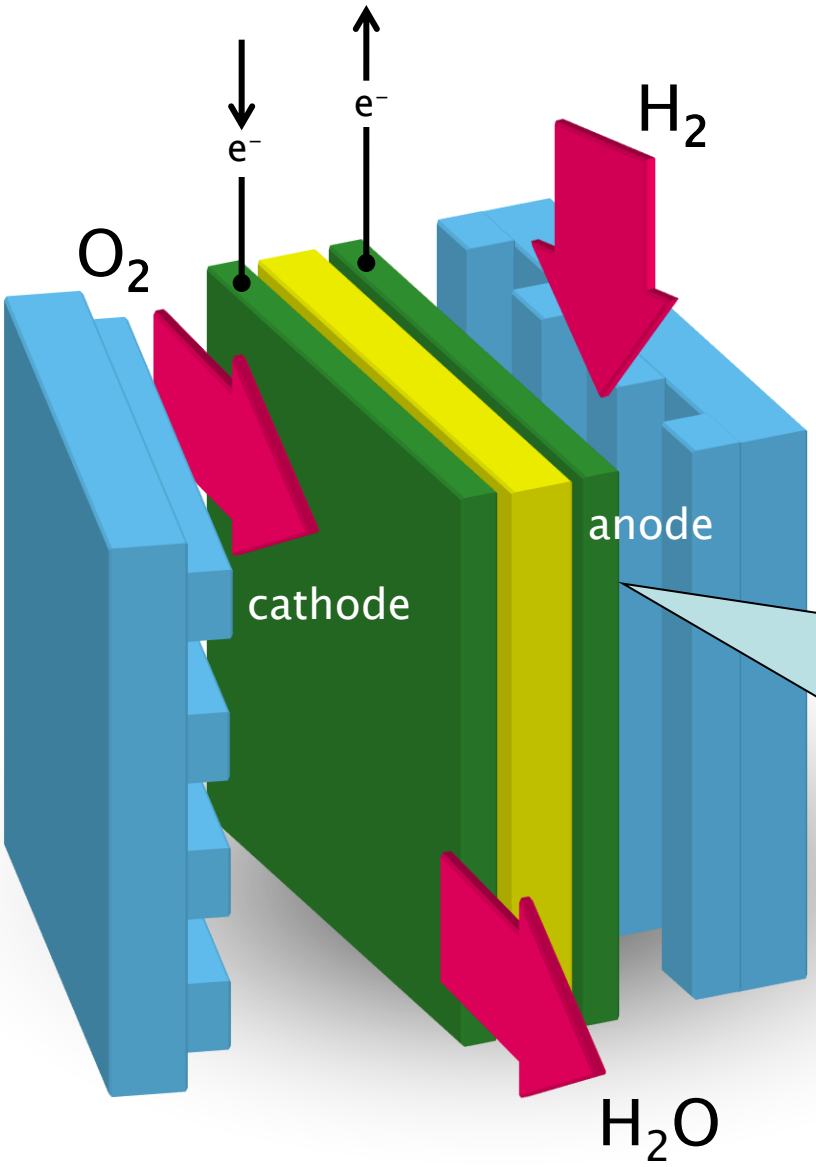




Quantum dynamics of dissociative adsorption of Hydrogen molecule



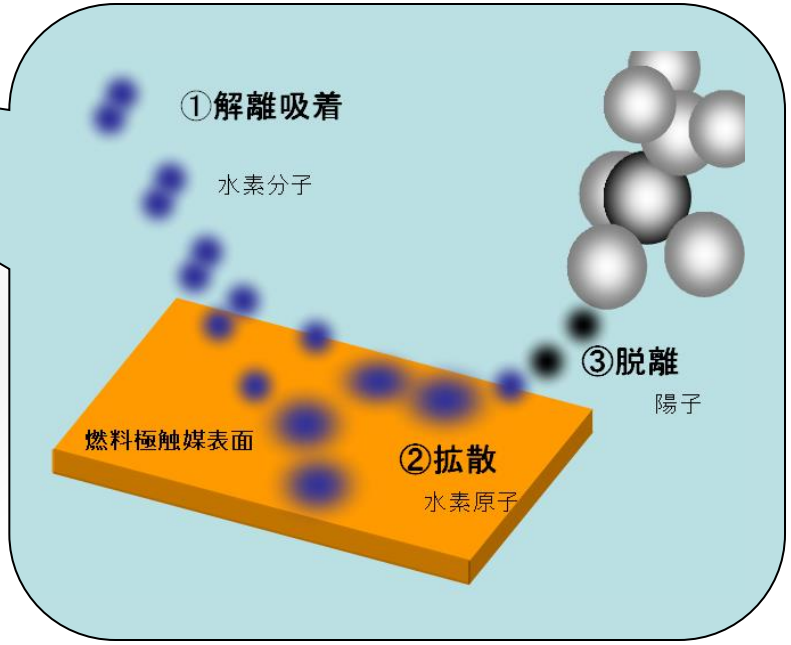
Some important reactions in the hydrogen fuel cell anode



① Dissociative adsorption of H_2 on the electrode surface (Pt)

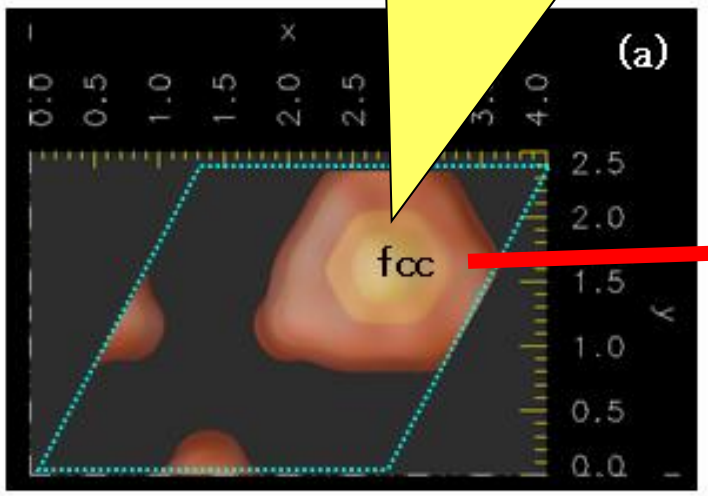
② Adsorption/migration of H (atoms) on the electrode surface

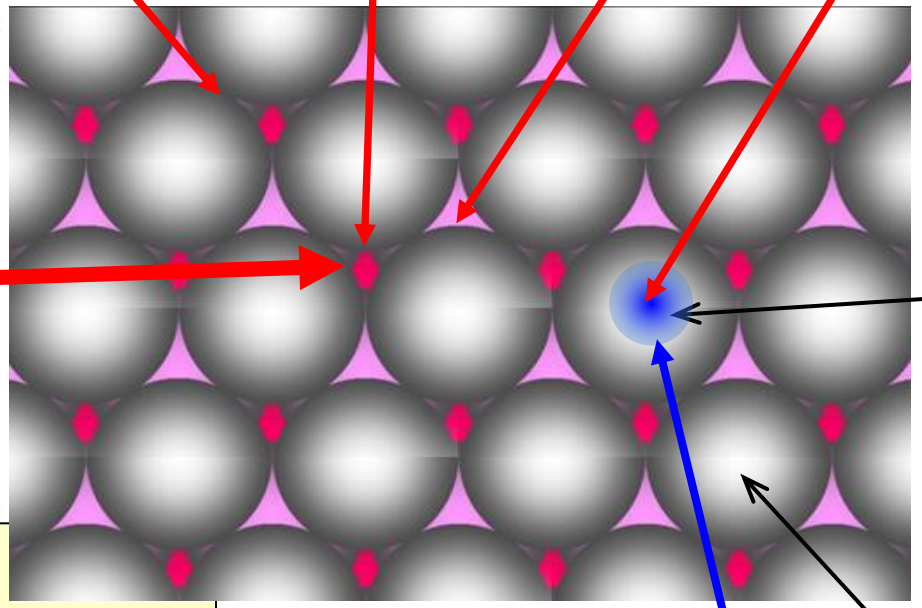
③ H^+ transmission from the electrode to the proton conducting membrane

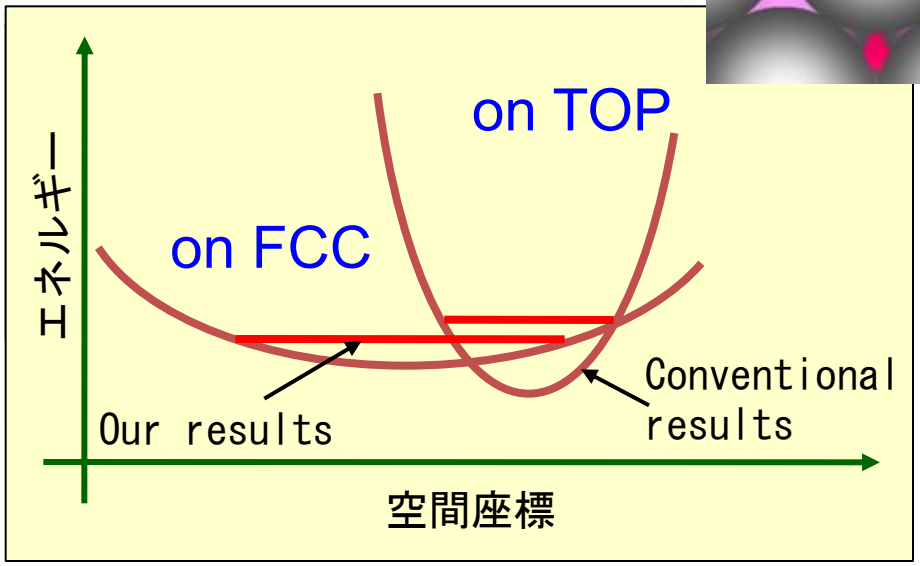


Quantum Adsorbed state of hydrogen atom

Quantum adsorbed states

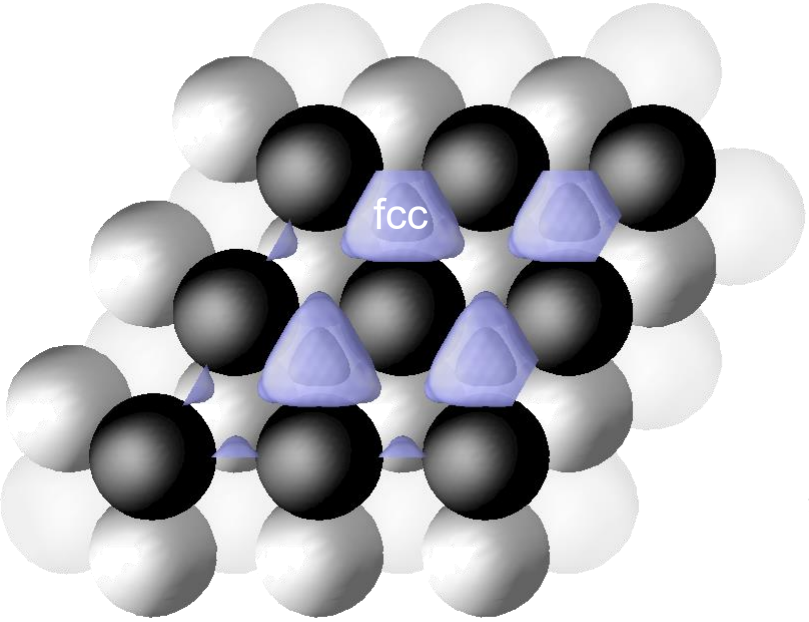






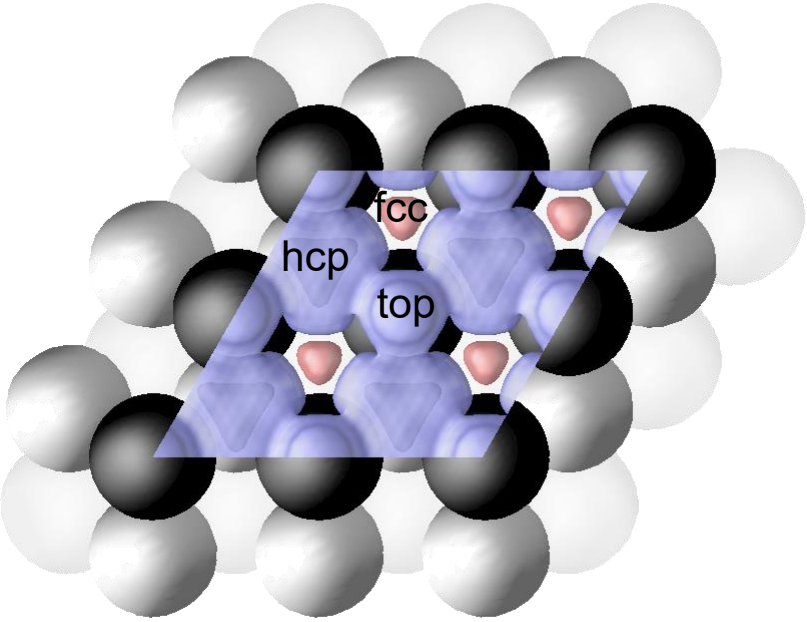
Wavefunctions of a hydrogen atom on Pt(111) surface

Ground state



E_0 = -2.461 eV

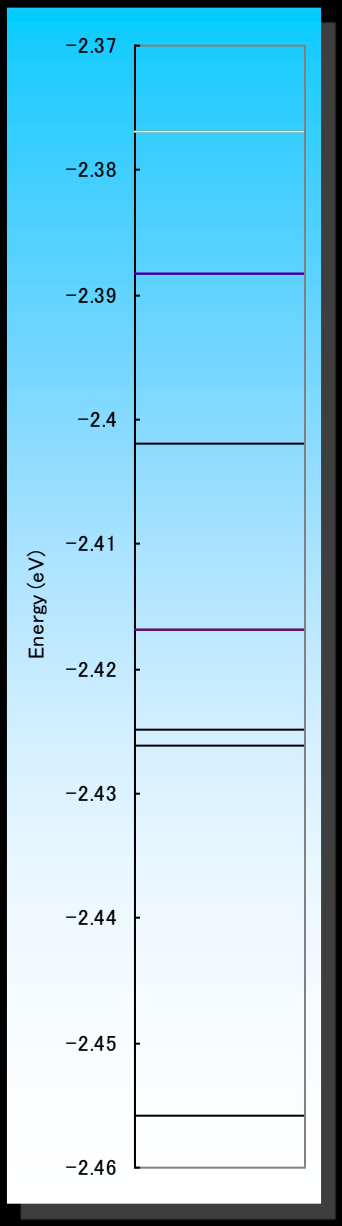
The first excited state



E_1-E_0 = 30 meV

Hydrogen diffusion can occur at typical fuel cell operational temperature !

1st Excited state



8th + 9th

6th + 7th

5th

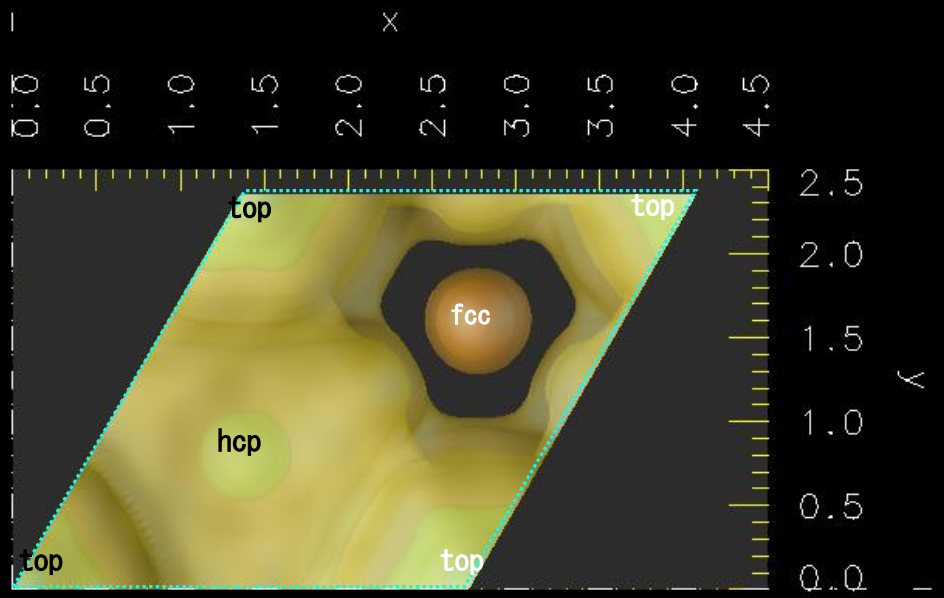
3rd + 4th

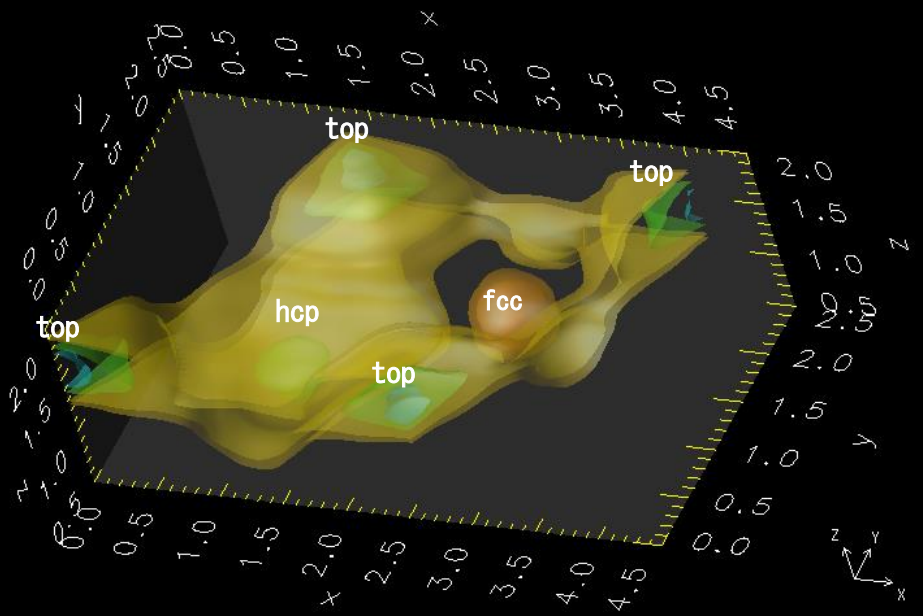
2nd
1st

Delocalized!

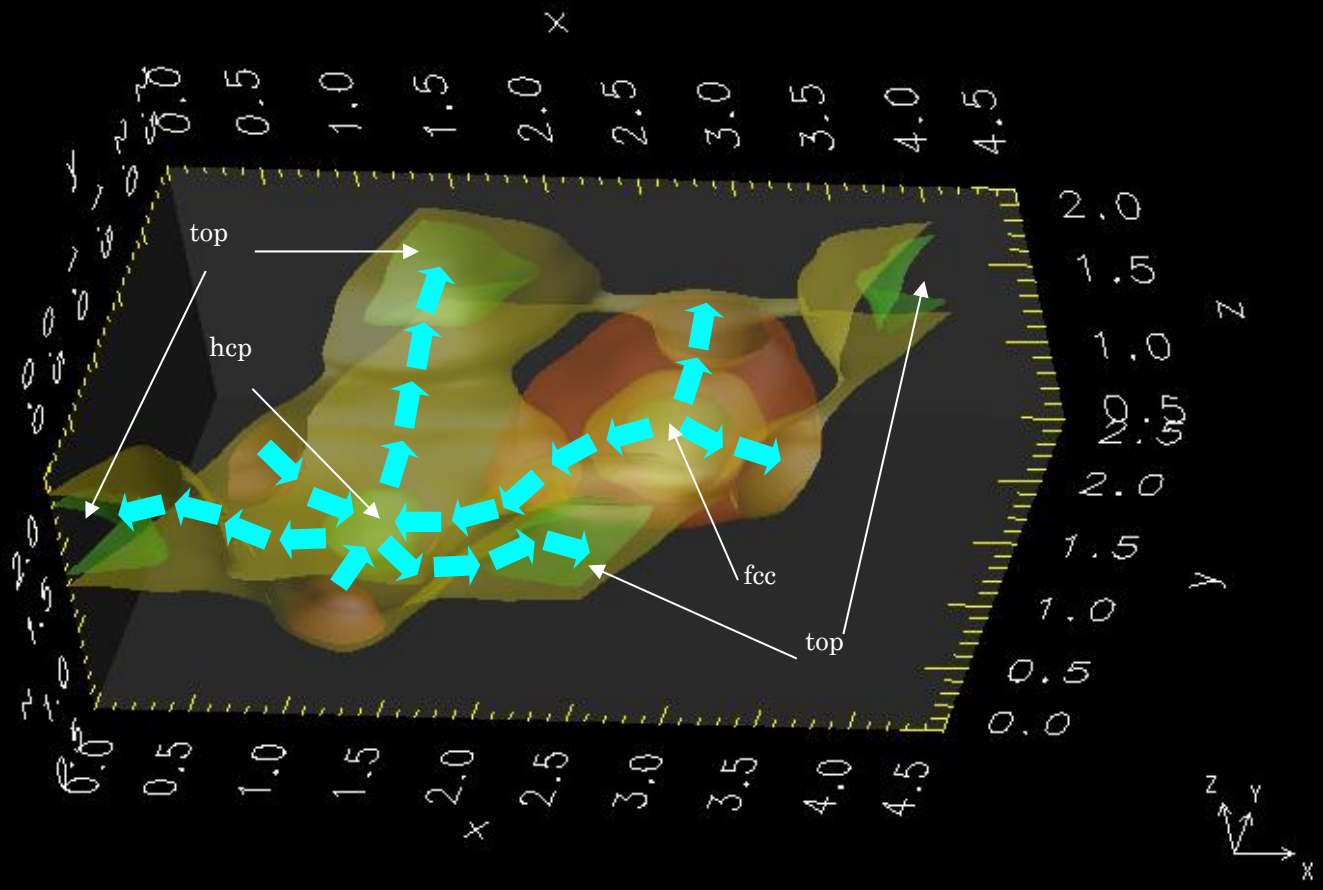
30 meV above the ground state

ground state



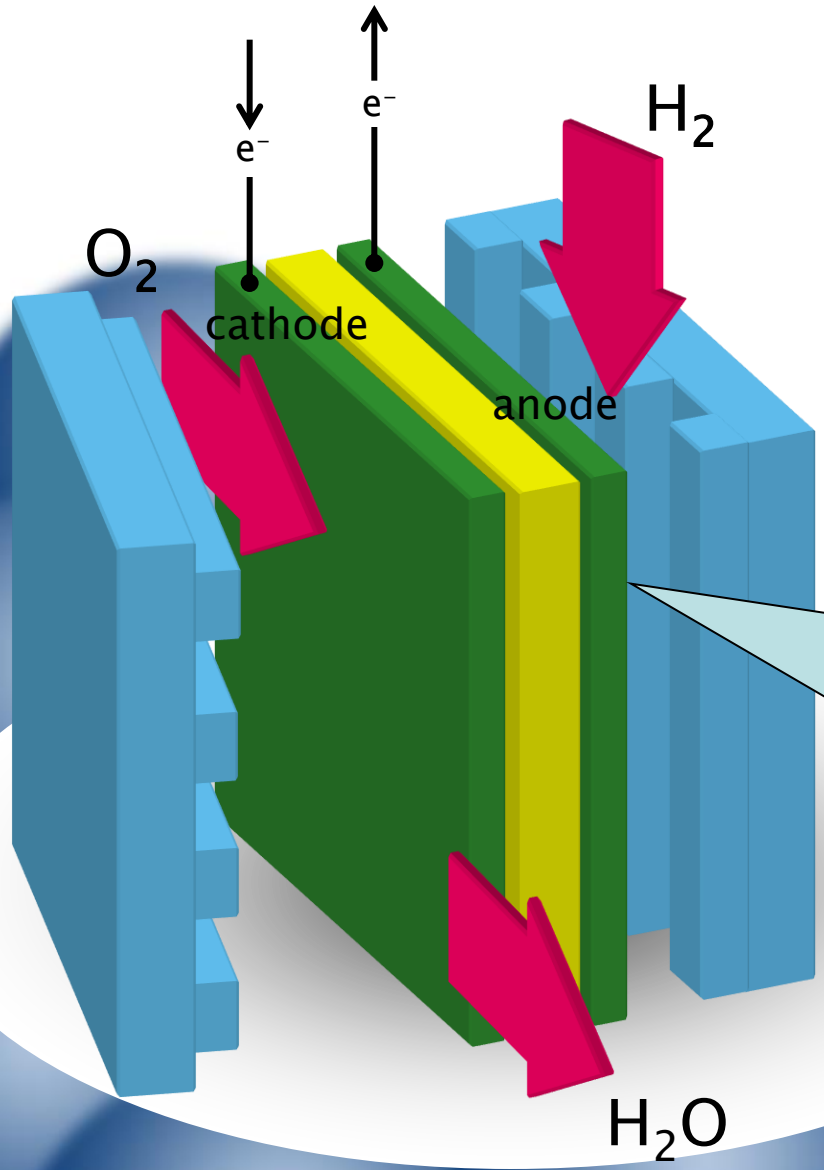


Diffusion process



拡散経路の古典的描像（青の矢印）。赤い部分は、
基底状態、緑-黄色部分は第一励起状態の
波動関数を表す。

Some important reactions in the hydrogen fuel cell anode



① Dissociative adsorption of H_2 on the electrode surface (Pt)

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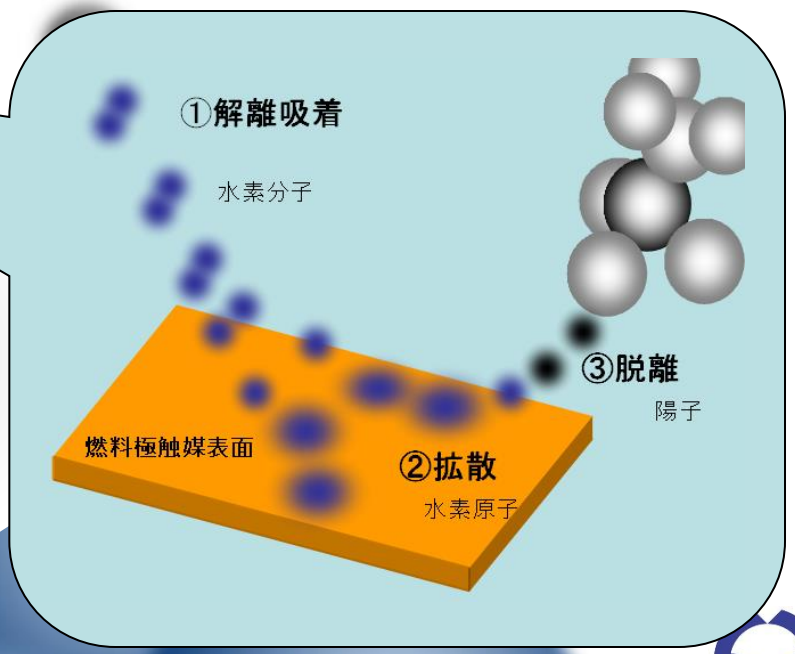
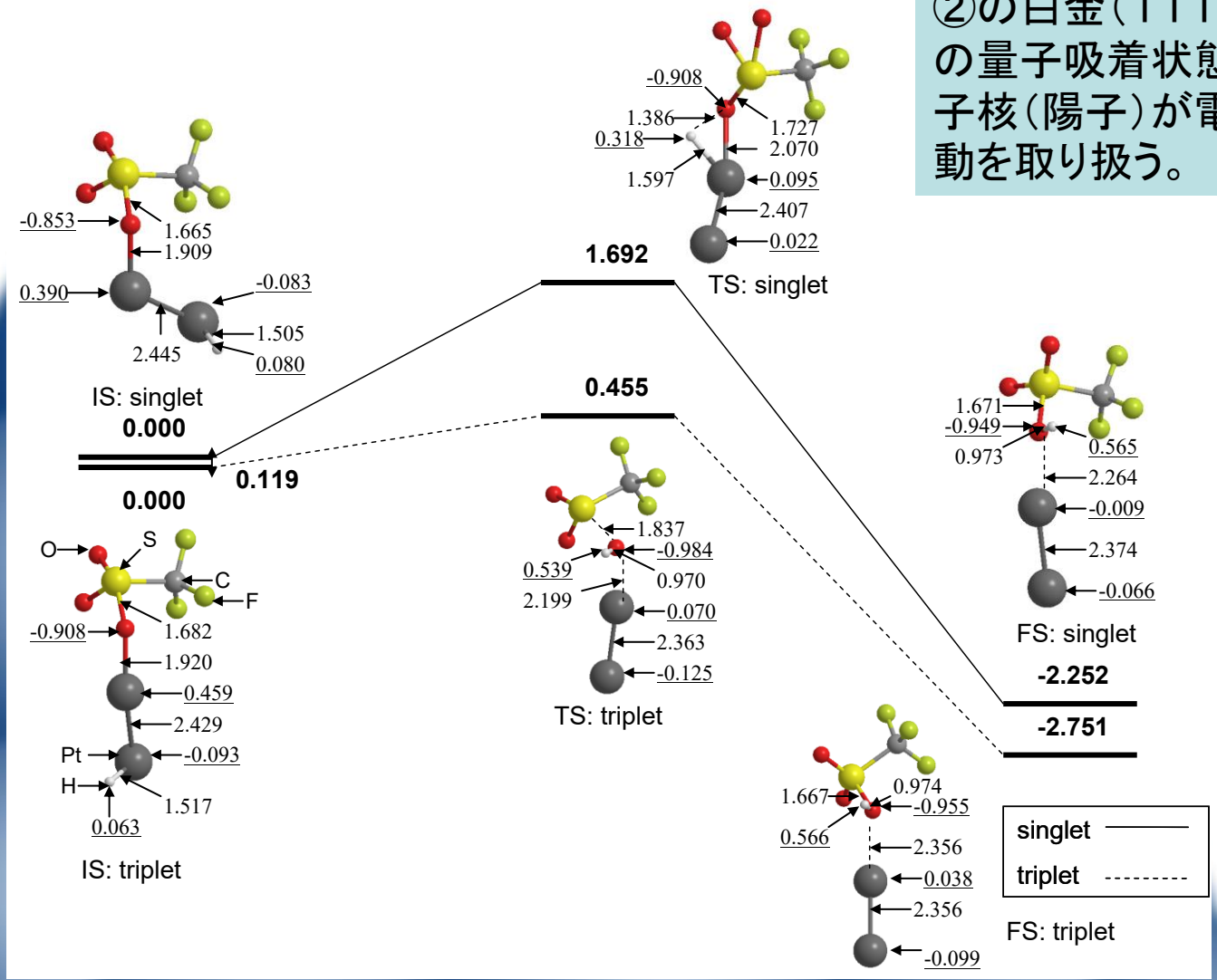


③ Dynamics of proton liberation from the Pt surface

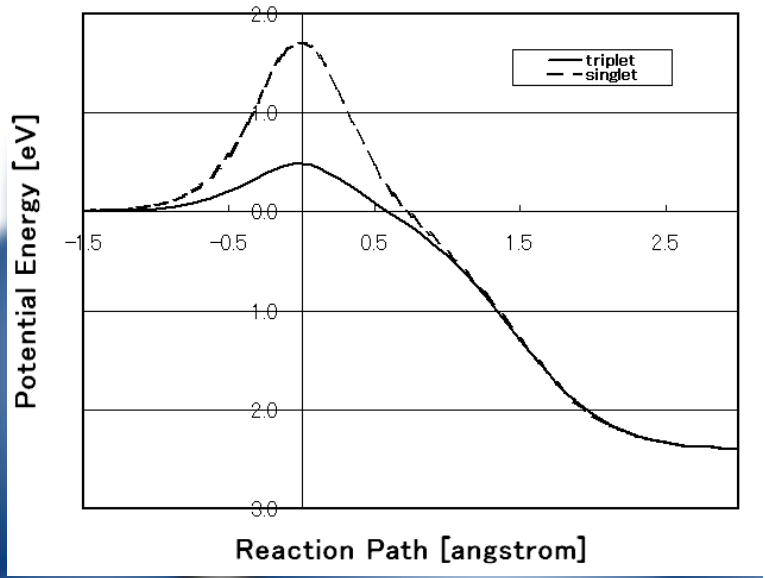
②の白金(111)面上での水素原子の量子吸着状態から水素原子の原子核(陽子)が電解質へ移動する運動を取り扱う。



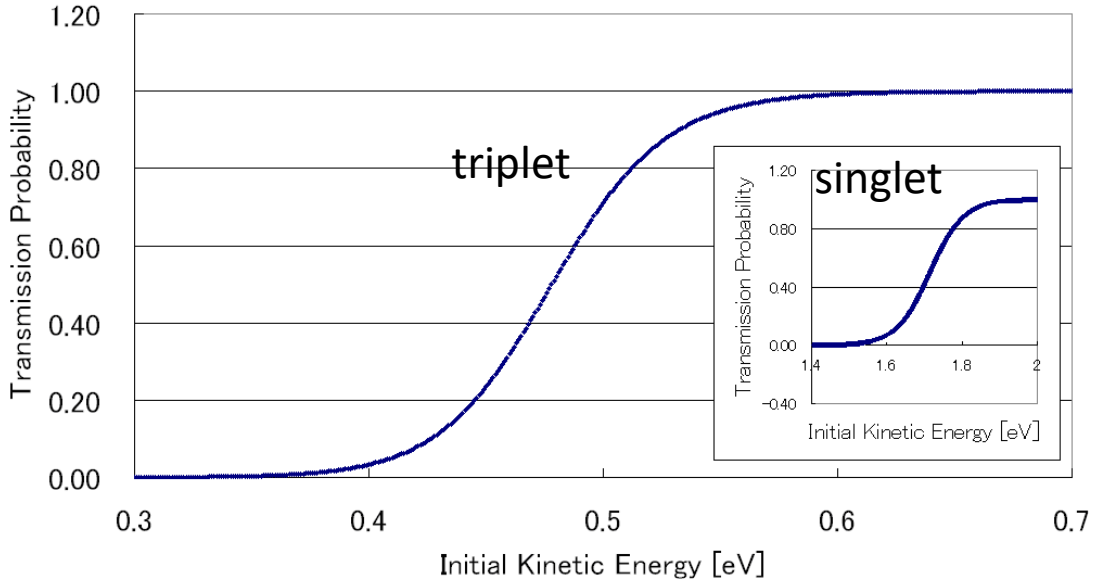
水素原子から白金触媒への電子移動が起こる

Potential energy for proton motion

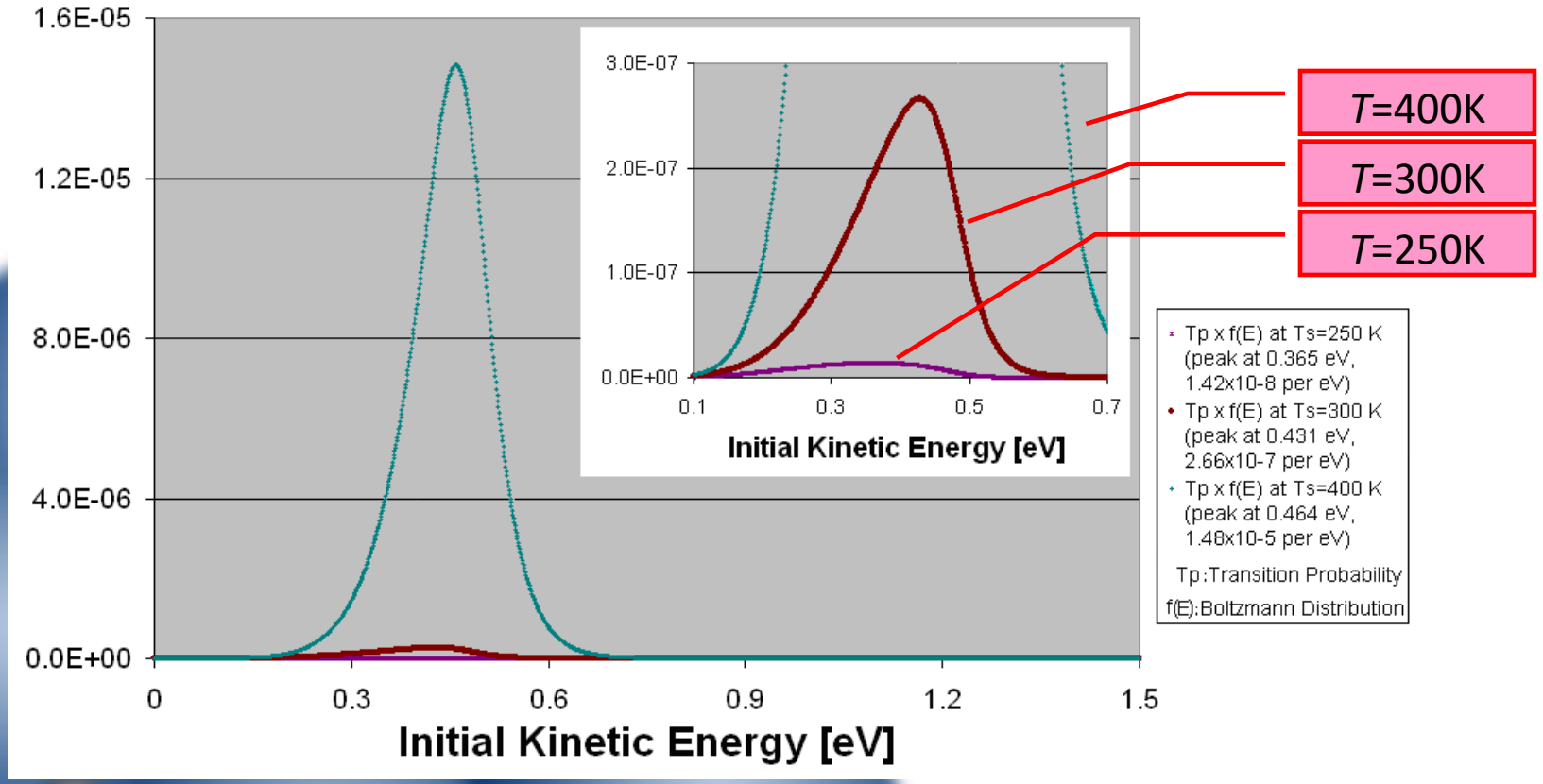
Initial transition final



Transmission probability



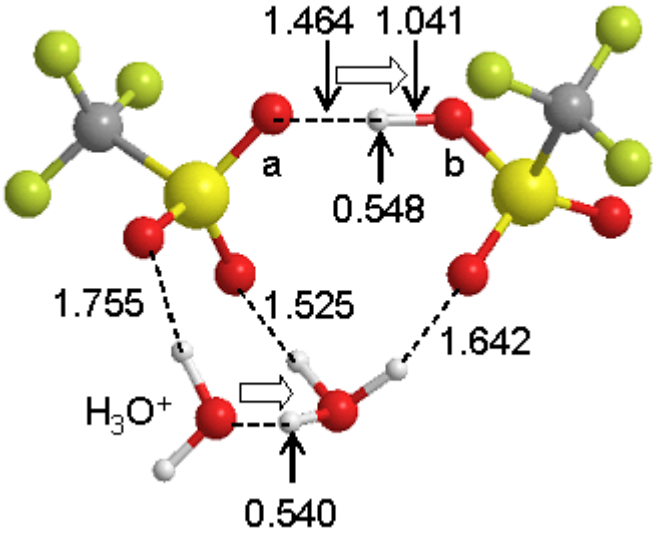
Surface temperature dependence



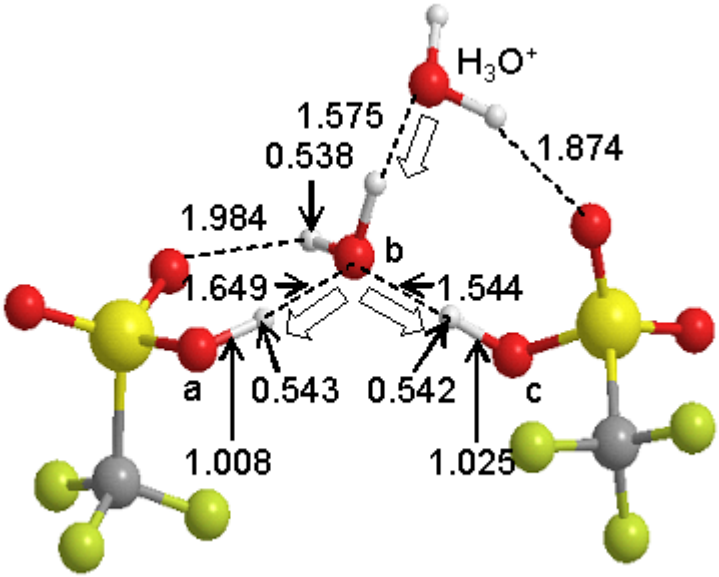
Quantum tunneling effects on this process

play an important roll even at *typical fuel cell operational temperature!!*

Proton conduction in the Proton Exchange Membrane



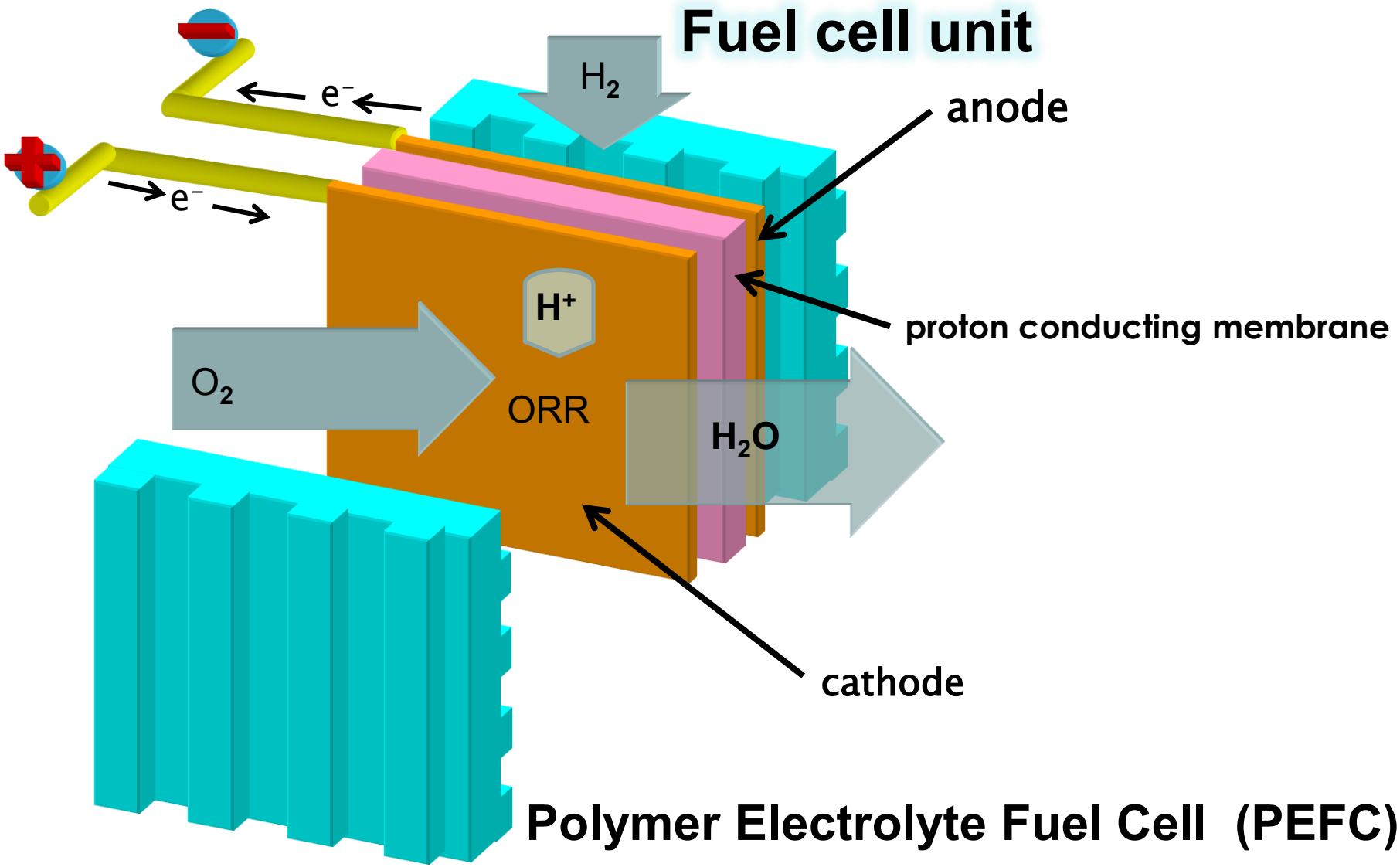
側鎖間の直接的な伝導



側鎖間の間接的な伝導

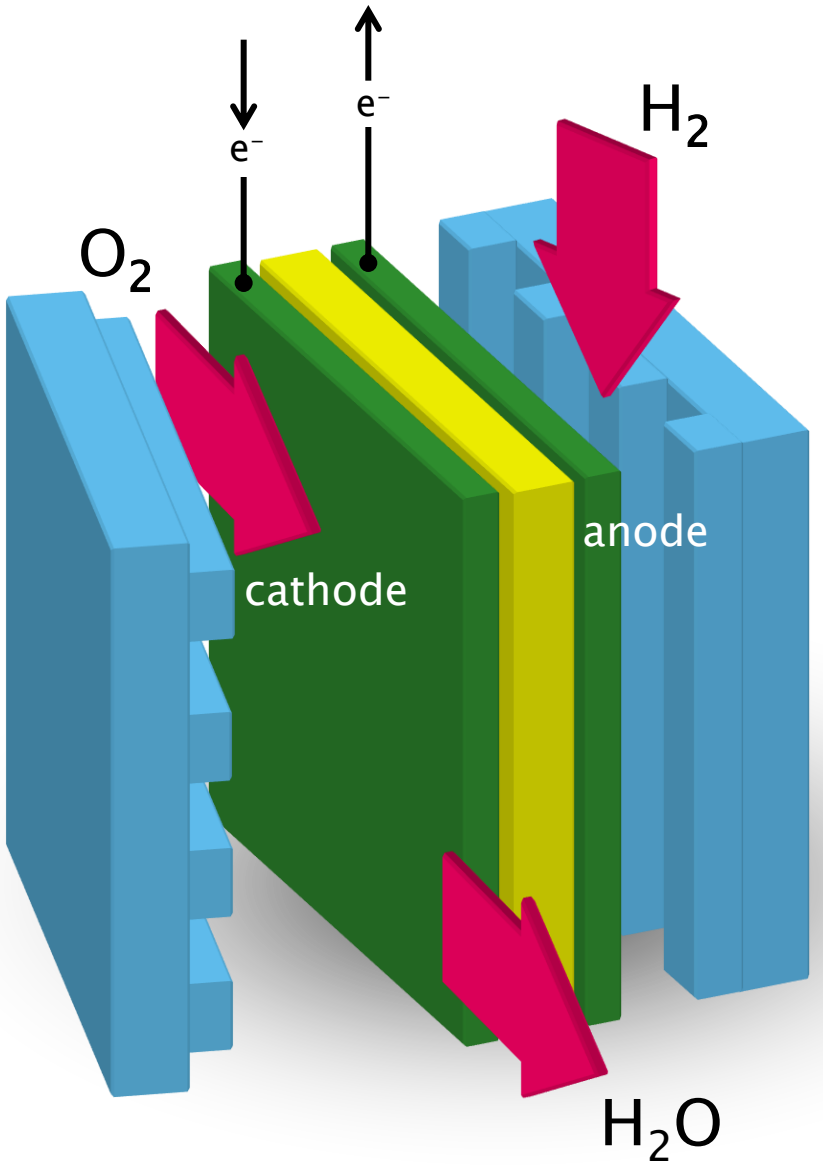
H_2O分子を介し，O-H結合の内部変換を伴う

Oxygen Reduction Reactions on Fuel Cell Cathode



Polymer Electrolyte Fuel Cell (PEFC)

Challenges in PEFC Development （課題）



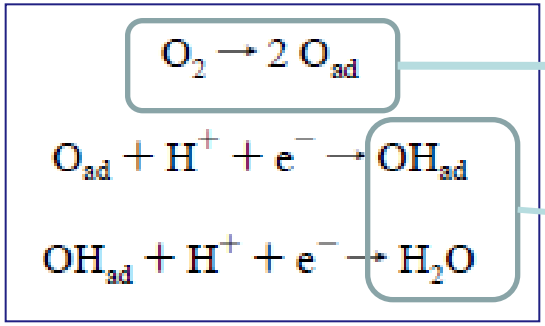
Major issues

1. Cathode reactions are slow even on Pt
2. Pt is very precious metal

Challenges in PEFC Development （課題）

Cathodic reaction:
Oxygen reduction reaction (ORR)

$$1/2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$



General reaction pathway for bimetallic systems

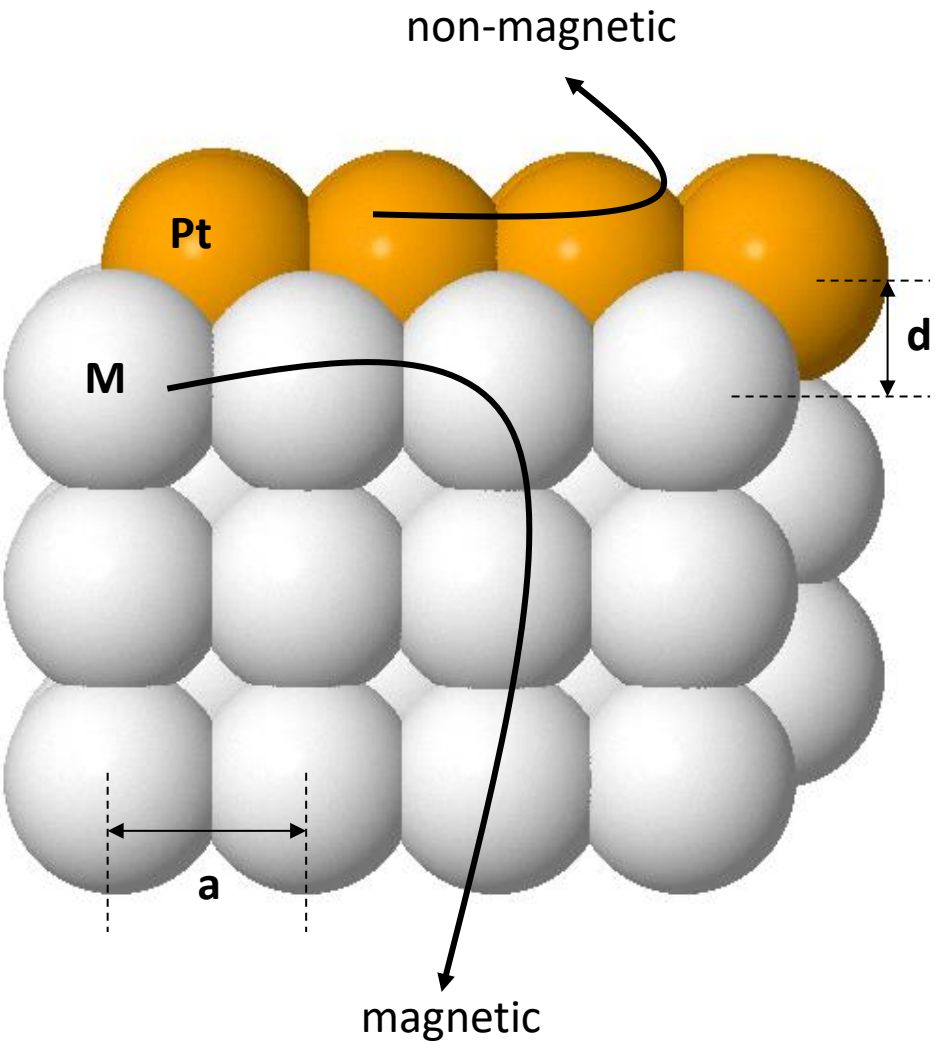
Easy dissociation is needed.

Less binding on catalyst IS NEEDED for easy subsequent reaction and desorption

O_2 activation in this respect (easy O2 dissociation but less binding of Oad on the surface) is therefore not easy to attain.

A. Udaykumar and M. Mavrikakis: Surf. Sci. 602 (2008) L89.

Tuning Reactivity using Non-magnetic layer (Pt) over Magnetic Substrate (Fe)



- Pt pseudomorphic overlayer on 3d transition metal (M). **a** and **d** are lattice constant of M and Pt-M interlayer distance, respectively.

- These bimetallic systems can offer up to 90% reduction in Pt loading.

- Comparable with Pt-based alloys under electro-catalytic measurements since **Pt segregation to surface forming Pt "skin" over base metal is generally observed.**

Toda, T.; Igarashi, H.; Watanabe, M. *J. Electroanal. Chem.* 1998, *446*, 213-220.

Ruban, A. V.; Skriver, H. L.; Nørskov, J. K. *Phys. ReV. B.* *1998, 59, 15990.*

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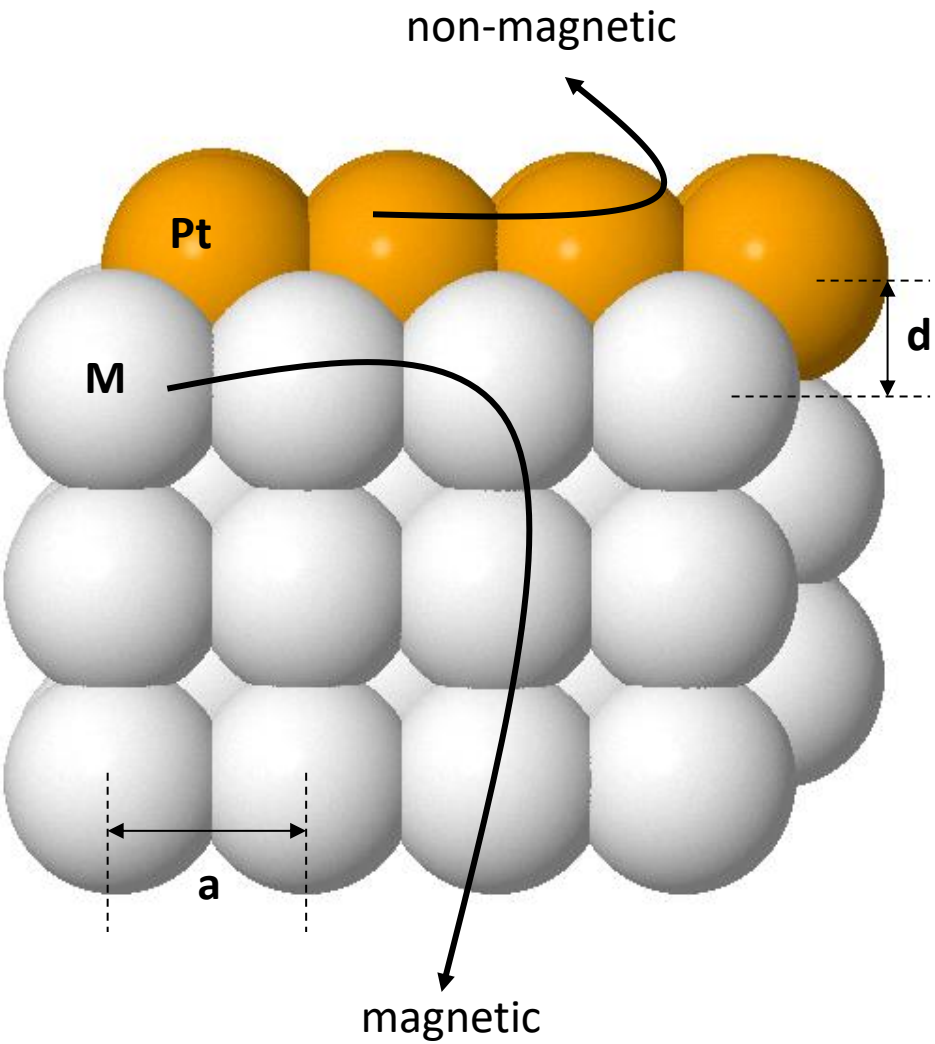

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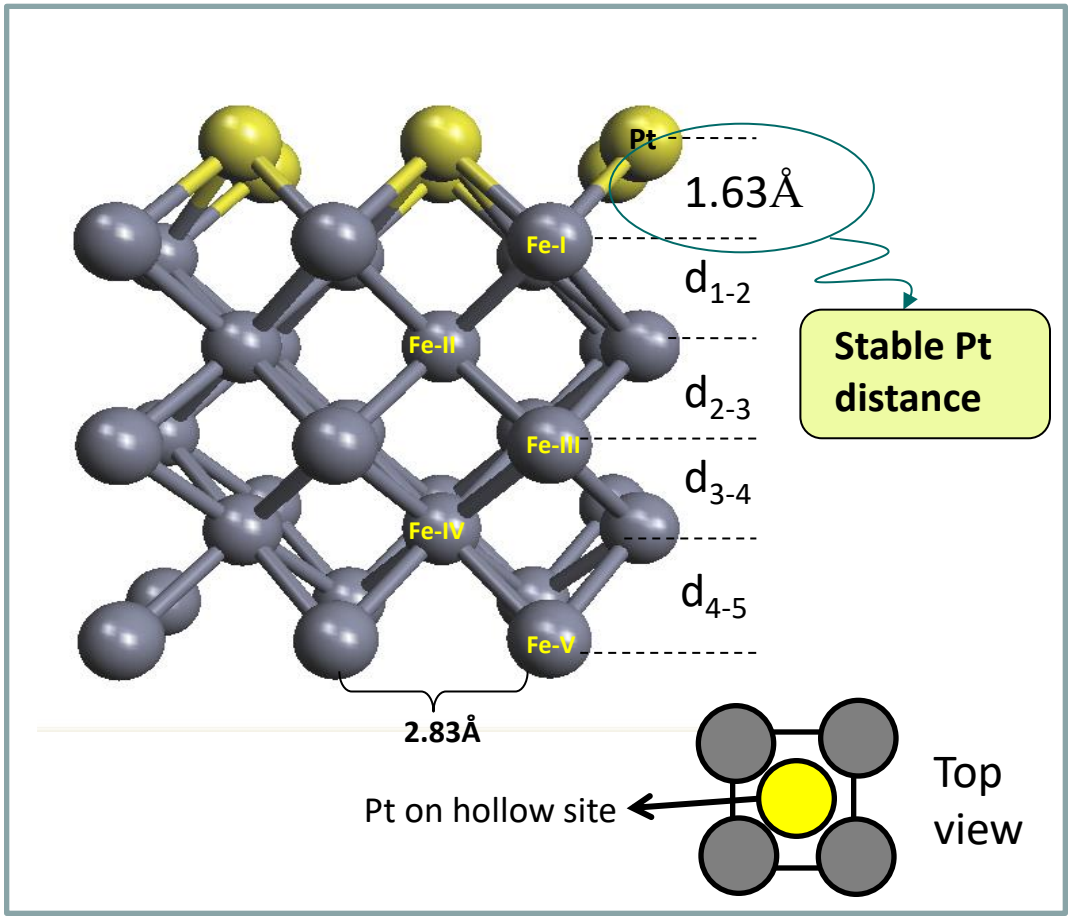
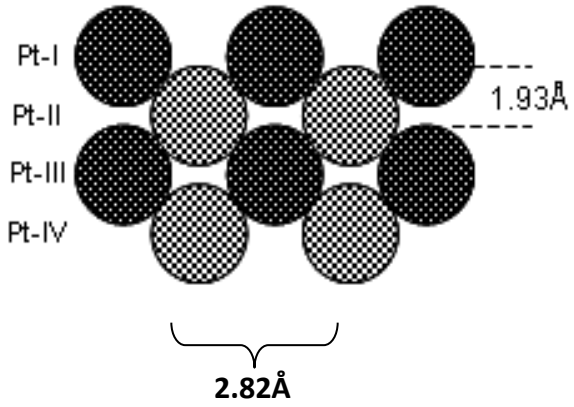
Atomic Structure of Pt/Fe(001)



Reference System: Pt(001) – (1 x1)

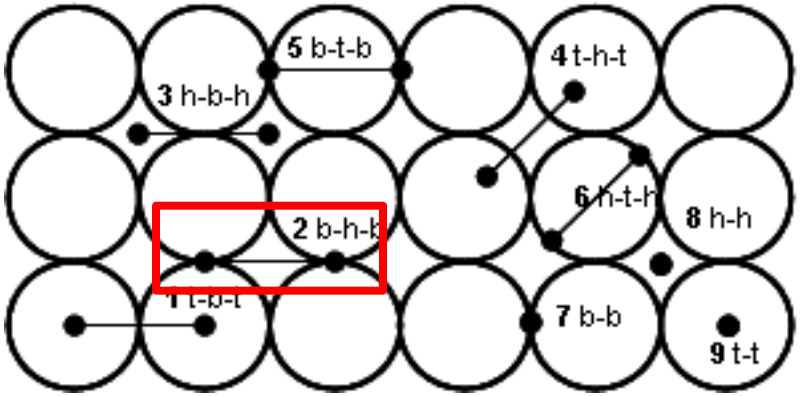


Pt(001)-(1x1) structure viewed along [010] direction

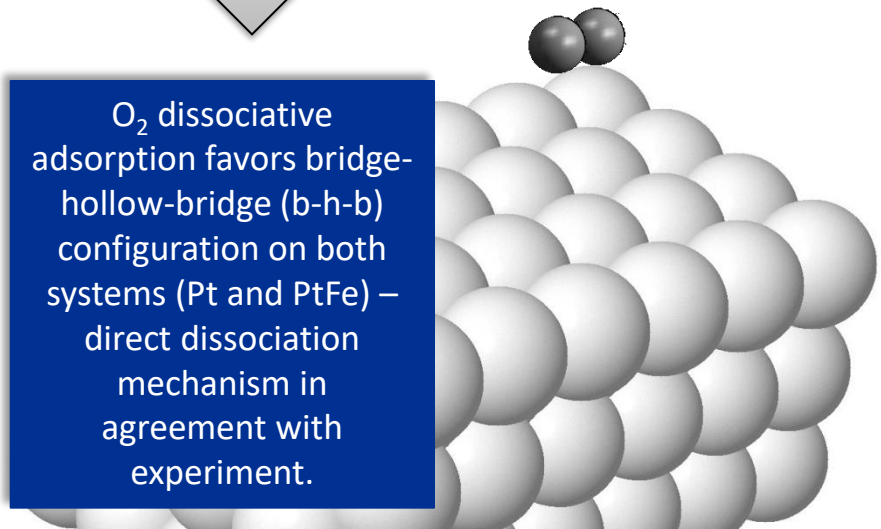
- Pt-Fe bond length is 2.50Å , a significant **contraction** with respect to the Pt-Pt bond in first interlayer of 4-layer fcc Pt (001) slab.

O_2 dissociative adsorption

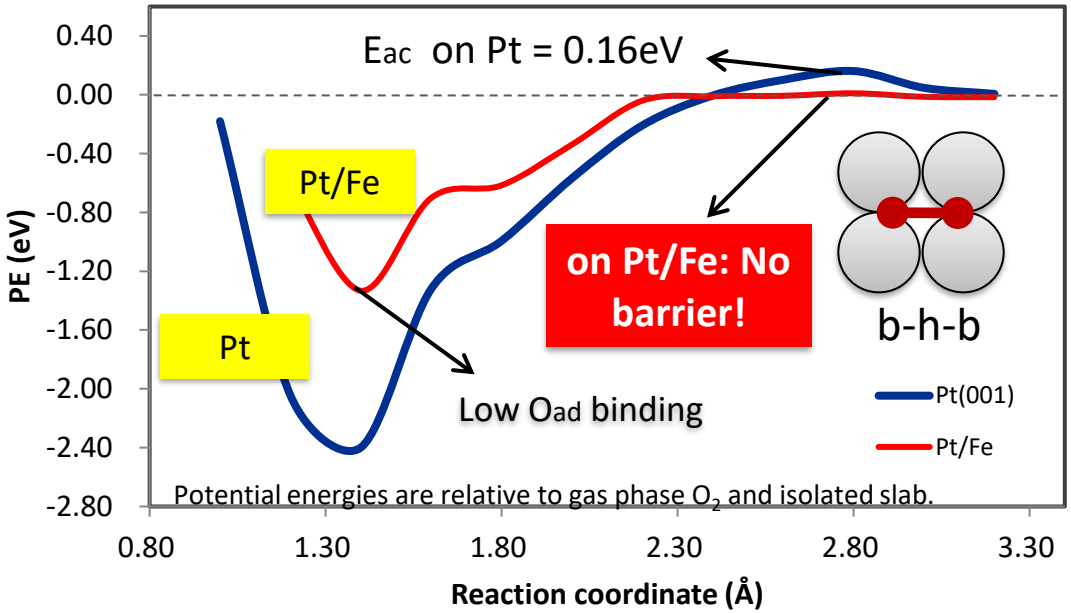
O_2 trajectories

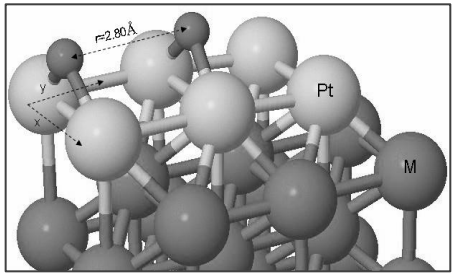


O_2 dissociative adsorption favors bridge-hollow-bridge (b-h-b) configuration on both systems (Pt and PtFe) – direct dissociation mechanism in agreement with experiment.



Potential energy curves for O_2 dissociative adsorption on Pt/Fe(001) and Pt(001)





Adsorbed:
O-O distance 2.80Å
O-Pt distance 1.30 Å

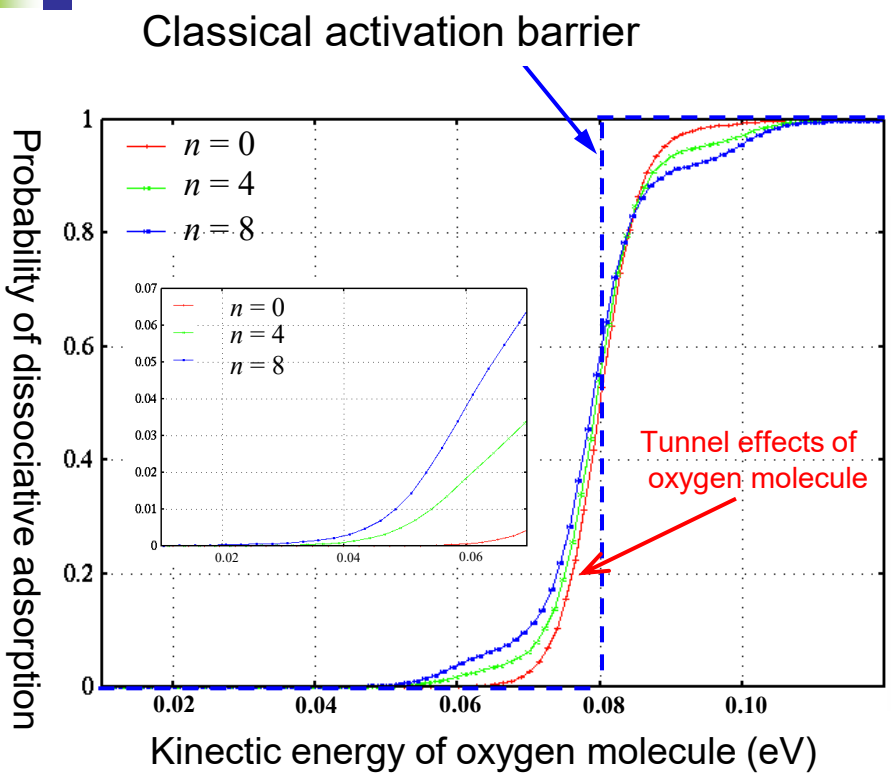
TS
O-O distance 1.30Å
O-Pt distance 2.80 Å

Bradley, J. M.; Guo, X. C.; Hopkinson, A.; King, D. A. *J. Chem. Phys. 1996, 104, 11. (exp)*
MC Escano, H. Nakanishi, H. Kasai JPC 113 52 (2009)

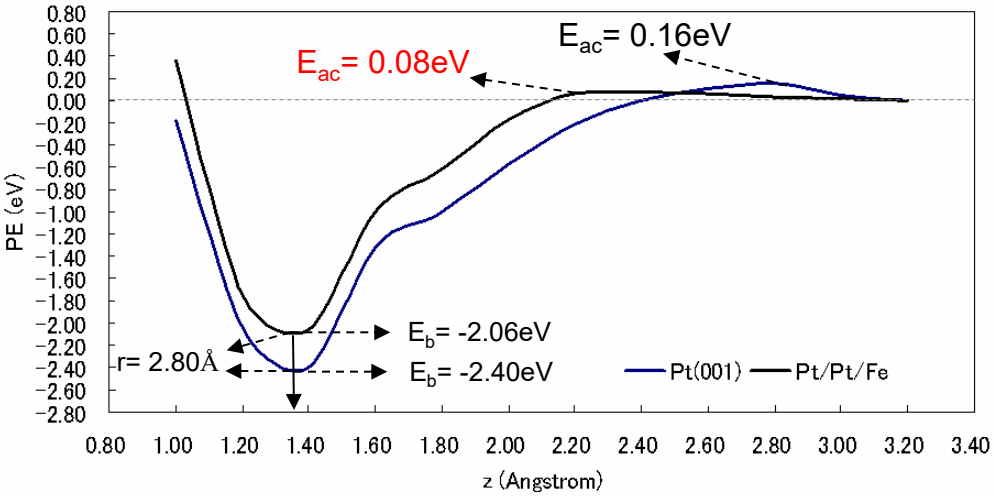
Result 2 : Cathode catalyst and its new design

- The dissociative adsorption reaction of oxygen molecule on cathode catalytic surface is rate limiting reaction proceed by the quantum tunnel effect even at room temperature.
- Designed surface: 2ML Pt coating Fe surface can enhance the dissociative adsorption reaction of oxygen molecule

Dissociative adsorption of oxygen molecule

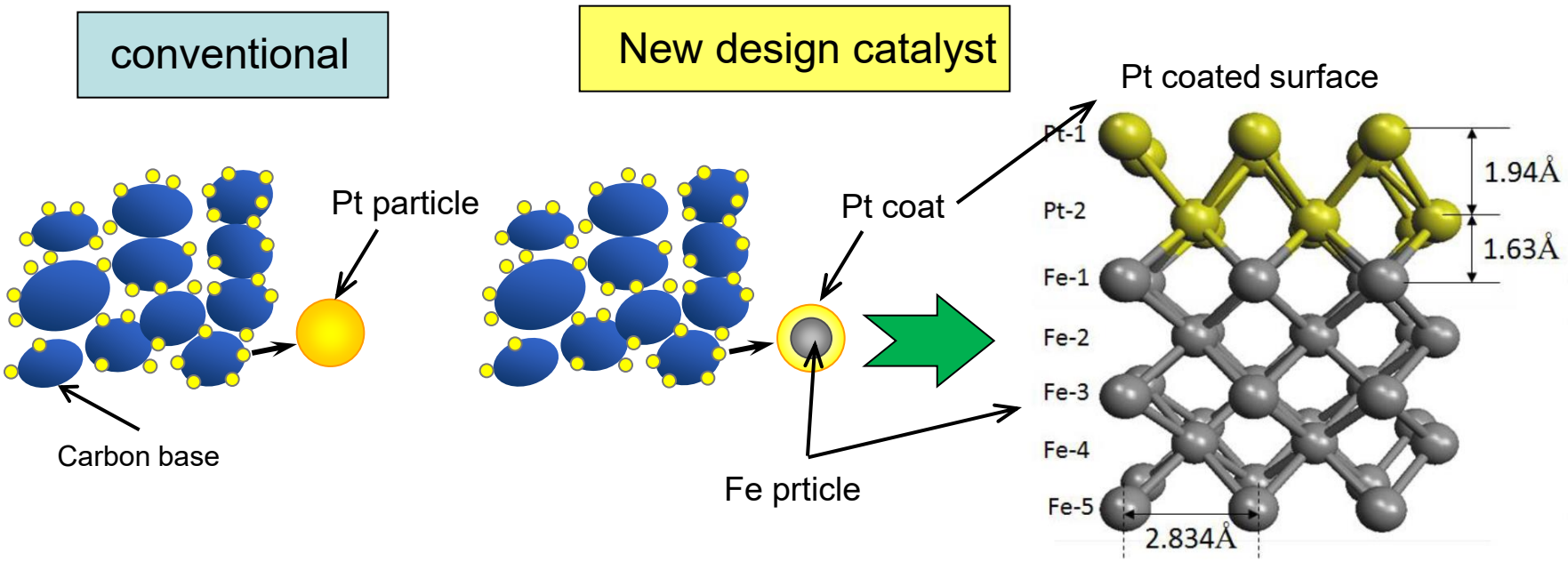


Potential energy curves for O_2 dissociative adsorption on Pt/Pt/Fe(001) and Pt(001)



Based on the classical mechanics theory, it is necessary that operation temperature is higher than 1000℃ for conventional Pt catalysis and 500℃ even for new designed Pt(2ML)/Fe catalysis surface. Actual possible room temperature operation is due to the quantum tunneling effects.

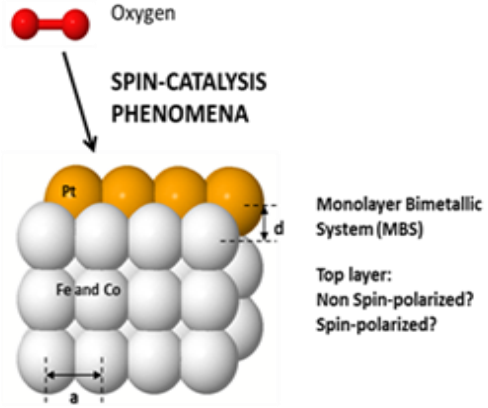
CMD for cathode catalyst

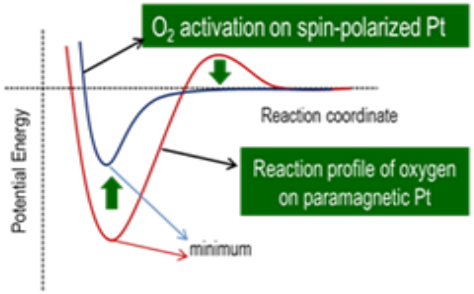


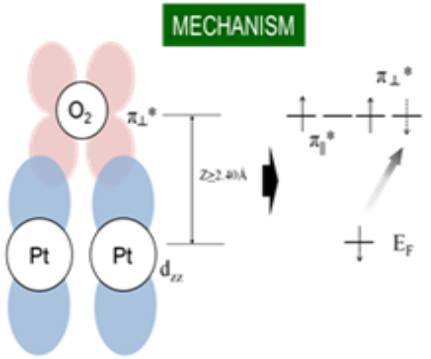
In this new designed catalysis surface, the Pt atoms have magnetic spins, which are induced by the Fe layers. Spin-polarized Pt has

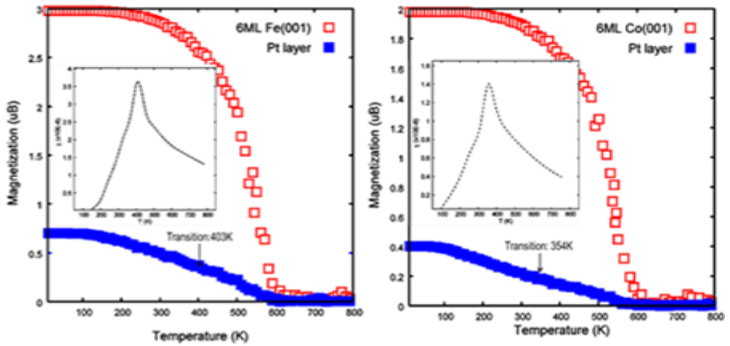
Cathode Catalyst for Fuel Cell

Spin polarization effects on oxidation of Pt





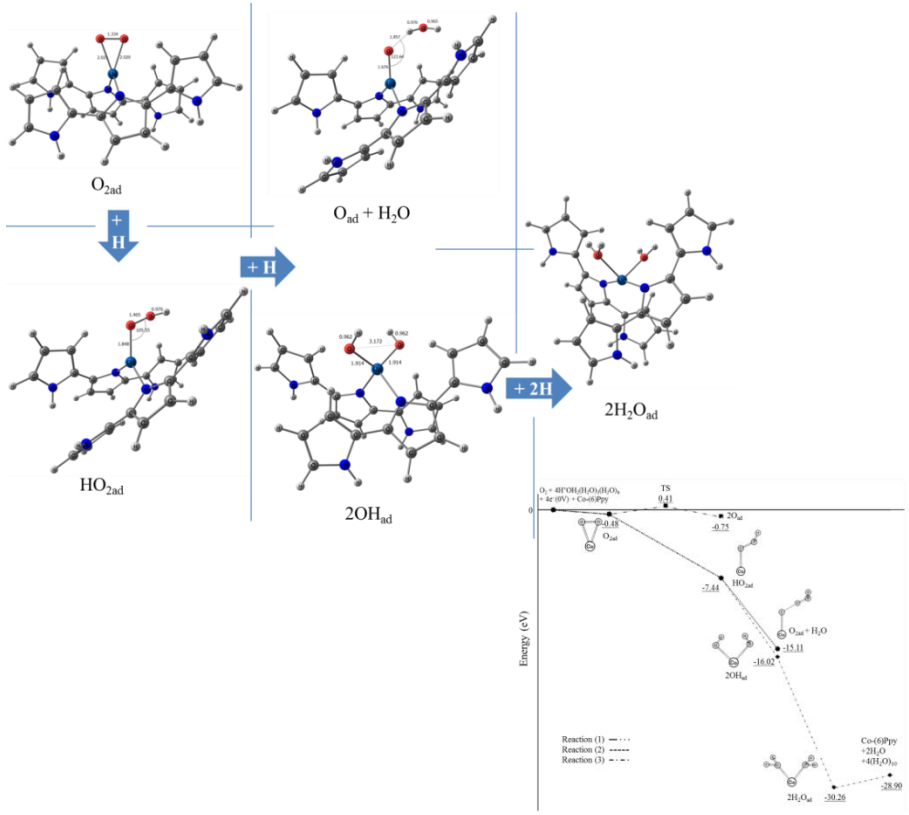




Magnetization curves and phase transition for Pt (on Fe) and Pt (on Co).

Dr. Mary Clare Escaño
PNU, BSPT 2000

Designing Non-Precious Metal Catalysts for Oxygen Reduction Reaction in the Direct Hydrazine Fuel Cells



Dr. Adhitya Gandaryus Saputro (Indonesia) 2014

Summary

- The first principles quantum calculation（Hyper-Naniwa） which can treat both the electrons and nuclei by quantum mechanical manner.
- Hydrogen Fuel Cell should be considered as the quantum mechanical machine.
- Computational Materials Design Method for fuel cell（FC-CMD） is constructed

to contribute to the Hydrogen Fuel Cell technology

JOURNAL OF APPLIED PHYSICS VOLUME 93, NUMBER 6 15 MARCH 2003

First principles studies for the dissociative adsorption of H_2 on graphene

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H. Kasai,[a] W. Diño, and H. Nakanishi
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T. Sugimoto
Toyota Motor Corporation, Toyota-cho, Aichi, 471-8572, Japan

(Received 9 September 2002; accepted 2 January 2003)

We investigate and discuss the interaction of H_2 with graphene based on density functional (DFT) theory. We calculate the potential energy surfaces for the dissociative adsorption of H_2 on highly symmetric sites on graphene. Our calculation results show that reconstructions of the carbon atoms play an important role in the H_2 -graphene interactions. Activation barrier for H_2 dissociation on an unrelaxed graphene is considerably high, ~4.3 eV for a T–H–T geometry and ~4.7 eV for a T–B–T geometry. The T–H–T(T–B–T) geometry means that the center of mass position of H_2 is at the hollow(bridge) site, and the two H atoms are directed towards the top sites on the graphene. On the other hand, when the carbon atoms are allowed to relax, the activation barrier decreases, and becoming 3.3 eV for the T–H–T geometry and 3.9 eV for the T–B–T geometry. In this case, the two carbon atoms near the hydrogen atoms move 0.33 Å towards the gas phase for the T–H–T geometry and 0.26 Å for the T–B–T geometry.
[DOI: 10.1063/1.1555701]

First Principles Studies on the Interaction of a Hydrogen Atom with a Single-Walled Carbon Nanotube

Yoshio MIURA[1,2], Hideaki KASAI[1,*], Wilson Agerico DIÑO[1], Hiroshi NAKANISHI[1] and Tsuyoshi SUGIMOTO[3]

[1]*Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan*
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(Received October 31, 2002; accepted for publication December 30, 2002)

We investigate the interaction of a hydrogen atom with an armchair-type, single-walled carbon nanotube, based on the density functional theory (DFT), and discuss how changes in the nanotube's diameter affect hydrogen adsorption on the carbon nanotube. We find that because the strong sp^2-like bonding and π-bonding network are enhanced with increasing nanotube diameter, hydrogen adsorption on the carbon nanotube becomes less stable with increasing nanotube diameter. We also find that with increasing nanotube diameter, the potential energy curves approach that for hydrogen interacting with a graphene sheet. These results can be explained in terms of the hydrogen-induced changes in the local density of states of the carbon nanotube. [DOI: 10.1143/JJAP.42.4626]

KEYWORDS: carbon nanotube, hydrogen, adsorption, first principles calculation, density functional theory

博士論文

第一原理計算による固体高分子形燃料電池要素材料及び水素貯蔵材料のデザイン(2007)

First Principles-Based CMD Design of Potential Materials for Proton Exchange Membrane Fuel Cell and Hydrogen Storage Applications

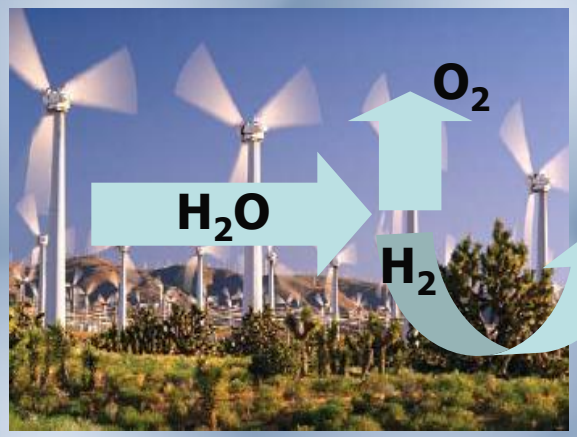
Dr. Muneyuki Tsuda (Toshiba)

Cyclic hydrocarbon dehydrogenation ***catalyst design***

白金を用いず、白金よりも
脱水素反応温度を低下！

Cyclohexane(C_6H_{12}) ⇔ Benzene(C_6H_6)

Cyclohexane
(C_6H_{12})



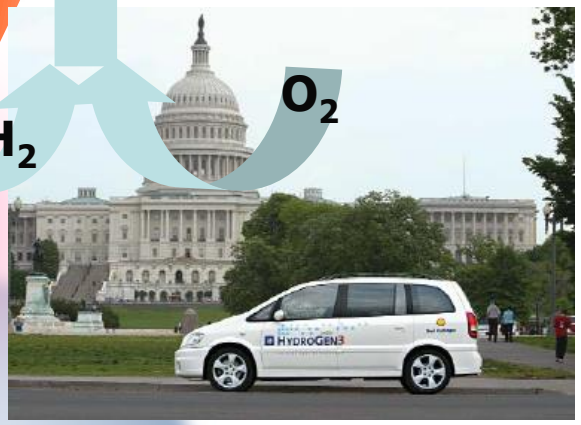
Hydrogen production

Benzene
(C_6H_6)

H_2O

H_2

O_2



Hydrogen fuel consumption

Cyclohexane (C_6H_{12}) as a hydrogen storage material

・常温常圧で液体である。

・貯蔵能に優れている

(7.2 wt%, 56.0 kgH_2/m^3 @$C_6H_{12} \rightarrow C_6H_6 + 3H_2$)

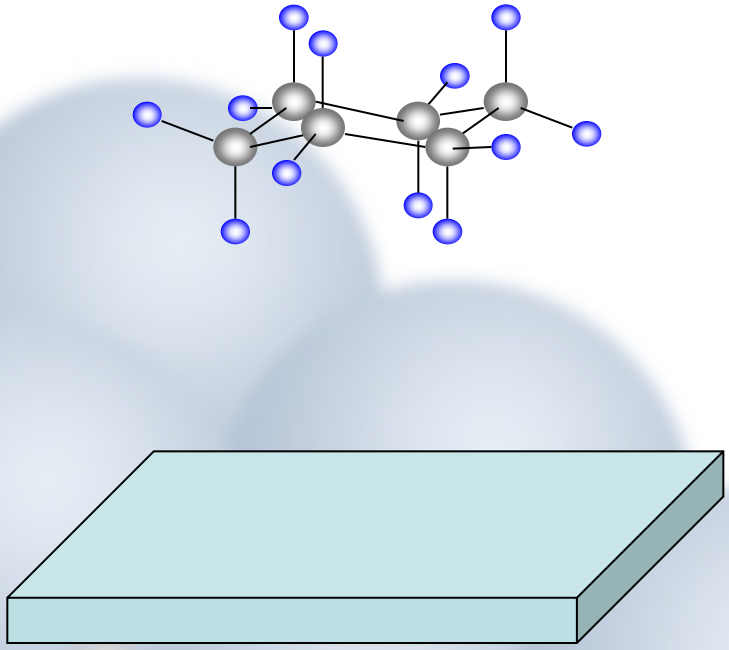
（cf. 目標値: 6.5 wt%, 62.0 KgH_2/m^3 @DOE目標値）

・白金触媒の下，高温(≈573 K)で脱水素反応を行う必要がある。

より低い温度で脱水素反応させる比較的安価な触媒が望まれる

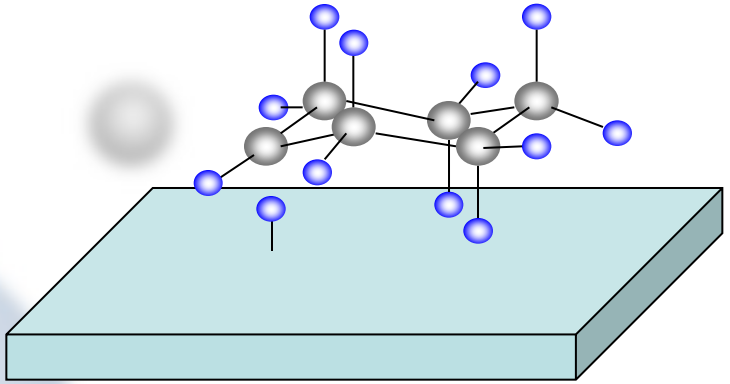
Cyclohexane ***dehydrogenation***

Step1



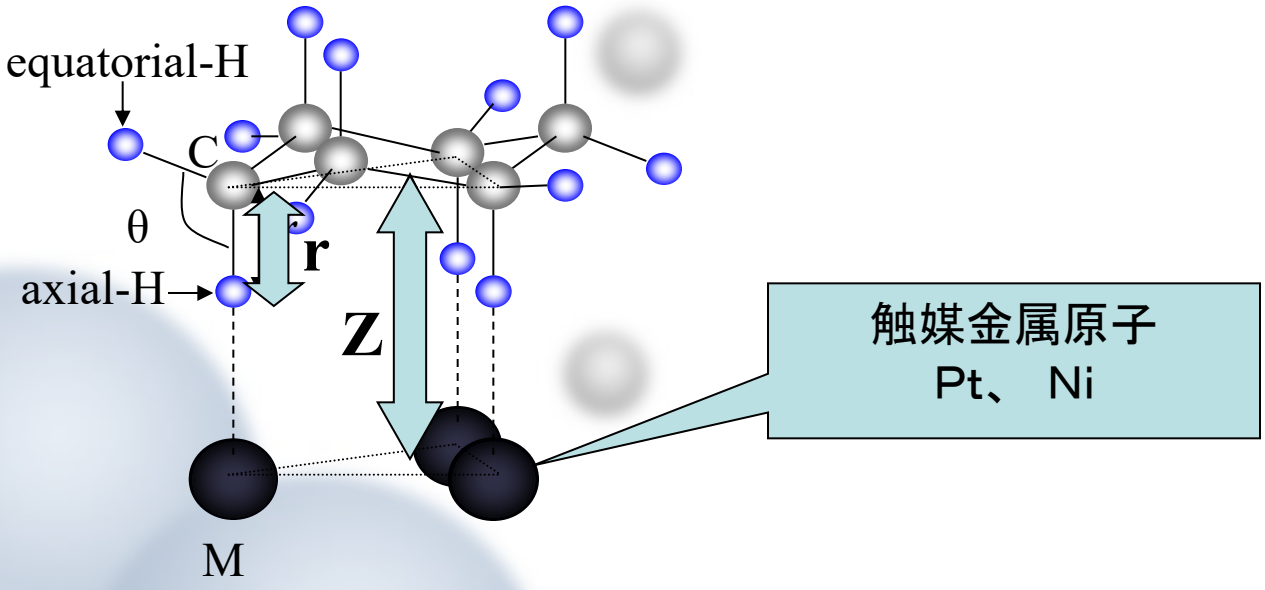
cyclohexaneが、触媒表面に接近

Step2



水素を触媒表面に残し脱離

Computational ***parameters***

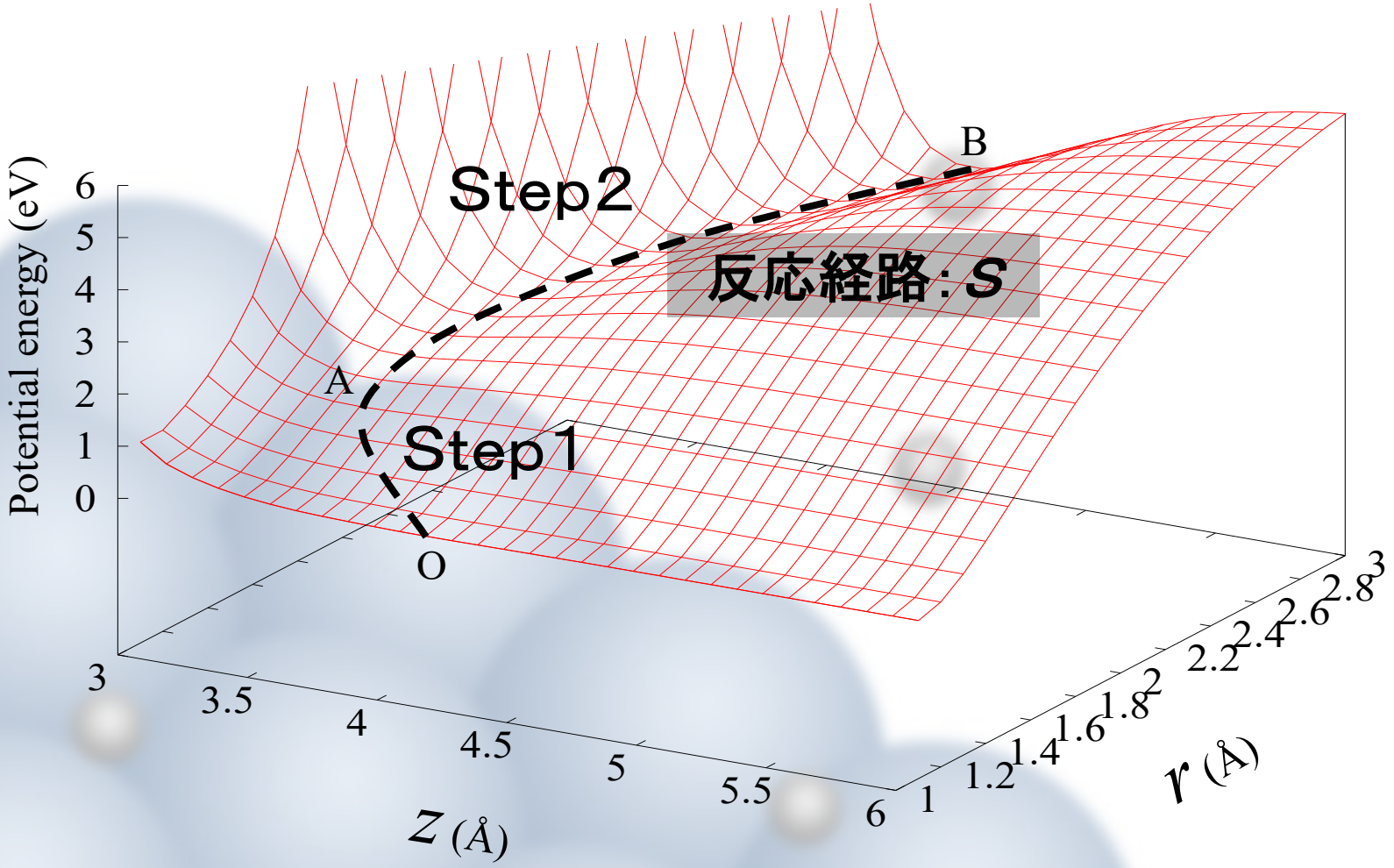


DFT-based total energy calculations

Becke three-parameter hybrid functionals

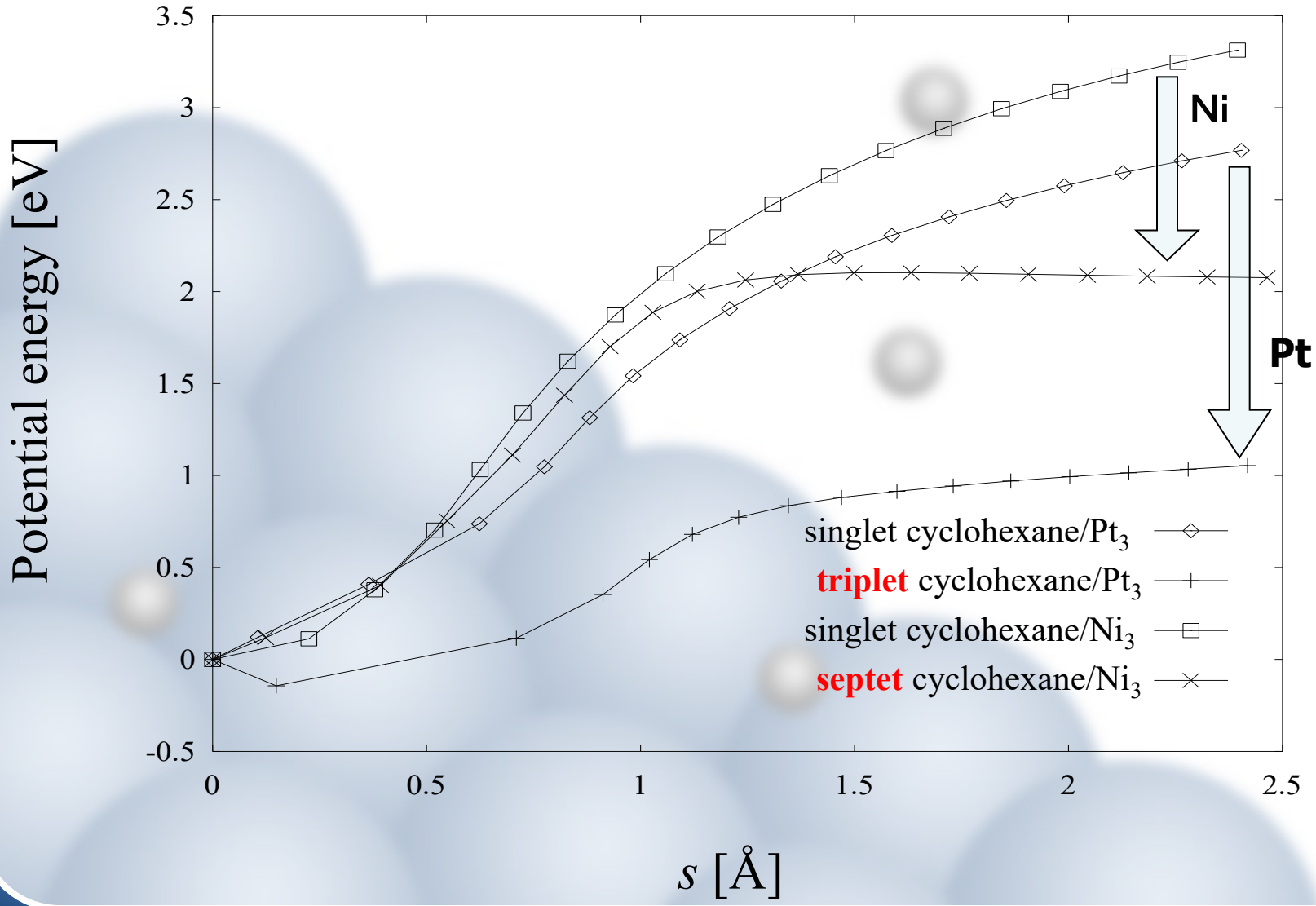
Perdew-Wang gradient-corrected correlation functional and Hay-Wadt basis sets

Cyclohexane dehydrogenation: ***Potential Energy Surface***



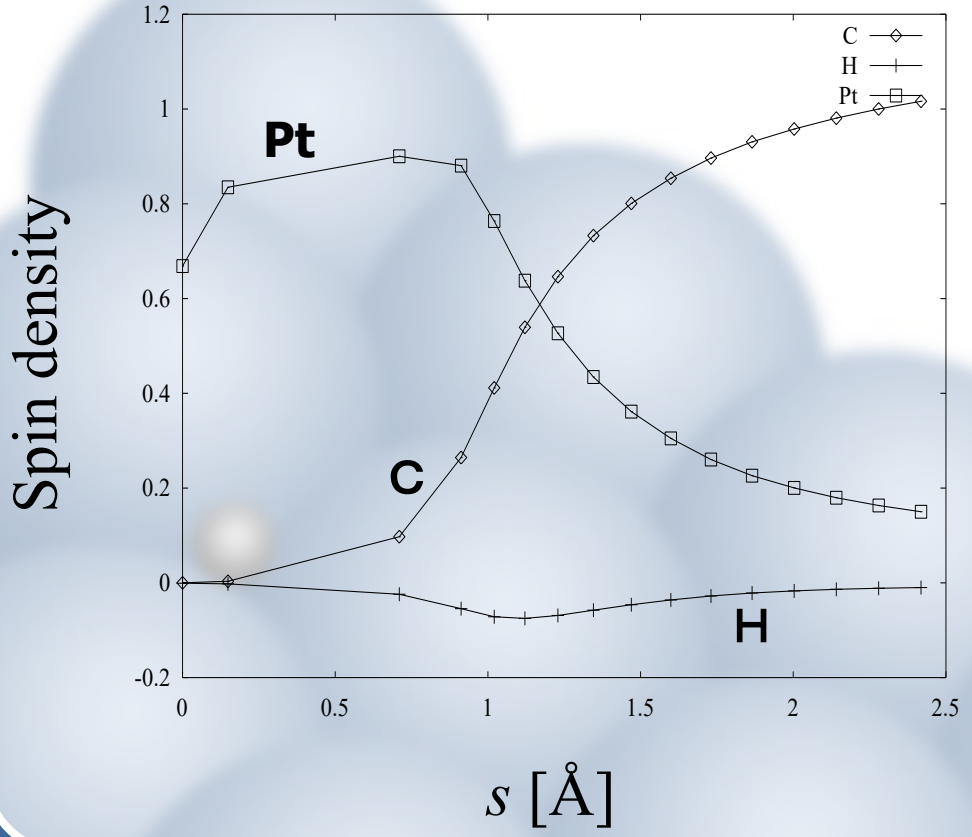
Potential energy along the reaction path

Spin effects

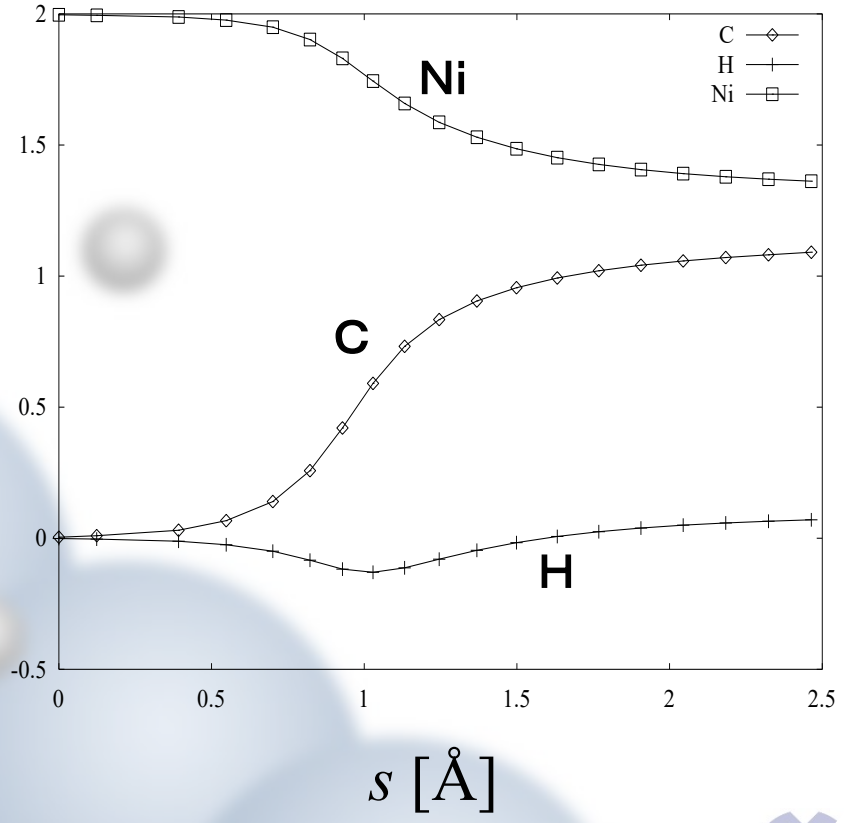


Spin changes along the reaction

Triplet cyclohexane/Pt_3



Septet cyclohexane/Ni_3



Spin effects

・Step 2 のプロセスに必要なエネルギーが劇的に減少。

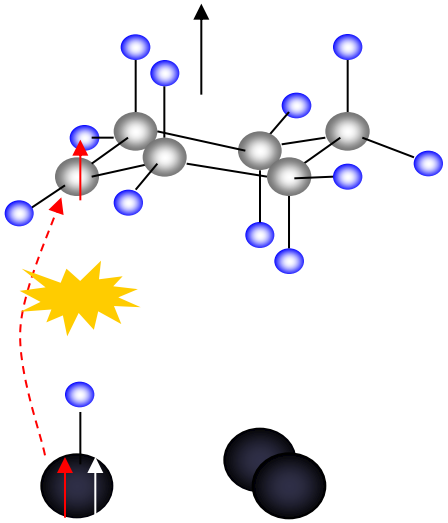
・磁化をもつNiは、Ptに匹敵する

・磁化をもったPtは、更に高効率

・触媒金属から炭素へスピンが移動

↓

C－H結合を弱める



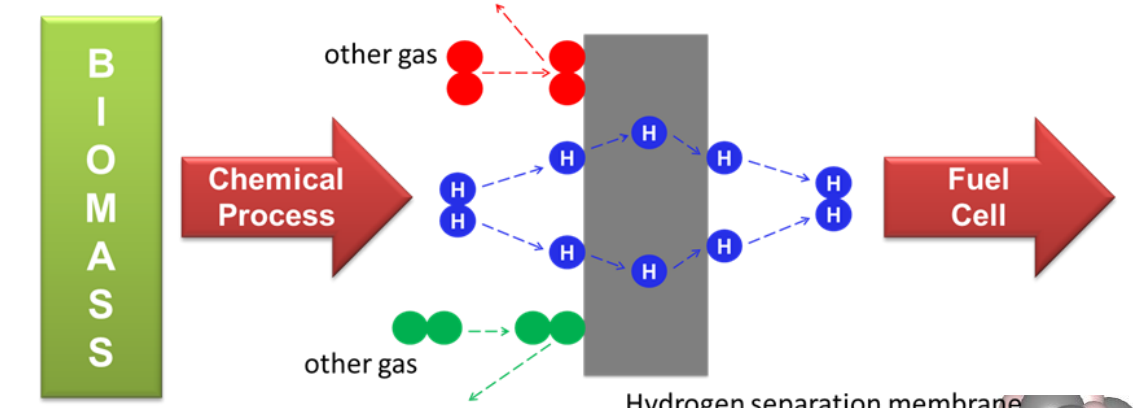
e.g., Chiyoda Corporation

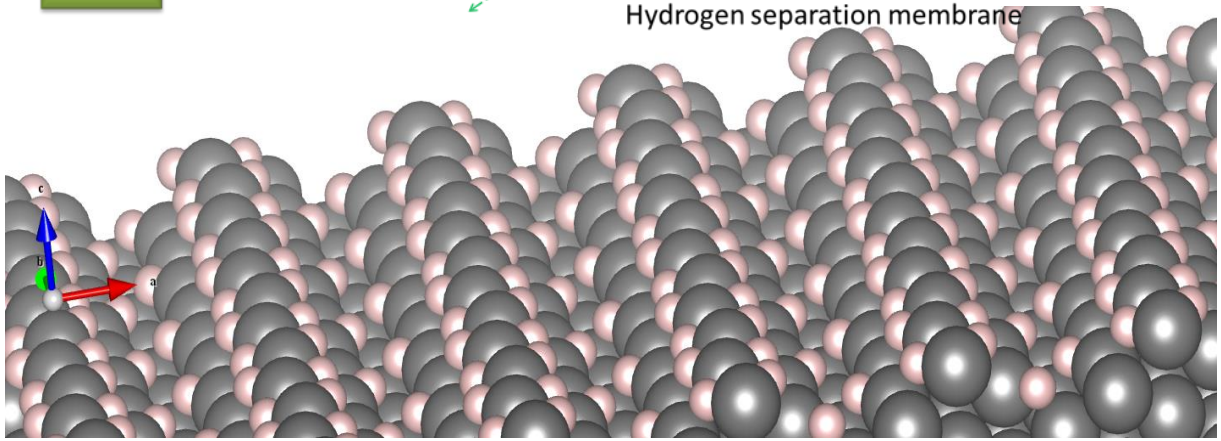
Shogo Shibuya

President & CEO

Hydrogen Separation Membrane

Understanding H absorption on (1X2) missing row reconstructed Pd(110) surface





Dr. Allan Abraham Padama
PNU, BSPT 2004

A clear description on the behavior of H atoms on surfaces, especially its absorption process will be significant for various applications such as storage and hydrogenation or dehydrogenation of different molecules.

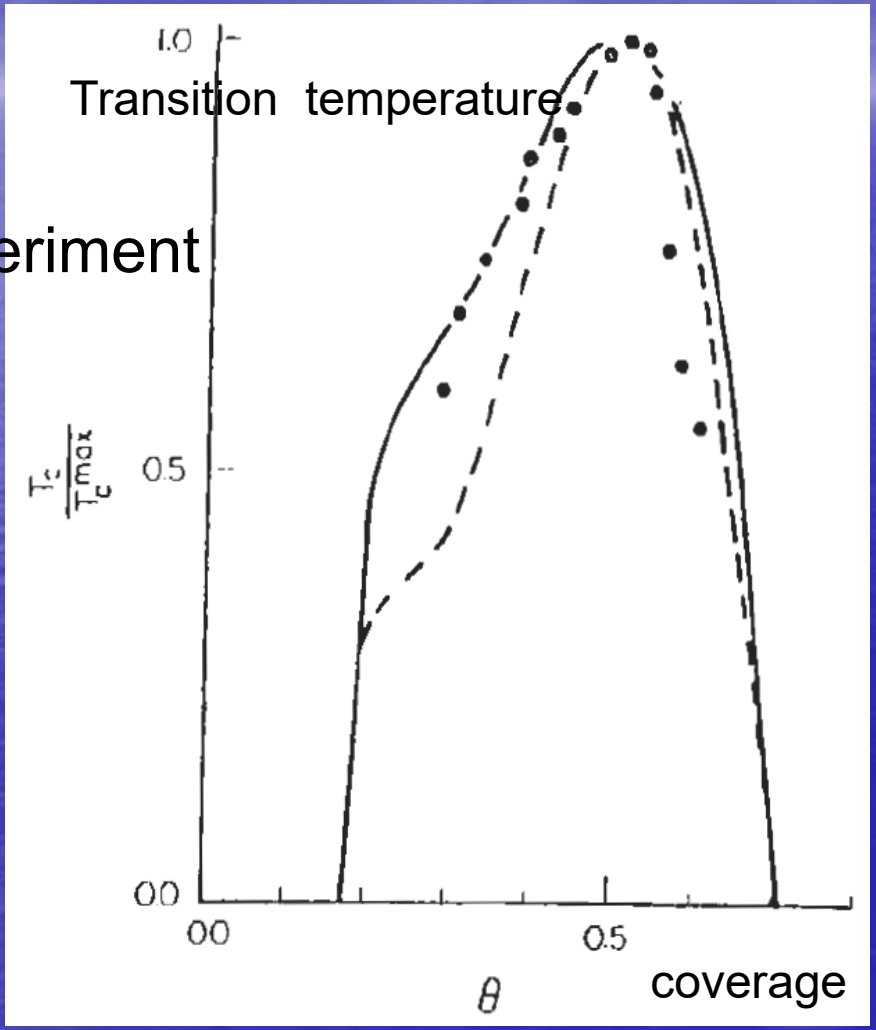
Towards Hydrogen-based Society

1. Fuel Cell Vehicle
2. Liquid Hydrogen Tanker
3. SOFC (Solid Oxide Fuel Cell)

On the order-disorder transition of chemisorbed H on Ni(111)

Ertl (1979) Experiment

LEED



Lattice gas model

Coherent scattering
& Domain structures

fcc-hollow sites
hcp-hollow sites
Low coverage
One of these sites
(Domain structures)
High coverage
Both sites

H. Kasai et al. (1981)

Electron Correlation Effects on Dissociative Adsorption of H_2 on Metal Surfaces (1982)

The eq. (2.10) contains F_0, $F_1 \cdots F_4$ as unknown valuables which can be determined self-consistently from eqs. (2.3)–(2.6) and eq. (2.10).

In terms of G and F in the surface cluster, the binding energy for the hydrogen molecule can be written as

$$\Delta E_B(t_{ab} \neq 0) = -\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{E_F} \left\{ \sum_\sigma (F_0 + E + \varepsilon_{eff}) G_0 + \sum_{ij\sigma} \frac{1}{2} (F_i + E + T) G_{ij} \right\} dE$$
$$- \left[-\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{E_F} \left\{ \sum_\sigma (F_0^0 + E + \varepsilon_{eff}) G_0^0 + \sum_{ij\sigma} \frac{1}{2} (F_i^0 + E + T) G_{ij}^0 \right\} dE \right], \quad (2.15)$$

where the summation of i is taken for the substrate sites. The binding energy for the two adatoms, $\Delta E_B(t_{ab}=0)$, can be calculated by replacing ε_{eff} and U_{eff} with ε_a and U_a (for atoms) in the expression (2.15). It is noted that the binding energy for the two adatoms obtained by the above method gives the same result as that obtained for the two independent adatoms in the framework of this numerical calculation.

§3. Numerical Results

As the purpose of this paper is to investigate the effect of the bulk property of the substrate on the hydrogen molecule chemisorption, V and t are taken variable. For simplicity, ε_{eff} and U_{eff} are chosen in such a way that $\varepsilon_{eff} + \frac{1}{2}U_{eff} = E_F$ which ensures the charge neutrality in the chemisorbed substrate, where E_F is the Fermi energy. This charge neutrality condition and the assumption that the vacuum level of the substrate given by $T+U$ is taken zero of energy lead to $U = 14.3$ eV and $T = -14.3$ eV, respectively. When two chemisorbed hydrogen atoms are completely isolated, $\varepsilon_a = -13.6$ eV and $U_a = 12.9$ eV are chosen from the ionization potential and the electron affinity for free hydrogen atom, respectively, while ε_{eff} for the hydrogen molecule may take different values. That is, U_{eff}, ε_{eff} and t_{ab}, the first two of which are subjected to the restriction mentioned above, are chosen so as to yield the observed dissociation energy for the hydrogen molecule[1,8] (see Appendix).

Two kinds of binding energies, $\Delta E_B(t_{ab}=0)$ and $\Delta E_B(t_{ab}\neq 0)$, have been defined in §2 as a function of V. There is a critical value V_c obtained by the condition, $|\Delta E_B(t_{ab}=0)| = |\Delta E_B(t_{ab}\neq 0) + \text{binding energy for a free molecule}|$. In the range of V larger than V_c, two chemisorbed hydrogen atoms may couple with the substrate more strongly in the dissociative form than in the molecular form. Figure 2 shows that the critical value V_c becomes large with increasing t. This indicates that a hydrogen molecule is likely to chemisorb in the dissociative form more easily on the substrate with small t than on the substrate with large t. This tendency can also be inferred from the result for the bond order as to a substrate atom and an atop adatom which has been obtained for the hydrogen chemisorption within the same framework.[6] Refer to Fig. 3. It is seen that the chemisorbed hydrogen is strongly coupled to the substrate with decreasing t. For finite

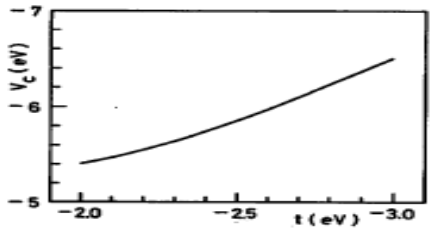


Fig. 2. Critical values V_c as a function of t.

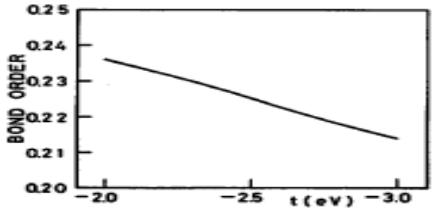


Fig. 3. The bond order between a substrate atom and an adatom as a function of t in the case of hydrogen atom chemisorption ($V = -4$ eV).

Hubbard Model

Dissociation can proceed as U/D increases

Hubbard U
Band Width D

Towards Hydrogen-based Society

1. Fuel Cell Vehicle
2. Liquid Hydrogen Tanker
3. SOFC (Solid Oxide Fuel Cell)

Towards Hydrogen-based Society

Hydrogen Business (水素ビジネス)

- PEST analysis (PEST 分析)

- P(Politics)政治的要因 （法規制、緩和）
- E(Economics)経済的要因（価格、助成）
- S(Society)社会的要因（世論、ライフスタイル）
- T(Technology)技術的要因（科学技術、革新）

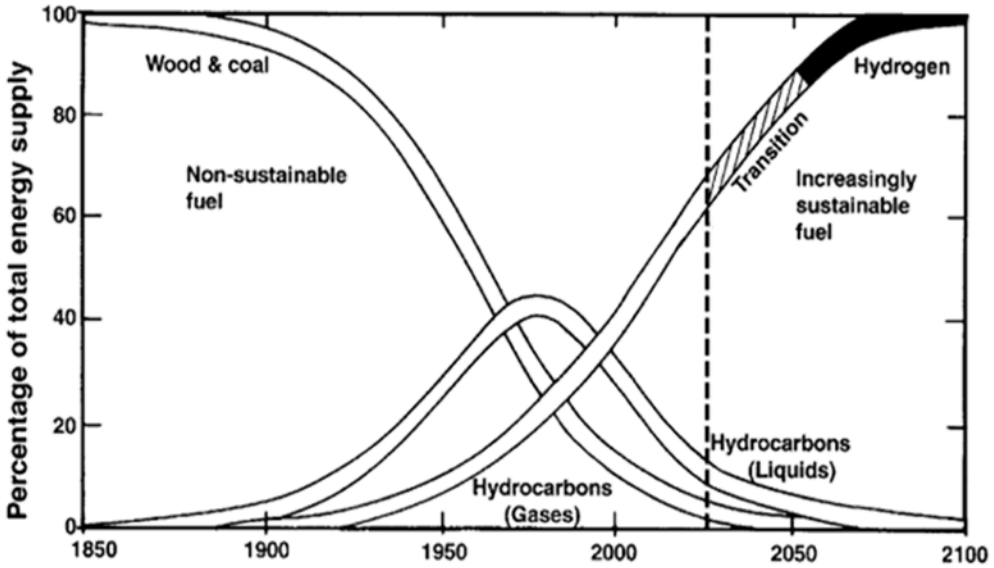
- PEST分析

- P(Politics)政治的要因 （法規制、緩和）
- E(Economics)経済的要因（価格、助成）
- S(Society)社会的要因（世論、ライフスタイル）
- T(Technology)技術的要因（科学技術、革新）

Our Present Scenario

Combustion of Conventional Fossil Fuel Leads to Emission of Greenhouse Gases

World's Energy Supply



T. Muneer et al., Energy Conversion and Management, 44 (2003) 35.

Alternative energy is the ultimate solution to the global energy problem and environmental concerns.

Alternative Energy Source Realization

Clean

Cheap

Efficient

- PEST分析

- P(Politics)政治的要因 （法規制、緩和）
- E(Economics)経済的要因（価格、市場）
- S(Society)社会的要因（世論、ライフスタイル）
- T(Technology)技術的要因（科学技術、革新）

The Rise of Hydrogen Economy

Inspired by the launch of hydrogen fuel cell cars by TOYOTA in 2014.

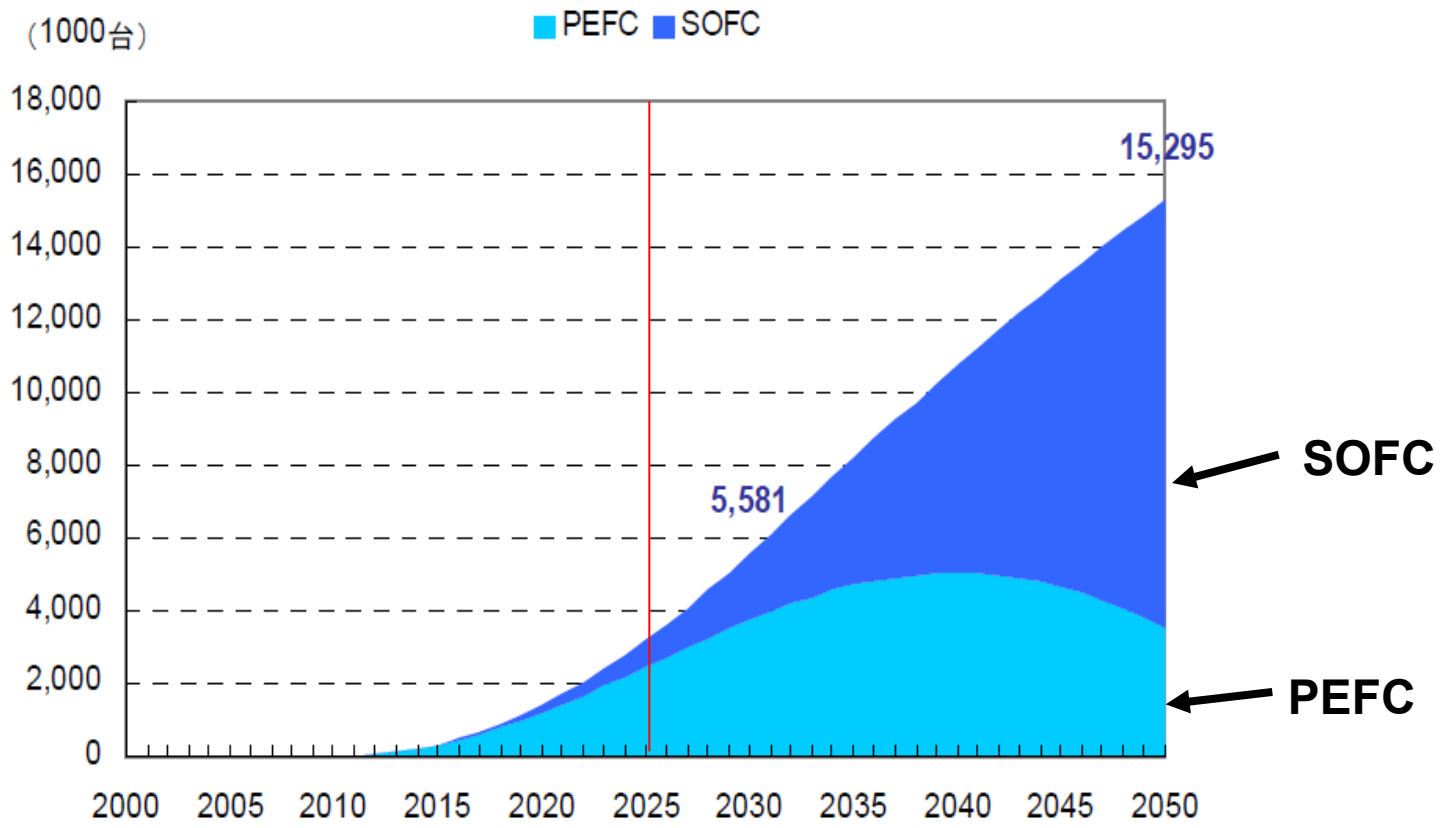
メーカー希望小売価格*1

7,236,000円
（消費税抜き6,700,000円）

Sales launch of Fuel Cell sedan in Japan before April 2015

SOFCとPEFCの市場推移予測

IEA（International Energy Agency）＋（財）日本エネルギー経済研究所の資料より



富士経済によれば、2025年の世界市場は5兆円、国内市場は1兆6千億円。国内市場におけるSOFCは、PEFCの1／5という規模。それ以降、SOFCの比率が徐々に拡大し、PEFCを凌駕すると予測されている。 ハズレ!

- PEST analysis (PEST分析)

- P(Politics)政治的要因 （法規制、緩和）
- E(Economics)経済的要因（価格、助成）
- S(Society)社会的要因（世論、ライフスタイル）
- T(Technology)技術的要因（科学技術、革新）

燃料電池自動車の普及拡大　FCV Popularization

- 2014年12月に市場投入された燃料電池自動車の普及に向け、2015年度までに4大都市圏を中心に100箇所程度の水素ステーションの整備を目指す。
- また、2025年頃に同車格のハイブリッド車同等の価格競争力を有する車両価格を目指す。燃料となる水素の価格については、2020年頃にハイブリッド車の燃料代と同等以下の水素価格を目指す。

燃料電池自動車
トヨタ自動車:2014年12月15日の一般販売開始

FCV普及 ＋ 水素ステーション整備
→ 双方に同時に取り組む必要

subsidy

①燃料電池自動車の導入支援
- 初期需要創出の観点から、燃料電池自動車の量産効果を下支えする導入補助（202万円を補助）

②燃料電池等の技術開発
- FCVの低コスト化、高耐久化に向けて、燃料電池に関する基盤技術開発、水素タンクに関する技術開発等を促進

③海外展開に向けた制度整備
- 世界統一基準と国内法令の調和や、相互承認を推進

①水素ステーションの整備補助
- FCVの市場投入に先行し、水素ステーションの整備費用の一部を補助（整備費用の1／2を補助）

②低廉な水素ステーションの開発等
- FCVの普及状況に見合った仕様の確立
- 圧縮機や蓄圧機等の構成機器の低コスト化に向けた技術開発
- パッケージ型や移動式ステーションの活用

③規制見直し
- 高圧ガス保安法等の規制について、欧米の規制を参考にしつつ、圧力容器の設計基準、使用可能鋼材の制約等を見直す
- 「規制改革実施計画」（2013．6）に基づき、25項目について規制見直しを加速化

Deregulation

燃料電池自動車及び水素ステーションについて

経済産業省　資源エネルギー庁　燃料電池推進室　平成27年1月26日

FCV Popularization

Subsidy

Deregulation

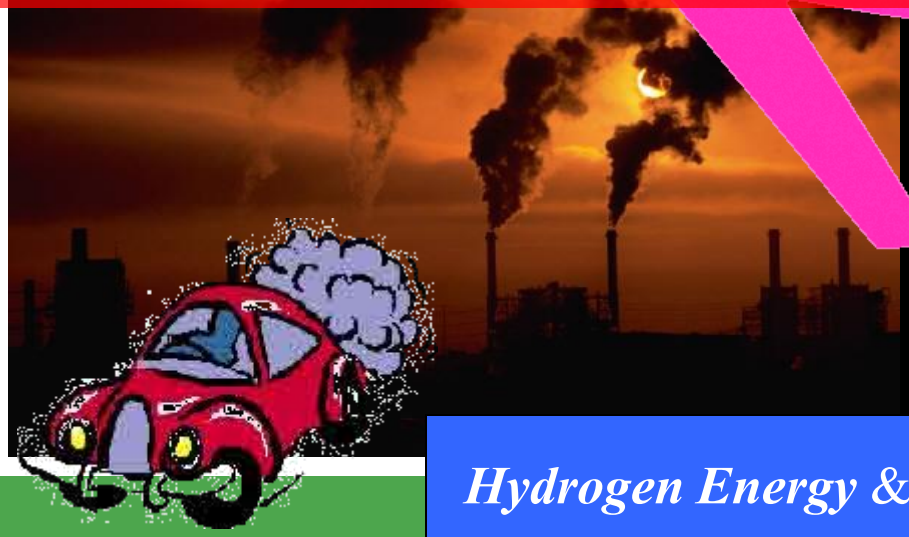
METI(**Ministry of Economy, Trade and Industry)**

Agency for Natural Resources and energy

MOTIVATION

FOSSIL FUELS

Fossil fuel depletion · Global warming · Air pollution



Hydrogen Energy & Fuel Cells

Production

Storage

Safe and efficient Utilization

HYDROGEN

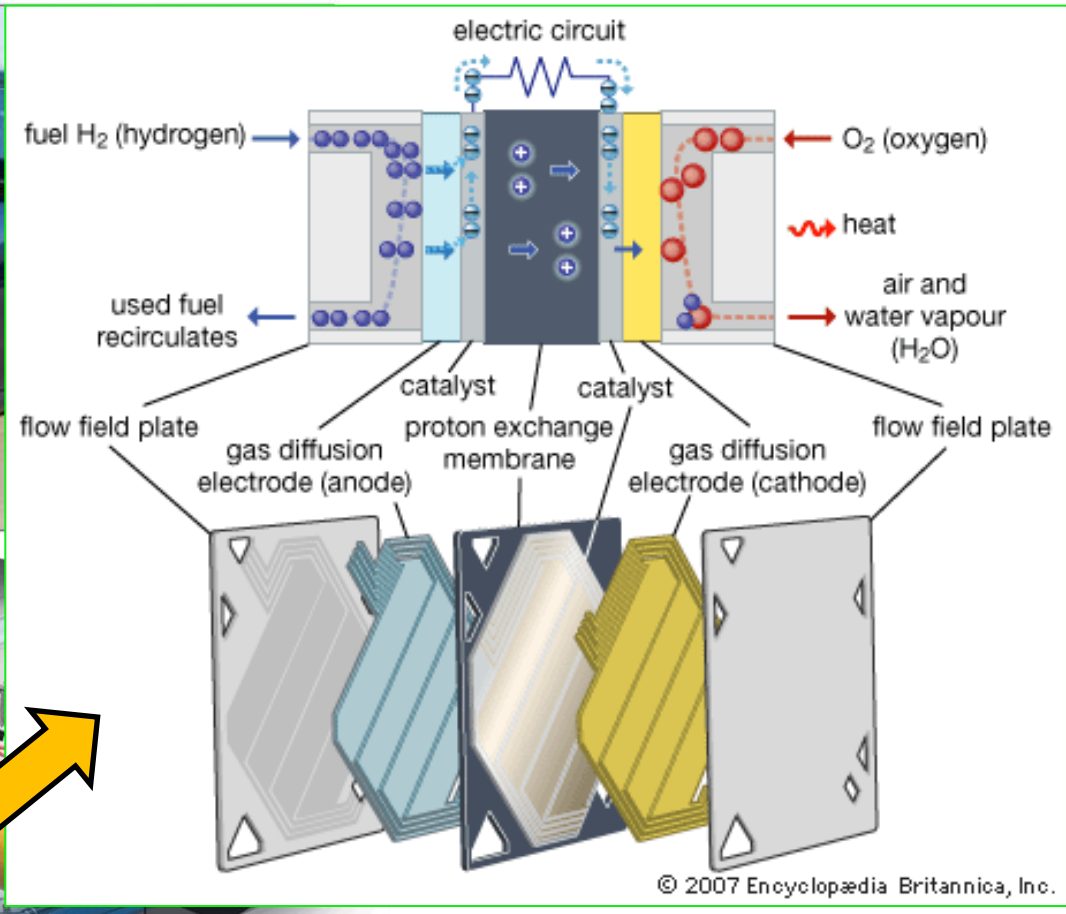
- PEST分析

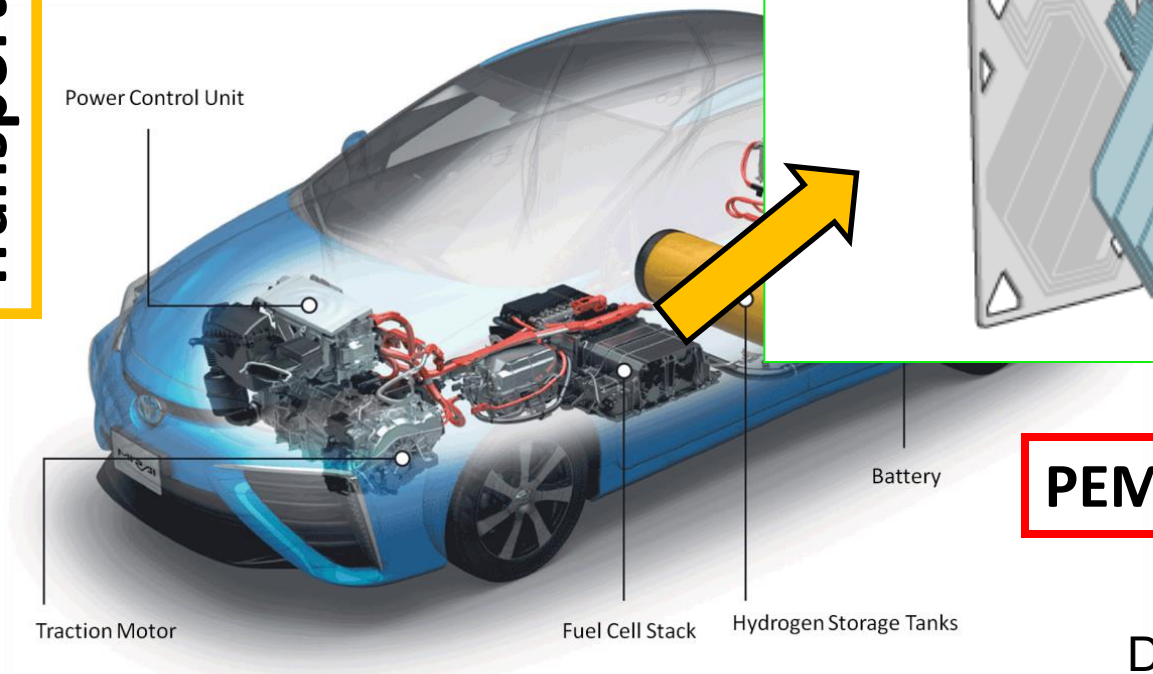
- P(Politics)政治的要因 （法規制、緩和）
- E(Economics)経済的要因（価格、助成）
- S(Society)社会的要因（世論、ライフスタイル）
- T(Technology)技術的要因（科学技術、革新）

Fuel Cell Introduction

Proton Exchange Membrane Fuel Cell (PEMFC)

Transportation





Zero Emissions Vehicle (ZEV)

PEMFC Production Cost ?

Dr. Ferensa Oemry

Cutting Edge R & D for Fuel Cell (PEMFC) 2001-

Toyota and OU R&D Hydrogen Storage Materials Design, etc.

Japanese Patent No.5110557 (2012)

Toyota - OU

- Kunihiro Nobuhara, Hideaki Kasai, Hiroshi Nakanishi, Wilson Agerico Diño
  電池用電極触媒の性能評価方法、探索方法、電池用電極触媒及びその電極触媒を用いた燃料電池
  特願2006-93546

Hydrogen ***storage*** and ***transportation***

fuel cell-powered vehicle

高圧水素ボンベ

メタノールやガソリンの改質

水素吸蔵合金

液体水素

炭素系ナノ構造材料

Carbon nanotube : CNT

Graphite nanofibers : GNF

水素4kgの体積　（約400km走行）

Liquid Hydrogen Tanker
大型液化水素運搬船

出典：山下誠二,ほか,低炭素社会に向けた水素チェーンの実現可能性検討,エネルギー・資源学会論文誌,vol35,No.2,2014.3,P33−38

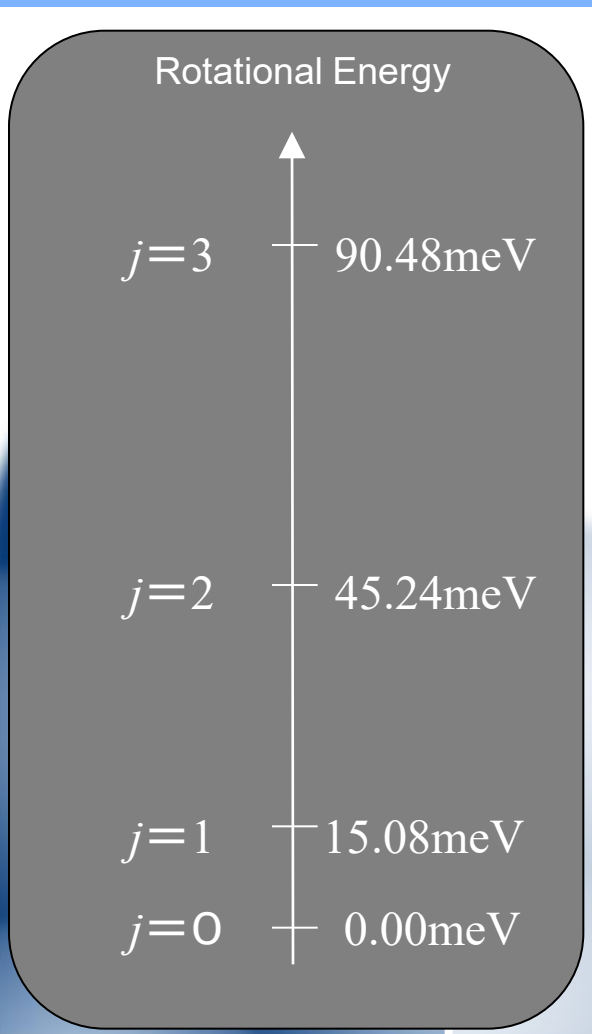
Kawasaki Heavy Industries-OU-UT
NEDO Project (2015-)

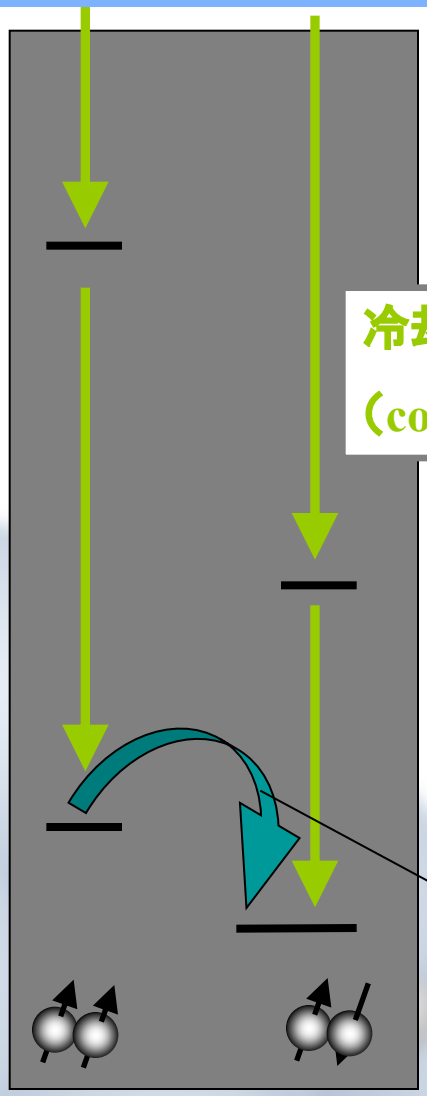
JAPANESE PATENT NO. 3765050 (2006)
JST (JAPAN SCIENCE AND TECHNOLOGY AGENCY)

2.Hideaki Kasai, Hiroshi Nakanishi, Yoshio Miura, Rifki Muhida
オルソ・パラ変換促進方法および水素液化促進方法
特願2002-327405

1.Hideaki Kasai, Hiroshi Nakanishi, Wilson Agerico Diño, Rifki Muhida
水素の液化促進法
特願2001-274461

・*Ortho-Para Conversion* Reaction Design

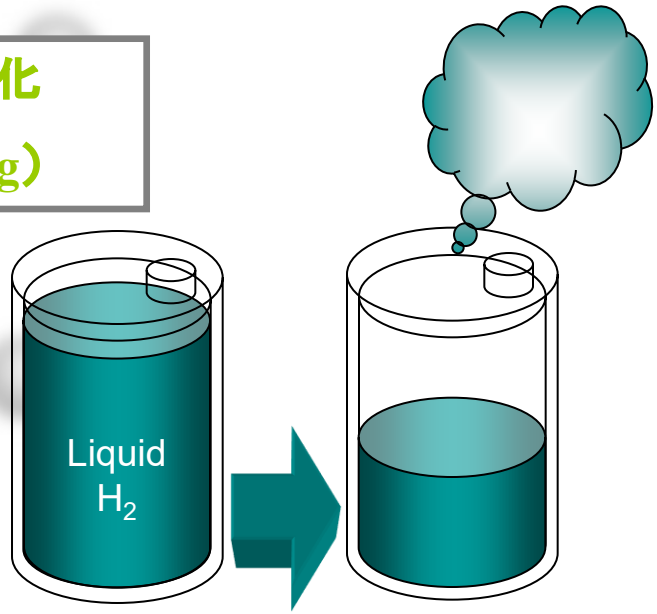




H_2 molecule nuclear spin states

水素液化時の
ボイリングオフ問題

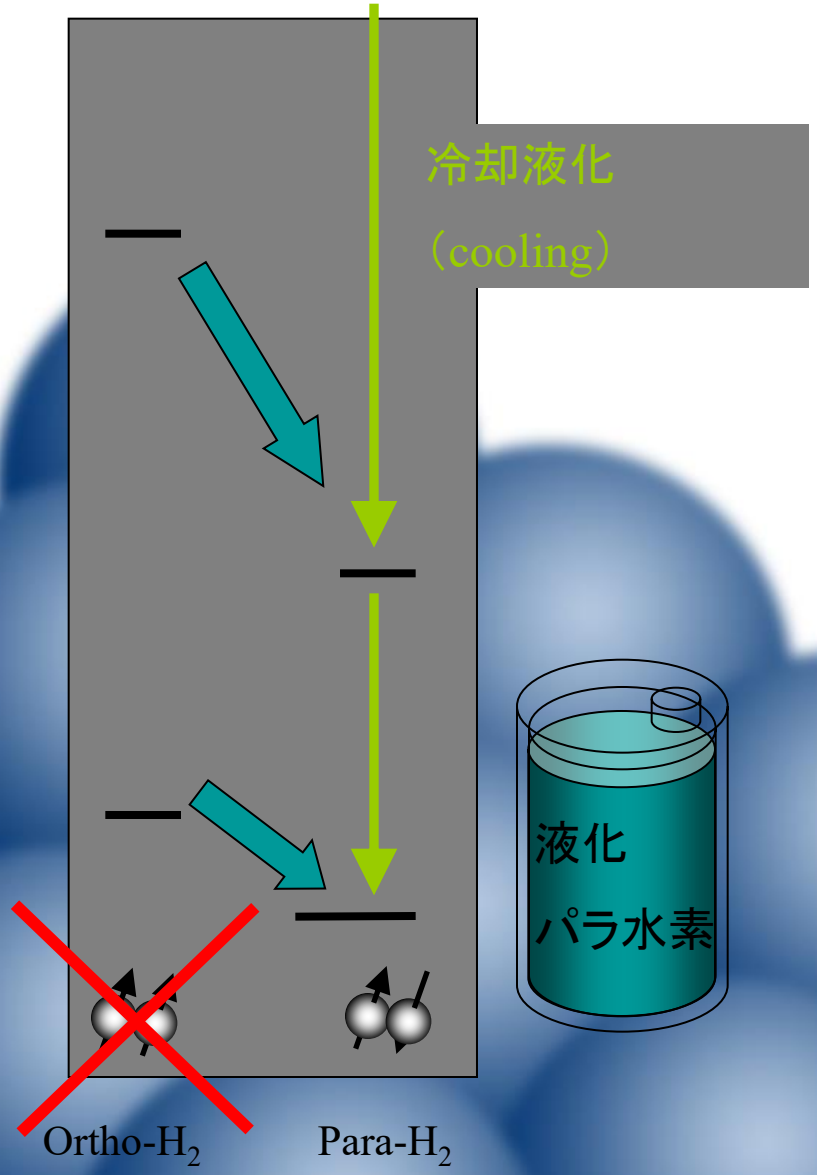
冷却液化
（cooling）



一週間後

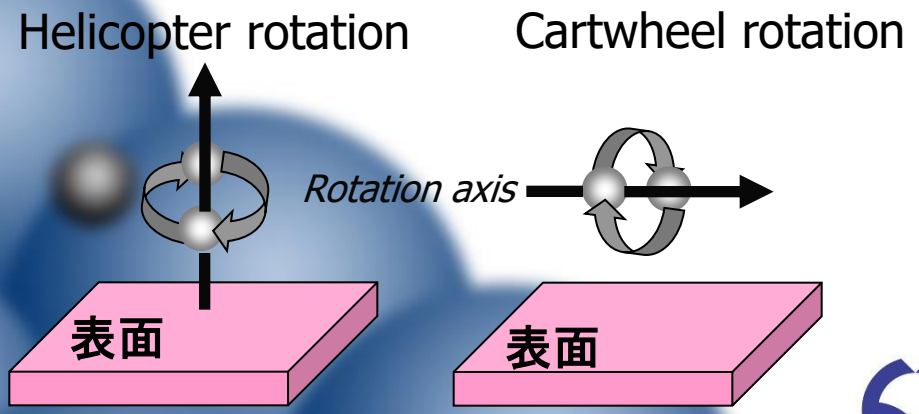
通常の転換確率は極めて小さい。
寿命　～　Day
数日かけて徐々に転換
⇒　発熱　→　蒸発熱を供給

Ortho-para conversion is necessitated before liquefaction.



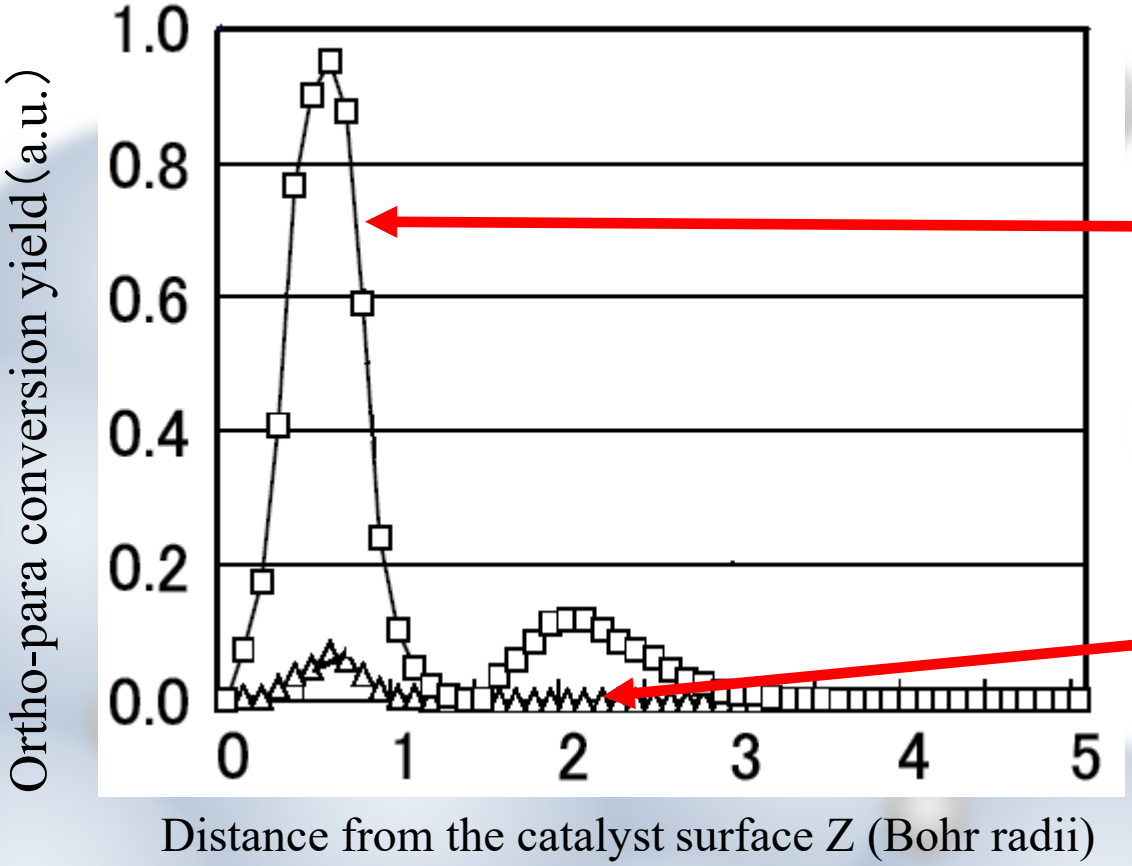
- 高効率転換を実現
- 従来：
  ・高効率転換触媒の開発

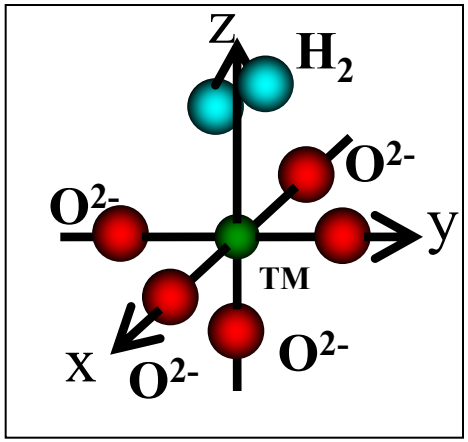
プロセスデザインの観点から：
・量子ダイナミクス効果を活用した
プロセス・デザイン



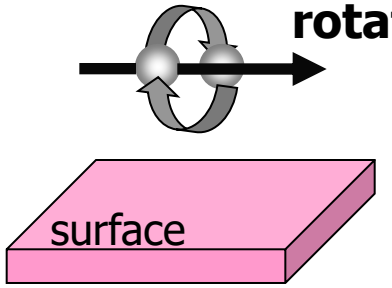
Molecular rotation dependence of ortho-para conversion

Quantum simulation results

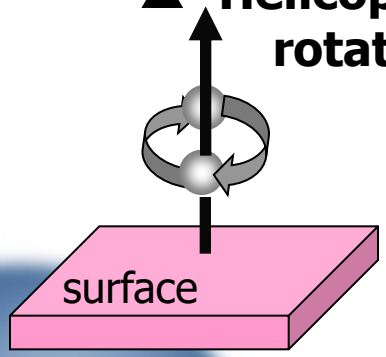




■ **Cartwheel rotation**



▲ **Helicopter rotation**



R.Muhida, et al : J. Vac. Soc. Jpn. 45 (2002) 448.

Liquid Hydrogen Tanker
大型液化水素運搬船

出典：山下誠二,ほか,低炭素社会に向けた水素チェーンの実現可能性検討,エネルギー・資源学会論文誌,vol35,No.2,2014.3,P33−38

Kawasaki Heavy Industries-OU-UT
NEDO Project (2015-)

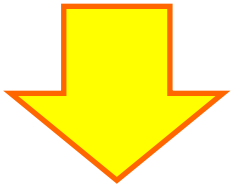
SOFC

M.Alaydrus et al., J.Phys.Soc. Jpn. 83,094707 (2014)
Mamoru Sakaue et al., ECS Transactions, 68(1) 3195 (2015)
M.Alaydrus et al., Phys. Chem. Chem. Phys. 18, 12938 (2016)

2. Hideaki Kasai, Hiroshi Nakanishi, Mamoru Sakaue, Musa Alaydrus
New material and structure of solid oxide type fuel cell
Japanese Patent Application No. 2013-212308

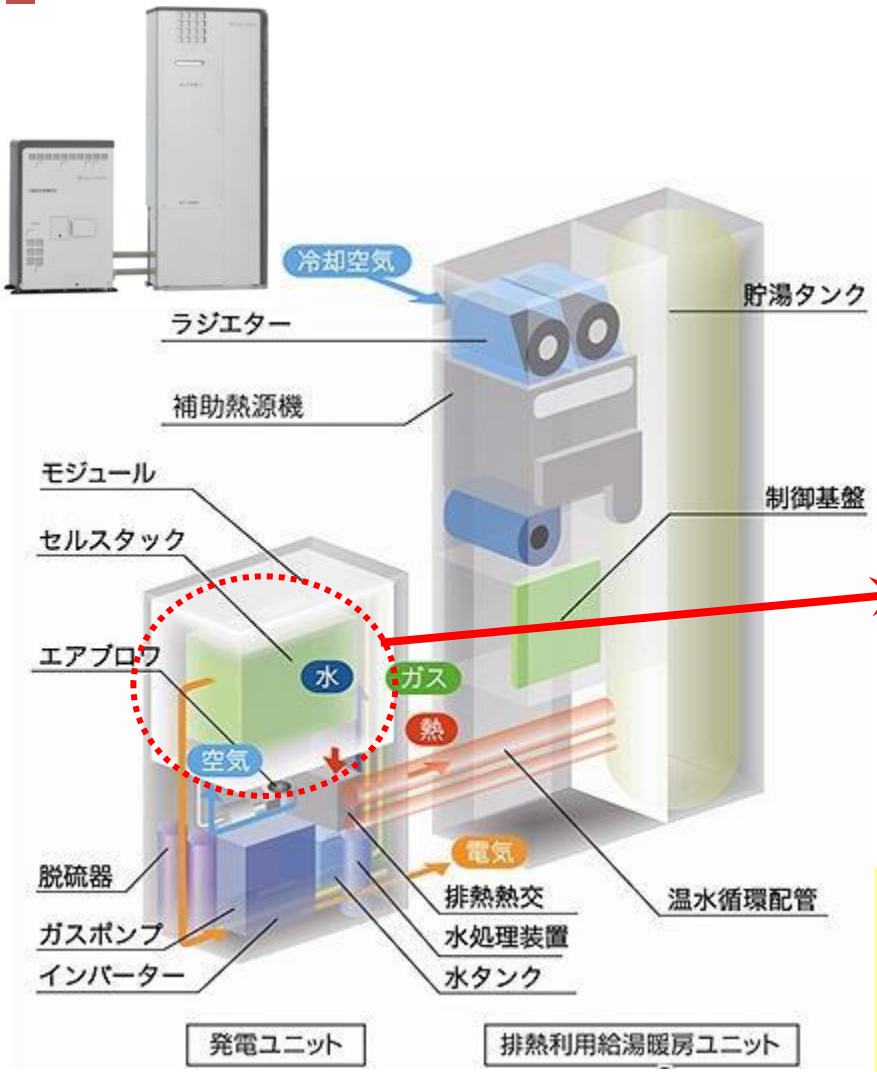
研究の背景

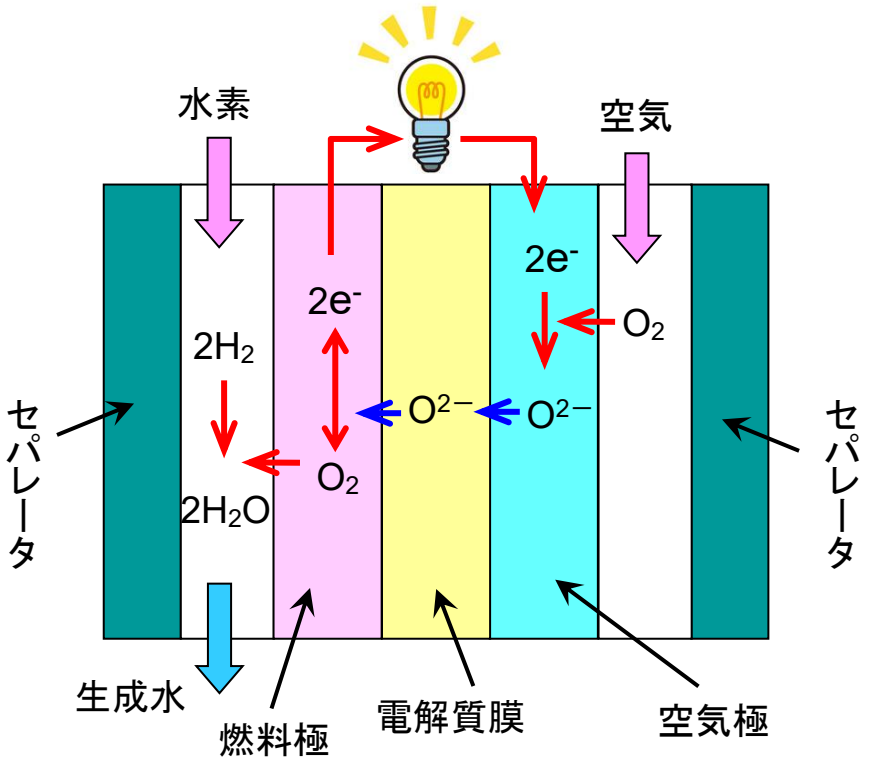
空気中の酸素と都市ガスから作る水素で発電する固体酸化物形燃料電池(SOFC)の長所は約45～65%という最大の発電効率（参考：PEFCでは35～40%）であり、短所は作動温度が約700から1000℃という高温動作に伴う高コスト・大型化および電解質の損傷・劣化を招きやすいことである。



低温作動SOFCが実現すれば、低コスト・小型化・長寿命が実現できる。そのために、電解質膜の反応メカニズムを原子スケールで解明し、設計方法を確立する必要がある。

固体酸化物形燃料電池（SOFC）の構造

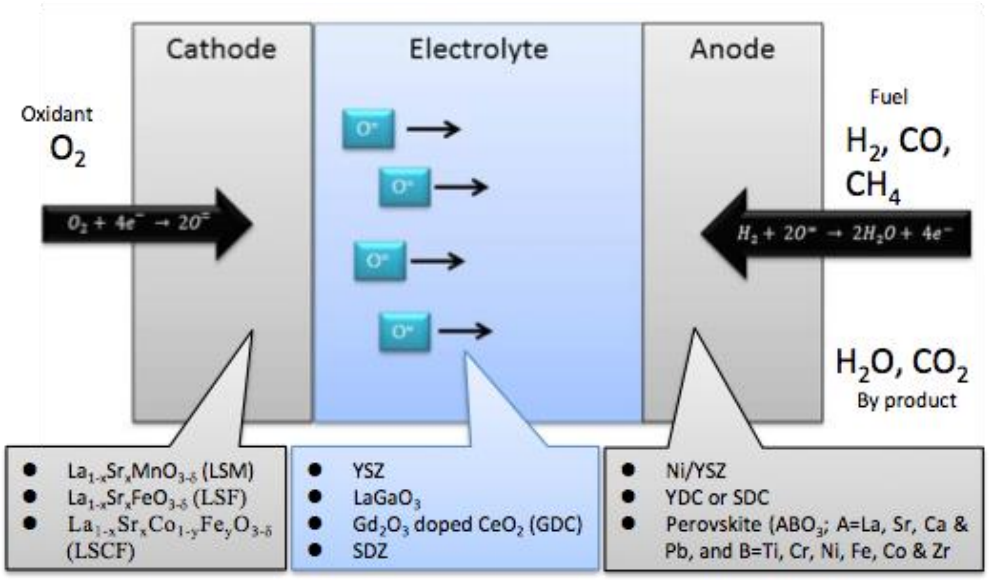




都市ガス（水素）と空気（酸素）で発電し、排出物は水のみ。貴金属不要なもう一つの究極のエコ電池。

固体酸化物形燃料電池（SOFC, Solid Oxide Fuel Cells）
大阪ガスHPより

Solid Oxide Fuel Cell



SOFC is a promising technology for efficient energy conversion device through electrochemical reactions

Overall Reaction

Cathode: $O_2 + 4e^- \longrightarrow 2O^{2-}$

Anode: $H_2 + O^{2-} \longrightarrow 2H_2O + 4e^-$

Advantages

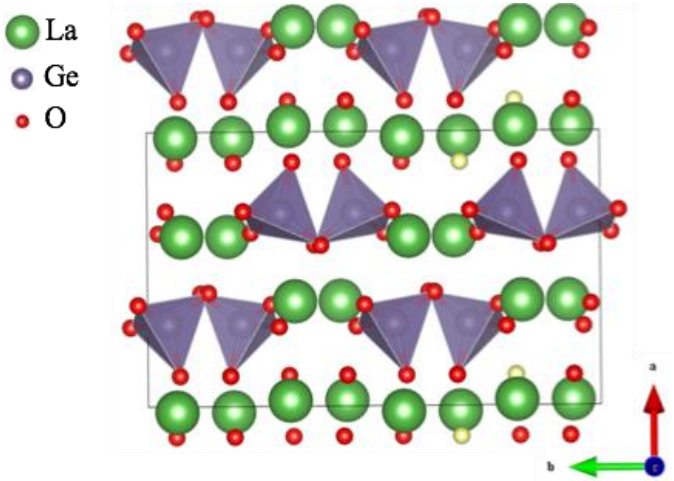
- ✓ Can have **efficiency of 60%** for fuel conversion to electricity and overall **efficiency of 80%** when the heat produce is harnessed
- ✓ Fuel can be reformed in the fuel cell itself which **allows fuel flexibility** (H_2, CO and CH_4)
- ✓ High temperature operations results to **improved reaction kinetics** thereby **removing the need for precious metal catalyst**

Areas of Improvement

- ✓ Usual operating temperature is high, 800˚C to 1000 ˚C
- ✓ Have long start-ups
- ✓ Must be constructed of robust, heat resistant materials
- ✓ Must be shielded to prevent heat lost

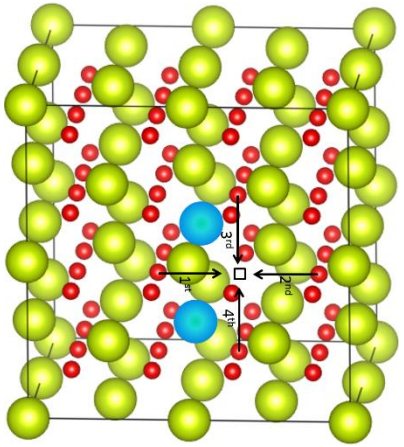
Candidate Materials

La_2GeO_5 - based (Lanthanum Germanate)



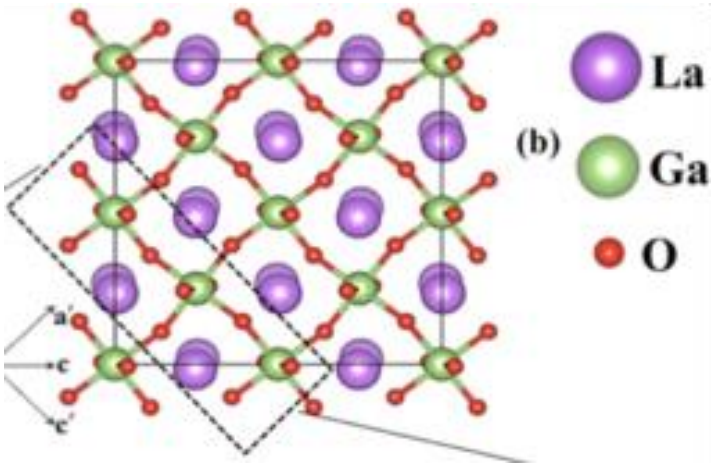
- ✓ Perovskite
- ✓ O migration through vacancies

CeO_2 –based (Ceria)



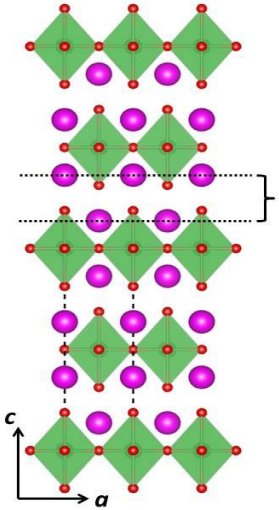
- ✓ Flourite structure
- ✓ O migration through vacancies

$LaGaO_3$ - based (Lanthanum Gallate)



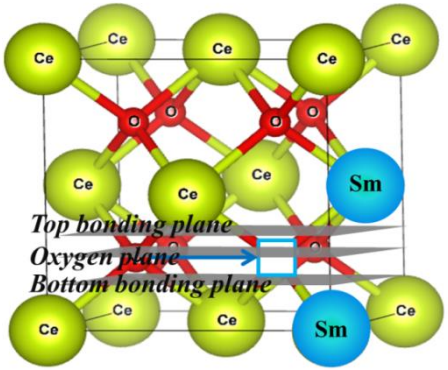
- ✓ Perovskite with $GdFeO_3$-type structure
- ✓ O migration through vacancies

Pr_2NiO_4 - based (Praseodymium Nickelate)

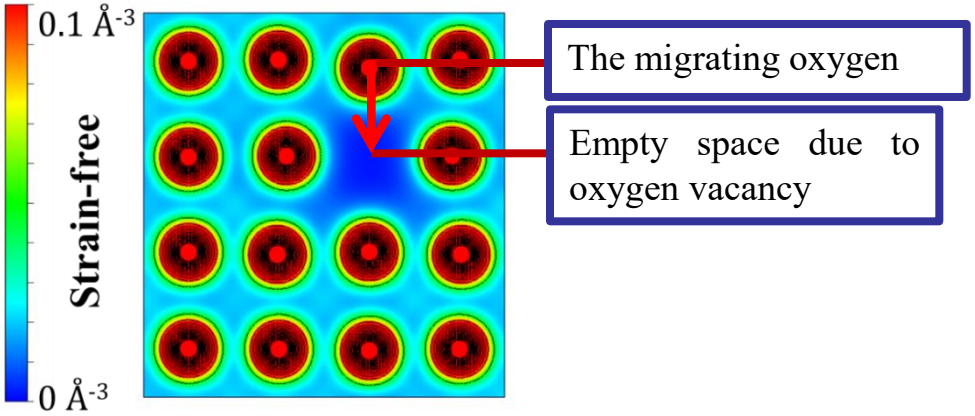


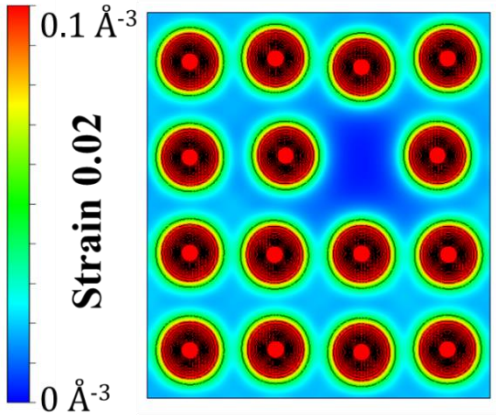
- ✓ Perovskite with K_2NiF_4-type structure
- ✓ O migration through interstitial
- ✓ Mixed ionic and electronic conductor

First-principles study of the Lattice Strain Effects on the Ionic Migration Barrier of Sm-doped Ceria for Solid Oxide Fuel Cell (SOFC) Application



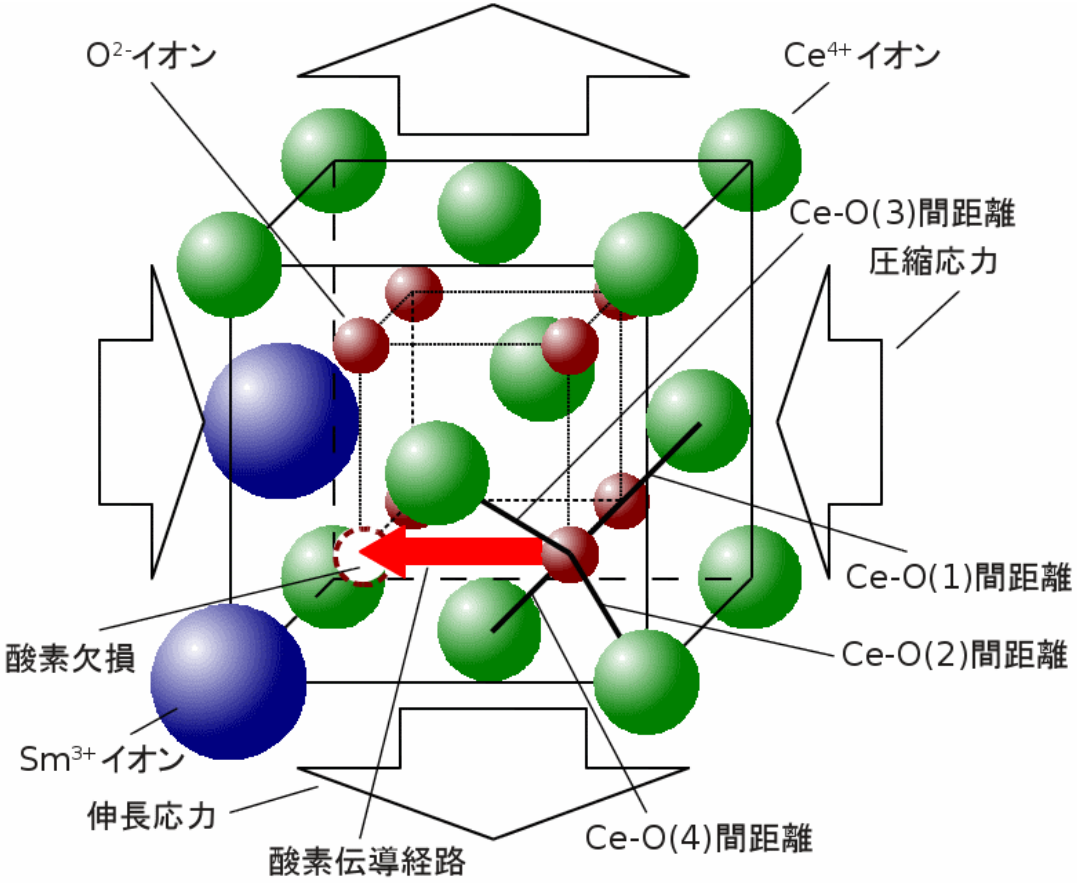
Dr. Musa Alaydrus (2015)





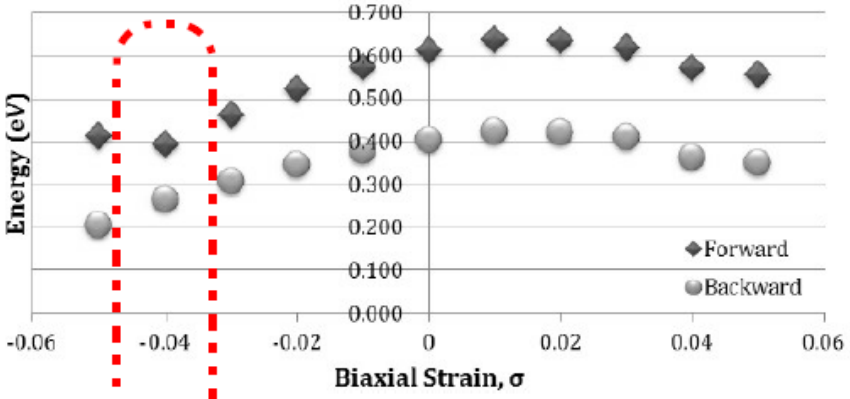
成果1:電解質の新材料を知的設計

電解質の新材料は、九大が発見した新SDC（サマリウムドープセリア、$Ce_{1-x}Sm_xO_{2-\delta}$）であり、応力印加型のSDC構造とすることで、低温作動性能が現れる。

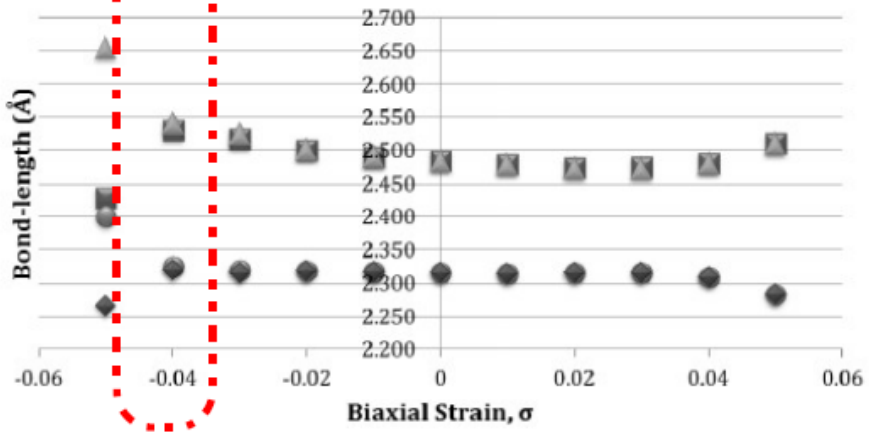


Lowering Activation Energy Barrier

酸素イオン伝導における活性化障壁

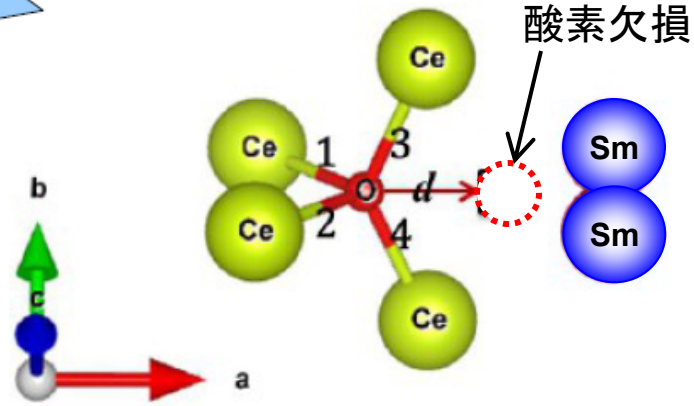


Ce-O原子間距離



Ce-O原子間距離が活性化障壁と強く相関。
（結合距離が長いほど結合が弱く、酸素移動が起こりやすい。）

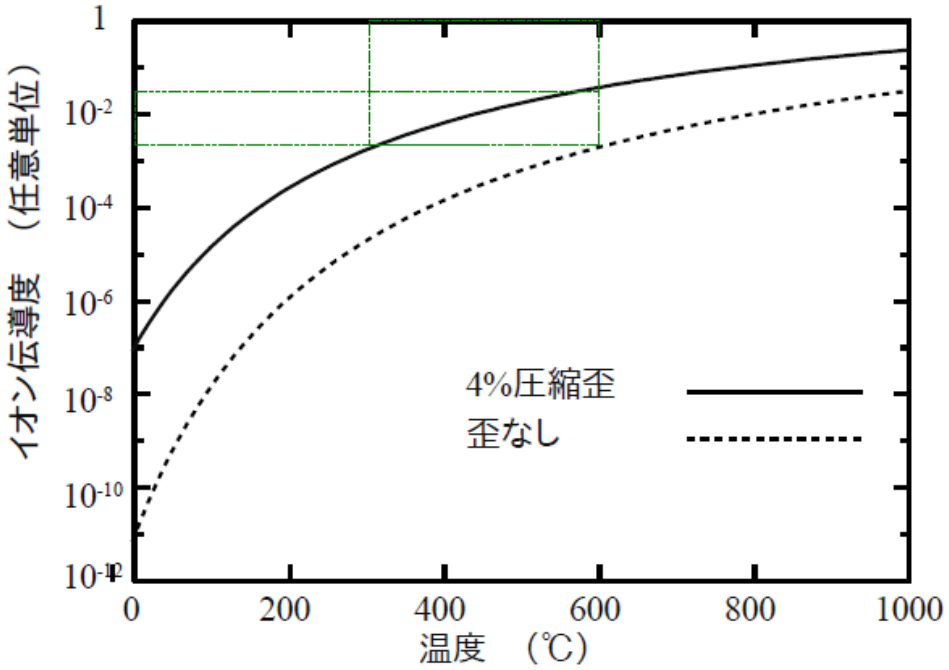
4%圧縮が最適。



SDCにおける酸素移動の微視的機構

応力印加SDC($Ce_{1-x}Sm_xO_{2-\delta}$)の低温作動

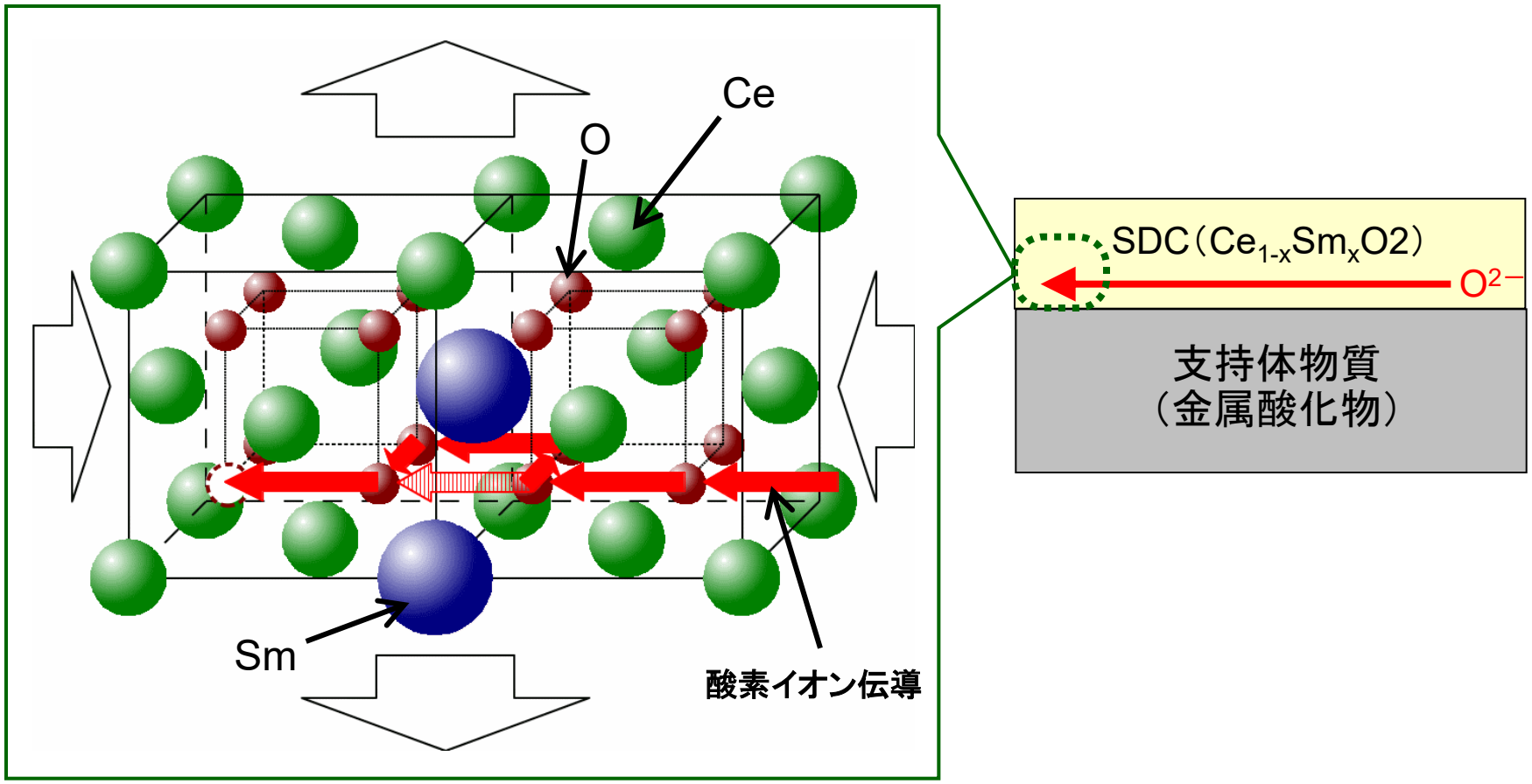
CMD-Naniwaによる計算結果から、4%の応力が印加された$Ce_{1-x}Sm_xO_{2-\delta}$の作動温度は低温側へ300℃シフトする。



300℃まで600℃と
同桁の伝導度を維持。

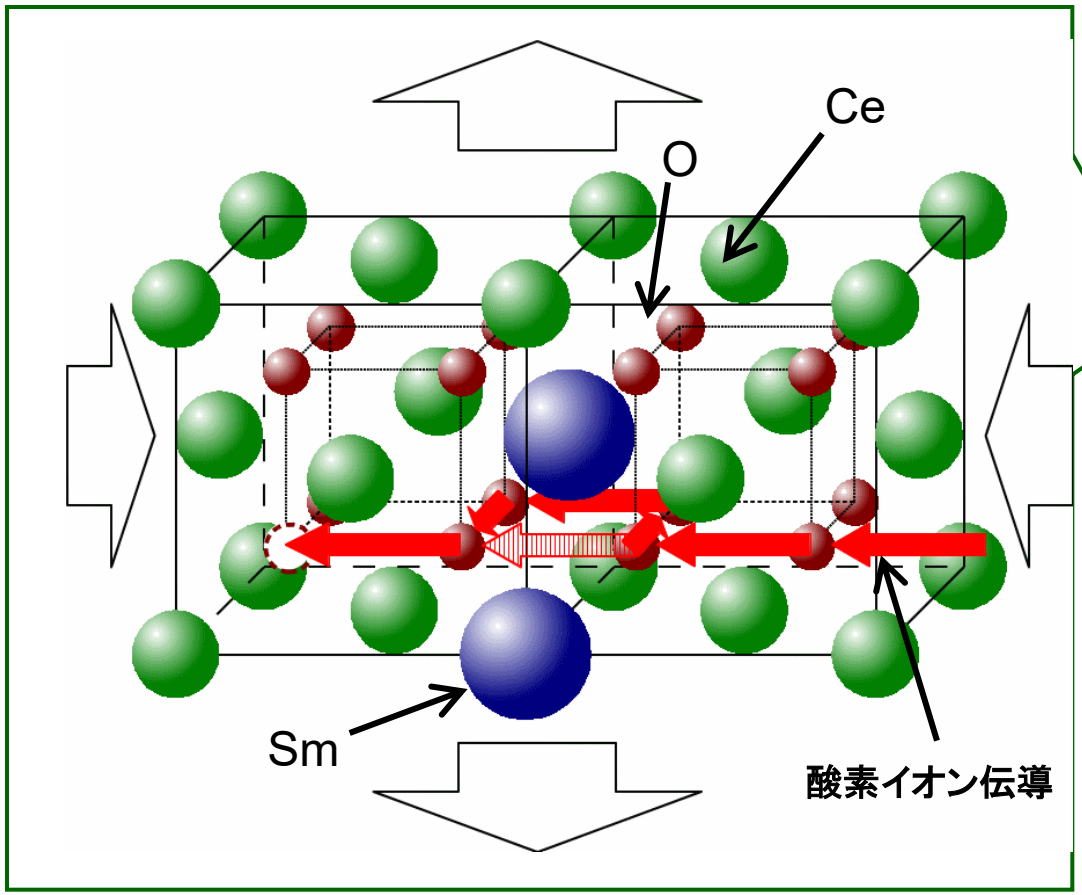
Substantial reduction of operating temperature can be realized.

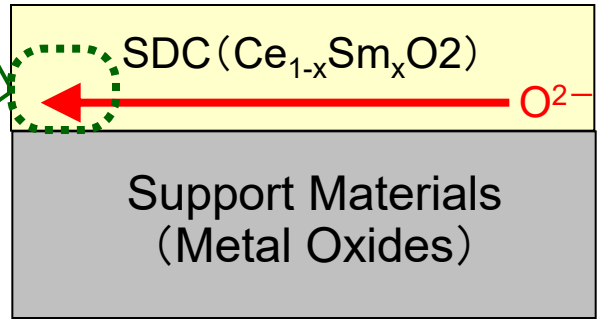
成果2：最適な応力印加構造を知的設計



格子定数の異なる支持体物質との接触により、酸素イオンの伝導方向に
4%の格子圧縮をもたらす応力印加により、酸素イオン伝導度が向上する。

1 :Electrolyte Materials Design





LAMINATE STRUCTURE

compressive stress

格子定数の異なる支持体物質との接触により、酸素イオンの伝導方向に
4%の格子圧縮をもたらす応力印加により、酸素イオン伝導度が向上する。

Something to Think About…

露の世は露の世ながらさりながら　一茶

Tsuyu no yo wa tsuyu no yo nagara
Sarinagara **Issa(1762-1826)**

This dewdrop world –
It maybe a dewdrop,
And yet – and yet –

Trans. R. H. Blyth