Newly-developed Technique for Real-time Observation of the Behavior of Platinum Fuel Cell Catalyst

May 18, 2015
Toyota Motor Corporation

1. **Development of microscopic electrochemical cells for fuel cells (FCs) to be embedded into a transmission electron microscope**

2. **Application of voltage to microscopic electrochemical cells in a transmission electron microscope, and recreation of platinum nanoparticle behavior on a nanometer level in the same chemical reaction state as when electricity is generated**

Successful real-time observation of the process leading to platinum nanoparticle coarsening, which is considered to cause decreased catalyst reactivity (deterioration)

Topics covered in these materials

1. **Role of platinum catalyst in fuel cells**
2. **Platinum nanoparticle observation techniques using conventional technology**
3. **New technique for observing platinum nanoparticle behavior**

1. **Role of platinum catalyst in fuel cells**
2. **Platinum nanoparticle observation techniques using conventional technology**
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Development of eco-cars to solve environmental and energy problems

Fuel diversification measures
Use of hydrogen

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Developing FCVs that can be mass-produced

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Further popularization of FCVs

- Increasing performance, lowering costs of FCs
- Encouraging the growth of hydrogen supply infrastructure

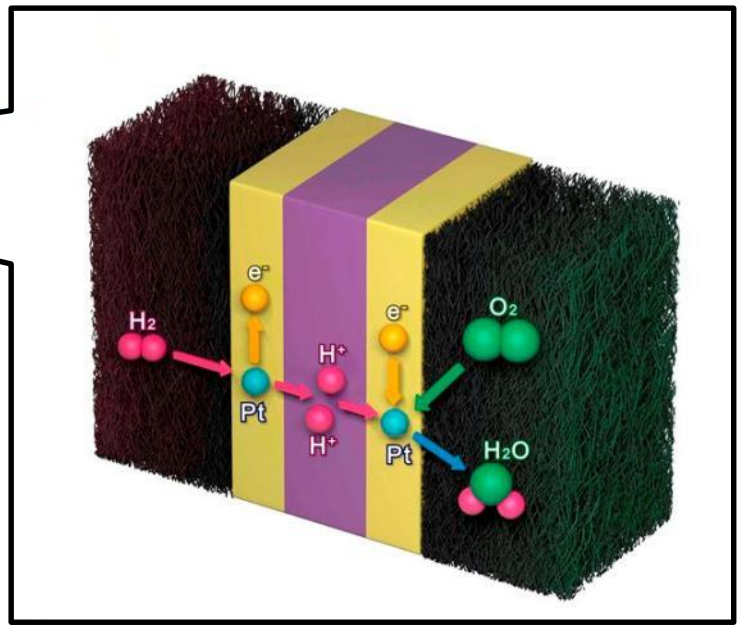
Mirai
(launched December 15, 2014)

To popularize FCVs, Toyota needs to improve performance and decrease costs of FCs

(2) Fuel cell stack installed in the Mirai

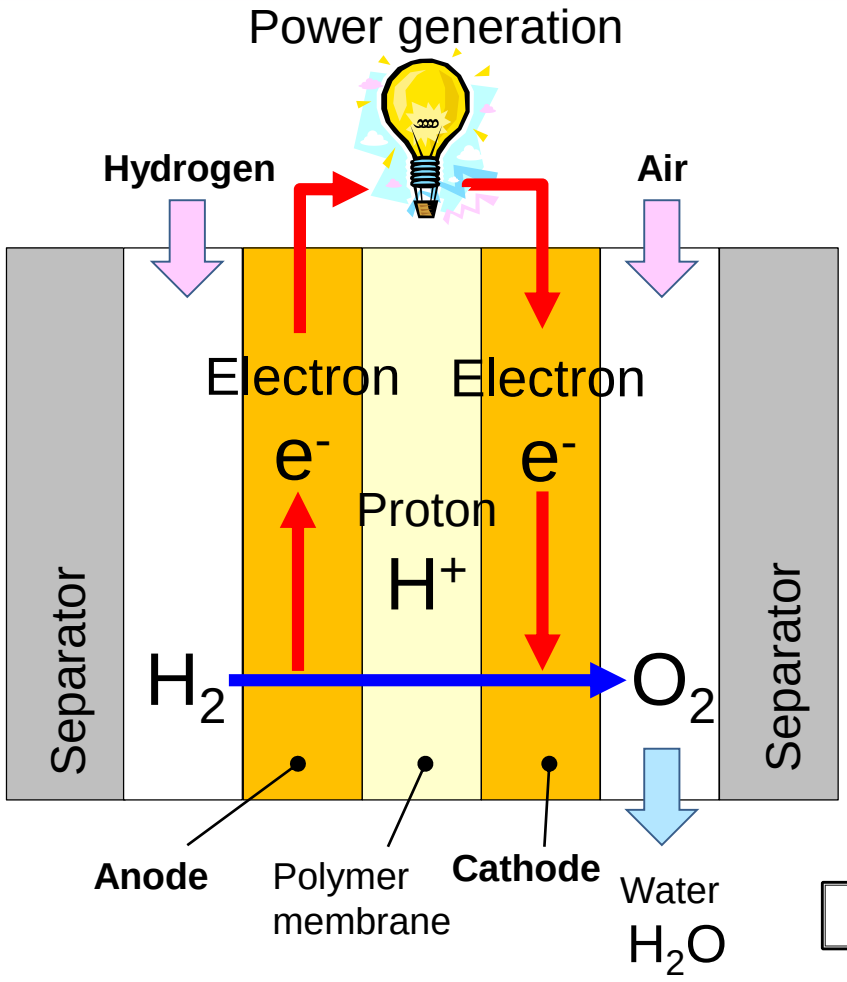
370 cells

Fuel cell cross-section



Series of 370 fuel cells for generating capacity of 114 kW

(3) Fuel cell schematic diagram

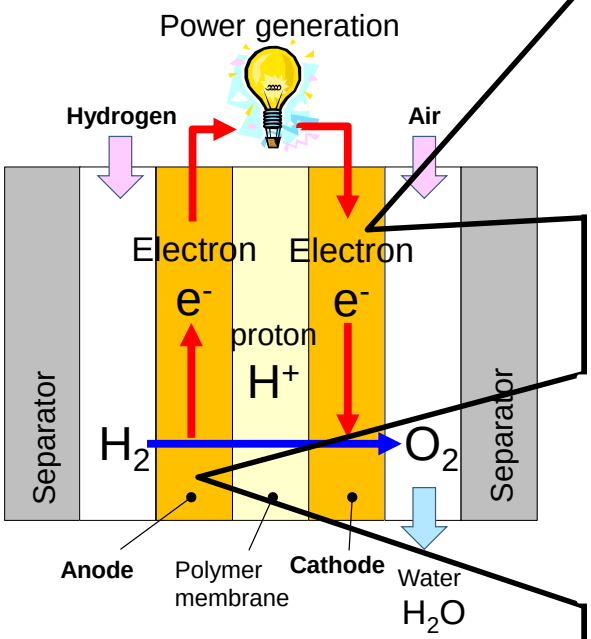


Reaction in fuel cell

$2H_2 + O_2 \rightarrow 2H_2O$ + electricity

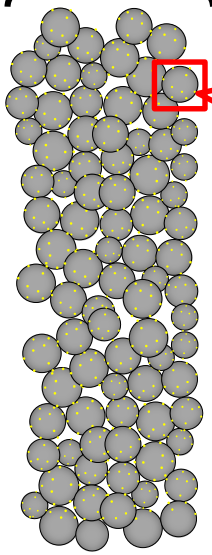
Extracts electrons by reacting hydrogen and oxygen to generate electricity (opposite of water electrolysis)

(4) Composition of anodes and cathodes



Catalyst layer

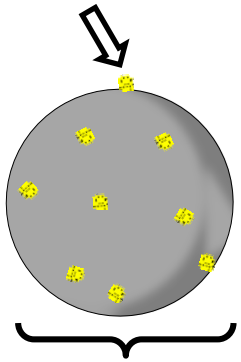
Thickness: tens of μm*1



Mixed layer of platinum, carbon and ion-conducting polymers

Platinum nanoparticle

Size: several nm*2



Carbon

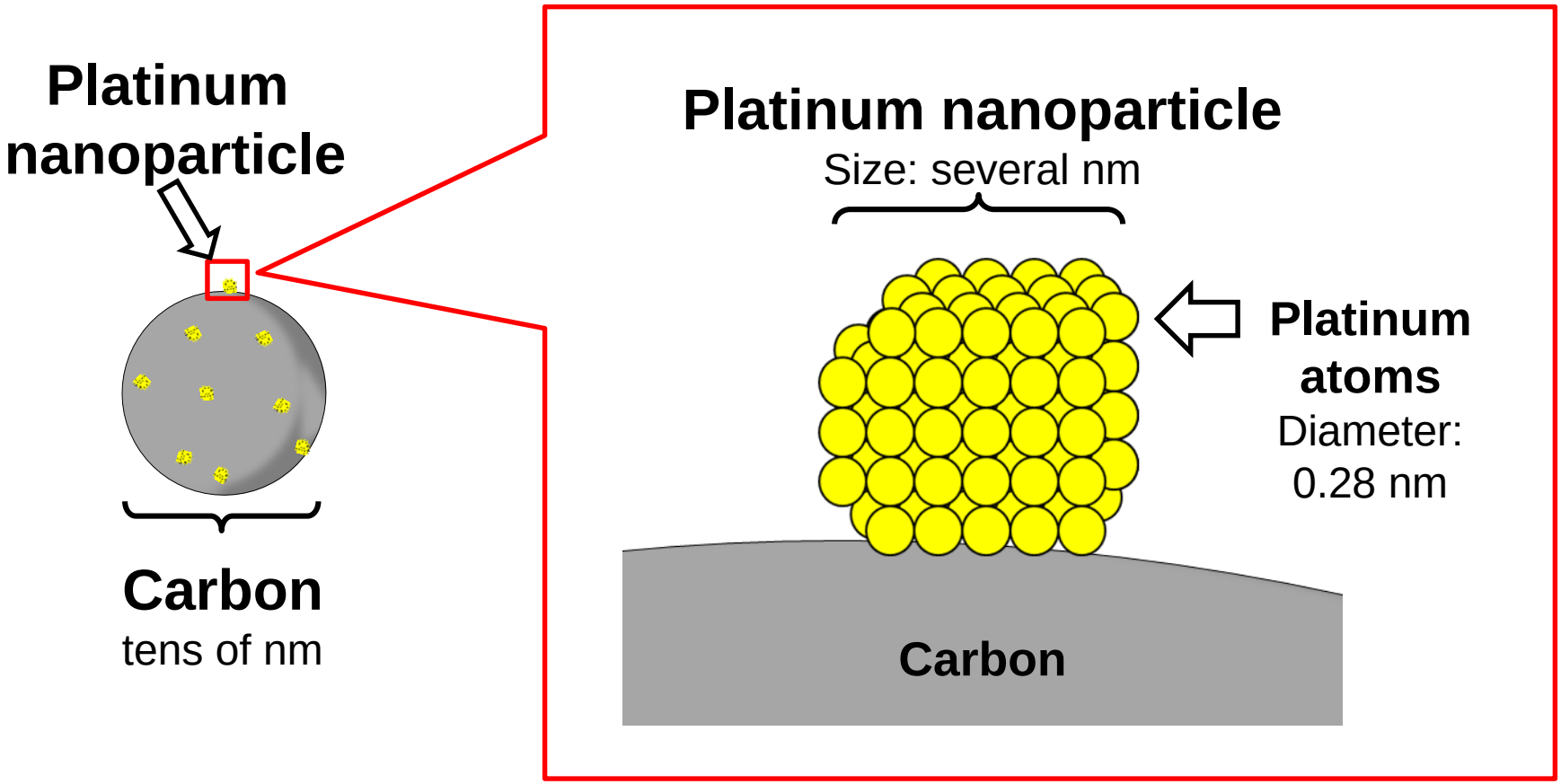
Diameter: tens of nm

*1: 1μm (micrometer) is one millionth of 1 meter

*2: 1 nm (nanometer) is 1 billionth of 1 meter

Anodes and cathodes are primarily composed of platinum nanoparticles and carbon

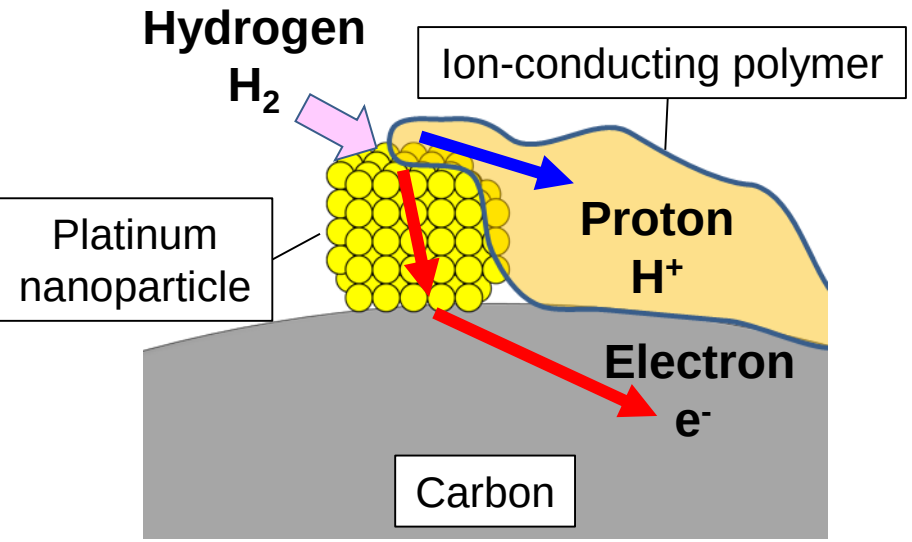
(5) Composition of platinum nanoparticles



Platinum nanoparticles are complex bodies of platinum atoms (hundreds of thousands to millions of atoms)

(6) Catalytic role of platinum nanoparticles

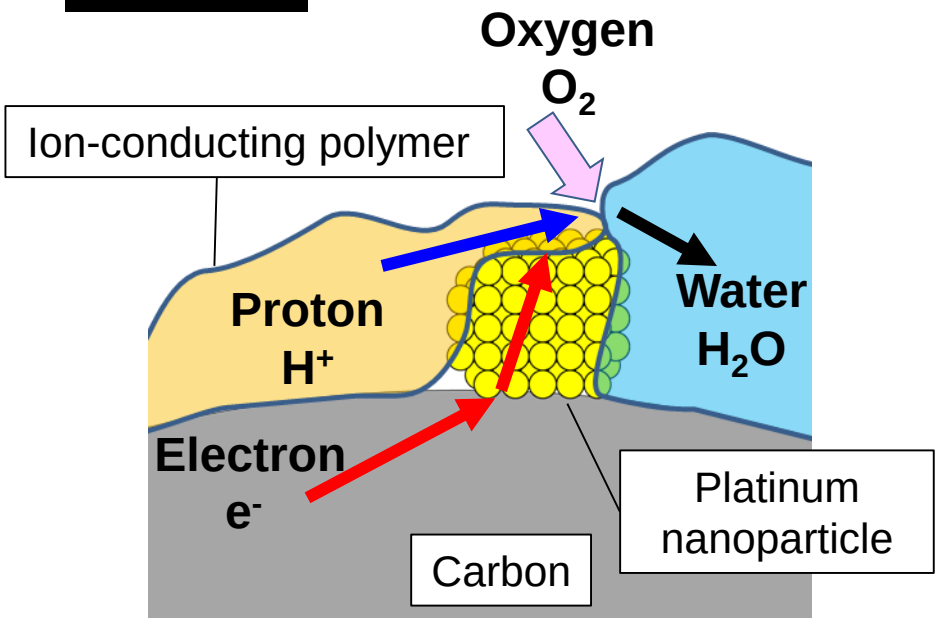
Anode



Chemical reaction: $H_2 \rightarrow 2H^+ + 2e^-$

Hydrogen broken down into protons and electrons

Cathode



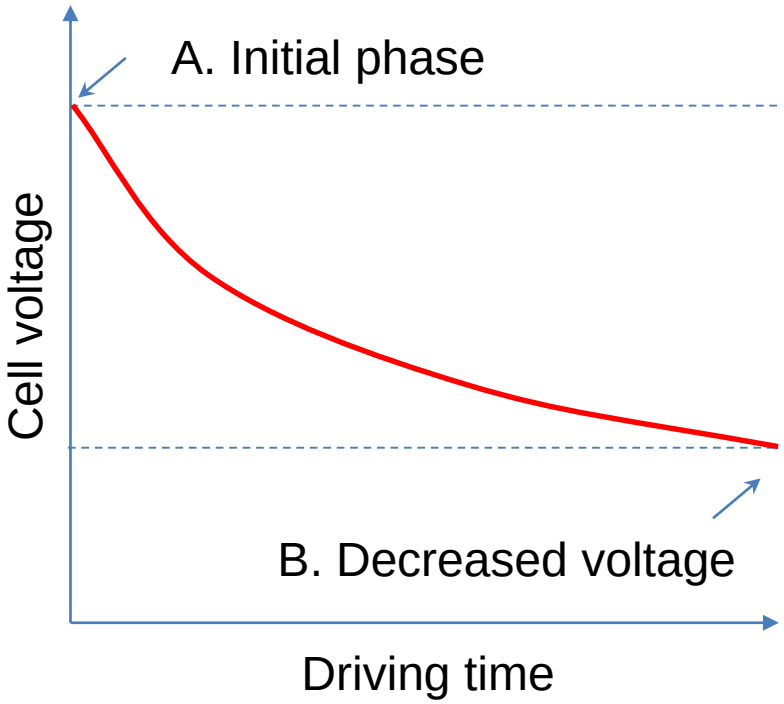
Chemical reaction: $4H^+ + O_2 + 4e^- + \rightarrow 2H_2O$

Water generated from protons, oxygen and electrons

Platinum nanoparticles catalyze fuel cell chemical reactions

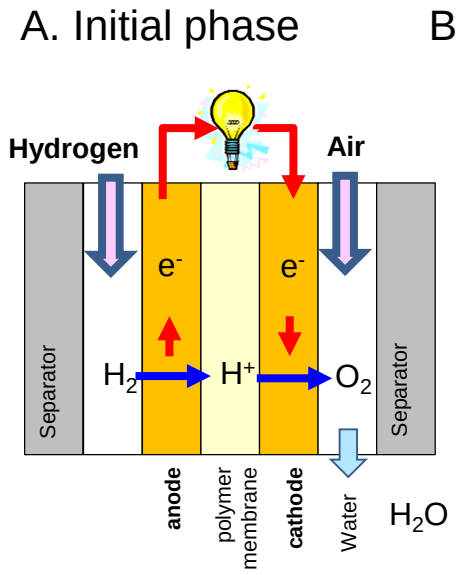
(7) Changes in fuel cell performance during driving

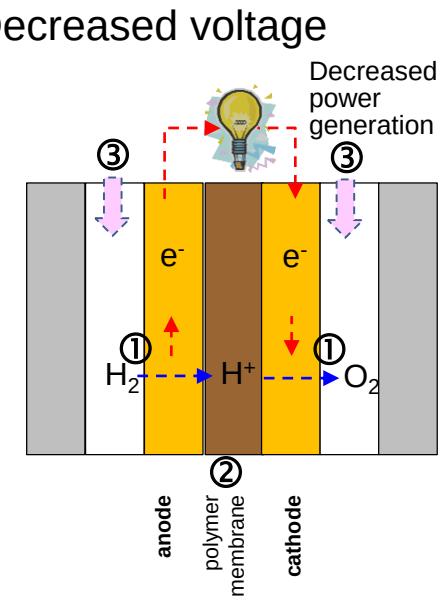
Decreased fuel cell voltage



Causes of decreased voltage

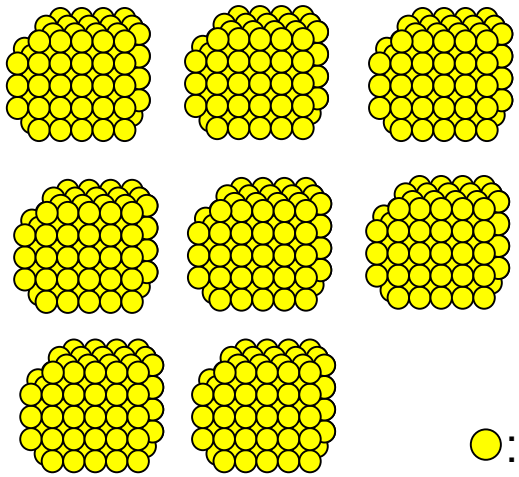
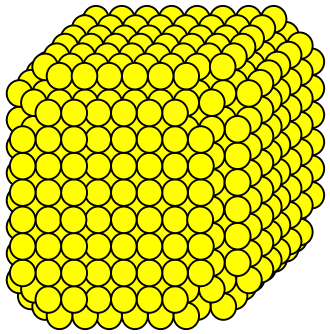
① **Decreased platinum nanoparticle catalyst reactivity**
② **Change in polymer membrane qualities**
③ **Decreased anode/cathode gas diffusibility etc.**





Decreased platinum nanoparticle reactivity may negatively affect fuel cell voltage

(8) Decreased platinum nanoparticle reactivity

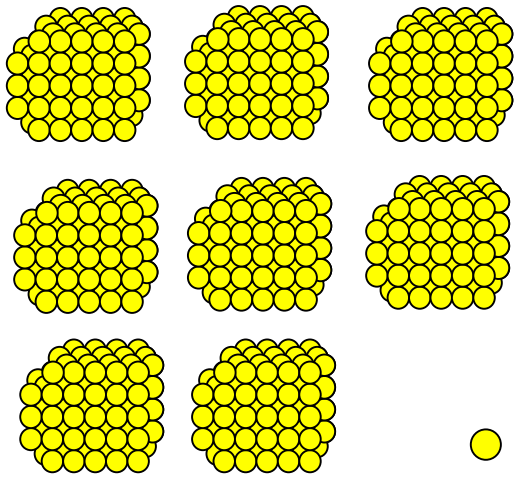
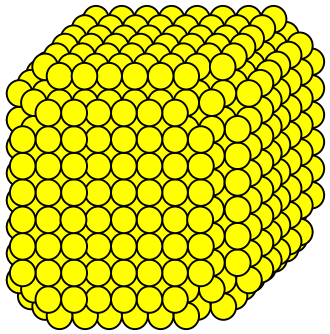
	A. Initial phase	B. Voltage decrease
Platinum nanoparticle state (1000 platinum atoms)		
Size	Small	Large
Reaction surface (surface area)	Large **High reactivity**	Small **Low reactivity**

●:platinum atoms

Decreased platinum nanoparticle reactivity is caused by coarsening (increase in size, decrease in surface area)

1. Role of platinum catalyst in fuel cells
2. **Platinum nanoparticle observation techniques using conventional technology**
3. New technique for observing platinum nanoparticle behavior

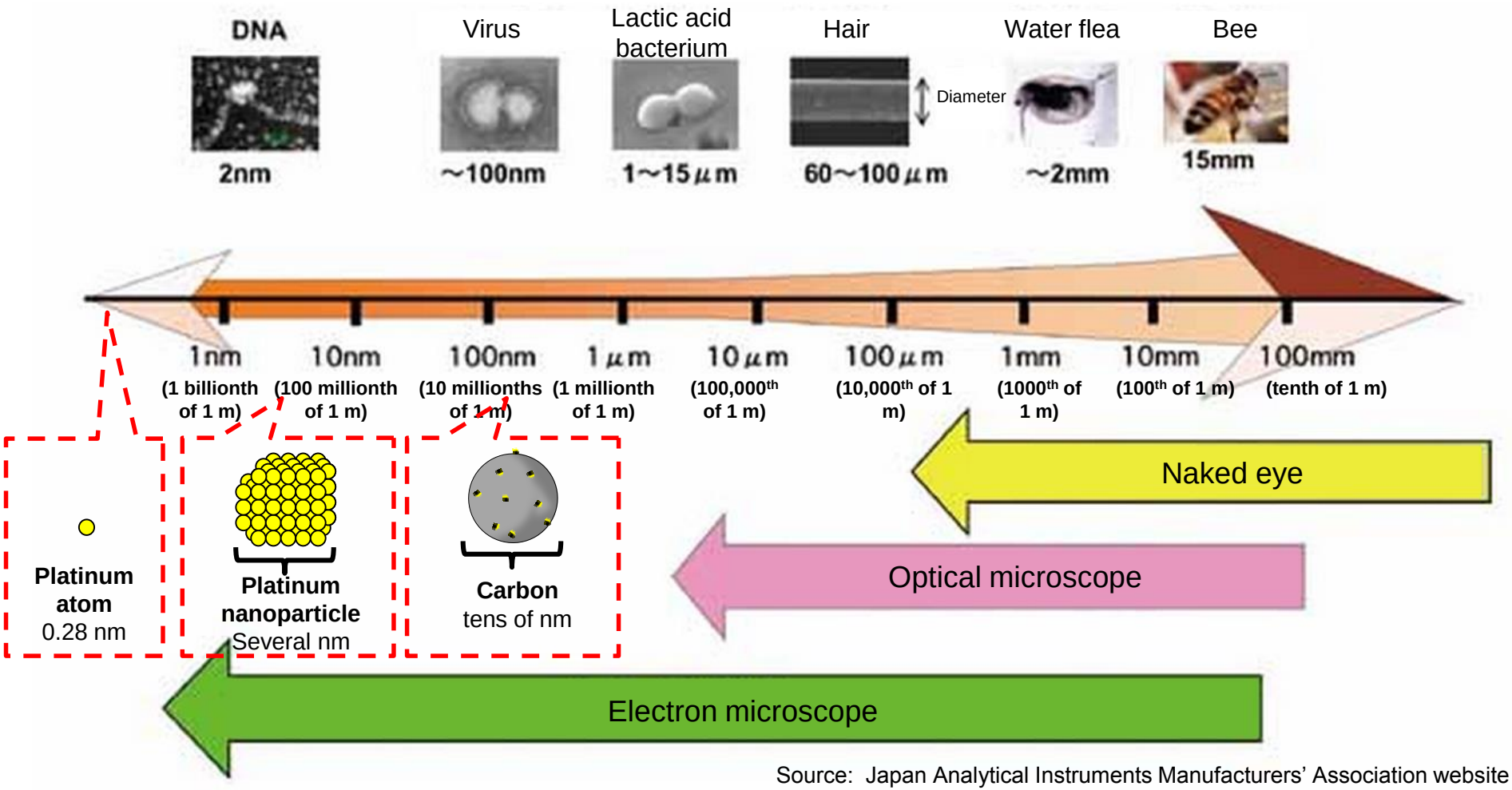
(1) Method for confirming platinum nanoparticle coarsening

	A. Initial phase	B. Voltage decrease
Platinum nanoparticle state (1000 platinum atoms)		
Observation		
Size	Small	Large
Reaction surface (surface area)	Large	Small
	High reactivity	**Low reactivity**

:platinum atoms

Observation of platinum nanoparticle **size**

(2) Technique for observing platinum nanoparticles



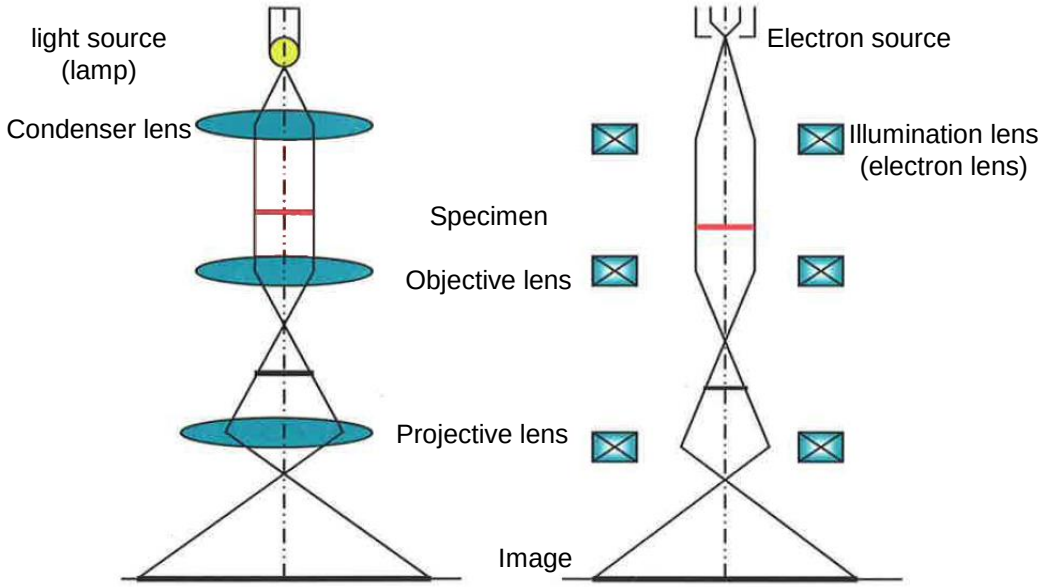
Source: Japan Analytical Instruments Manufacturers' Association website

Platinum nanoparticles can be observed using an transmission electron microscope

(3) Observation with a transmission electron microscope

Optical microscope vs. **Transmission electron microscope**

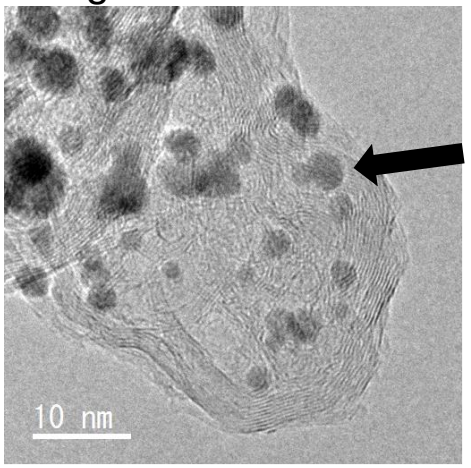
Light source: light rays vs. electron beam



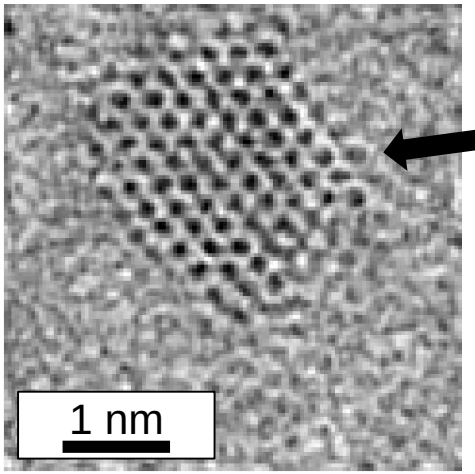
Source: Hitachi High-Technologies Corporation, “Become a friend of TEM“

Enlarging and observing specimens with electron beams

Transmission electron microscope image



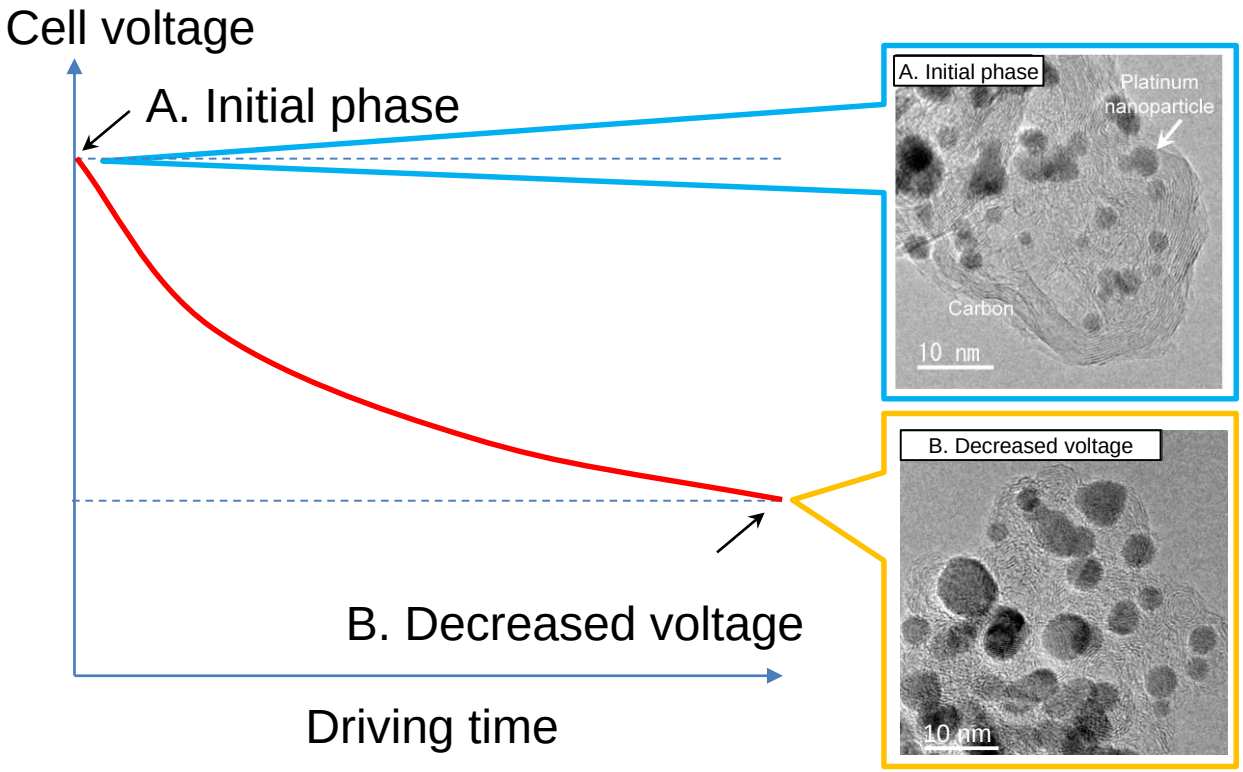
Platinum nanoparticle



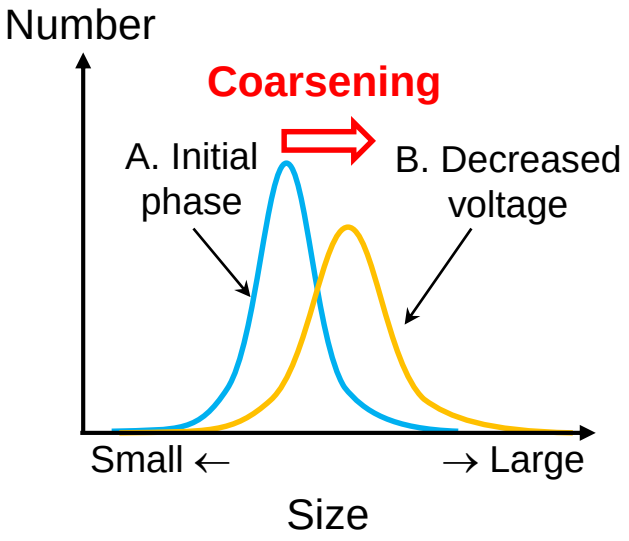
Platinum atom

Transmission electron microscopes enable observation of platinum nanoparticles on a nanometer/atomic level

Decreased fuel cell voltage

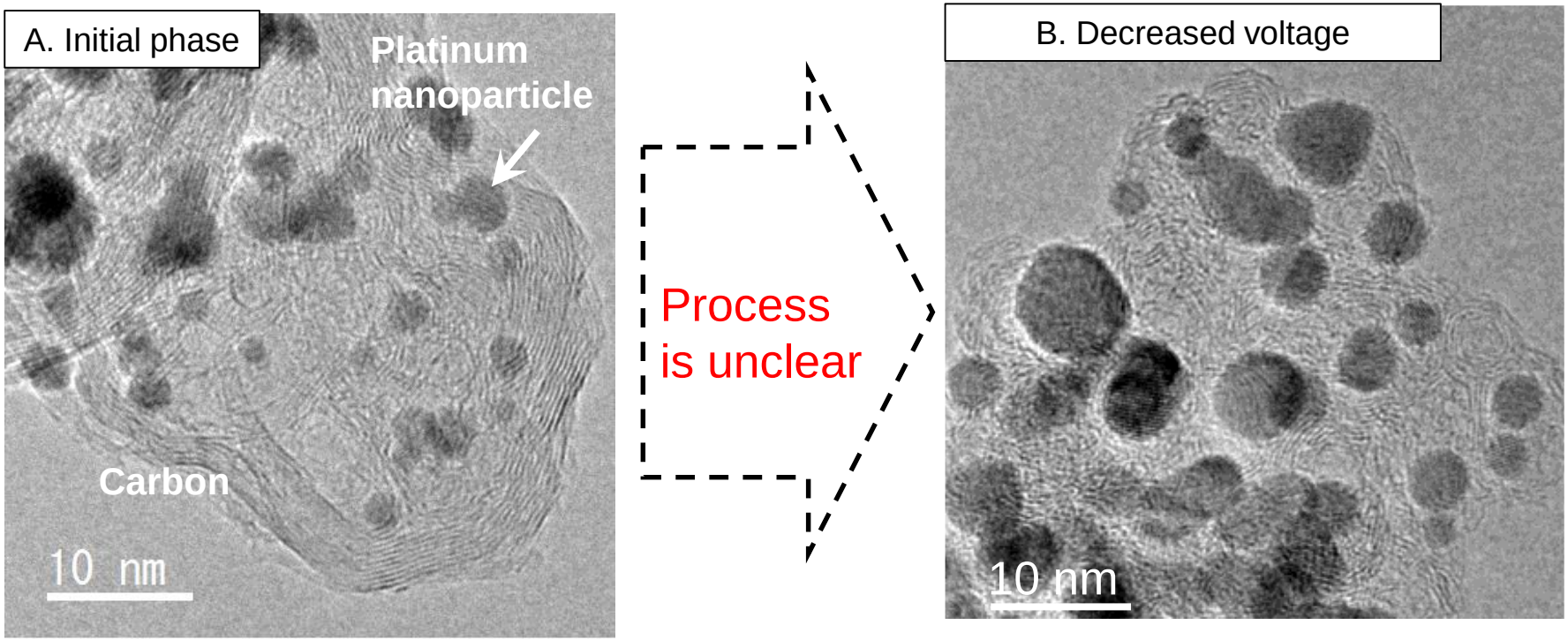


Distribution of platinum nanoparticles by number and size



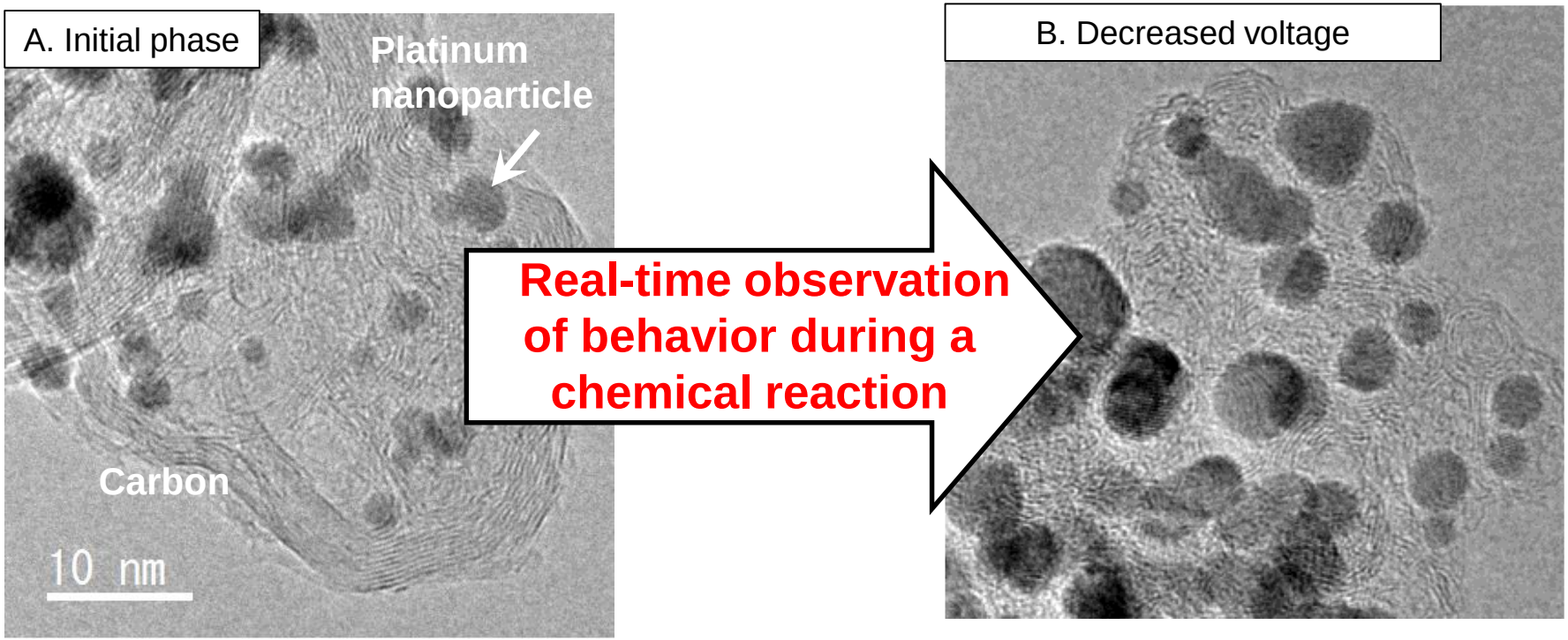
Conventional technology compares platinum nanoparticle size during the initial phase and after voltage is decreased

(5) Problems with conventional observation techniques



The process of platinum nanoparticle coarsening cannot be fully understood using conventional techniques

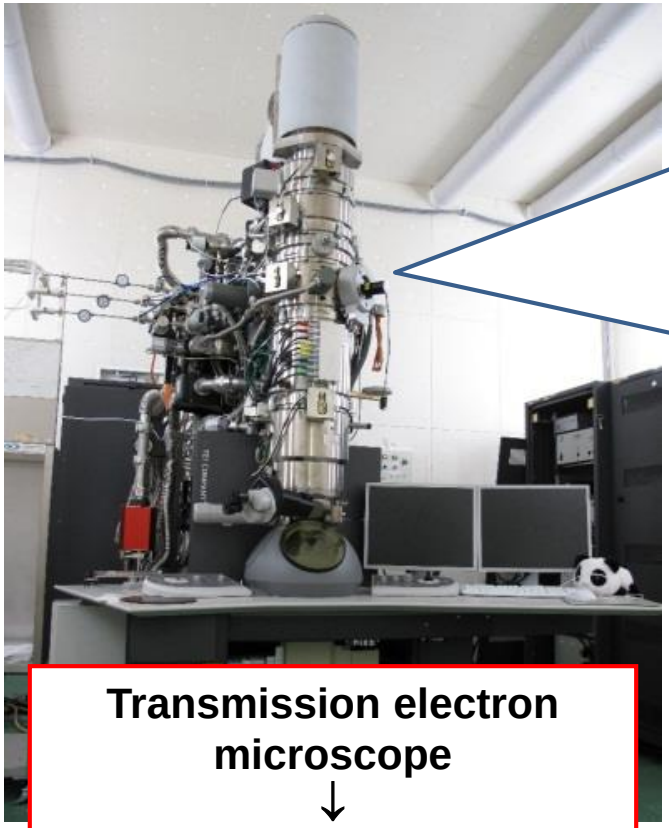
(6) Goal of developing new observation technique



Aim: identify behavior, conditions and materials that make platinum nanoparticles prone to coarsening

1. Role of platinum catalyst in fuel cells
2. Platinum nanoparticle observation techniques using conventional technology
3. **New technique for observing platinum nanoparticle behavior**

(1) Technique for observing platinum nanoparticle behavior



Transmission electron microscope

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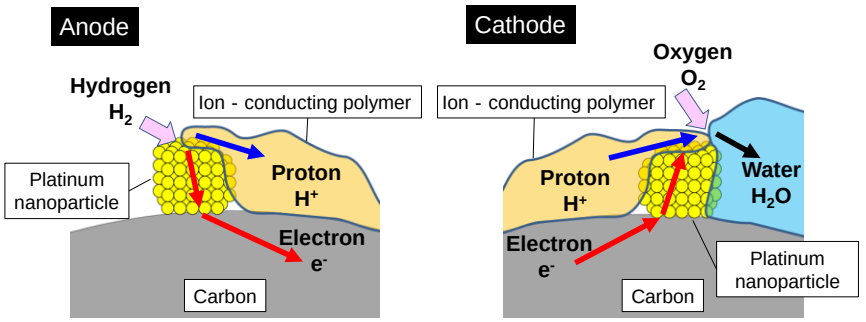
Observation on nanometer/atomic level

Sample holder



Incorporate electrochemical cells into equipment

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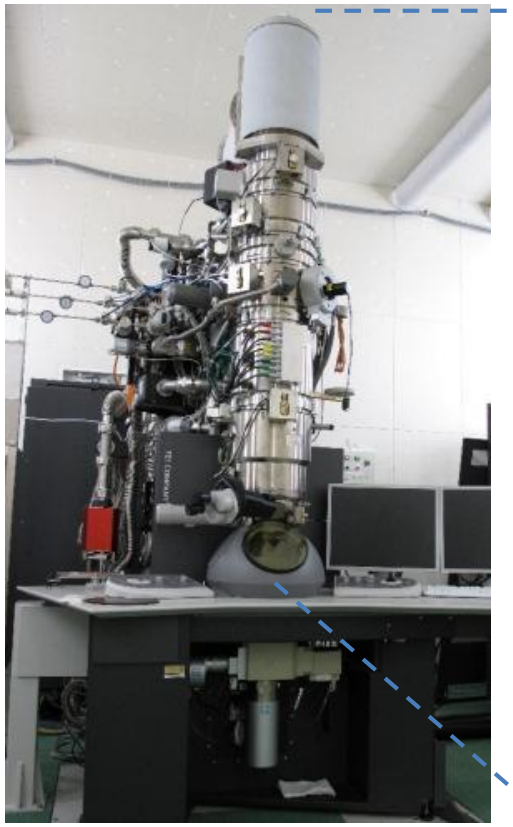
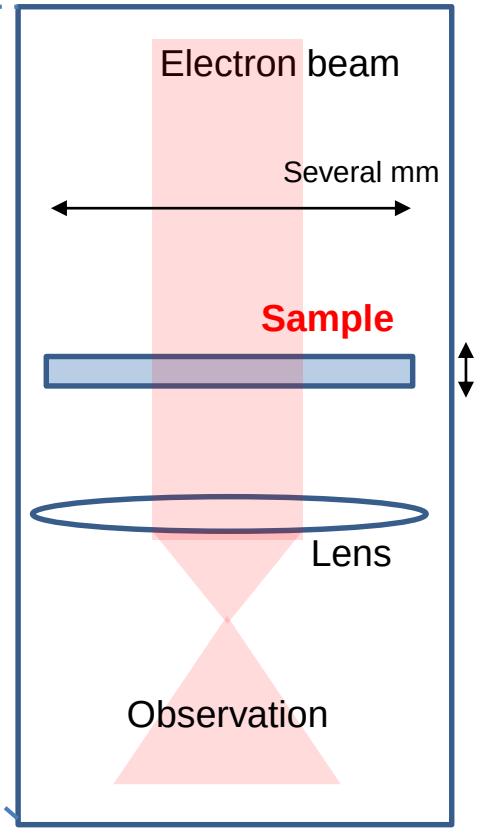
Recreate catalyst behavior

Recreate a fuel cell catalyst chemical reaction in a transmission electron microscope





Requirements for observation by transmission electron microscope

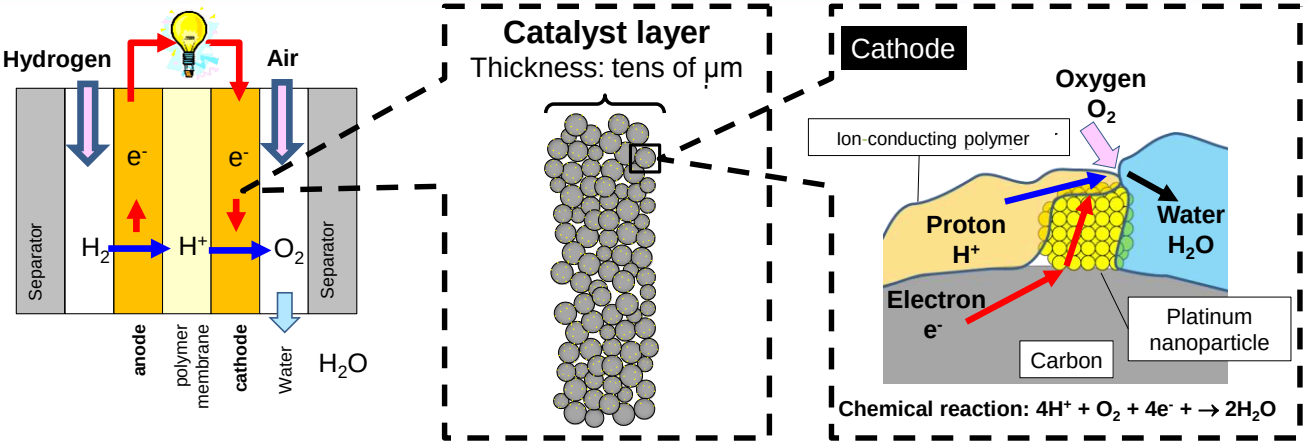
The electron beam must pass through the sample

Generally, samples must have thickness of several 100 nm or smaller

The site of the fuel cell catalyst chemical reaction must be extremely small

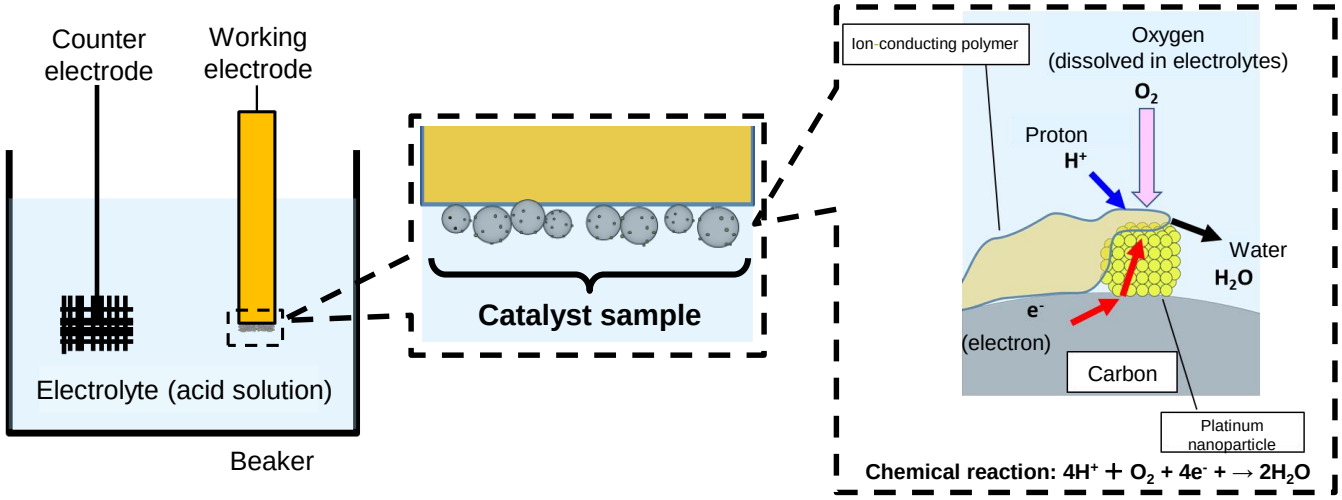
(3) Reproducing a fuel cell chemical reaction (conventional technique)

Fuel cell



General catalyst evaluation method

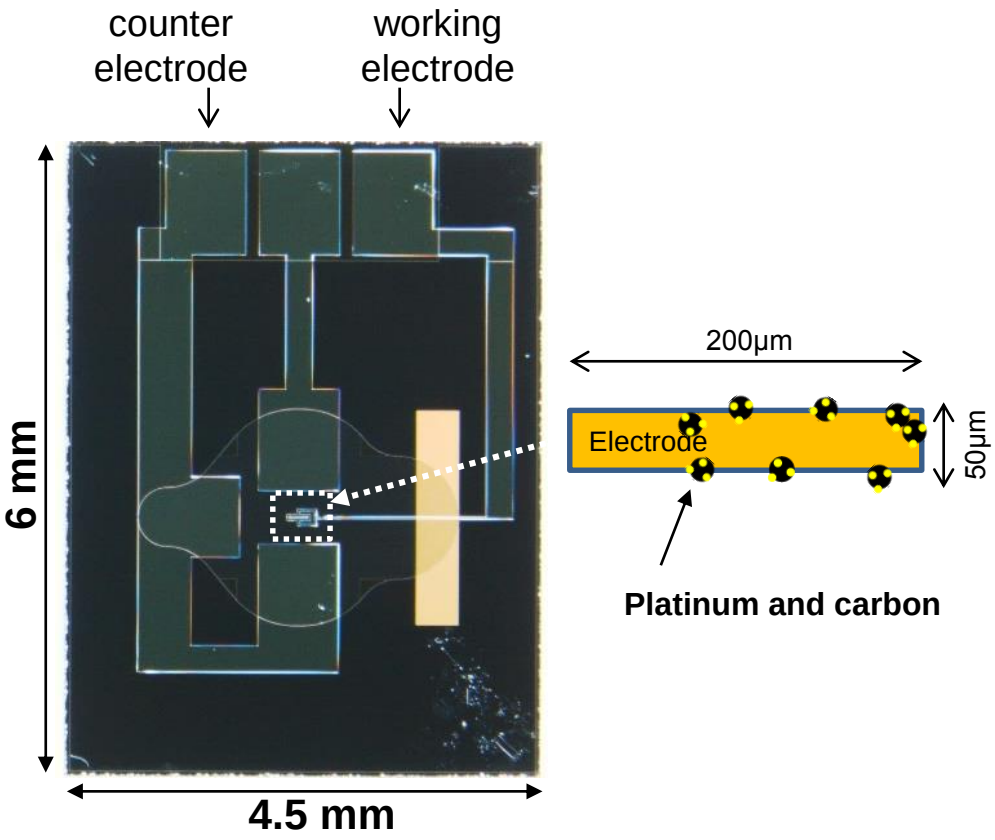
Use two electrodes and electrolyte to produce a chemical reaction



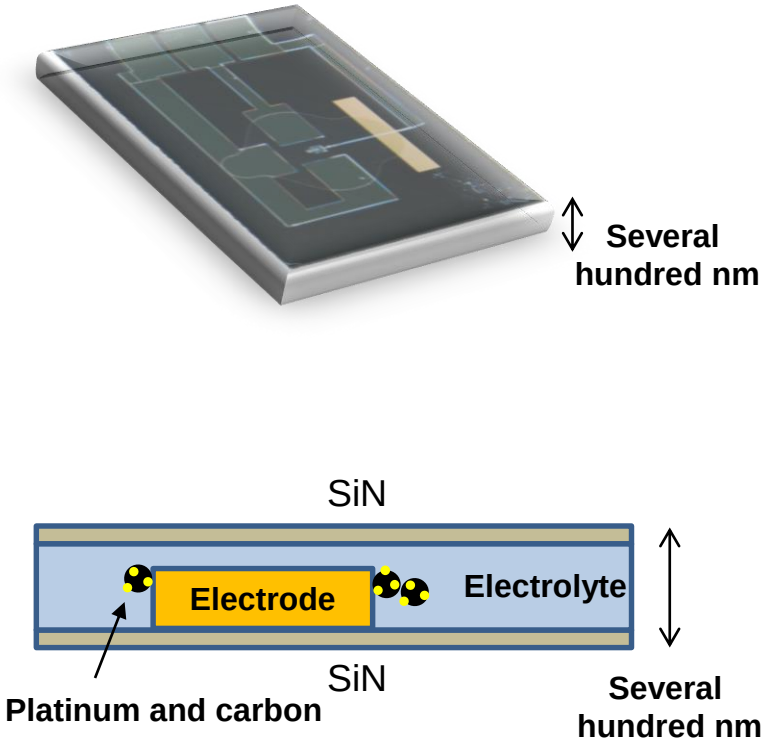
The conventional technique uses the general catalyst evaluation method to reproduce the chemical reactions that occur in fuel cells

(4) Use of microscopic electrochemical cells as samples

Using micro-electromechanical systems technology to create millimeter-sized microscopic electrochemical cells (plane view)

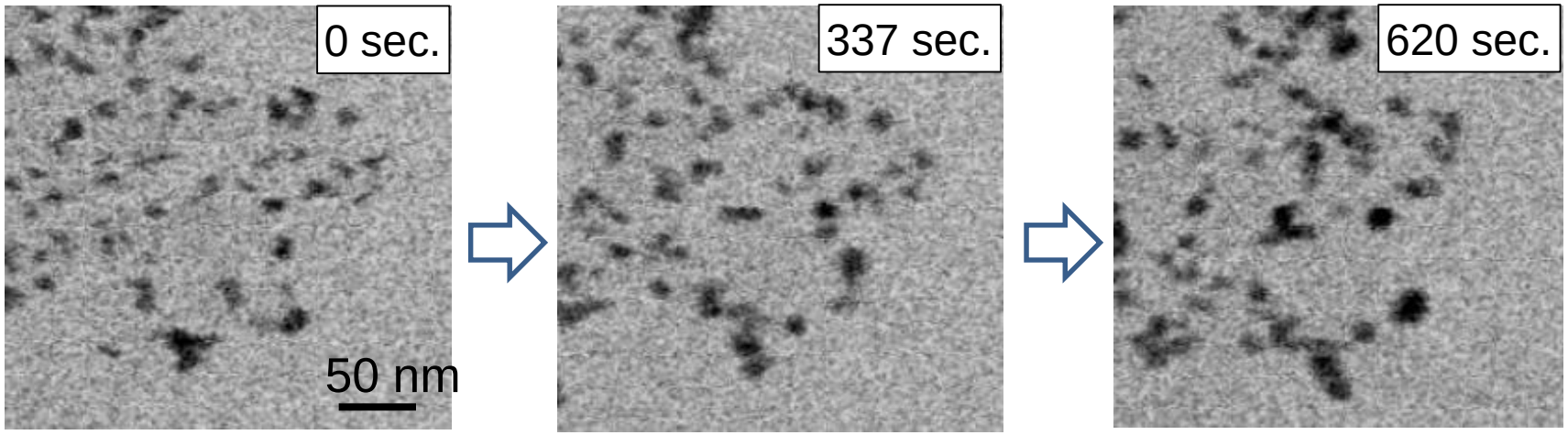


Using silicon nitride (SiN) film to confine electrolytes within a thickness of several 100 nm (cross-section)



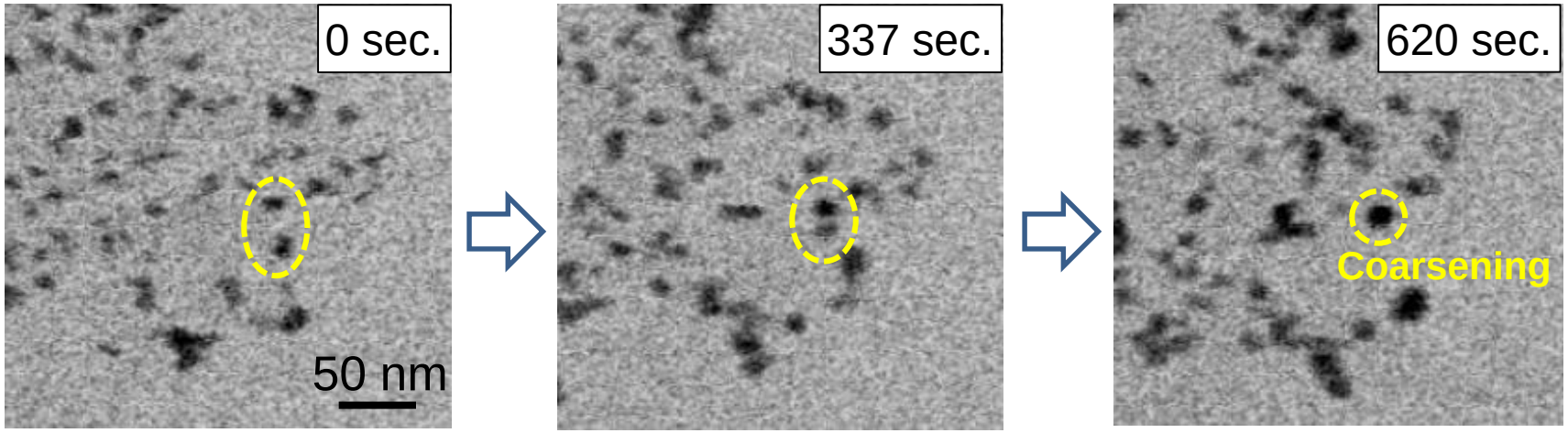
Using micro-electromechanical systems technology to create microscopic electrochemical cells that can be observed via transmission electron microscope

(5) Real-time observation results

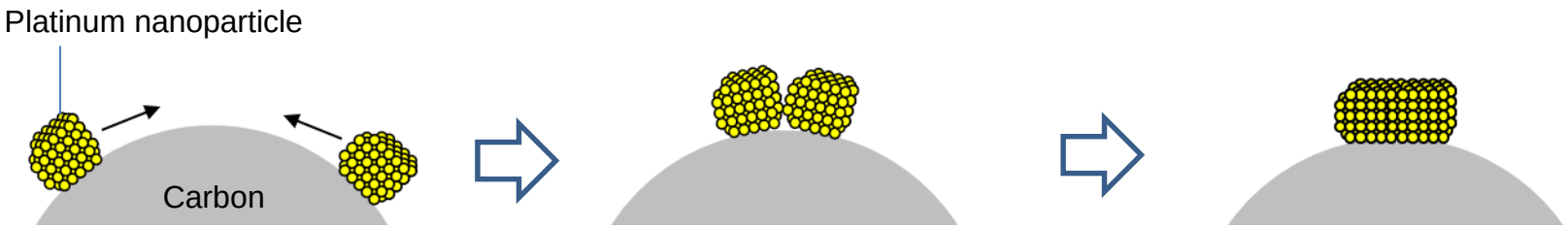


Successful real-time observation of platinum nanoparticle behavior at nanometer levels during a chemical reaction leading to coarsening

(6) Real-time observation results



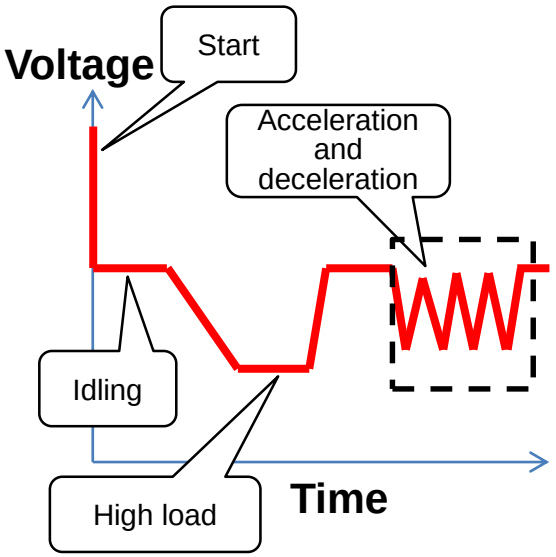
Phenomenon observed (schematic diagram)



Platinum nanoparticles migrate over carbon and coarsen

(7) Future uses of this new observation technique

Voltage changes during driving



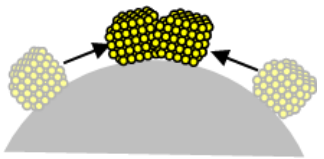
Aim: Increase lifespan of fuel cells and reduce platinum used

Driving conditions
- Voltage
- Voltage changes

Materials
- Carbon type
- Platinum nanoparticle size

Analyze relationship

Platinum nanoparticle behavior



Analysis of relationship between voltage changes during driving and platinum nanoparticle behavior changes

(Reference) Exhibit at Automotive Engineering Exposition

- Exhibit at the Automotive Engineering Exposition (held May 20 – 22 at Pacifico Yokohama)
- Lecture at 2015 JSAE Annual Congress (Spring) held concurrently (May 20, from 9:30)

TOYOTA