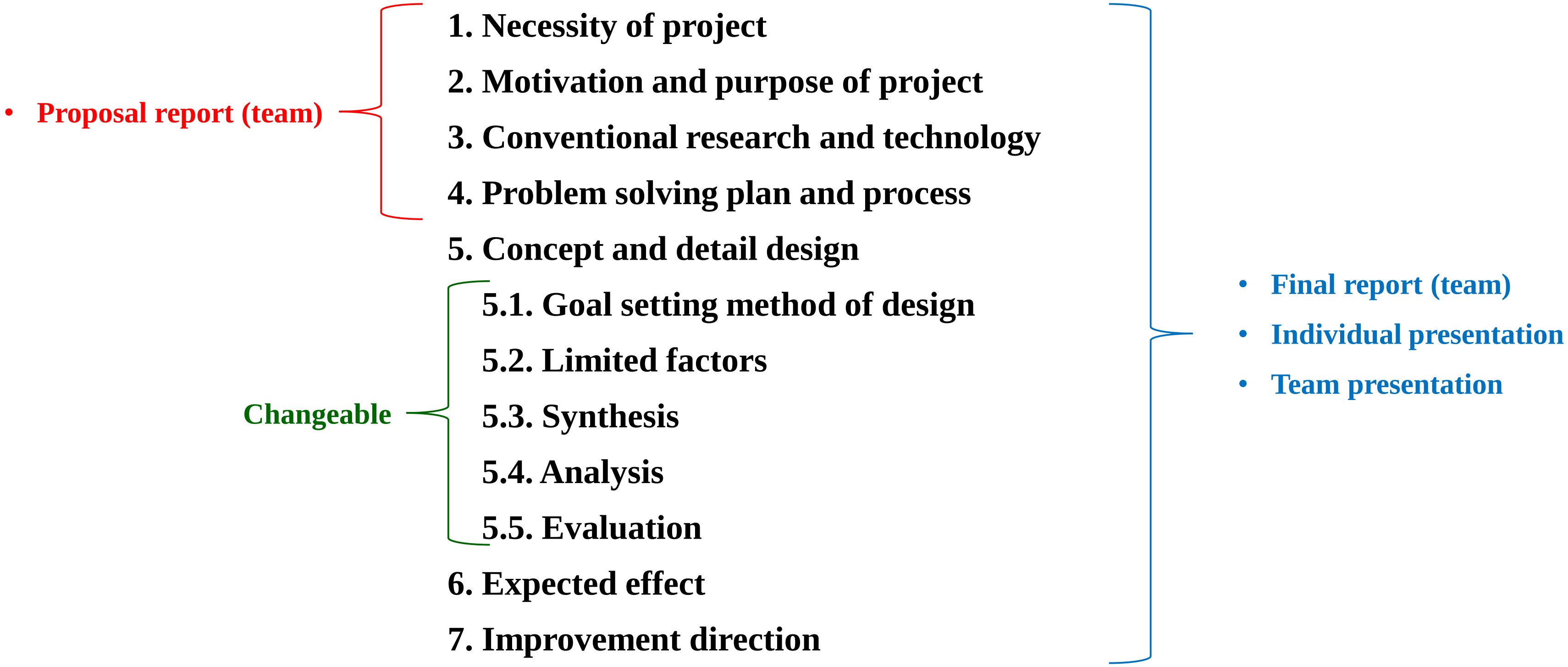
Chemical Engineering Fundamentals and Design

Lecture 03

How to Prepare the Reports and Presentation? (Case Study)

How to prepare the reports and presentation?

Your reports and presentation should include…



- Proposal report (team)

1. Necessity of project
2. Motivation and purpose of project
3. Conventional research and technology
4. Problem solving plan and process
5. Concept and detail design

Changeable

   - 5.1. Goal setting method of design
   - 5.2. Limited factors
   - 5.3. Synthesis
   - 5.4. Analysis
   - 5.5. Evaluation
6. Expected effect
7. Improvement direction

- Final report (team)
- Individual presentation
- Team presentation

All reports and presentation materials should be prepared by English.

How to prepare the reports and presentation?

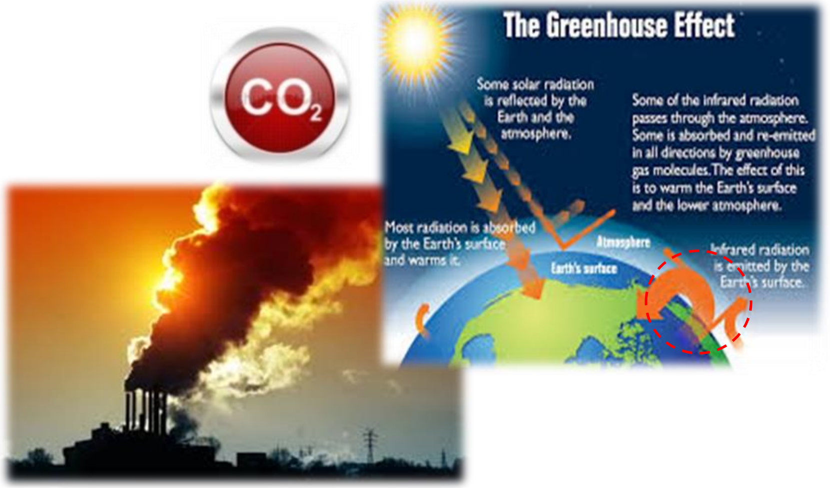
Development of clean energy for future (case study)

1. Necessity of project

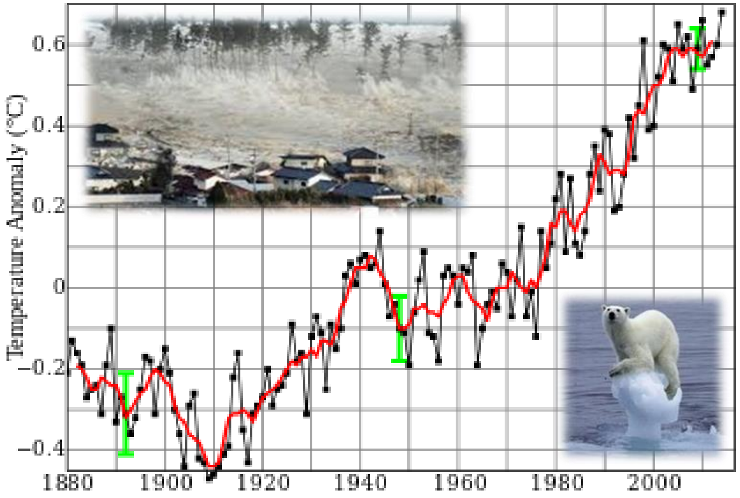
1. Necessity of project

Energy issues: environmental problem

Greenhouse effect



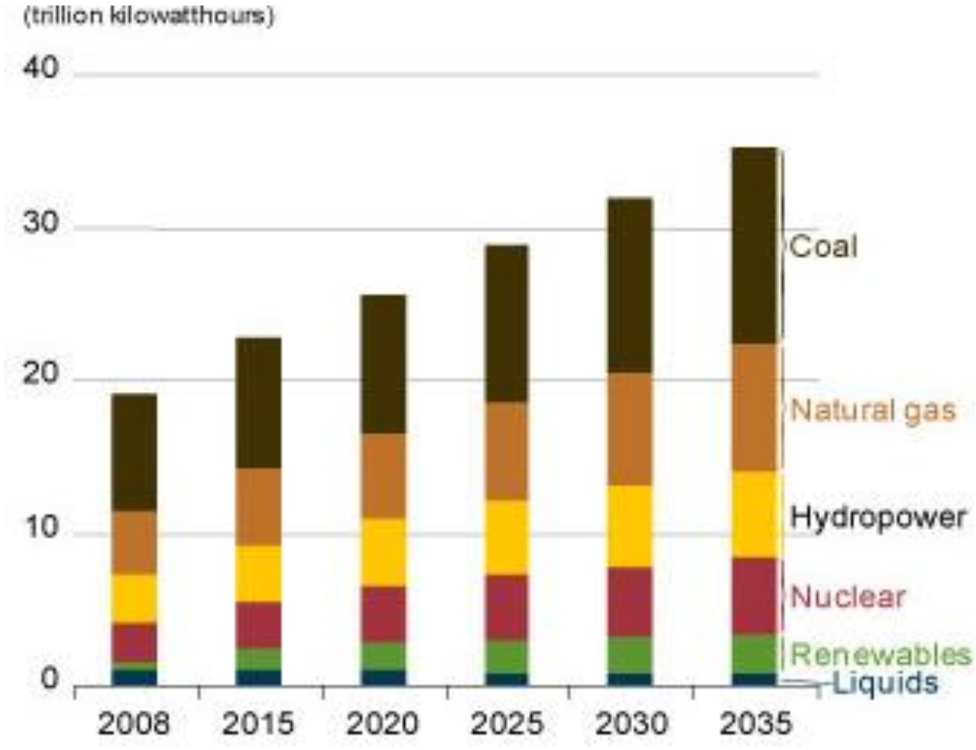
Global warming



1. Necessity of project

Energy issues: dependence

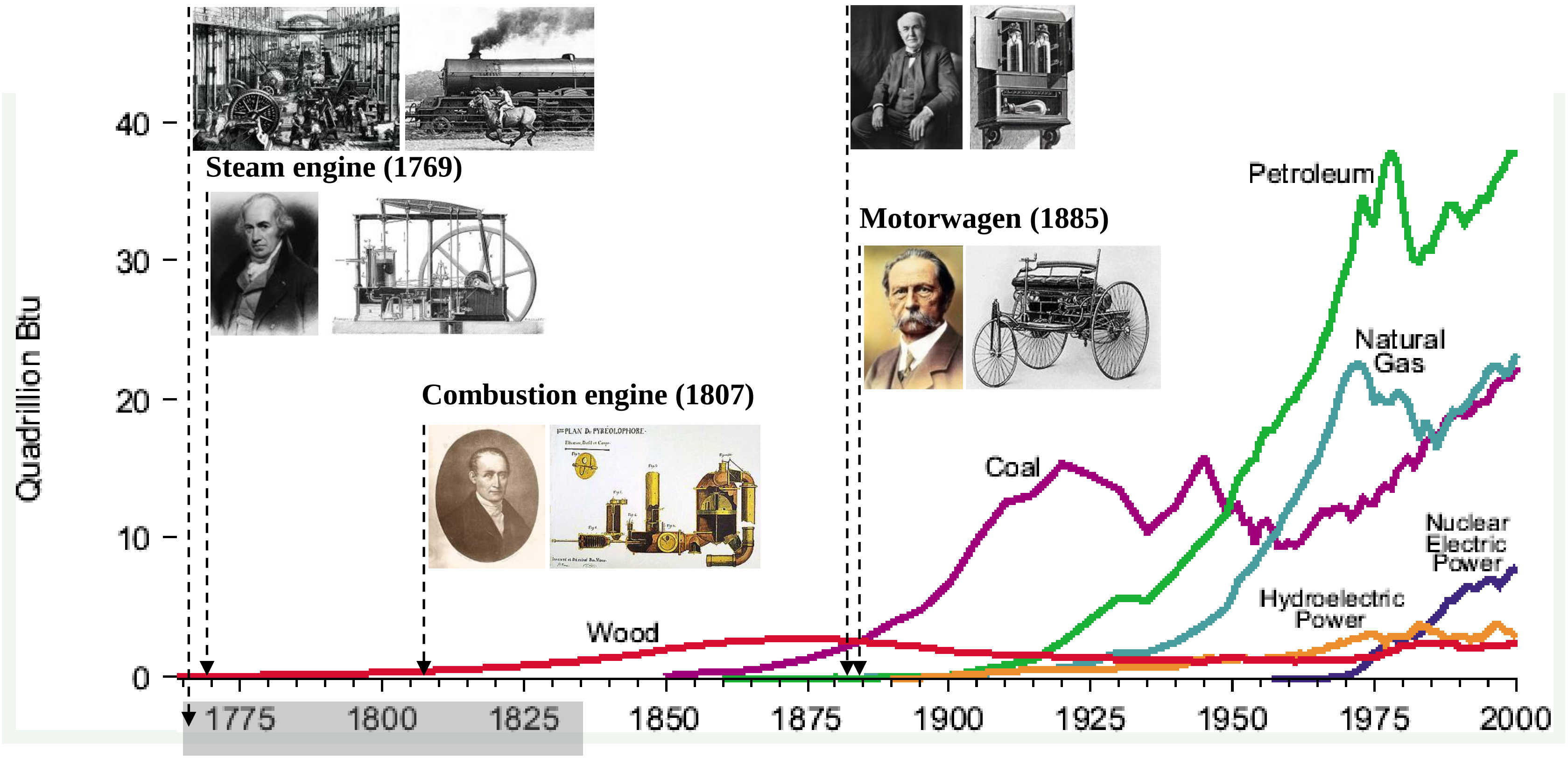
World electricity generation



Source: http://www.eia.gov/forecasts/

1. Necessity of project

Energy issues: dependence (historical time line)


Industrial revolution (1760 ~ 1830)

Steam engine (1769)

Combustion engine (1807)

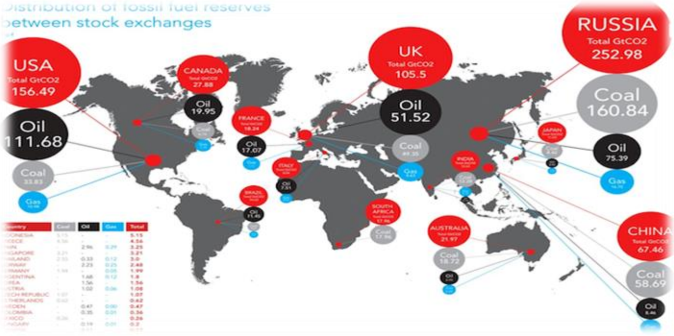
Power station (1882)

Motorwagen (1885)

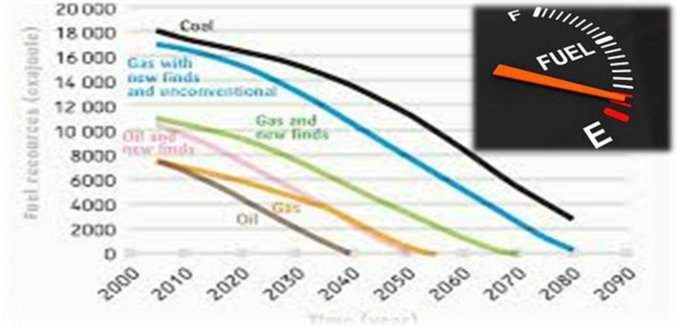
1. Necessity of project

Energy issues: international conflict

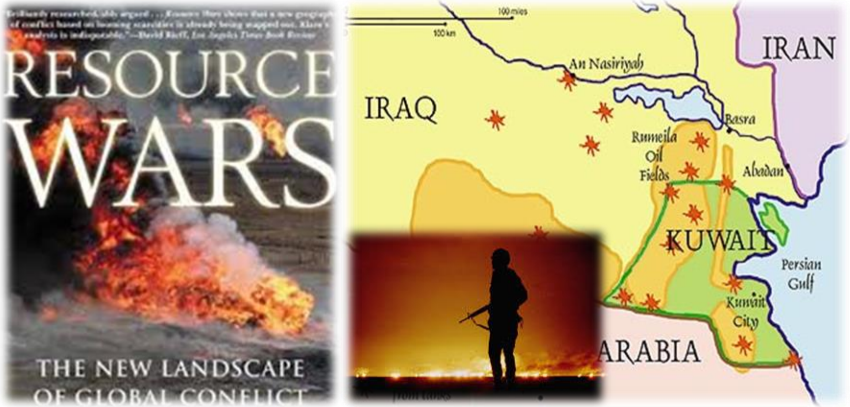
Energy reserves distribution



Energy depletion



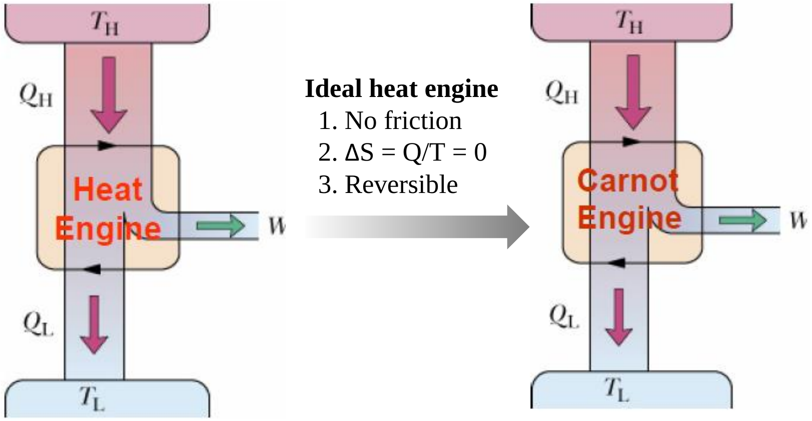
Resources war



1. Necessity of project

Energy issues: conversion efficiency

Power plant



Ideal heat engine

1. No friction
2. $\Delta S = Q/T = 0$
3. Reversible

Efficiency at T_H = 673 K (400 °C) and T_L = 298 K (25 °C)

$$\varepsilon = \frac{Useful\ output}{Total\ input} = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H} = 0.56$$

$$|W| = |Q_H| - |Q_L|$$

1st law: conservation of energy

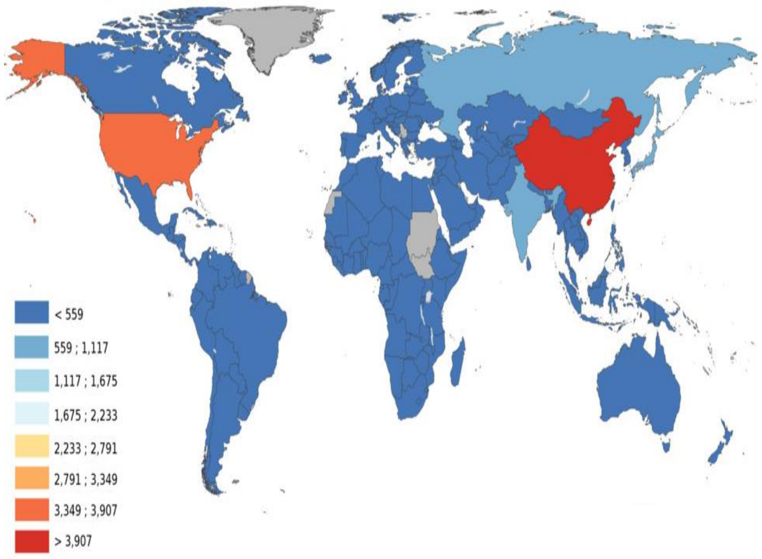
$$\Delta S = 0 = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L}$$

$$\rightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

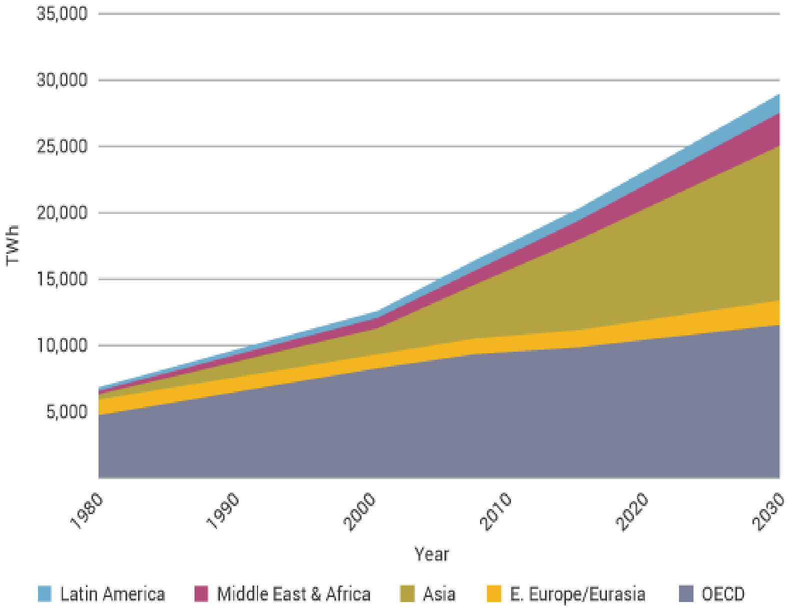
1. Necessity of project

Energy issues: energy consumption

Electricity consumption (billion – kWh)



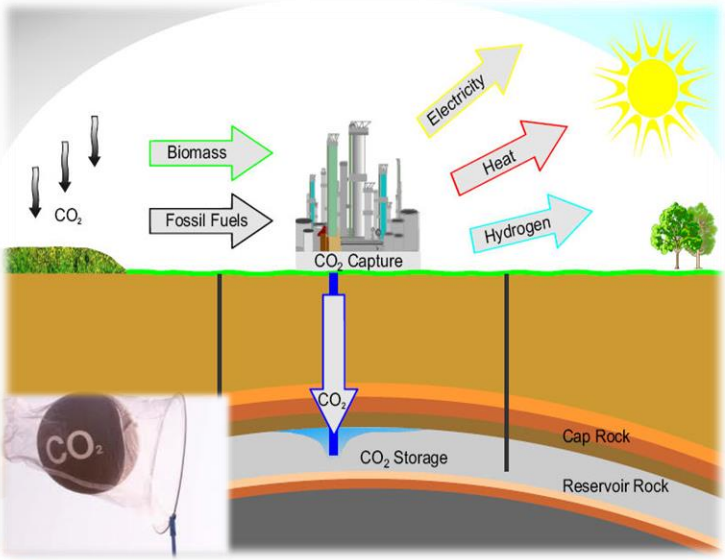
World electricity consumption by region



1. Necessity of project

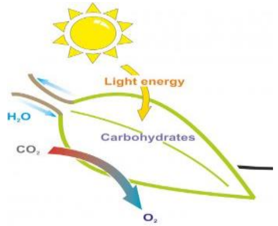
Solutions for energy issues: environmental problem (carbon cycle)

Carbon capture and storage

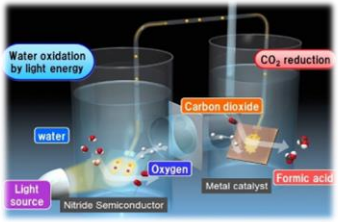


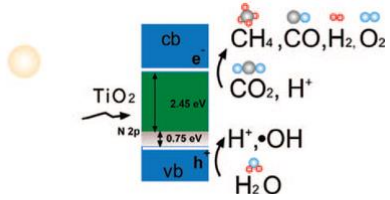
CO_2 conversion (utilization)

Biochemical

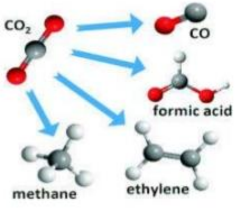


Photochemical





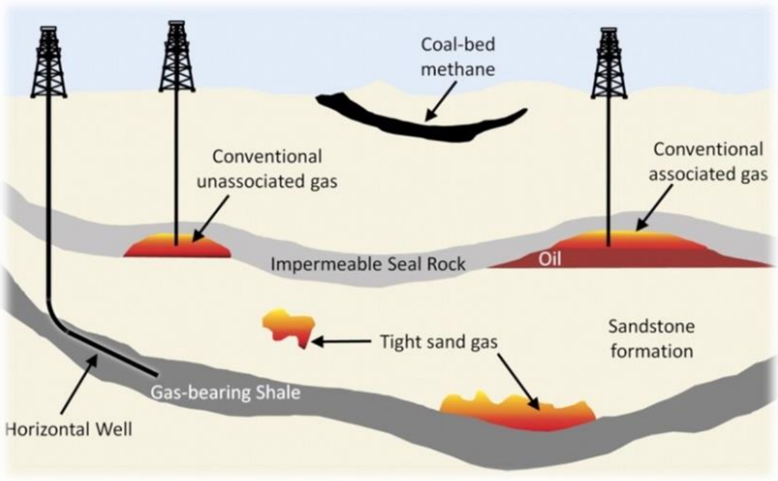
Electrochemical



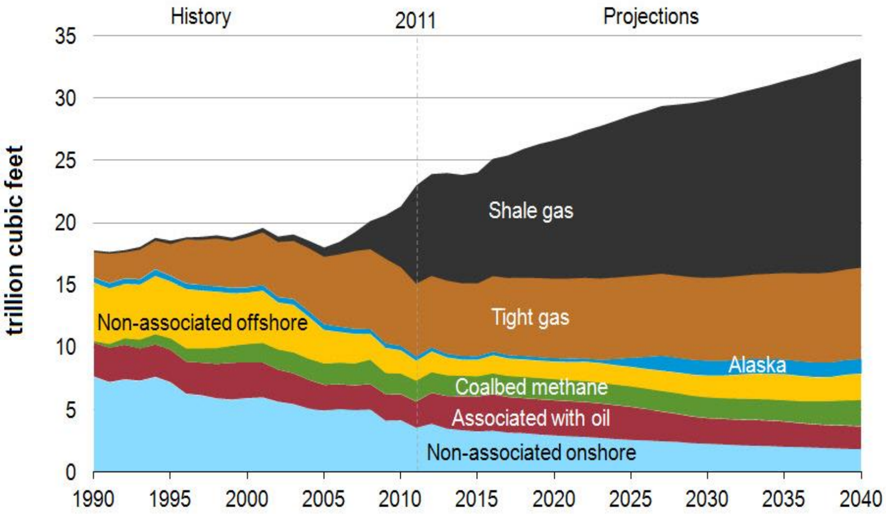
1. Necessity of project

Solutions for energy issues: international conflict (advanced technology)

Shale gas



Prediction of gas production portion



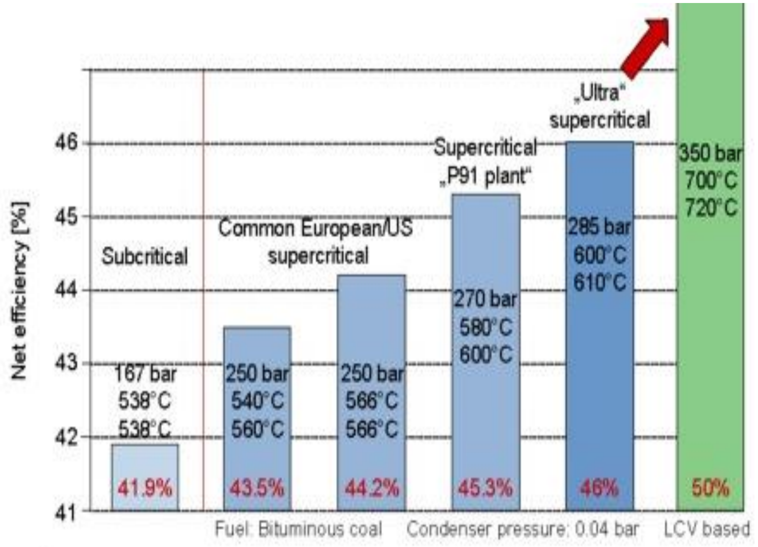
Chemical composition of shale gas is very similar with that of conventional gas.

Production of shale gas will be hugely increased.

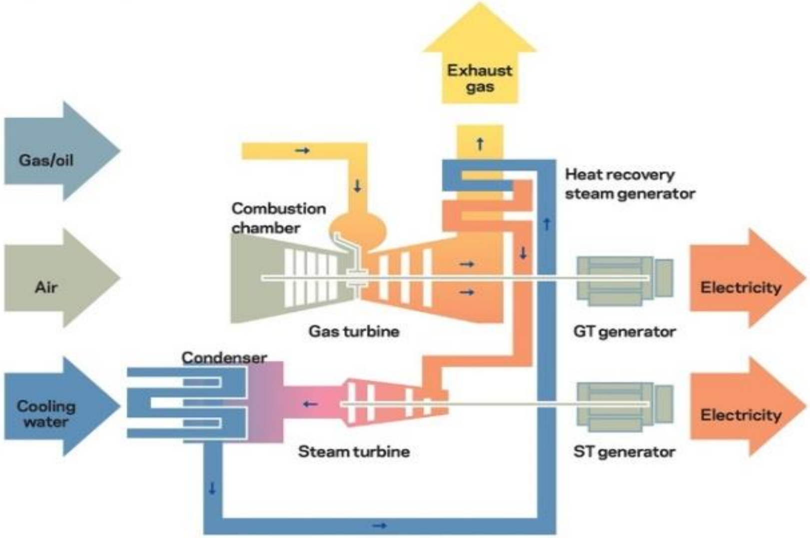
1. Necessity of project

Solutions for energy issues: conversion efficiency (development of new type power plant)

Ultra-supercritical power plant



Combined cycle power plant



Ultra-supercritical and combined cycle power plants are expected to increase the efficiency compared with conventional power plant.

2. Motivation and purpose of project

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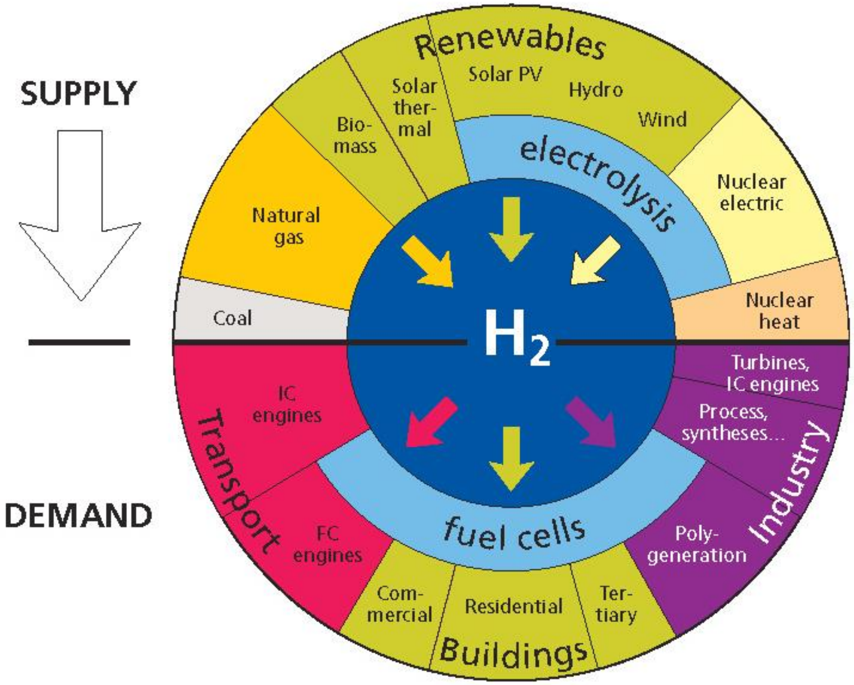
Hydrogen as a future energy

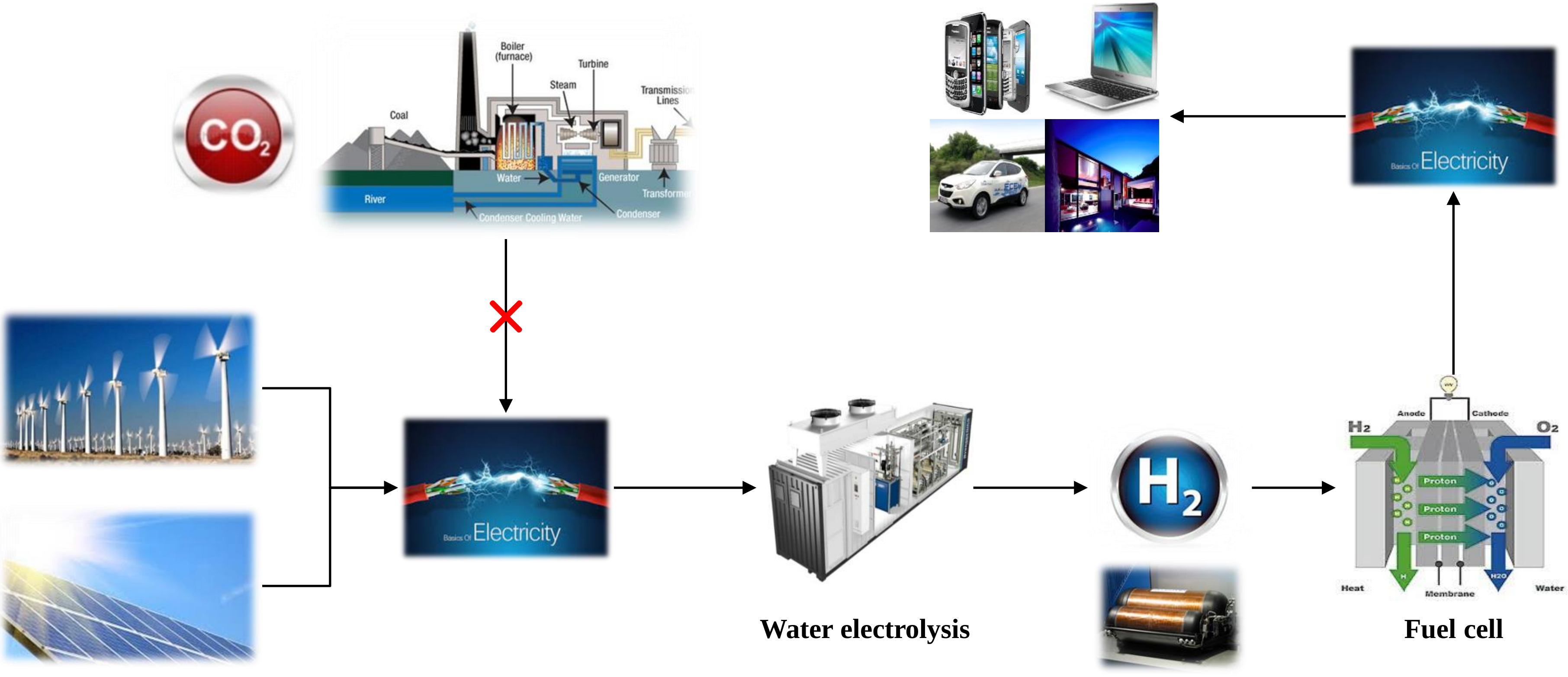
2. Motivation and purpose of project

How to produce and utilize hydrogen?



2. Motivation and purpose of project

How to produce and utilize hydrogen?



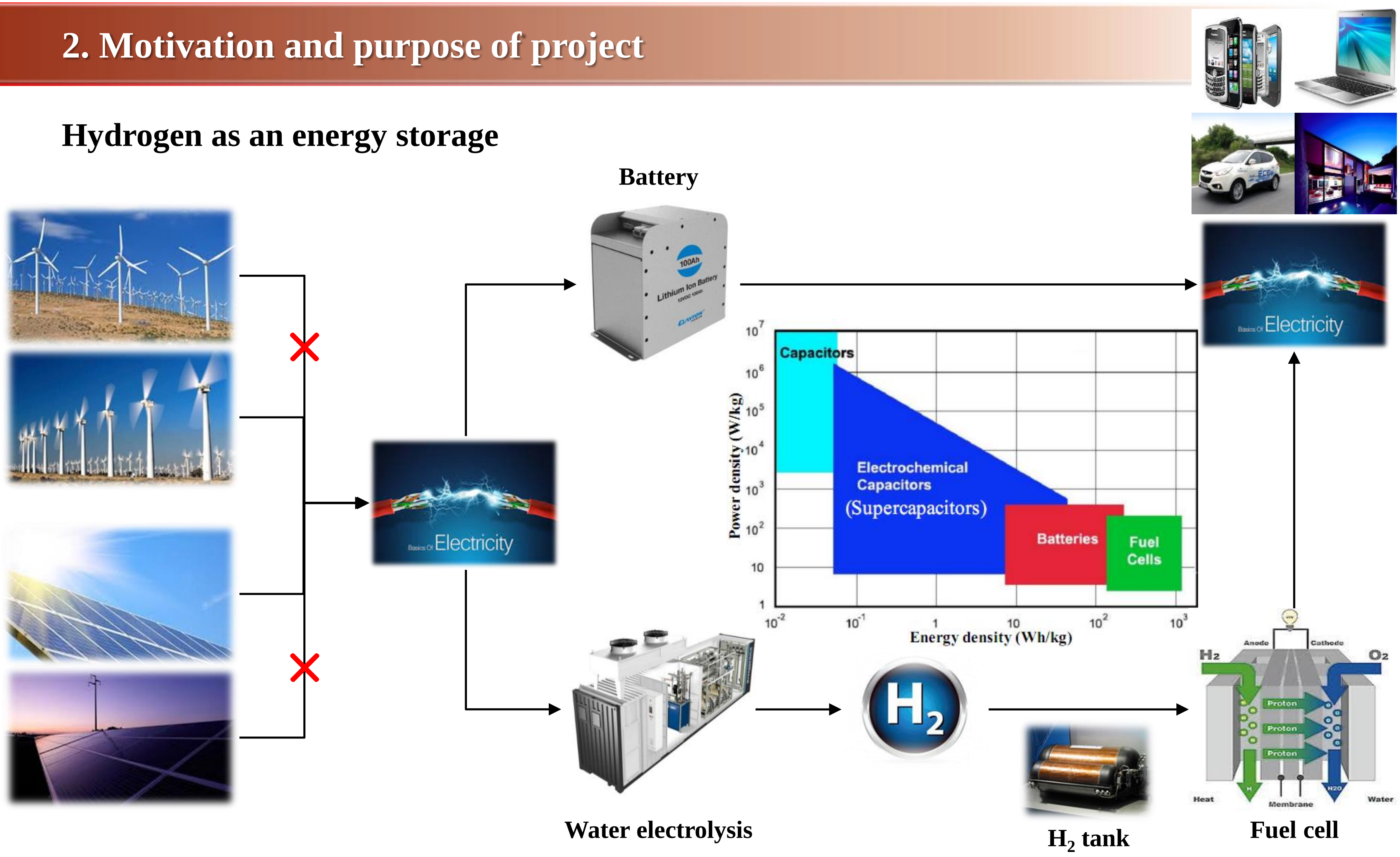
Water electrolysis

H_2 tank

Fuel cell

2. Motivation and purpose of project

Hydrogen as an energy storage



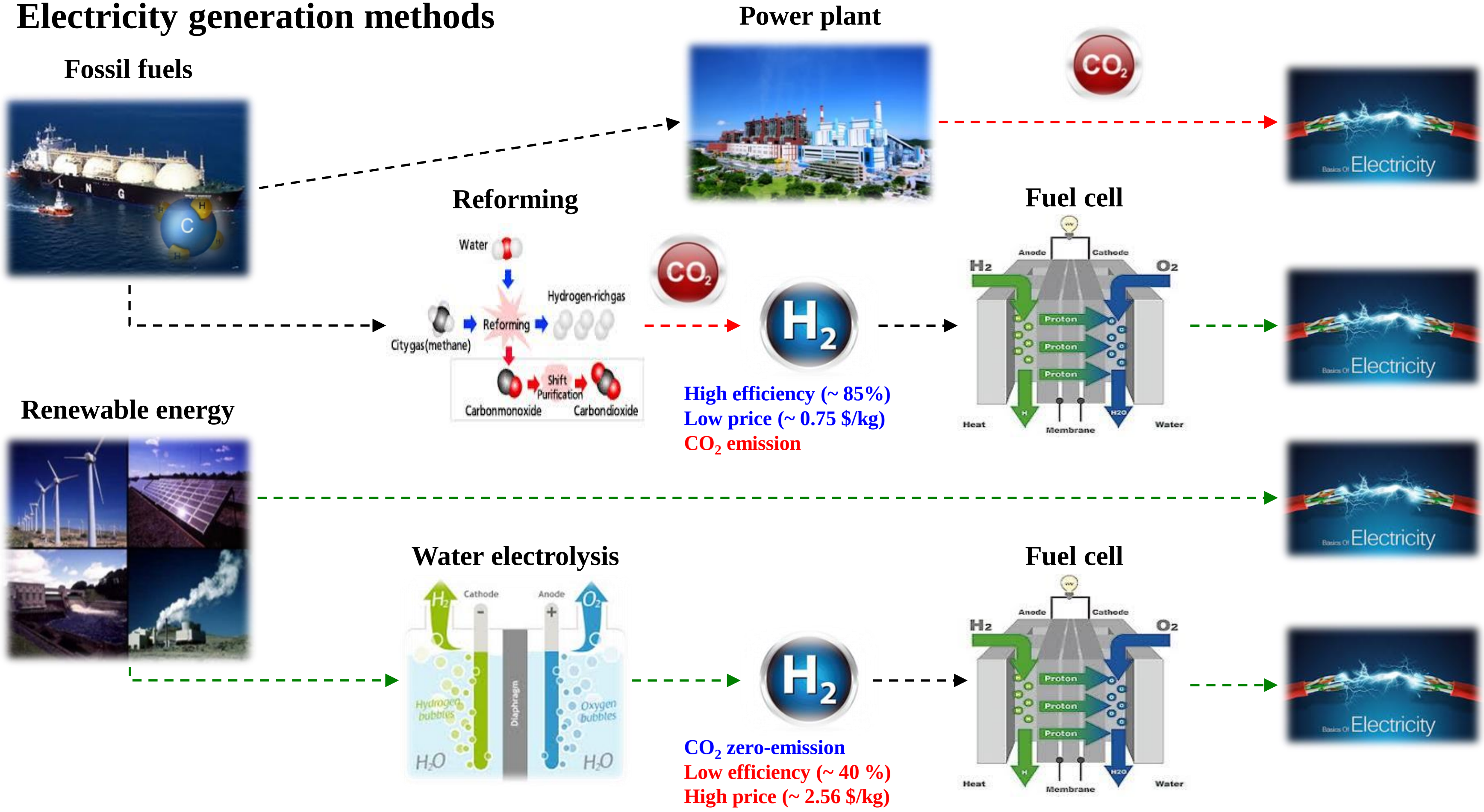
2. Motivation and purpose of project

Current status of environmental-friendly energy system

3. Conventional research and technology

3. Conventional research and technology

Electricity generation methods



Power plant

Fossil fuels

Reforming

Fuel cell

High efficiency (~ 85%)
Low price (~ 0.75 \$/kg)
CO_2 emission

Renewable energy

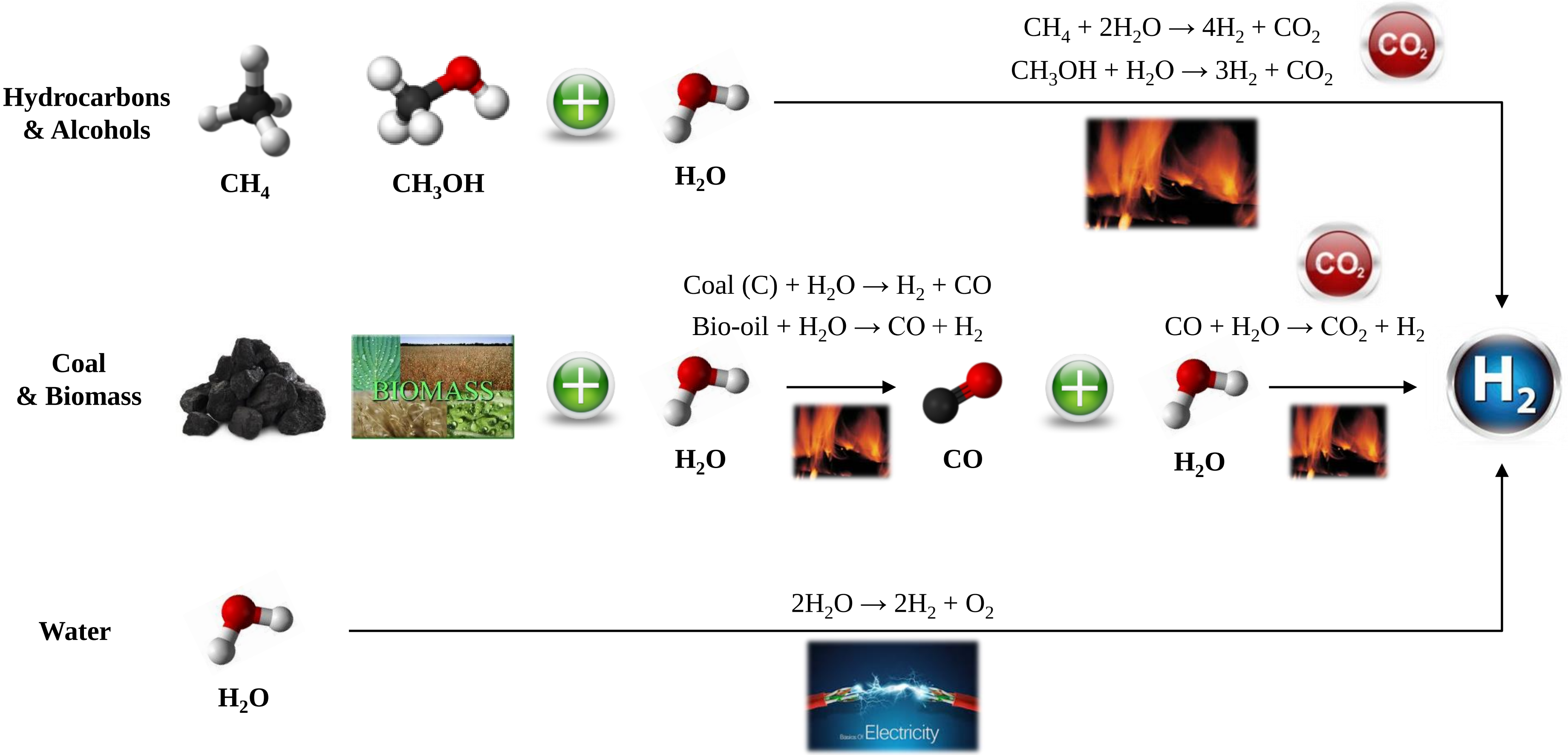
Water electrolysis

Fuel cell

CO_2 zero-emission
Low efficiency (~ 40 %)
High price (~ 2.56 \$/kg)

3. Conventional research and technology

Hydrogen production methods



Hydrocarbons & Alcohols

CH_4 **CH_3OH** + **H_2O**

$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$

Coal & Biomass

Coal (C) + $H_2O \rightarrow H_2 + CO$

Bio-oil + $H_2O \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

H_2O **CO** + **H_2O**

Water

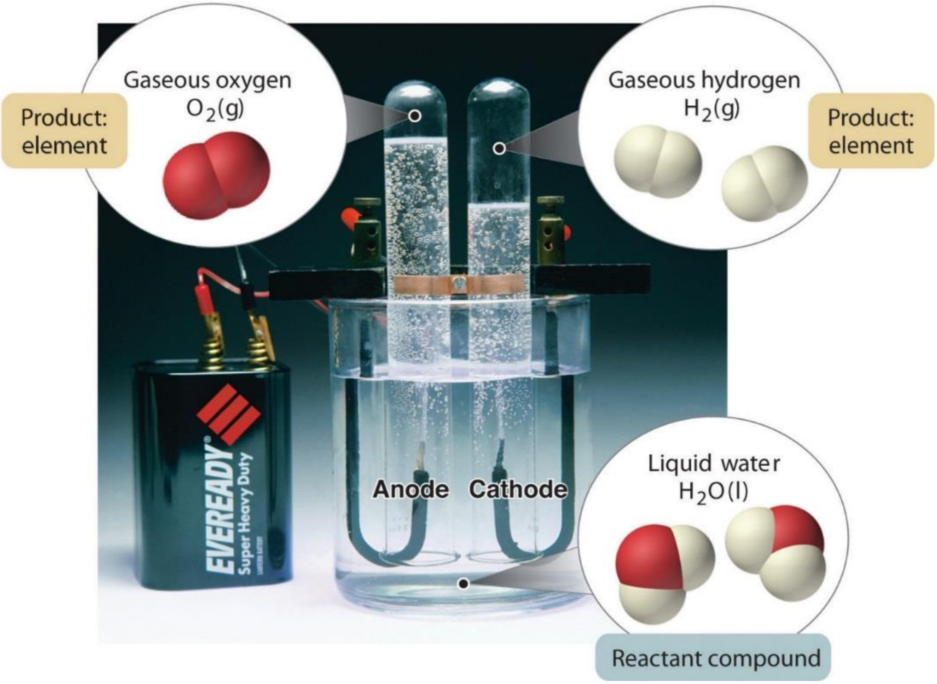
H_2O

$2H_2O \rightarrow 2H_2 + O_2$

3. Conventional research and technology

Hydrogen production methods: water electrolysis

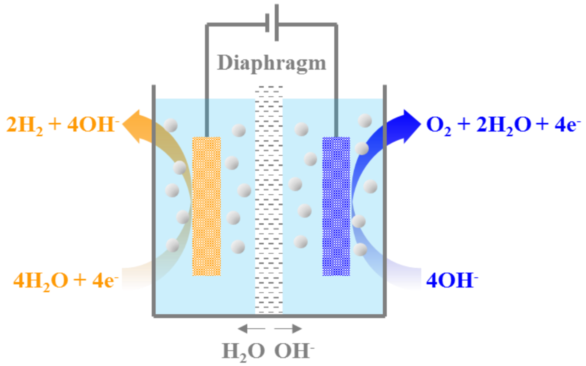
$$2H_2O \rightarrow 2H_2 + O_2$$



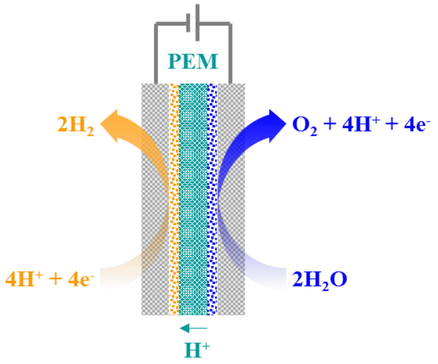
3. Conventional research and technology

Hydrogen production methods: water electrolysis

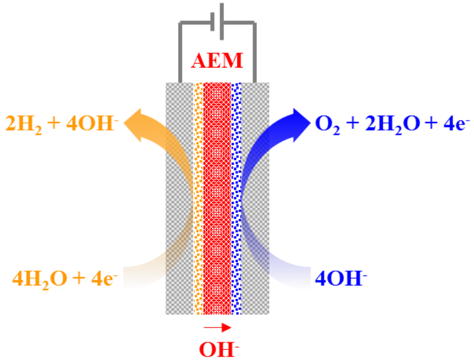
Classic Alkaline Water Electrolysis

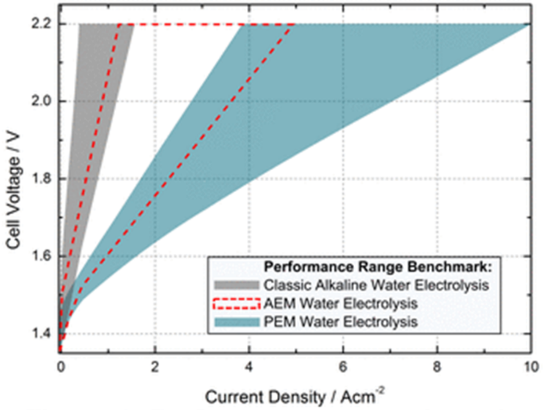


Proton Exchange Membrane Water Electrolysis



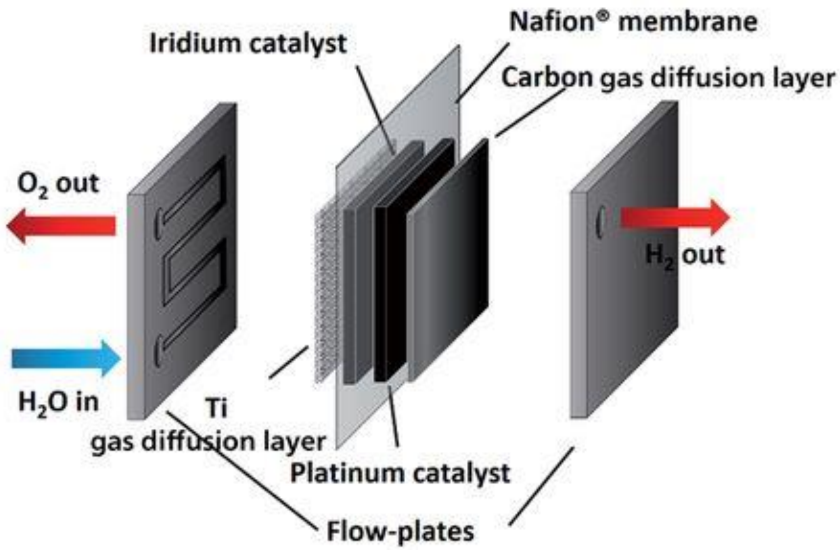
Anion Exchange Membrane Water Electrolysis





3. Conventional research and technology

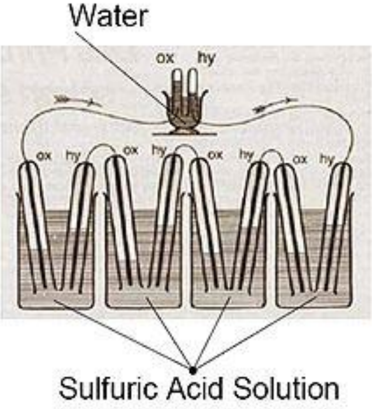
Hydrogen production methods: proton exchange membrane water electrolysis (PEMWE)

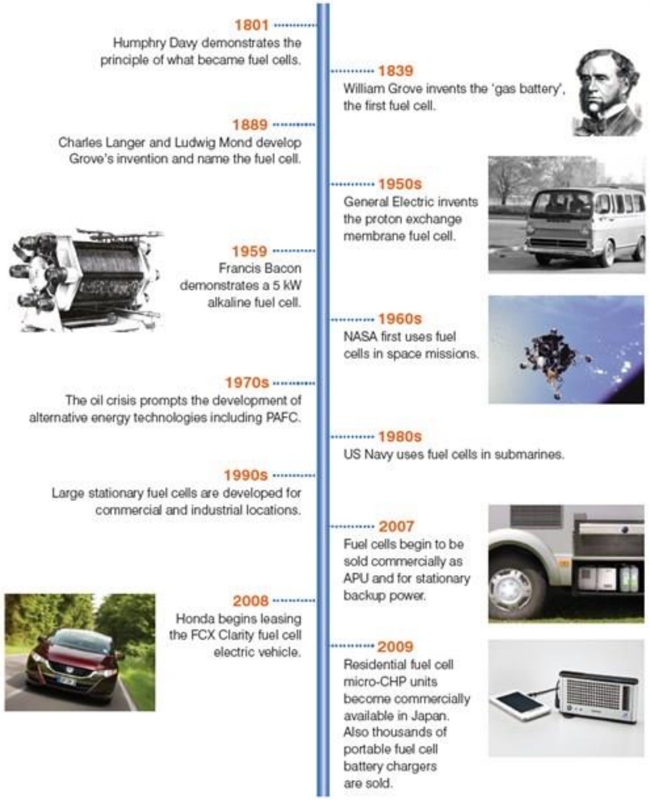


3. Conventional research and technology

Hydrogen utilization methods: fuel cell

Sir William Grove (1811 ~ 1896)





1801
Humphry Davy demonstrates the principle of what became fuel cells.

1839
William Grove invents the 'gas battery', the first fuel cell.

1889
Charles Langer and Ludwig Mond develop Grove's invention and name the fuel cell.

1950s
General Electric invents the proton exchange membrane fuel cell.

1959
Francis Bacon demonstrates a 5 kW alkaline fuel cell.

1960s
NASA first uses fuel cells in space missions.

1970s
The oil crisis prompts the development of alternative energy technologies including PAFC.

1980s
US Navy uses fuel cells in submarines.

1990s
Large stationary fuel cells are developed for commercial and industrial locations.

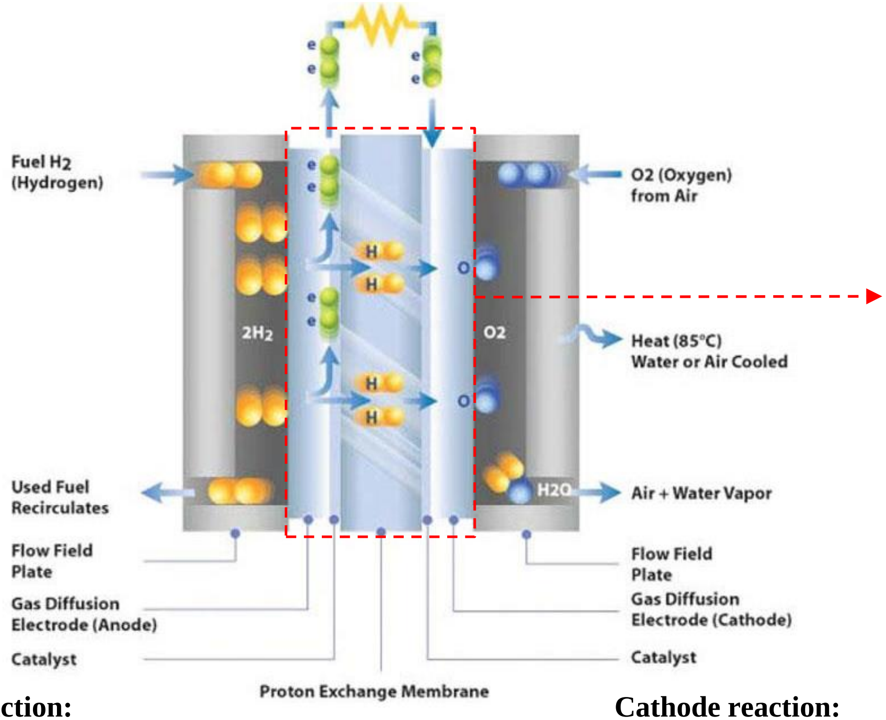
2007
Fuel cells begin to be sold commercially as APU and for stationary backup power.

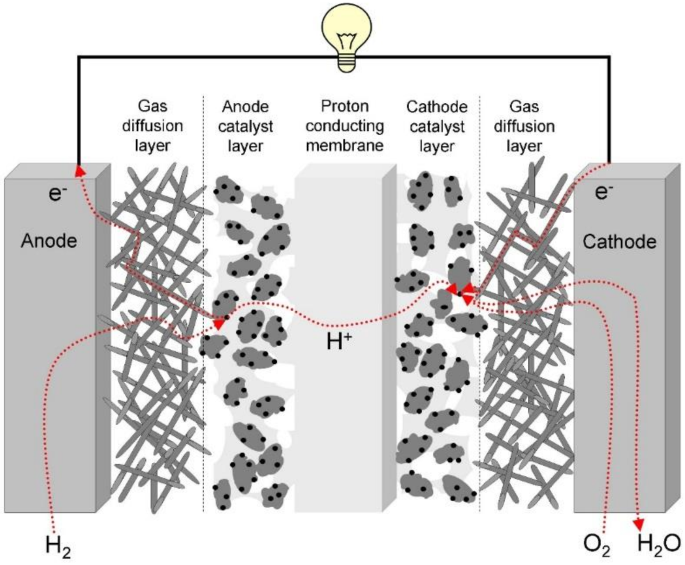
2008
Honda begins leasing the FCX Clarity fuel cell electric vehicle.

2009
Residential fuel cell micro-CHP units become commercially available in Japan. Also thousands of portable fuel cell battery chargers are sold.

3. Conventional research and technology

Hydrogen utilization methods: proton exchange membrane fuel cell (PEMFC)





Anode reaction:

$2H_2 \rightarrow 4H^+ + 4e^-$

Cathode reaction:

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

Overall reaction:

$2H_2 + O_2 \rightarrow 2H_2O$

3. Conventional research and technology

Hydrogen production methods: economical problem of water electrolysis

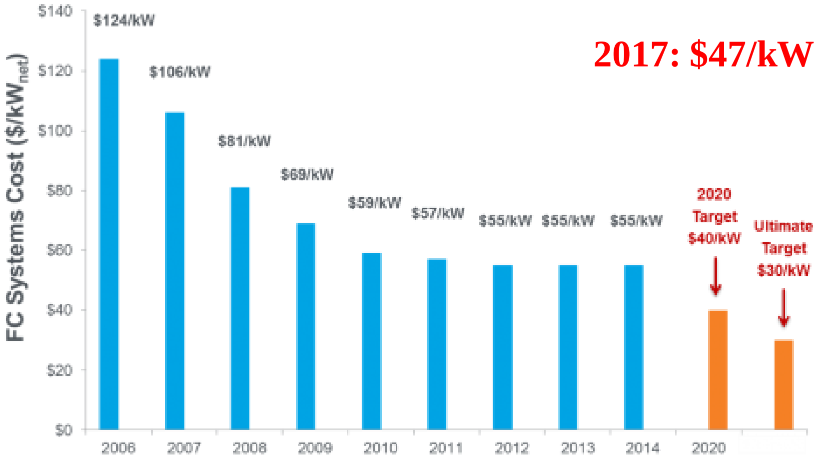
H_2 production technique	**Energy efficiency**	**Estimated price**	**Reaction**	**Major advantages**
Steam reforming of methane	85%	\$0.75/kg	$CH_4 + H_2O \rightarrow 2H_2 + CO$ $2CO \rightarrow CO_2 + C$ $CO + H_2O \rightarrow CO_2 + H_2$	High efficiency Economically favorable Methane pipelines already in place
Coal gasification	63%	\$0.92/kg	Coal (C) + $H_2O \rightarrow H_2 + CO + I$ $CO + H_2O \rightarrow CO_2 + H_2$	Economically favorable Abundance of coal resources in U.S.
Biomass pyrolysis	56%	\$1.26~2.19/kg	Biomass + Energy → Bio-oil + Char + I Bio-oil + $H_2O \rightarrow CO + H_2$ $CO + H_2O \rightarrow CO_2 + H_2$	Renewable Not dependent on fossil fuels
Water electrolysis	40~60%	\$2.56~2.97/kg	$H_2O \rightarrow 0.5O_2 + H_2$	Emissions free when paired with a renewable energy sources

3. Conventional research and technology

Hydrogen utilization methods: economical problem of fuel cell

Fuel cell vehicle: ~ 70,000 $

Gasoline vehicle: ~ 30,000 $

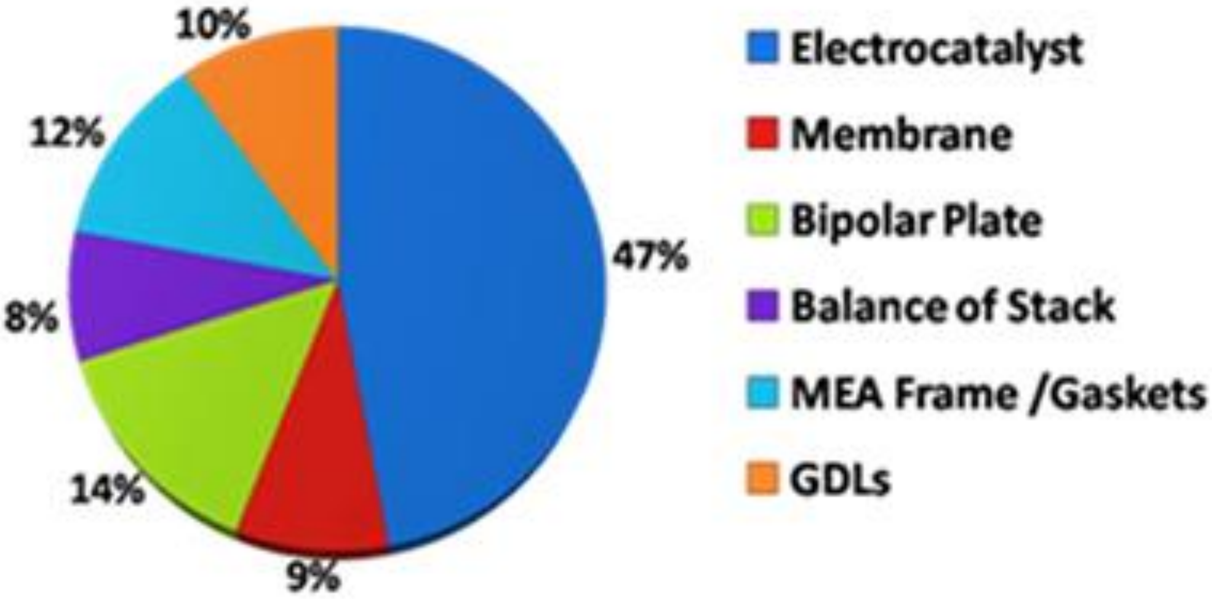


2017: $47/kW

3. Conventional research and technology

What is main cause of economical problem?

Breakdown of cost by PEMFC components



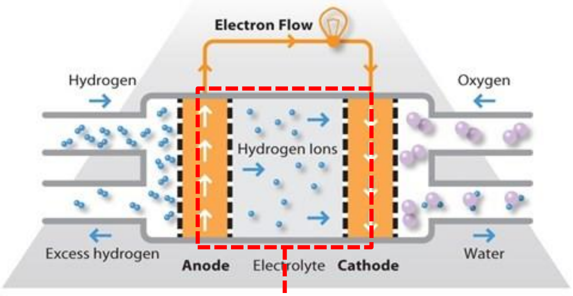
3. Conventional research and technology

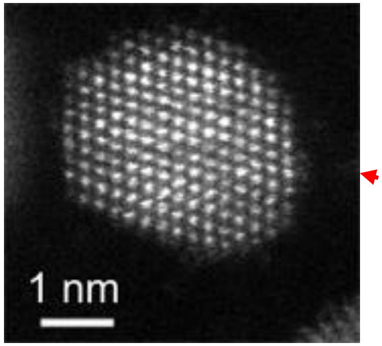
Cost problem for hydrogen production and utilization methods

Fuel cell car

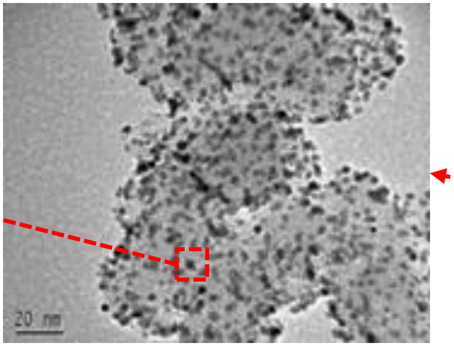
Fuel cell engine (stack)

Single fuel cell

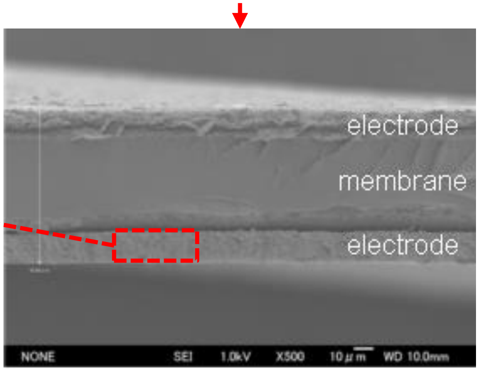




Single Pt nanoparticle



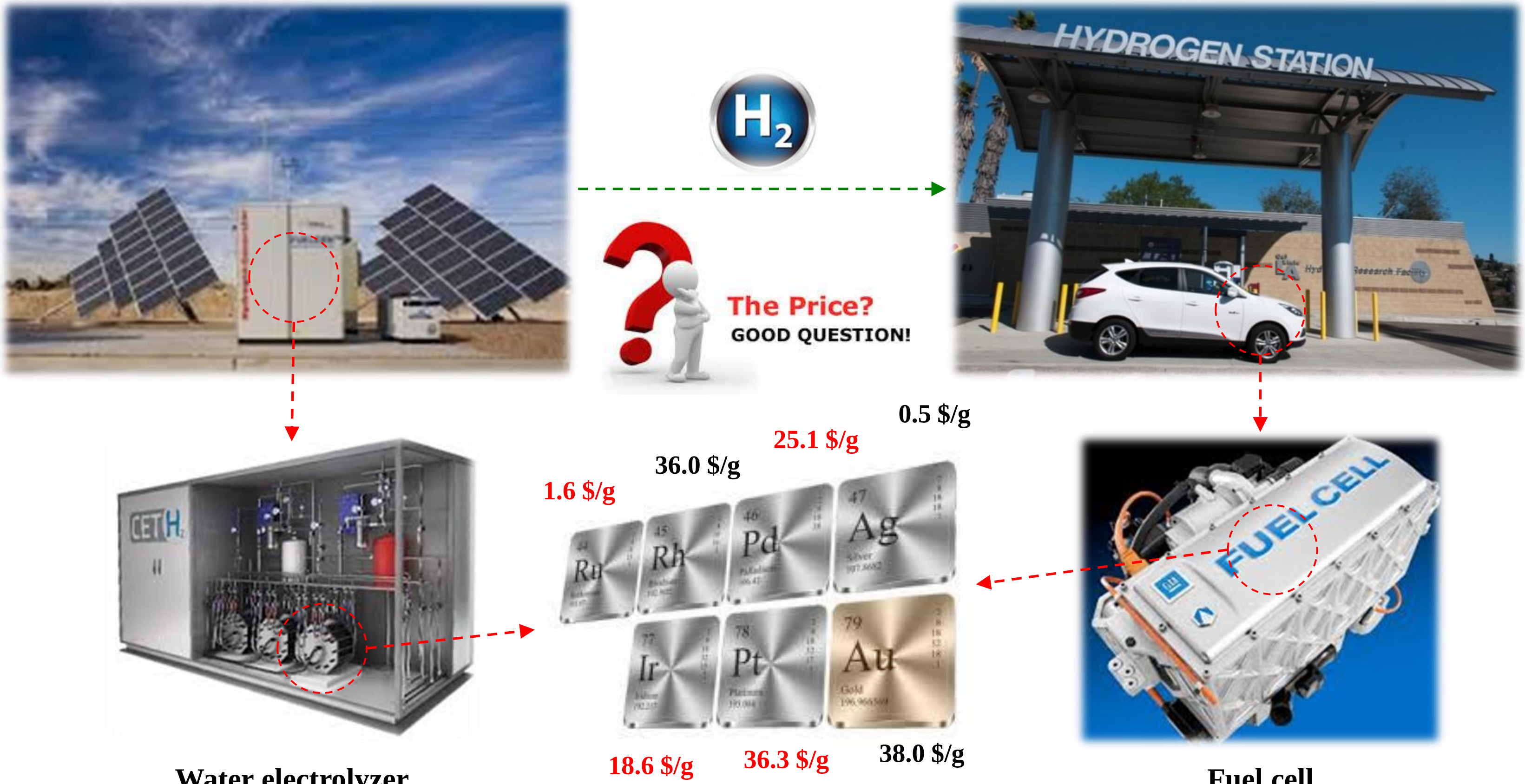
Pt/C catalysts



Membrane electrode assembly

3. Conventional research and technology

Cost problem for hydrogen production and utilization methods



Water electrolyzer

Fuel cell

3. Conventional research and technology

Catalysts for water electrolysis and fuel cell

Water electrolysis reactions

In acid

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

Cathode: $4H^+ + 4e^- \rightarrow 2H_2$

In alkaline

Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Fuel cell reactions

In acid

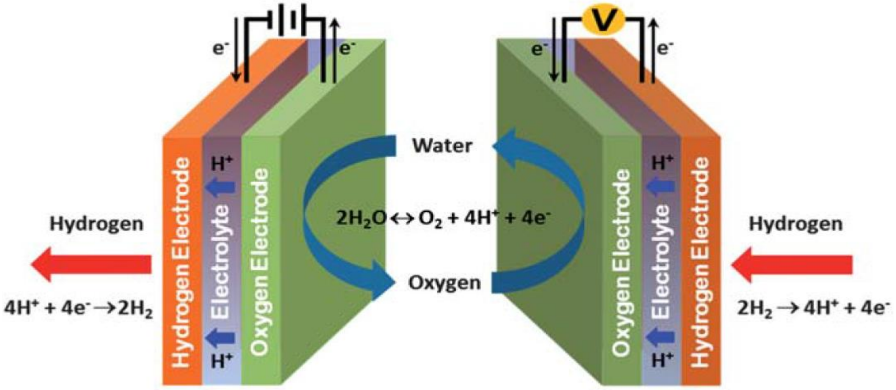
Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

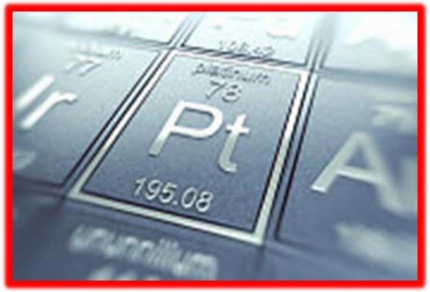
Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

In alkaline

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

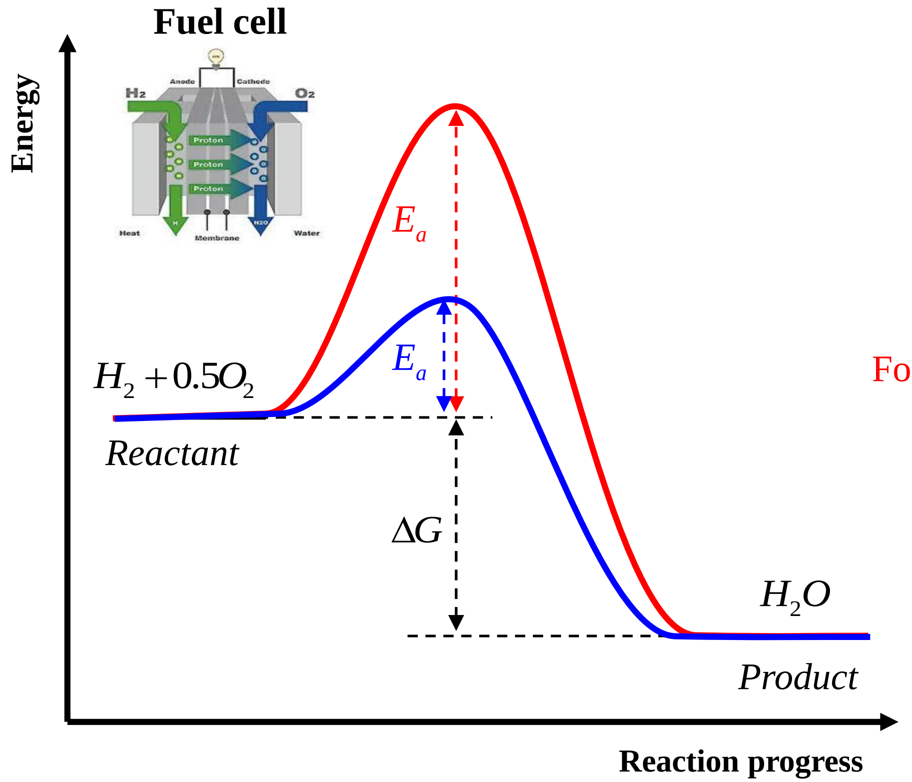
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$





3. Conventional research and technology

Catalyzed reaction



Fuel cell reactions

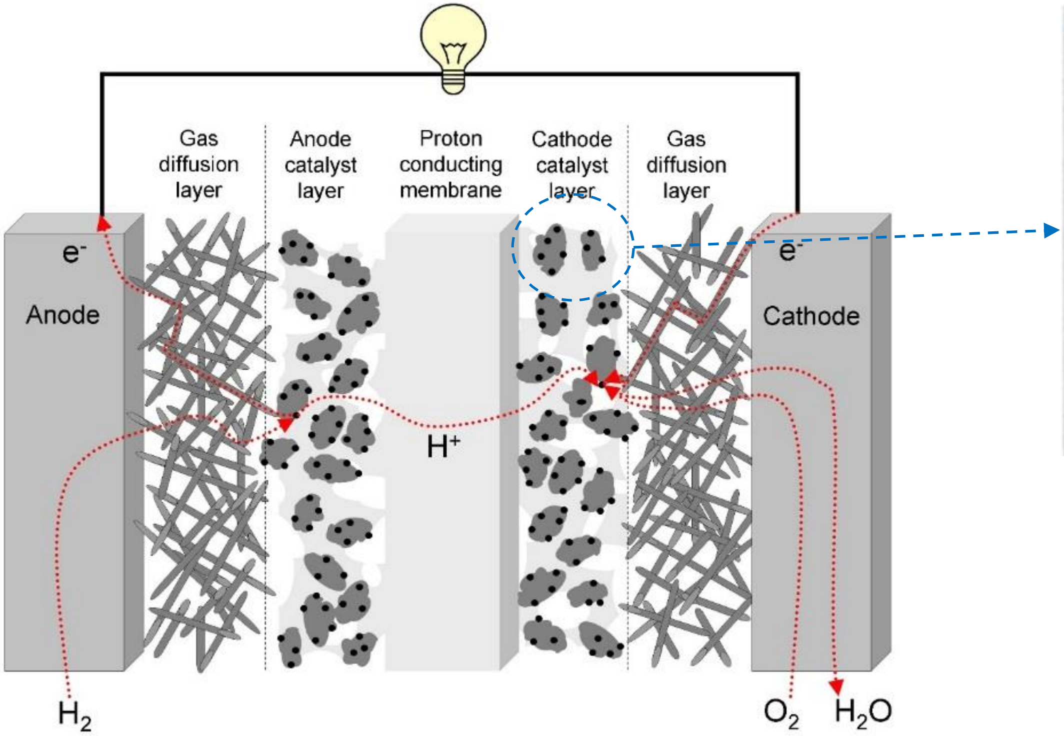
$$H_2 + 0.5O_2 \xrightarrow{r} H_2O$$

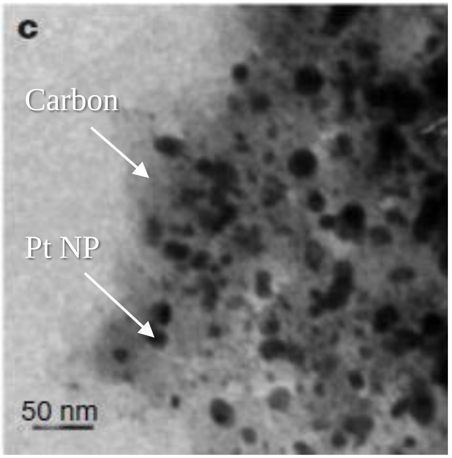
$$r = kC_{reatant}, \quad k = Ae^{-E_a/RT}$$

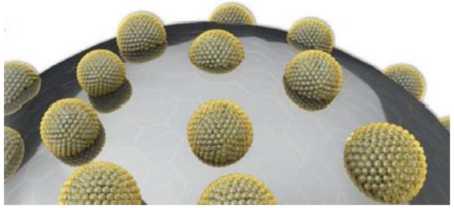
For non-catalyzed reaction $k = Ae^{-Ea/RT}$ $<$ For catalyzed reaction $k = Ae^{-Ea/RT}$

3. Conventional research and technology

Pt/C catalyst





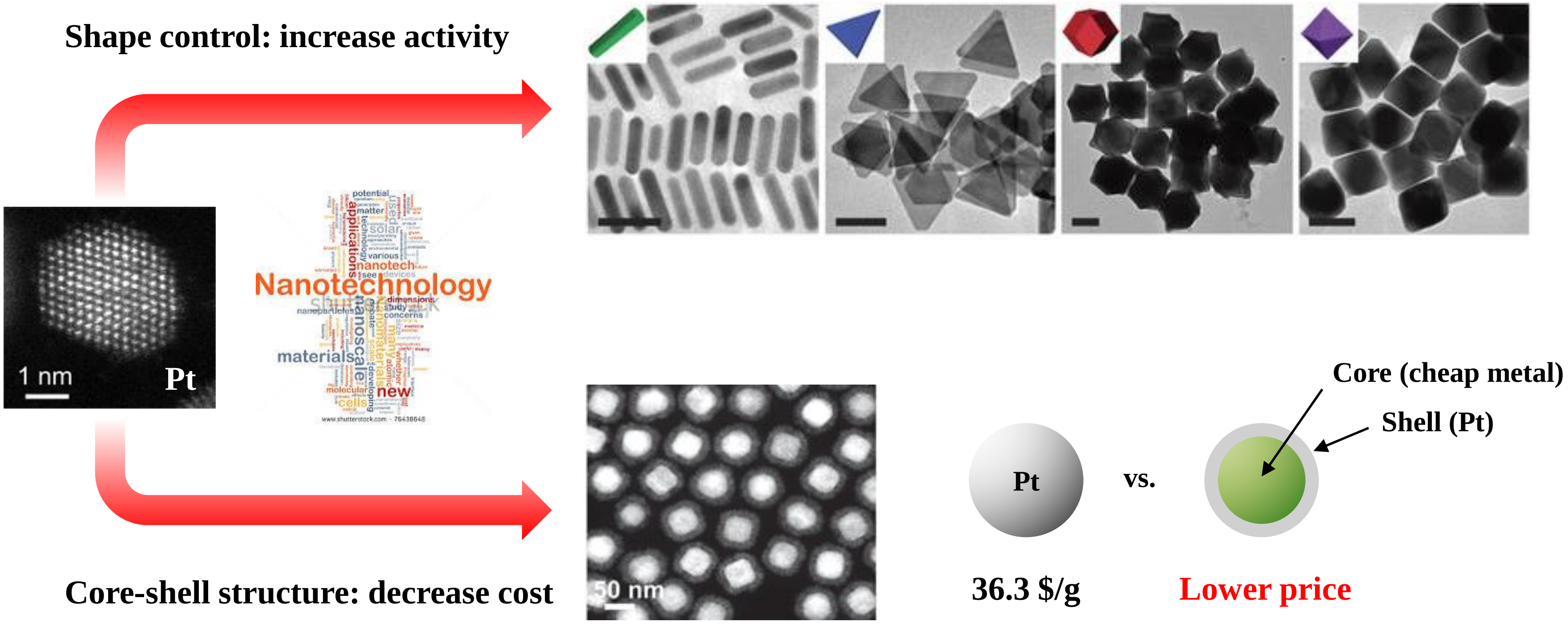


At least 70 g of Pt should be loaded to fuel cell engine to operate vehicle (~ KRW 10,000,000).

4. Problem solving plan and process

4. Problem solving plan and process

Strategies to increase activity and decrease cost of Pt catalyst



Shape control: increase activity

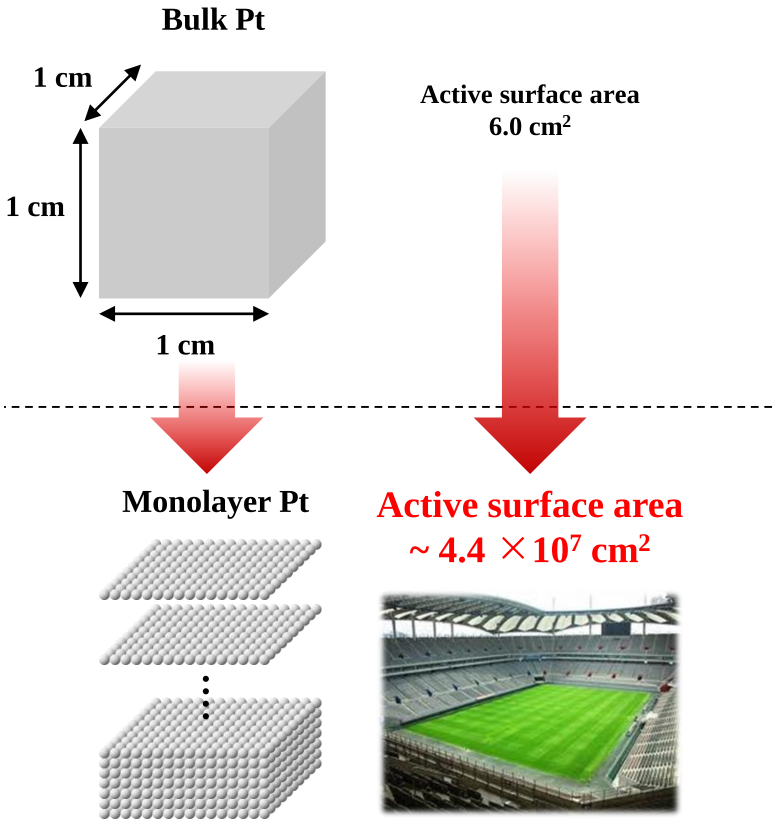
Core-shell structure: decrease cost

36.3 $/g

Lower price

4. Problem solving plan and process

Advantages of core-shell catalyst



Bulk Pt

1 cm

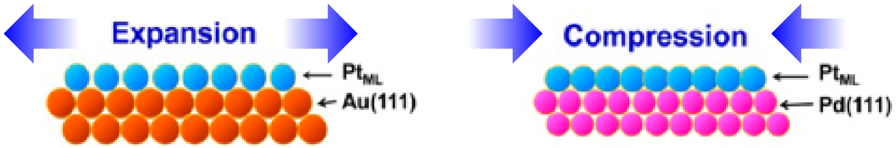
1 cm

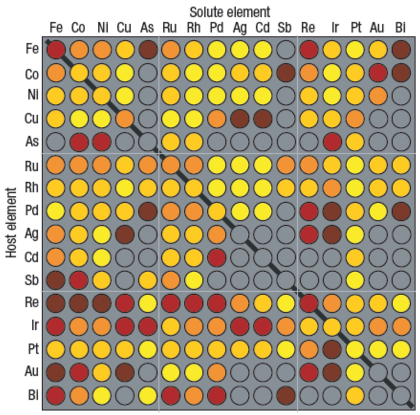
1 cm

Active surface area
6.0 cm^2

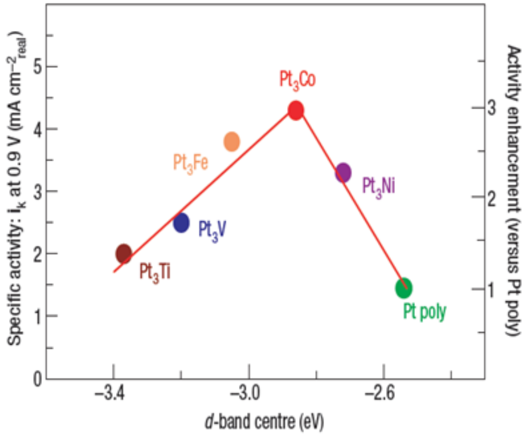
Monolayer Pt

Active surface area
~ 4.4 ×10^7 cm^2





[*Nat. Mater.*, **5** (2006) 909-913.]



[*Nat. Mater.*, **6** (2007) 241-247.]

4. Problem solving plan and process

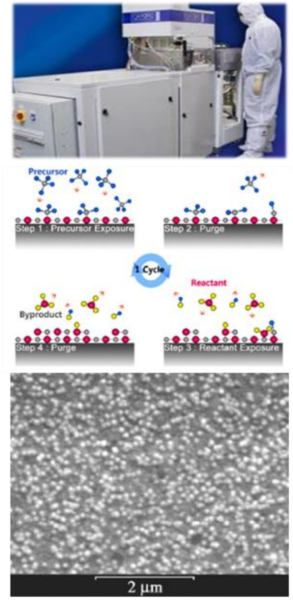
Fabrication methods for core-shell catalyst

Physical methods	Chemical methods	Lithographic techniques
Ball milling	Chemical reduction synthesis	Photolithography
Inert gas condensation	Solvothermal synthesis	Electron-beam lithography
Arc discharge	Photochemical synthesis	Focused ion beam lithography
Ion sputtering	Electrochemical synthesis	Nanoimprint lithography
Laser ablation	Sonochemical synthesis	
Spray pyrolysis	Micelles and microemulsions	
Flame pyrolysis	Chemical vapor deposition	
Thermal evaporation	Sol-gel process	
Pulsed laser deposition		
Molecular beam epitaxy		

4. Problem solving plan and process

Advantages and disadvantages of current technologies

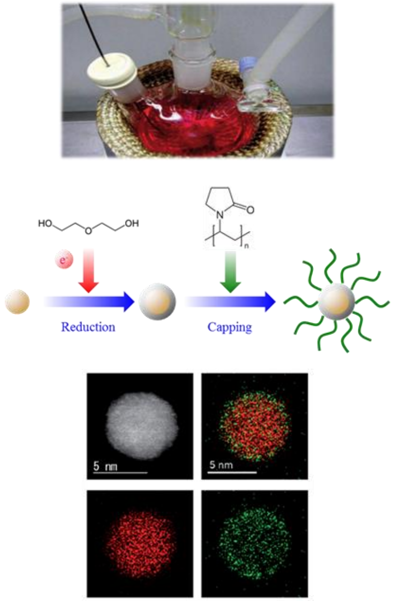
Physical method (atomic layer deposition)



[*Chem. Mater.* **15** (2003) 1924-1928.]

High temperature & vacuum
Expansive instrument
Slow deposition rate

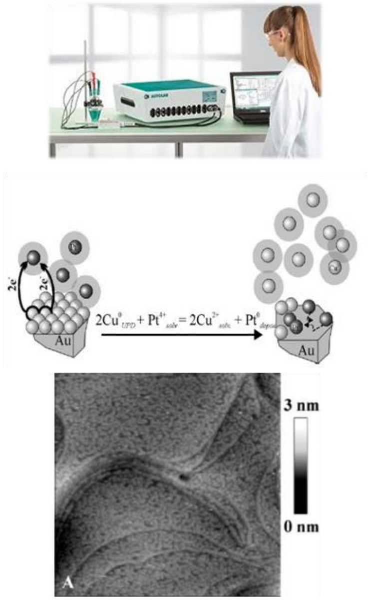
Chemical method (chemical reduction)



[*Angew. Chem. Int. Ed.* **46** (2007) 4630-4660.]

Relatively high temperature
Removal of capping agent

Chemical method (electrochemical synthesis)



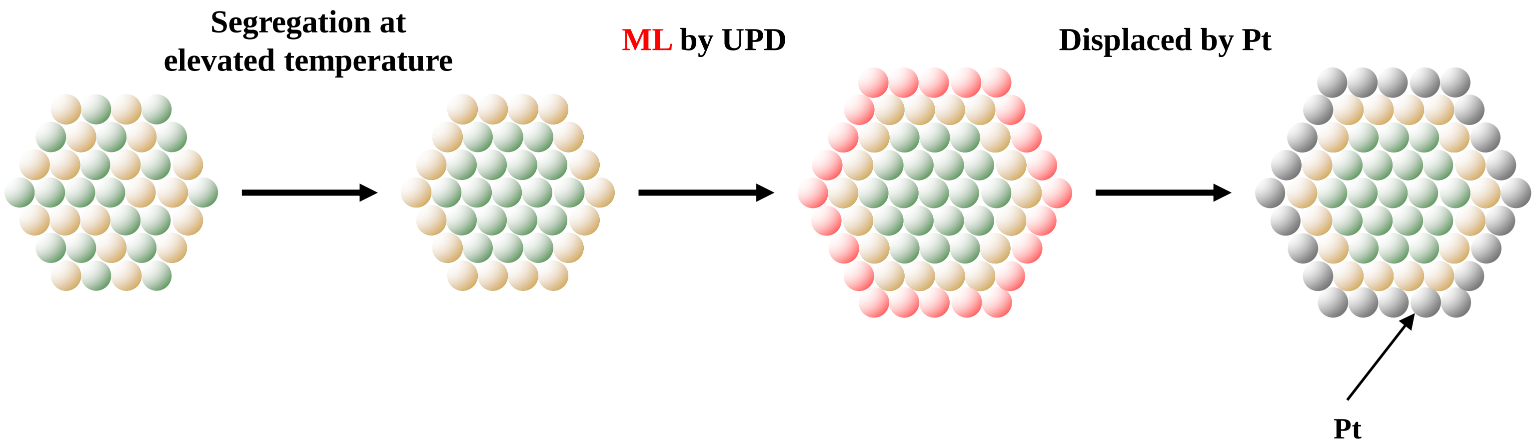
[*Sur. Sci.* **474** (2001) L173-L179.]

Room temperature
Short time & easy control

5. Concept and detail design

5.1. Goal setting method of design

Fabrication process of Pt core-shell catalyst

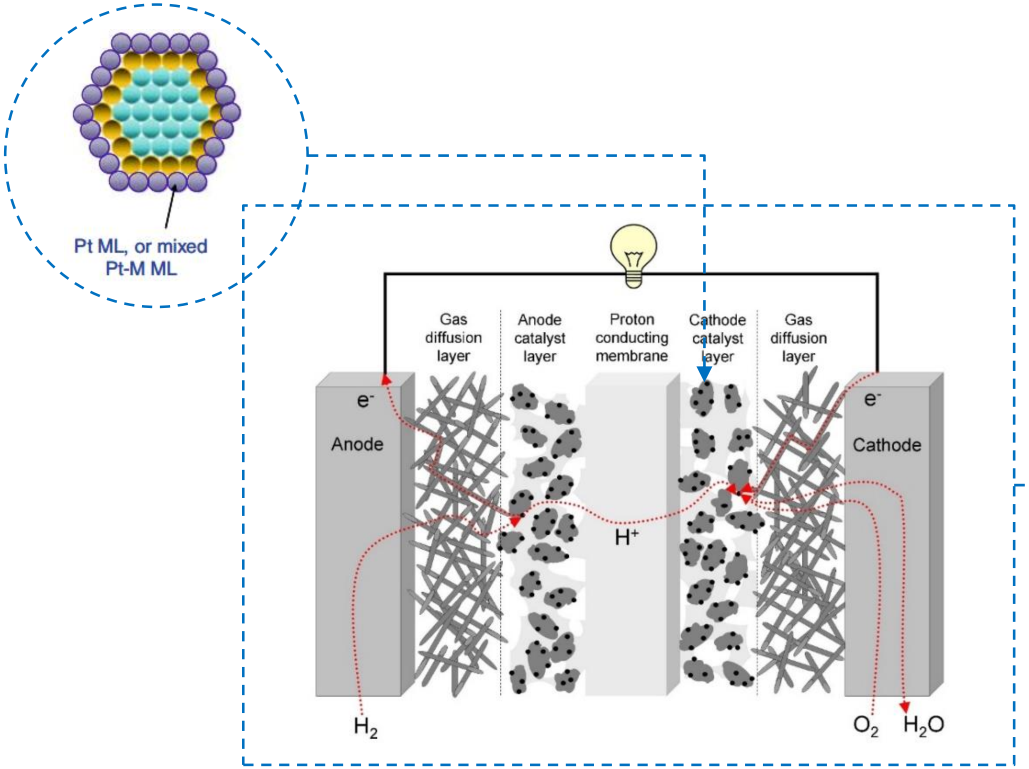


ML: monolayer

UPD: under potential deposition

5.1. Goal setting method of design

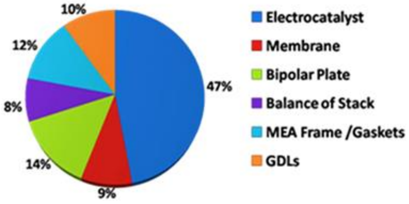
Application of Pt core-shell catalyst to fuel cell engine



5.1. Goal setting method of design

Application of Pt core-shell catalyst to fuel cell engine

Fuel cell vehicle ~ 70,000 $



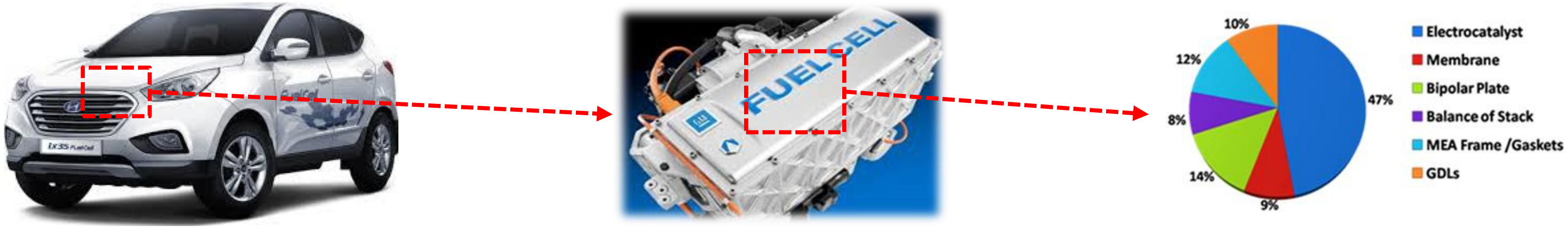
5.2. Limited factors

Cost of Pt core-shell catalyst

Fuel cell vehicle:
~ 70,000 $

Fuel cell engine:
~ 18,000 $

Fuel cell catalyst:
~ 8,500 $ (Pt: ~ 70 g)



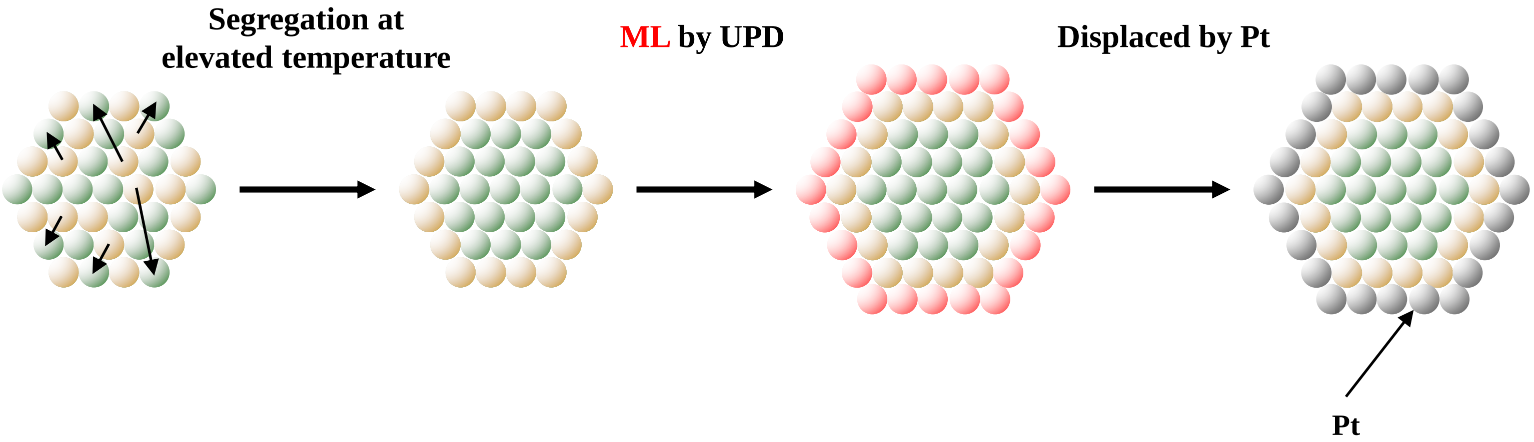
New fuel cell vehicle:
< 64,000 $

New fuel cell engine:
< 12,000 $

New fuel cell catalyst:
< 2,500 $

5.2. Limited factors

Material selection: feasibility for fabrication process



Segregation at elevated temperature

ML by UPD

Displaced by Pt

Pt

● Metal A: cheap and earth-abundant metals (e.g. Ni, Co, Cu, Sn and etc.)

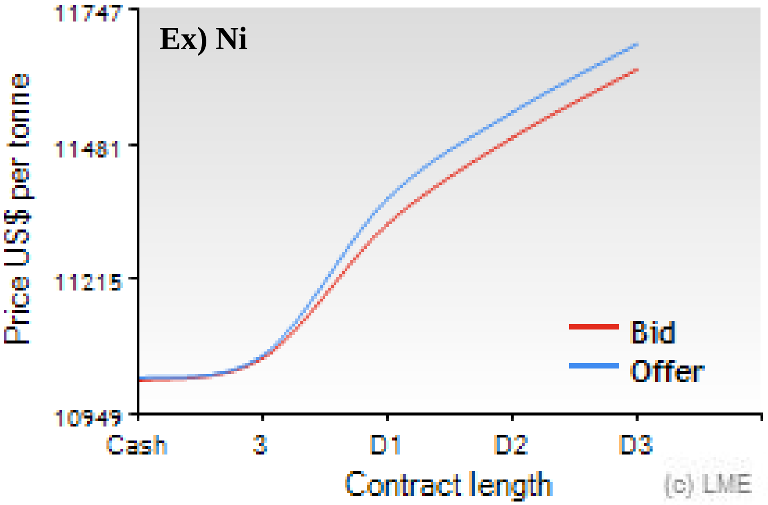
● Metal B: more stable than metal A

● Metal C: less stable than metal B and Pt

5.2. Limited factors

Material selection: cost

- Metal A: cheap and earth-abundant metals (e.g. Ni, Co, Cu, Sn and etc.)



London Metal Exchange (http://www.lme.com)

Metal prices

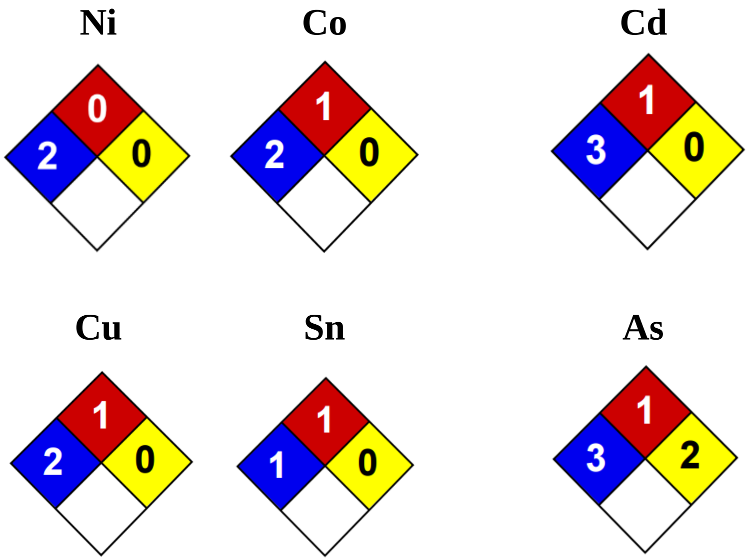
- Ni: 0.011 $/g
- Co: 0.048 $/g
- Cu: 0.006 $/g
- Sn: 0.020 $/g
- Pt: 36.3 $/g

5.2. Limited factors

Material selection: safety

- Metal A: cheap and earth-abundant metals (e.g. Ni, Co, Cu, Sn and etc.)

Material
Safety
Data
Sheets



5.2. Limited factors

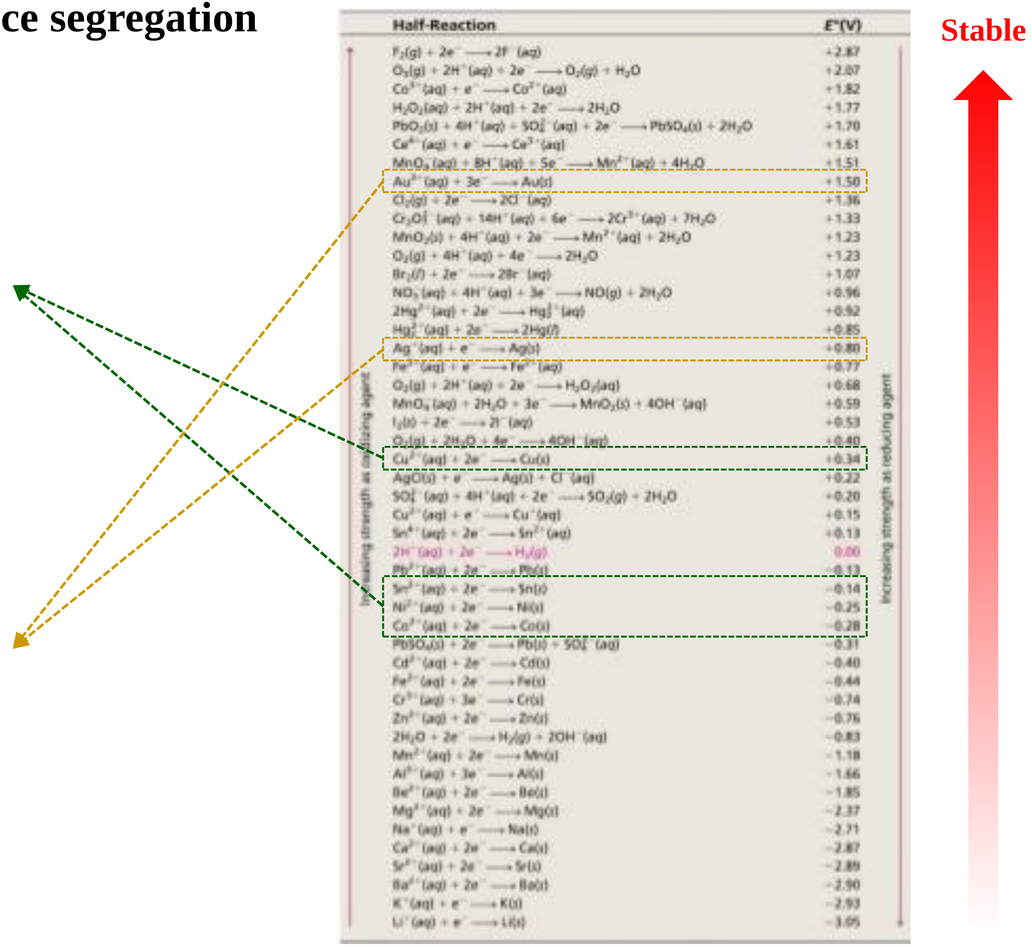
Material selection: feasibility for surface segregation

- Metal B: more stable than metal A

Fe^{3+} (aq) + $3e^-$ → Fe (s)	+0.77 V
Cu^{2+} (aq) + $2e^-$ → Cu (s)	+0.34 V
Sn^{2+} (aq) + $2e^-$ → Sn (s)	-0.14 V
Ni^{2+} (aq) + $2e^-$ → Ni (s)	-0.25 V
Co^{2+} (aq) + $2e^-$ → Co (s)	-0.28 V

Au^{3+} (aq) + e^- → Au (s)	+1.50 V
Pt^{2+} (aq) + $2e^-$ → Pt (s)	+1.19 V
Ir^{3+} (aq) + $3e^-$ → Ir (s)	+1.16 V
Pd^{2+} (aq) + $2e^-$ → Pd (s)	+0.92 V
Ag^+ (aq) + e^- → Ag (s)	+0.80 V

Standard reduction potential table



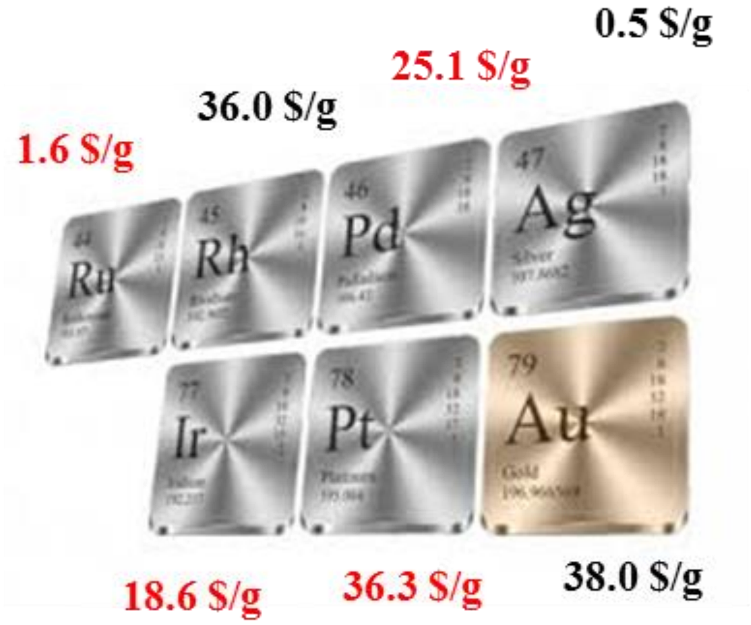
Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

5.2. Limited factors

Material selection: cost

- Metal B: more stable than metal A

Au^{3+} (aq) + e^- → Au (s)	+1.50 V
Pt^{2+} (aq) + $2e^-$ → Pt (s)	+1.19 V
Ir^{3+} (aq) + $3e^-$ → Ir (s)	+1.16 V
Pd^{2+} (aq) + $2e^-$ → Pd (s)	+0.92 V
Ag^+ (aq) + e^- → Ag (s)	+0.80 V



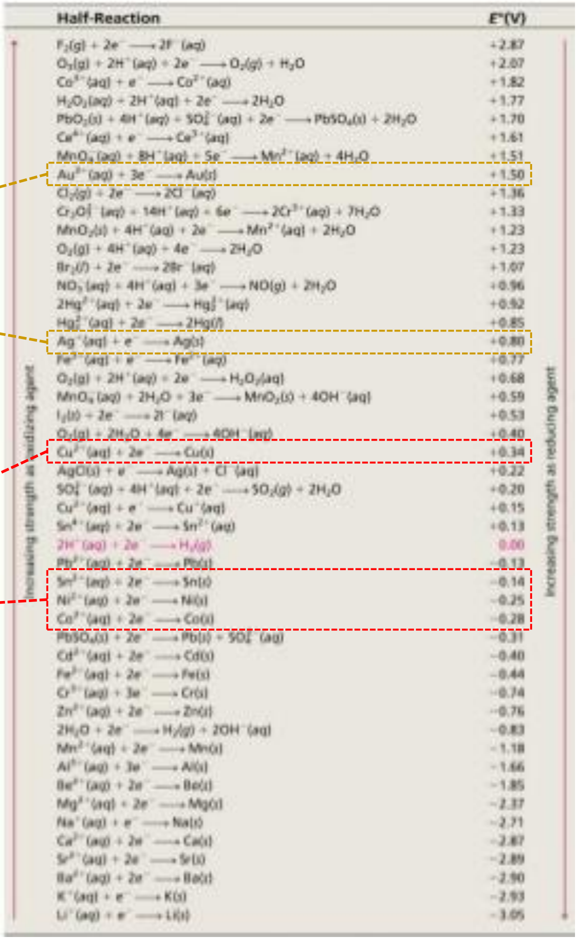
5.2. Limited factors

Material selection: feasibility for Pt displacement

- **Metal C: less stable than metal B and Pt**

Au^{3+} (aq) + e^- → Au (s)	+1.50 V
Pt^{2+} (aq) + $2e^-$ → Pt (s)	+1.19 V
Ir^{3+} (aq) + $3e^-$ → Ir (s)	+1.16 V
Pd^{2+} (aq) + $2e^-$ → Pd (s)	+0.92 V
Ag^{+} (aq) + e^- → Ag (s)	+0.80 V
Fe^{3+} (aq) + $3e^-$ → Fe (s)	+0.77 V
Cu^{2+} (aq) + $2e^-$ → Cu (s)	+0.34 V
Sn^{2+} (aq) + $2e^-$ → Sn (s)	-0.14 V
Ni^{2+} (aq) + $2e^-$ → Ni (s)	-0.25 V
Co^{2+} (aq) + $2e^-$ → Co (s)	-0.28 V

Standard reduction potential table



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$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
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$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
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$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

Stable

5.3. Synthesis: nanoparticle

Thermodynamic approaches

$$dG = -SdT + VdP + \sum_{i=1}^{c}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i$$

Gibbs free energy for
mixed solution or mixed gas

G: Gibbs free energy
S: Entropy
T: Temperature

V: Volume
P: Pressure
n_i: concentration for i species

Raoult's law

$$P_i = P_i^0 X_i$$

Henry's law

$$\lim_{x_i \to \infty}\left(\frac{dP_i}{dX_i}\right) = P_i^*$$

Activity

$$a_i = X_i$$

Chemical potential

$$d\mu_i = -\overline{S_i}dT + \overline{V_i}dP$$

Volumetric Gibbs
free energy change

$$\Delta G_v = -\frac{kT}{V_m}\ln\left(\frac{C}{C_0}\right) = -\frac{kT}{V_m}\ln\sigma < 0$$

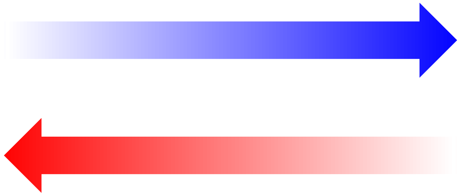
G_v: Volumetric Gibbs free energy
k: Boltzmann constant
V_m: Molar volume of bulk crystal

C: Solute concentration
C_0: Equillibrium concentration
σ: Supersaturation $\sigma = \dfrac{C}{C_0}$

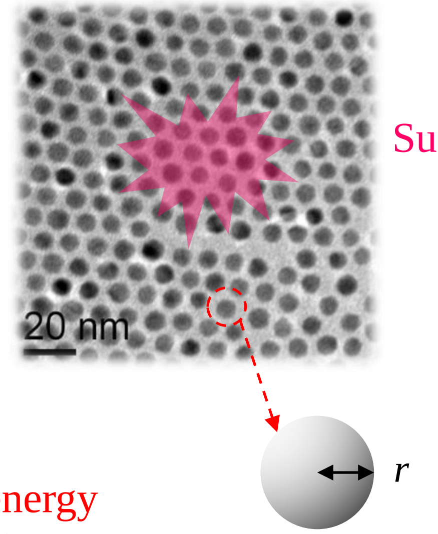
5.3. Synthesis: nanoparticle

Thermodynamic approaches

Supersaturated solution



Nanoparticles



Surface energy increase

Assumption
: produced nanoparticle is sphere.

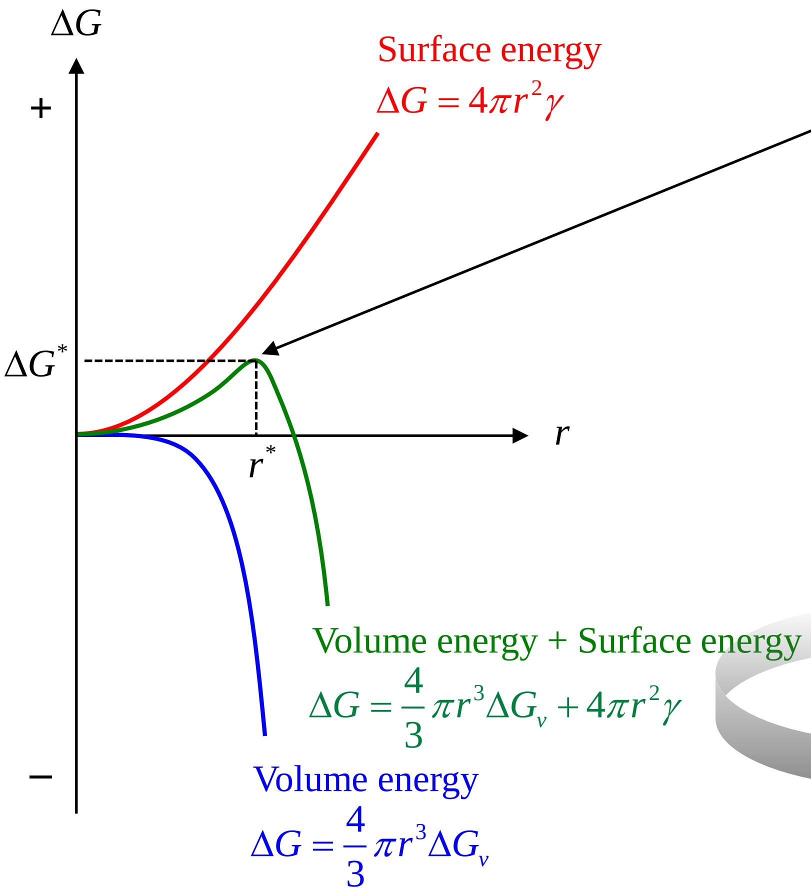
Volume energy (minus)

Surface energy (plus)

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

5.3. Synthesis: nanoparticle

Thermodynamic approaches



Surface energy

$$\Delta G = 4\pi r^2 \gamma$$

Volume energy + Surface energy

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Volume energy

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v$$

Always,
$r > 0$

r^*: critical radius of nucleation
When $r = r^*$, $d(\Delta G)/dr = 0$

$$\frac{d(\Delta G)}{dr} = 4\pi r^2 \Delta G_v + 8\pi r \gamma$$

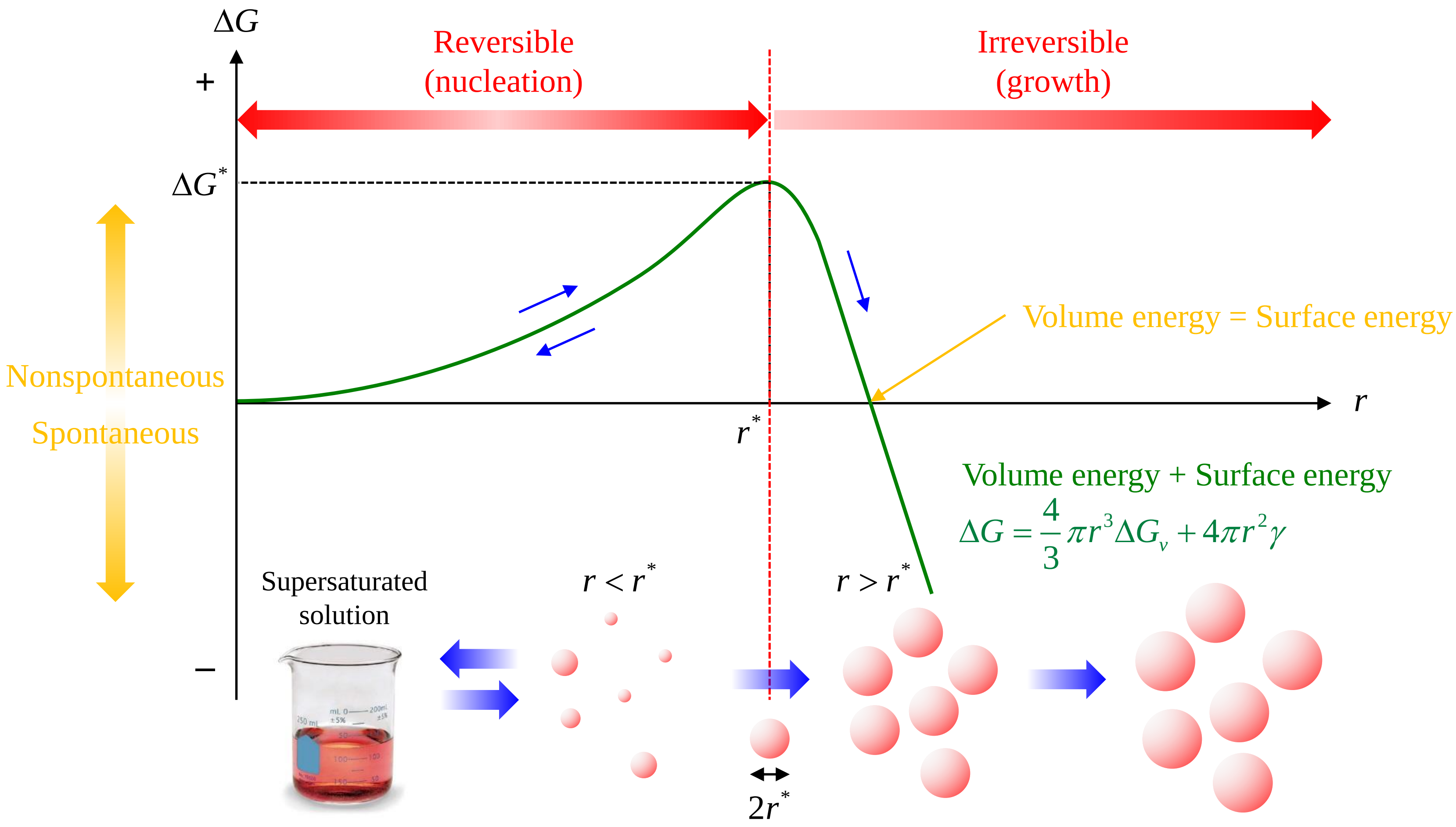
$$4\pi \left(r^*\right)^2 \Delta G_v + 8\pi r^* \gamma = 0$$

Critical radius of nucleation r^* is…

$$r^* = -2\frac{\gamma}{\Delta G_v} = \left(\frac{2V_m}{kT}\right)\frac{\gamma}{\ln \sigma}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\left(\Delta G_v\right)^2} = \left(\frac{16\pi V_m^2}{3k^2T^2}\right)\frac{\gamma^3}{\left(\ln \sigma\right)^2}$$

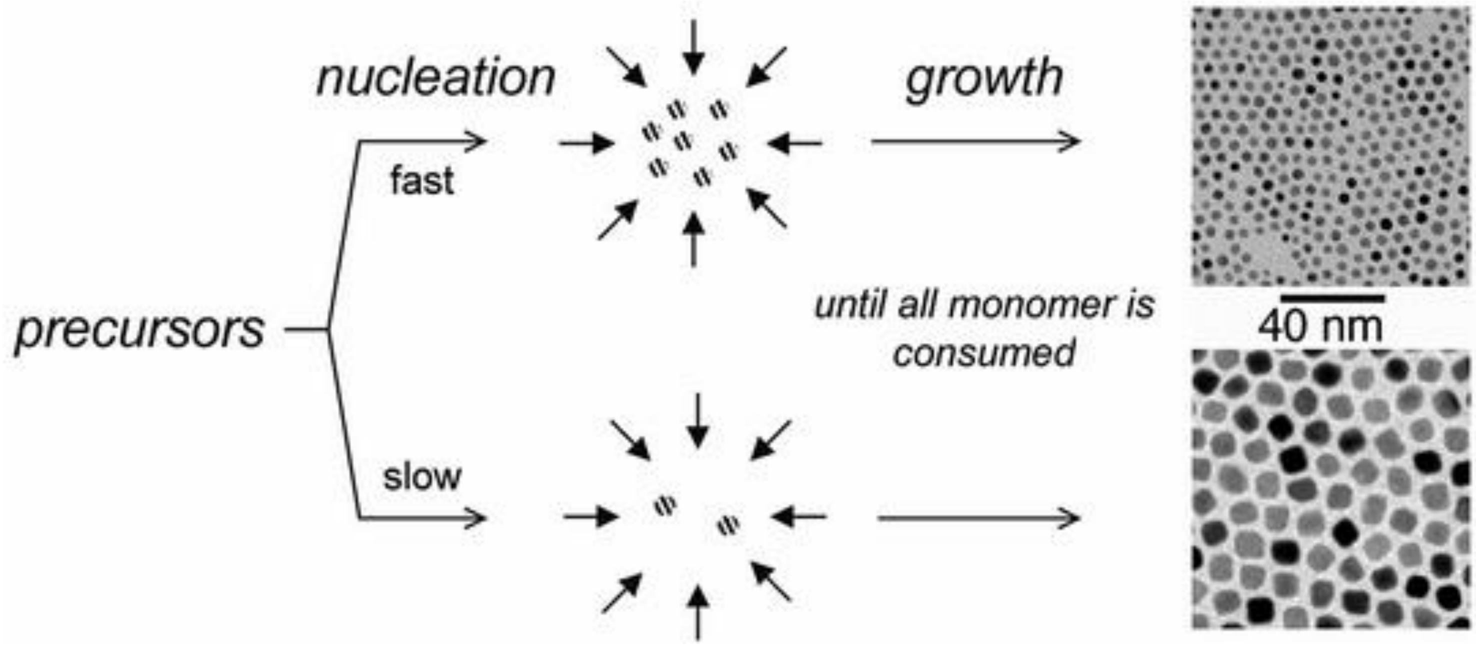
5.3. Synthesis: nanoparticle



$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

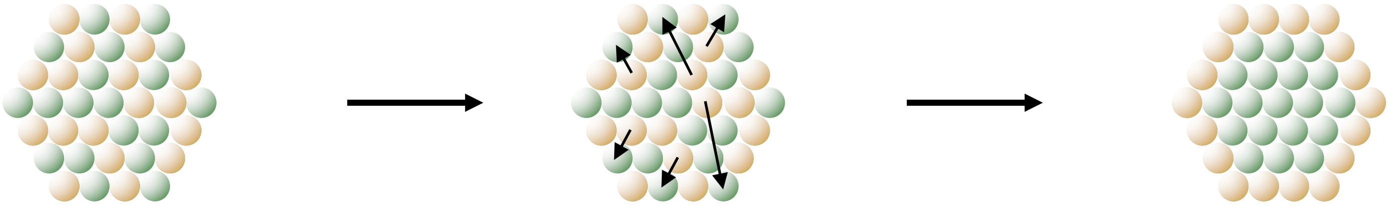
5.3. Synthesis: nanoparticle

Thermodynamic approaches



5.3. Synthesis: annealing

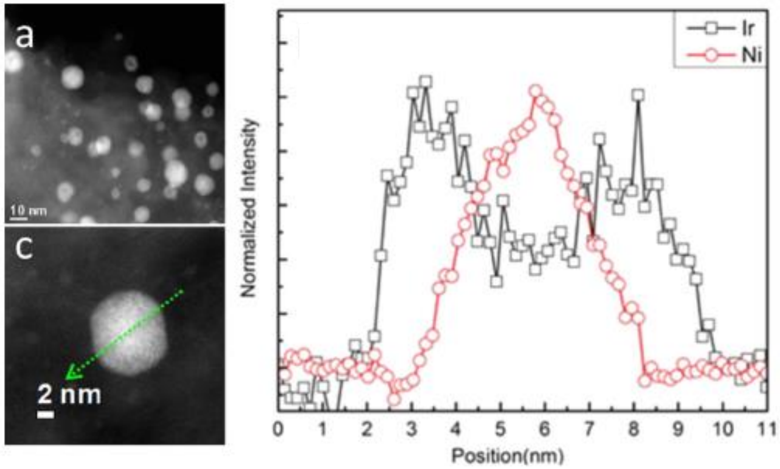
Thermodynamic approaches: surface energy difference



5.4. Analysis

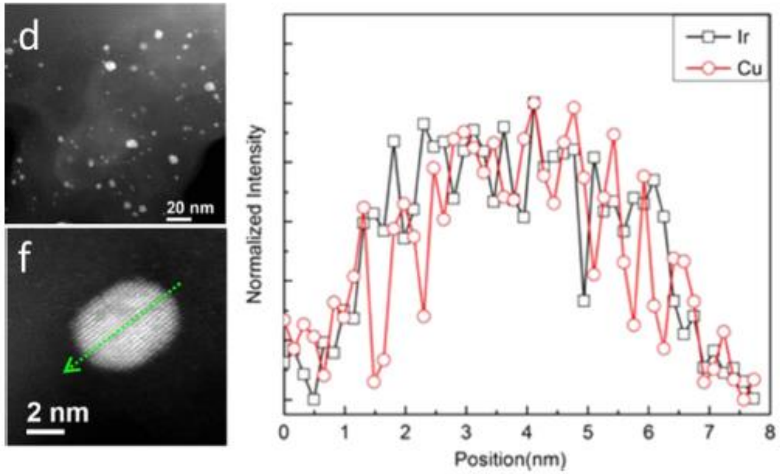
Elemental analysis

- Metal A: cheap and earth-abundant metals
- Metal B: more stable than metal A
- Metal C: less stable than metal B and Pt



$\mathrm{Ni^{2+}\ (aq) + 2e^{-} \rightarrow Ni\ (s)}$ -0.25 V

$\mathrm{Ir^{3+}\ (aq) + 3e^{-} \rightarrow Ir\ (s)}$ +1.16 V

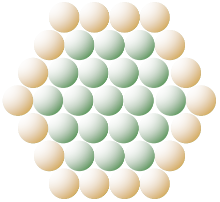


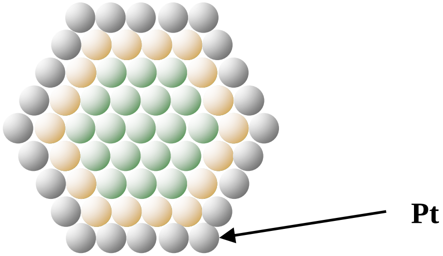
$\mathrm{Cu^{2+}\ (aq) + 2e^{-} \rightarrow Cu\ (s)}$ +0.34 V

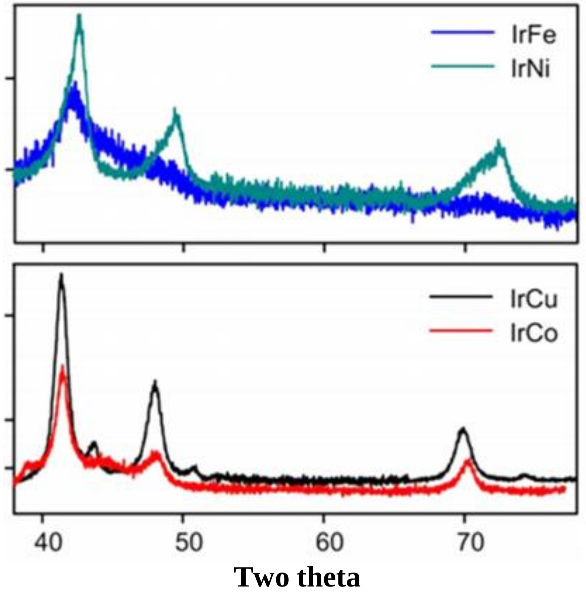
$\mathrm{Ir^{3+}\ (aq) + 3e^{-} \rightarrow Ir\ (s)}$ +1.16 V

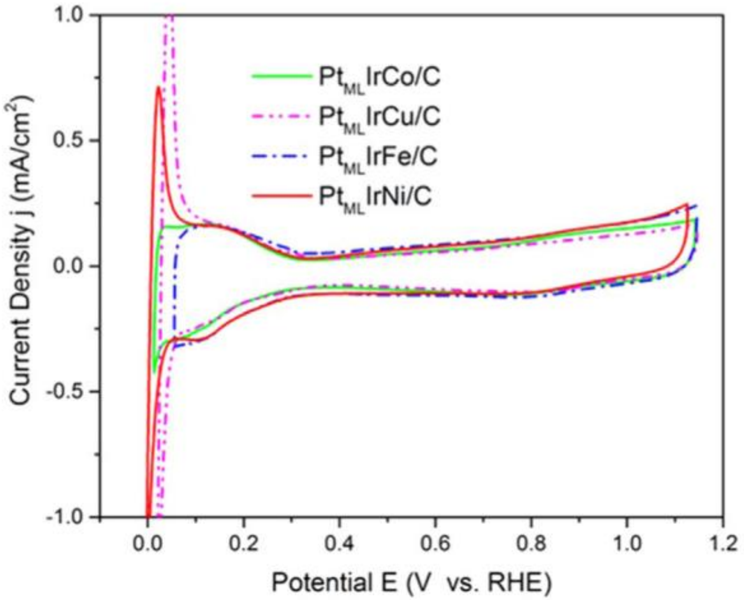
5.4. Analysis

Crystal structure and electrochemical measurement



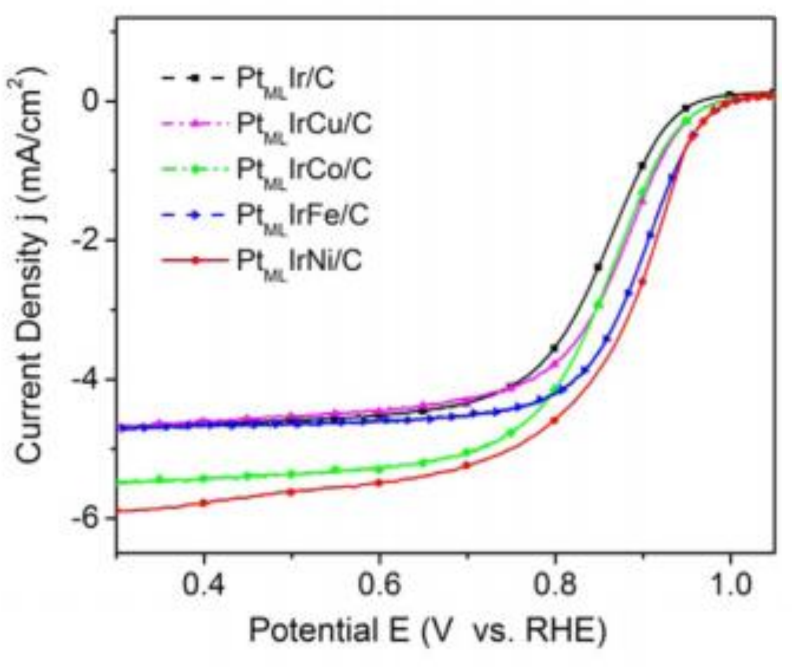


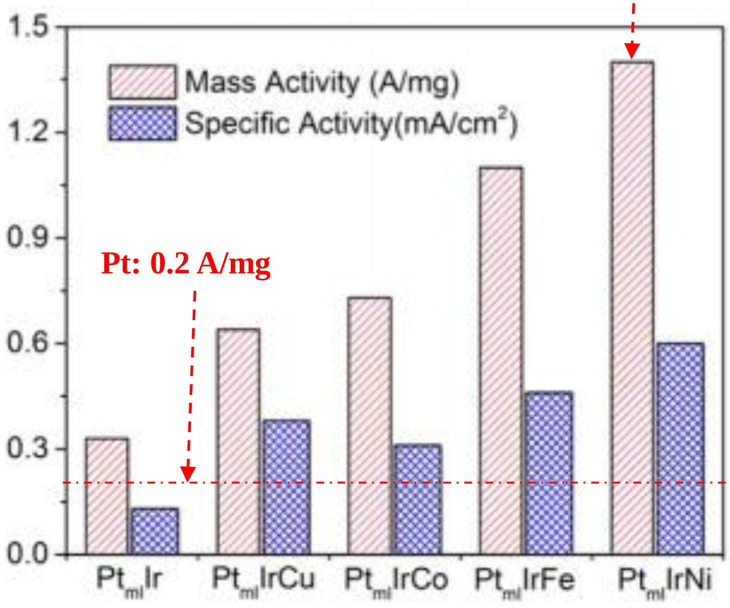




5.5. Evaluation

Pt mass based activity





$Pt_{ml}IrNi$: 1.4 A/mg

Pt: 0.2 A/mg

6. Expected effect

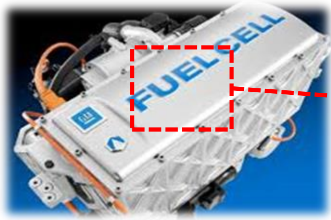
6. Expected effect

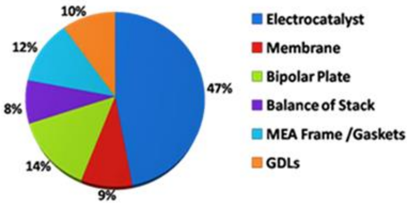
Price reduction of fuel cell vehicle

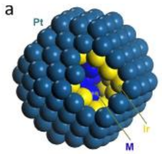
Fuel cell vehicle:
~ 70,000 $

Fuel cell engine:
~ 18,000 $

Fuel cell catalyst:
~ 8,500 $ (Pt: ~ 70 g)







New fuel cell vehicle:
~ 62,700 $

New fuel cell engine:
~ 10,700 $

New fuel cell catalyst:
~ 1,200 $ (Pt: ~ 10 g)

6. Expected effect

Relieving environmental problem

Gasoline vehicle

CO_2, NO_x, SO_x

Fuel cell vehicle

H_2O

6. Expected effect

Fuel conservation

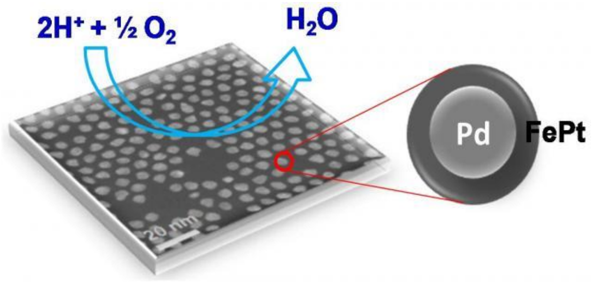
Fuel cell vehicle

If just 20% of the cars in America used fuel cells (50,000,000),

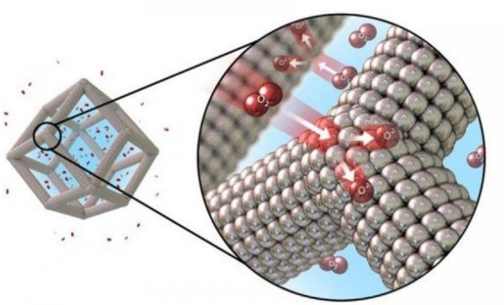
We could cut oil imports by 1.5 million barrels per day (= $44 billion per year).

7. Improvement direction

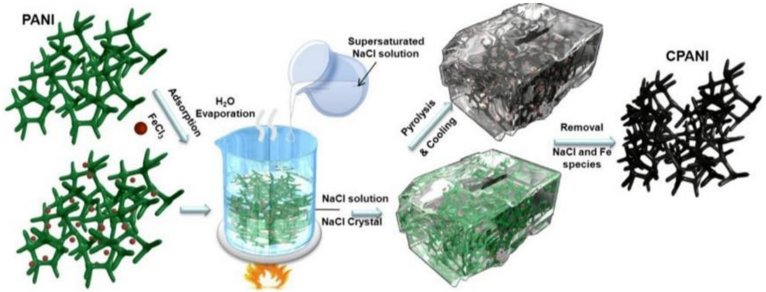
New core-shell catalyst



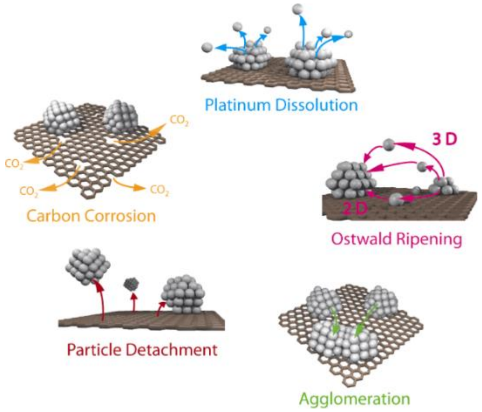
Shape-controlled catalyst



Non-metal catalyst



Mechanism analysis



How to prepare the reports and presentation?

Your reports and presentation should include…

- **Proposal report (team)**

1. **Necessity of project**
2. **Motivation and purpose of project**
3. **Conventional research and technology**
4. **Problem solving plan and process**
5. **Concept and detail design**

Changeable

   - **5.1. Goal setting method of design**
   - **5.2. Limited factors**
   - **5.3. Synthesis**
   - **5.4. Analysis**
   - **5.5. Evaluation**

6. **Expected effect**
7. **Improvement direction**

- **Final report (team)**
- **Individual presentation**
- **Team presentation**

All reports and presentation materials should be prepared by English.