# Fuel Cell Electrode Materials with Durability and Flexibility

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**Faculty of Engineering & Hydrogen Technology Research Center**

**Presented at ETH-Zürich**

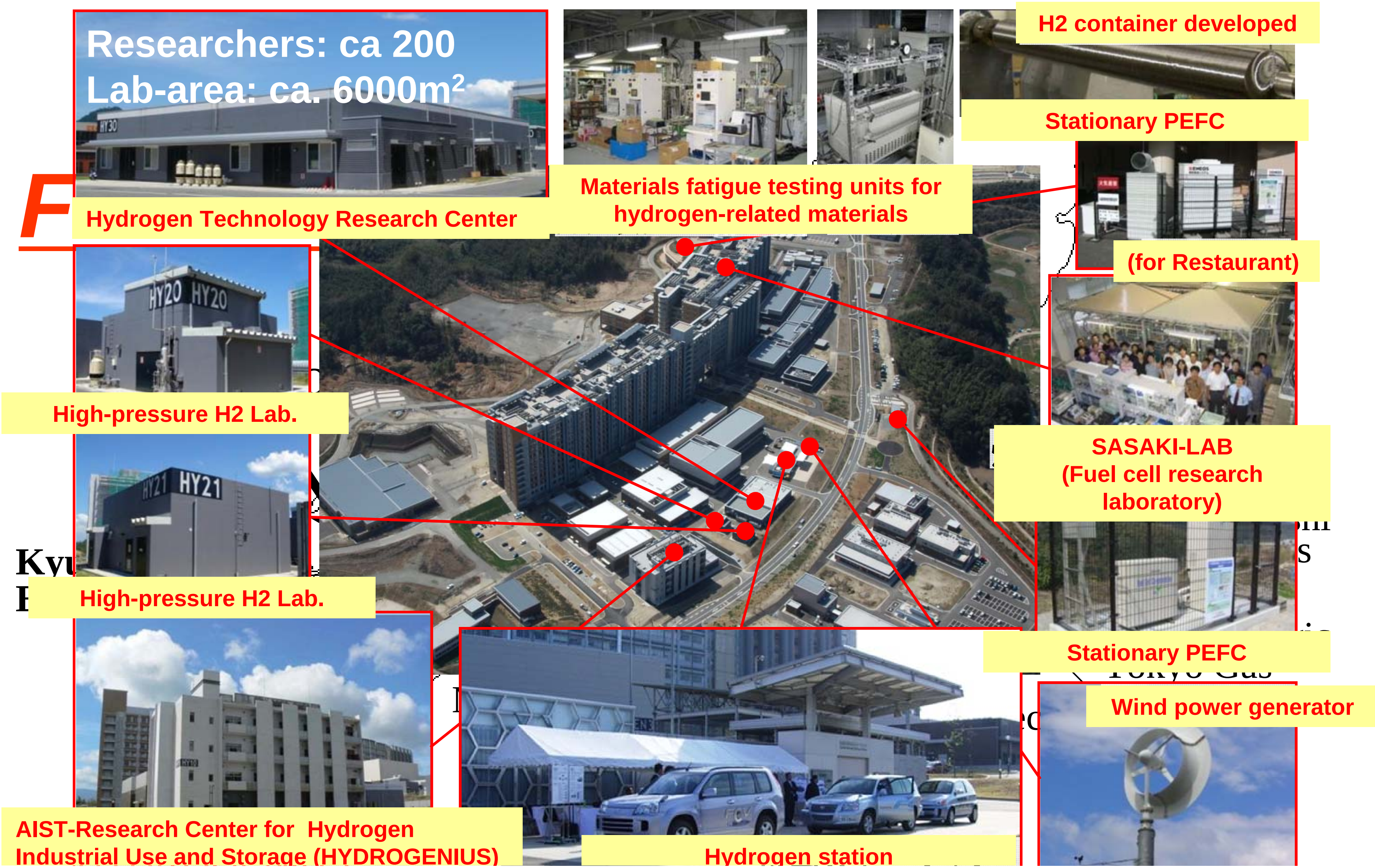
September 5, 2008

# Kazu. Sasaki c/o Prof. Gauckler (1989-95)


(Cited from the HP of ETHZ-NMW)

# Kyushu University "Hydrogen Campus":

## Towards realizing clean energy society with FUEL CELLS



# Kyushu University "Hydrogen Campus":

## A Center-of-Excellence on Fuel Cells and Related Hydrogen Technologies

**Kyushu University,**
**Hydrogen Technology Research Center**

Research topics:
Fuel cells, Electrolysis,
Sensors, Combustion, Safety etc

**Fukuoka Hydrogen Strategy Conference**
**(collaborating with**
**ca. 330 private companies)**

**Kyushu Univ. ITO-campus**

**AIST-Hydrogenius**
**(Research Center for Hydrogen**
**Industrial Use and Storage)**

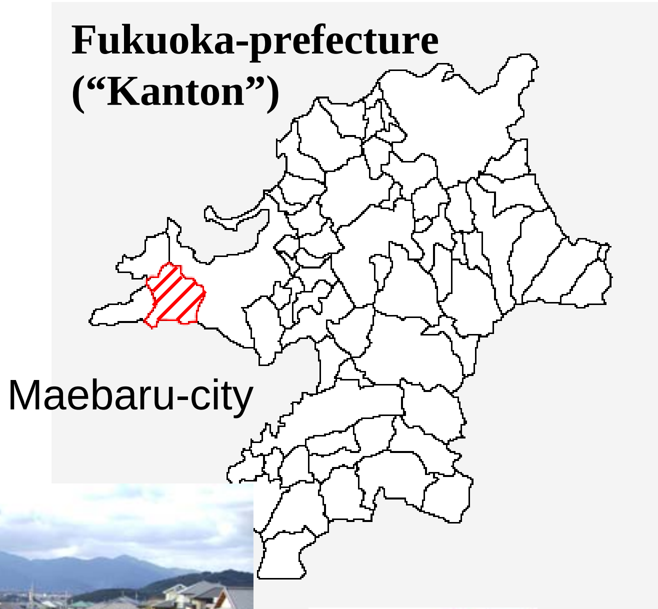

Research topics:
Structural materials for high-pressure
hydrogen energy systems,
Tribology, Simulation techniques

**Kyushu University,**
**INAMORI Frontier Research Center**

Research topics:
Energy, Environment,
Electronics, Nanotechnologies

# Fukuoka “Hydrogen-Town” and “Hydrogen-Highway”

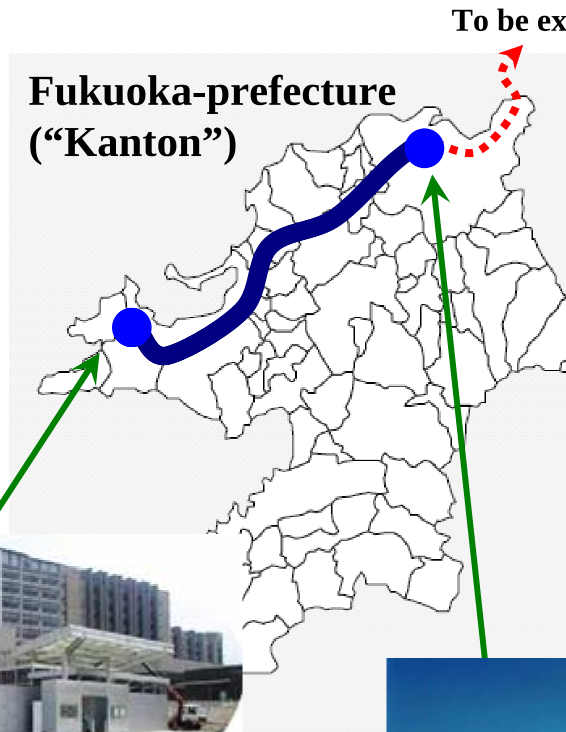
## “Hydrogen-Town”




Hydrogen-town near the Hydrogen Campus of Kyushu University

**150 stationary PEFCs will be installed !**

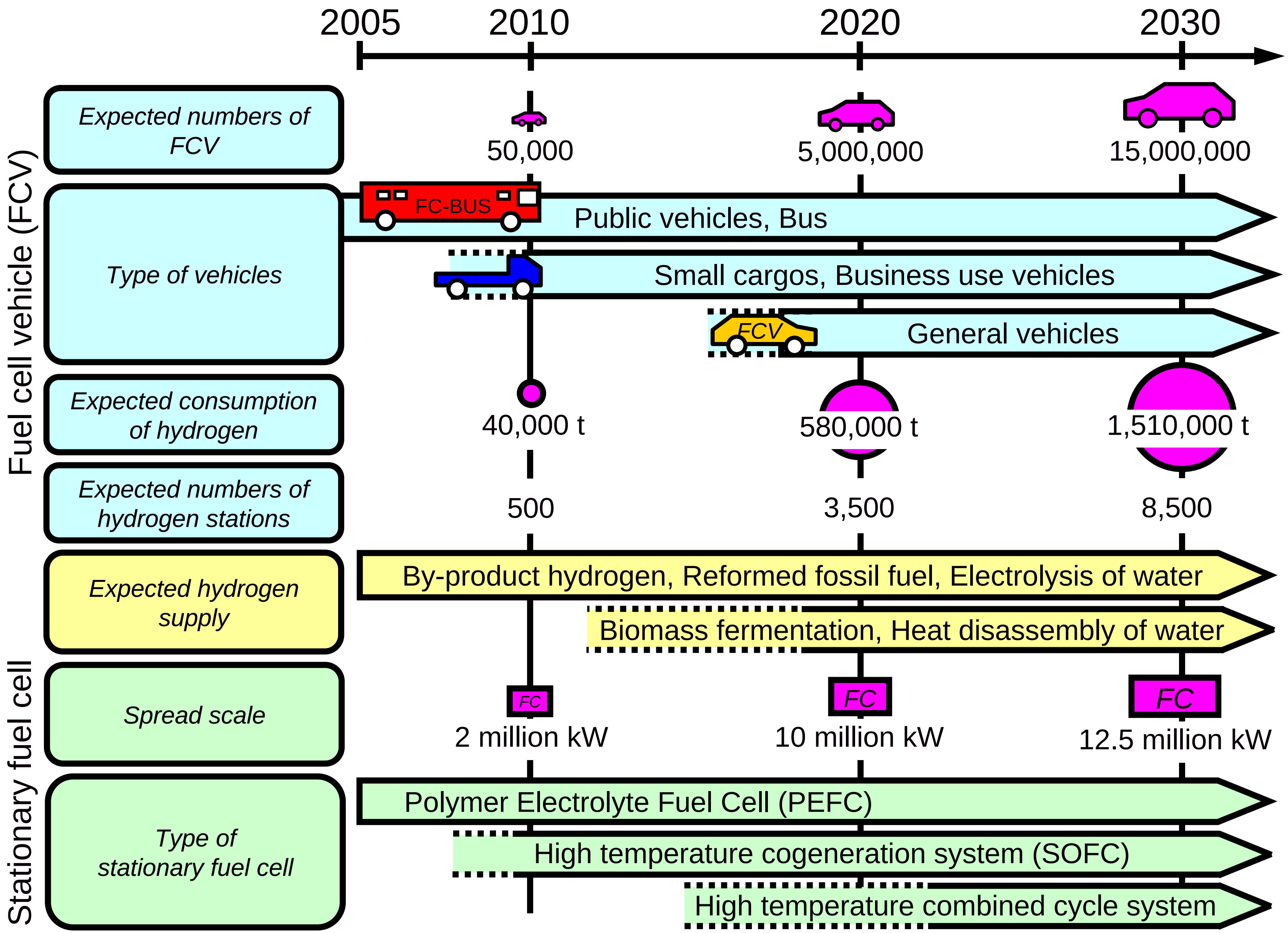
## “Hydrogen-Highway”



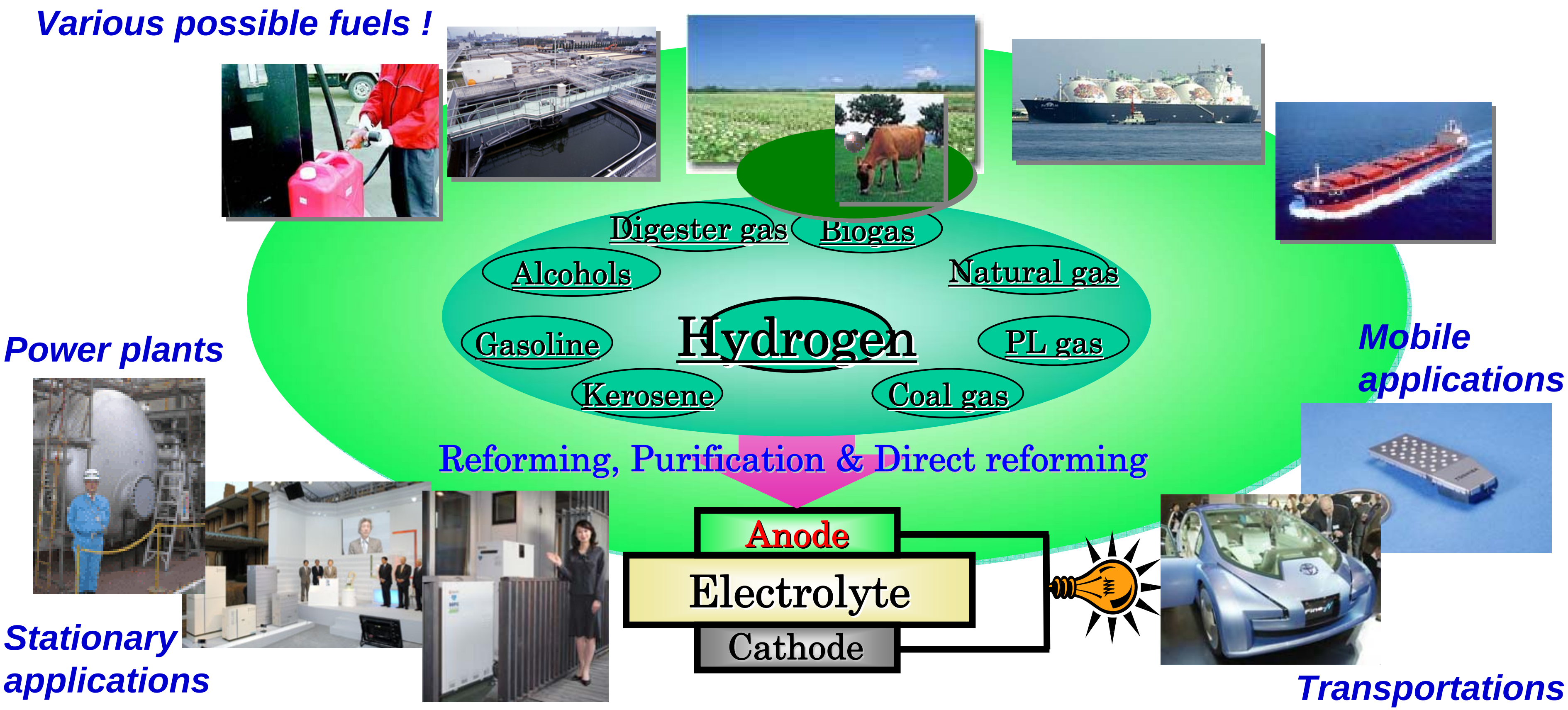

Hydrogen Station in Hydrogen Campus of Kyushu University

**Suitable for driving fuel cell vehicles**

# Hydrogen Society Proposed by Japanese Government for Fuel Cell Commercialization



# Hydrogen Energy based on Fuel Cell Technologies




- **Durability**
- **High performance**
- **Low cost**

  **⇒Alternative electrode materials are desired !**

# Durable high-performance fuel cell electrodes

**<u>＜ Alternative Electrode Materials for PEFC/DMFC＞</u>**

- **<u>Pt/Semiconducting oxide support</u>**
- Pt/Carbon nanofiber support
- Pt alloy/Carbon black support

＜ Alternative Electrode Materials for SOFC＞

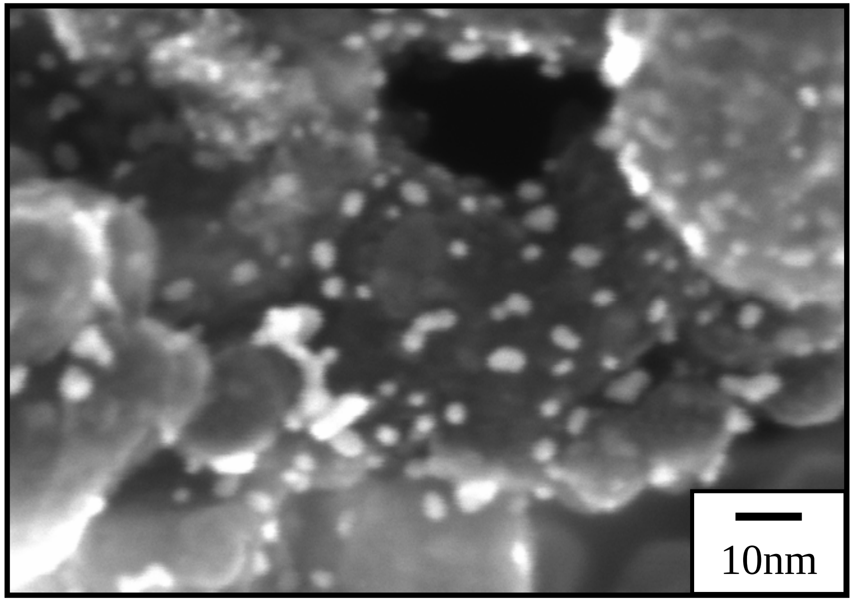
- Degradation mechanisms
- Ni nanocomposite/Zirconia

***Thermochemical stability is a key to ensure long-term durability of fuel cells !***

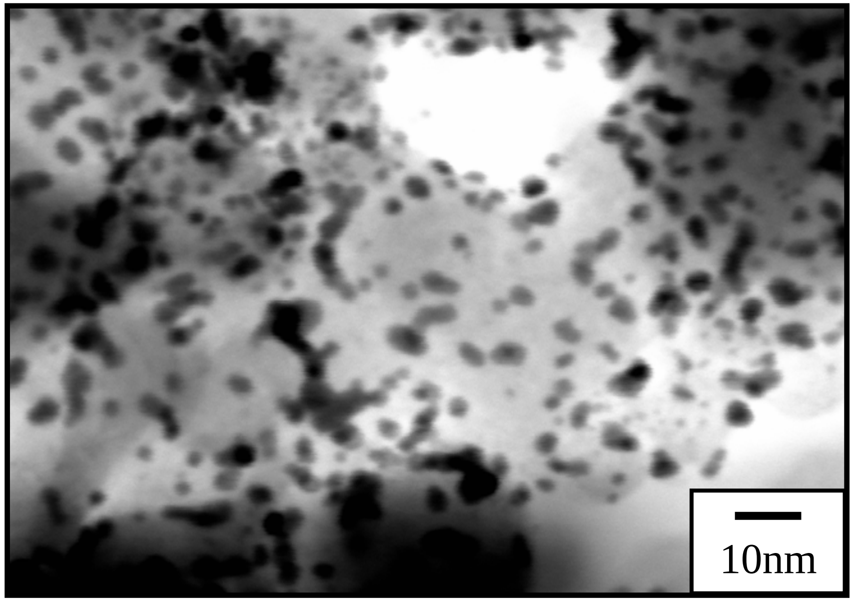
# Nanostructure: Pt/C(Carbon black, Vulcan)

FESEM-STEM observation

**Colloidal impregnation**

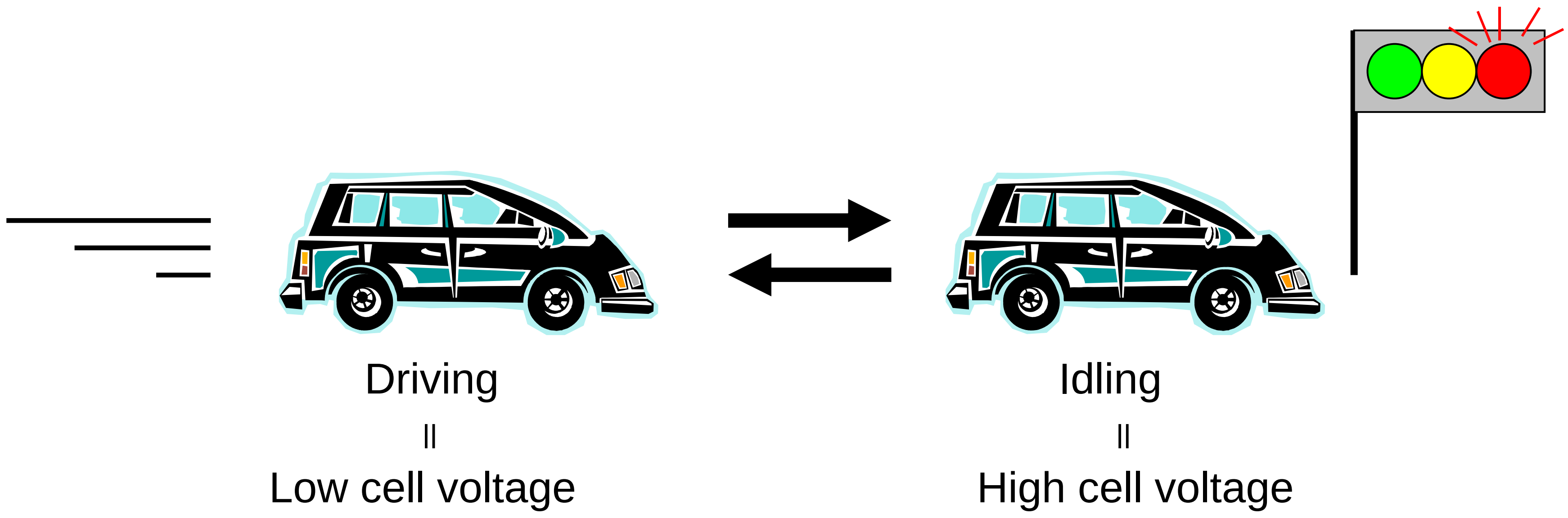



FESEM secondary-electron image




STEM image

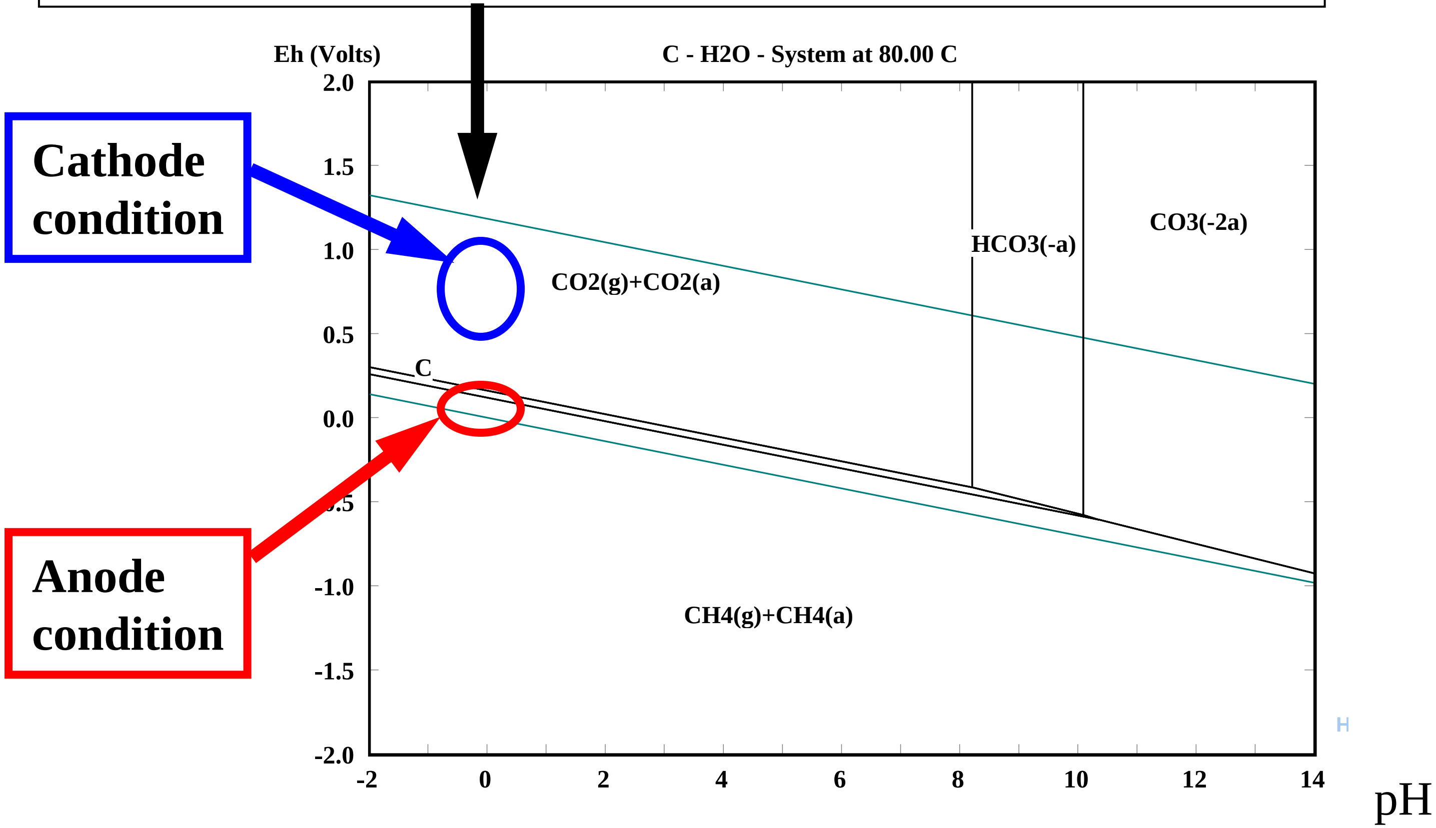
# PEFC electrocatalysts without catalyst support corrosion are desired!




**Electrocatalysts tolerant against voltage cycling are desired!**

# Pourbaix diagram of C-$H_2O$ systems at 80°C

strongly-acidic condition (PEFC electrolyte: Nafion)




**Carbon (graphite) is thermochemically *not stable* especially under cathodic conditions!**

# Pourbaix diagram of Sn-$H_2O$ systems at 80ºC

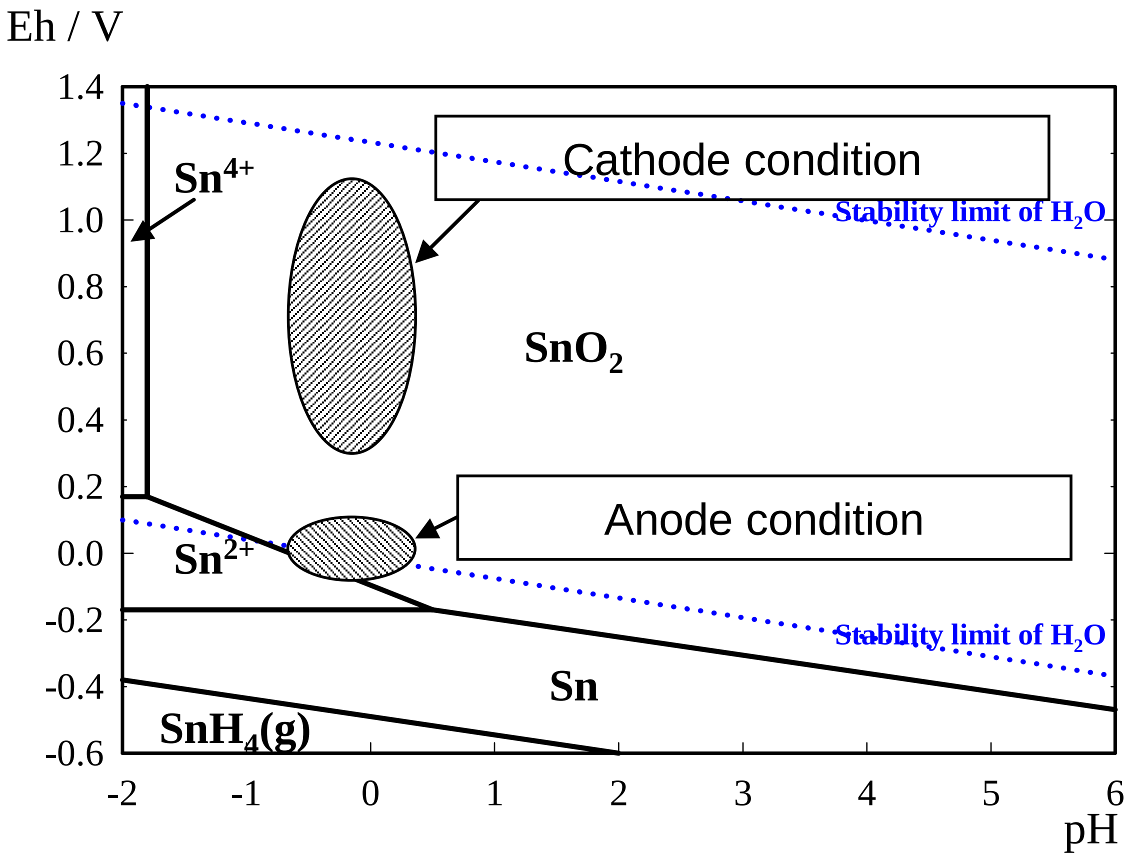
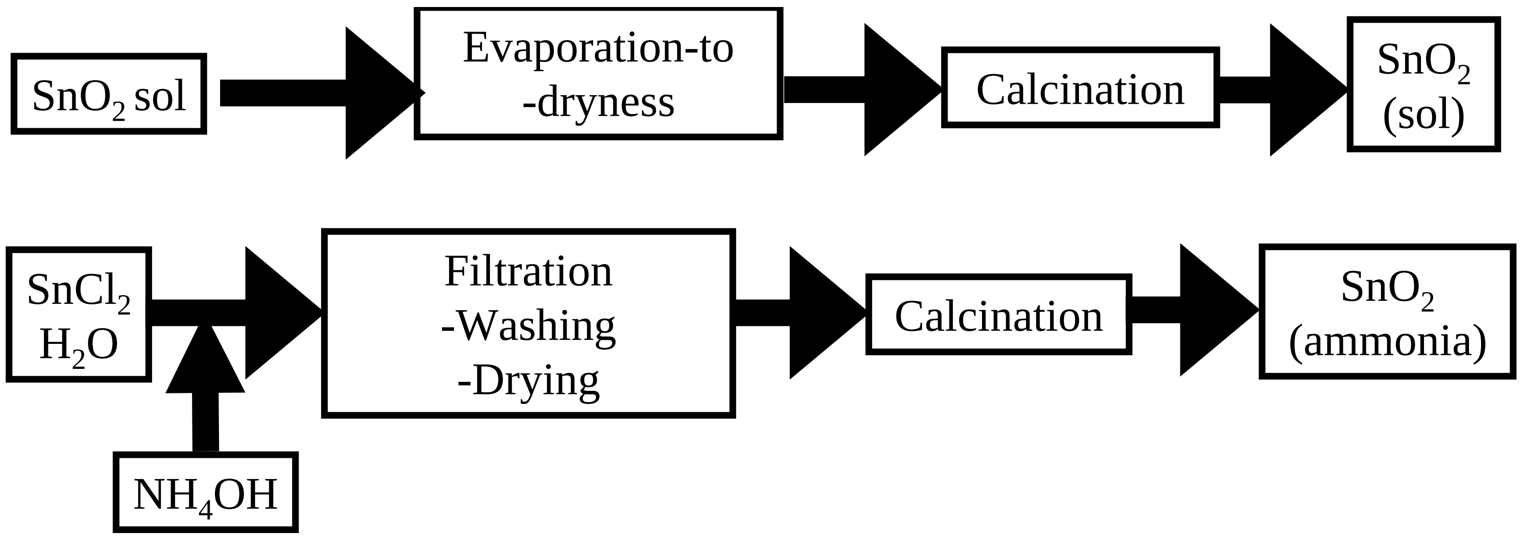



Fig. Pourbaix diagram of the Sn-$H_2O$ system

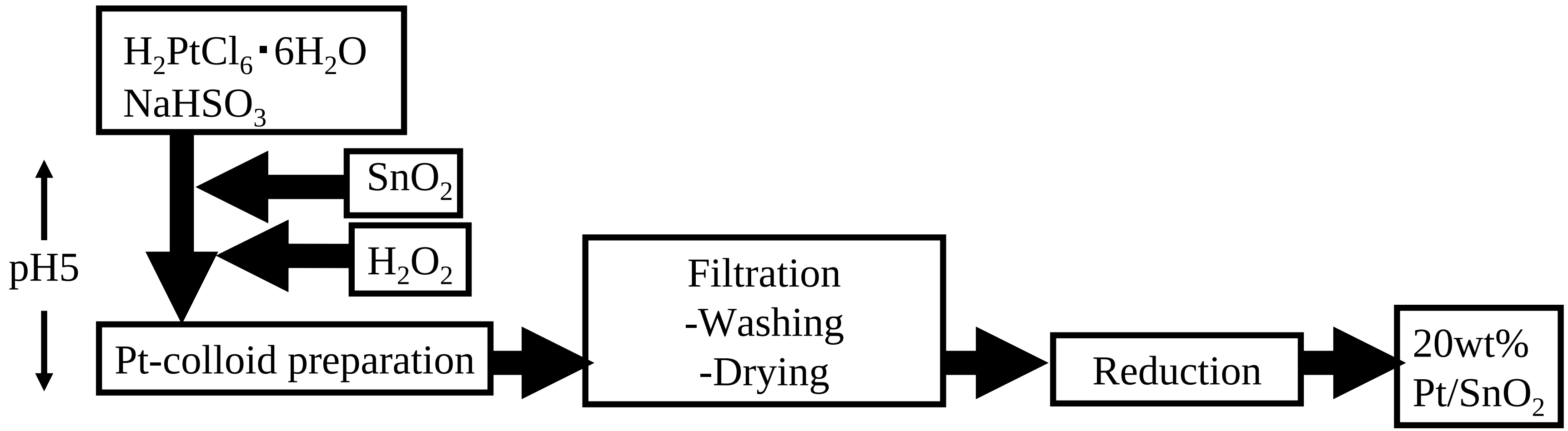
$SnO_2$-supported ***carbon-free*** electrocatalysts !?

# Preparation procedures of PEFC electrocatalysts

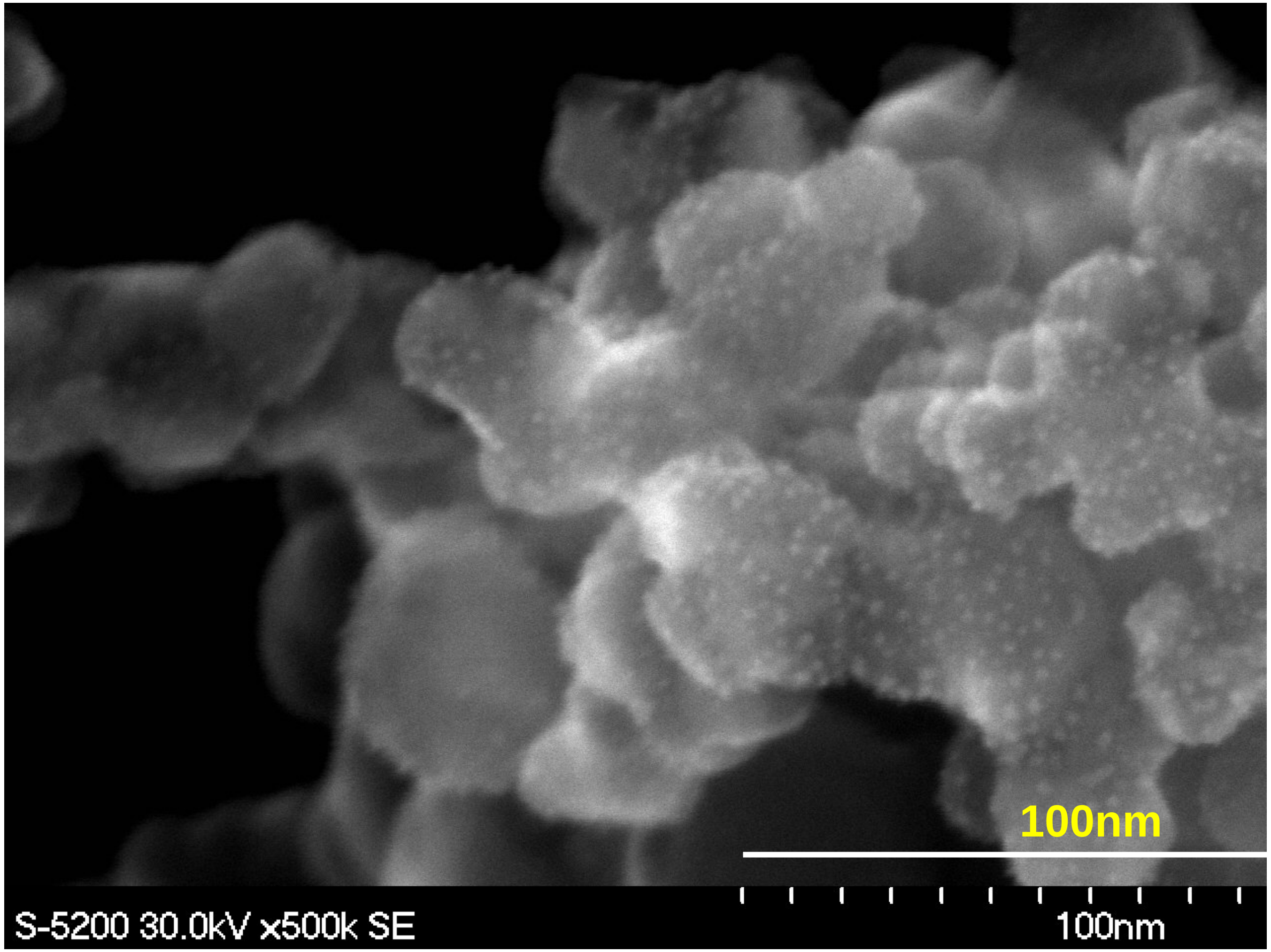
## *Preparation of catalyst supports*




## *Colloidal impregnation of electrocatalysts*



# *Carbon-free* Pt electrocatalysts successfully prepared !




**SEM micrograph of Pt/$SnO_2$**

**Pt nanoparticles of ca. 2-3 nmϕ are supported on $SnO_2$.**
**Metal(Pt) / semiconductor($SnO_2$) junctions !?**

# I-V of MEA using $SnO_2$-supported Pt electrocatalysts

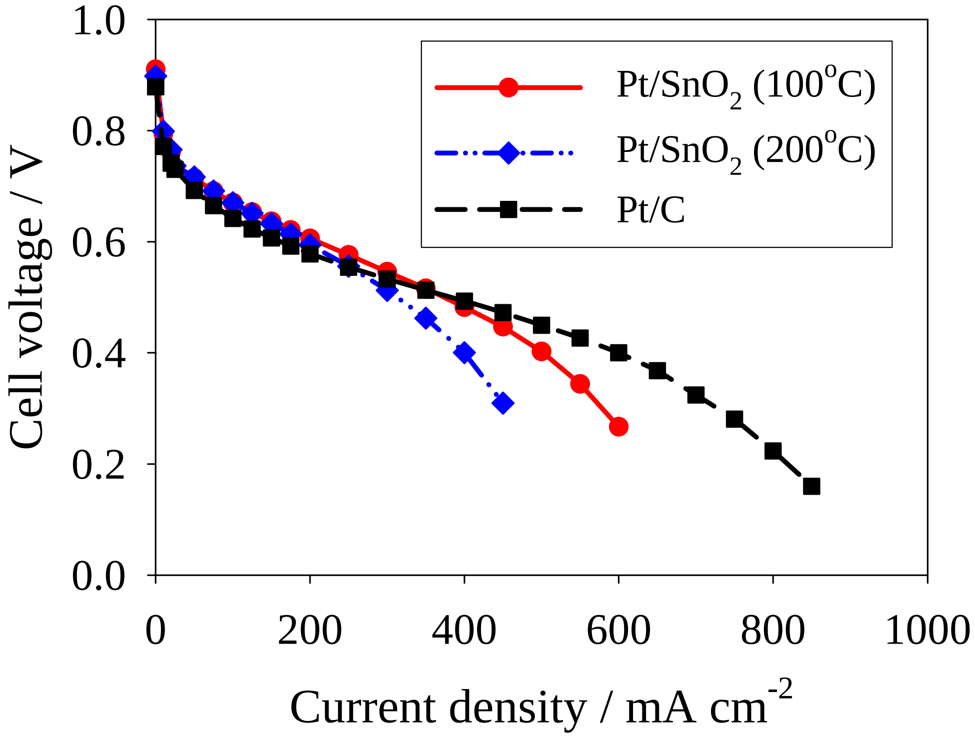



Fig. I-V characterization of single cells with 20% $Pt/SnO_2$ (0.6 mg-Pt $cm^{-2}$), and 20% Pt/C (0.6 mg-Pt $cm^{-2}$), cathodes. Anode catalyst: 46% Pt/C (0.4 mg-Pt $cm^{-2}$). The cell was operated with $H_2$/Air at a rate of 150 ml $min^{-1}$, Cell temperature at 80°C, atmospheric pressure, and humidification temperature at 80°C. Temperature in the figure indicates the calcination temperature of $SnO_2$.

**Comparable performance of $Pt/SnO_2$ with conventional Pt/C has been obtained.**

# Durability of Pt/C and Pt/$SnO_2$

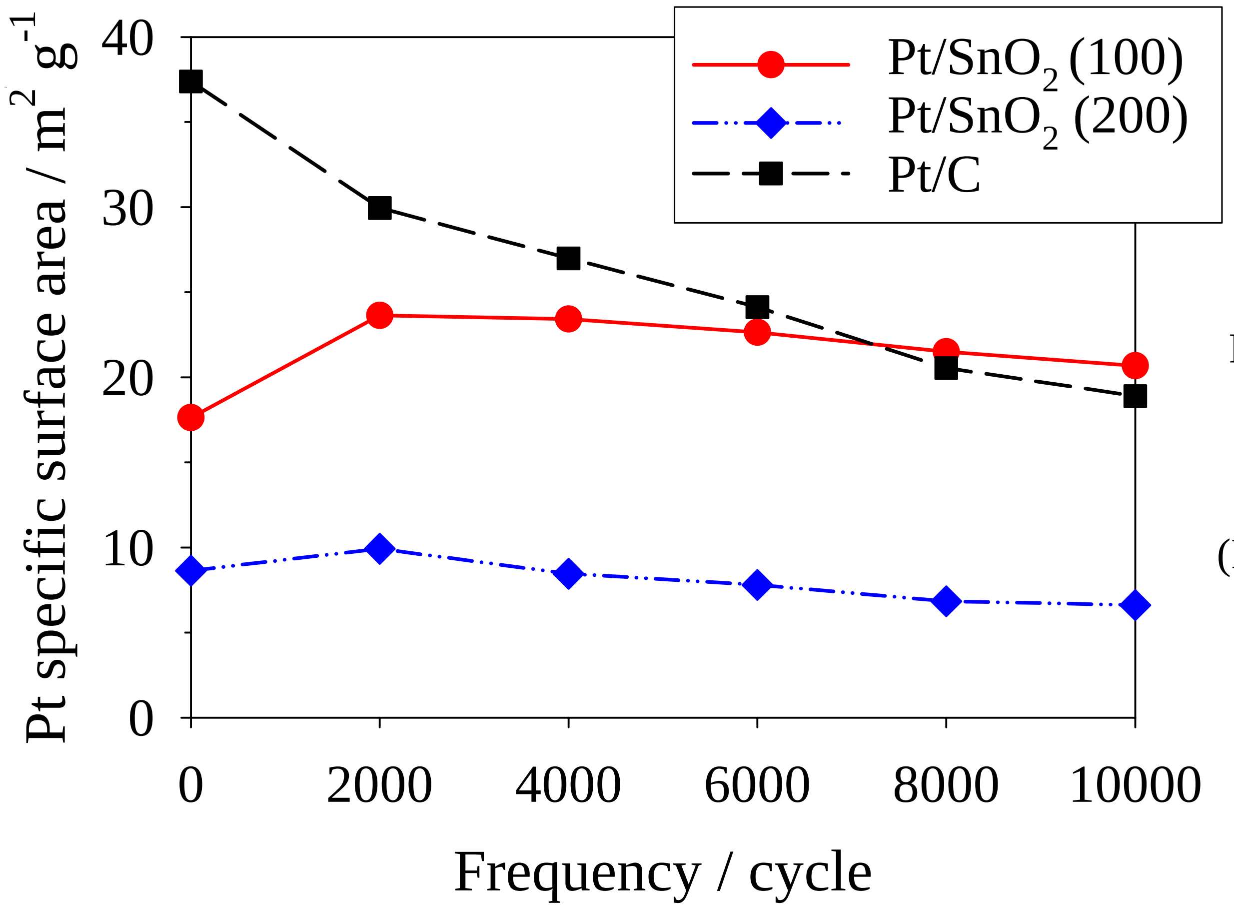



Fig. Change of ECSA of Pt up to 10000 cycles. (From 0.6 to 1.1 $V_{RHE}$)

**Electrochemical surface area (ECSA) of Pt remained almost constant, while Pt/C lost ECSA with cycles.**

# Durable high-performance fuel cell electrodes

**＜ Alternative Electrode Materials for PEFC/DMFC＞**

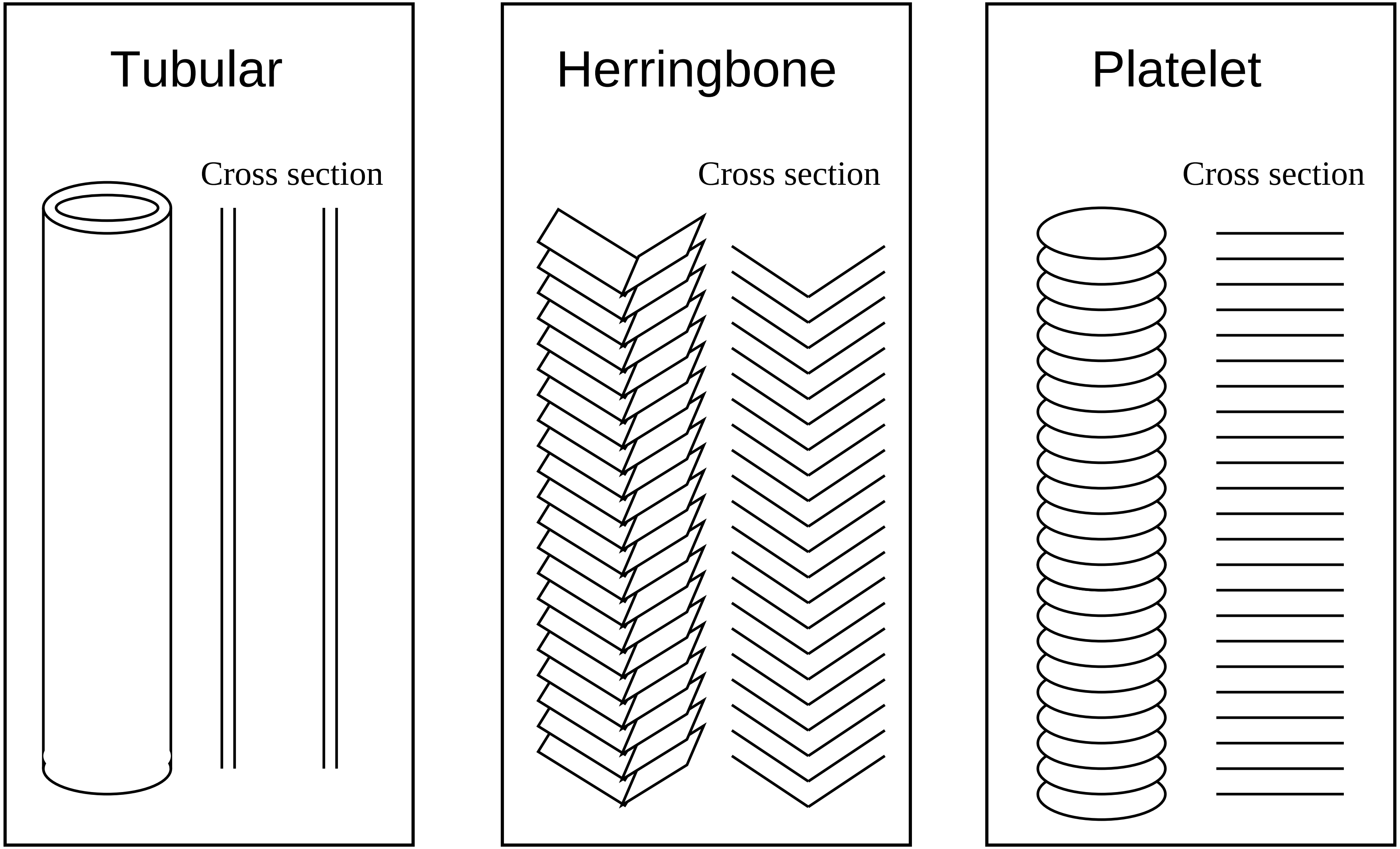
- Pt/Semiconducting oxide support
- **Pt/Carbon nanofiber support**
- Pt alloy/Carbon black support

＜ Alternative Electrode Materials for SOFC＞

- Degradation mechanisms
- Ni nanocomposite/Zirconia

***Thermochemical stability is a key to ensure long-term durability of fuel cells !***

# Structure of carbon nanofibers as catalyst supports



# PEFCs with Pt/CNF electrode catalysts

Pt/CNF(VGCF) electrocatalyst layers

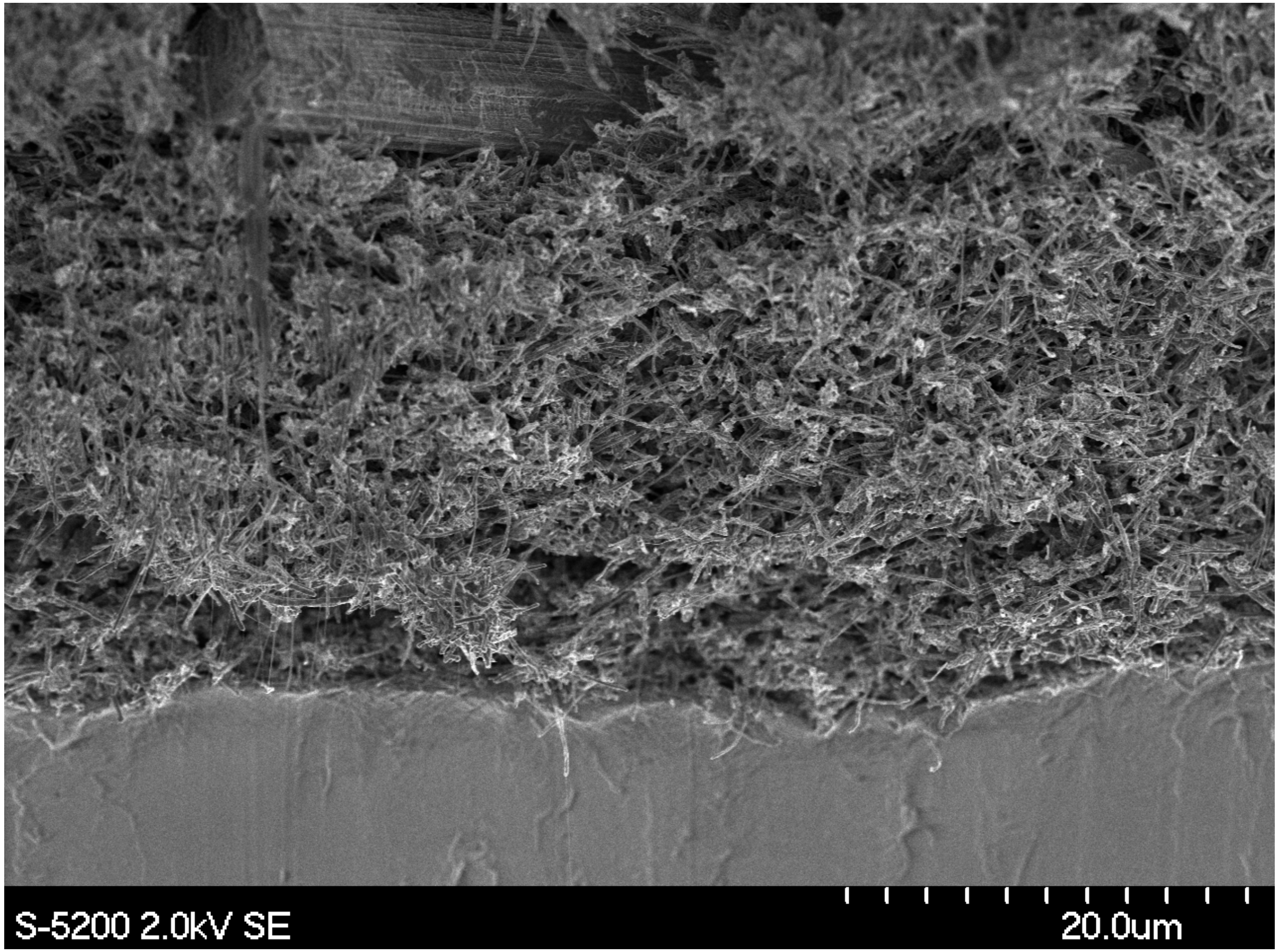
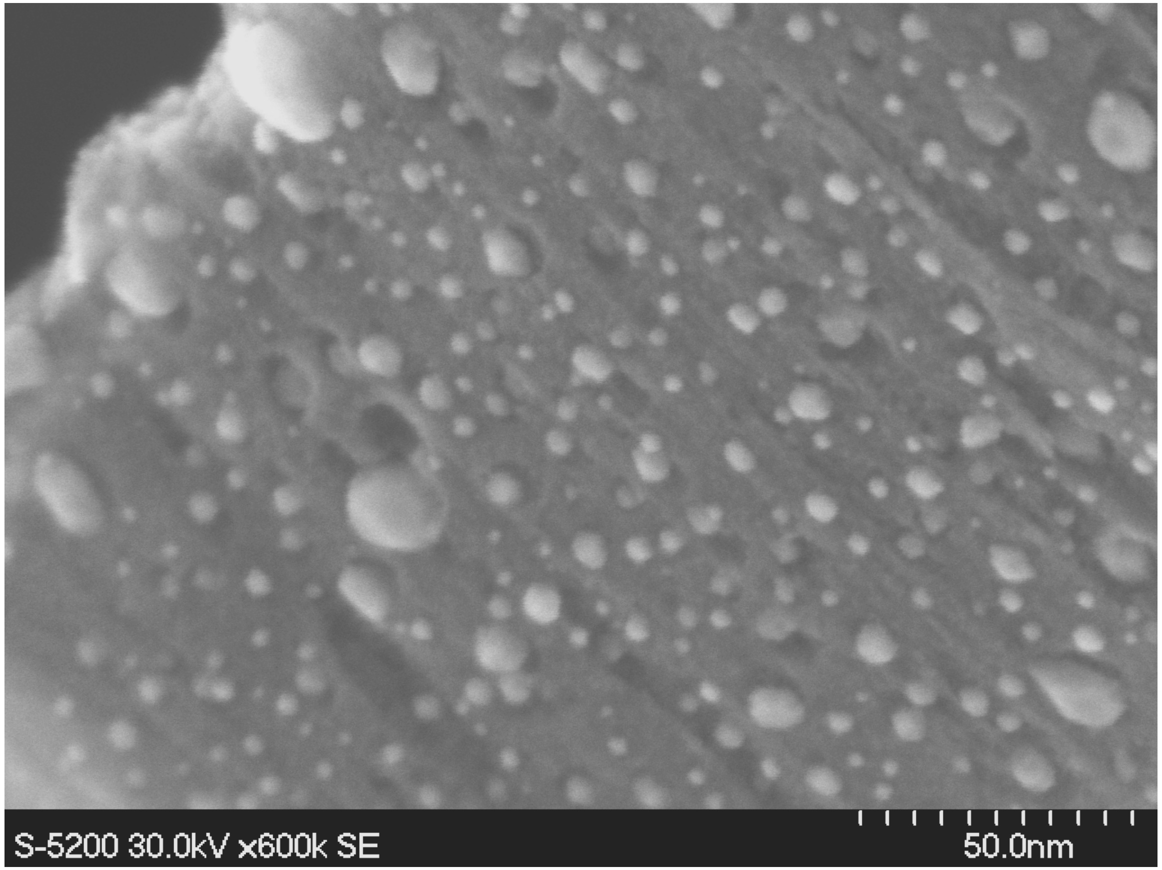



Fig.: FESEM micrograph of catalyst layer using CNF electrode supports

# Pt/CNF surface modified by activation procedures




Pt/Platelet electrocatalyst after steam-activation

**Pt particles are well impregnated “into” the surface.**

# Durable high-performance fuel cell electrodes

**＜ Alternative Electrode Materials for PEFC/DMFC＞**

- Pt/Semiconducting oxide support
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- **Pt alloy/Carbon black support**

＜ Alternative Electrode Materials for SOFC＞

- Degradation mechanisms
- Ni nanocomposite/Zirconia

***Thermochemical stability is a key to ensure long-term durability of fuel cells !***

# Pourbaix diagram of Ti-$H_2O$ systems at 80ºC

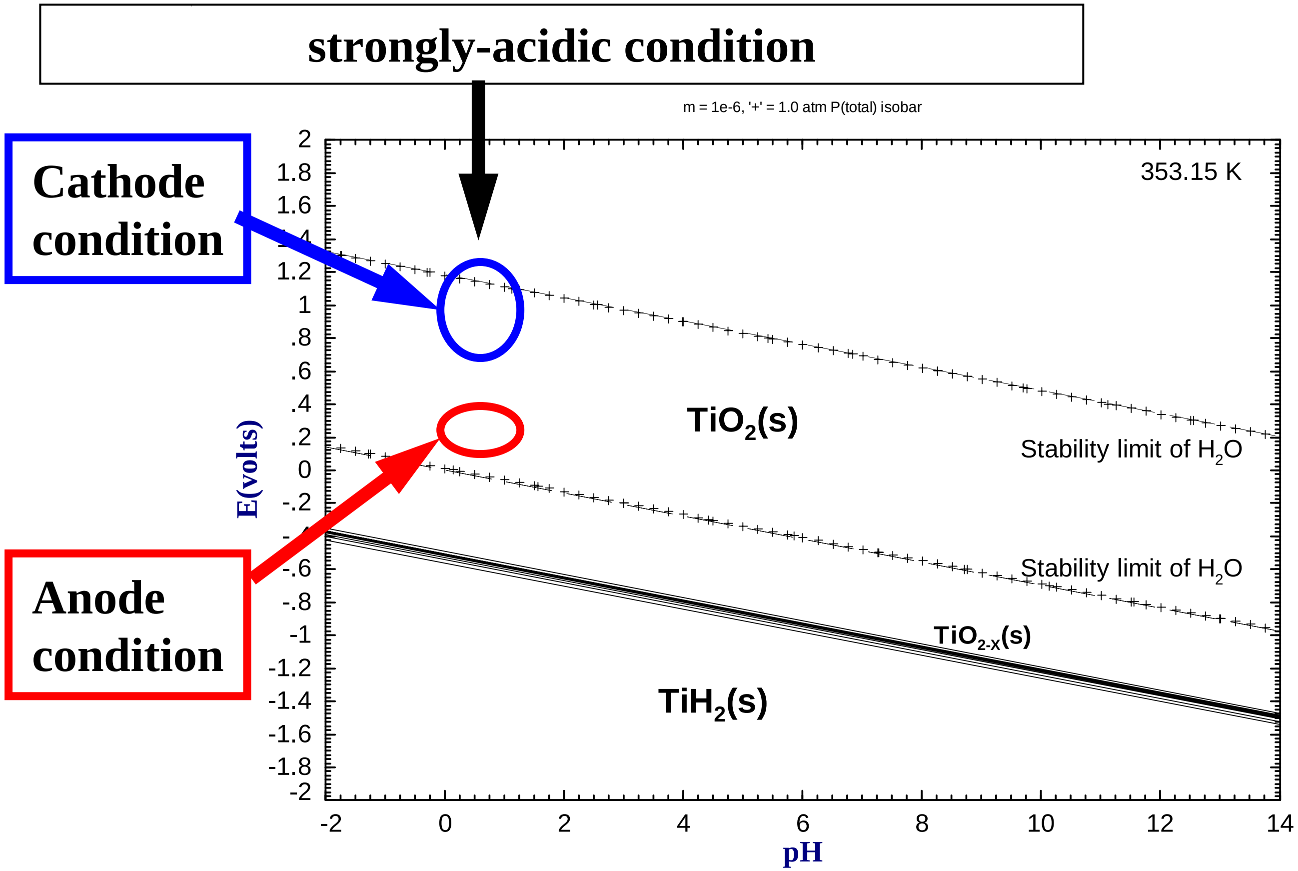



Fig. pH-potential equilibrium diagram for system Ti-$H_2O$

**Ti is a stable element under PEFC conditions.**

**→ Pt/Ti alloy electrocatalysts**

# Pt-Ti electrocatalysts are successfully prepared !

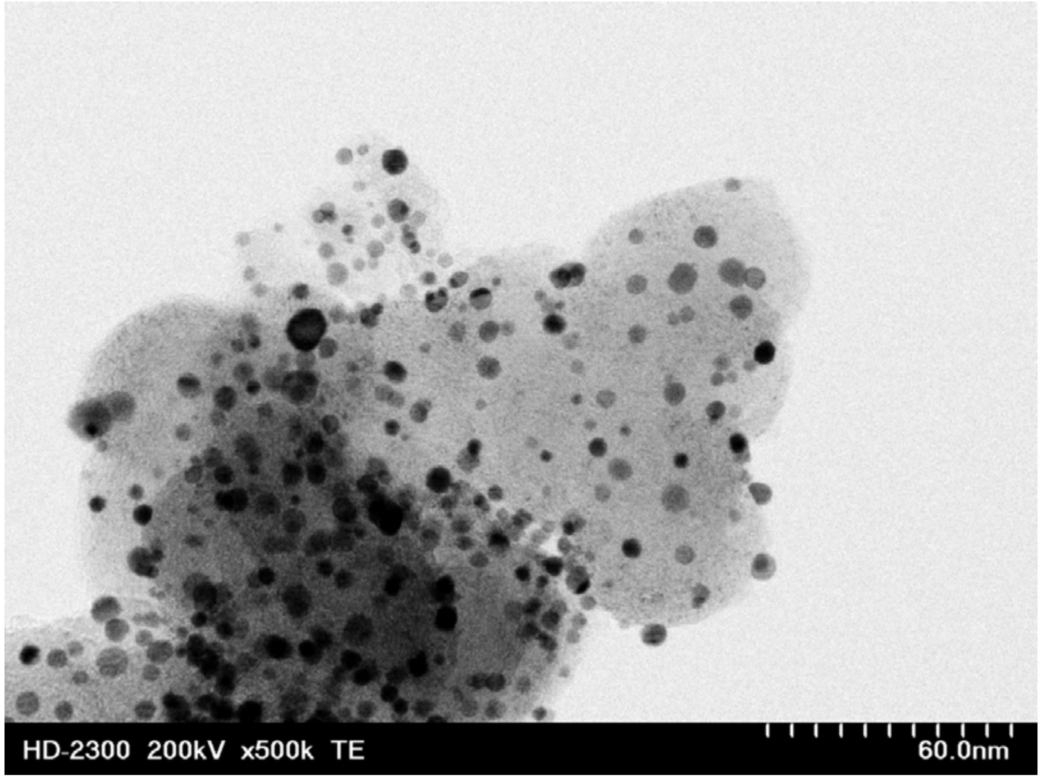



**Fig. STEM micrograph of PtTi/C electrocatalysts, showing nanocrystalline Pt-Ti alloy particles, where surface Ti may be oxidized.**

**Table: Particle size.**

| Catalyst | Particle size / nm |
|---|---|
| Pt(200) | 3.5 |
| Pt(450) | 3.9 |
| Pt(700) | 4.7 |
| Pt3Ti1(900) | 4.2 |
| Pt1Ti1(900) | 4.6 |
| Pt1Ti3(900) | 4.3 |

(Kawasoe et al., *J. Electrochem. Soc.*, **154**, B969 (2007))

**Pt-Ti alloy or Pt-$TiO_2$ nanocomposite?**

# Catalytic activity of Pt-Ti electrocatalysts

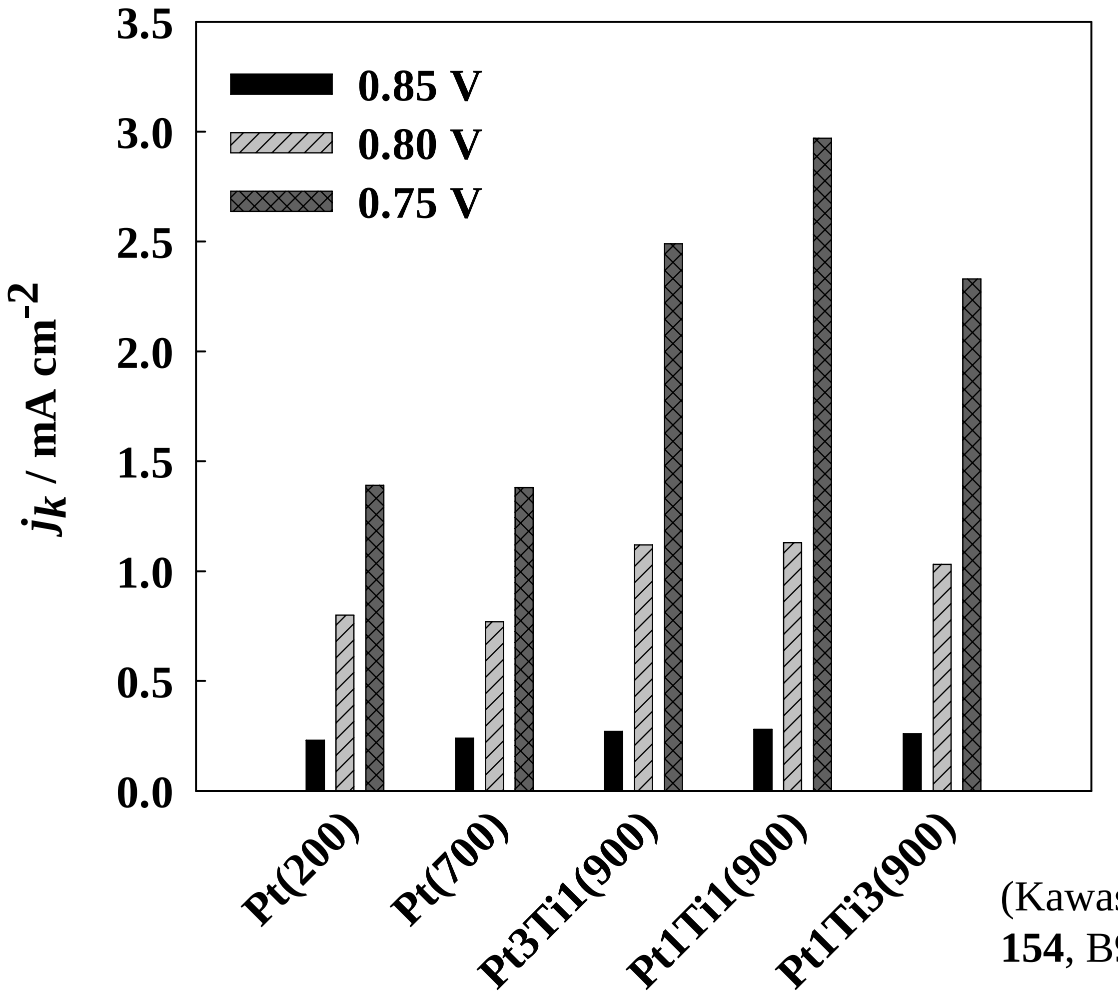



**Figure .** Kinetic current densities ($j_k$) at 0.85, 0.80 and 0.75 V vs. RHE in 0.1 M $HClO_4$ solution saturated with $O_2$. Sweep rate: 10 mV/s, temperature: 25 °C. The current density was normalized to ECSA measured by CV.

(Kawasoe et al., *J. Electrochem. Soc.*, **154**, B969 (2007))

**Comparable or even higher catalytic activity was obtained for Pt-Ti catalysts. But, Pt-Ti alloy or Pt-$TiO_2$ nanocomposite?**

# Durable high-performance fuel cell electrodes

＜ Alternative Electrode Materials for PEFC/DMFC＞

- Pt/Semiconducting oxide support
- Pt/Carbon nanofiber support
- Pt alloy/Carbon black support

**＜ Alternative Electrode Materials for SOFC＞**

- **Degradation mechanisms**
- Ni nanocomposite/Zirconia

***Thermochemical stability is a key to ensure long-term durability of fuel cells !***

# Importance of “chemical degradation” of SOFCs

**Chemical degradation**

Major origins:
- Practical fuels
- Ambient air
- System components

## *Practical fuels*

$H_2$, CO, Alcohol, Natural gas, Gasoline, Biogas, LP gas, Kerosene, Coal gas

Various energy resources

**Minor constituents in practical SOFC fuels**

**Sulfur-related impurities**
(City gas, LP gas, Coal gas, Coke oven gas, Biogas, Petroleum-related fuels)

**Halogen-gas** ($Cl_2$ gas in water, HCl in coal gas etc.)

**Ammonia** (Biogas)

**Aromatic compounds** (Petroleum-related fuels)

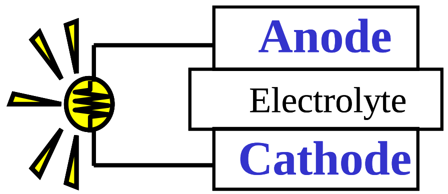
↓ Internal or external reforming

## *System components*

**Impurities from system components**

Heat insulation materials
Structural components
Electric insulator
Materials for heat exchanger
Fuel supply tubes
Air supply tubes
Bonding materials

→ Evaporation




Anode poisoning

Cathode poisoning

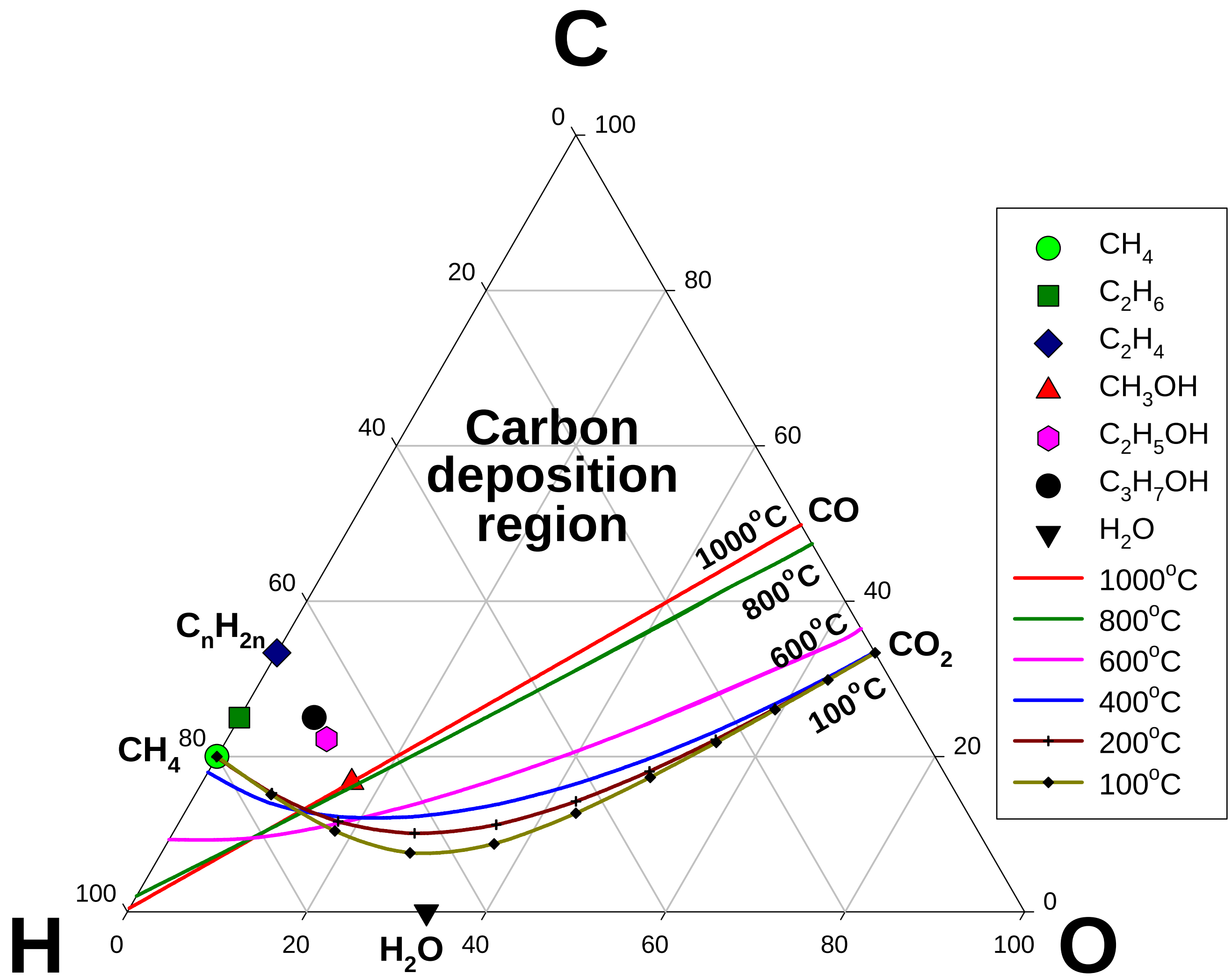
↑ Direct supply

## *Ambient air*

**Minor constituents in ambient air**

SOx in contaminated air
Salt-containing mist near seashore
Humidity in ambient air

# C-H-O ternary diagram: Carbon deposition region




**Equilibrium compositions can be specified by the C:H:O ratio.**

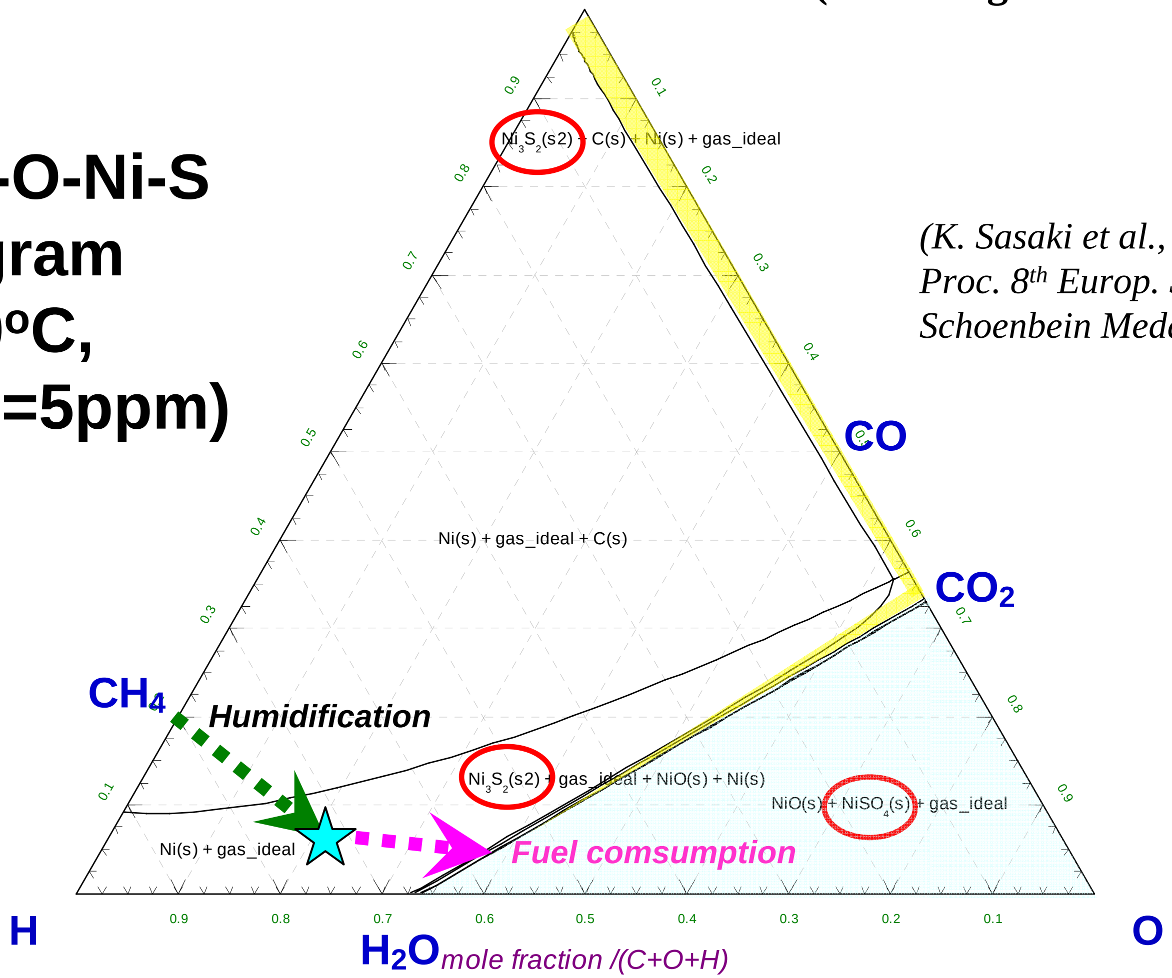
K. Sasaki and Y. Teraoka, *J. Electrochem. Soc.*, **150** [7] A885 (2003).

# C-H-O ternary diagram: Reactivity of Ni with S

(Assuming C+H+O>>Ni>Impurity)

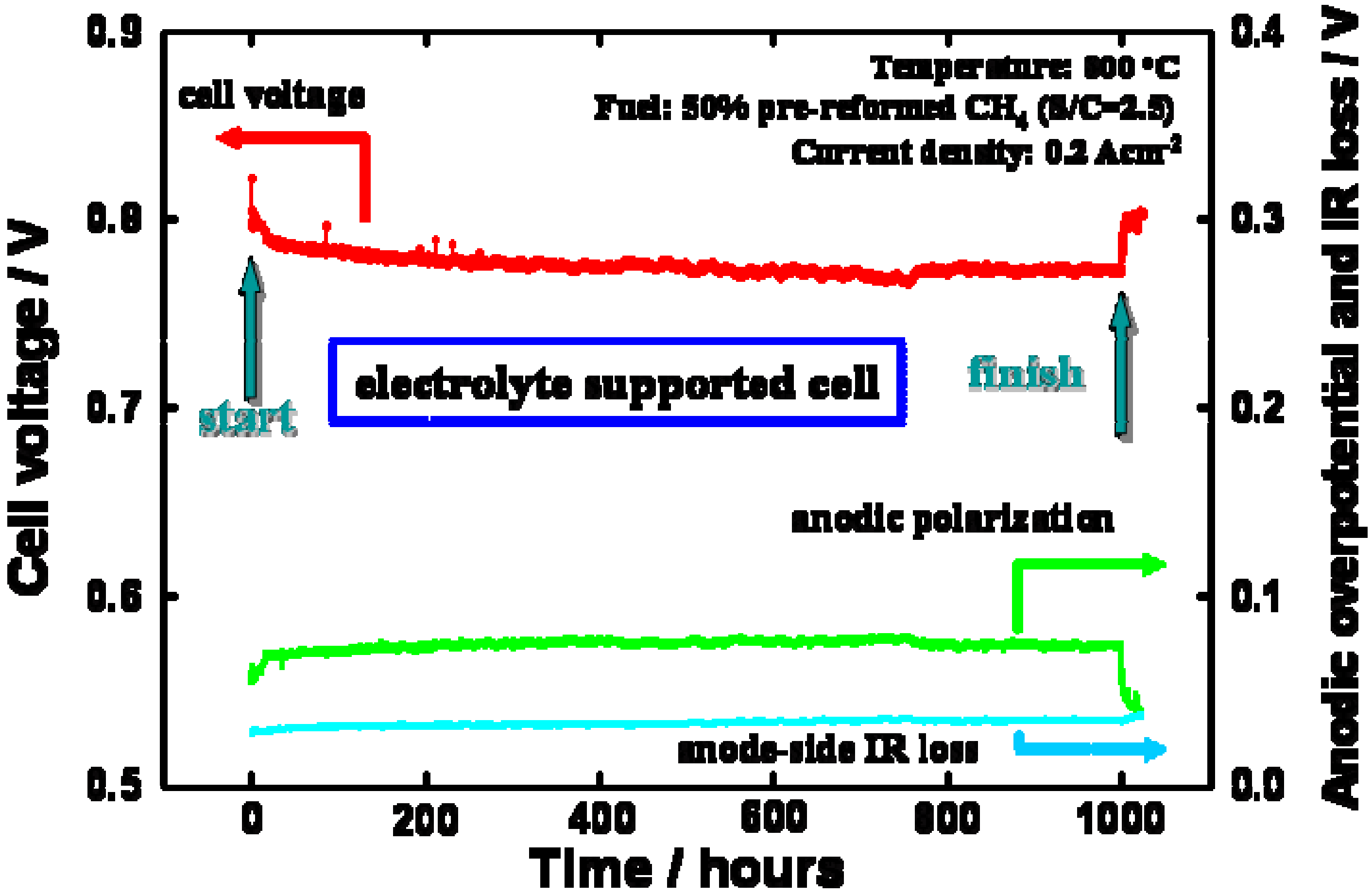
**C-H-O-Ni-S diagram (600°C, $P_{H2S}$=5ppm)**

*(K. Sasaki et al., Proc. 8th Europ. SOFC Forum, Schoenbein Medal 2008 awarded!)*




**Reactivity of Ni with minor impurities can be described in the C-H-O diagrams !**

# Poisoning by $H_2S$ up to 1000 hours

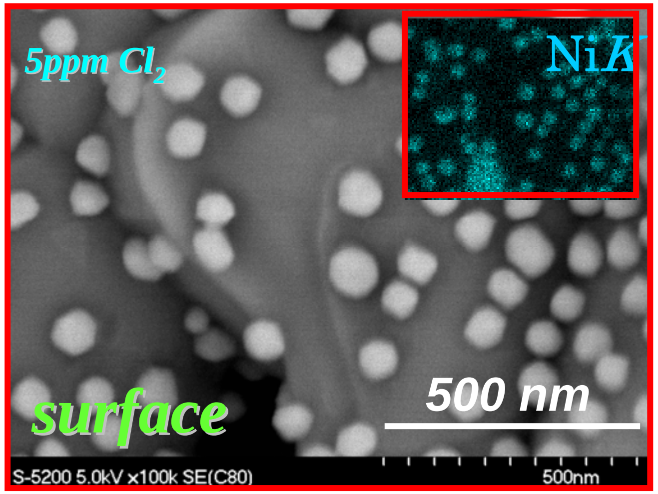



**Stable cell voltage up to 1000 hours is confirmed.**
**Cell voltage drop is reversible.**

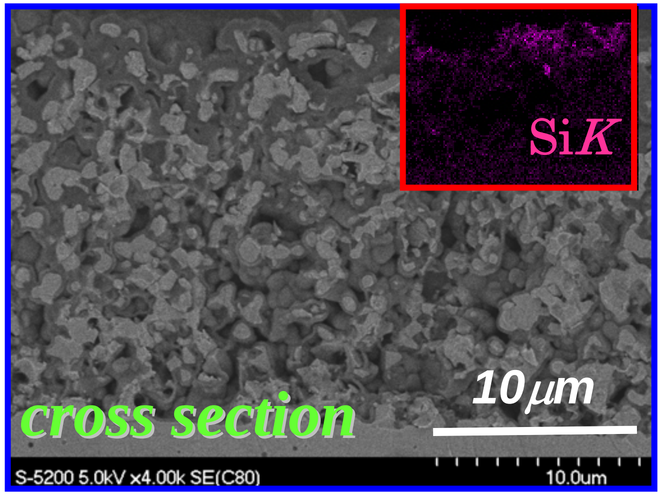
(K. Haga et al., *Solid State Ionics*, in press)

# Degradation mechanisms for each impurities

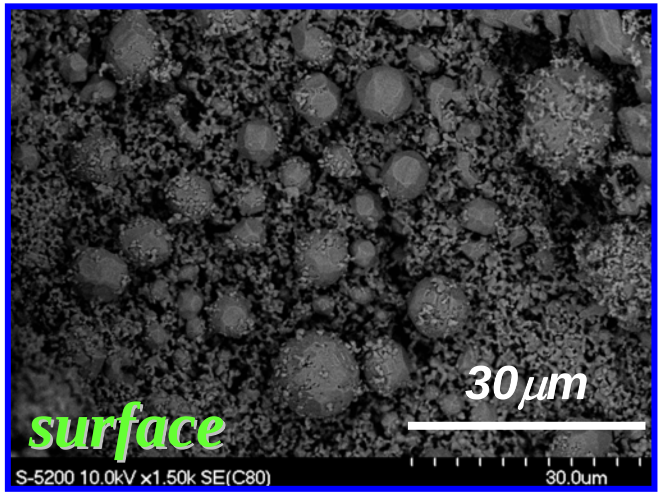
$Cl_2$



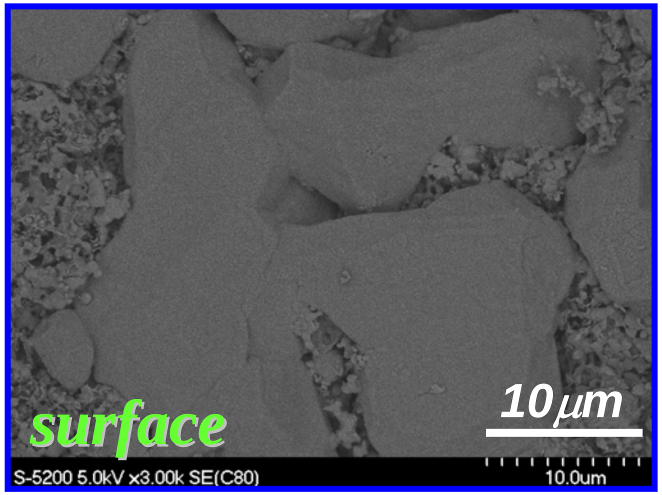

Siloxane




P



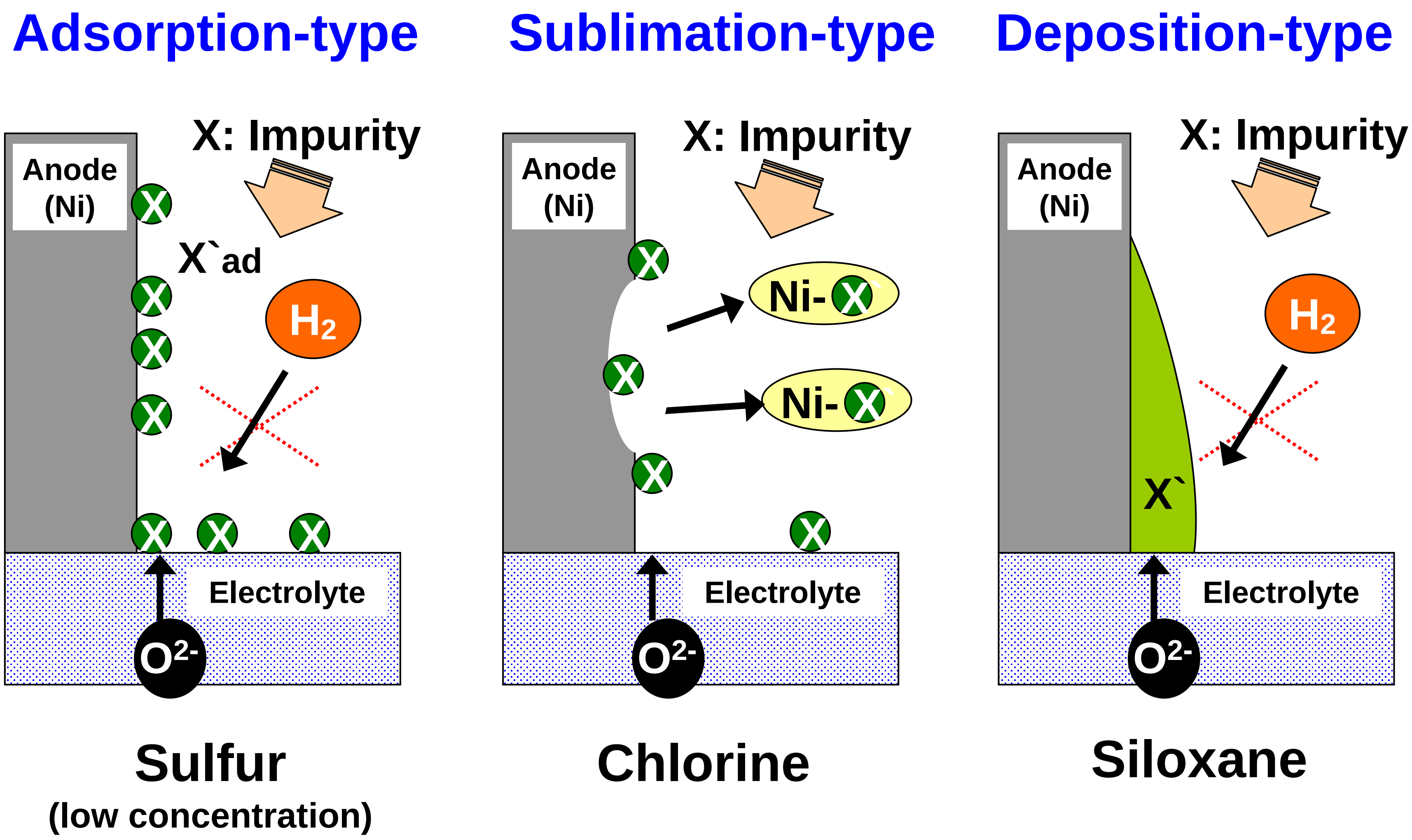

B




**$Cl_2$: sublimation&precipitation type**
**Siloxane: precipitation (deposition) type**
**P, B: eutectic-type, grain-growth-type**

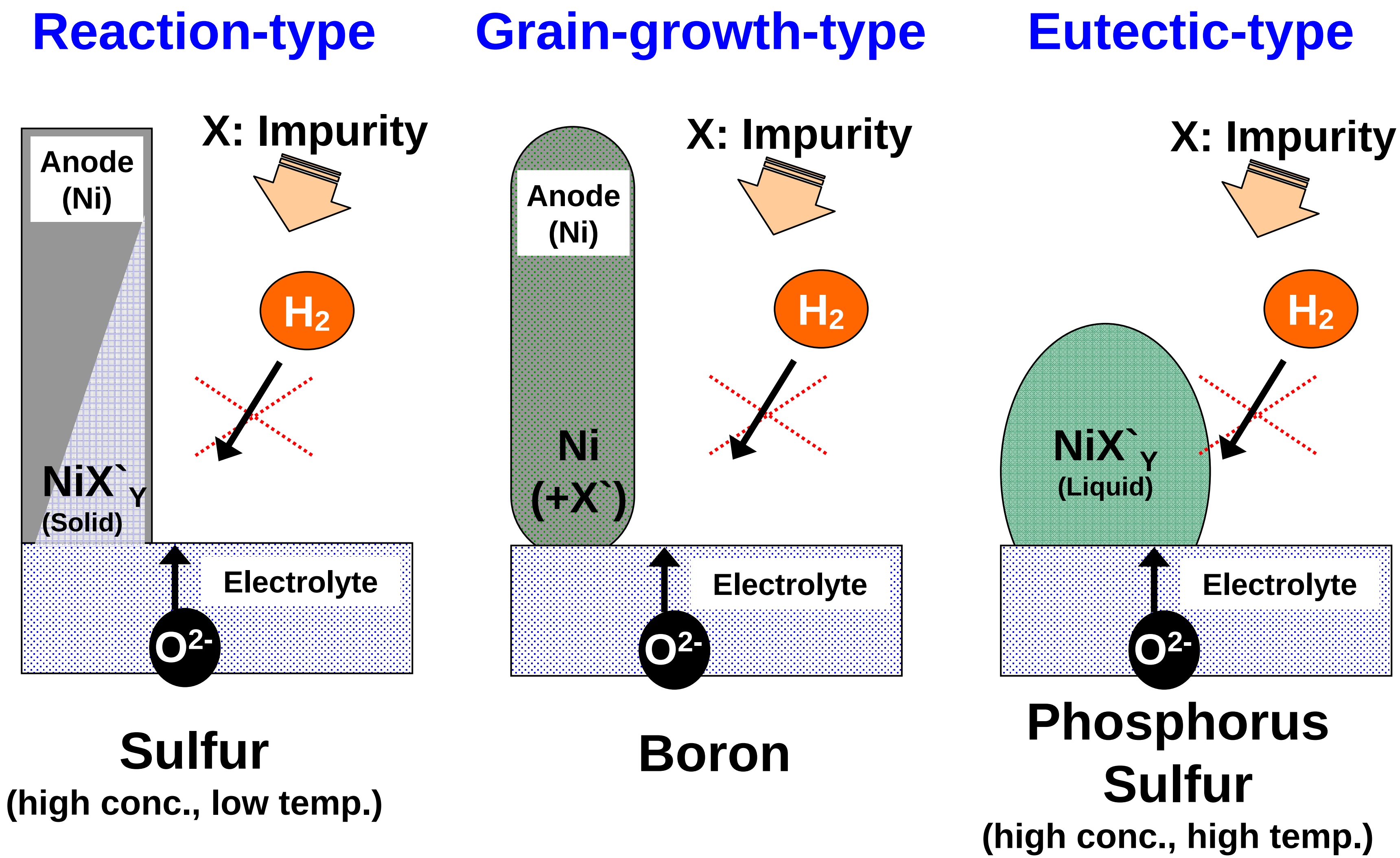
(K. Haga et al., *Solid State Ionics* & J. Electrochem. Soc., in press)

# Poisoning / degradation mechanisms- I




*(K. Sasaki et al., Proc. 8th Europ. SOFC Forum, Schoenbein Medal 2008 awarded!)*

# Poisoning / degradation mechanisms- II




*(K. Sasaki et al., Proc. 8th Europ. SOFC Forum, Schoenbein Medal 2008 awarded!)*

# Durable high-performance fuel cell electrodes

＜ Alternative Electrode Materials for PEFC/DMFC＞

- Pt/Semiconducting oxide support
- Pt/Carbon nanofiber support
- Pt alloy/Carbon black support

<u>**＜ Alternative Electrode Materials for SOFC＞**</u>

- Degradation mechanisms
- <u>**Ni nanocomposite/Zirconia**</u>

***Thermochemical stability is a key to ensure long-term durability of fuel cells !***

# Stable compounds in the SOFC anode atmosphere

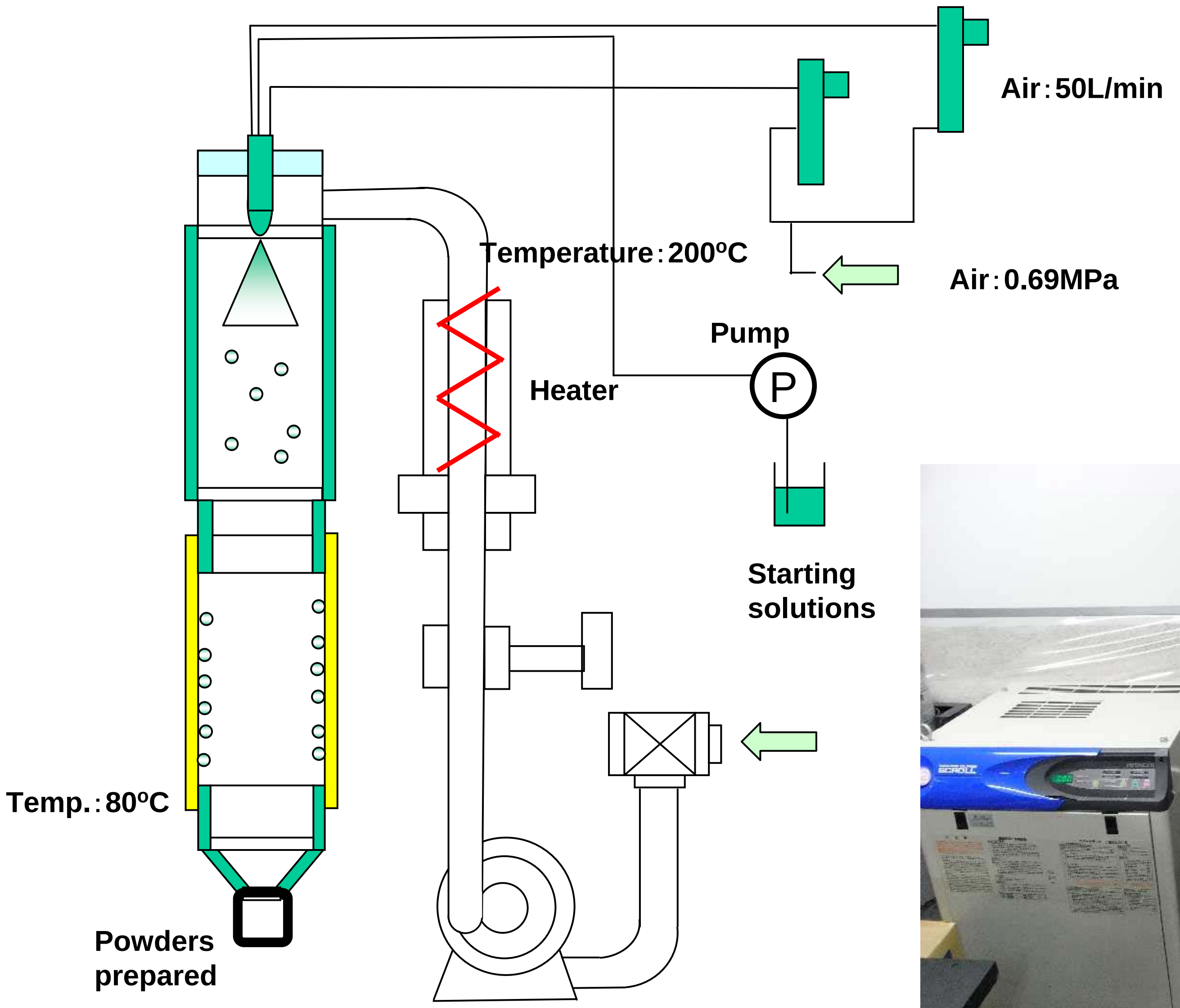
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | |
| 2 | | BeO | | | | | | | | | | | | | | | |
| 3 | | MgO | | | | | | | | | | | $Al_2O_3$ | | | | |
| 4 | | CaO | $Sc_2O_3$ | $TiO_2$ | $V_2O_3$ | $Cr_2O_3$ | MnO | Fe | Co | Ni | Cu | | $Ga_2O_3$ | | | | |
| 5 | | SrO | $Y_2O_3$ | $ZrO_2$ | $NbO_2$ | Mo | | Ru | Rh | Pd | | | | | | | |
| 6 | | BaO | $La_2O_3$ | $HfO_2$ | $Ta_2O_5$ | W | | | Ir | Pt | | | | | | | |
| 7 | | | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanides | $CeO_2$ | $Pr_2O_3$ | $Nd_2O_3$ | | $Sm_2O_3$ | $Eu_2O_3$ | $Gd_2O_3$ | $Tb_2O_3$ | $Dy_2O_3$ | $Ho_2O_3$ | $Er_2O_3$ | $Tm_2O_3$ | $Yb_2O_3$ | $Lu_2O_3$ |
| Actinides | $ThO_2$ | | $UO_2$ | $NpO_2$ | $PuO_2$ | | | | | | | | | |

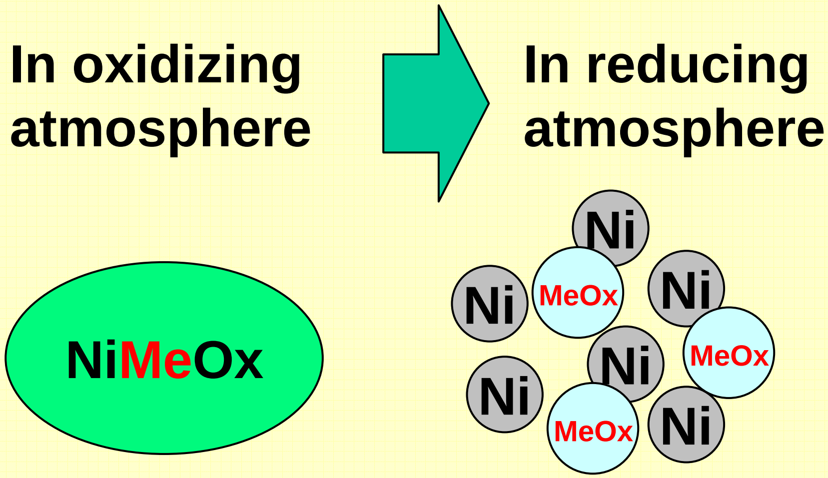
: **Stable as an oxide in $H_2$-3%$H_2O$ at 1000$^oC$**

: **Stable as a metal in $H_2$-3%$H_2O$ at 1000$^oC$**

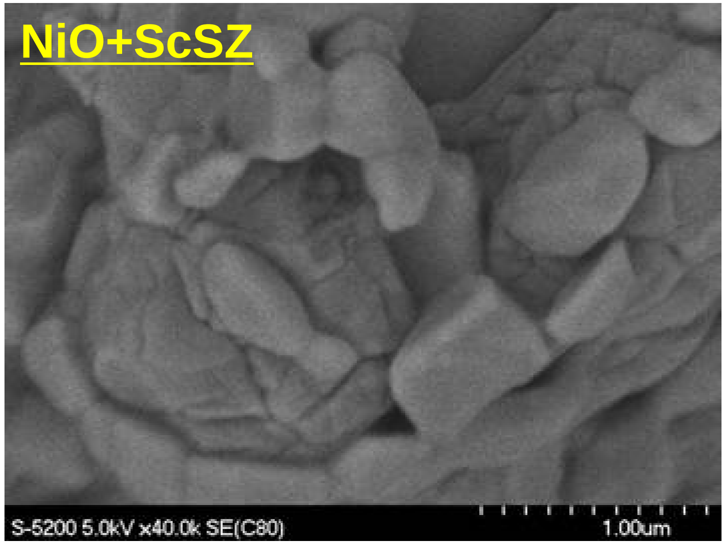
# Preparation of anode materials via spray-mist dryer

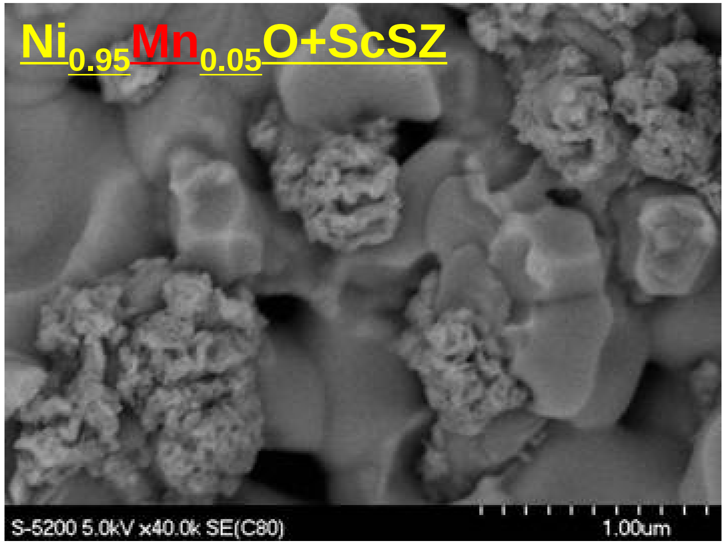



# Spray-mist-dryer for anode materials synthesis




***<u>Pinning effect</u> to keep***
***<u>larger electrode reaction area</u>***
***against poisoning and***
***to <u>prevent Ni agglomeration</u>!***

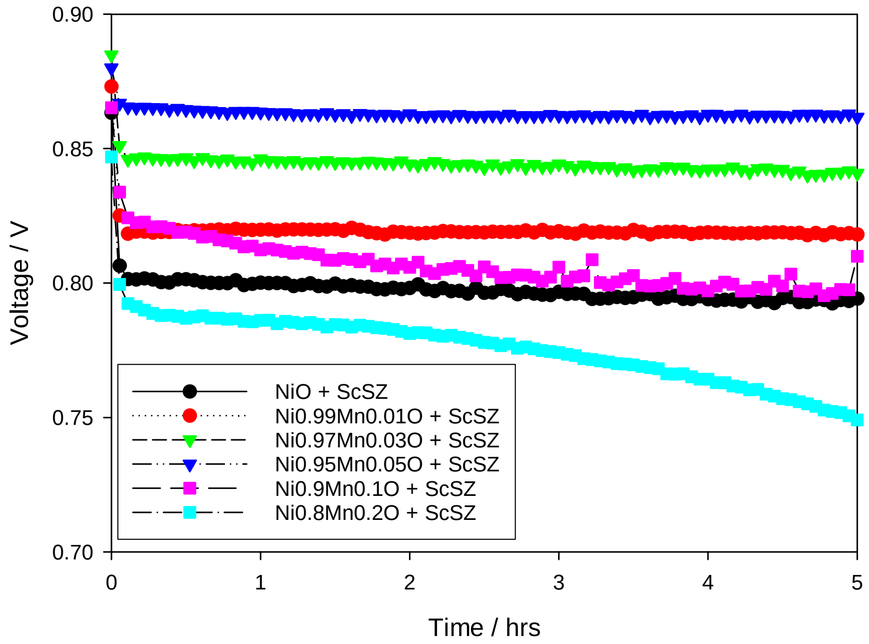


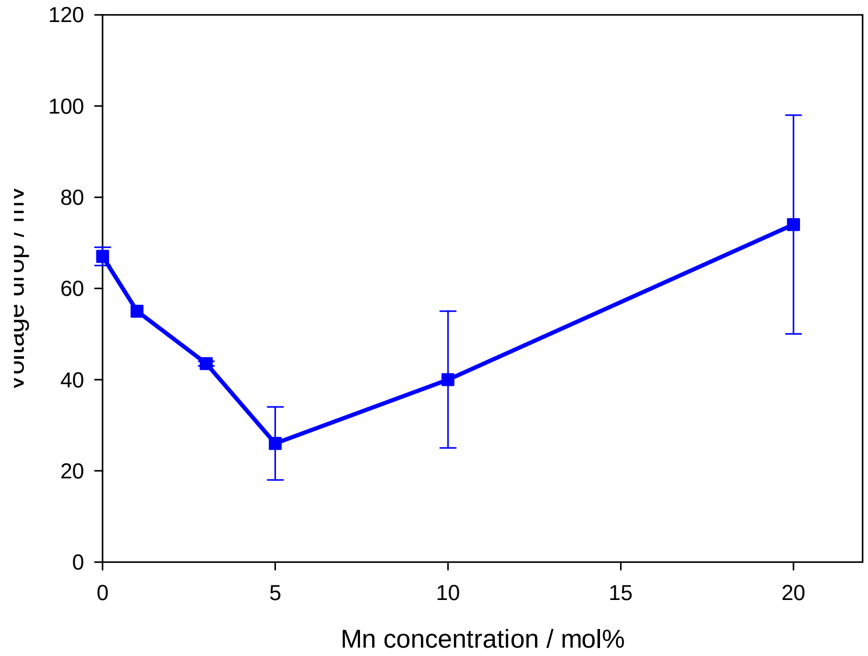




**⇒ Larger electrode reaction area**

(J. Yamamoto et al.)

# Ni-MnO/Zirconia nanocomposite anodes




**Impurity tolerant anode, Ni-MnO/Zirconia, has been developed.**
Cell voltage drop due to sulfur poisoning decreased considerably.

(J. Yamamoto et al.)

# Summary

**Various electrode materials have been developed for fuel cells with high durability and flexibility, based on thermochemical stability and nanostructuring:**

## ＜PEFC/DMFC＞

**Carbon-free electrocatalysts have been developed using semiconducting oxide support.**

**Various nanostructured electrocatalysts have been developed with thermochemical and geometrical stability.**

## ＜SOFC＞

**Degradation mechanisms by foreign species have been specified.**

**Sulfur-tolerant Ni-Mn based nanocomposite anode has been developed.**

# Sasaki-Lab. in Kyushu University

***Contributing to various fuel cell applications via materials synthesis, cell preparation, electrochemical / materials characterizations !***

**Fuel Cell Laboratory**

**Fuel Cell Evaluation Systems (30 systems available)**

- **Fuel cell materials preparation facilities** (Apparatus for various wet-chemical procedures)
- **Fuel cell fabrication facilities** (Automated spray-coating systems, Hot-press etc.)
- **Fuel cell evaluation facilities** (30 evaluation systems available for SOFC/PEFC/DMFC, 20 are full-automated.)
- **Electrochemical experimental apparatus** (4 impedance analyzers, 5 CV, RDE etc.)
- **Microscopes** (FESEM-STEM-EDX, AFM-STM) (Own STEM-EDX-EELS & FIB-MS will be installed in this year.)
- **Materials analytical instruments** (XRD, XPS, DTA-TG-MS etc.)
- **Gas analytical instruments** (GC-MS, automated GC etc.)
- **Materials database**