Technical Bottle-Necks for SOFC Operation in Conjunction with Biomass Gasification
バイオマスのガス化と連動したSOFC（固体酸化物形燃料電池）運用の技術課題

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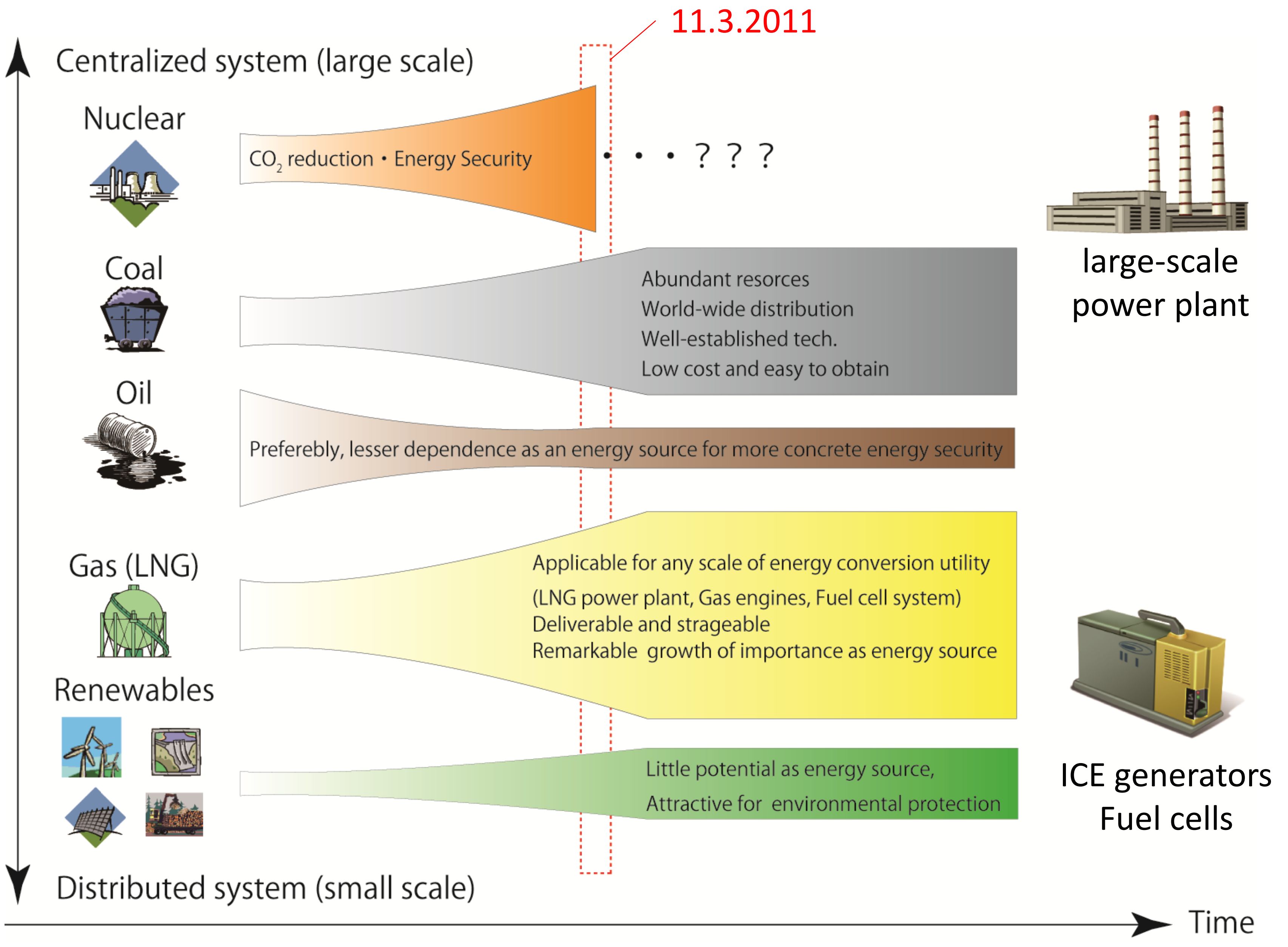
主任研究員　倉本浩司


11.3.2011
Centralized system (large scale)
Nuclear
CO_2 reduction • Energy Security
• • • ? ? ?
Coal
Abundant resorces
World-wide distribution
Well-established tech.
Low cost and easy to obtain
large-scale power plant
Oil
Preferebly, lesser dependence as an energy source for more concrete energy security
Gas (LNG)
Applicable for any scale of energy conversion utility
(LNG power plant, Gas engines, Fuel cell system)
Deliverable and strageable
Remarkable growth of importance as energy source
Renewables
Little potential as energy source,
Attractive for environmental protection
ICE generators
Fuel cells
Distributed system (small scale)
Time

Type of fuel cells

https://www.slideshare.net/Ramaraj90033/fuel-cell-43347517

Type	PEM	AFC	PAFC	DMFC	MCFC	SOFC
Name	Proton Exchange Membrane	Alkaline	Phosphoric Acid	Direct Methanol	Molten Carbonate	Solid Oxide
Applications	Vehicles, Mobiles, CHP	Space application	Large scale CHP	Mobiles from micro to small scale	Medium and Large scale CHP up to MW	All sizes of CHP up to multi MW
Operating Temp.[C]	50-100	50-200	ca. 220	ca. 70	ca. 650	500-1000
Reaction Ion	H^+	OH^-	H^+	H^+	CO_3^{2-}	O^{2-}
Fuel	Hydrogen	Hydrogen	Hydrogen	Methanol	H_2, CO, CH_4	H_2, CO, CH_4
Cell Components	Carbon-based	Carbon-based	Graphite-based	Carbon-based	Stainless-based	Ceramic
Catalyst	Platinum	Platinum	Platinum	Platinum/ ruthanium	Nickel	Nickel, Perovskites
Efficiency	40-50%	60%	37-42%	30-40%	> 50%	> 50%
Anode Reaction	$H_2 = 2H^+ + 2e^-$	$H_2 + 2(OH)^- = 2H_2O + 2e^-$	$H_2 = 2H^+ + 2e^-$	$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$	$H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$	$H_2 + O_2^- = H_2O + 2e^-$
Cathode Reaction	$1/2O_2 + 2H^+ + 2e^- = H_2O$	$1/2O_2 + H_2O + 2e^- = 2(OH)^-$	$1/2O_2 + 2H^+ + 2e^- = H_2O$	$3/2O_2 + 6H^+ + 6e^- = 3H_2O$	$1/2O_2 + CO_2 + 2e^- = CO_3^{2-}$	$1/2O_2 + 2e^- = O^{2-}$

Conversion with FC 91.8%

Conversion with ICE 31.8%

Elec.

Electricity
Exergy 3779.7 [kJ]
Energy 3779.7 [kJ]

Chem.

4.62mol-CH_4
Exergy 3779.7 [kJ]
Energy 4116.2 [kJ]

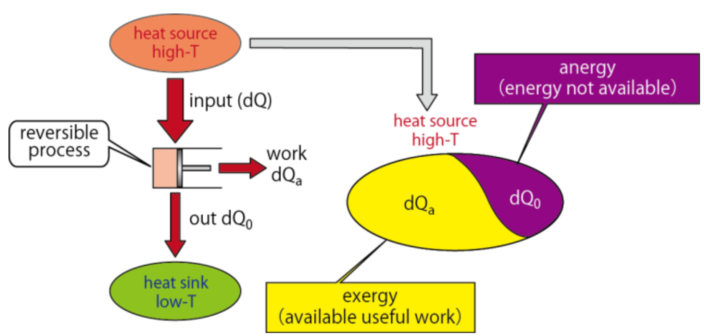
Ther.

Exhausted Heat
Exergy 0.0 [kJ]
Energy 336.5 [kJ]

$E = (H_2-H_1) - T_0(S_2-S_1)$

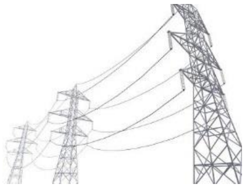
Ther.

Steam(1073K)
Exergy 1309.3 [kJ]
Energy 4116.2 [kJ]



Elec.

Electricity
Exergy 1309.3 [kJ]
Energy 1309.3 [kJ]

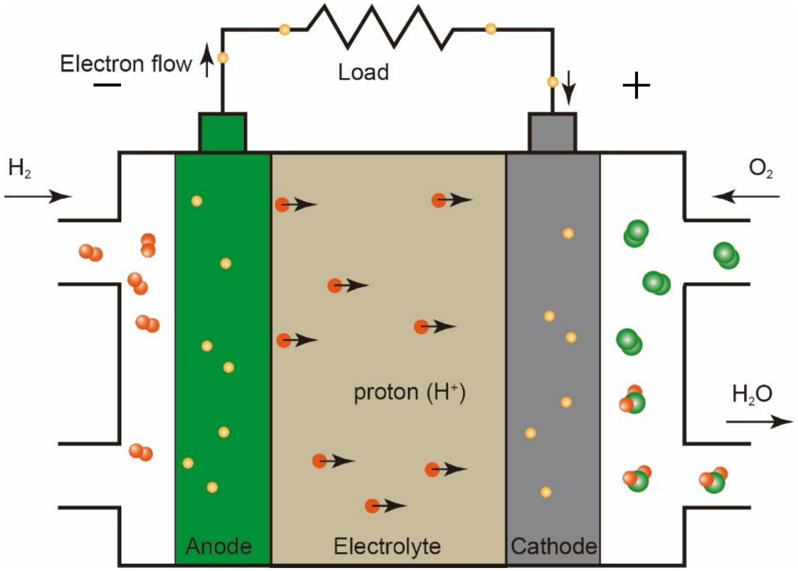


Ther.

Exhausted Heat
Exergy 0.0 [kJ]
Energy 2806.6 [kJ]

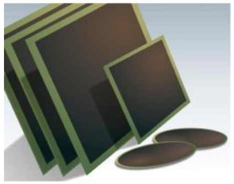
Working principle in PEMFC and SOFC

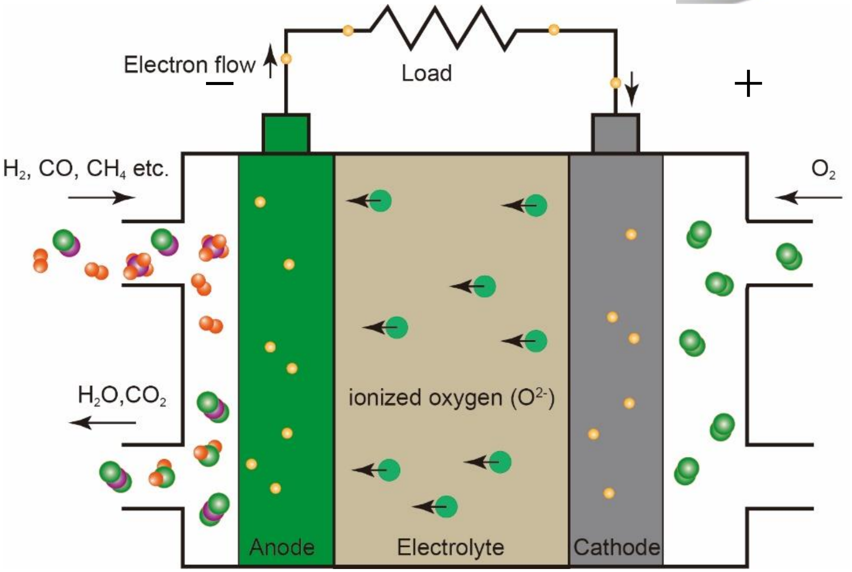
Proton Exchange Membrane FC



Temp.	: 50-100℃
Fuel.	: H_2 only (City Gas with reformer)
Electrolyte	: Solid polymer membrane
Reaction ion	: Proton (H^+)
Catalyst	: Pt-based
Application	: Vehicles, Mobiles, CHP
Operation	: Quick start/stop

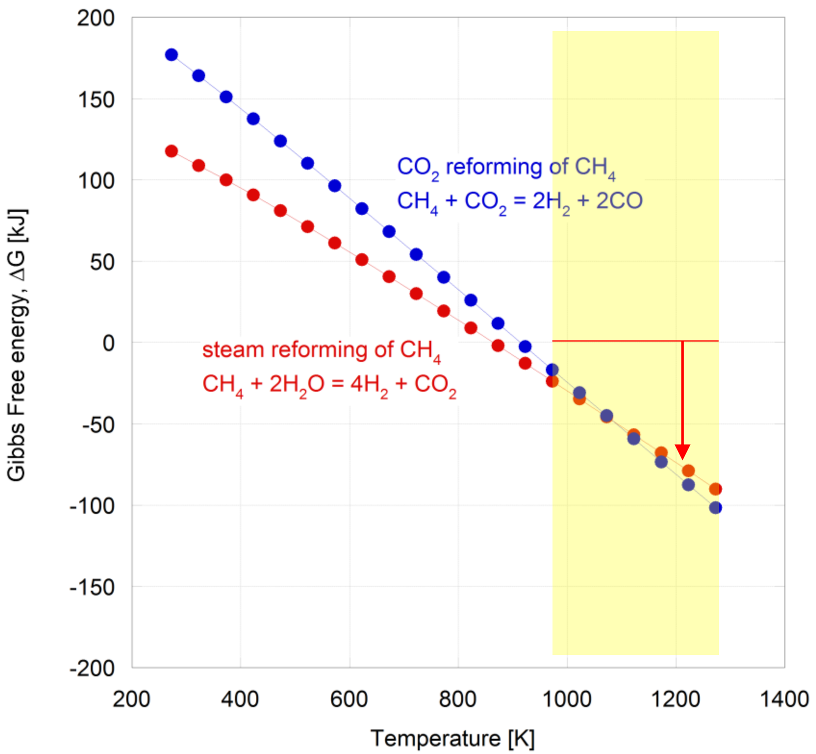
Solid Oxide FC





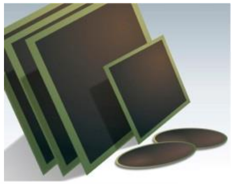
Temp.	: 500-1000℃
Fuel.	: H_2, Hydrocarbons (without reformer)
Electrolyte	: Ceramic oxide
Reaction ion	: Ionized oxygen (O^{2-})
Catalyst	: Ni, Perovskite
Application	: large scale CHP
Operation	: Steady operation

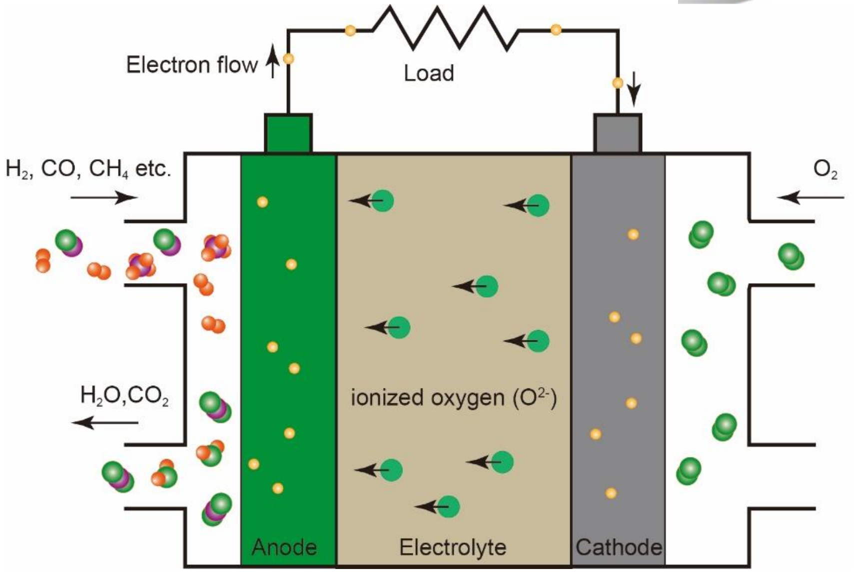
Fuel flexibility in SOFC: Internal and spontaneous reforming in high-T SOFC.



When ΔG is negative, a process will proceed spontaneously.

Solid Oxide FC





Temp.	: 500-1000℃
Fuel.	: H_2, Hydrocarbons (without reformer)
Electrolyte	: Ceramic oxide
Catalyst	: Ni, Perovskite
Application	: large scale CHP
Operation	: Steady operation

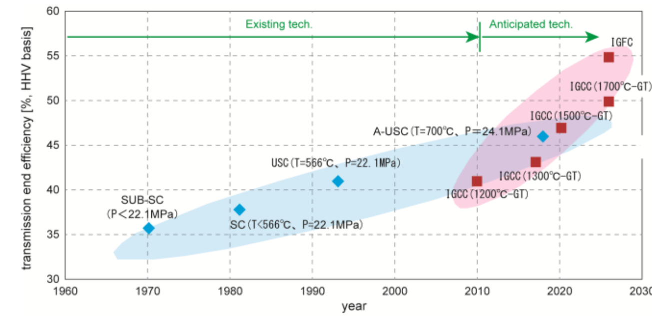
SOFC Operation in conjunction with biomass gasification.

Lessons learned from our previous works about degradation behaviors of SOFC due to the chemical interaction between trace gaseous impurities in coal syngas and Ni-YSZ anode.

Relevant papers on this topics:

Kuramoto et al., ECS Transactions, 25(2) 2149-2154 (2009)
Kuramoto et al., ECS Transactions, 41(12) 81-90 (2012)
Kuramoto et al., ECS Transactions, 57(1) 3077-3086 (2013)
Kuramoto et al., Fuel Processing Technology, 160 8-18 (2017)

Advancement in coal conversion tech.



Pulverized Coal Fired Power Generation

Coal — Boiler — Steam Turbine

Integrated Gasification Combined Power Generation (IGCC)

Coal — Gasification — [gas cleaning] — Gas turbine — Heat Recovery Boiler — Steam Turbine

gas cleaning

Integrated Gasification Fuel Cell Combined Power Generation (IGFC)

→ CO/H_2 mixtures

Coal — Gasification — [gas cleaning] — Gas turbine / Fuel Cell — Heat Recovery Boiler — Steam Turbine

gas cleaning

Integrated Gasification Fuel Cell Combined Power Generation with CCS (A-IGFC)

→ H_2 enriched gas

Coal — Gasification — CCS — [ ] — Gas turbine / Fuel Cell — Heat Recovery Boiler — Steam Turbine

SHIFT: $CO + H_2O \rightarrow H_2 + CO_2$

CO_2 to be fixed

IGCC in Japan: Past, present and future

IGCC
↓
IGCC+CCS

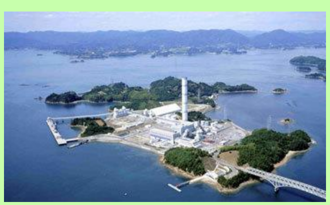
x8 Scale-up

IGCC
↓
IGCC+CCS
↓
IGFC with CCS

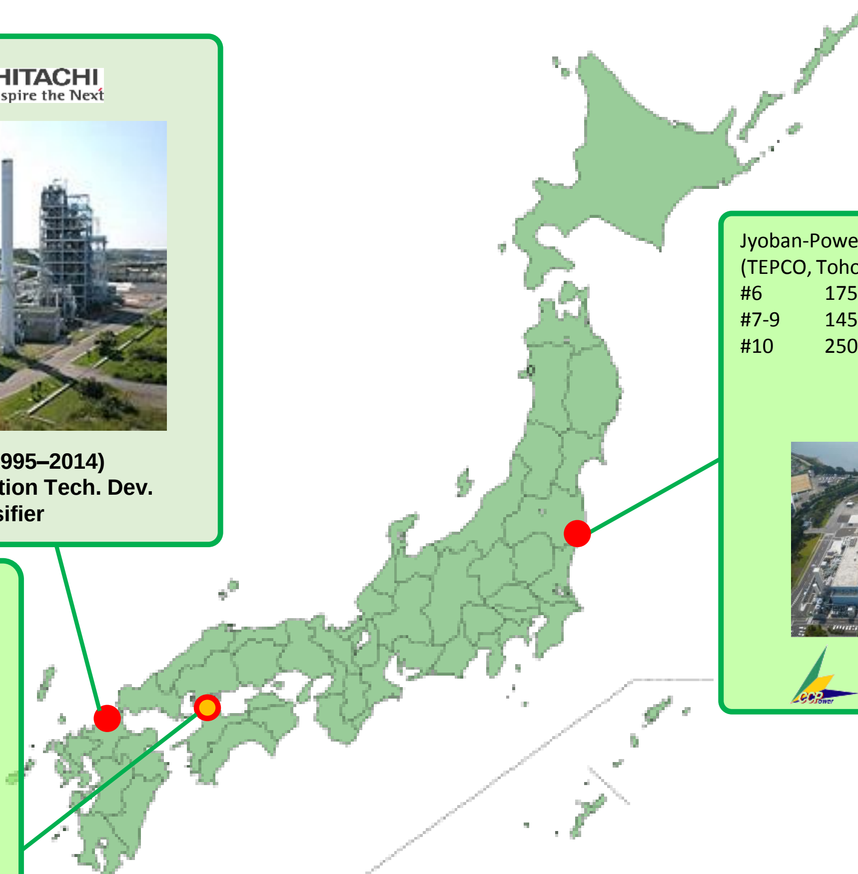
J-POWER, NEDO, HITACHI Inspire the Next

EAGLE demonstration PJ (1995–2014)
Multi-purpose Coal Gasification Tech. Dev.
8MW (150t/d)、O_2-blown gasifier

J-POWER, Energia 中国電力



Osaki CoolGen PJ (2012-)
170MW (1180t/d)



Jyoban-Power co. at Nakoso
(TEPCO, Tohoku-EPCO)

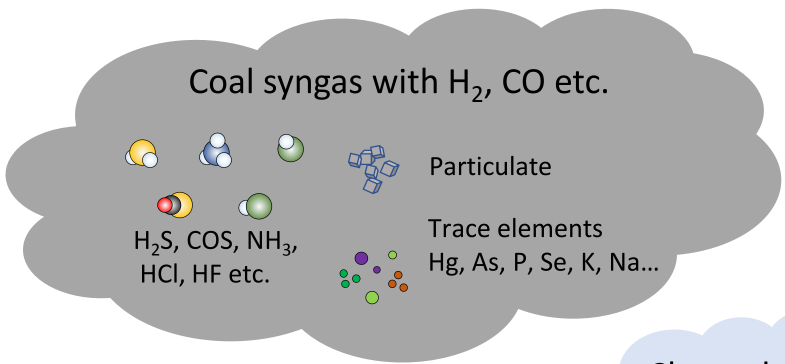
#6	175MW (Oil-fired)
#7-9	1450MW (PCC)
#10	250MW (IGCC-1700t/d)

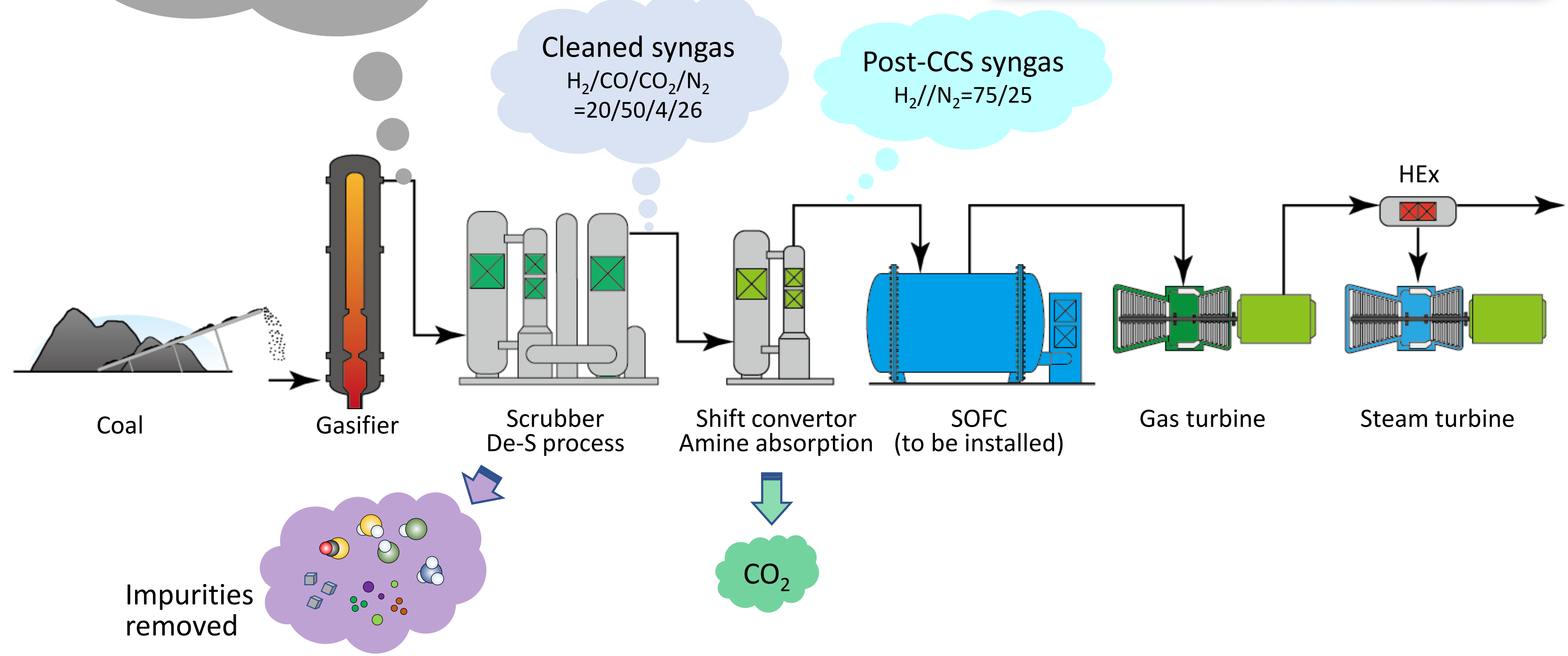
三菱重工 この星に、たしかな未来を

OCG PJ.: Large-scale IGCC, CCS, IGFC demonstration plant in Hiroshima

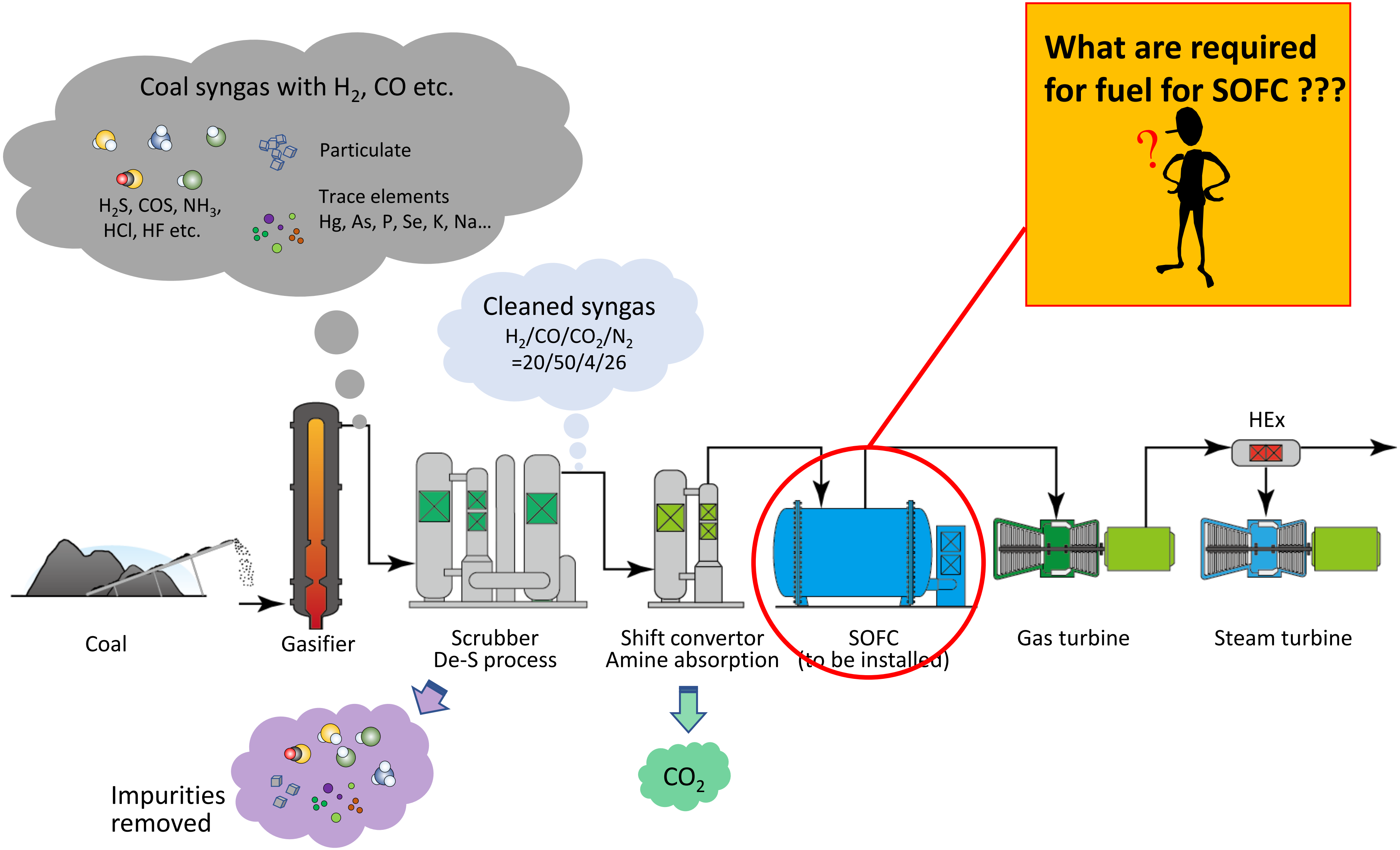
Demonstration PJ on IGCC+CCS/A-IGFC in Japan
http://www.osaki-coolgen.jp/english/index.html

Integrated Gasification Fuel Cell (IGFC) power plants (Anticipated)

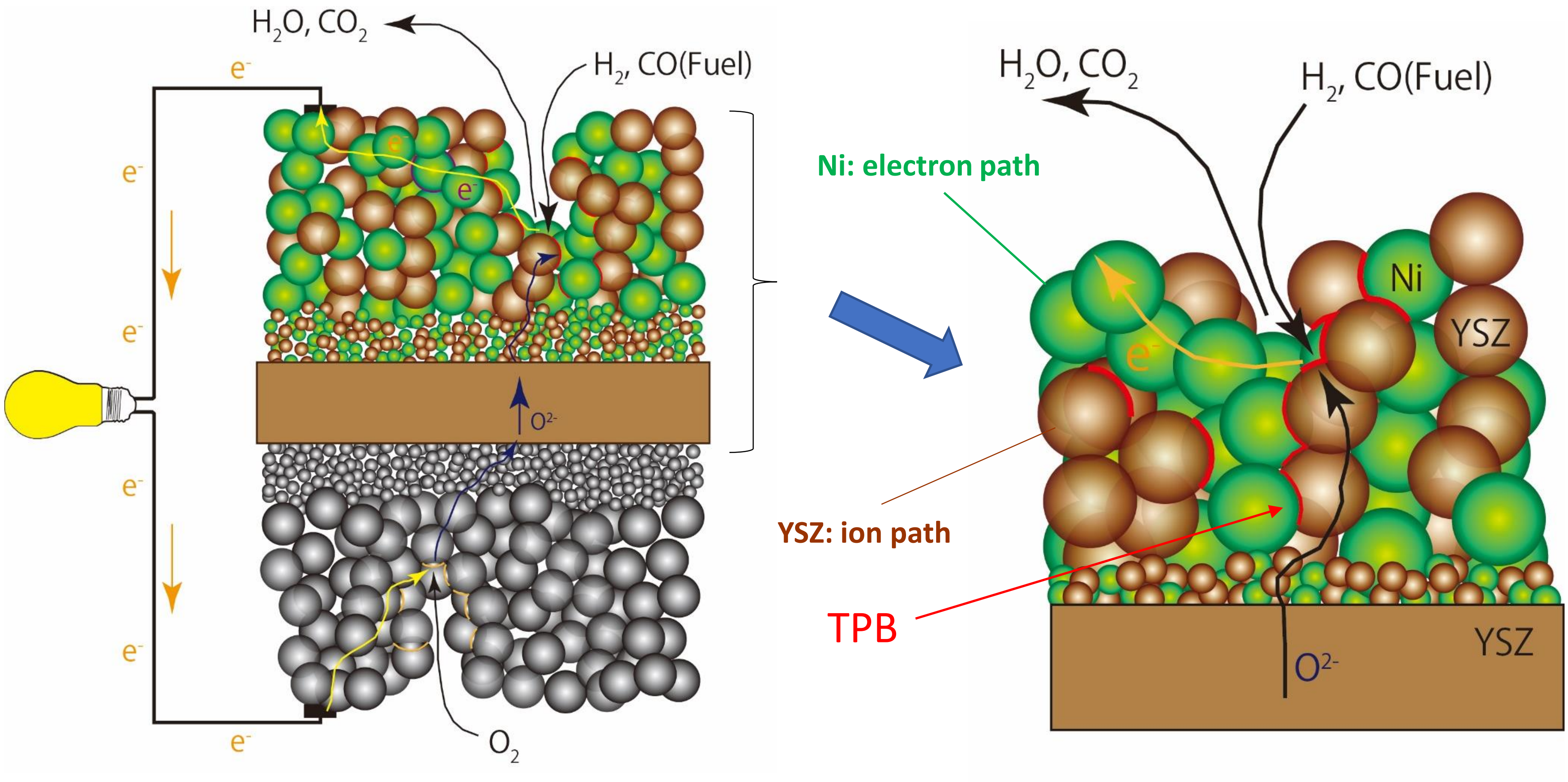




Integrated Gasification Fuel Cell (IGFC) power plants (Anticipated)



Relevant reactions in SOFC power generation

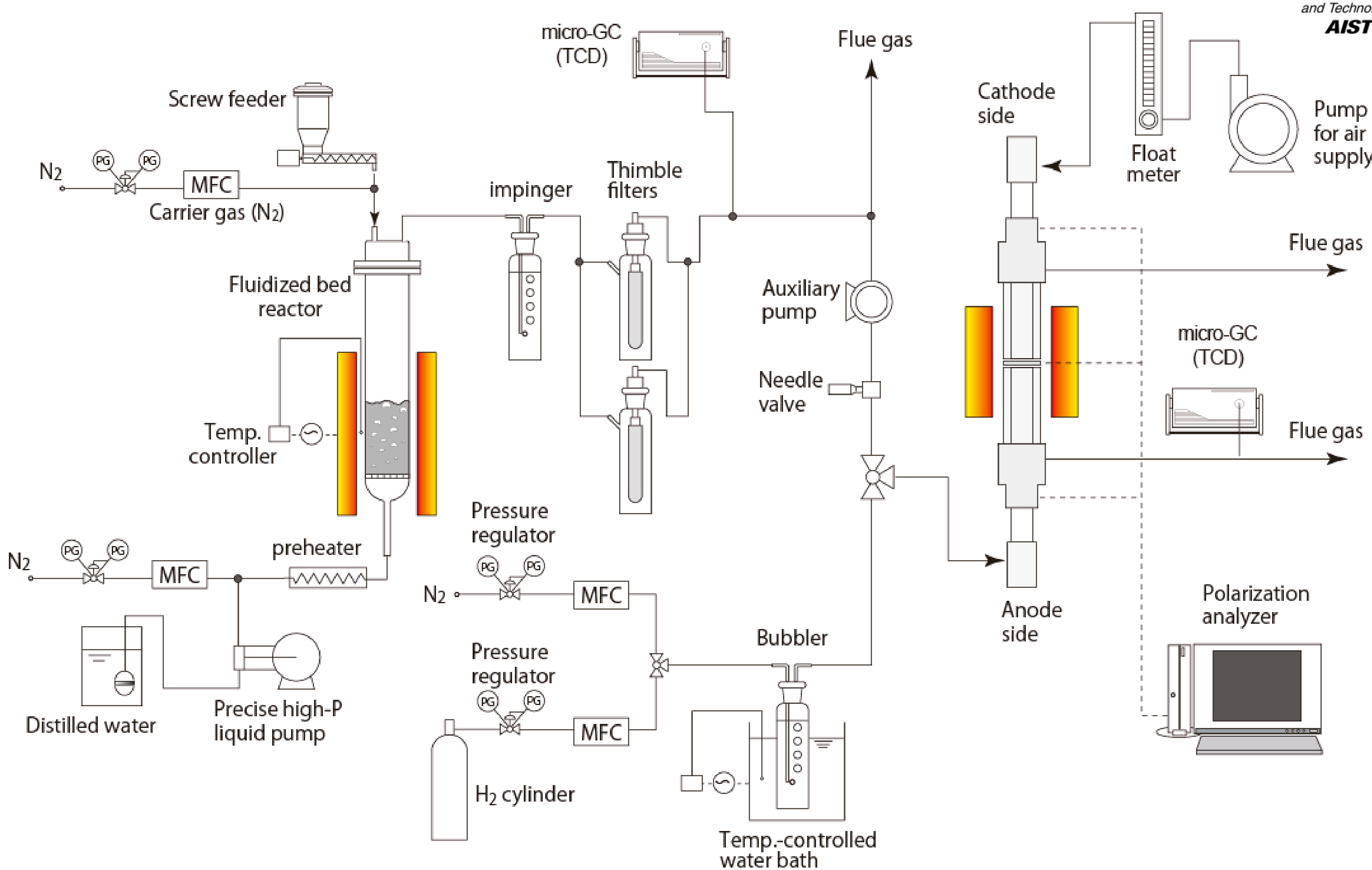


Anodic reaction: $2H_2 + 2O^{-2} \rightarrow 2H_2O + 4e^-$ & $CO + O^{-2} \rightarrow CO_2 + 2e^-$

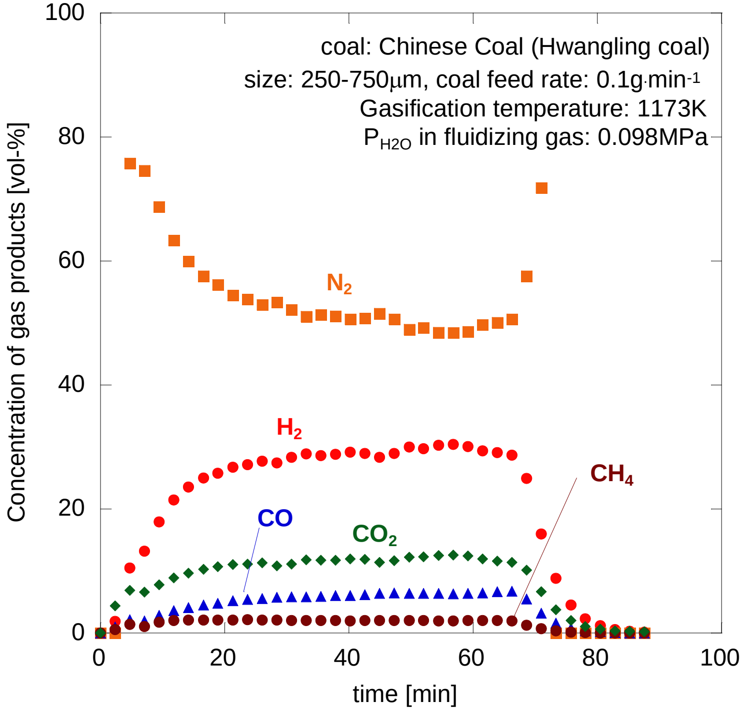
Cathodic reaction: $O_2 + 4e^- \rightarrow 2O^{-2}$

Total reaction: $2H_2 + O_2 \rightarrow 2H_2O$ & $2CO + O_2 \rightarrow 2CO_2$

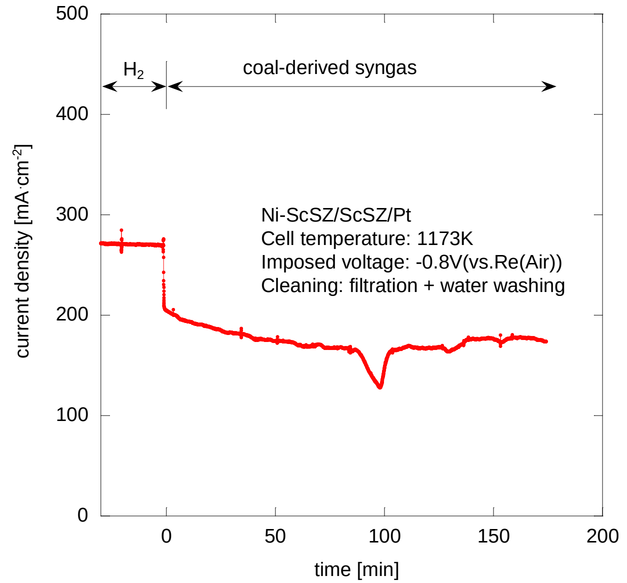
Experimental setup for SOFC power generation tests with direct feed of syngas from steam reforming of coal



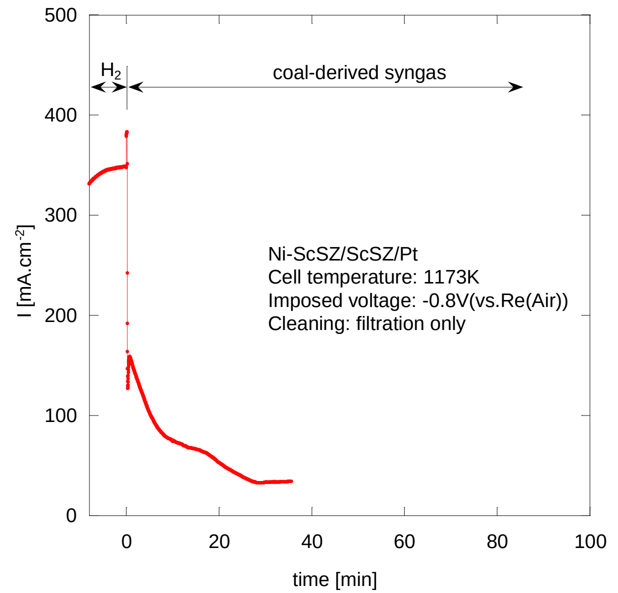
Raw syngas-feed test: Remarkable performance loss of SOFC



with filtration plus water washing

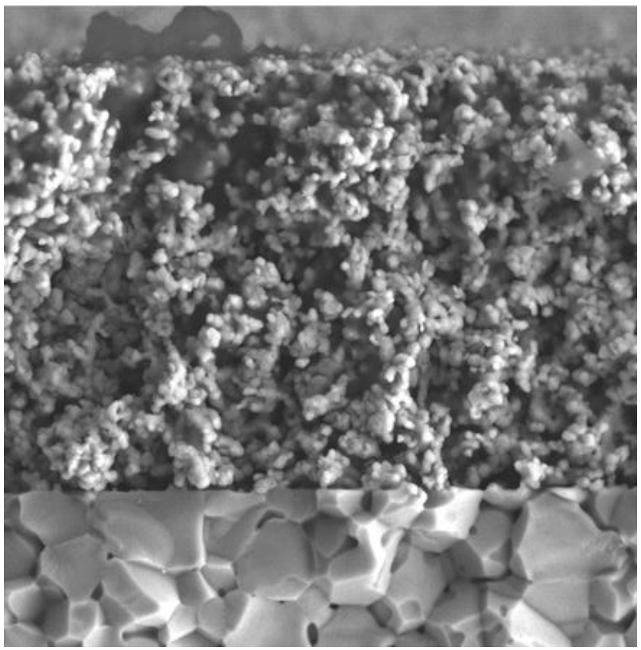


with filtration only



SEM observation of spent SOFC anode: wet H_2 (left) and coal syngas (right)

spent cell in test fueled by wet H_2



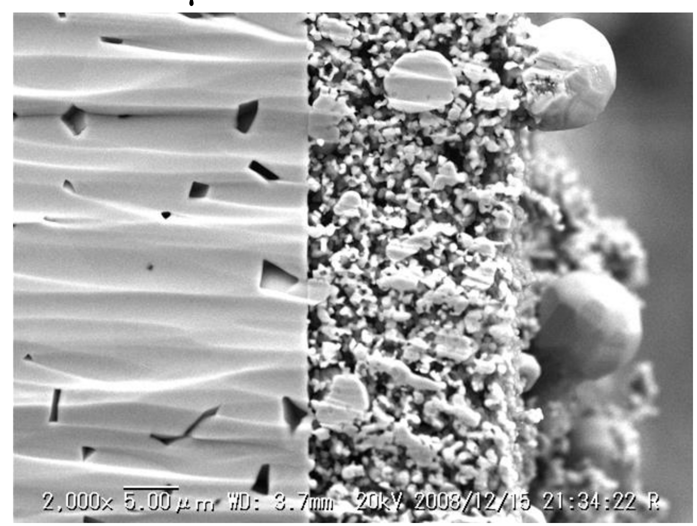
anode (Ni-based)

electrolyte

5μm

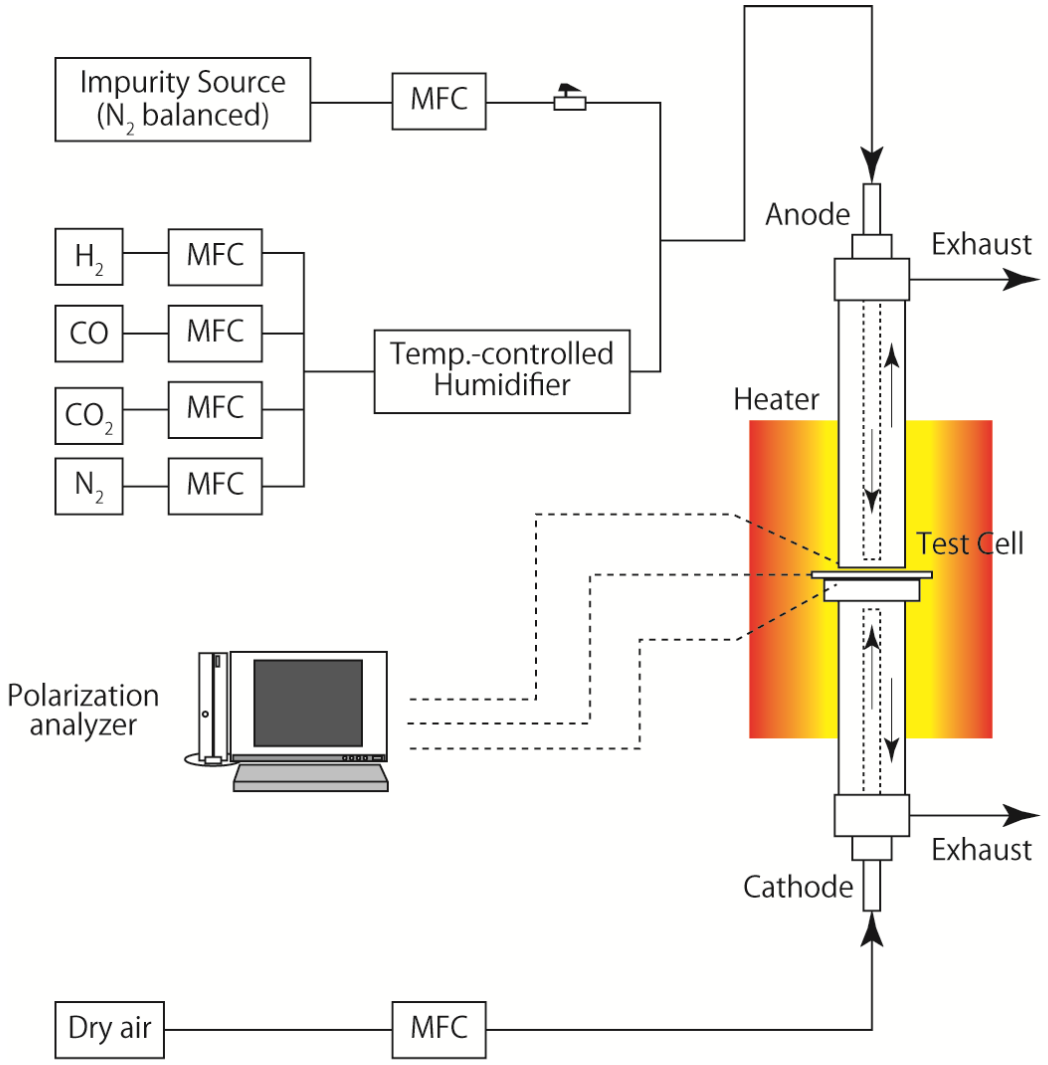
spent cell in test fueled by coal syngas

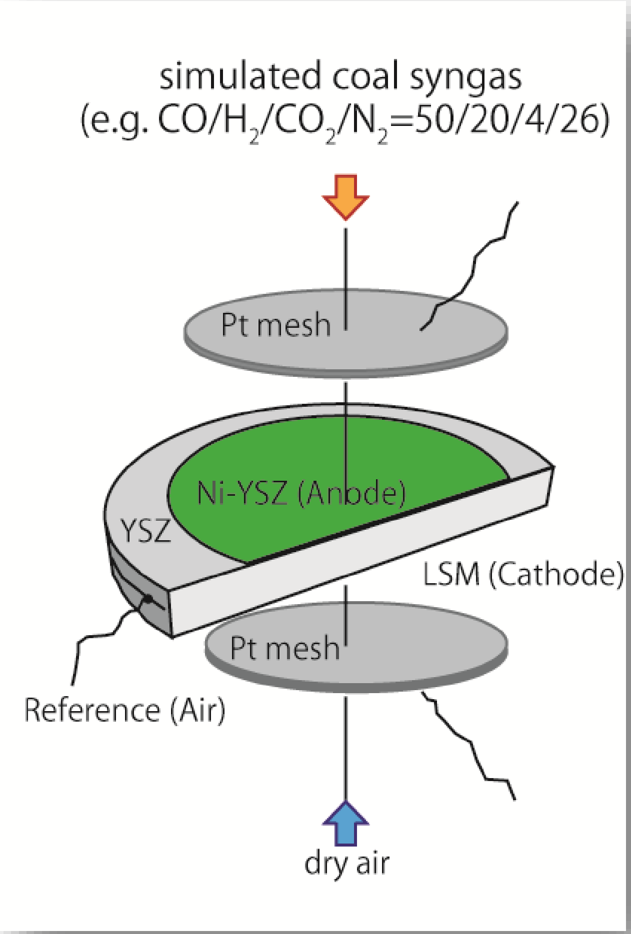
10μm



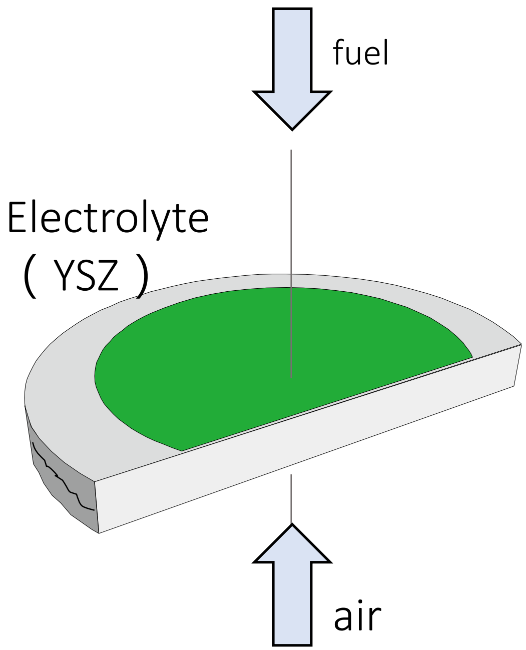
5μm

Experimental apparatus for fuel cell test at AIST ~ Simulated coal syngas injection test ~





Attempts to clarify the allowable range of H_2S under different fuel operations with post-CCS gas and coal syngas



- **Fuel gas**

  Case 1: Simulated coal syngas
  ($CO/H_2/CO_2/N_2/H_2O$ = 42/17/22/3/17 [mol%])

  Case 2: Hydrogen-enriched fuel gas (Post-CCS)
  ($H_2/N_2/H_2O$ = 80/3/17 [mol%])

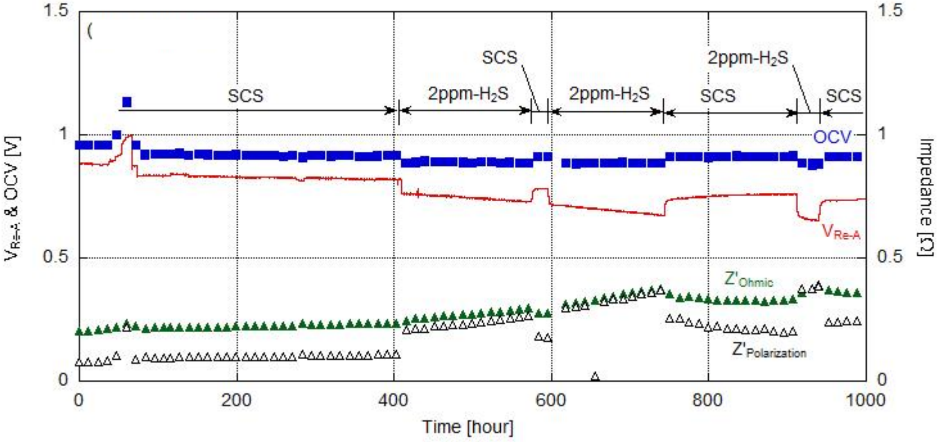
- **Trace H_2S as a possible impurity in practice**

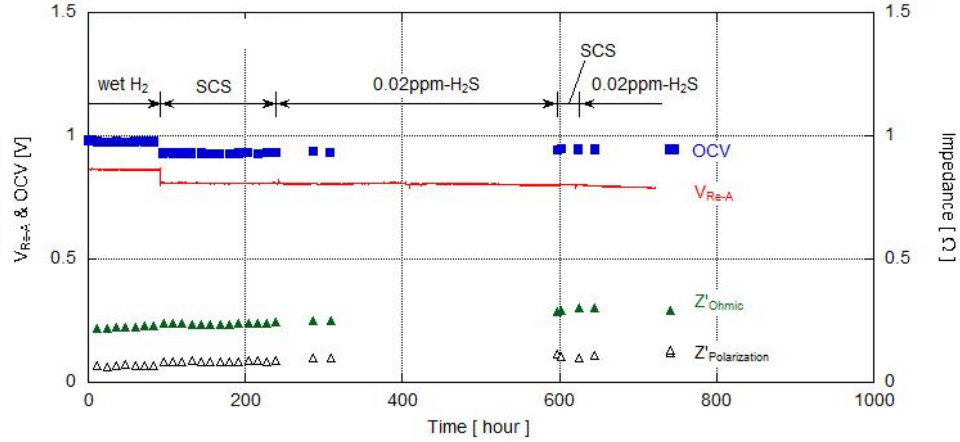
  0.02, 0.5 or 2.0ppm-H_2S

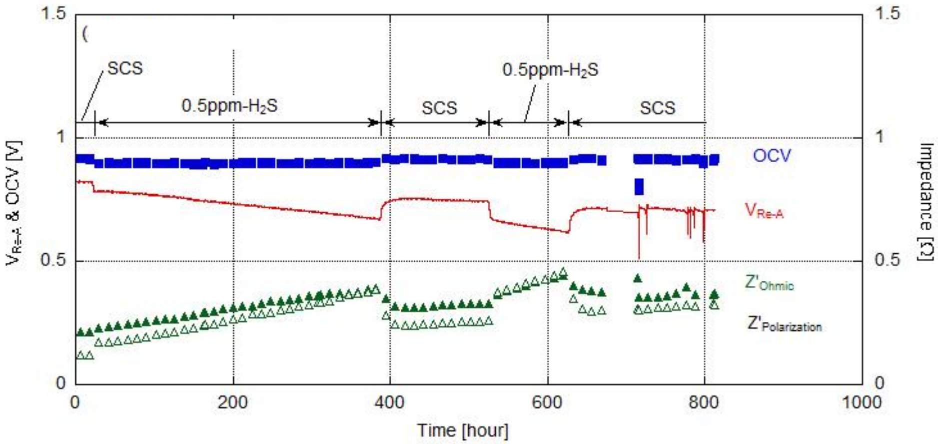
- **Test cells used**

  Nextcell (by FUEL CELL MATERIALS, USA)

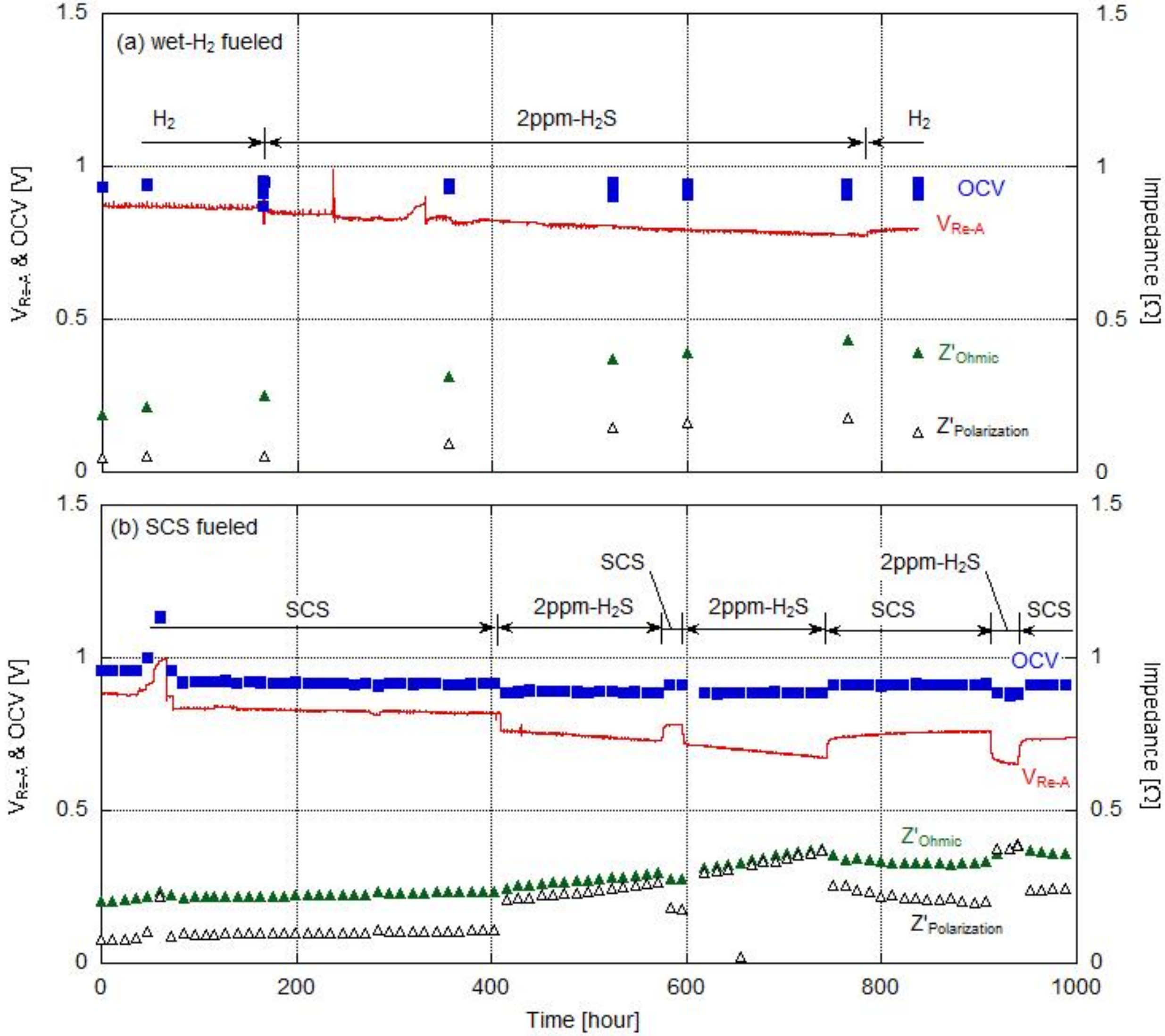
Effects of H_2S concentration on performance loss of SOFC fueled by simulated coal syngas







Effect of fuel composition on the SOFC performance loss caused by 2ppm-H_2S

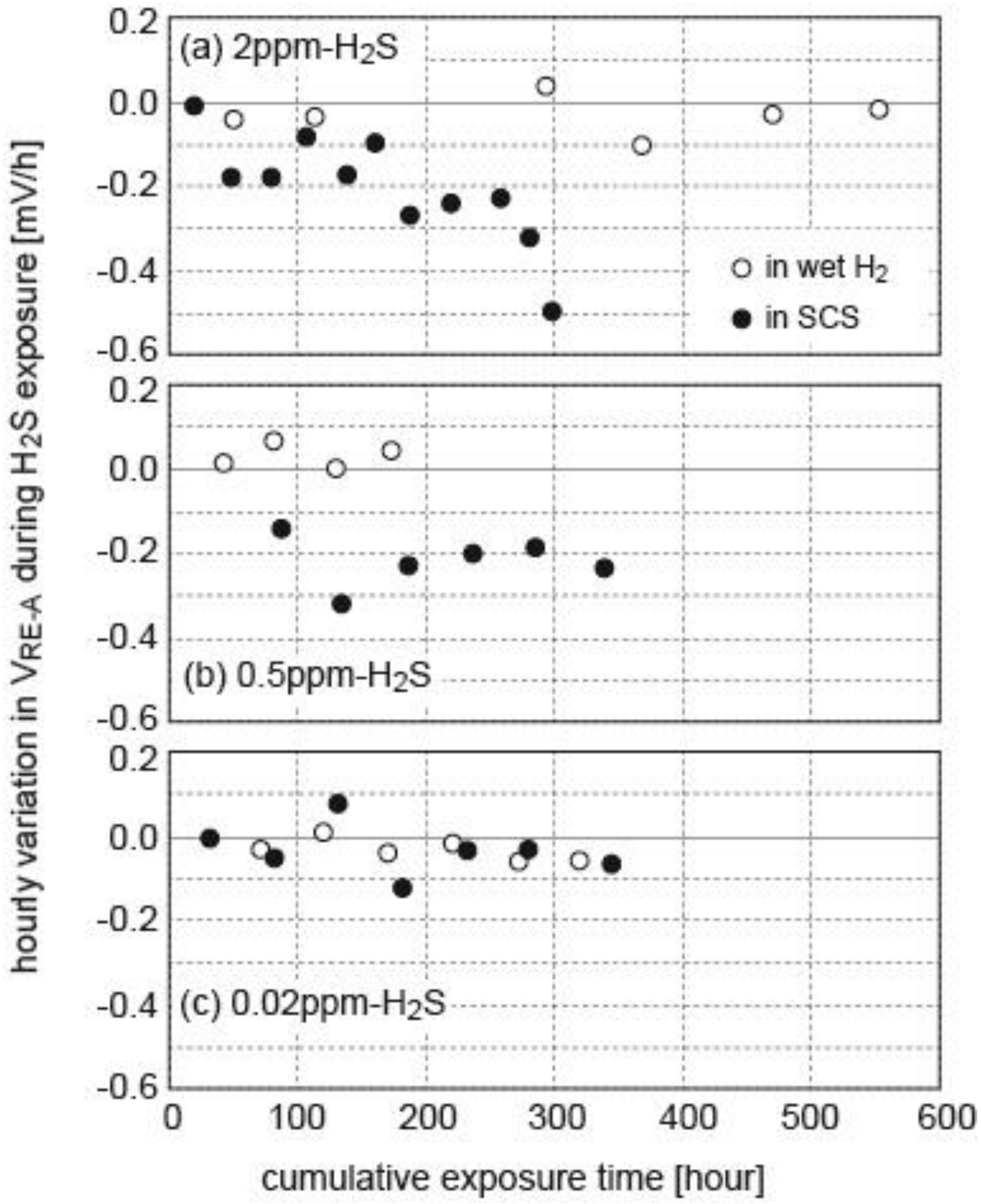


Observed change with time in the performance during the injection of trace H_2S with different concentrations.

High P_{CO} in fuel gas might cause chemical deactivation of Ni catalysis because;

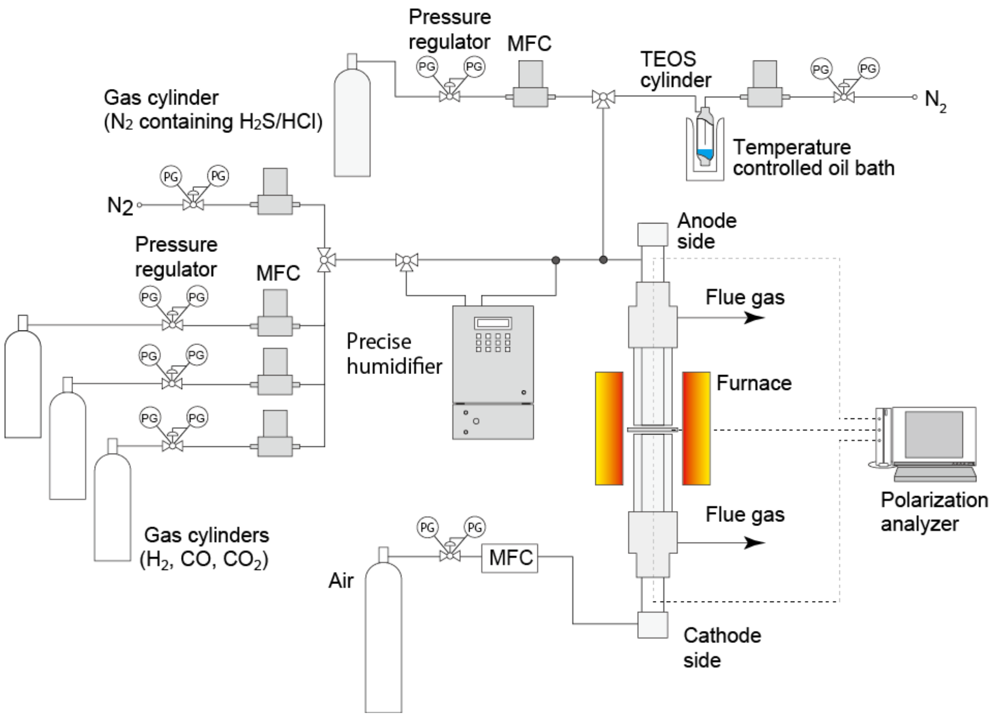
→ enhancement of S activity*

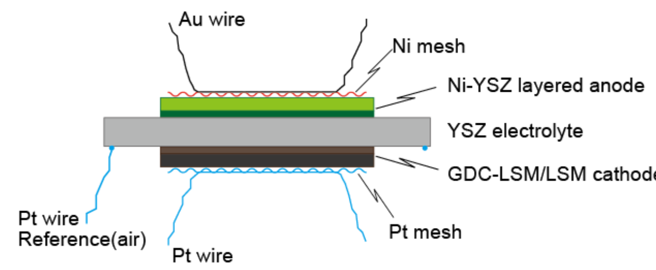
→ partial solid solution of C to Ni**



* Kishimoto et al, *J. ECS*, **157(6)**、B802 (2010)、
** Yang et al., J. Crystal Growth, 187, 81(1998)

Experimental setup for H_2S/HCl/TEOS exposure tests

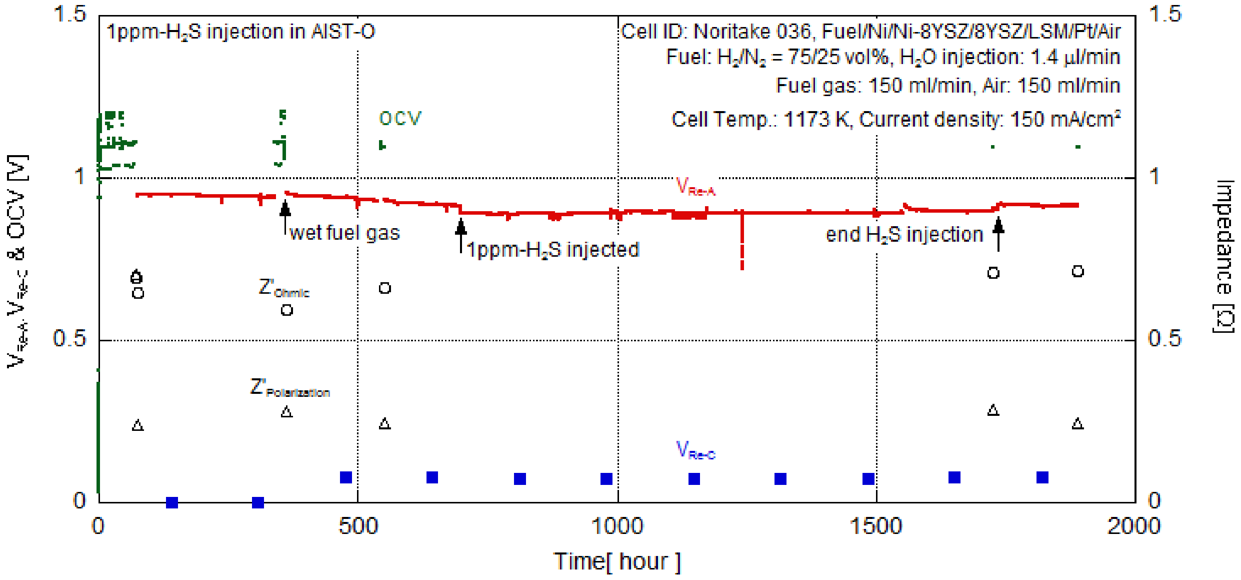




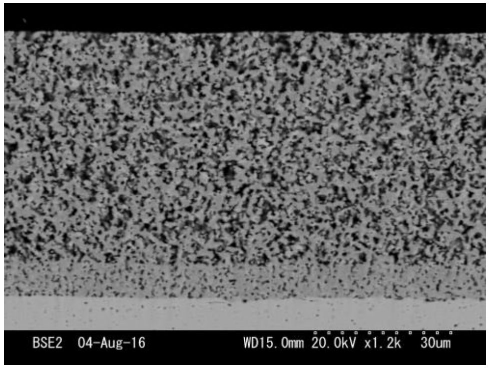
For Power generation test of SOFC single cell

- Cell temperature ： 1173K (900℃)
- Configuration ： Fuel gas/Ni mesh/Ni-YSZ/YSZ/LSM-GDC/LSM/Pt mesh/dry air
- Fuel gas ： H_2/N_2 = 75/25 [vol-%] (simulated post CCS fuel gas)
- Impurities doped ： H_2S 1, 3.3, 6.6ppm
  HCl 1, 10ppm
  $Si(OC_2H_5)_4$ 0.14, 0.24ppm (TEOS)

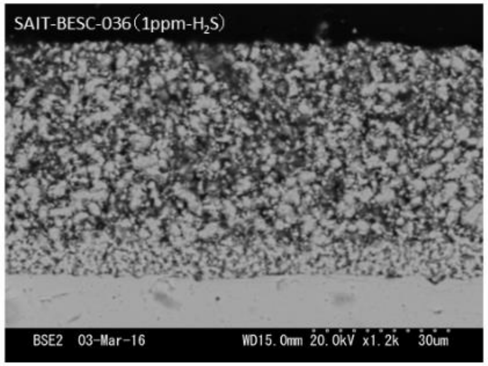
H_2S Exposure test: Effect of time of H_2S exposure on the cell performance



Before

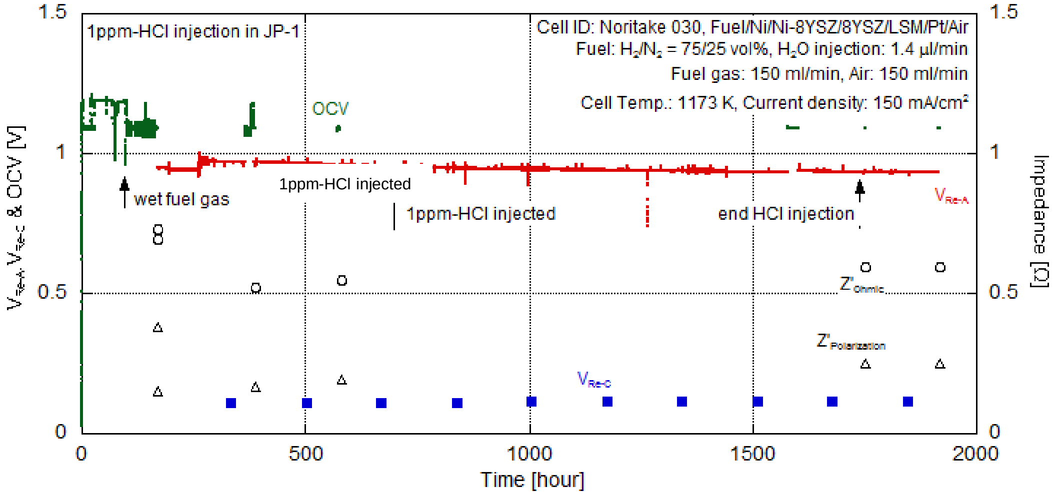


after

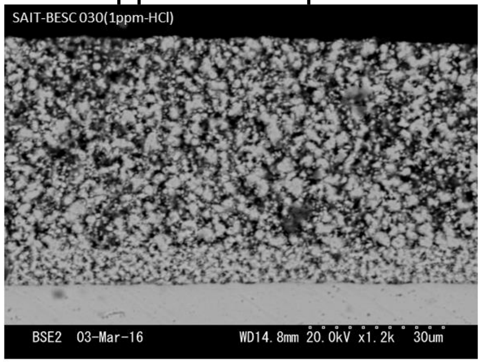


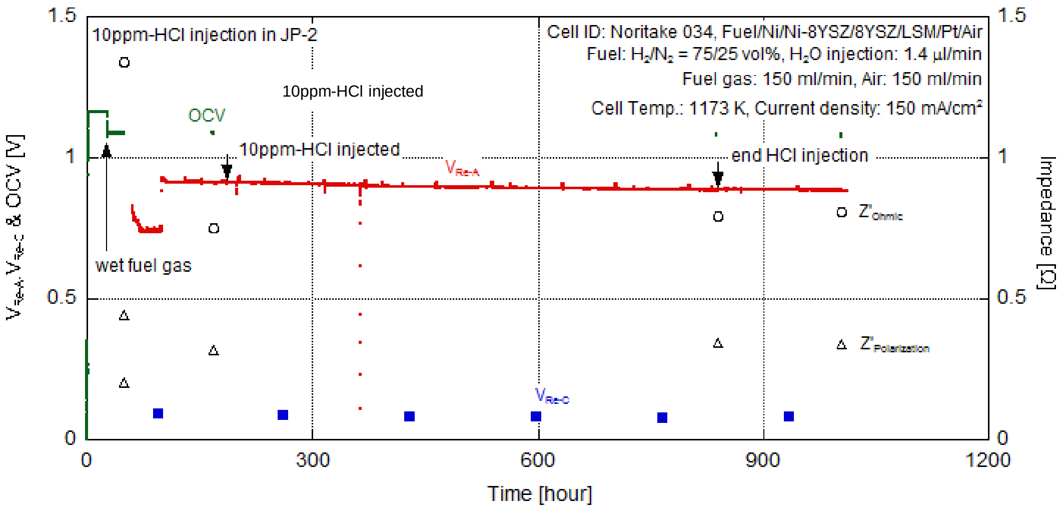
- A step-wise voltage drop was observed soon after the 1ppm-H_2S introduction.
- No further performance loss can be seen after the initial voltage drop for 1000hours.
- The voltage was recovered to initial level even after the 1000-hours H_2S exposure. (recoverable)
- SEM observation confirms that there is a little progression of sintering of component particles in anode.

HCl Exposure test: Effect of HCl conc. on the cell performance

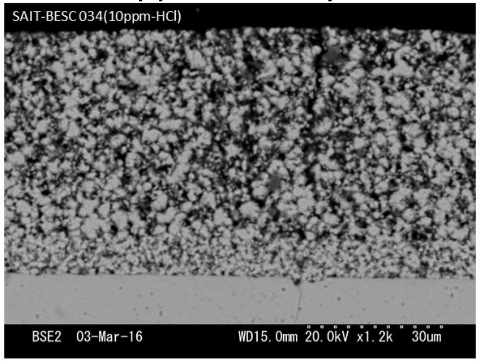


After 1ppm-HCl exposure





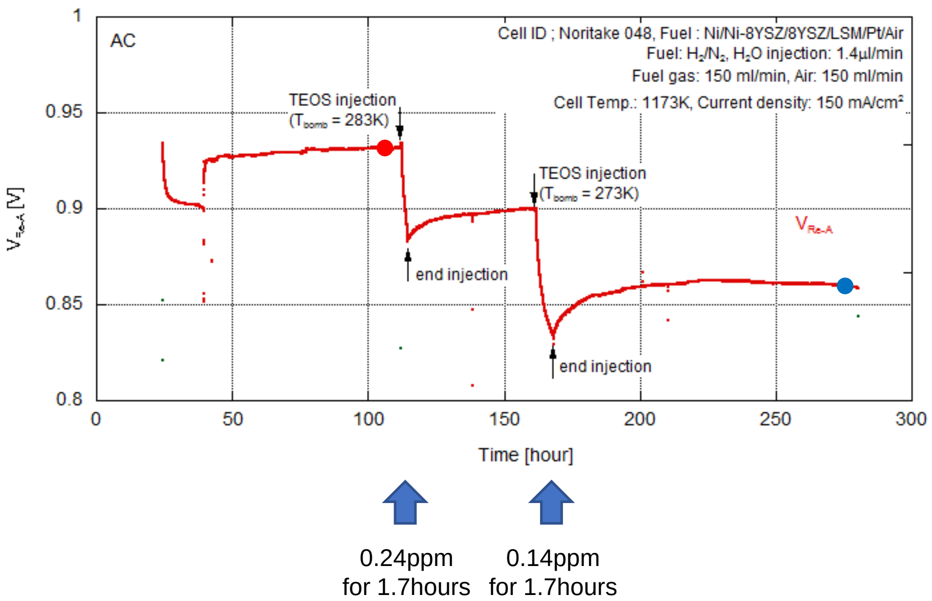
After 10ppm-HCl exposure

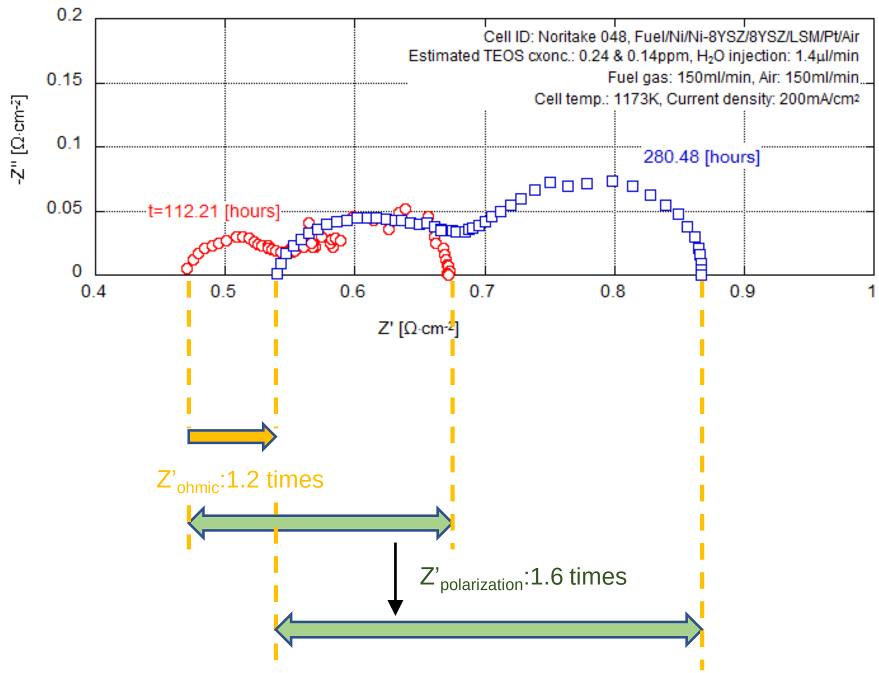


- No performance loss can be seen during the injection of 1- and 10ppm-HCl.

TEOS exposure test: Effect of Si impurities on the cell performance

Change in $V_{RE\text{-}A}$ during TEOS exposure test

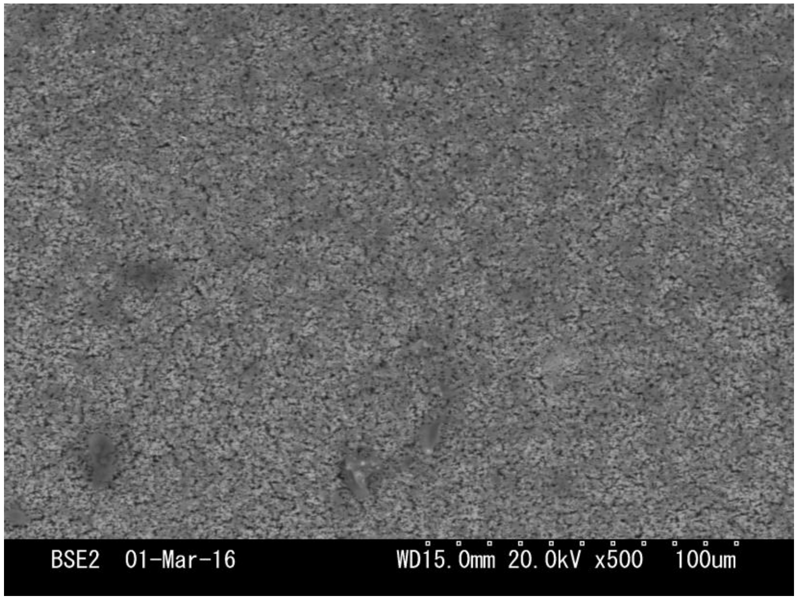


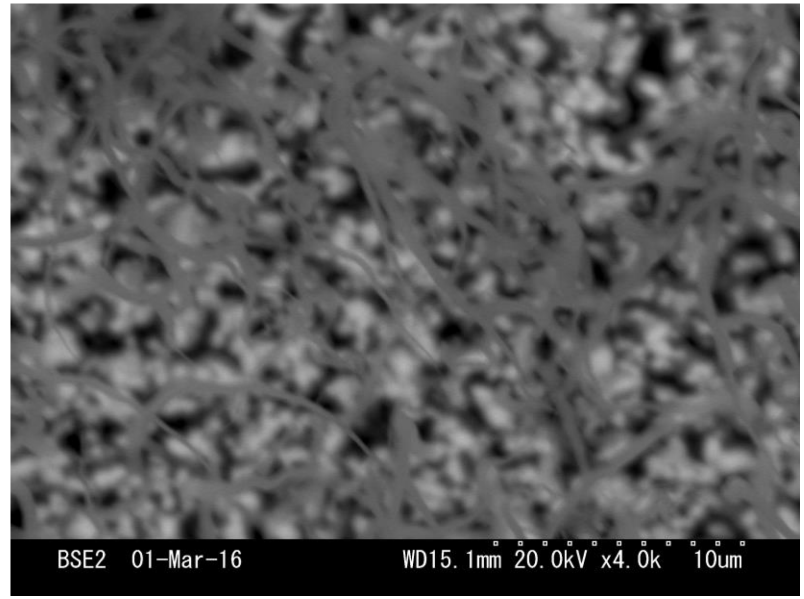


$\Delta Z'_{Ohmic} < \Delta Z'_{Polarization}$:

TEOS injection causes the increase in resistance in electrochemical oxidation and/or transportation of reactant in the anode.

BSE images of the surface of the anode exposed to TEOS vapor





Possible Si polymerization took place over the anode surface through the following reactions*:

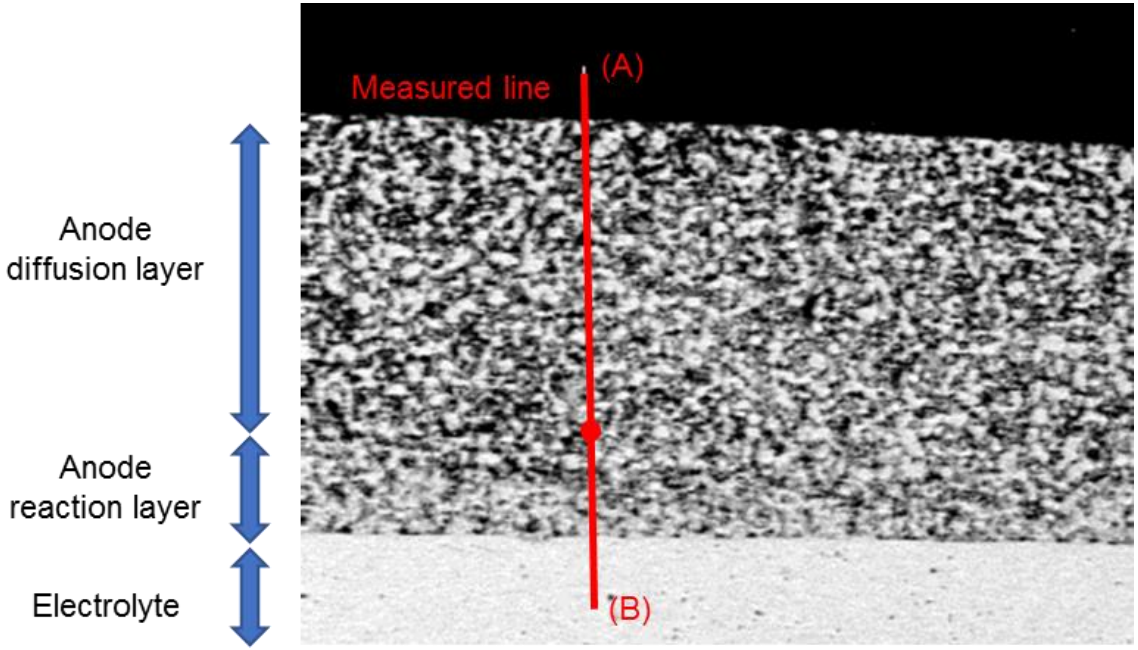
$$Si(OC_2H_5)_2 + 4H_2O = Si(OH)_4 + 4C_2H_5OH$$

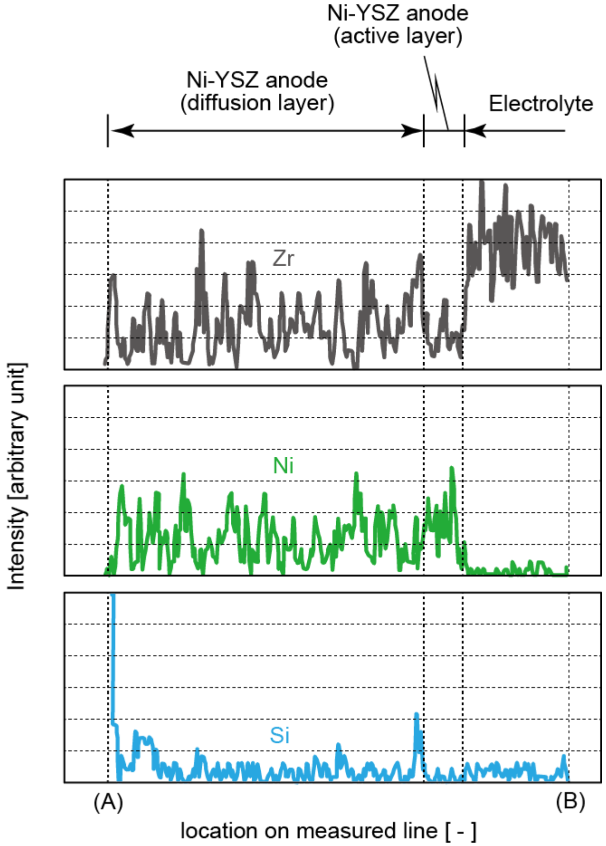
$$Si(OH)_4 = SiO_2\ (s) + 2H_2O$$

- Si deposits having a string-like appearance can be seen over the anode surface.

*Barberena-Fernández et al., Cement and Concrete Composites 55 (2015) 145–152.

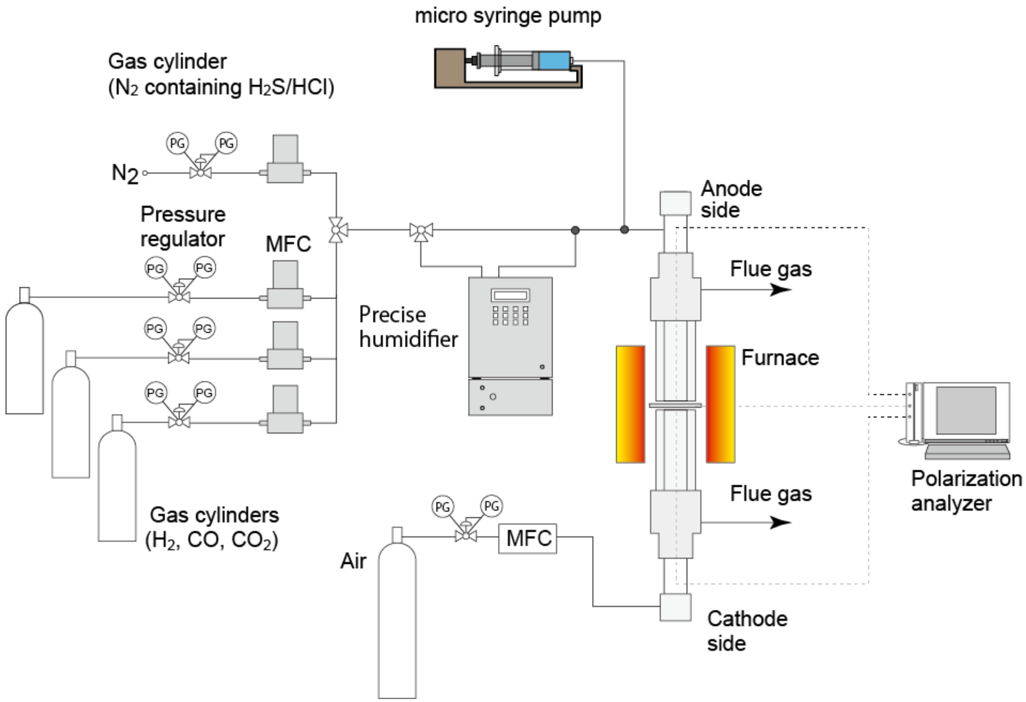
Accumulation of Si in the boundary between diffusion and reaction layers

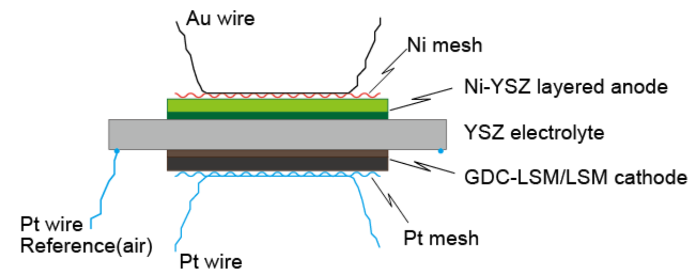




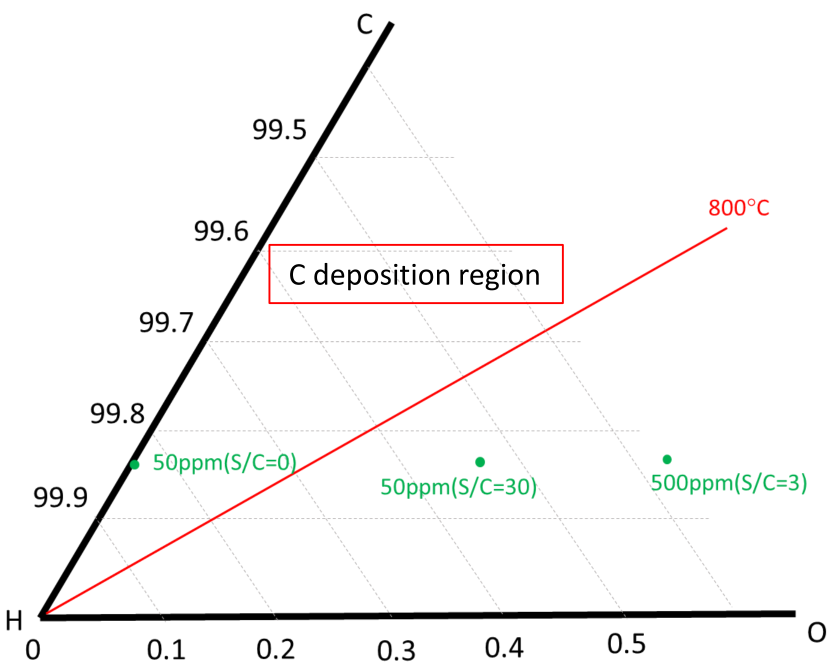
- The preferential accumulation of Si took place between the coarse diffusion layer and fine reaction layer.
- This preferentially accumulated Si might act as an obstacle for the electrochemical oxidation process.

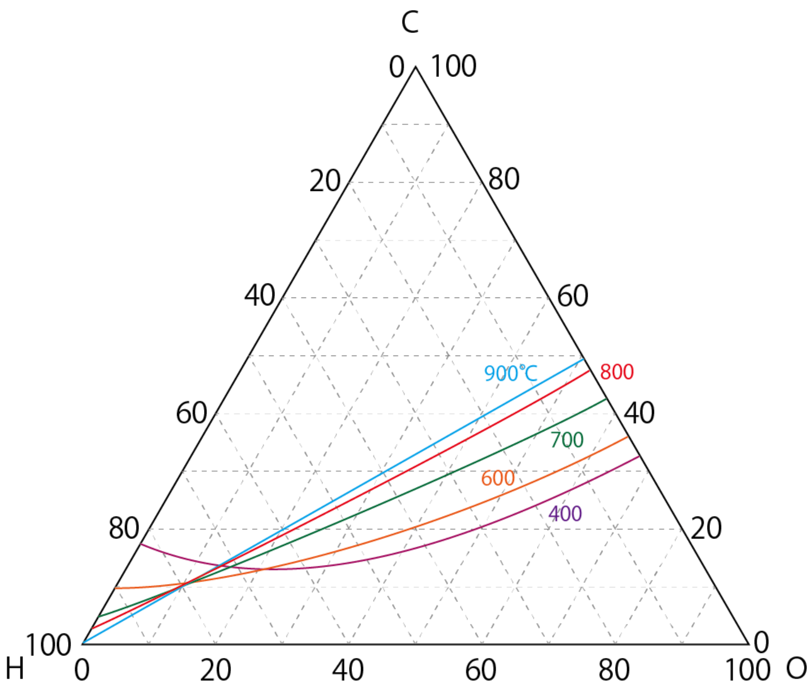
C_7H_8 Exposure test: Effect of concentration of tar on the cell performance





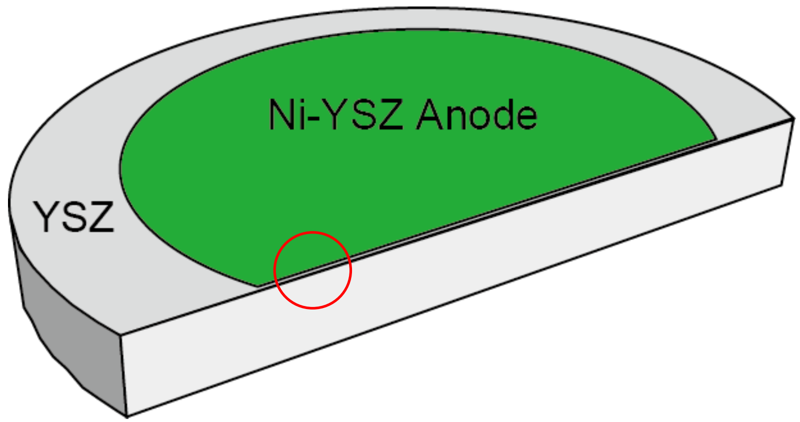
The boundary of carbon deposition region in the C–H–O phase diagram at 1 atm

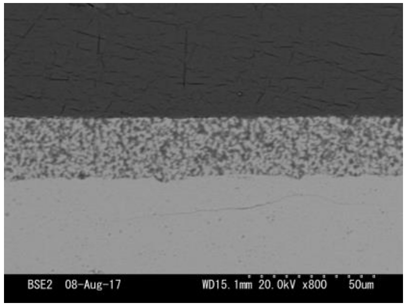




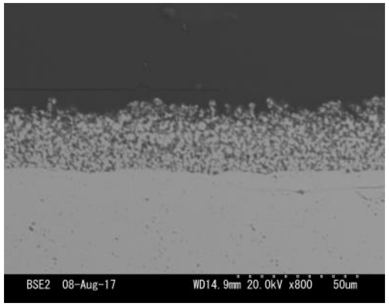
K. Eguchi, et al: *Solid State Ionics*, 152, (2002), 411-416

Partial collapsing of Ni-YSZ anode caused by carbon deposition

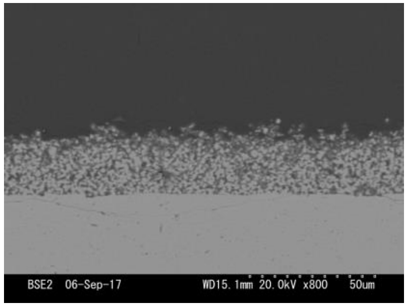




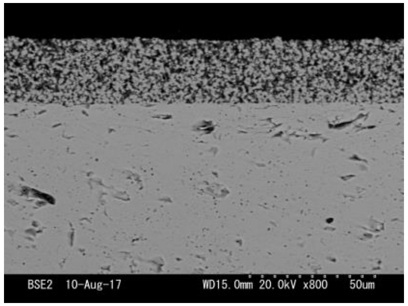
wet H_2 injected



500ppm-C_7H_8 at S/C = 3



50ppm-C_7H_8 at S/C = 0



50ppm-C_7H_8 at S/C = 30

What we found are:

1. Melting of Ni in SOFC anode occurred due to chemical interaction with trace impurities contained in coal-derived fuel gas.

2. The Ni-YSZ SOFC anode showed little performance loss during the 1000-hour 1ppm-H_2S exposure tests.

3. A step-wise voltage drop occurred soon after the H_2S injection and the extent of the voltage drop increased with H_2S concentration and current density.

4. Impact of 1-10ppm HCl contamination on performance of the Ni-YSZ anode was invisible during the present 1000-hour exposure tests.

5. Trace TEOS injection test resulted in the preferential accumulation of Si in the boundary region between the (coarse) diffusion layer and (dense) reaction layer, where the chemical oxidation of fuel proceeded.

6. The ppm levels of tar (toluene) caused partial C deposition, resulting in severe collapsing of Ni-YSZ cermet.

7. For the SOFC with biomass gasification, chemical impacts of AAEM (e.g. Na, K) on the SOFC performance are needed to be clarified.