

# Effects of Impurities on the Degradation of SOFC Stacks

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## **1. Introduction**

Degradation by impurities,  
NEDO SOFC reliability project,  
Approach to analyses

## **2. Impurity analysis of cell/stack components**

## **3. Interface analysis at cathode/interlayer/electrolyte**

(local compositional changes during operation)

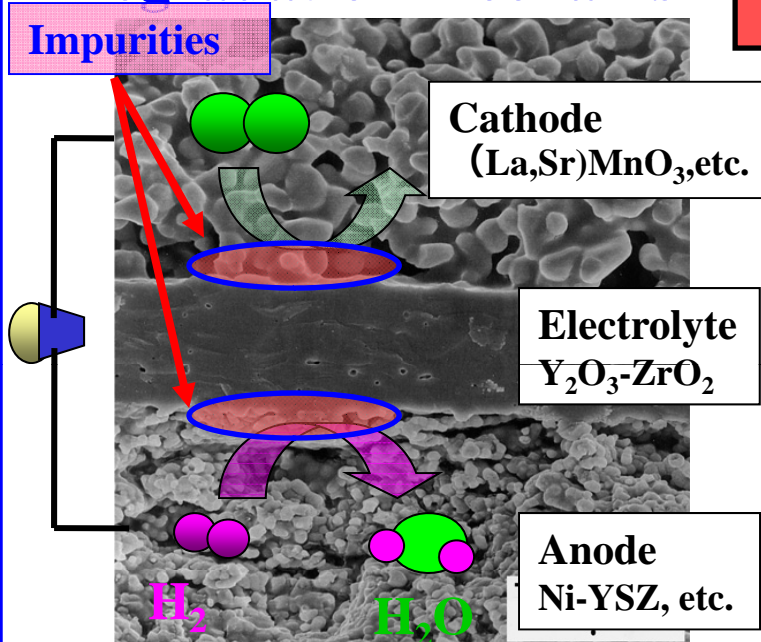
## **4. Summary**

# 1. Introduction

**Degradation by impurities,  
NEDO SOFC reliability project,  
Approach to analyses**

# Degradation by Impurities and Life Estimation

## Degradation mechanism



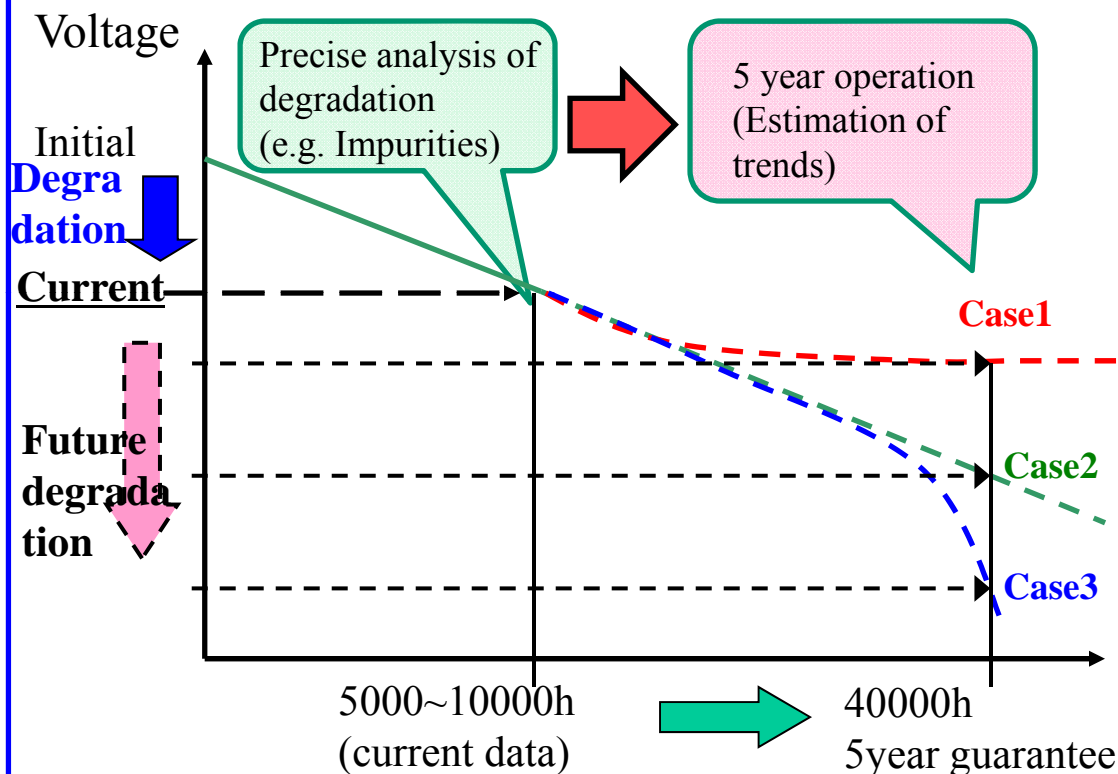
**Impurities associated with degradation**  
(Impurity level; ppm)

**Electrode activity degradation**  
(Chemical reactivity, Microstructures)

**Application of SIMS**

## Estimation of SOFC life

=necessary to commercialization



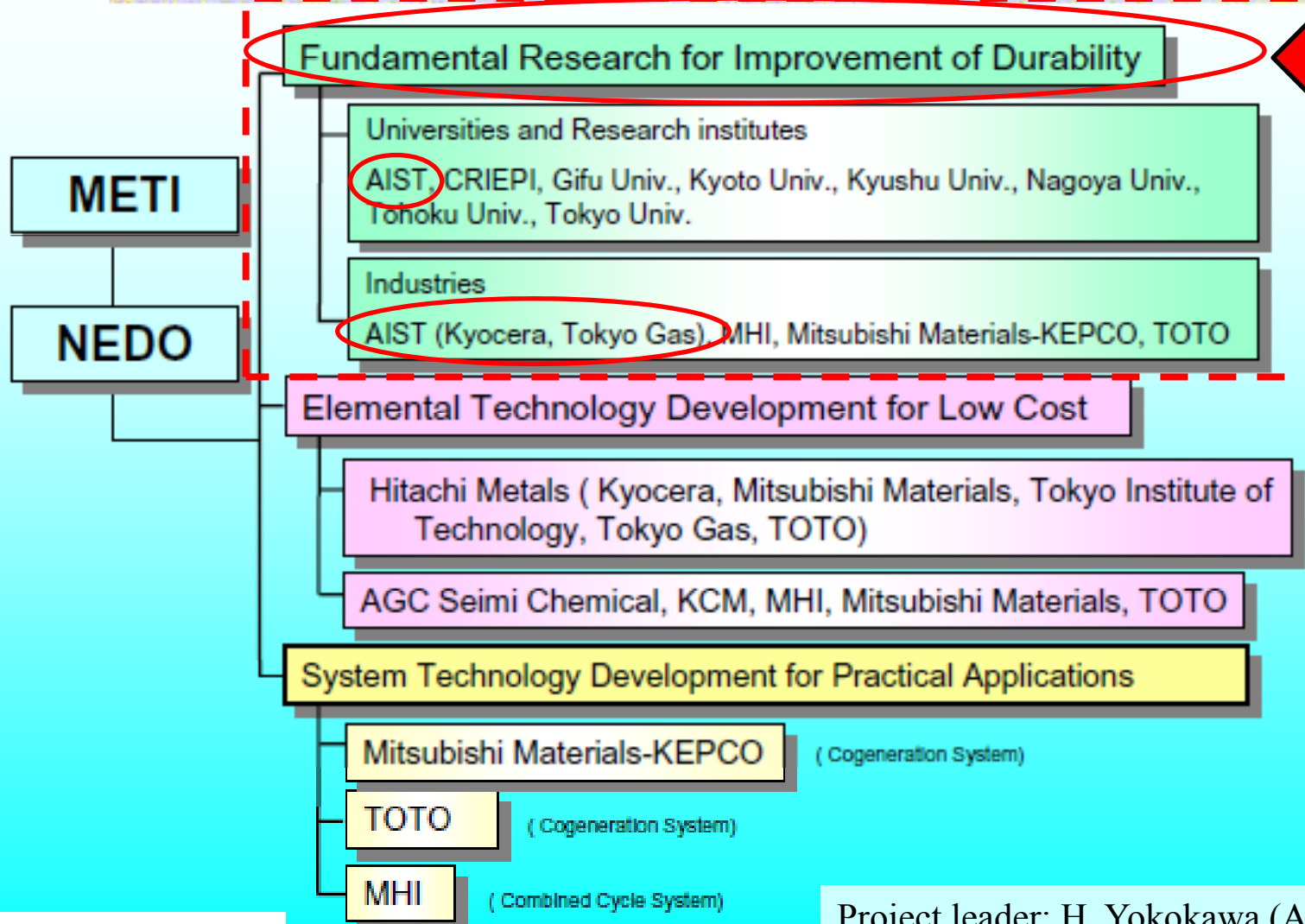
Target voltage loss: 0.25%/1000h  
If the impurity concentration is proportional to the degradation, the detection limit of impurity should be;  
**0.1 mass %=1000ppm**

# National Project for SOFC developments in JP



Project Scheme for Development of System and Elemental Technology on SOFC (2008-2012)

*This talk*



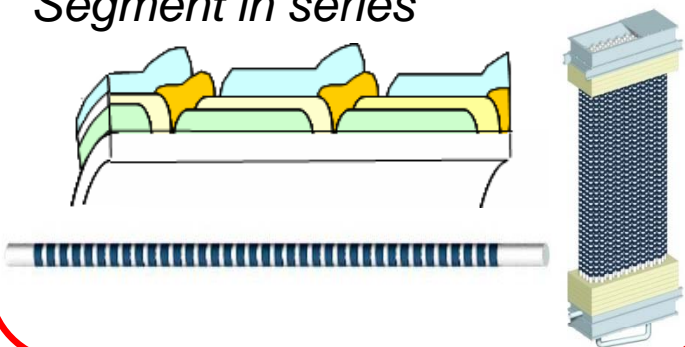
Project leader: H. Yokokawa (AIST)

# SOFC stacks for durability tests

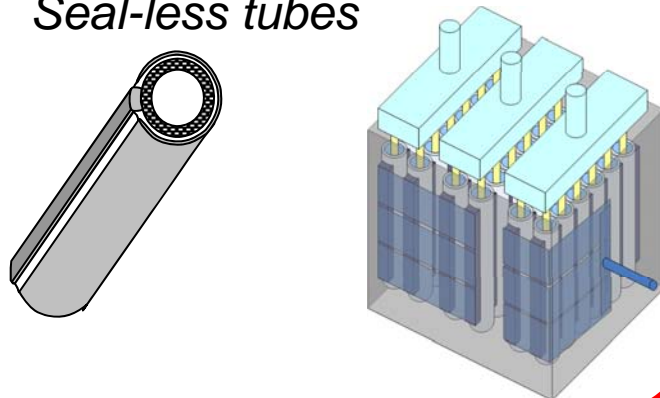
Medium temperature(700-750°C)

High temperature(900-1000°C)

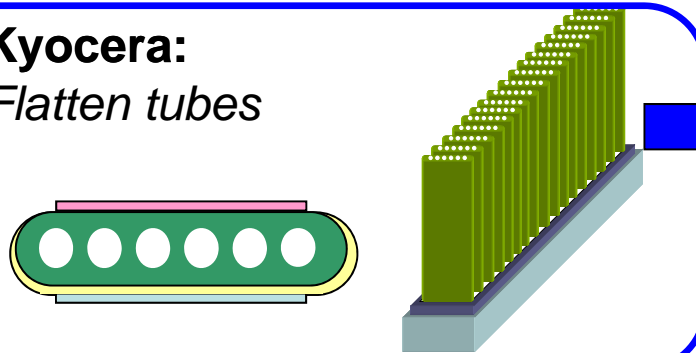
**Mitsubishi Heavy Industries:**  
*Segment in series*



**TOTO:**  
*Seal-less tubes*

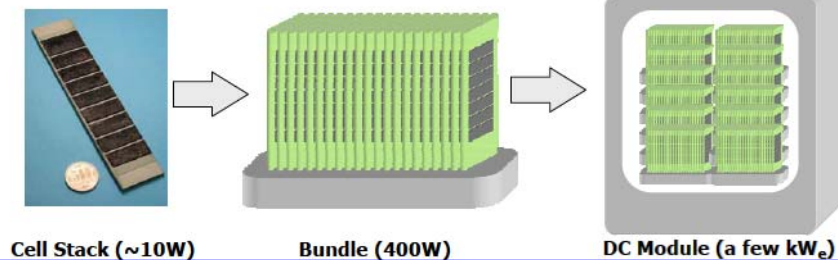


**Kyocera:**  
*Flatten tubes*

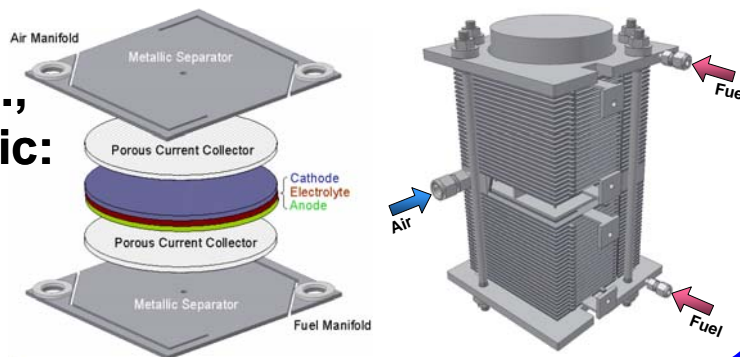


Demonstration stack/system

**Tokyo Gas-Kyocera:**  
*Segment in series (Flatten tube)*



**Mitsubishi Material Corp., Kansai Electric:**  
*Disk-type*

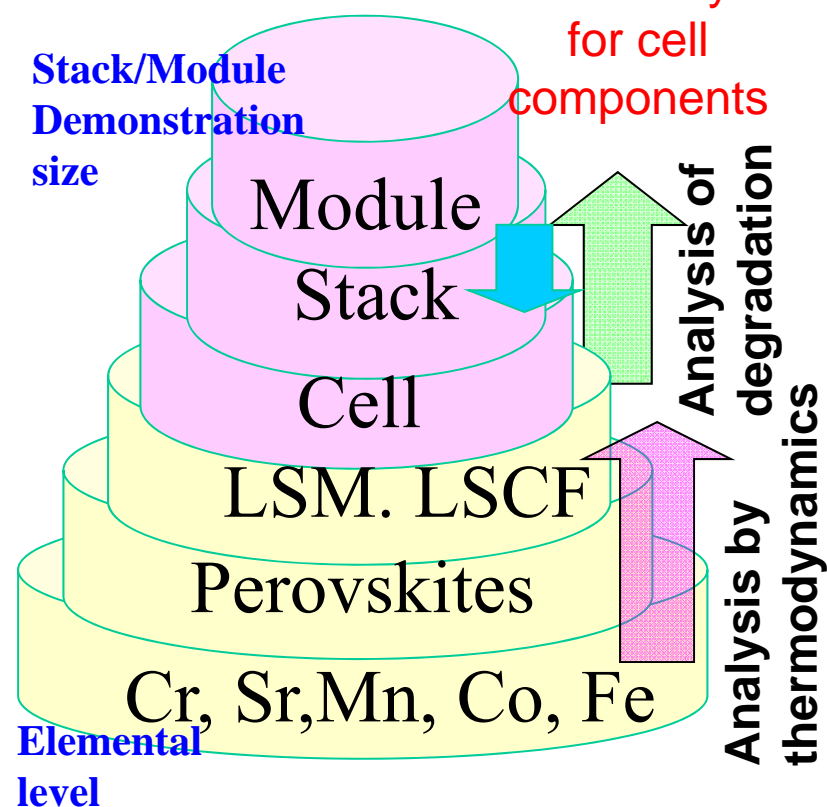


# Purpose and Approach

## Purpose:

- 1) List up of degradation phenomena of main components,
- 2) Determination of impurity levels of SOFC stacks

## Sketch of Analyses



## Challenges and approach

- 1) Operation of 5 stack/modules and evaluation of the degradation rates (for 5000-10000 h)
- 2) Impurity level analyses of cell components after long-term operation and correlation of voltage loss by using **SIMS technique**

Impurity effects on the degradation of stacks (ppm levels analysis)

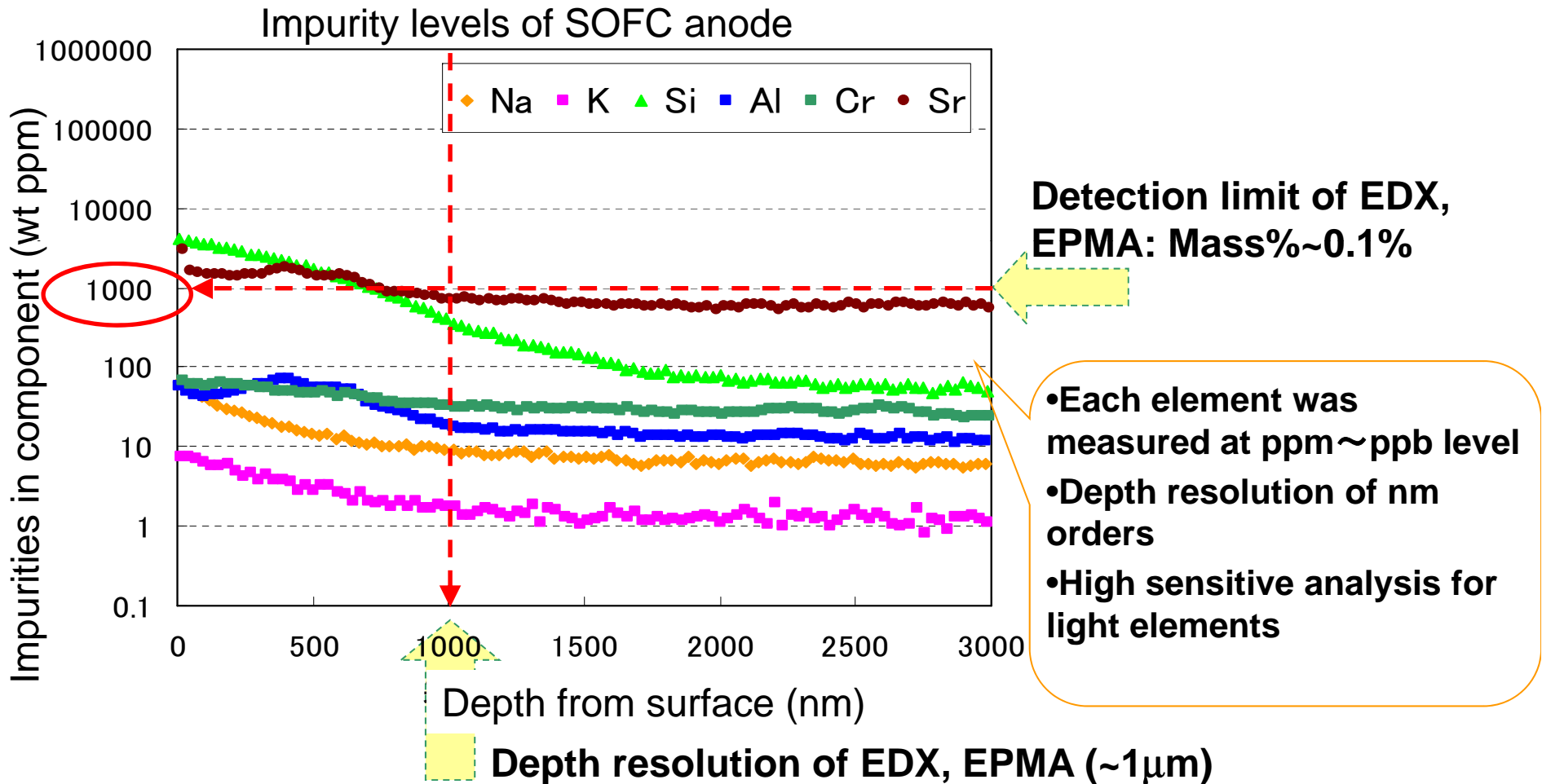
## **2. Impurity analysis of stacks and modules (by using SIMS technique)**

# Outlook of SIMS (Secondary Ion Mass Spectrometry) (ims-7f, CAMECA)

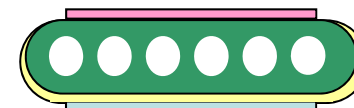
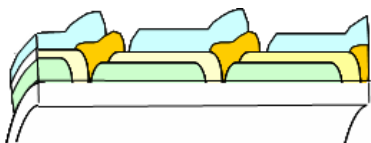


# Example of impurity level analysis by SIMS

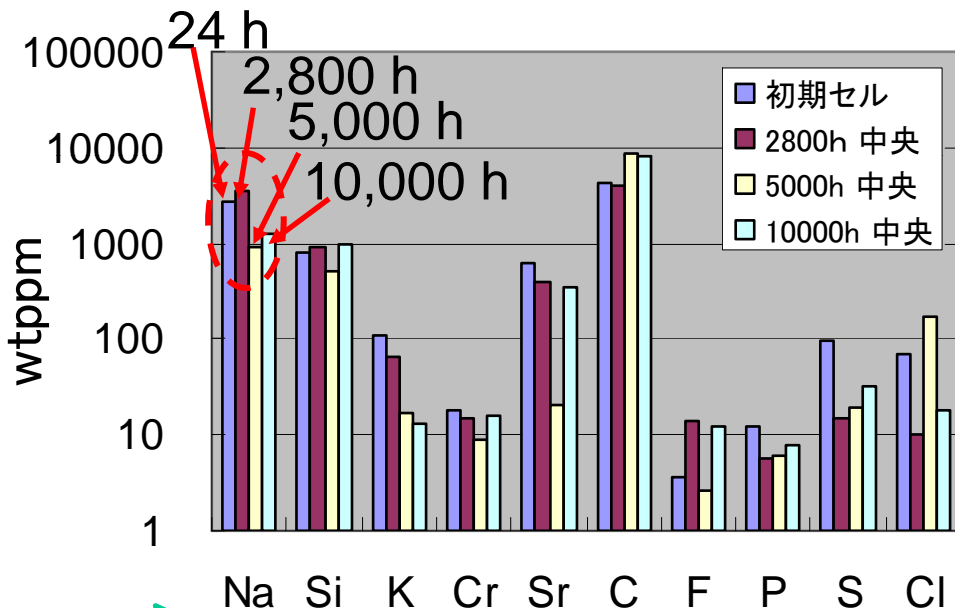
Key point: High sensitivity for light elements and depth resolution



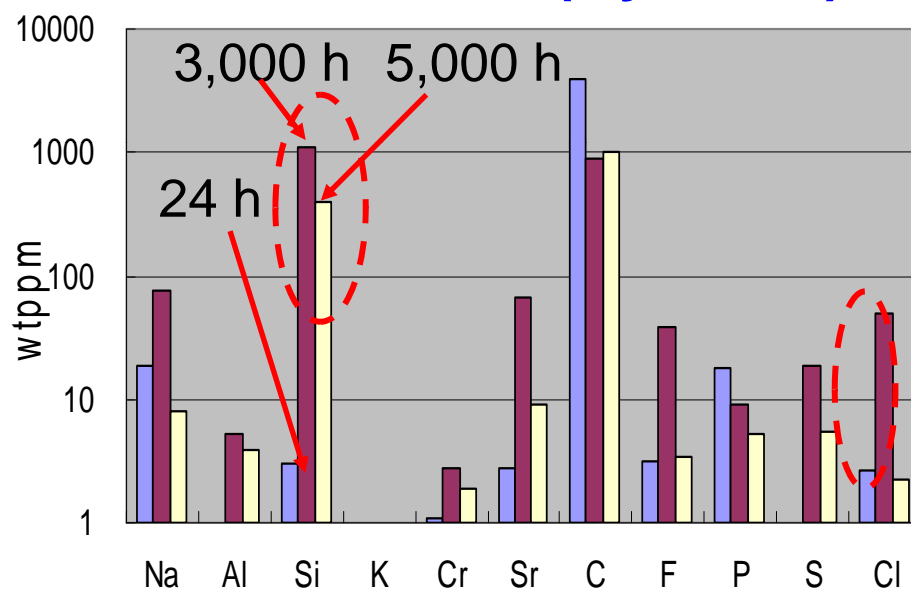
# Impurity analysis: Anode for different stacks



## Segmented in-series (MHI)



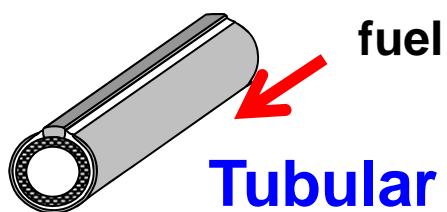
## Flatten tube (Kyocera)



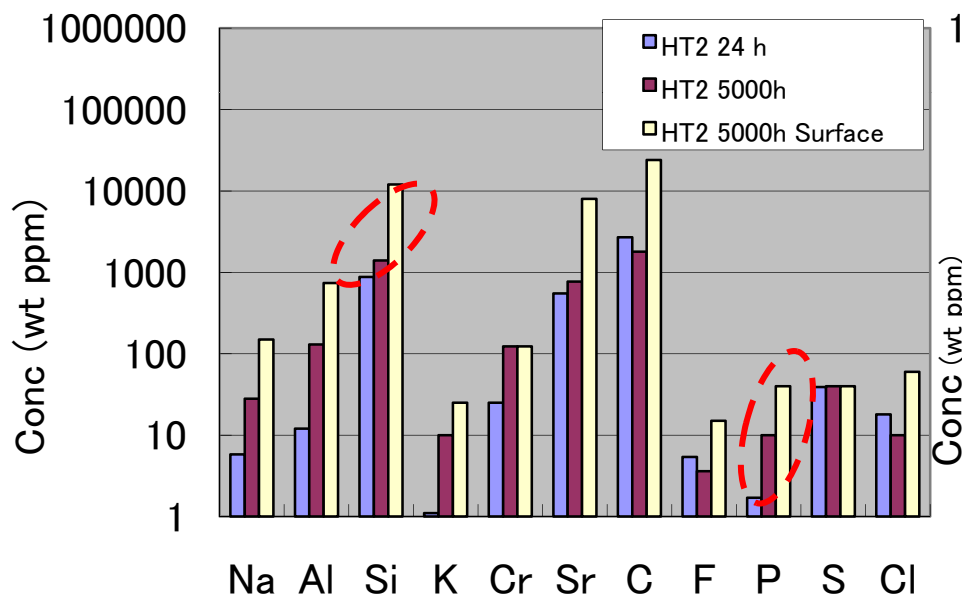
Impurity elements

1. The impurity level is different depending on the stack/modules
2. The increase of Na, Al, Si concentration can be due to the thermal insulators

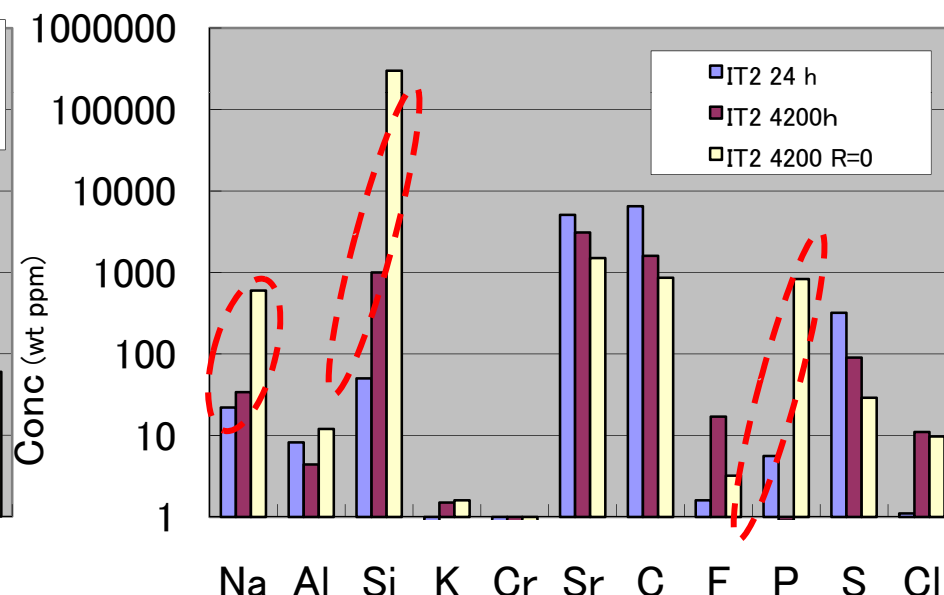
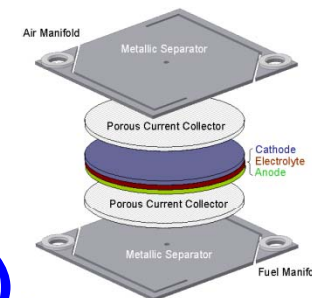
# Impurity analysis: Anode for different modules



## Tubular (TOTO)

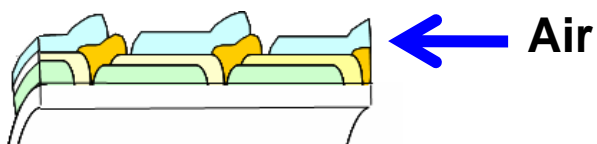


## Disk type (MMC)

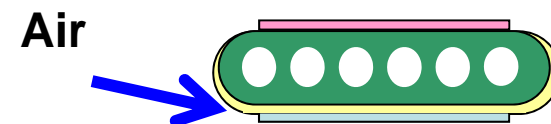


1. A significant increase of Na, Al, Si, and K concentrations,
2. C, S, P and Cl and some other elements show strange behaviors.

# Impurity analysis: Cathode for different stacks

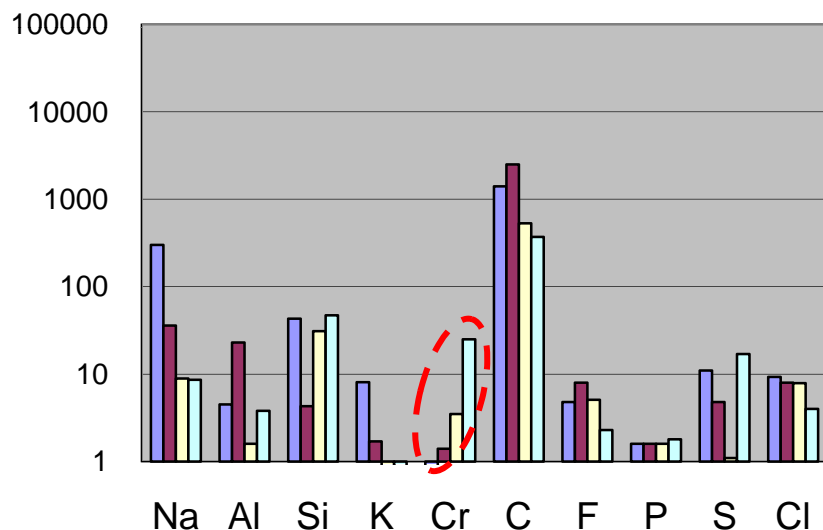


**Segmented in-series (MHI)**

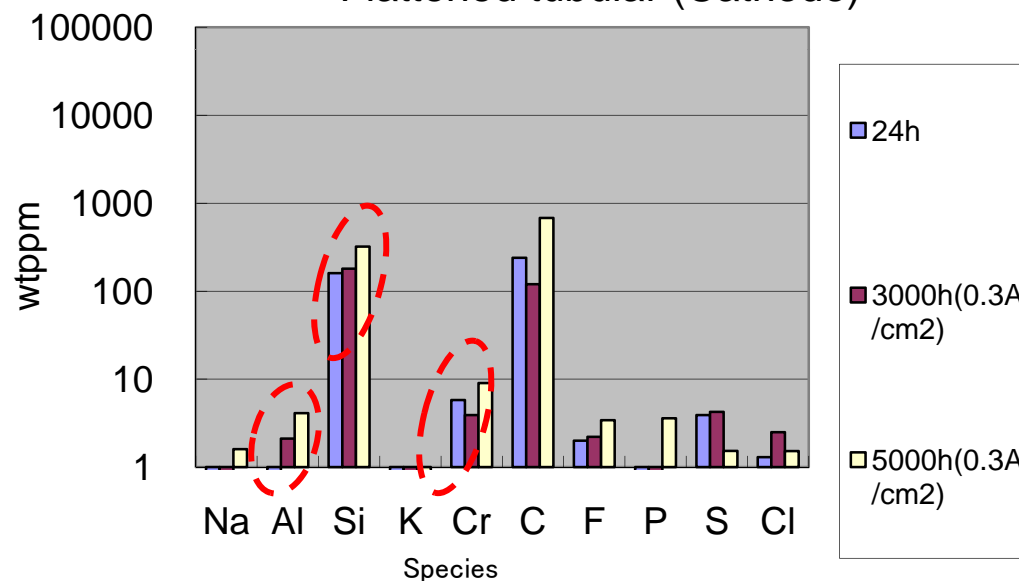


**Flatten tube (Kyocera)**

Segment in Series (Cathode)

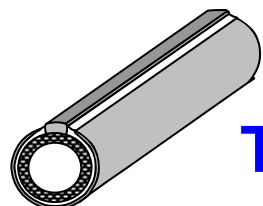


Flattened tubular (Cathode)

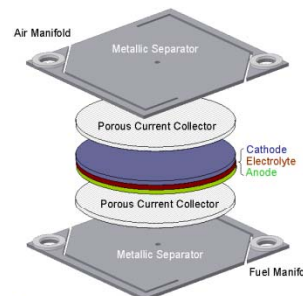


Impurities of Al, Si, Cr are increasing with time  
Exposed in air side and easy to deposit impurities from air

# Impurity analysis: Cathode for different modules

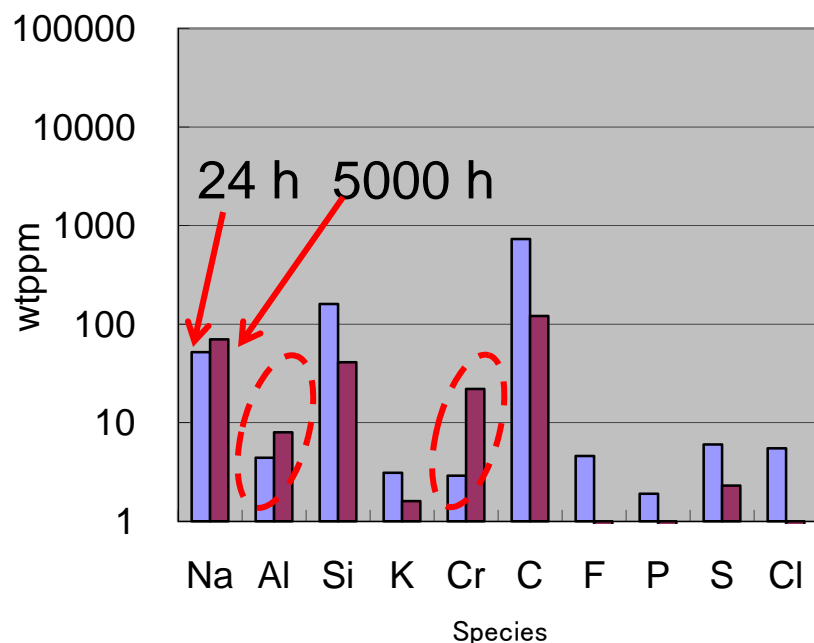


**Tubular (TOTO)**

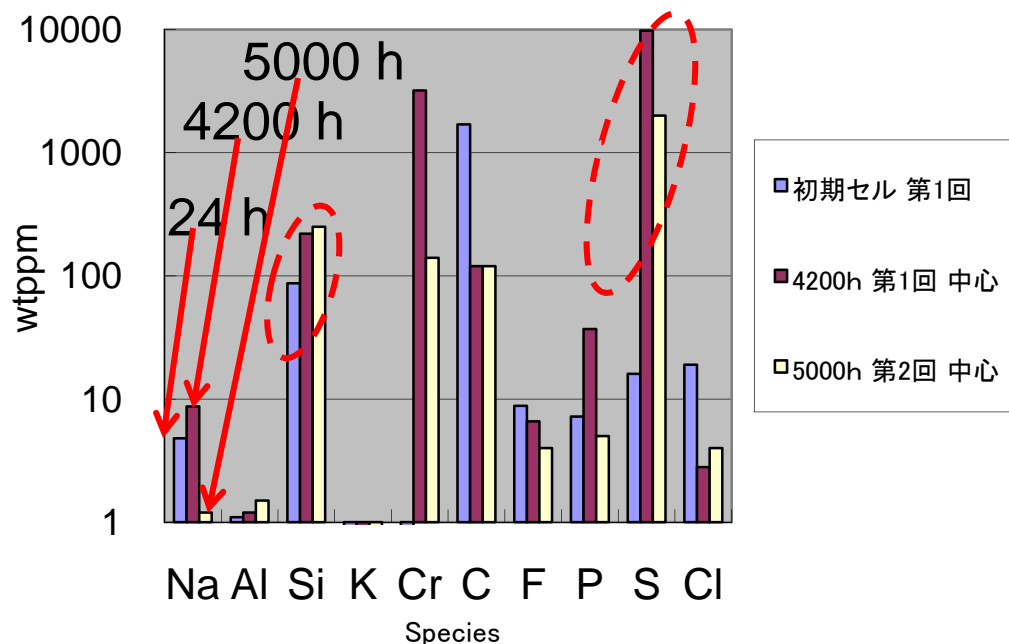


**Disk type (MMC)**

Sealless Tubular (cathode)



Flat Disk Type (cathode)



# Summary of impurities detected in the stacks

Type	Team (developers)	Average voltage degradation rate (loss%/1000h)	Detected foreign impurities <b>(red :more than 100 ppm)</b>
<b>Flatten tube</b> (750°C)	AIST-Kyocera	0.9	Si, P, Sr (interlayer), Corrosion at metallic IC
<b>Segment in series, Flatten Tube</b> (750°C)	AIST-Tokyo gas	0.42	Al, Si, Cr (cathode) F, P, Cl (interlayer)
<b>Tubular</b> (900°C)	TOTO	0.38 (single cell)	P, Si (anode/electrolyte) <b>Al, Si</b> , Cr (anode)
<b>Disk</b> (700-750°C)	MMC-KEPCO	0.25	<b>Si</b> , P, S (Anode) <b>S</b> , Cr (cathode)center of electrodes Corrosion at metallic IC
<b>Segment in series, Tubular(900°C)</b>	MHI	0.83	<b>Cr</b> (cathode)

AIST: National Institute of Advanced Industrial Science and Technology, Japan

TOTO: TOTO Corporation. Ltd., Japan

MMC: Mitsubishi Material Corporation, Japan

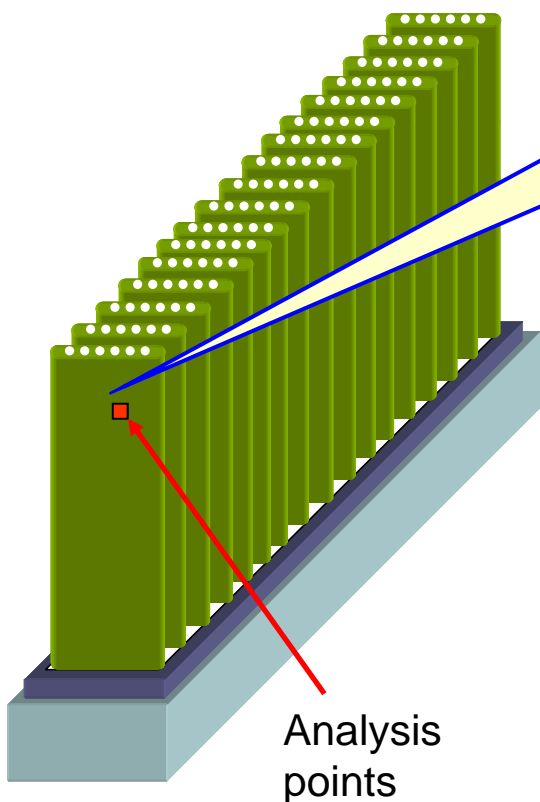
KEPCO: Kansai Electric Power Corporation Inc., Japan

MHI: Mitsubishi Heavy Industries

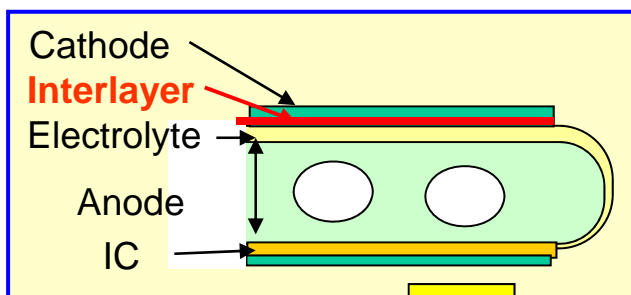
**Updated July 2009**

# Impurity analysis: Flat Tube stack

Schematic view of 20 cell stack

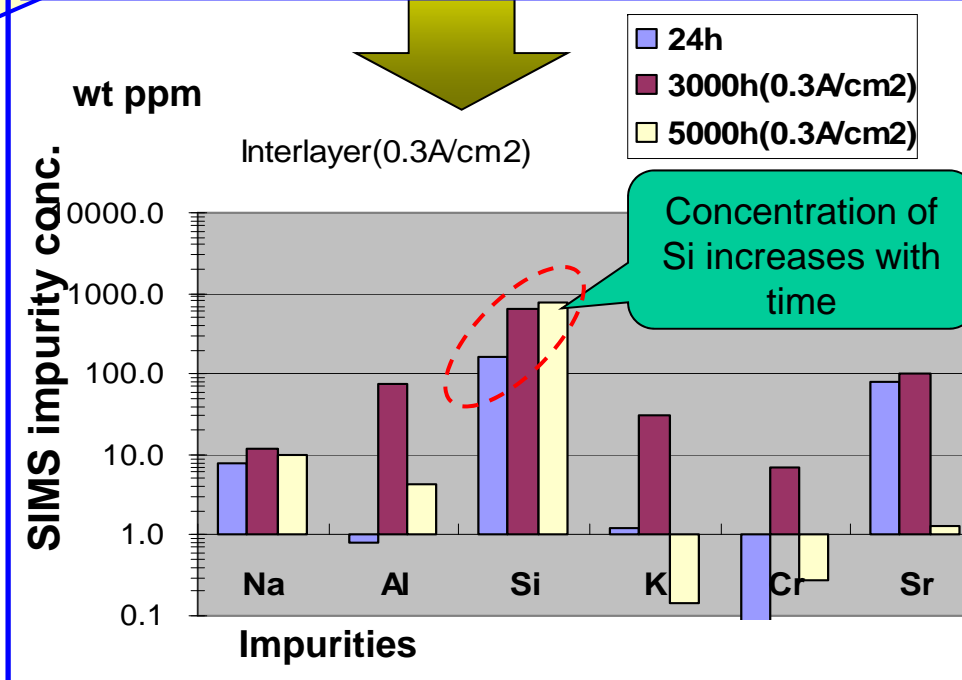


## Schematic view of cross section



Concentration level change was determined in ppm level by SIMS

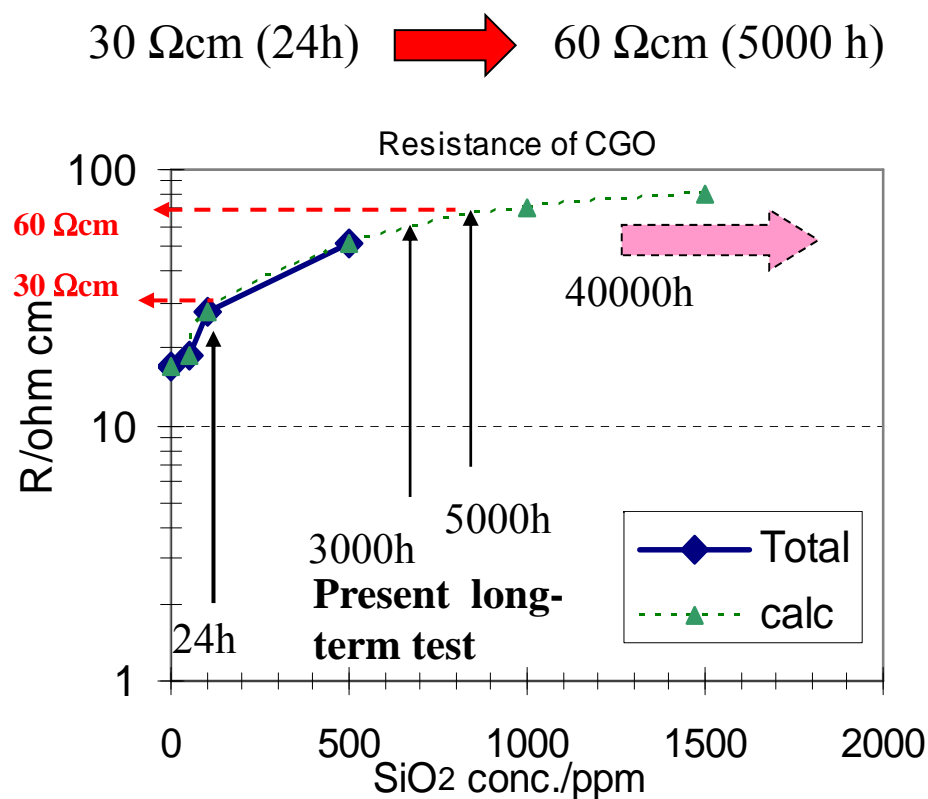
Impurities of **Interlayer** around Cathode/Electrolyte Interface



T. Horita et al., J. Power, Vol.193, 194(2009)

# Estimation of resistance due to impurity Si: at cathode/interlayer/electrolyte

## Resistance change due to Si in GDC

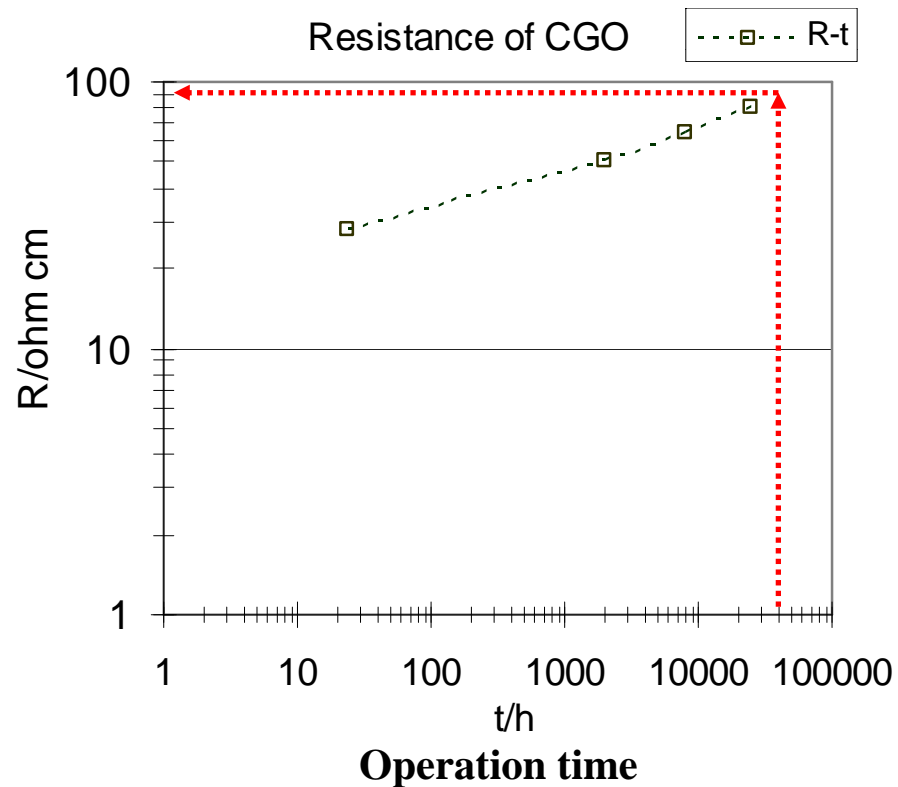


J.A.Lane et al., SSI177(2006)1911-1915

## Resistivity change by Si in GDC

(linear increase of Si-concentration and resistance)

Resistance of GDC interlayer after 40000 hour: 90  $\Omega\text{cm}$  (3 times of initial)



# Impurity Analysis of Demonstration Stacks

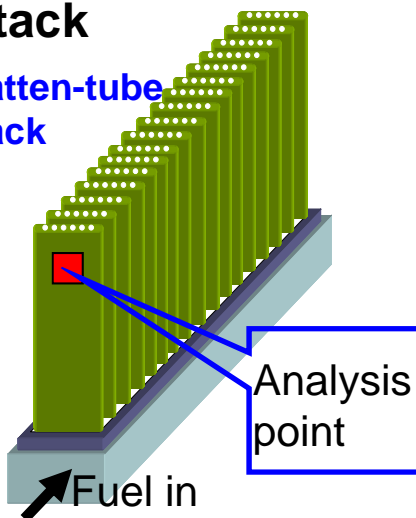
**First results of impurity levels in real operating conditions !**

Demonstration system

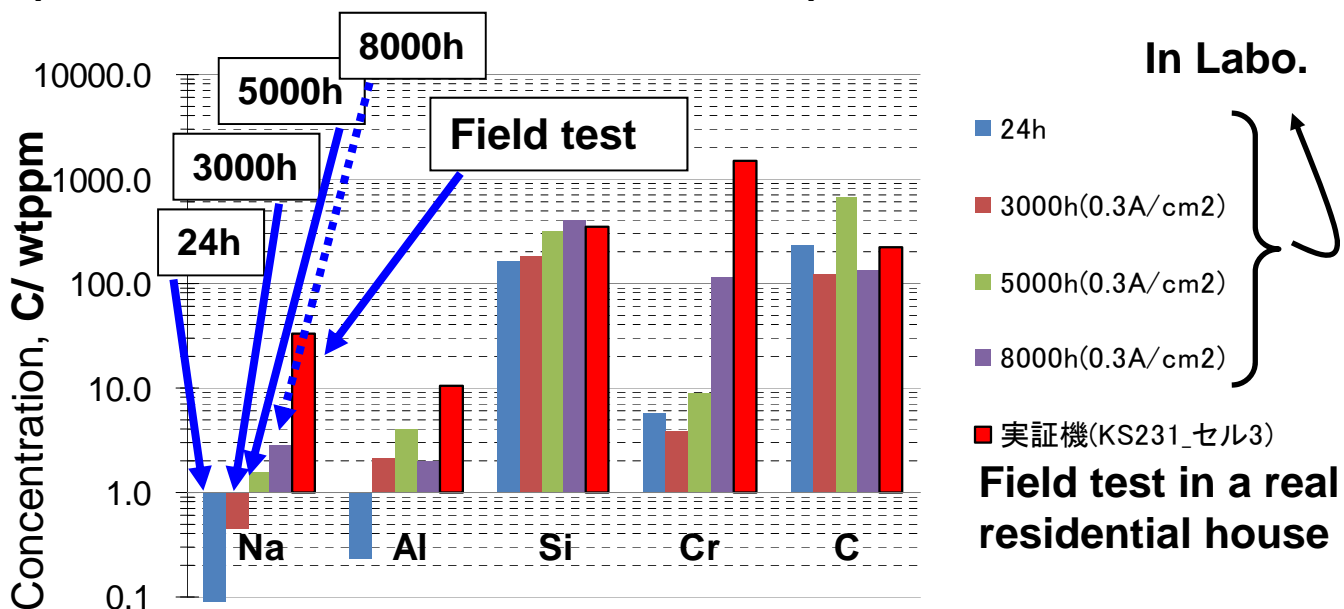


Schematic of 20 cells stack

Flatten-tube stack



**High sensitive analysis for impurities: cathode**  
( field tested for more than 3500 h )

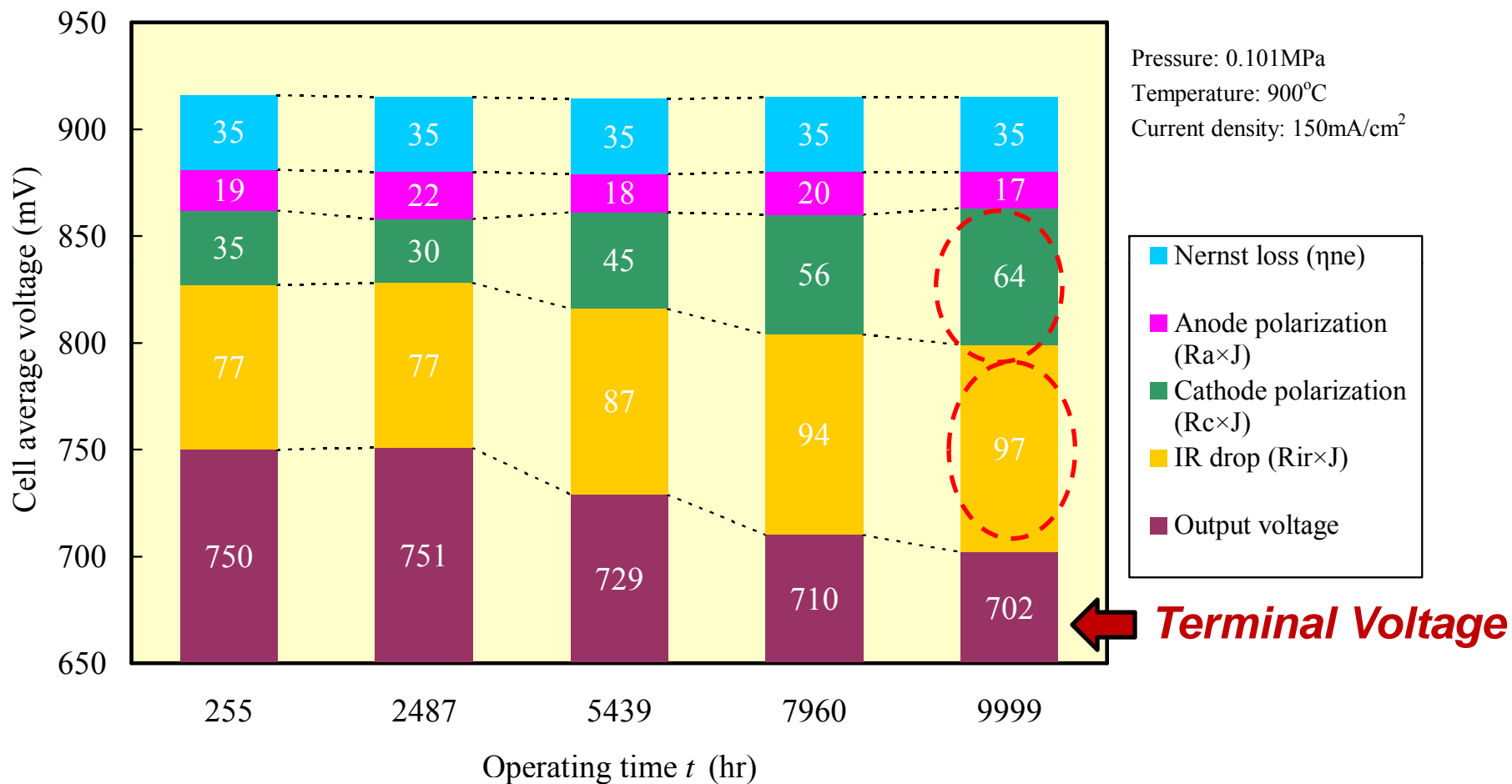


- Left 4 bars indicates the concentration in Labs
- Higher concentration of Na,Al,Si,Cr in the field test

T. Horita et al., J. Power , Vol. 190, 180(2009)

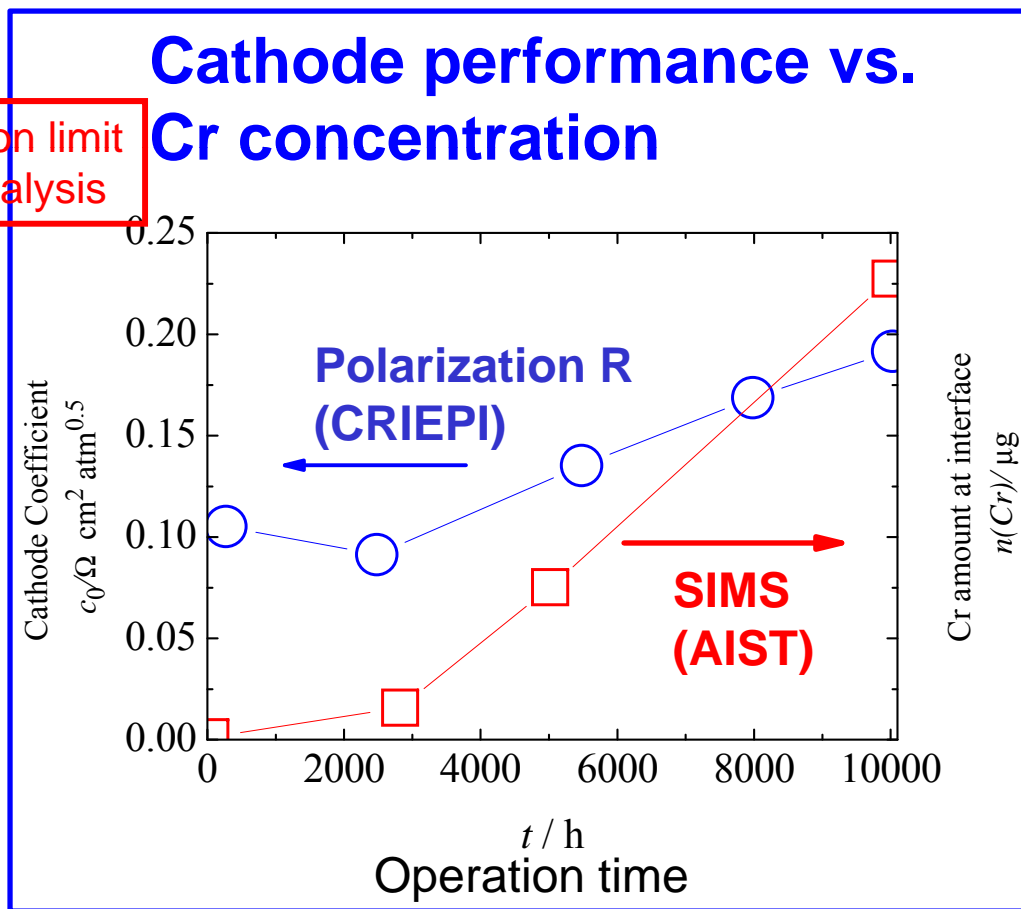
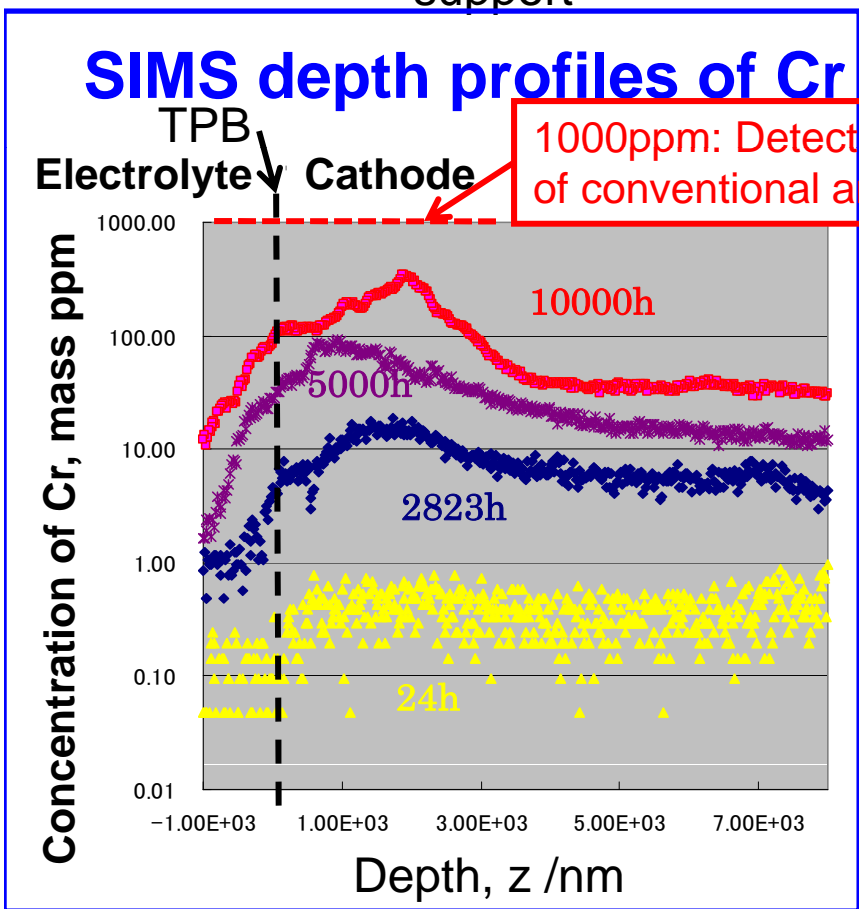
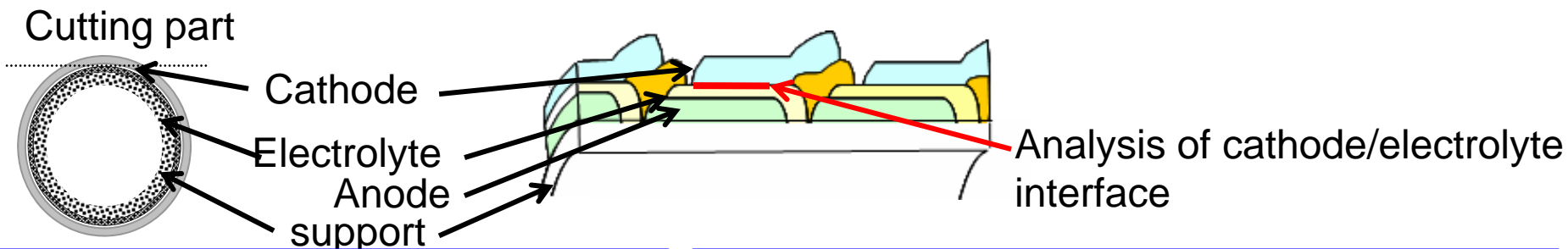
**Fundamental data to estimate the life of SOFC stacks**

# Electrochemical performance analysis: Segmented in-series stack (by CRIEPI)

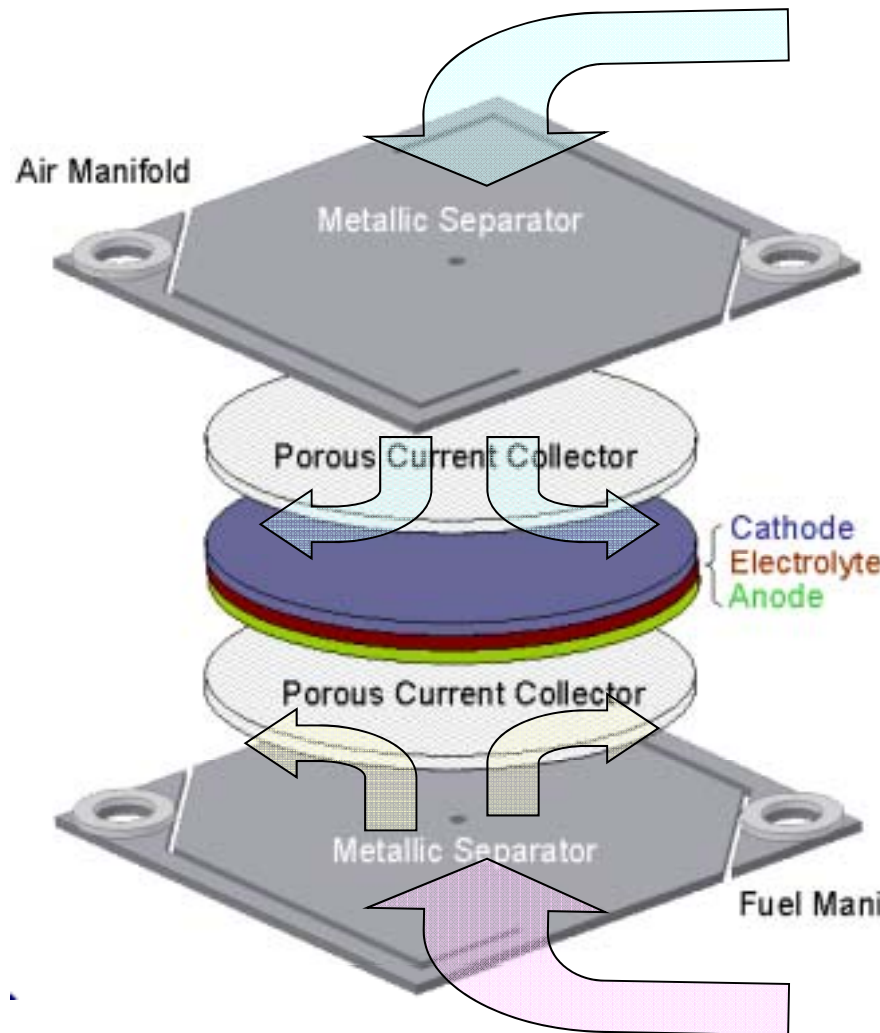


Cell degradation is due to the 1)IR drop and 2)cathode polarization

# Impurity analysis: Segmented in-series stack



# Impurity analysis: Disk planer type



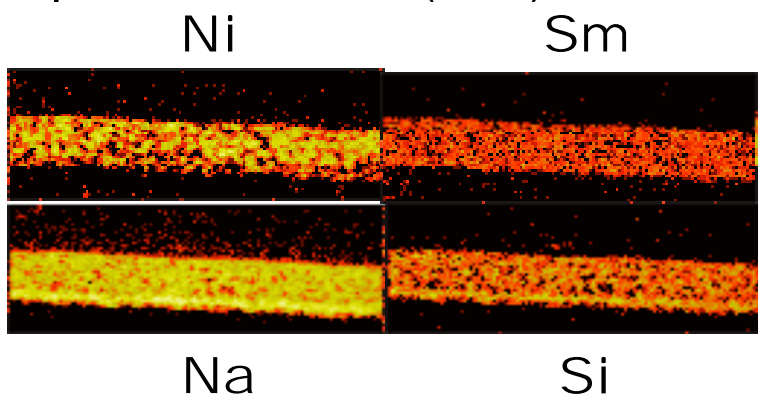
Air  
(impurities: P, S, Cr)

Fuel  
(impurities: S, Cl, Ca, Na, Si)

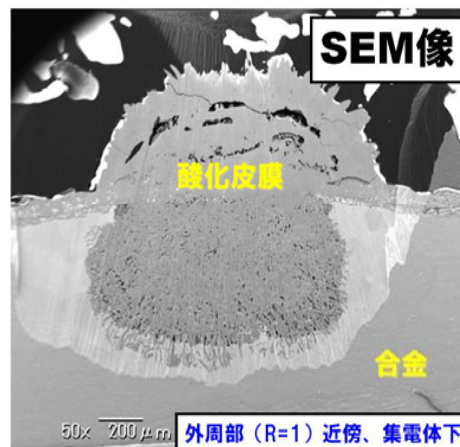
# Degradation of Disk Planer type: Impurities from filtered water

## Center of Anode: Concentration of Na and Si

Operation: 4200h (R=0)

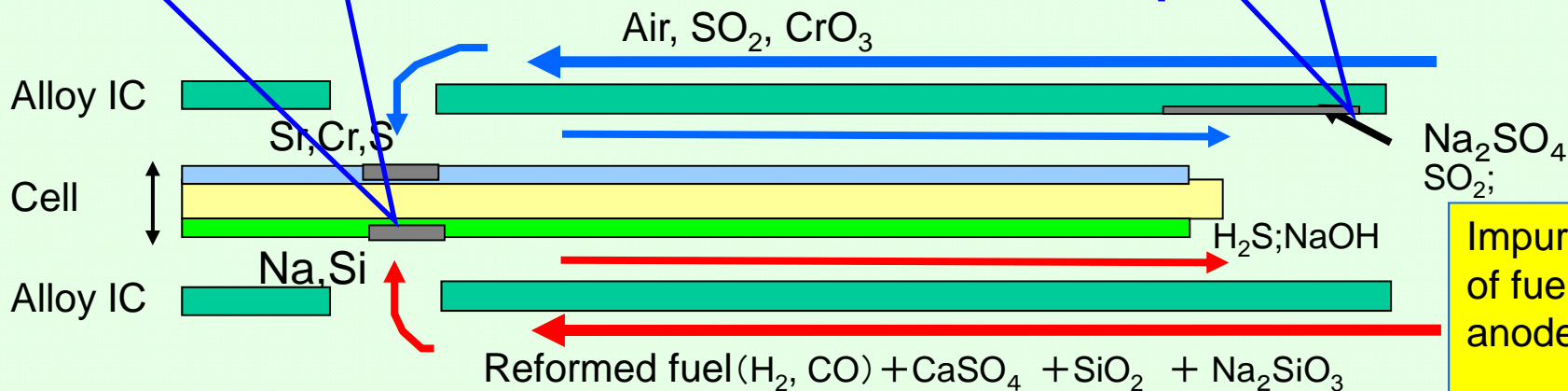


## Anomalous Oxidation of IC

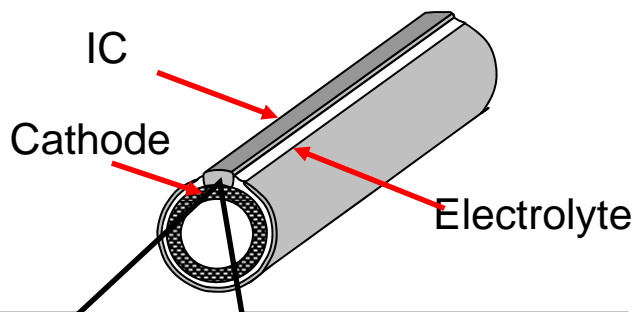


The formation of anomalous oxide scale was improved by coating.

## Gas flow and condensation of impurities

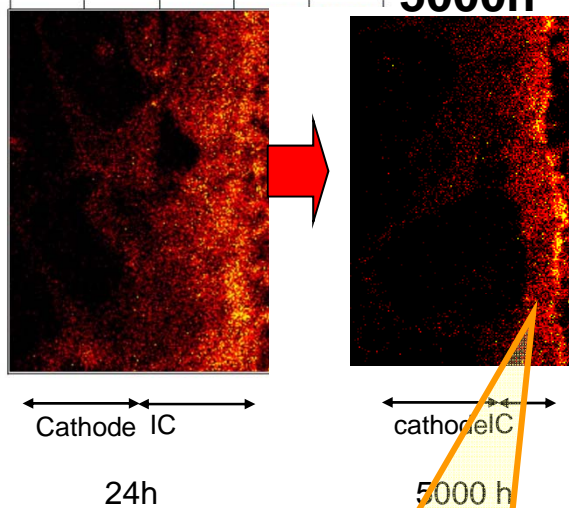


# Degradation of Tubular stack



## Elemental distribution at cathode/IC

### SIMS image of Ca



Increase of Ca concentration

## Concentration of Impurity on electrolyte surface

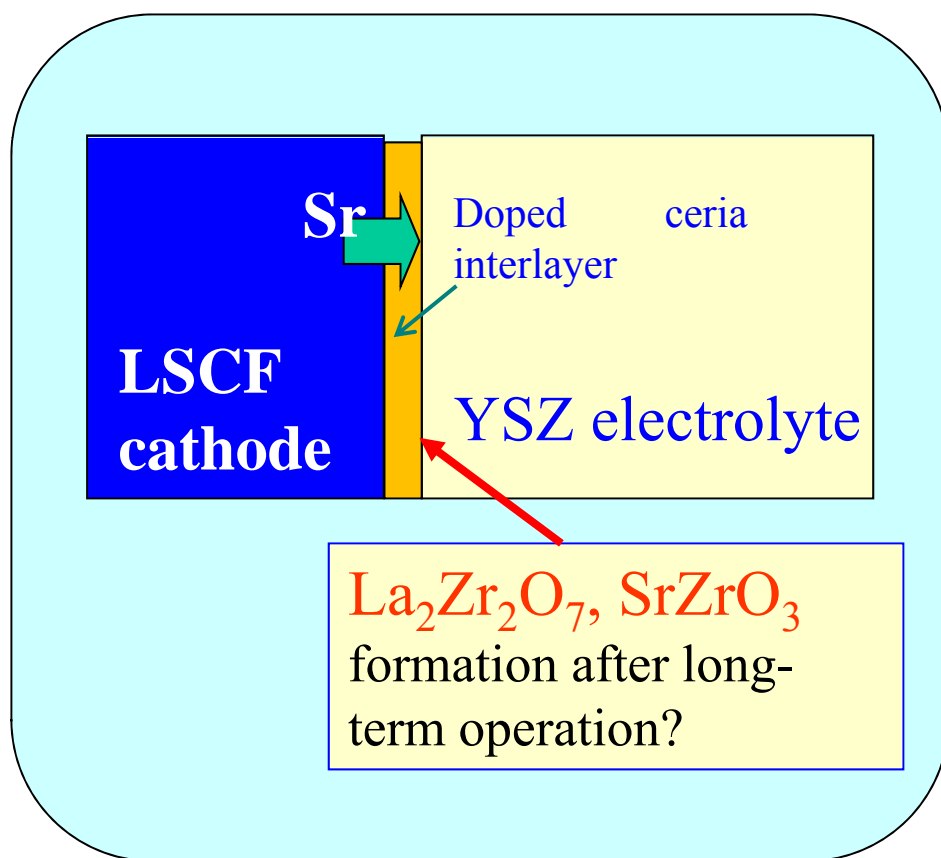
\* 表面から2~3ミクロンの、強度が安定したところを計算したデータ

濃度/wppm	Na	Al	K	Cr	Sr	Mg	C	F	Si	P	S	Cl	
初期	7	8.5	1.6	2.5	4000	20	280	0.5	41	41	0.3	1.2	
5000時間後	上	1000	4400	1000	12.5	5500	150	6500	50	11000	8	4	120
	中	6	350	3	1200	2600	350	900	3	1200	38	2.8	7
	下	10	600	1	10	2200	100	2000	20	900	200	30	20

Concentration of Si and Al increased at Anode, Electrolyte, IC surfaces:  
 → Impurity react with components and increased the resistance  
 → One of the degradation factors

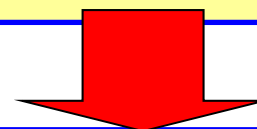
### 3. Interface analysis at cathode/interlayer/electrolyte

Local compositional changes at cathode/interlayer/electrolyte interface during operation



#### Points to be focused:

Inter-diffusion of elements at cathode/interlayer interface (blocking of Sr diffusion from cathode)

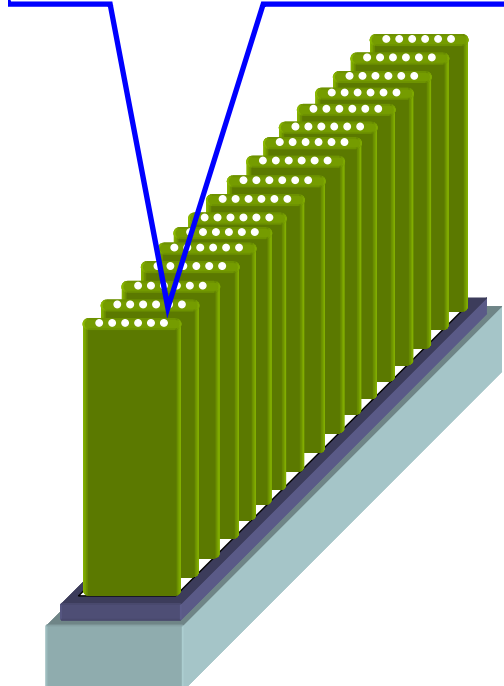
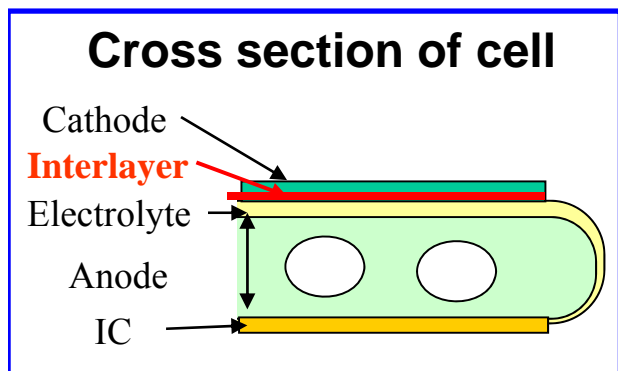


#### Challenges:

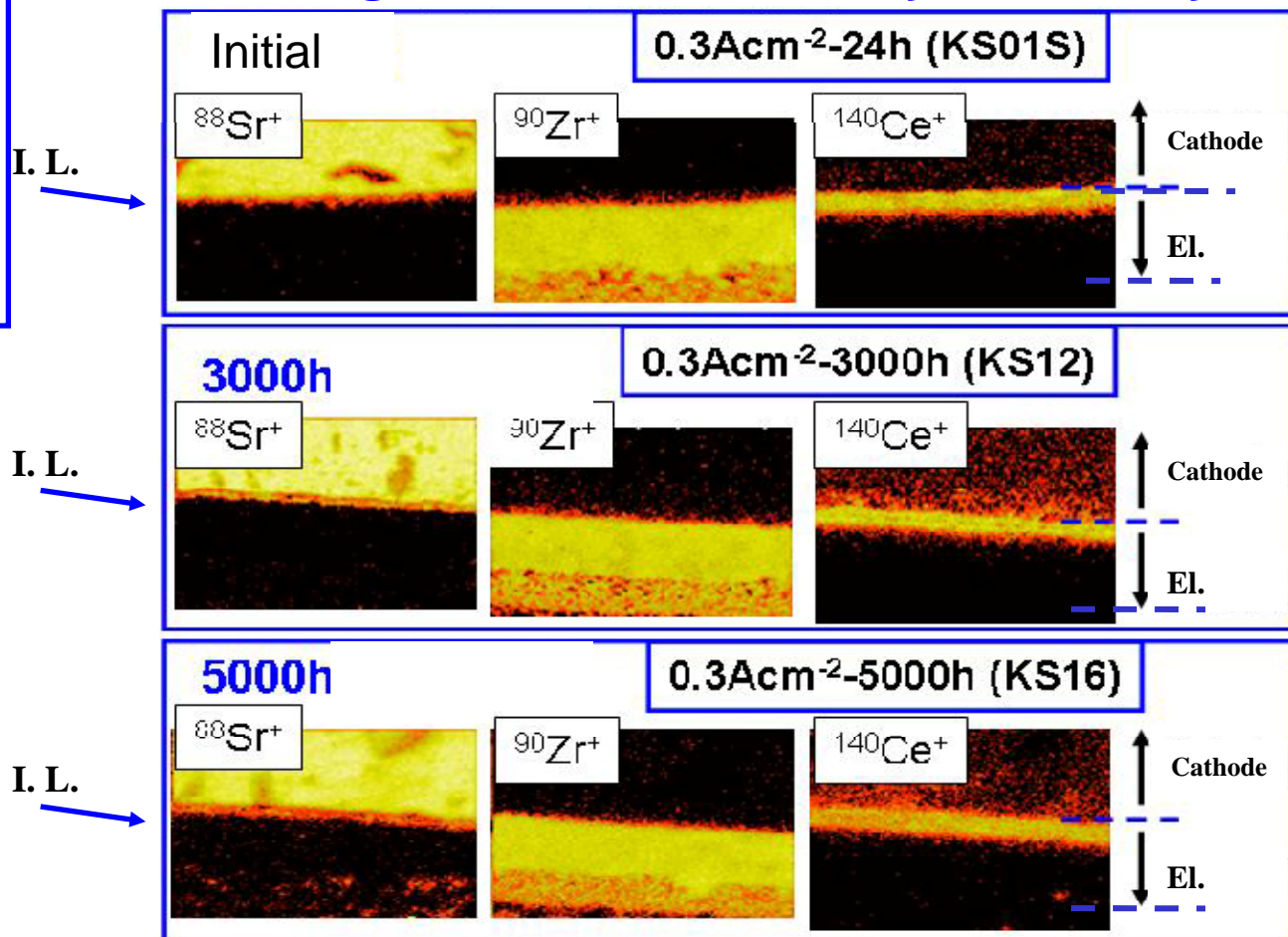
- 1) Evaluation of interface stability,
- 2) Clarification of elemental diffusion for estimating the long-term operation

# Interface analysis: Flatten tube of cathode/electrolyte

SIMS images of cathode/interlayer/electrolyte

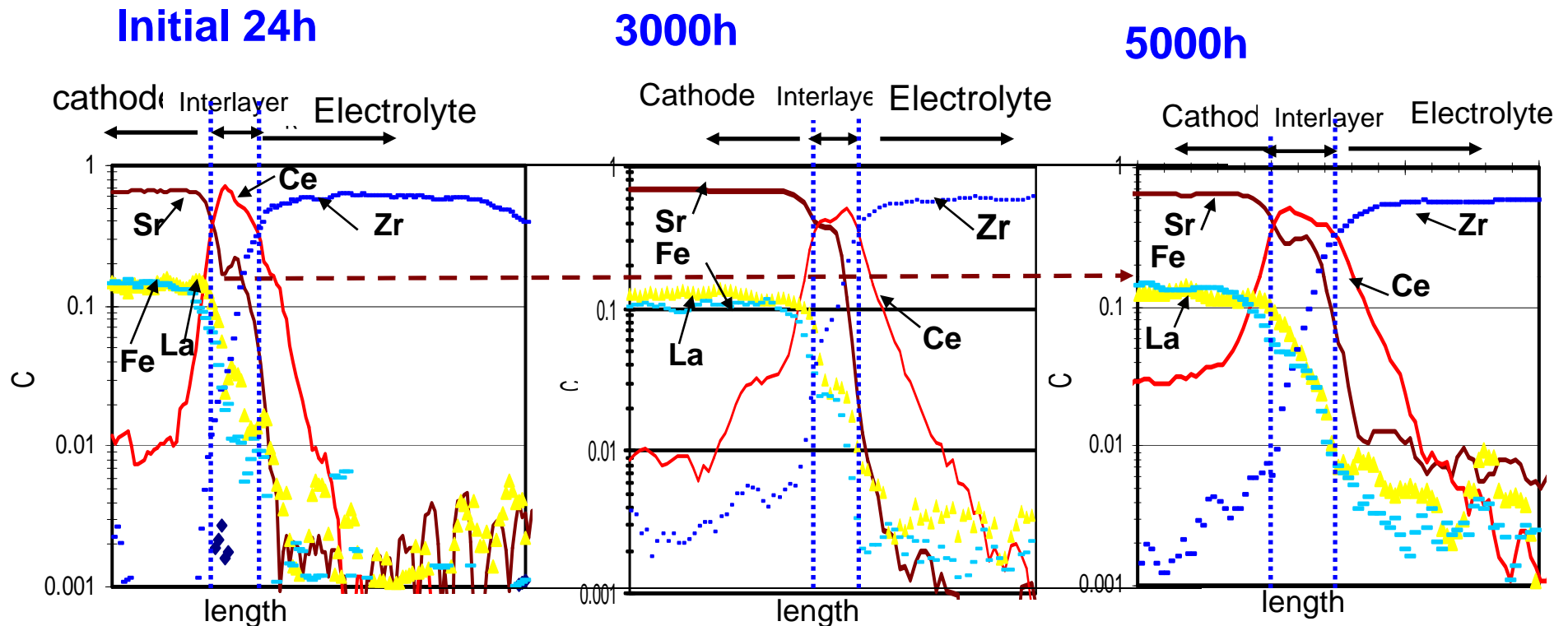


Schematic drawing of stack



High Sr concentration in  $\text{CeO}_2$ , but no diffusion in YSZ

# SIMS Line scan for cathode/electrolyte Interface of Flat-tube stacks operated at $0.3 \text{ Acm}^{-2}$



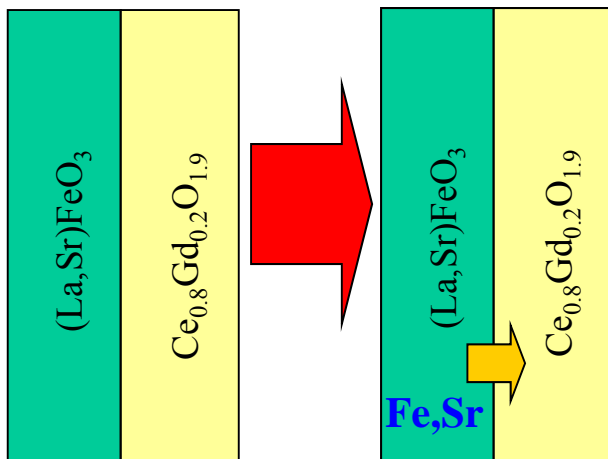
## Compared with Initial state

- Sr content increased in  $\text{CeO}_2$  interlayer.
- Although Sr level increased in electrolyte, no apparent  $\text{SrZrO}_3$  formation.

# Diffusion couple tests: LSF/GDC

## Annealing of diffusion couple

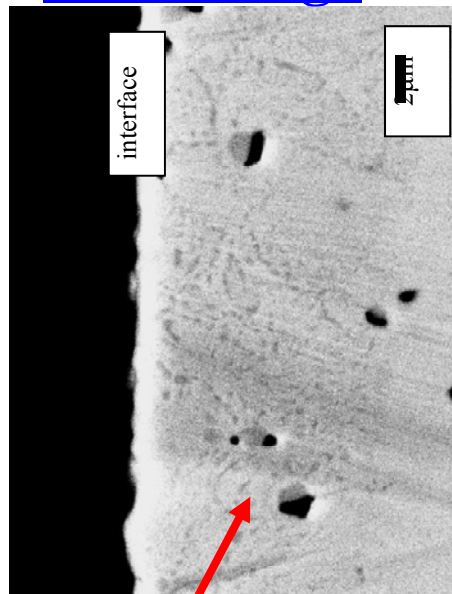
Initial **1100°C** Over 100h After diffusion



Diffusion phenomena:

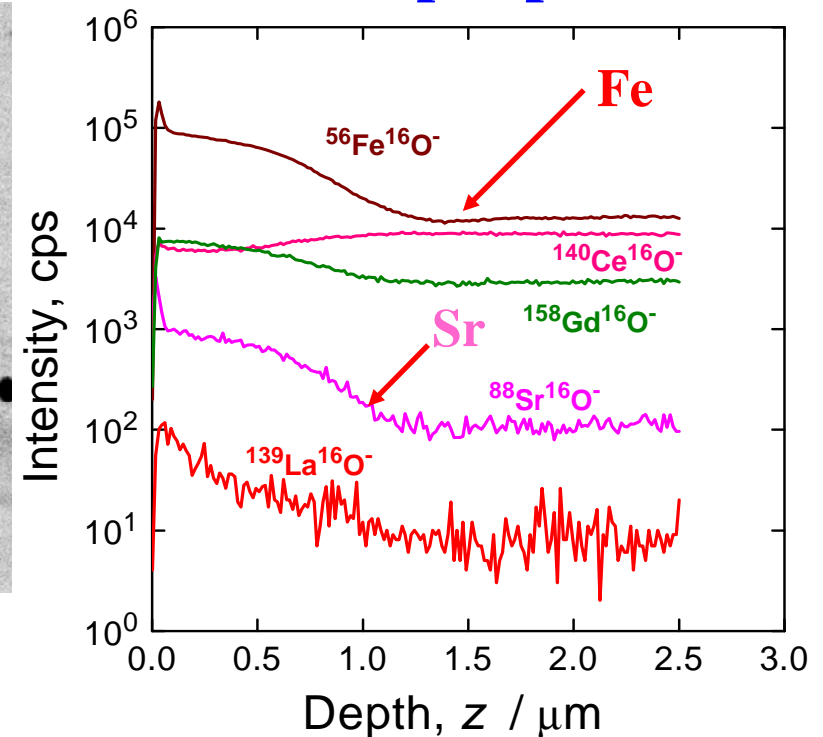
- 1) Formation of  $\text{GdFeO}_3$ ,
- 2) Grain boundary diffusion of Sr, Fe
- 3) Fast elemental diffusion

## SEM image



Fast diffusion of Fe

## SIMS depth profiles



# Summary

1. Some degradation factors were clarified for 5 different stacks/modules operated more than 5000 h.
2. The concentration of impurities was examined by SIMS sensitive analysis for stacks/modules.
3. Several kinds of degradation phenomena were extracted from the SIMS analyses.
4. Local composition changes at the component interfaces were examined by measuring the diffusion profiles.

Acknowledgements: This study was supported by NEDO.