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Sn-anode infiltration for Direct-biogas SOFC operation

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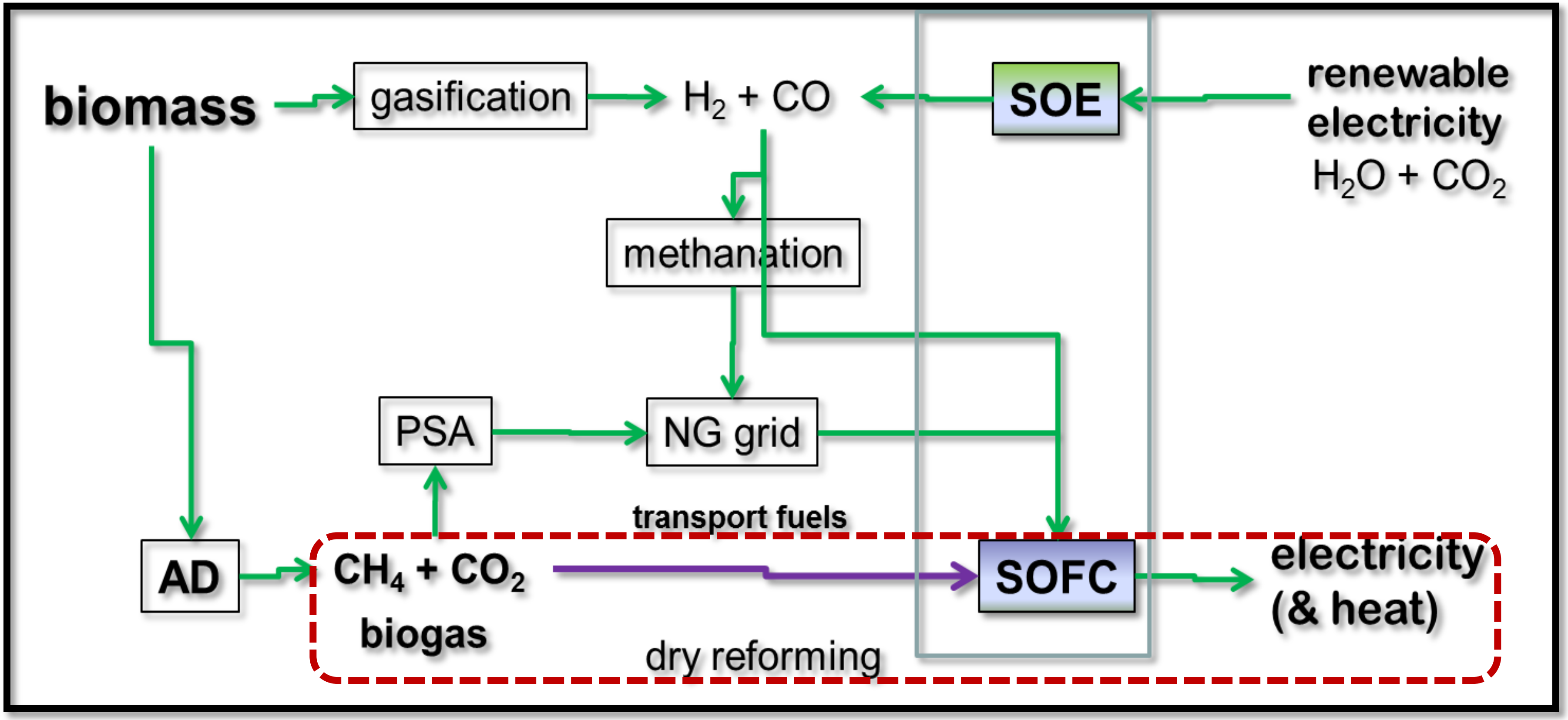
Aim: to contribute to sustainable direct-biogas SOFC operation



Reactions of biogas fuel at anode

Dry reforming of CH_4

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2$$

Which occurs via dissociative adsorption of CH_4 followed by C oxidation

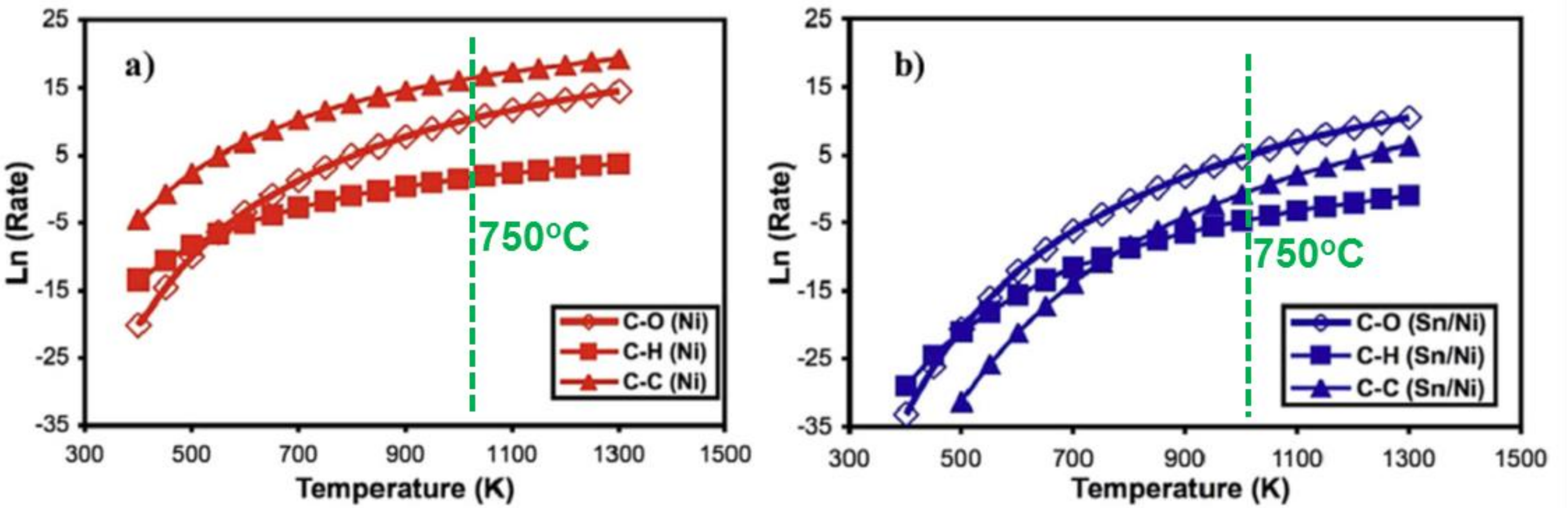
$CH_4 \rightarrow C + 2\,H_2$ → The risk of carbon build up is present

$C + CO_2 \rightarrow 2\,CO$ → carbon can be removed by reaction with CO_2 provided suitable catalyst is present

- ✓ Supported Ni (on zirconia, silica, alumina, magnesia) are among the widely used catalysts for methane reforming
- ✓ Bimetallic Ni catalysts are already developed to assist in carbon removal. Ni-Sn catalyst system is one of them.

Trimm, D.L., *Catalysts for the control of coking during steam reforming.* Catalysis Today, 1999. 49(1–3): p. 3-10

Reference results from Calculation using Density Functional Theory (in steam reforming)



At 750°C, on both SnNiYSZ (blue) and NiYSZ (red) C-H bond activation is the rate limiting step

On NiYSZ (red) C-C bond formation is faster than C-O bond formation

On SnNiYSZ (blue) C-O bond formation is faster than C-C bond formation

Question: Will these behavior apply in dry reforming? Let's investigate!

Nikolla, E., J. Schwank, and S. Linic, *Comparative study of the kinetics of methane steam reforming on supported Ni and Sn/Ni alloy catalysts: The impact of the formation of Ni alloy on chemistry.* Journal of Catalysis, 2009. 263(2): p. 220-227

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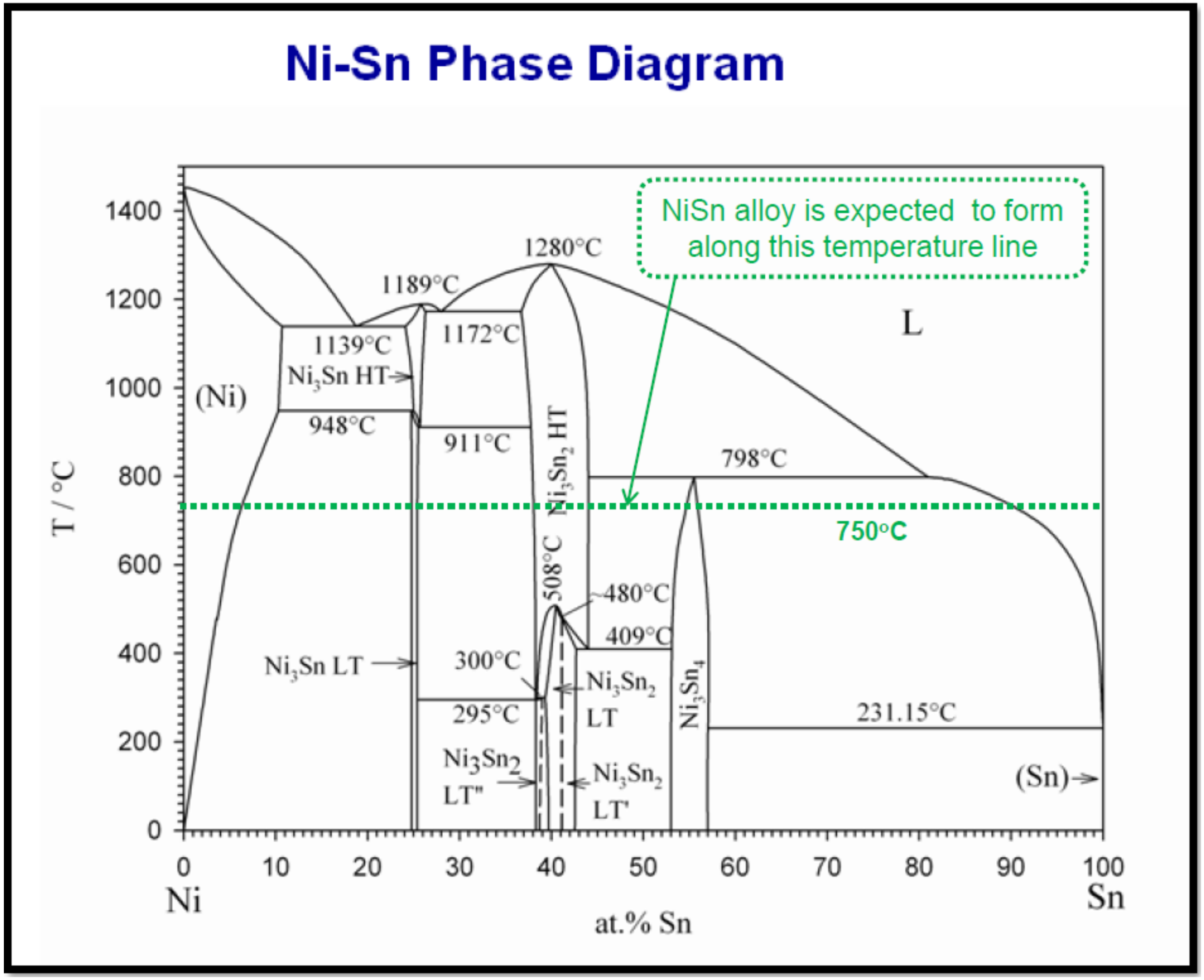
Formation of Ni-Sn alloy at typical SOFC operating condition is expected

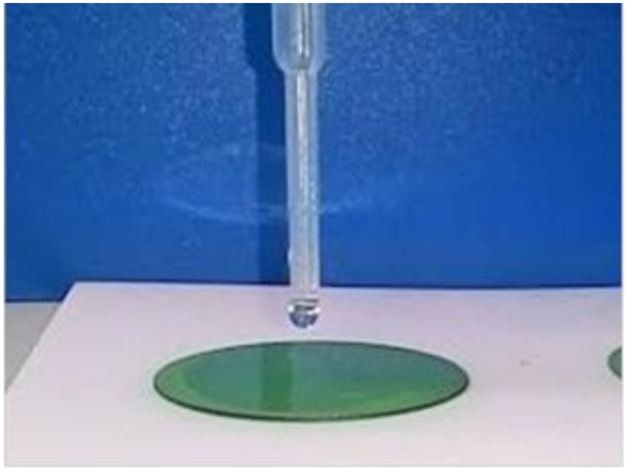


Possible phases:

- ✓ Ni_3Sn Low Temp.
- ✓ Ni_3Sn High Temp.
- ✓ Ni_3Sn_2 Low Temp.
- ✓ Ni_3Sn_2 High Temp.
- ✓ Ni_3Sn_4

Chart adapted from Schmetterer, C., et al., *A new investigation of the system Ni–Sn.* Intermetallics, 2007. 15(7): p. 869-884

Sn-infiltration method



- ✓ Infiltration by pipette-drop on commercial NiYSZ anode surface
- ✓ Ø 30mm, 600mg Ni
- ✓ Multiple drops were performed

Dopant solution: $SnCl_2$ in ethanol

1 mg Sn/drop solution

1 drop = 20 µl

Method:

- Drop on sintered anode surface
- Air dry at ambient temperature
- Oven dry at 100-120^{o}C
- Calcine at 600^{o}C
- Reduce in H_2/He at 750^{o}C
- Perform dry reforming
- Monitor outlet gas composition using mass spectrometer

TGA and possible reactions of $SnCl_2.2H_2O$ as dopant to form Ni-Sn alloys

Infiltration stage	Reactions	TG Region
Drying at 70 °C and 100 °C (Solvent evaporation)	$C_2H_5OH_{(liq)} \rightarrow C_2H_5OH_{(vap)}$ $H_2O_{(liq)} \rightarrow H_2O_{(vap)}$	1
First stage heating up to 200 °C (anhydrous $SnCl_2$ formation)	$SnCl_2.2H_2O \rightarrow SnCl_2 + 2H_2O_{(vap)}$	2
Further heating to 600 °C during calcinations ($SnCl_2$ evaporation and calcinations)	$SnCl_{2(solid)} \rightarrow SnCl_{2(liq)}$ Partial $SnCl_{2(liq)} \rightarrow SnCl_{2(vap)}$ Partial $SnCl_2 + ½ O_{2(g)} \rightarrow SnO + Cl_{2(g)}$	3
	$SnO + ½ O_{2(g)} \rightarrow SnO_2$	4
Reduction with H_2 at 750 °C	$SnO_2 + 2H_{2(g)} \rightarrow Sn + 2H_2O_{(vap)}$ $NiO + H_{2(g)} \rightarrow Ni + H_2O_{(vap)}$	
Alloy formation at 750 °C	$Ni + Sn \rightarrow$ Ni-Sn alloys	

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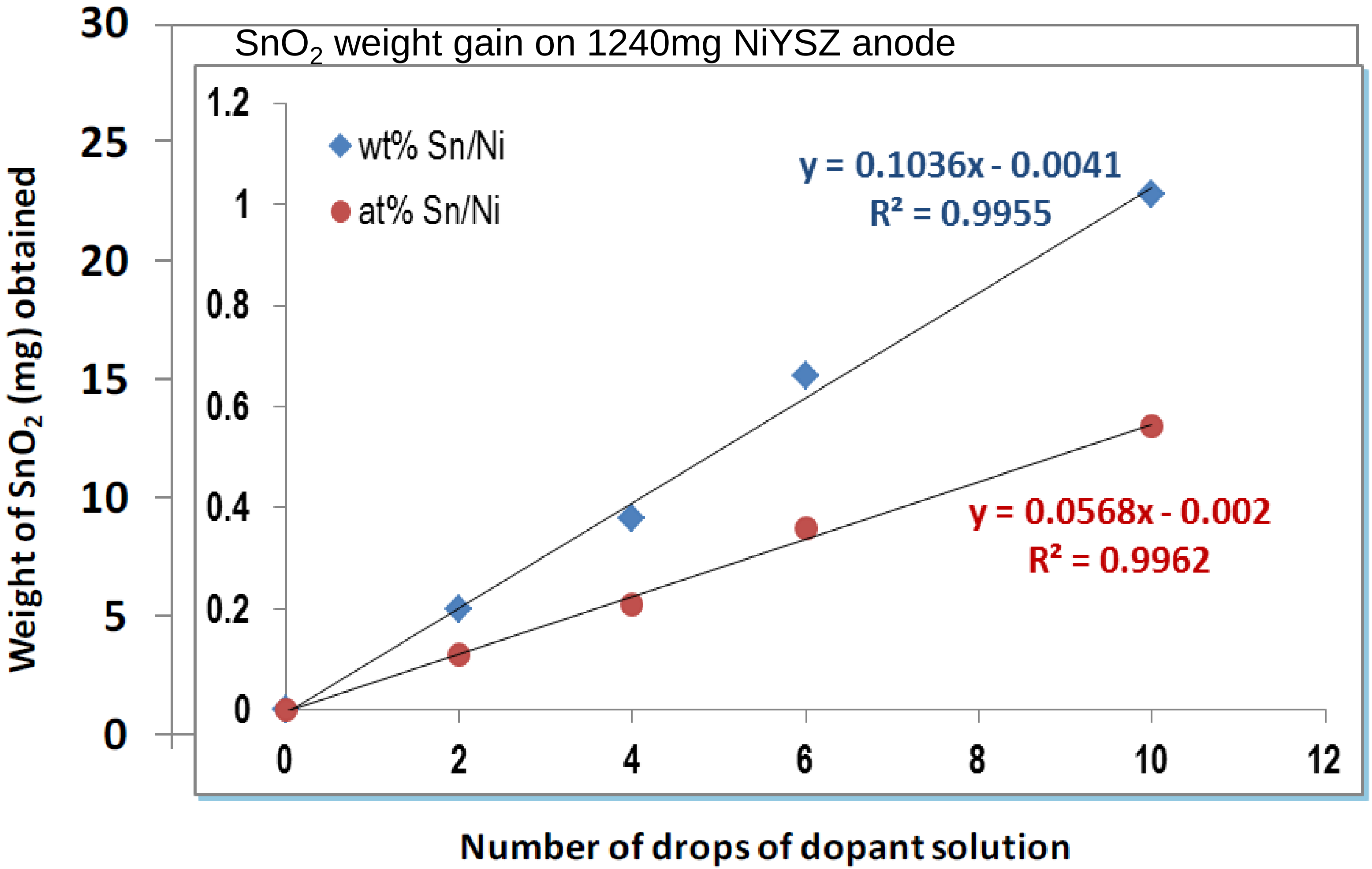
Repeatable infiltration on sintered commercial SOFC anodes with different Sn loading



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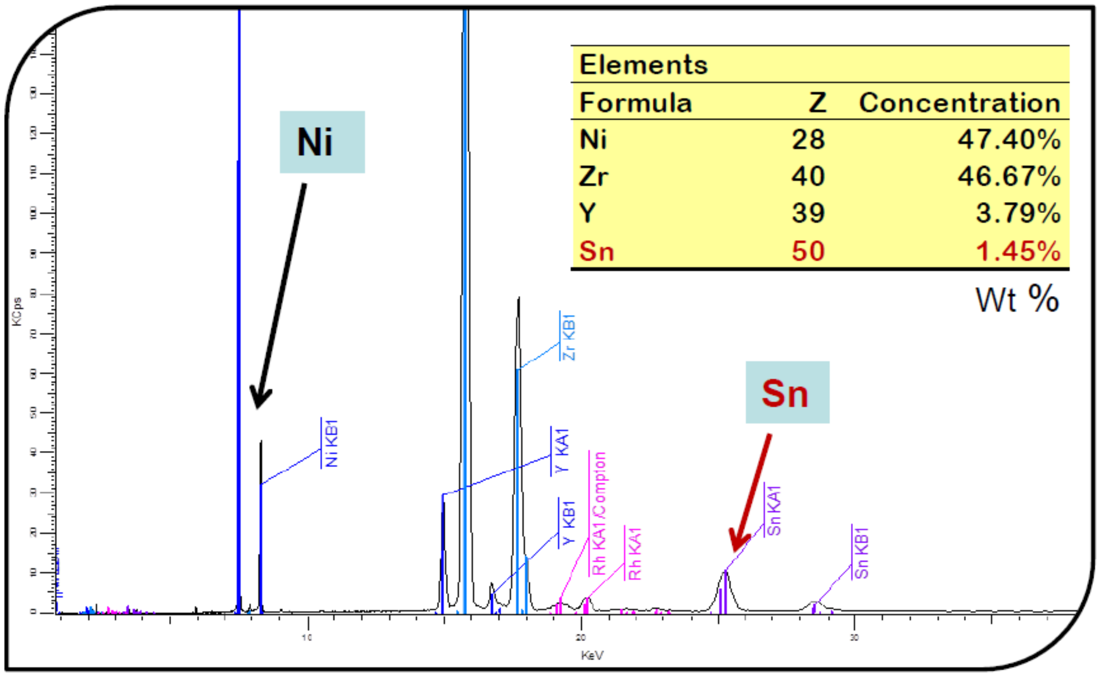
Evidence of doped Sn

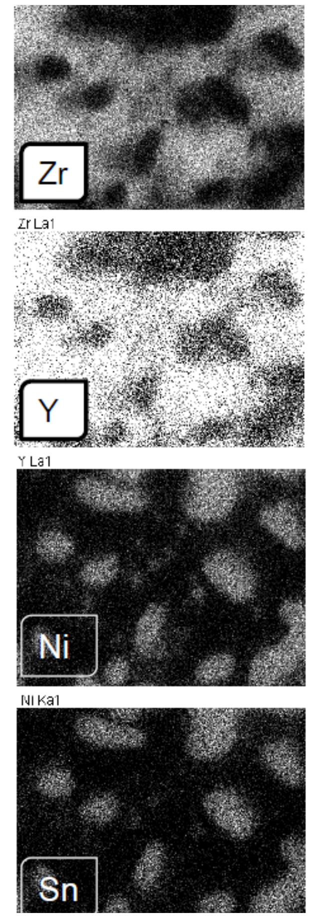
X-ray Fluorescence

Energy-dispersive X-ray spectroscopy

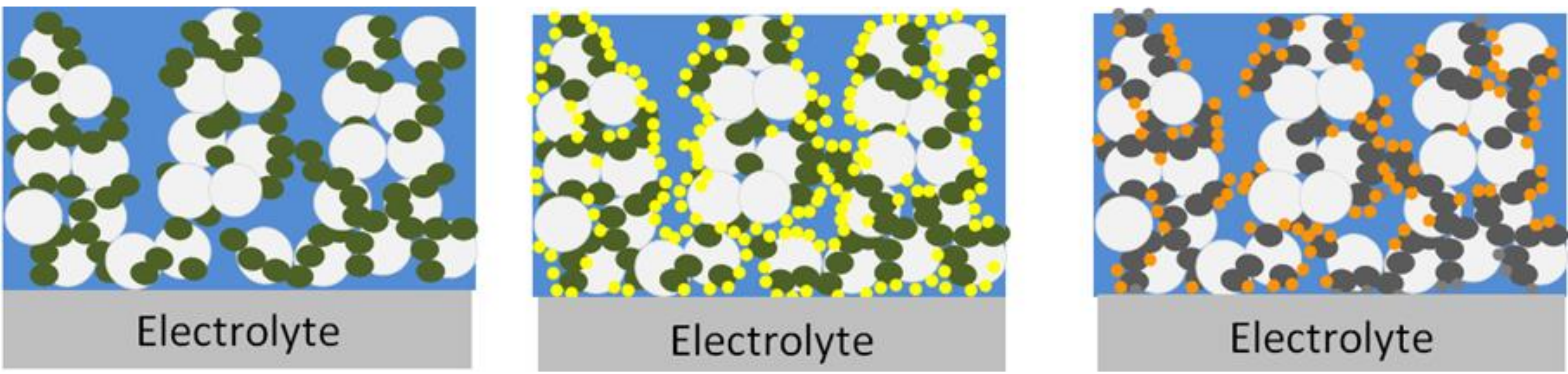


Elements		
Formula	Z	Concentration
Ni	28	47.40%
Zr	40	46.67%
Y	39	3.79%
Sn	50	1.45%

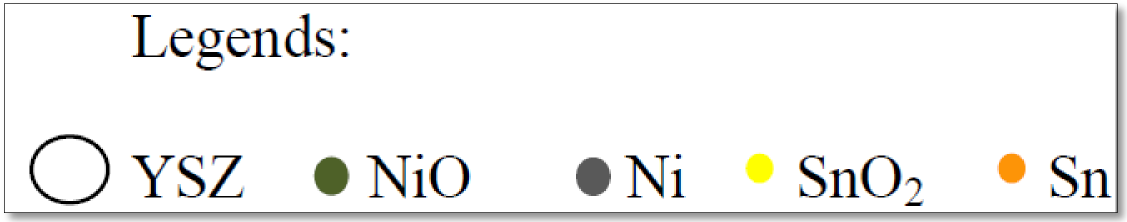
Wt %



Proposed simple structural model
of Sn-infiltration using pipette-drop method on NiYSZ anode



a. Before infiltration **b. after infiltration** **c. after infiltration and reduction**



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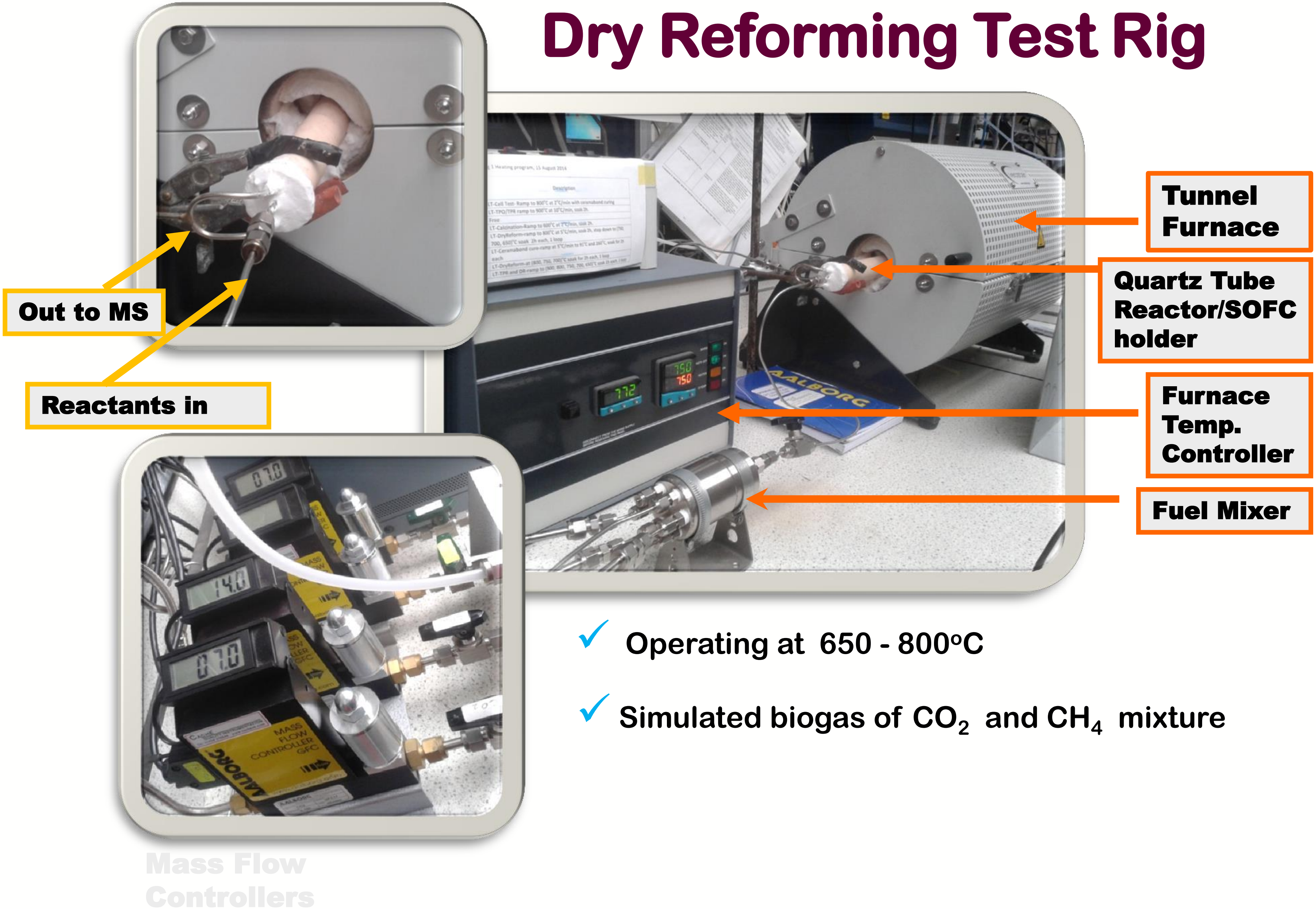
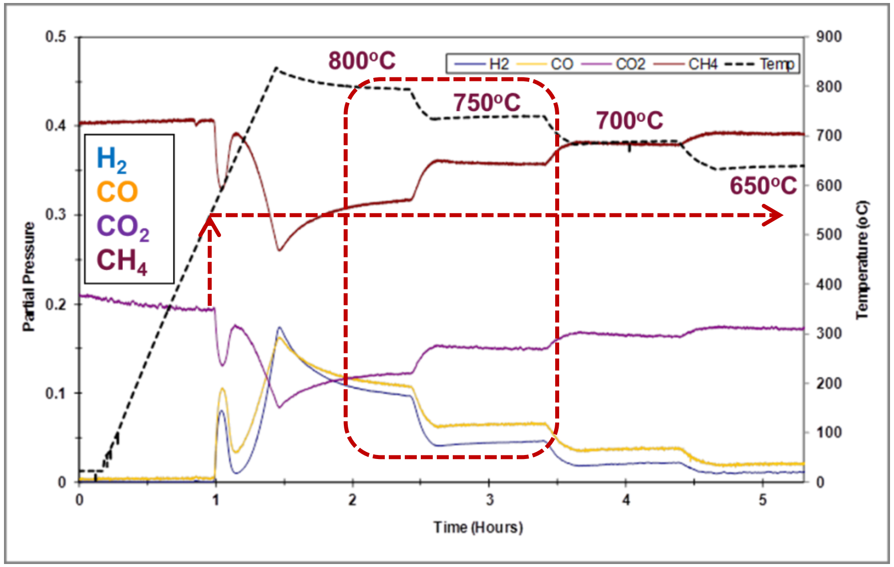
Dry Reforming Test Rig



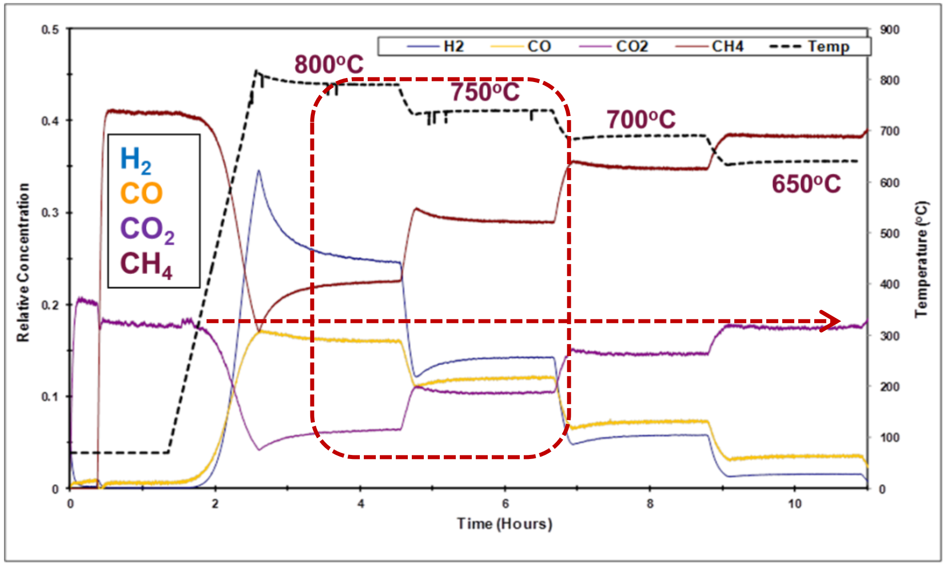
- ✓ Operating at 650 - 800°C
- ✓ Simulated biogas of CO_2 and CH_4 mixture

Dry reforming product gas composition at varied temperature

A. on non-infiltrated SOFC anode chips



B. on Sn-infiltrated SOFC anode chips



- ✓ **Sn-infiltrated anode chips**
  - ✓ **started to produce H_2 and CO at 330°C while non-infiltrated ones at 550°C**
  - ✓ **produced much more H_2 and CO than non-infiltrated ones.**
- ✓ **Catalyst-activity-wise: operating SOFCs at 750-800°C in DR mode is feasible.**

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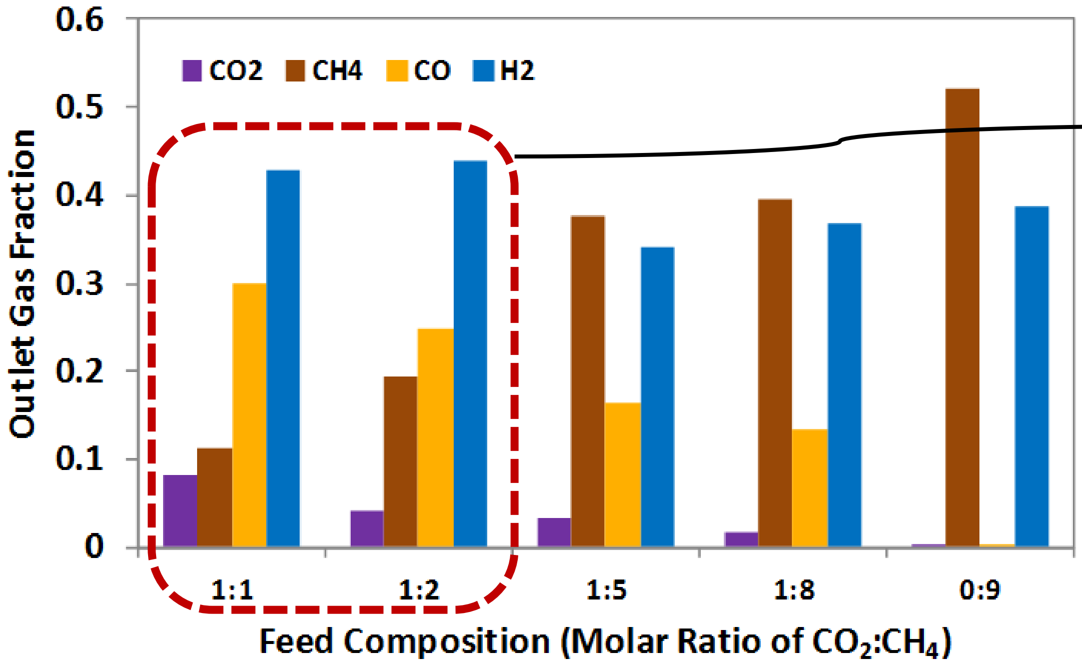
Product gas composition of DR on 4D Sn-infiltrated SOFC chips at different CO_2 : CH_4 ratio, at 800°C



Common CO_2:CH_4 compositions in biogas produced relatively high quantities of CO and H_2.
These compositions will be used for SOFC operation

The bar chart is derived from Mass Spectra that records only gaseous components; so solid carbon as one of the reforming products is not shown above.

As low as 1:8 CO_2:CH_4 ratio produces significant amount of H_2 and CO.
Highest reactants conversions and amount of CO was obtained at 1:1 CO_2:CH_4,
Reforming at 1:2 CO_2:CH_4 produced similar quantity of CO and H_2 to that at 1:1 ratio

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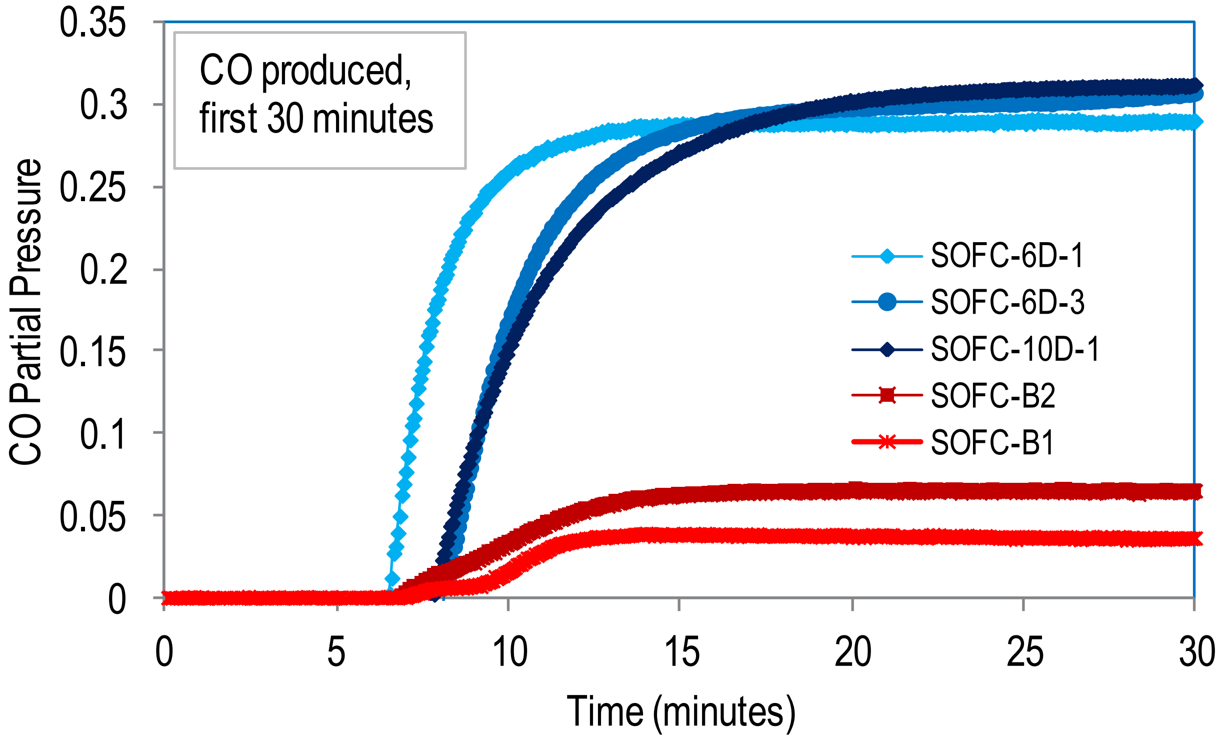
Mass spectra of SOFC outlet gas collected from 6 SOFCs at OCV when fuel is switched from H_2 to biogas (1:2 CO_2:CH_4 at 750°C)



Sn-infiltrated SOFCs: 6D1, 6D3, 10D-1

Non infiltrated SOFCs: B1 and B2

- ✓ **CO level appears much higher on Sn-infiltrated SOFCs than on non-infiltrated SOFCs.**
- ✓ **The slope of the curves show that formation of C-O bond is faster on Sn-Ni catalysts than that on Ni catalysts which promise less carbon formation is expected on Sn-Ni/YSZ SOFCs compared to that on NiYSZ SOFCs. Further investigations are still needed.**

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Conclusions

- Sn- anode infiltration was successfully carried out on sintered anode surface, using commercially available NiYSZ anodes,
- Sn/Ni alloy presence on NiYSZ have significantly increased CH_4 conversion in biogas dry reforming. This finding forms a firm ground for operating SOFC directly on biogas with high power output
- Further work is on going to further
  - characterise the catalysts,
  - elucidate mechanism of biogas dry reforming,
  - elaborate on how Sn improves NiYSZ catalytic activity in DR
  - evaluate carbon formation and
  - evaluate Sn-doping on in-house SOFC anodes

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Thank you for your attention

Any Questions?

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