Composite Mixed Ion-Electron Conducting (MIEC) Membranes for Hydrogen Generation and Separation

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Outline of the Presentation

- Motivations.
- Description of hydrogen generation and separation process.
- Fabrication and microstructure of the membranes.
- Hydrogen generation experiments.
- Effect of the surface catalyst on hydrogen generation process.
- Conclusions.
- Suggested future work.

Motivations and Research Objectives

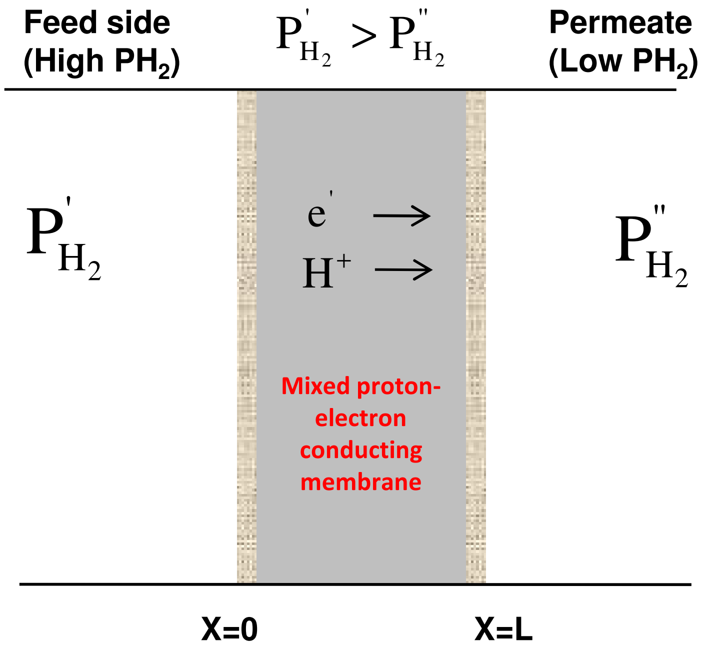
Motivations:

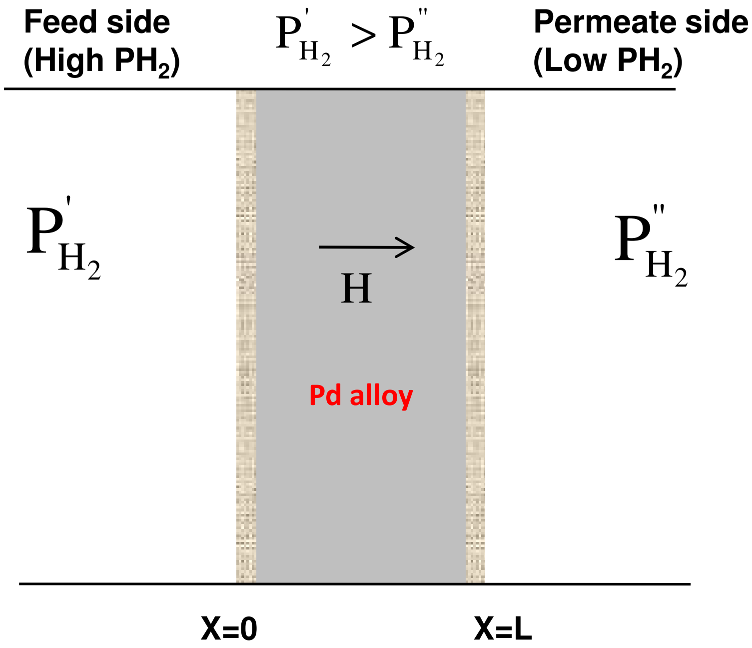
- Currently, more than 600 billion cubic meters of hydrogen consumed each year.
- Simultaneous generation of pure hydrogen and syn-gas production at commercially attractive rates.

Research Objective:

- Develop and analyze a new approach for hydrogen generation and separation from steam employing a MIEC based membrane architecture.

Conventional Membranes for Hydrogen Separation





Approach 1: (dense ceramics)
Hydrogen separation using mixed proton-electron conducting membrane

Permeation mechanism:
Coupled diffusion of protons and electrons

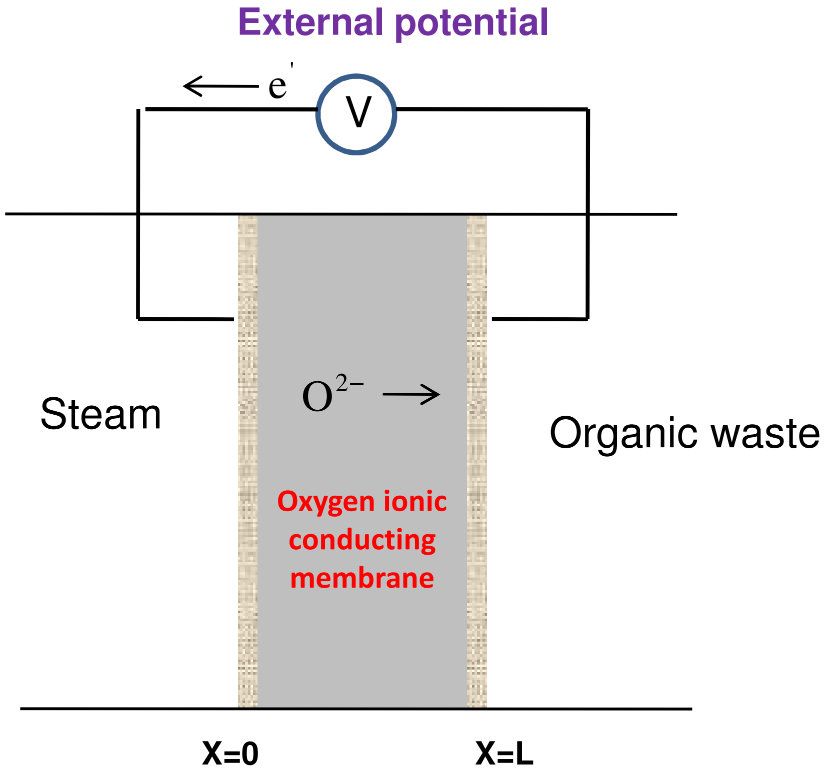
Drawback:
Low hydrogen production rate

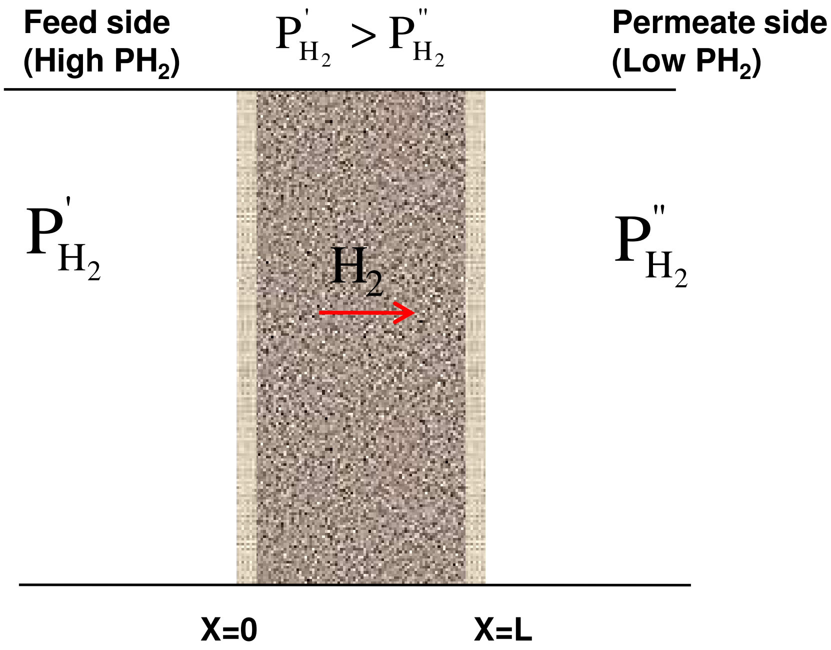
Approach 2: (dense metals and alloys)
Hydrogen separation using Pd and its alloys

Permeation mechanism:
Solution-diffusion mechanism

Drawback:
Unstable when exposed to sulfur hydrogen

Continued:





Approach 3: (Ionic conducting membrane)

Hydrogen production from organic waste using oxygen ionic conducting membrane

Permeation mechanism:

Oxygen ions transport through the dense membrane

Drawback:

Complicated device

Approach 4: (Microporous membrane)

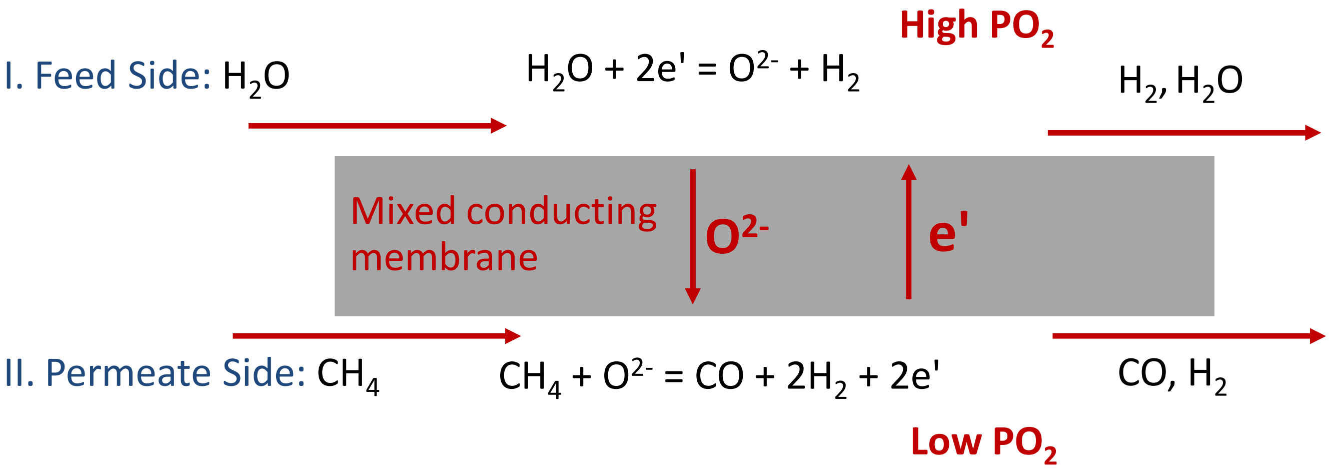
Permeation mechanism:

Hydrogen gas diffuse through the pores of the membrane.

Drawback:

Low selectivity

Our Hydrogen Separation Approach
(Simultaneous production of hydrogen and syn-gas)



MIEC dense membrane

Material Selection: $Gd_{0.2}Ce_{0.8}O_{1.9}$(GDC)/$Gd_{0.08}Sr_{0.88}Ti_{0.95}Al_{0.05}O_{3\pm\delta}$(GSTA)

- GDC: Ionic conducting phase

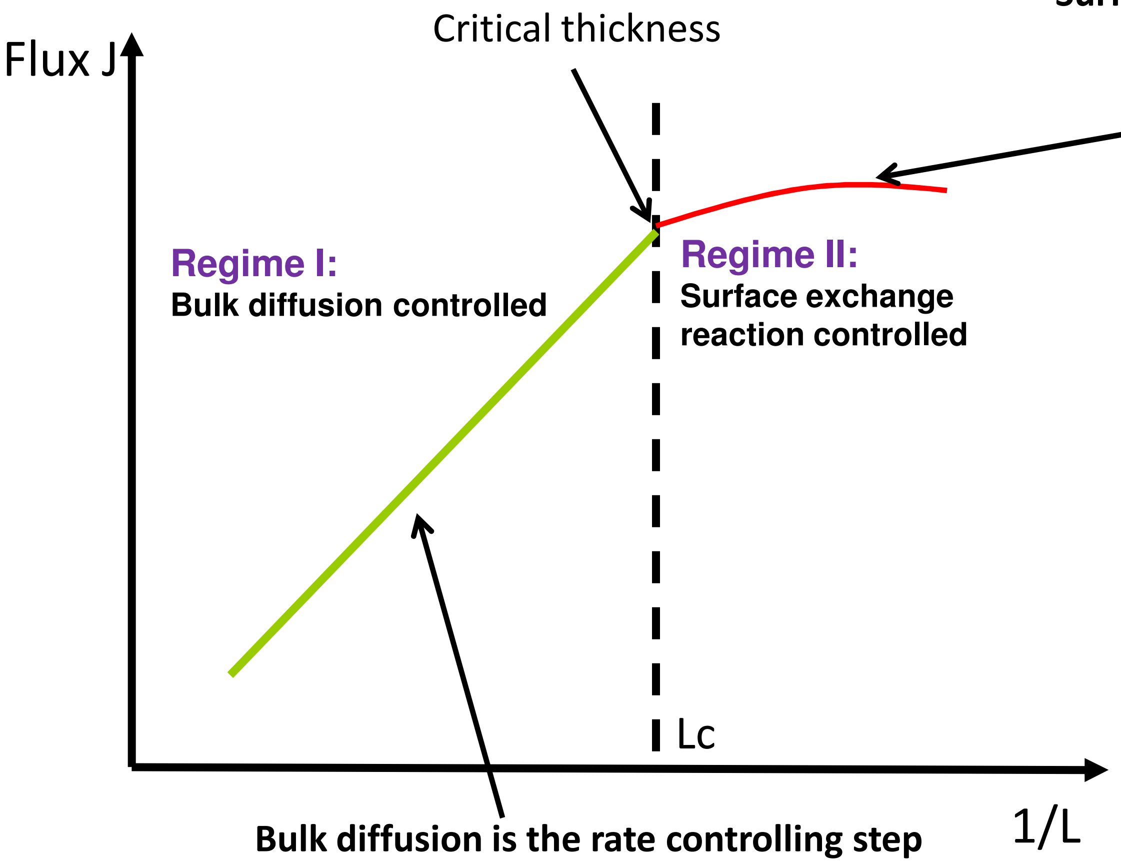
$$Gd_2O_3 \xrightarrow{2CeO_2} 2Gd'_{Ce} + 3O_O^{\times} + V_O^{\cdot\cdot}$$

- GSTA: n-type electronic conducting phase

$$Gd_2O_3 + 2TiO_2 \xrightarrow{2SrTiO_3} 2Gd^{\cdot}_{Sr} + 2Ti'_{Ti} + 6O_O^{\times} + \frac{1}{2}O_2(g) \qquad Ti_{Ti}^{\times} + e' = Ti'_{Ti}$$

$$O_O^{\times} \to \frac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e'$$

Critical Thickness of the Membrane



Flux J

Critical thickness

Regime I:
Bulk diffusion controlled

Regime II:
Surface exchange reaction controlled

Lc

1/L

Bulk diffusion is the rate controlling step

$$J_{H_2}=\frac{D_v k_r}{L k_f}(1/\sqrt{P_{O_2}^{permeate}}-1/\sqrt{P_{O_2}^{feed}})$$

Surface exchange is the rate controlling step

$$J_{H_2}=\frac{\frac{2k_r}{k_f}(1/\sqrt{P_{O_2}^{permeate}}-1/\sqrt{P_{O_2}^{feed}})}{\frac{1}{K_{ex}^{permeate}}+\frac{2L}{D_v}+\frac{1}{K_{ex}^{feed}}+k\frac{\tau L_s}{PD_{H_2\text{-}H_2O}}}$$

$\frac{1}{K_{ex}^{permeate}}$	Resistance of surface exchange reaction on permeate side
$\frac{1}{K_{ex}^{feed}}$	Resistance of surface exchange reaction on feed side
$\frac{2L}{D_v}$	Bulk diffusion resistance
$k\frac{\tau L_s}{PD_{H_2\text{-}H_2O}}$	Resistance of gas diffusion through porous support

L: membrane thickness

S. J. Xu and W. J. Thomson, *Chem. Eng. Sci.*, **54**, 3839 (1999).

Derivation of the Permeation Equation

(a) Five steps involved in the oxygen permeation through mixed ion-electron conducting membrane:

(b) Two Steps not considered:

Step 1: gas phase mass transfer of gaseous species on feed side
Step 5: gas phase mass transfer of gaseous species on permeate side

(c) Three important steps are considered:

Step 2: surface exchange reaction on feed side

$$J_{O_2} = k_f P_{O_2}^{'0.5} C_V^{'} - k_r$$

Step 3: oxygen bulk diffusion process

$$J_{O_2} = \frac{1}{2} J_V = \frac{D_V}{2L}(C_V^{''} - C_V^{'})$$

Step 4: surface exchange reaction on permeate side

$$J_{O_2} = k_r - k_f P_{O_2}^{''0.5} C_V^{''}$$

k_f and k_r The forward and reverse reaction rate constants for oxygen incorporation reaction. Functions of gas compositions, microstructure and properties of the membrane surface

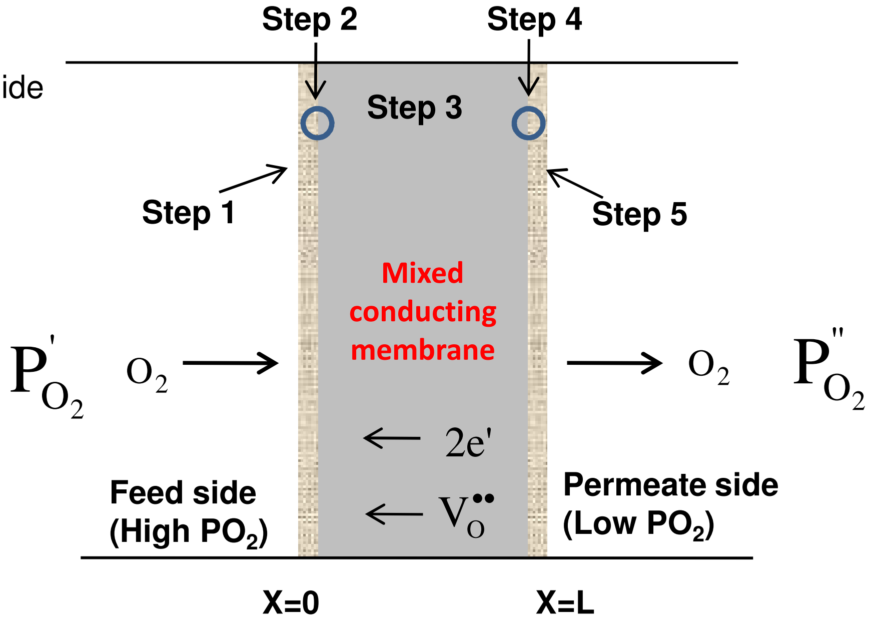
D_V Oxygen vacancy diffusivity

Interface I

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e^{'} \underset{k_r}{\overset{k_f}{\rightleftarrows}} O_O^x$$

Interface II

$$O_O^x \underset{k_f}{\overset{k_r}{\rightleftarrows}} \frac{1}{2}O_2 + V_O^{\bullet\bullet} + +2e^{'}$$



$$P_{O_2}^{'} > P_{O_2}^{''}$$

L is the membrane thickness

$C_V^{''}, C_V^{'}$ Oxygen vacancy concentration at the low and high oxygen partial pressure sides of the membrane

S. J. Xu and W. J. Thomson, *Chem. Eng. Sci.*, **54**, 3839 (1999).

Continued:

Derivation of the Permeation Flux Equation

Oxygen permeation flux equation:

$$J_{O_2} = \frac{D_V k_r (P_{O_2}^{'0.5} - P_{O_2}^{''0.5})}{2Lk_f P_{O_2}^{'0.5} P_{O_2}^{''0.5} + D_V (P_{O_2}^{'0.5} + P_{O_2}^{''0.5})}$$

Equation (4) can be further simplified as:

$$J_{O_2} = \frac{\frac{k_r}{k_f}(P_{O_2}^{'-0.5} - P_{O_2}^{''-0.5})}{\frac{2L}{D_V} + \frac{1}{k_f P_{O_2}^{''0.5}} + \frac{1}{k_f P_{O_2}^{'0.5}}}$$

Continued:

Derivation of the Permeation Flux Equation

The area specific hydrogen generation rate can be expressed as:

$$J_{H_2} = 2J_{O_2} = \frac{\frac{2k_r}{k_f}(P_{O_2}^{'-0.5} - P_{O_2}^{''-0.5})}{\frac{2L}{D_V} + \frac{1}{k_f P_{O_2}^{''0.5}} + \frac{1}{k_f P_{O_2}^{'0.5}}} = \frac{\frac{2k_r}{k_f}(P_{O_2}^{'-0.5} - P_{O_2}^{''-0.5})}{\frac{2L}{D_V} + \frac{1}{K_{ex}^{permeate}} + \frac{1}{K_{ex}^{feed}}}$$

(both surface exchange reactions and bulk diffusion process are included)

$(P_{O_2}^{'-0.5} - P_{O_2}^{''-0.5})$ Driving force for the permeation process

$\frac{1}{k_f P_{O_2}^{''0.5}} = \frac{1}{K_{ex}^{permeate}}$ Resistance on the permeate side

$\frac{1}{k_f P_{O_2}^{'0.5}} = \frac{1}{K_{ex}^{feed}}$ Resistance on the feed side

$\frac{2L}{D_V}$ Bulk diffusion resistance

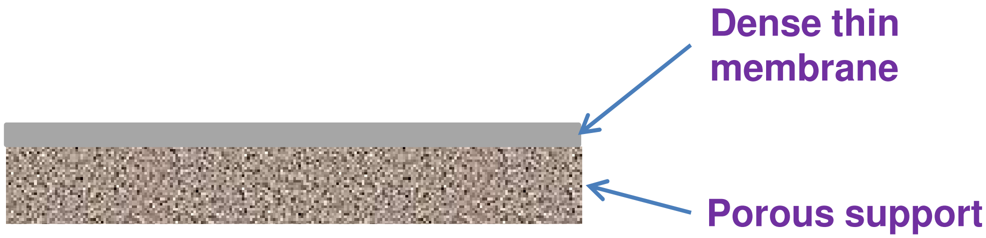
For the bulk diffusion controlled permeation process with small surface exchange resistances:

$$J_{H_2} = 2J_{O_2} = \frac{D_V k_r}{L k_f}(P_{O_2}^{'-0.5} - P_{O_2}^{''-0.5})$$

(Only bulk diffusion process is included)

Membranes Architectures

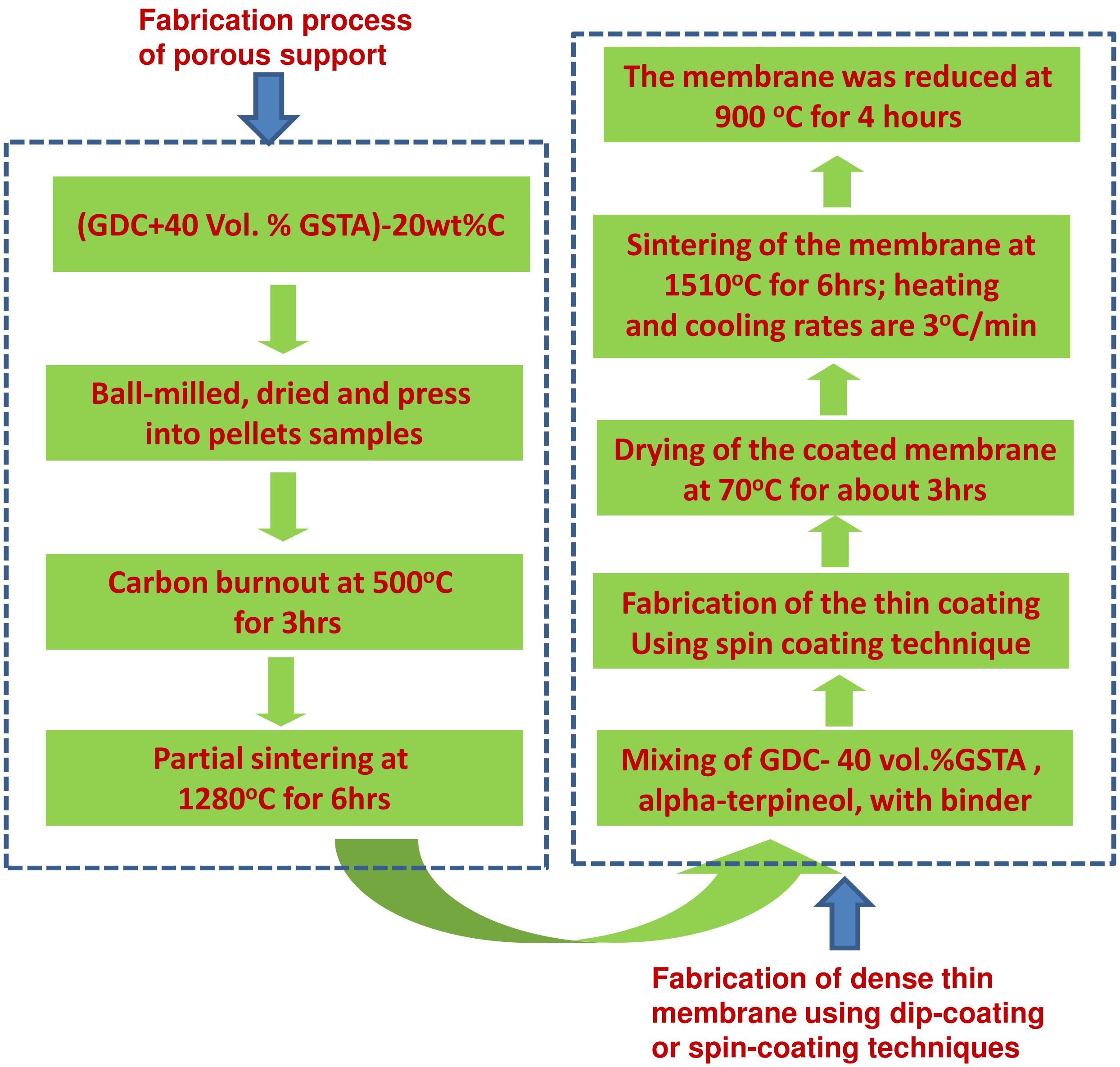
Self-supported thick membrane



Porous supported dense thin membrane

Thickness of the porous support: 2 mm
Thickness of the dense membrane: 10-45 microns

Fabrication Process of the Porous Supported Dense Thin Membranes



Fabrication process of porous support

(GDC+40 Vol. % GSTA)-20wt%C

Ball-milled, dried and press into pellets samples

Carbon burnout at 500^{o}C for 3hrs

Partial sintering at 1280^{o}C for 6hrs

The membrane was reduced at 900 ^{o}C for 4 hours

Sintering of the membrane at 1510^{o}C for 6hrs; heating and cooling rates are 3^{o}C/min

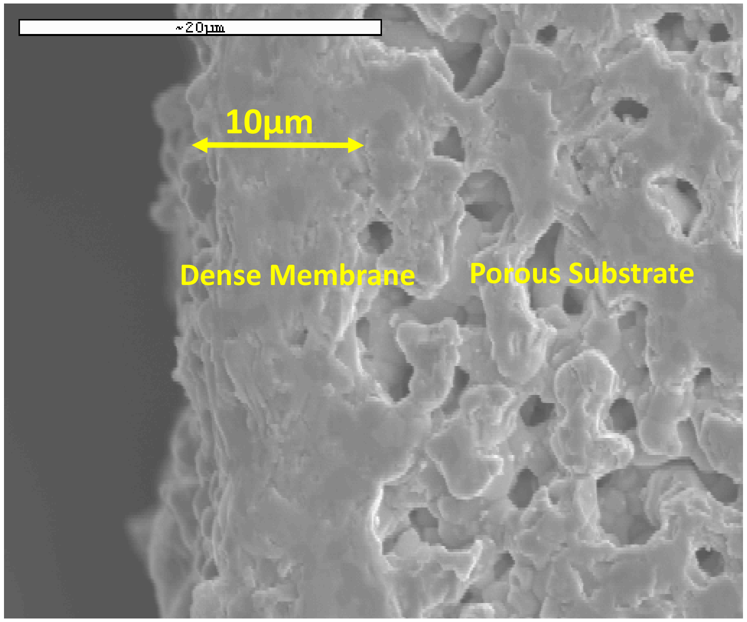
Drying of the coated membrane at 70^{o}C for about 3hrs

Fabrication of the thin coating Using spin coating technique

Mixing of GDC- 40 vol.%GSTA , alpha-terpineol, with binder

Fabrication of dense thin membrane using dip-coating or spin-coating techniques

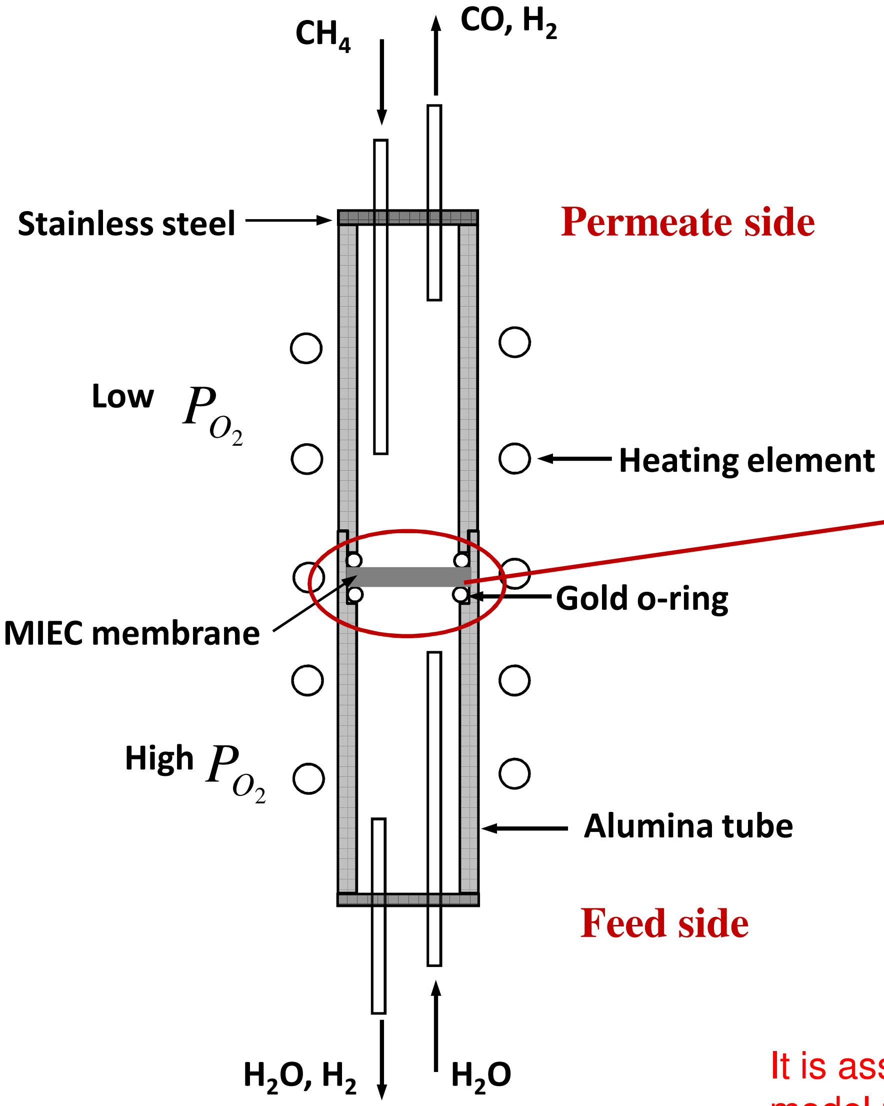
Typical Microstructure of the Porous Supported Membrane

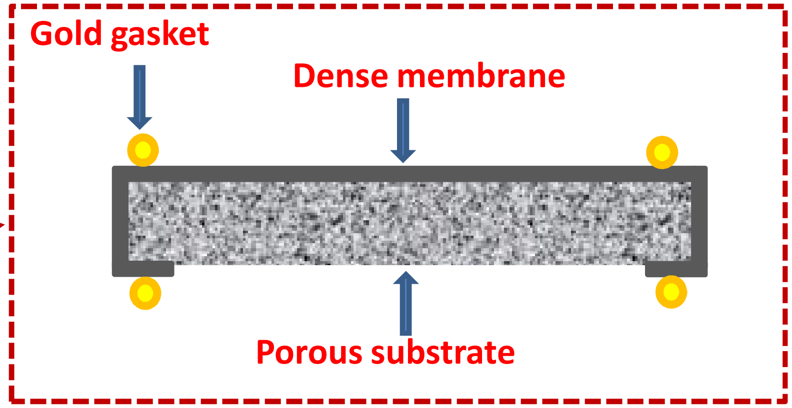


Micrograph of the dense membrane

- Thickness of the dense membrane can be decreased to **10** μm or even thinner using a spin coating technique.
- The porosity of the porous support is around 36%

Set-up for Permeation Experiment

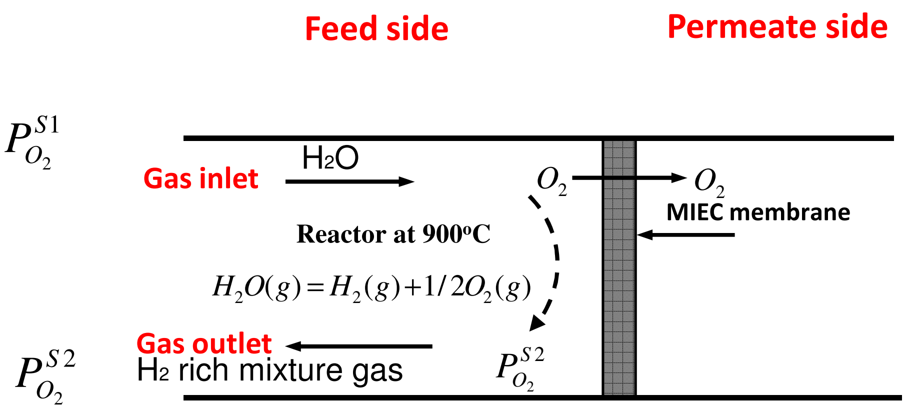




Schematic of dense membrane supported on porous substrate

It is assumed that CSTR (continuous stirred-tank reactor) model may be applied to membrane reactor

Calculation of the Area Specific Hydrogen Generation Rate



Feed side

Permeate side

$P_{O_2}^{S1}$

Gas inlet H_2O

O_2 → O_2

MIEC membrane

Reactor at 900°C

$H_2O(g) = H_2(g) + 1/2O_2(g)$

Gas outlet

H_2 rich mixture gas

$P_{O_2}^{S2}$

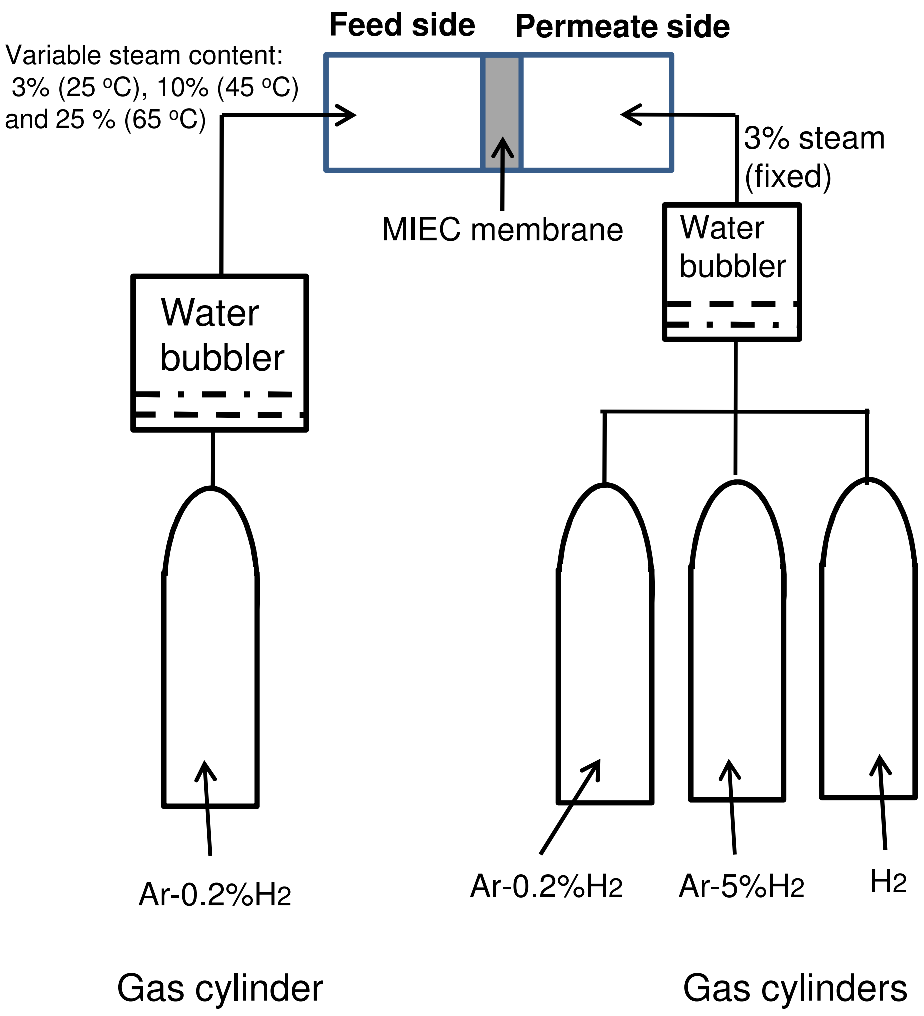
$P_{O_2}^{S2}$

$$J_{H_2} = \frac{F_{H_2}^{in}[(P_{O_2}^{S1})^{0.5} - (P_{O_2}^{S2})^{0.5}]}{A \cdot [(P_{O_2}^{S2})^{0.5} + K_{eq}]}$$

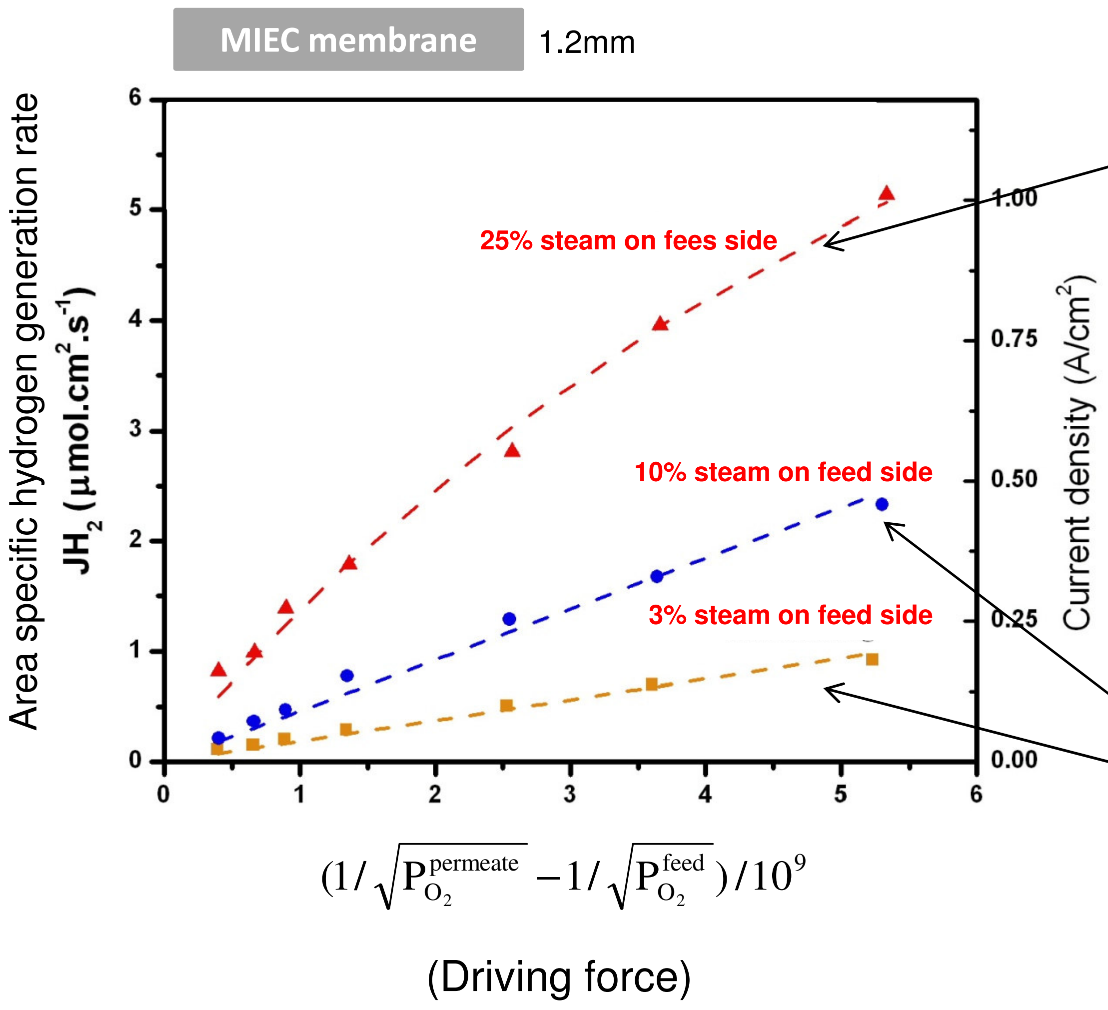
$P_{O_2}^{S1}$	The oxygen partial pressure on the feed side inlet
$P_{O_2}^{S2}$	The oxygen partial pressure on the feed side exit
K_{eq}	The equilibrium constant of the steam dissociation reaction
A	The area of the membrane surface
$F_{H_2}^{in}$	Hydrogen flow rate in the feed side inlet.

Inlet Gas Compositions on the Feed Side and Permeate Side

Exp. #	**Feed side flow rate (cc/min)**		**Permeate side flow rate (cc/min)**		
	Ar-0.2%H_2		Ar-0.2%H_2	Ar-5%H_2	H_2
1	400		400	0	0
2	400		380	20	0
3	400		350	50	0
4	400		300	100	0
5	400		200	200	0
6	400		100	300	0
7	400		0	400	0
8	400		0	380	20
9	400		0	360	40
10	400		0	340	60
11	400		0	300	100
12	400		0	200	200
13	400		0	0	400



Results for the 1.2 mm Self-Supported Membrane



Nonlinear fitting equation:

$$J_{H_2}=\frac{\frac{2k_r}{k_f}(1/\sqrt{P_{O_2}^{permeate}}-1/\sqrt{P_{O_2}^{feed}})}{\frac{1}{K_{ex}^{permeate}}+\frac{2L}{D_v}+\frac{1}{K_{ex}^{feed}}}$$

$\frac{1}{K_{ex}^{permeate}}$ Resistance of surface exchange reaction on permeate side

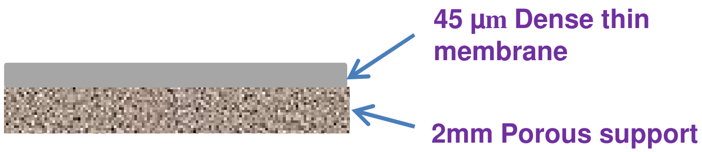
$\frac{1}{K_{ex}^{feed}}$ Resistance of surface exchange Reaction on feed side

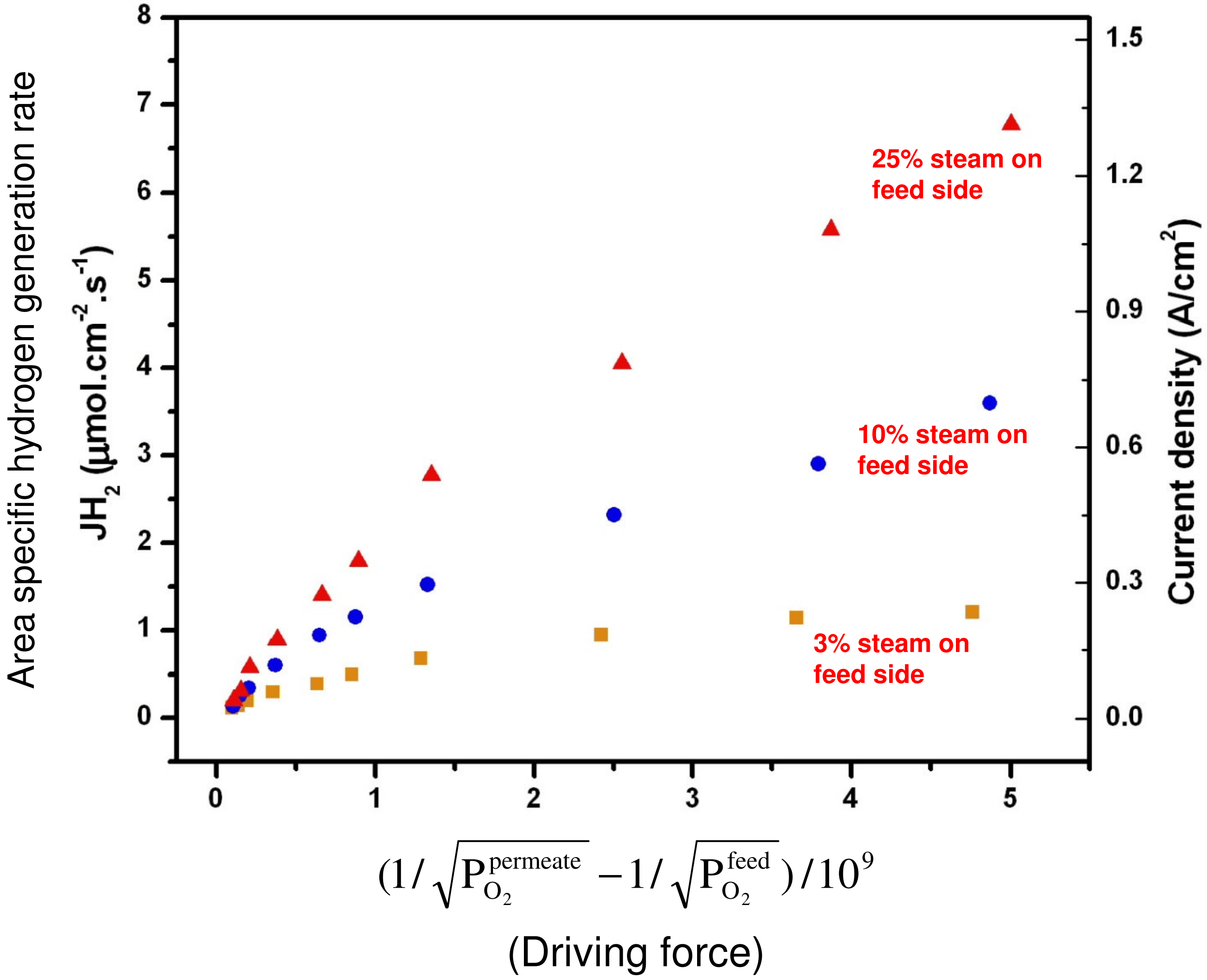
$\frac{2L}{D_v}$ Bulk diffusion resistance

Linear fitting equation:

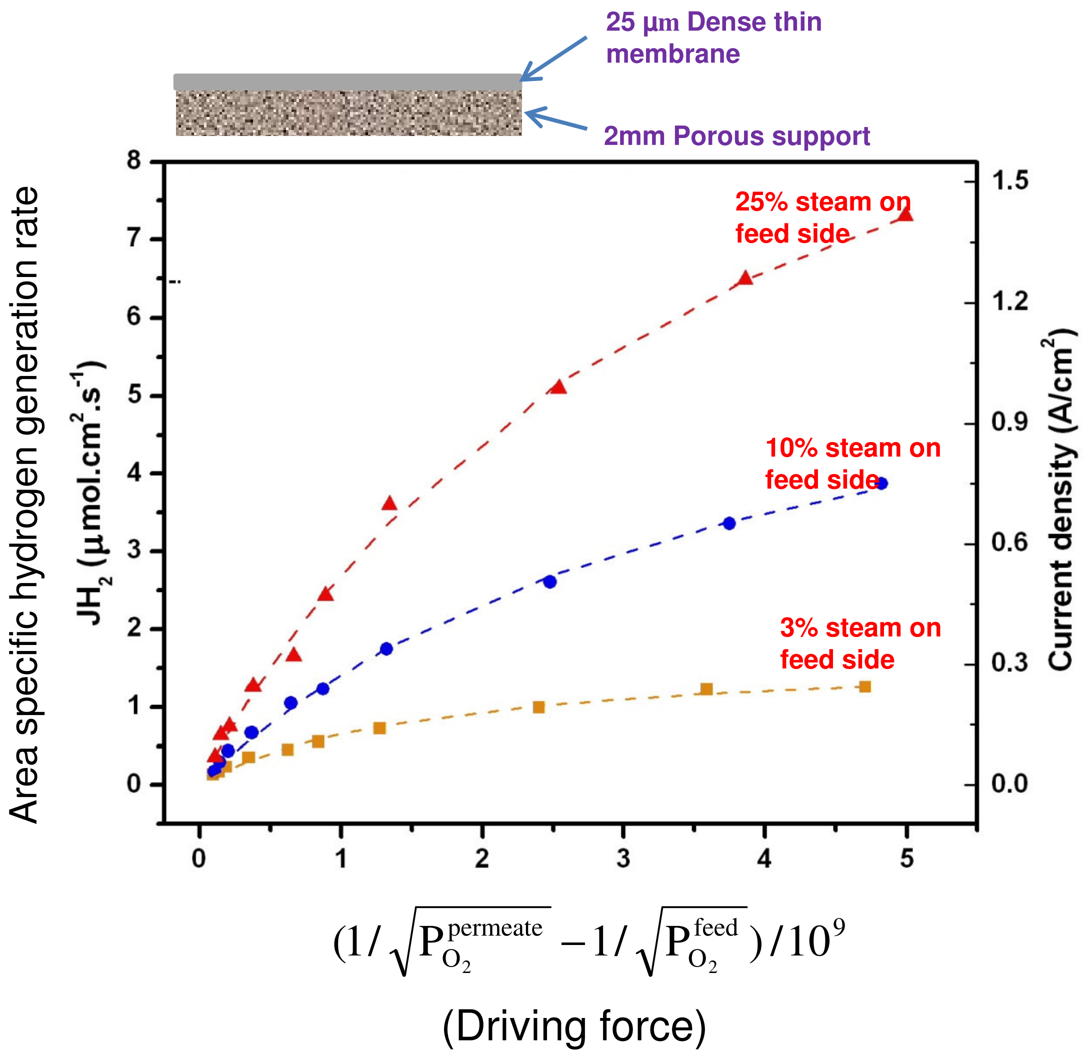
$$J_{H_2}=\frac{D_v k_r}{Lk_f}(1/\sqrt{P_{O_2}^{permeate}}-1/\sqrt{P_{O_2}^{feed}})$$

Results for the 45 µm Porous Supported Membrane





Results for the 25 μm Porous Supported Membrane



Nonlinear fitting equation:

$$J_{H_2} = \frac{\frac{2k_r}{k_f}(1/\sqrt{P_{O_2}^{permeate}} - 1/\sqrt{P_{O_2}^{feed}})}{\frac{1}{K_{ex}^{permeate}} + \frac{2L}{D_v} + \frac{1}{K_{ex}^{feed}}}$$

$\frac{1}{K_{ex}^{permeate}}$	Resistance of surface exchange reaction on permeate side
$\frac{1}{K_{ex}^{feed}}$	Resistance of surface exchange reaction on feed side
$\frac{2L}{D_v}$	Bulk diffusion resistance

Fitted Parameters for 25 μm Porous Supported Membrane

Fitted parameters	3% steam	10% steam	25% steam
k_r (μmol/cm^2.s)	0.84	3.43	6.3
k_f (cm/atm$^{0.5}$.s)	9.2×10^6	2.3×10^7	2.2×10^7

Calculated parameters	3% steam	10% steam	25% steam
$1/K_{ex}^{feed}$ (s/cm)	0.701-40.5	0.152-11.1	0.048-3.84
$1/K_{ex}^{permeate}$ (s/cm)	0.982-552	0.393-221	0.411-231
$2L/D_V$ (s/cm)	167	167	167

$$H_2O(g) \Leftrightarrow H_2(g) + 1/2O_2(g)$$

$$K_{ex}^{feed} = k_f \sqrt{P_{O_2}^{feed}}$$

Resistance on the feed side

$$\sqrt{P_{O_2}^{feed}} = \frac{P_{H_2O}^{feed}}{P_{H_2}^{feed}} \cdot K_{eq}$$

$$K_{ex}^{permeate} = k_f \sqrt{P_{O_2}^{permeate}}$$

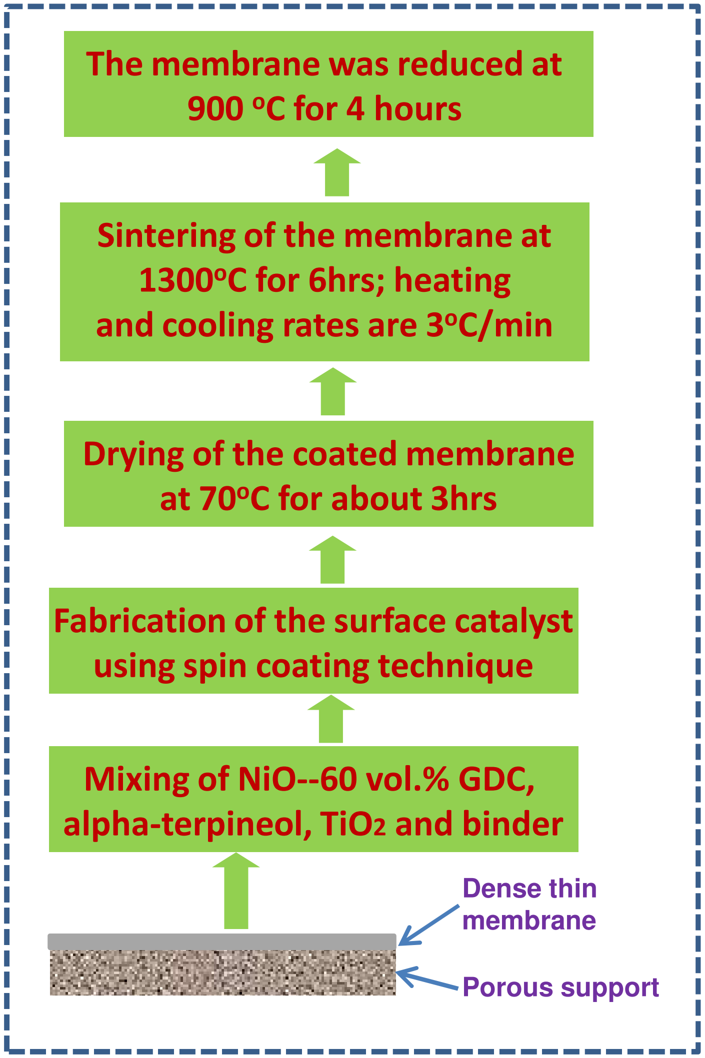
Resistance on the permeate side

$$\sqrt{P_{O_2}^{permeate}} = \frac{P_{H_2O}^{permeate}}{P_{H_2}^{permeate}} \cdot K_{eq}$$

An Example of the Measured Oxygen Partial Pressures

Exp. #	PO_2 on permeate side outlet	PO_2 on feed side outlet
1	1.23E-14	9.16E-13
2	1.28E-15	4.67E-13
3	6.06E-16	2.58E-13
4	2.16E-16	1.74E-13
5	7.73E-17	8.87E-14
6	4.11E-17	3.43E-14
7	2.10E-17	2.60E-14
8	6.65E-18	9.67E-15
9	2.20E-18	5.67E-15
10	1.21E-18	2.47E-15
11	5.28E-19	9.93E-16
12	1.49E-19	4.08E-16
13	6.49E-20	2.04E-16

Fabrication Architecture of Porous Supported Membrane Coated with Surface Catalyst



The membrane was reduced at 900 °C for 4 hours

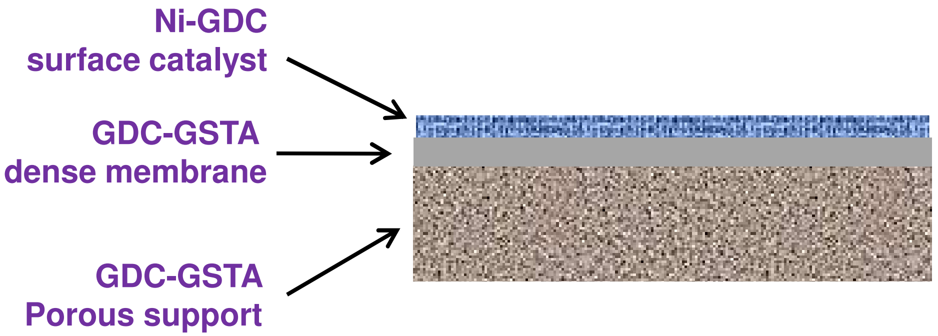
Sintering of the membrane at 1300°C for 6hrs; heating and cooling rates are 3°C/min

Drying of the coated membrane at 70°C for about 3hrs

Fabrication of the surface catalyst using spin coating technique

Mixing of NiO--60 vol.% GDC, alpha-terpineol, TiO_2 and binder

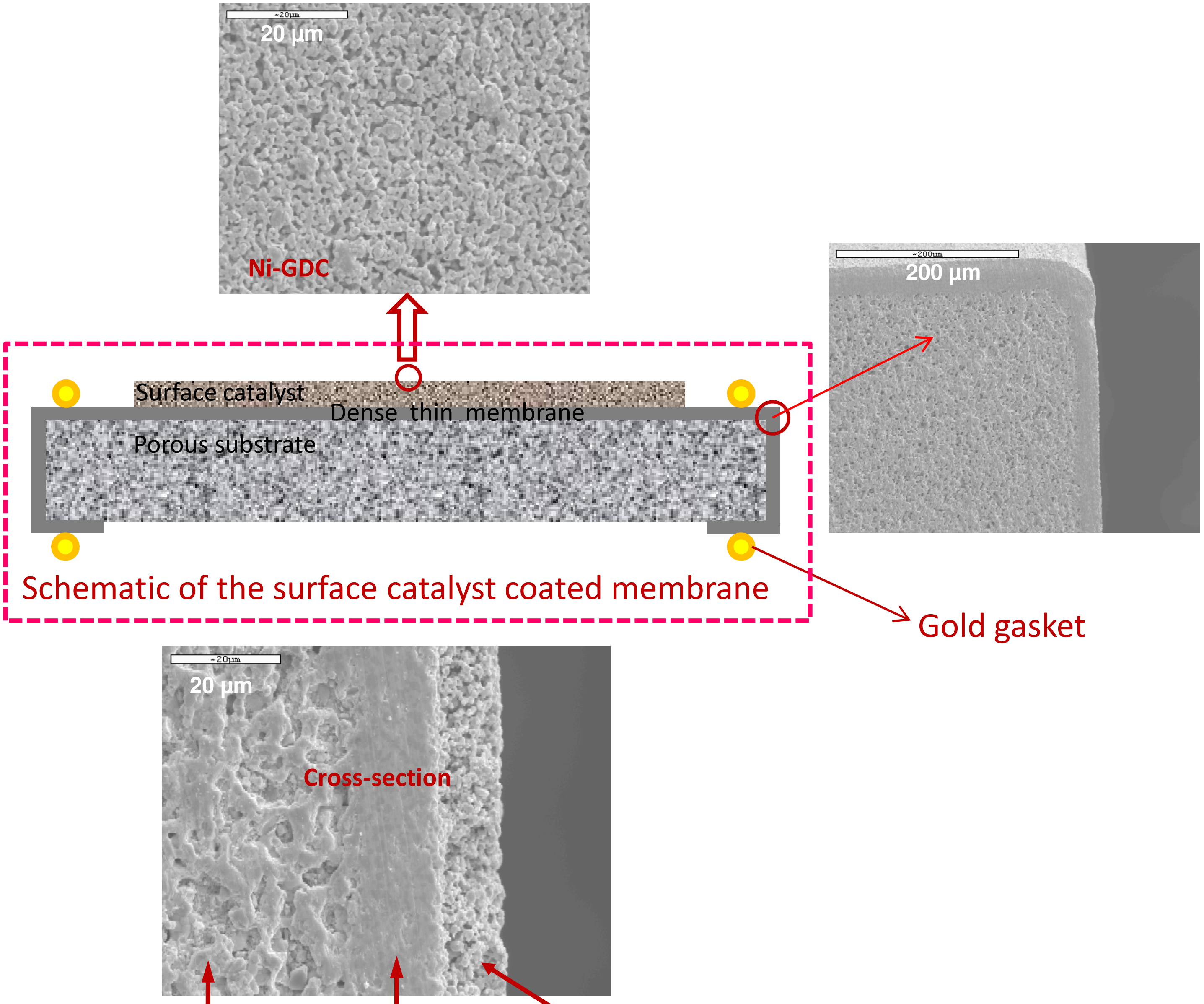
Fabrication process of the surface catalyst coated membrane



Schematic membrane architecture

H. Cui, A. Karthikeyan, S. Gopalan, and U. B. Pal, *Electrochemical and Solid-State Letters*, **9**, A179-A181 (2006)

Microstructure of MIEC Membrane Coated with Surface Catalyst



Surface catalyst

Dense thin membrane

Porous substrate

Schematic of the surface catalyst coated membrane

Gold gasket

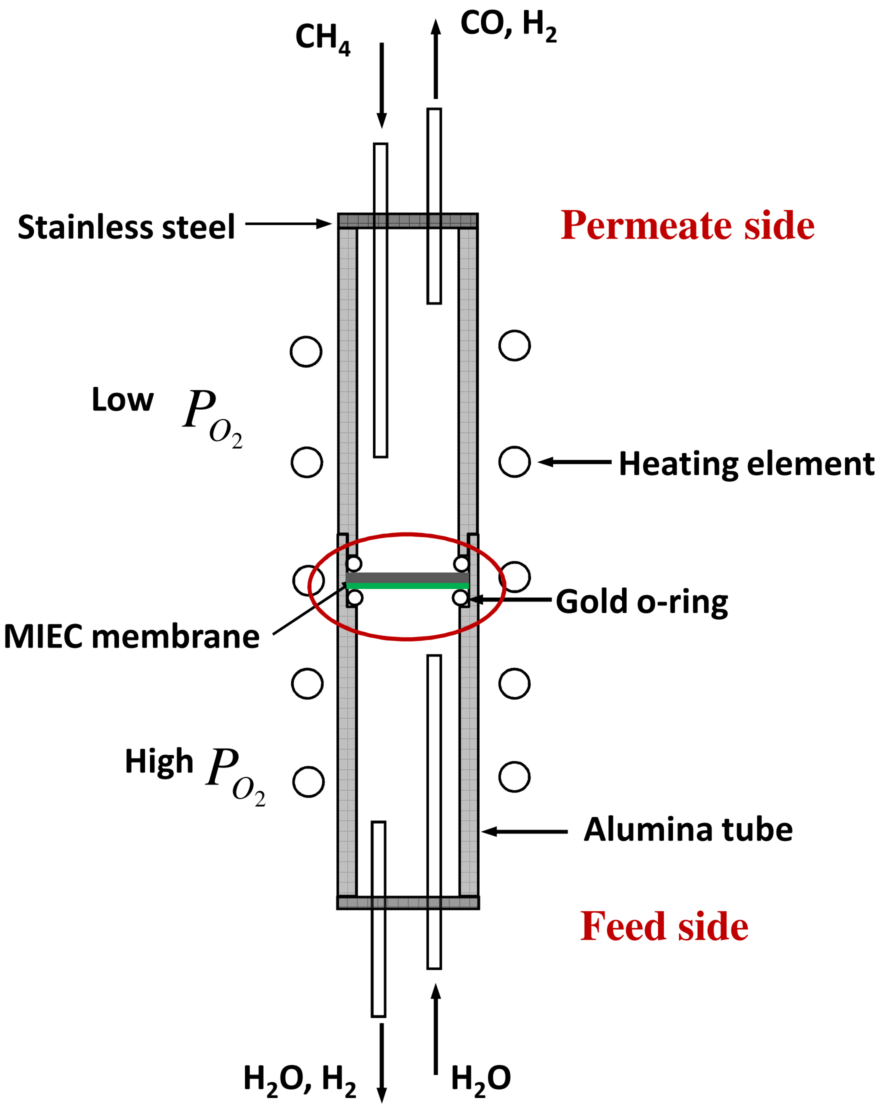
Porous substrate

Dense thin membrane

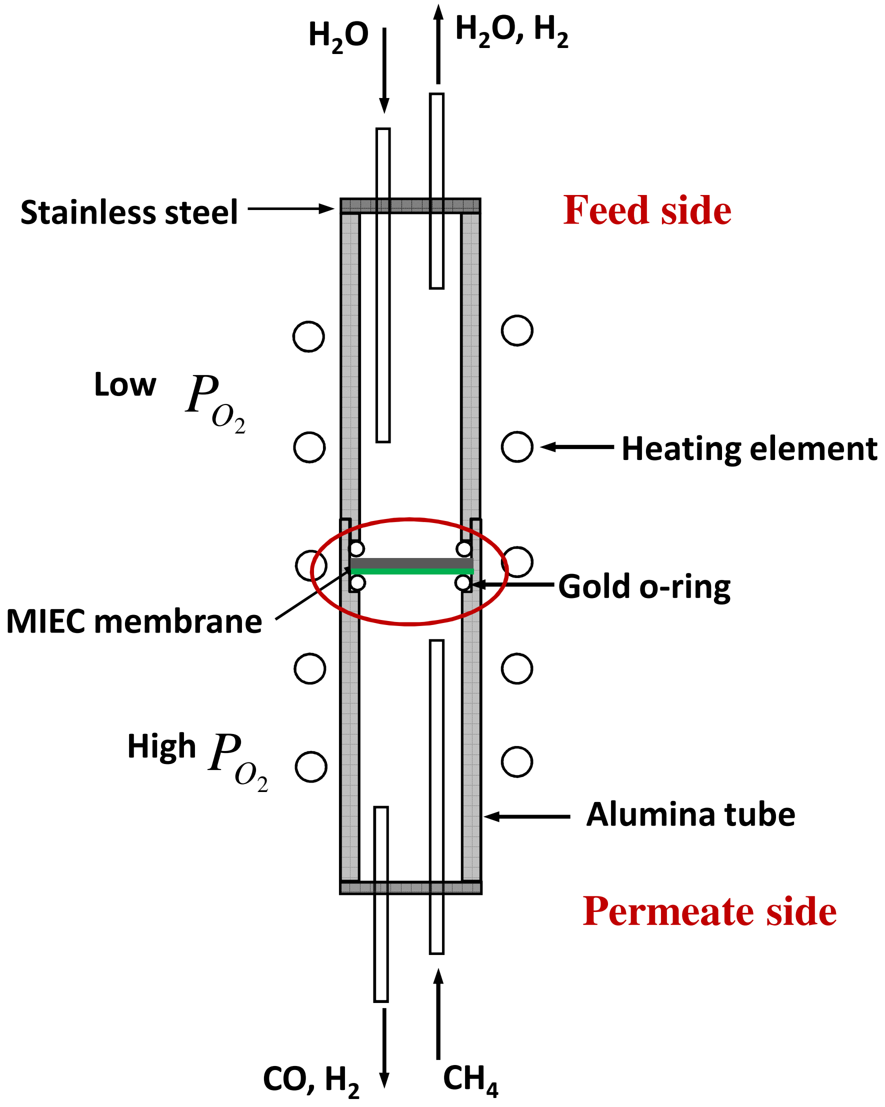
Surface catalyst

Permeation Experiment for Membranes with Surface Catalyst

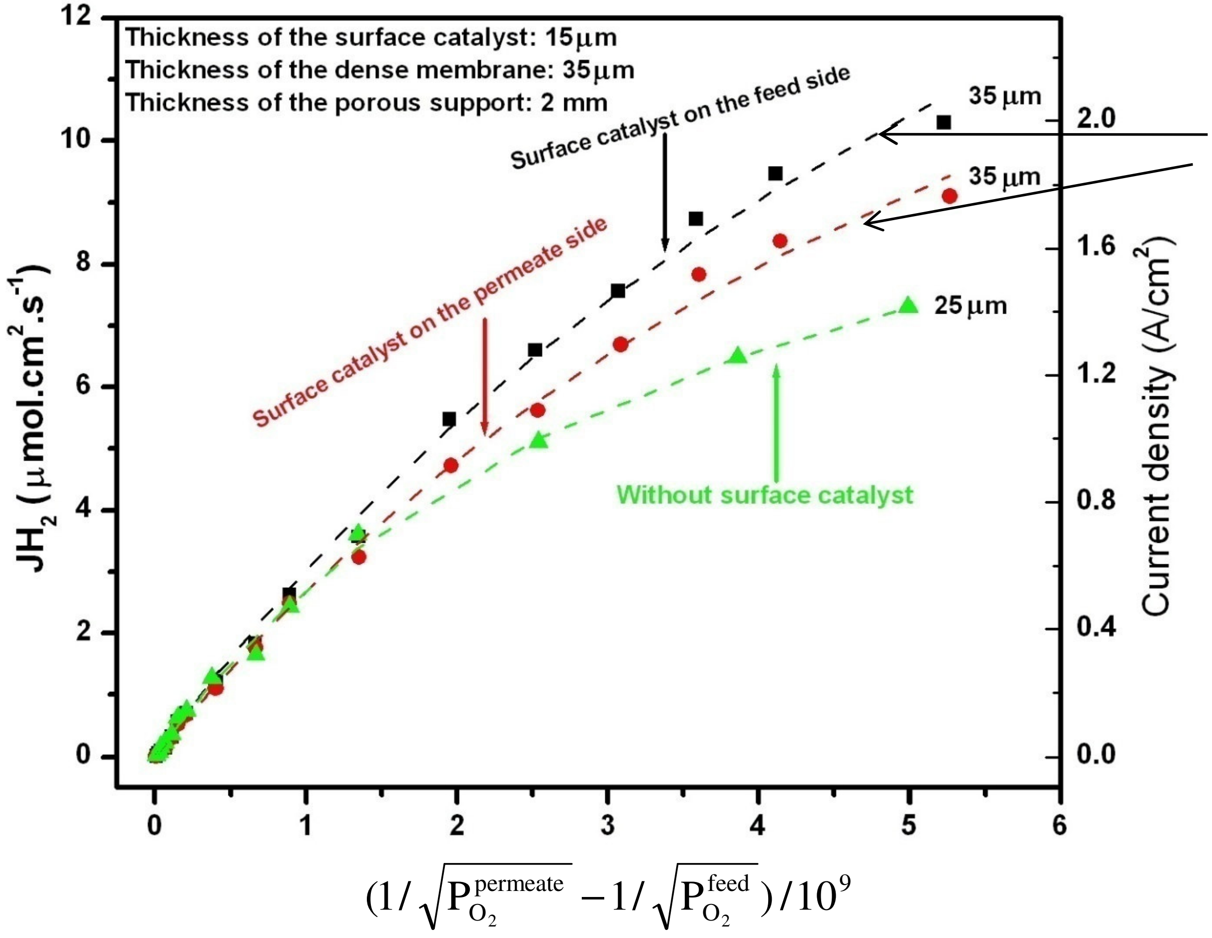
Surface catalyst exposed to the feed side



Surface catalyst exposed to the permeate side



Effect of the Surface Catalyst on the Hydrogen Generation Rates

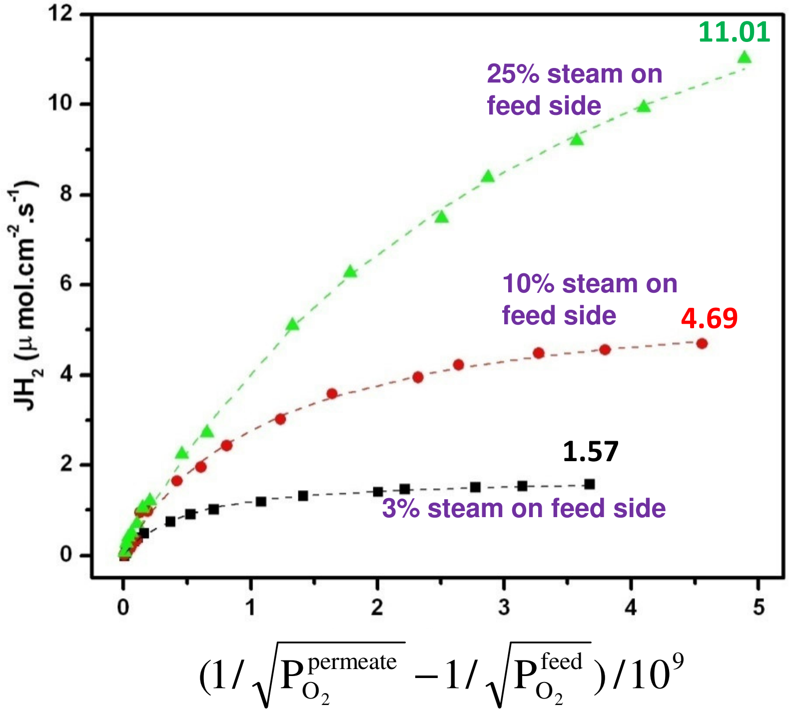


Surface catalyst coated membrane

Steam content on the feed side of the membrane: 25%

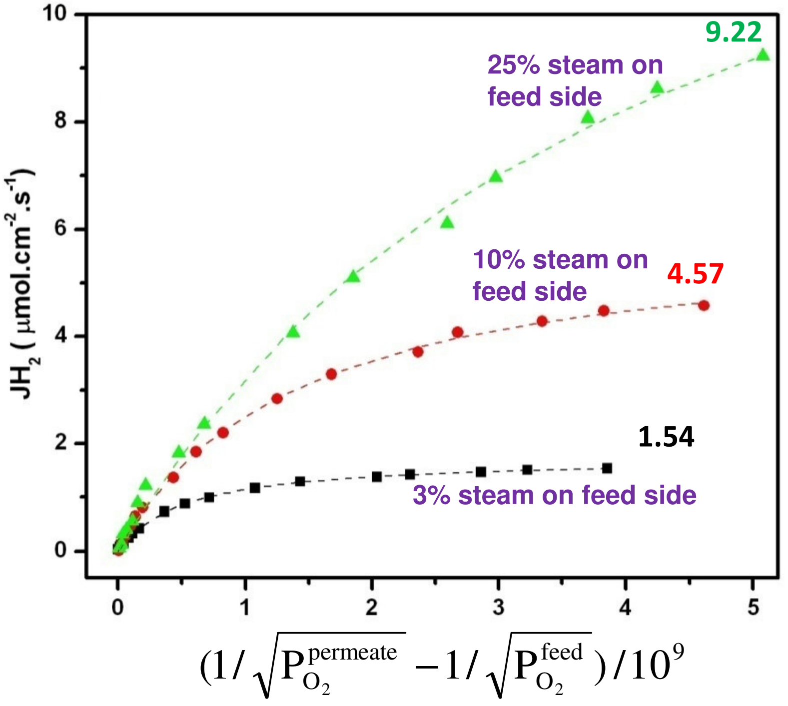
Effect of Surface Catalyst on Feed Side and Permeate Side

Surface catalyst exposed to the feed side



Feed side catalyzed

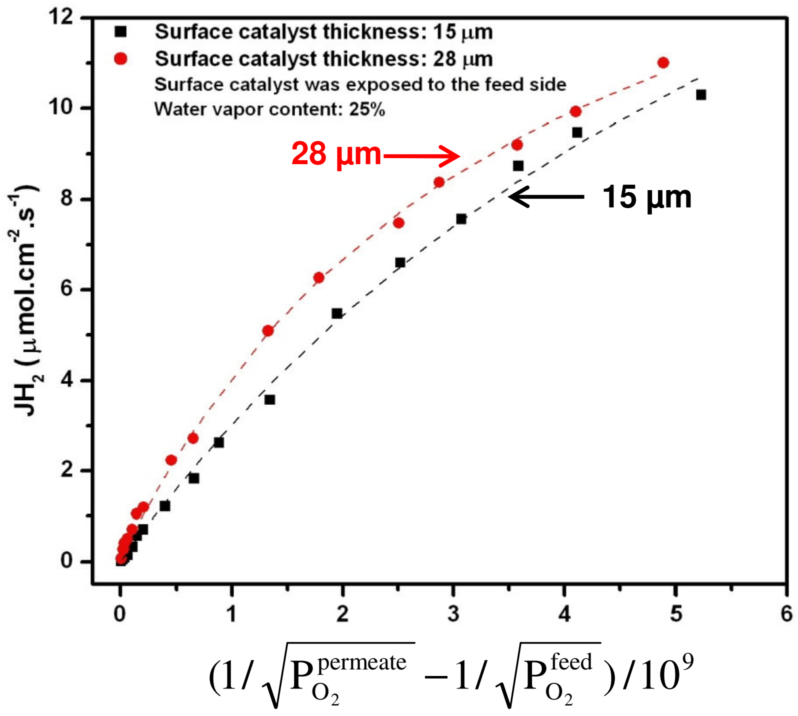
Surface catalyst exposed to the permeate side



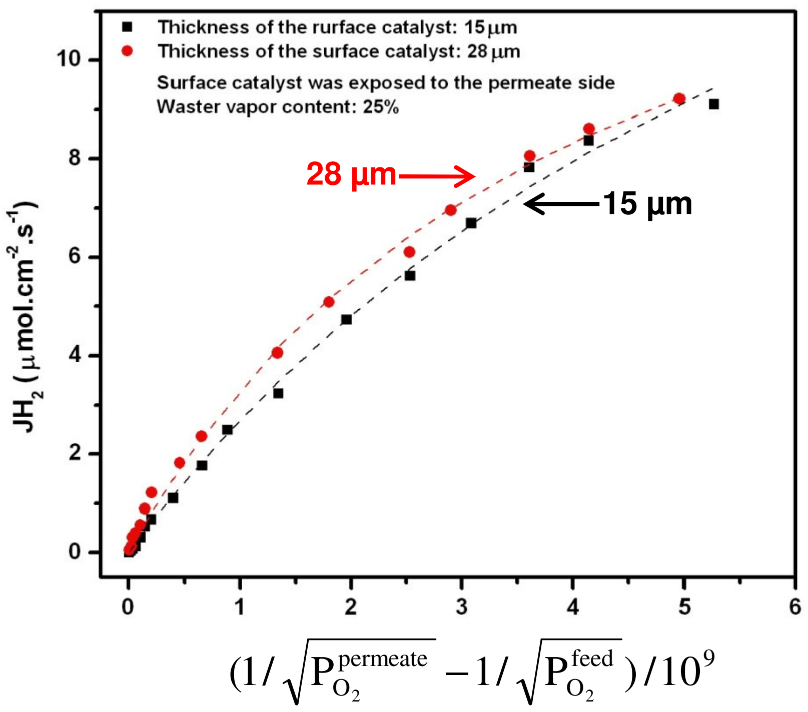
Permeate side catalyzed

Thickness of the dense membrane: 35 μm
Thickness of the surface catalyst : ～28 μm
Thickness of the porous support: 2 mm

Effect of Catalyst Thickness on Hydrogen Generation Rate



Surface catalyst exposed to the feed side
Steam content on feed side: 25%



Surface catalyst exposed to the permeate side
Steam content on feed side : 25%

Comparison of the Hydrogen Generation Rates using Different Membrane Technologies

Materials	Hydrogen generation rate	Membrane thickness	Operating temperature
GDC-GSTA	11 μmol•cm-2•s^{-1}	35 μm membrane coated with surface catalyst	1173 K
$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$	1.5 μmol•cm-2•s^{-1}	2 μm membrane	950 K [a] [c]
Pd-40Cu	151 μmol•cm-2•s^{-1}	1.3 μm membrane	638 K [b]

In actual membrane reactor for hydrogen production using our approach, the steam content on the feed side will be increased to ～100% and a much higher hydrogen production rate is expected.

[a]: Satoshi Hamakawa et al. *Solid State Ionics*, 48 (2002) 71-81

[b]: Paul M. Theon et al, *Desalination*, 193 (2006) 224-229

[c]: S. Gopalan, A. V. Virkar, *Journal of The Electrochemical Society*, **140**, 1060-1065 (1993)

Conclusions and Future Work

Conclusions:

- Porous supported dense membrane as thin as 10 µm was fabricated using dip-coating and spin coating techniques.
- A mathematical model for the calculation of the area specific hydrogen generation rates was derived based on the measured oxygen partial pressures, gas compositions, and gas flow rates of the inlet and outlet gases on the feed side.
- Hydrogen generation/oxygen permeation process for the self standing thick membranes is mainly controlled by the oxygen bulk diffusion process, while the hydrogen generation for the porous supported dense thin membranes is controlled by both the surface exchange reactions and bulk diffusion process.
- The effect of the surface catalyst is more pronounced when it is exposed to the feed side rather than the permeate side, and a high area specific hydrogen generation rate ($11.01 \mu mol.cm^{-2}.s^{-1}$) was obtained.

Work In Progress:

- Catalyze both surfaces of the membrane to get higher hydrogen generation rates.
- Investigate alternative surface catalyst for partial oxidation of hydrocarbons.
- Incorporation of pore diffusion resistance in the transport model.

$$J_{O_2} = \frac{\frac{k_r}{k_f}\left(1/\sqrt{P_{O_2}^{permeate}} - 1/\sqrt{P_{O_2}^{feed}}\right)}{\frac{1}{K_{ex}^{permeate}} + \frac{2L}{D_V} + \frac{1}{K_{ex}^{feed}} + k\frac{\tau L_s}{PD_{H_2\text{-}H_2O}}}$$

$k\frac{\tau L_s}{PD_{H_2\text{-}H_2O}}$ is the resistance of the gas diffusion through the porous substrate

L_s is the thickness of the porous support

τ is the tortuosity of the porosity

P is the porosity of the porous support

$D_{H_2\text{-}H_2O}$ is the binary diffusivity of the H_2–H_2O system

k is a parameter including the partial pressure of gas composition