Newly developed H_2 Generator using Highly-Oxygen-Permeable Ceria-based Membrane

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1. Advantages of MPOX (Partial Oxidation of Methane by using Oxygen Permeable Membranes)

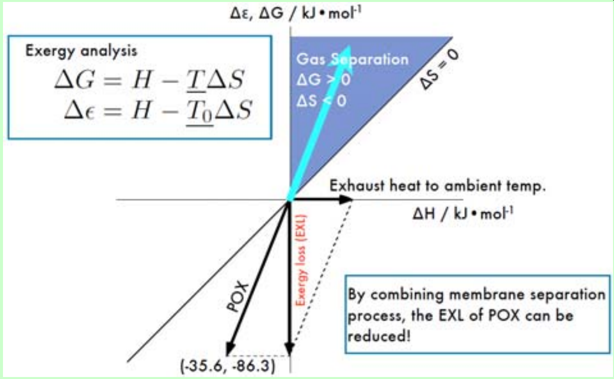
- Objective : Hydrogen generation from natural gas
- Comparison of candidate reaction

	Reaction Formula	ΔG^0_{298} (kJ/mol)	ΔH^0_{298} (kJ/mol)	ΔS^0_{298} (kJ/mol)	drawbacks
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	150.843	250.176 (endothermic)	333.164	Slow Start-Ups: Approx. 1h
Partial oxidation	$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	-86.347	−35.654 (exothermic)	170.024	Large Exergy Loss

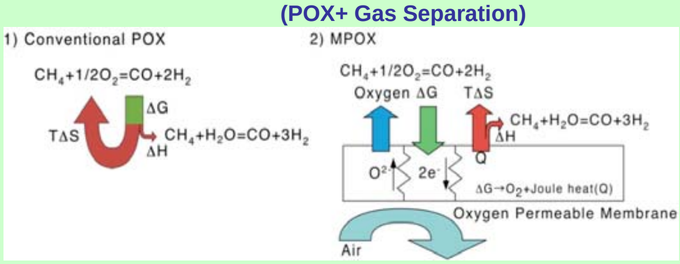
- Partial Oxidation of Methane (POX)
  Can Large Exergy loss (EXL) of POX be reduced?

Exergy Analysis
Combination with the reaction with exergy vector having opposite direction to POX is promising.

- MPOX : Membrane separation process + POX ($\Delta G > 0, \Delta S < 0$)
- Reduction of EXL of POX is achieved.



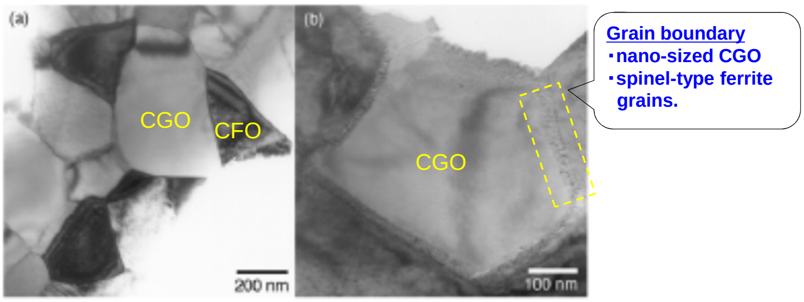
Exergy Analysis shows the advantage of MPOX (POX+ Gas Separation)



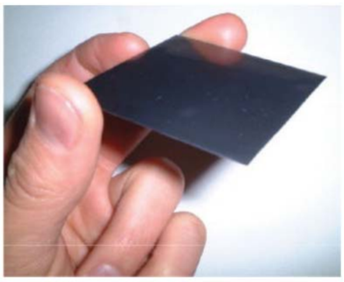
MPOX effectively utilizes the free energy generated from partial oxidation reaction to Oxygen separation

2. Ceria-based oxygen permeable membranes

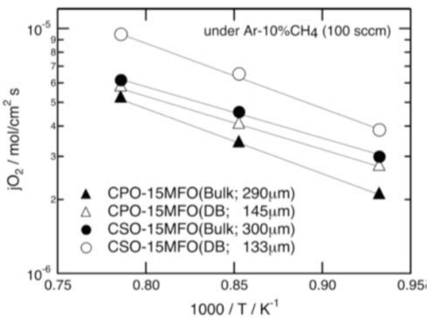
	Composition	Oxygen flux density μmol • cm⁻² • s⁻¹	Temp. °C	Ref.
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$	8.6	875	Shao *et al.*, 2001
LSGF	$La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_3$	8.2	1000	Ishihara *et al.*, 2002
PSAF	$Pr_{0.7}Sr_{0.3}Fe_{0.8}Al_{0.2}O_3$	8.2	1000	Takamura *et al.*, 2002
Ceria-MFO	$(Ce, Sm)O_2$-15vol%$MnFe_2O_4$	10.0	1000	Takamura *et al.*, 2002
LBSFI	$(La_{0.5}Ba_{0.3}Sr_{0.2})(Fe_{0.6}In_{0.4})O_3$	10.6	1000	Aizumi *et al.*, 2004



Ceria-MFO : $(Ce,Gd)O_2$-17vol%$CoFe_2O_4$ fired at 1300℃ for 2 h



CSO membrane made by tape-casting tequnique: 5cm×5cm



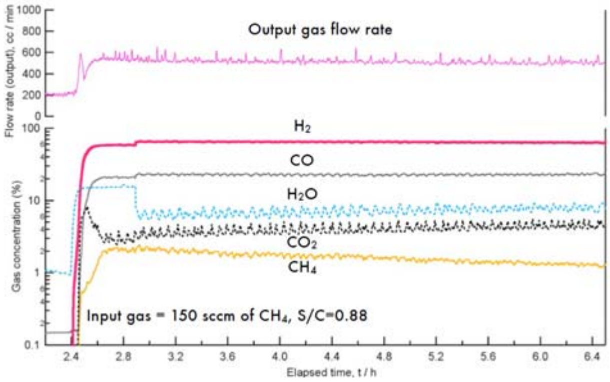
Oxygen permeation properties

Ceria-MFO: $(Ce,Re)O_2 + MeFe_2O_4$
- $(Ce,Re)O_2$: Oxygen Conductive Phase (Re is an acceptor) (CGO (Re=Gd), CSO (Re=Sm) and CPO (Re=Pr))
- $MeFe_2O_4$: Electron Conductive Phase

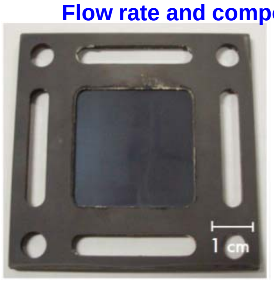
3. Characteristics of MPOX reformer

No. of modules	CH_4 (sccm)	Air (sccm)	Temp. (°C)	S/C	jO_2 (μmol/cm² s)	CH_4 conv. (%)	CO selectivity (%)	H_2 selectivity (%)
1	150	500	780	0.88	3.3	96	84	89

※C-balance: 150 sccm (input); 151.8 sccm (output)



Flow rate and composition of reformate gas



MPOX reformer module comprising of CSO.15MFO and ZMG232R (left) and its 20 stacks (right)

To produce 10 liter/min of hydrogen, stack of 20 modules is required.

4. Patent available for licensing

Patent No. : WO2003/084894,WO2007/046314 (JP,US,EP)

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