

การร่วมผลิตไฮโดรคาร์บอน C2 และกำลังไฟฟ้าจากมีเทน
โดยใช้เครื่องปฏิกรณ์ชนิดเซลล์เชื้อเพลิงแบบออกไซด์แข็ง



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CO-GENERATION OF C₂ HYDROCARBONS AND
ELECTRIC POWER FROM METHANE
IN A SOLID OXIDE FUEL CELL TYPE REACTOR

Mr. Worapon Kiatkittipong

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for the Degree of Doctor of Engineering in Chemical Engineering

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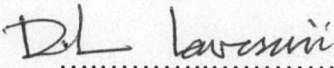
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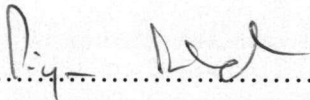
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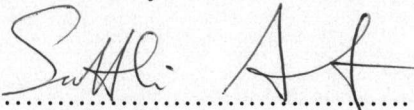
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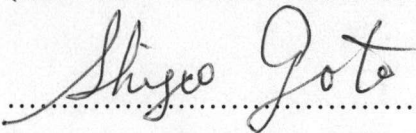
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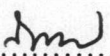
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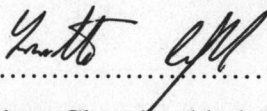
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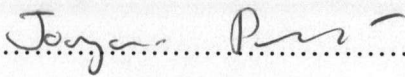
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การศึกษาร่วมผลิตไฮโดรคาร์บอน C2 และกำลังไฟฟ้าจากมีเทนโดยใช้เครื่องปฏิกรณ์ชนิดเซลล์เชื้อเพลิงแบบออกไซด์แข็งซึ่งใช้ ขั้วแคโทดคือ $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) อิเล็กโทรไลต์คือ 8% โมล yttria-stabilized zirconia (YSZ) และแอโนดคือ $\text{La}_{1.8}\text{Al}_{0.2}\text{O}_3$ (LaAlO) แบ่งได้เป็น 3 ส่วนหลักคือ การศึกษาพฤติกรรมของออกซิเจนสปีชีส์โดยเทคนิคการหลุดออกด้วยการโปรแกรมอุณหภูมิ การศึกษาการแพร่ของออกซิเจนผ่านเซลล์ LSM/YSZ/LaAlO และการสร้างแบบจำลองของการเกิดปฏิกิริยาคู่ควบของมีเทนแบบใช้ออกซิเจนในเครื่องปฏิกรณ์ชนิดเซลล์เชื้อเพลิงแบบออกไซด์แข็ง ออกซิเจนสปีชีส์ที่ได้จากเครื่องปฏิกรณ์ชนิดเซลล์เชื้อเพลิงแบบออกไซด์แข็งนั้นมีผลต่อปฏิกิริยาการเผาไหม้ และปฏิกิริยาคู่ควบของมีเทน ซึ่งสอดคล้องเช่นเดียวกันกับออกซิเจนสปีชีส์ที่ได้จากศึกษาตัวเร่งปฏิกิริยา LaAlO ในรูปแบบผงโดยเทคนิคการหลุดออกด้วยการโปรแกรมอุณหภูมิ (Tagawa และคณะ, 2003) การจ่ายศักย์ไฟฟ้าระหว่างการเตรียมการดูดซับออกซิเจนเป็นการเพิ่มปริมาณออกซิเจนที่หลุดออกและลดพลังงานกระตุ้นในการหลุดออกด้วย พลังงานในการแพร่ของออกซิเจนผ่านเซลล์มีค่า 8.90×10^{-8} โมล เมตร⁻² วินาที⁻¹ ที่ 1173 เคลวิน และมีค่าพลังงานกระตุ้น 170 กิโลจูลต่อโมล และเมื่อจ่ายศักย์ไฟฟ้า พลังงานในการแพร่ของออกซิเจนมีค่าเพิ่มขึ้นขณะที่พลังงานกระตุ้นมีค่าลดลง อีกทั้งเมื่อเปลี่ยนชนิดของก๊าซตัวพาจากฮีเลียมเป็นมีเทน ค่าพลังงานในการแพร่เพิ่มขึ้นอยู่ในช่วง 10-100 เท่า สำหรับการศึกษาร่วมผลิตของมีเทนในเครื่องปฏิกรณ์ชนิดเซลล์เชื้อเพลิงแบบออกไซด์แข็งนั้นได้ทำการศึกษาทั้งการทำทดลองและการสร้างแบบจำลองทางคณิตศาสตร์ โดยค่าการเลือกเกิดของสารผลิตภัณฑ์ C2 มีค่า 91.7 % และค่าการเปลี่ยนของมีเทนเท่ากับ 23.7 % ที่ 1273 เคลวิน แบบจำลองทางคณิตศาสตร์ที่เสนอสมมติเป็นการไหลแบบปลั๊กและพิจารณาจลนพลศาสตร์ของการเกิดปฏิกิริยาโดยแยกชนิดของออกซิเจนสปีชีส์ที่ต่างกัน การเพิ่มภาวะภายนอกทำให้ค่าการเปลี่ยนของมีเทนลดลง ในขณะที่ไม่มีผลต่อค่าการเลือกเกิดของ C2 นัก การดำเนินการที่อุณหภูมิและความดันสูงทำให้ได้กำลังไฟฟ้าและไฮโดรคาร์บอน C2 เพิ่มขึ้นได้ เครื่องปฏิกรณ์ชนิดเซลล์เชื้อเพลิงแบบออกไซด์แข็งนี้เป็นเครื่องปฏิกรณ์ที่ดีในการผลิตสารประกอบไฮโดรคาร์บอน C2 อย่างไรก็ตามปริมาณกำลังไฟฟ้าที่ได้จากการร่วมผลิตนี้ยังน้อยกว่าที่ได้รับเซลล์เชื้อเพลิงแบบออกไซด์แข็งทั่วไปอยู่มาก

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WORAPON KIATKITTIPONG: CO-GENERATION OF C2

HYDROCARBONS AND ELECTRIC POWER FROM METHANE IN A SOLID OXIDE FUEL CELL TYPE REACTOR. THESIS ADVISOR: ASSOC. PROF. SUTTICHAJ ASSABUMRUNGRAT, Ph.D., THESIS CO-ADVISOR: PROF. SHIGEO GOTO, Ph.D., 111 pp. ISBN 974-17-6758-7

The research studies the co-generation of C2 hydrocarbons and electric power from methane in a solid oxide fuel cell (SOFC) reactor using $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) as the cathode catalyst, 8 mol% yttria-stabilized zirconia (YSZ) as the electrolyte and $\text{La}_{1.8}\text{Al}_{0.2}\text{O}_3$ (LaAlO) as the anode catalyst. The study is divided into 3 main parts: Investigation the behaviors of oxygen species by fuel cell type temperature-programmed desorption (FC-TPD) measurement, oxygen permeation through the LSM/YSZ/LaAlO cell and modeling of the oxidative coupling of methane (OCM) in SOFC reactor. The two oxygen species responsible for a combustion reaction and for a coupling reaction are observed as suggested in previous TPD study of the LaAlO anode catalyst powder (Tagawa *et al.*, 2003). The increase of the applied potential during the pretreatment increases the amount of desorbed oxygen and decreases the activation energy of oxygen desorption. The oxygen permeation flux through the cell is $8.90 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$ at 1173 K with the activation energy of 170 kJ mol^{-1} . By applying an external potential, the oxygen permeation flux increases while the activation energy of oxygen permeation decreases. The oxygen permeation fluxes under methane feed in the anode side are 1-2 orders of magnitude higher than those under helium feed. A model of the oxygen permeation is proposed. In the OCM in SOFC reactor studies, both experiments and simulations are carried out. The C2 selectivity and the methane conversion are 91.7 % and 23.7 % at 1273 K, respectively. A mathematical model of the OCM in the SOFC reactor is developed. The plug flow condition is assumed and the kinetic rate expression with two different oxygen species is proposed. The effect of external load is investigated both by performing experiments and calculations. Methane conversion decreases with increasing the external load resistance while C2 selectivity is insignificantly affected. When operating at higher temperature and pressure, higher electric power and C2 production can be obtained. The results suggest that our SOFC system is a good reactor for C2 production; however the obtained power density is much lower than that of the conventional SOFC.

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NOMENCLATURE

A_d	pre-exponential factor of oxygen desorption	[s ⁻¹]
A_j	pre-exponential factor of conductivity	[S K m ⁻¹]
A_{Per}	pre-exponential factor of oxygen permeation	[mol m ⁻² s ⁻¹]
E	electromotive force	[V]
E_d	activation energy of desorption	[kJ mol ⁻¹]
E_j	activation energy of conductivity	[J mol ⁻¹]
E_{Per}	activation energy of oxygen permeation	[J mol ⁻¹]
F	Faraday's constant, 96485	[C mol ⁻¹]
$F_{CH_4,0}$	feed molar flow rate of methane	[mol s ⁻¹]
$-\Delta H_k$	heat of reaction	[J mol ⁻¹]
I	current density	[A m ⁻²]
J_{O_2}	oxygen permeation flux	[mol m ⁻² s ⁻¹]
k	reaction rate constant	[m ² kg ⁻¹ Pa ⁻¹]
k_{O_2-perm}	overall oxygen ions recombination and diffusion coefficient	[mol m ⁻² s ⁻¹]
k_{O_2-Rxn}	oxygen surface reaction coefficient	[mol m ⁻² s ⁻¹ Pa ⁻¹]
k_V	proportional constant	[mol m ⁻² s ⁻¹ V ⁻¹]
L	thickness of material	[m]
P	electric power	[W]
P_i	pressure of component i	[Pa]
$Per_{,O_2}$	specific oxygen permeability	[mol m ⁻¹ s ⁻¹]
P_{feed}	oxygen partial pressure at feed side (cathode side)	[Pa]
P_{perm}	oxygen partial pressure at permeate side (anode side)	[Pa]
P_{rich}	oxygen partial pressure at rich side of materials	[Pa]
P_{lean}	oxygen partial pressure at lean side of materials	[Pa]
$P_{O_2(I)}$	oxygen partial pressure at the gas-membrane interface	[Pa]
$P_{O_2(II)}$	oxygen partial pressure at membrane-gas interface	[Pa]
r_j	rate of reaction j	[mol kg ⁻¹ s ⁻¹]
R	area-specific resistance	[Ω m ²]
R_g	gas constant	[J mol ⁻¹ K ⁻¹]
S	membrane surface area	[m ²]

T	temperature	[K]
T_{st}	standard temperature, 298	[K]
T_m	temperature for the maximum of amount of desorbed oxygen	[K]
V_P	applied external potential during pretreatment	[V]
V_{Per}	applied external potential during steady state permeation	[V]
V_T	applied external potential during TPD	[V]
W	mass of anode catalyst	[kg]
x	dimensionless axial length divided by the total length of reactor	[-]
y	mole fraction	[-]
$y_{O_2, cou}$	mole fraction of oxygen for coupling site	[-]
$y_{O_2, oxy}$	mole fraction of oxygen for oxygenate site	[-]

Greek Letter

α	permeation rate constants in interface diffusion step	[mol m ⁻² s ⁻¹ Pa ^{-1/2}]
β	rate of temperature increase	[K s ⁻¹]
δ	permeation rate constants in bulk diffusion step	[mol m ⁻¹ s ⁻¹ Pa ^{-1/4}]
γ	molar flow rate ratio ($= F_i / F_{T0}$)	[-]
η	efficiency	[-]
φ	surface concentration	[mol m ⁻²]
σ	conductivities	[S m ⁻¹]

<Subscript>

CCI	closed circuit current
e	electronic
i	ionic
i	component i
I	inert gas
int	internal
j	reaction j
L	load
$O_{2, cou}$	oxygen for coupling site
$O_{2, oxy}$	oxygen for oxygenate site
OCV	open circuit voltage

OV overall
s shell side (cathode side)
t tube side (anode side)
T total
0 feed