$La_{0.5}Ce_{0.5}O_{1.75}$-Catalytic Layer For Methane Conversion Into C_2 Products Using Solid Oxide Fuel Cell

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Contexte

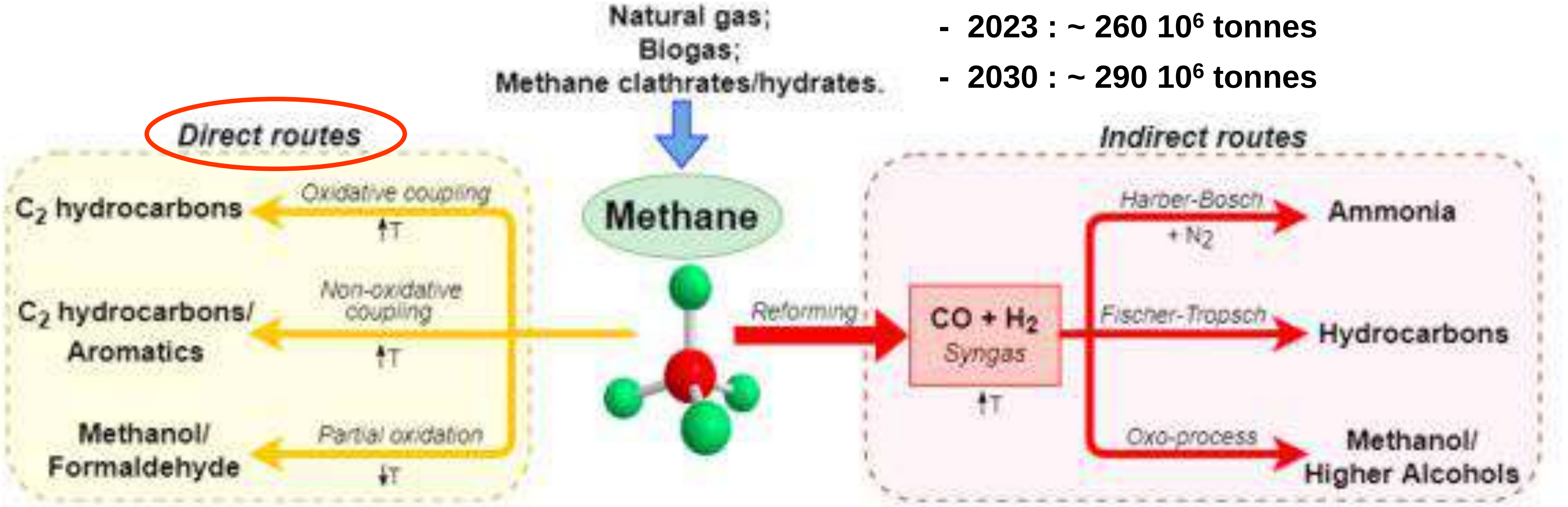
➢ Utilisation de CH_4 dans le compartiment anodique d'une cellule SOFC

- **CH_4 ?**

→ - **Gaz abondant : gaz naturel, biogaz (40 – 60 % CH_4)**
  - **Utilisations multiples : par exemple, synthèse de C_2H_4**

- **Ethylène C_2H_4 ?**

→ **Matière première pour l'industrie pétrochimique** ☑
- **2018 : ~ 185 10^6 tonnes**
- **2023 : ~ 260 10^6 tonnes**
- **2030 : ~ 290 10^6 tonnes**



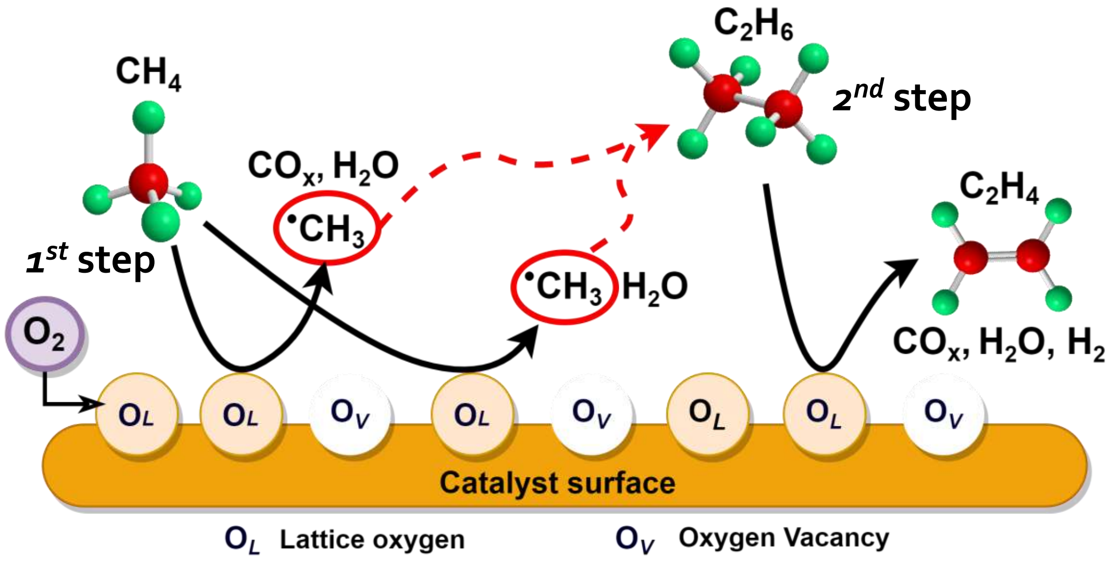
V. V. Thyssen et al., Chemical Reviews, 122 (2022) 3966−3995

OXIDATIVE COUPLING OF METHANE (OCM)
"Couplage Oxydant du Méthane"

The OCM reaction can take place with different oxidant species (such as O_2, CO_2, N_2O, etc.);
It occurs in two stages:

(i) The heterogeneous step → formation of $•CH_3$ in the gaseous form via CH_4 hydrogen abstraction by active oxygen species available on the surface of catalyst;

(ii) The homogeneous step → the $•CH_3$ is coupled to another $•CH_3$, forming the primary product C_2H_6 that is dehydrogenated to C_2H_4.



<u>STEP 1:</u> M^+O^- (catalyst) + $CH_{4\,(g)} \rightarrow M^+OH^- + {}^{\bullet}CH_3$

<u>STEP 2:</u> $2\,{}^{\bullet}CH_3 \rightarrow C_2H_{6\,(g)}$

$C_2H_{6\,(g)} + O^- \rightarrow {}^{\bullet}C_2H_5 + OH^-$

${}^{\bullet}C_2H_5 + O^- \rightarrow OC_2H_5^- +$ e-

$OC_2H_5^- \rightarrow C_2H_{4\,(g)} + OH^-$

Bilan : $2CH_4 + O_2 \rightleftarrows C_2H_4 + 2H_2O$ ☺

Lunsford, J. H. *Angewandte Chemie International* ***34***(9), 970–980 (1995).

OXIDATIVE COUPLING OF METHANE (OCM)
"Couplage Oxydant du Méthane"

- Difficult activation of CH_4 → high stability
- High operational temperature (700 – 900°C)
- Oxidation parallel products (CO, CO_2) + C_{3+}: **decrease in C_2 selectivity**
- Risk of explosion with the co-feed of CH_4/O_2 mixture
- Reactor hot spots

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$CH_4 + O_2 \rightarrow CO + H_2O + H_2$

$CO + ½O_2 \rightarrow CO_2$

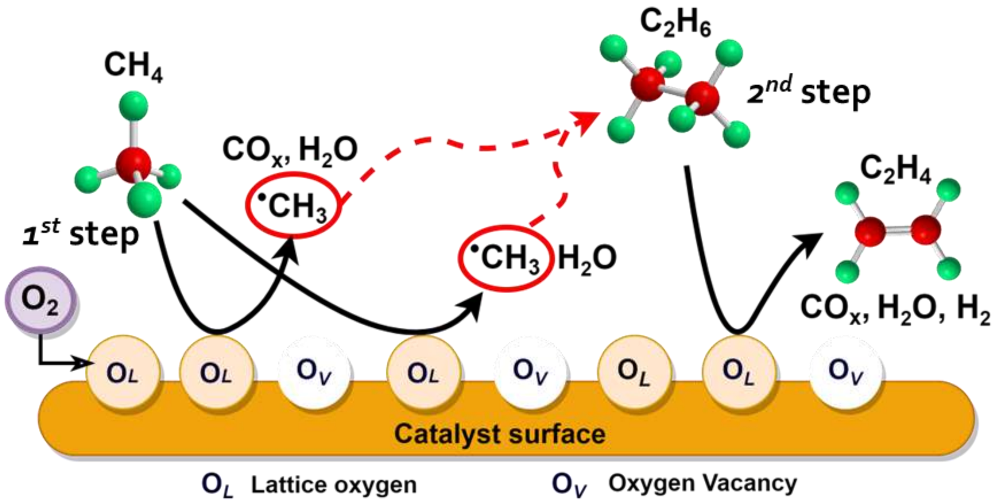
$CH_4 + H_2O \rightarrow 3H_2 + CO$

$C_2H_4 + 2H_2O \rightarrow 4H_2 + 2CO$

$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

...



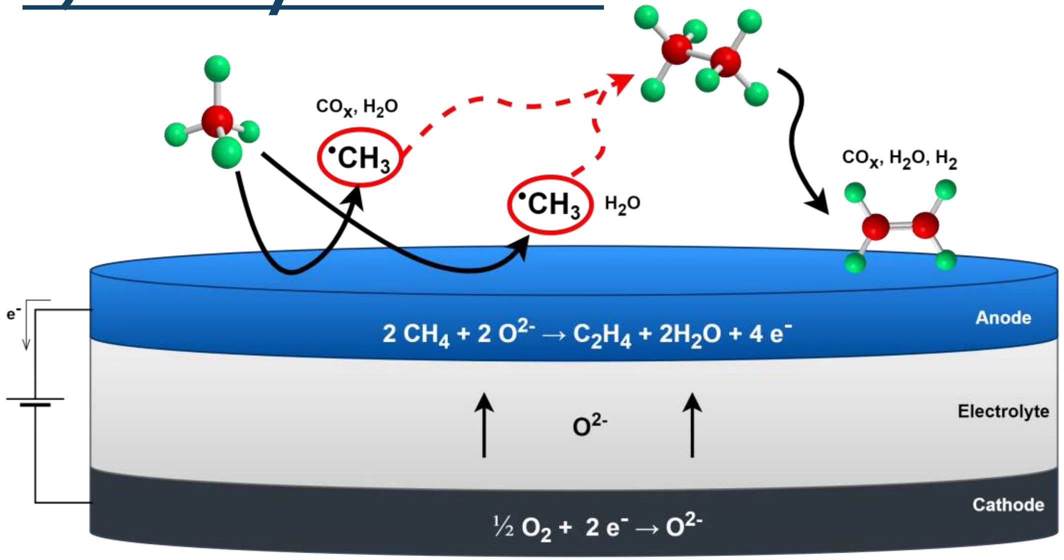
How to make this process viable?

↓

Electrochemical Oxidative Coupling of Methane (EOCM)

Electrochemical Oxidative Coupling of Methane (EOCM) : SOFC Reactors

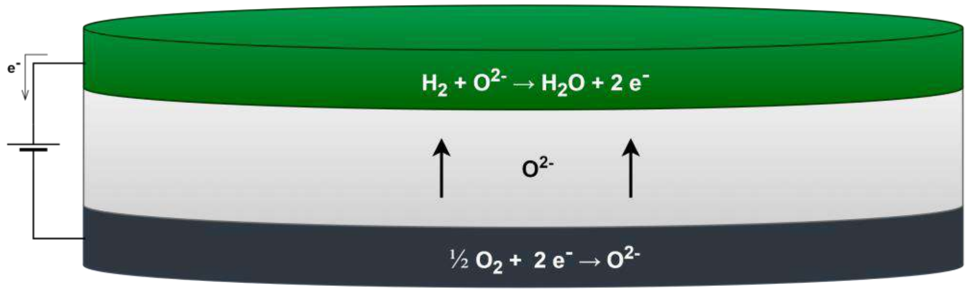
1) Catalytic Anode



Five basic requirements that an anode must satisfy:

1. Catalytic activity
2. Thermal compatibility
3. Chemical stability
4. Porosity
5. Electronic conductivity

2) Catalytic Anodic Membrane



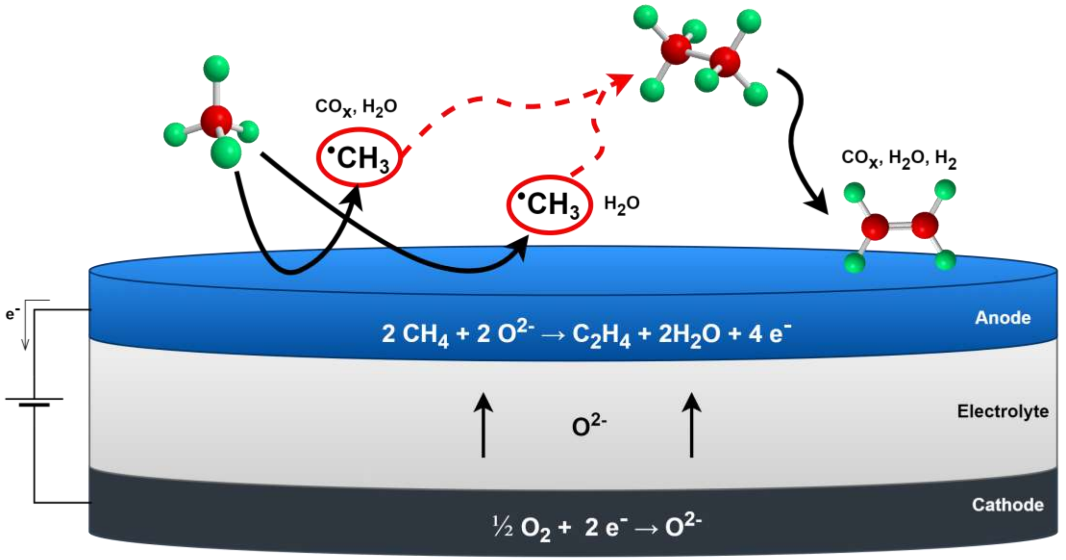
Nickel based anodes
+
Fuels containing carbon

$CH_4 + Ni \rightarrow C\text{-}Ni + 2\ H_2$

Coke deposition

Electrochemical Oxidative Coupling of Methane (EOCM) : SOFC Reactors

1) Catalytic Anode



Five basic requirements that an anode must satisfy:

1. **Catalytic activity**
2. **Thermal compatibility**
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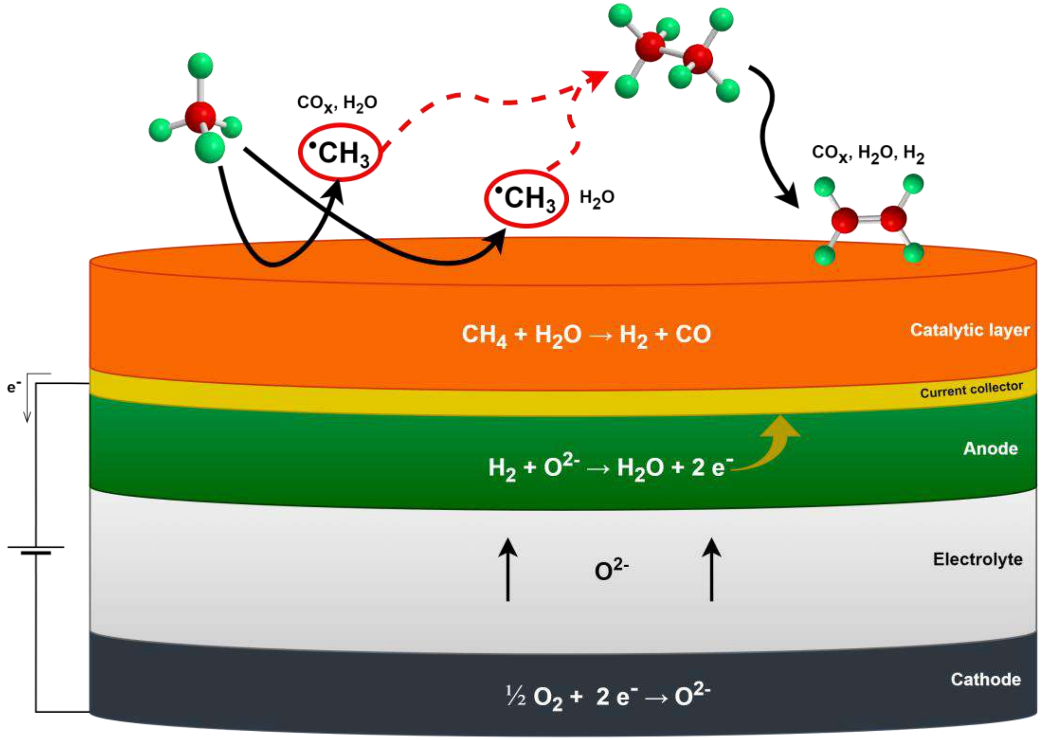
4. **Porosity**
5. **Electronic conductivity**

2) Catalytic Anodic Membrane

A strategy to avoid deactivation and improve the efficiency of SOFC

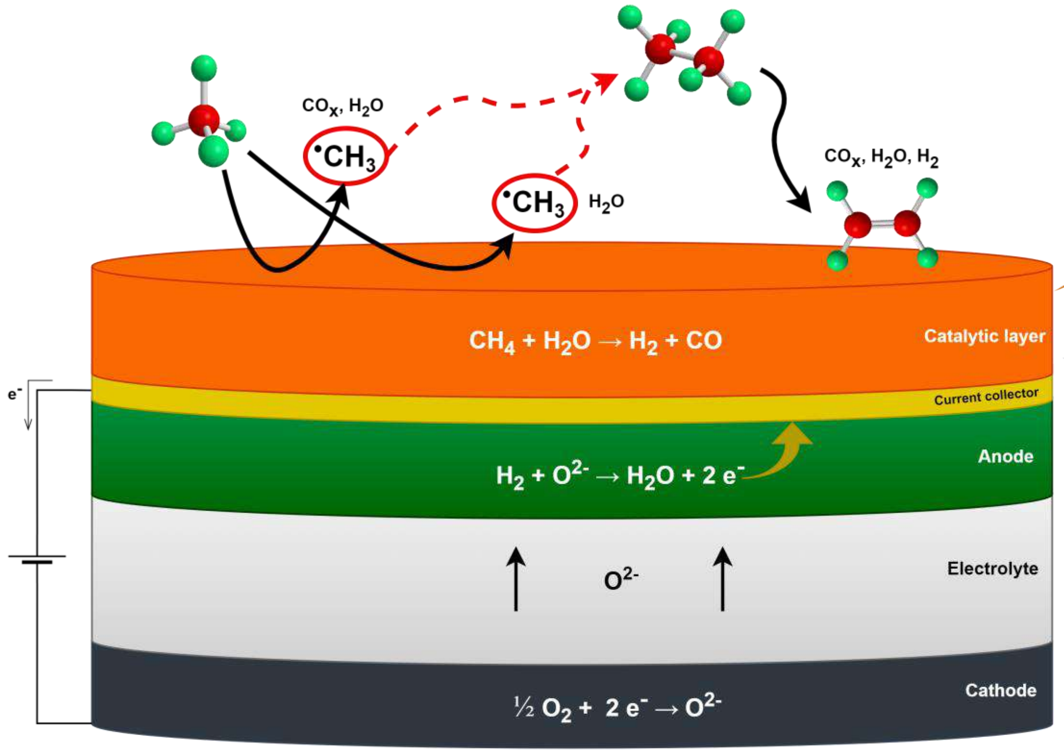


- **In this case, the catalyst has two roles: steam reforming and OCM**

What is the oxidant for OCM reaction?

2) Catalytic Anodic Membrane

A strategy to avoid deactivation and improve the efficiency of SOFC



Internal Reforming

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

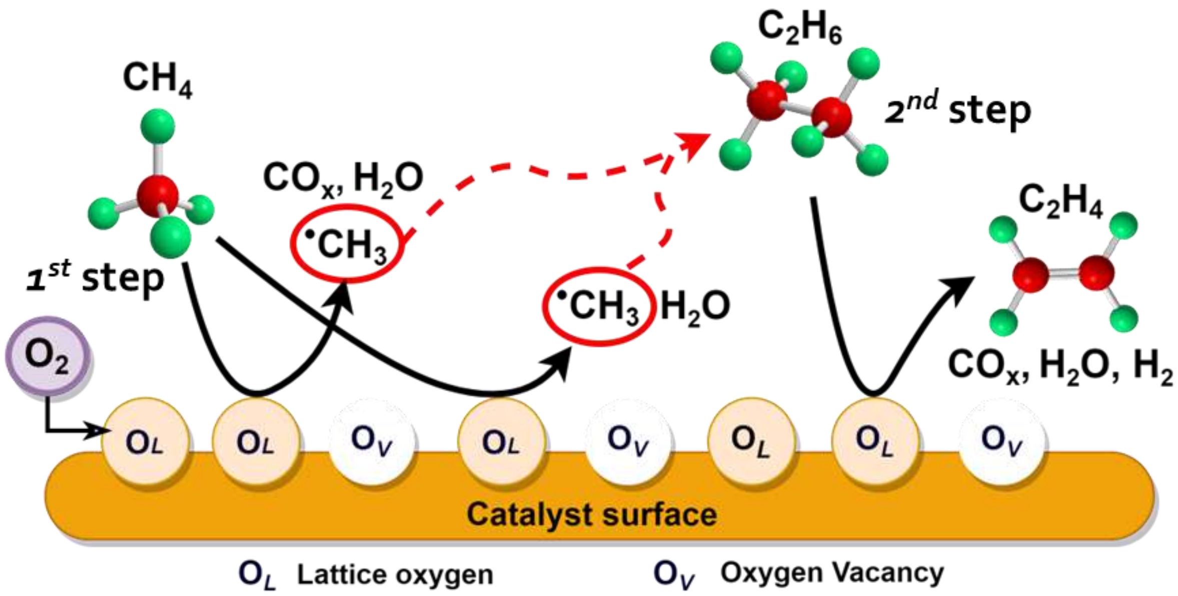
Oxidative Coupling

$$2CH_4 + CO_2 \rightarrow C_2H_6 + H_2O + 2CO$$
$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2H_2O + 2CO$$

Development of active catalytic materials for both reactions:
Oxidative coupling and internal reforming of CH_4
to be used as a catalytic layer in a SOFC

CATALYTIC MATERIAL

- **Thermal and Mechanical Stability**
- **Suitable alkaline sites**
- **Selective mobile oxygen sites**
- **Structural defects and oxygen vacancies**



Mixed oxide

$La_xCe_{1-x}O_{2-\delta}$

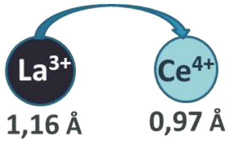
La_2O_3
↑ Alkalinity
↑ Selectivity

CeO_2
↑ Conversion
↓ Selectivity

ORTIZ-BRAVO, C. A. et at, *Journal of Natural Gas Science and Engineering* ***2021*** (96)

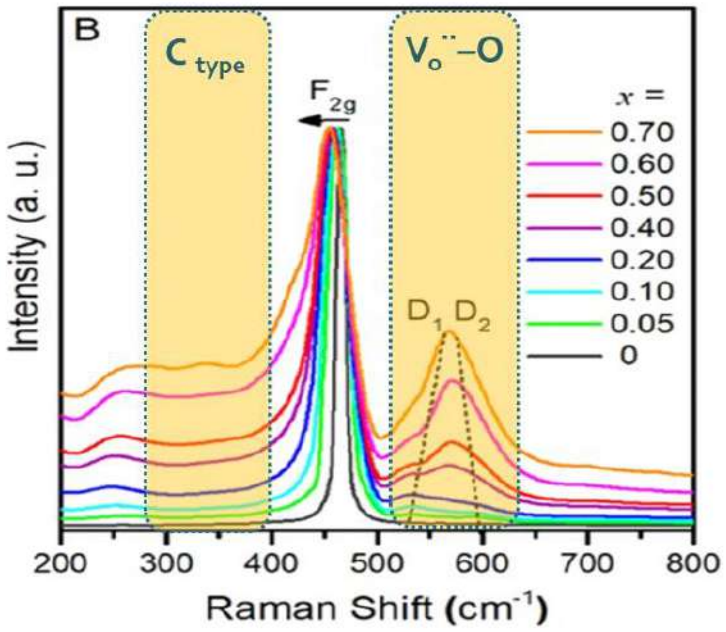
$La_xCe_{1-x}O_{2-\delta}$ (0 ≤ x ≤ 0.7) system

XRD: Solution Solide



→ Fluoryte + C-type cristaline structure

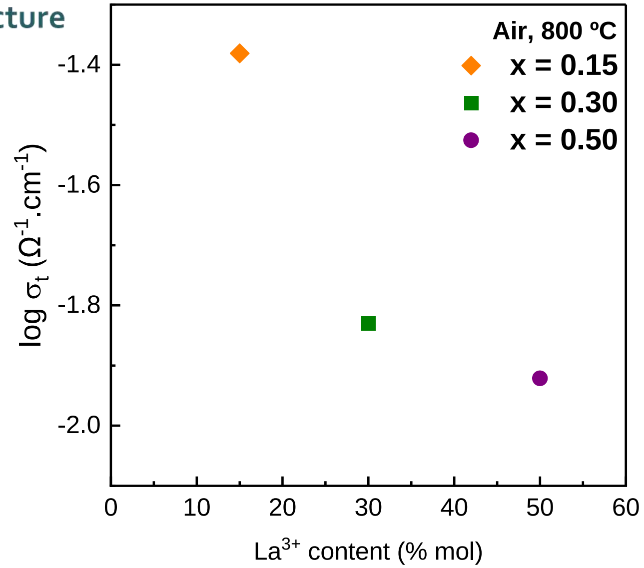
Raman

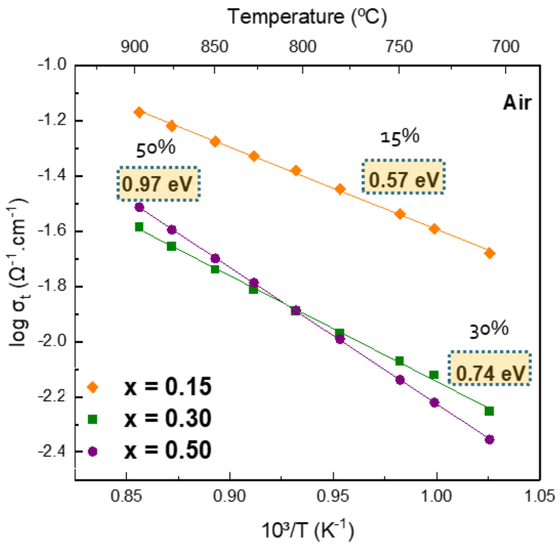


↑ La^{3+} content ↑ $V_o^{\cdot\cdot}$ formation

→ C-type structure → $V_o^{\cdot\cdot}$ ordering

Electrical Conductivity





x > 0.15
↓ Conductivity ↑ Ea → Oxygen mobility ↓

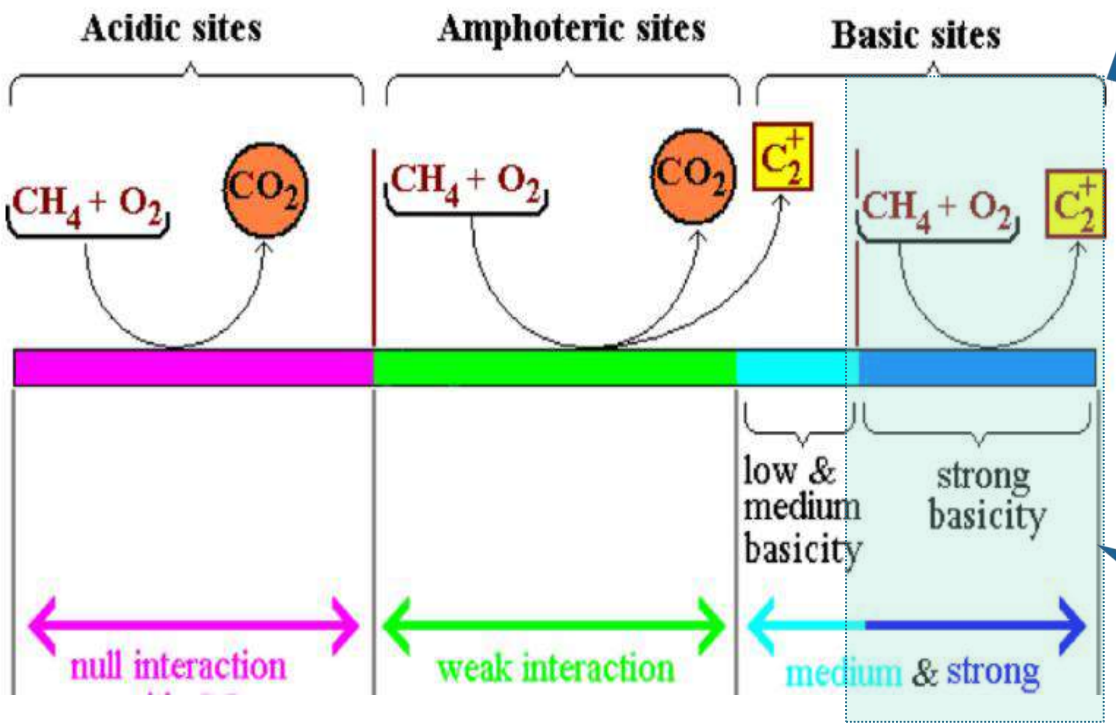
Increase C_2 selectivity, while keeping its activity on CH_4 activation.

$La_{0.5}Ce_{0.5}O_{1.75}$

TRINDADE, F. *et al*. Paper under writing process.

CATALYTIC MATERIAL

For OCM reaction

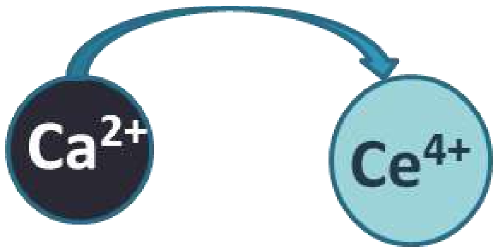


Mixed oxide

$La_{0.5}Ce_{0.5}O_{1.75}$

La_2O_3	CeO_2
↑ Alkalinity	↑ Conversion
↑ Selectivity	↓ Selectivity

Improving the alkaline sites by doping process



PAPA, F. *et al.*, *Journal of Molecular Catalysis A: Chemical* **(346)**, 46–54 (2011)

CATALYST PREPARATION

COMBUSTION METHOD

Stire and heat

Combustion reaction

Deagglomeratio
n

As-prepared powder

LCO

$La_{0.5}Ce_{0.5}O_{1.75}$

Doping
Ca^{2+}

LCCaO-25

$La_{0.5}Ce_{0.44}Ca_{0.06}O_{1.75}$

$La_{0.5}Ce_{0.38}Ca_{0.12}O_{1.75}$

LCCaO-50

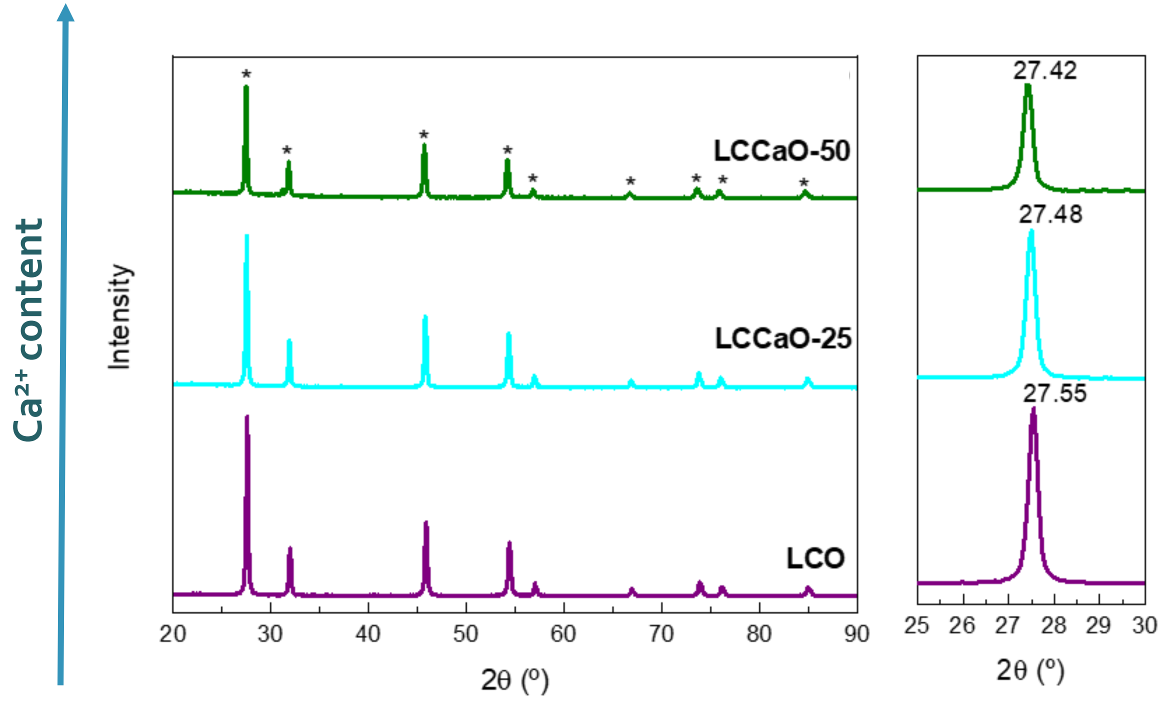
Characterization
Cal. 800 °C (S_{BET} = 8 m²/g)

OCM tests
EOCM tests

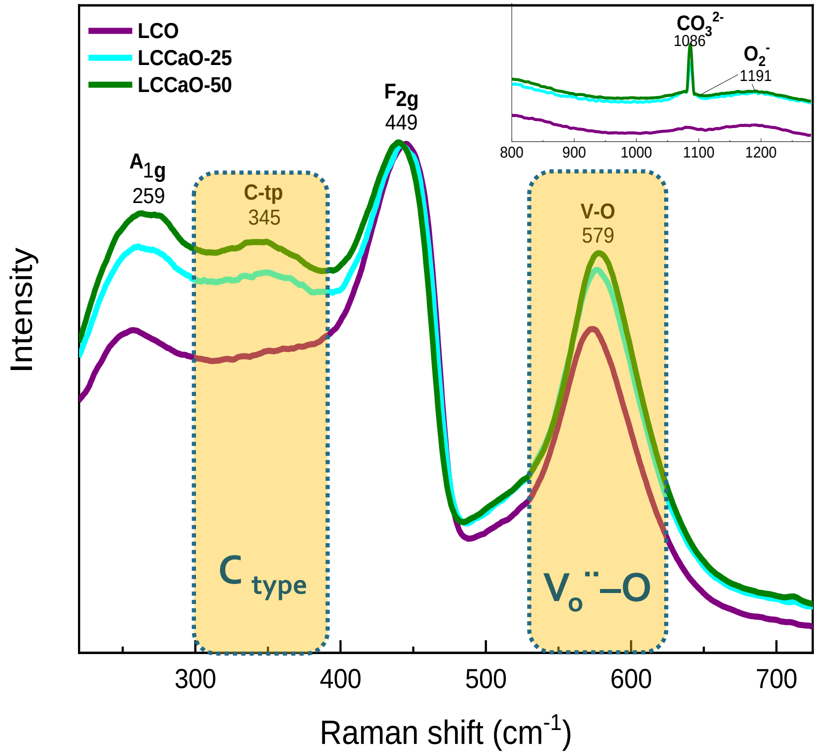
VILELA, V. B. *et al*, *ECS Trans* **103**(1), 1917–1925 (2021)

Ca^{2+}-doped LCO samples

XRD



Raman



Similar behavior of La^{3+}-doped CeO_2 samples → ↑ Ca^{2+} content ↑ $V_o^{\cdot\cdot}$ formation

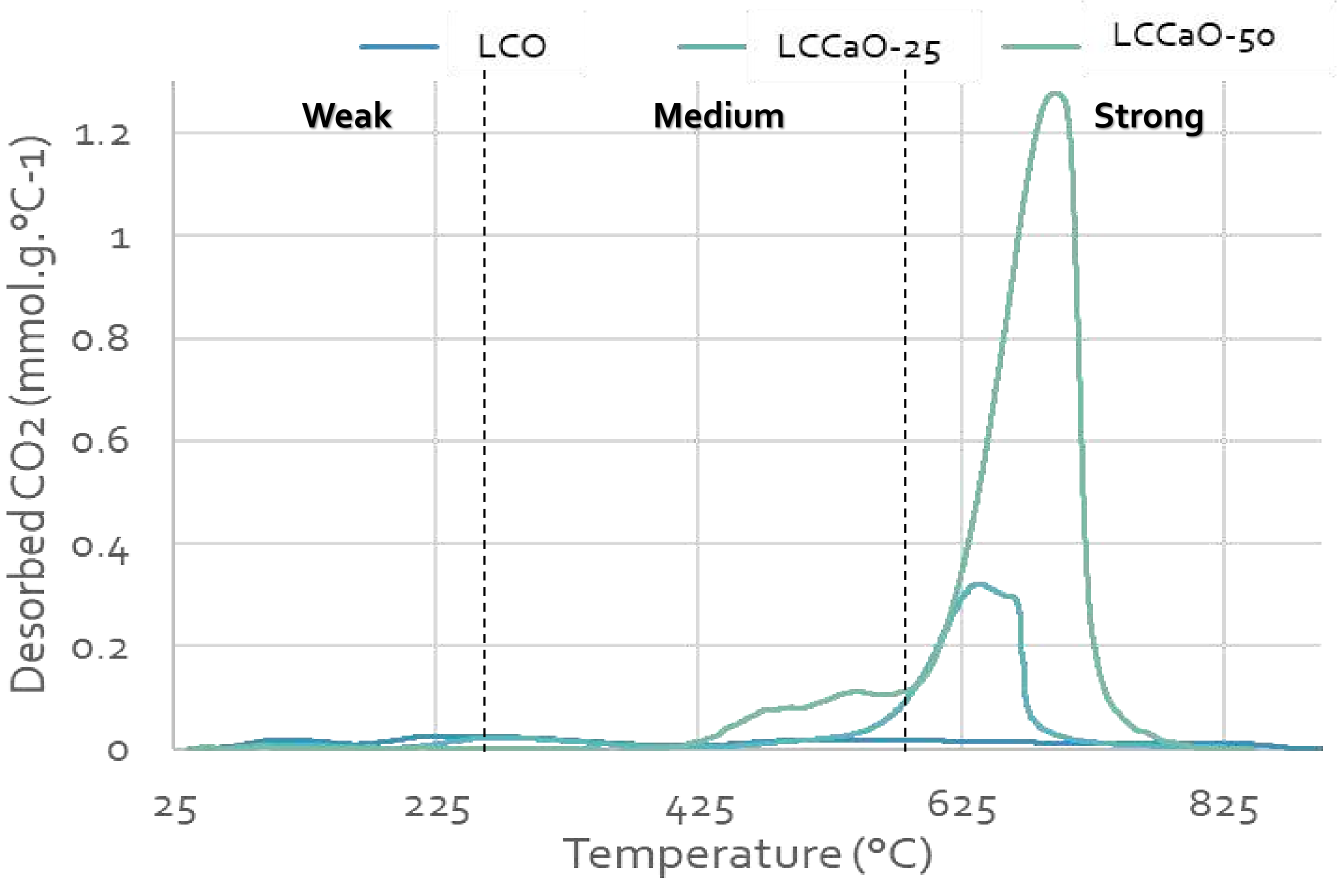
↳ C-type structure → $V_o^{\cdot\cdot}$ ordering

CO_2-Temperature Programmed Desorption

Ca^{2+}-doped LCO samples

Ircelyon

Ph.D. Antoine SALICHON
Dr. Stéphane LORIDANT



↑ Ca^{2+} content

↑ Strong basic sites

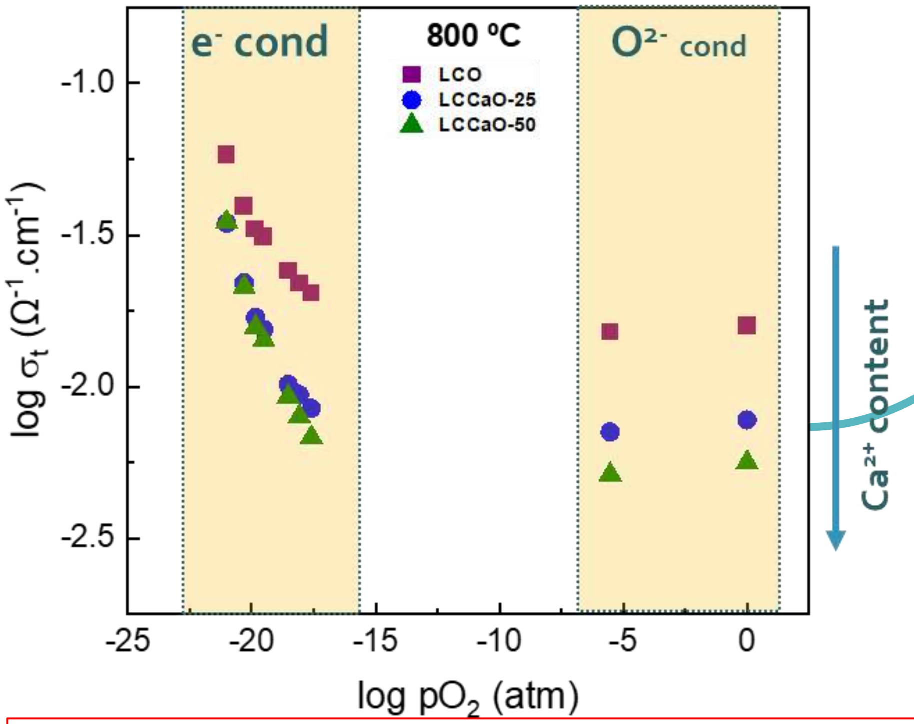
For OCM reaction

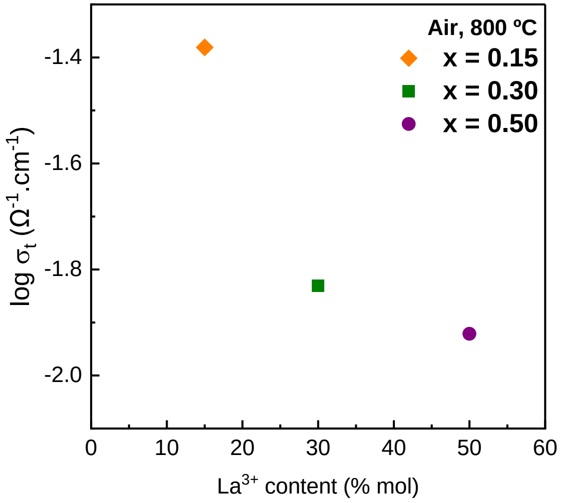
Electrical Conductivity (EIS)

Ca^{2+}-doped LCO samples

↑ Ca^{2+} content ↓ σ_{ionic}

- C-type structure contibutes to the $V_O^{\cdot\cdot}$ ordering, reducing the ionic mobility.





Similar behavior of La^{3+}-doped CeO_2 samples

- Atmosphères réductrice : $Ce^{4+} \longrightarrow Ce^{3+}$
- Création des $V_O^{\cdot\cdot}$

σ_{e-} augmente σ_{ionic} (~ stable ou diminue)

Selectivity?

Internal Reforming

$CH_4 + H_2O \rightarrow 3H_2 + CO$

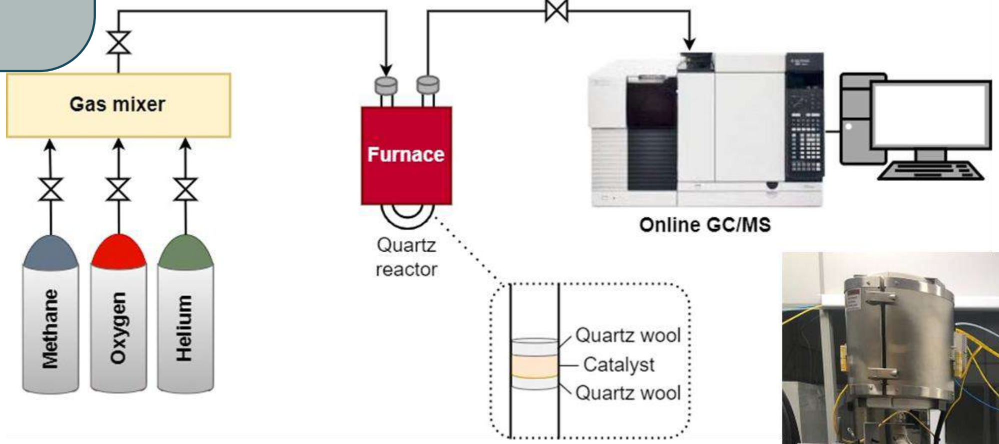
$CO + H_2O \rightarrow CO_2 + H_2$

Oxidative Coupling

$$2\ CH_4 + O_2 \rightleftarrows C_2H_4 + 2H_2O$$

The Catalytic Activity

Schematic of the heterogeneous catalysis test system with an online gas analyzer (GC/MS)



OCM test conditions

CH_4:O_2 molar ratio - 4:1

Reactor feed - 60 mL.min^{-1}

50 mg of catalyst

Temperature - 750 ºC

During - 20 h

LCCaO-25

$La_{0.5}Ce_{0.44}Ca_{0.06}O_{1.75}$

$La_{0.5}Ce_{0.38}Ca_{0.12}O_{1.75}$

LCCaO-50

CH_4 conversion → X_{CH_4} (%) = 100 × moles$CH_{4(consumed)}$ ÷ moles$CH_{4(feed)}$

O_2 conversion → X_{O_2} (%) = 100 × moles$O_{2(consumed)}$ ÷ moles$O_{2(feed)}$

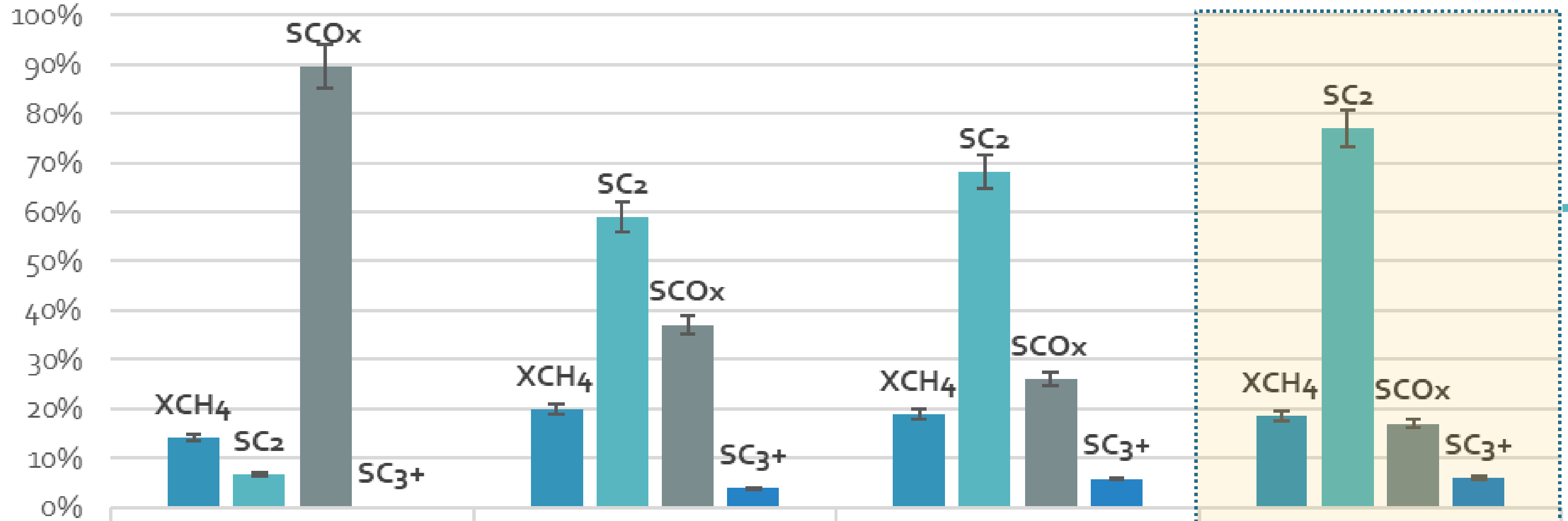
C_2 selectivity → S_{C_2} (%) = 100 × (2 × moles$C_{2(formed)}$) ÷ moles$CH_{4(consumed)}$

CO_x selectivity → S_{CO_x} (%) = 100 × moles$CO_{x(formed)}$ ÷ moles$CH_{4(consumed)}$

Yield → Y_X (%) = S_X × X_{CH_4}

The Catalytic Activity

Doped-LCO: 750 °C, $4CH_4:1O_2$, 50 mg



	CeO2	LCO	LCCaO-25	LCCaO-50
XCH4	14%	20%	19%	19%
SC2	7%	59%	68%	77%
SCOx	90%	37%	26%	17%
SC3+	0%	4%	6%	6%

XCH4 SC2 SCOx SC3+

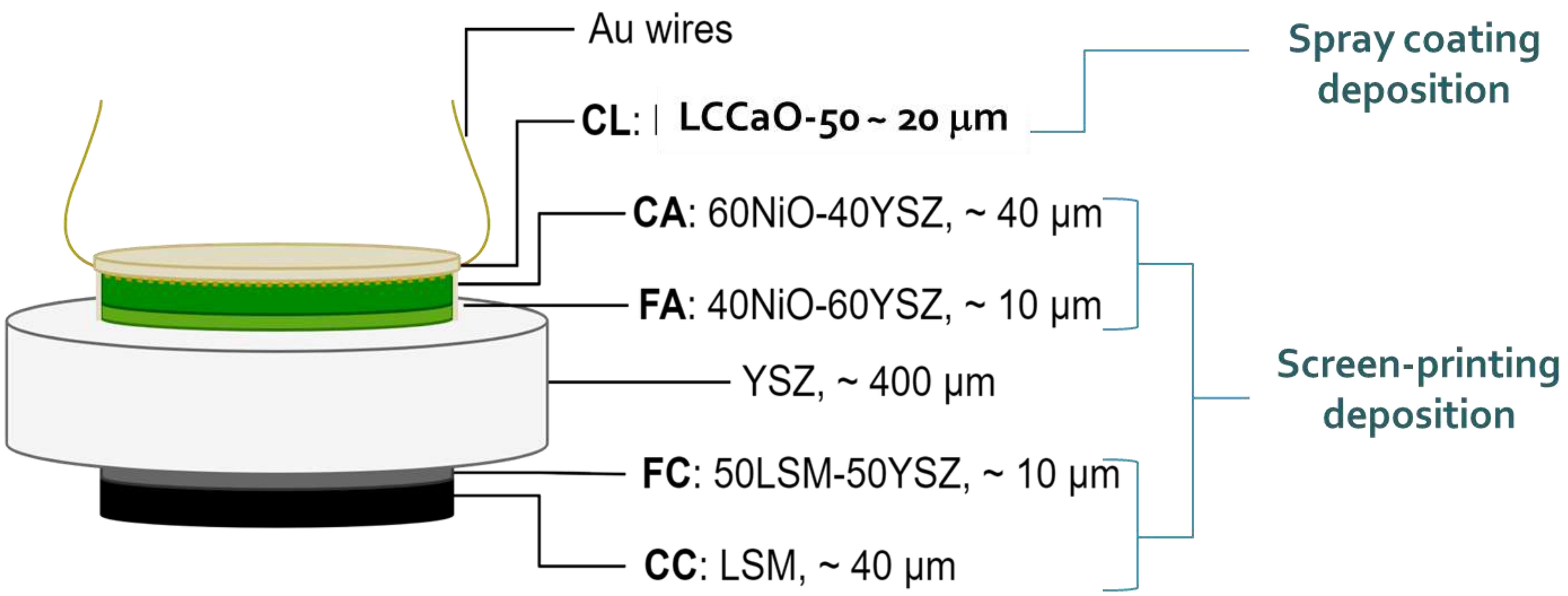
Ca^{2+}-doped LCO

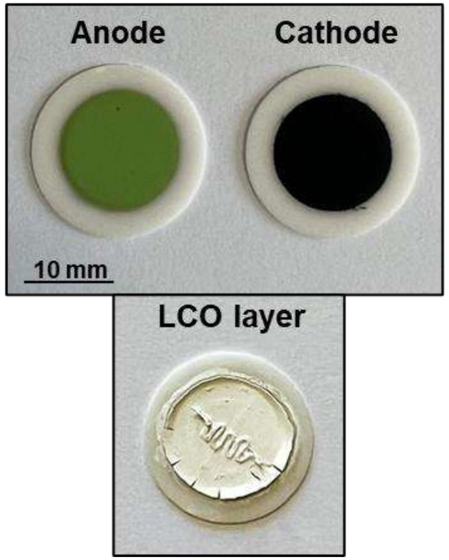
- ↑ C_2 selectivity
- ↑ C_2 yield
- ↓ CO_x selectivity

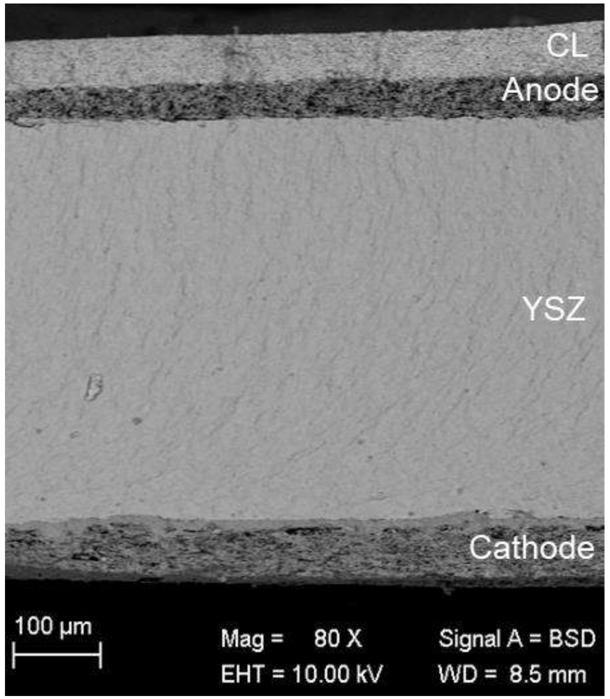
Ca^{2+}-doped LCO

- ↑ $V_o^{\cdot\cdot}$ formation
- ↑ $V_o^{\cdot\cdot}$ ordering
- ↓ σ_{ionic}
- ↑ Strong basic sites

Fuel Cell Fabrication



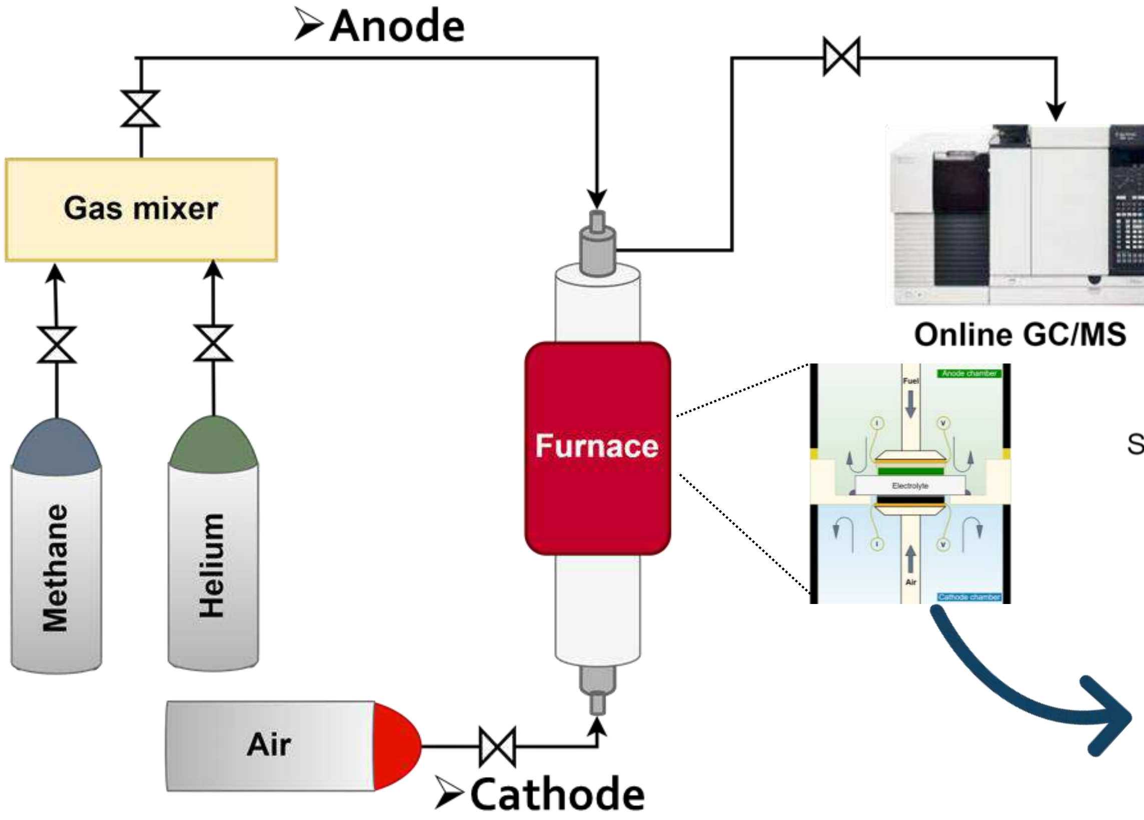


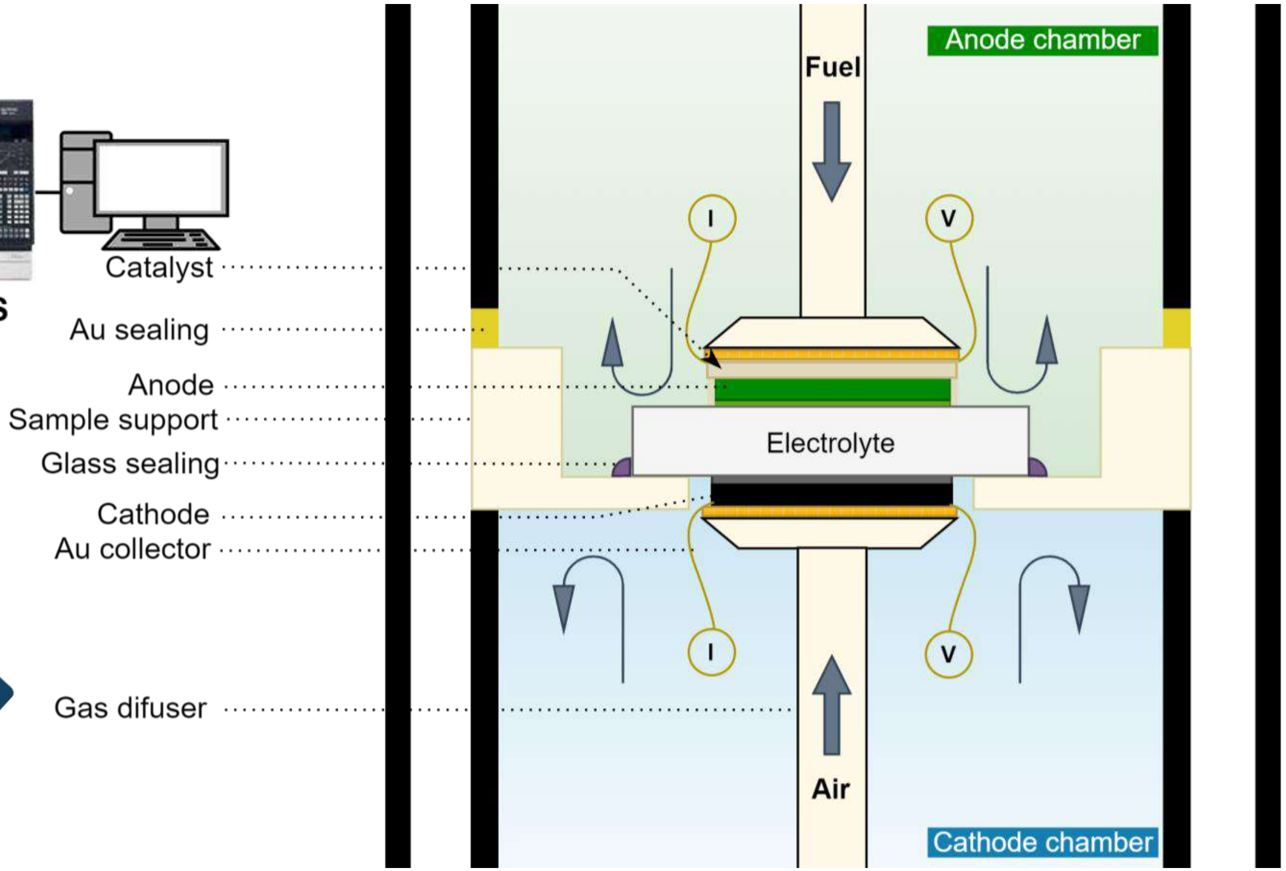


- Diameter Electrolyte = 19 mm
- Diameter Electrodes = 12 mm

Electrochemical Oxidative Coupling of CH_4 (EOCM)

SETUP (LEPMI)

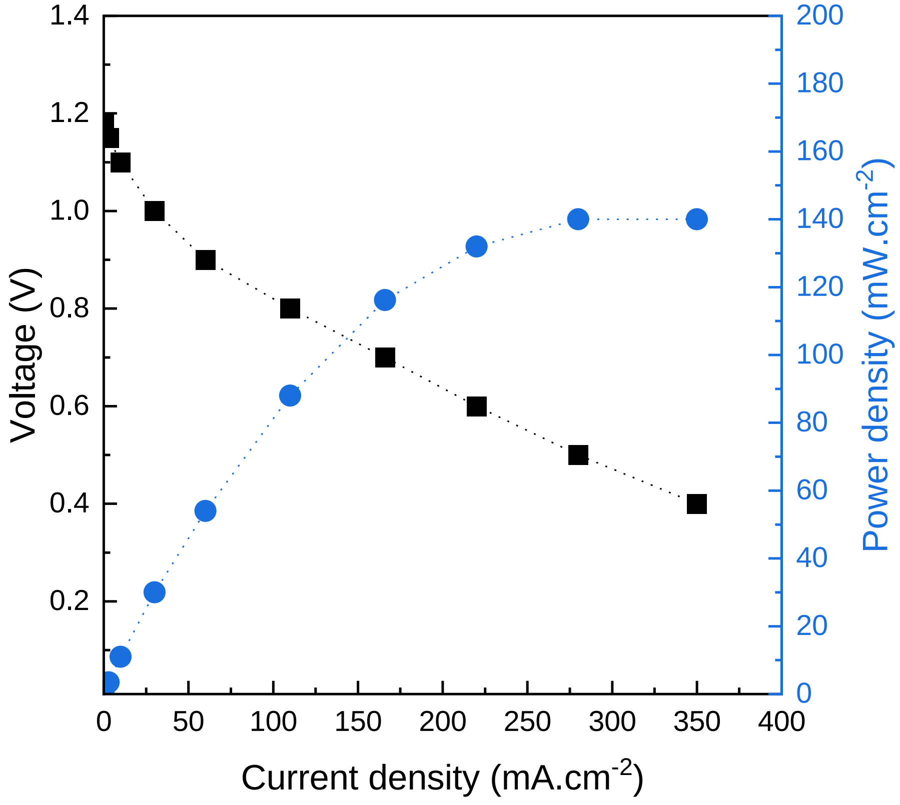




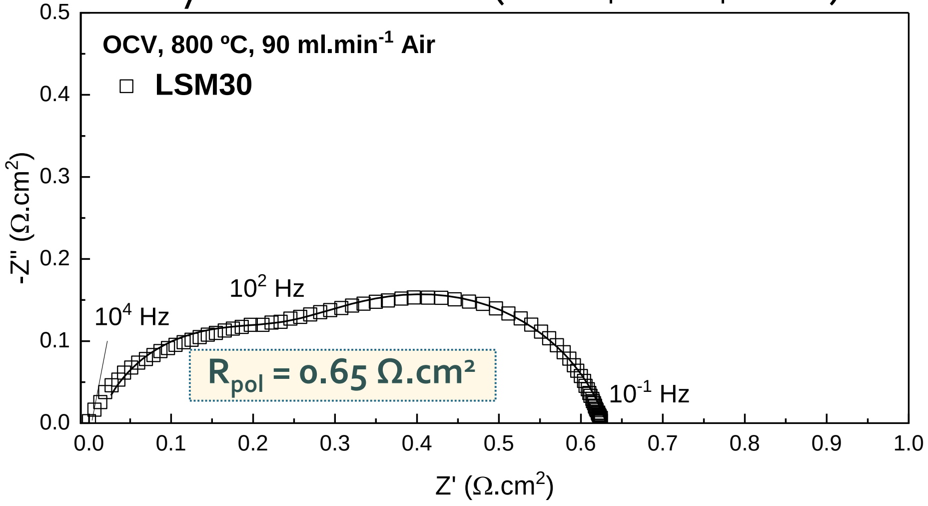
Fuel Cell Characterization

Electrochemical Oxidative Coupling of CH_4 (EOCM)

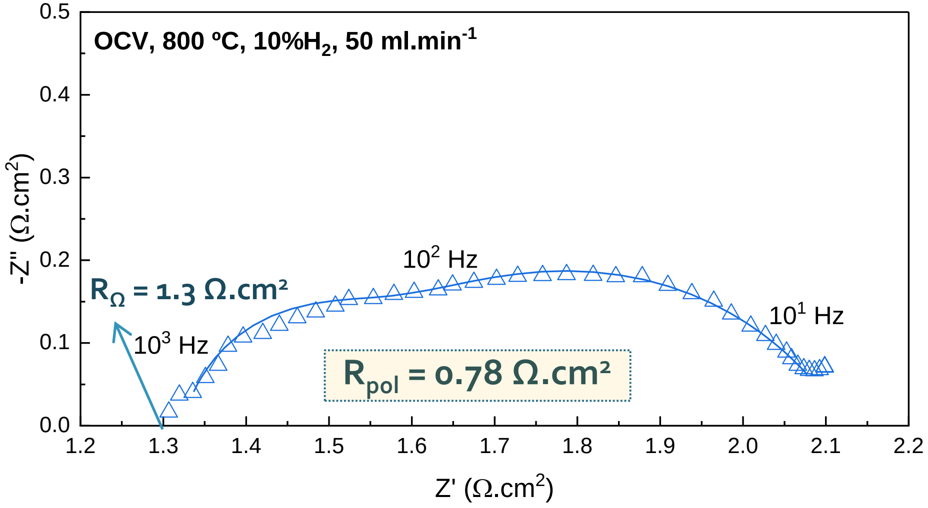
Temperature → 800 ºC
Anodic side → H_2/He (10/90%), 50 mL.min^{-1}
Cathodic side → Synthetic air, 90 ml.min^{-1}



Symmetrical cell (LSM | YSZ | LSM)



Fuel Cell



EOCM Tests

Total amount of oxygen feed for the EOCM tests is related to the applied current, and it can be calculated by the Faraday law.

$$J\ (mol.s^{-1}) = I \div (2 \times F)$$

$O^{2-}/CH_4 = 0.01$

Test condition I

20 mA

50%CH_4/He, 25 mL.min^{-1}

Synthetic air, 90 mL.min^{-1}

800 ºC

LCO

LCCaO-50

$O^{2-}/CH_4 = 0.02$

Test condition II

40 mA

50%CH_4/He, 25 mL.min^{-1}

Synthetic air, 90 mL.min^{-1}

800 ºC

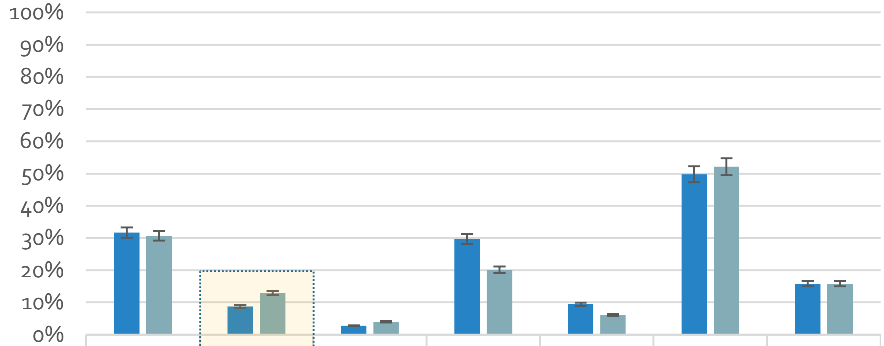
LCO

LCCaO-50

Electrochemical Oxidative Coupling of CH_4 (EOCM)

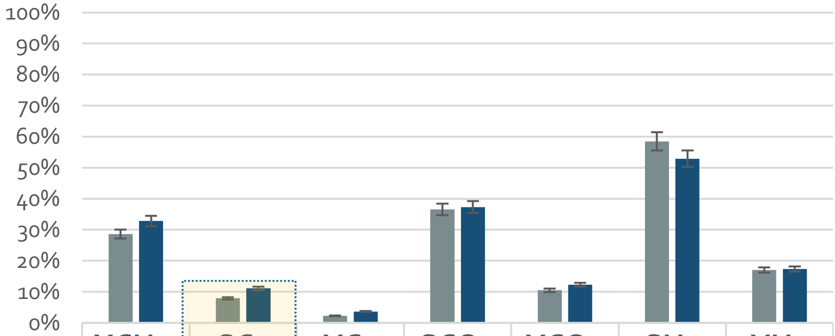
EOCM Tests

20 mA
$O^{2-}/CH_4 = 0.01$

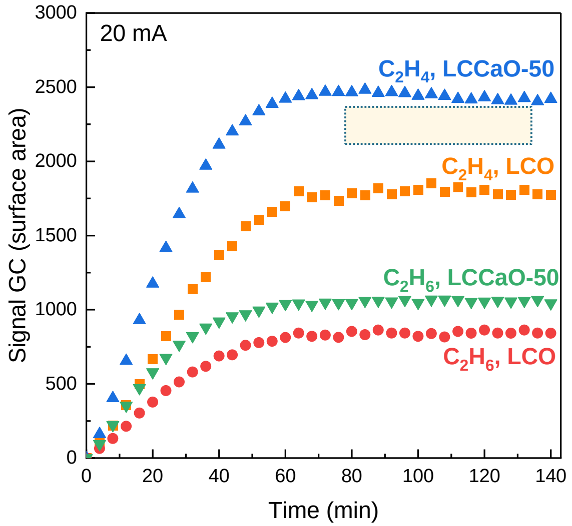


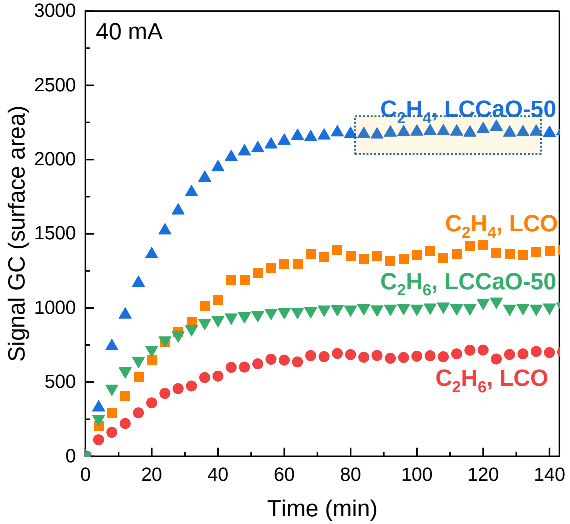
	XCH4	SC2	YC2	SCOx	YCOx	SH2	YH2
20mA - LCO	32%	9%	3%	30%	9%	50%	16%
20mA - LCCaO-50	31%	13%	4%	20%	6%	52%	16%

40 mA
$O^{2-}/CH_4 = 0.02$



	XCH4	SC2	YC2	SCOx	YCOx	SH2	YH2
40mA - LCO	29%	8%	2%	37%	10%	58%	17%
40mA - LCCaO-50	33%	11%	4%	37%	12%	53%	17%





Applied current

Higher the current:

↓ C_2 selectivity

↑ CO_x selectivity

2) Ca-doping

↑ C_2 selectivity

↑ C_2H_4/C_2H_6 ratio

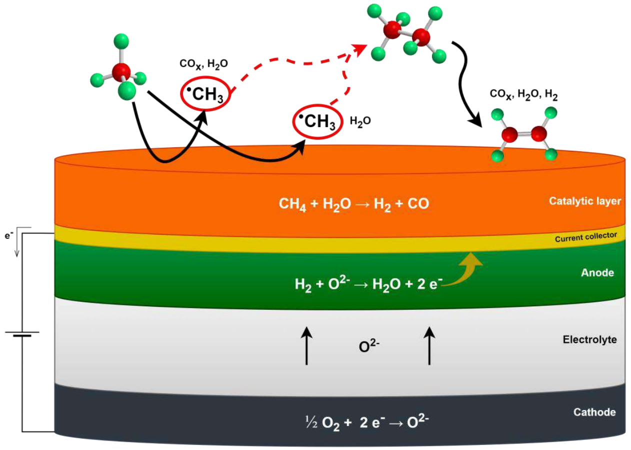
Conclusion

Ca^{2+}-doped $La_{0,5}Ce_{0,5}O_{1,75}$

Formation de lacunes d'oxygène ordonnées (DRX et RAMAN)	✚	Diminution de σ_{ionic} (Lacunes d'oxygène moins mobiles)	✚	Matériau Basicité augmentée

➢ **Tous ces facteurs ont conduit à une activité catalytique améliorée pour la réaction OCM**

Electrochemical Oxidative Coupling of CH_4 (EOCM)



➢ LCO et LCCaO-50 sont actifs comme couche catalytique pour les deux réactions : OCM et reformage interne.

➢ La sélectivité des produits C_2 dépende du rapport O^{2-}/CH_4 : teneur en oxygène plus élevée favorise l'oxydation profonde conduisant au reformage ($CO + H_2$).

➢ Des rapports C_2H_4/C_2H_6 et une sélectivité C_2 plus élevés ont été obtenus avec LCCaO-50.

Perspectives

- **EHT + OCM**

- anode :

$$2\ CH_4 + 2\ O^{2-} \rightarrow C_2H_4 + 2\ H_2O + 4\ e^-$$

- cathode :

$$2\ H_2O + 4\ e^- \rightarrow 2\ H_2 + 2\ O^{2-}$$

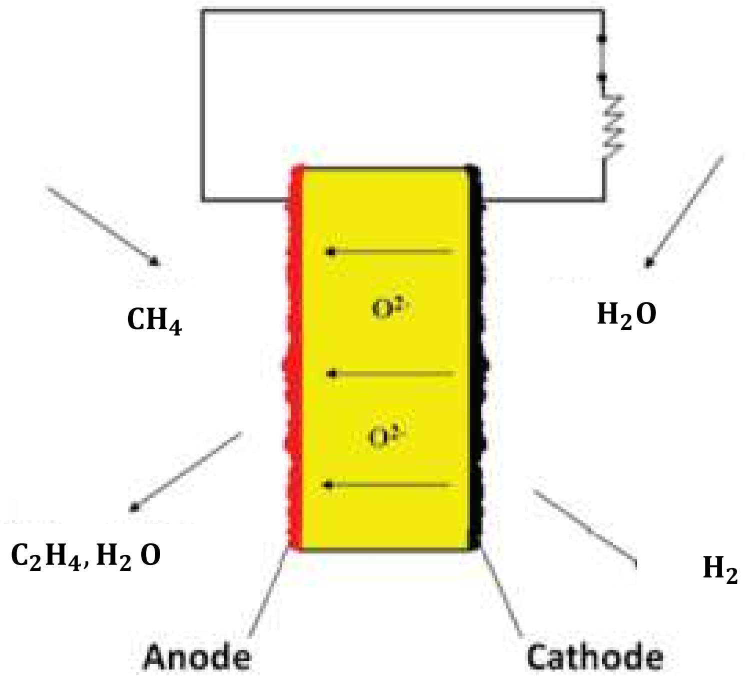
$\rightarrow$ **diminution de $V_{cellule}$**

$$OCV = E^o + \frac{R \times T}{2 \times F} \times \ln\left(\frac{P_{H_2} \times (P_{O_2})^{1/2}}{P_{H_2O}}\right)$$

$$H_2O + 2\ e^- \rightarrow 2\ H_2 + O^{2-}$$

$$O^{2-} \rightarrow \frac{1}{2} O_2 + 2\ e^-$$

$V_{cellule} : 0,8 - 1,1V$

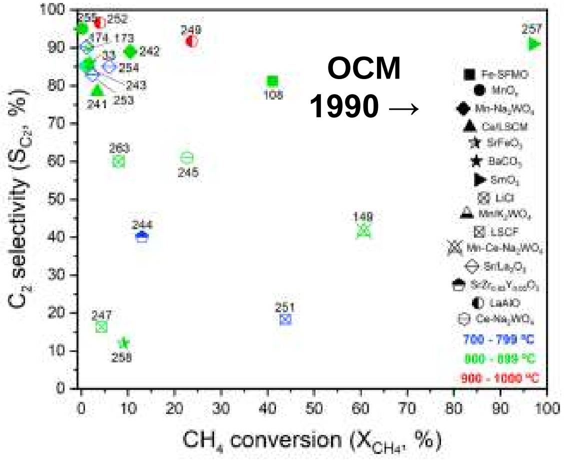


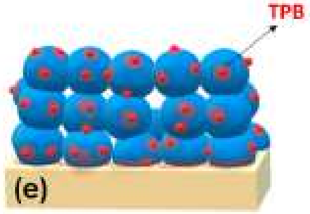
Projet (sep 2023 / sep 2024)
LEPMI (Labex CEMAM) - IPEN (CNPQ-Brésil)

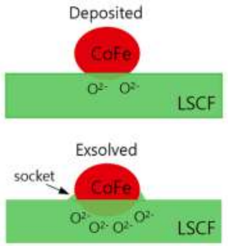
J.T. Grant et al., Chemical Reviews, 118 (2018) 2769–2815
I. Garagounis et al., Industrial Engineering Chemistry Research, 50 (2011) 431-472
Butler et al., Renewable and Sustainable Energy Reviews, 82 (2018) 2440-2454

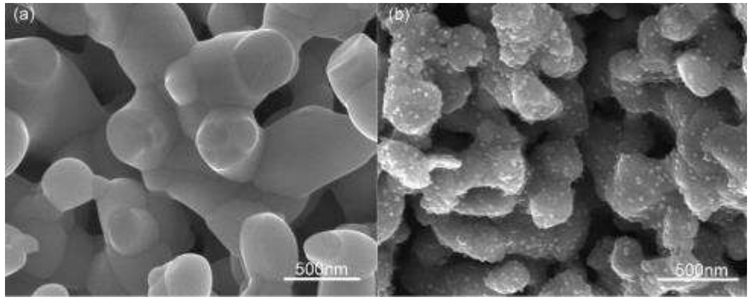
Je vous remercie pour votre attention

- Architecture
  - → - anode : composite MIEC/LCO
  - - cathode : MIEC dopé avec cation métallique (m-MIEC)
- Anode
  - → - imprégnation d'une couche poreuse de MIEC
  - - nanoparticules de LCO
- Cathode
  - → - réduction de m-MIEC
  - - nanoparticules métalliques (Fe, Ni)

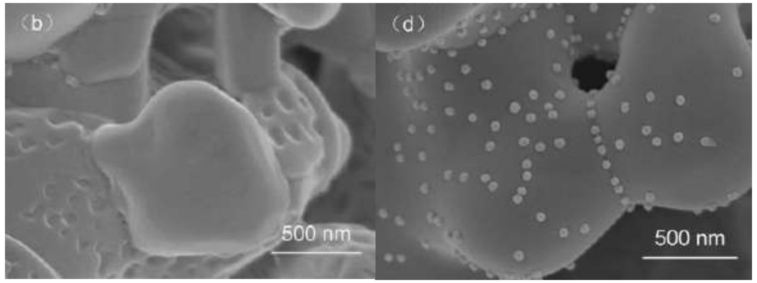








$CeO_{0,8}Gd_2O_3/La_{0,8}Sr_{0,2}Co_{0,8}Ni_{0,2}O_{3-\delta}$



$La_{0,4}Sr_{0,4}Sc_{0,9}Ni_{0,1}O_{3-\delta}$

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$La_xCe_{1-x}O_{2-\delta}$ (0 ≤ x ≤ 0.7) system

TRINDADE, F. *et al*, *ACS Applied Nano Materials* **5**(7), 8859-8867 (2022)

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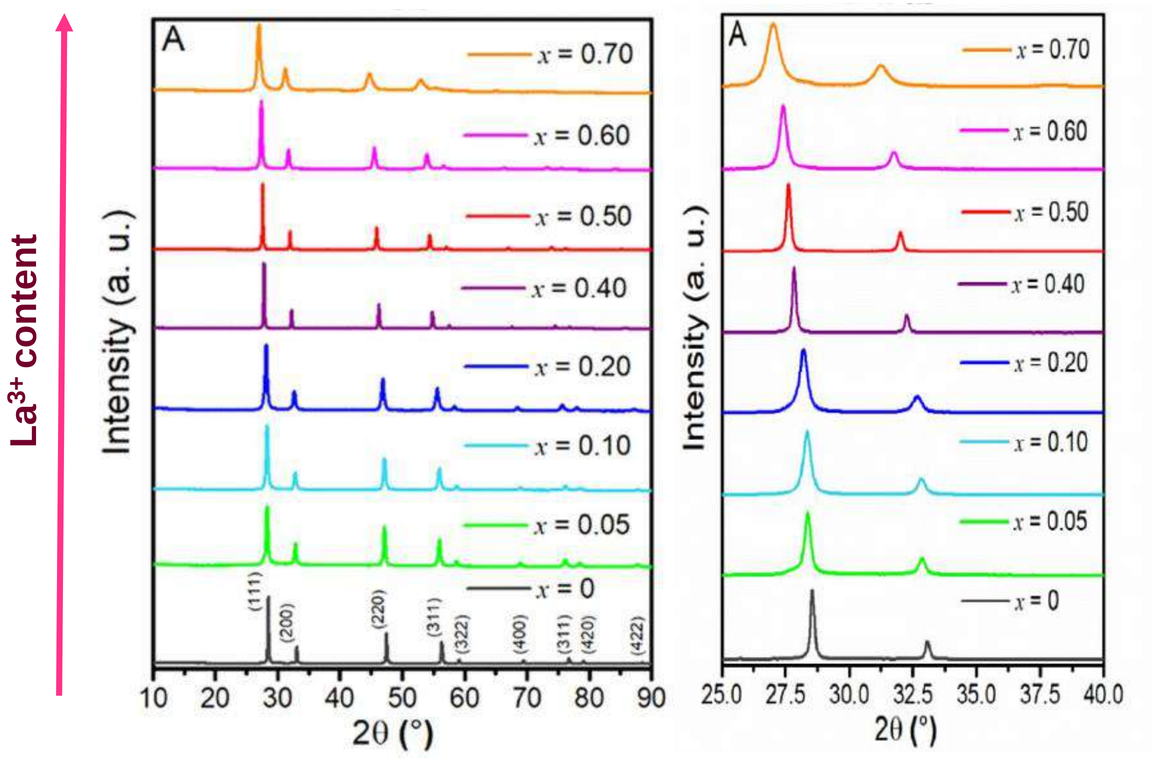
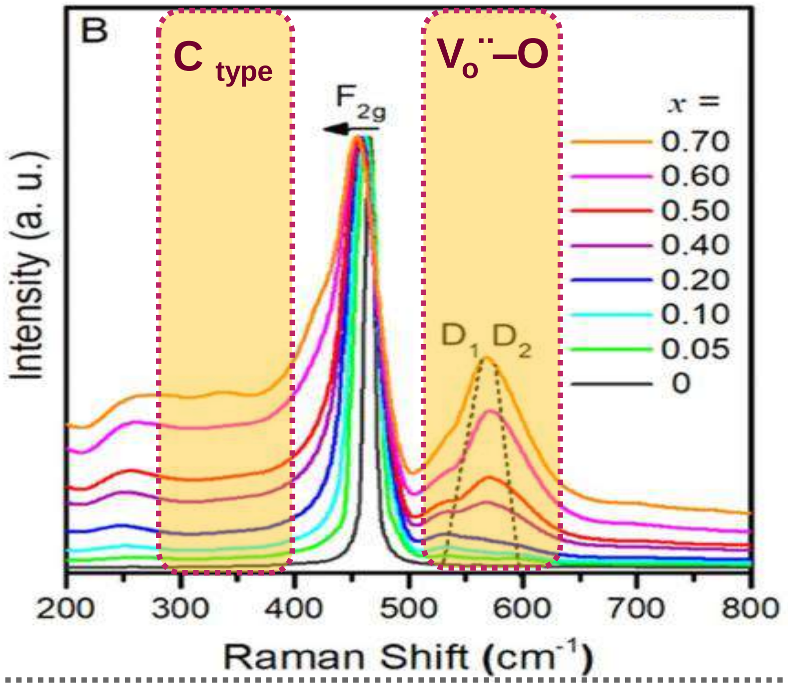
XRD



Raman



→ **Fluoryte + C-type cristaline structure**

↑ **La^{3+} content** ↑ **$V_o^{\cdot\cdot}$ formation**

└→ **C-type structure → $V_o^{\cdot\cdot}$ ordering**

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