Intermediate-Temperature Electrogenerative Cells for Flexible Cogeneration of Power and Liquid Fuel

DOE ARPA-E Award # DE-AR0000496

ARPA-E Program Director: Dr. John Lemmon

Greg G. Tao[1], Xingbo Liu[2], Fanxing Li[3], and John Sofranko[4]

1. Materials & Systems Research, Inc.; 2. West Virginia University; 3. North Carolina State University; 4. Bio2Electric, LLC

16th Annual SOFC Workshop

Pittsburgh, PA, July 14-16, 2015

Materials & Systems Research Inc.

MSRI specializes in materials and electrochemical engineering for power generation and energy storage applications: fuel cells/electrolyzers, storage batteries, and thermoelectric converters.

"Powder in → Power & Liquid Fuel out"

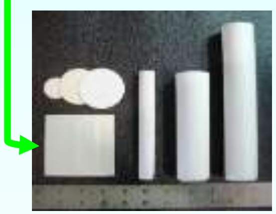
Fuel Cell/Electrolyzer

- Start from off-the-shelf powders
- Both planar and tubular cells
- Per-cell active area varying from 1 to 400 cm^2
- Stacks/bundles from 10 W to 4 kW

Sodium-beta Battery

- Advanced Na^+-conducting ceramic electrolyte
- Unique battery designs

MSRI's Technology processing & solutions



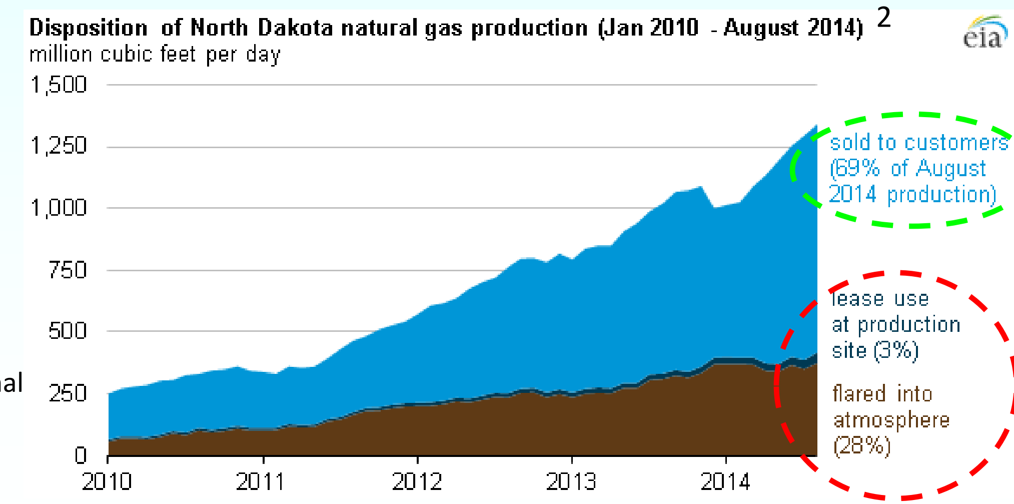
Outline

- Project Overview
- Accomplishments
- Summary

Opportunity

- 75% CO_2
- 16% methane
- others

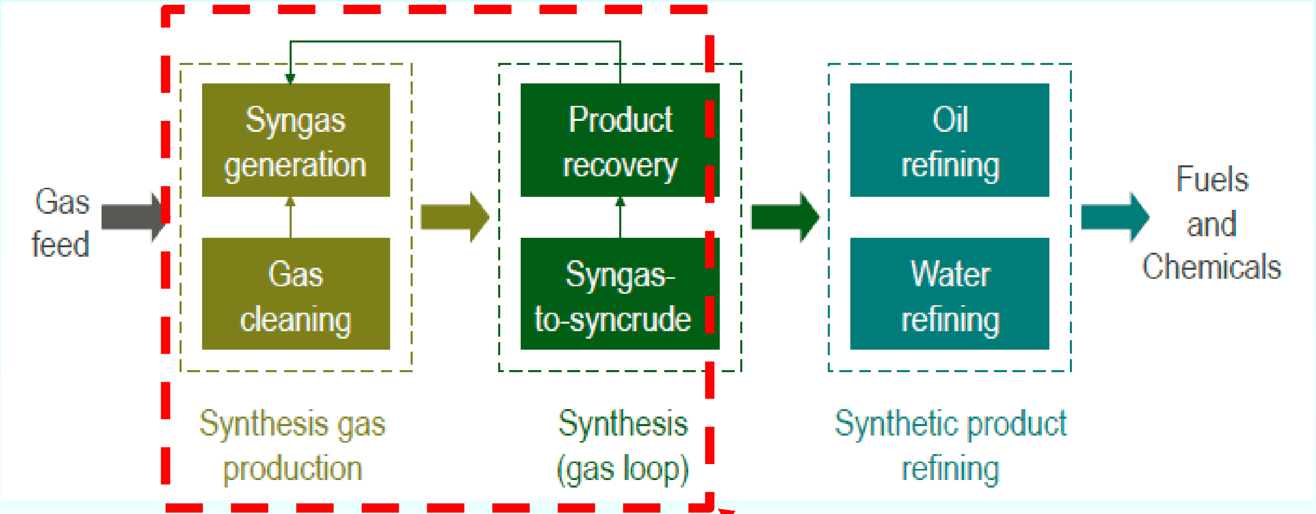
- **Global NG flaring[3]**
  - 5 quadrillion BTU yearly
  - ~ 27% U.S. power production
- **Flared/vented gas wells**
  - Negative value gas
  - 50% produce < 1000 bpd



1. K.A Johnson and D.E. Johnson, Methane Emissions from Cattle, J. Animal Science, 1995
2. http://www.eia.gov/todayinenergy/detail.cfm?id=18451#
3. World Bank, Global gas flaring reduction partnership, 2012

Introduction - GTL

Fischer-Tropsch GTL Process (A. De Klerk, U of Albany, 2011)



A drop-in reactor for small-scale GTL, replacing >50% cost?

GTL Economics

GTL Facility	Company	Capacity	Capital Cost[5]
Pearl	Shell	140,000 bpd[3]	~ $110,000/bpd
Escravos	Sasol-Chevron	33,000 bpd[4]	~ $180,000/bpd
Sasol I expansion	Sasol	---	~ $200,000/bpd

3. A. De Klerk, ARPA-E workshop, Houston TX, January 2012; 4. Pearl GTL – an overview. Shell 2012; 5. B. Reddall. Thomson Reuters, Feb. 24, 2011

REBELS Category 3 – Gas to Power/Liquid

Description	Symbol	Unit	Sample Products* Pentane	Bezene	Methanol
Reaction			$5CH_4=C_5H_{12} + 4H_2$	$6CH_4=C_6H_6 + 9H_2$	$CH_4 + 0.5O_2=CH_3OH$
Number of electrons	n	mol/mol	8	18	2
Faraday Constant	F	C/mol	96,485	96,485	96,485
Membrane Active Area	A	cm^2	100	100	100
Cell unit thinkness	t	cm^2	1	1	1
Current density	j	A/cm^2	0.100	0.100	0.100
Molar mass product	M	g/mol	72.2	78.1	32
Density of product	ρ	g/mL	0.626	0.877	0.792
Enthalpy of combustion	$\Delta_c H^o$	kJ/mol	3509	3273	715
Volumetric product output	$P_V=jAM/\rho nF$ (x86400)	mL/D	129	44	181
Areal product output	$P_A=j\Delta_c H^o/nF$ (÷70.8)	bpd/cm^2	6.42E-06	2.66E-06	5.23E-06
Process Intensity	$PI=j\Delta_c H^o/nFt$ (x28,317÷70.8)	bpd/ft^3	0.18	0.08	0.15
Cell material cost	C_A	$\$/cm^2$	0.50	0.20	0.50
Cell cost per product output	C_A/P_A	$/bpd	77,870	75,136	95,540

*. ARPA-E FOA No. DE-FOA-0001026, page 21

Organization	Team Leader	Functions
MSRI	Greg Tao	Cell design; cathode enhancement; fabrication process; material integration; experimental evaluation; PoC demonstration, T2M
WVU	Xingbo Liu	Highly performing, redox-stable anode development; anode catalyst implementation
NCSU	Fanxing Li	Methane to methanol catalyst development; GTL process simulation
B2E	John Sofranko	Methane to methanol catalyst development; cost analysis; T2M

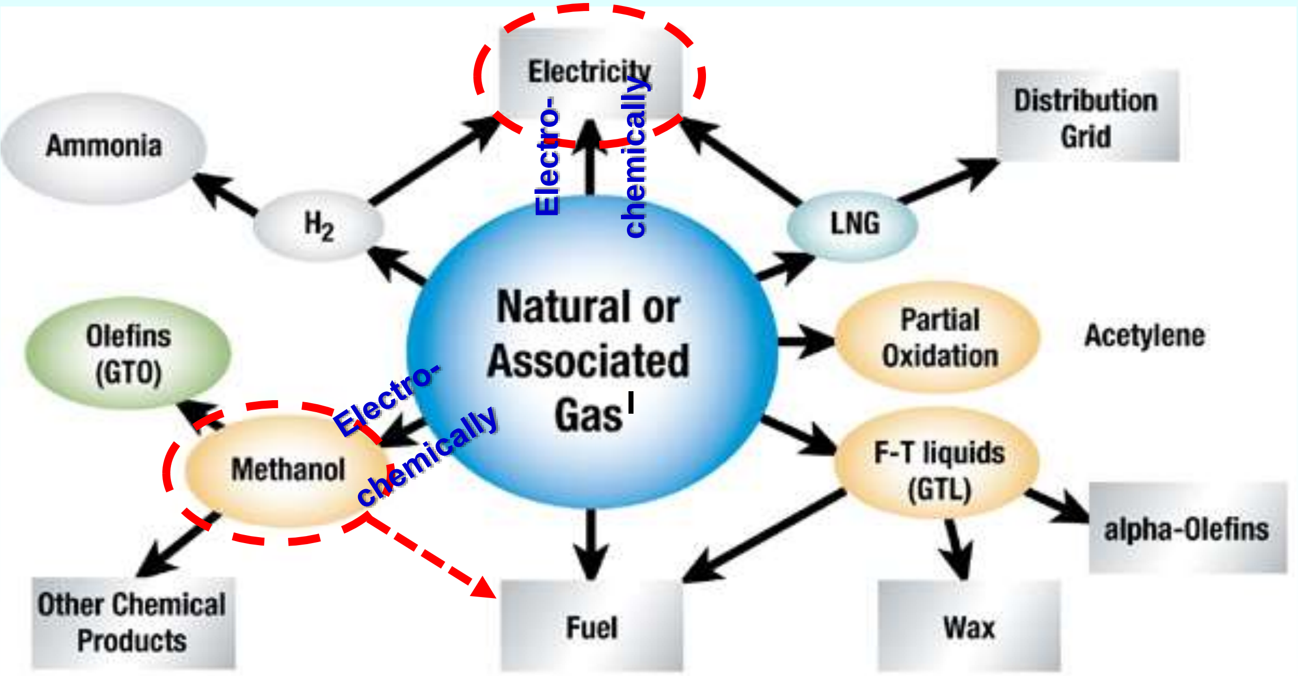
Overall Project Description

Goal: to develop an intermediate-temperature (IT) electrogenerative device for converting natural gas electrochemically into electricity or liquid fuel in a single step:

(1) power generation;

(2) fuel production;

(3) operating conditions

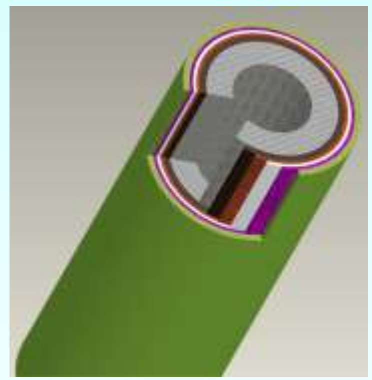


I: http://www.oilgasmonitor.com/monetization-natural-gas/2453/

Proposed Technology

To integrate state-of-the-art fuel cell technologies, advanced methane-oxidation catalyst development, and unique cell design with the cost-effective cell fabrication technique to produce low-cost electricity and liquid fuel with enhanced durability.

MSRI 4kW SOFC/SOEC stack



MSRI 300W portable SOFC module

$\frac{1}{2}O_{2,c} + 2e^{-} \rightarrow O_{c}^{-2}$ ORR on cathode

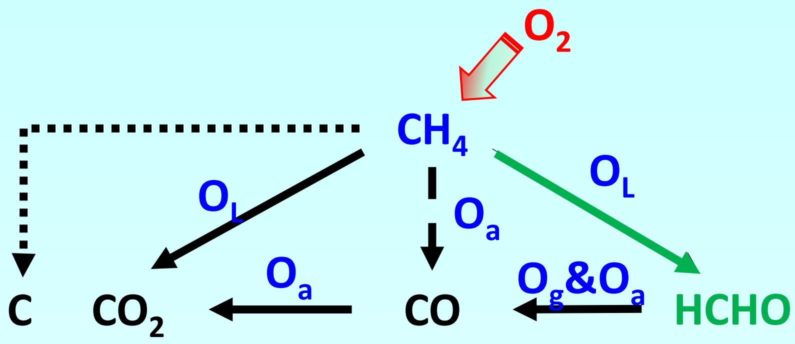
$O_{c}^{-2} \rightarrow O_{a}^{-2}$ O^{-2} transport through electrolyte

$O_{a}^{-2} + CH_{4,a} \rightarrow CH_{3}OH + 2e^{-}$ fuel oxidation on cathode

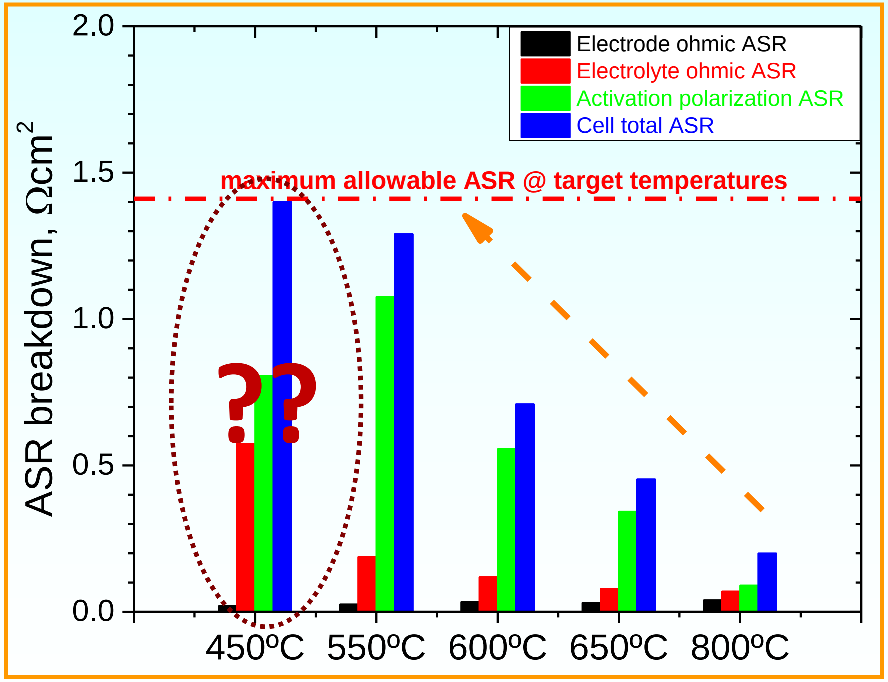
$\frac{1}{2}O_{2,c} + CH_{4,a} \rightarrow CH_{3}OH$ overall electrochemical reaction

Tubular, porous **M**etal-**S**upported **E**lectrogenerative **C**ell **(TMS-EC)**

Major Challenges



Methane Partial Oxidation



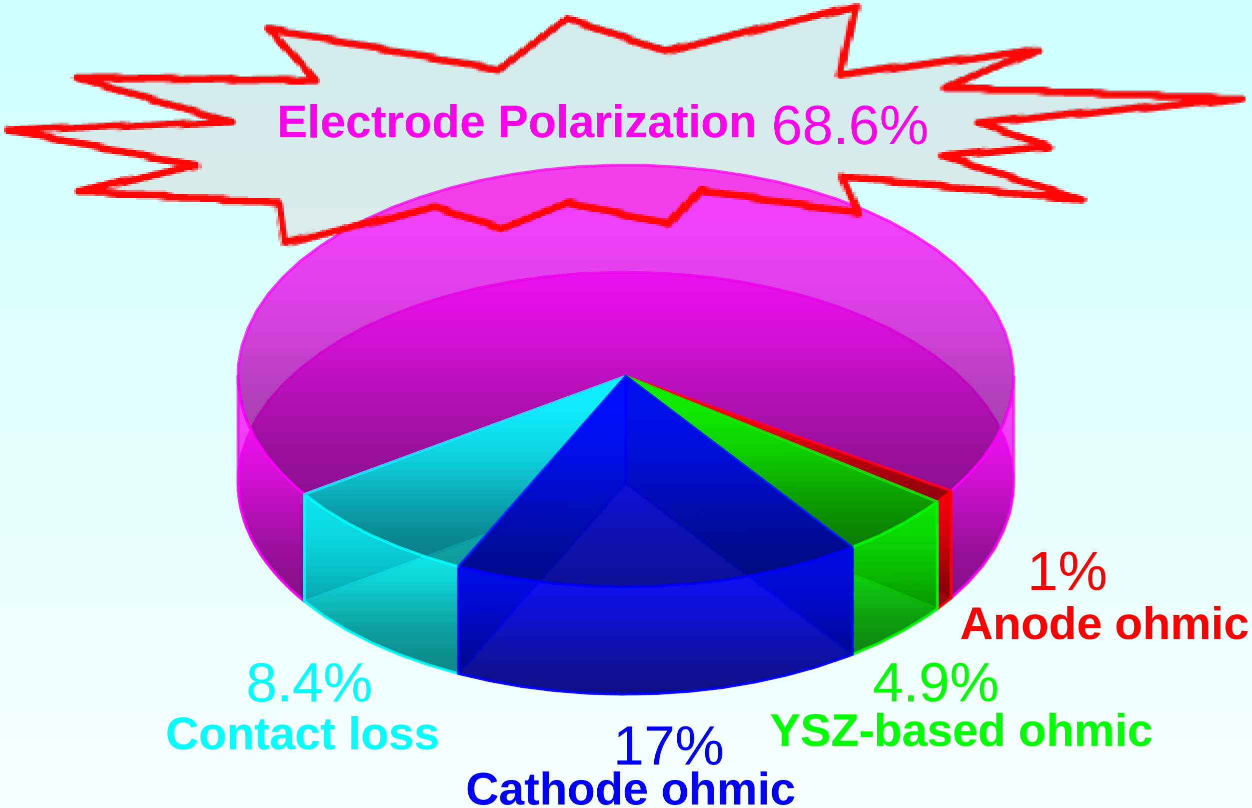
- Methane oxidation catalyst selectivity for methanol/formaldehyde
- Tailoring catalyst structure to enhance activity & selectivity
- Refining catalyst/electrode design
- Improving catalyst compatibility to anode/electrolyte materials

- Highly performing-cell components (electrodes & electrolyte) at low temperatures
- Electrochemical reaction sites extension
- Methane oxidation catalyst and electrocatalyst implementation
- Cell design to incorporate catalysts
- Cost-effective cell fabrication process development
- Scaling –up challenges

Approaches

- **TMS-EC Design**
  - Tubular form factor
  - Porous metal supports with all thin-film structures (electrodes/electrolyte)
- **Materials Development**
  - Methane oxidation catalysts
  - Anode materials
  - Cathode materials
  - Materials integration
- **TMS-EC Fabrication Development**
  - Thermal spray process
  - Dissimilar cell materials integration
  - Scaling-up (100 cm^2)
  - Experimental evaluation for proof-of-concept demonstration
- **Technology-to-Market (T2M)**
  - Techno-economic analysis
  - System design (MTG)
  - T2M development

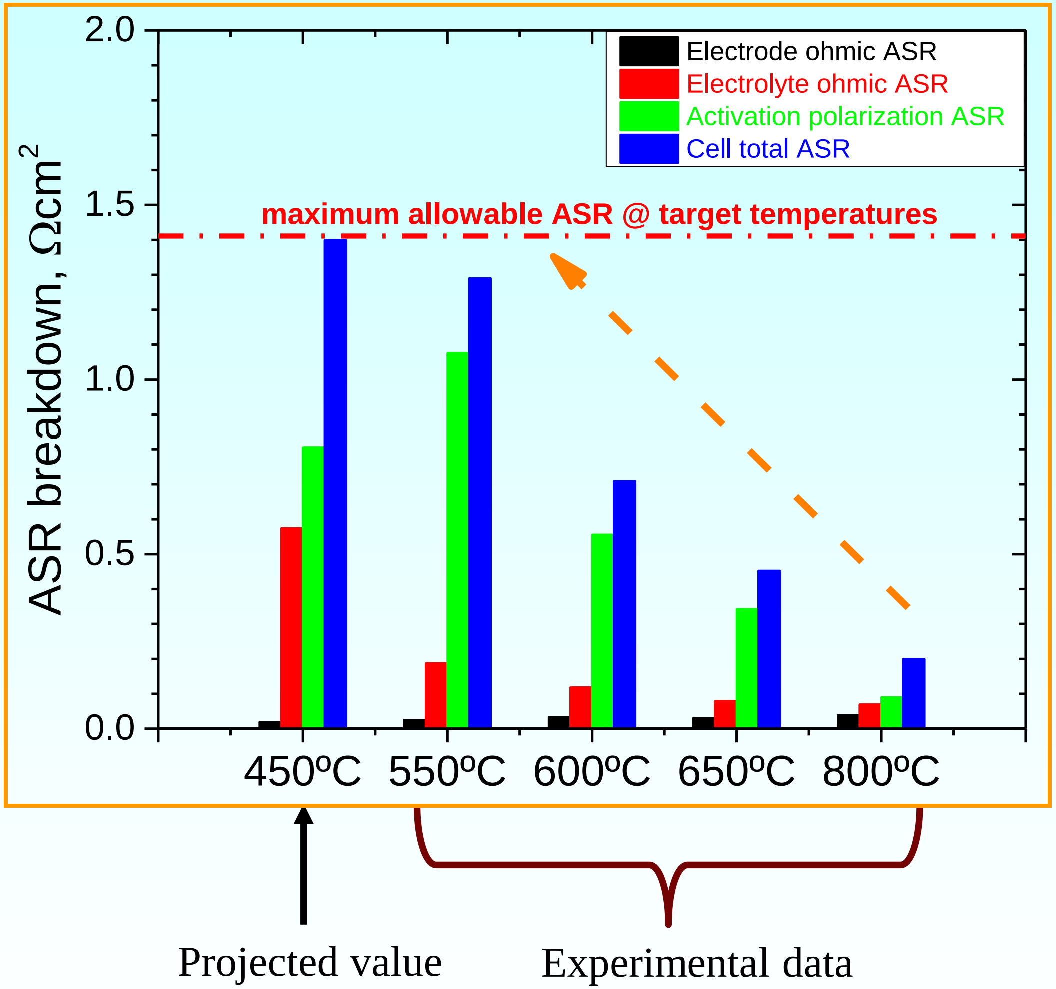
Cell Materials Development



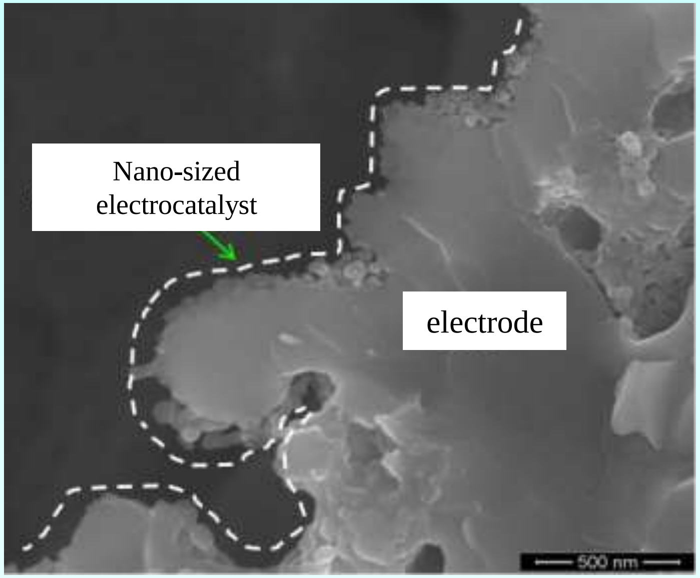
Overpotential breakdown at a cell level for a typical MSRI anode-supported cell

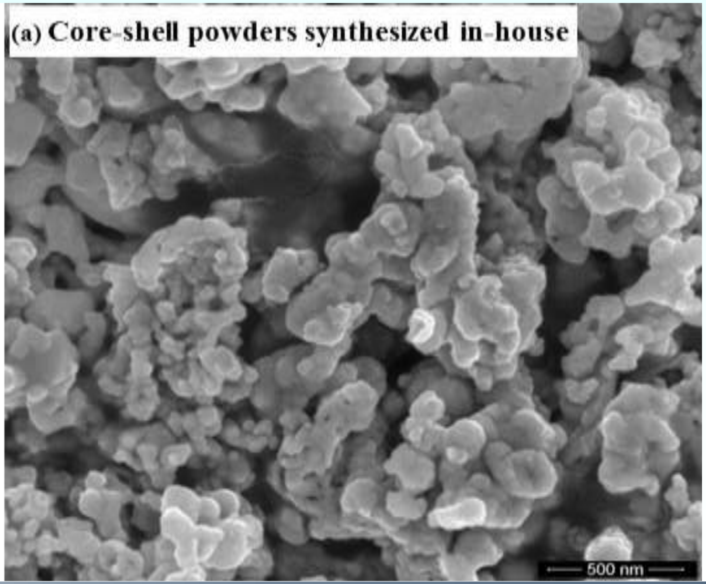
$$\eta_{total} = \eta_{act,an} + \eta_{conc,an} + \eta_{ohmic,an} + \eta_{act,ca} + \eta_{conc,ca} + \eta_{ohmic,ca} + \eta_{ohmic,EL} + \Sigma\eta_{ohmic,cont} + \eta_{ohmic,sp}$$

Cathode Development



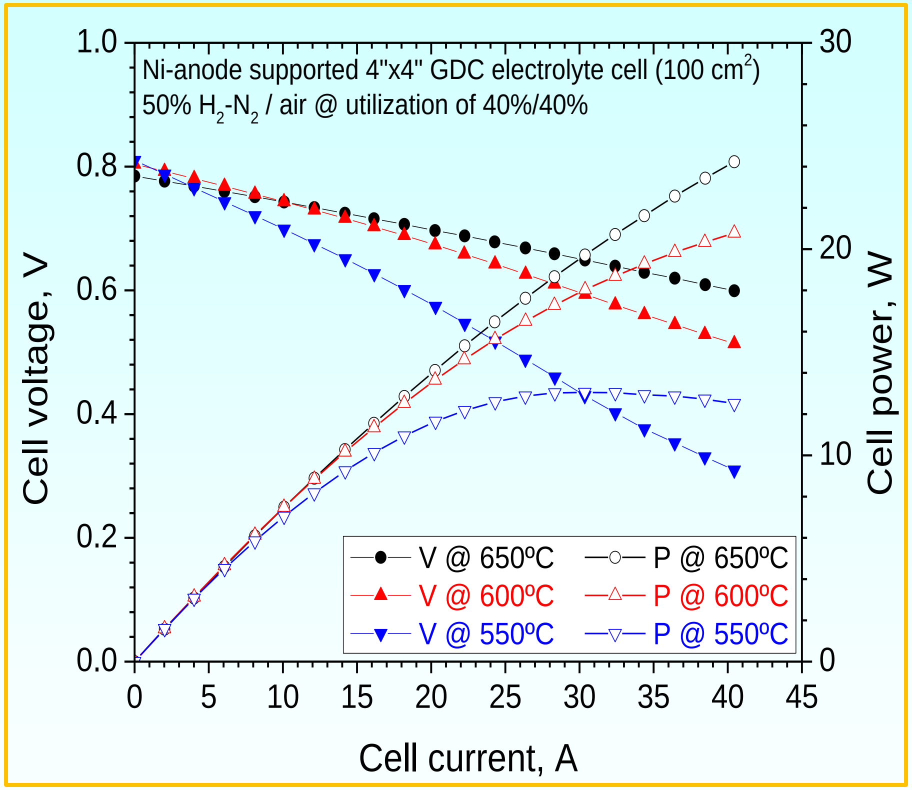
Button cell ASR breakdown (in SOFC operating conditions)

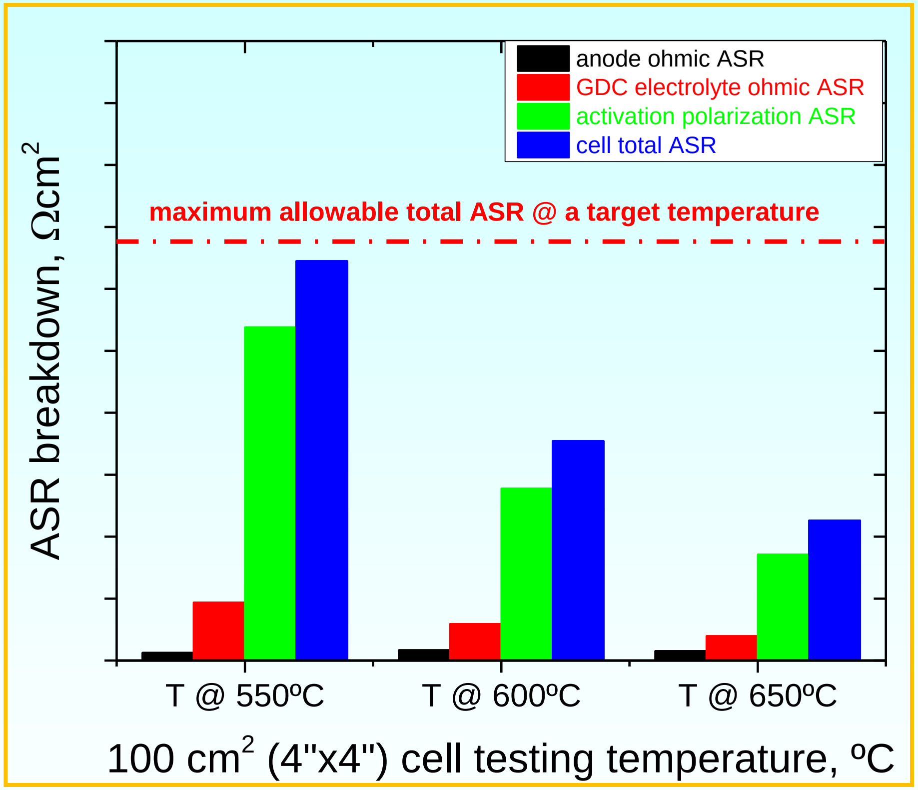




Ceria-Based Electrolyte Cell (4”x4”- 100cm^2)

- ❑ **Beyond 8YSZ-based Electrolyte – for ITFC**





A single, planar, Ni+YSZ-supported SOFC (100 cm^2) tested at 550ºC, 600ºC, and 650ºC w/50% H_2-N_2 as the fuel. Both U_f & U_{air} fixed @ 40%

Anode Requirements

Requirements	Ni-YSZ(GDC,SSZ)	Ceramic anodes	Infiltrated anodes
Catalytic activity: electrochemical oxidation of fuel	H_2 dissociation: **Good** dry CH_x: **Bad**	H_2 and CH_x: **OK** but not good; **Coking resistant;**	**OK/Good/Super**: depending on infiltrated catalysts
Impurity tolerance:	**Bad**	**Good**	**OK/Good**
Stability: Chemically, morphologically	**Bad:** large volume change of Ni/NiO	**Good for redox**	**OK/Good** Depending on backbone and infiltrated material
Conductivity: high σ_e & σ_i	**High σ_e** (~1000 S/cm) High σ_i at high T	**σ_e OK**(0.1~100S/cm) **Poor σ_i**	**OK/Good** Depending on catalyst loading and backbone
TEC Compatibility:	OK but generally higher TEC than other components	**Better TEC match**	**TEC: cat. >> backbone** is allowed
Microstructure: Porosity, percolation	Sufficient for normal operating conditions	**Important**	**Very important**

Design of Highly Performing Anodes

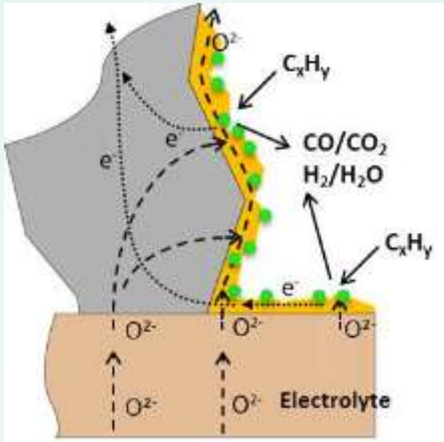
Routes:

Ceramic anode materials

or/and

Nano-catalyst infiltrated anodes

A desirable anode structure:



1 phase (very good MIEC & cat.)
or
2 phases ($\sigma_{el} + \sigma_i$ & cat.)
(co-sintered mix-powders
or one layer coating the other)
or
3 phases (2 phases + nano-catalyst decorations)

Anode Material Choices

MIEC

- **Mixed conductor** in reducing atmosphere: whole surface could be "active" and not limited to the TPBs;
- **Moderate performance** as single component anode material for oxidation of hydrogen;
- **Low electronic conductivity**;

Alloy

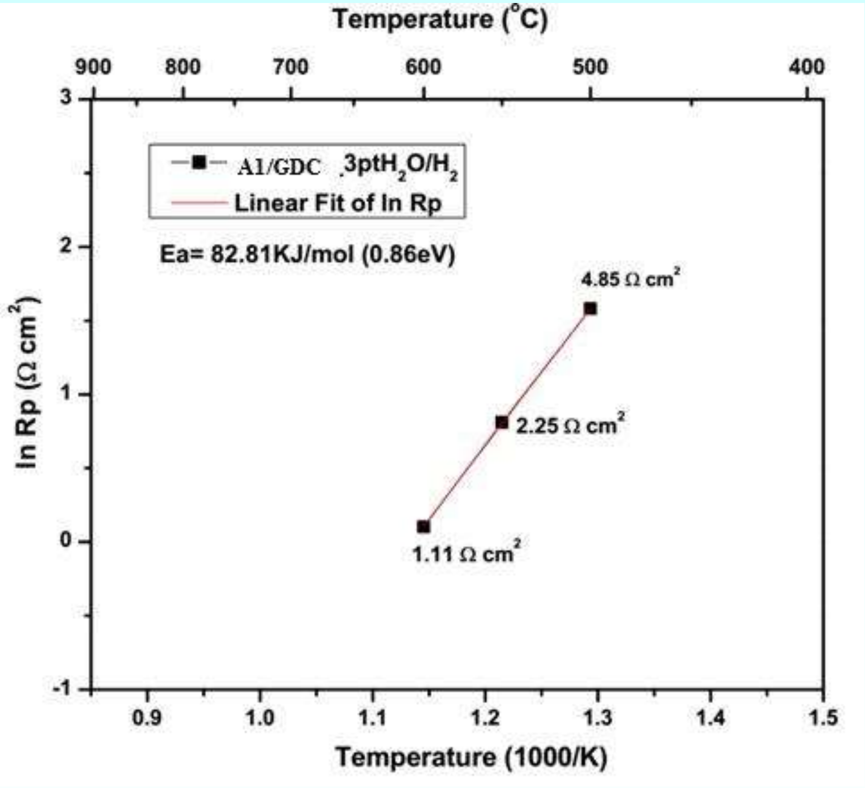
Very good electronic conductivity;

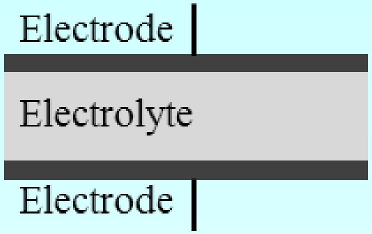
Coking resistant; lower catalytic property

Doped oxides

- Electrical conduction in reducing atmosphere;
- Chemical stability, redox stable; S-tolerant;
- Electrochemical properties for oxidation of H_2;

Anode System #1|GDC|SSZ





Gas atmospheres:

a) Wet (1 % H_2 + 99 % N_2);
b) Wet (10 % H_2 + 90 % N_2);
c) Wet (100 % H_2 + 0 % N_2);

No electronic leaking current through the SSZ electrolyte under the reducing atmosphere;

Rp = 2.3 Ωcm^2 @550°C for this type anode

A1 Electrode Wet (100% H_2 + 0% N_2)	450 °C	500 °C	550 °C
Rp (Ωcm^2)_GDC support	**2.7**	0.6	0.2
Rp (Ωcm^2)_SSZ support	-	4.9	**2.3**

Anode Nano-Catalyst Development

- **Methane catalytic oxidation by active oxygen species into C1 oxygenates**

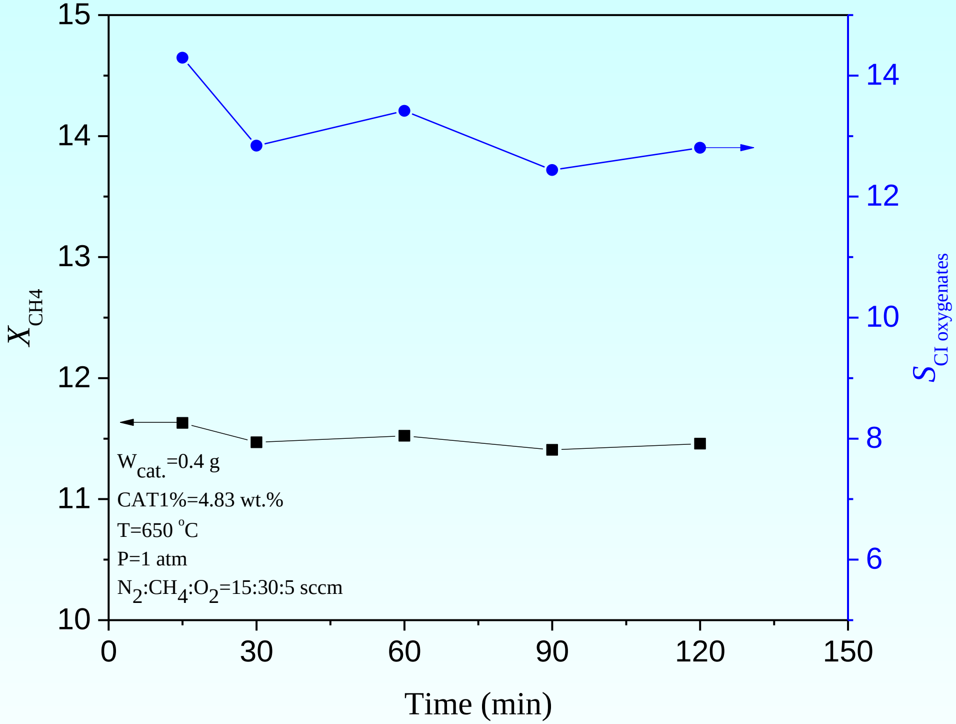
$$Anode: \quad CH_4 + O^{x-} = CH_3OH + xe \quad or \;\; CH_4 + O^{x-} = CHOH + H_2O + xe$$

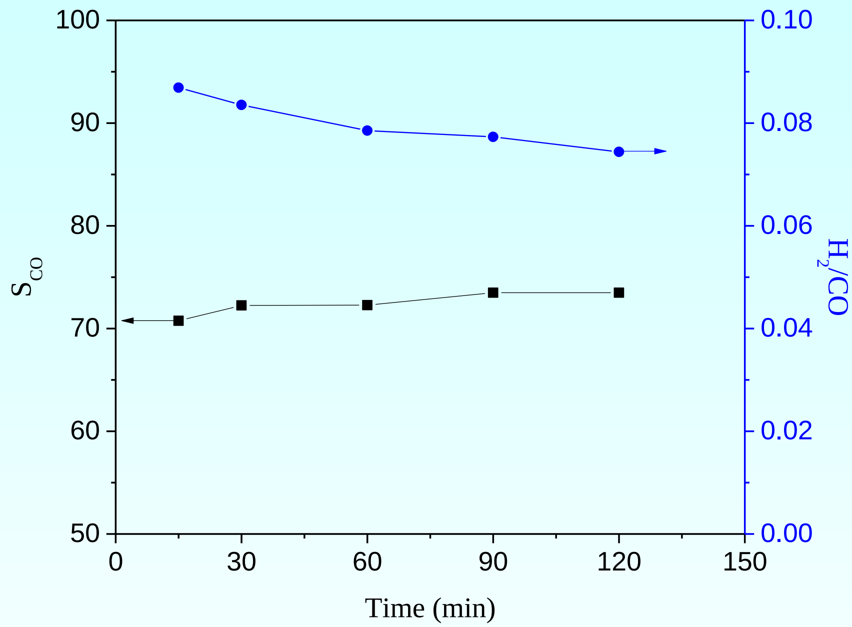
- **Synthesis methods for supported metal oxide catalysts**
  - **Incipient wet impregnation**
    - Precursor of catalyst
    - Drying & calcination
  - **Thermal spreading**

- **Catalytic testing:** direct conversion of methane to C1 oxygenates was carried out in a continuous flow fixed-bed reactor with co-feed mode (1 atm)

  - 0.4 g catalyst particles in a U-type quartz tube
  - 550~650ºC
  - Flow w/ 10%O_2 bal. He for 1 hr
  - Flow w/ reactant of $CH_4/O_2/N_2/H_2$ at 60%/10%/20%/10% respectively, or different ratios

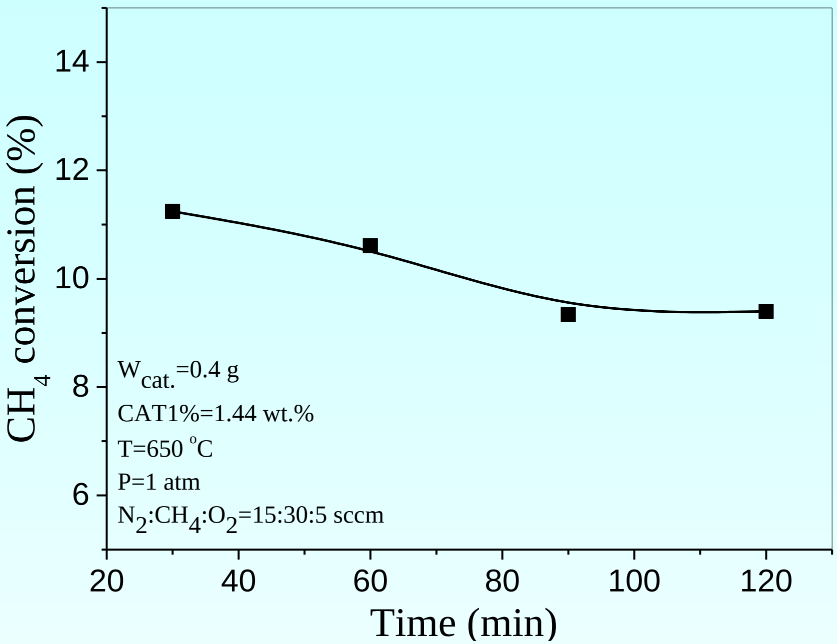
Selective oxidation over CAT1/MCM-41

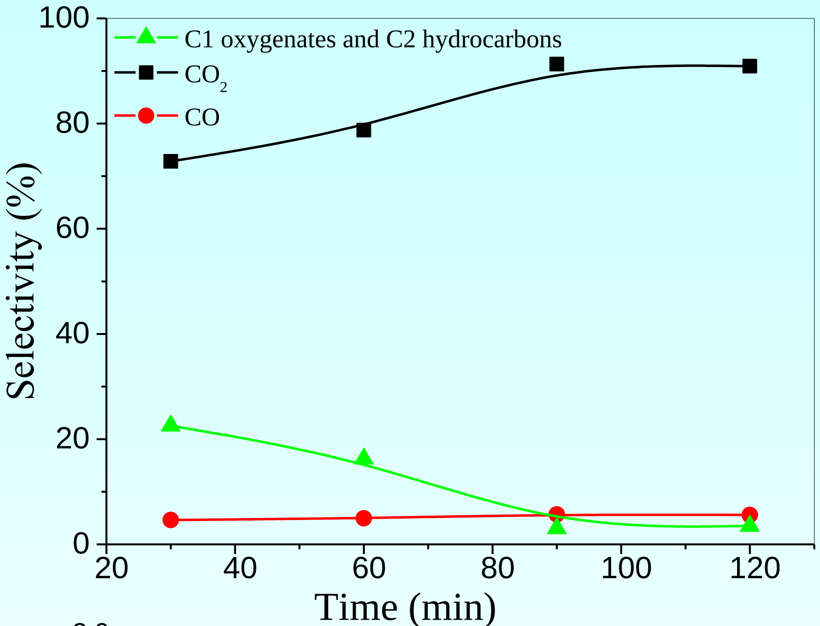


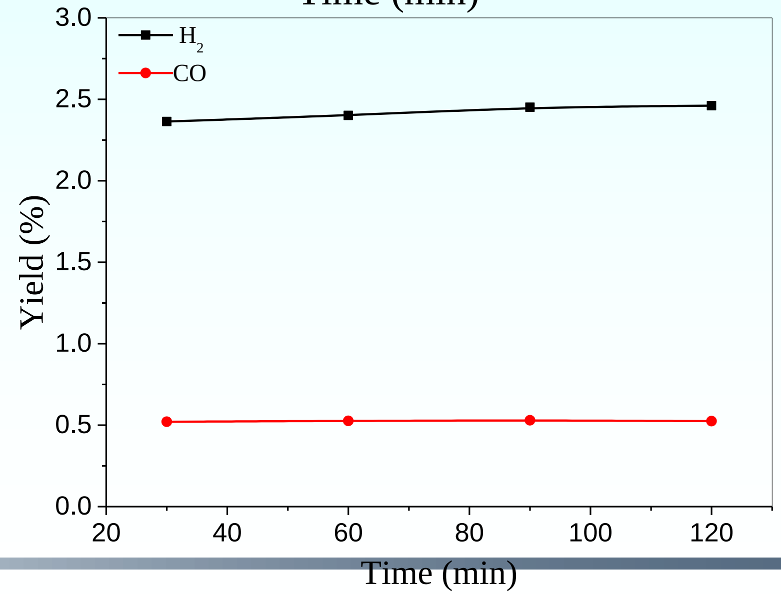


- Methane conversion is 11%
- The selectivity of C1 oxygenates is 12%
- CO selectivity is 70%

Selective oxidation over CAT1/Support-1



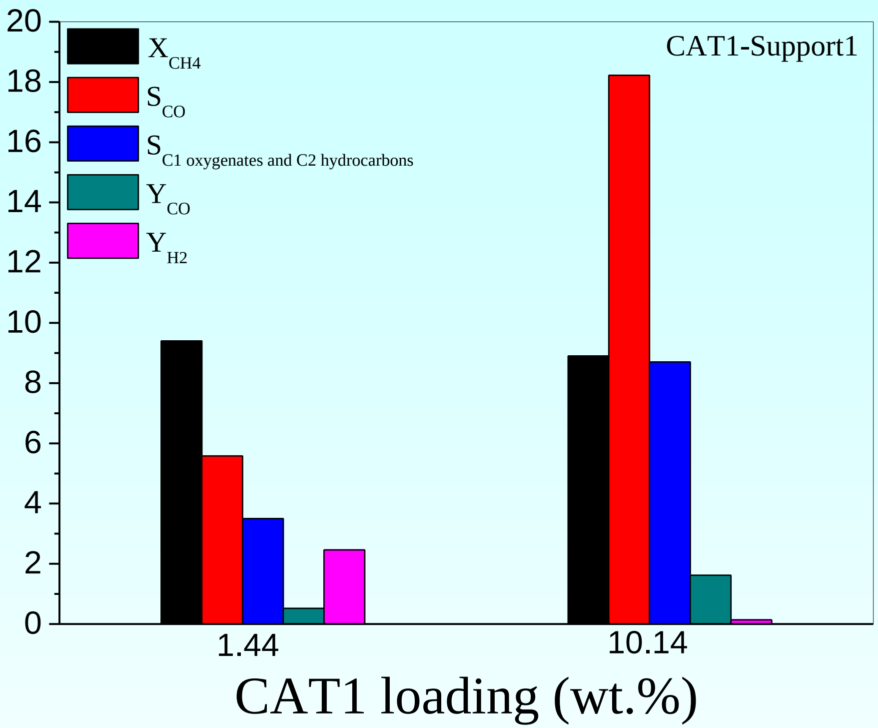


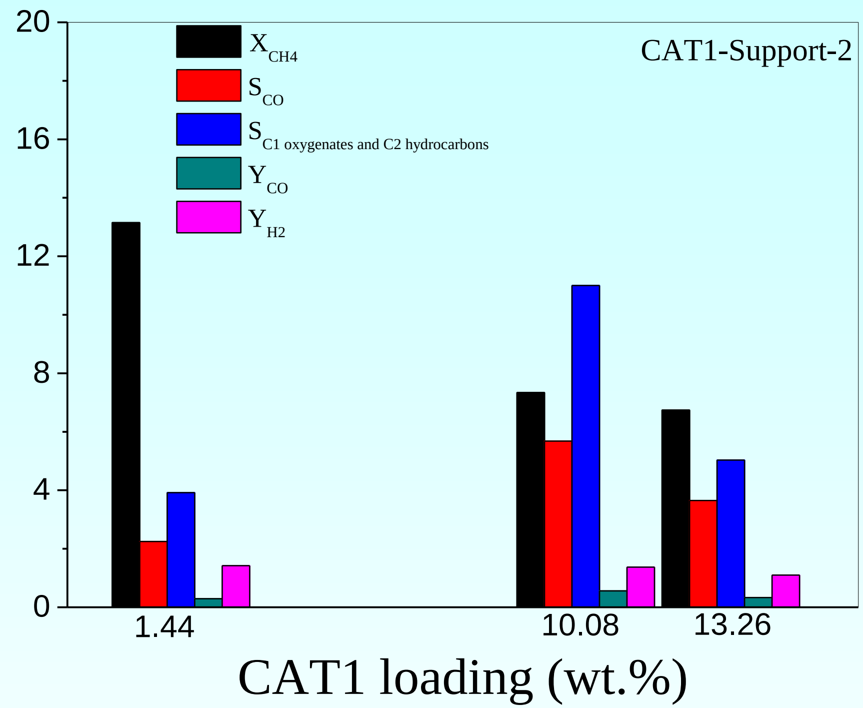


CAT1=1.44 wt.%

- The initial low selectivity toward CO_2 is due to time lag in GC sampling
- The selectivity of CO_2 is around 90 %
- The molar ratio of H_2/CO_2 is 0.58

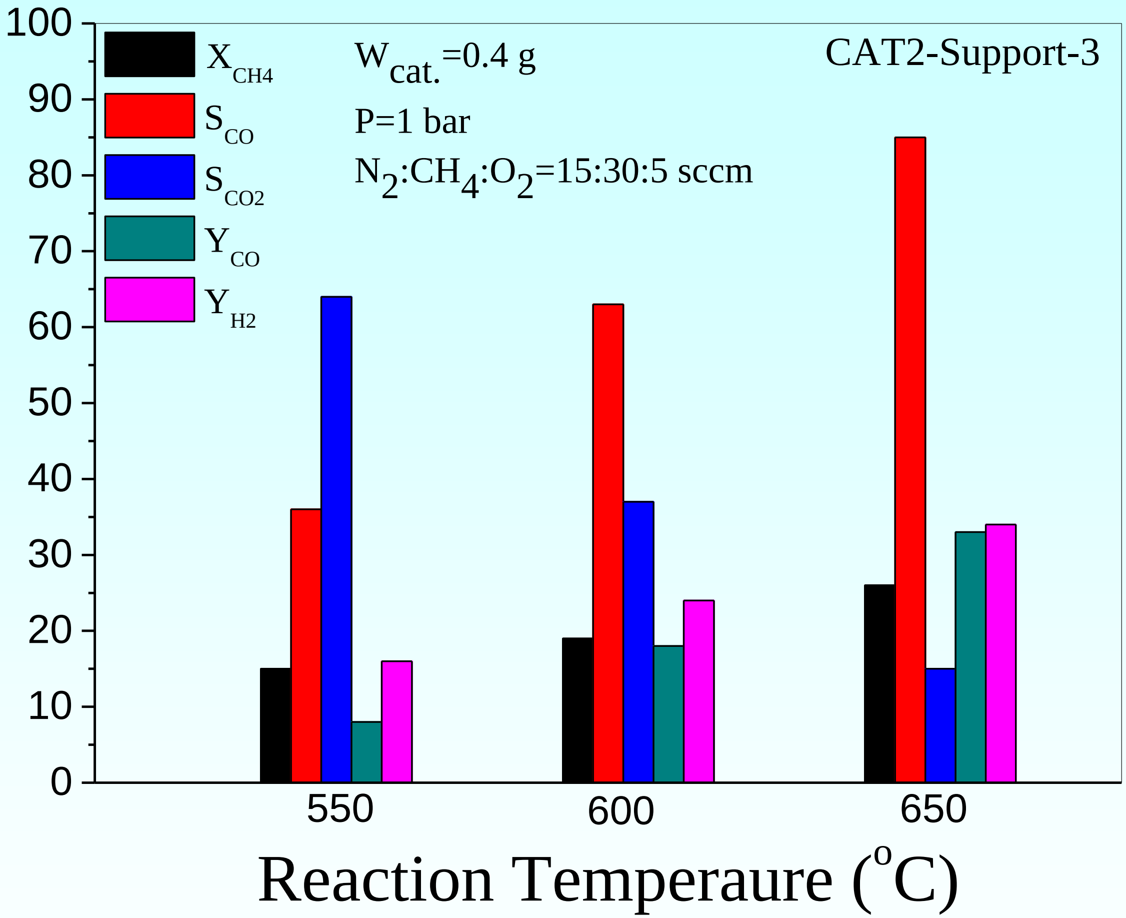
Effects of CAT1 Loadings





- CO_2 is the main product
- The selectivity of CO (16 mol.%) plus C_1 oxygenates+C_2 hydrocarbons (10 mol.%) maximizes at 10 wt.% of CAT1

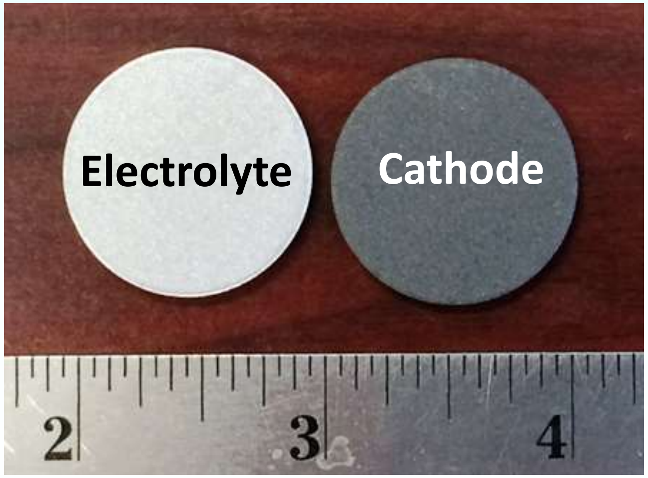
Effects of Temperatures

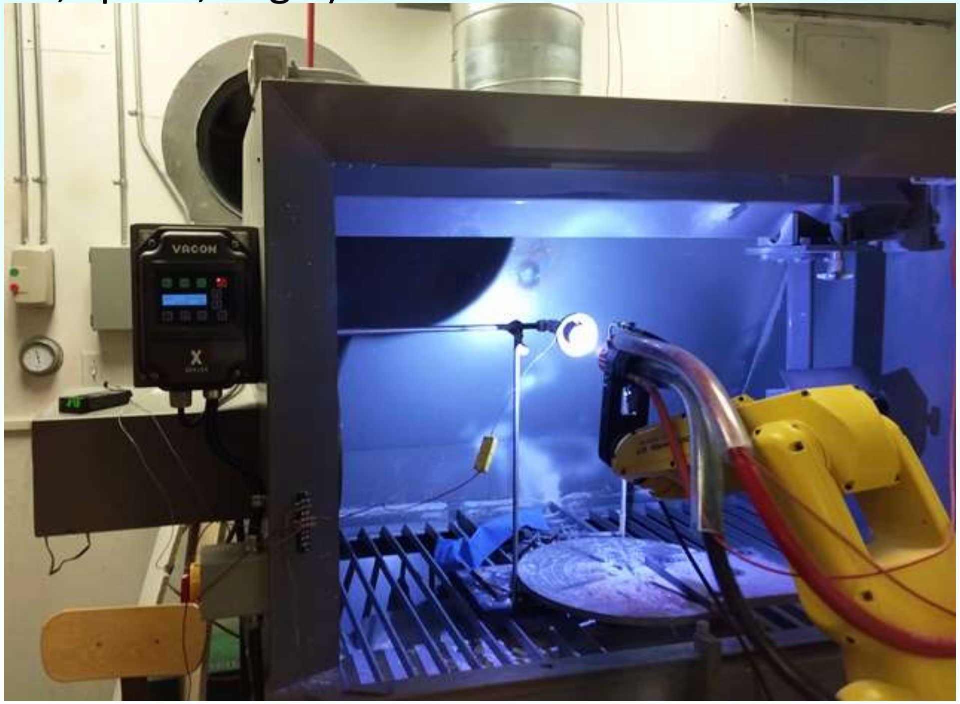


- The conversion of O_2 is 100 % at three temperatures
- Highest CH_4 conversion is 13%

Cell Manufacturing Process Development

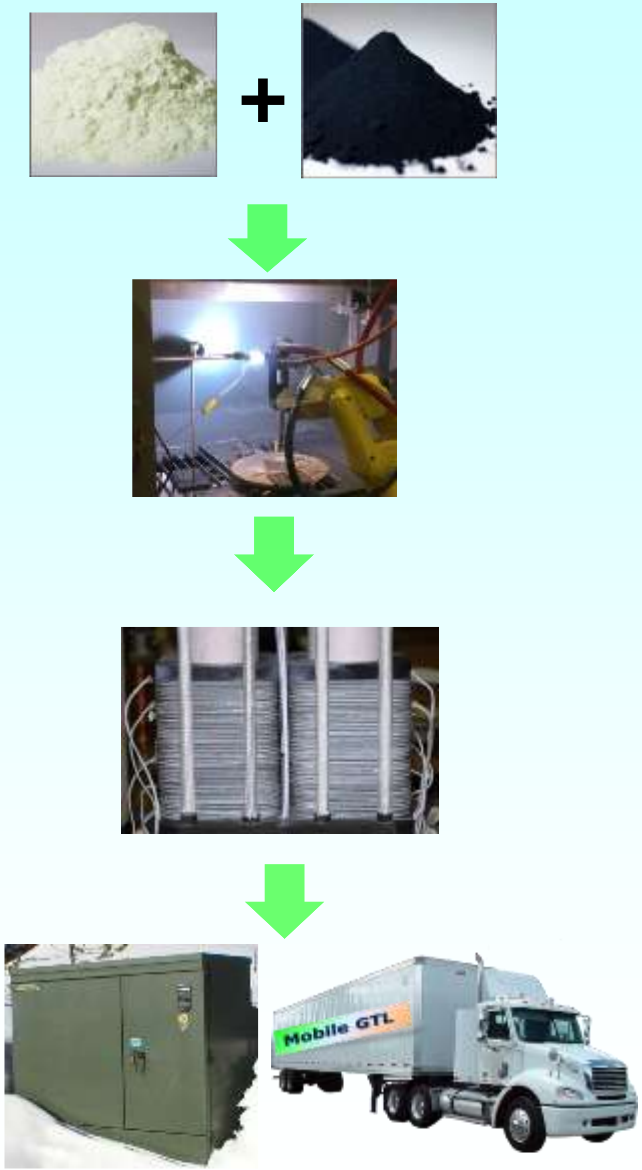
- DoE development for the deposition of all thin-film structures supported on a porous metal substrate
    - Thermal spraying parameters
        - ✓ Feedstock parameters (granulate sizes, feed rate)
        - ✓ Gun operating parameters (gas compositions, V/I)
        - ✓ Gun movement parameters (SoD, speed, angle)
    - Mapping "sweet spot"
    - Substrate temperature





Summary

- Flexible operation for power generation or/and fuel production
  - Modularity
  - Less complexity
  - Suitable for remote site applications (well pads)
  - minimum O&M costs
  - low financial risks
- Greenhouse gases emission reduction
  - Turning flaring gas (negative value) into marketable products (fuel or power)
- Enable small GTL modules integration with MTG process
- Mobile GTL reactors
- Distributed power generation



Acknowledgement

- This material is based upon work supported by the Advanced Research Projects Agency – Energy Program under contract # DE-AR0000496

- ARPA-e REBELS Program management team Drs. John Lemmon, Mark Pouy, John Tuttle, and Scott Litzelman

Thank you!