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

DOE ARPA-E Award # DE-AR0000496

ARPA-E Program Director: Dr. Grigorii Soloveichik

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17th Annual SOFC Workshop

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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/Project Roles
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
EcoCatalytic	John Sofranko	Methane to methanol catalyst development; cost analysis; T2M

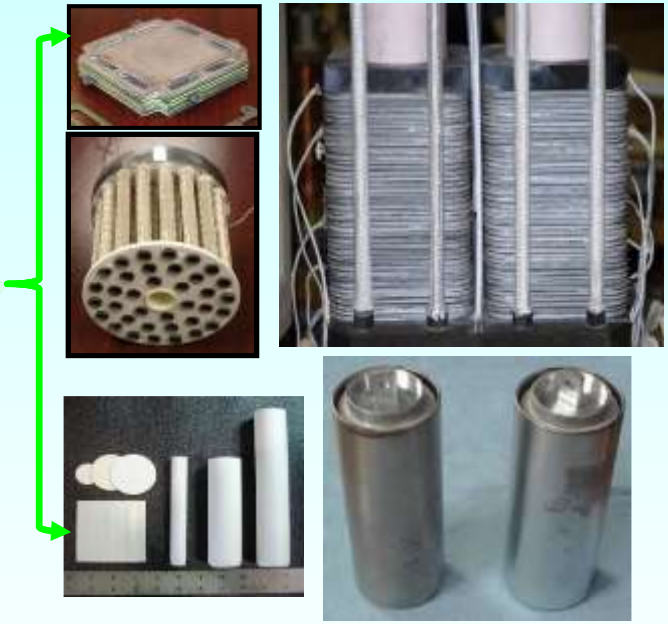
Materials & Systems Research Inc.

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

- 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

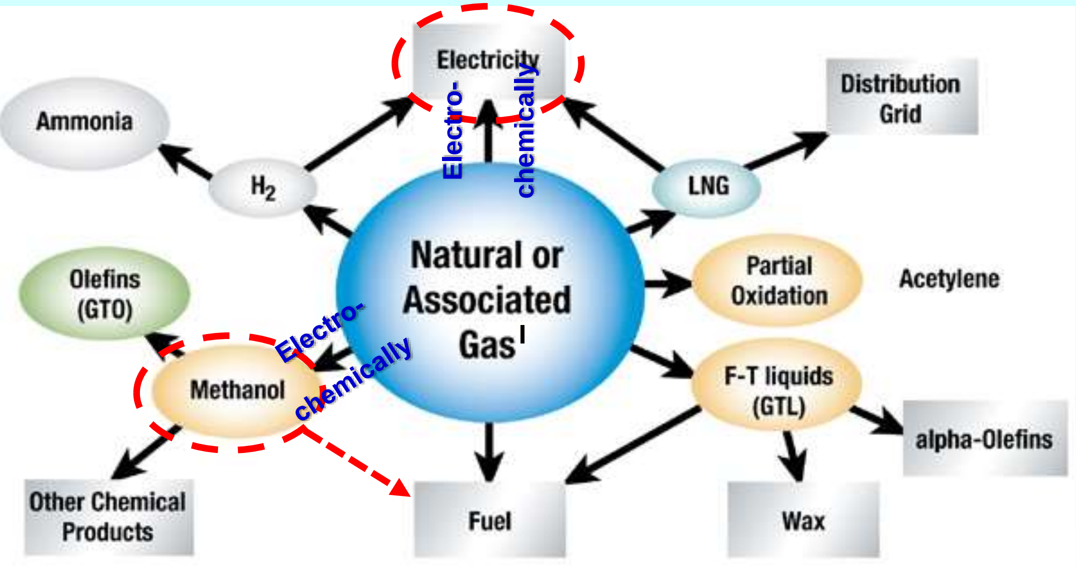
- Advanced Na$^+$-conducting ceramic electrolyte
- Unique battery designs (planar & tubular)

Outline

- Project Overview
- Up-to-Date Accomplishments
  - Electrogenerative Cell Design
  - EC Materials Development
  - EC Manufacturing Process Development
- Summary

Objective and Challenges

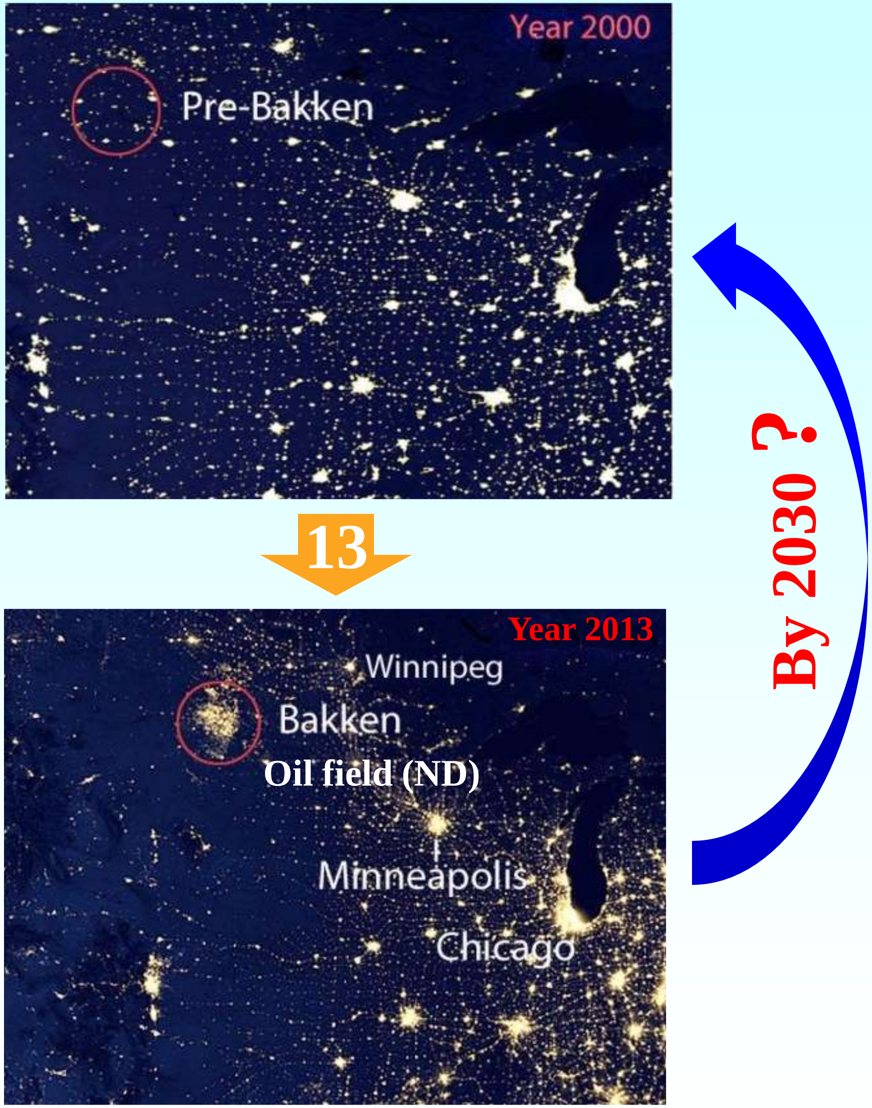
- **Objective:** to develop an intermediate-temperature (IT) electrogenerative device for converting natural gas electrochemically into electricity and liquid fuel cost-effectively.
  - (1) power generation
  - (2) fuel production
  - (3) operating conditions



- **Key Challenges Addressed**
  - Electrogenerative cell design enabling operating directly on dry methane
  - Electrogenerative cell materials development for operating at intermediate temperatures
    - ✓ Methane oxidation catalysts; anode materials; cathode performance enhancement; materials integration
  - Advanced cell manufacturing process development:
    - ✓ Cost-effective manufacturing process; dissimilar cell materials integration
  - Scaling-up and proof-of-concept demonstration

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

Value Proposition



- ○ **Natural gas flaring[1]**
  - 28% of North Dakota NG production is flared into atmosphere (~ 250 million cubic feet/day)
  - Global NG flaring > 5 quadrillion BTU/year
  - > 300 million tons of CO_2 emission (or equivalent to 70 mission cars emission)
  - ~ equivalent to 750 billion kWh of electricity
- ○ **Turning the flare gas to value added products**
  - Small scale modular reactor for flare gas (a negative market value gas) into fuel and electricity (~1000 bpd)
  - Mobile reactor, and easy integration w/ MTG process
  - Minimize financial risks
  - Flexible operation for fuel & power cogeneration – suitable for remote site applications (well pads), minimum O&M costs

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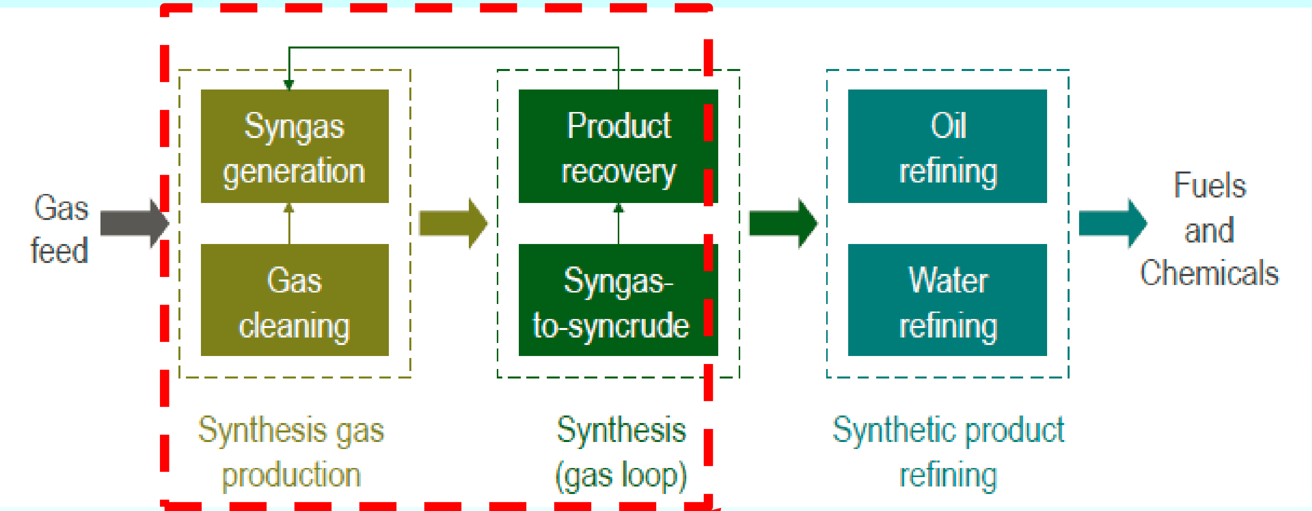
[1] World Bank, Global gas flaring reduction partnership, 2012; http://www.worldbank.org/en/programs/zero-routine-flaring-by-2030

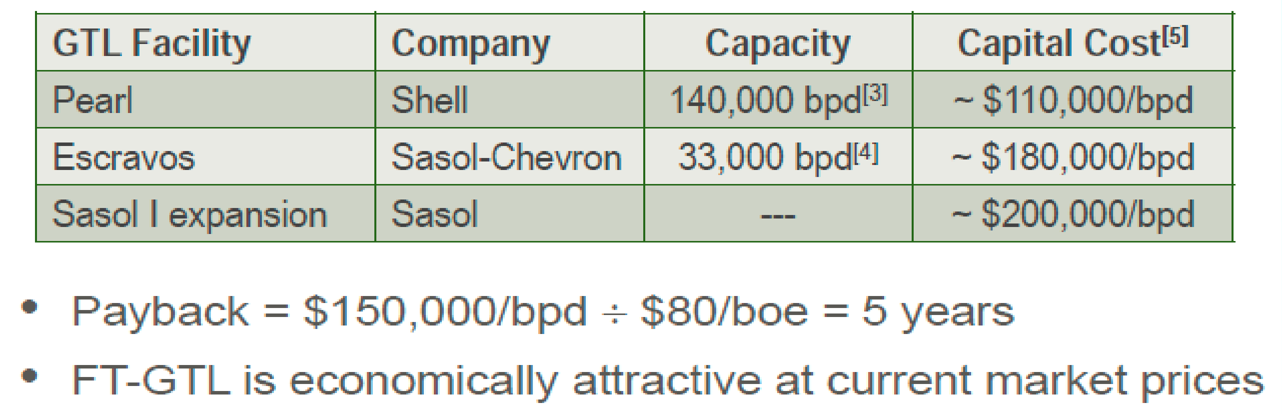
Gas to Liquids

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

- Payback = $150,000/bpd ÷ $80/boe = 5 years
- FT-GTL is economically attractive at current market prices

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

Objective and Challenges

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Key Challenges Addressed

- Electrogenerative **cell design** enabling operating directly on dry methane
- Electrogenerative **cell materials** development for operating at intermediate temperatures
  - ✓ Methane oxidation catalysts; anode materials; cathode performance enhancement; materials integration
- Advanced cell manufacturing process development:
  - ✓ **Cost-effective manufacturing process**; dissimilar cell materials integration
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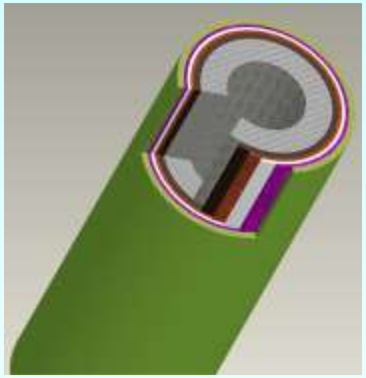
Electrogenerative Cell Design

Tubular Metal-Supported Electrogenerative Cell

Unique cell design would be capable of integrating state-of-the-art fuel cell technologies, advanced methane-oxidation catalyst development, with the cost-effective cell manufacturing process development.

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

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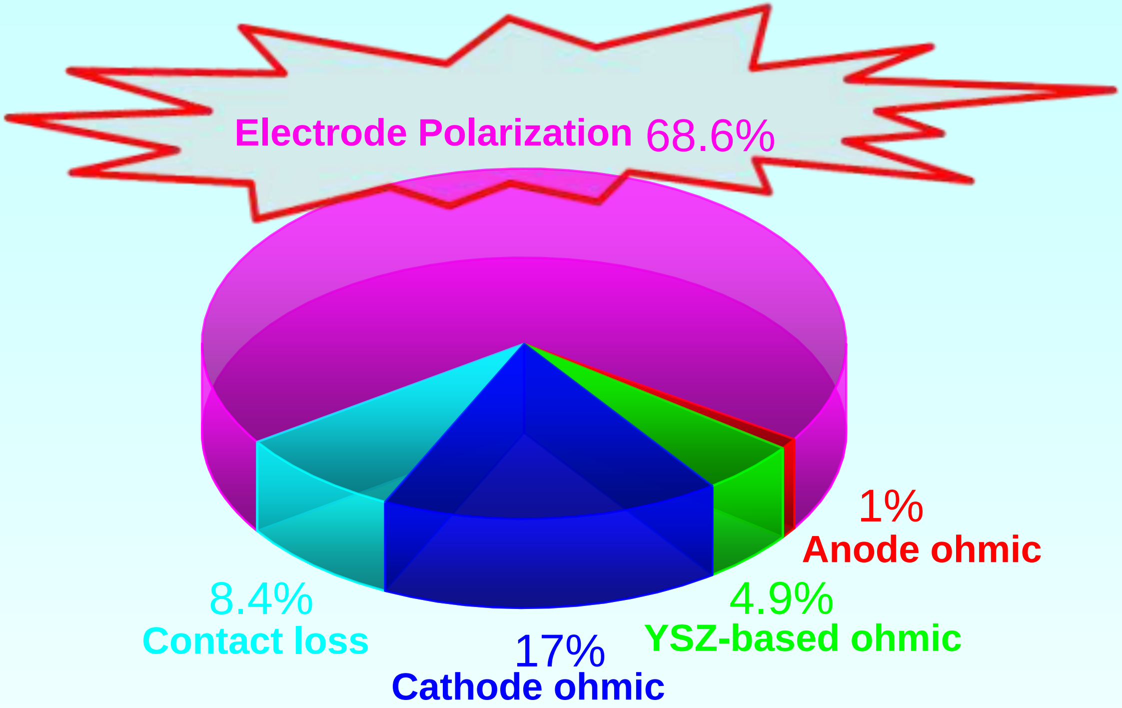
$\frac{1}{2}O_{2,c} + CH_{4,a} \rightarrow CH_{3}OH$ overall electrochemical reaction

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

Electrogenerative Cell Materials Development:

cathode + anode + anode methane catalyst

ASR Breakdown

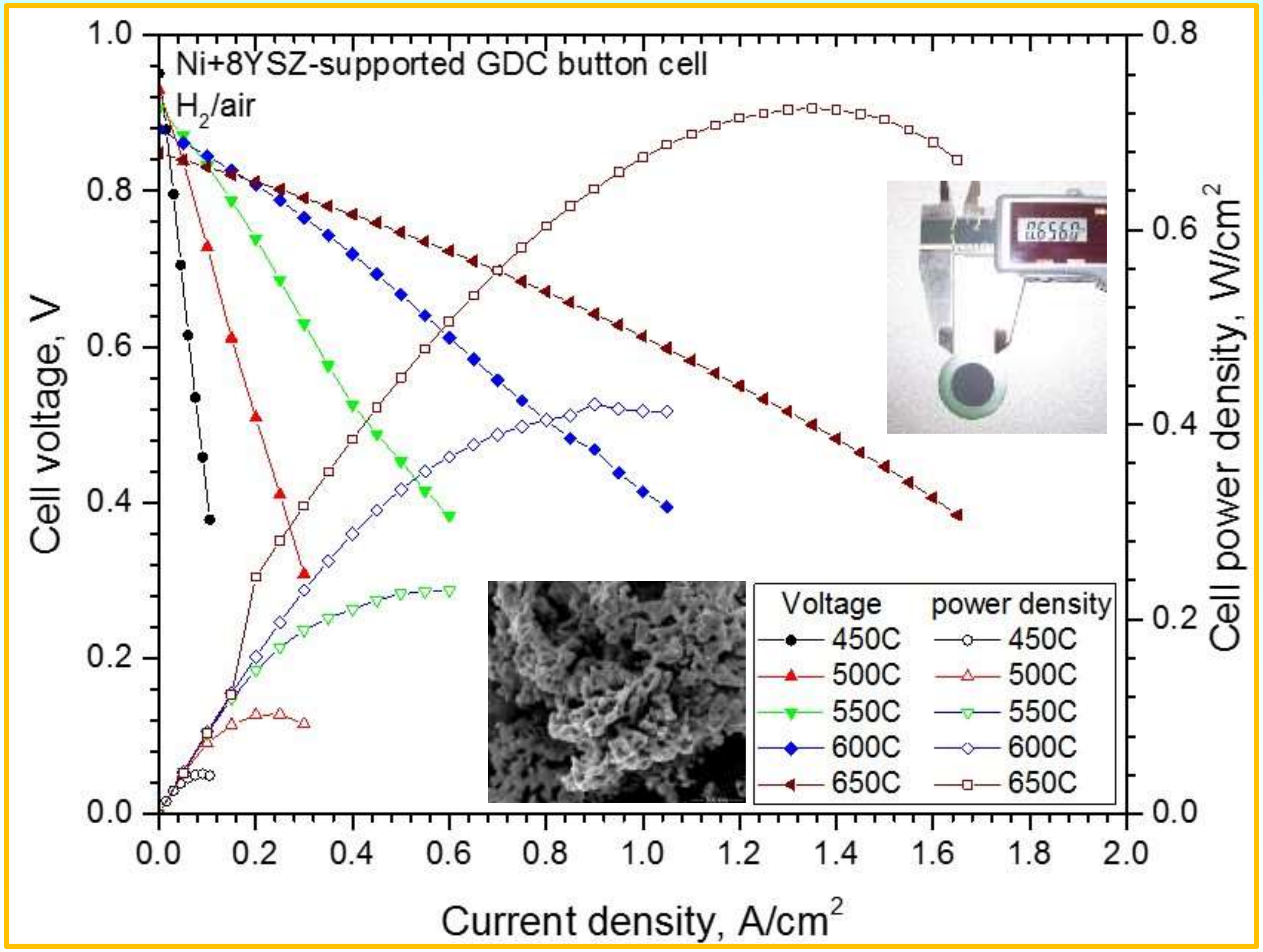


Overpotential breakdown at a cell level for a typical MSRI anode-supported cell

Metal-supported TMS-EC < 500°C

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

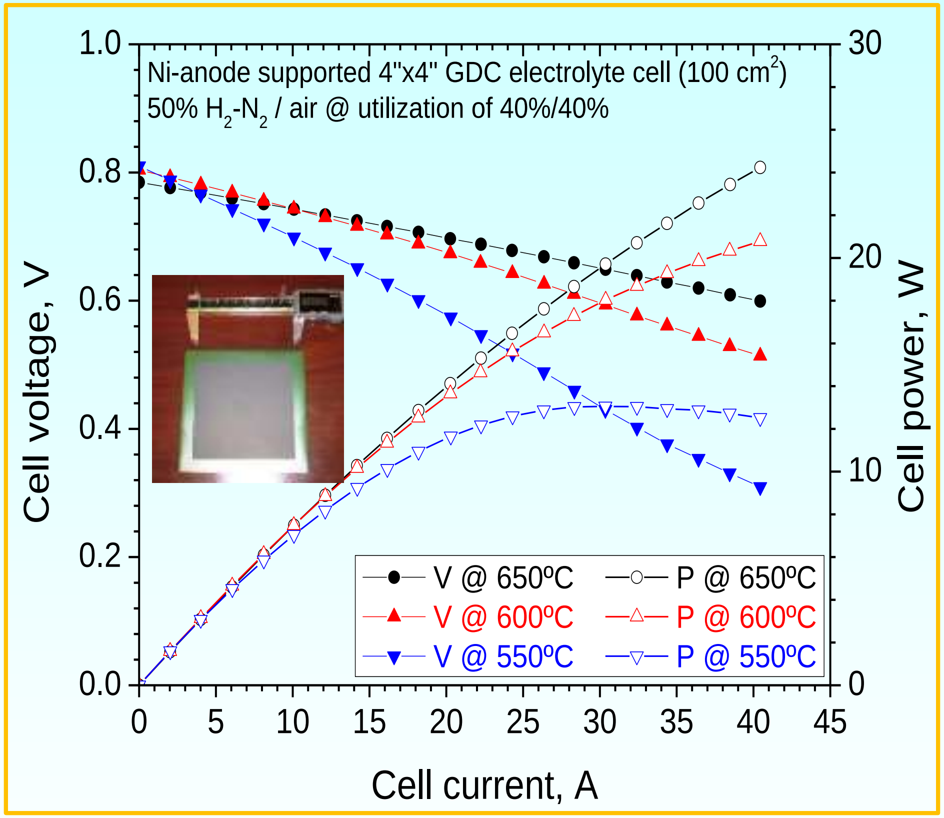
Cathode Development

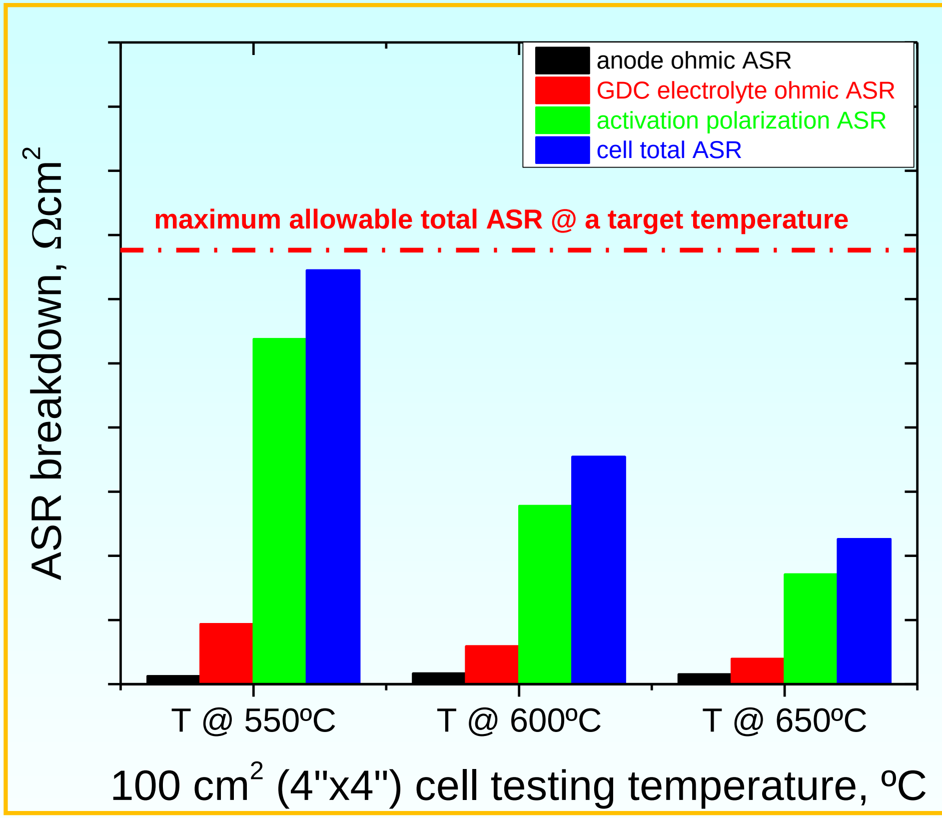


Two approaches to reduce cathode R_p:

- Single-step infiltration technique to infiltrate nano-sized electrocatalyst into engineered cathode skeletons.
- Core-shell structured nano-catalysts.
- $Rp_{\_ca}$ = 0.37 Ωcm^2 and 0.92 Ωcm^2 at 550ºC and 500ºC, respectively.

Cathode Scale-up to 10x10cm^2





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%

Design of Highly Performing Anodes

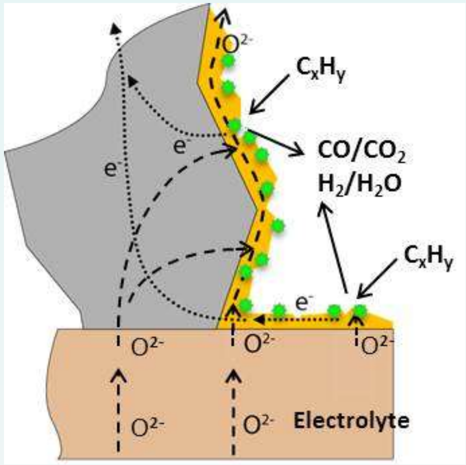
Routes:

Ceramic anode materials

or/and

Nano-catalyst infiltrated anodes

Desirable anode structure:



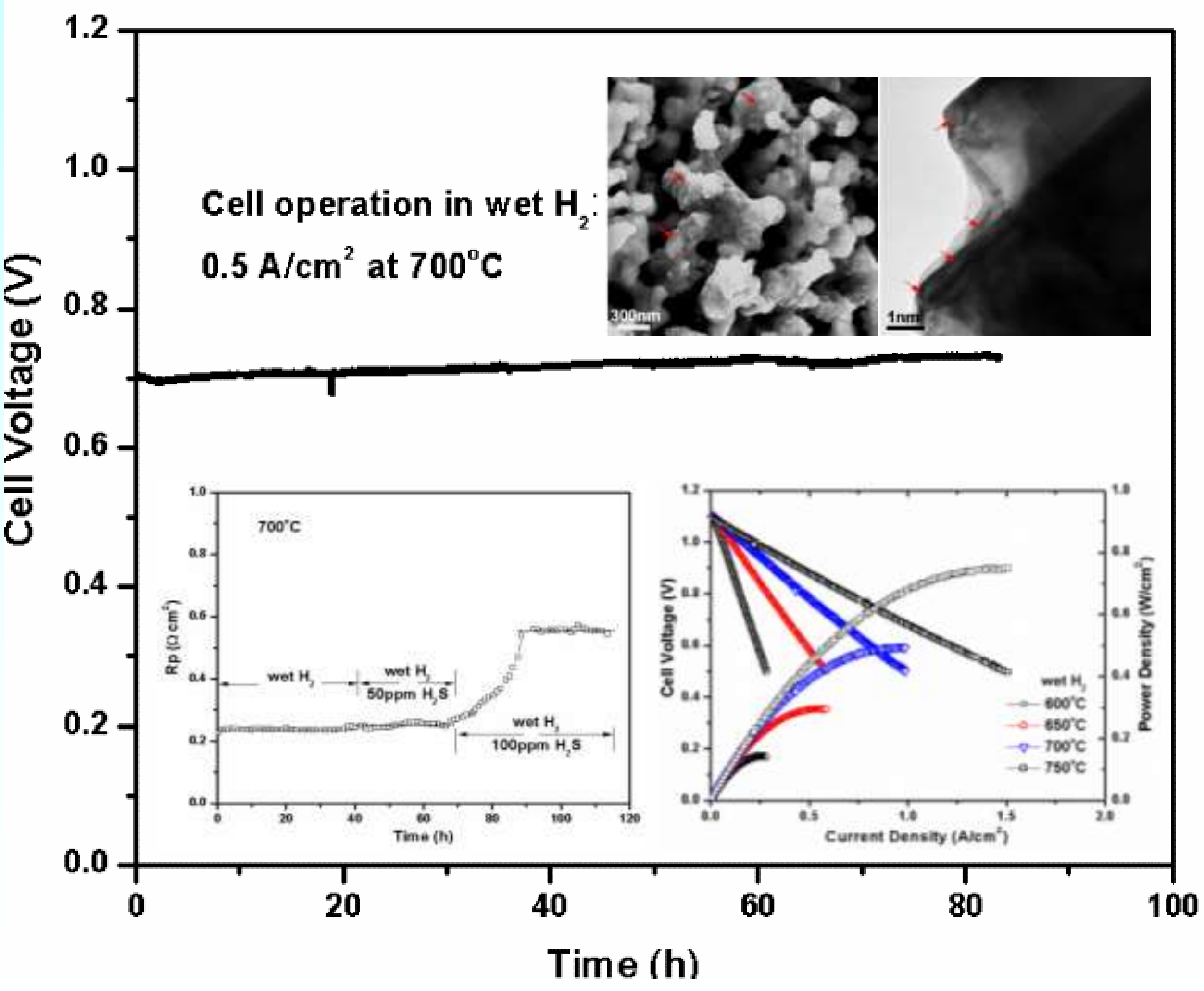
1 phase (very good MIEC & cat.)
or
2 phases (σ_{el} + σ_i & cat.)
(co-sintered mix-powders
or one layer coating the other)
or
3 phases (2 phases + nano-catalyst decorations)

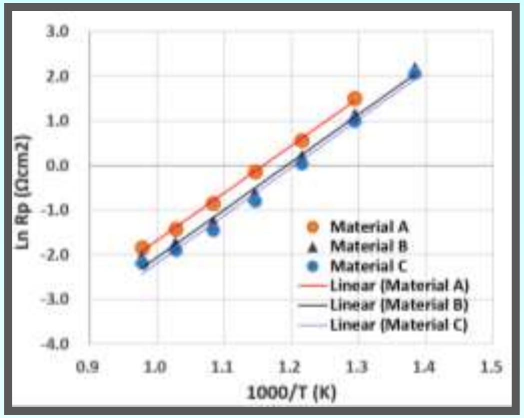
Super anode for operating at T ~ 500ºC

- **Super MIEC** – high ionic and electronic conductivity, and excellent catalytic activity (essentially, declined σ_i at low T + declined σ_{el} at low Po_2 + slowed kinetics of surface reaction at low T)
- **Super catalyst** – not too fast cause coking, but active enough for partial oxidation of methane (Ni is good catalyst but risk coking, whereas other catalysts are not active enough)

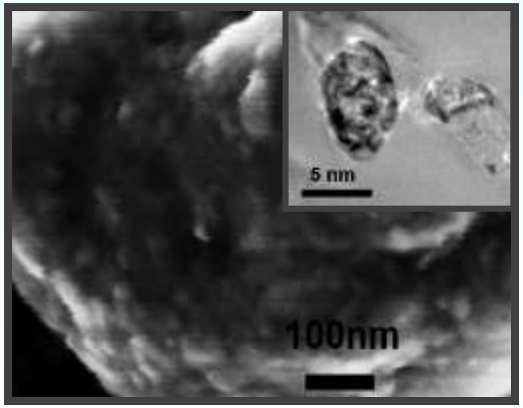
Promising Anode Systems

Full-ceramic anodes with record low Rp (Ωcm^2) in H_2 @600°C: A=0.87; B=0.52; C=0.45;





Perovskite_C:



Precipitation of Nano-catalyst in the reducing atmosphere

Methane Catalyst Development

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

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

- **Synthesis methods for supported metal oxide catalysts**
  - ☐ **Incipient wet impregnation**
  - ☐ **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) & Redox mode
  - ○ 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

Summary of CH_4 Conversion (Redox)

Catalyst Systems	Best Results			
	Operating T, ºC	%, Conversion	% Selectivity	Productivity, mol/kg-cat-hr
# 1	650	8.1%	88% Ethane	7.9
#2	600	23.9%	74.5% CO/H_2; 24.1% CO_2	11.3
#3	650	5.8%	92.8 C^{2+}	1.4
	750	24.1%	88.6 C^{2+}	11.8

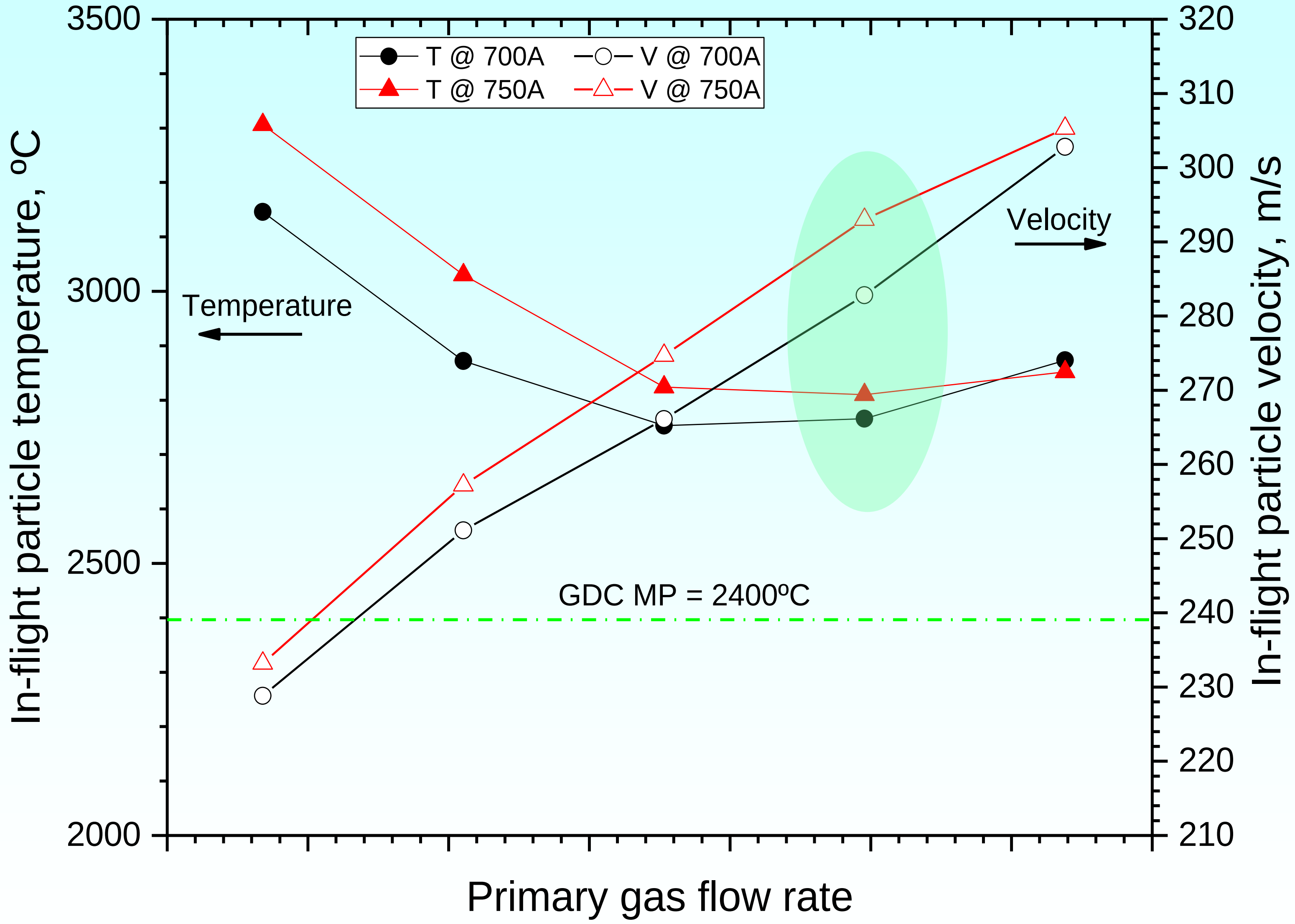
Electrogenerative Cell Manufacturing Process Development:

protective layer; graded cathode layers; electrolyte layer; graded anode layers

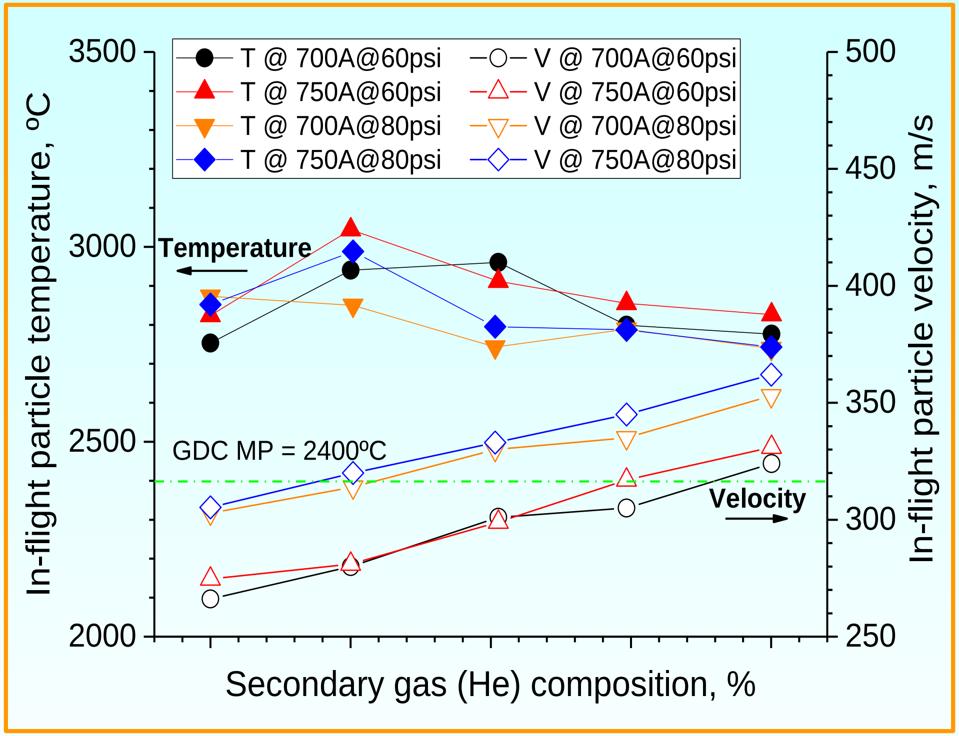
Thermal Spray Enabled TMS-EC Manufacturing

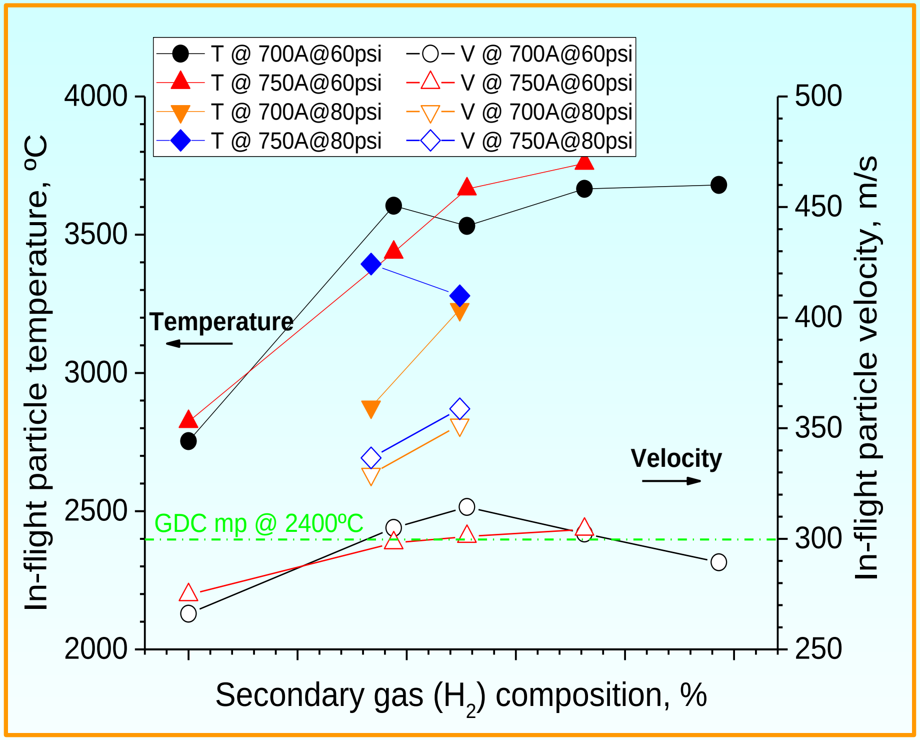
- DoE matrix to investigate thermal spray optimum parameters for the deposition of a all thin-film structure supported on a porous metal substrate.
- Characterized In-flight particles’ T&V, mapping plume “sweet spots” for desirable coating quality and deposition efficiency.
- Qualified deposits properties (strength, phases, conductivity & microstructures).

Effects of Primary Gas on T&V

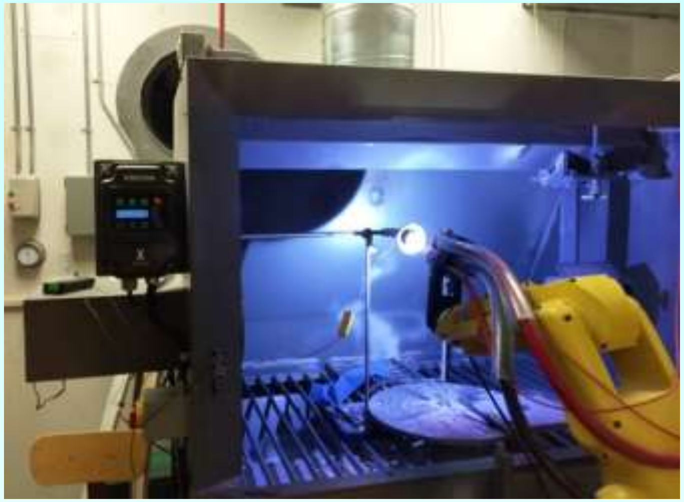


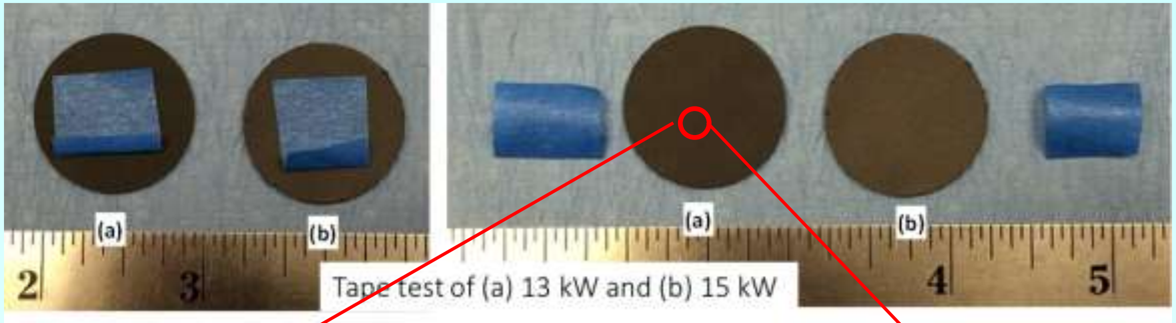
Effects of 2nd Gas on T&V





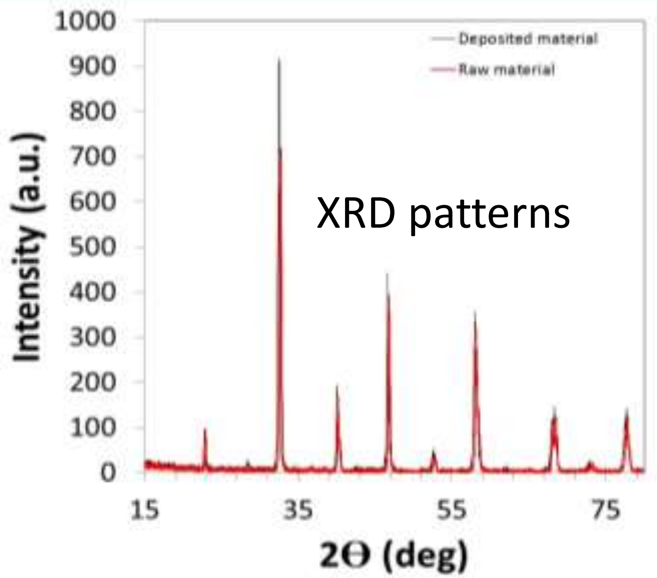
Qualification of APS Deposits



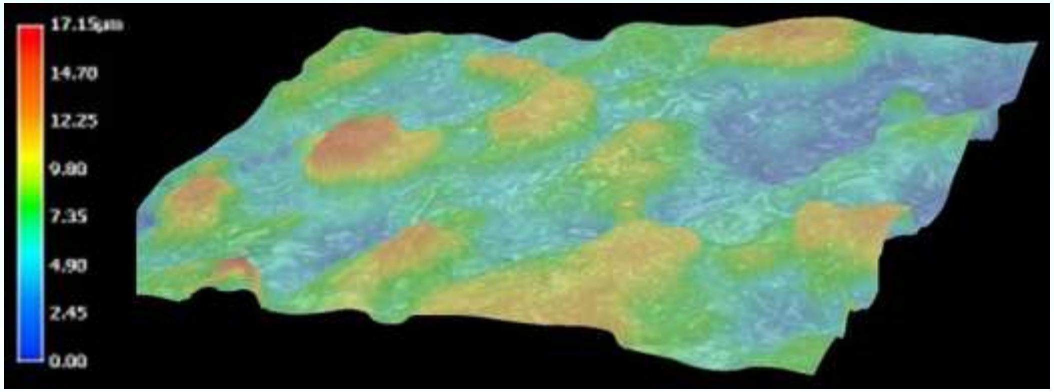


Tape test of (a) 13 kW and (b) 15 kW

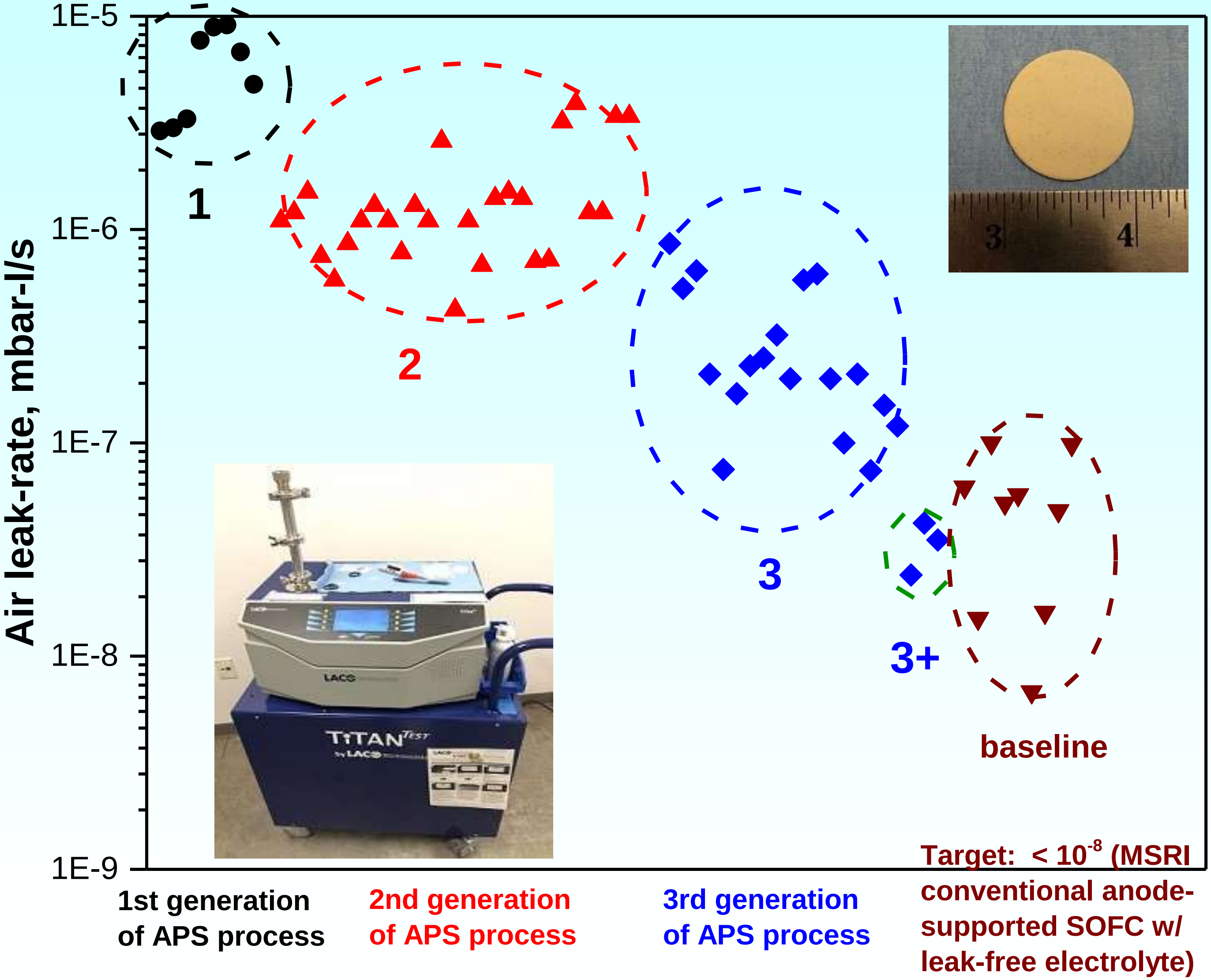
Tape test to ensure sufficient bonding strength between two adjacent layers



XRD patterns

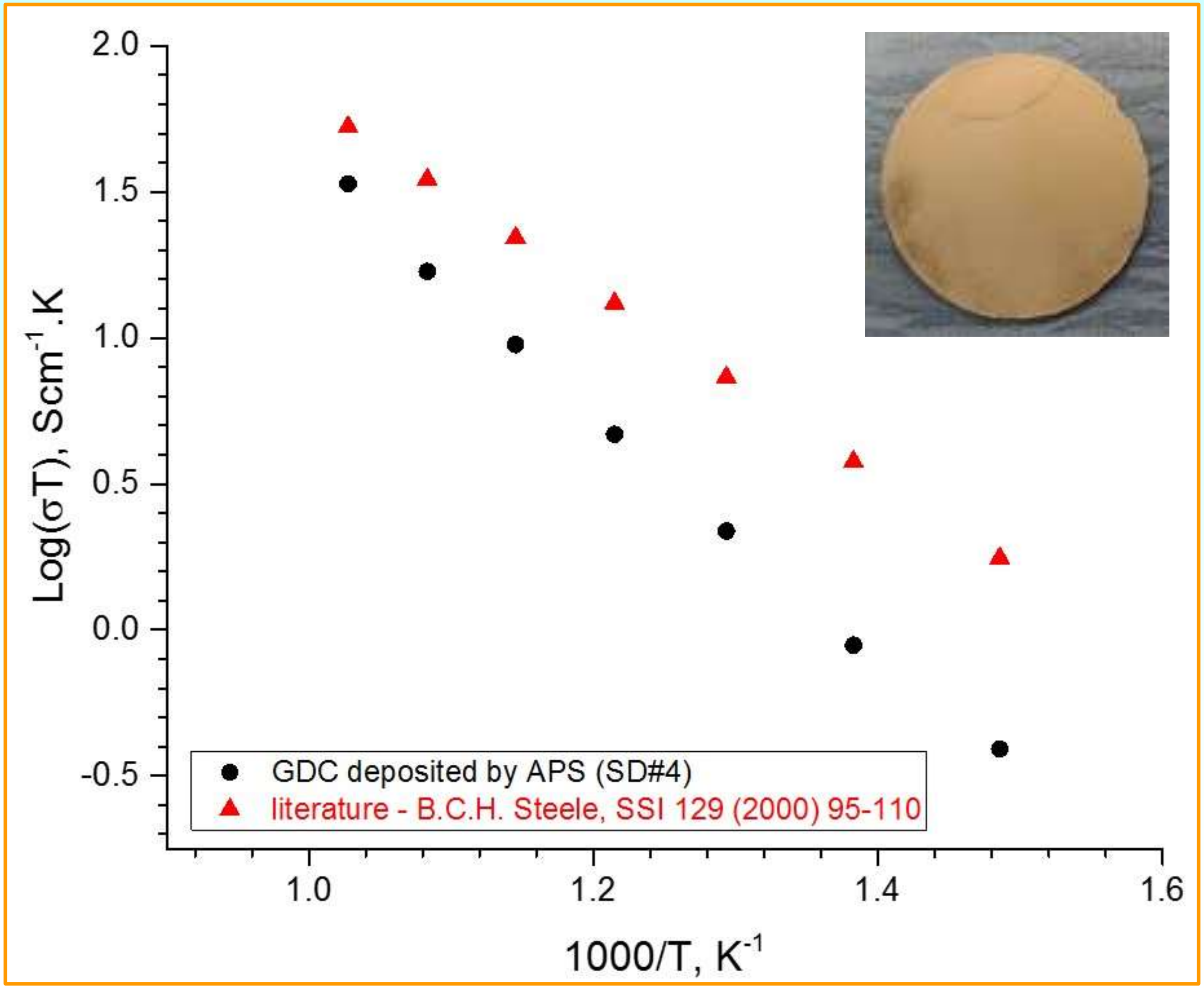


Metal-supported EC Leak Rate (half cell)



> 100 discs manufactured through three generations' development efforts

Qualification of Freestanding GDC Discs



Summary & Remaining Challenges

Results of 1.5 years' Efforts

- Extensive methane-oxidation catalyst systems were evaluated with high productivity/selectivity towards syngas & C^{2+}.
- Cell active materials development showed much promising for electrode polarization reduction.
- Thermal spray-based fabrication processes were developed for depositing multiple layers, from protective coating layer, electrodes, to electrolyte.
- Fully functioning, porous meal-supported button cells were fabricated by thermal spraying technology.

Remaining challenges

- Working towards fuel producing catalysts w/ high yield and productivity.
- ASR needs further reduction (<500ºC).
- Thermal spray process optimization for fabricating high quality electrogenerative cells with desirable features.
- Integration of optimum cell materials and fabrication processes for proof-of-conception demonstration.

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Thank you!