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Plasma-Assisted Methane Reforming and Catalyst Decoking

DE-SC0019664

Yue Xiao
Advanced Cooling Technologies, Inc.

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U.S. Department of Energy
National Energy Technology Laboratory
2023 Carbon Management Project Review Meeting

Project Overview (1/2)

- Funding and Performance Dates
  - Source: DOE SBIR
  - Phase I: $149,998 (02/2019 – 11/2019)
  - Phase II: $1,049,923 (04/2020 – 04/2022)
  - Phase IIA: $1,149,997 (04/2022 – 04/2024)

- Project Participants
  - Dr. Yue Xiao, Dr. Jay Uddi, Dr. Chien-Hua Chen (Advanced Cooling Technologies, Inc.)

  - Prof. Jonas Baltrusaitis (Lehigh University)

Project Overview (2/2)

Overall Project Objectives

- Low-temperature syngas production through plasma-assisted methane reforming

$$CO_2 + CH_4 = 2H_2 + 2CO$$

$$CO_2 + CH_4 + H_2O \rightarrow xH_2 + CO, x=1\text{—}3$$

- Improve reactor performance
- Evaluate coke formation and decoking techniques
- Plasma physics modeling
- Scaling analysis and scaled-up reactor design
- Industrial process flow analysis and TEA

Outline (1/1)

- Background
- Major Progress
  - New Stacked Wire Dielectric Barrier Discharge (SWDBD) reactor design
  - Plasma chemistry modeling
  - Plasma-catalysis methane reforming and decoking tests
  - Industrial Flow Analysis
- Future Work
- Summary

Background (1/2)

Syngas ($CO+H_2$): critical mid-product

Syngas H_2:CO Ratio	Products
≤1	Ethanol
~2	Methanol → Acetic Acid, Ethylene-Propylene, etc.
≥2	Fischer-Tropsch Process → Wax, Gasoline, etc.
≥50	Hydrogen

Hernández et al., *Green Chem.*, **19** (10) 2326–2346 (2017).

Current mainstream: Steam Methane Reforming (SMR)

$CH_4 + H_2O \rightarrow 3H_2 + CO$, ΔH=206 kJ/mol

- High H_2/CO ratio: 3—5

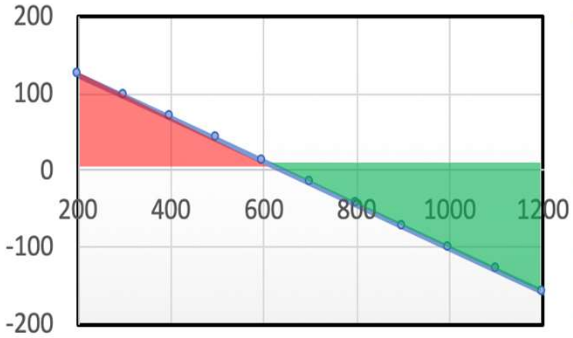
Alternative: Dry Methane Reforming (DMR) or Bi-Reforming

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$; ΔH=247 kJ/mol

$H_2O + CH_4 + CO_2 \rightarrow XH_2 + CO$; $1<X<3$

- CO-rich syngas; Consumes CO_2
- Problems:
  - <u>High temperature</u>: 700 °C —900 °C
  - <u>Coking</u>: deactivates catalyst, reformer clogging

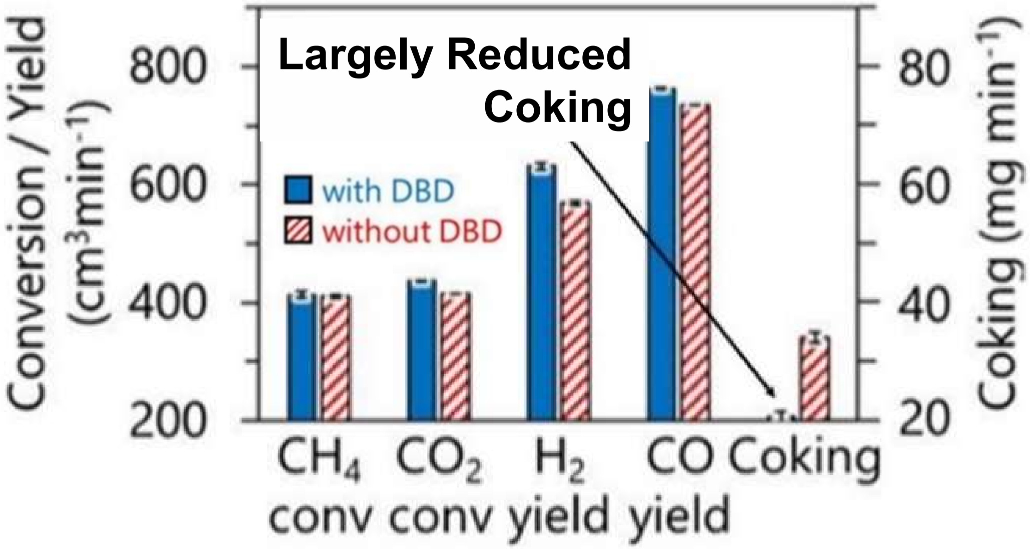
T (°C) vs.ΔG (kJ/mol)



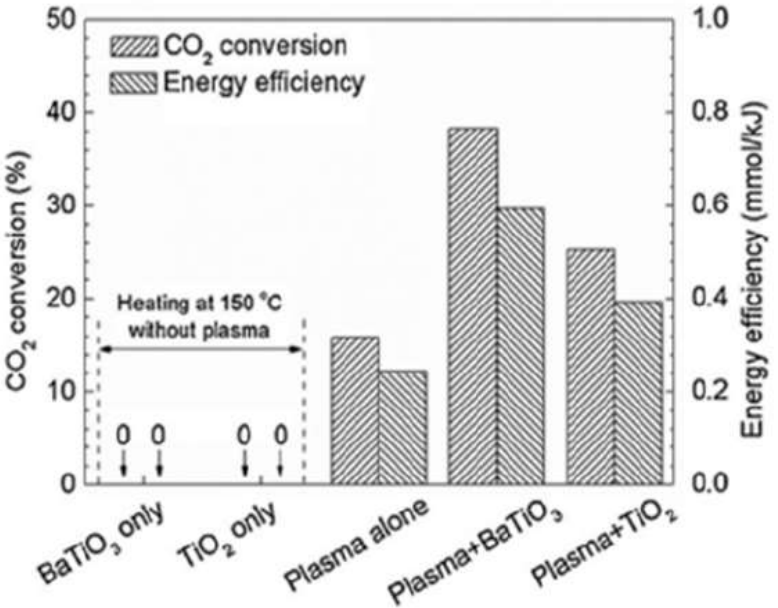
Background (2/2)

Plasma-Assisted Dry/Bi Methane Reforming (PADMR/PABMR) and catalyst decoking

- Non-thermal plasma → Lower temperature reactions
- High energy electrons enables unique reaction pathways → Coke reduction
- Synergistic effects of plasma-catalysis reactions
- Dielectric barrier discharge (DBD) plasma adopted

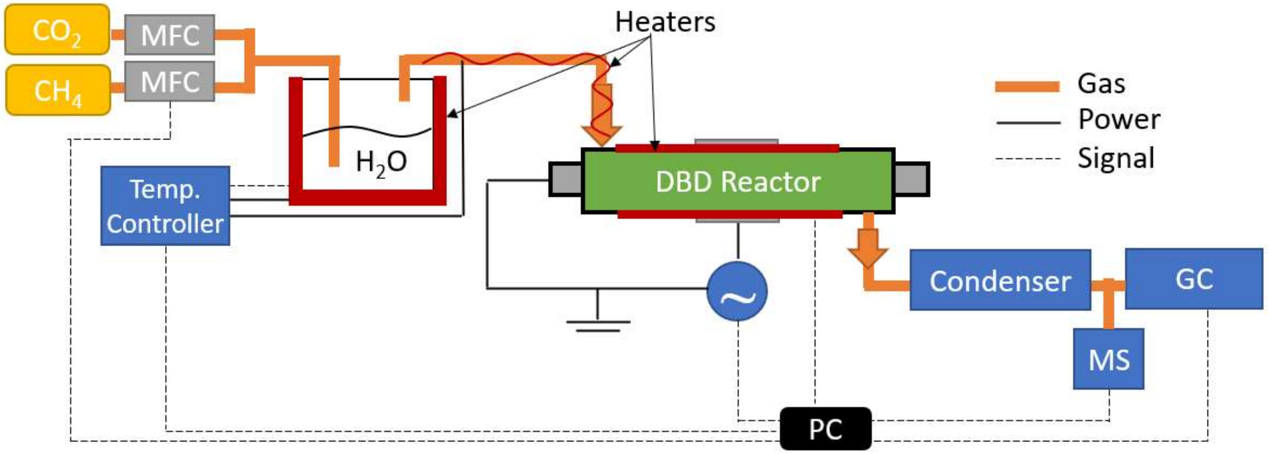


Kameshima et al., *Int'l J. of Plasma Enviro. Sci. & Tech.* **9**(1),201797785 (2015).



Li et al. *Nanomaterials* **9**, 1428 (2019).

Concept (1/1)



Test Setup

MFC: Mass flow controller; GC: Gas Chromatography; MS: Mass Spectroscopy

Plasma-Assisted Methane Reforming

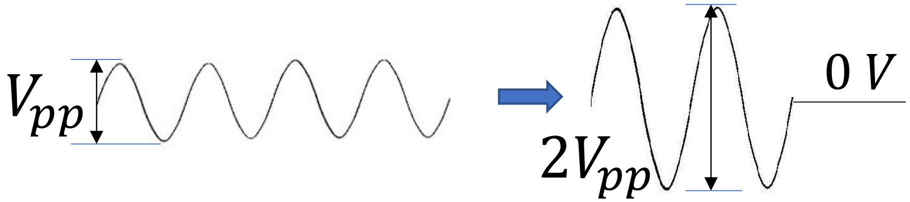
- Cylindrical DBD plasma reactor in Phase I and Phase II
- Discharge gap l_g: 0.5–5 mm for packed bed and catalyst loading
- Additional heating and insulation

Progress (1/12): Novel Plasma Reactor Design

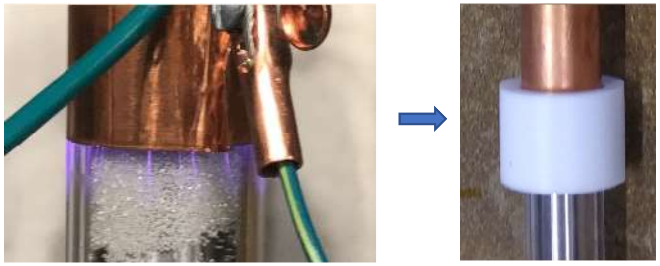
Recap: Cylindrical Reactor in Phase II

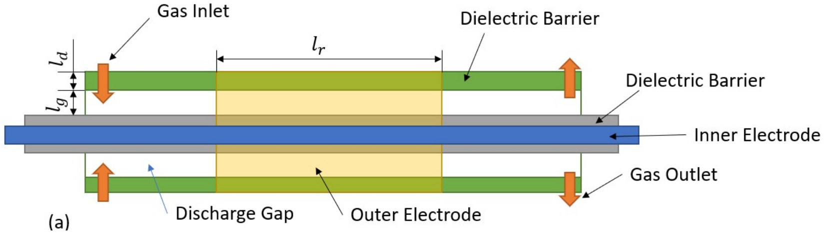
1. Reduced Gap size l_g: Electric field V/l_g ↑

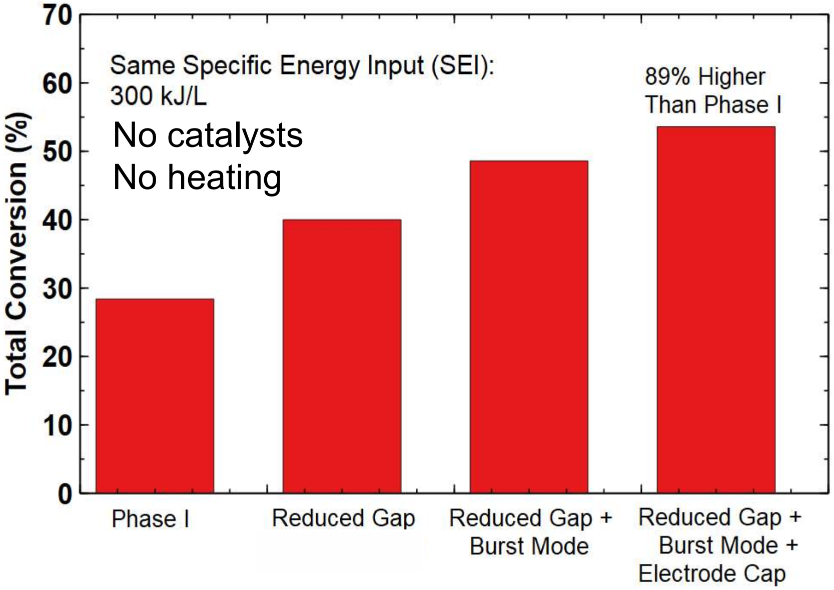
2. “Burst Mode” power



3. Eliminate secondary surface discharge
→ Energy Waste ↓



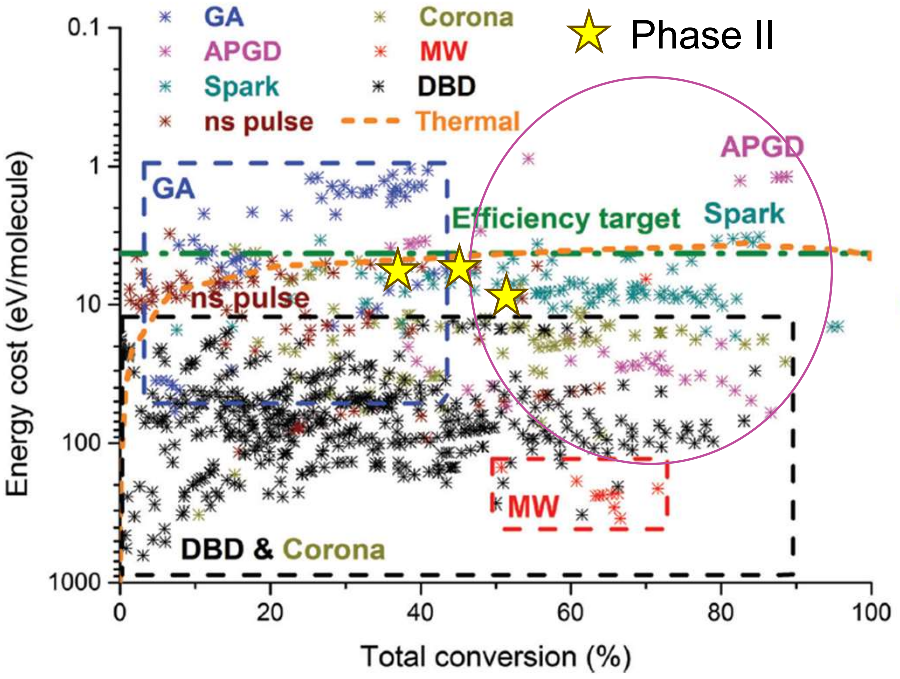




- Phase II: 89% higher than Phase I results at room temperature.

Progress (2/12): Novel Plasma Reactor Design

Creating Atmospheric Pressure Glowing Discharge (APGD)

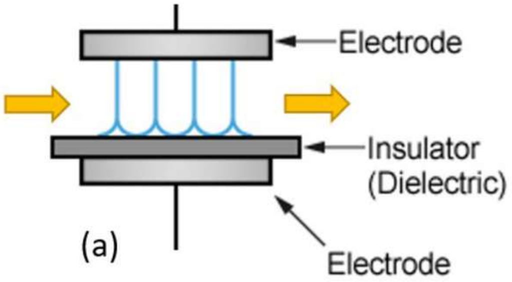


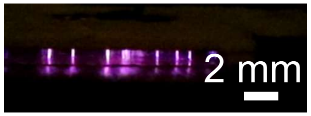
Snoeckx & Bogaerts, *Chem. Soc. Rev.* **46**, 5805-5863 (2017).

APGD: Maintain homogeneous glow or filamentary glow without vacuum condition

Additional Design Challenges:

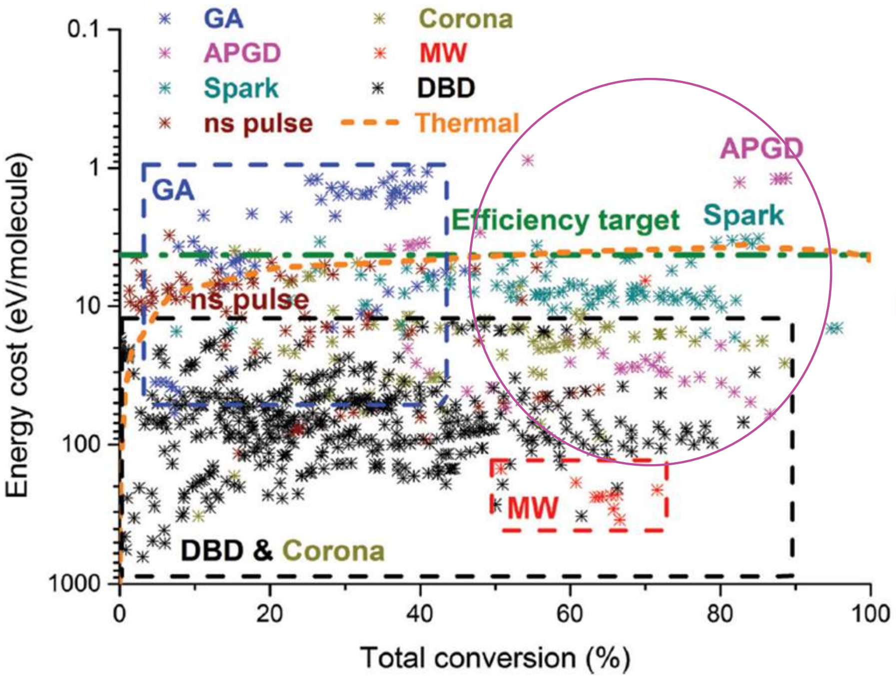
- Catalyst compatible
- Easy to scale up





Progress (2/12): Novel Plasma Reactor Design

Creating Atmospheric Pressure Glowing Discharge (APGD)



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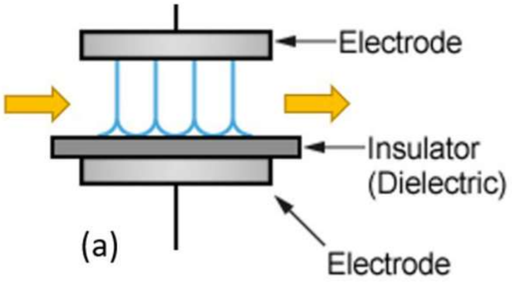
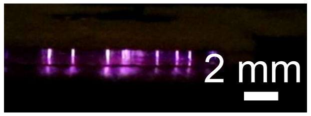
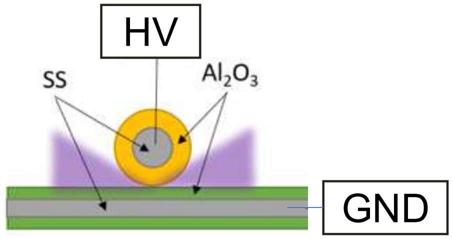
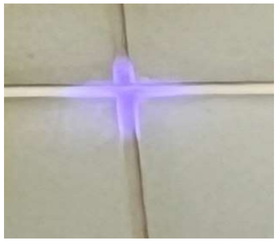






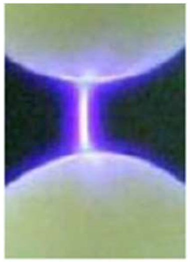


Stacked Wire Dielectric Barrier Discharge (SWDBD) reactor:

- Generate glow discharge at 1 atm
- Uniform gas treatment → energy efficiency ↑

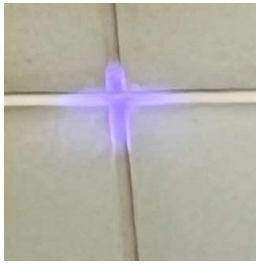
Progress (3/12): Novel Plasma Reactor Design

Suppress the Filament Formation



Single filament DBD
(1 mm gap, air)

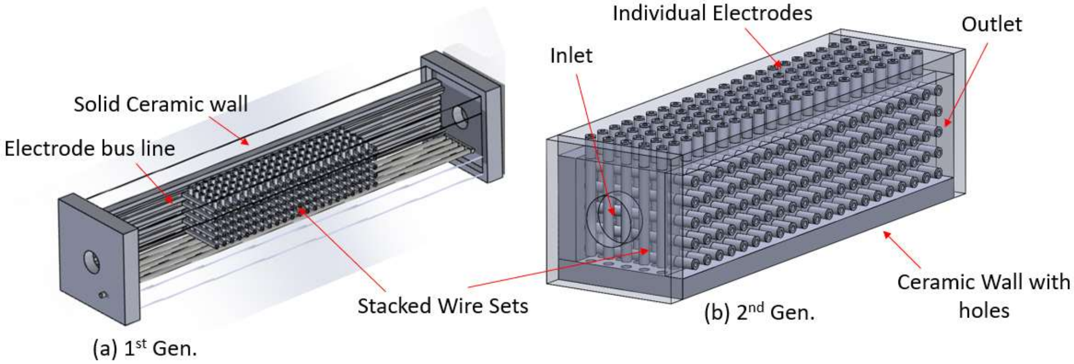
Kettlitz et al., *J. Phys. D: Appl. Phys.* **45**, 245201 (2012).

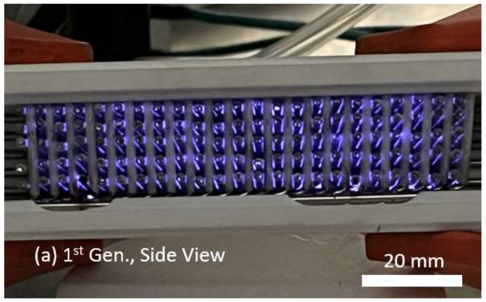


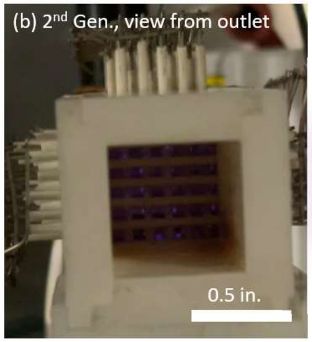
Al_2O_3 diameter 0.062”

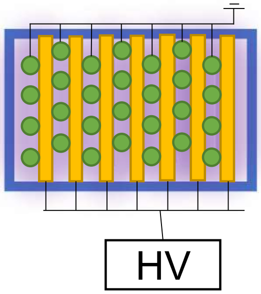
- Eliminate the discharge space at the contact point
- Create an area with high electron energy

Stacked Wire DBD Reactor Prototype Build



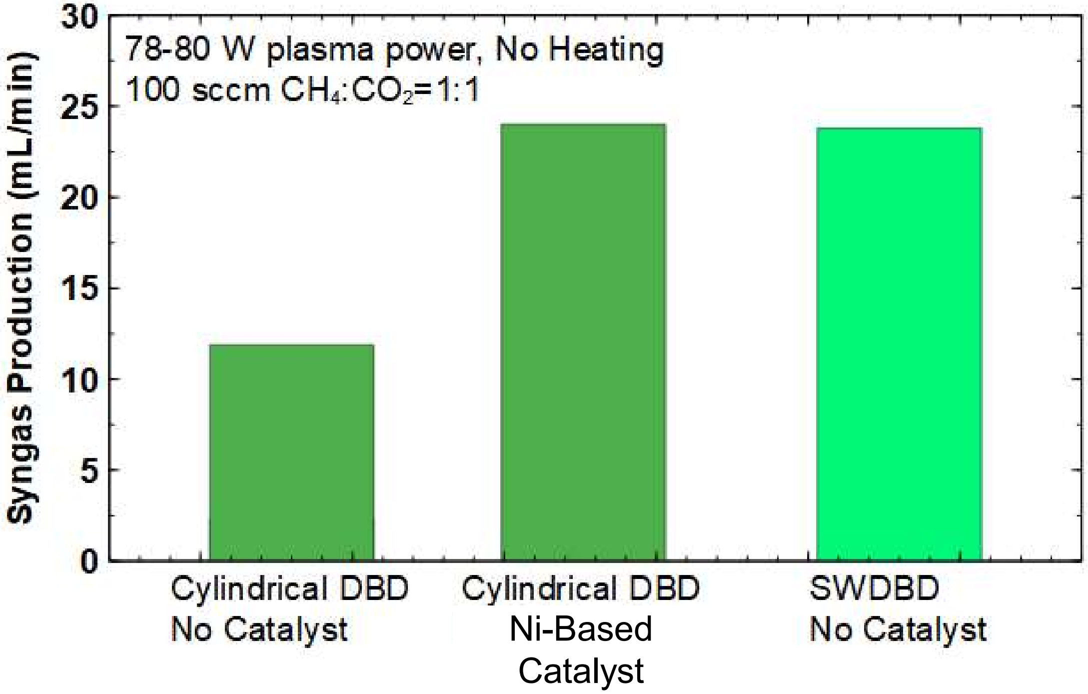






- Staggered electrode pattern
- Easy to load catalyst
- Easy to scale up compared to cylindrical DBD

Progress (4/12): Novel Plasma Reactor Design



SWDBD vs. Cylindrical DBD:

- Same electrode spacing (1.5 mm)
- Same Reactor volume
- Same plasma power

- ~90% performance improvements

- Expect to further increased conversion with catalyst or with reduced electrode spacing

- Currently testing different design configurations

Progress (5/12): Plasma-Assisted Reaction Modeling

Aim: Utilize the plasma chemistry modeling to study and optimize the SWDBD reactor

Density of species p

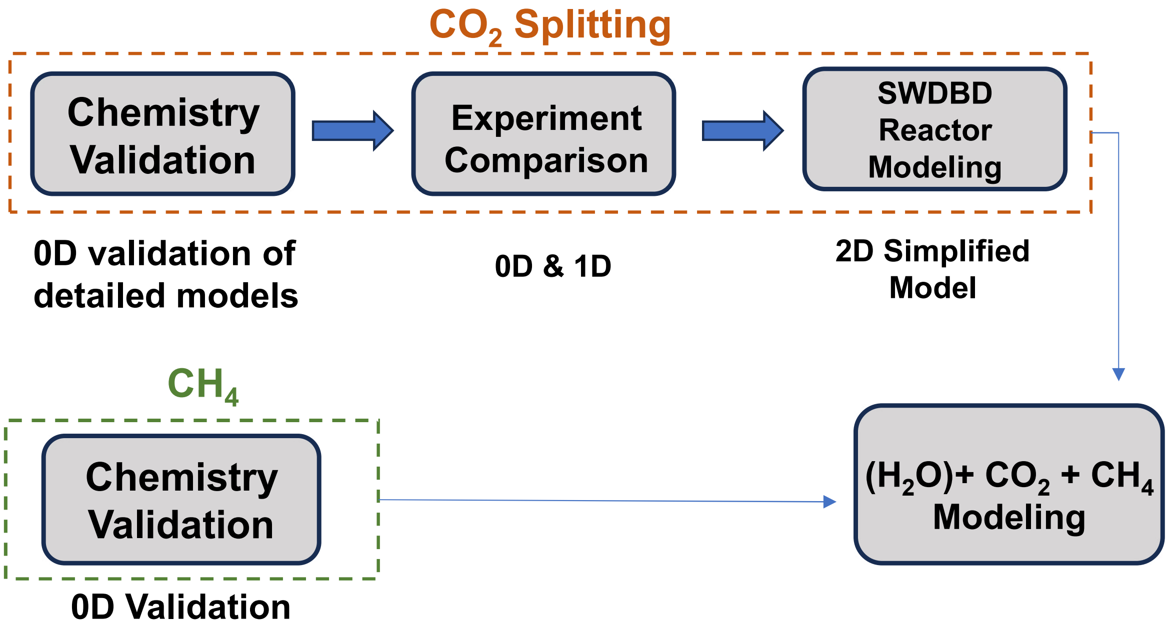
0 for 0D case

$$\frac{\partial n_P}{\partial t} + \boxed{\nabla \cdot \overrightarrow{\Gamma_p}} = S_P$$

Time

Particle flux density

Net source term (Chemistry related)



CO_2 Splitting

Chemistry Validation

Experiment Comparison

SWDBD Reactor Modeling

0D validation of detailed models

0D & 1D

2D Simplified Model

CH_4

Chemistry Validation

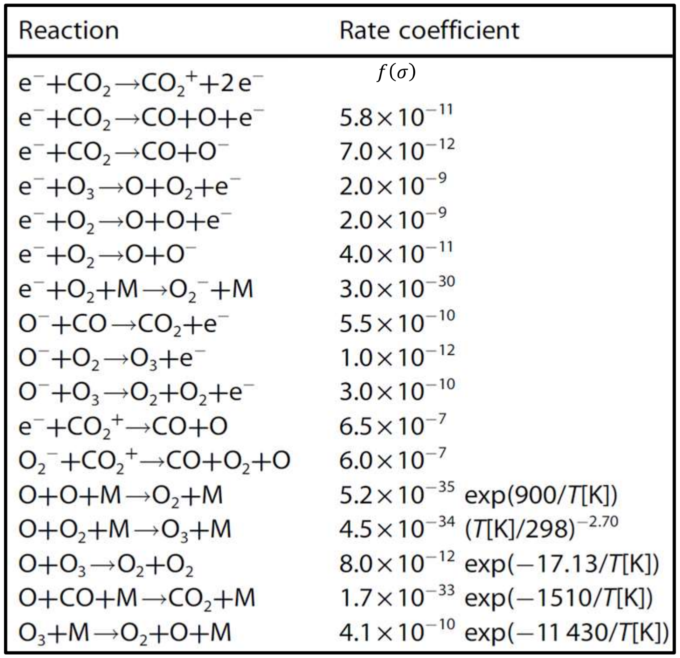
0D Validation

$(H_2O)+ CO_2 + CH_4$ Modeling

- Starting with 0D (spatial uniform) CO2 splitting, eventually move to 2D Dry/Bi-reforming simulation
- Currently completed preliminary SWDBD modeling with simplified 2D model
- Simulations performed in COMSOL Multiphysics

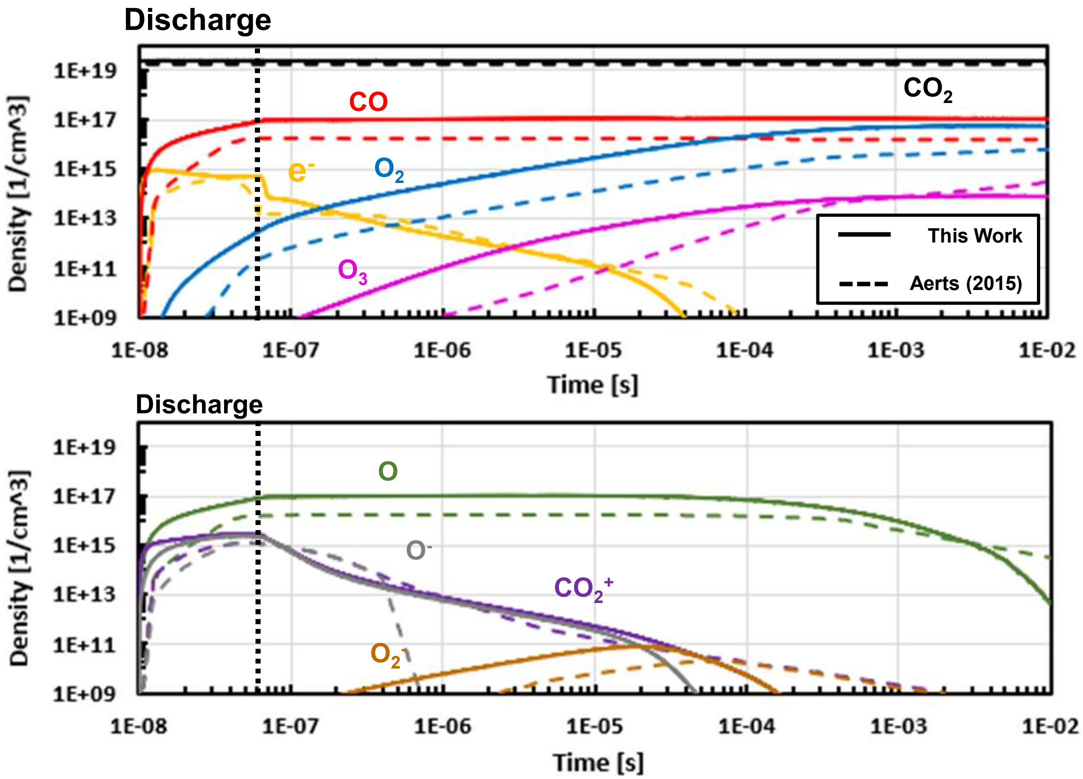
Progress (6/12): Plasma-Assisted Reaction Modeling

0D chemistry set calibration



Reaction	Rate coefficient
$e^- + CO_2 \rightarrow CO_2^+ + 2e^-$	$f(\sigma)$
$e^- + CO_2 \rightarrow CO + O + e^-$	5.8×10^{-11}
$e^- + CO_2 \rightarrow CO + O^-$	7.0×10^{-12}
$e^- + O_3 \rightarrow O + O_2 + e^-$	2.0×10^{-9}
$e^- + O_2 \rightarrow O + O + e^-$	2.0×10^{-9}
$e^- + O_2 \rightarrow O + O^-$	4.0×10^{-11}
$e^- + O_2 + M \rightarrow O_2^- + M$	3.0×10^{-30}
$O^- + CO \rightarrow CO_2 + e^-$	5.5×10^{-10}
$O^- + O_2 \rightarrow O_3 + e^-$	1.0×10^{-12}
$O^- + O_3 \rightarrow O_2 + O_2 + e^-$	3.0×10^{-10}
$e^- + CO_2^+ \rightarrow CO + O$	6.5×10^{-7}
$O_2^- + CO_2^+ \rightarrow CO + O_2 + O$	6.0×10^{-7}
$O + O + M \rightarrow O_2 + M$	$5.2 \times 10^{-35} \exp(900/T[K])$
$O + O_2 + M \rightarrow O_3 + M$	$4.5 \times 10^{-34} (T[K]/298)^{-2.70}$
$O + O_3 \rightarrow O_2 + O_2$	$8.0 \times 10^{-12} \exp(-17.13/T[K])$
$O + CO + M \rightarrow CO_2 + M$	$1.7 \times 10^{-33} \exp(-1510/T[K])$
$O_3 + M \rightarrow O_2 + O + M$	$4.1 \times 10^{-10} \exp(-11\,430/T[K])$

Aerts, et al., *Chem. Sus. Chem.* **10**, 02818 (2015).

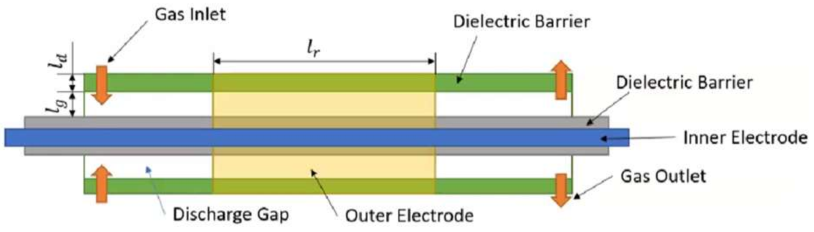


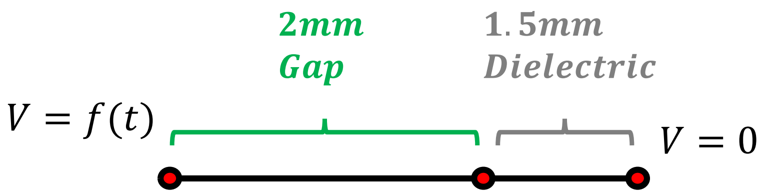
- 60 ns single pulse discharge, P_{avg}=40 W. Gas flow 18.6 sccm
- CO_2 ionization replaced with energy-dependent model
- Good agreement particularly in electron density

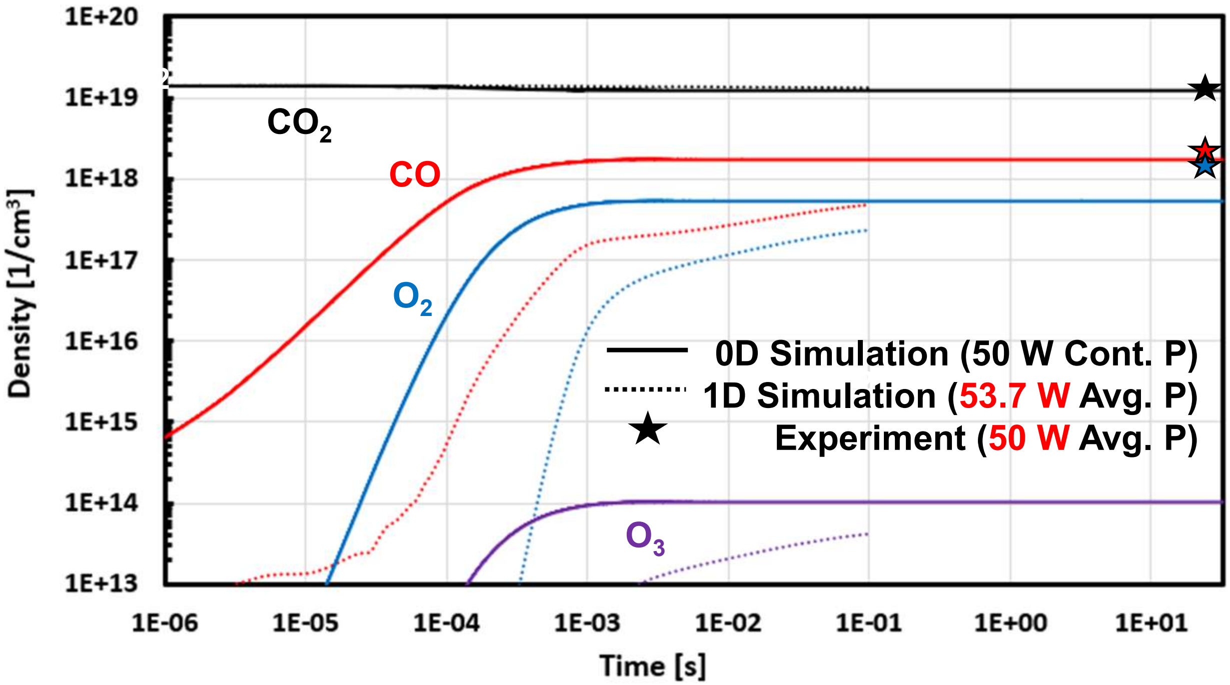
Progress (7/12): Plasma-Assisted Reaction Modeling

0D & 1D Simulation vs. Experiments

- Same dimension as the experiments



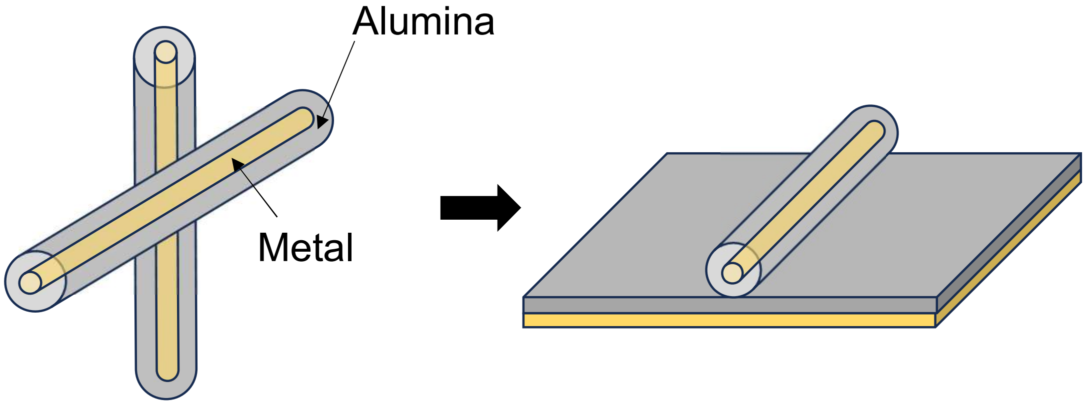


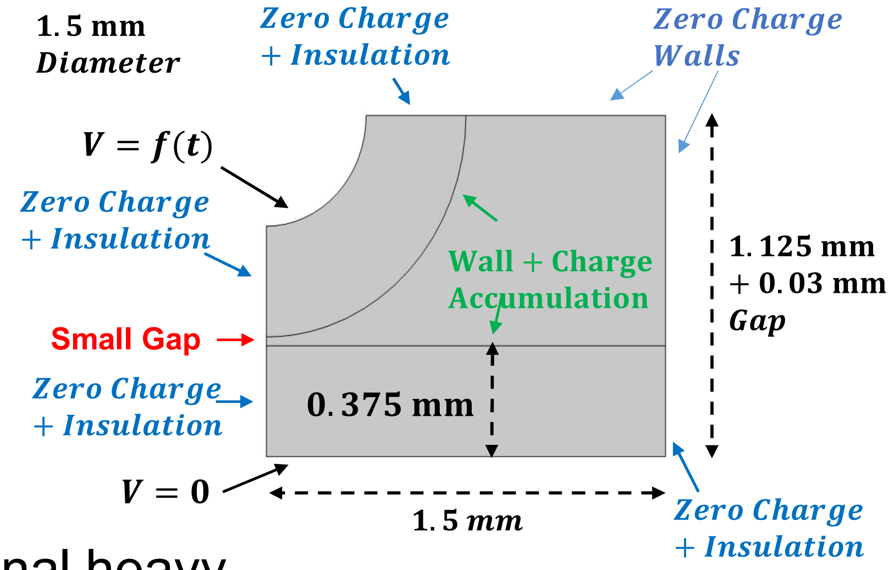


- 0D have good agreement with experiments in CO generation and CO_2 conversion
- Conditions in 1D modeling: Continuous AC (5.2 kV, 30.8 kHz), 20 sccm CO_2 flow rate.
- 1D: Very good power consumption agreement with experiments, reasonable agreement in species density within limited computational time

Progress (8/12): Plasma-Assisted Reaction Modeling

2D SWDBD Modeling

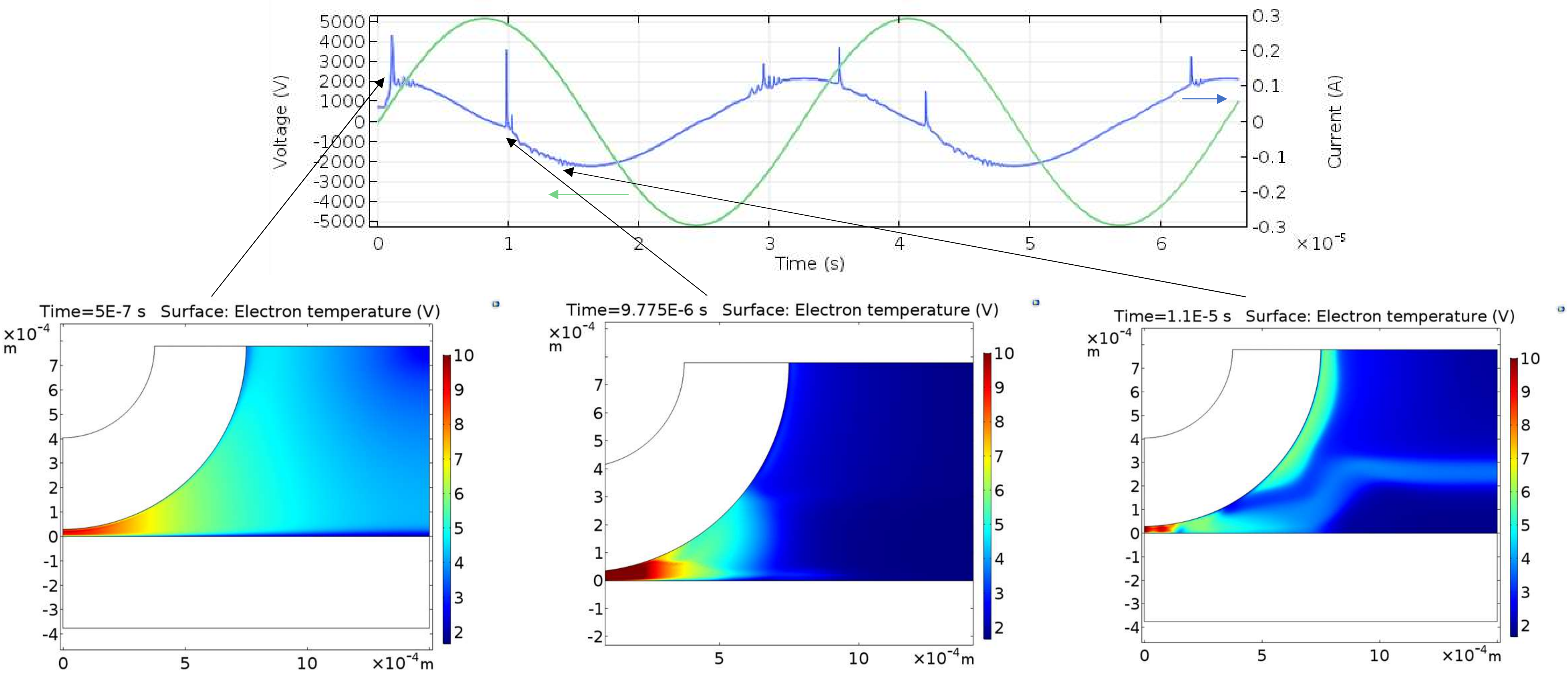


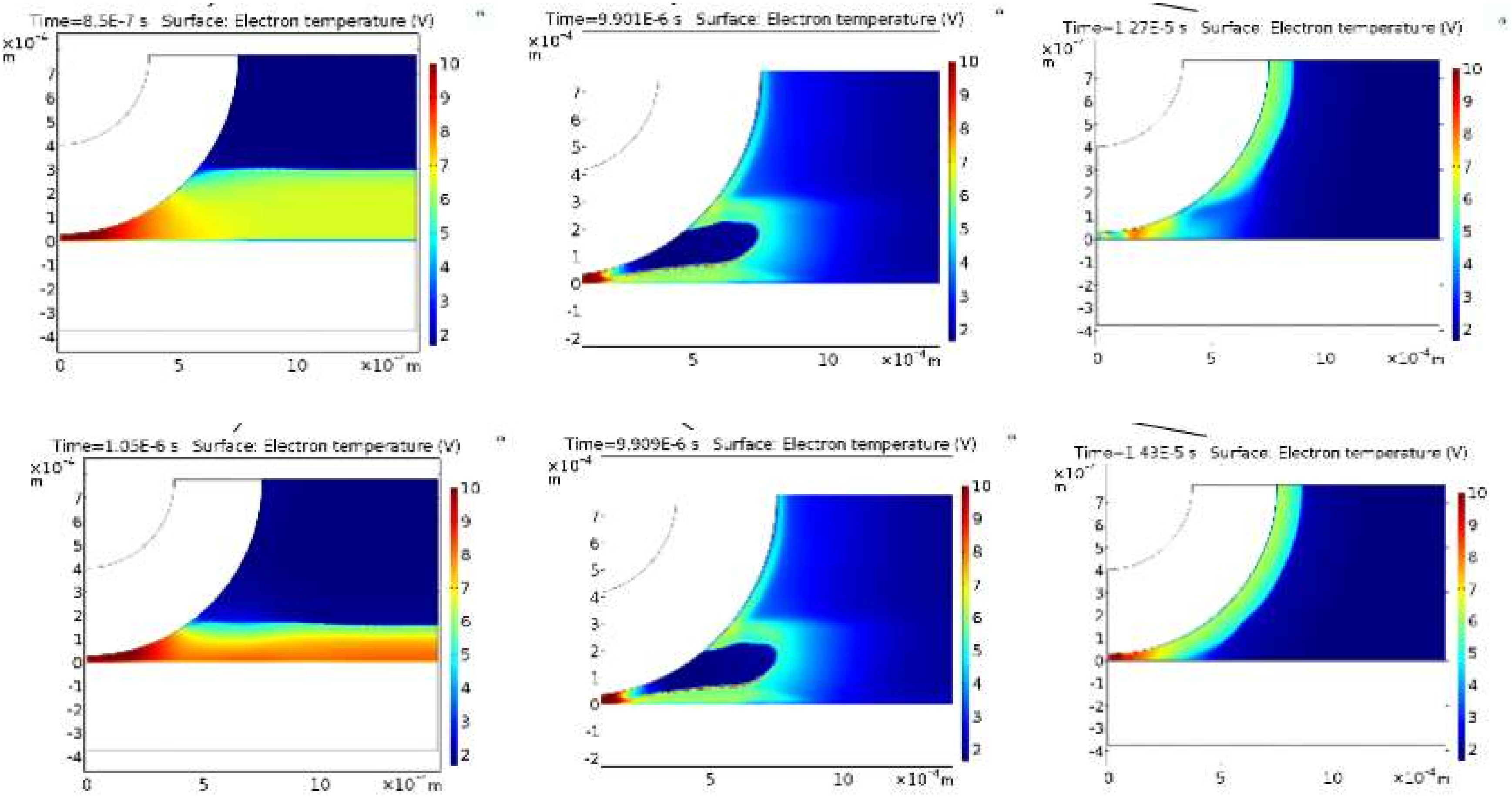


- 3D modeling is extremely computational heavy
  → Simplified 2D model
- Other dimensions same as the experiments
- Small gap for easier convergence
- ~8 days to simulate two periods (5 kV, 30 kHz), 12-Core workstation

Progress (9/12): Plasma-Assisted Reaction Modeling

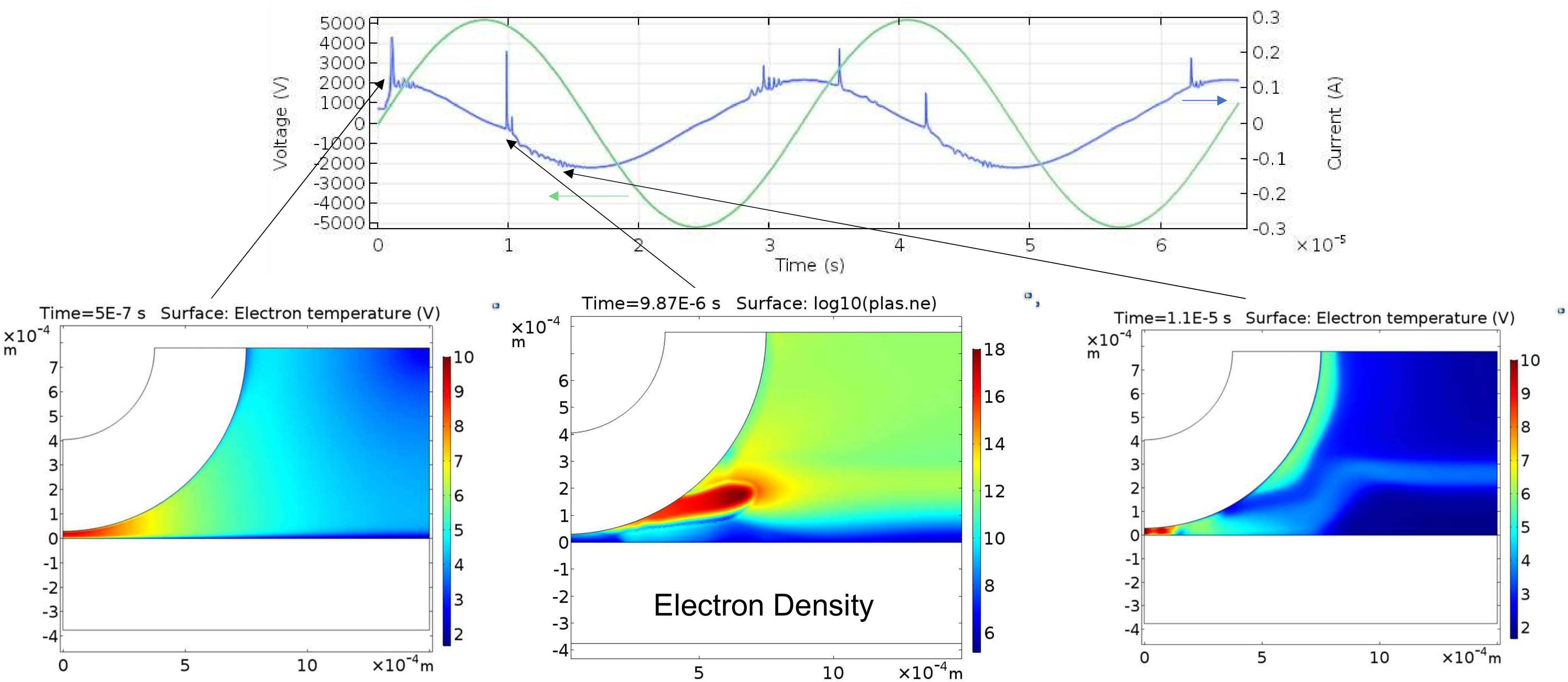
2D SWDBD Modeling: high energy layer transits from one electrode to another




Time=8.5E-7 s Surface: Electron temperature (V)
Time=9.901E-6 s Surface: Electron temperature (V)
Time=1.27E-5 s Surface: Electron temperature (V)
Time=1.05E-6 s Surface: Electron temperature (V)
Time=9.909E-6 s Surface: Electron temperature (V)
Time=1.43E-5 s Surface: Electron temperature (V)
×10⁻⁴ m
0
5
10
×10⁻⁴ m
10
9
8
7
6
5
4
3
2

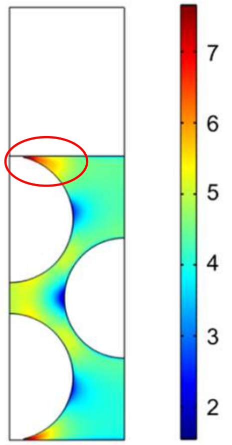
Progress (9/12): Plasma-Assisted Reaction Modeling

2D SWDBD Modeling: high energy layer transits from one electrode to another

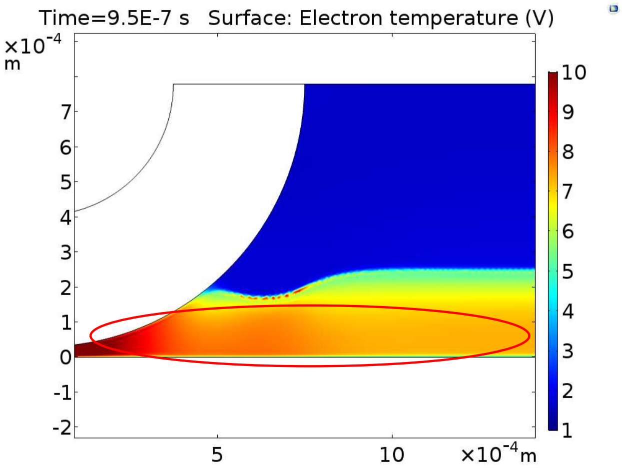


Progress (10/12): Plasma-Assisted Reaction Modeling

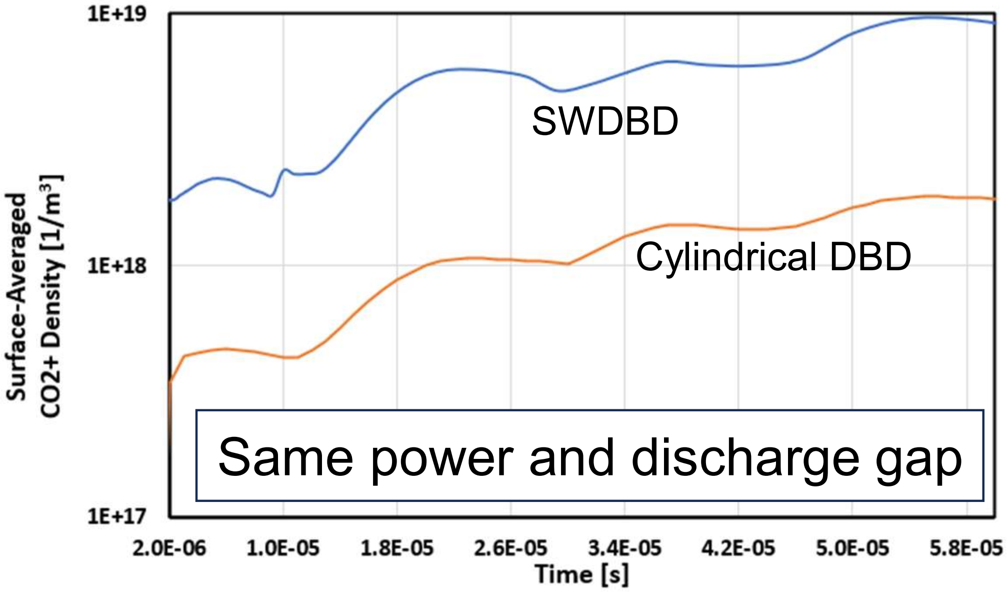
- A uniform layer with high-electron energy formed at the surface of dielectric barrier, connected by a transitioning discharge towards the outside
- Compared with 2D modeling on packed beds: More uniform high electron energy layer



Van Laer & Bogaerts, *Plas. Sources Sci. Tech.* **25**, 015002 (2016).

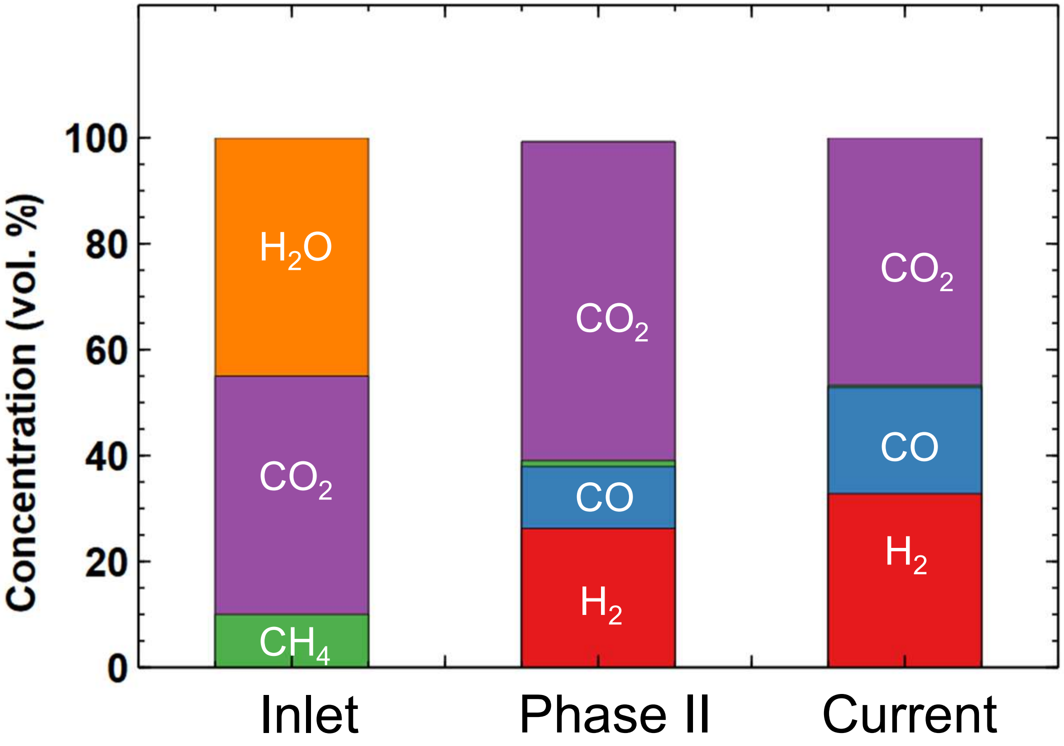


Comparison: SWDBD and Cylindrical DBD



- Same power, discharge gap, and frequency
- Generally 5x to 10x higher in electron density and related species

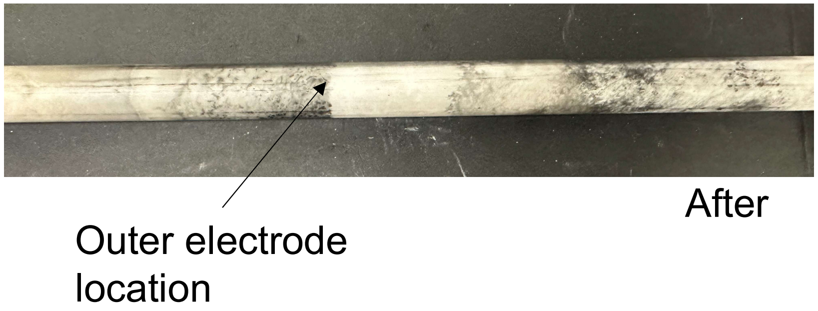
Progress (11/12): Catalyst testing for Bi-Reforming



Continuous development and testing of catalyst:

- H_2:CO=1.7:1
- CH_4 95% conversion, CO_2 26% conversion
- CO_2 cycling cost further reduced


Before

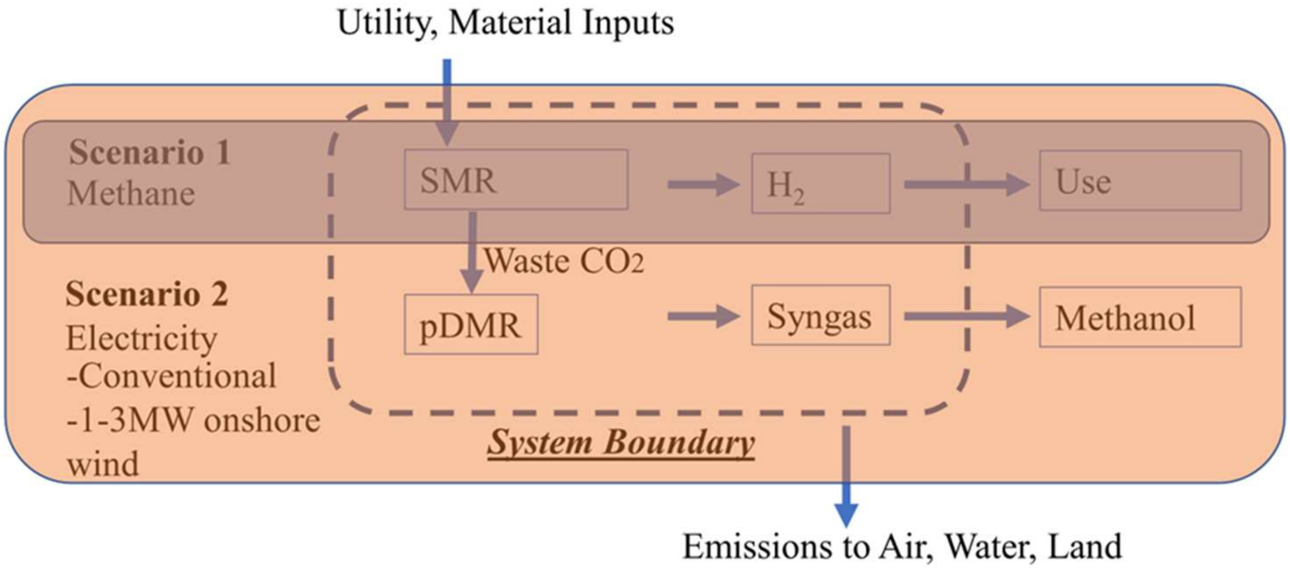


After

- Net coke reduction at low Steam-to-Carbon ratio (S:C)=0.81 vs. 0.90 in industry
- Testing combined with SWDBD in progress

Progress (12/12): Industrial Process Flow

Currently Developing a bi-reforming process flow with an SMR co-location for CO_2 utilization



- Compared to our work that stops at Syngas last year, sequential methanol synthesis is added to further evaluate the economical viability
- Various energy sources will also be simulated

Summary (1/1)

- SWDBD reactor was build and tested for higher conversion
- 2D model developed for SWDBD and shows higher reaction rates
- Plasma-assisted bi-reforming provides syngas with suitable composition and excellent coke reduction
- Industrial process design now considers sequential chemical production using syngas

Future Plan (1/1)

- Continue the SWDBD optimization, modeling, and testing
- Continue the catalyst tests and decoking evaluation
- Test with simulated impurities
- Scaled-up system build
- Detailed techno-economic analysis for bi-reforming process

Acknowledgement

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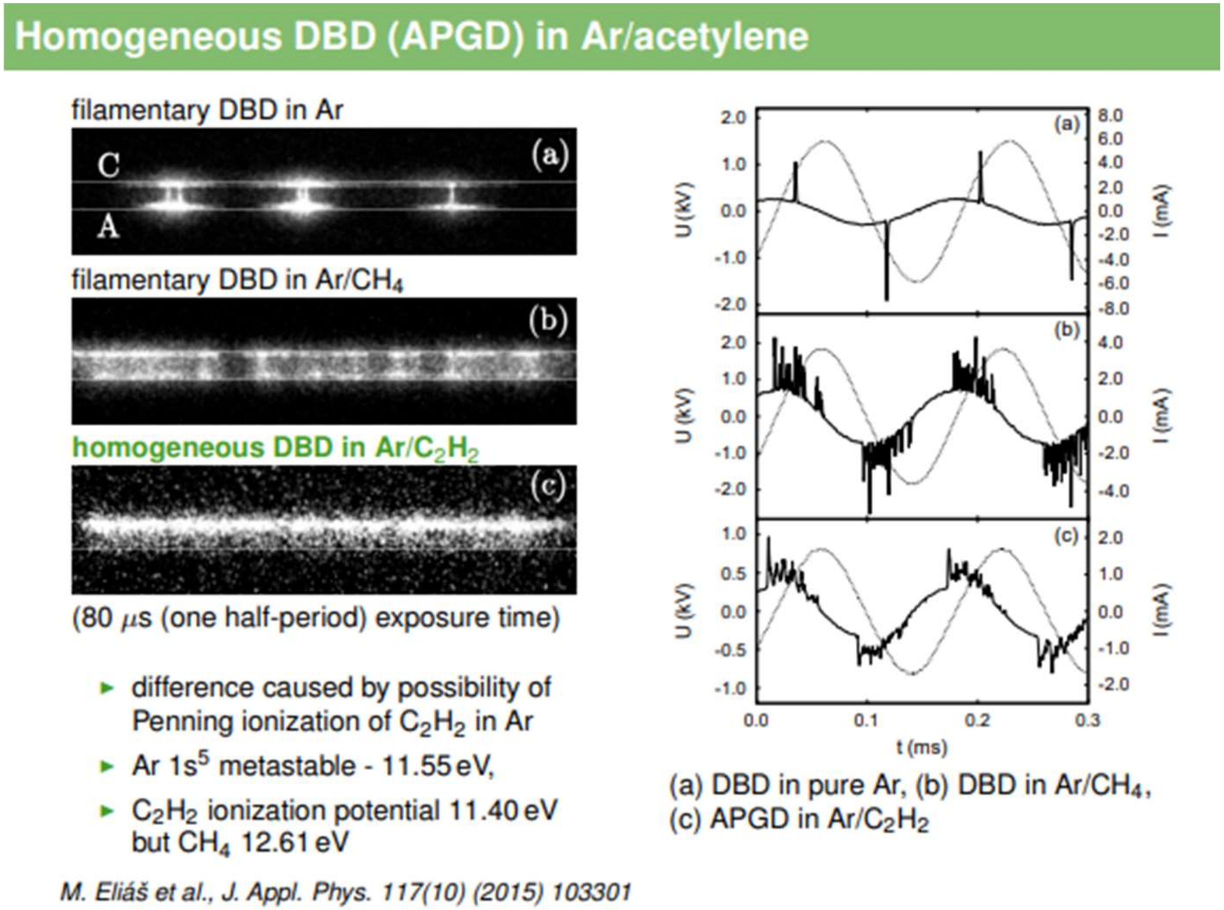
Program Managers: Dr. Akhil Sathish, Dr. Lei Hong.

LEHIGH UNIVERSITY

Prof. Jonas Baltrusaitis
Dept. of Chemical Engineering, Lehigh University

THANK YOU!

Backup



Homogeneous DBD (APGD) in Ar/acetylene

filamentary DBD in Ar

filamentary DBD in Ar/CH_4

homogeneous DBD in Ar/C_2H_2

(80 μs (one half-period) exposure time)

- difference caused by possibility of Penning ionization of C_2H_2 in Ar
- Ar $1s^5$ metastable - 11.55 eV,
- C_2H_2 ionization potential 11.40 eV but CH_4 12.61 eV

(a) DBD in pure Ar, (b) DBD in Ar/CH_4, (c) APGD in Ar/C_2H_2

M. Eliáš et al., J. Appl. Phys. 117(10) (2015) 103301