IAEA
International Atomic Energy Agency

Technical Meeting on Emerging Applications of Plasma Science and Technology
Vienna, Sept. 19-22, 2023

Catalysis and plasma processing:
The tip of the iceberg

Sylvain Coulombe, ing., Ph.D.

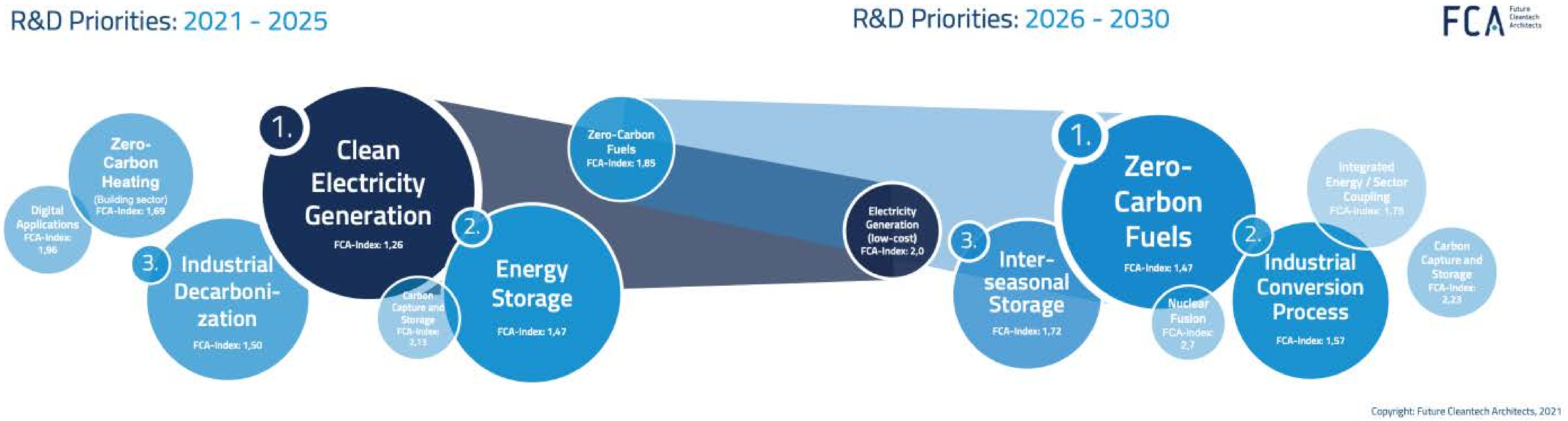
Professor, Chemical Engineering

Co-leader, Catalytic and Plasma Process Engineering

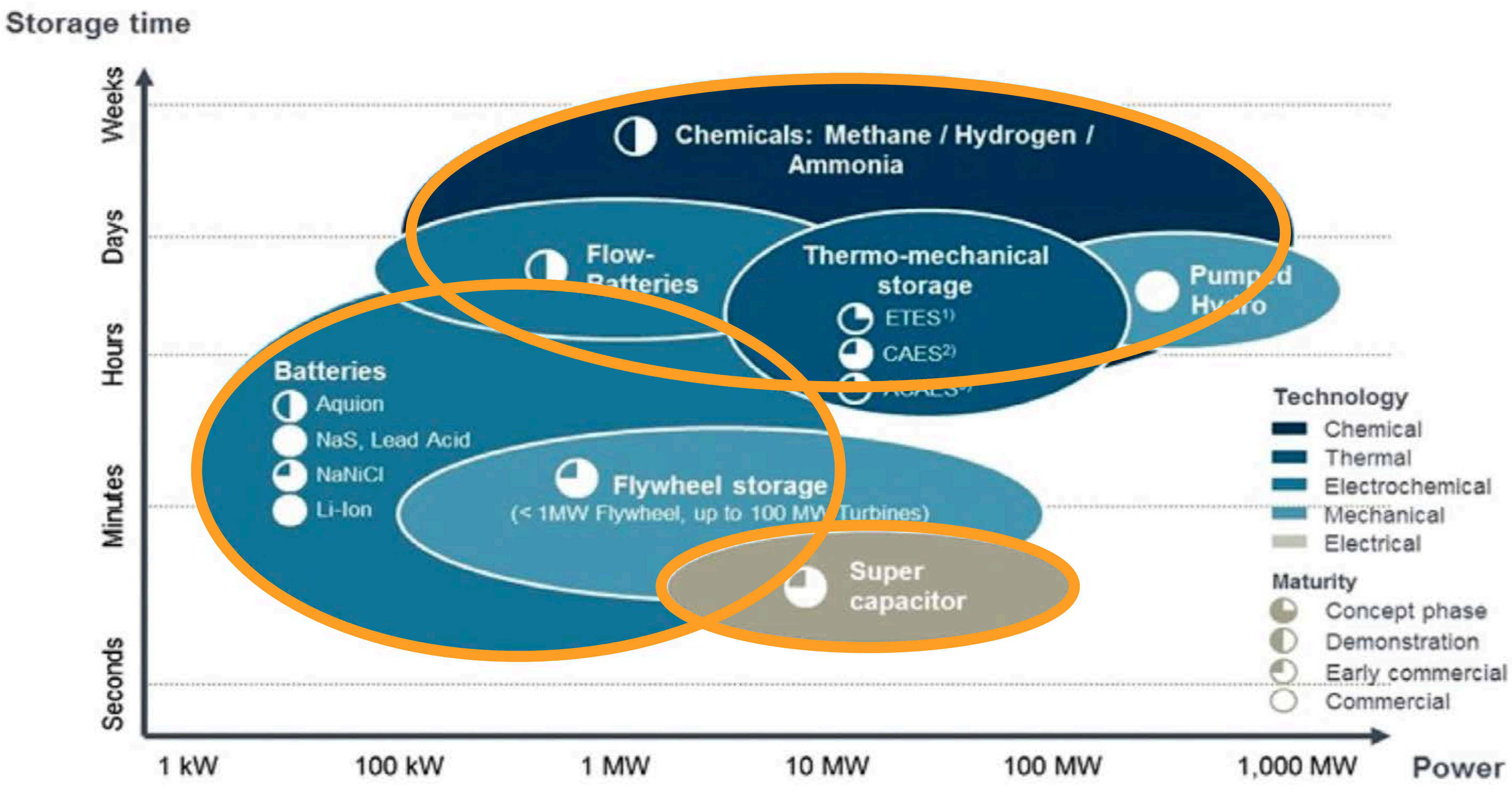
Director, Centre for Innovation in Storage and Conversion of Energy

Climate Change | Energy | Decarbonizing Energy

Top cleantech R&D priorities to help tackle climate change



Plasma-related activities at CPPE

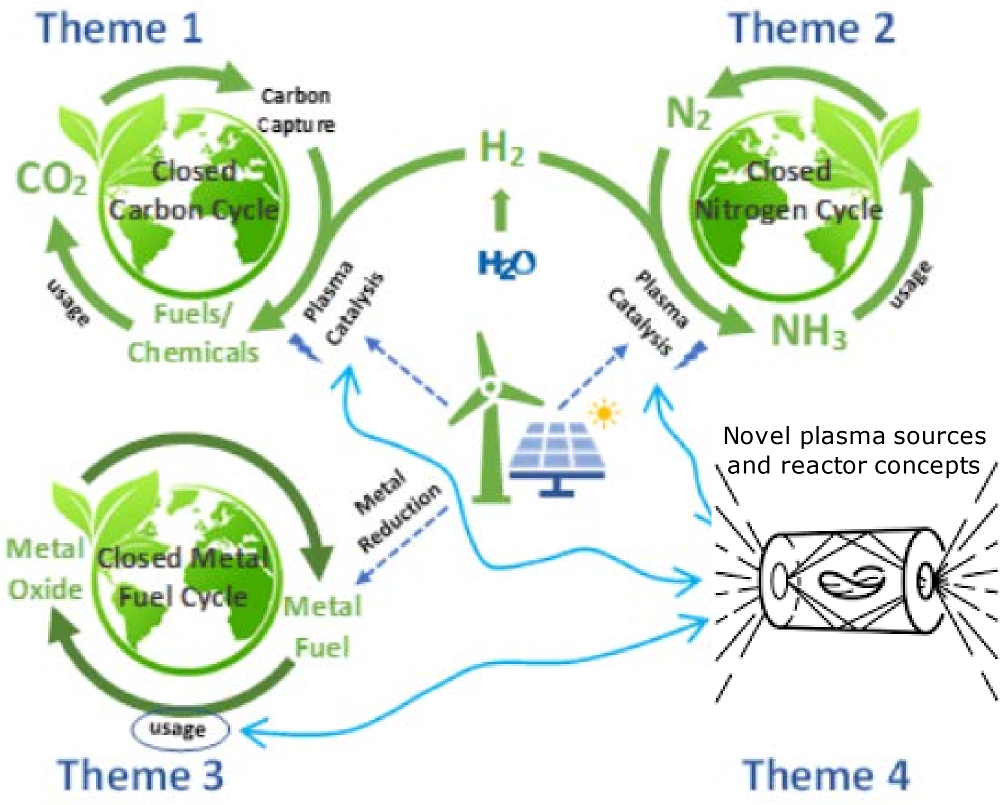


[1] Electro-Thermal Energy Storage [2] Compressed Air Energy Storage [3] Adiabatic Compressed Air Energy Storage

Plasma sources & processes for:

- Gas conversion
- Catalyst synthesis
- Energy storage material
- Regeneration/recycling

Plasma-related activities at CPPE



Circular Fuels:

Alternative fuels with closed-loop logistic and utilization solely powered by renewable energy

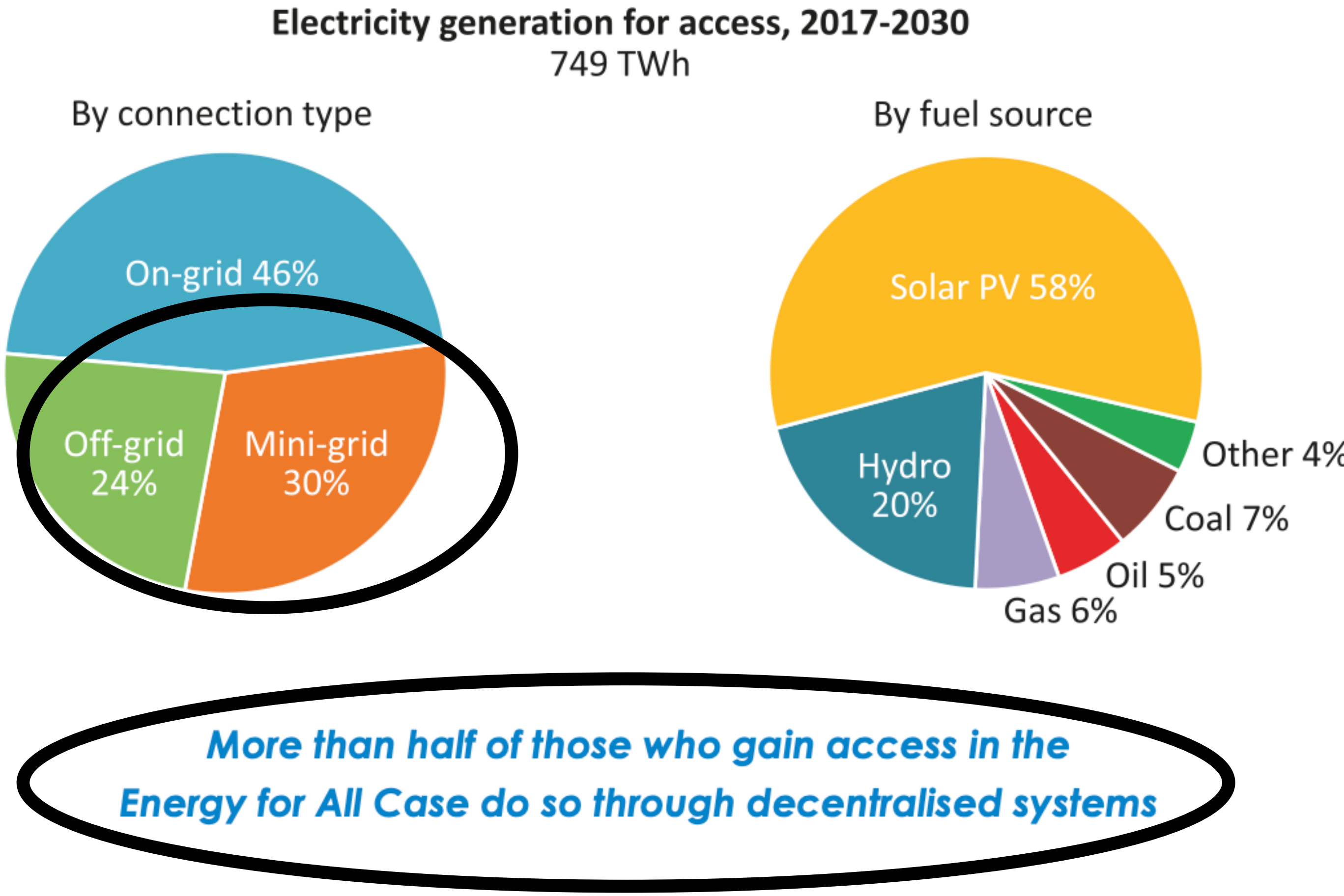
Clean electricity opens opportunities for plasma technologies

- Share of renewables in global electricity generation jumped to 29% in 2020, up from 27% in 2019.

- Renewables could produce more than half of the world's electricity by 2035, at lower prices than fossil-fuel generation.

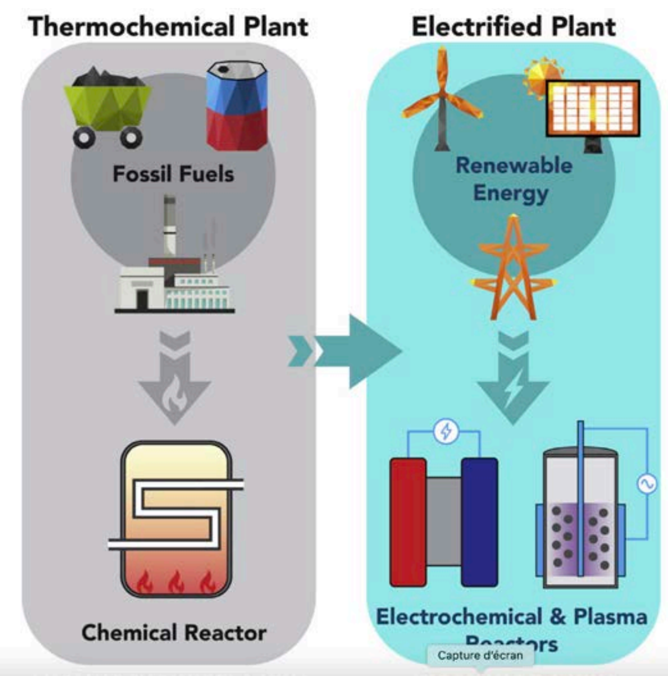
! Revision by IEA 2022: Renewable capacity expansion in the next five years will be much faster than what was expected just a year ago!

- Renewable electricity intermittency and decentralization add interest to plasma processes



Unique properties of plasma technologies w/r energy transition & decarbonization

- Direct utilization of renewable electricity
- Access to energy levels not otherwise reachable through electrons
- Can perform chemistry under non-equilibrium conditions
- No solvent / dry conversion and synthesis processes
- Fast light-up/turn-down, more compatible with intermittent electricity
- Allows to move away from the traditional bigger + more powerful approach, with decentralized on-demand use



Joule

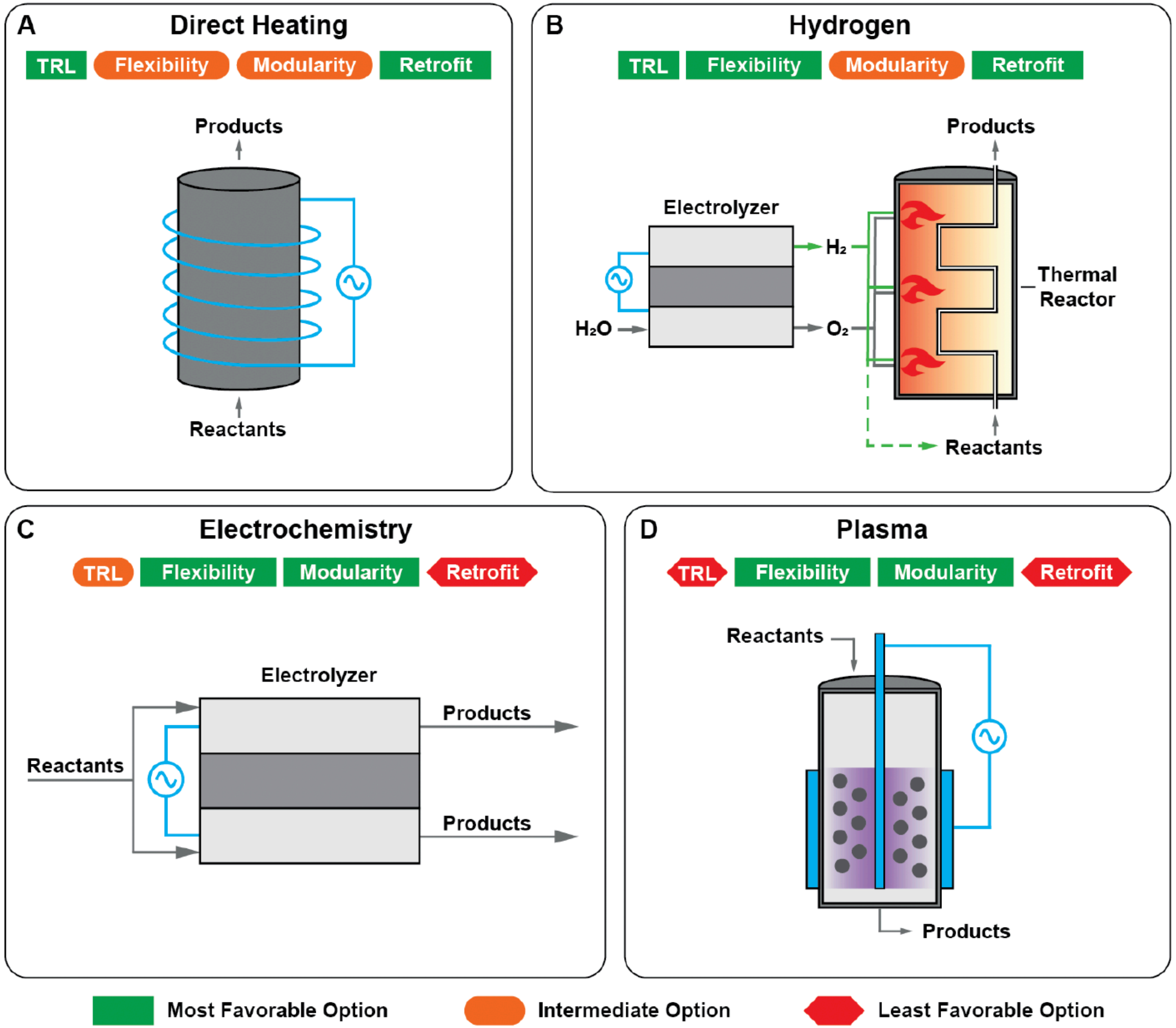
CellPress

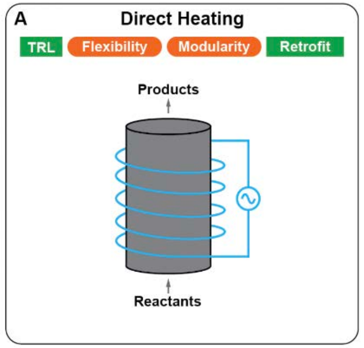
Volume 7, Issue 1, 18 January 2023, Pages 23-41

Perspective

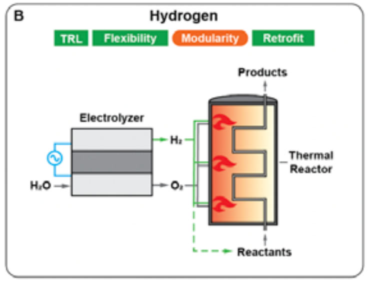
Decarbonization of the chemical industry through electrification: Barriers and opportunities

Dharik S. Mallapragada [1], Yury Dvorkin [2], Miguel A. Modestino [3], Daniel V. Esposito [4], Wilson A. Smith [5 6 7], Bri-Mathias Hodge [6 7 8], Michael P. Harold [9], Vincent M. Donnelly [9], Alice Nuz [10], Casey Bloomquist [3], Kyri Baker [11], Lars C. Grabow [9 12], Yushan Yan [13], Nav Nidhi Rajput [14], Ryan L. Hartman [3], Elizabeth J. Biddinger [15], Eray S. Aydil [3], André D. Taylor [3]

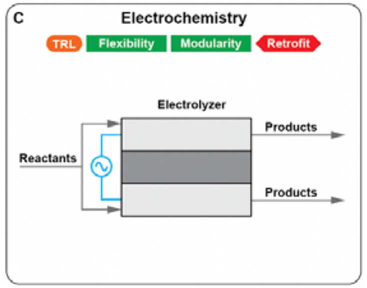




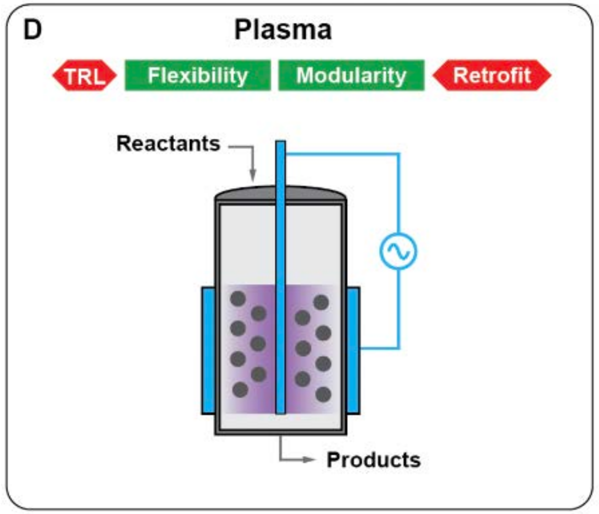
Electric arc furnace (EAF, DRI)
Waste-to-energy (syngas)
Plasma spraying
Plasma pyrolysis
Resource recovery
...



Plasma pyrolysis
Waste-to-energy (syngas)
Plasma electrolysis
Nanocatalyst synthesis
Surface functionalization (wetting)
...

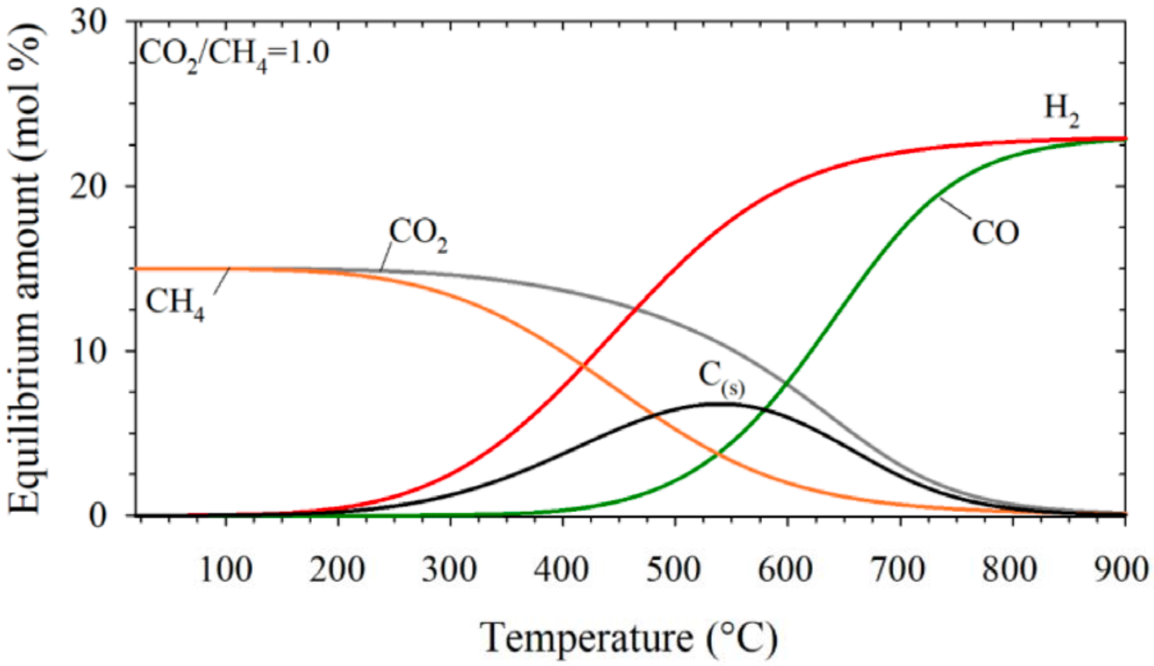


Plasma electrolysis
Nanocatalyst synthesis
Surface functionalization (wetting)
Supercapacitor electrodes
...

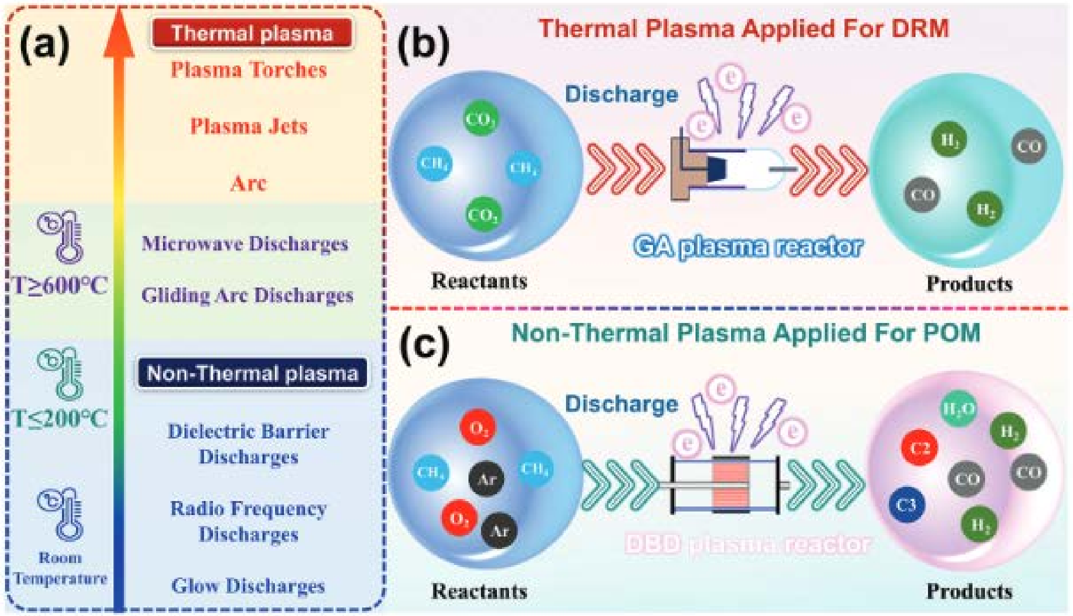


Non-thermal gas conversion (e.g. ozone)
Pollution control (e.g. DeNOx, PFAS)
Surface modification
Plasma activation (gas and liquid)
Coatings
Material synthesis (s, l, g)
Plasma-catalysis
...

Plasma heating/chemistry: CH4 oxidation



DRM: CH_4+CO_2 => 2CO + H_2, 123.5 kJ/mol (H_2)



Plasma-Assisted Reforming of Methane

Jiayu Feng, Xin Sun, Zhao Li, Xingguang Hao, Maohong Fan, Ping Ning,* and Kai Li**

Adv. Sci. **2022**, *9*, 2203221

H_2 synthesis via CH_4 pyrolysis

H_2O => H_2 + ½ O_2, 285 kJ/mol (H_2)

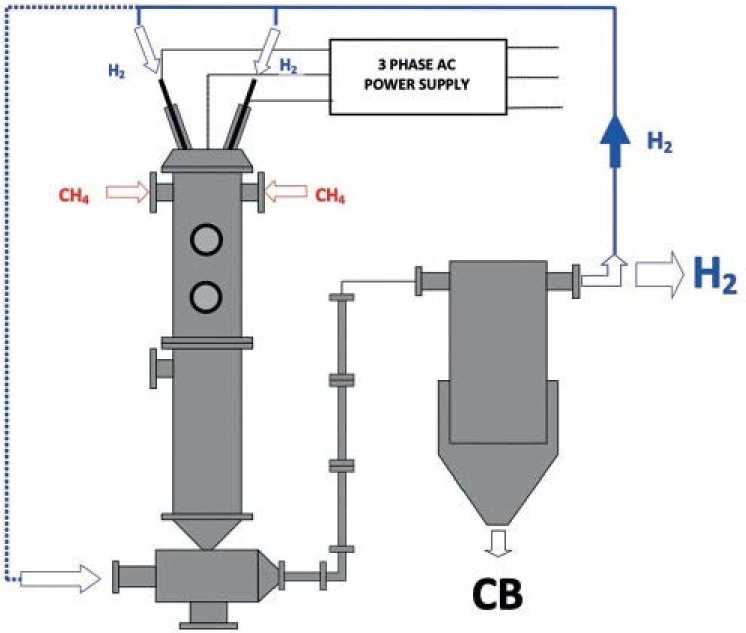
CH_4+H_2O => CO + 3H_2, 68 kJ/mol (H_2)

CH_4 => C + 2H_2, 37.5 kJ/mol (H_2)

2NH_3 => N_2 + 3H_2, 30.7 kJ/mol (H_2)

Electrolysis: *~80 kWh/kg.H_2 + Pt/Ir catalysts*

Plasma pyrolysis: 10-20 kWh/kg.H_2 no-catalyst
750 kg C(s) per ton of CH_4…



Production d'hydrogène décarboné : la troisième voie

Laurent Fulcheri

Dans Annales des Mines - Responsabilité et environnement 2020/3 (N° 99), pages 93 à 100

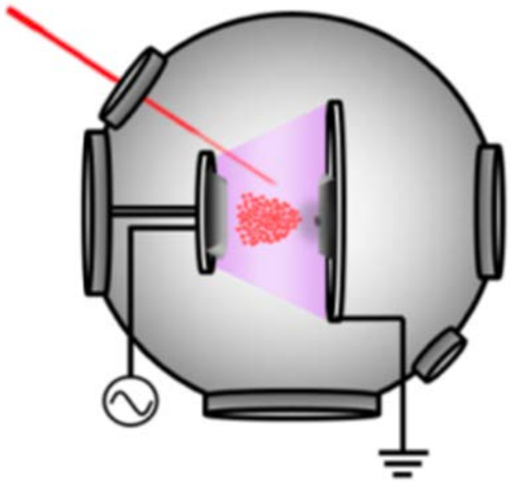
Éditions Institut Mines-Télécom

ISSN 1268-4783
DOI 10.3917/re1.099.0093

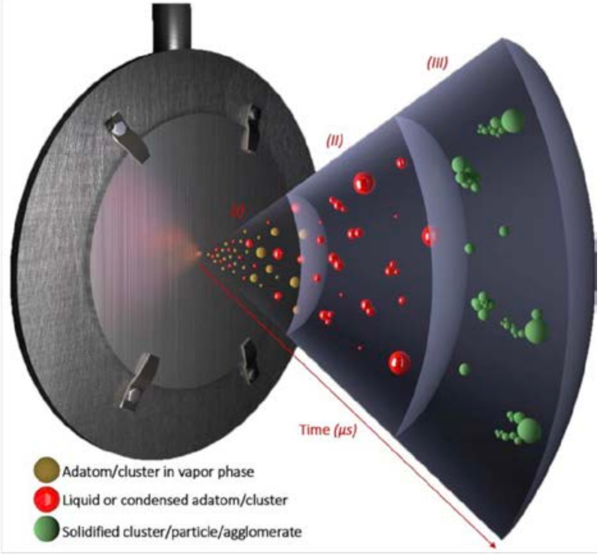
monolith

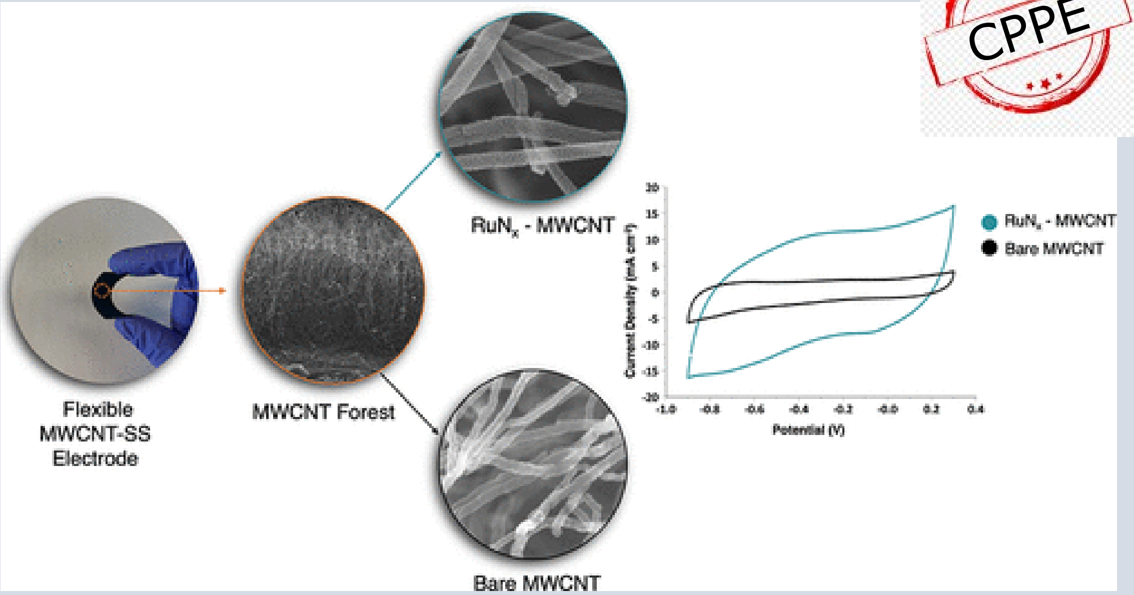
Nanocatalyst synthesis

Pulsed-laser ablation +
Plasma-enhanced CVD

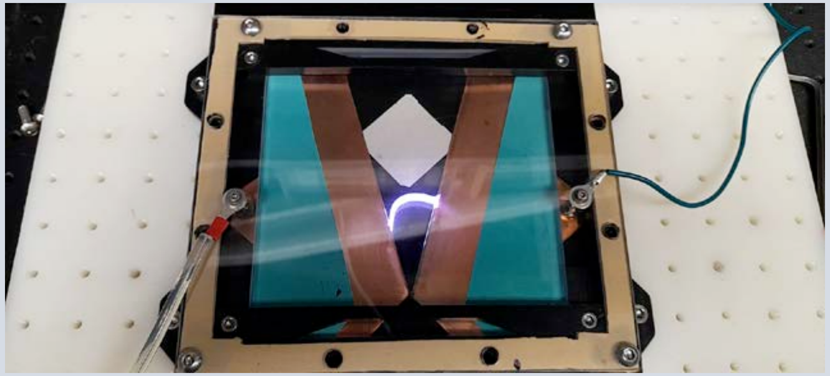


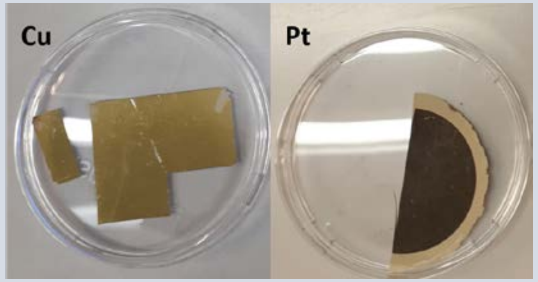
PLA-PECVD



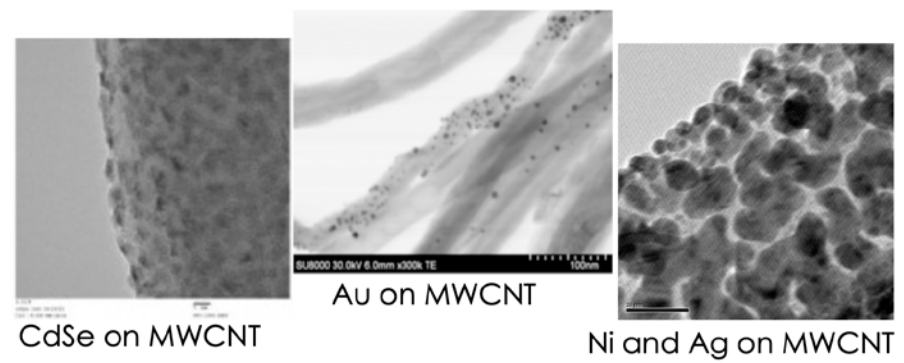


Binder-free RuNx-MWCNT flexible supercapacitors





NPs on BNNT paper



Well-dispersed (~5nm) NPs on nanostructures

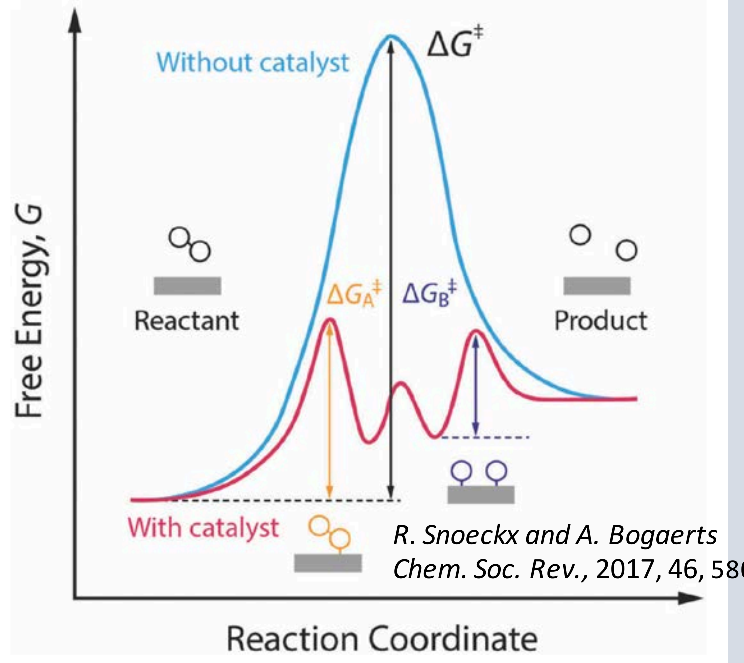
Plasma-Catalysis

"Catalysis-based chemical synthesis accounts for 60 percent of today's chemical products and is a factor in 90 percent of current chemical processes." ACS 1996

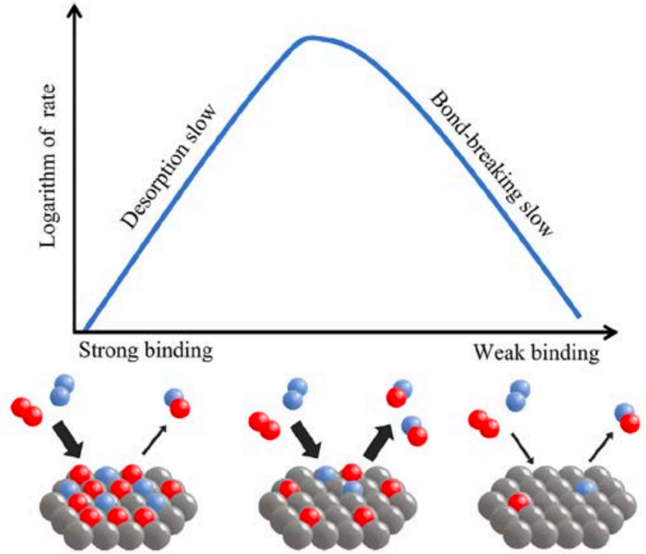
Thermocatalytic processes have ruled the chemical industry since the beginning of the fossil fuels era

Why adding a plasma?

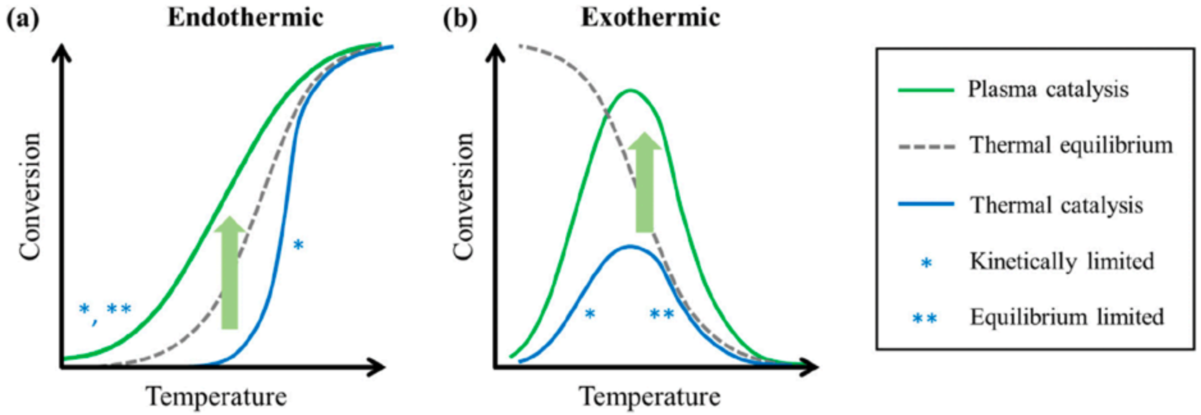
- ✓ Operation at lower gas temperature, yet high T_{exc}
- ✓ Access to more catalyst materials, non-PCM
- ✓ Enhanced activity/selectivity
- ✓ Synergetic effects?



R. Snoeckx and A. Bogaerts
Chem. Soc. Rev., 2017, 46, 5805



B. Loenders, R. Michiels and A. Bogaerts
Journal of Energy Chemistry 85 (2023) 501–533



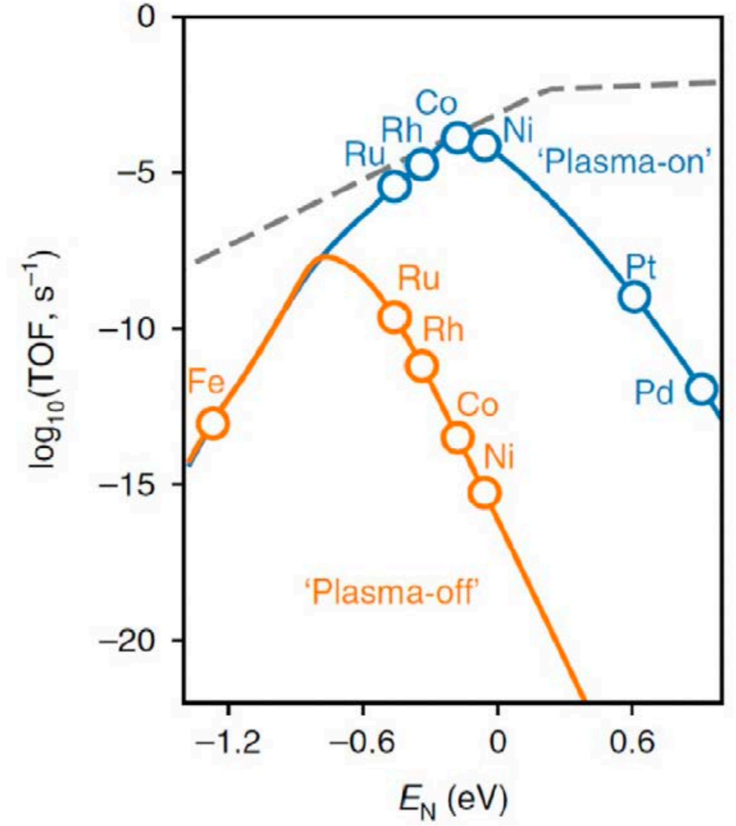
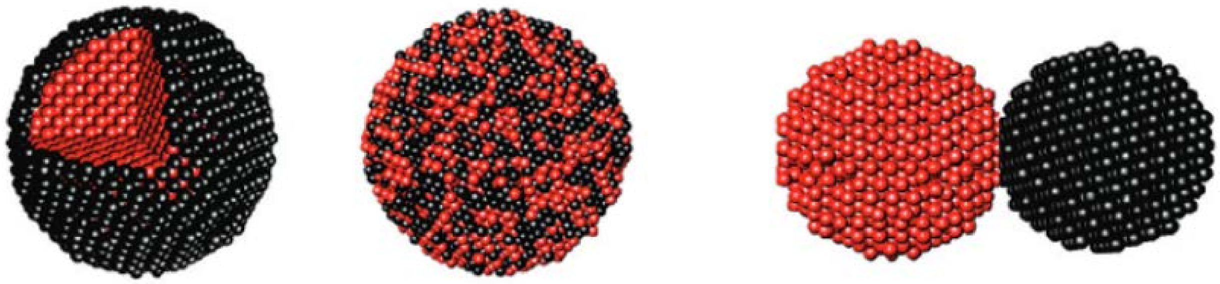


Fig. 7. Predicted effect of N_2 vibrational excitation on the TOFs of NH_3 synthesis (plasma-on), compared to those for thermal catalysis (plasma-off). Rates on (211) surfaces with reaction conditions: 1 atm, T_{gas} = 473 K, T_{vib} = 3000 K, conversion = 1%. The dashed lines are the maximum possible rates for the hydrogenation reactions according to Sabatier analysis. Lower (negative) values of E_N correspond to catalysts that bind N* strongly, and high (positive) values of E_N correspond to catalysts that bind N* weakly. Reproduced with permission from ref. [70]. Copyright 2018, Springer Nature.

[70] P. Mehta, P. Barboun, F.A. Herrera, J. Kim, P. Rumbach, D.B. Go, J.C. Hicks, W.F. Schneider, Nat. Catal. 1 (2018) 269–275.



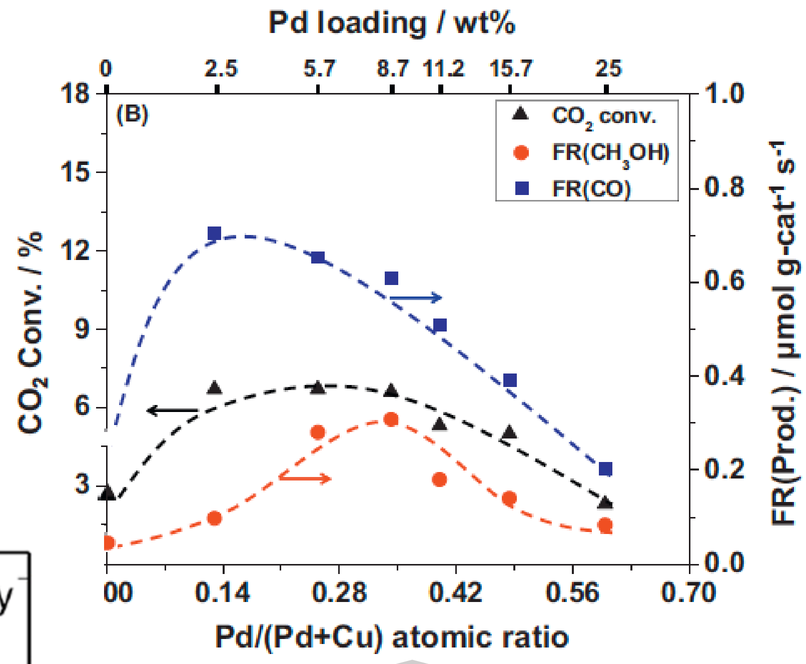
Core/Shell — Ru@Pt

Alloys — RuPt (1:1) alloy

Aggregate Mixtures — Ru + Pt monometallic NPs

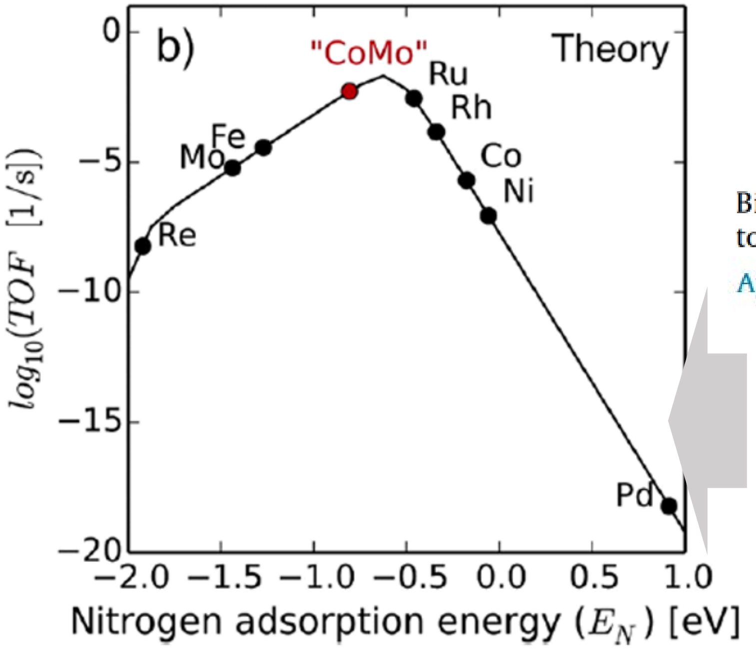
Structural and Architectural Evaluation of Bimetallic Nanoparticles: A Case Study of Pt−Ru Core−Shell and Alloy Nanoparticles

VOL. 3 • NO. 10 • 3127–3137 • 2009 ACS NANO



Bimetallic Pd–Cu catalysts for selective CO_2 hydrogenation to methanol

Applied Catalysis B: Environmental 170-171 (2015) 173–185



Ammonia synthesis catalysts, N_2+3H_2=>$2NH_3$

J. Catal. **2015**, *328*, 36−42.

With a Langmuir-Hinshelwood (LH) mechanism, where both reactants are dissociatively adsorbed on the surface before any reaction between their fragments takes place, a dual metal catalyst may perform better.

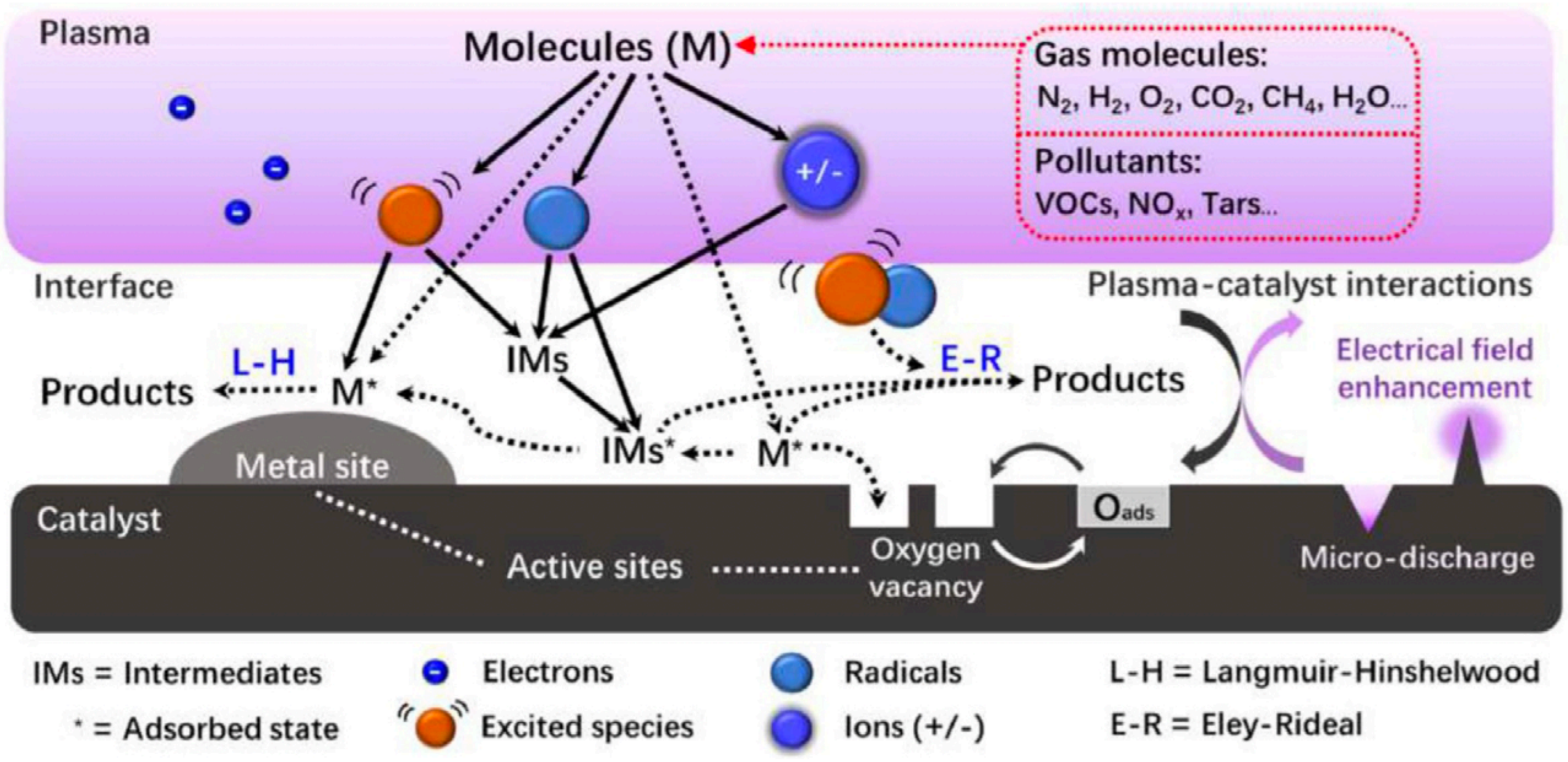
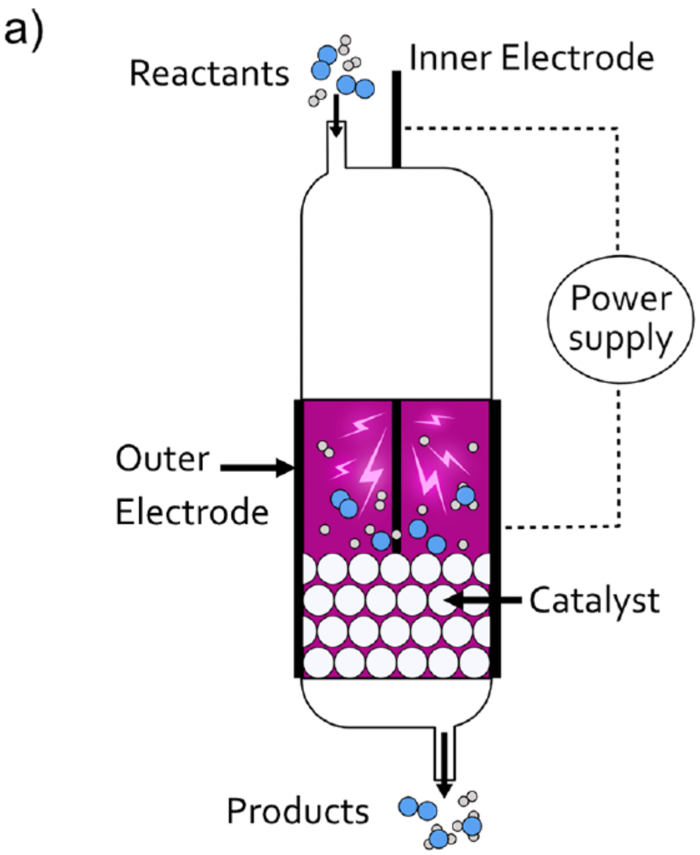


Figure 1. Overview of the key mechanisms and species in the plasma and at the catalytic surface, showing the complexity of plasma catalysis.

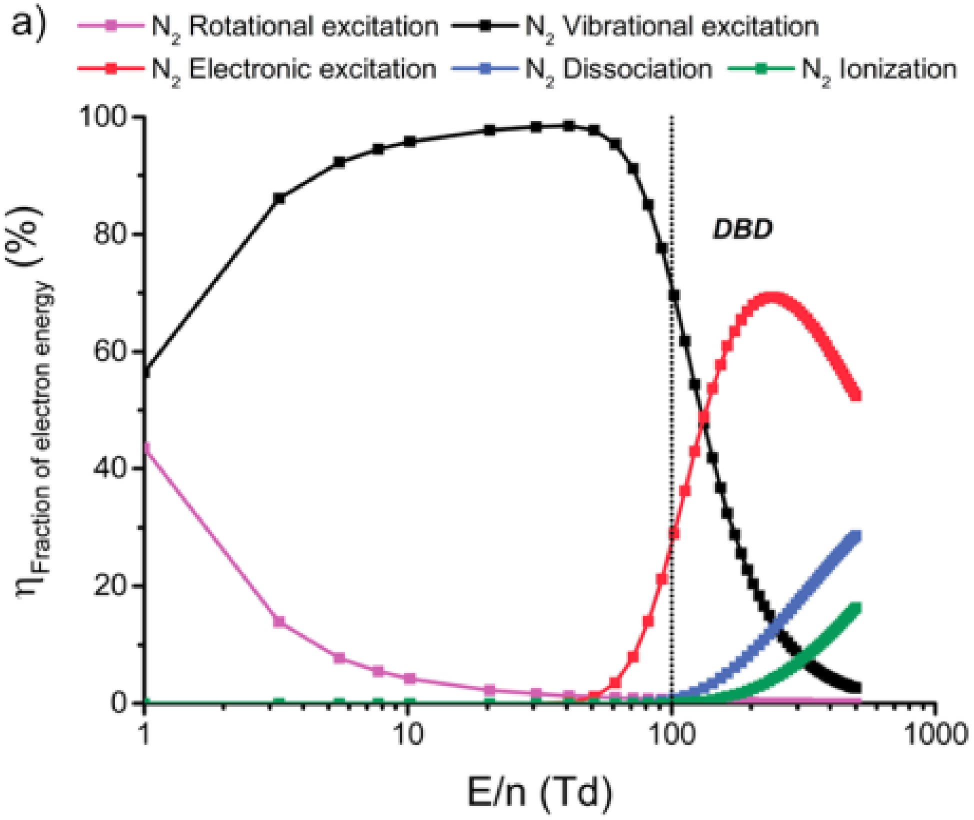
The 2020 plasma catalysis roadmap

Annemie Bogaerts[1], Xin Tu[2], J Christopher Whitehead[3], Gabriele Centi[4,5], Leon Lefferts[6], Olivier Guaitella[7], Federico Azzolina-Jury[8], Hyun-Ha Kim[9], Anthony B Murphy[10], William F Schneider[11], Tomohiro Nozaki[12], Jason C Hicks[11], Antoine Rousseau[7], Frederic Thevenet[13], Ahmed Khacef[14] and Maria Carreon[15]

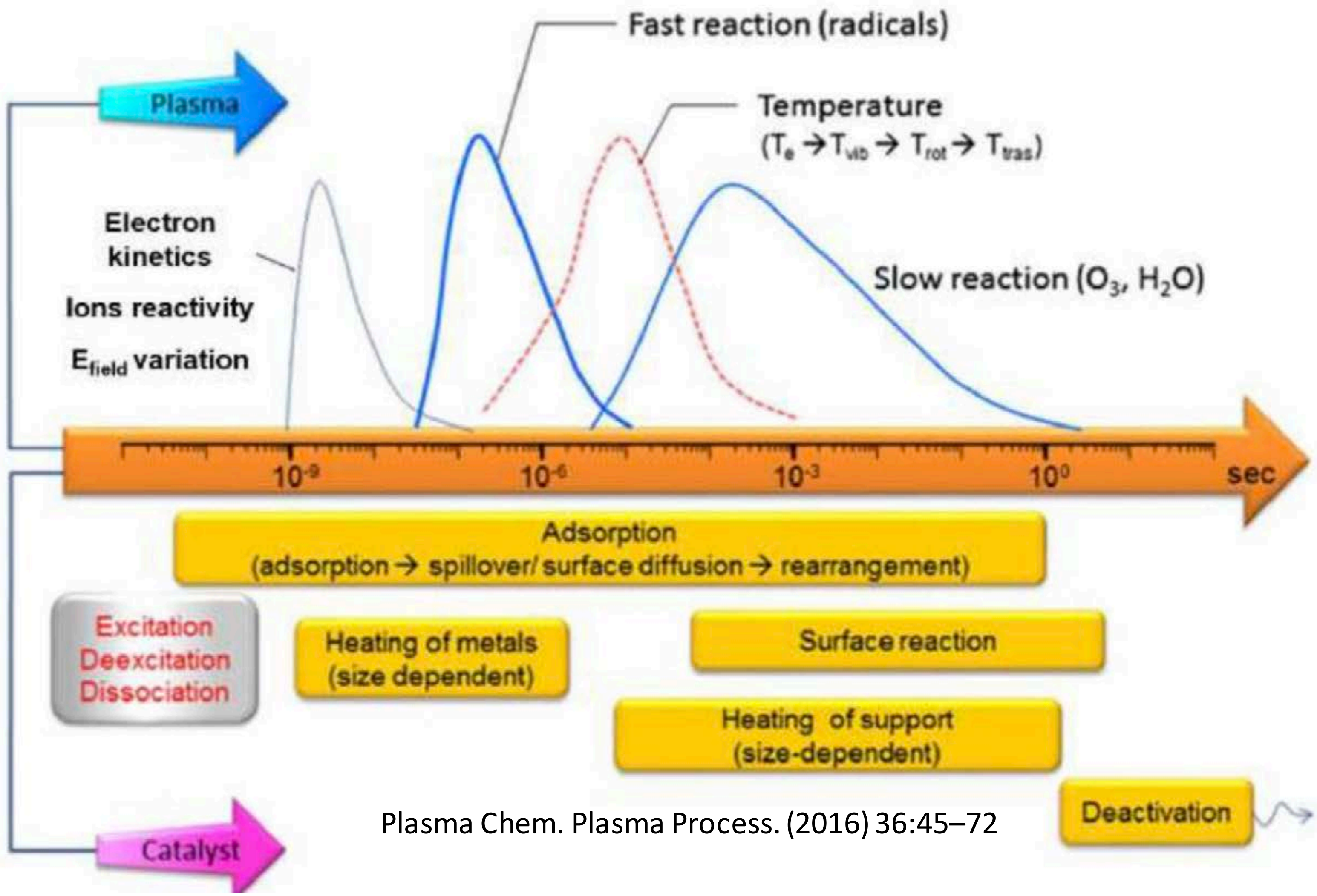
J. Phys. D: Appl. Phys. **53** (2020) 443001 (51pp)



ACS Energy Lett. 2019, 4, 1115−1133

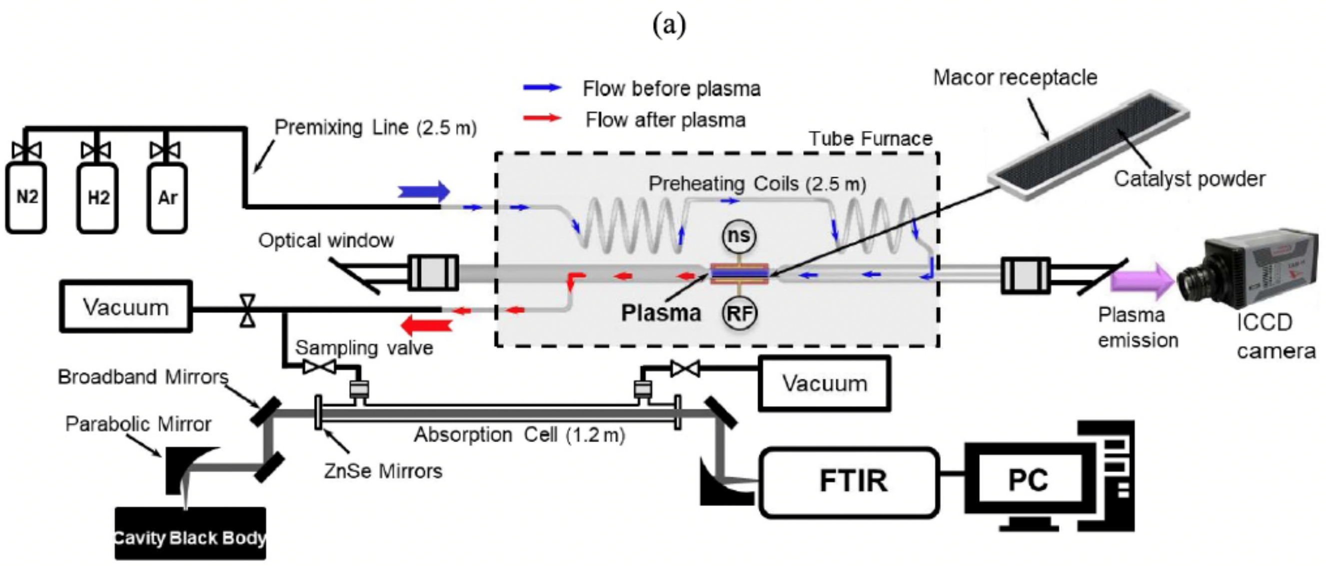


Bogaerts, A.; Neyts, E. C. Plasma Technology: An Emerging Technology for Energy Storage. ACS Energy Lett. 2018, 3, 1013−1027.



Plasma Chem. Plasma Process. (2016) 36:45–72

Presented in 2016... Not much has been done since then on dynamic control

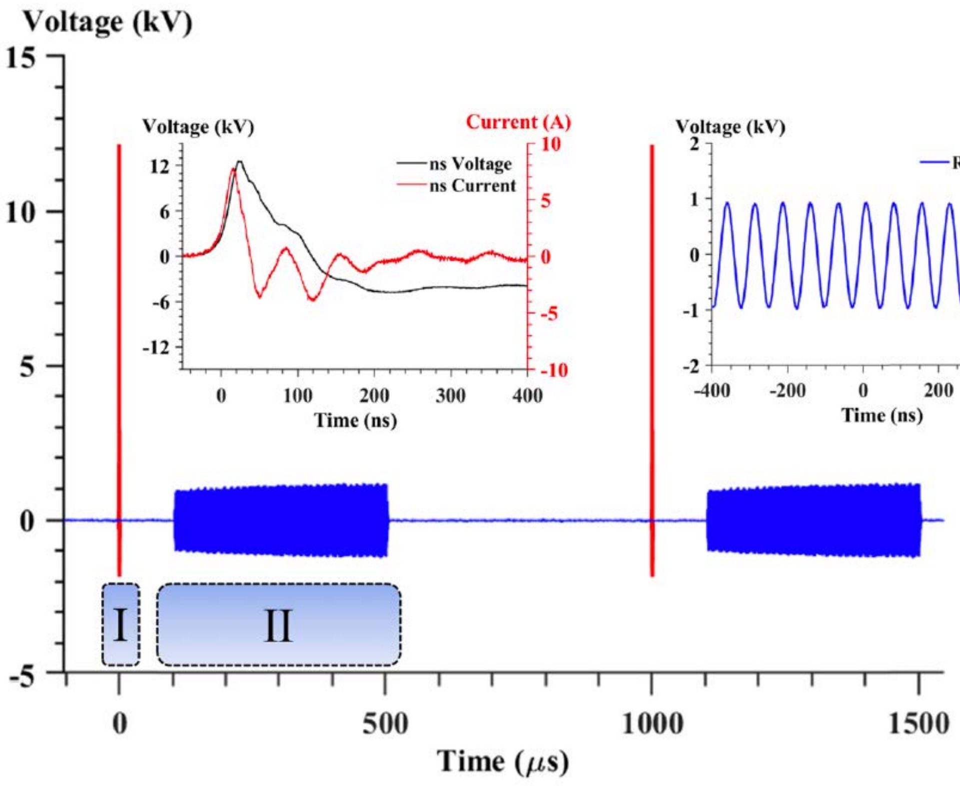


Ammonia generation in Ns pulse and Ns pulse/RF discharges over a catalytic surface

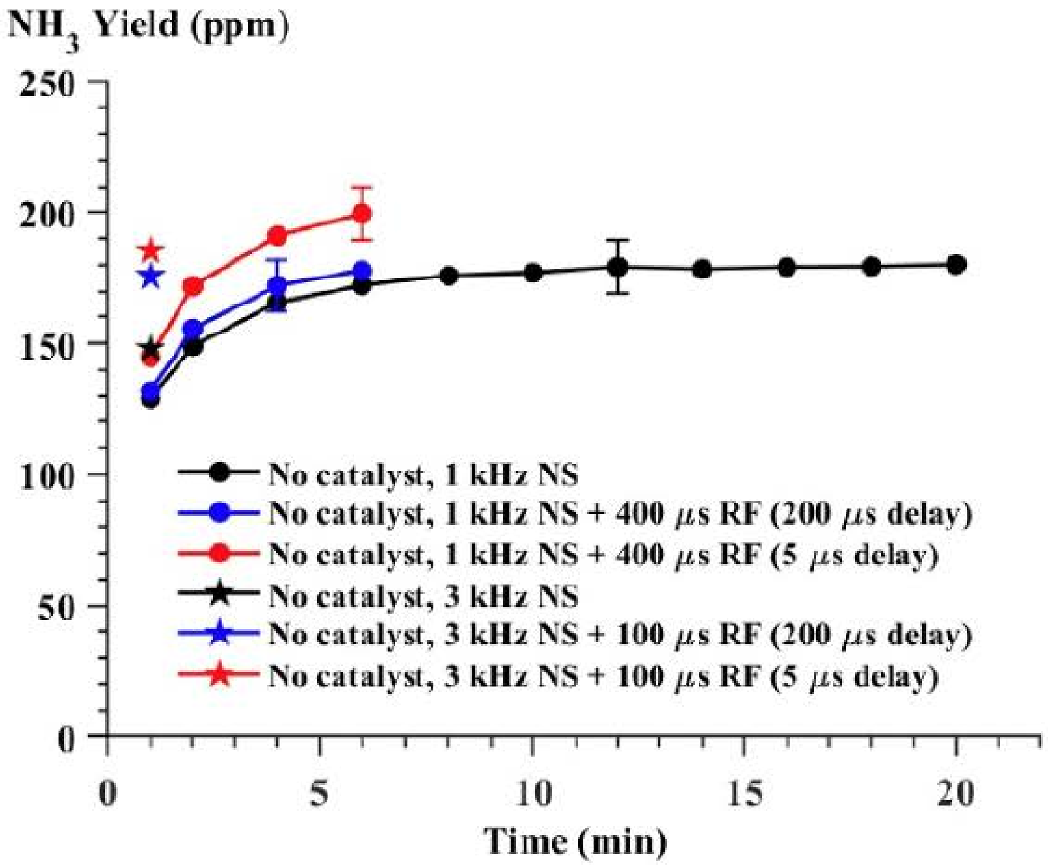
Xin Yang*, Caleb Richards and Igor V Adamovich*

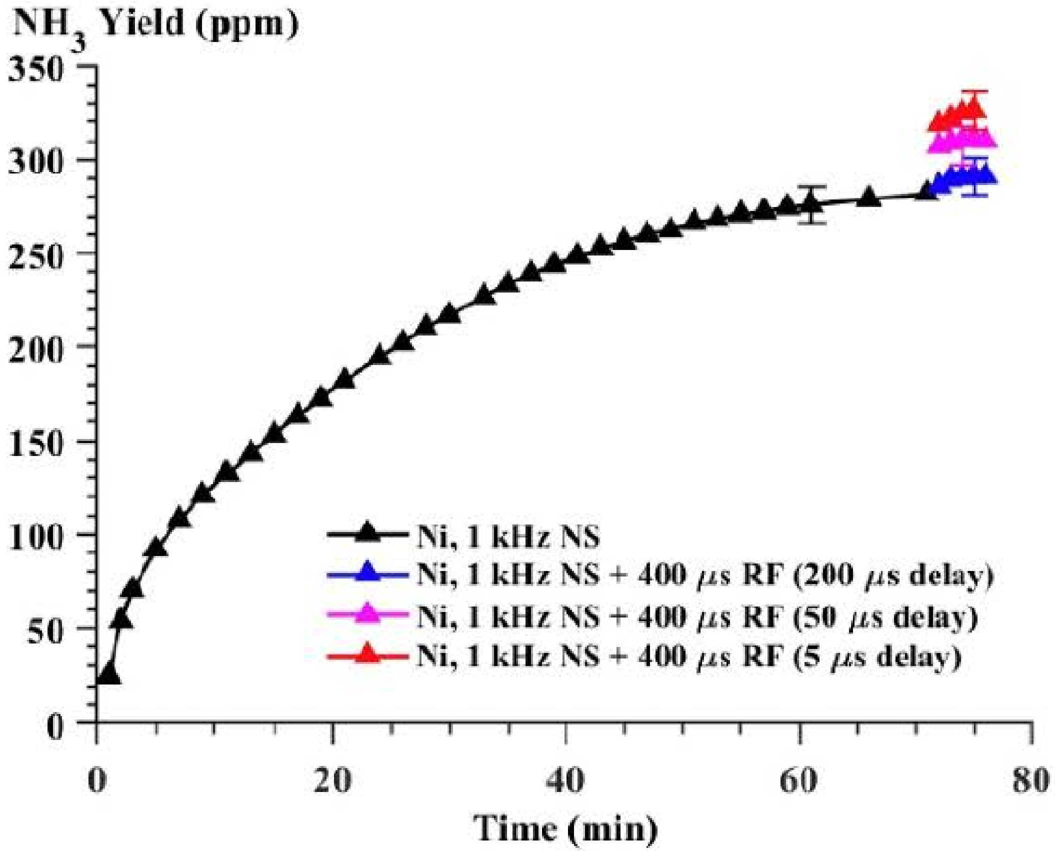
Nonequilibrium Thermodynamics Laboratory, Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH 43210, United States of America

Plasma Sources Sci. Technol. **32** (2023) 064003 (13pp)



P=190 Torr, 573 K, 10% H_2-N_2 mixture





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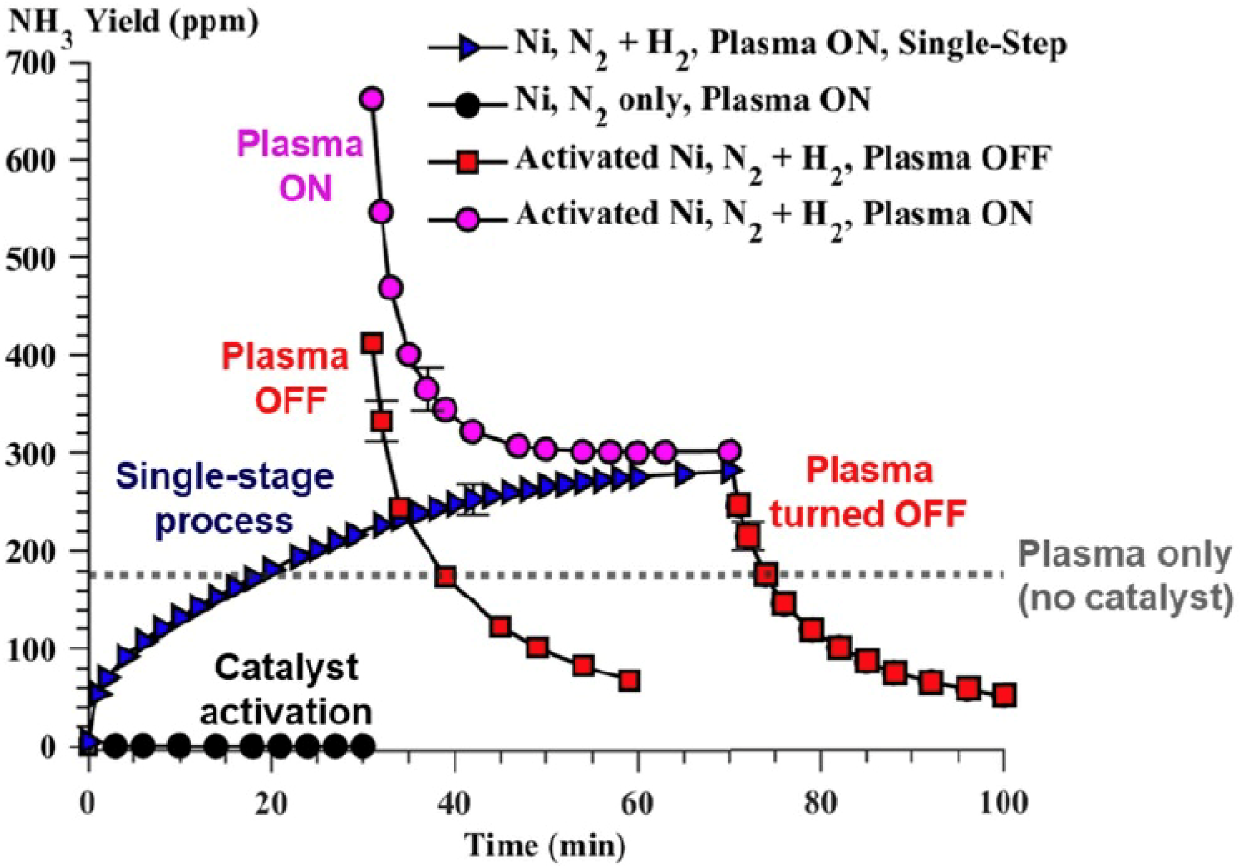
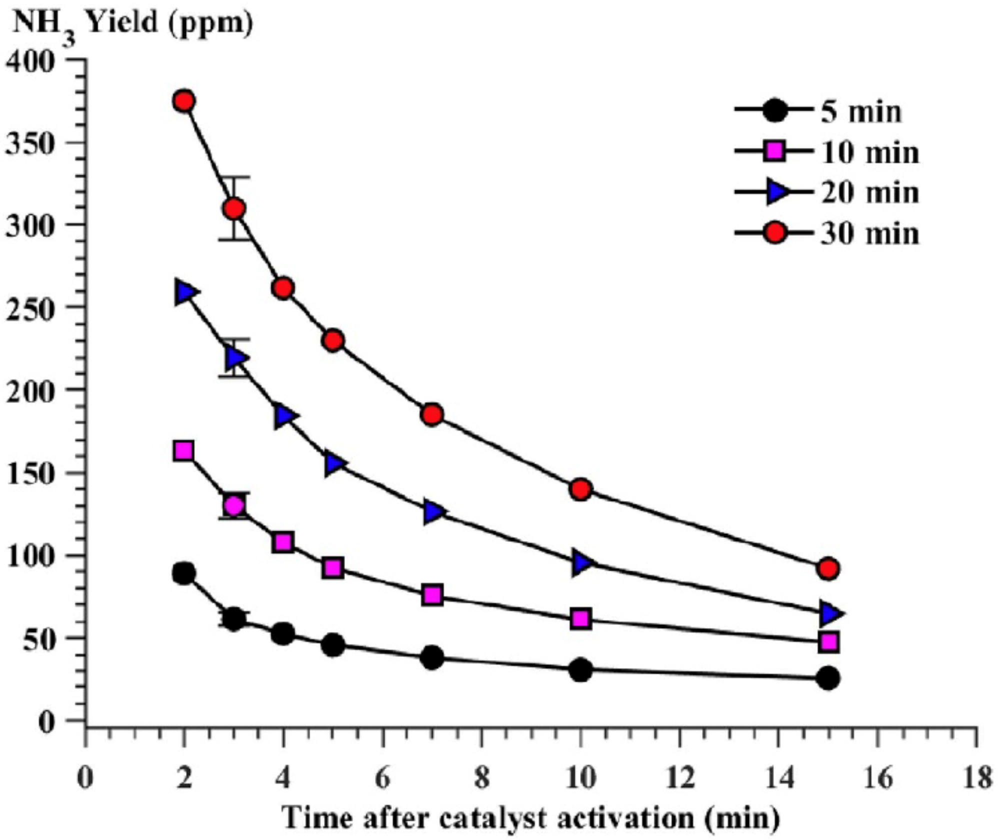
Plasma Sources Sci. Technol. **32** (2023) 064003 (13pp)

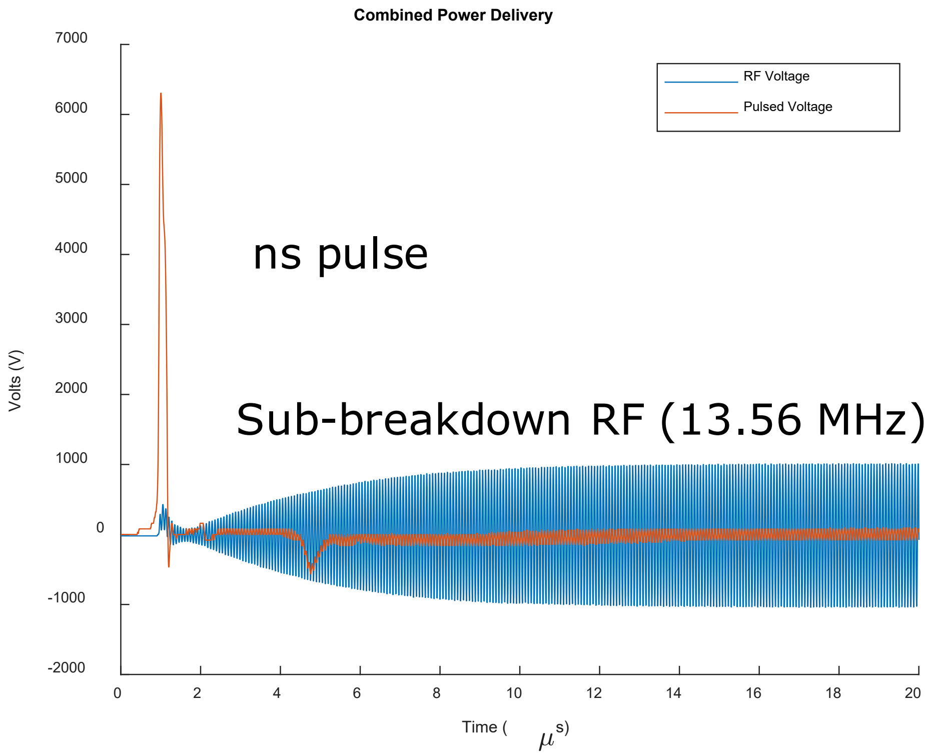


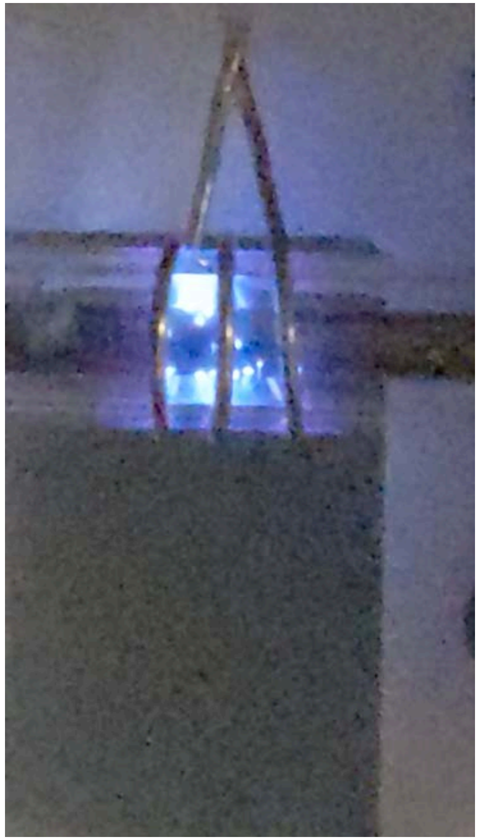


P=190 Torr, 573 K, 10% H_2-N_2 mixture

Plasma Sources Sci. Technol. **32** (2023) 064003 (13pp)

Plasma source design: Electrical power deposition <=> Plasma chemistry



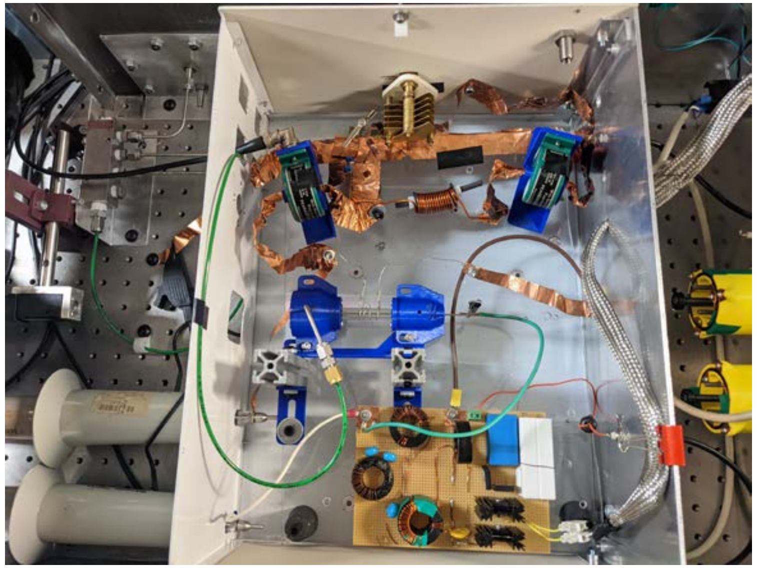


1 kHz ns pulsing

followed by

500 Hz (50%) pulsed RF

Pure CO_2, 1 atm, No catalyst



Conclusions and perspective

Plasma-catalysis is a nascent field. Much remains to be done from the 2020 roadmap. We need to better use the non-equilibrium.

- One needs to pay far more attention to the power delivery <=> plasma chemistry relation
- Distributed arrangement for the timely excitation/contact of reactive with catalyst?
- In-situ separation or chemical rxn freezing?
- Multi-function catalysts tuned to gas mixtures?
- Sequencing: Use of time- and spatially-distributed excitation?
- For nanocatalysts synthesized by plasma, can we test them in-situ?

Acknowledgements

IAEA’s technical meeting organizers

CPPE laboratory

National Research Council of Canada

NSERC CRSNG

NRC·CNRC

sylvain.coulombe@mcgill.ca

/mcgill.ca/cppe/

Thank you!