A Round Table Discussion

LOW TEMPERATURE PLASMAS: OUR DISCIPLINE IN 2030

Annemie Bogaerts, Jean-Paul Booth, Peter Bruggeman, William Graham, Walter Lempert and Stephane Mazouffre

Moderated by: Mark J. Kushner
Created by: Francisco J. (Paco) Gordillo-Vazquez

ICPIG, 2013

eV PHYSICS – SOCIETAL BENEFIT

- In a letter to the editor to Physics Today (July, 1988) Dr. John Waymouth described "eV physics".

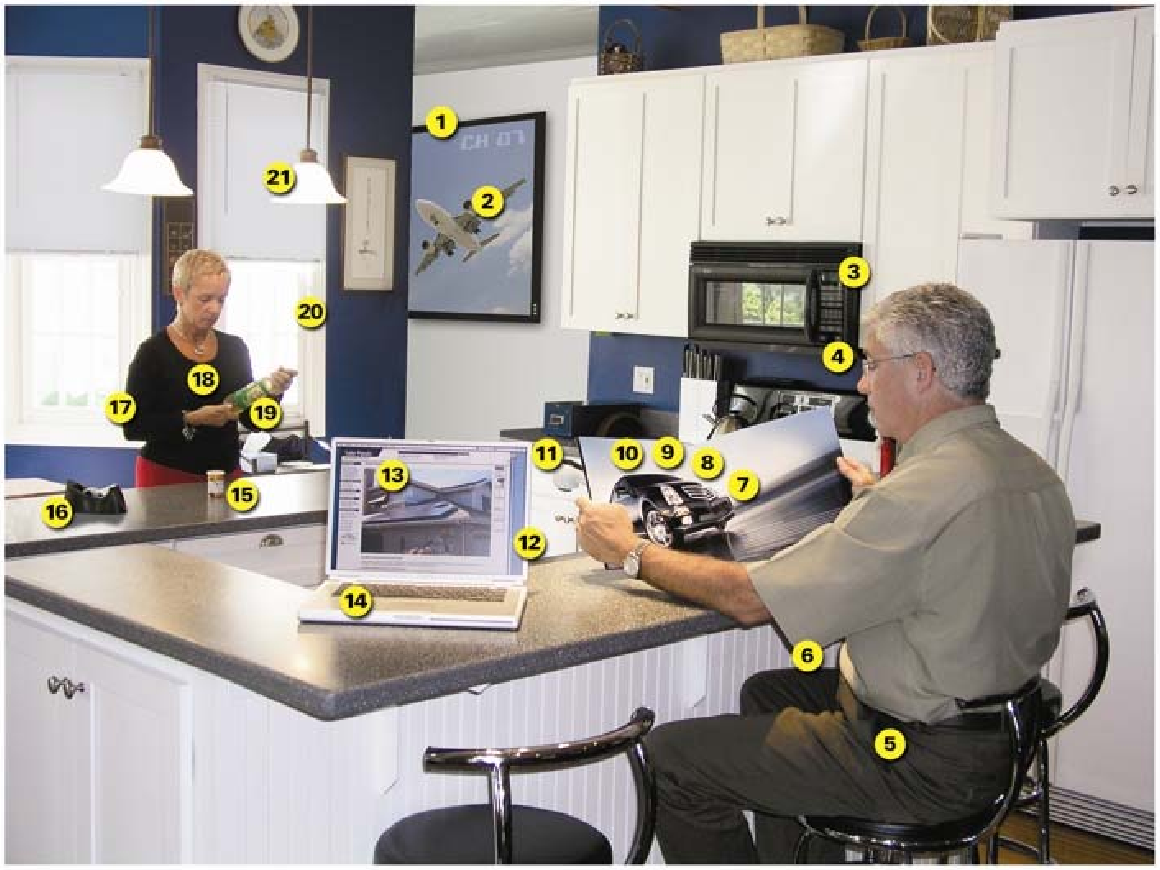
"…Electron-volt physics, in which energy exchanges on an atomic, molecular or electronic scale are less than 100,000 volts…is the science of things that happen on Earth, with…contributions of what happens in the nearby Sun and the intervening space."

"Every single member of our society has been touched in very substantial ways by the accomplishments of eV physics…"

- Dr. John Waymouth, Former Director of Research, GTE/Sylvania Lighting

- eV Physics is that part of our discipline that provides near term, and often real time, societal benefit – from materials processing and electronics, to water purification.
- It is important as we look forward to acknowledge this legacy of providing societal benefit.

ROBUST SCIENCE, SOCIETAL BENEFIT



01—Plasma TV
02—Plasma-coated jet turbine blades
03—Plasma-manufactured LEDs in panel
04—Diamondlike plasma CVD eyeglass coating
05—Plasma ion-implanted artificial hip
06—Plasma laser-cut cloth
07—Plasma HID headlamps
08—Plasma-produced H_2 in fuel cell
09—Plasma-aided combustion
10—Plasma muffler
11—Plasma ozone water purification
12—Plasma-deposited LCD screen
13—Plasma-deposited silicon for solar cells
14—Plasma-processed microelectronics
15—Plasma-sterilization in pharmaceutical production
16—Plasma-treated polymers
17—Plasma-treated textiles
18—Plasma-treated heart stent
19—Plasma-deposited diffusion barriers for containers
20—Plasma-sputtered window glazing
21—Compact fluorescent plasma lamp

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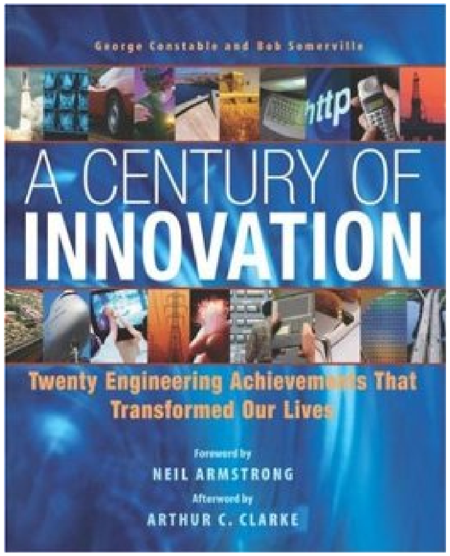
- **Research in low temperature plasmas addresses science issues that translate into technologies in our daily lives.**

Ref: Adapted from *"Plasma 2010: Plasma Science: Advancing Knowledge in the National Interest*", US National Research Council, 2007.

University of Michigan
Institute for Plasma Science & Engr.

US NATIONAL ACADEMY OF ENGINEERING: GREATEST ENGINEERING ACHIEVEMENTS OF 20TH CENTURY



- **The role of low temperature plasmas in 20th century technology.**

1. **Electrification**
2. **Automobile**
3. **Airplane**
4. **Water Supply and Distribution**
5. **Electronics**
6. **Radio and Television**
7. **Agricultural Mechanization**
8. ***Computers (via Electronics)***
9. ***Telephone (via Electronics)***
10. **Air Conditioning & Refrigeration**
11. **Highways**
12. **Spacecraft**
13. ***Internet (via Electronics)***
14. **Imaging**
15. **Household Appliances**
16. **Health Technologies**
17. **Petroleum & Petrochemical Technol.**
18. **Laser and Fiber Optics**
19. **Nuclear Technologies**
20. **High-performance Materials**

LTP Impact
Absolutely Critical
Major Contribution
Minor Contribution

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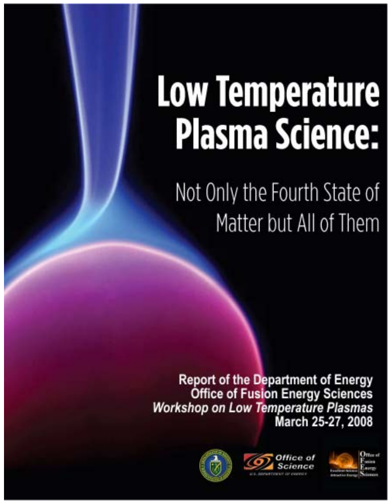
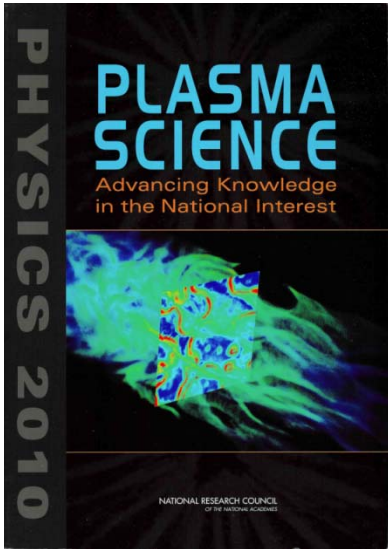
http://www.greatachievements.org/

University of Michigan
Institute for Plasma Science & Engr.

PLASMA 2010; LOW TEMPERATURE PLASMA WORKSHOP (2008)

- ***Priority 1: Predictive Control of Plasma Kinetics:*** **Predictably controlling *f(v,r,t)* through fundamental understanding of energy coupling into LTPs underlies ability to provide societal benefit.**
- ***Priority 2: Collective Behavior and Non-linear Transport:*** **LTPs produce unique collective behavior and nonlinear transport in part due to broad array of positive and negative ions (and electrons).**
- ***Priority 3: Interfaces and Multiple Phases in Plasmas:*** **LTPs uniquely interact with multiple phases: solid, liquid and gas. Optimizing plasmas in contact with multiple phases based on fundamentals is beyond current abilities.**
- ***Cross-cutting Priority: Diagnostics, Modeling, Fundamental Data:*** **Advances in all areas require a state-of-the-art foundation in diagnostics and modeling supported by knowledge bases of fundamental data.**





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US NATIONAL ACADEMY OF ENGINEERING: 21st CENTURY GRAND CHALLENGES

- **What will the role of low temperature plasmas be in addressing these (and similar) challenges?**
- **What are the science and technology issues we must address by 2030?**
- **How would you mentor a young colleague entering the field?**

- Make solar energy economical
- Provide energy from fusion
- Develop carbon sequestration methods
- Manage the nitrogen cycle
- Provide access to clean water
- Restore and improve urban infrastructure
- Advance health informatics
- Engineer better medicines
- Reverse-engineer the brain
- Prevent nuclear terror
- Secure cyberspace
- Enhance virtual reality
- Advance personalized learning
- Engineer the tools of scientific discovery

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http://www.engineeringchallenges.org/

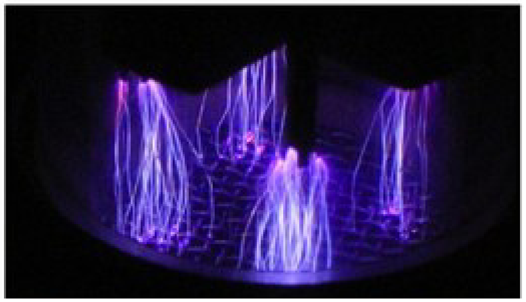
OUR SPEAKERS

- Prof. Annemie Bogaerts, Universiteit Antwerpen
  - Energy and the Environment
- Dr. Jean-Paul Booth, Laboratoire de Physique des Plasmas, CNRS
  - Plasma Materials Processing – Microelectronics
- Prof. Peter Bruggeman, University of Minnesota
  - Biotechnology and Liquids
- Prof. Walter Lempert, Ohio State University
  - Combustion and Aeronautics
- Dr. Stephane Mazouffre, Institut de Combustion, Aerothermique, Reactivite et Environment, CNRS
  - Space Plasmas and Propulsion
- Prof. William Graham, Queen's University Belfast
  - "The Big Picture"

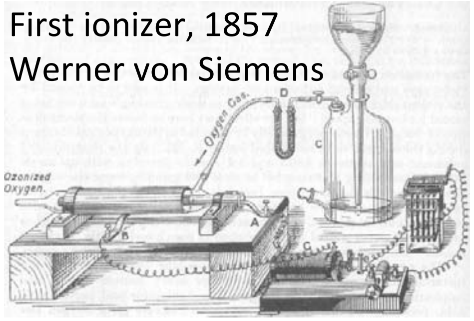
Prof. Annemie Bogaerts
Energy and the Environment

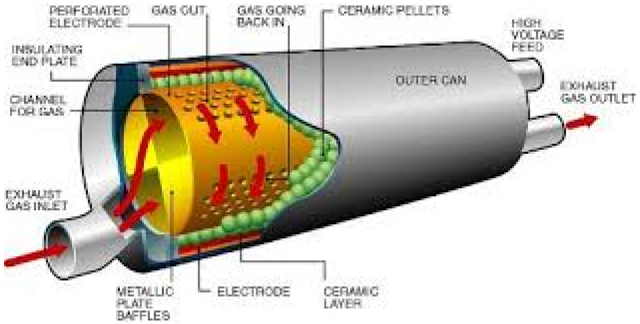
Challenges for plasma in environmental / energy applications

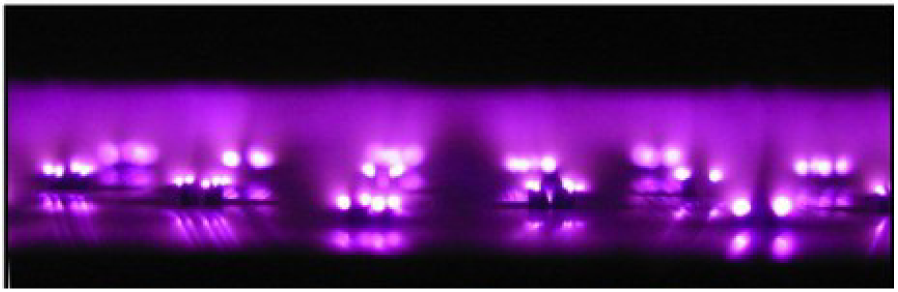
Annemie Bogaerts



- VOC remediation
- Exhaust treatment (NOx removal)
- Water purification
- Waste destruction
- Fusion
- …
- **Greenhouse gas conversion into new fuels / chemical feedstock**


First ionizer, 1857
Werner von Siemens





Situation of the problem (1)

Source: Richard Smalley, Rice University, 2003

Situation of the problem (2)

1) Worldwide: 80 % of energy consumption: fossil fuels

→Greenhouse gases

→Global warming

Catalytic conversion of greenhouse gases (CH_4, CO_2) into value-added chemicals or new fuels (CCU)
= one of the grand challenges for the 21st century
(The Strategic Research Agenda of the European Technology Platform for Sustainable Chemistry)

Processes include:
CO_2 splitting, CO_2 / CH_4, CO_2 / H_2O, CH_4 / O_2, CH_4 / H_2O,...
(= inert molecules, activation energy, endothermic reactions)

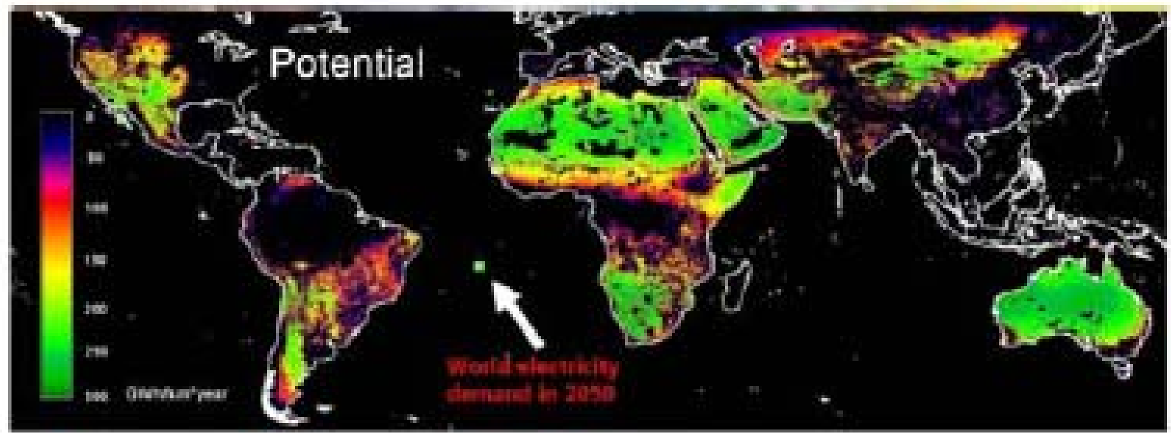
→ Need for energy-efficient processes

Situation of the problem (3)

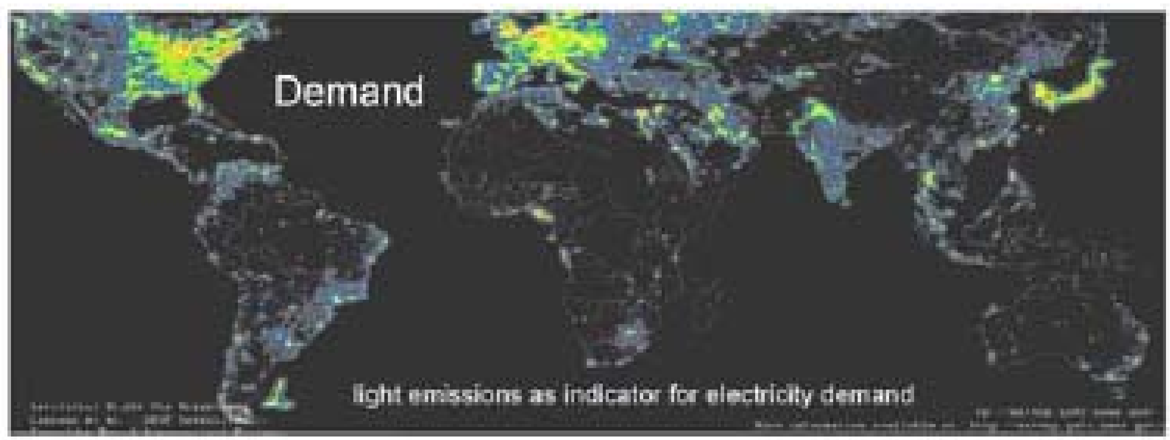
2) Sustainable energy sources (solar, wind,...): peak powers

Problem of electricity storage + transport

e.g.: Solar generation



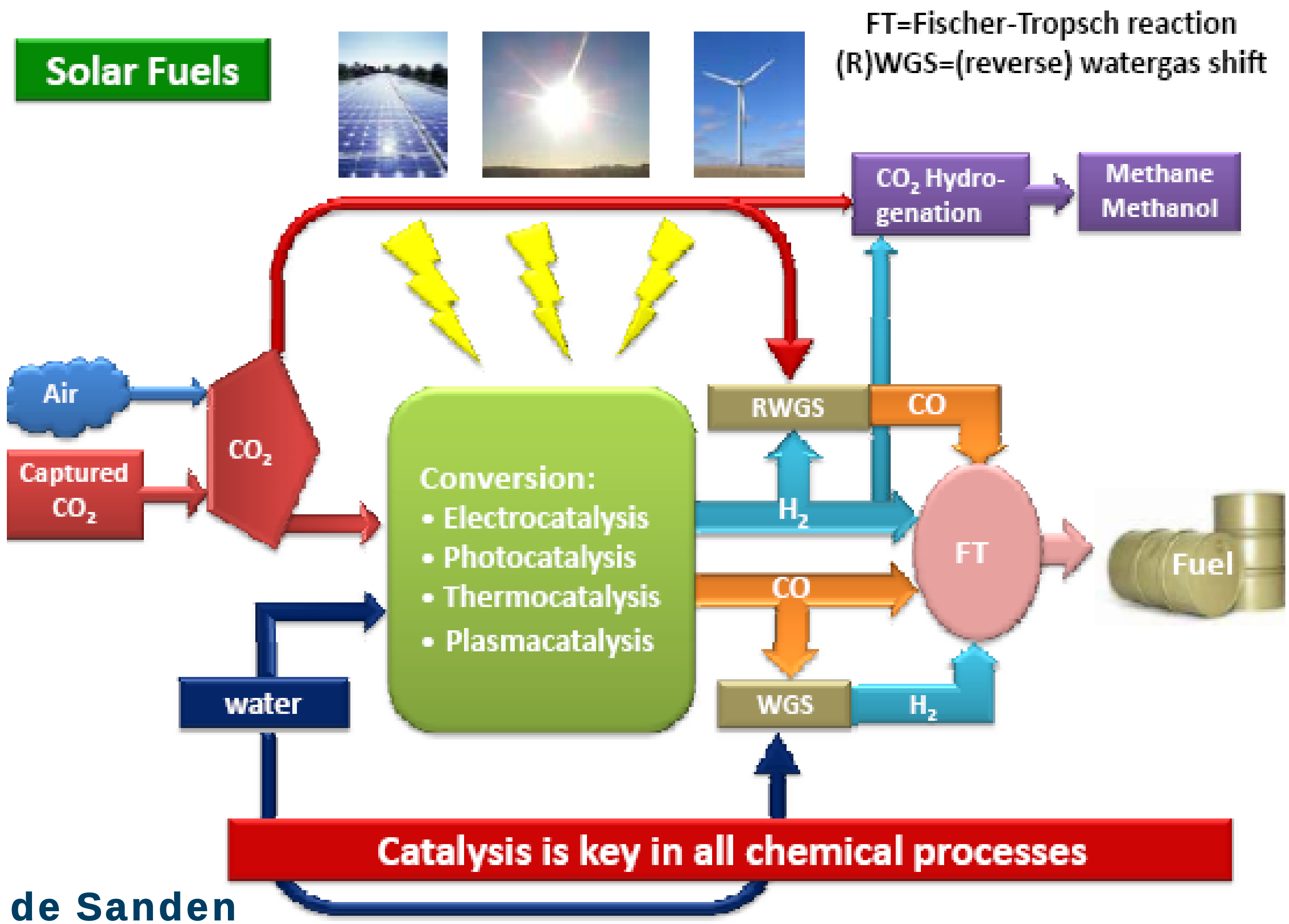
Energy demand



→ **Need for processes that can store energy**

"Dream" solution: "Solar fuels"

Production of **fuels** (hydrocarbons, alcohols,...)
(or **value-added chemicals as feedstock** for chemical industry)
from **sustainable energy sources** (solar, wind,...),
using CO_2



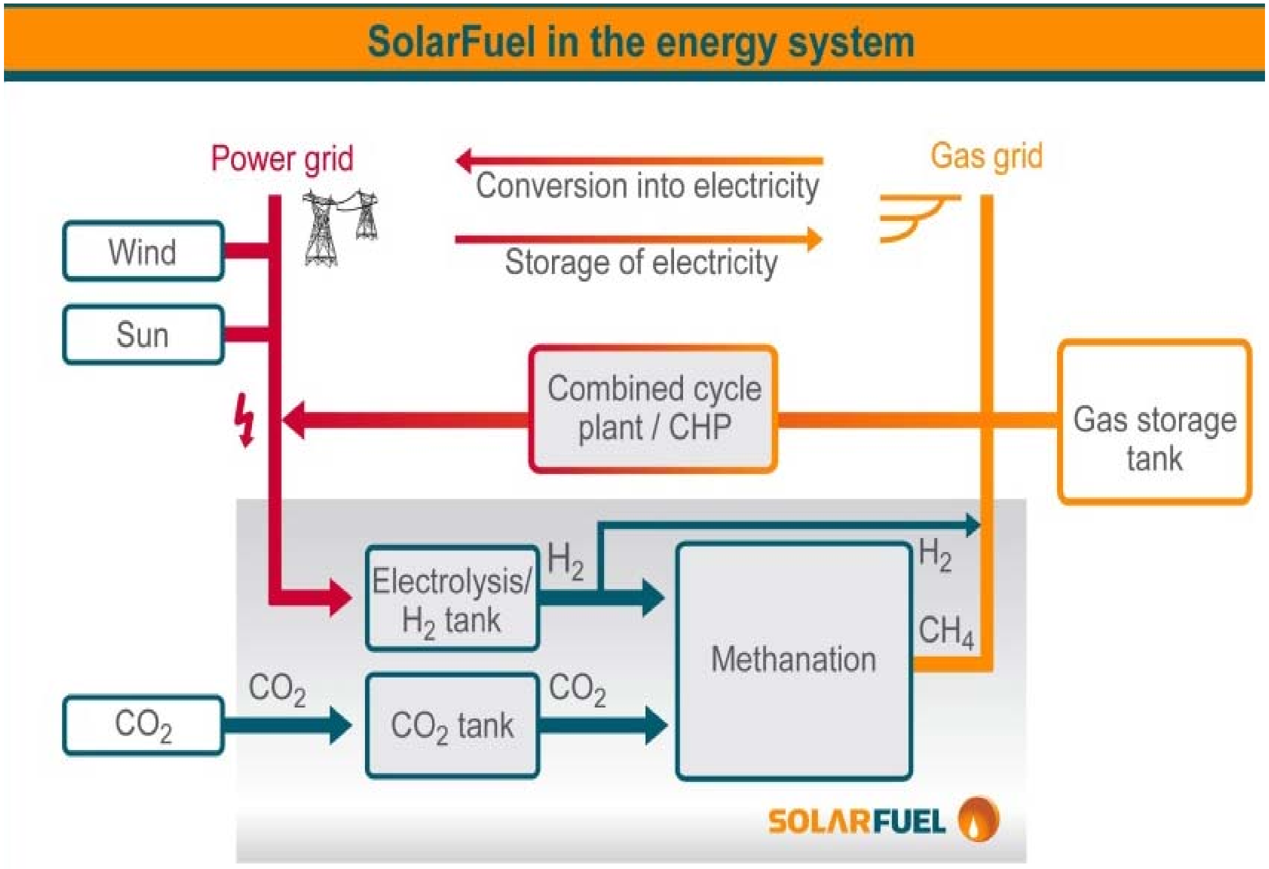
Source: Richard van de Sanden

Example: Sabatier Reaction

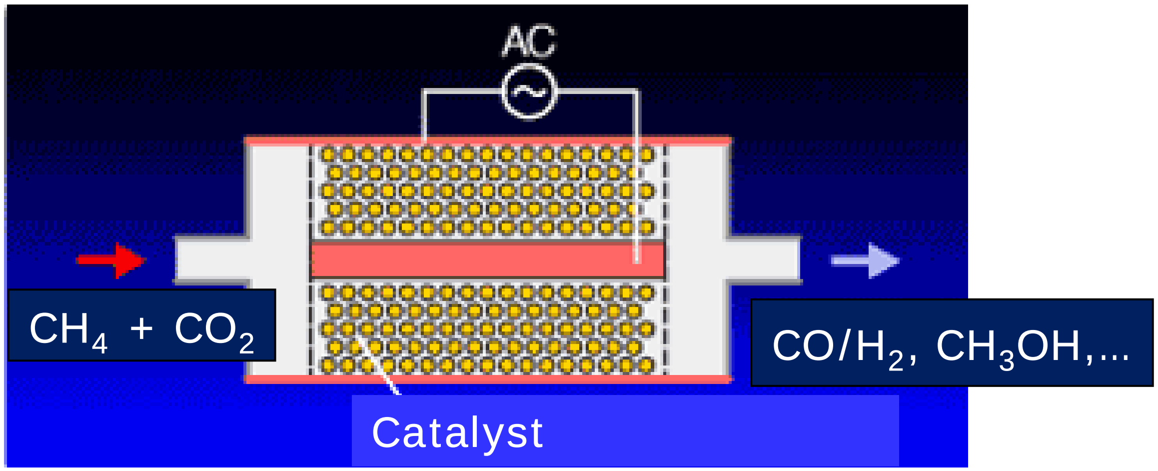
$CO_2 + 4\ H_2 \leftrightarrow CH_4 + 2\ H_2O$ (reversible, exothermic reaction)

(Electrolysis by solar/wind energy: $2\ H_2O \rightarrow 2\ H_2 + O_2$)

Power-to-gas: Storage of fluctuating solar/wind energy into fuels (synthetic natural gas, but also other: H_2, hydrocarbons,...)



Can plasma be a suitable alternative to existing (thermal) processes ?



Non-equilibrium plasma:

Energetic electrons: Dissociation of inert molecules (thermodynamically unfavorable reactions can take place)

Role of vibrational excitation !!

Moreover: plasmas can easily be switched on/off:

Suitable for temporary energy storage

But: is plasma energy-efficient enough?

Ideal plasma ?

Low temperature plasma (DBD, corona, GD,...):

High ionization cost (~ 100s eV); SER only “reasonable” if:

-Ionization products used very effectively for chemical reactions

-Significant fraction in **vibrational states**

Thermal plasma (arc, ICP):

-Ionization cost low, because mainly stepwise ionization

-But: high heating cost + to maintain high temperature (thermal losses at walls + product outflow)

Warm plasma (microwave, gliding arc, spark, APGD, microdischarge):

-T_e = 1-3 eV >> T_0 ~ 2000 K

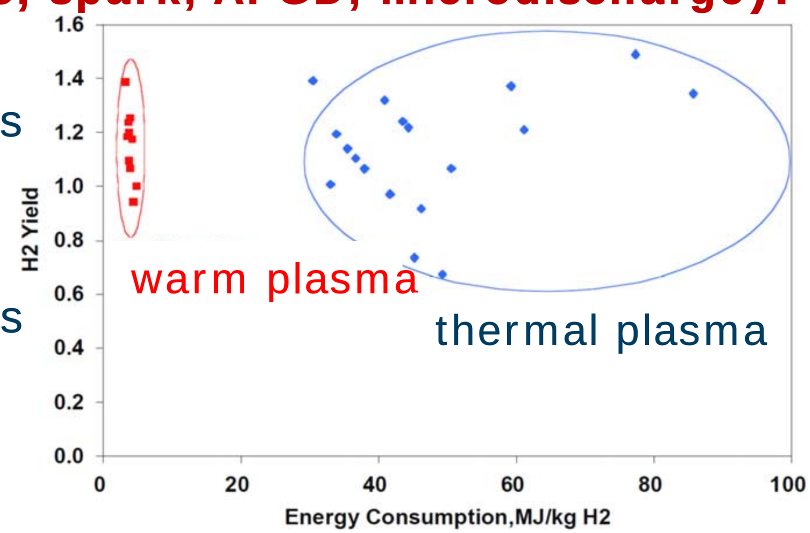
-Temp. high enough to support chem.reactions (excit.molec, stepwise ioniz.)

-Lower energy cost

-Easier to design/maintain than therm.plasmas

-Transition regime thermal/non-thermal (gliding arc, microwave moderat pressure)

(Ref: Gutsol et al., J.Phys.D, 2011)



State of the art:
plasma for greenhouse gas conversion

Some figures for CO_2 splitting

Type of plasma	Max E-efficiency (%)	Corresponding conversion (%)	Reference
Thermal plasma	43 (theoretical)	/	Fridman, 2008
Arc discharge	15	/	Polak, 1977
RF discharge (280 mTorr)	3	20	Spencer, 2011
RF discharge	60	/	Butylkin, 1981
DC glow discharge	17	1	Wang, 1999
Low pressure glow discharge	8	/	Metel, 1977
Plasma radiolysis (0.5-2 atm)	30	0.5-1	Legasov, Vakar, 1978
Low pressure plasma beam discharge	50	/	Nikiforov, 1979
Pulsed microwave (300 Torr)	60	/	Asisov, 1977
Non-equilibrium microwave (subsonic flow) (50-200 Torr)	80	/	Legasov, 1978
Non-equilibrium microwave (supersonic flow) (50-200 Torr)	**90**	/	Asisov, 1981, 1983
Microwave plasma (atm.pressure)	20	10	Spencer, 2011
Gliding arc	25	18	Indarto, 2007
Gliding arc (reverse vortex flow)	**43**	**9**	Nunnally, 2011
DBD	13	/	Paulussen, 2012
DBD	**64**	**0,66**	Michielsen, 2013
DBD	**21**	**6,66**	Michielsen, 2013

Warm plasmas (microwave, gliding arc): better E-efficiency (SEI ~ 1 eV/molec)

Experimental + calculated E-efficiencies for different plasma types

Ref: Fridman, Plasma Chemistry, 2008

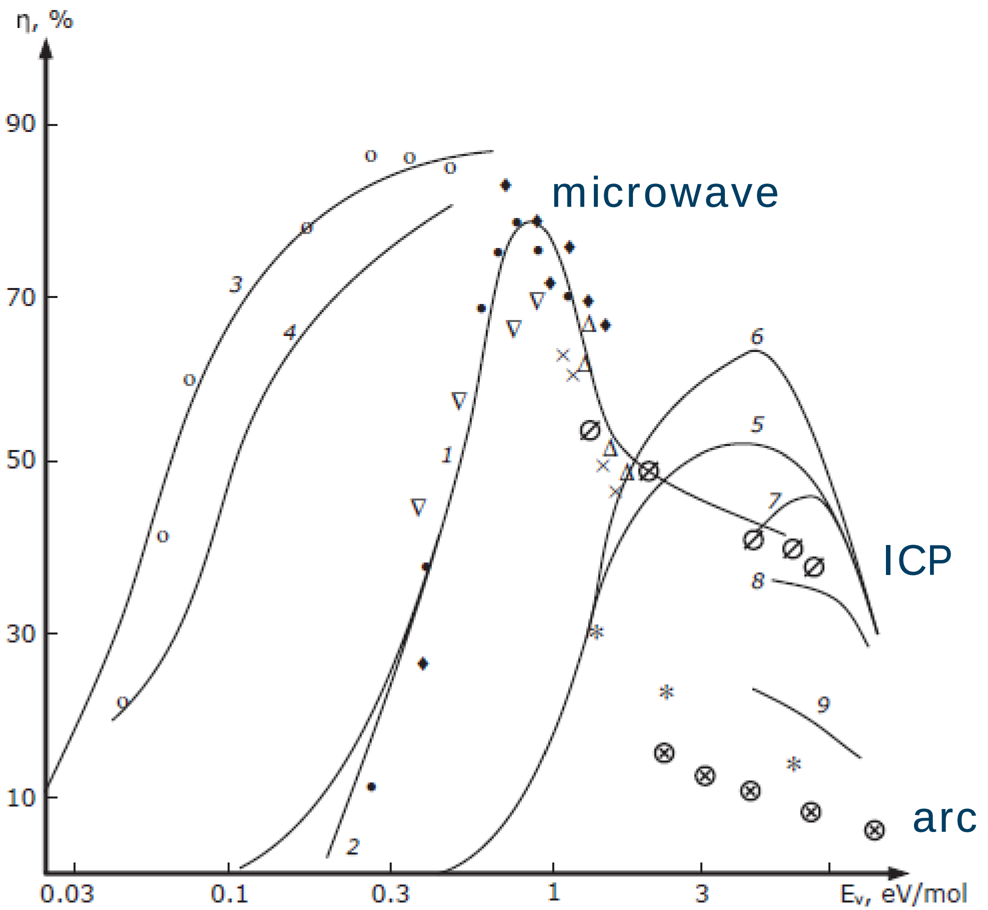
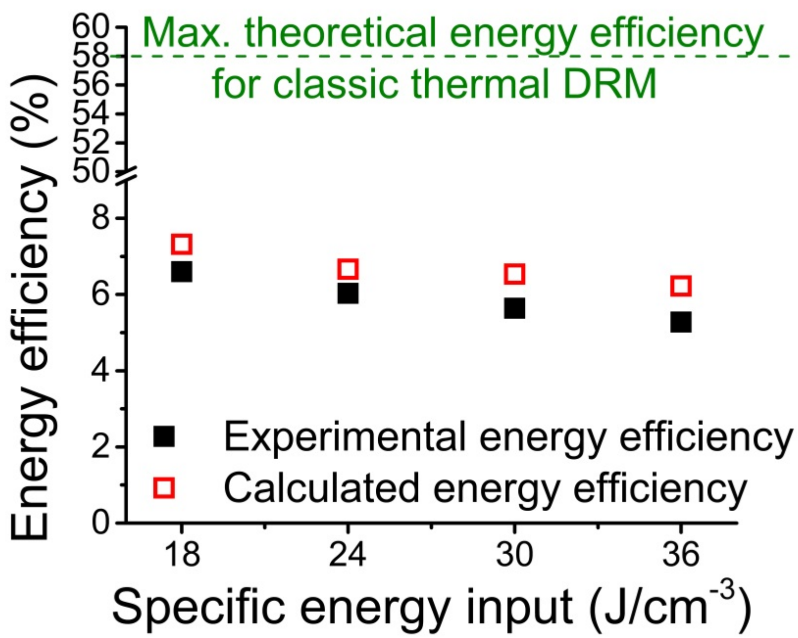


Illustration: DBD (CH_4+CO_2)

$$\text{Energy cost}\left(\frac{\text{eV}}{\text{molec}}\right)=\frac{\text{SEI (J/cm}^3)\cdot\text{plasma volume (cm}^3)\ x\ 6.210^{18}\left(\frac{\text{eV}}{\text{J}}\right)}{\text{molecules of }CH_4\text{converted}+\text{molecules of }CO_2\text{ converted}}$$

$$\eta\ (\%)=\frac{\chi\ (\%)\cdot\Delta H^0_{298K}(eV\cdot molecule^{-1})}{SEI\ (eV\cdot molecule^{-1})}$$



Highest η at lowest SIE (18 J/cm³)

$X(CH_4)$ = 16%, $x(CO_2)$ = 8%

E-cost = 35 eV/molec

E-efficiency = 7,3%

(Still ~factor 8 < classical processes)

→ **Need for Optimization**

(plasma conditions, plasma catalysis, packing, other plasmas)

Challenges for plasma technology to become an alternative to classical techniques

Energy efficiency !! (conversion, throughput)

(needs to be (at least) competitive with classical techniques)

Type of plasma (warm plasma, packed bed DBD, microplasma,...)?

Better understanding of underlying processes:

-Plasma catalysis (is there a real synergy ?)

-Role of vibrational levels, and how can we "steer" this?

(~ type of plasma)

-Effect of up-scaling

-...

Convince stakeholders of this alternative technology

(cf plasma medicine) (but first needs to demonstrate potential)

Which plasma is most suitable?

Will plasma really be able to contribute to CCU ?

(economically feasible?) **= real challenge !!**

Dr. Jean-Paul Booth
Plasma Materials Processing- Microelectronics

Plasma processing for microelectronics/materials: the future

- Large area plasmas/ uniformity
- New structures to etch / smaller features
- New materials
- Productivity
- What tools can we use?

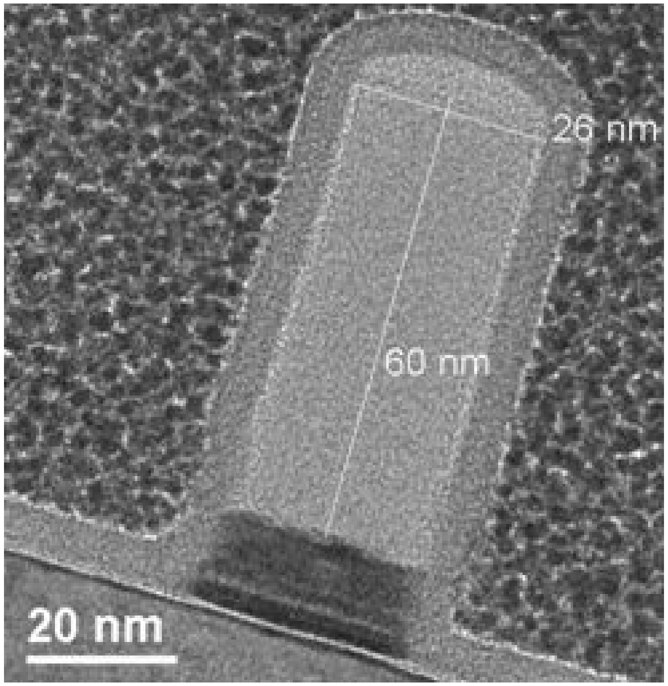
- Large area plasmas/ uniformity
  - Transition 300→450mm
  - Large area solar cells
  - Uniformity of
    - Plasma
    - Chemistry
    - Temperature

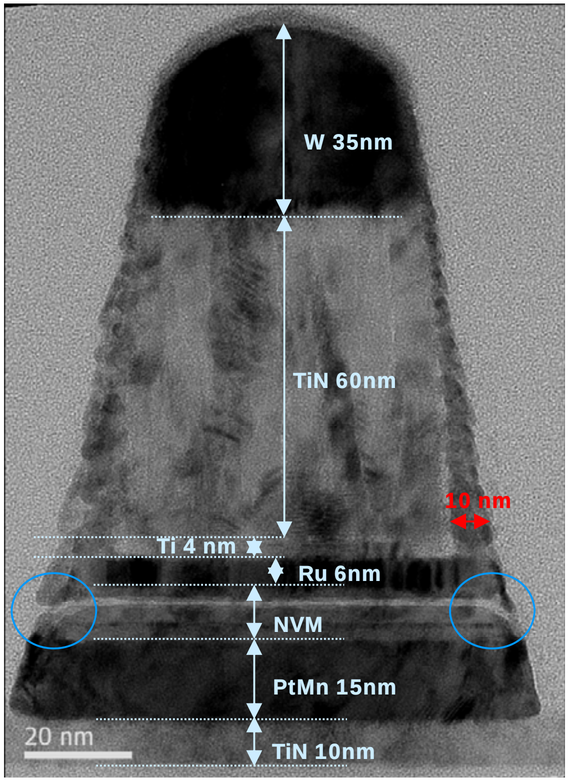
- New structures to etch:
  - finFET
  - 3D integration

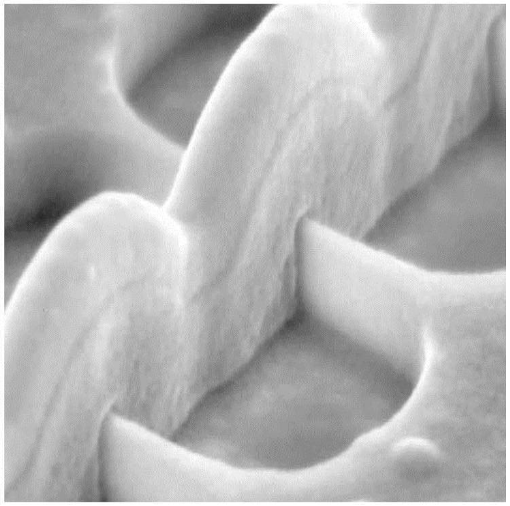
Etch challenges

Miniaturization of IC circuits

Necessity to etch nanostructures in complicated stacks of ultrathin layers







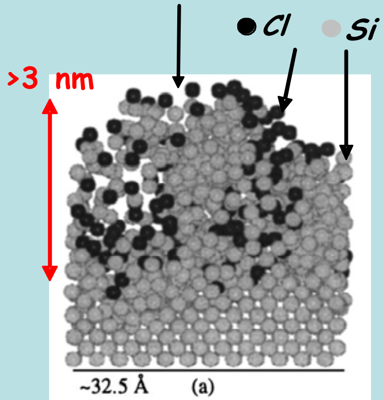
Respectivement: grille métal, MRAM et finfet

→Typical HDP plasma reactor show severe limitations
(in terms of anisotropy and selectivity)

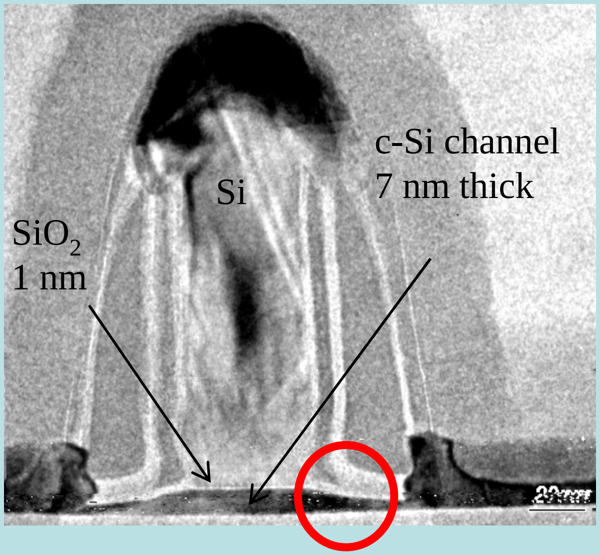
- New materials to etch:
  - non-volatile materials (high-k gates, magnetic RAM)
  - Low-k (organic) dielectrics (avoid damage)
  - Selectivity between very similar materials
  - Low damage
- Productivity:
  - plasma-wall interactions must be mastered!
  - Process control : drift, maintenance, tool lifetime

Limitations of typical CW plasmas processes

1) Ion induced damage



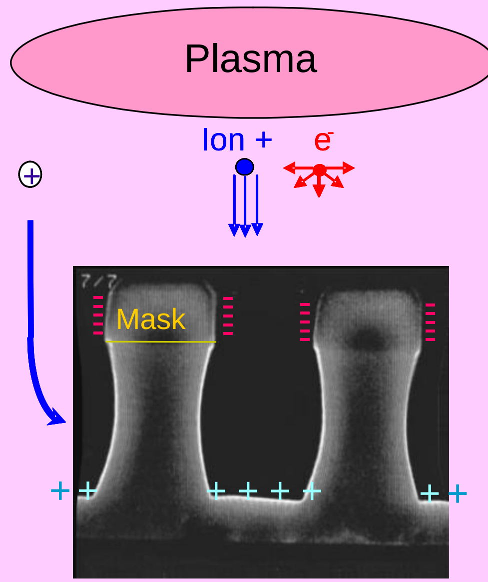
(Y. Zhang et al, PESM 2011)

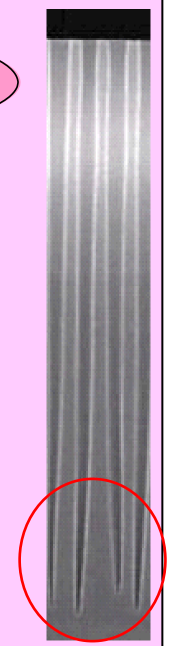


Ion energy > 15 eV

➔Issue to etch stacks of ultrathin layer

2) Charging effects





➔ Profile control issue

Today's etching processes are not adapted to nanometric dimensions (vertical, lateral)

Tools we can use:

- Ion energy control
  - Critical applications:
    - ultra-low energy etching : graphene, gate dielectrics
    - ultra-low energy deposition : photo-voltaics
    - Chamber cleaning / conditioning processes
- EEDF control
- Solutions :
  - Pulsed plasmas
  - Frequency (VHF, microwave...)
  - Electrical Asymmetry effect/ Tailored waveforms
- Reactor and process design via modeling:
  - Achieve model maturity :
    - systematic comparison to sophisticated diagnostics
    - Start with simpler, archetype systems

Prof. Peter Bruggeman
Biotechnology and Liquids

Low temperature plasmas: our discipline in 2030

plasma and liquids – biomedical applications

Peter J. Bruggeman

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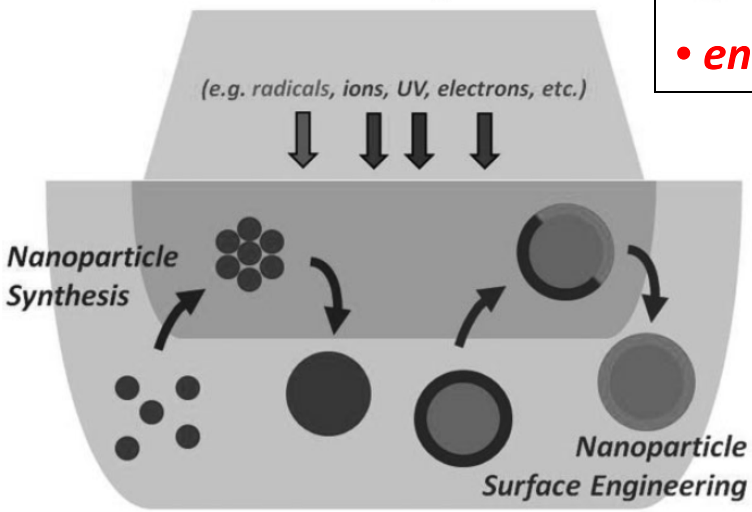
The status of the applications

- *synthesis*
- *medicine*
- *environmental*



Mariotti et al PPP (2012) (9) 1074-1085

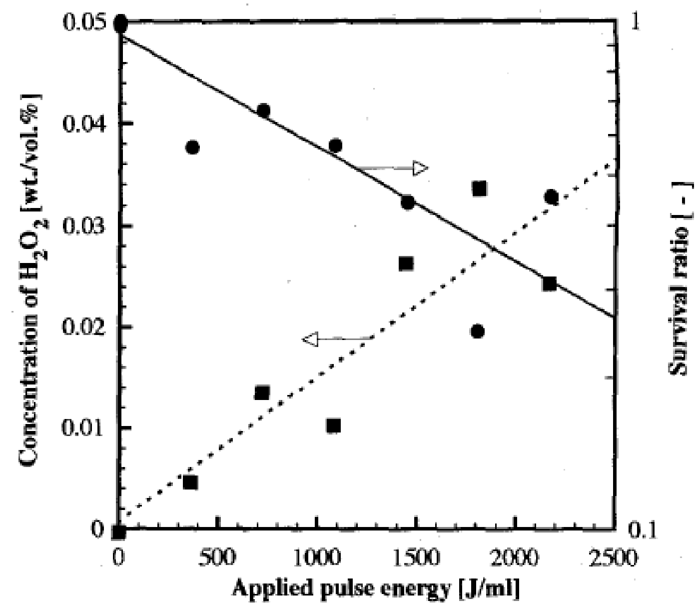


Fig. 9. Cell survival ratio and H_2O_2 concentration in distilled water as a function of total pulse energy applied (pulse voltage: 19 kV).

Sato M et al (1996) IEEE Trans. Ind. Appl. **32** (1) 1996

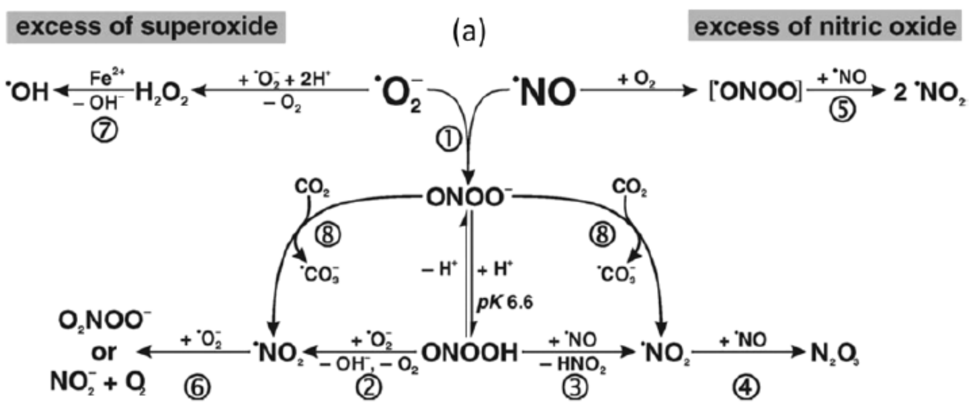
(J. Heinlin et al. 2010)

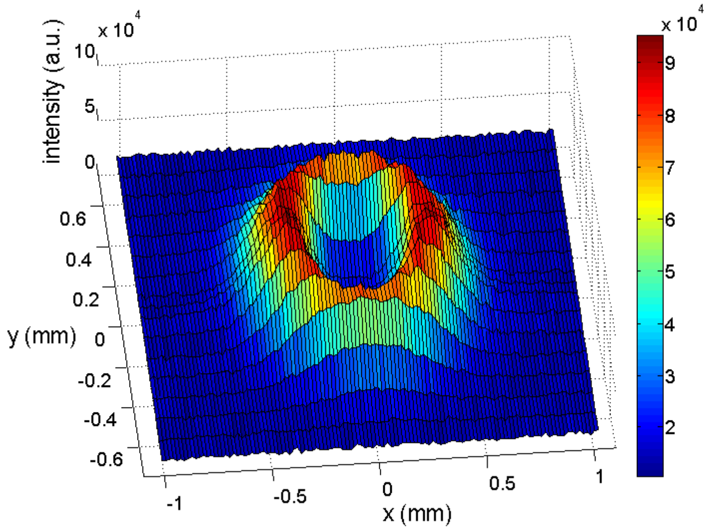
- *promising opportunities*
- *few technologies emerged*
- *large expectations*

What is known?

Necessities:

- the efficient production of reactive species (UV, shockwaves,…)
- efficient transport of the reactive species (to liquid phase / biosample)
- specificity of certain species (ROS-RNS)

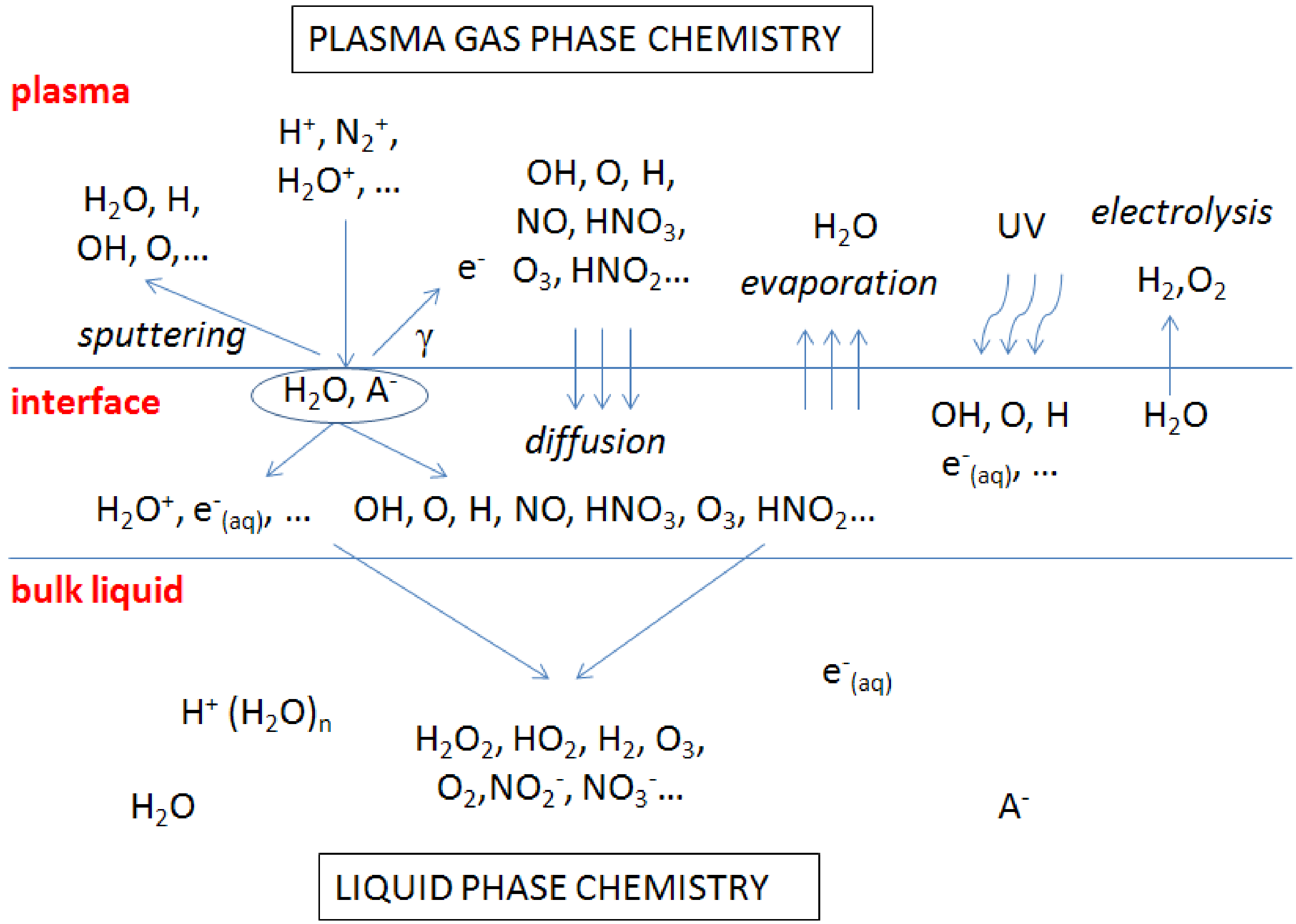




Tools:

- basic chemistry models
- extensive set of plasma gas phase diagnostics
- limited amount of (selective) liquid based diagnostics

Plasma chemistry vs. liquid chemistry



WOUND TISSUE

Samukawa, Hori, Rauf, Tachibana, Bruggeman et al, The 2012 Plasma Roadmap, J. Phys. D (2012)

Key challenge: application control

plasma control → electric excitation

→ gas composition

electron kinetics

gas heating

non-equilibrium chemistry

reactive species and short lived radicals

transport – interfaces

application

Source design and optimization

Laser scattering

Optical emission spectroscopy

Absorption and fluorescence techniques

Mass spectrometry

Development efforts necessary

Interdisciplinary research

What is the challenge for plasma physics – chemistry within the framework of the application?

Plasma as `handoff` technology for biomedical field or `every day` role of plasma engineer necessary?

(coupling between bio-sample and plasma properties)

Necessities

Diagnostics:
- more reliable diagnostics for mapping electron kinetics
- standards in interpretation of non-equilibrium characteristics of plasmas
- development of more selective liquid based diagnostics
- time resolved liquid based diagnostics
- techniques to monitor in situ the plasma-liquid/wound interface

Modeling:
- cross sections and rate coefficient (in liquid and gas phase)
- rates and yields of reactive chemistry at the liquid interface (ions, neutrals, UV,…)
- interface models including heat and mass transfer
- clarity in assumptions / access to data used in models

Applications:
- simplified relevant reference application case studies
- reference conditions (comparison between different groups)
- is there an adequate physical language to describe bio-experiments?

Prof. Walter Lempert
Combustion and Aeronautics

Low Temperature Plasmas have been demonstrated to enhance a variety of flow and combustion phenomena including:

- Reduction in ignition delay time.
- Increase in laminar flame speed.
- Increase in extinction strain rate (turbulent combustion).
- Increase in lean flammability limit.
- Distributed ignition (improved "spark plugs")
- Reduction in NO_x.
- Enhanced mixing.
- Boundary layer flow acceleration – separation control (thermal and non-thermal).
- Shock control.
- Acoustic noise abatement.

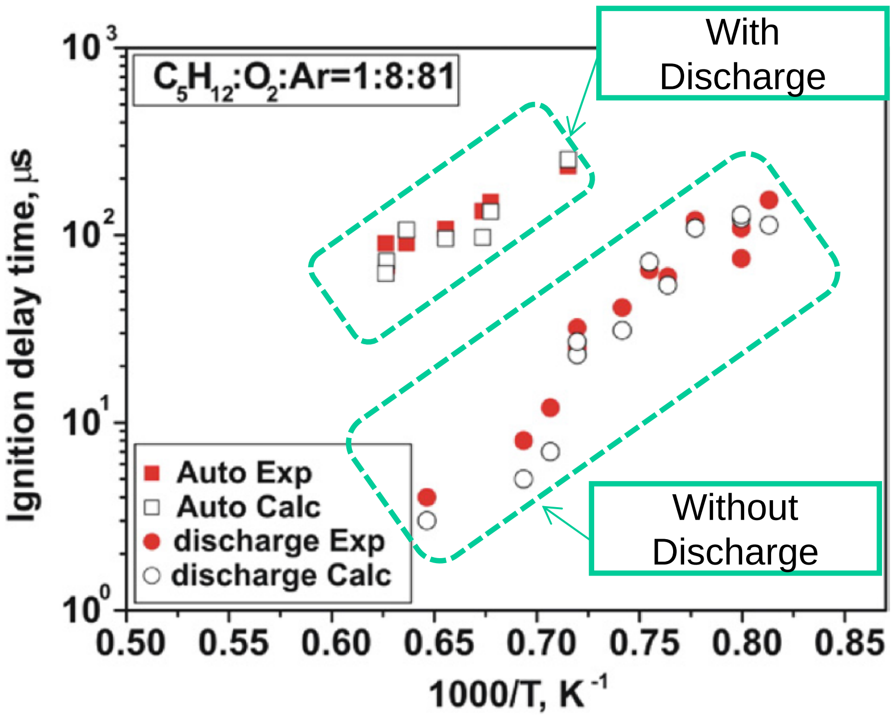
But Fundamental Understanding is Often Lacking or Incomplete.

Some Recent Examples

The Ohio State University *Nonequilibrium Thermodynamics Laboratory*

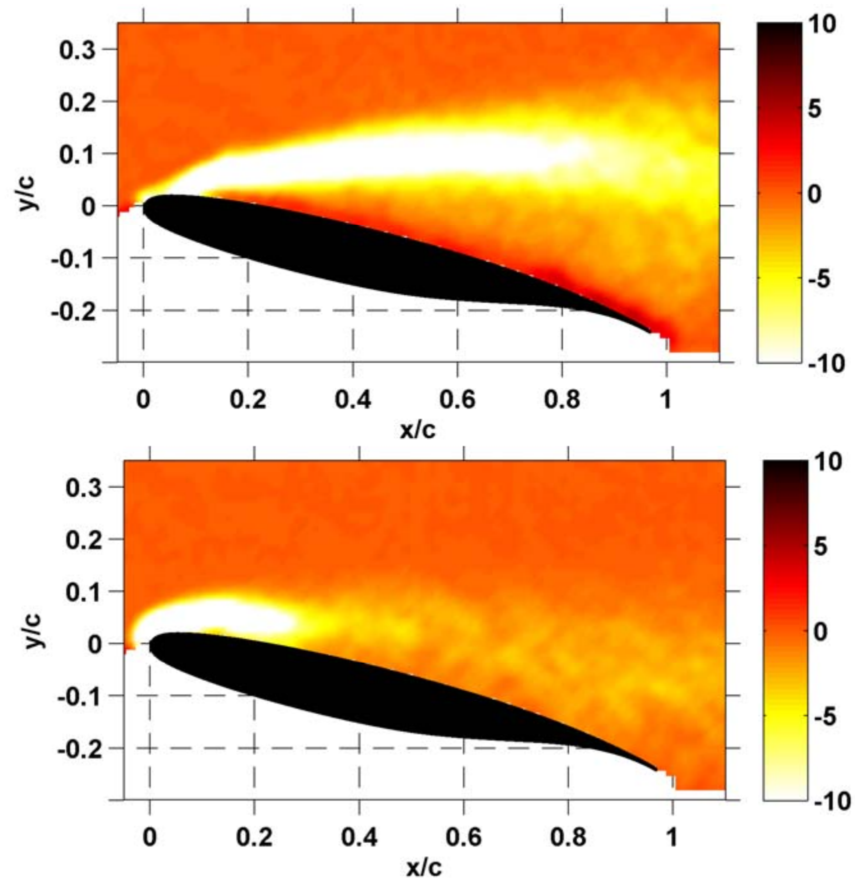
Ignition Delay Reduction by Nsec Pulsed Discharge

(Kosarev et al., Combust. Flame, 2009)



NS Surface DBD - 45 m/sec (thermal interaction)

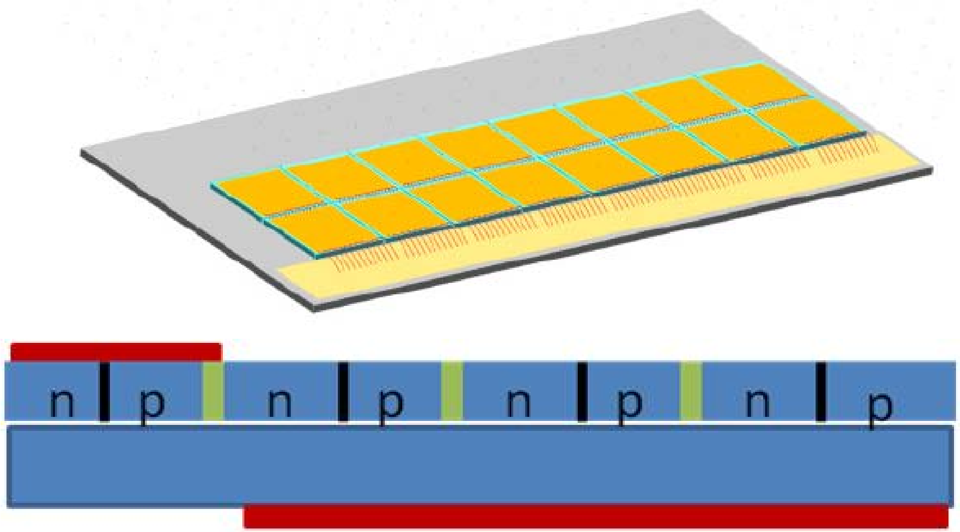
Little et al, AIAA J., 2012



Some Opportunities and Future Directions
(Plasma Aerodynamics)

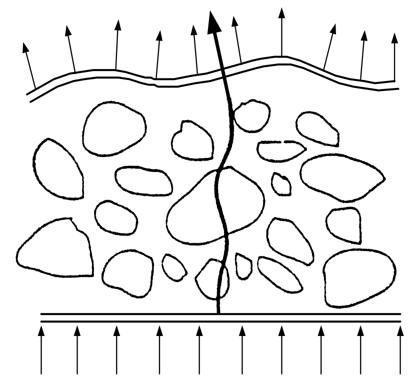
The Ohio State University *Nonequilibrium Thermodynamics Laboratory*

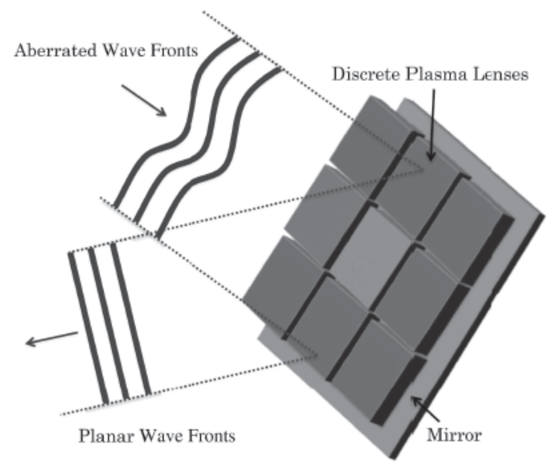
Surface NS SDBD Diode Array
(Miles, Starikovskiy, Princeton)



i. Rising edge of ns pulse creates propagating wave on surface, producing "forward" momentum transfer to boundary layer flow.
ii. Falling edge creates return current path within array, suppressing "backwards" boundary layer momentum transfer (ie, cancellation).

Plasma Aero-Optics
(E. Jumper, T. Corke, Notre Dame U.)



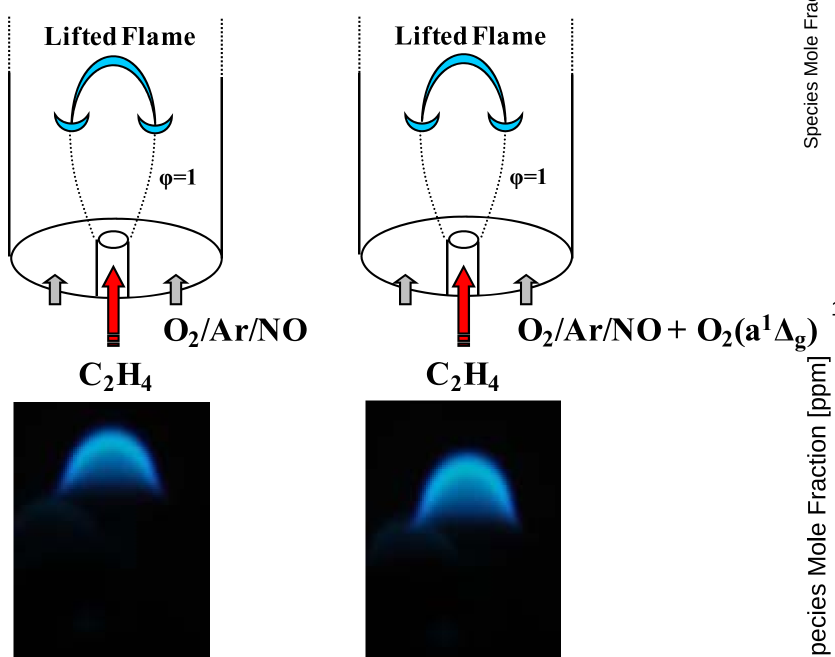


Some Opportunities and Future Directions
(Plasma Assisted Combustion)
NEQ Kinetic Mechanisms (Radicals, Excited Electronic/Vibrational States)

The Ohio State University — *Nonequilibrium Thermodynamics Laboratory*

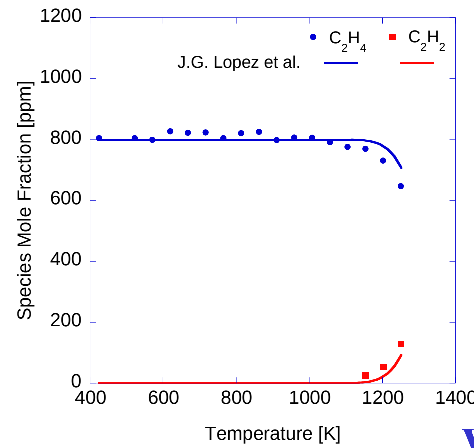
Effect of O_2 ($a^1\Delta_g$) on flame propagation speed
(T. Ombrello, AFRL – WPAFB)

$C_2H_4/O_2/Ar$ at 6.7 kPa



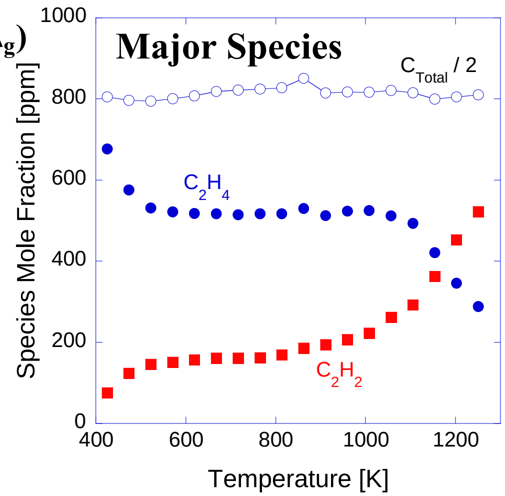
Non-Equilibrium Fuel Pyrolysis/Reforming
(R. Yetter – Penn St)

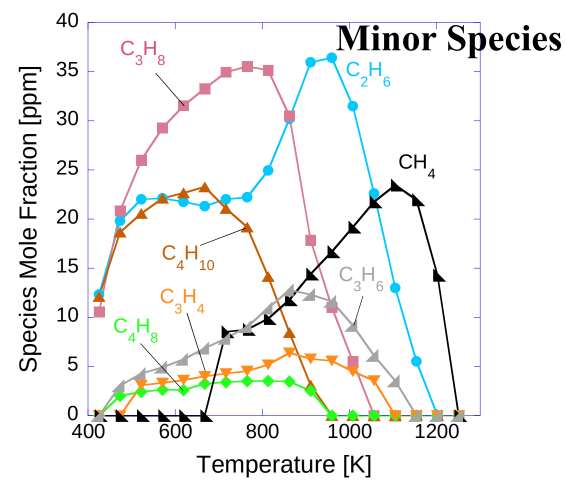
Baseline (Thermal)



- **Thermal pyrolysis initiates at T ~1100 K.**
- **Plasma reduces onset to ~400 – 500 K.**
- **Plasma generates multitude of minor species at T < 500 K.**
- **Could alleviate need for catalyst.**

With NS Plasma

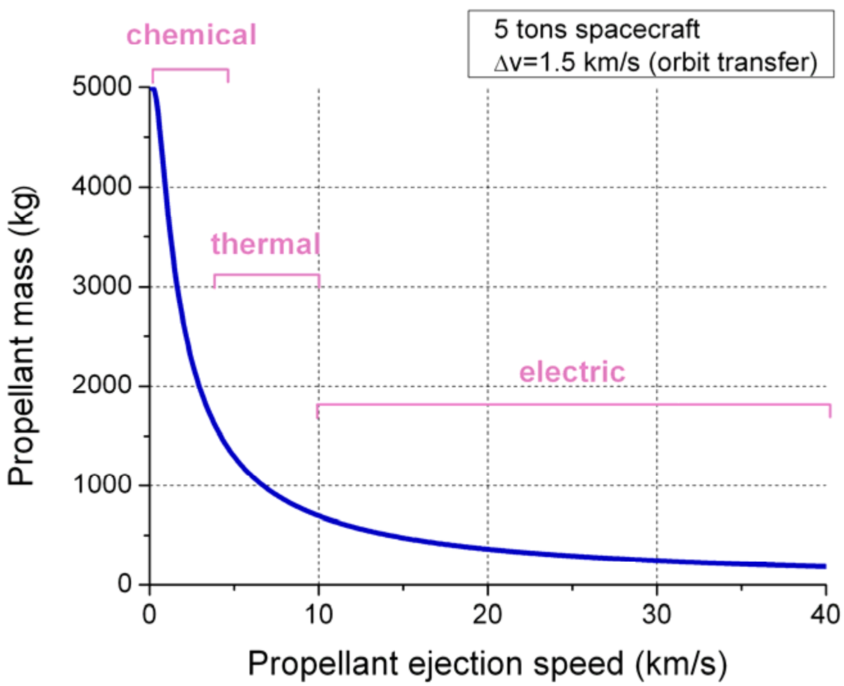




Dr. Stephane Mazouffre
Space Plasmas and Propulsion

Electric space propulsion - Basics

EP: high propellant ejection velocity
→ main advantage: low propellant consumption

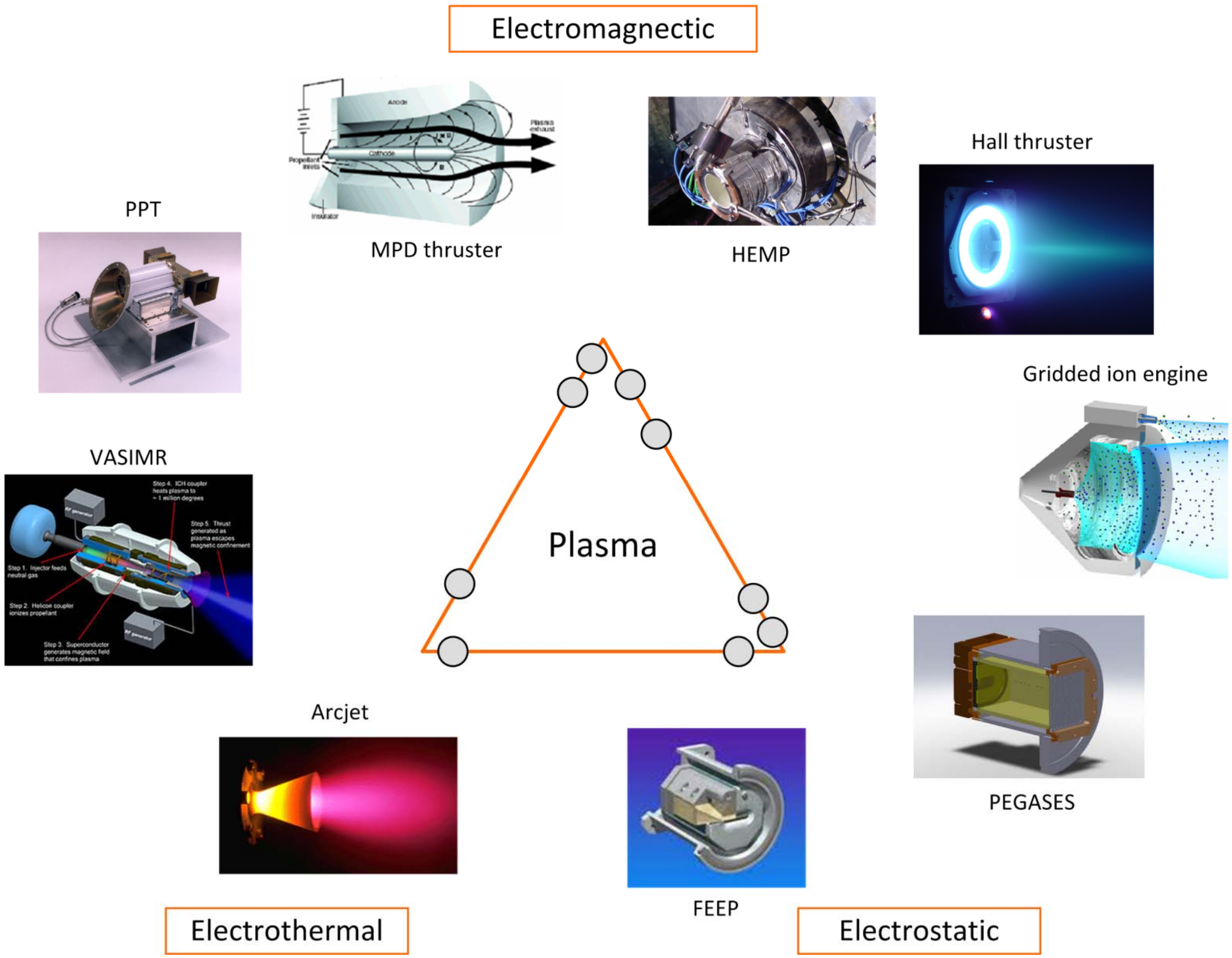


EP characteristics

Advantages
High specific impulse
Long operation period
High efficiency
Ignition, Flexibility

Drawbacks
Low thrust level
Complexity
Propellant type
Power sources

Electric space propulsion - Classification



Electric space propulsion - Status

Current status

Technologies

Many, yet HT and GIE dominate
Moderate Thrust and Isp
Xenon propellant
Moderate power
Short lifetime
Plume/spacecraft interactions

Missions/Maneuvers

Station keeping, attitude control
Satcom orbit transfer
  NEOSAT, ELECTRA
First exploration trips

→ growing role of EP

Mid/Long term objectives

Technologies

Other concepts
Large thrust, large T/P, high Isp
Clusters
New propellants
Low interaction: Neutral beams?
High power: Nuclear?

Missions/Maneuvers

Create a broad market
High ΔV missions
  quick orbit transfer
  deorbiting (space debris)
  interplanetary, exploration

Electric space propulsion – Plasma physics PoV

High efficiency ions sources (low pressure magnetized discharges) in Ar, Iodine, Bi, H_2, He

- transport phenomena, instabilities
- discharge control and stabilization

Magnetic nozzle / plasma detachment

Plasma-wall interactions (role of SEE, etching)

Physics of ion-ion plasmas

Extraction/acceleration of ion-ion plasmas

Neutralization

Electric space propulsion – Plasma physics PoV

Modelling and numerical simulation

for source, beam, beam-spacecraft interaction

- towards self-consistent 3D PIC codes
- tools for deisgn and optimization

Diagnostics

non intrusive technique (e.g. EEDF acquisition) with high temporal resolution

examination of PSI

Power sources

high-efficiency solar-cells

Fusion reactor (compact)

Prof. William Graham
“The Big Picture”