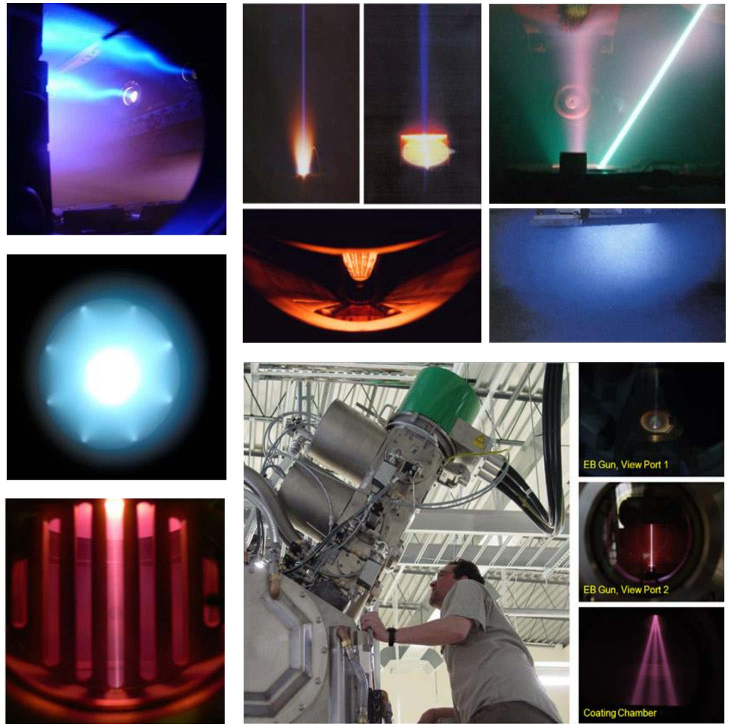
POTENTIAL OF ELECTRON BEAM SUSTAINED HYBRID PLASMAS FOR POWER-TO-X PROCESSES: AN OUTLOOK

David J. Schreuder, Lars Dincklage, Burkhard Zimmermann, Ralf Blüthner, Björn Meyer, Gösta Mattausch

Source: BMBF - KOPERNIKUS



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DEPARTMENT “CUSTOMIZED EB SYSTEMS AND TECHNOLOGIES”

Head: Prof. Dr. Gösta Mattausch

- **Team CEB** (customized electron beams):

  Dr. Burkhard Zimmermann
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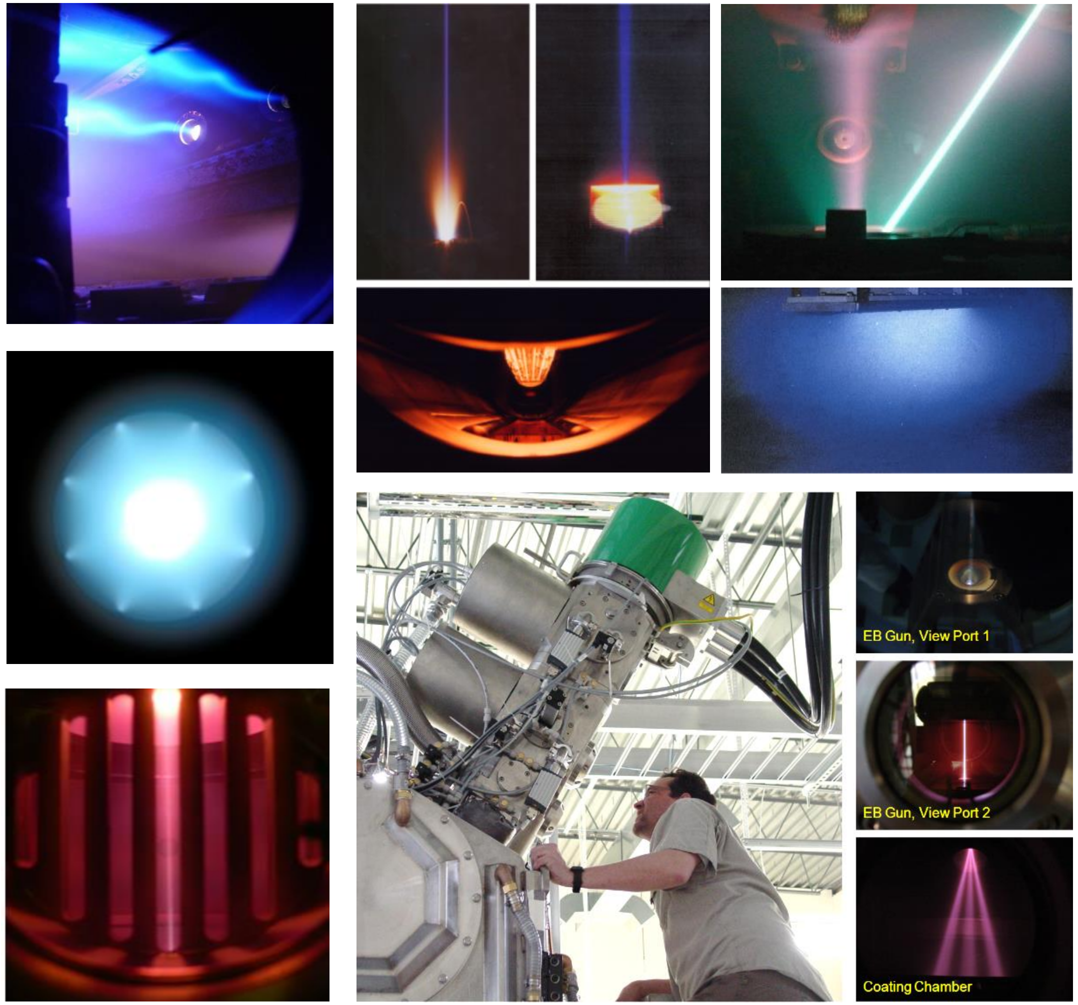
- **Team NTH** (non-thermal applications):

  Dr. Tobias Teichmann
  Ralf Blüthner, André Poremba,
  Lotte Ligaya Schaap (D), David Schreuder (D)

Topic of today:

- Non-thermal plasmachemical conversion through EB-assisted hybrid plasmas



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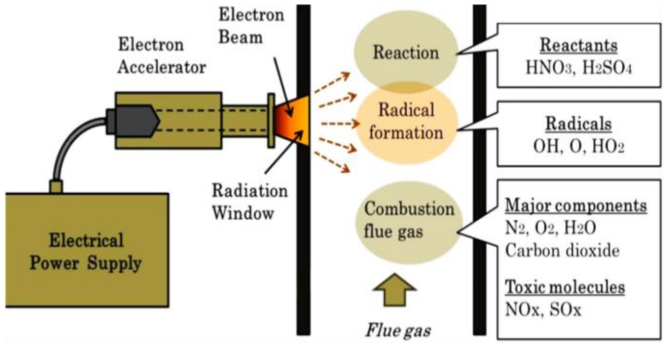
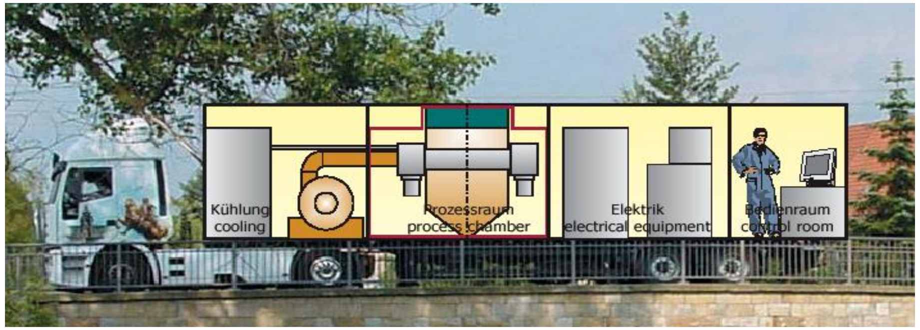
NTH - Technologies:

Electron Beams for Green Technologies

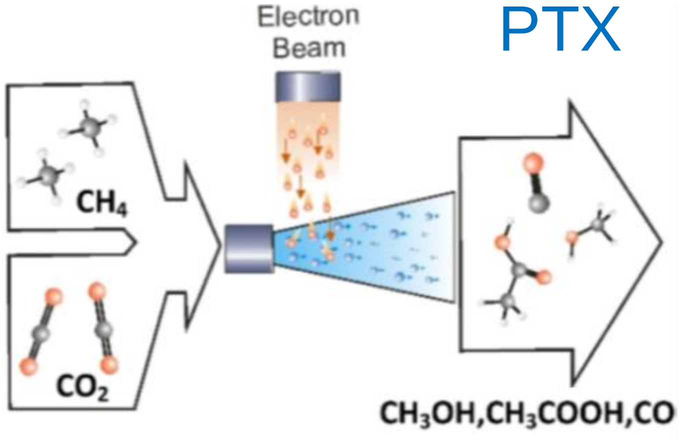
Exhaust Gas Cleaning



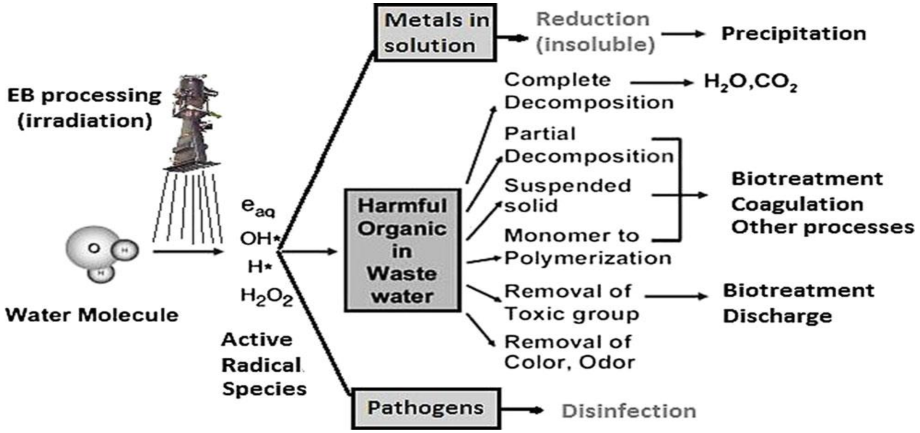
Sustainable Agriculture



EB-Plasma Chemistry PTX



Waste Water Treatment

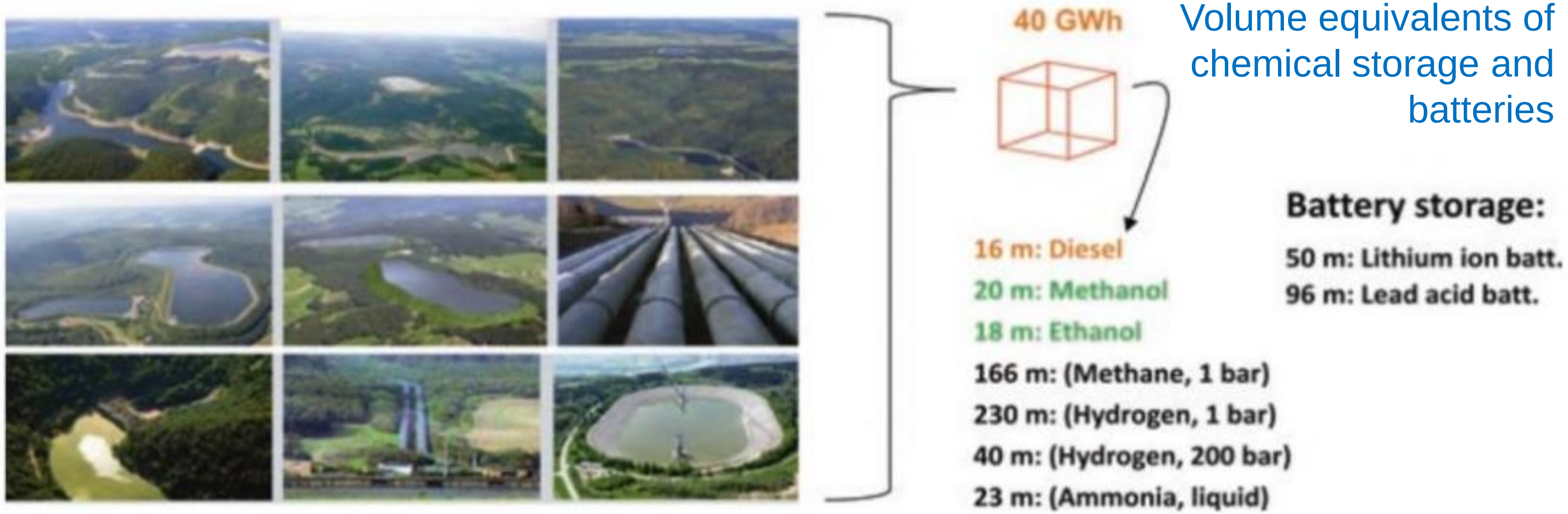


Synthetic chemical energy

… is essential for a succesfull energy transition and defossilization

- Seasonal balancing of the fluctuating solar – and wind energy requires inexpensive high-density energy storage
- Energy-intensive sectors such as aviation and shipping industry
- Carbon cycle: CO_2 as a starting material for synthesis of basic chemicals

Volume equivalents of chemical storage and batteries

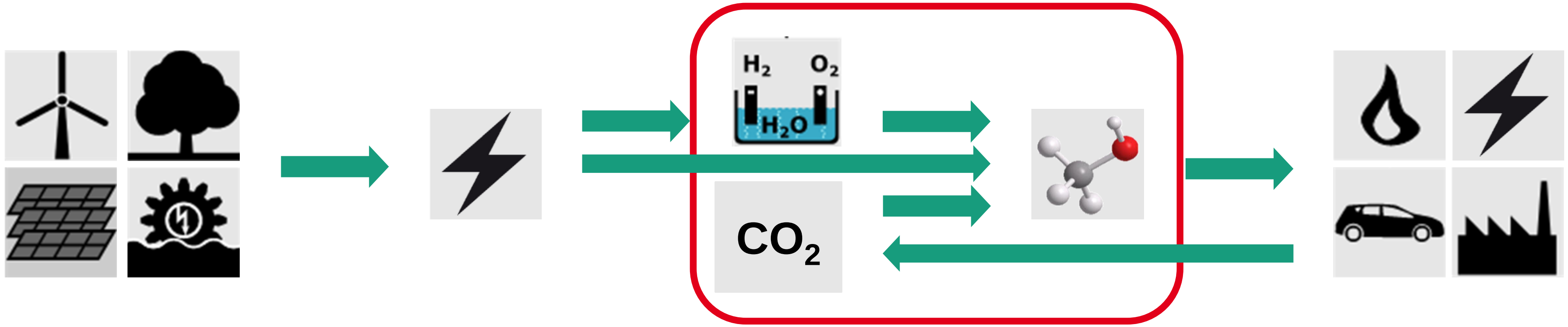


Capacity of pump storage plants in Germany: 40 GWh

Required capacity for complete electrified industry in Germany: 40.000 GWh

Wolfgang Maus (2019)
Zukünftige Kraftstoffe: Energiewende des Transports als ein weltweites Klimaziel.
Springer-Verlag

POWER-TO-X: CONVERSION OF RENEWABLE ENERGY IN CHEMICAL ENERGY



$CO_2 \rightarrow CO + \frac{1}{2} O_2$

- Demands for efficient Power-to-X process:
  - High reaction process efficiency for high solar-to-fuel efficiency
    - Target CO_2 conversion process efficiency: ~60%
  - Flexibility in operation conditions (fluctuation renewable energy)
    - Establishing a `turn-key process‘

CHEMICAL CONVERSION REACTIONS WITH CO_2 – COREACTANTS

- Ideally, chemical energy synthesis is achieved for
  - Reactions with a high gain in enthalpy
  - Bridge technology: dry reforming of methane

PHOTOSYNTHESIS:	$CO_2 + 2\,H_2O \rightarrow CH_3OH + 3/2\,O_2$	$\Delta H^0 = +\,676$ kJ/mol
ELECTROLYSIS:	$2\,H_2O \rightarrow 2\,H_2 + O_2$	$\Delta H^0 = +\,572$ kJ/mol
SPLITTING:	$CO_2 \rightarrow CO + 1/2\,O_2$	$\Delta H^0 = +\,283$ kJ/mol
DRY REFORMING OF METHANE (DRM):	$CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2$	$\Delta H^0 = +\,247$ kJ/mol
PARTIAL HYDROGENATION:	$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$	$\Delta H^0 = -\,50$ kJ/mol
SABATIER-PROCESS:	$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$	$\Delta H^0 = -\,165$ kJ/mol

METHODS FOR POWER-TO-X

	Use of rare earth metals	Renewable energy	Turnkey process	Conversion and yield	Separation step needed	Oxygenated products (e.g. alcohols, acids)	Investment cost	Operating cost	Overall flexibility
Traditional catalysis	Yes	-	No	High	Yes	Yes	Low	High	Low
Catalysis by MW-heating		Indirect						Low	Low
Electro-chemical	Yes	Indirect	No[b]	High	Yes[c]	Yes	Low	Low	Medium
Solar thermo-chemical	Yes	Direct	NA	High	No	No	High	Low	Low
Photo-chemical	Yes	Direct[a]	Yes	Low	Yes	Yes	Low	Low	Low
Biochemical	No	Direct[a]	No	Medium	Yes[d]	Yes	High /low	High	Low
Plasma-chemical	No	Indirect	Yes	High	Yes[e]	Yes	Low	Low	High

Overview of traditional thermal catalysis and the different emerging technologies, indicating their distinctive key advantages and disadvantages

Bogaerts, A., Snoeckx, R.; *Chem. Soc. Rev.*, **2017**, 46 (19)

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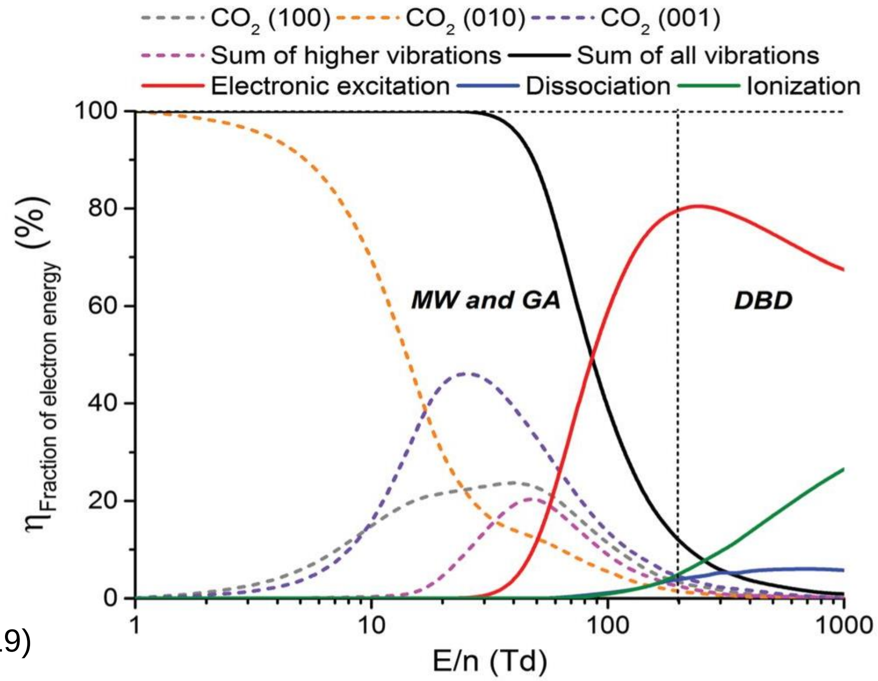
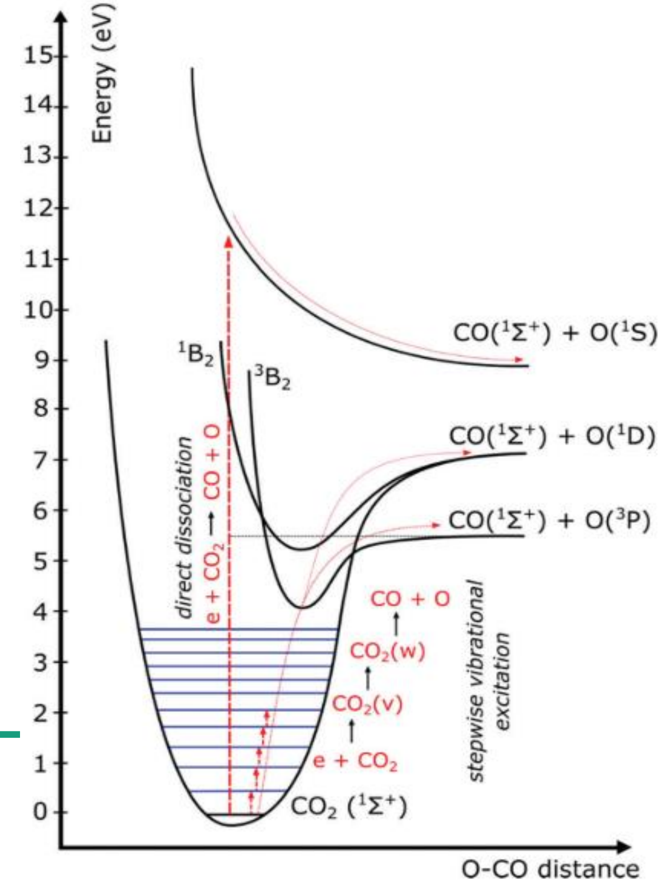
Td = Townsend = 10^{-17} V cm²

- *Hence, the same applied field E [V/m] at increased particle density n [cm³] results in a lower reduced electric field*
- *Geometry of discharge gap and pressure determine required field for plasmachemical processes ('pd parameter')*

- Non-equilibrium plasmas:
  $(T_e) >> (T_g)$
- Energy transfer pathways dependent on reduced electric field strength E/n [Td]
  - for small E/n mainly vibrational excitation
    - efficient stimulation of (endothermic) CO_2 conversion reactions
- Vibrational-induced dissociation requires:

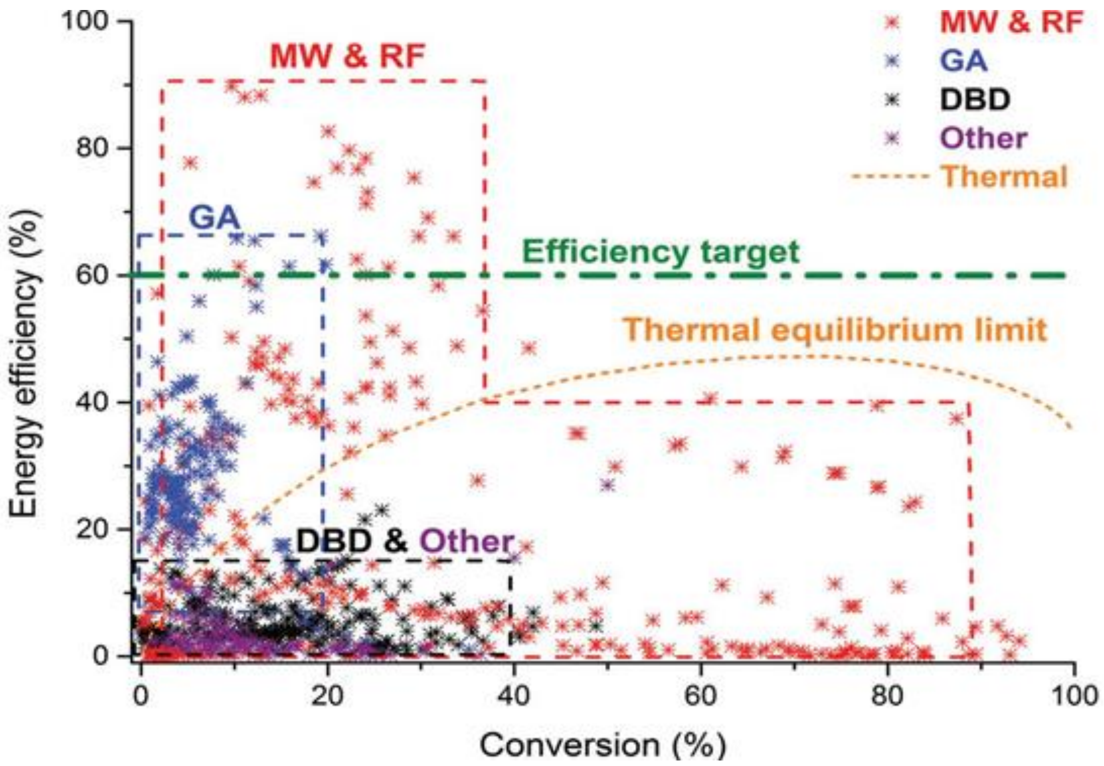
$$\frac{n_e}{n_0} \gg \frac{k_{VT}(Tg)}{k_{eV}(Te)}$$

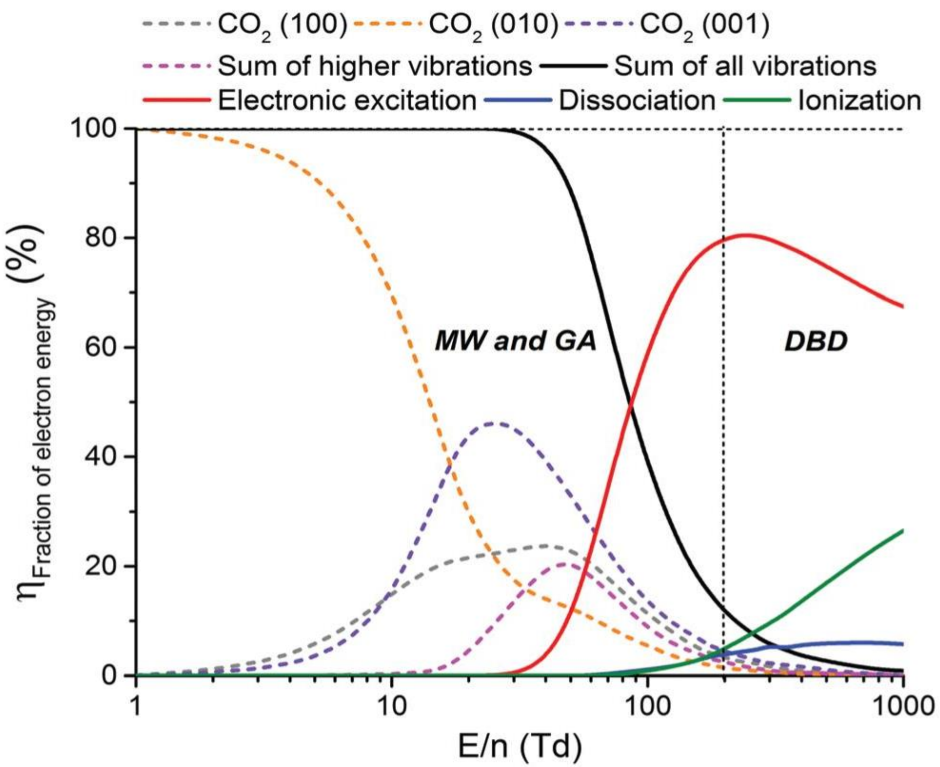




Figures: Bogaerts, A., Snoeckx, R.; *Chem. Soc. Rev.*, **2017**, 46 (19)

ENERGY EFFICIENCY AND CONVERSION DEGREE FOR NON-EQUILIBRIUM PLASMACHEMICAL CONVERSION





- *Conversion degree (%)*
  the amount of CO_2 molecules converted as a fraction of the total CO_2 particles
- *Energy efficiency (%)*
  the fraction of energy input being utilized in conversion of CO_2

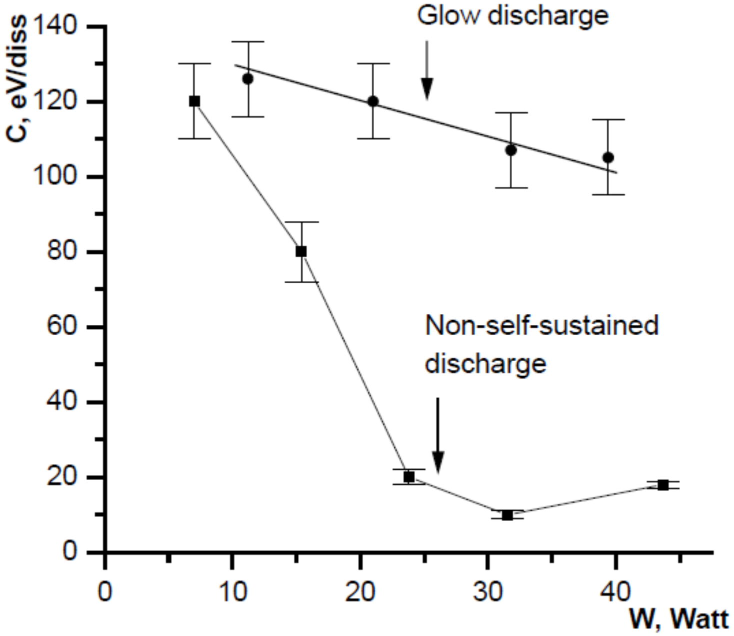
Bogaerts, A., Snoeckx, R.; *Chem. Soc. Rev.*, **2017**, 46 (19)

LIMITATIONS OF CURRENT PLASMACHEMICAL POWER-TO-X METHODS

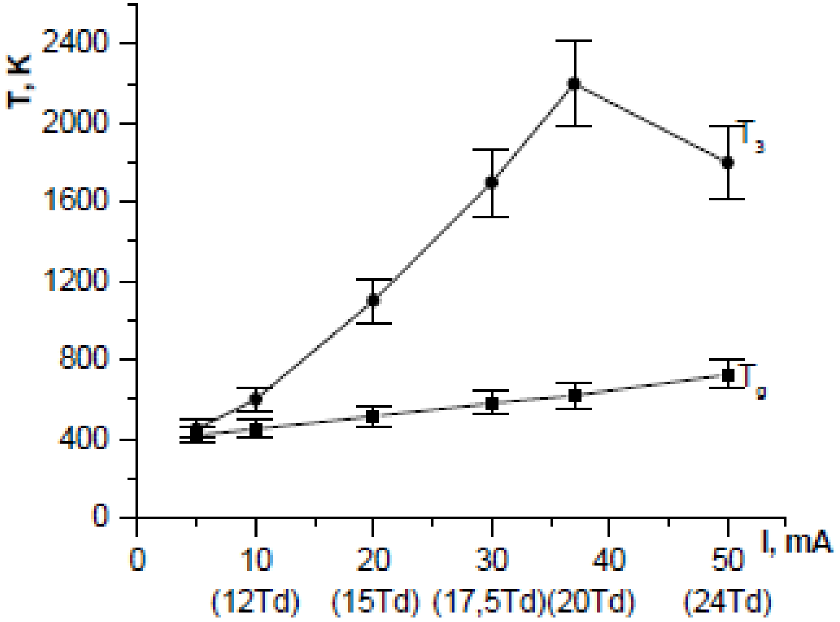
- Trade-off energy efficiency and conversion:
  not able to simultaneously obtain a high conversion degree and energy efficiency
  - Vibrational excitation and ionization occur at a different energy
    (< 0.4 eV and >10 eV, respectively)
- When increasing pressure: plasma contraction → lower non-equilibrium degree
  → disrupts energy efficient dissociation pathway
  - Ionization-overheating instability:
    local increases in gas temperature T_g causes for more heating (positive feedback mechanism)
    - Increased gas temperature
      → loss of energy stored in vibrational modes and faster back reactions
- Solution:
  - **External ionized discharge = non-self-sustained discharge = hybrid discharge**

RESEARCH EXAMPLE CHEMICAL CONVERSION BY NON-SELF-SUSTAINED DISCHARGES

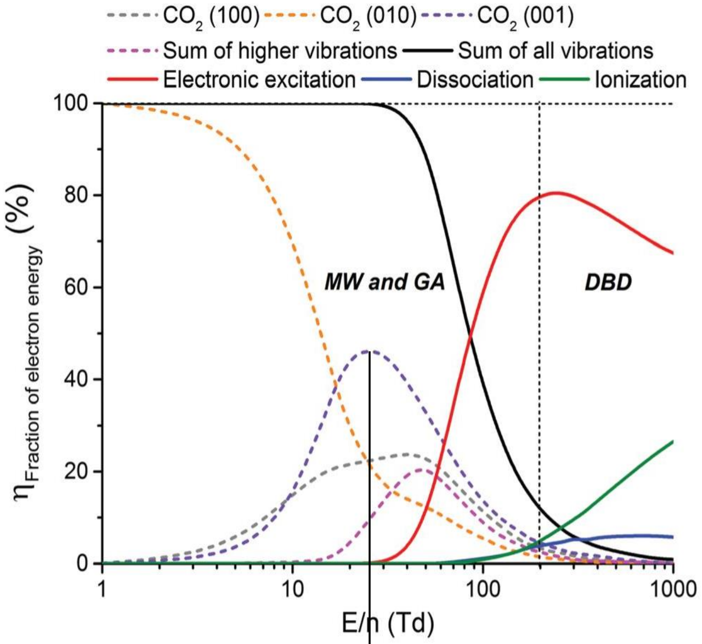
- **$CO_2 \rightarrow CO + ½ O_2$**



Energy cost per dissociation as a function of DC discharge power for a self-sustained and a non-self-sustained discharge.(1)



Increase in the translational temperature (T_g) and vibrational temperature (T_v) as a function of plasma current (reduced field strength.(1)



Optimal E/n for vibrational excitation

Ext ionization: high voltage pulse (10 kV, 0,5 µs)
Additional source: DC
Pressure: 1550 Pa

(1) Andreev, S.N., Zhakarov, V.V., Ochkin, V.N., Savinov, S.Y.; *Spectrochim. Acta A*, **2004**, 60, 14, pp. 3361 – 3369.

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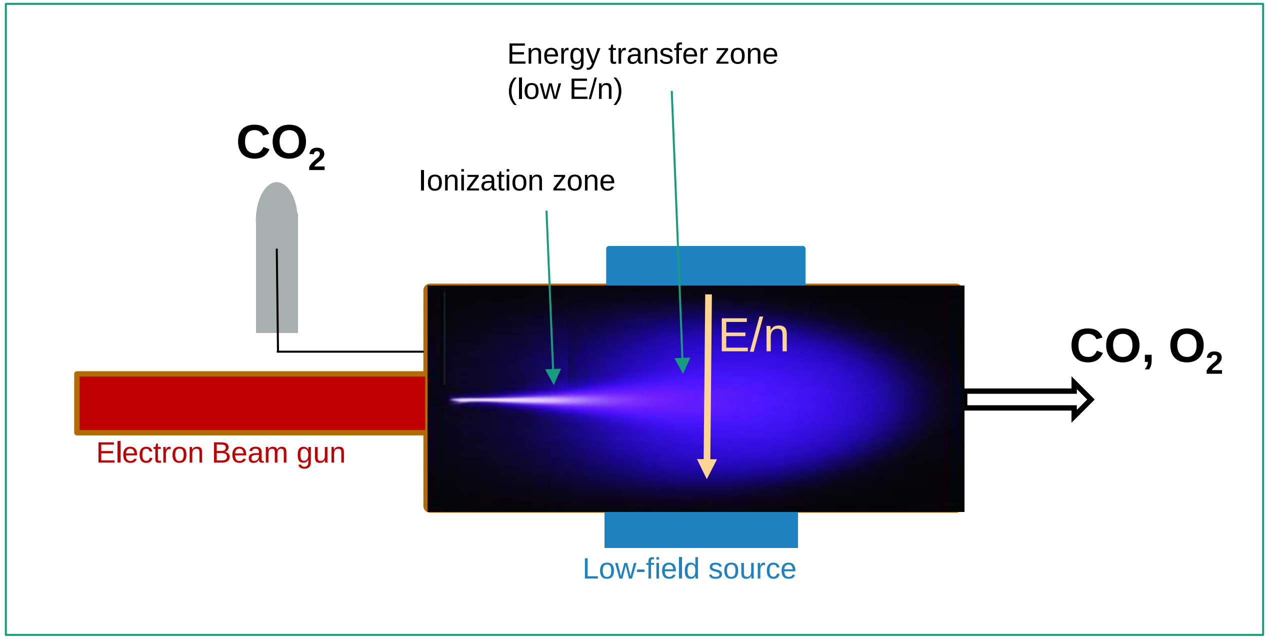
NON-SELF-SUSTAINED USING ELECTRON BEAM TECHNOLOGY

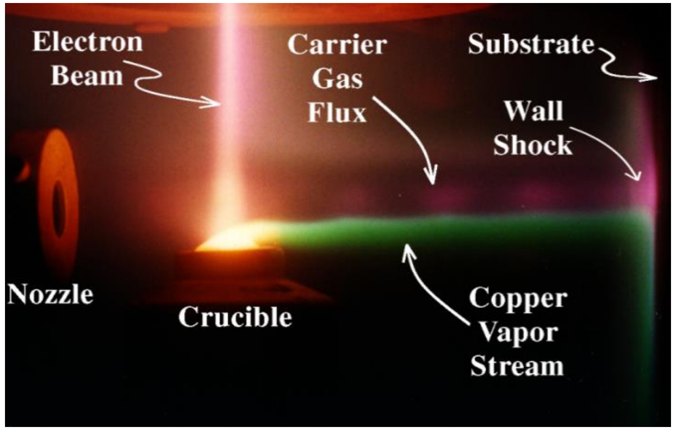
- Chemical dissociation promoted through external ionization and additional coupling of energy to free electrons source
  - External ionization: high degree of ionization → high conversion degree
  - Additional source: reduced fields (E/n) → vibrational excitation → energy efficient dissociation



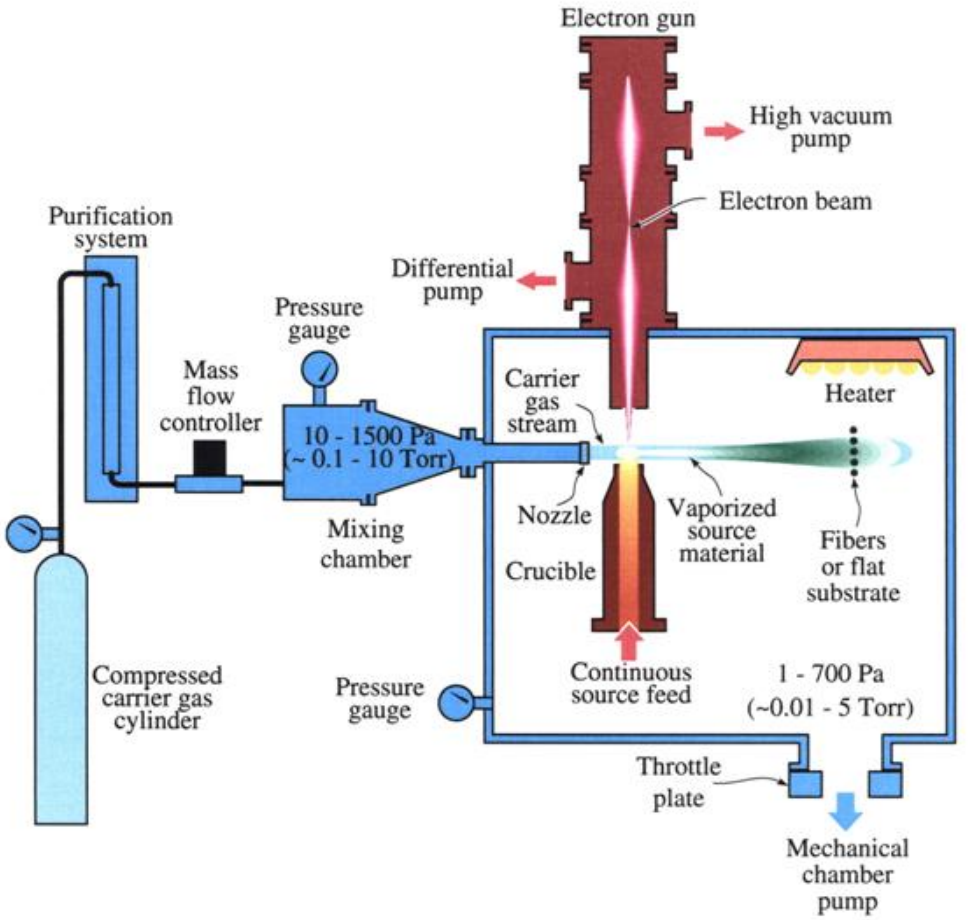
Schematic example of a non-self-sustained discharge flow reactor for CO_2 conversion

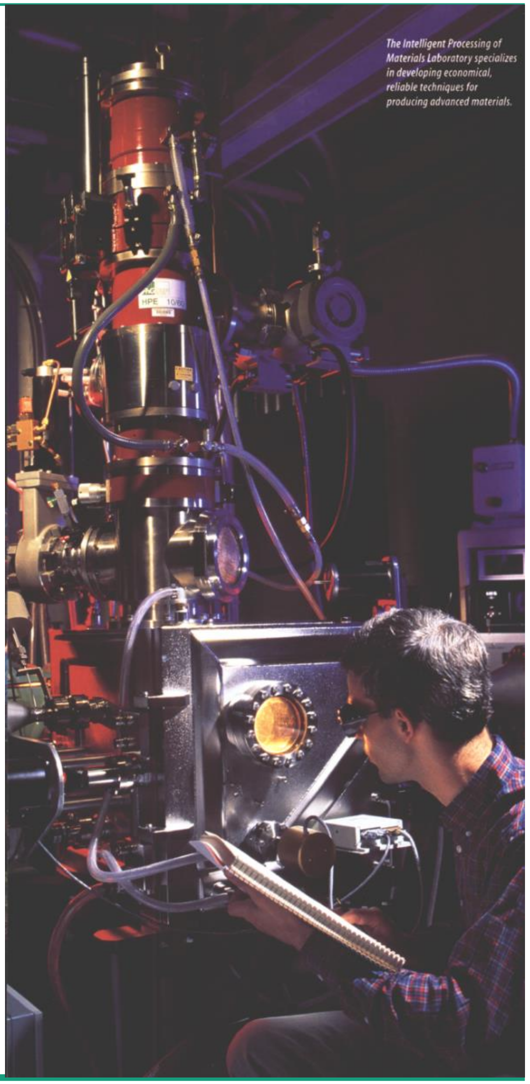
- $P_1 >> P_2$
  - Most power originates from additional source, yielding energy efficient dissociation
- $(E/n)_1 << (E/n)_2$
  - Ionization requires stronger reduced electric field than vibrational dissociation

EXAMPLE: ELECTRON BEAM HYBRID DISCHARGE WITH DIFFERENTIAL PUMPING



- Differential pumping:
  - Bring high vacuum electron beam to moderate pressure working gas (~1-5 mbar)

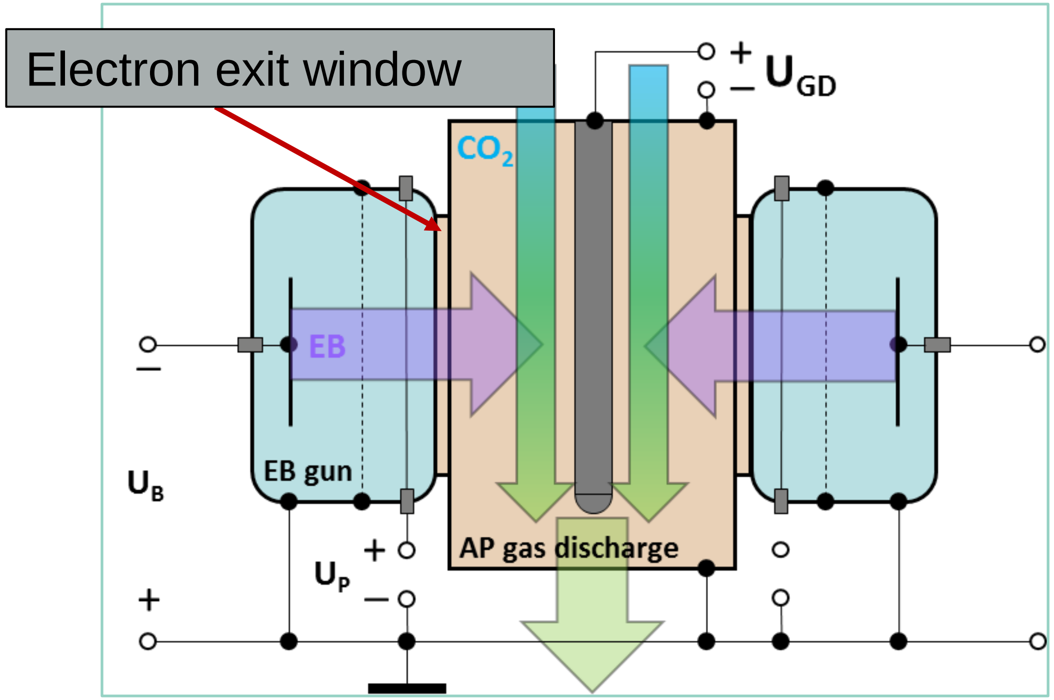


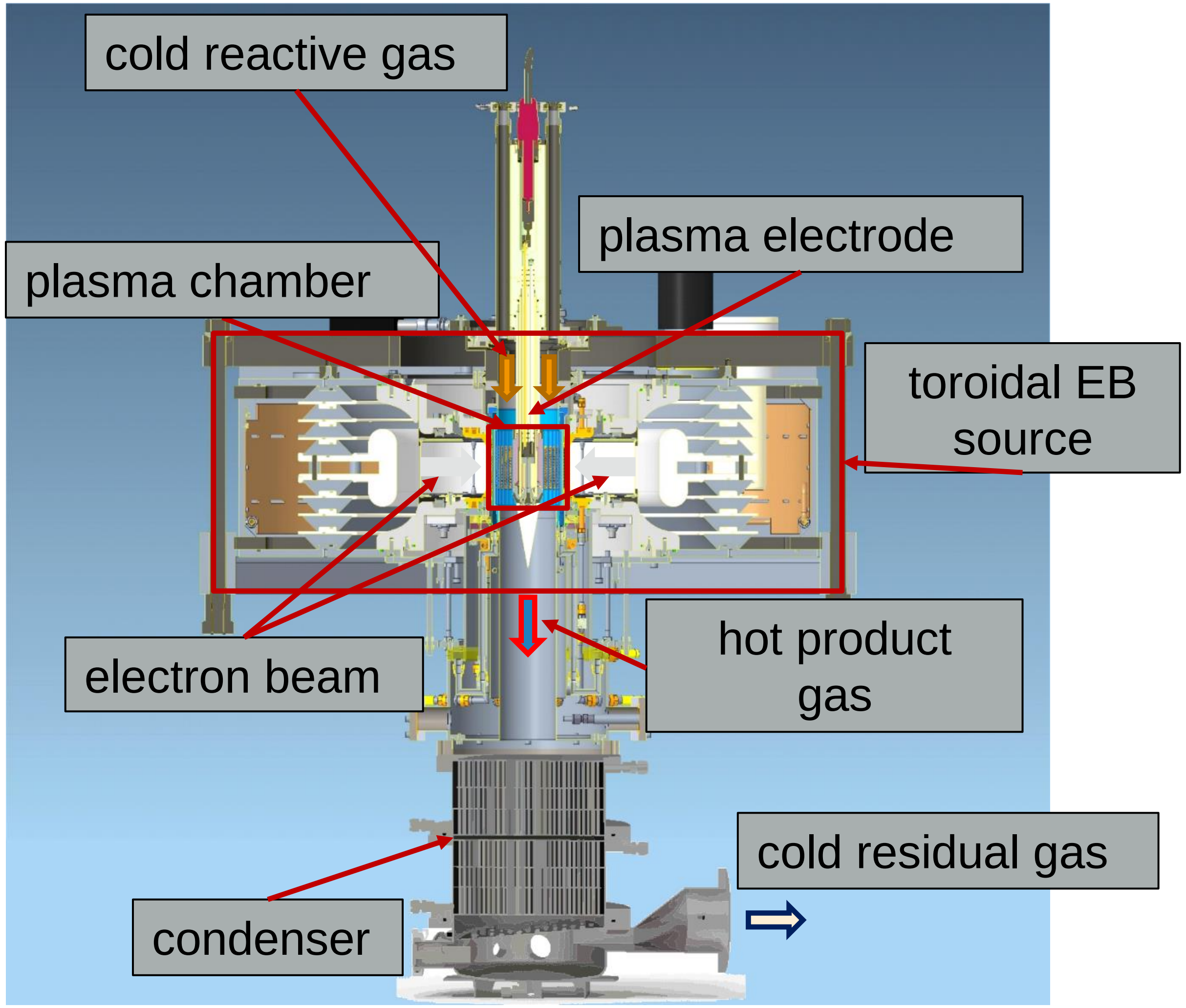


Groves JF (1998)
DIRECTED VAPOR DEPOSITION
PhD thesis, University of Virginia

EXAMPLE: ELECTRON BEAM HYBRID DISCHARGE WITH ELECTRON EXIT WINDOW

- Torodial electron beam gun
- Electron Beam operates in working gas ~ 1 bar
  - Electron exit window





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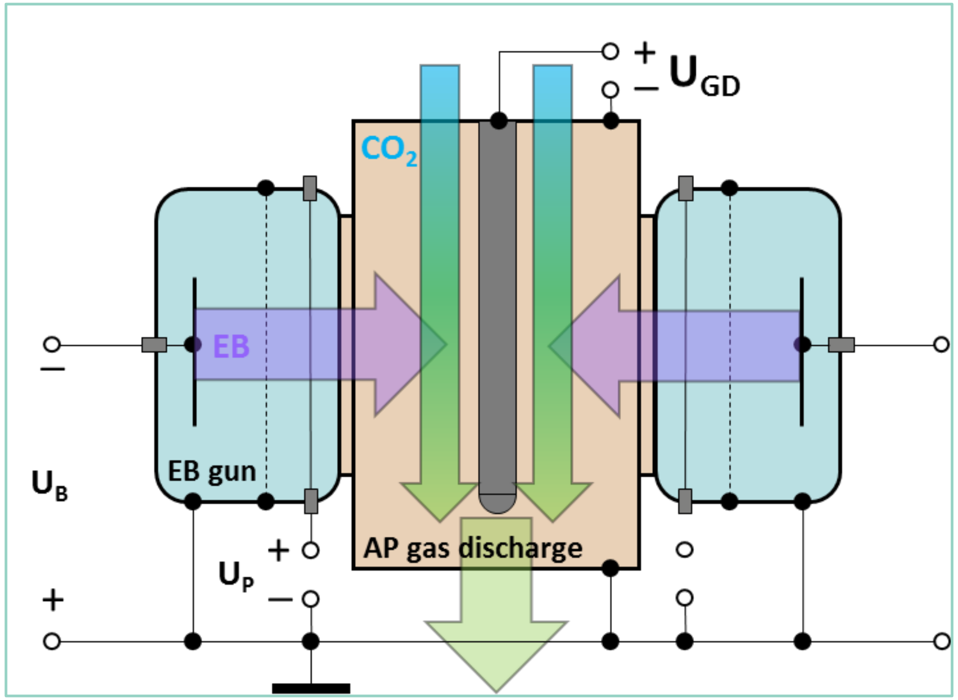
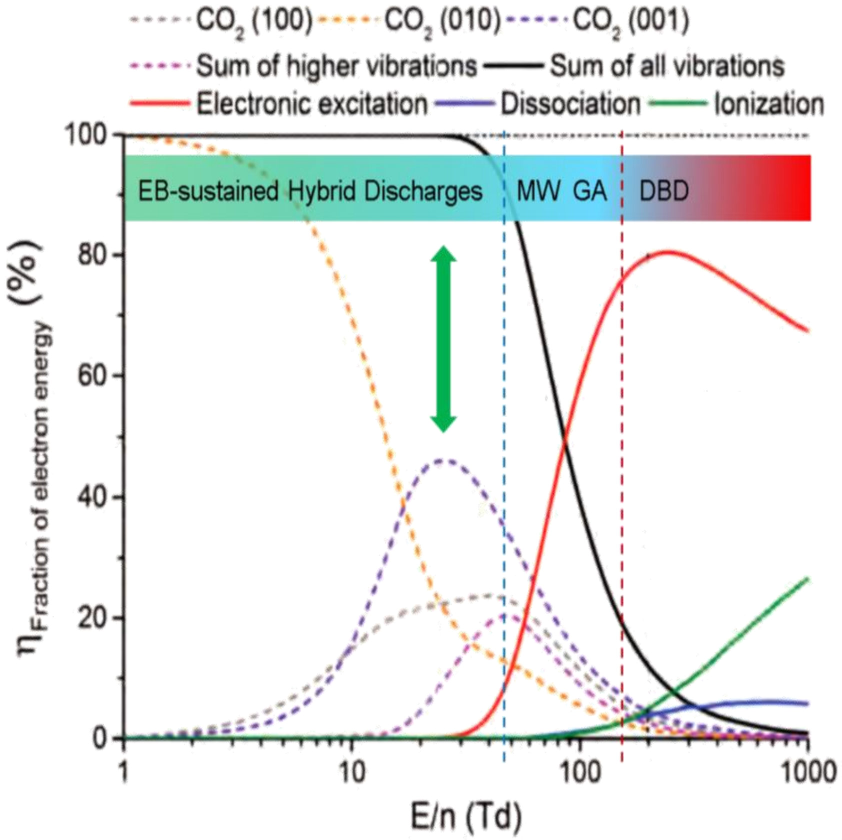
ELECTRON BEAM SUSTAINED HYBRID DISCHARGES FOR CHEMICAL CONVERSION

- very economic energy from gas discharge (up to 90..95 % !)
- EB stabilizes volume character of high-power gas discharge
- EB pre-ionization of gas discharge for low field strengths
- Selective excitation of vibrational modes: optimized efficiency





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CONCLUDING REMARKS

- Non-equilibrium plasmas for Power-to-X methods:
  - Operate at low (gas) temperatures → flexible operation conditions
- Limitations of conventional plasmachemical conversion processes:
  - Trade-off in conversion degree and energy efficiency
  - Non-equilibrium insufficient due to plasma instability
    - **Suggested solution: non-self-sustained discharges (`hybrid plasmas`)**
      - Employment of external ionization source (i.e. electron beam gun)
→ ionization
      - Secondary source of low electric field
→ vibrational excitation
        - → Decoupling of ionization (conversion degree) and vibrational excitation (energy efficiency)

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Thank you for your attention!