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Development of high temperature PEM fuel cells. Simplification and CO tolerance mapping

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Development of

high temperature PEM fuel cells.

Simplification and CO tolerance mapping

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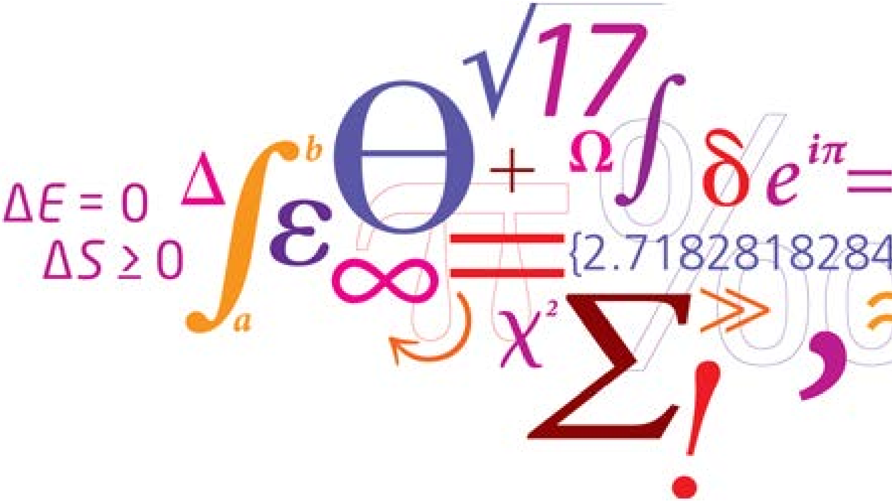
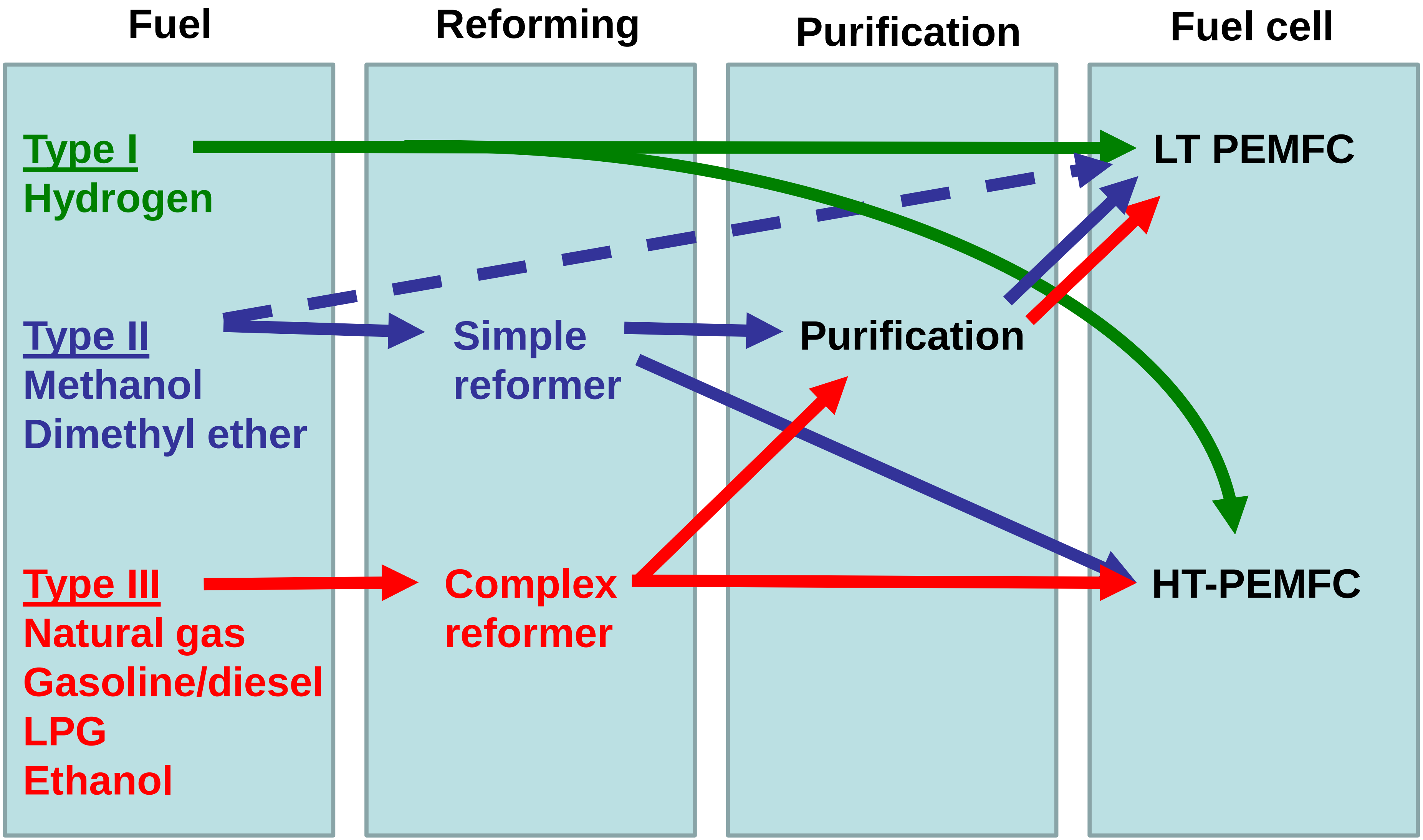


Outline

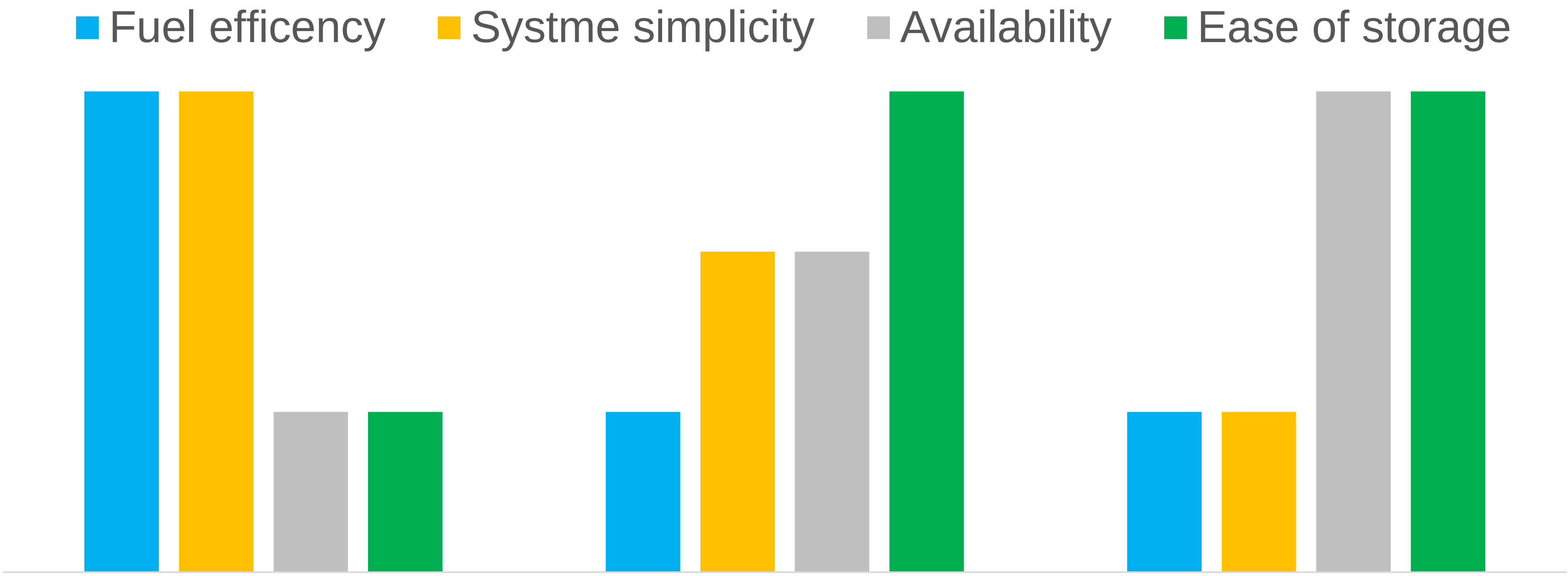
- The choice of fuel
- CO effect on the PEM fuel cell
- Binderless electrodes
- Lowering the platinum loading

Fueling of fuel cells



J.O. Jensen – at "Neptune's Hydrogen and Fuel Cells", Naples, Dec. 15, 2015

Fueling of fuel cells

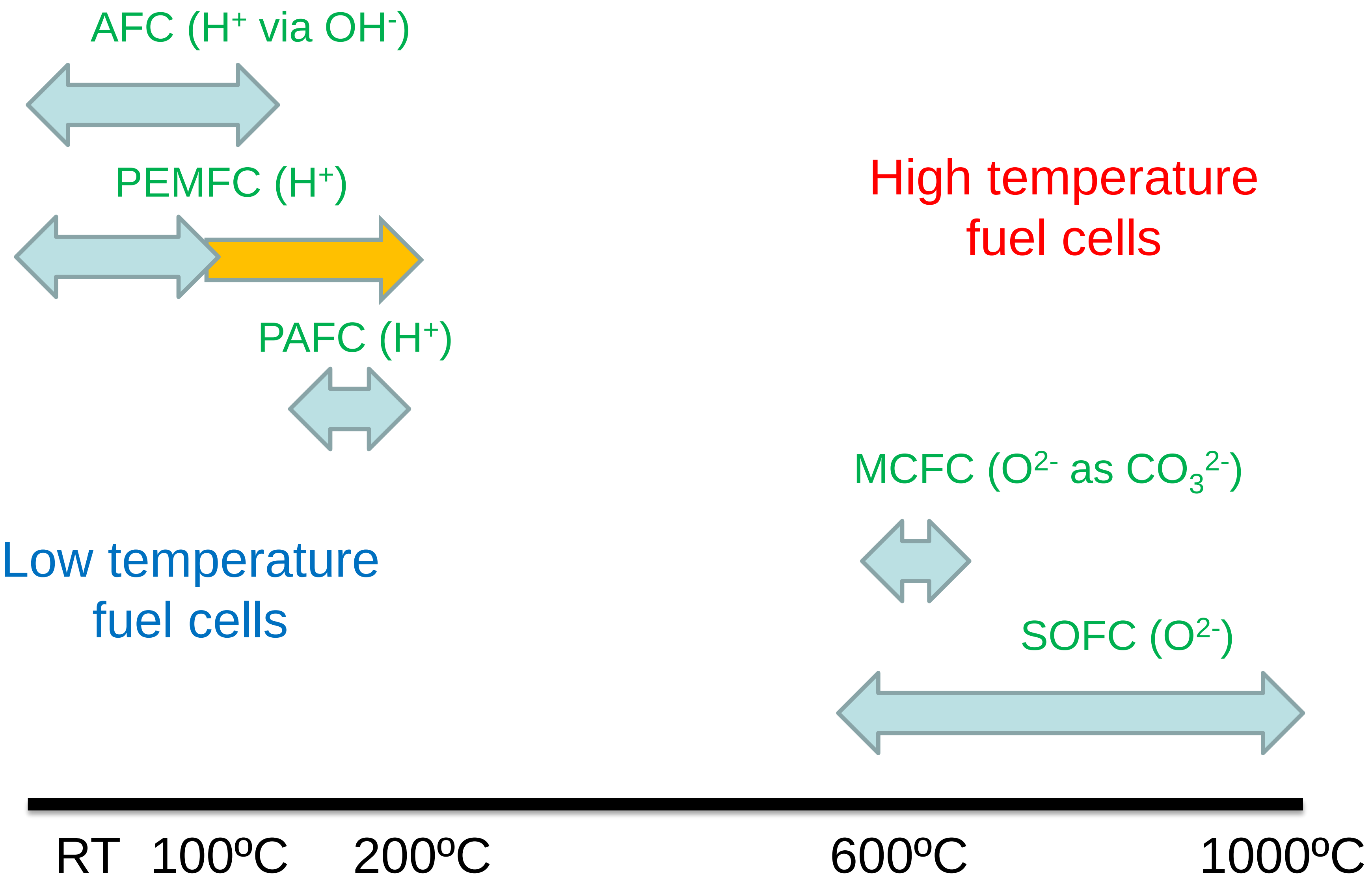


Type I
Hydrogen

Type II
Methanol
Dimethyl ether

Type III
Natural gas
Gasoline/diesel
LPG
Ethanol

FC temperatures



AFC (H^+ via OH^-)

PEMFC (H^+)

PAFC (H^+)

High temperature fuel cells

MCFC (O^{2-} as CO_3^{2-})

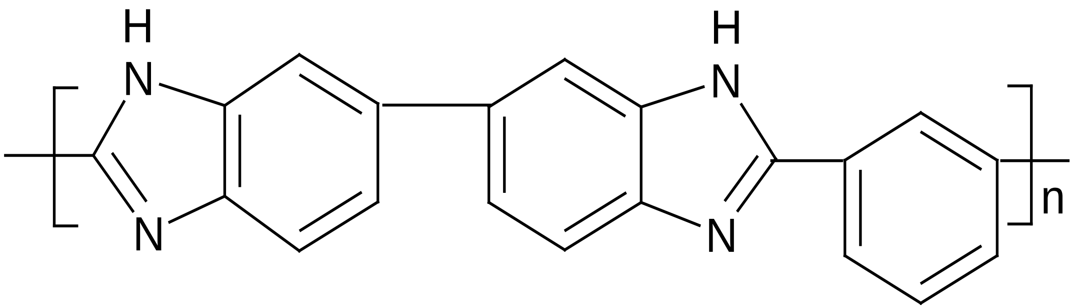
Low temperature fuel cells

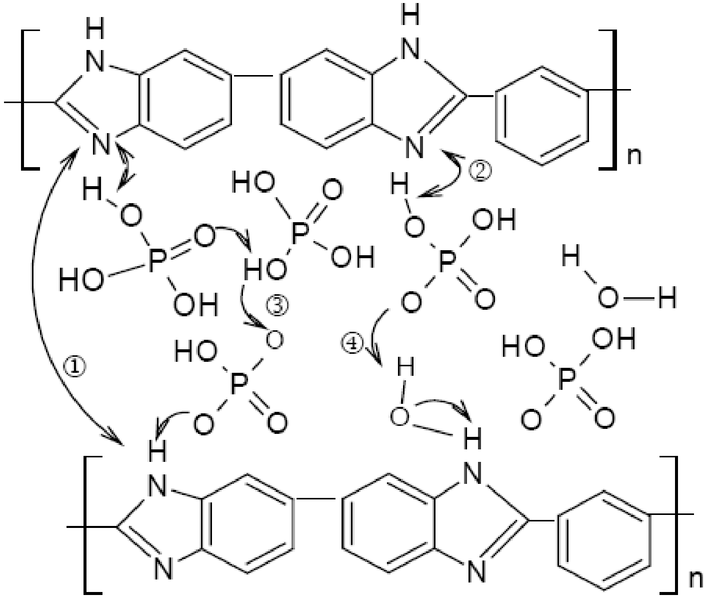
SOFC (O^{2-})

RT 100ºC 200ºC 600ºC 1000ºC

Results with PBI membranes

Polybenzimidazole





Poly (2,2´-*m*-(phenylene)-5,5´-bibenzimidazole)

Well-known temperature resistant polymer

T_g = ~430ºC

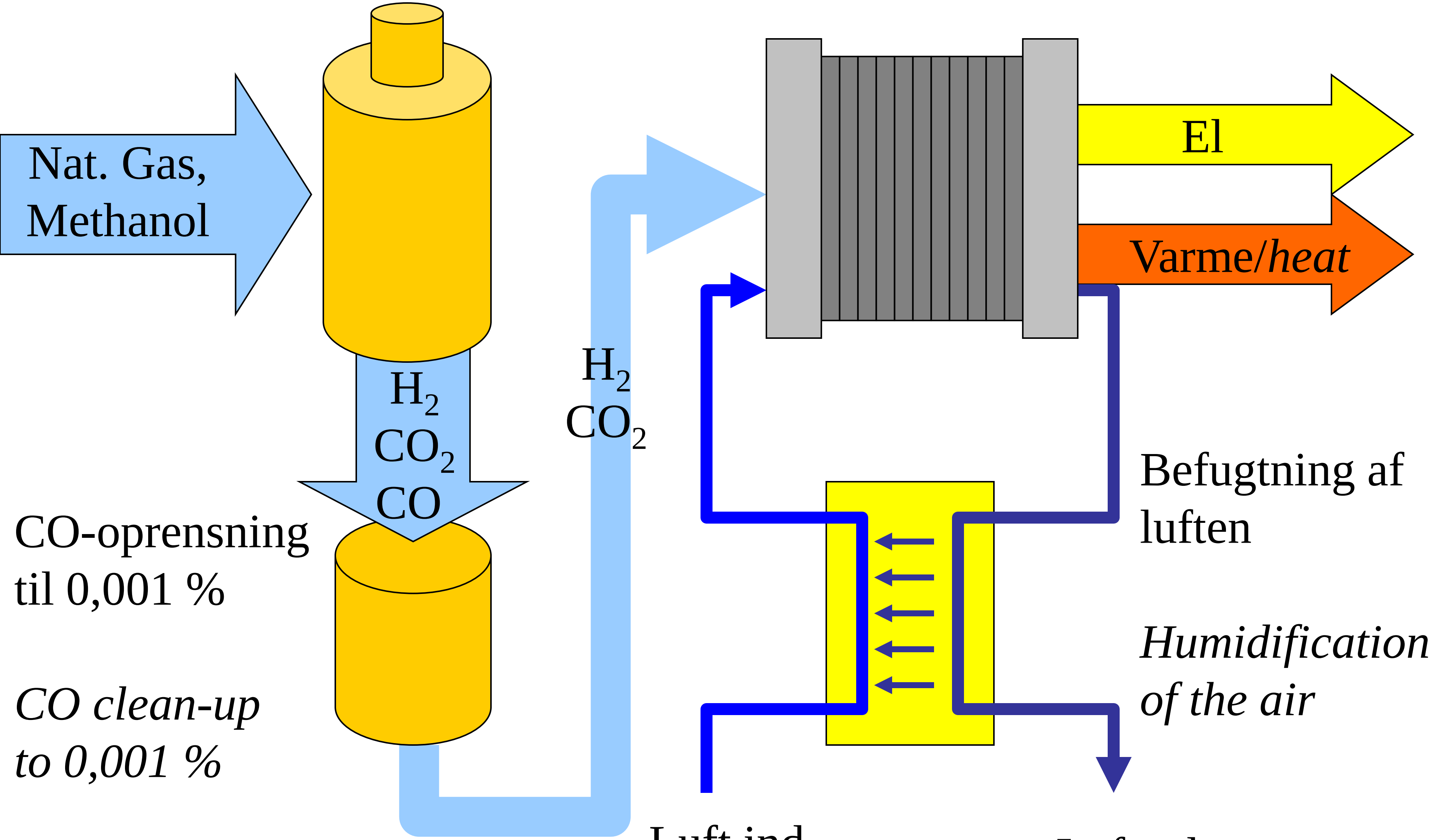
When doped with phosphoric acid:

Proton conductor

Wainright and Savinell. J. Electrochem. Soc. 142 (1995) L121

Reformer / *Reformer*

Brændselscelle / *Fuel cell*



Nat. Gas, Methanol

H_2
CO_2
CO

CO-oprensning til 0,001 %

CO clean-up to 0,001 %

H_2
CO_2

El

Varme/*heat*

Befugtning af luften

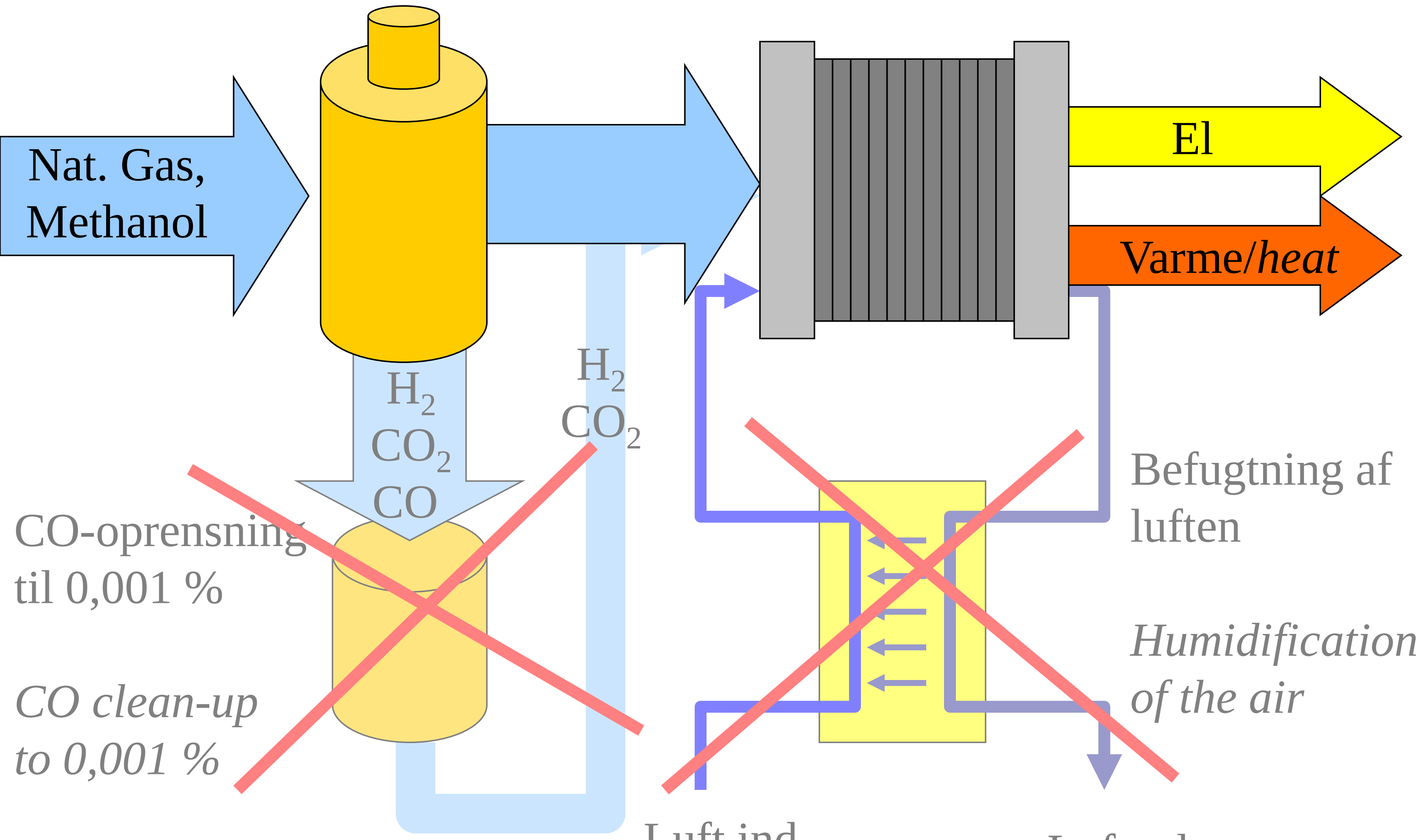
Humidification of the air

Luft ind
Air in

Luft ud
Air out

Reformer / *Reformer*

Brændselscelle / *Fuel cell*



Nat. Gas,
Methanol

El

Varme/*heat*

H_2
CO_2
CO

H_2
CO_2

CO-oprensning
til 0,001 %

CO clean-up
to 0,001 %

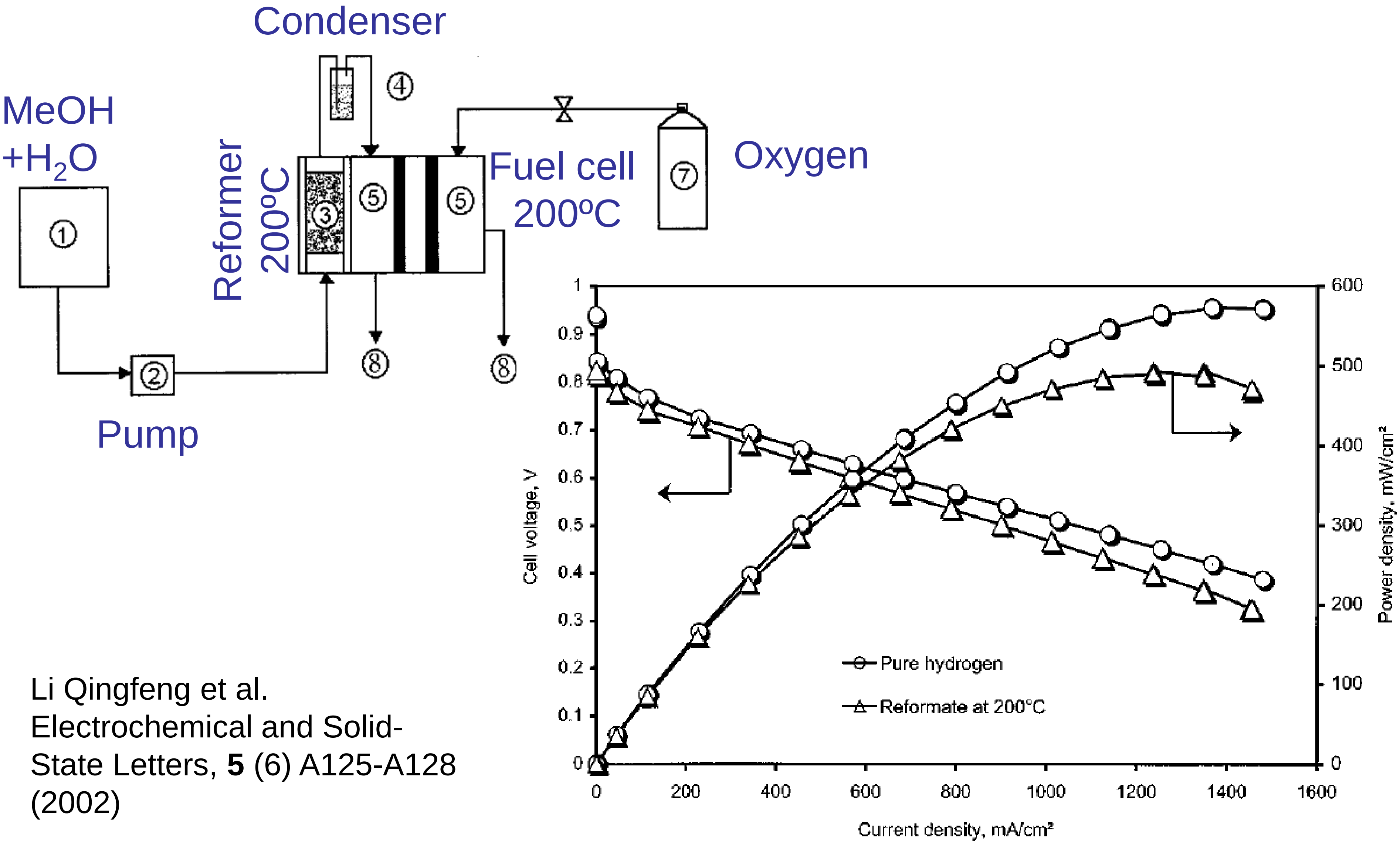
Befugtning af
luften

Humidification
of the air

Luft ind
Air in

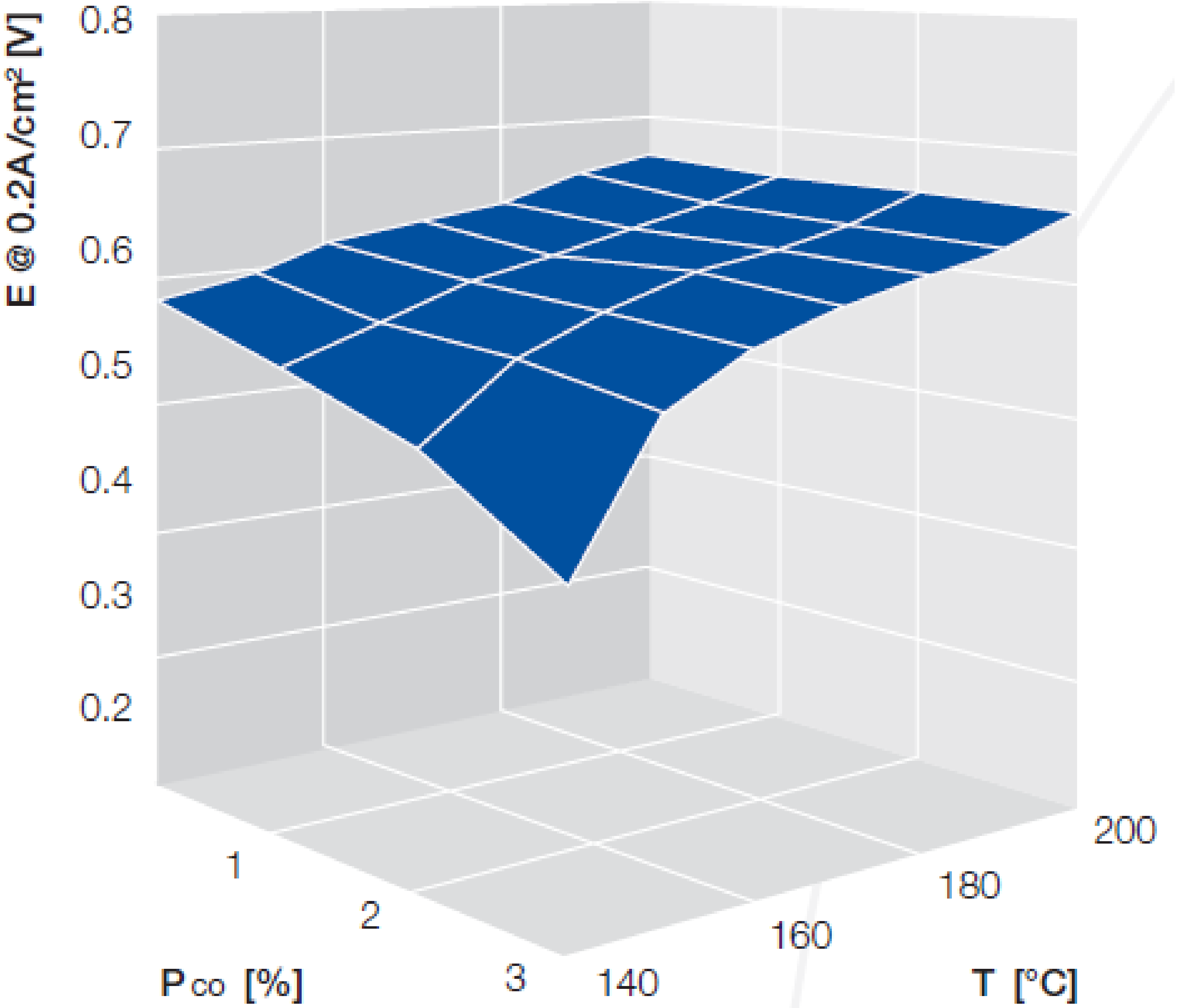
Luft ud
Air out

Integration with methanol reformer



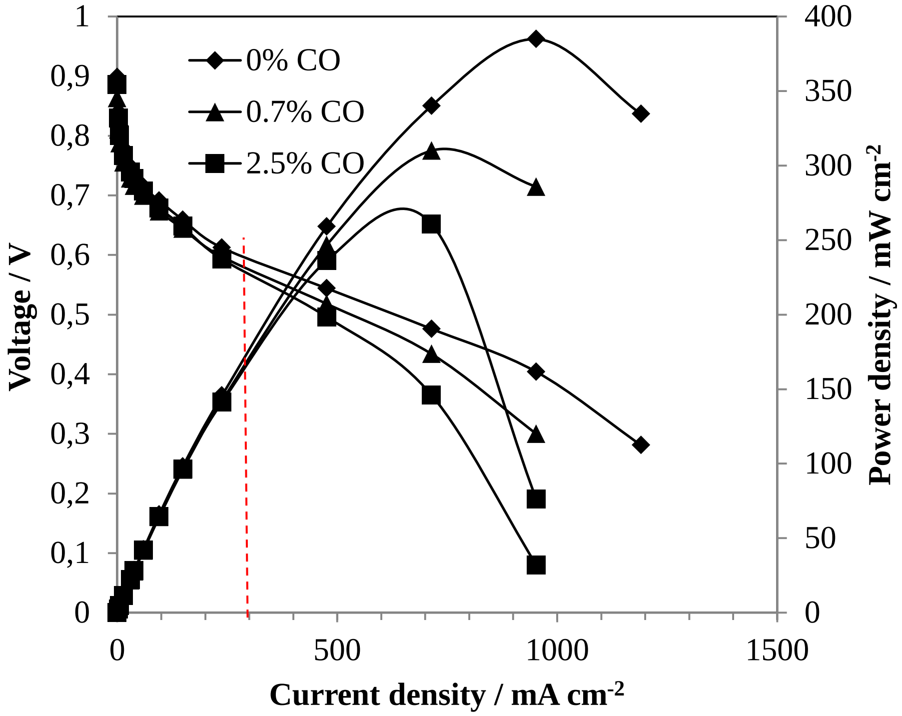
Li Qingfeng et al. Electrochemical and Solid-State Letters, **5** (6) A125-A128 (2002)

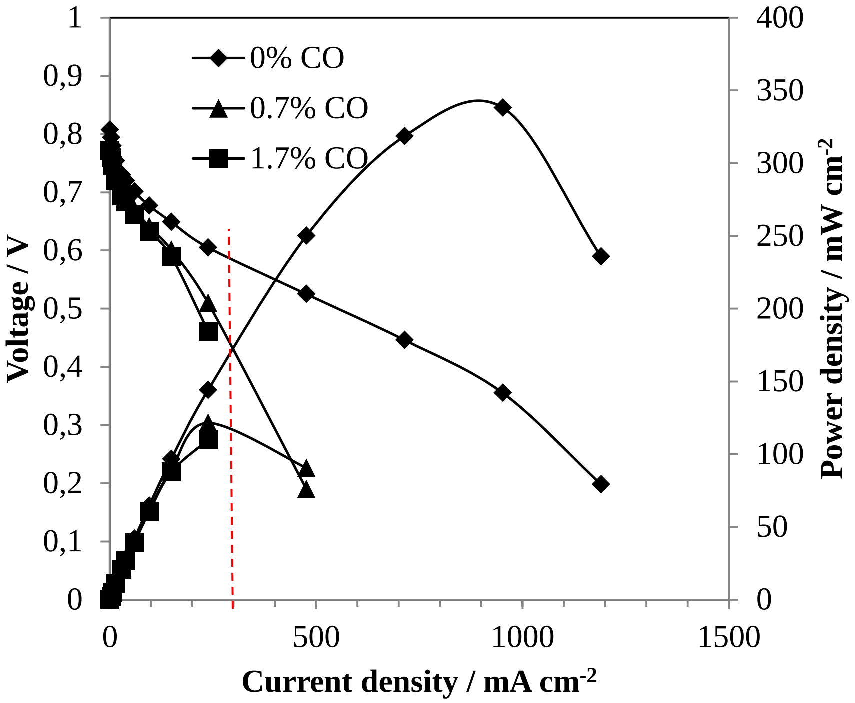
CO tolerance



BASF, Celtec® P1100W prospect

Response to diluted hydrogen





Model composition:

CO: 0.7%; H_2: 34.8%; N_2: 64.5%

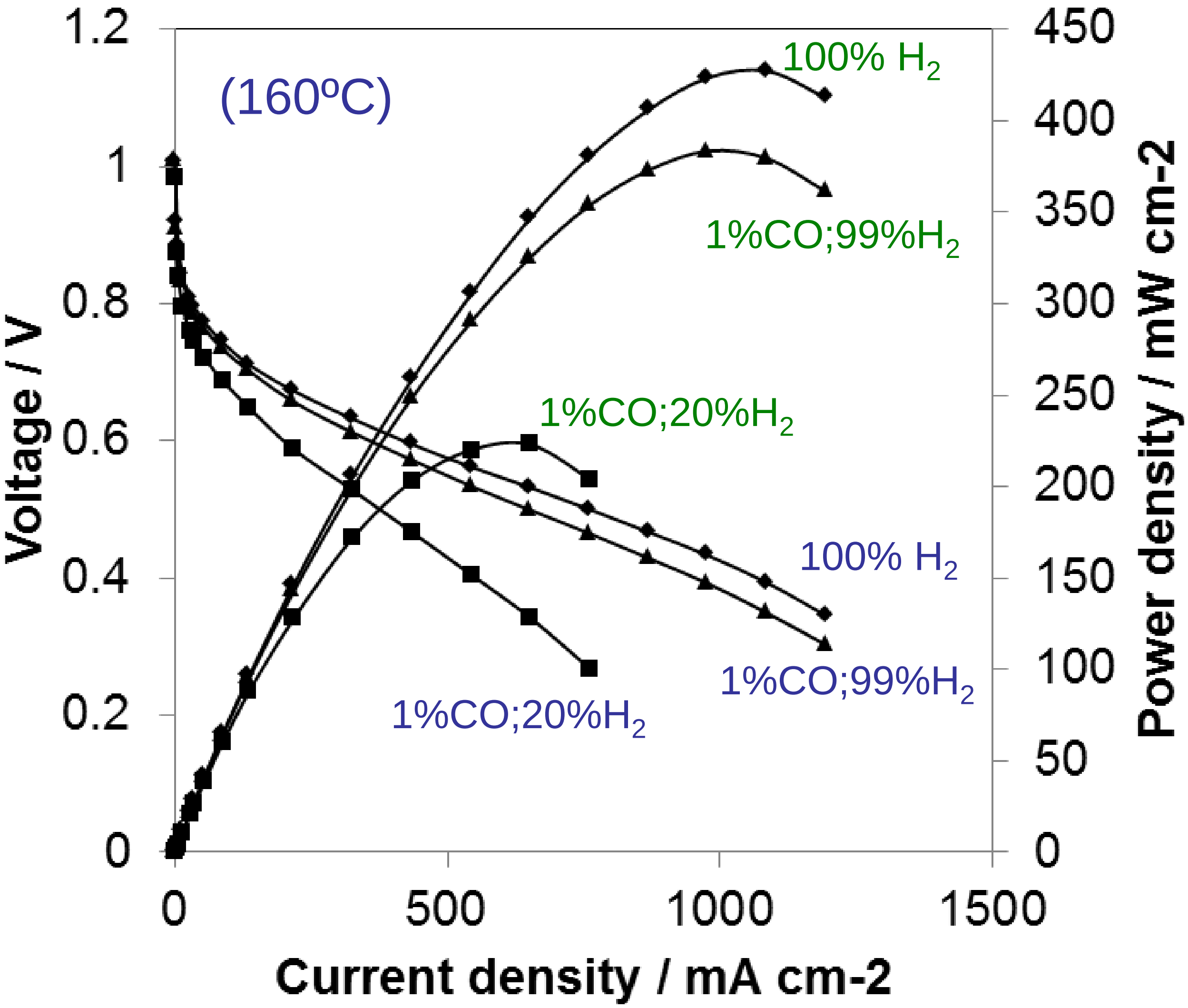
CO: 1.7%; H_2: 33.9%; N_2: 64.4%

λ_{H2} = 1.2 (0.35 mg_{Pt} cm^{-2})

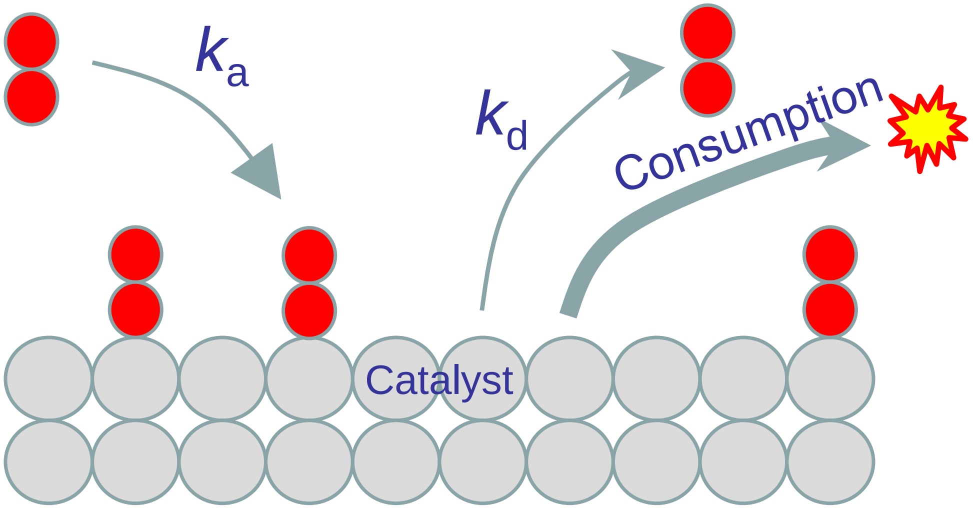
λ_{air} = 2.0 (0.83 mg_{Pt} cm^{-2})

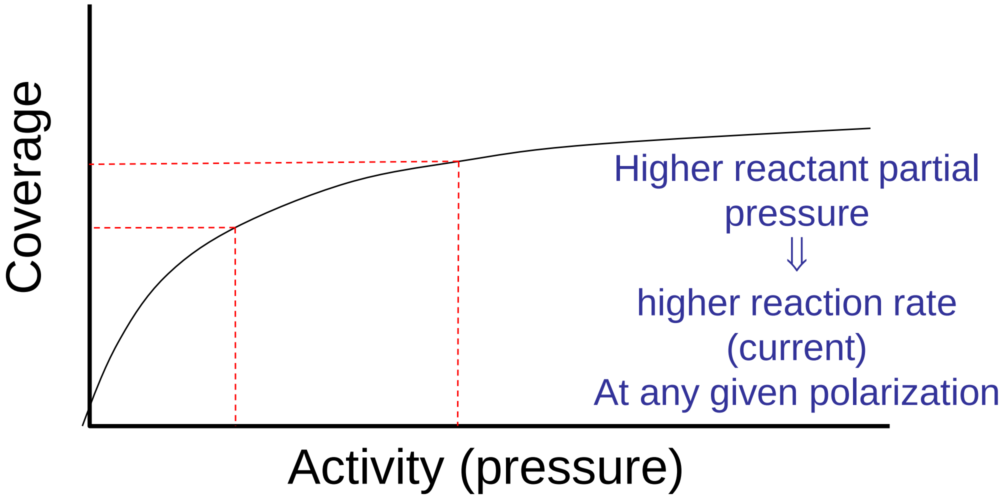
Dilution of hydrogen with CO

λ(air): 2, λ(H_2): 1.5
Cathode: 1.3 mg_{Pt} cm^{-2}
Anode: 1.3 mg_{Pt} cm^{-2}.



High surface adsorption, Langmuir





Higher reactant partial pressure
⇓
higher reaction rate (current)
At any given polarization

Equilibrium:

$$k_a PN(1-\theta) = k_d N\theta$$

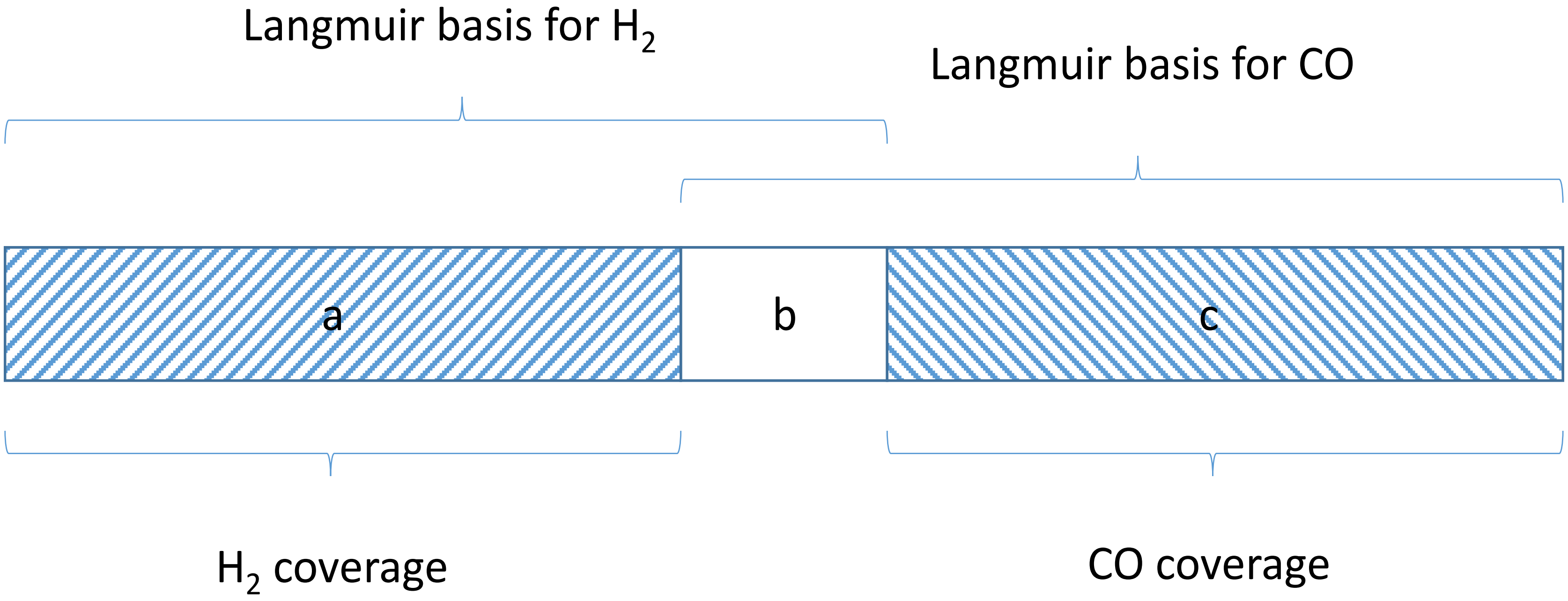
or:

$$\theta = \frac{\frac{k_a}{k_d}P}{1+\frac{k_a}{k_d}P} = \frac{KP}{1+KP}$$

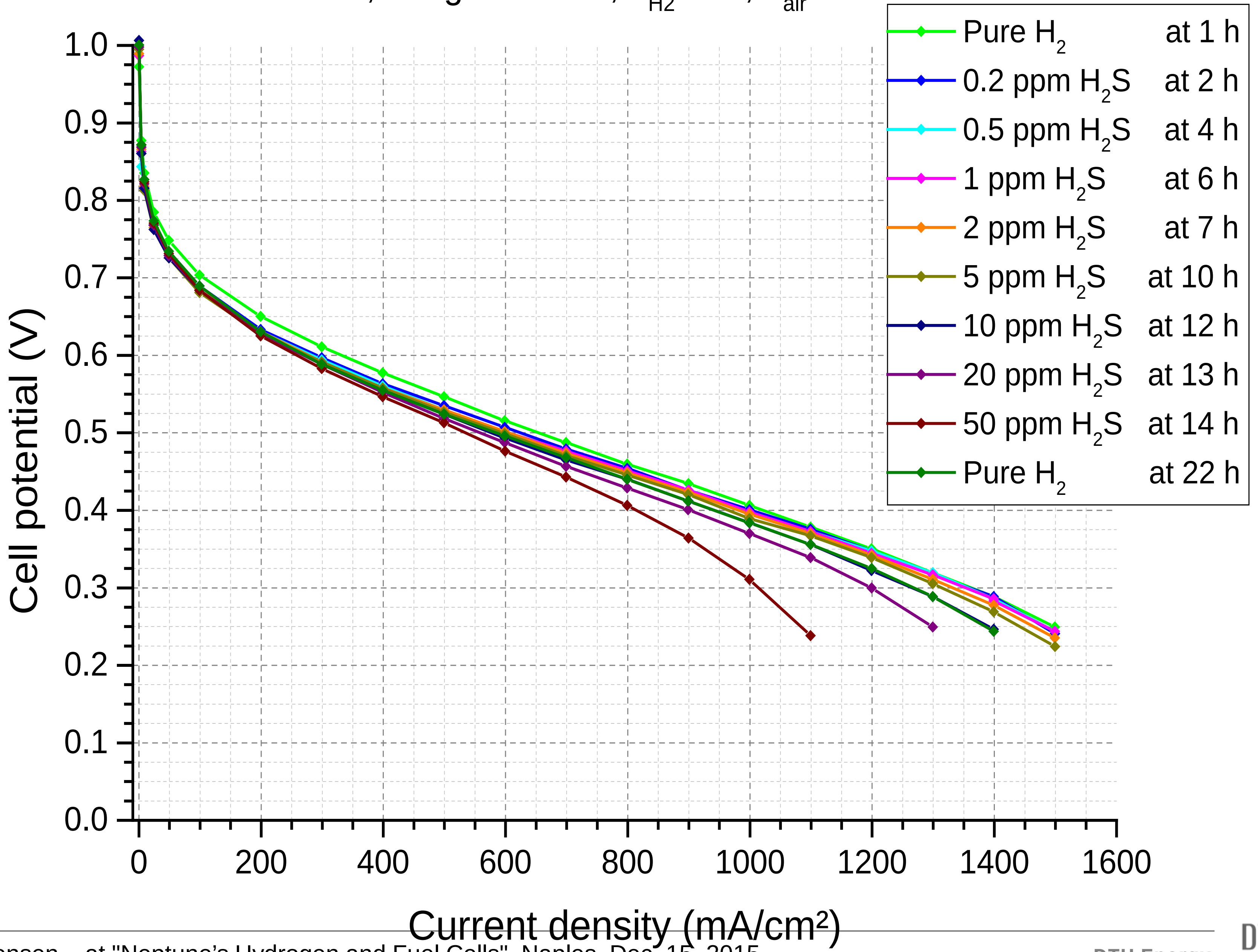
N: no. of sites
θ: surface fraction occupied
P: pressure
t: time
k_a, k_d: rate constants for adsorption and desorption

$K = K(T)$

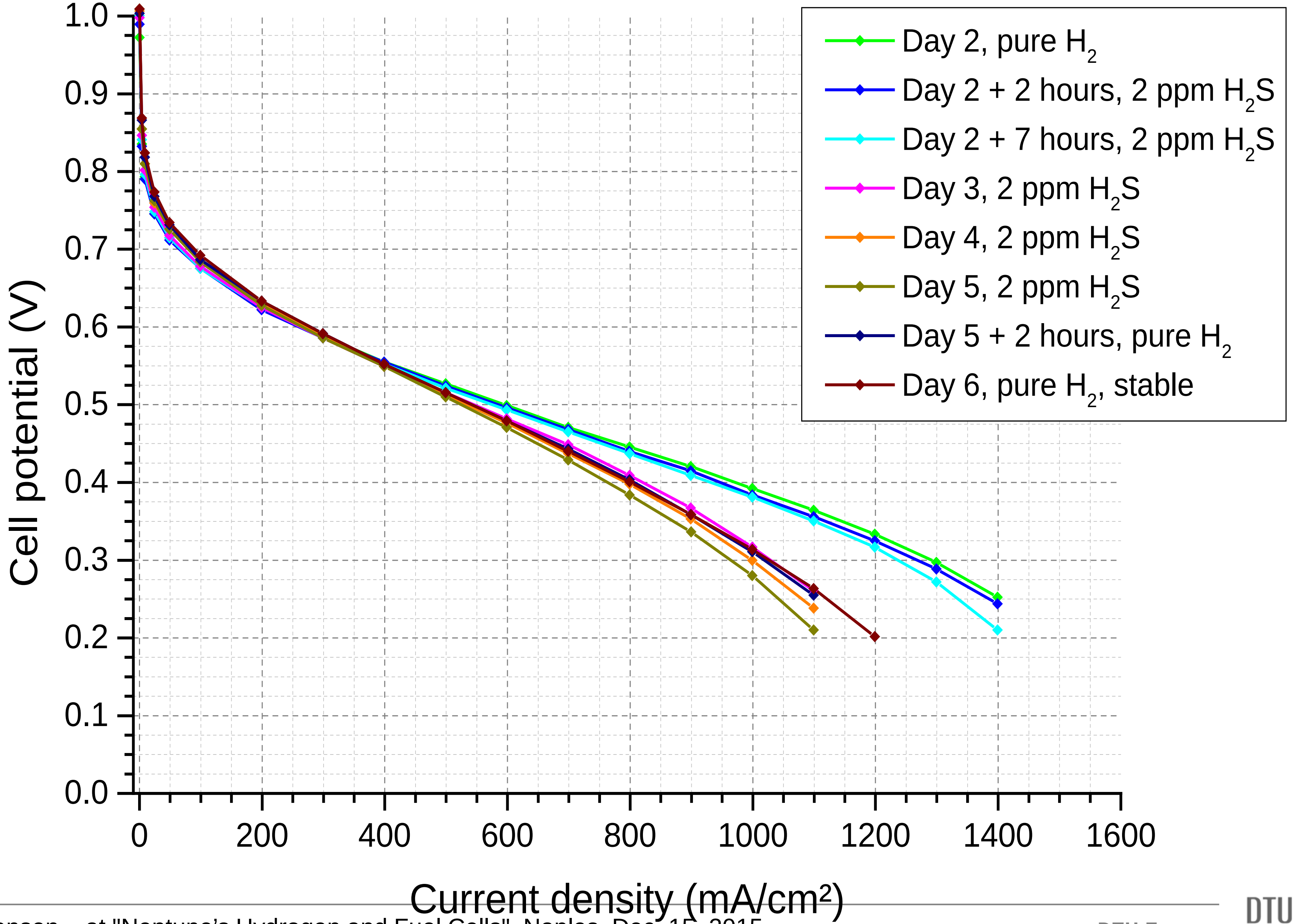
Competition with CO



160 °C, 1 mg/cm² Pt/C, λ_{H2}=1.2, λ_{air}=2



160 °C, 1 mg/cm² Pt/C, λ_{H2}=1.2, λ_{air}=2



Reduction of binder

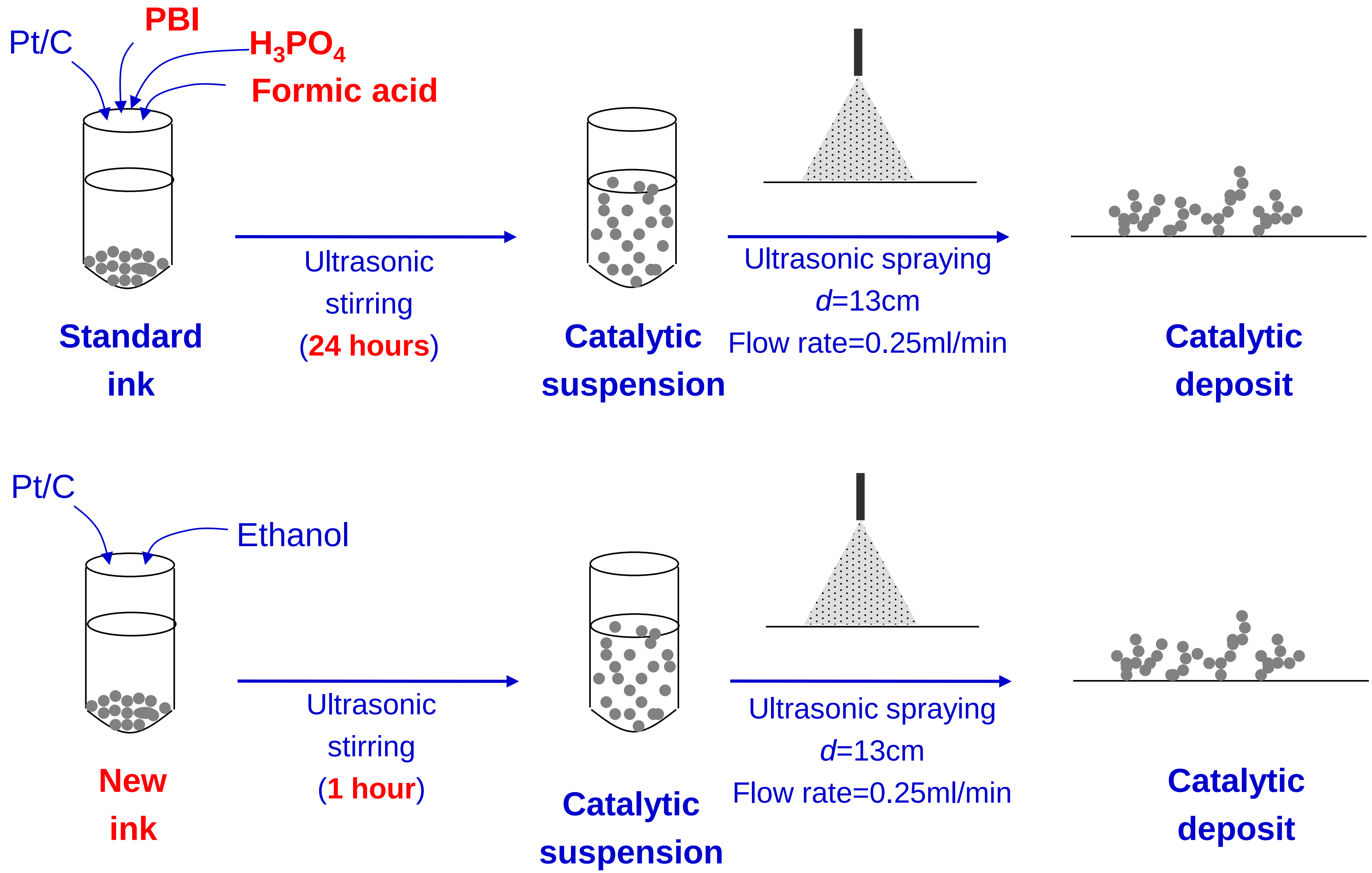
Experiments say:
Less binder (PBI) gives better performance.

What is the optimum/minimum?

What happens if we go to the extreme and make electrode completely without the binder?

1. Nothing. The binder is not needed
2. The catalyst layer falls off too easily
3. The proton transport is mostly blocked
4. Reduction to a certain level improved performance and then it breaks down

Single cell dev., binderless electrodes



Pt/C

PBI

H_3PO_4

Formic acid

Standard ink

Ultrasonic stirring (**24 hours**)

Catalytic suspension

Ultrasonic spraying

d=13cm

Flow rate=0.25ml/min

Catalytic deposit

Pt/C

Ethanol

New ink

Ultrasonic stirring (**1 hour**)

Catalytic suspension

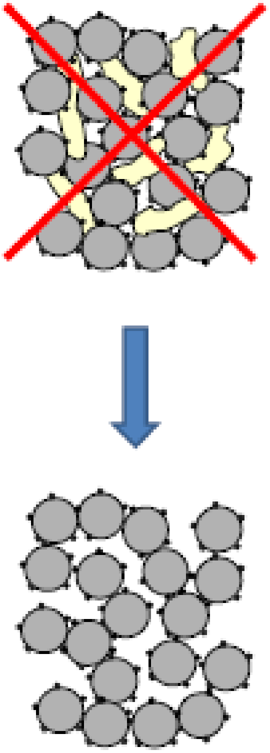
Ultrasonic spraying

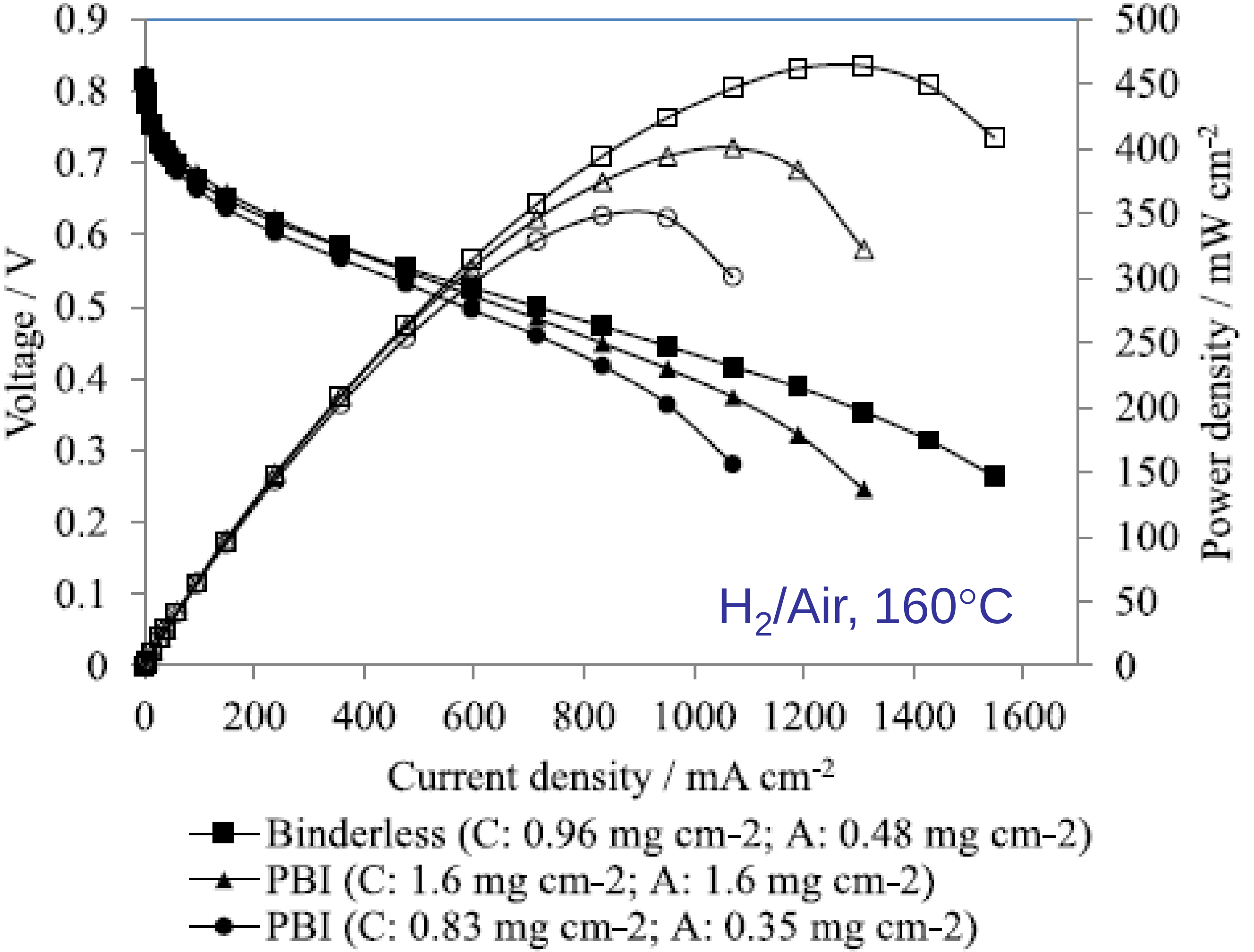
d=13cm

Flow rate=0.25ml/min

Catalytic deposit

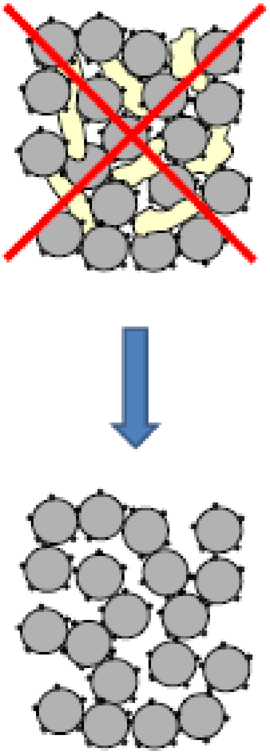
Binderless electrodes

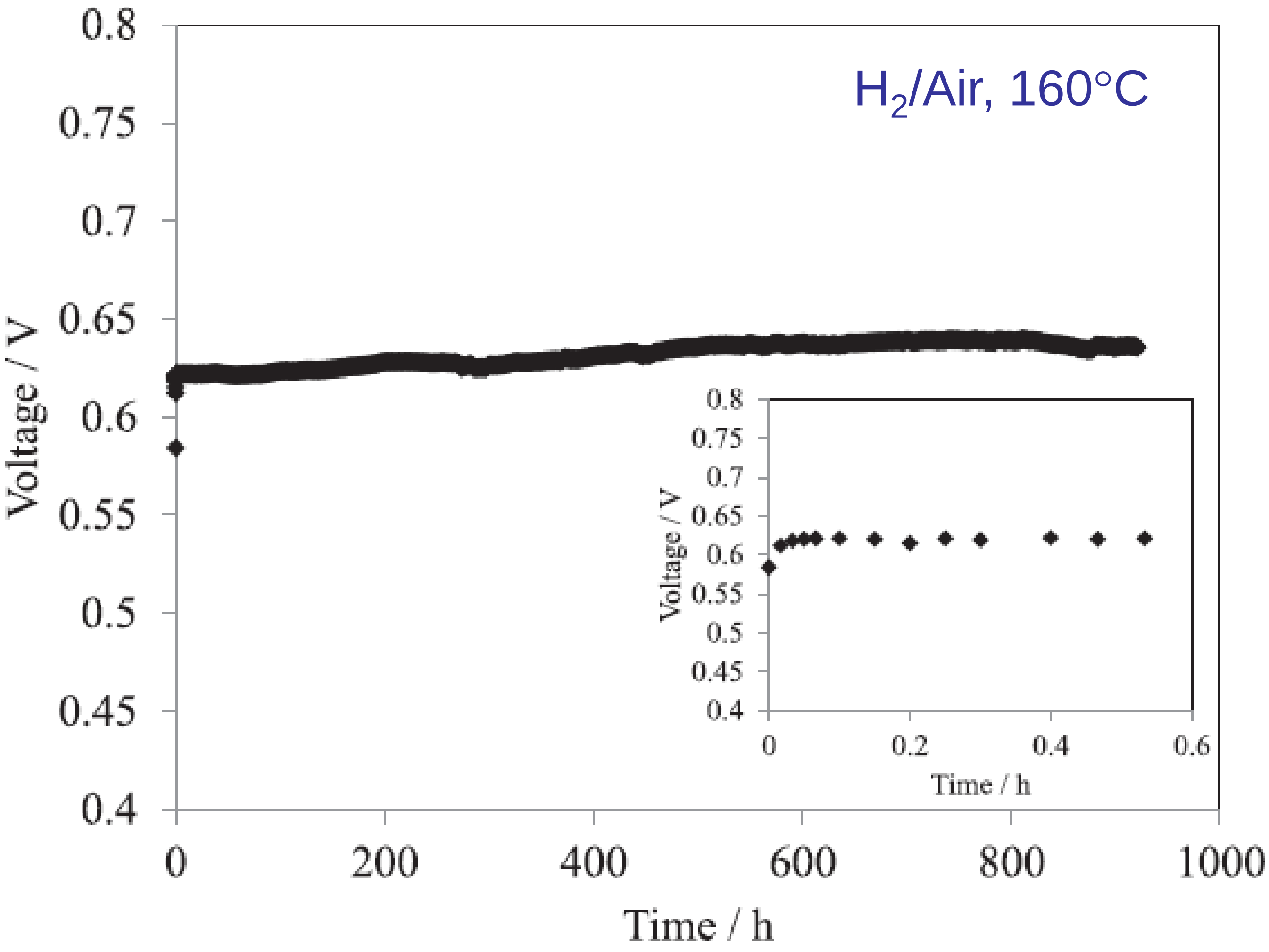




S. Martin, Q. Li, T. Steenberg, J.O. Jensen.
J. Power Sources 272 (2014) 559-566

Binderless electrodes





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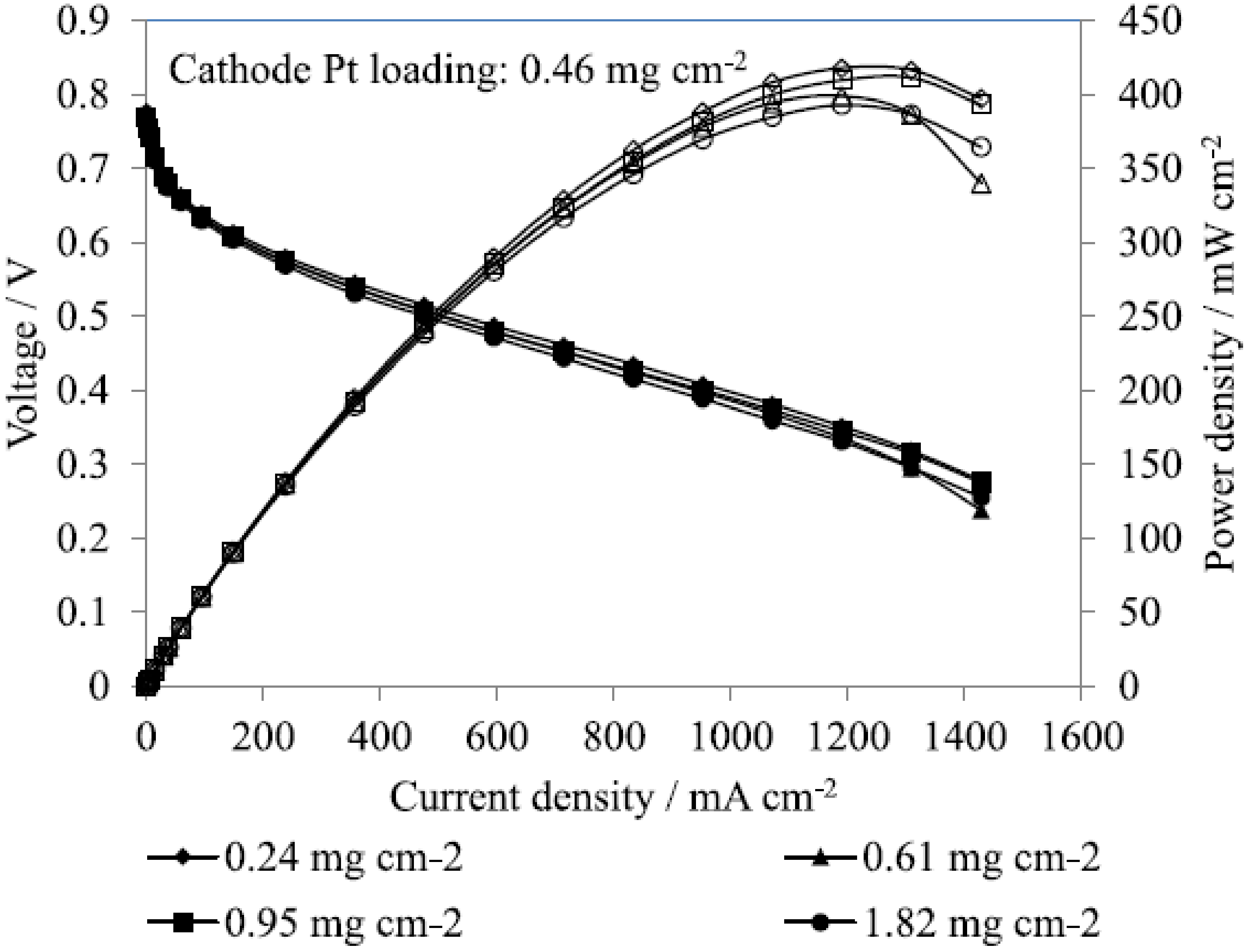
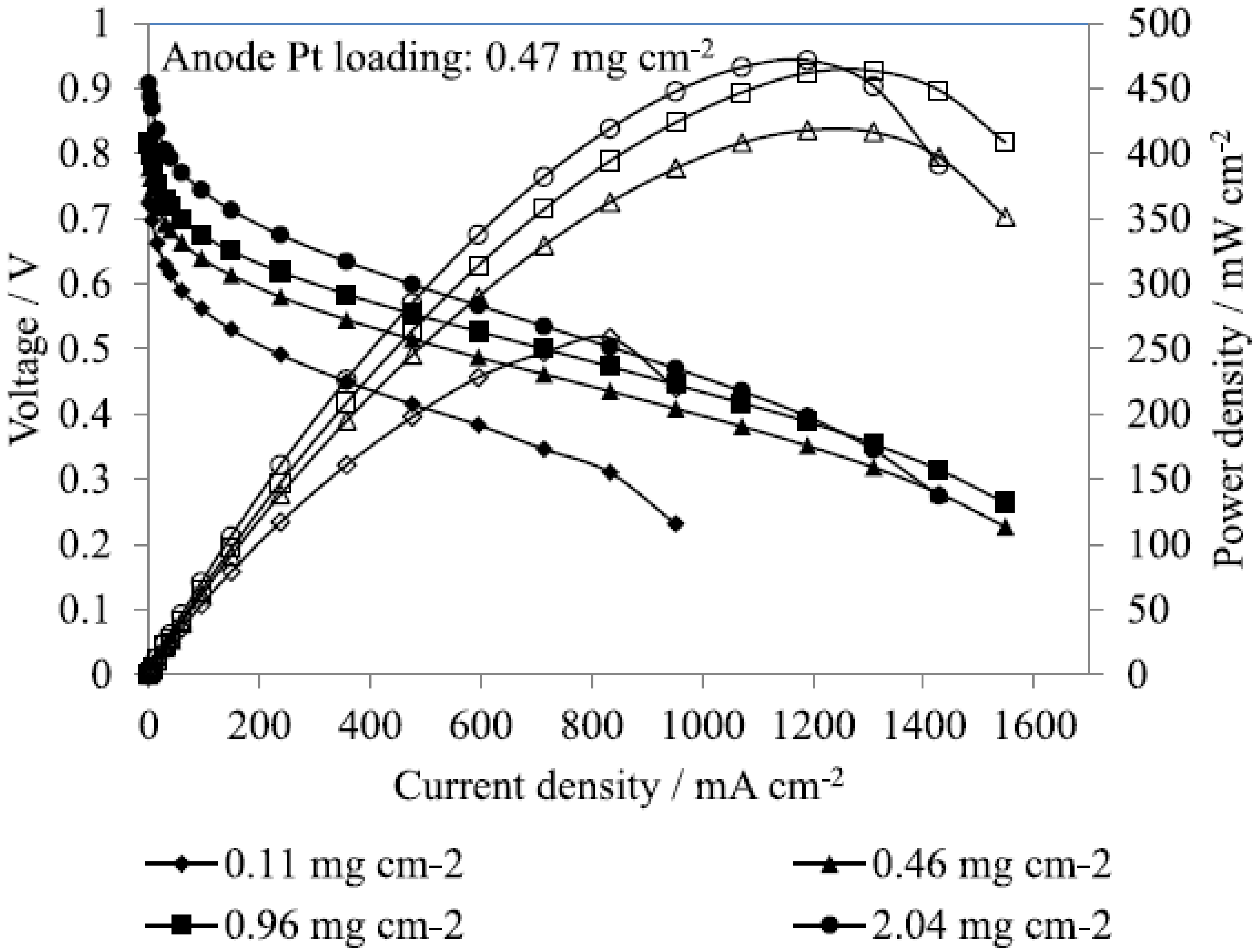
Reducing Pt loading on anode



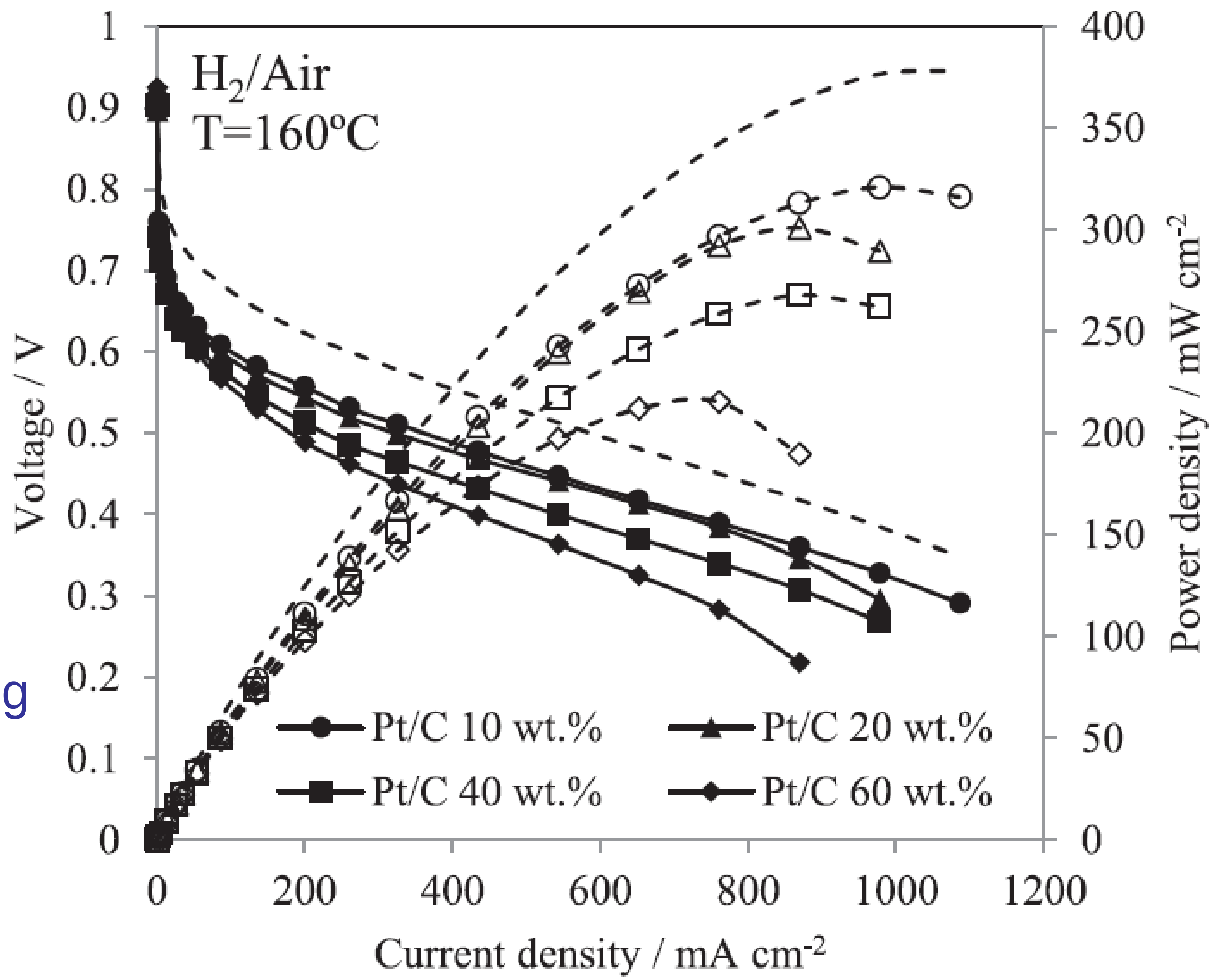
S. Martin, Q. Li, T. Steenberg, J.O. Jensen.
J. Power Sources 272 (2014) 559-566

Reducing Pt loading on cathode



S. Martin, Q. Li, T. Steenberg, J.O. Jensen.
J. Power Sources 272 (2014) 559-566

Reducing Pt loading to 0.1 mg_{Pt} /cm^2 (each)

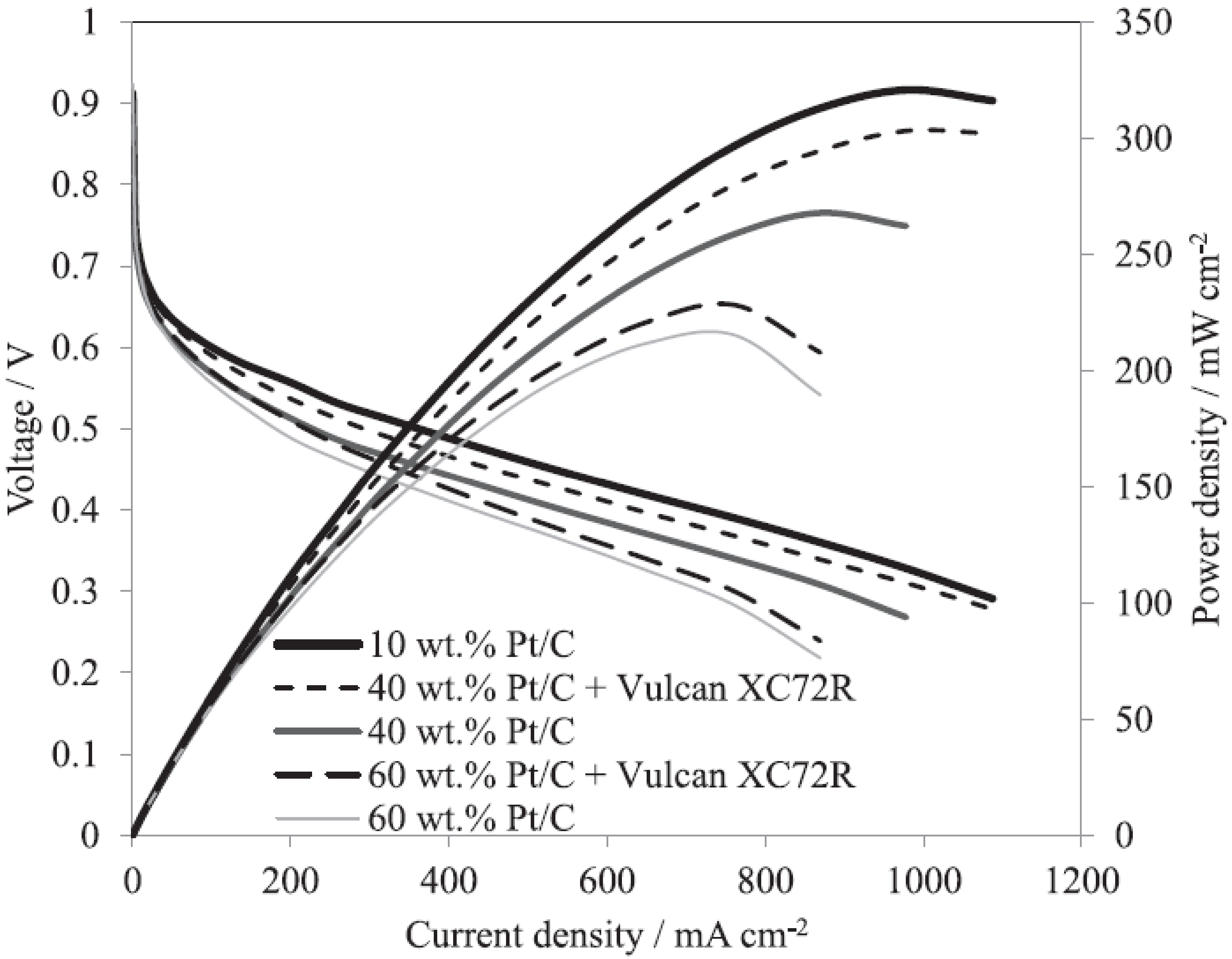


No markers:
SOA, 0.6/0.6 mg

Markers:
0.1/0.1 mg

S. Martin, Q. Li, J.O. Jensen.
J. Power Sources 293 (2015) 51-56

Reducing Pt loading to 0.1 mg_{Pt} $/cm^2$



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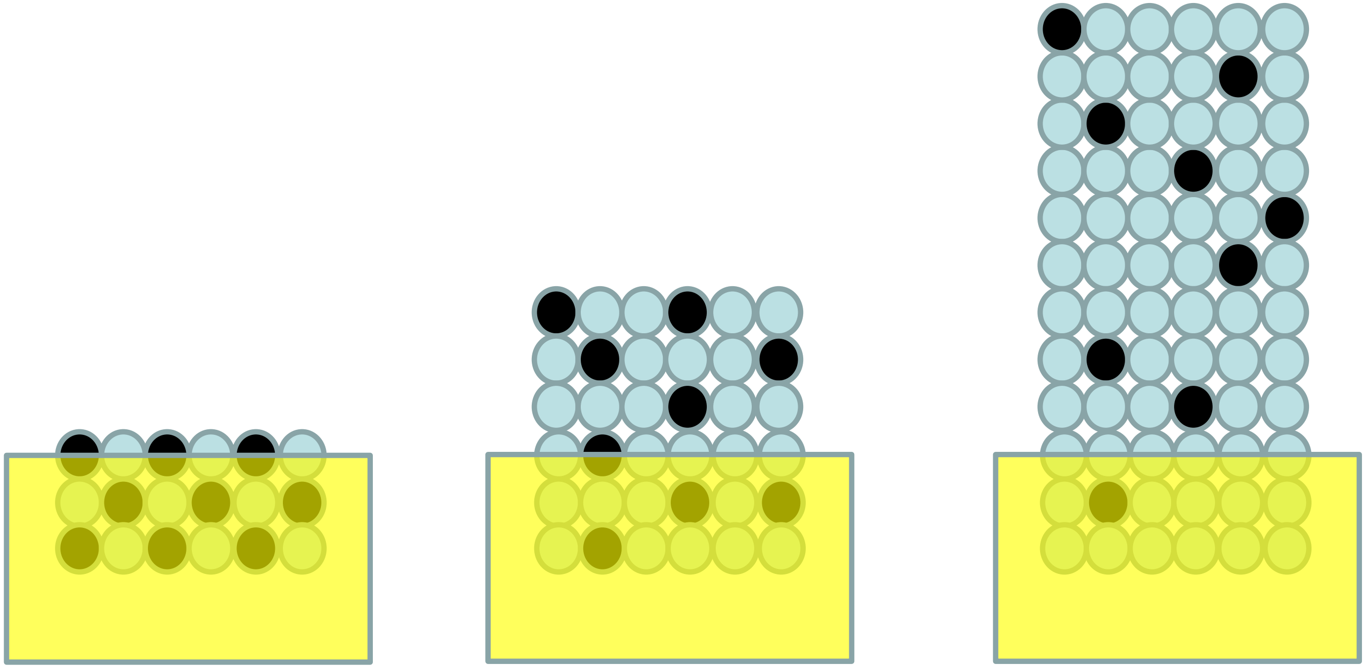
J. Power Sources 293 (2015) 51-56

A closer look a the catalyst materials (JM)

Pt on carbon / wt.%	**10**	**20**	**40**	**60**
Pt loading cathode/anode / mg cm^{-2}	0.098/0.094	0.098/0.094	0.098/0.096	0.098/0.098
Peak power density^{a} / mW cm^{-2}	321(482)	301	268	215
Pt utilization^{a} / kWg$_{Pt}^{-1}$				
overall	1.67(2.51)	1.57	1.38	1.10
cathodic	3.27(4.92)	3.08	2.73	2.19
Voltage at 200 mA cm$^{-2,a}$ / V	0.557(0.618)	0.544	0.513	0.489
Catalyst layer thickness / µm	~ 18	~ 8	~ 3.5	~ 2.5
Pt XRD crystallite size^{b} / nm	2.5	2.7	3.3	3.2

Partial flooding?



Acknowledgement

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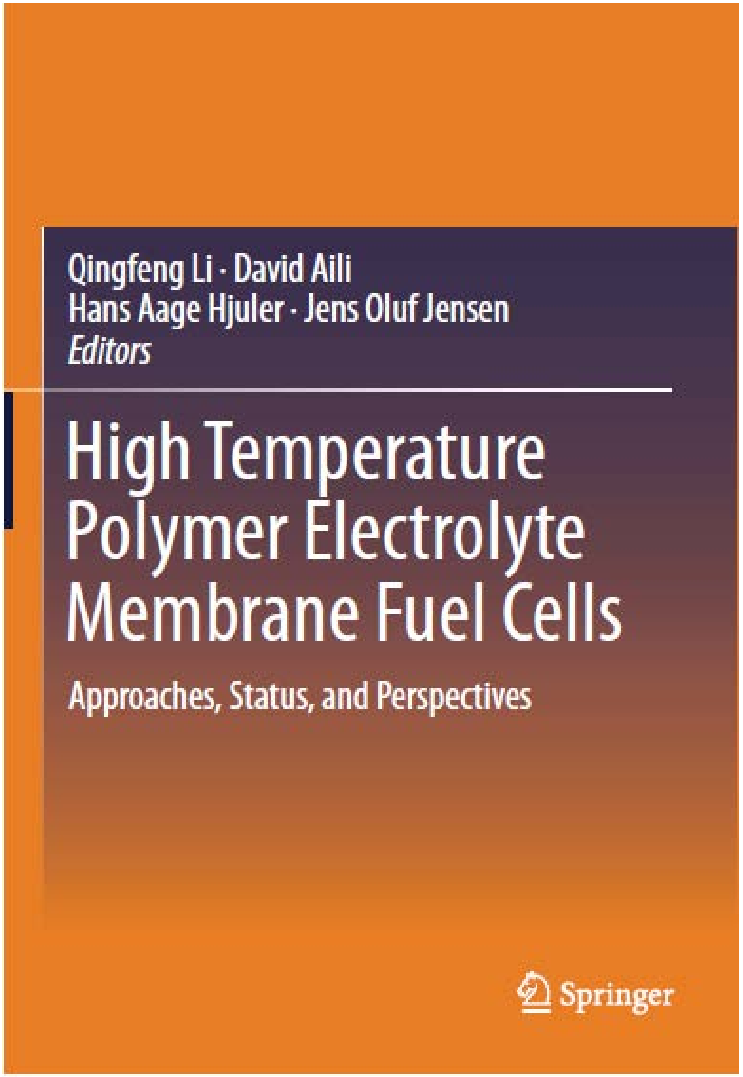

Qingfeng Li · David Aili
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High Temperature Polymer Electrolyte Membrane Fuel Cells

Approaches, Status, and Perspectives

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Book, Springer 2015