Why an Open Circuit Voltage of 1.23 V Cannot be Obtained

Ulf Bossel
Fuel Cell Consultant

Hannover Messe 2017
Hydrogen + Fuel Cells + Batteries
Group Exhibit

Technical Forum
April 25, 2017
11:40 h

Accepted Equation for Hydrogen Oxidation in Fuel Cells

$$2\ H_2 + O_2 \Rightarrow 2\ H_2O$$

Accepted Faraday Equation for Open Circuit Voltages

$$\mathbf{OCV = -\Delta_f G^0(T) / (n_e\ F)}$$

with $\Delta_f G^0(T) = \Delta_f H^0(T) - T\ \Delta S^0(T)$ Gibbs Free Energy
n_e = number of exchanged electrons = 4
F = Faraday constant = 96'485 C/mol

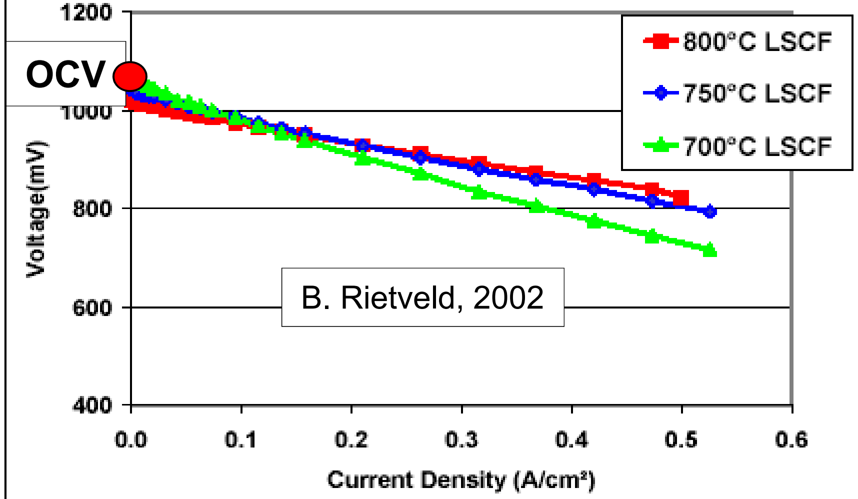
Janaf Tables for 298K = 25°C:

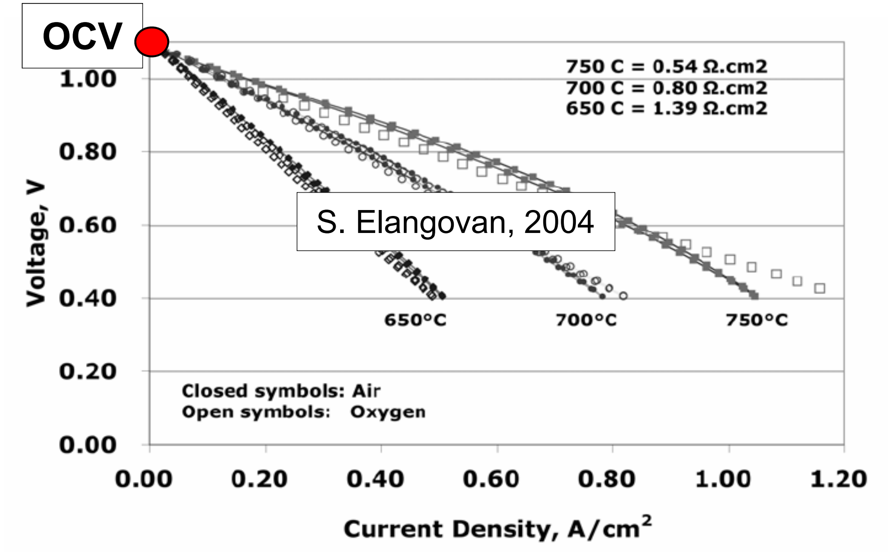
H_2:	$\Delta_f G^0 = 0$
O_2:	$\Delta_f G^0 = 0$
H_2O:	$\Delta_f G^0 = -237'141$ J/mol

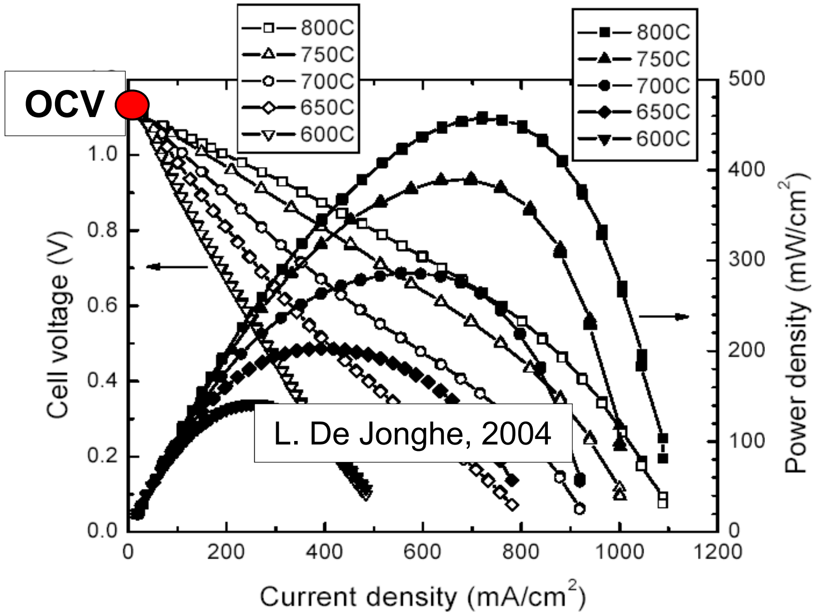
Reaction $\Delta_f G^0(T) = -2 \times 237'141 - (0 + 0) = -474'282$ J/mol

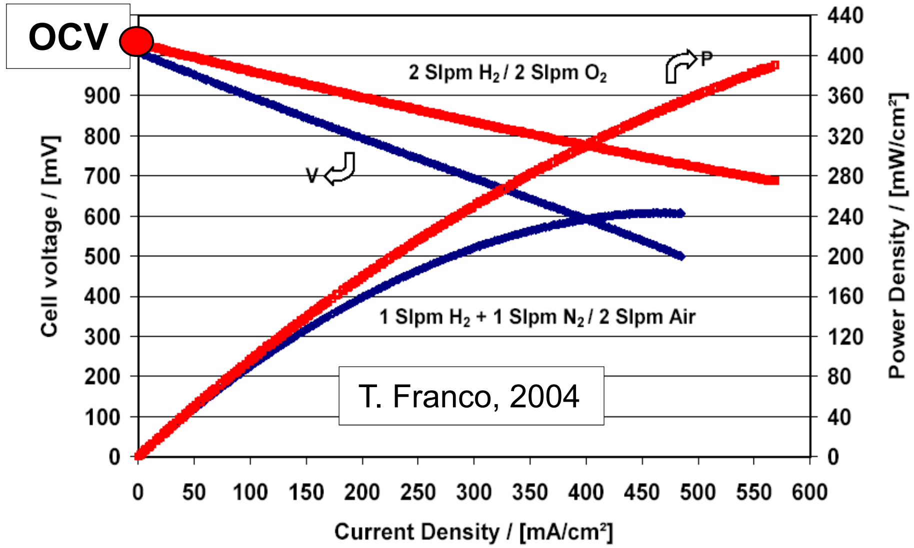
at 25°C: OCV = 1.23 Volt ?
at 727°C: OCV = 1.00 Volt !

Representative SOFC Characteristics





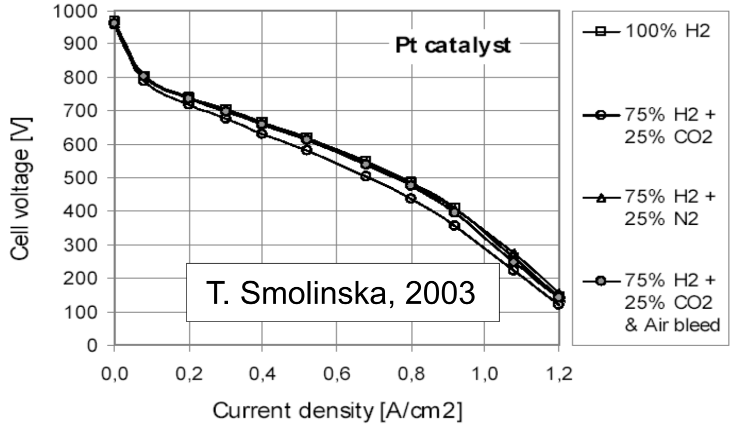


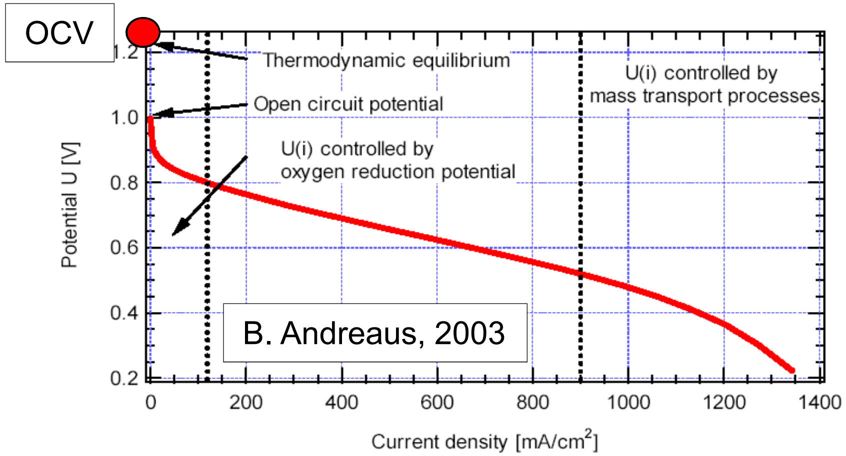


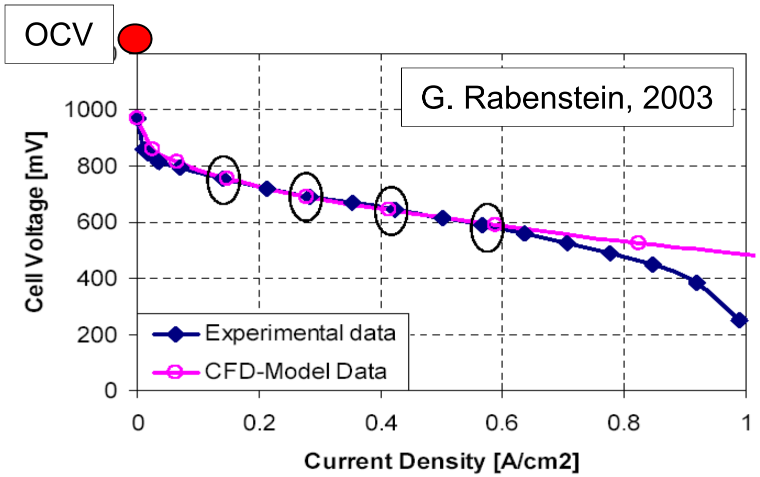
Representative PEFC Characteristics

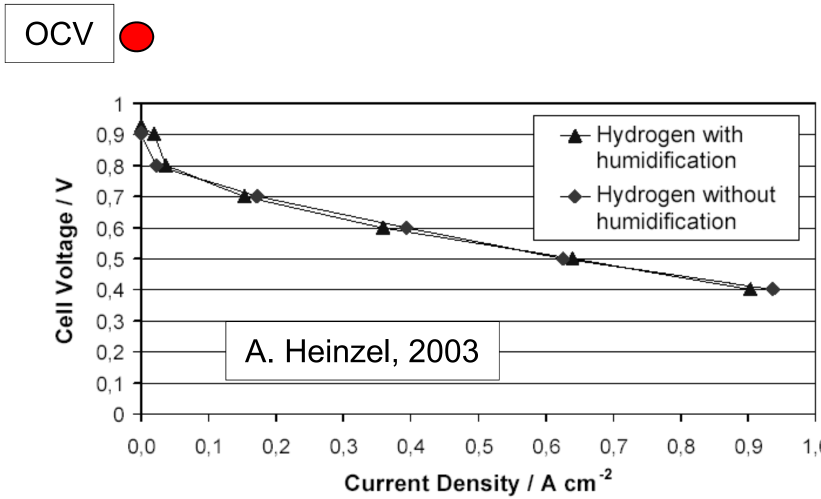
OCV

Theoretical OCV = 1.23 V









Hydrogen Oxidation in Fuel Cells

T

All fuel cell reactions are unforced or spontaneous!

$2\ H_2 + O_2 \Rightarrow 2\ H_2O$

Across electrolyte => HT-OCV

"High Temperature Oxidation of Hydrogen" (HT-OCV)

Spontaneous Ignition Temperature for H_2 and O_2 .... 585°C

"Low Temperature Oxidation of Hydrogen" (LT-OCV)

$H + O \Rightarrow HO^-$ (Hydroxyl)

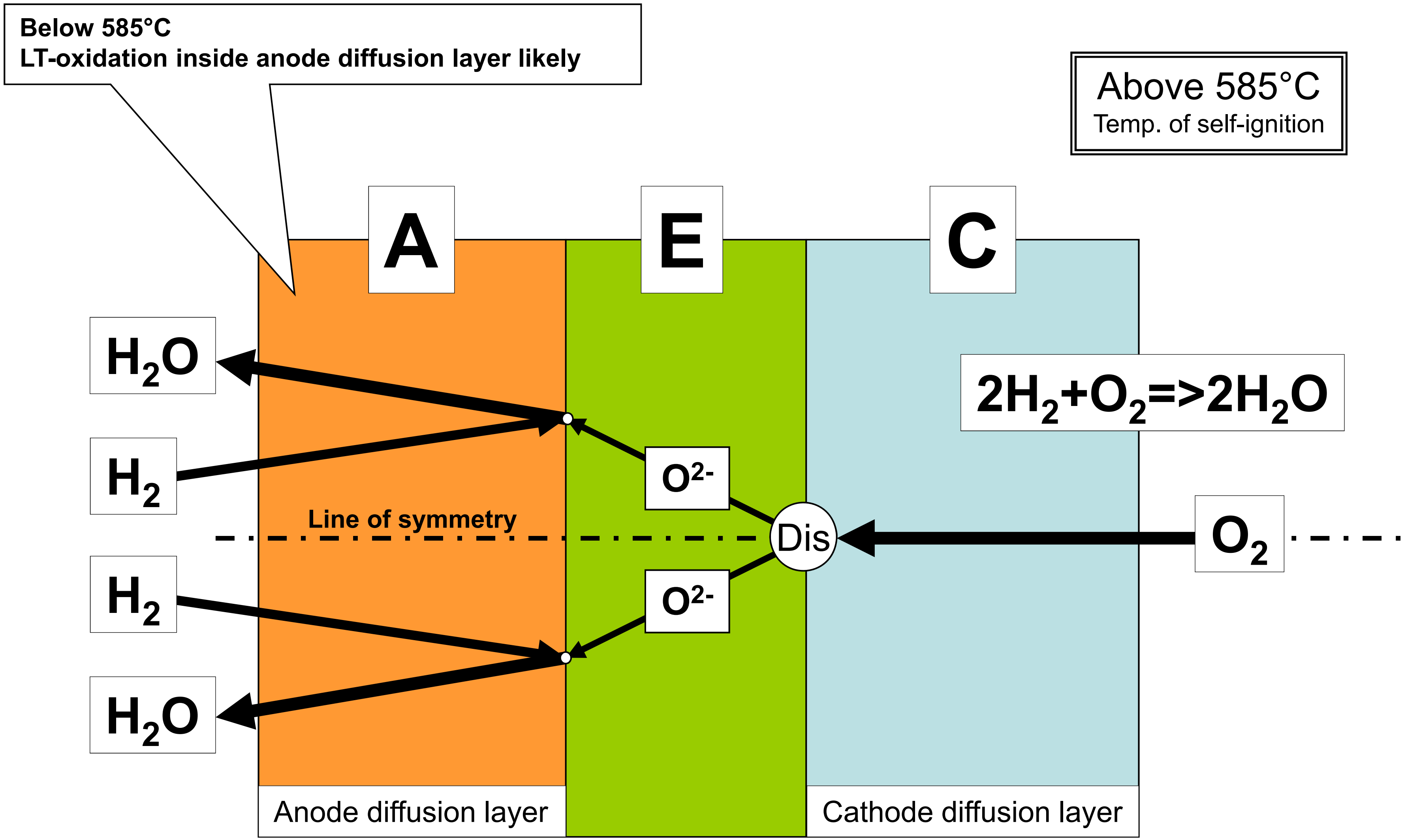
Across electrolyte => LT-OCV

followed by:

2 chemical reactions inside cathode diffusion layer => heat

$2\ HO^- \Rightarrow H_2O_2$ and $H_2O_2 \Rightarrow H_2O + O$

Below 585°C no spontaneous HT oxidation of hydrogen possible

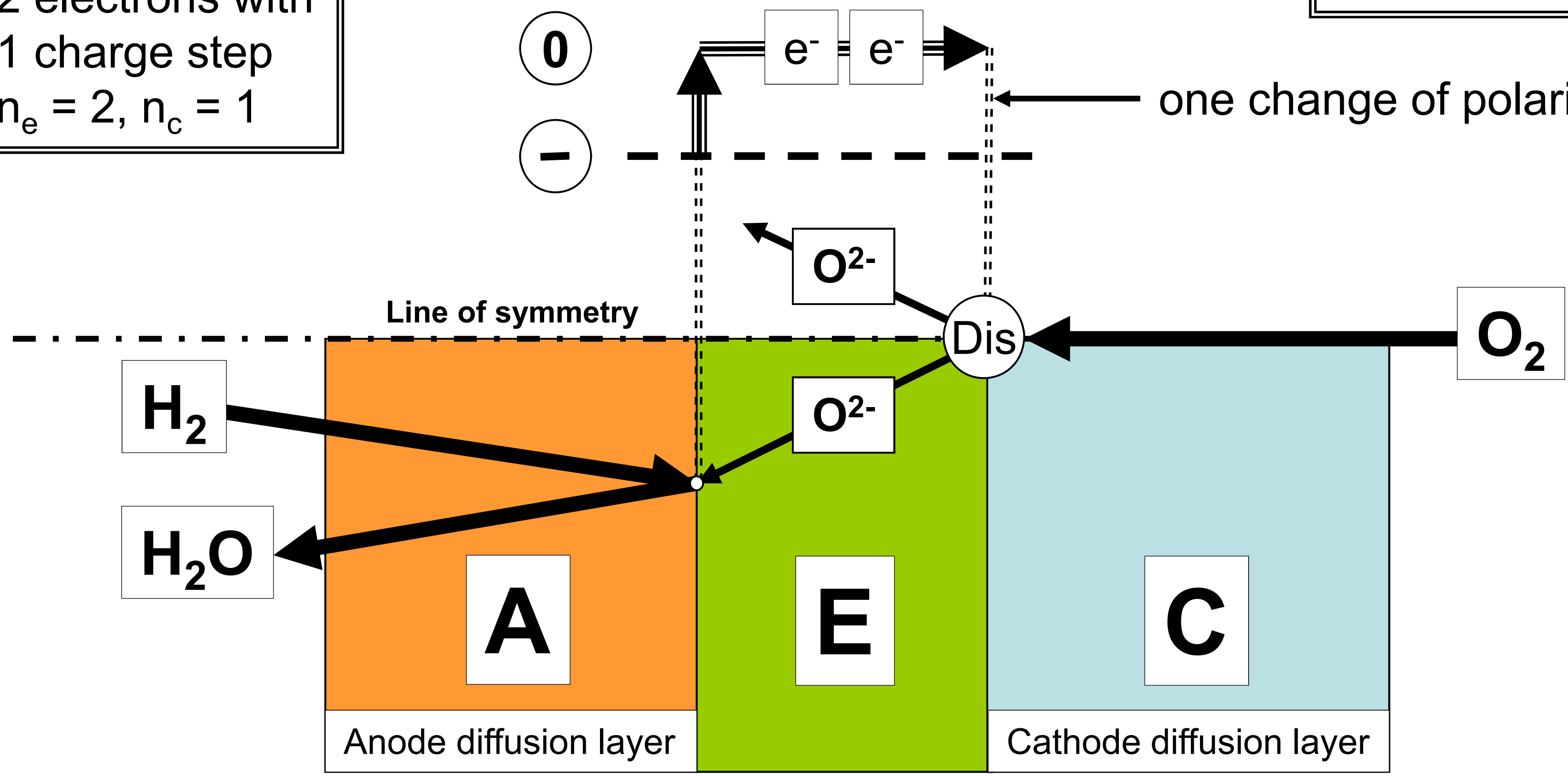


HT Oxidation of Hydrogen in SOFCs

Ulf Bossel
Fuel Cell Consultant
Oberrohrdorf / Switzerland

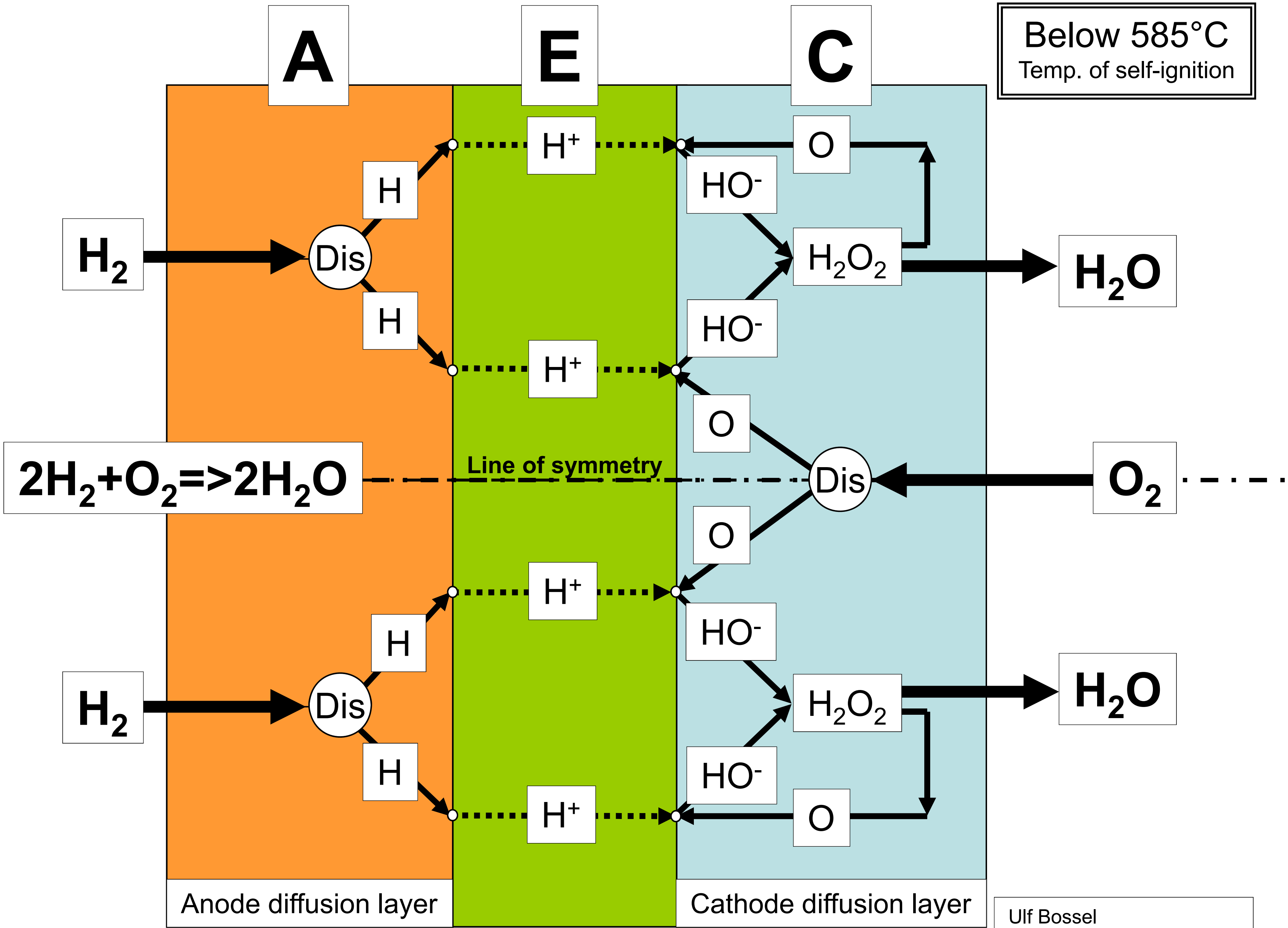
For each H_2O
2 electrons with
1 charge step
$n_e = 2$, $n_c = 1$

Above 585°C
Temp. of self-ignition



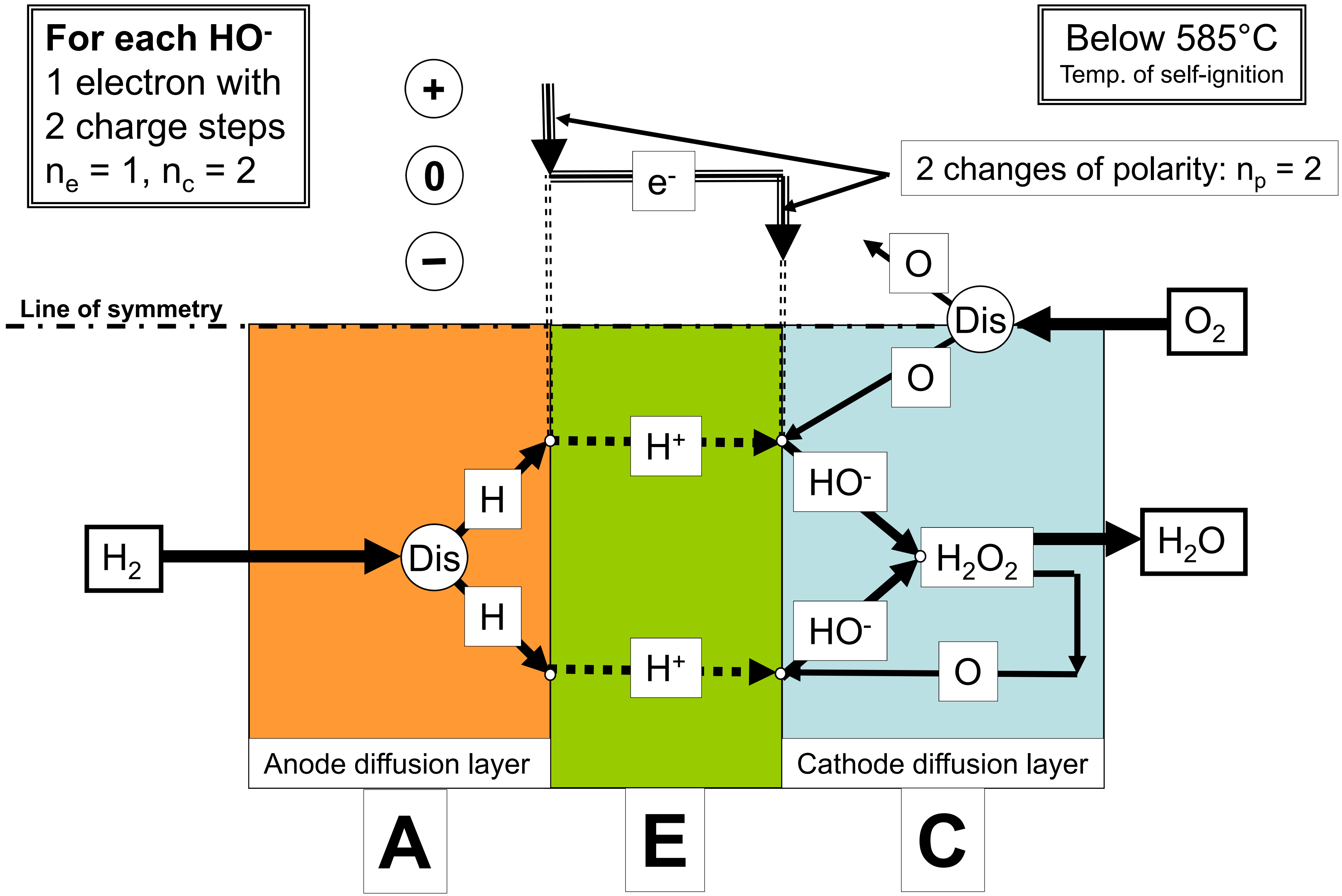
HT Charge Transfer in SOFCs

Ulf Bossel
Fuel Cell Consultant
Oberrohrdorf / Switzerland



LT Oxidation of Hydrogen in Protonic FCs

Ulf Bossel
Fuel Cell Consultant
Oberrohrdorf / Switzerland



LT Charge Transfer in Protonic FCs

Ulf Bossel
Fuel Cell Consultant
Oberrohrdorf / Switzerland

HT Oxidation of Hydrogen in Fuel Cells (above 585°C)

$$2\ H_2 + O_2 \Rightarrow 2\ H_2O$$

HT-OCV

1.23V at 25°C and 1.00V at 700°C

LT Oxidation of Hydrogen in Fuel Cells (below 585°C)

$$H + O \Rightarrow HO^-$$

(across electrolyte)

$$OCV = -\,\Delta_f G^0 / (n_e\ n_p\ F)$$

with $\Delta_f G^0$ Gibbs Free Energy, F = Faraday constant = 96485 C/mol
n_e = number of exchanged electrons = 1, n_p = number of polarity change steps = 2

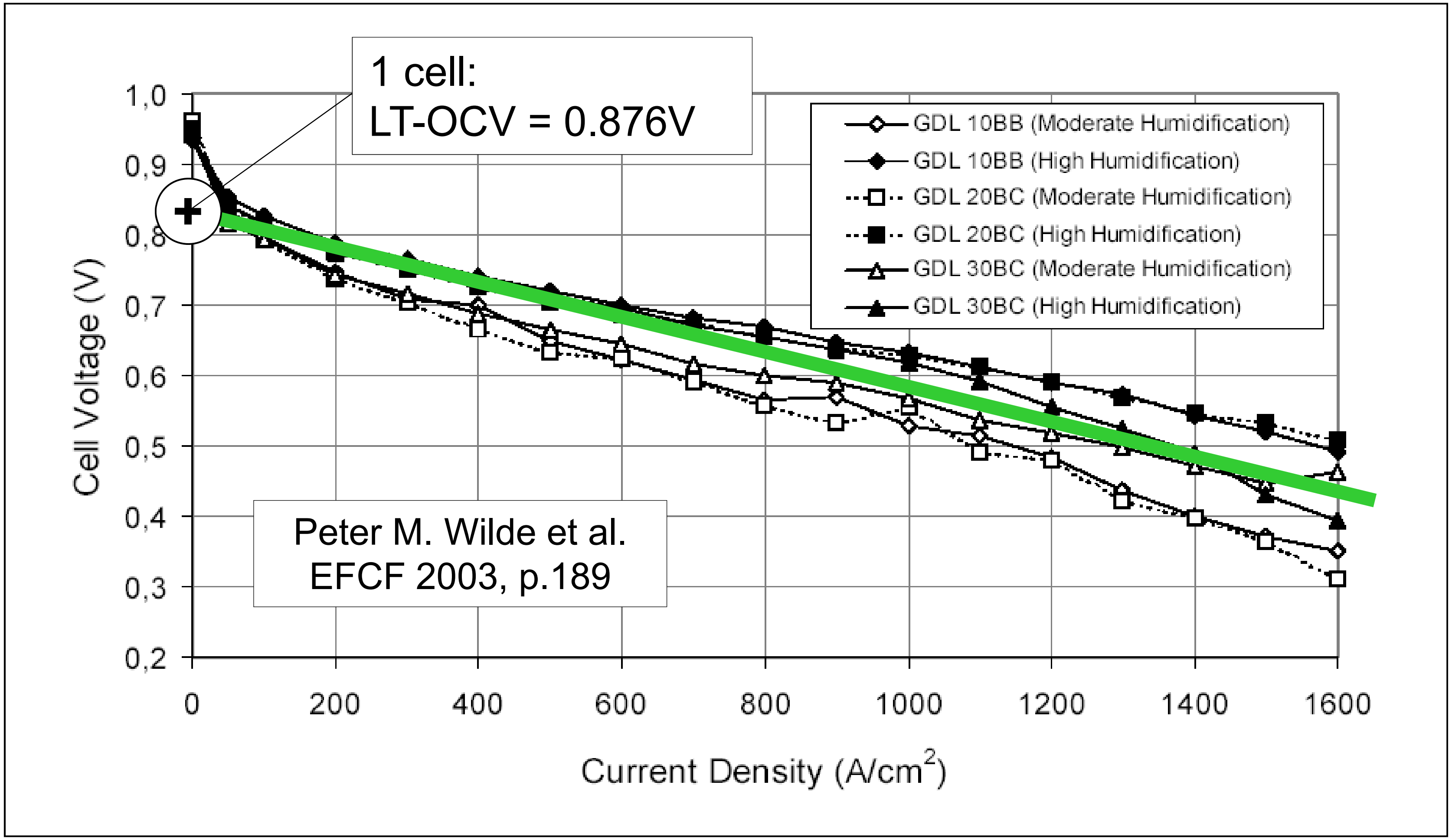
Janaf Tables for 298K = 25°C:
H: $\Delta_f G^0$ = -203278 J/mol, O: $\Delta_f G^0$ = 0, HO: $\Delta_f G^0$ = +34277 J/mol

Reaction $\Delta_f G_0$ = - (34277 – (-203278)) = -169001 J/mol

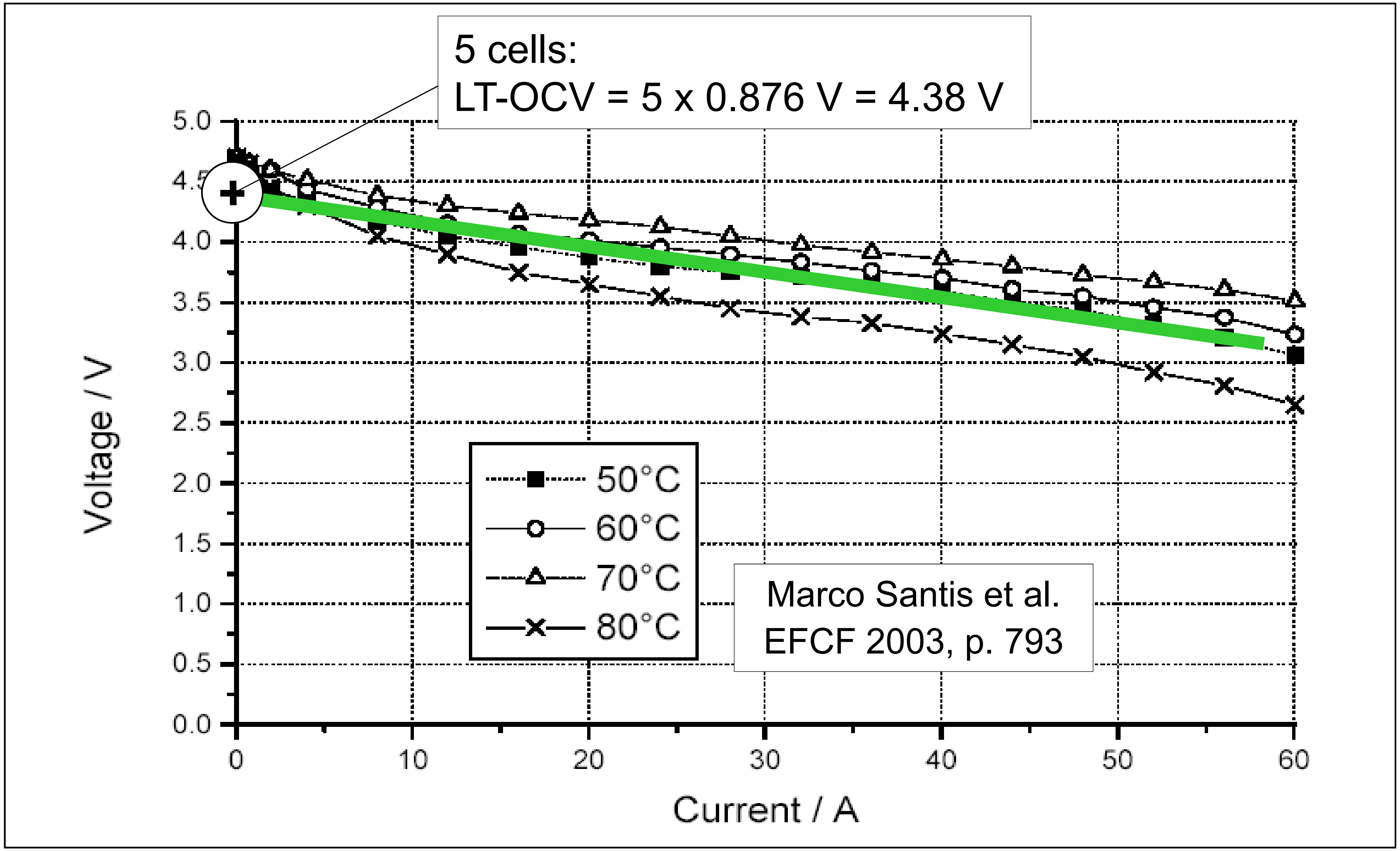
LT-OCV

0.876V at 25°C and 0.767V at 585°C

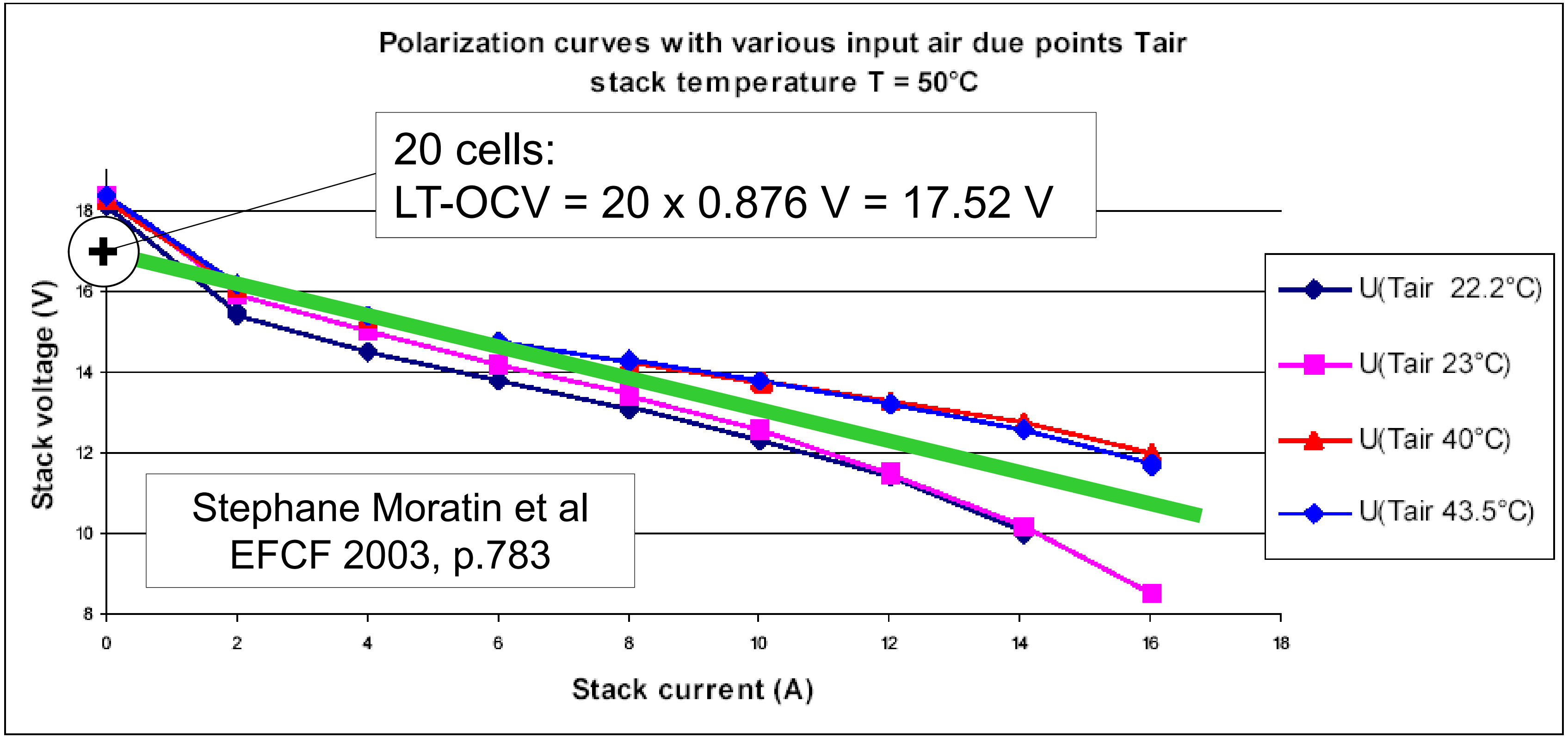
Open Circuit Voltage of a PEFC



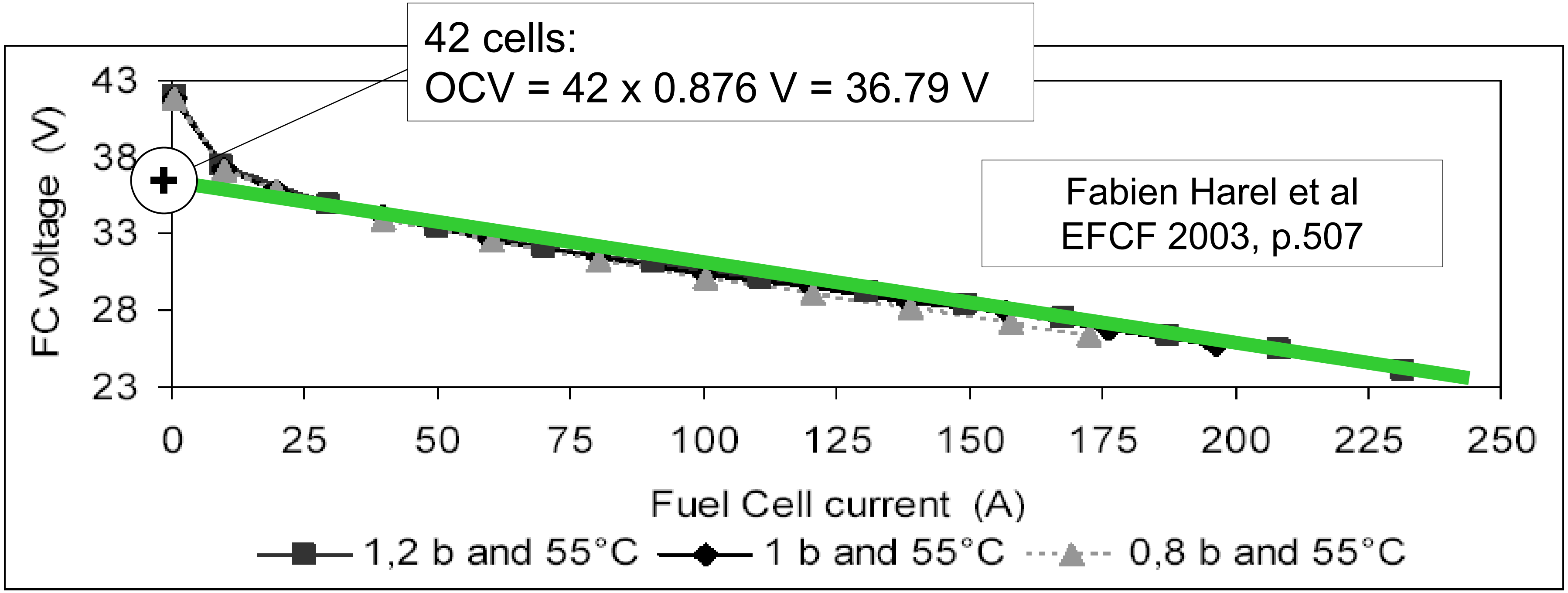
Open Circuit Voltage of a PEFC



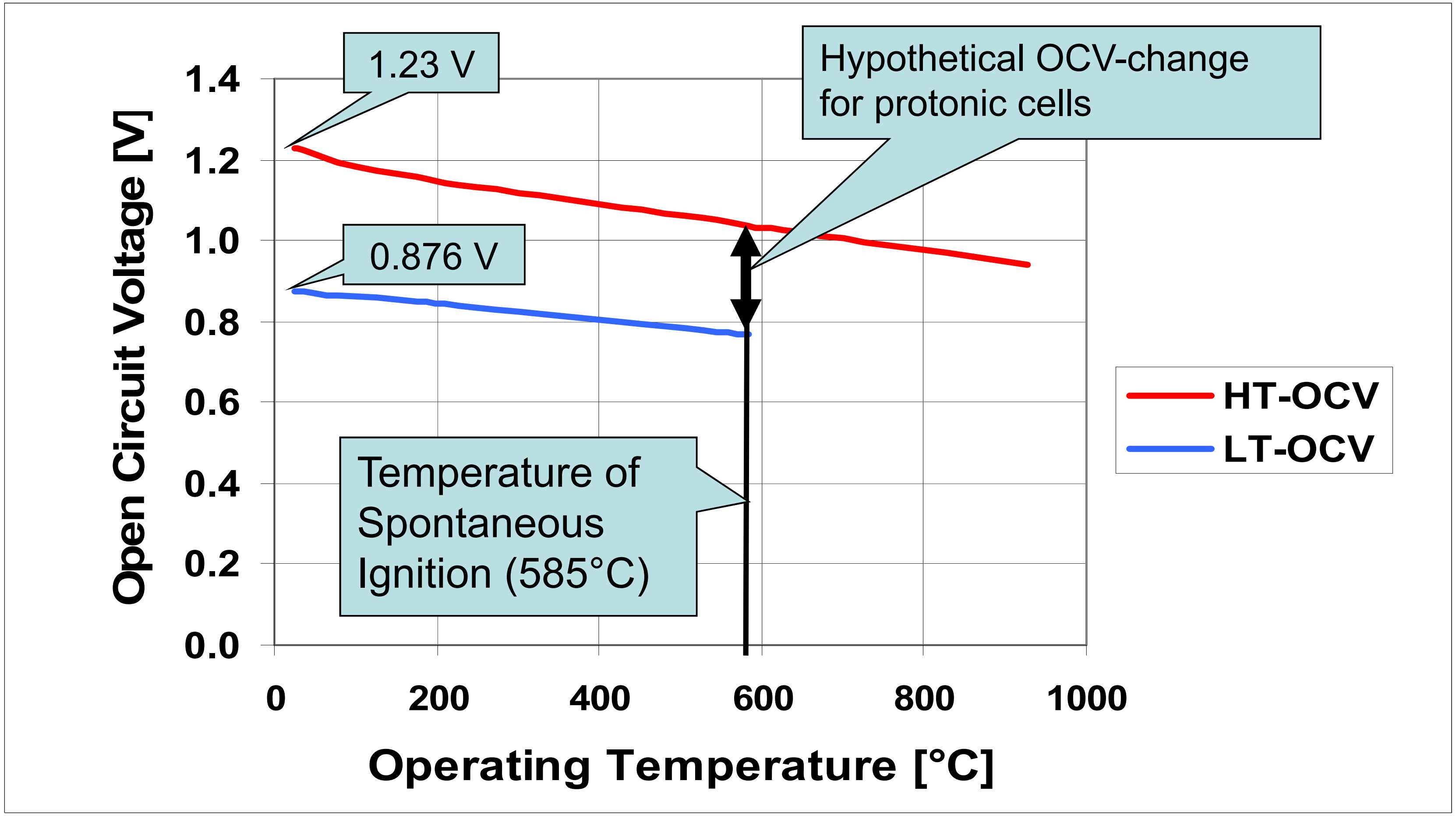
Open Circuit Voltage of a PEFC



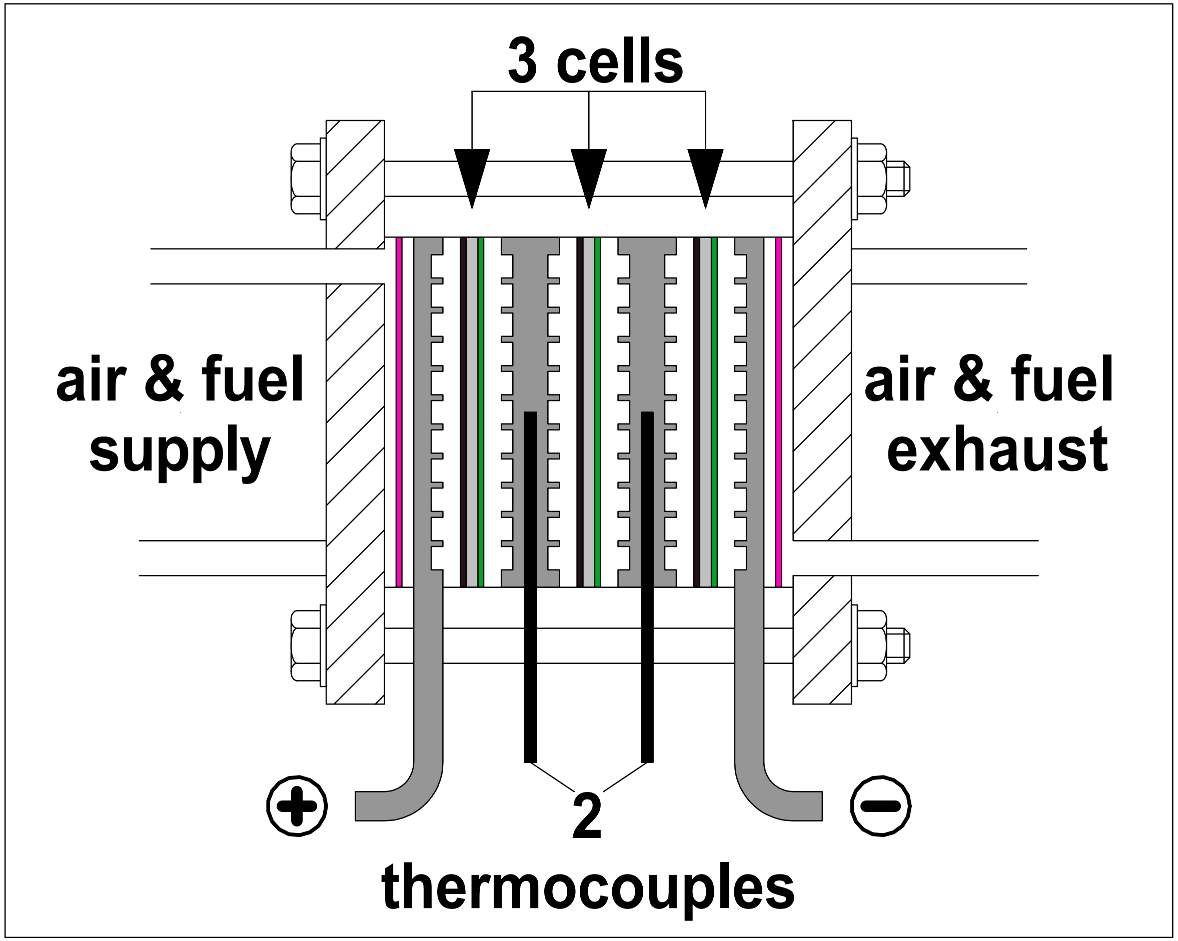
Open Circuit Voltage of a PEFC



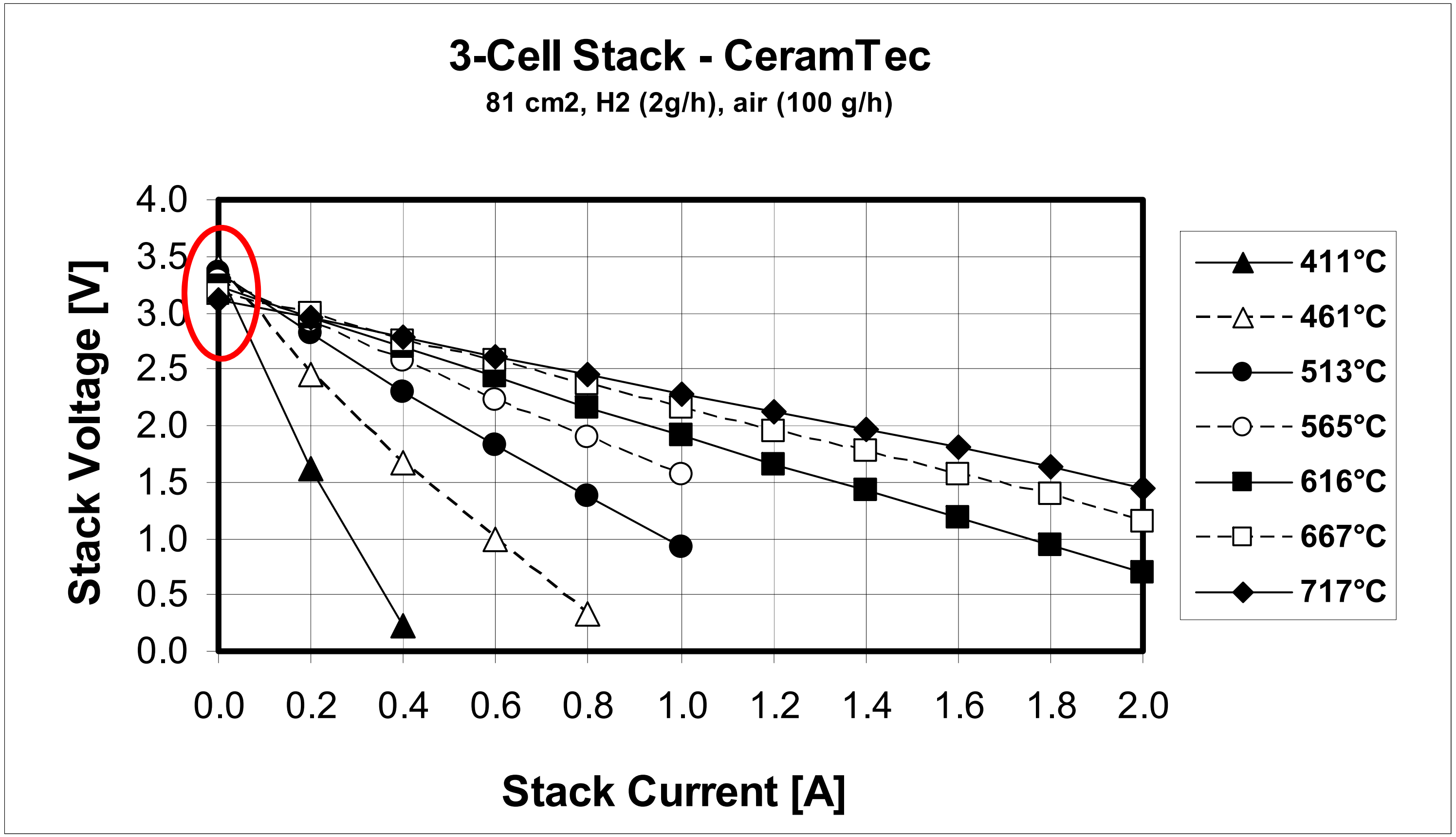
Hypothetical OCV Change at Temperature of Spontaneous Ignition



SOFC Setup for H_2-O_2 OCV Studies above and below the Spontaneous Ignition Temperature (585°C)

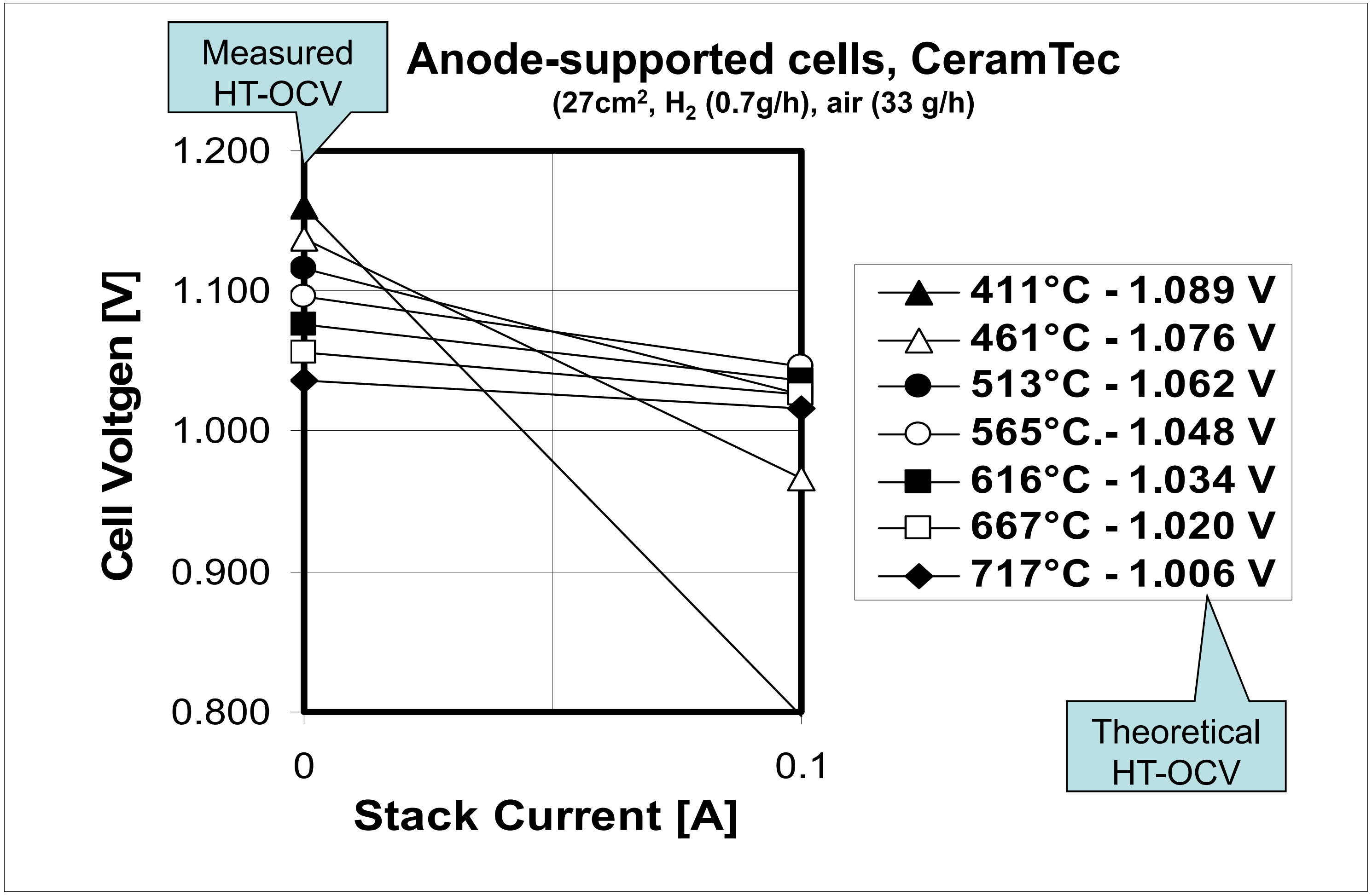


3-Cell OCV vs. Stack Temperature

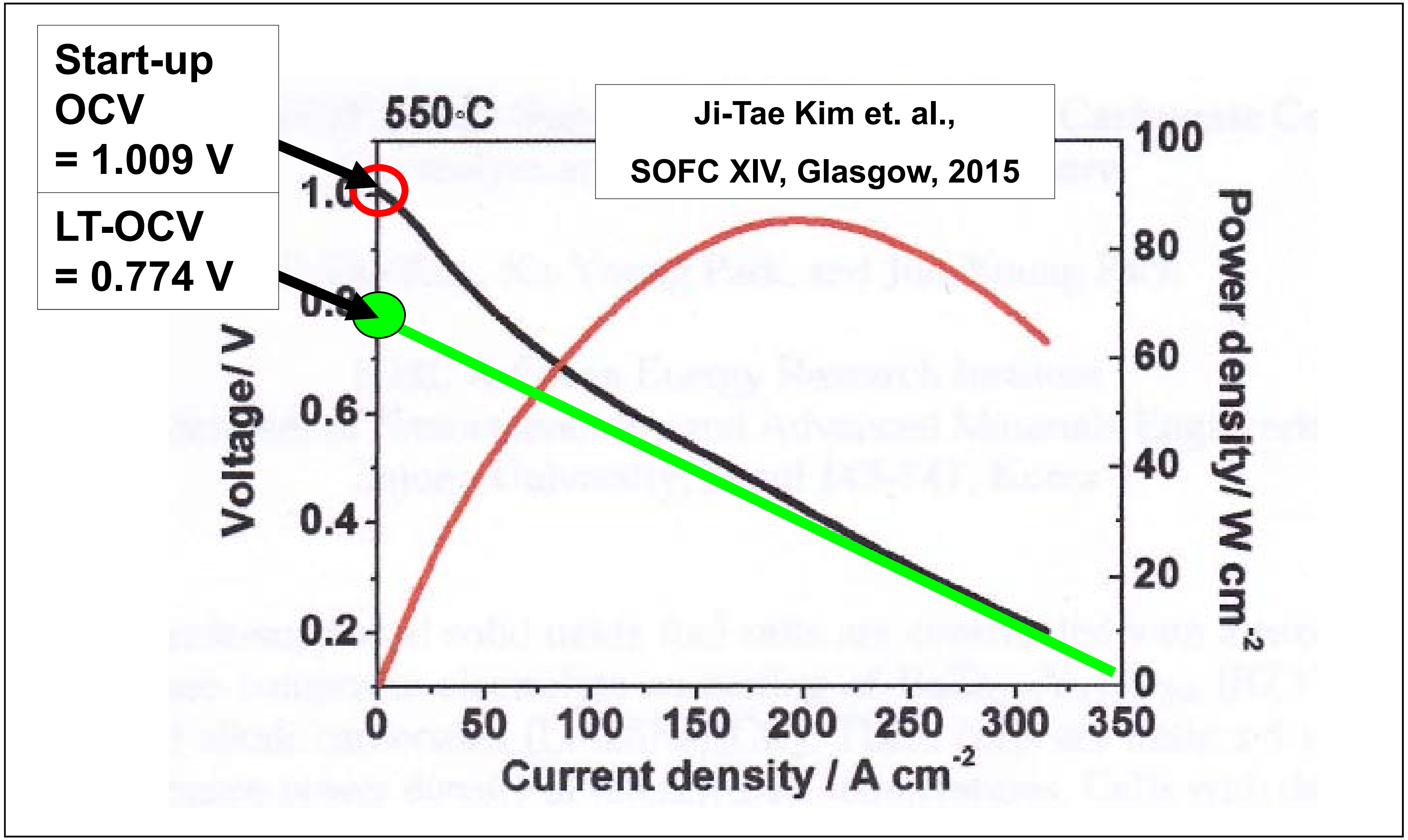


Single Cell OCV vs. Stack Temperature

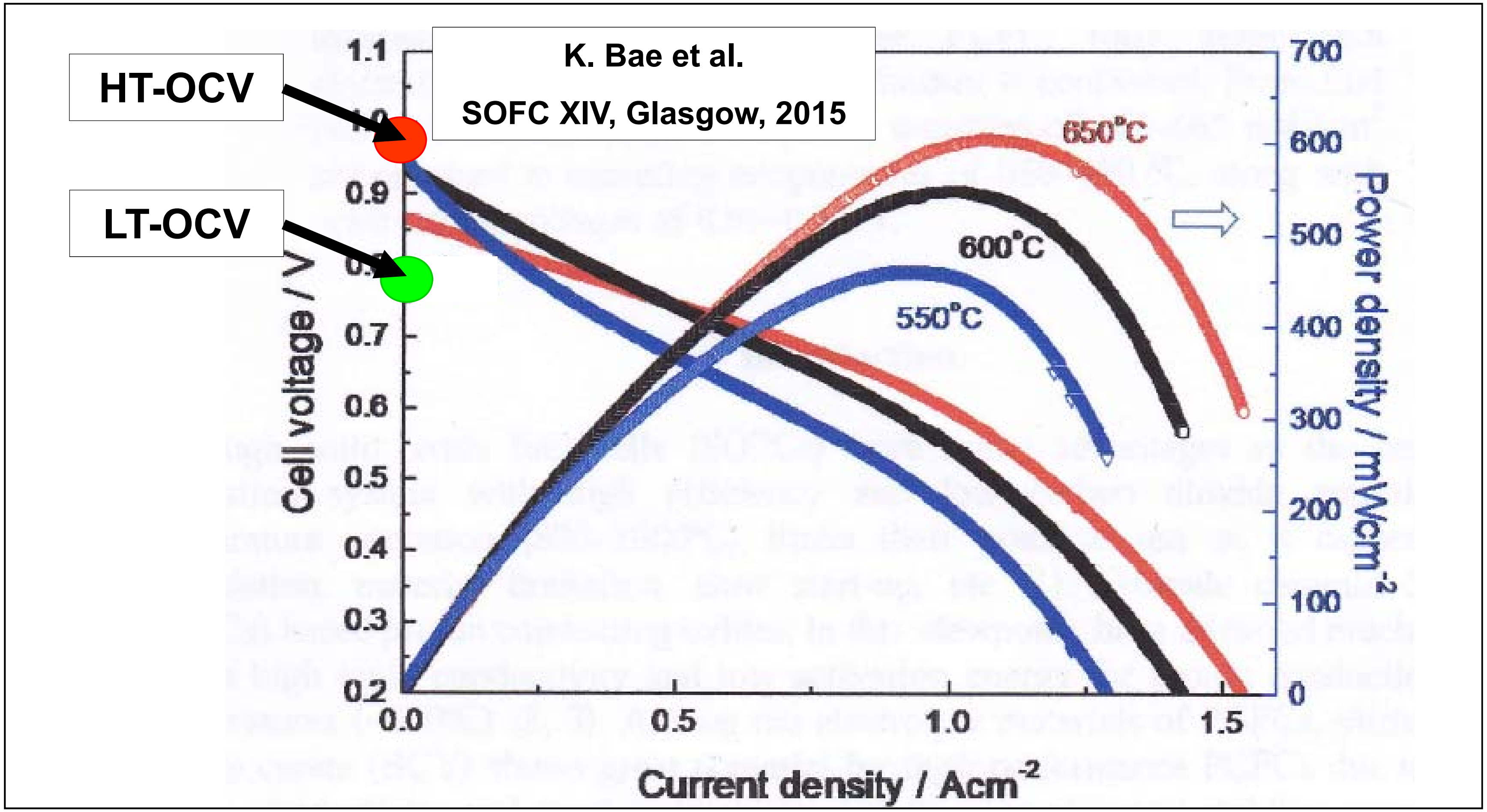
Details for i < 0.1 A



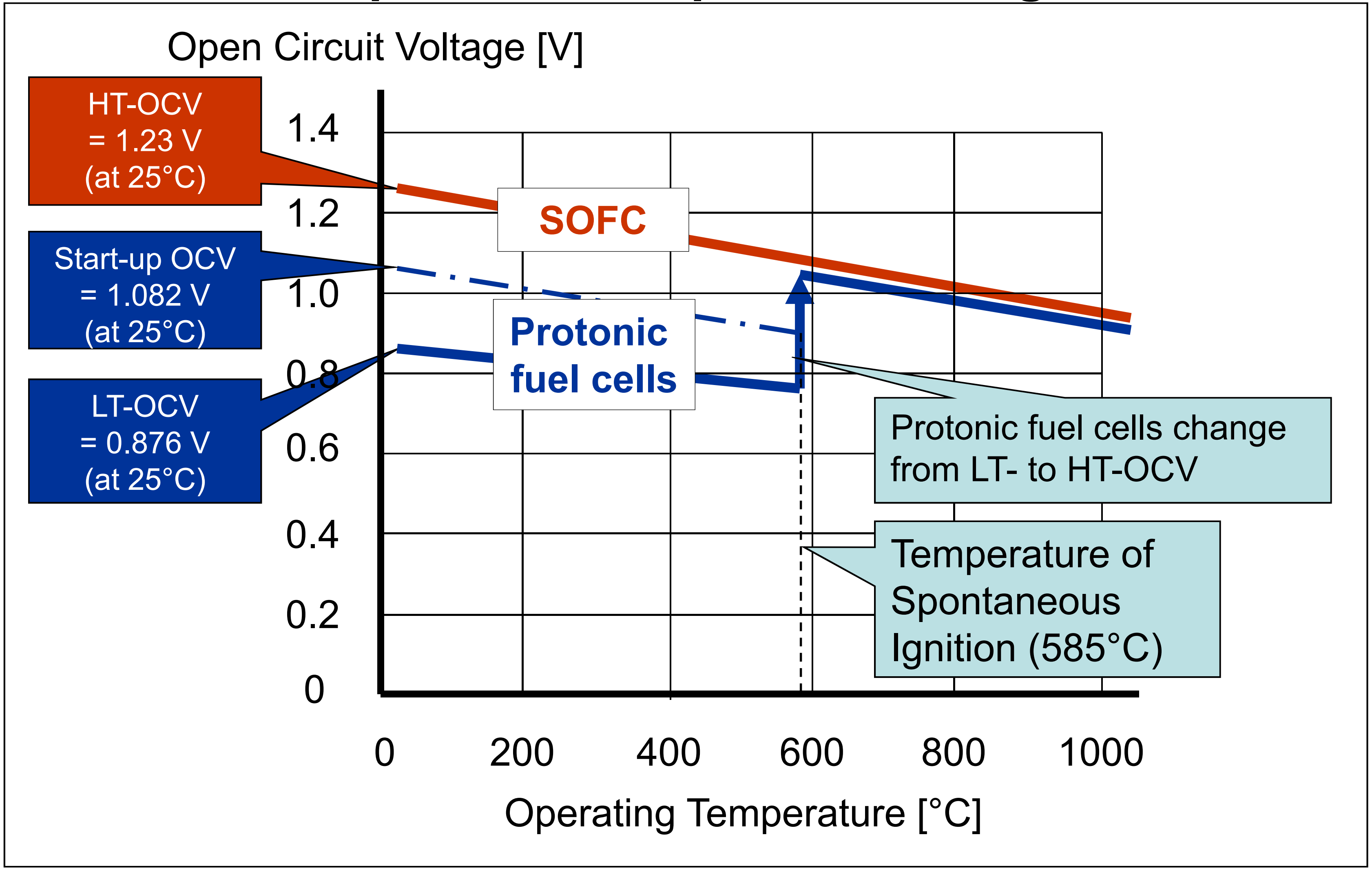
Protonic Ceramic Fuel Cell (PCFC)



Protonic Ceramic Fuel Cell (PCFC)



Hypothesis for Protonic Fuel cCells: Switch of LT-OCV to HT-OCV at Temperature of Spontaneous Ignition



The Role of Platinum in Protonic Fuel Cells

„Finely dispersed in the diffusion layers of both electrodes“

Apparently, Pt is not involved in the electrochemical exchange processes
at both electrode-electrolyte interfaces

What role does Platinum play in the diffusion layers?

Guess:

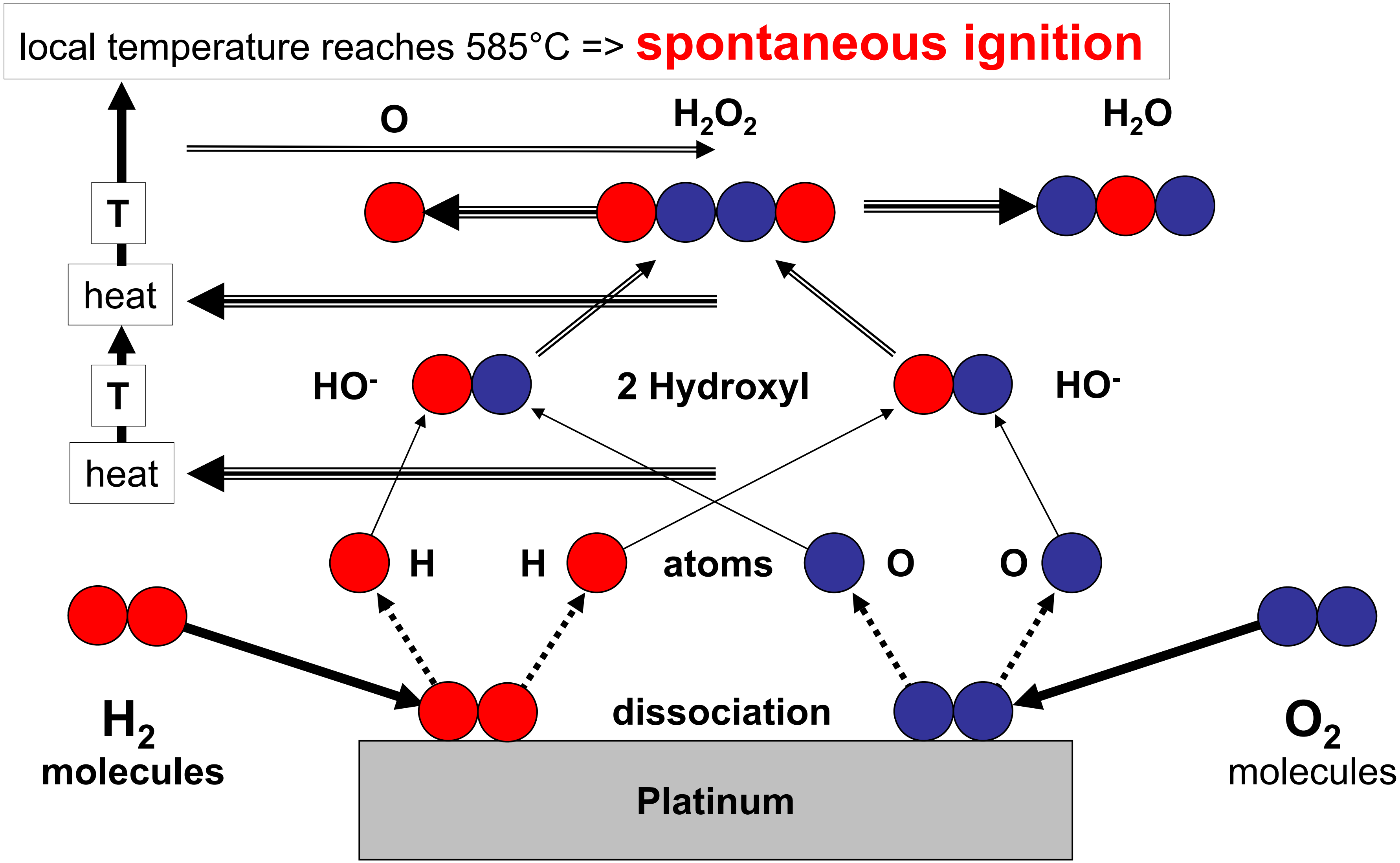
Hydrogen and Oxygen molecules are dissociated by Pt
inside both diffusion layers

Hydroxyl formation

$$H + O \Rightarrow HO^-$$

becomes possible,
because Hydrogen and Oxygen are in “status nascendi”

Ignition of H_2 and O_2 on Platinum



LT-Oxidation of H_2 and O_2 on Platinum
(fuel cells or else)

At ambient temperatures
Hydrogen and Oxygen can be ignited by Platinum
(known since 1820?)

Likely sequence of reactions:

1. Hydrogen and Oxygen molecules are dissociated by Pt
2. Hydrogen and Oxygen atoms combine to Hydroxyl by $H + O \Rightarrow OH^-$
   This reaction is exothermic. Heat is generated locally
4. Two Hydroxyl ions combine: $OH^- + OH^- \Rightarrow H_2O_2$
   This reaction is exothermic. Heat is generated locally
5. H_2O_2 splits up: $H_2O_2 \Rightarrow H_2O + O$
   This reaction is endothermic. Some heat is absorbed locally
6. Temperature rises locally
7. Start of chain reaction $2\,H_2 + O_2 \Rightarrow 2\,H_2O$
   when Spontaneous Ignition Temperature (585°C) is reached locally
8. Hydrogen and Oxygen burn as expected: $H_2 + O \Rightarrow H_2O$

Recommendations:

Check the presented hypothesis
Publish critical results
Establish general consent
Update teaching
Revise textbooks

Thank you for your patience!

Questions?