

Oxygenates and Ammonia as SOFC Fuels

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**The First European Fuel Cell Technology
and Applications Conference
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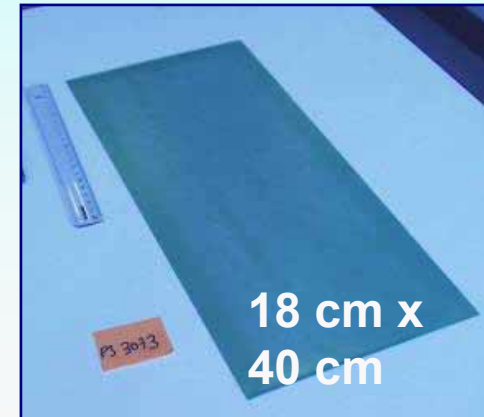
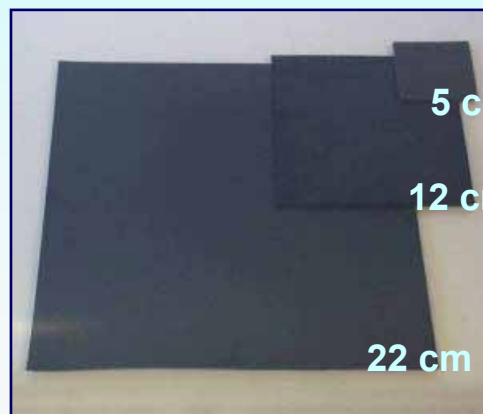
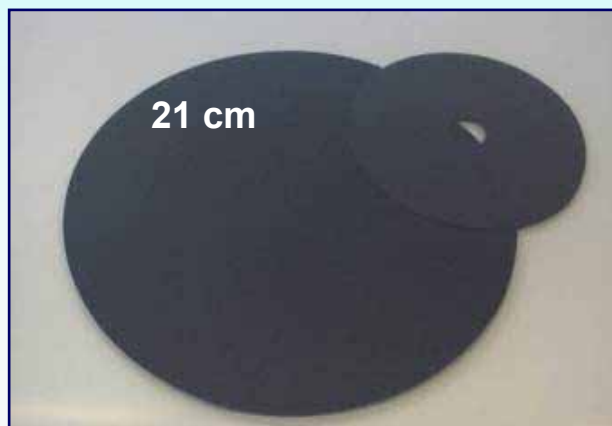
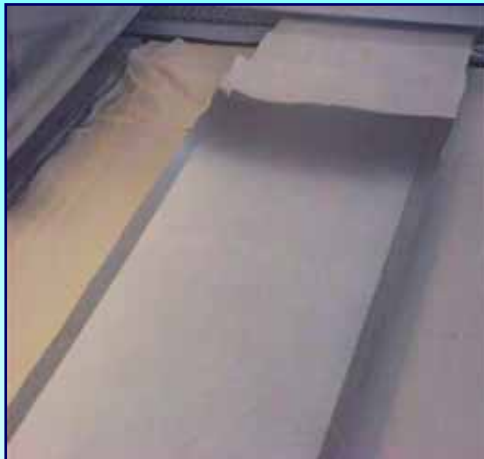
**Catalysis
Materials
Fuel Processing
Energy Technology
Solid Oxide Fuel Cell Consortium**

Haldor Topsøe A/S

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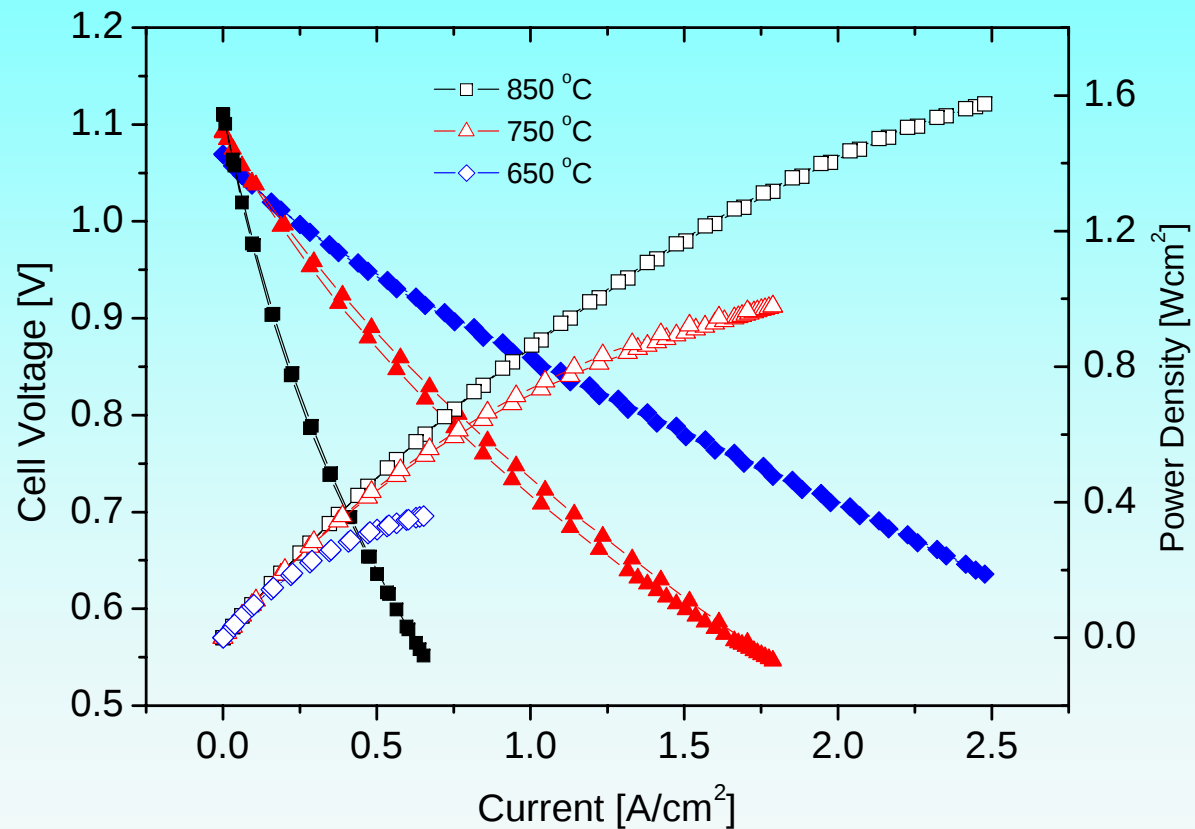


Manufacture of Anode-supported Cells

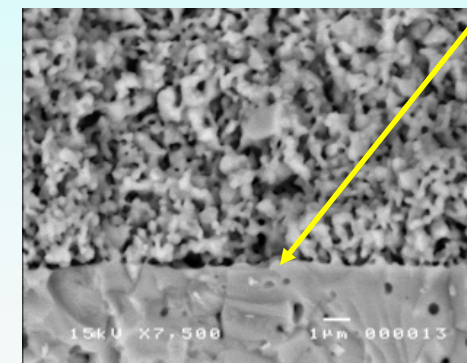
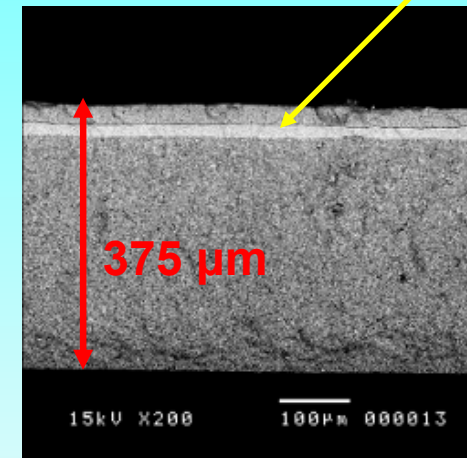


Single Cell Test

Cell Performance



Wide temperature operation window



Stack Development

- **Materials**

- Cells

- Metallic Interconnects

- Coatings

- Seals

- **Design**

- Flow configuration

- Internal manifold

- Stack size and geometry

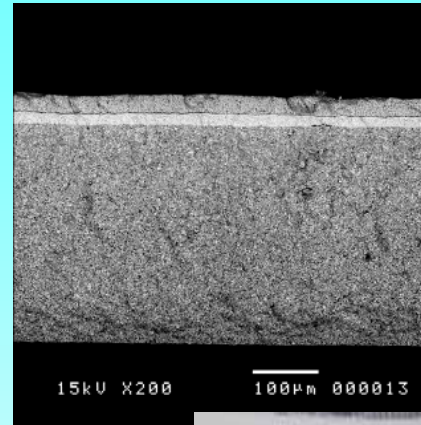
- **Manufacturing**

- Tolerances

- Success rate

- Reproducibility

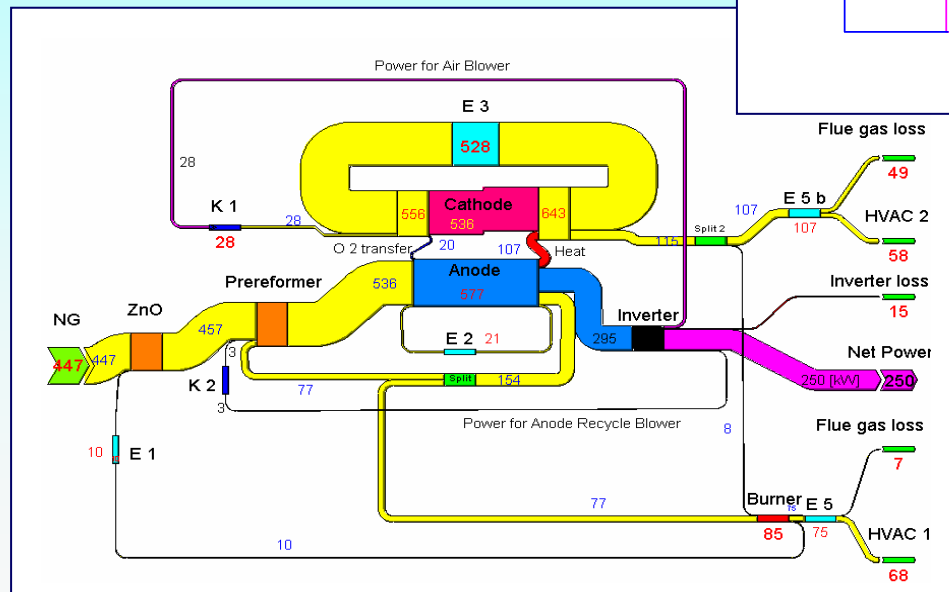
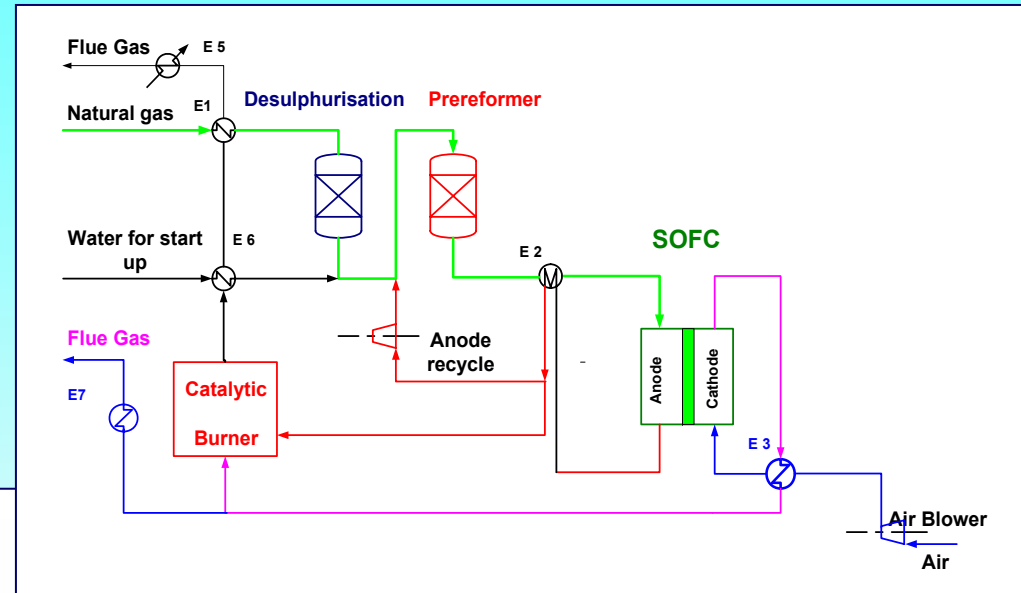
- **Reliability & Cost**



SOFC System Modelling

Natural gas base case - Conceptual Study 250 kW

56 % Net el. efficiency
84 % Cogen. efficiency



Energy Flows (kJ/s)



TOFC- Wärtsilä Collaboration



5 kW Test Stand

September 17. 2004:

1,25 kW

FU = 40%, O/C = 2



20 kW SOFC α-prototype

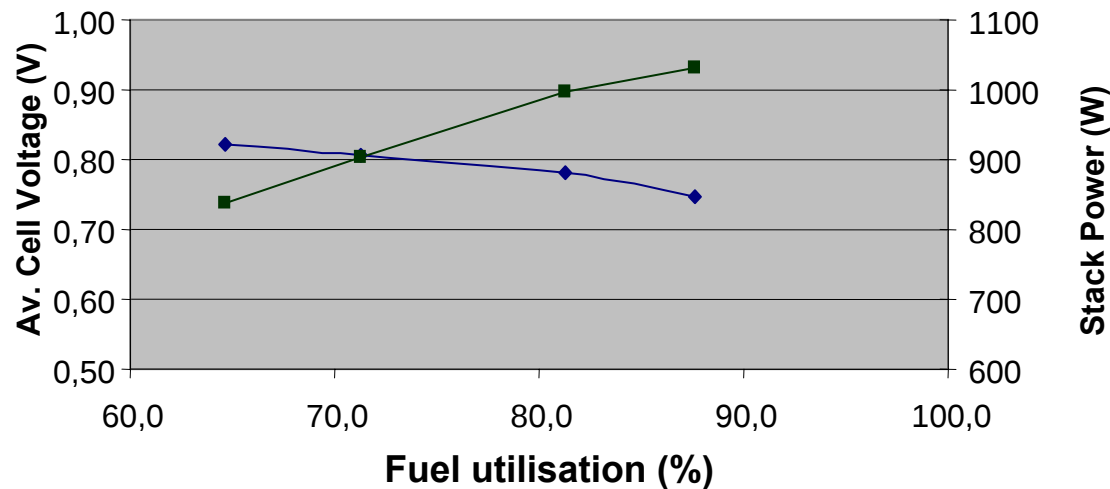
AVL APU Stack Test

50 Cell Stack (12 x 12 cm²)

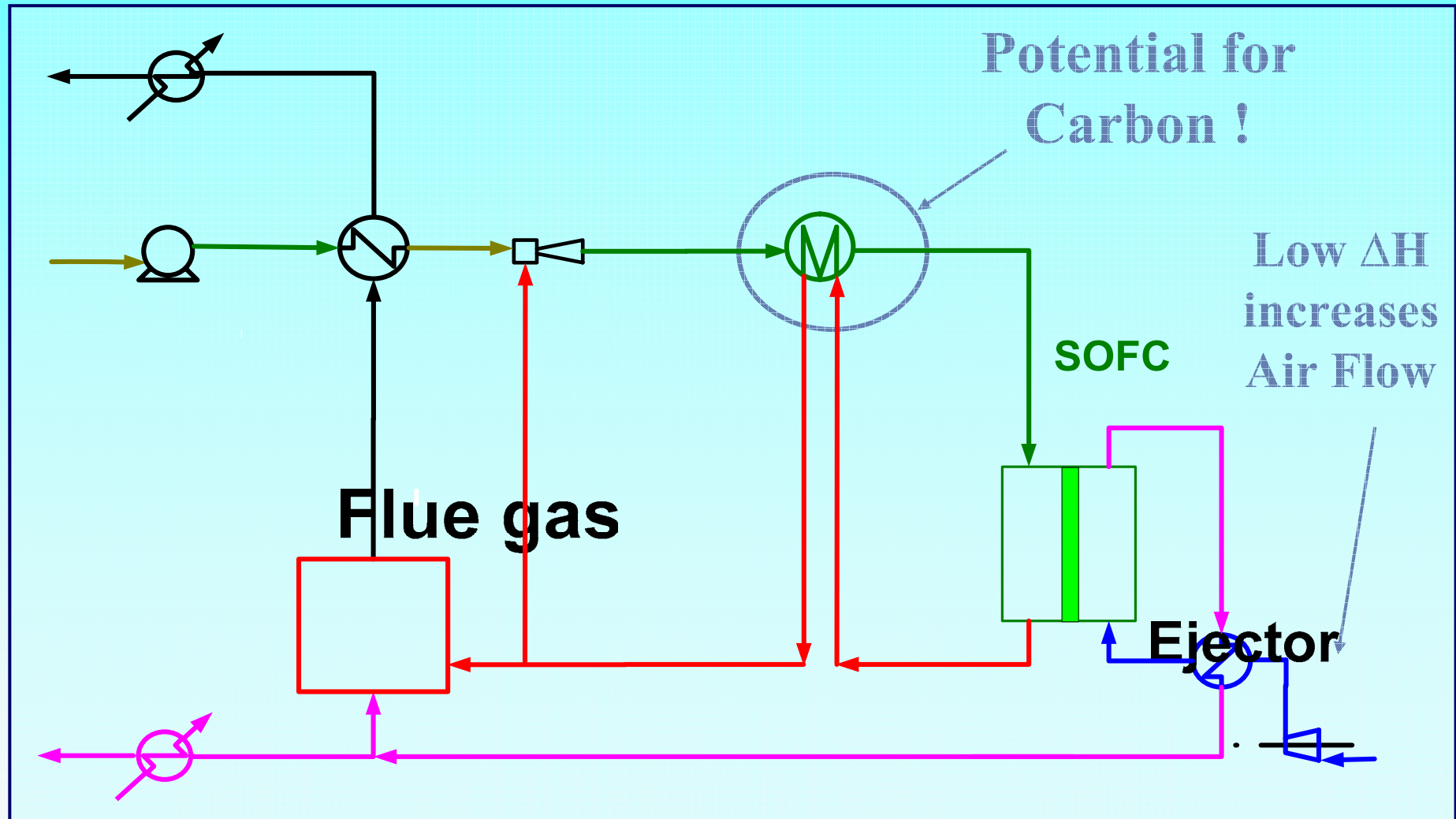
Thermally self-sustained operation
200 W heat loss to surroundings
35% H₂, 4% CO, 11% CO₂, 50% CH₄
Fuel utilisation = 92 %



Voltage and stack power with mix gas



Direct use of Methanol for SOFC

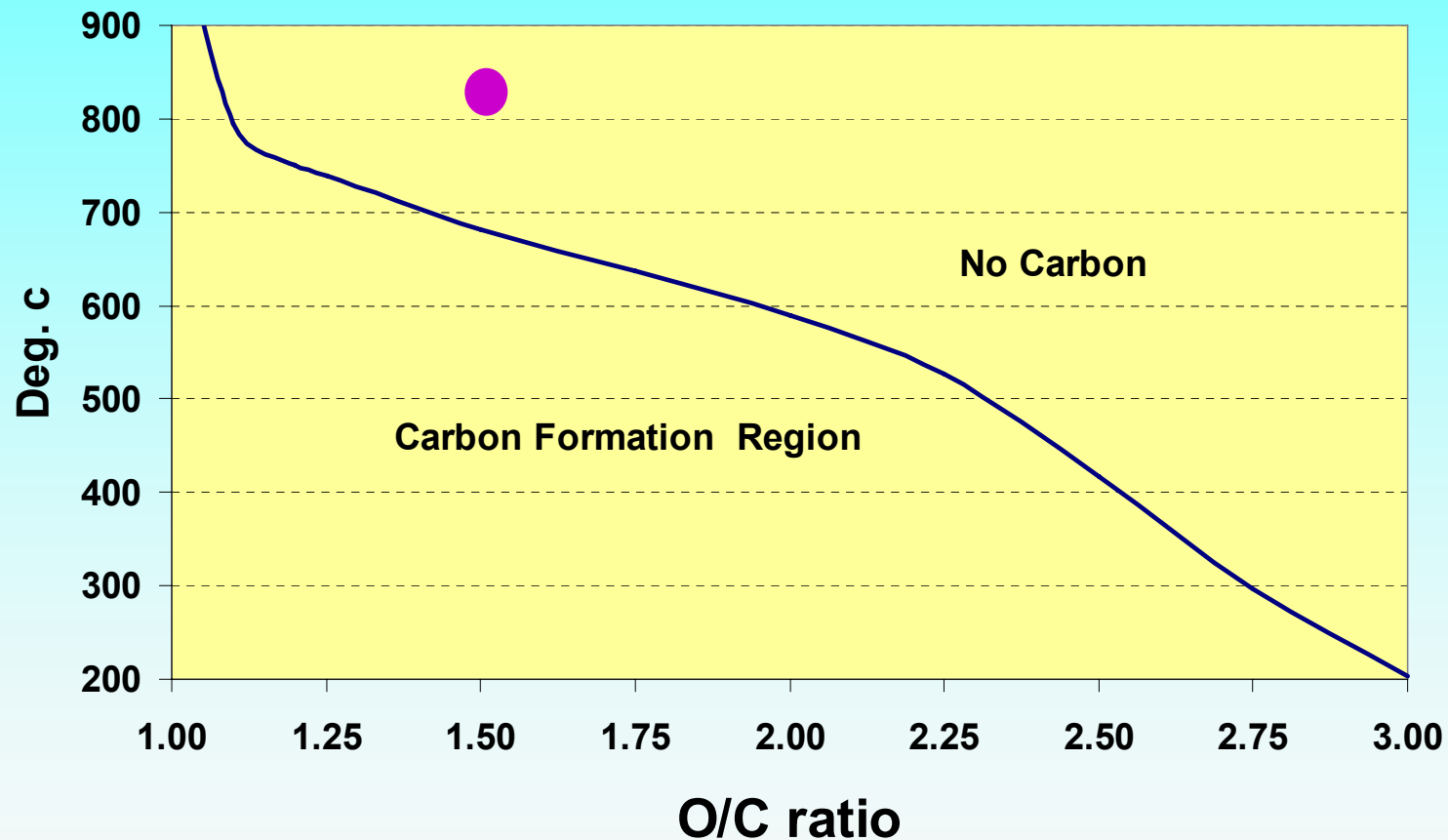


Methanol



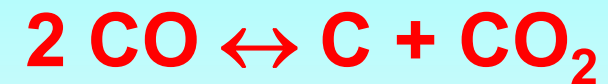
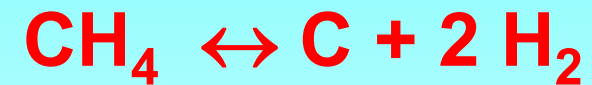
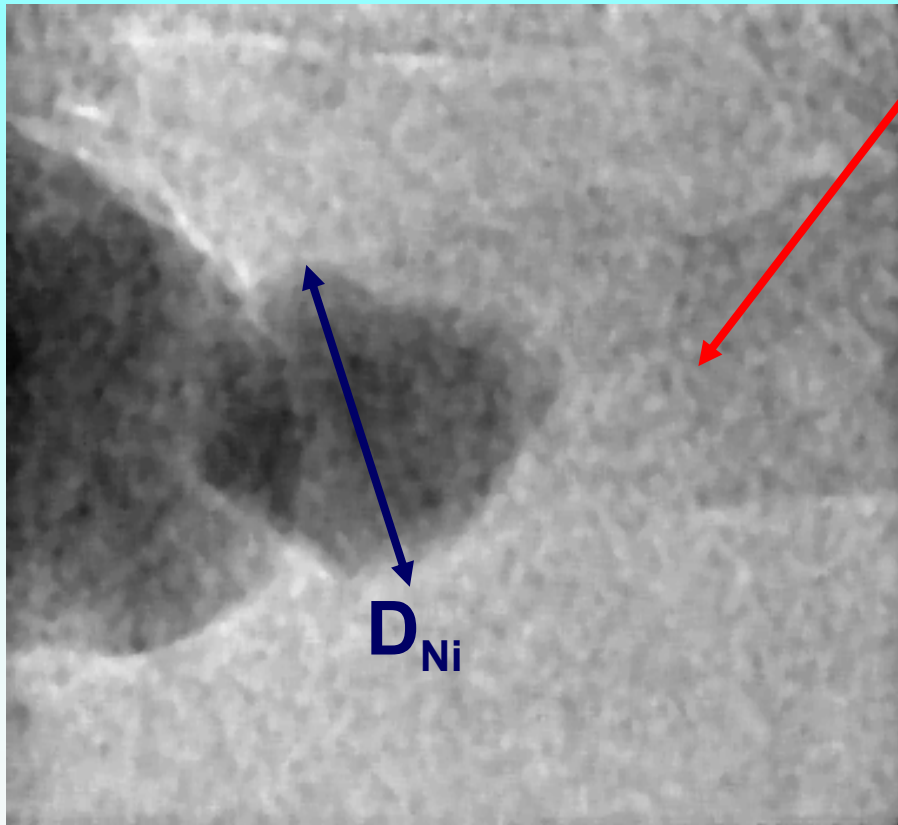
Carbon Formation - Graphite Data

$H/C = 3$ - $P = 1.5$ bar



Formation of Whisker Carbon

In situ HRTEM



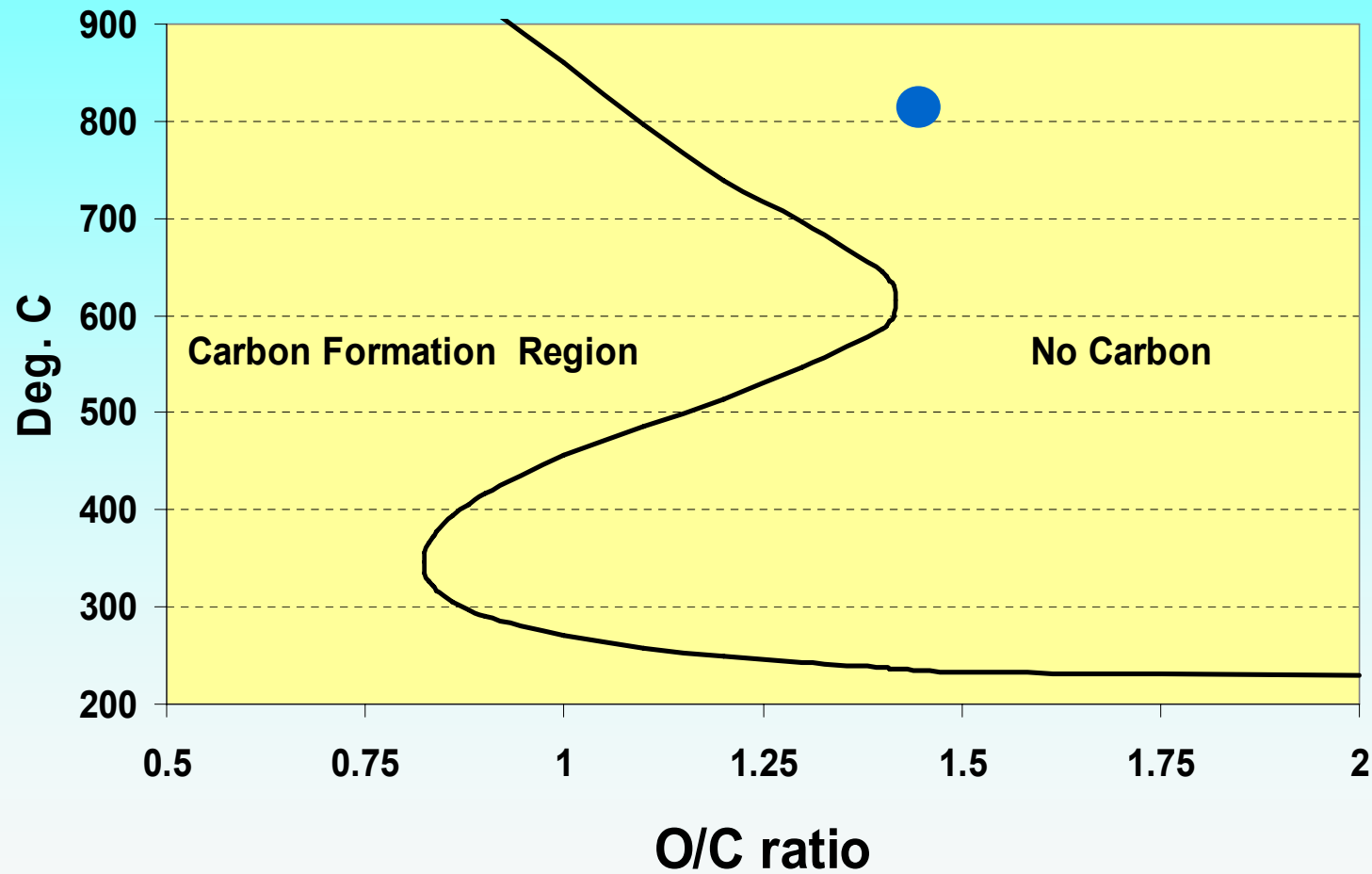
$$\Delta G = \Delta G_{\text{"Graphite"}} - \Delta G_{\text{ExcessWhisker}}$$

$$\ln K_p = a - \frac{b}{D_{\text{crystal}}}$$

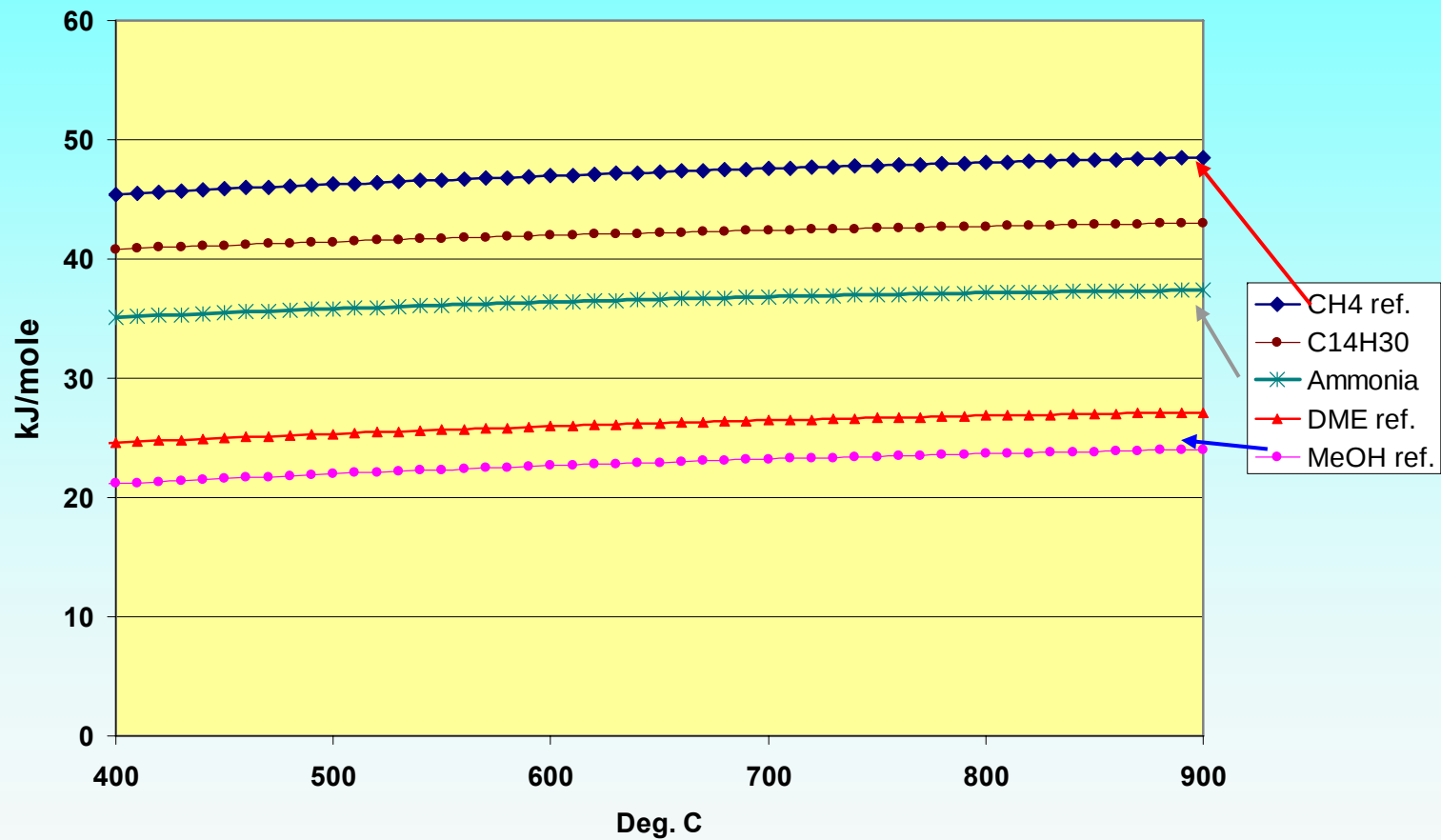


Carbon Formation - 250 nm Ni Crystals

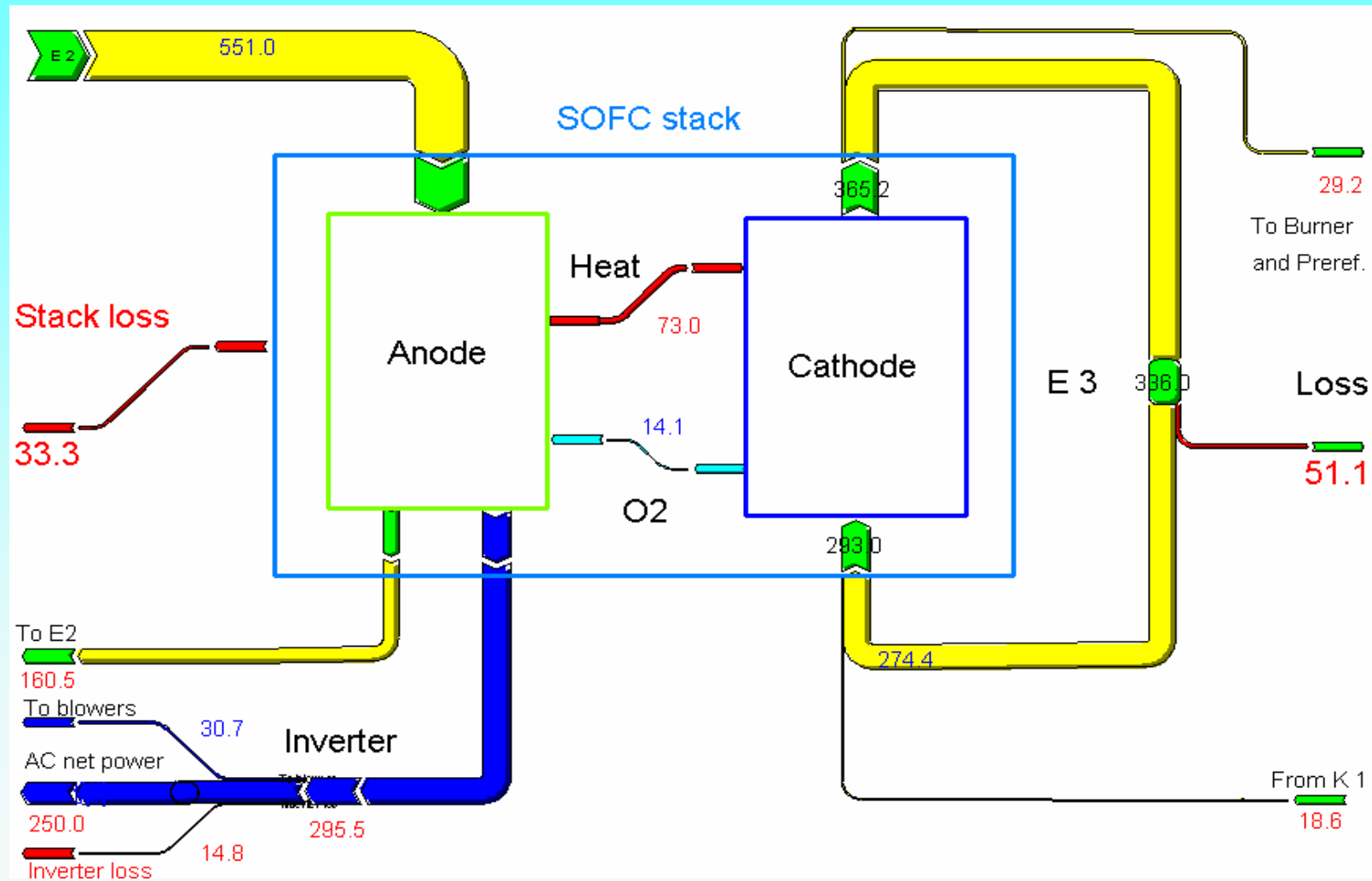
$H/C = 3$ - $P = 1.5$ bar



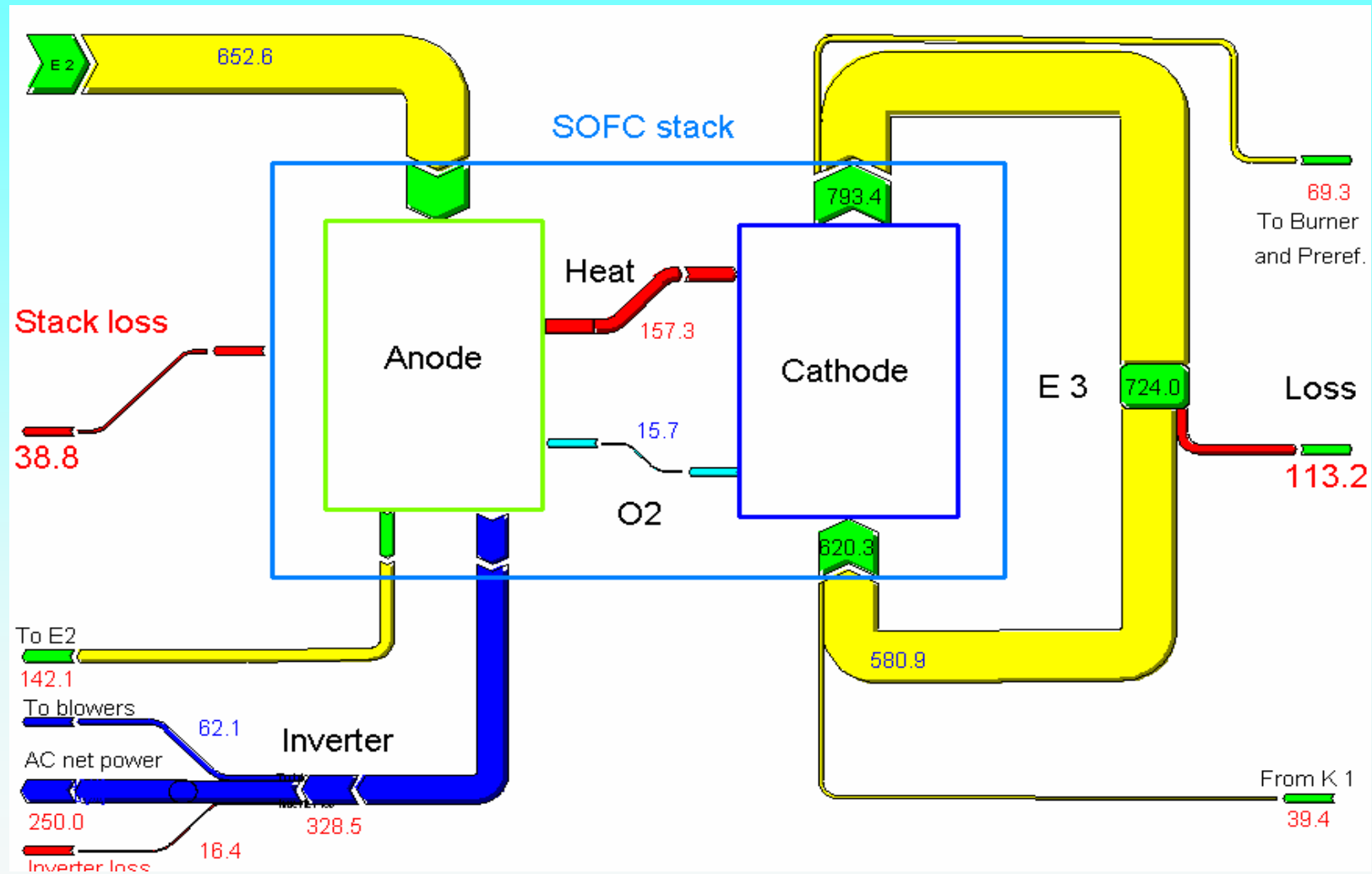
Reforming Enthalphies Shift and CPO Reaction Heats *per mole H_2 formed*



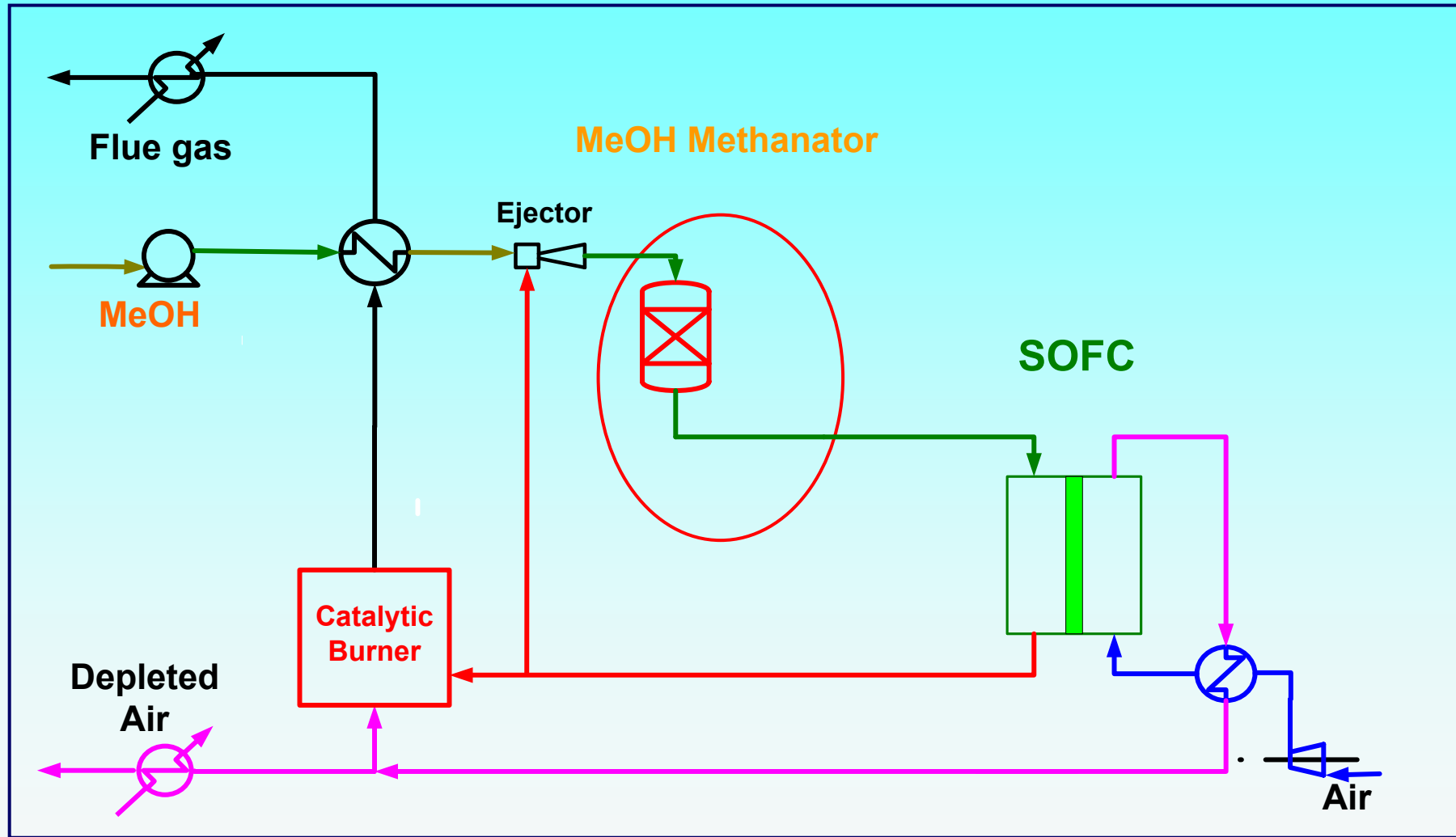
Exergy flows (kJ/s) in SOFC stack Base Case



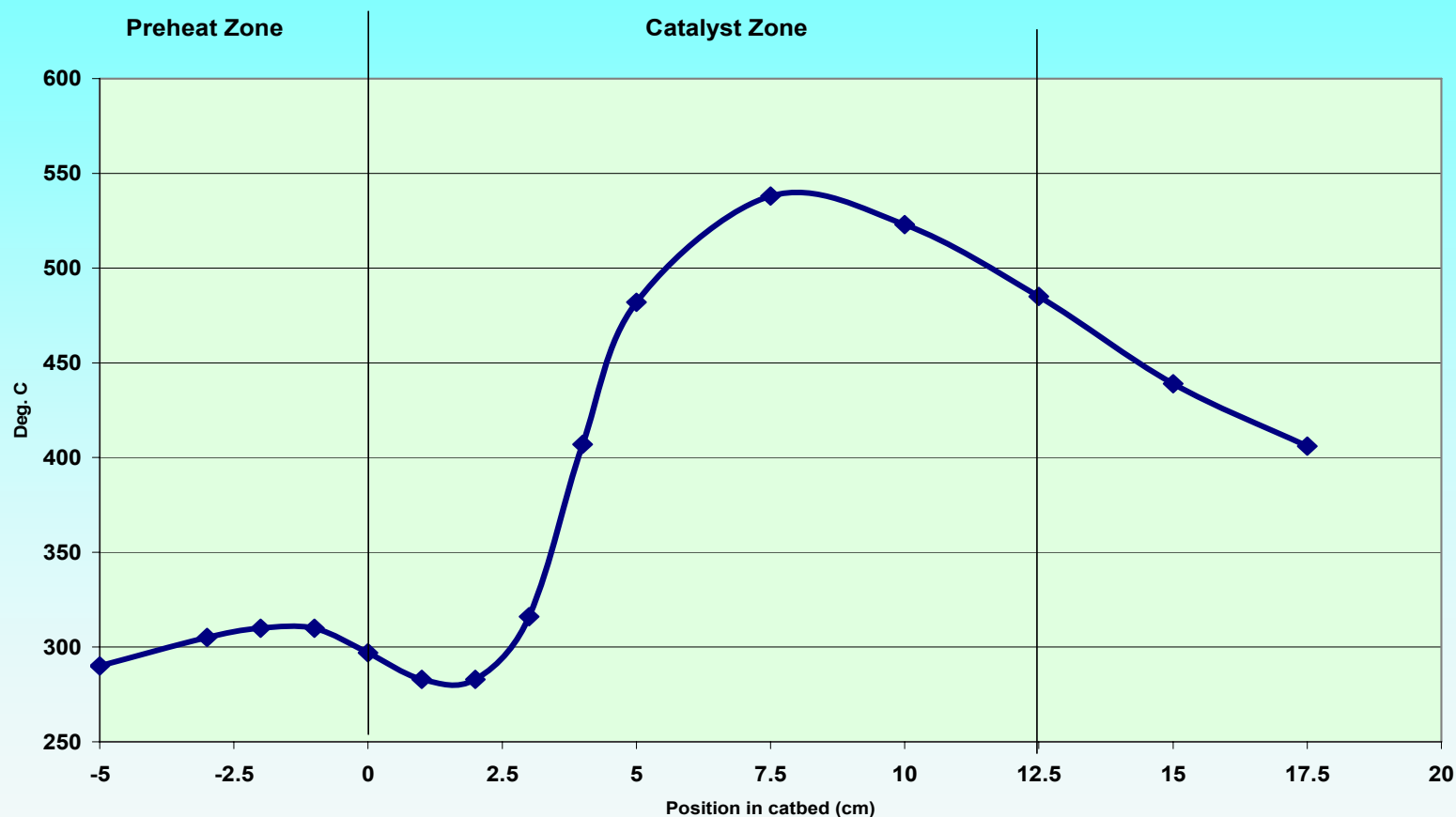
Exergy flows (kJ/s) in SOFC stack Pure Hydrogen as Feed



New Concept - Patent Pending Methanation of Methanol for SOFC



Temperature profile after 770 hours



More than 99.99 % MeOH conversion with 8 kg MeOH/h/kg cat !

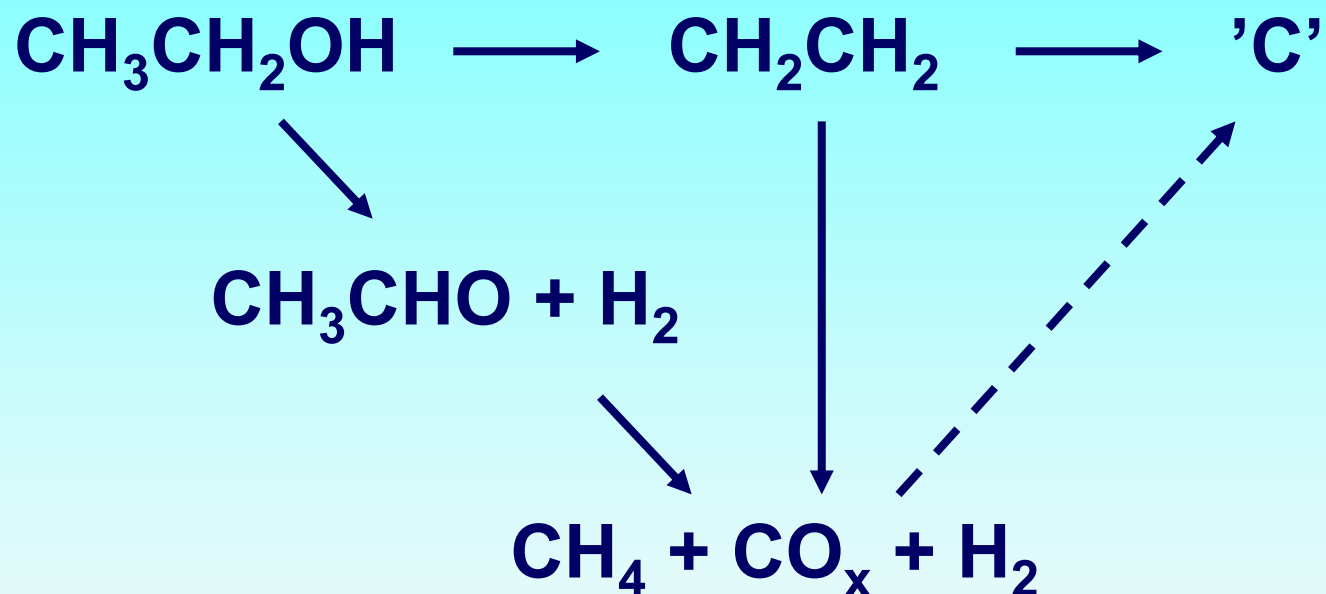


Benefits of DME Methanation

- **Eliminates potential carbon formation problems**
- **Eliminates the need for an anode in/out heat exchanger**
- **Increases the electric efficiency by 2 % relative.**
- **Reduces the combined heat exchanger duties by 20 %**
- **Reduces the air compressor work by 18 %**
- **Reduces the stack size by approx. 10 %**



Methanation of Ethanol



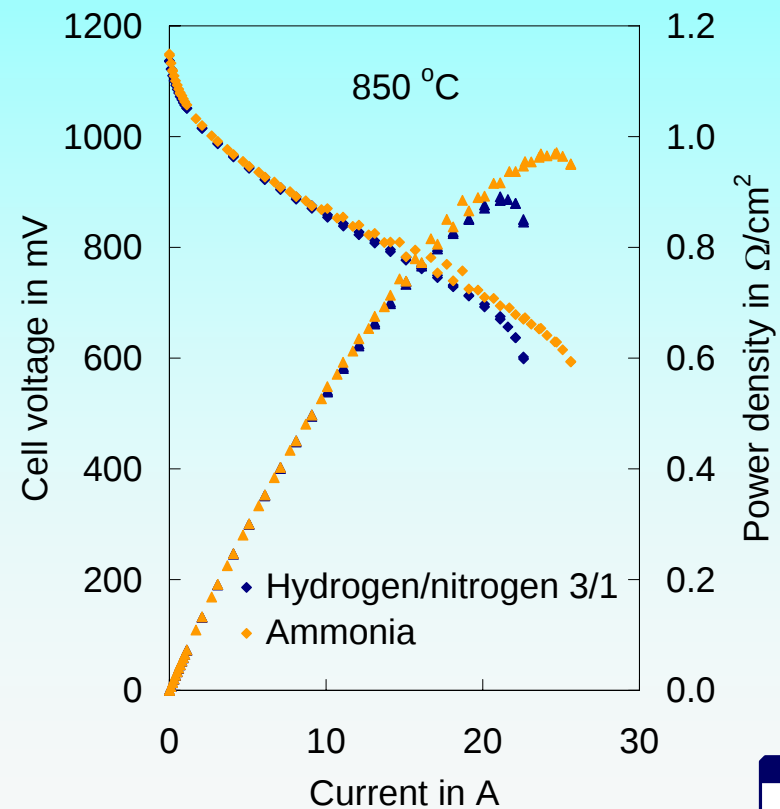
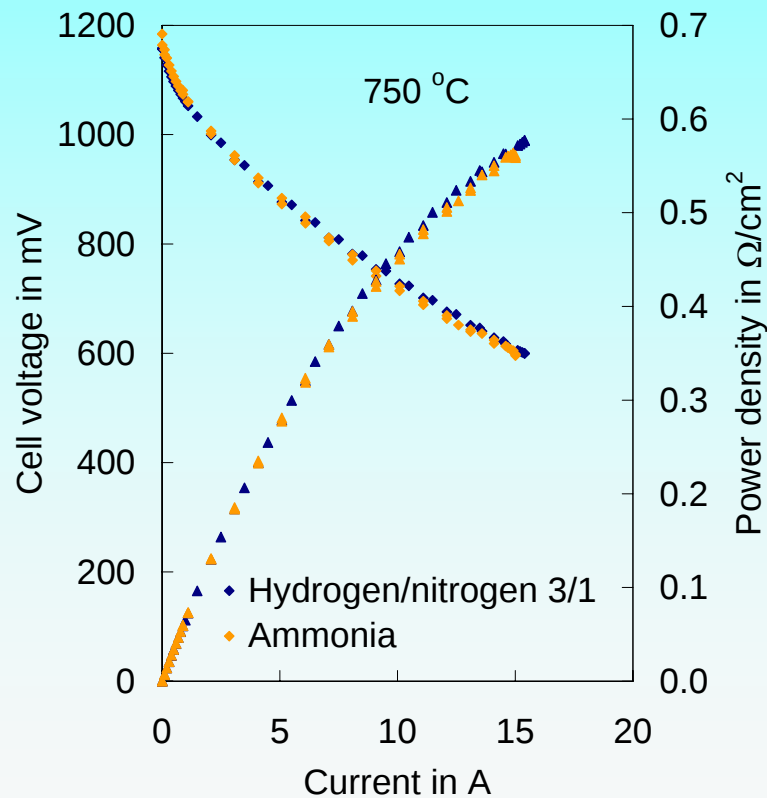
Challenge: Find catalyst that breaks C-C bond much faster than C-O bond in ethanol



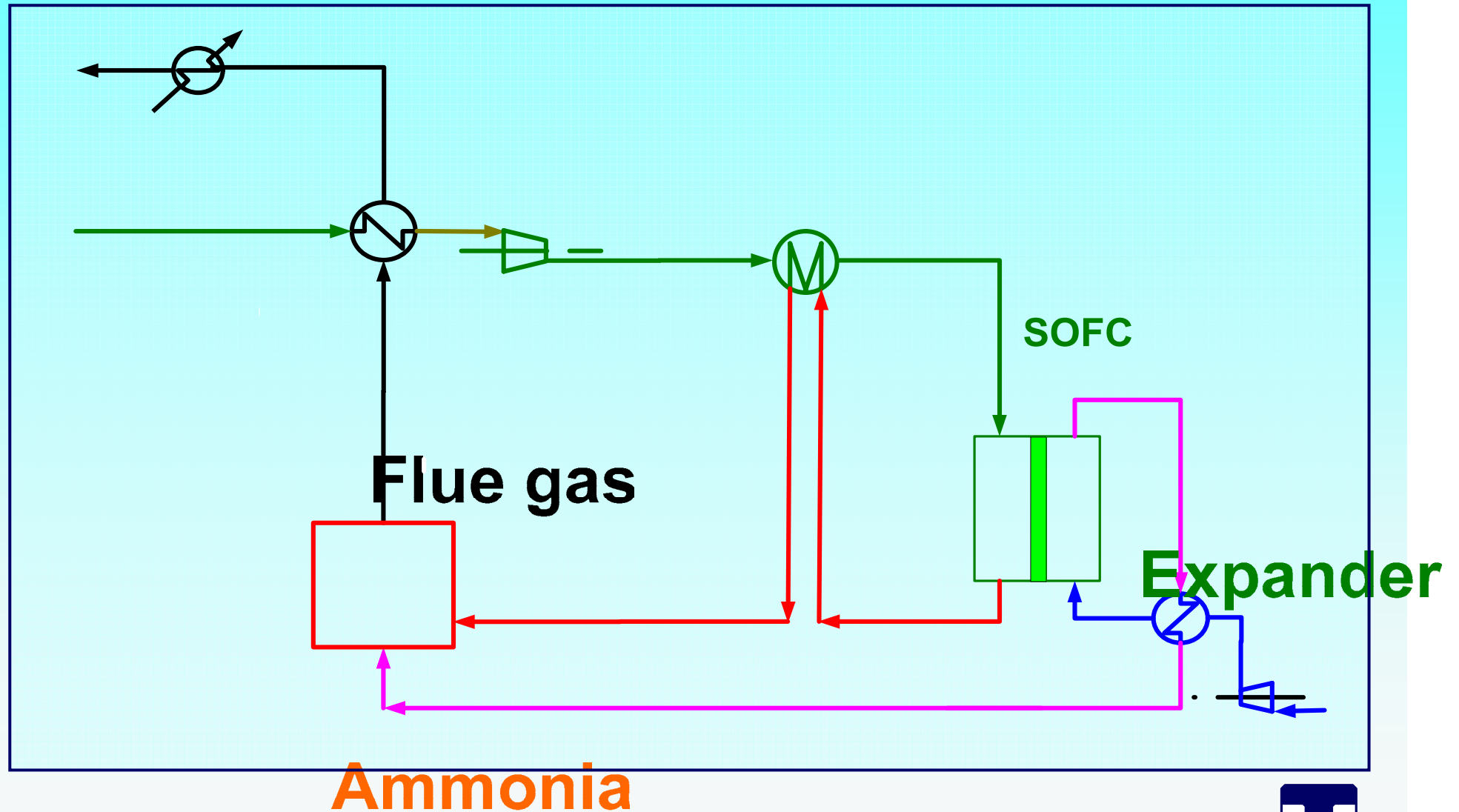
Direct Ammonia SOFC



Same or better performance with ammonia as with $\text{H}_2 + \text{N}_2$ mixture



Direct use of Ammonia for SOFC



System Efficiencies for SOFC Power Plants and traditional APU

Case	El Eff. %	Cogen Eff %
<i>Base NG Stationary Prereform</i>	55.5	83.6
<i>Methanol</i>	53.3	84.6
<i>DME</i>	53.0	82.5
<i>Ammonia</i>	55.0	84.0
<i>Diesel CPO O₂/C = 0.35</i>	40.7	85.4



Conclusions

- **Methanol and DME can be an excellent SOFC fuels if methanated, which provides better stack cooling**
- **Ethanol is somewhat more difficult to process**
- **Ammonia provides the simplest lay-out and lowest water content in anode, but provides less cooling by internal reforming and safety remain an issue**



Some numbers on Auxiliary Power Unit for Diesel Trucks in the USA

- **3.6 billion litres used annually for idling**
- **2.5 % of total Diesel consumption**
- **Emissions:**
 - **10 million tons CO₂**
 - **200,000 tons NO_x**
- **9100 liters of Diesel per truck per year**
- **Electric efficiency below 10 %**

Sources: EPA and EIA - 2003



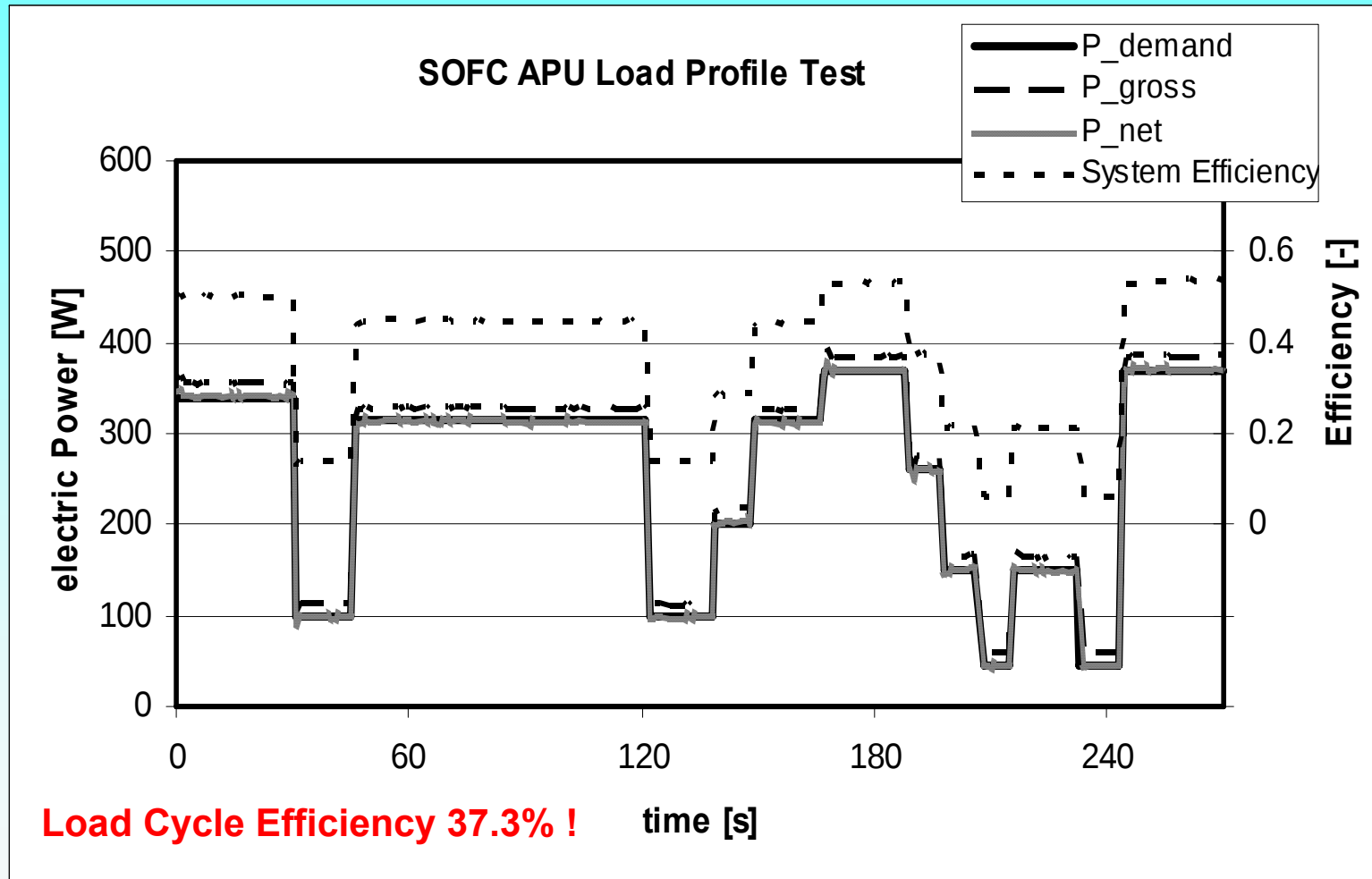
Caveat: Carbon Formation

Three Routes

- Irreversible decomposition of the hydrocarbon on the nickel surface leading to the **whisker carbon**
- Accumulation of hydrocarbon species on the nickel surface which may slowly be converted into a **polymer film** blocking the surface
- **Pyrolytic carbon** from olefins in the gas phase encapsulating the catalyst pellet



Transient Tests at AVL



Wärtsilä 20 kW SOFC α -prototype

