COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

Hybrid System Thermodynamics

Robert (Rob) Braun
Department of Mechanical Engineering
College of Engineering & Computational Sciences
Colorado School of Mines
Golden, CO USA
(http://aes.mines.edu)

ARPA-E Fuel Cell Engine Workshop

27 January 2017

AESG
Advanced Energy Systems Group

Outline – Motivate Discussion

I. Overview: Fuel cell thermodynamics and basic characteristics

A. Operation and Polarization basics

B. Performance sensitivity (T, p, fuel utilization/composition, fuel type)

II. Fuel Processing & Thermal Management

A. Reforming

B. Carbon deposition

III. Hybrid System Integration

A. Process Design Considerations

B. Exergy Analysis – where are the losses?

- Basic SOFC, GT, ICE

C. Hybrid System Concepts

- SOFC-GT and SOFC-ICE architectures

D. Pathways to 70% efficiency

IV. Closing Thoughts

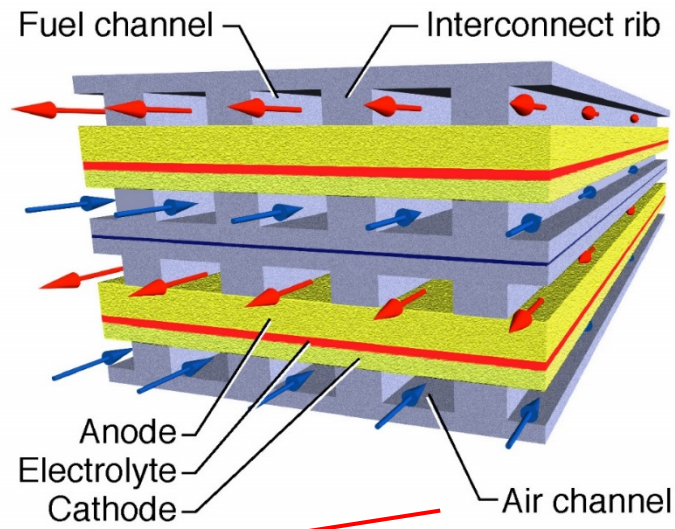
- Practical integration challenges, complexity, control, durability

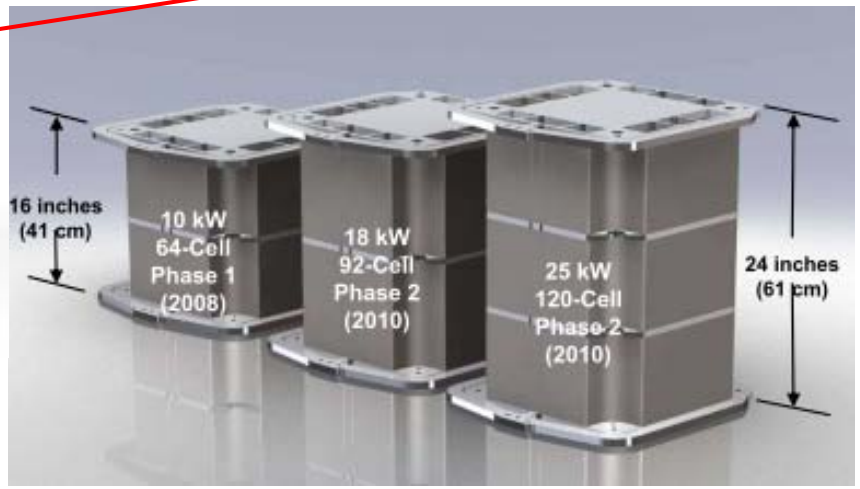
High temperature fuel cell systems are comprised of cell-stack hardware and balance-of-plant equipment

300-kW FCE (MCFC)

100-kW Bloom Box (SOFC)

2-kW BlueGen CFL (SOFC)



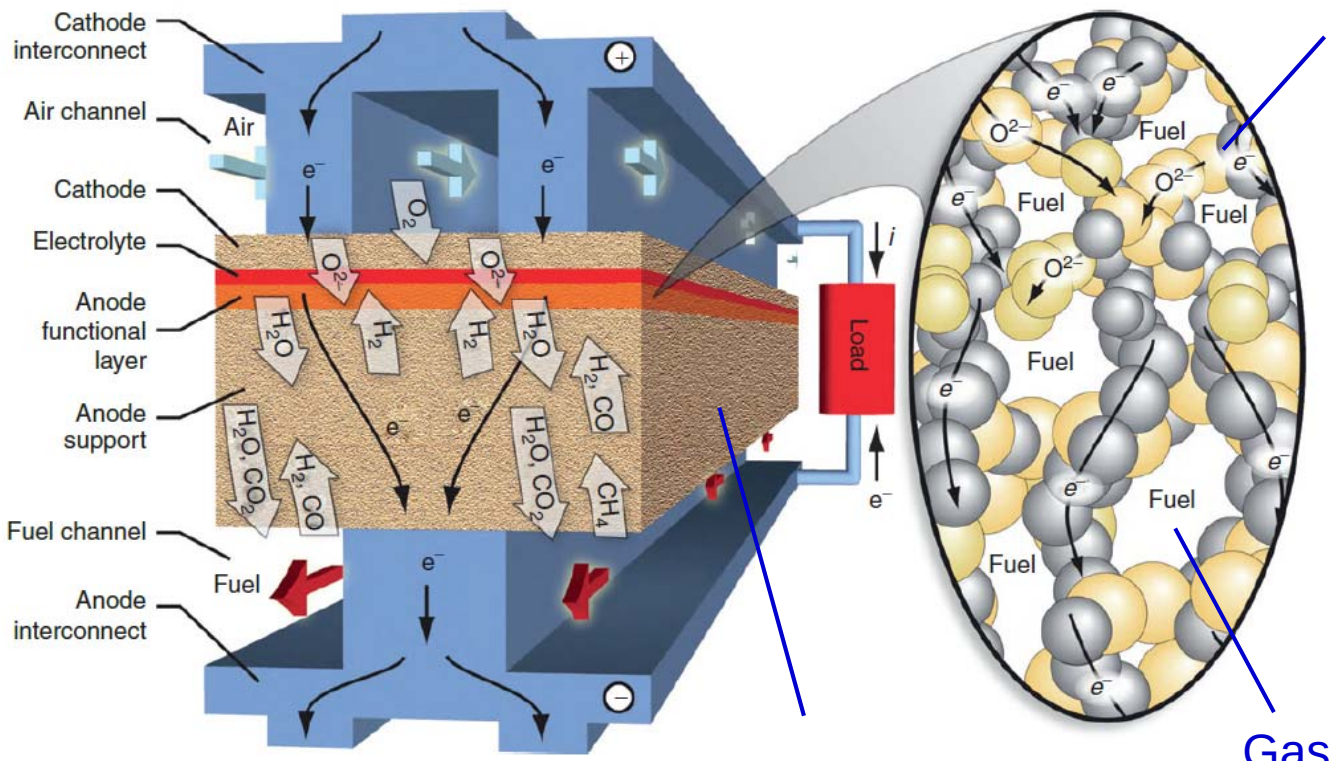


10-25 kW stacks Versa Power (SOFC)

*Figure: Kee et al., Proc. Combustion Institute **30** (2005)*

The repeating layers direct feed gases, and enable gas transport and electrochemistry

Anode-supported Planar configuration



Ion and electron transport

Heterogeneous Internal reforming of fuel gas

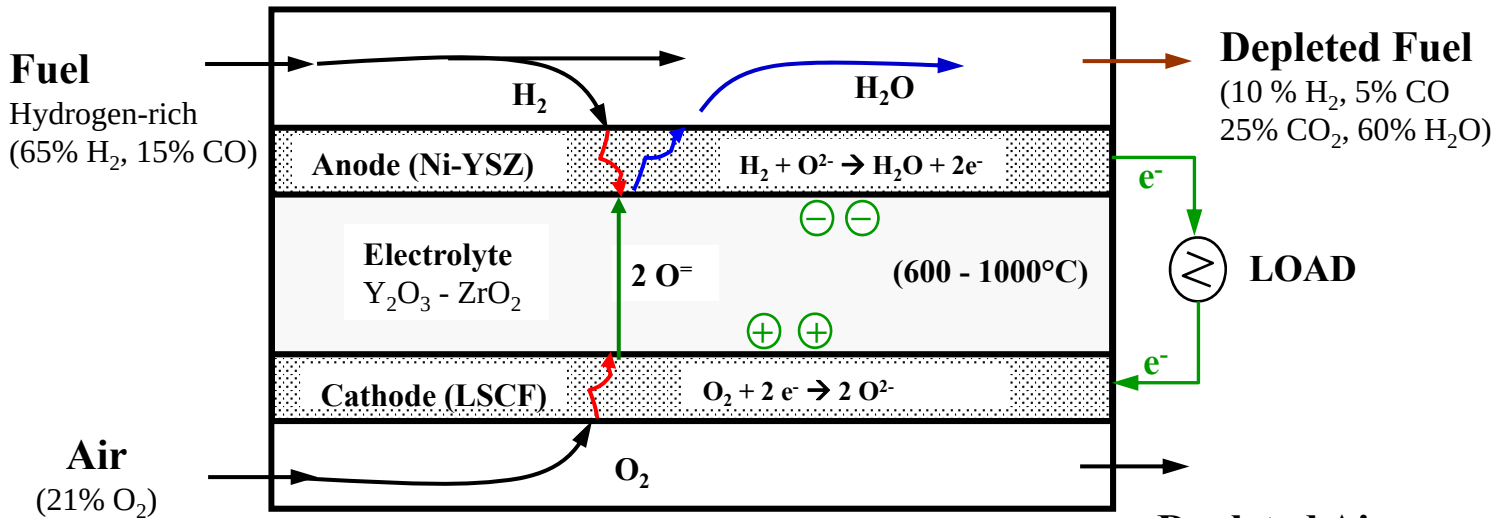
Gas diffusion in ceramic-metallic electrode

Characteristic dimension: 1 mm
- Channel diameter
- Anode thickness

Characteristic temperature: 750˚C

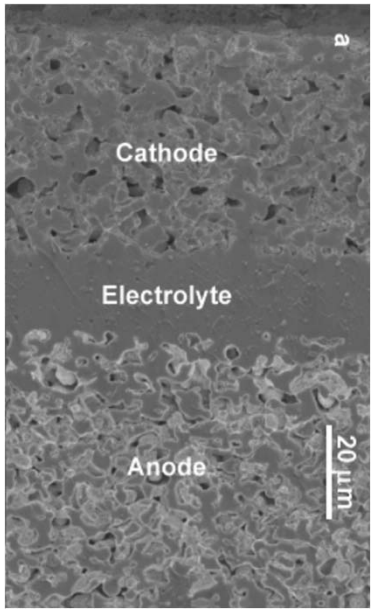
Figure: Kee et al., *Encycloped. Electrochem. Power Sources* (3) 2009

SOFC performance is sensitive to T, p, composition and are relatively fuel flexible allowing CH_4, CO, and H_2 fuels



Overall Reactions: $H_2 + ½\ O_2 \rightarrow H_2O$ **(R1)**

$CO + ½\ O_2 \rightarrow CO_2$ **(R2)**



SEM of "MEA"

Theoretical (reversible) Voltage :

$$OCV = E_N = -\frac{\Delta G^o_{R1}}{nF} + \left(\frac{RT}{nF}\right)\ln\left(\frac{P_{H2}\sqrt{P_{O2}}}{P_{H2O}}\right) \Rightarrow V = V(T, p, x_j)$$

Gibbs free energy of reaction for R1

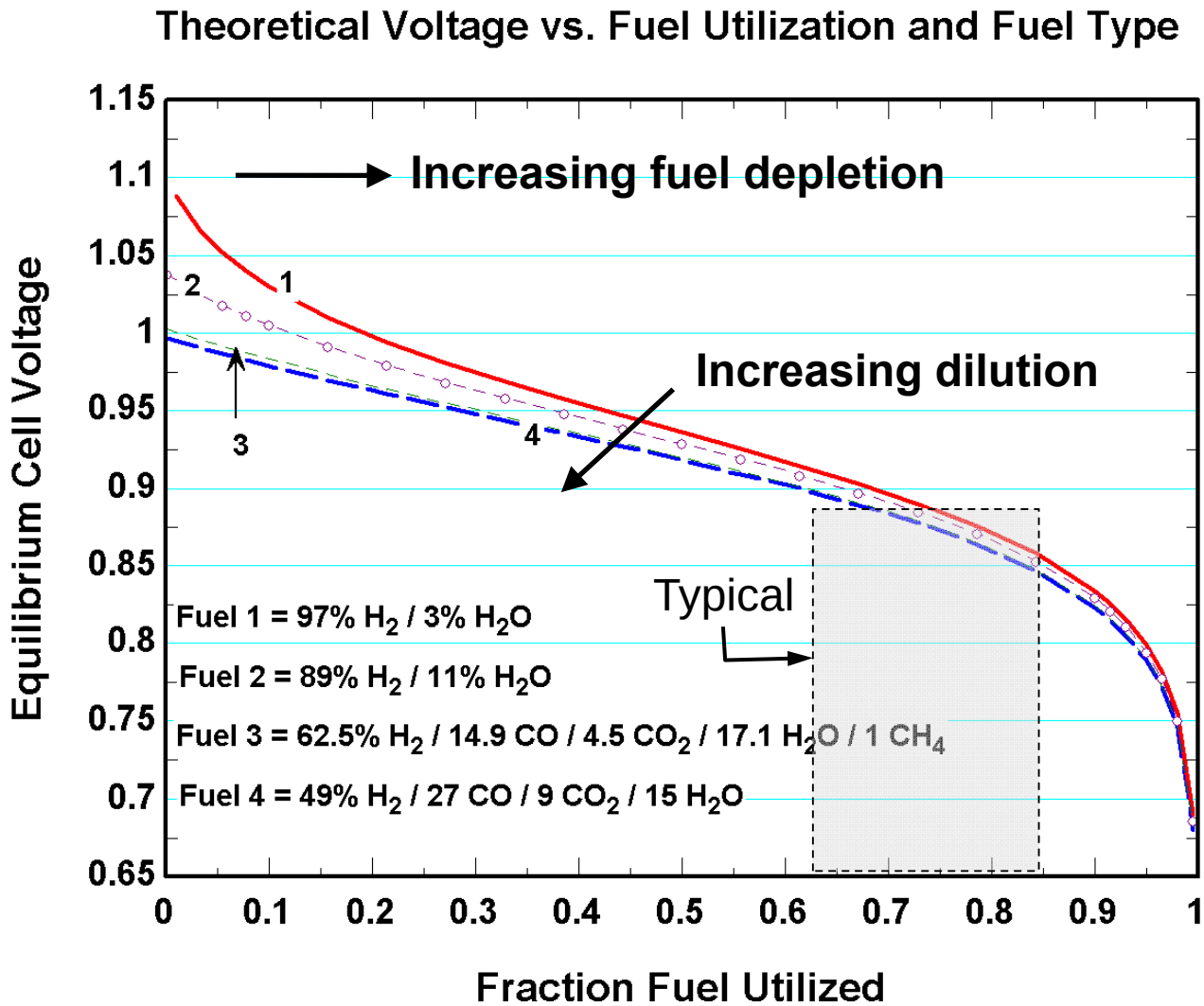
Correction for Fuel Composition

Fuel Utilization

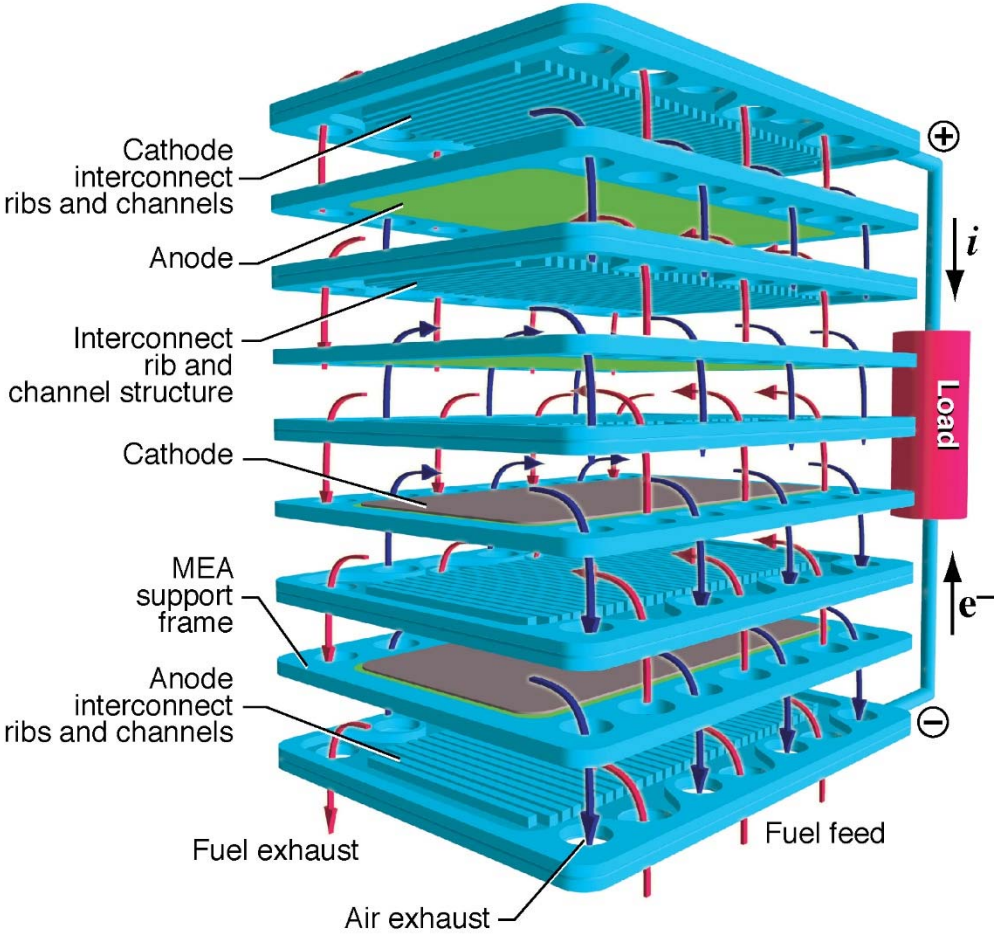
$$U_F = \frac{\dot{N}_{H_2,consumed}}{(\dot{N}_{H_2} + \dot{N}_{CO} + 4\dot{N}_{CH_4})} = \frac{j}{j_{max}}$$

Figure: Braun, Ph.D. Thesis, Univ. of Wisconsin (2002)

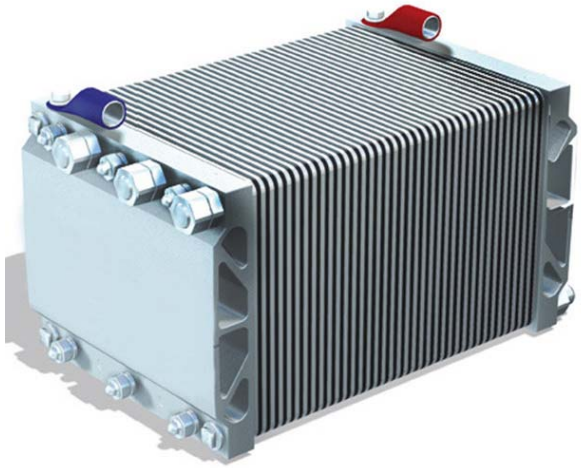
The electrical potential of the cell depends on the fuel type, composition, and degree of utilization



Stacking of cells is required to generate appreciable voltage & power and compression / seals to maintain integrity



Internal counter-flow geometry (modeled after a Juelich design)



Cell-stack with endplates and compression

Tubular configuration

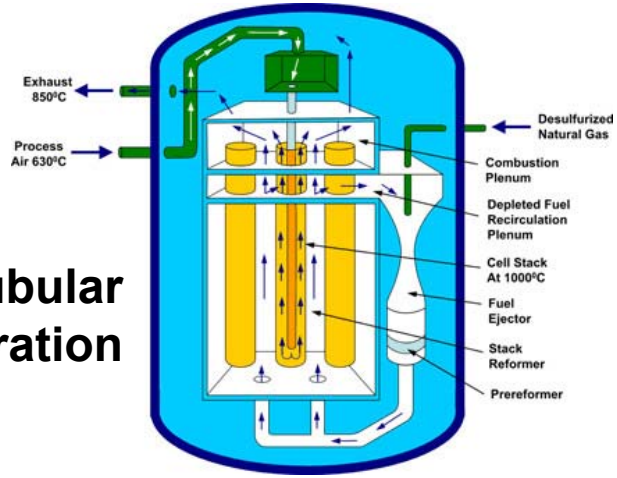
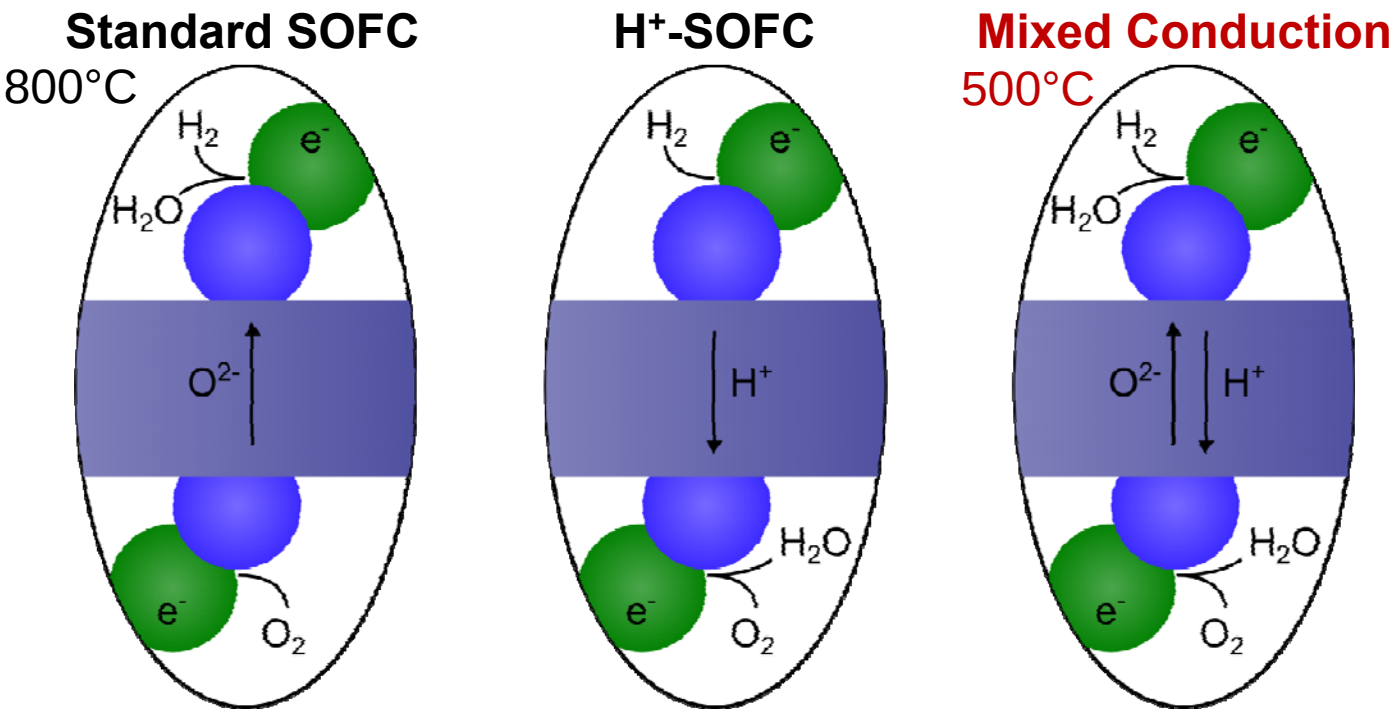


Figure credit: Bob Kee

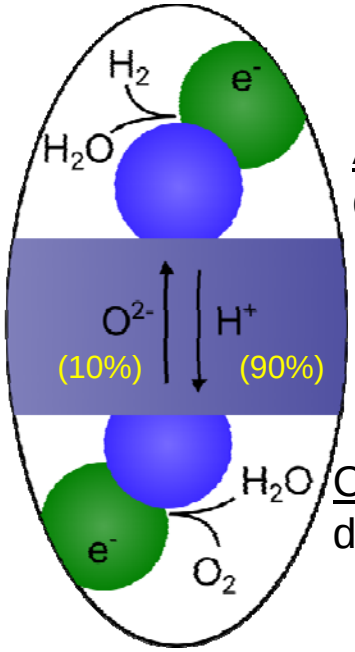
Planar protonic ceramics could improve fuel cell viability and decrease stack/system costs



- Cost effective manufacturing by solid state reactive sintering[1,2]
- Inexpensive cathode materials (Ba, Zr, Fe) and low # processing steps
- Low temperature (500°C) operation enabled by transport of protons
- Faster start-up time and cheaper heat exchangers

1. Tong et al., *Solid State Ionics* (181) 2010
2. Tong et al., *J. Materials Chemistry* (20) 2010

Proton conducting fuel cells are also fuel flexible and exhibit oxidation via mixed ionic conduction

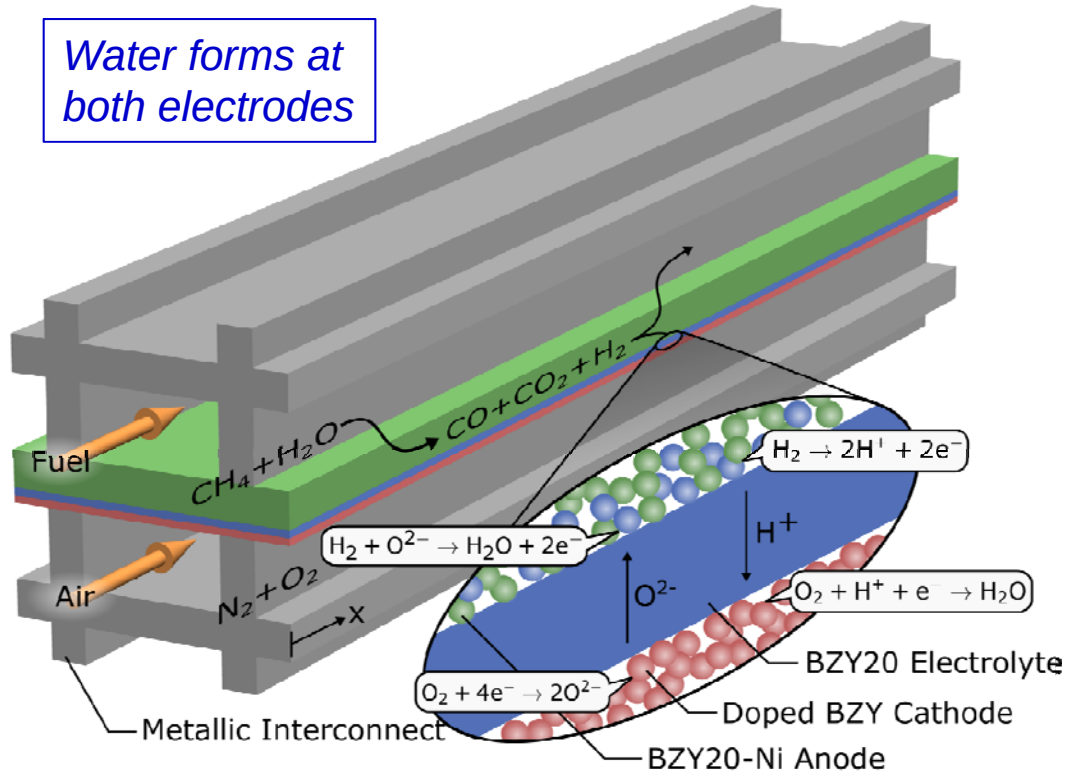


Anode: NiO doped BZY

BZY, BCZY, or BCZYYb

Cathode: Co/Fe doped BZY

Water forms at both electrodes



- Yttrium-doped barium zirconates conduct oxygen ions, H protons, e^- holes
- Can also enable *internal reforming* like SOFCs
- **Water formation** primarily on cathode side → negates use of anode gas recycle
- Thus the type of ion conductor is important

Figure: Albrecht et al., ECS Transactions, 68 (1) 3165-3175 (2015)

Fuel cell performance map is expressed in terms of Voltage-Current at different conditions

$$V_{cell} = E_N - \underbrace{\eta_{conc,an} - \eta_{act,an} - \eta_{ohm} - \eta_{act,c} - \eta_{conc,c}}_{f(T,p,j_{cell},x_j) \rightarrow ASR \cdot j_{Cell}} - \eta_{leak}$$

Concentration overpotentials
- Species transport through electrodes

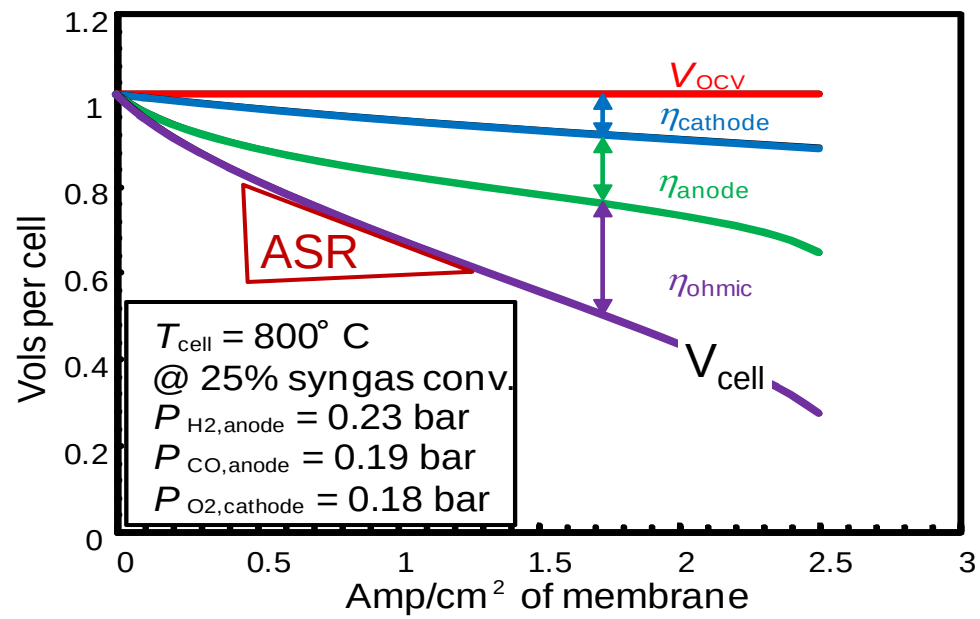
Activation overpotentials
- Electrochemistry at TPB

Ohmic overpotential
- Resistive losses in electrolyte

Interface overpotentials
- Resistance at materials interfaces

Leakage overpotential
- Electrical conduction in electrolyte

Voltage vs. current density for reformate

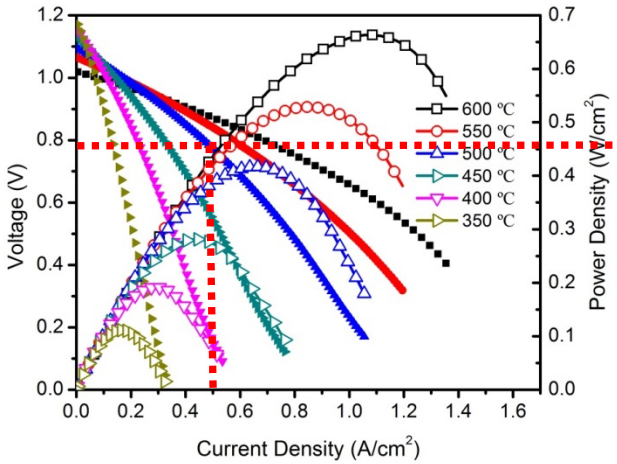


Area-specific resistance (ASR) = $\frac{E_N - V_{cell}}{j_{cell}}$ ← Slope - Lumped resistance that is a broad measure of cell performance

$[\Omega - cm^2]$

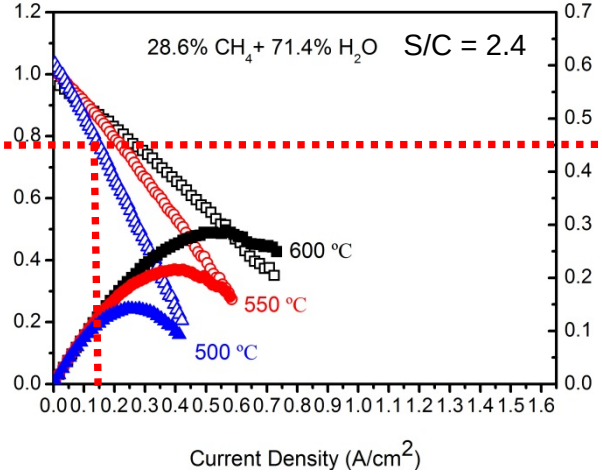
Temperature and fuel type performance sensitivity of protonic ceramic fuel cells demonstrated[1]

Hydrogen + 3% Steam



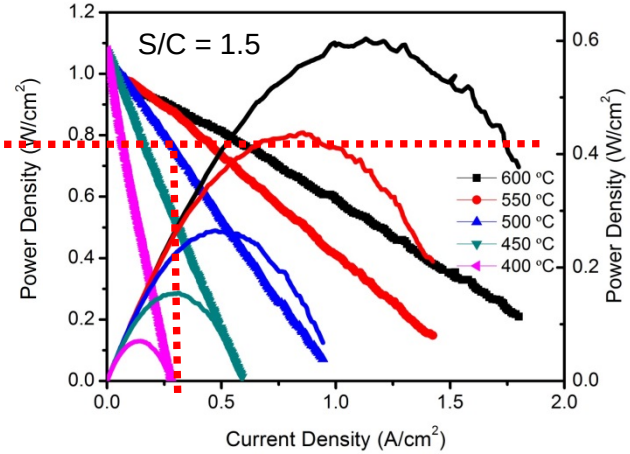
j = 500 mA/cm²

28.6% Methane + 71.4% H_2O(g)



j = 150 mA/cm²

Renewable Biogas
24% CH_4+16% CO_2+ 60% H_2O

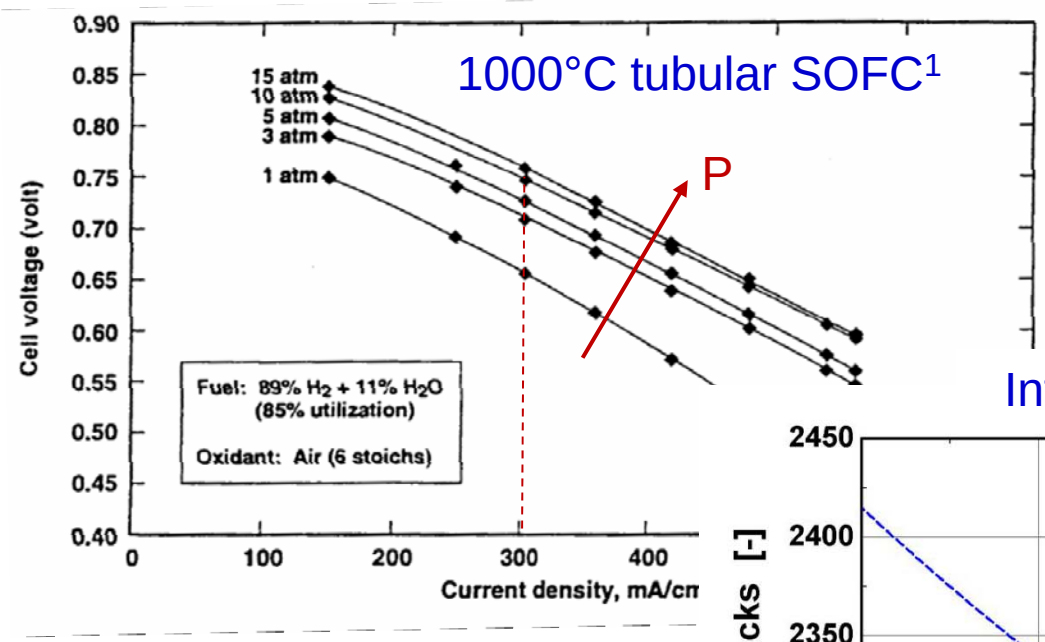


j = 250 mA/cm²

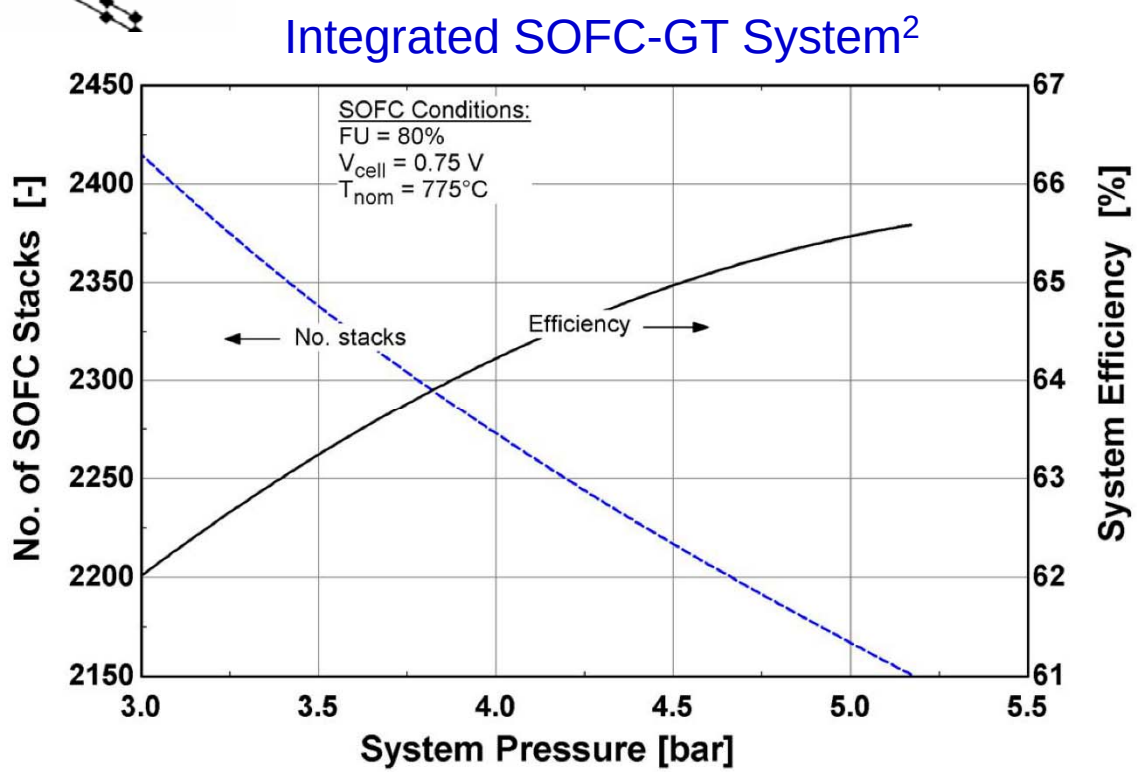
- 19mm diameter, BZY20 button cell tests (BZY20 = $BaZr_{0.8}Y_{0.2}O_{3-\delta}$)
- Single cells developed which demonstrate non-coking, fuel flexible operation while reaching power densities of 120 to 390 mW/cm2
- Stack cost reduction of >25% possible over SOFC[2]
- Efficiency & Voltage directly related: $\eta_{cell} = \frac{V_{cell}\, j\, A_{cell}}{\dot{m}_{\text{fuel,in}}\, LHV_{\text{fuel,in}}} = \frac{\text{Cell power}}{\text{Fuel energy}}$

[1]C. Duan, et al., Science, 23 July 2015
[2]Dubois and Braun, JPS submittal (2017)

Pressurization increases cell performance

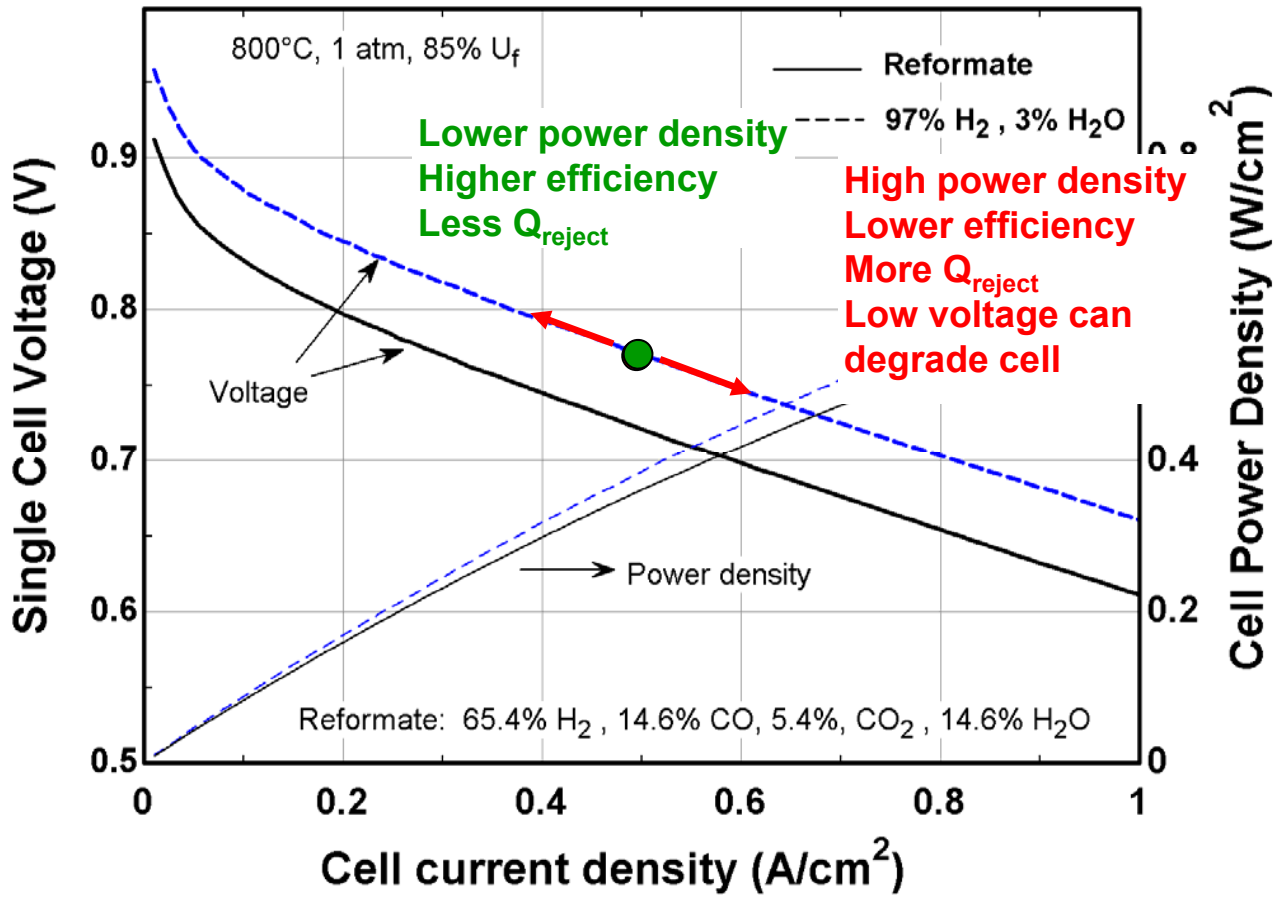


- **More power at same current (10-15%)**
- **Most of voltage gain at <10 bar**



[1]*Vora, SECA Annual Workshop (2004)*
[2]*Braun et al, ASME J. Engr Gas Turb and Power 134 (2012)*

Selection of the design point voltage considers trade-offs between efficiency and capital and operating costs



- Typical design cell voltages range between 0.70 V to 0.80 V
- Voltage degradation of 20% expected over 5-year stack life requires end-of-life system design strategy

Figure: Braun et al. J Power Sources 158 (2006)

Outline

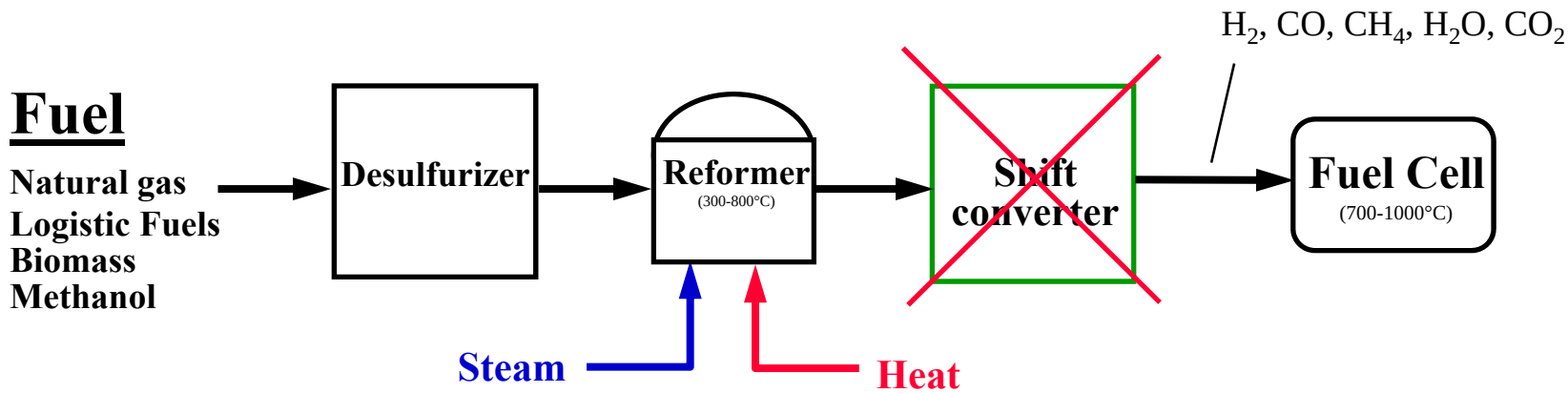
I. Overview: Fuel cell thermodynamics and basic characteristics
   A. Operation and Polarization basics
   B. Performance sensitivity (T, p, fuel utilization/composition, fuel type)

II. Fuel Processing & Thermal Management
   A. Reforming
   B. Carbon deposition

III. Hybrid System Integration
   A. Process Design Considerations
   B. Exergy Analysis – where are the losses?
      - Basic SOFC, GT, ICE
   C. Hybrid System Concepts
      - SOFC-GT and SOFC-ICE architectures
   D. Pathways to 70% efficiency

IV. Closing Thoughts
   - Practical integration challenges, complexity, control, durability

Fuel preparation requires removal of sulfur and may include pre-reforming/External reforming processes



Fuel Processing:

Steam Reforming (800°C) $CH_4 + H_2O \leftrightarrow 3\ H_2 + CO$ (**endothermic:** 227.5 kJ/mol$_{CH4}$)

Water-Gas Shift (250-800°C) $CO + H_2O \leftrightarrow H_2 + CO_2$ (**exothermic:** -32.2 kJ/mol$_{CO}$)

Overall: $CH_4 + 2\ H_2O \leftrightarrow 4\ H_2 + CO_2$ **(195.3 kJ/mol)**

Fuel Cell Reactions:

Overall Reaction: $H_2 + 1/2\ O_2 \rightarrow H_2O$ **(exothermic: -249.3 kJ/mol$_{H2}$)**

High temperature and nickel-based anodes allow in-situ fuel processing of hydrocarbons within the stack

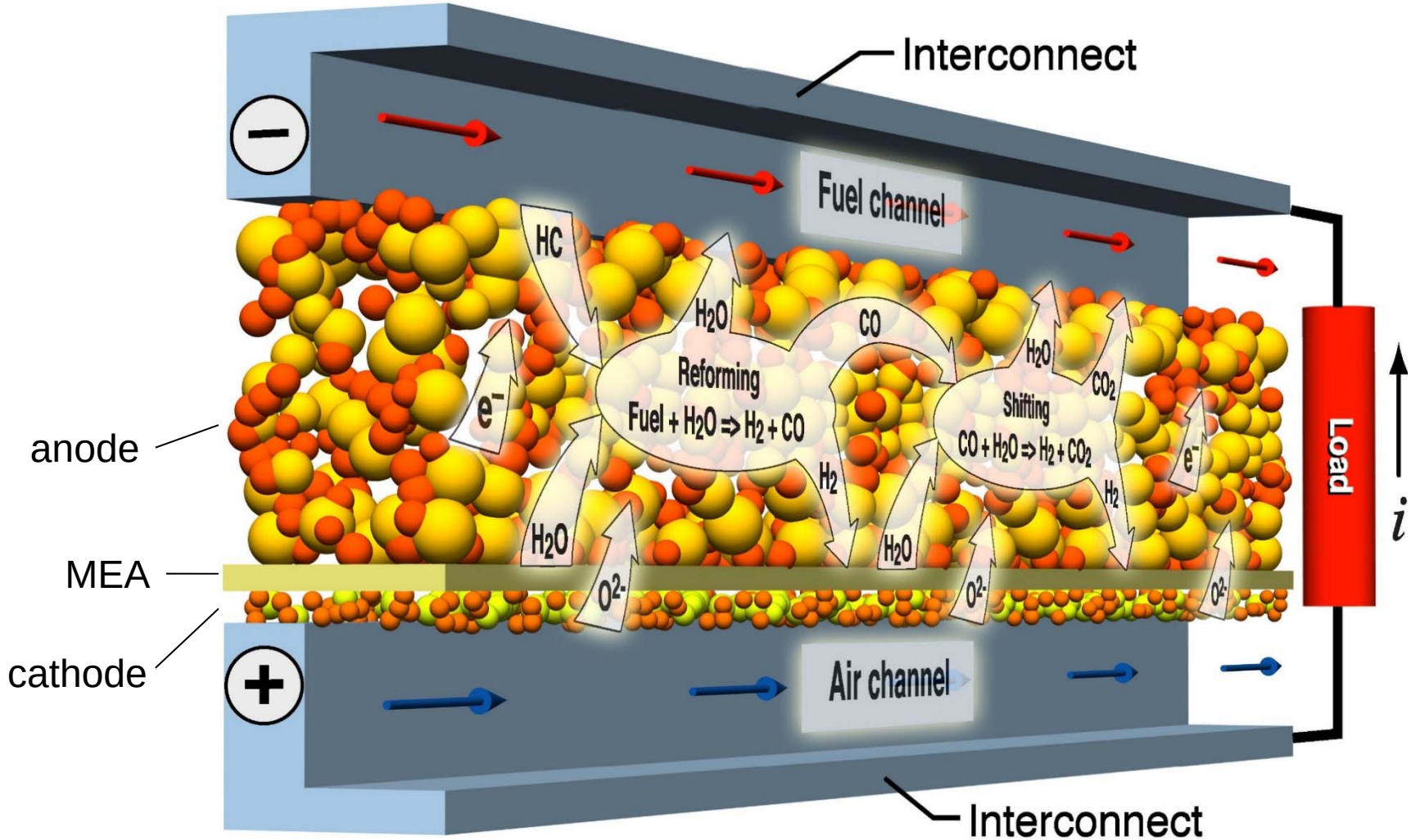
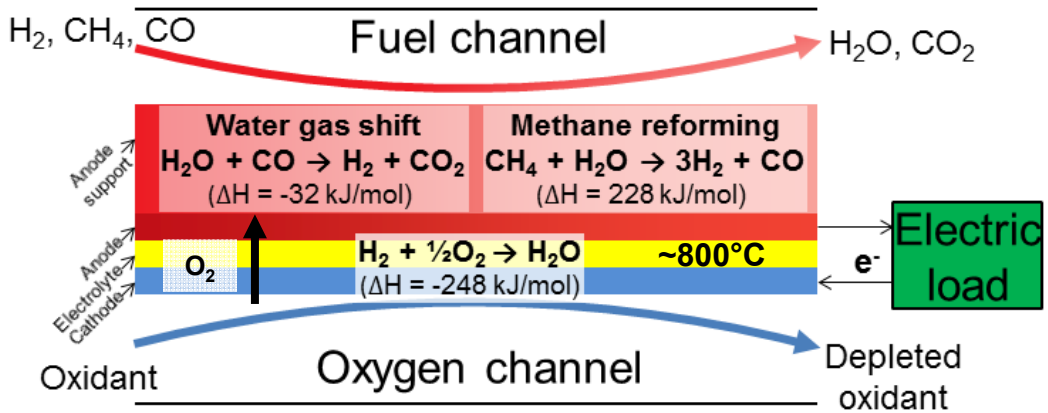


Figure: Zhu et al., J. Electrochem. Soc. ***152*** *(2005)*

Internal Reforming is advantageous for thermal management and system efficiency

- **SOFCs are air-cooled**
- **Operation on hydrogen means high air flow requirements**
- **Nickel-based anode enables internal reforming**
- **Heat sink and source matched!**



Note: Use of high temperature 'waste' heat effectively enhances hydrogen production, cell thermal management, and overall efficiency*

$$\eta_{sys} = \frac{\dot{W}_{el}}{\dot{m}_f LHV_f}$$

- *SOFC **system** efficiency better with natural gas hydrocarbons vs. pure hydrogen*

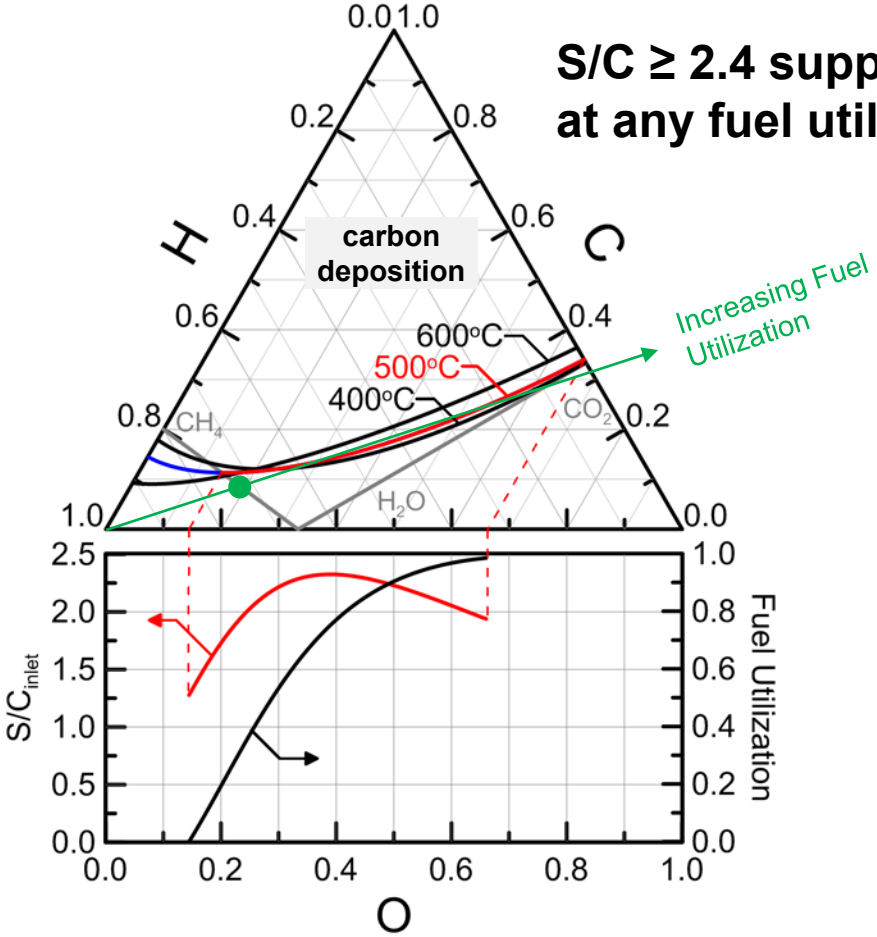
Challenge: high degree of internal reforming can lead to high temperature gradients and thermally-induced stress within the cell-stack

**See Braun et al., J Power Sources 158 (2006)*

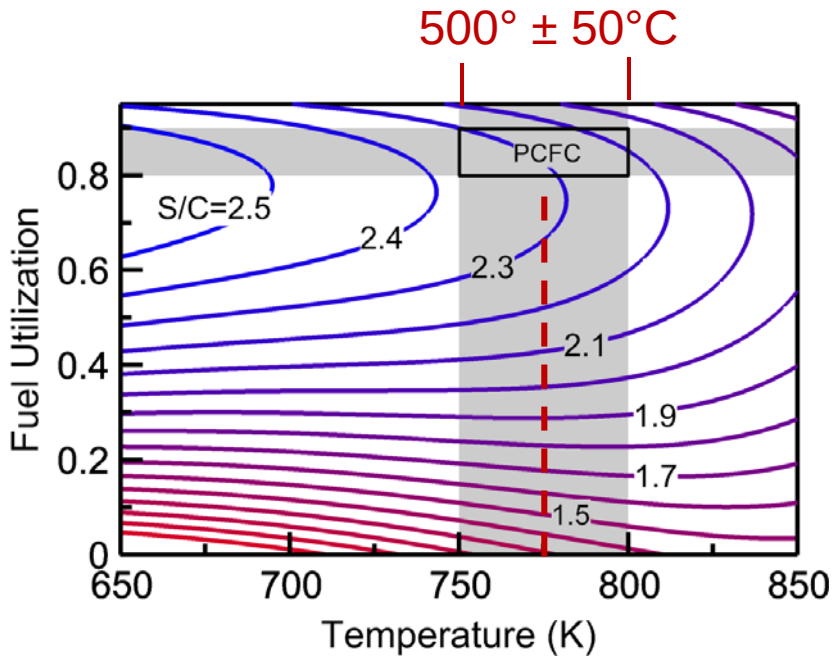
Hydrocarbon fuels necessitate an understanding of operating conditions which avoid carbon deposition

Selection of Inlet Steam-to-Carbon Ratio:

- Gibbs free energy minimization calculation to predict carbon deposition
- Proton conductors are sensitive to temperature and fuel utilization



S/C ≥ 2.4 suppresses solid carbon deposition at any fuel utilization and temperature above 750 K



Albrecht et al., ECS Transactions, 68 (1) 3165-3175 (2015)

Outline

I. **Overview: Fuel cell thermodynamics and basic characteristics**
   A. Operation and Polarization basics
   B. Performance sensitivity (T, p, fuel utilization/composition, fuel type)

II. **Fuel Processing & Thermal Management**
   A. Reforming
   B. Carbon deposition

III. **Hybrid System Integration**
   A. Process Design Considerations
   B. Exergy Analysis – where are the losses?
      - Basic SOFC, GT, ICE
   C. Hybrid System Concepts
      - SOFC-GT and SOFC-ICE architectures
   D. Pathways to 70% efficiency

IV. **Closing Thoughts**
   - Practical integration challenges, complexity, control, durability

Thermodynamic limits indicate hybrid system efficiencies near 80% (LHV) are possible

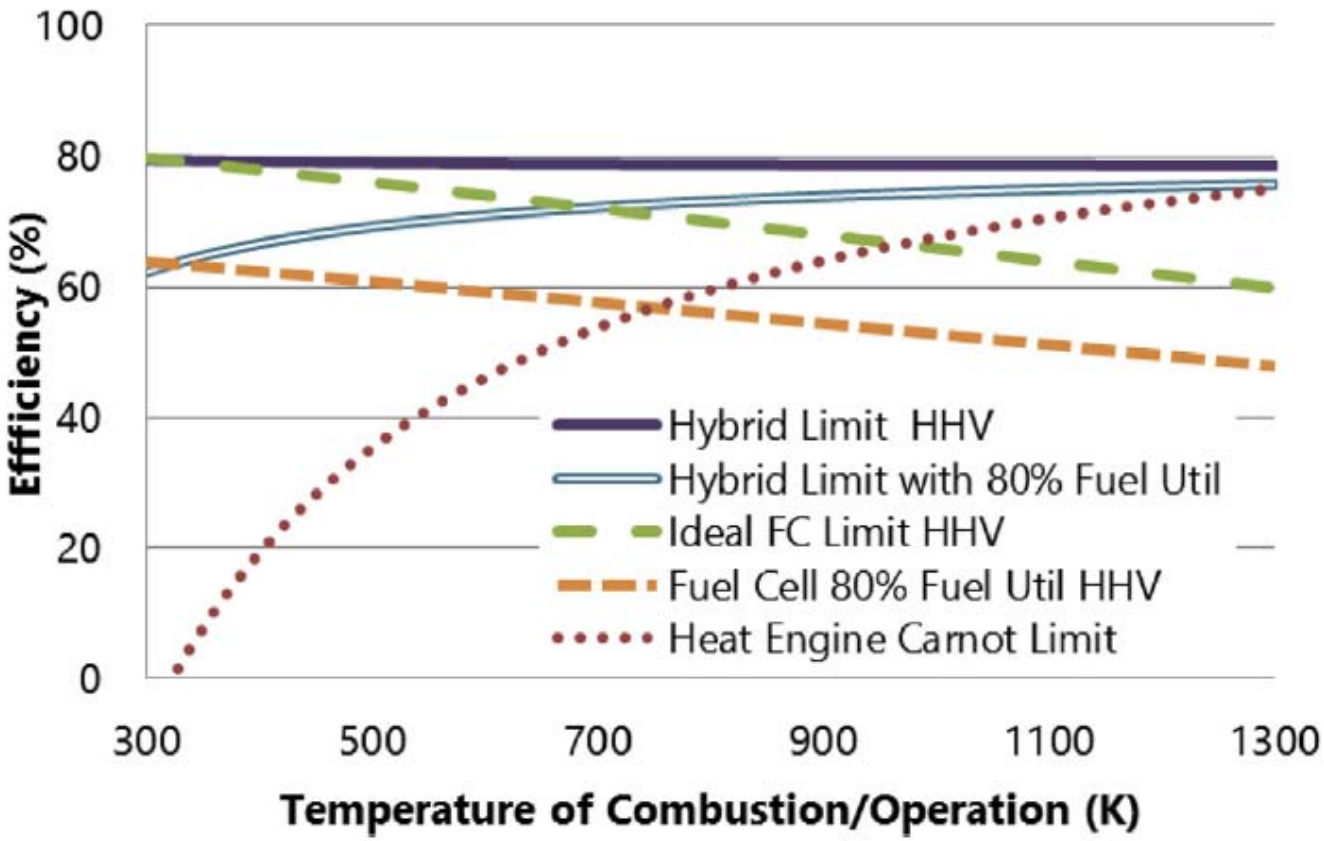
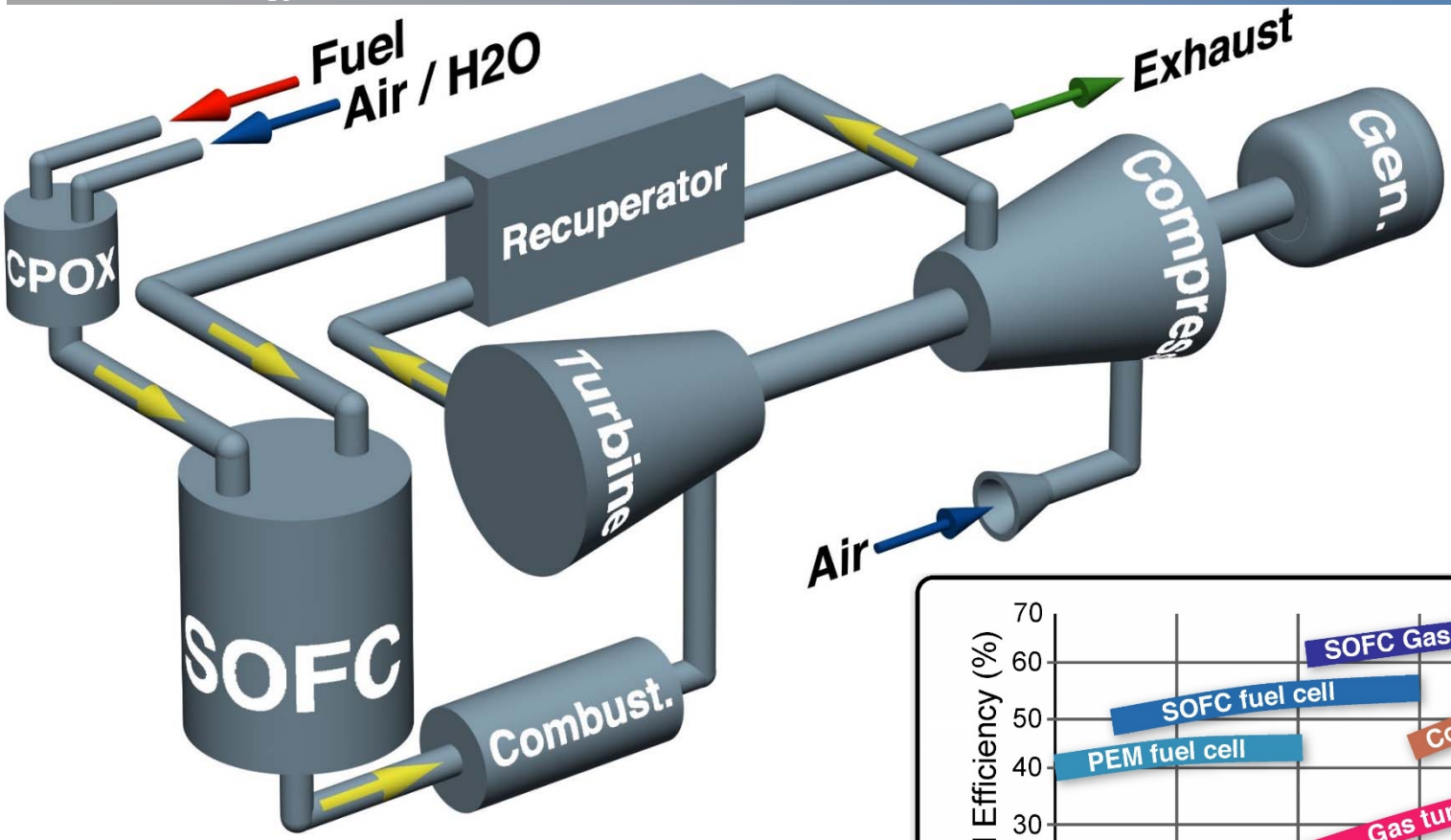
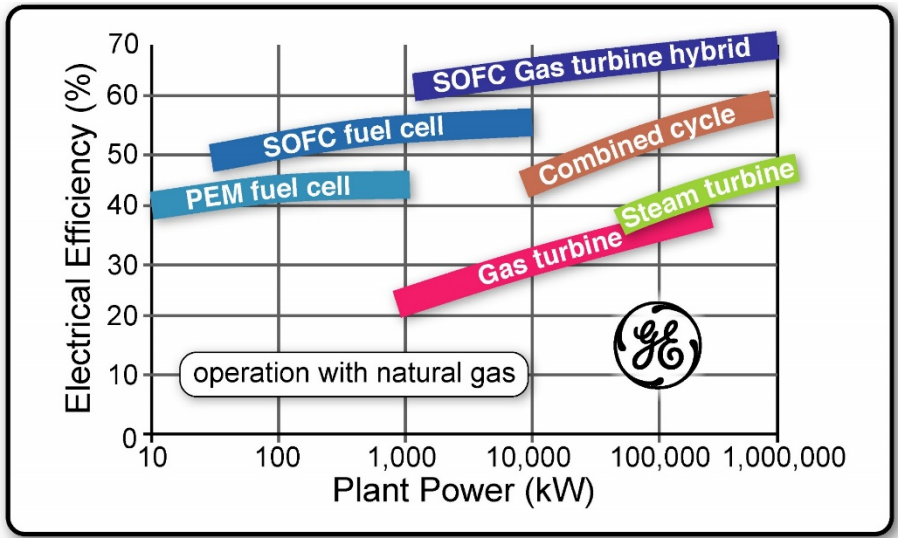


Fig. 1. Ideal efficiency comparison of fuel cells, gas turbines, and hybrids.

McLarty et al., J. Power Sources 257 (2014)

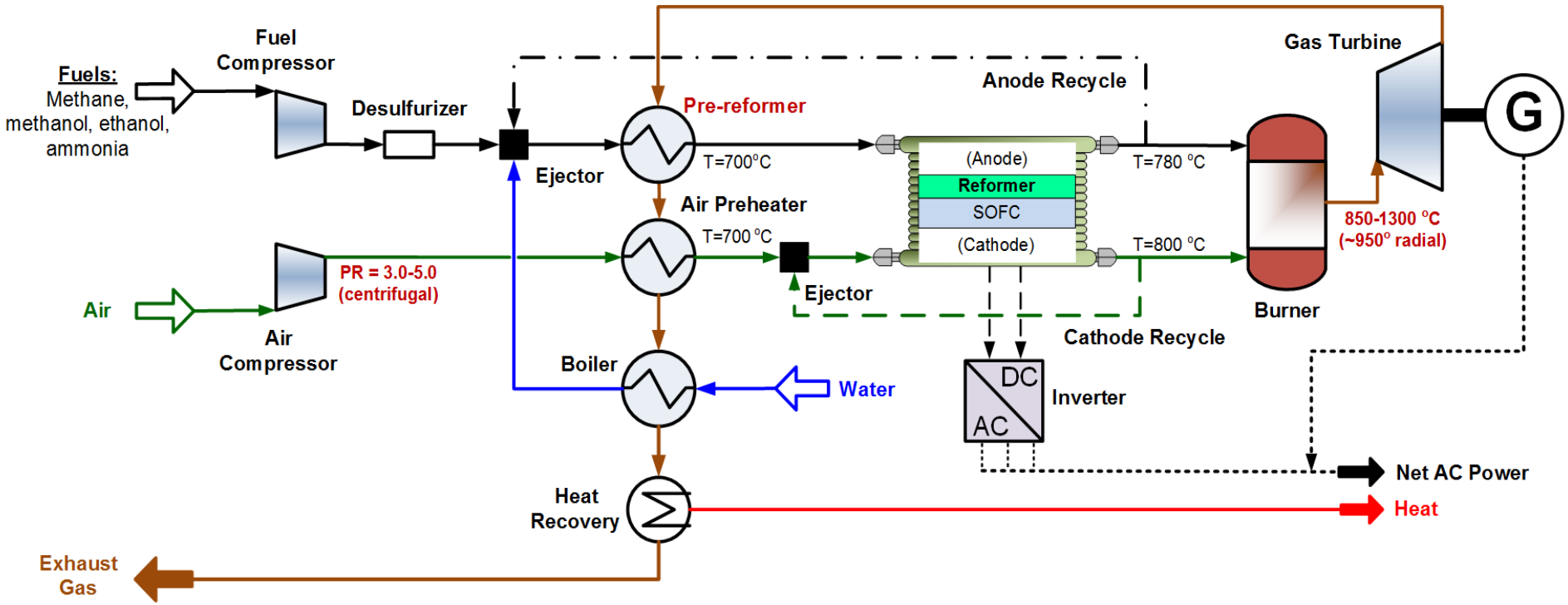
Hybrid cycles with performance limitations shown to offer system efficiencies of >70%-LHV





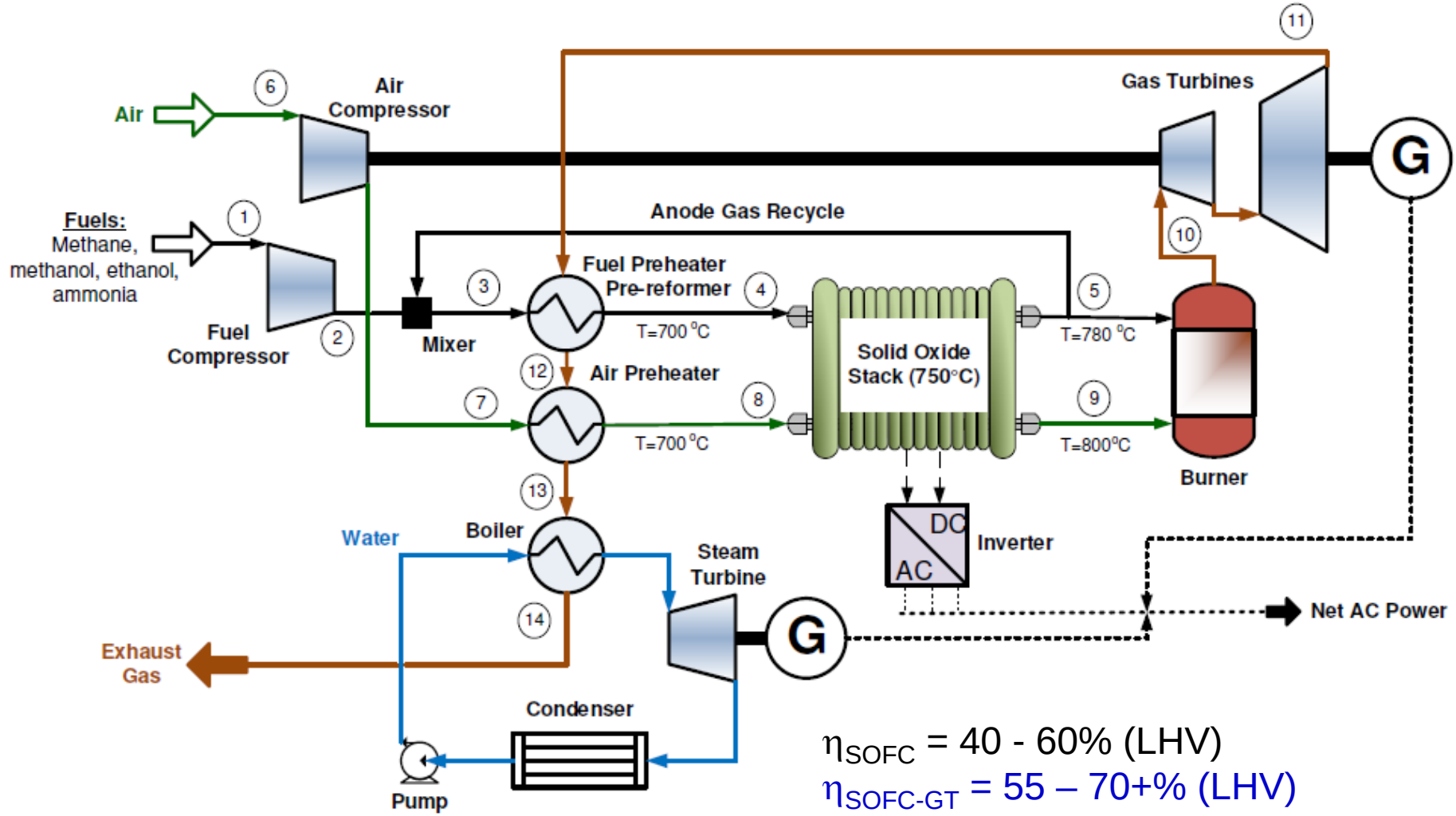
- Hydrocarbon fuels
- Biomass-derived fuels

There are numerous decisions in process design for viable high efficiency architectures



- **Reforming Method**
  $CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2$
- **Water Supply Methods**
- **Steam Reforming (Internal/Reforming)**
- **Cathode Gas Recycle**
- **Gas Turbine Integration**
- **Exhaust Heat Recovery or Bottoming Steam Cycle**

GT and Steam Rankine cycle integration increases efficiency, but also complexity

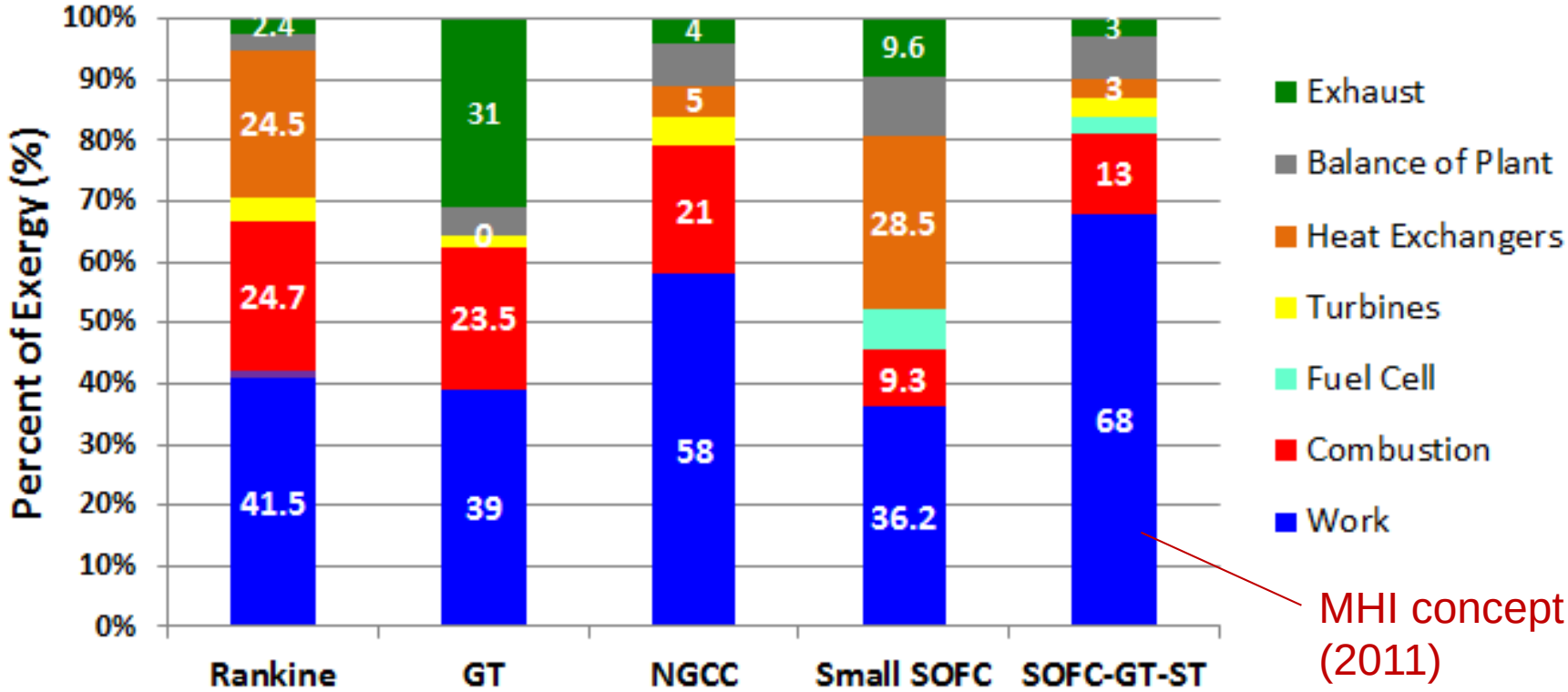


η_{SOFC} = 40 - 60% (LHV)

$\eta_{SOFC\text{-}GT}$ = 55 – 70+% (LHV)

$\eta_{SOFC\text{-}GT\text{-}SRC}$ = 60 – 75+% (LHV)

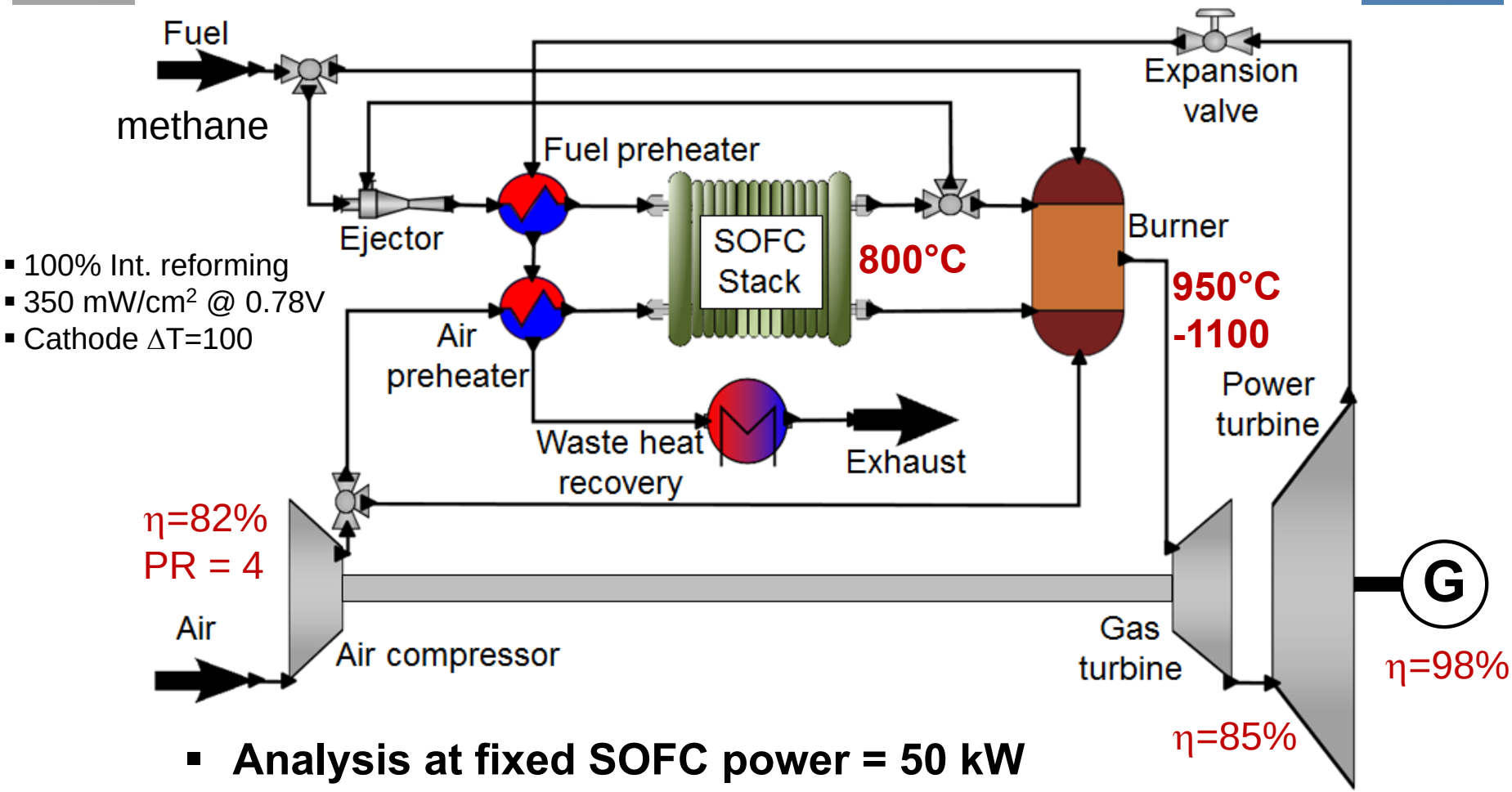
Exergetic analysis illustrates magnitude and location of system losses – combustion is a key loss source



- **Combustion losses dominate conventional power generation (20-25%)**
- **Hybridization of conventional technology does not reduce combustion loss**
- **Fuel cell integration lowers combustion loss even in simple systems**

Dunbar et al. Energy 16 (1991)
Braun et al., J. Power Sources 158 (2006)
Fyffe et al., Int. J. Engine Res (2017)

A design study of a simple SOFC-GT hybrid system can help motivate our discussions

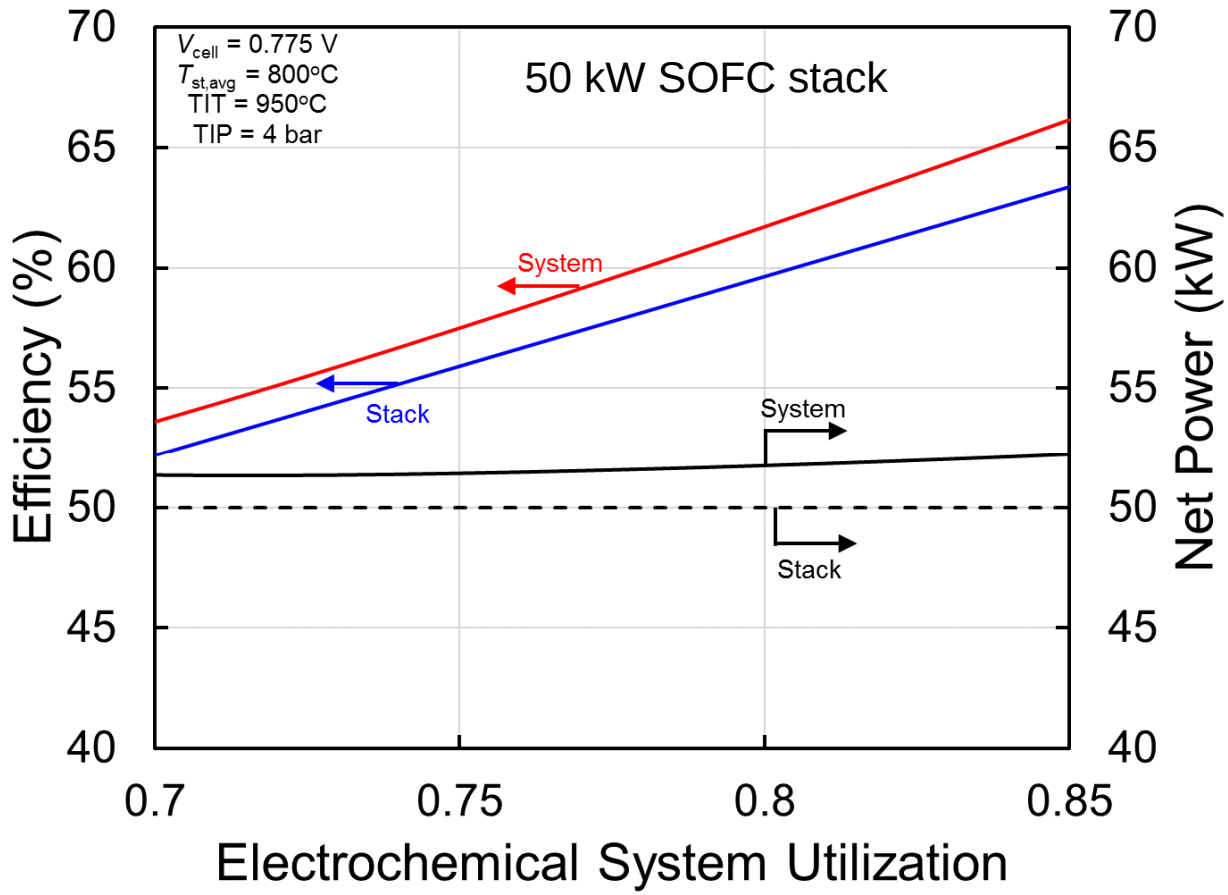


- 100% Int. reforming
- 350 mW/cm^2 @ 0.78V
- Cathode ΔT=100

- **Analysis at fixed SOFC power = 50 kW**
- **SOFC topping Radial gas turbine at PR = 4**
- **Bypass flows to cat burner for temperature control**
- **Pinch temperature constraint for air preheater (≥30°C)**

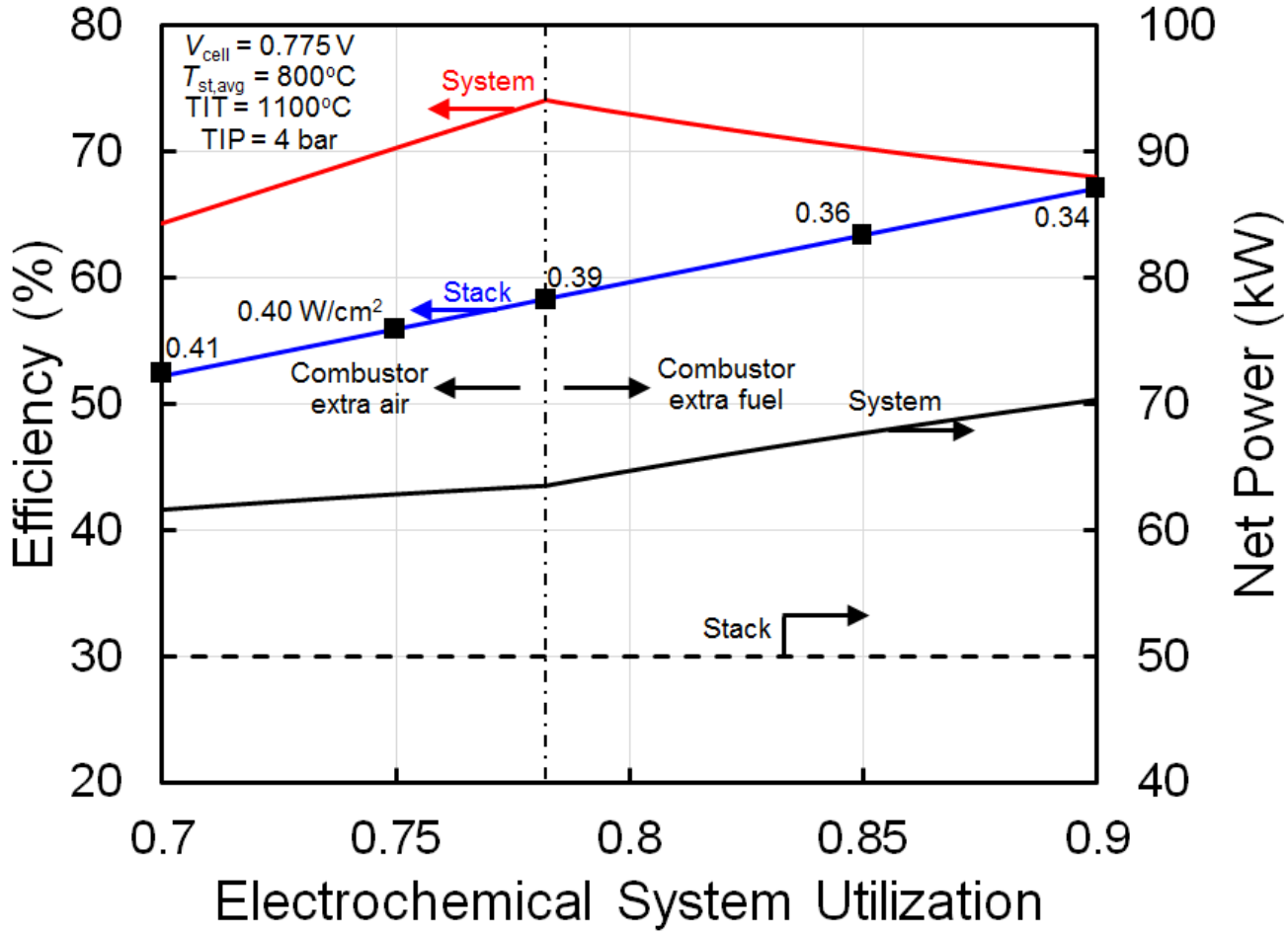
Fuel utilization analysis at fixed V_{cell} and 950°C turbine inlet illustrates simple hybrid efficiencies exceed 65% (LHV)

- η_{stack} increases due to lower fuel flow
- System efficiency is driven by stack efficiency
- Air preheater pinch limits full expansion of turbine
- Small net turbine power
- >65% efficiency possible



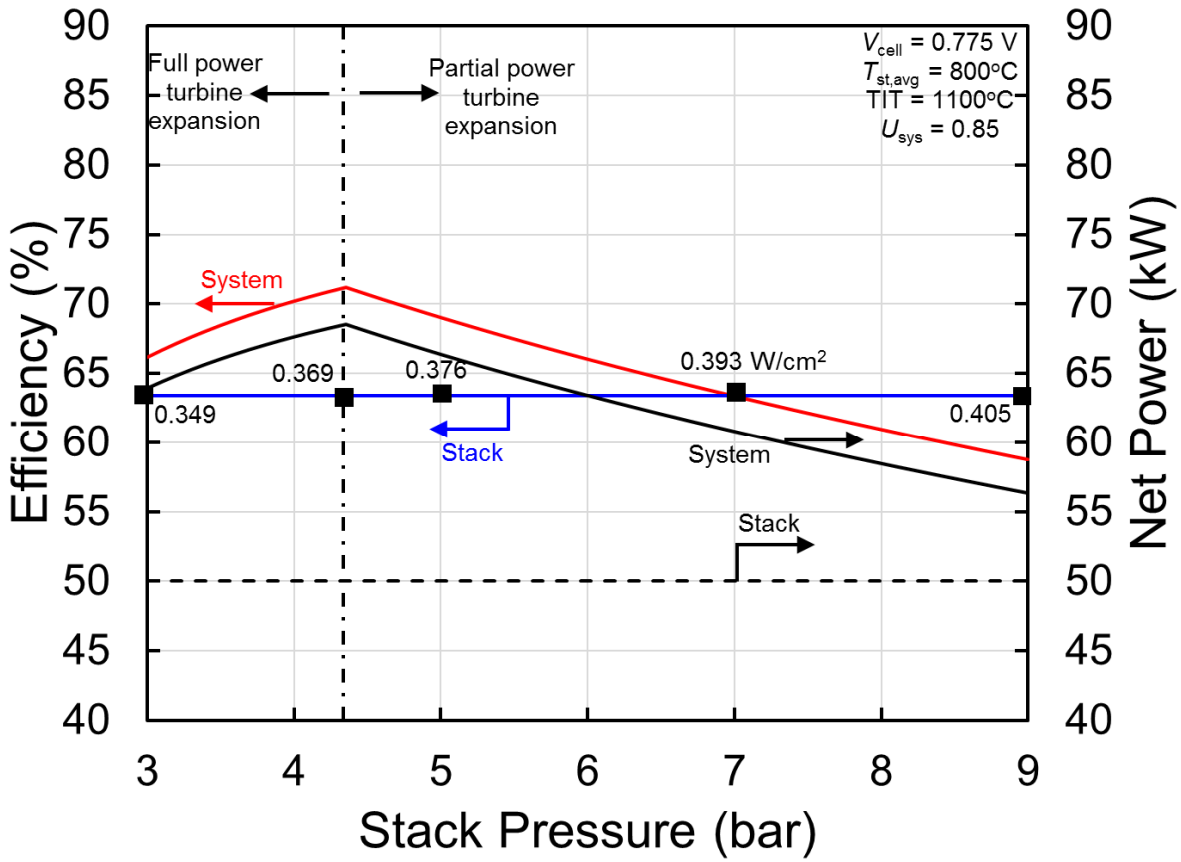
Efficiencies can exceed 70% by raising the turbine inlet to 1100°C at optimal fuel utilization

- η_{stack} increases due to lower fuel flow
- Power density affects economics
- Turbine amounts to 18-29% of total power
- Above Usys = 78%
  - Extra fuel supplied to meet TIT
  - Total fuel flow increases, decreasing η_{sys}
- Below Usys = 78%
  - η_{sys} driven by stack efficiency
  - Excess air to burner to limit TIT



Pressurization benefits performance, but maximum efficiency limited by constraints in this configuration

- Stack efficiency constant – constant voltage
- Below 4.35 bar
  - Air preheat pinch met with full turbine expansion
  - Pressurization benefit
- Above 4.35 bar
  - Turbine throttled to meet air preheat pinch
  - Decreases net power and efficiency

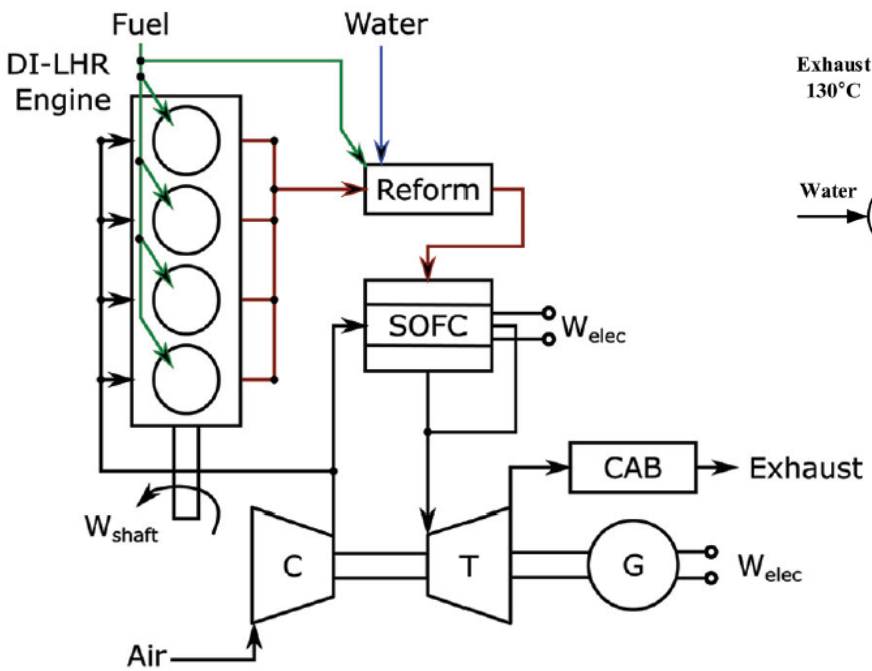


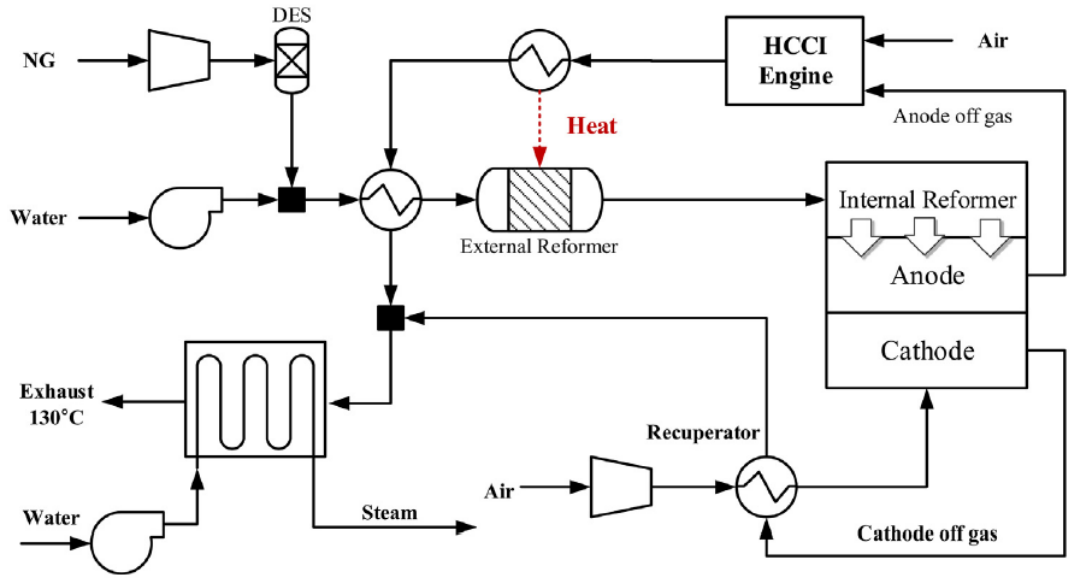
➢ <u>Redesign</u> – consider higher turbine inlets, higher fuel cell temperature, cathode recycle or other measures to address pinch constraints

Hybrid system concepts also include SOFC-ICE combinations using latest engine technology

Efficiency = ~56% LHV

Turbocharged, Direct-Injection, LHR engine bottomed w/ 1000°C SOFC





100 kW, 850°C SOFC-topped HCCI Engine

Efficiency = ~71% LHV

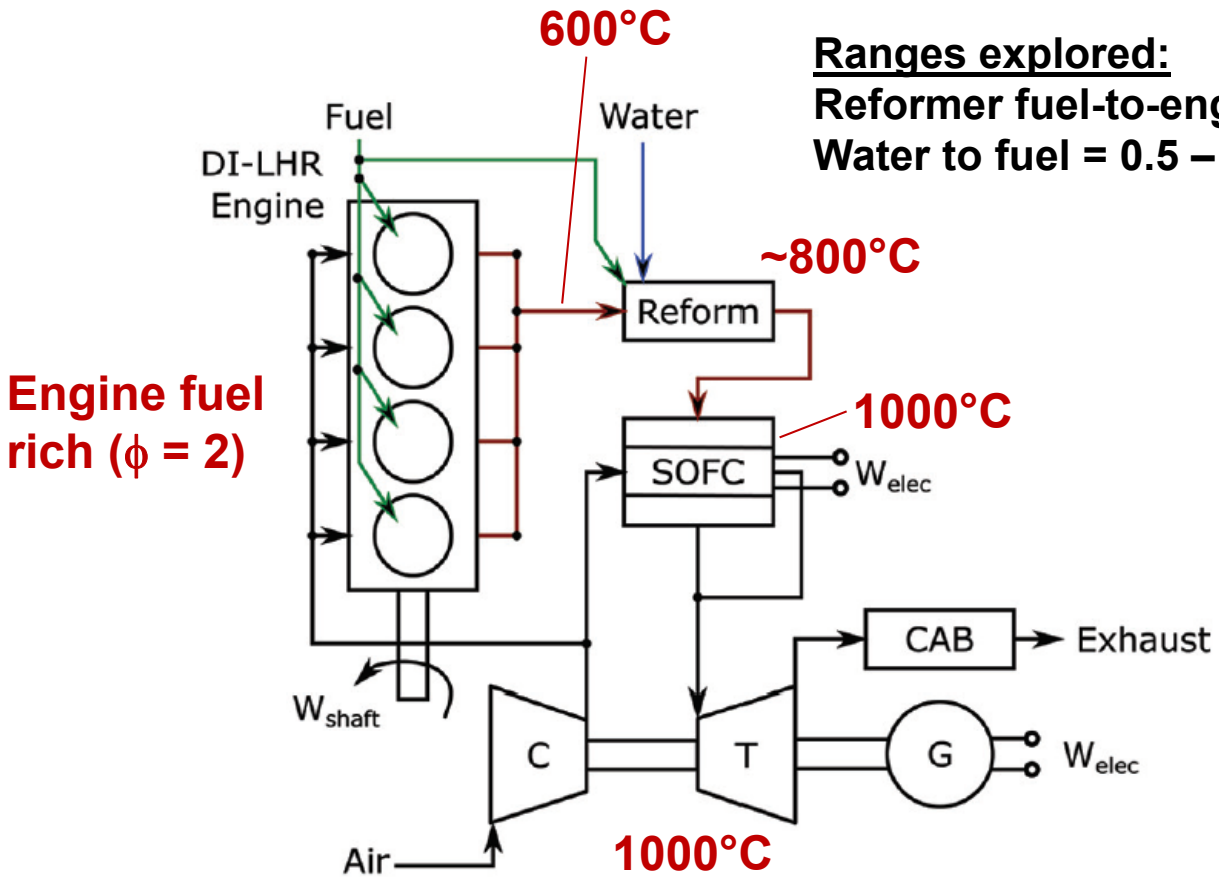
Fyffe et al. Int. J Engine Res (2017)

Park et al. Int. J Hydrogen Energy 39 (2014)

Bottoming the ICE with SOFC enables fuel reforming in the engine and upstream of the SOFC

Turbocharged, Direct-Injection, LHR engine bottomed w/ 1000°C SOFC

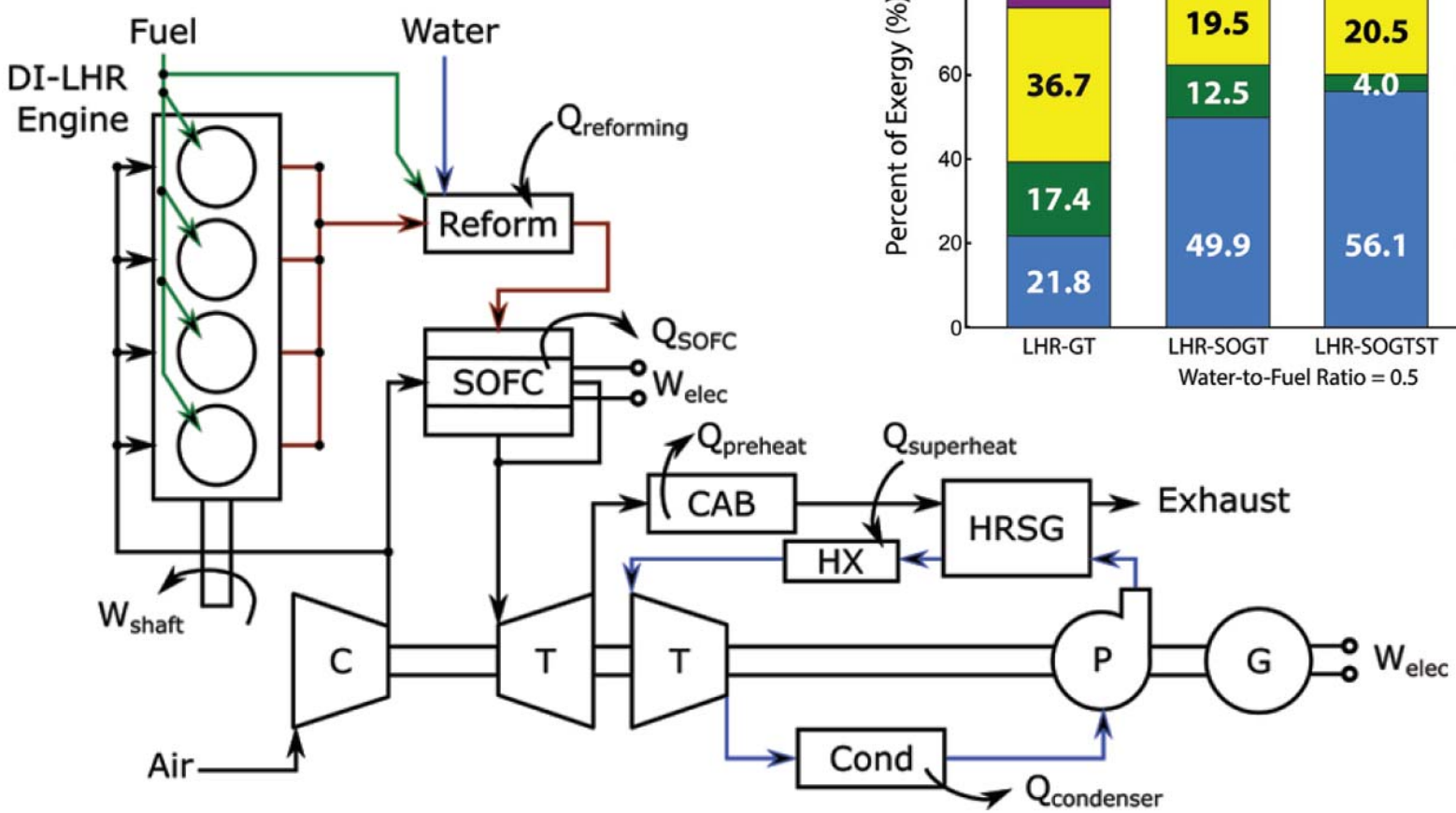
Ranges explored:
Reformer fuel-to-engine fuel = 0 – 2.0
Water to fuel = 0.5 – 2.0

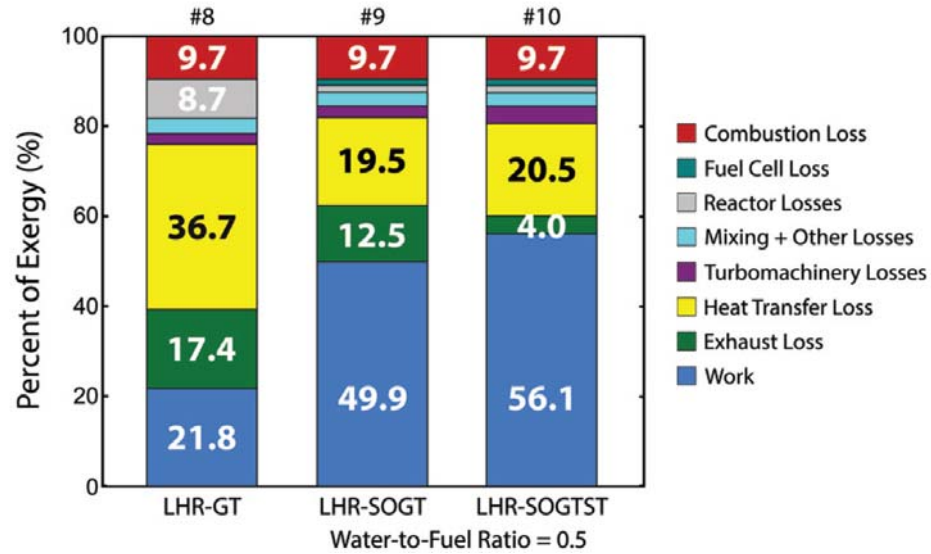


Fyffe et al. Int. J Engine Res (2017)

Adding a bottoming steam cycle to hybrid SOFC-ICE systems further increases efficiency to ~58% (LHV)

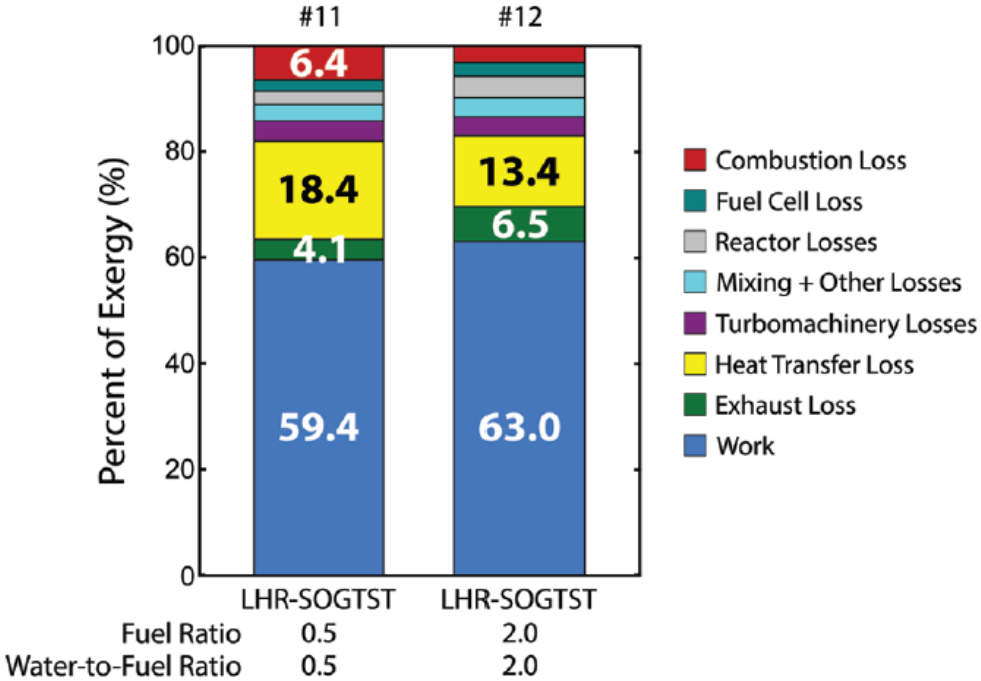
Lowered exhaust loss



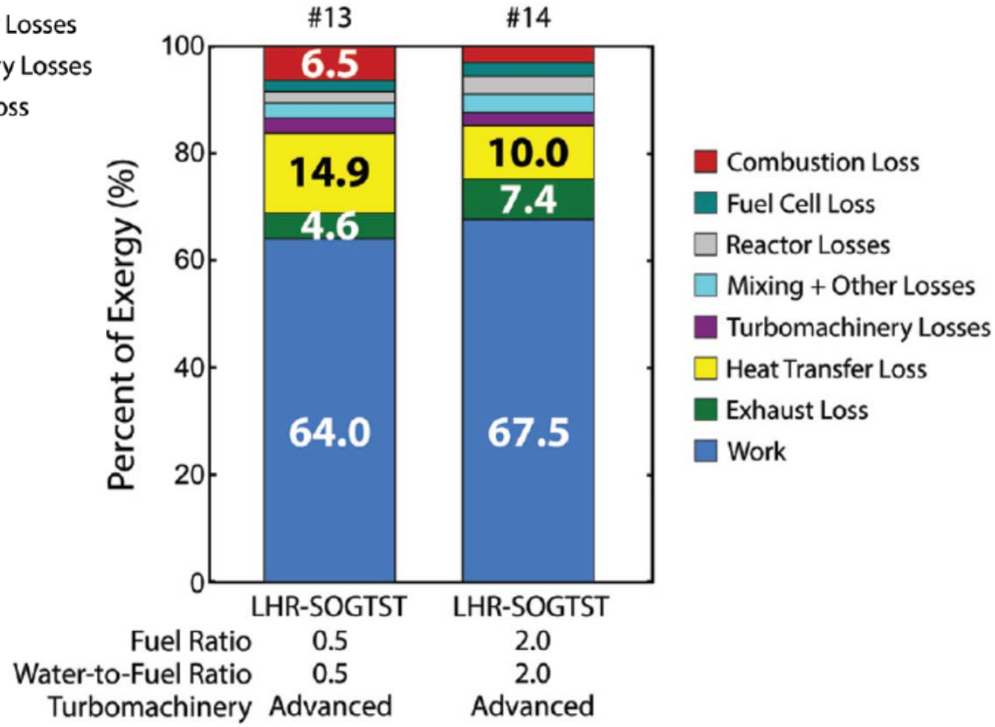


Fyffe et al. Int. J Engine Res (2017)

Changing operating conditions and advancing turbomachinery pushes efficiency to 70% (LHV)



Change in design conditions



Advanced turbomachinery

Fyffe et al. Int. J Engine Res (2017)

Concluding Thoughts

- >70% LHV efficiency is theoretically viable, but requires higher temperature turbine inlet temperatures and careful integration
- System architectures, **compressor surge margin** and process integration affect efficiency, required RIT, and operability throughout load range
- Off-the-shelf gas turbine vs. custom? OTS more practical → may mean designing around existing turbomachine performance maps
- High efficiency turbomachinery and synchronous generators at smaller scales would be a plus
- Internal reforming preferred for thermal management
- More than one fuel cell type may be an option, but pressurized planar fuel cell stacks required for >70% efficiency
- Many studies, few hybrid demonstrations at small or large-scale
- Practical integration issues remain – Modeling integration of systems and processes, FC durability at pressure, dynamics and control, etc.