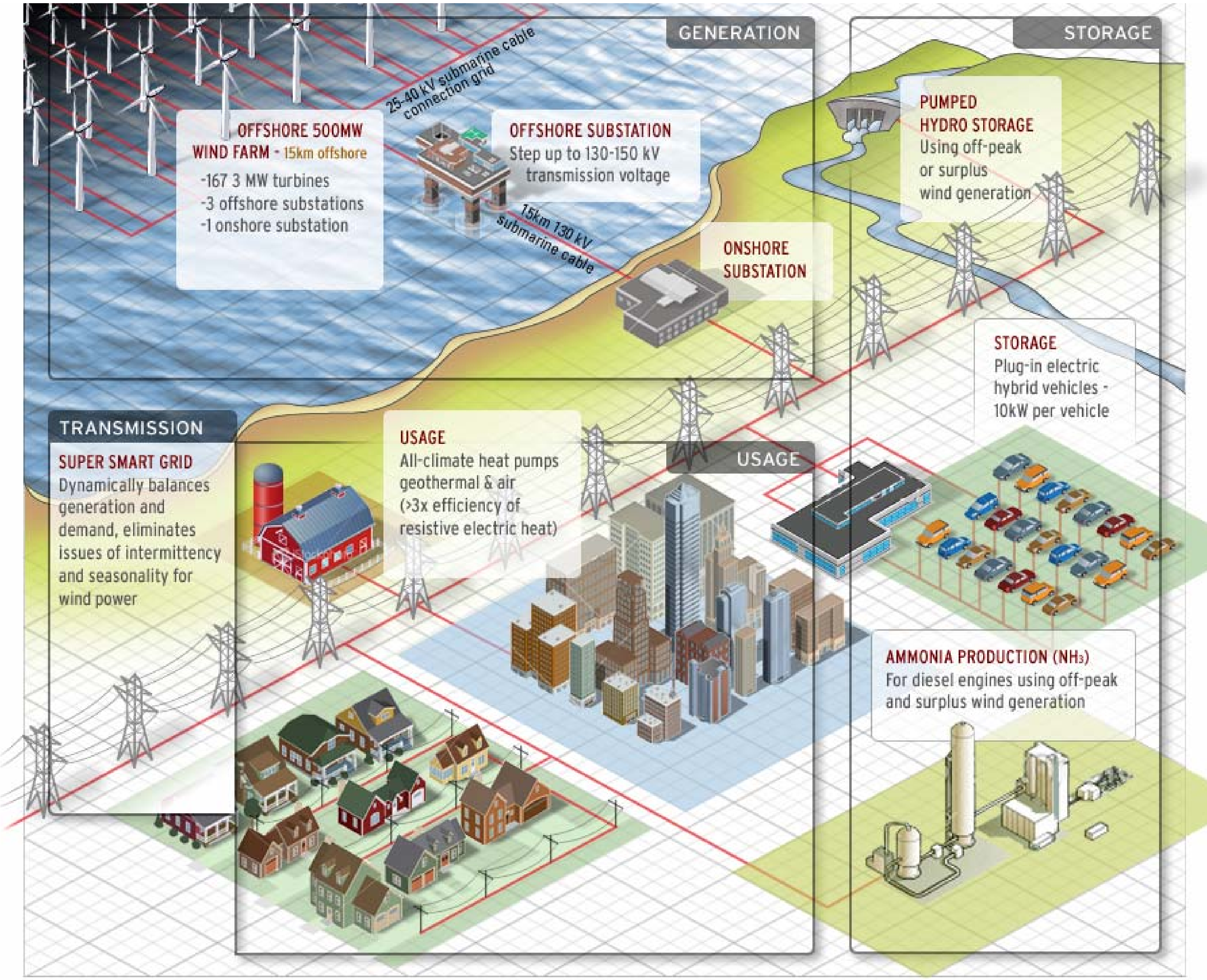
Hydrogen Production

- What we have
- What we want
- What is promising

A Green Energy Utopia?



Some Facts about H2

- Darn hard to store and manage
- Do we have a hydrogen mine, anyone?
- It’s sort of an energy medium, not a source (if nuclear fusion is not considered)

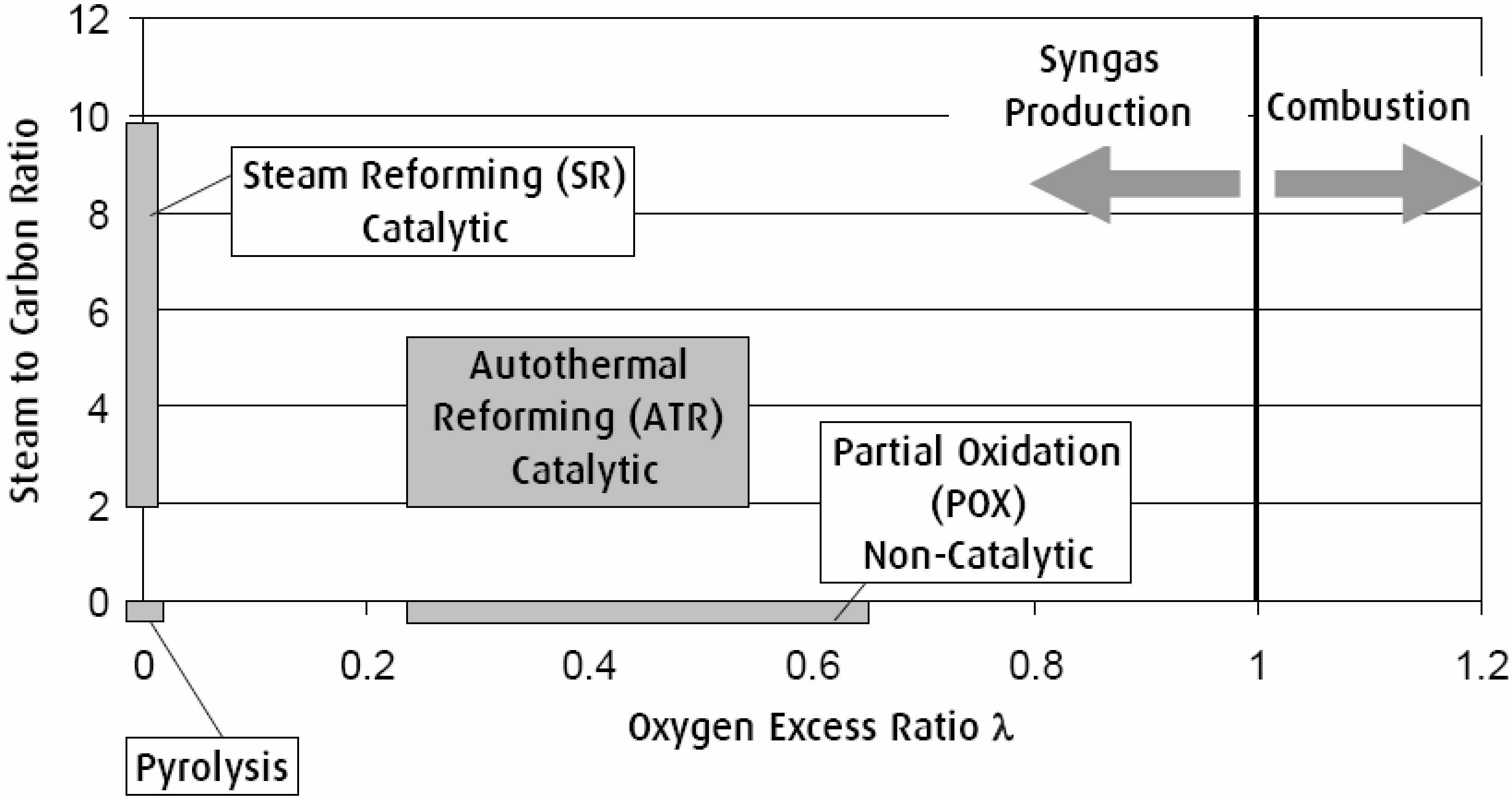
Where do we get H2 today?

- Steam reforming of methane (Dominating technology) or other hydrocarbons, alcohols
- The Syn-Gas process
- Electrolysis

Feedstocks

Light Hydrocarbons	Heavy Hydrocarbons
▪ Refinery Gases ▪ LPG (Propane, Butane) ▪ Natural Gas (48 %) ▪ Naphtha	▪ Fuel Oil (30 %) ▪ Vacuum Tar ▪ Asphalt ▪ Petroleum Coke ▪ Coal (18 %)
Process	**Process**
▪ Steam Reforming ▪ Partial Oxidation	▪ Partial Oxidation

Various reforming processes



Various reforming reactions

Non Oxygen Consuming:

- Steam Methane Reforming (SMR)
  $CH_4 + H_2O \rightarrow CO + 3\ H_2$ endothermal
- Carbon Monoxide Conversion (CO-Shift)
  $CO + H_2O \rightarrow CO_2 + H_2$ exothermal

}Steam Reforming

Oxygen Consuming

- Hydrocarbon Conversion
  $C_nH_m + n/2\ O_2 \rightarrow nCO + m/2\ H_2$ exothermal
- H_2 Oxidation
  $2\ H_2 + O_2 \rightarrow 2\ H_2O$ exothermal
- Carbon Monoxide Oxidation
  $2\ CO + O_2 \rightarrow 2\ CO_2$ exothermal

}Partial Oxidation, Autothermal Reforming

- **Synthesis Gas contains H_2, CO, H_2O, CO_2, unreacted Hydrocarbons, Impurities**
- **Requested Products are H_2, CO, CO+H_2**
- **H_2 Separation + Purification required**

Issues for reforming

- New bottle, old wine
- Non sustainable fossil fuels
- Hydrogen purification
- Its not really a cyclic hydrogen production; more like a mining and leaching of H2

Existing issues with electrolysis

- Energy intensive
- Using high quality energy (electricity)
- Electrolyzers are costly (corrosion, noble metals, PEM, etc.)

What hurts electrolysis

- Overpotential in the hydrogen evolution reaction (HER)
- Stability of electrodes in a certain pH range

- How to improve?
- High temperature electrolysis

Thermochemical H2 production

Approaches to Water Splitting using Nuclear Energy

$H_2O \longrightarrow H_2 + \_\ O_2$ $\Delta H = 242$ kJ/mol

(Direct Thermolysis requires ≥ 2500 °C)

- Conventional Electrolysis _ = 20-36%
  - Thermal ⟶ Electricity ⟶ Hydrogen
- High Temperature (Steam) Electrolysis _ = 40-50%
  - Use of both Electricity and Direct Heat
- Thermochemical Cycles _ = 45-55%
  - Series of Linked Chemical Reactions
  - Thermal Energy Only or Hybrid

_ = H_2 (HHV)/Nuclear heat

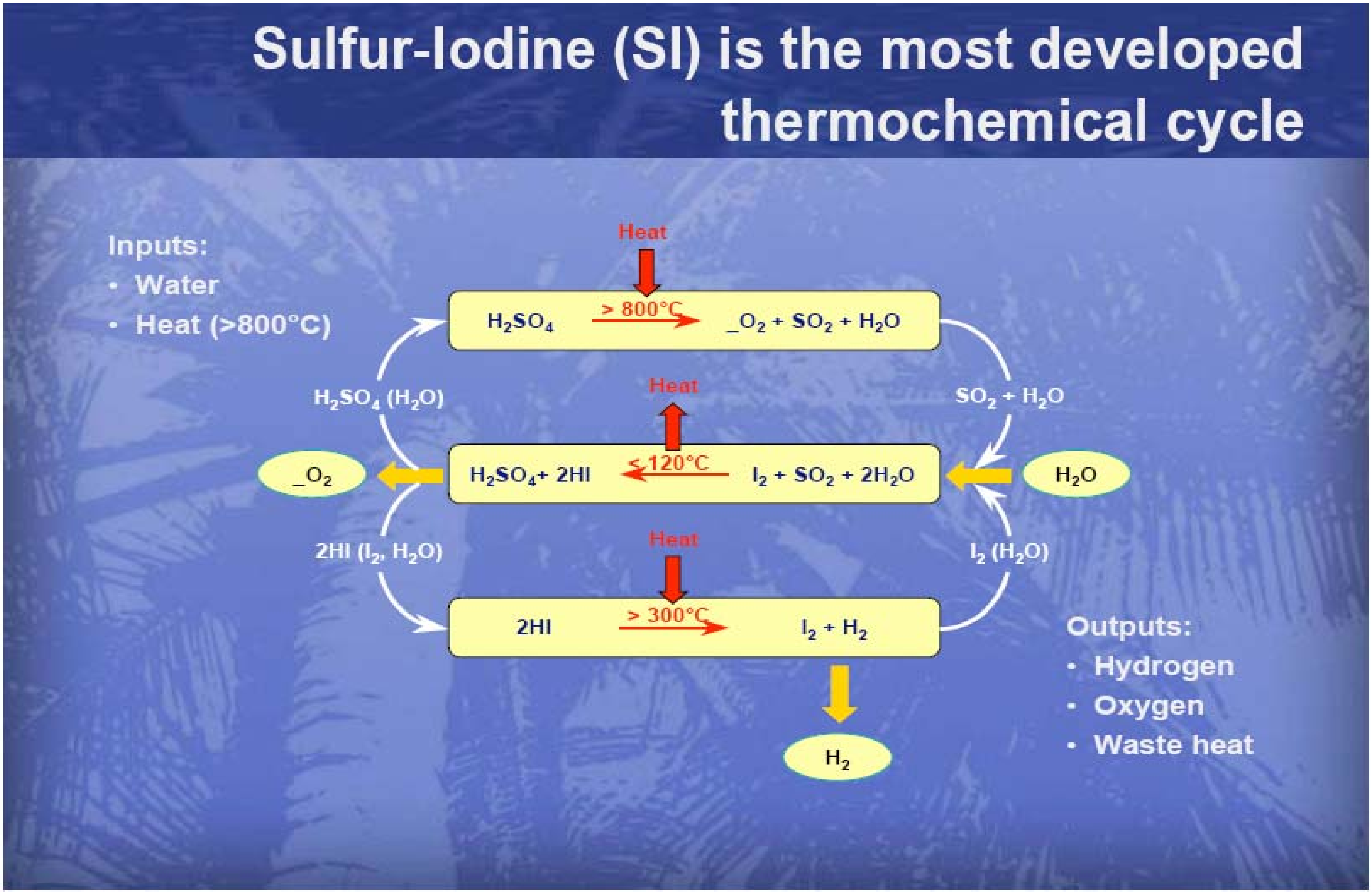
Thermochemical H2 production

- Potentially the highest cycle efficiency
- Negligible electrochemical corrosion
- Bulk reaction instead of an interfacial one (as in electrolysis) -> higher yield

Thermochemical H2 production Wish List

- All reactants in fluid phases
- Proper phase separation of some reaction intermediates
- Good isolation and purification of the products

Thermochemical H2 production

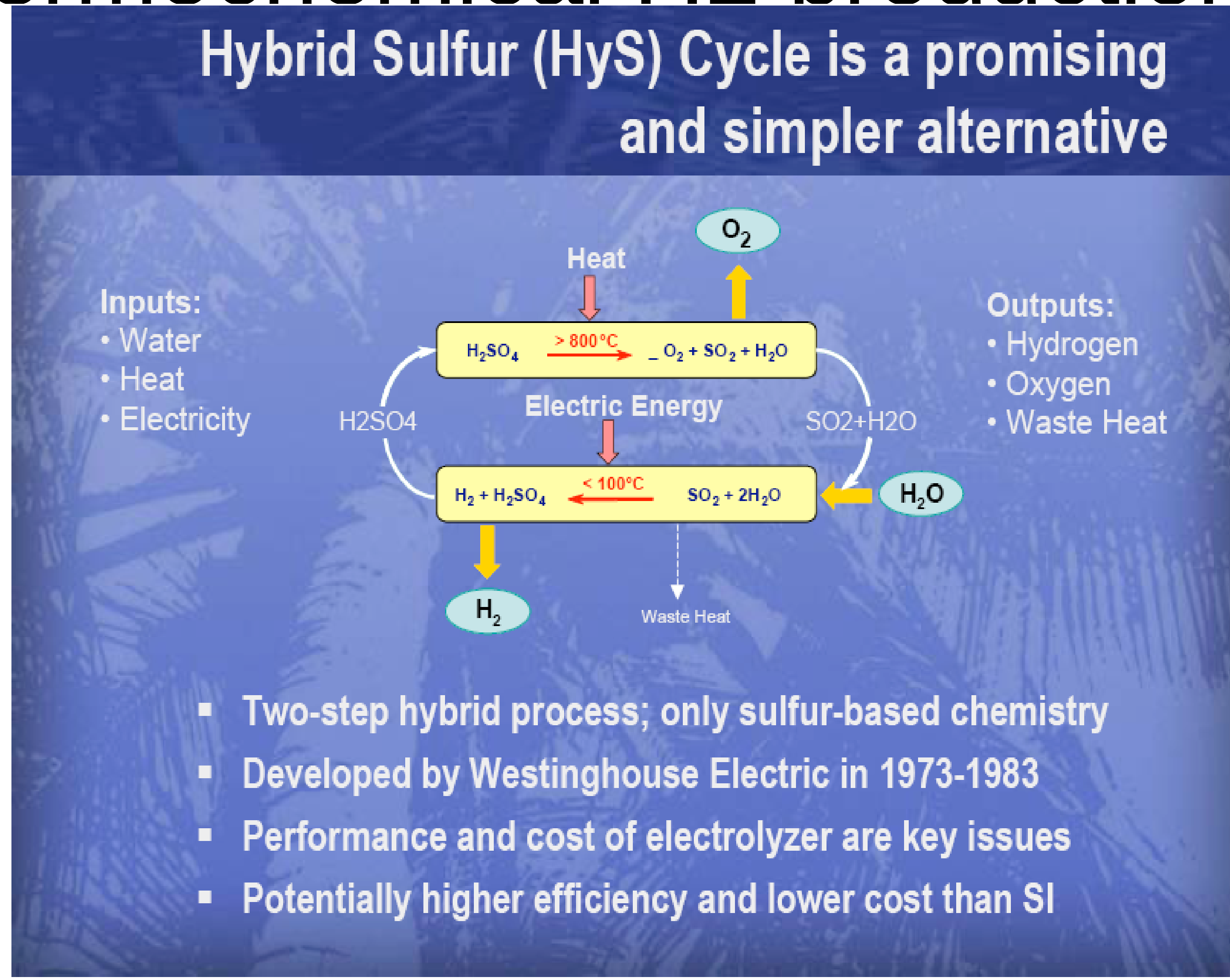


Neat features of the S-I process

- Sulfur-Iodine
- All reactants can be a fluid if the cycle temperature is properly chosen
- A natural phase separation exist in the intermediate HI and H2SO4
- Thermo-only process.

Thermochemical H2 production

Some Variations



Neat features of the S-I process

- In comparison, the Sulfur-Bromine process needs an electrolysis to split HBr

$$2HBr \rightarrow H_2 + I_2 \qquad \sim 1.066V$$

Neat features of the S-I process

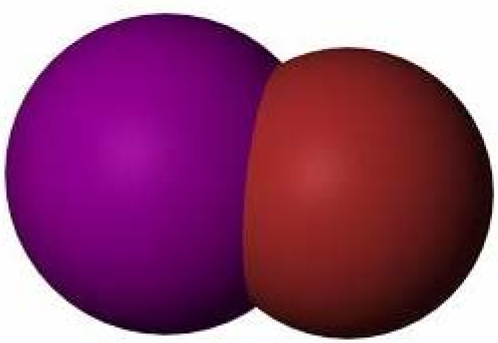
- Issues
- The first step is exothermic, and is preferably carried out at a T lower than 120 C.
- Iodine is relatively not very abundant and so the cost could be high.

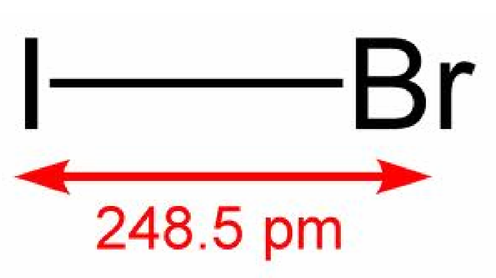
Any idea on improving the S-I?

- Think about your suggestions/improvements
- No need to demo in labs yet, but at least the concept please.
- This could be one problem for the HW#2

Improving the S-I, some options

- Heat exchange to recuperate the heat from $I_2 + SO_2 + 2\ H_2O \rightarrow 2\ HI + H_2SO_4$ (120°C)
- How about the thing called iodine bromide? IBr
- What? What is this darn thing?





So what's funny about IBr?

- Melting point: 40 degree Celsius!
- Almost room temperature
- Should be cheaper than iodine alone

How about the downside?

- Phase equilibrium of I_2, Br_2 and IBr?
- Phase separation of HI and the sulfuric acid?
- …
- We need to figure it out as HW#2

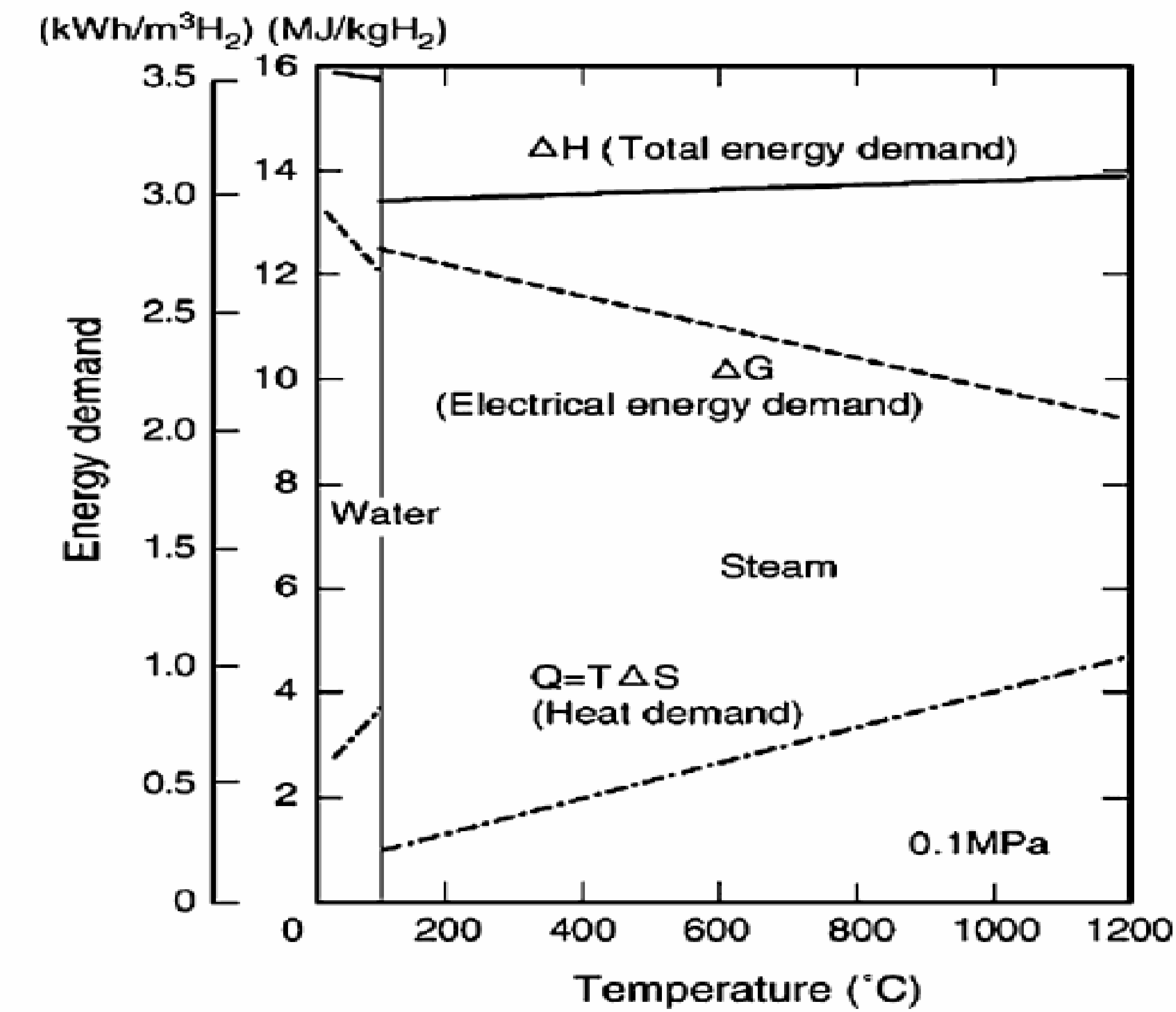
High T electrolysis

- Why High T?

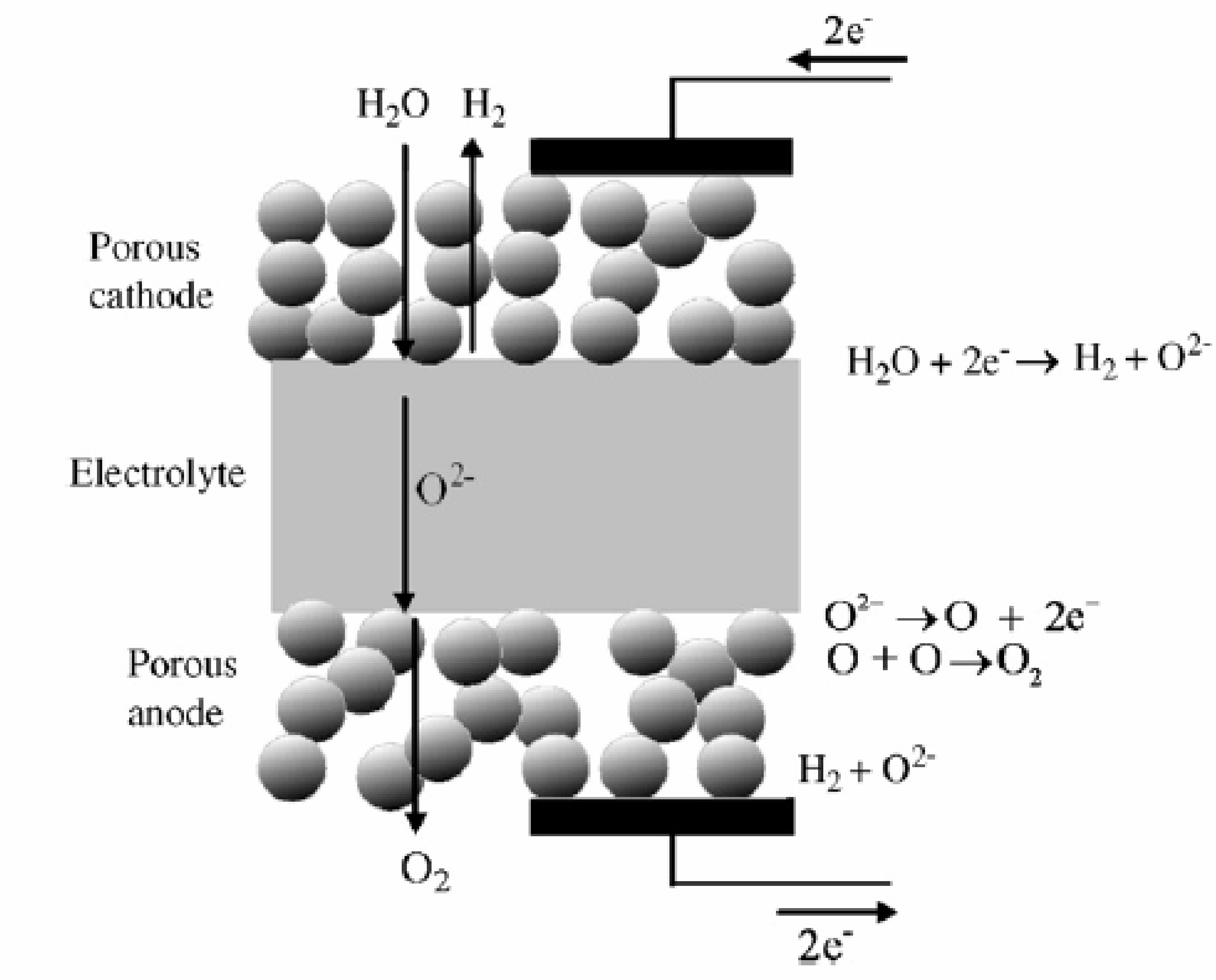
  High quality energy (electricity) – rare
  Low quality energy (heat) – abundant

- ¾ - 2/3 of energy is wasted as thermal energy in average power stations

High T electrolysis



High T electrolysis



Structure of
Single cell
Solid oxide
Electrolysis cell
(SOEC)

High T electrolysis

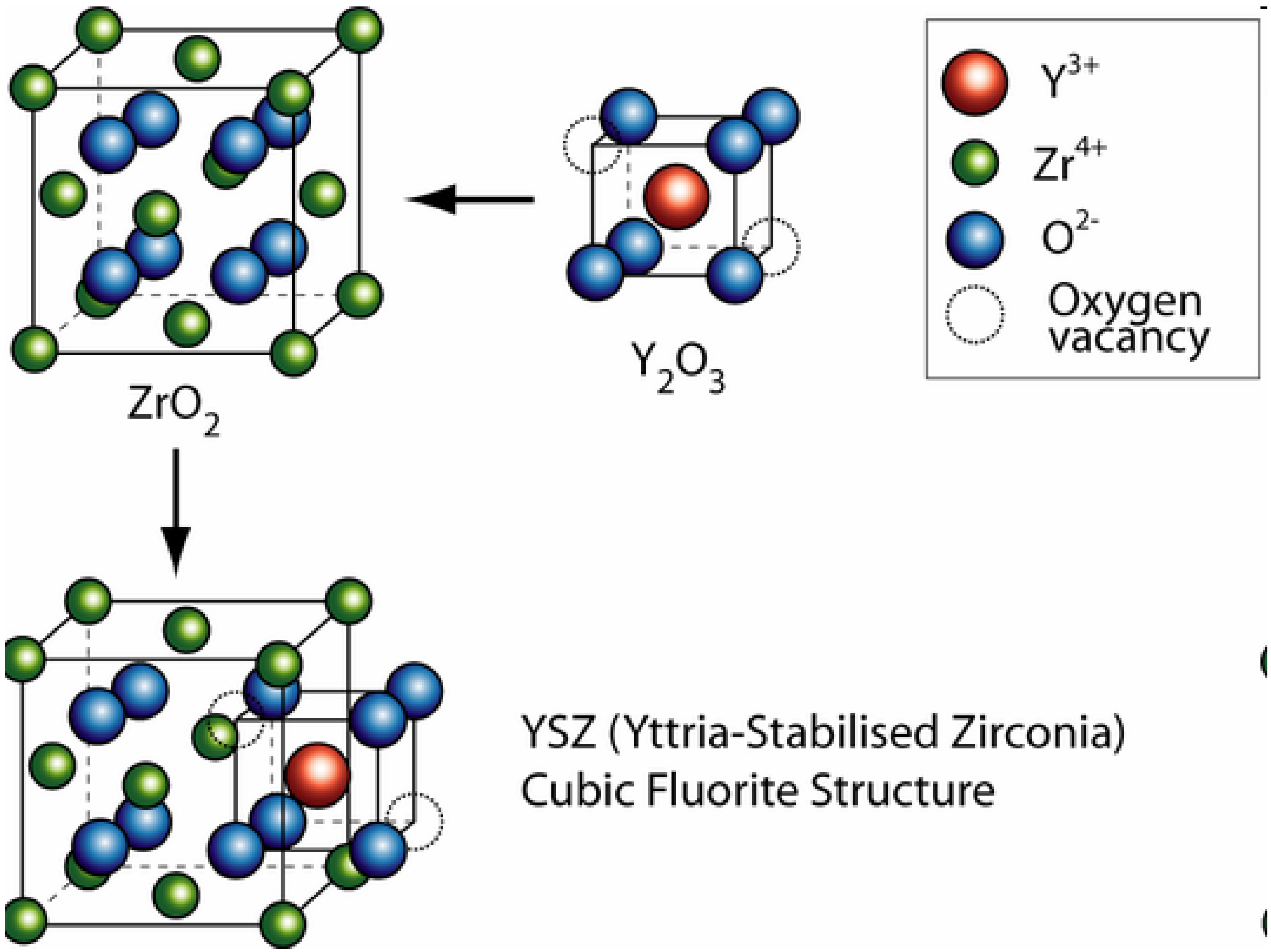
- Electrolyte:

Table 1 – Reported ionic conductivity of different

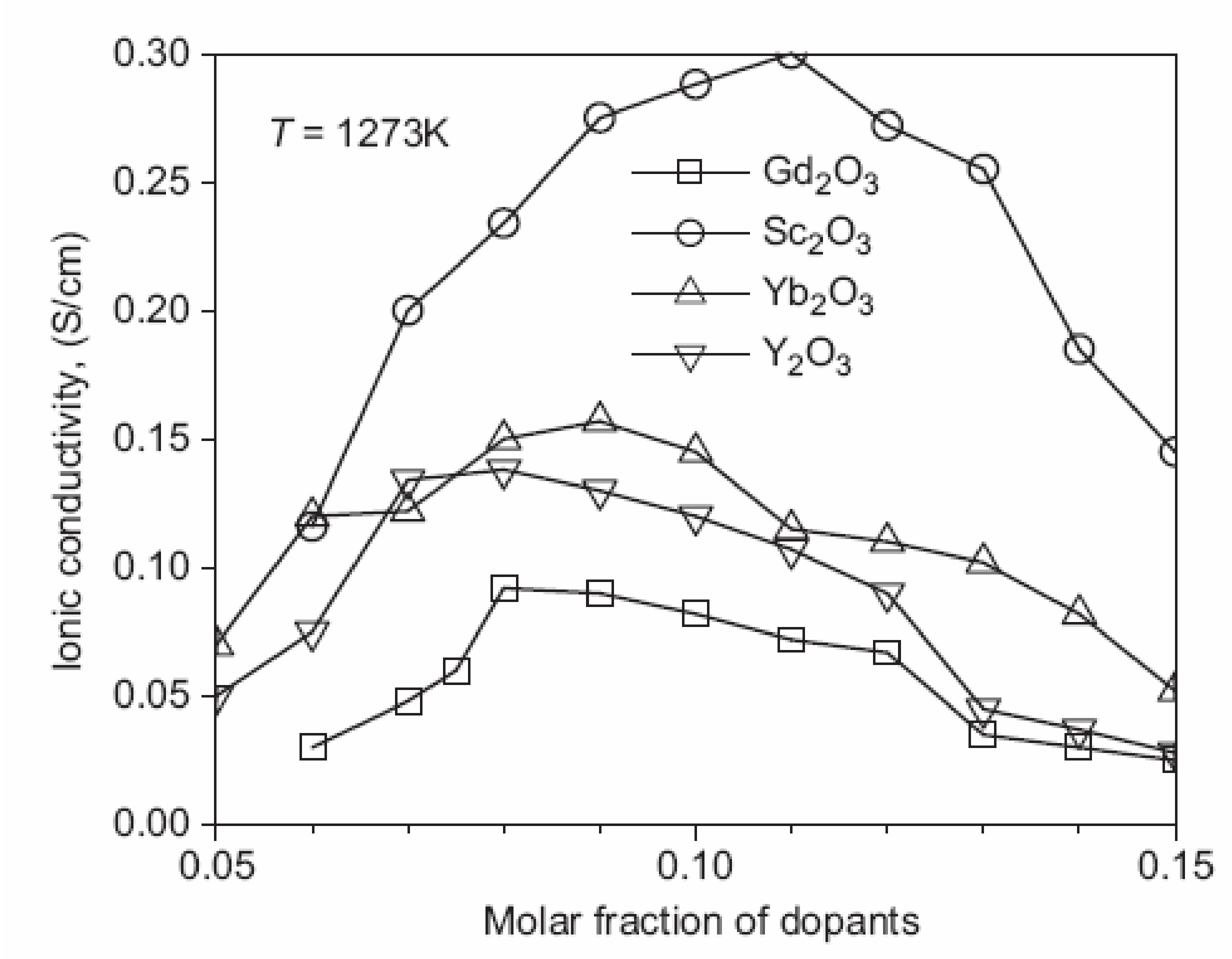
Material	Conductivity (S/cm)	Temperature (K)
8YSZ	0.13	1273
10.5YSZ	0.034	1073
10YSZ	4.52×10^{-6}	673
9.5YSZ	0.057	1173
8YSZ	0.083	1173
$CaO–ZrO_2$ with 12.5 mol% CaO	0.055	1273
$La_2O_3–ZrO_2$ with 5 mol% La_2O_3	0.0044	1273
$MgO–ZrO_2$ with 13.7 mol% MgO	0.098	1273
$Sc_2O_3–ZrO_2$ with 9–11 mol% Sc_2O_3	0.28–0.34	1273
$Sc_2O_3–ZrO_2$ with 6 mol% Sc_2O_3	0.18	1273

High T electrolyte materials

- YSZ



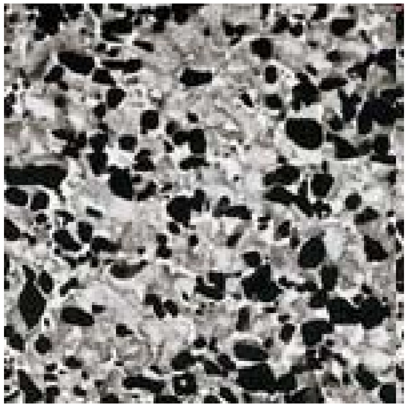
High T electrolyte materials



ionic conductivity versus dopant concentration

High T electrode materials

- Cathode: cermet Ni–YSZ
- Cermet: ceramic (cer) and metallic (met)

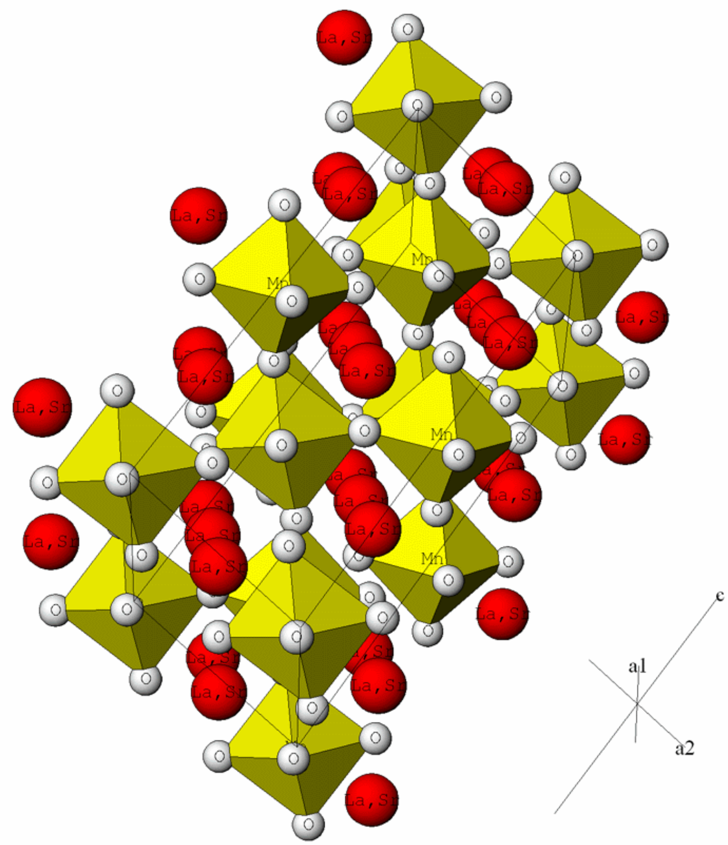


- Anode: cermet Ni-LSM – lanthanum strontium manganate (LSM)

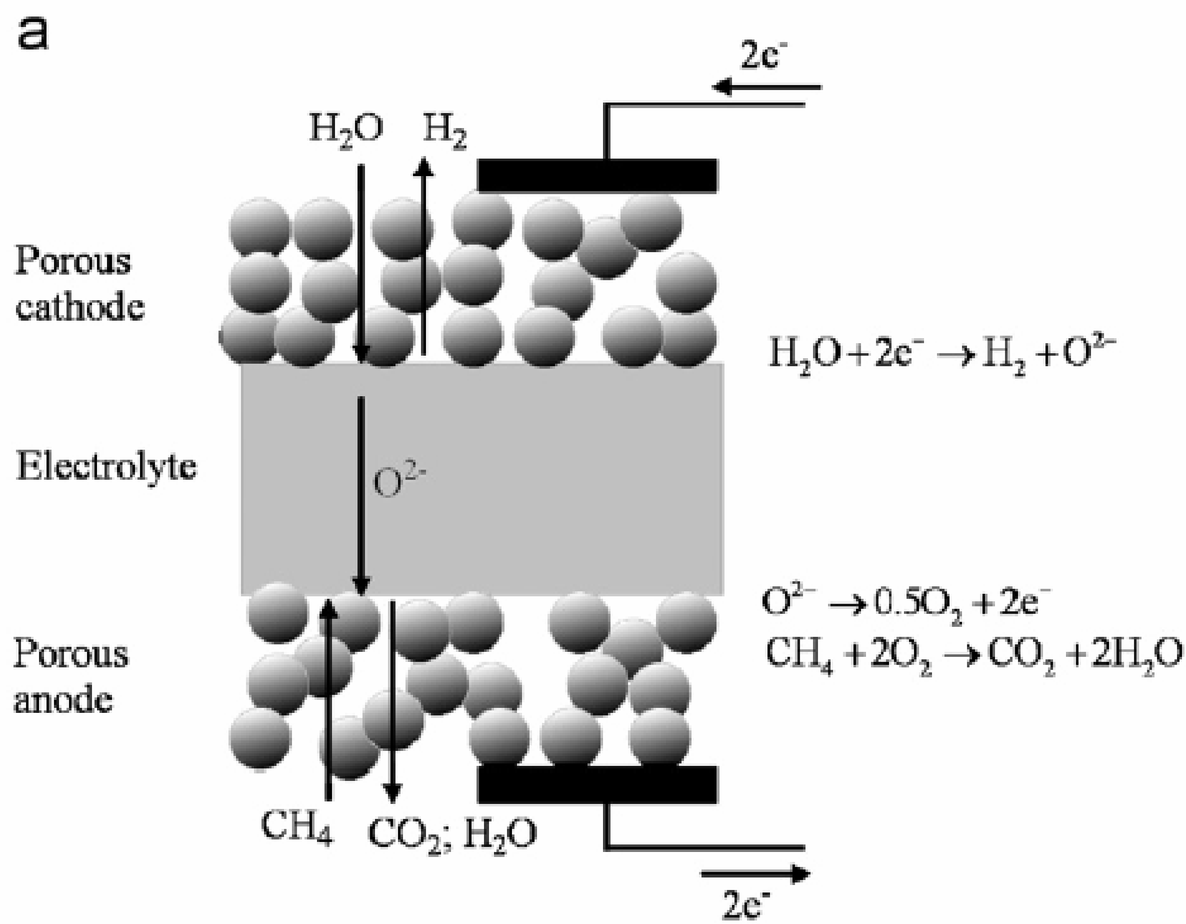
High T electrode materials

- lanthanum strontium manganate (LSM)

La1-xSrxMnO3

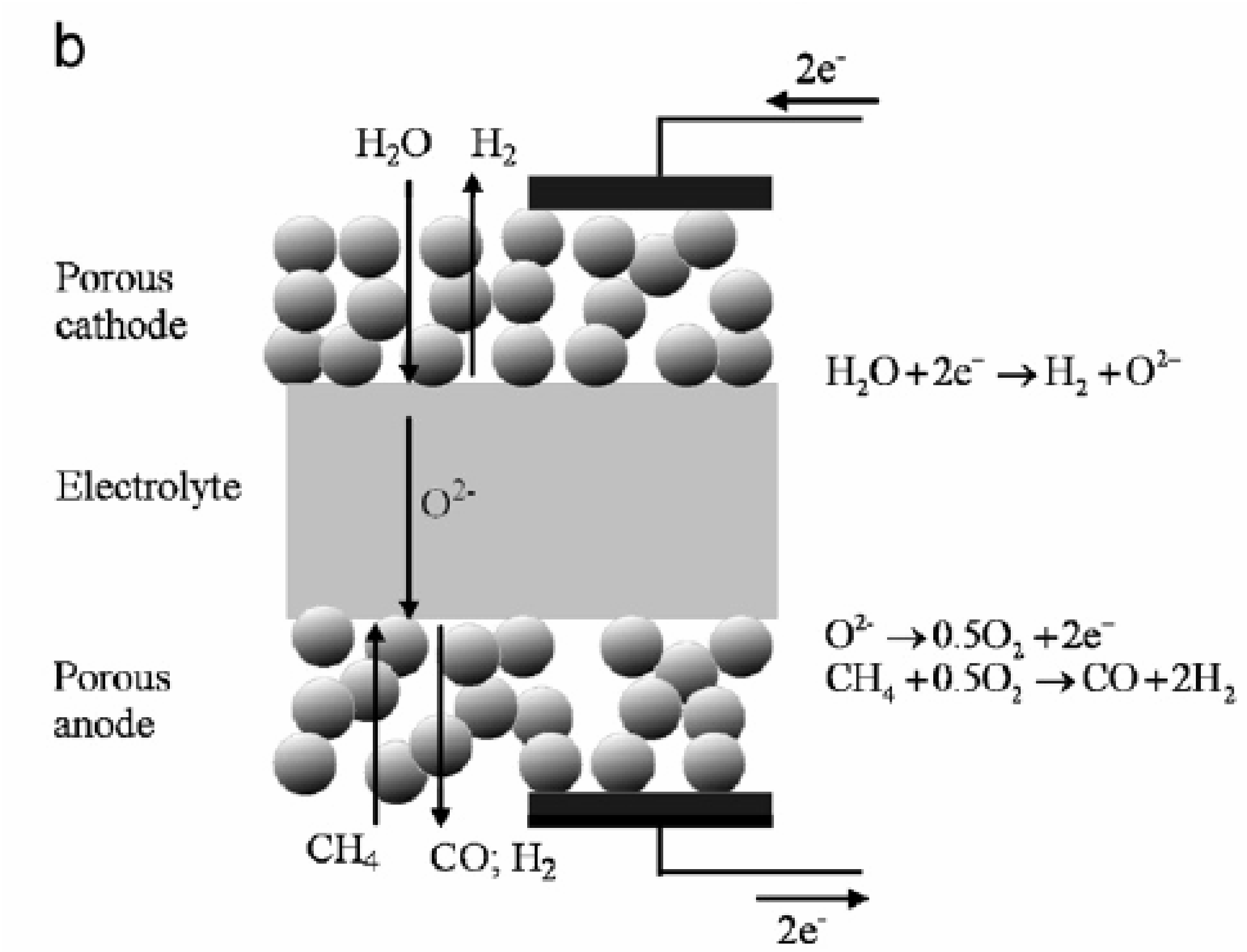


High T SOEC combos



natural gas-assisted SOEC, total oxidation

High T SOEC combos



natural gas-assisted SOEC, partial oxidation