UNIVERSITY OF CAMBRIDGE

Novel methods for producing hydrogen

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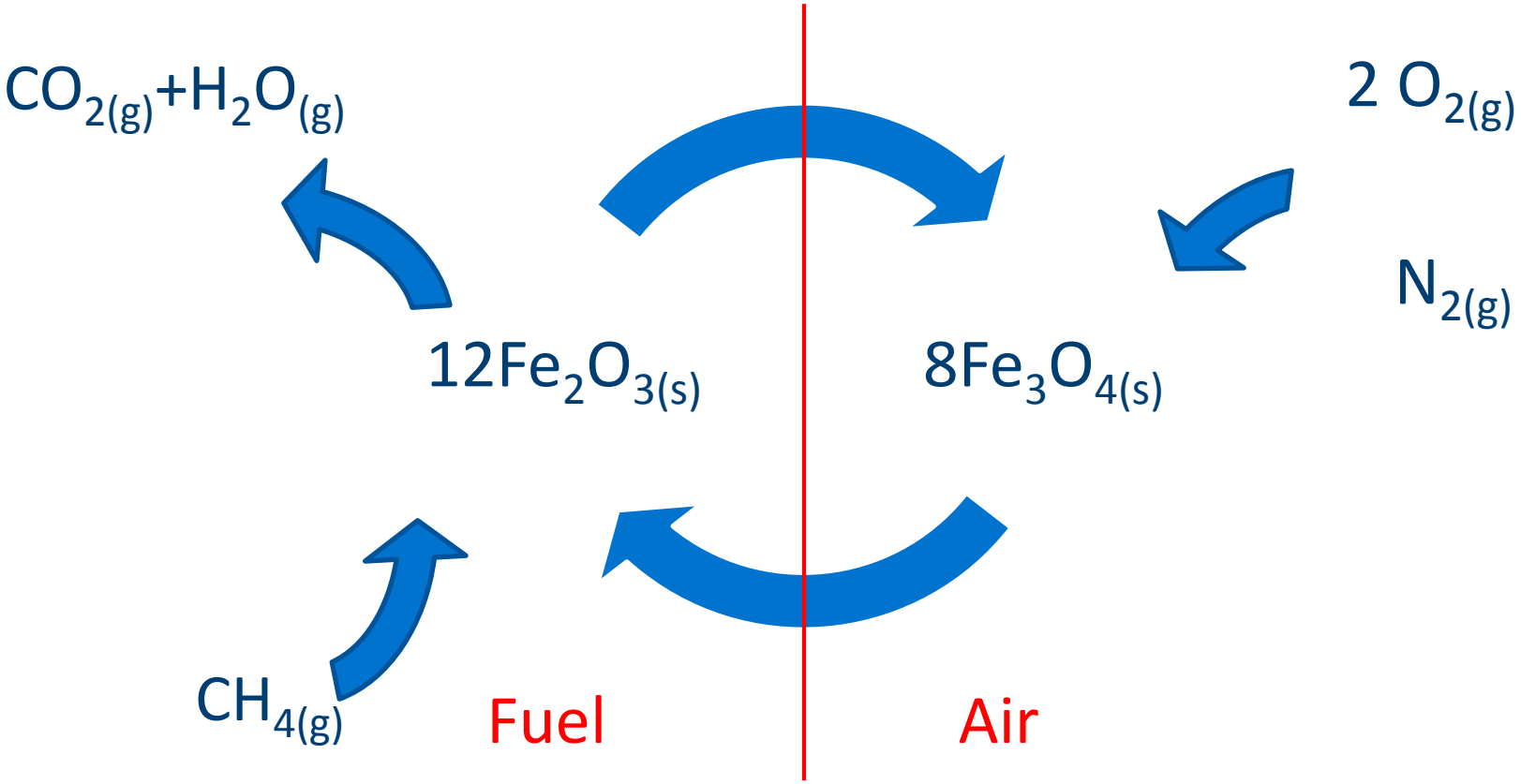
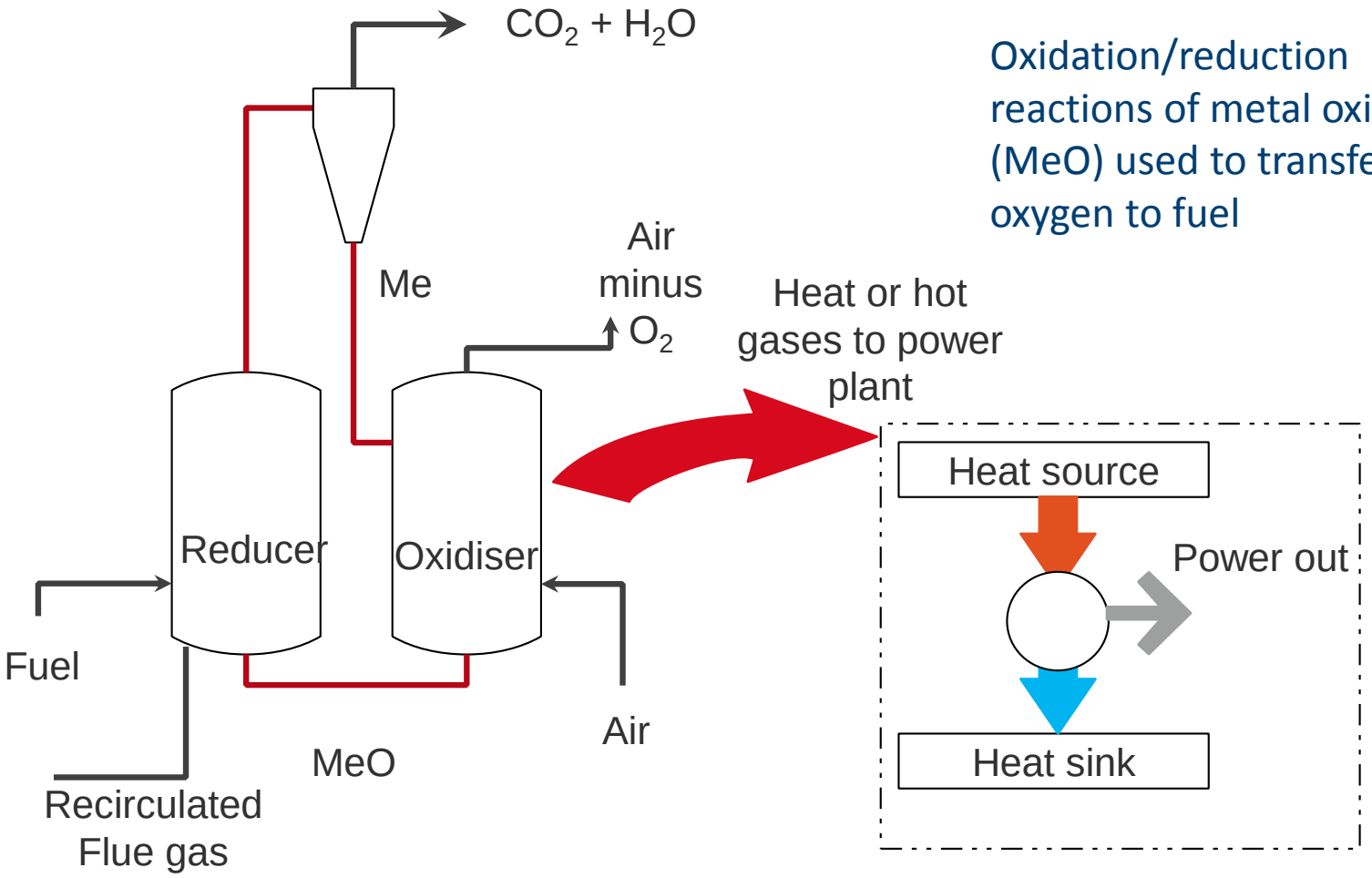
Chemical looping combustion for power generation



$$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)}+H_2O_{(g)}$$

Chemical looping combustion for power generation



Oxidation/reduction reactions of metal oxide (MeO) used to transfer oxygen to fuel

Some history …..

- Until 1906 Oxygen was produced industrially using the Brin process [1]. Their company later become known as the British Oxygen Company and switched to liquefaction.

  $BaO + 0.5\ O_2 <-> BaO_2$

  [at around 700 °C with air pressure swinging between atm and 0.05 atm]

- Lewis and Gilliand (1954) Patented a method for producing CO_2 which is essentially chemical looping combustion

[1] W. B. Jensen, "The Origin of the Brin Process for the Manufacture of Oxygen," *J. Chem. Educ.*, vol. 86, no. 11, p. 1266, Nov. 2009.
[2] Lewis and Gilliland, " Production of Pure CO2", US2665972A

Oxygen transfer materials

The oxygen transfer reaction used for chemical looping is characterised by the equilibrium for

$$Me + \frac{1}{2}O_2 \rightarrow MeO$$

Or equivalently the equivalent equilibrium oxygen pressure

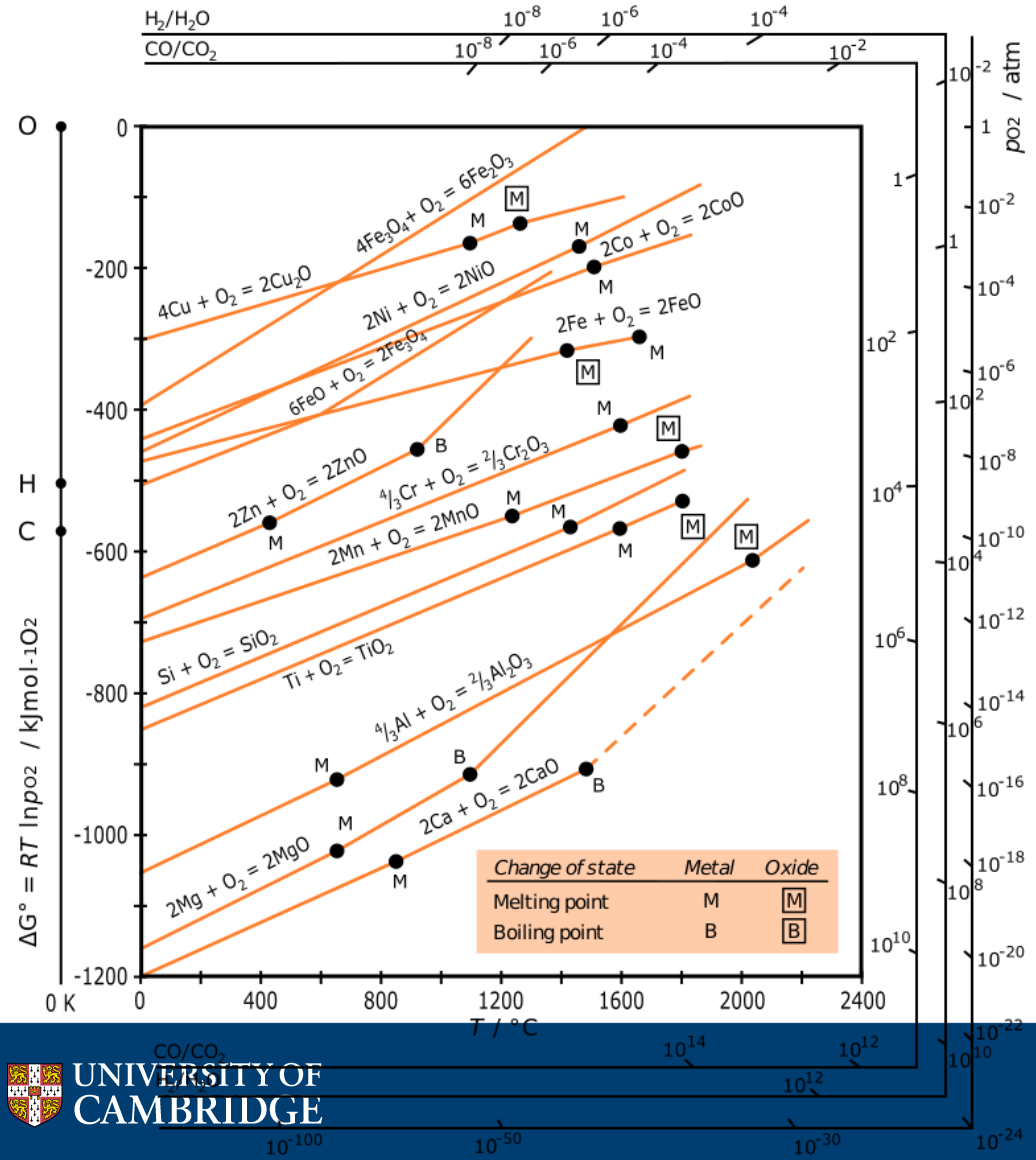
$$\left(P_{O_2}\right)^{-\frac{1}{2}} = e^{-\Delta G_{comb}/RT}$$

More the oxygen chemical potential

$2MeO \rightarrow O_2 + 2MeO$

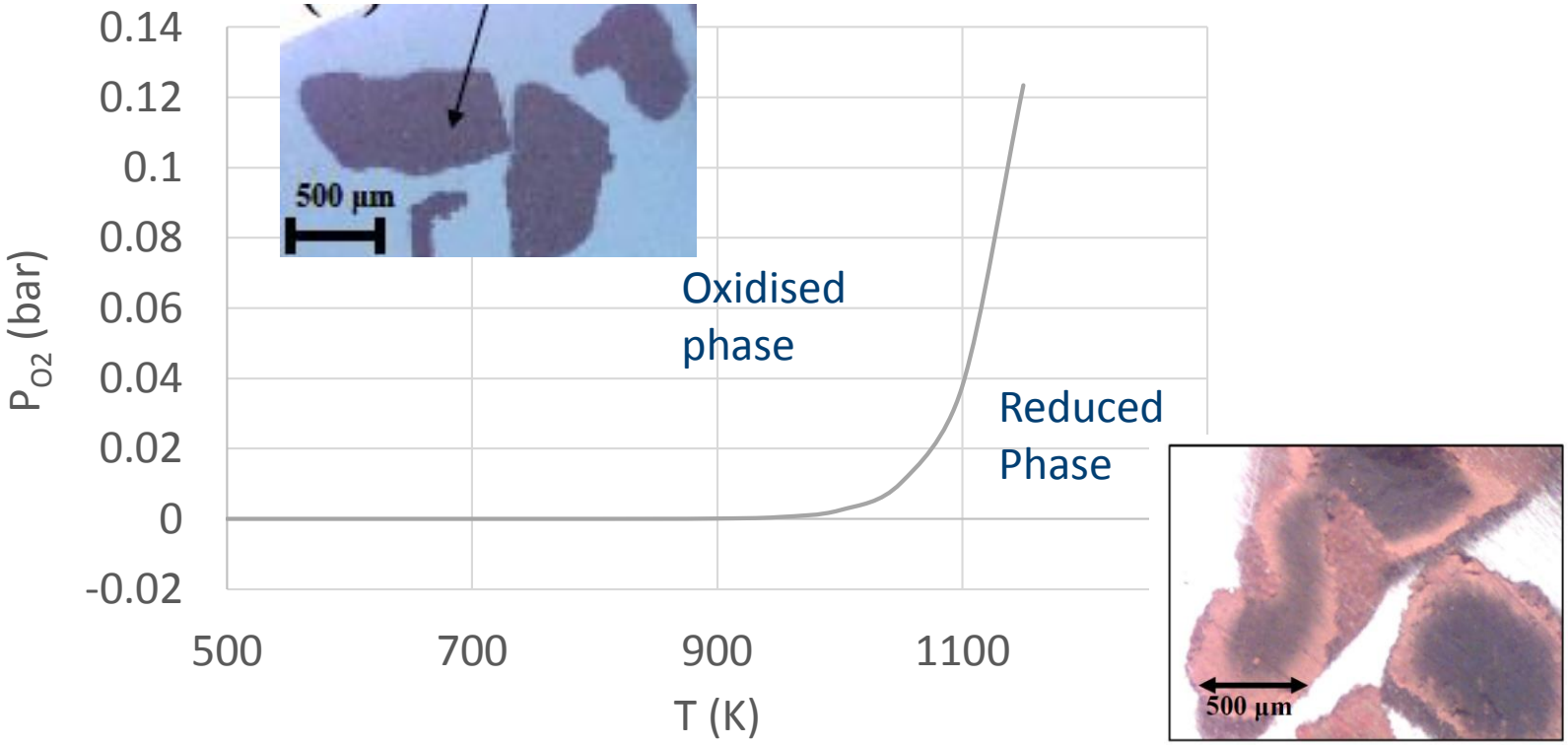
ΔG_{comb}: $\ln(PO_2) = -\Delta G_{comb}/RT$

Novel?



Source: https://en.wikipedia.org/wiki/Ellingham_diagram#/media/File:Ellingham_Richardson-

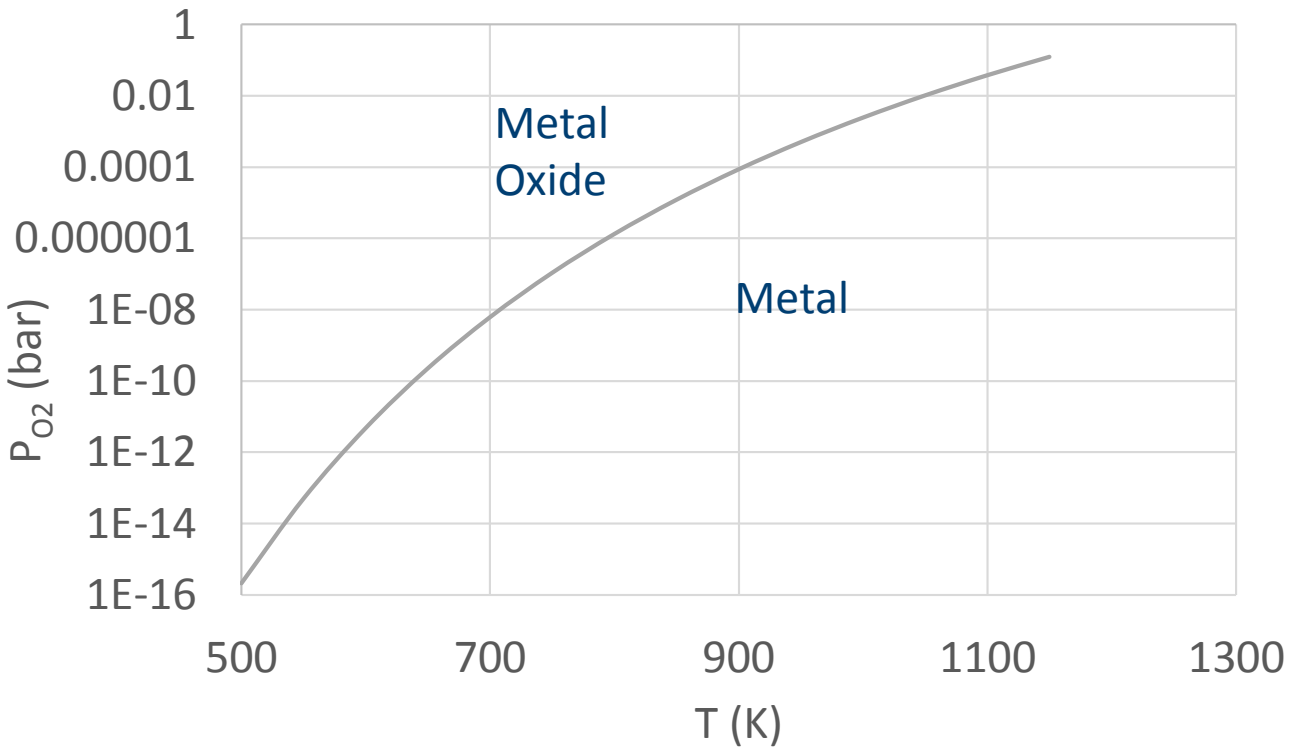
Oxygen transfer materials



$$Me + \frac{1}{2}O_2 \rightarrow MeO \qquad e.g.\ CuO \rightarrow Cu_2O + ½\ O_2$$

Images: Chuang , PhD thesis Cambridge

Oxygen transfer materials



$$Me + \frac{1}{2}O_2 \rightarrow MeO$$

More the oxygen chemical potential

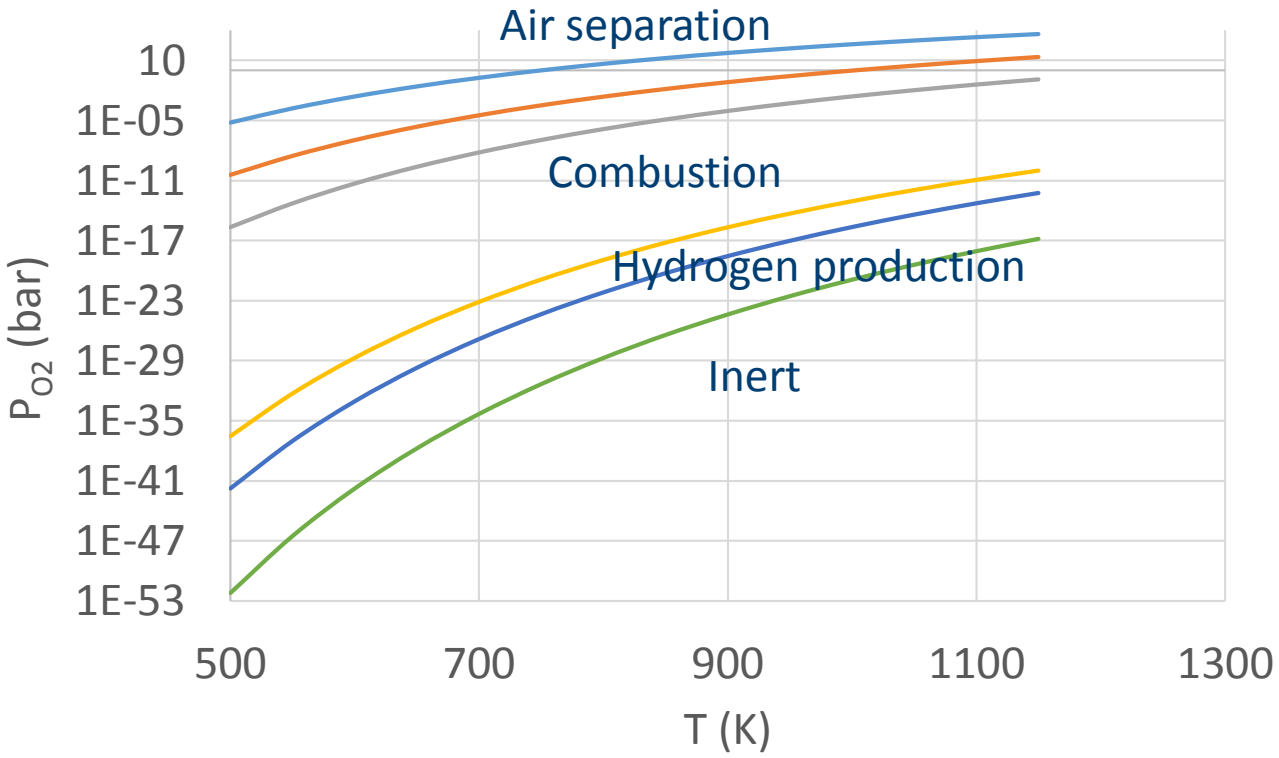
$2MeO \rightarrow O_2 + 2MeO$ $\quad\quad$ ΔG_{comb}: $\ln(PO_2) = -\Delta G_{comb}/RT$

$MeO + H_2 \rightarrow Me + H_2O$ $\quad\quad$ $\ln\left(\frac{P_{H2}}{P_{H2O}}\right) = Fn\,(\Delta G_{comb})$

$MeO + CO \rightarrow Me + CO_2$ $\quad\quad$ $\ln\left(\frac{P_{CO}}{P_{CO2}}\right) = Fn\,(\Delta G_{comb})$

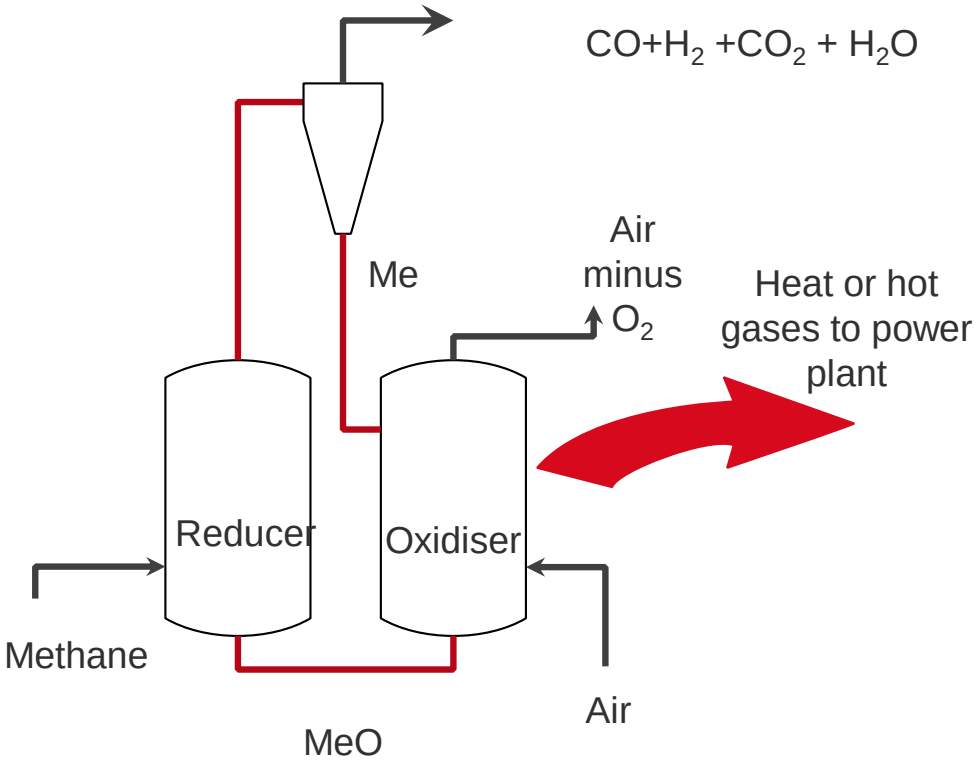
Materials that are reluctant to release oxygen and fully combust a fuel have hydrogen combustion reactions that can be easily reversed.

Oxygen transfer materials



Reforming or hydrogen

Reforming can be achieved by restricting the amount of oxygen supplied to the fuel.



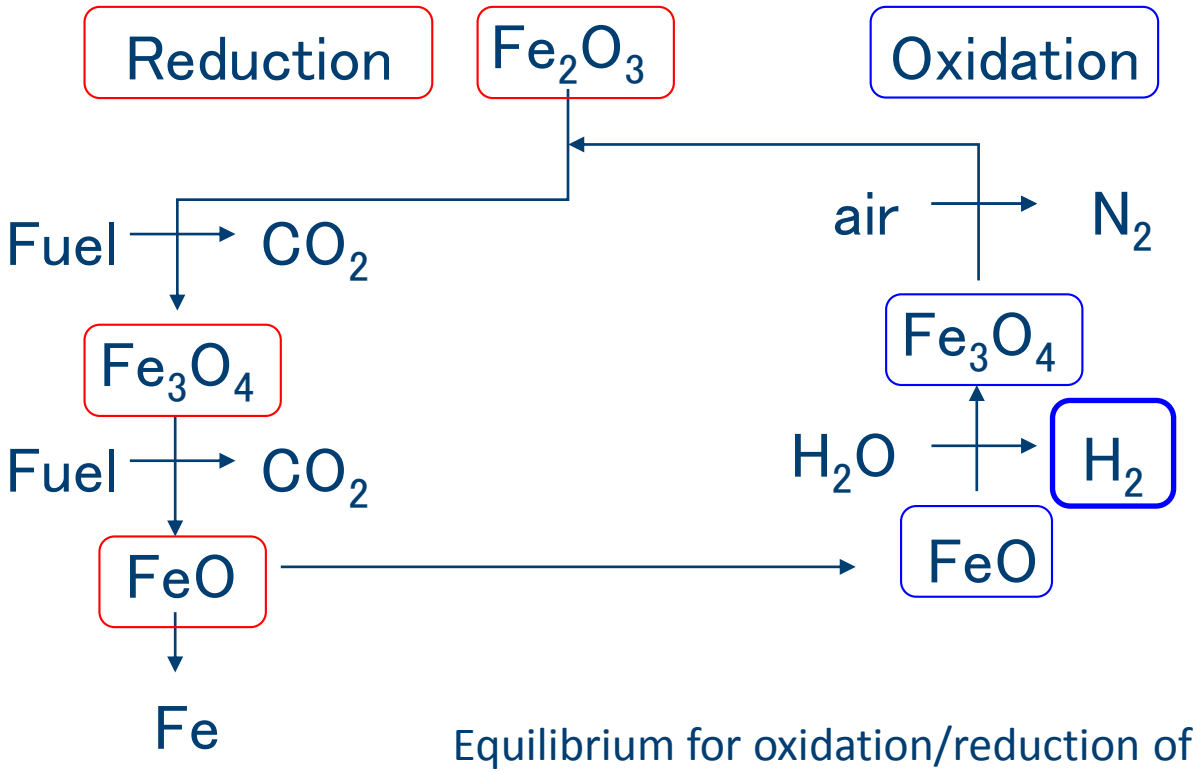
Demonstrated with NiO

Reforming using iron oxides

Nickel is expensive and toxic.

Iron oxide is a popular choice as it is cheap and not toxic, but often quite un-reactive towards methane, unless the temperature is very high. Iron oxide has phase transitions which can restrict the oxygen chemical potential.

Chemical looping/reforming for hydrogen



Equilibrium for oxidation/reduction of FeO and Fe is ideal for hydrogen production – but not suitable for complete combustion

Some history …..

Hydrogen was produced commercially using iron oxide as the oxygen transfer material (e.g. the Lane process, 1903 [1], and the Messerschmitt process). Lane introduced a cyclic processes

$$Fe_3O_4 + syngas \rightarrow Fe$$

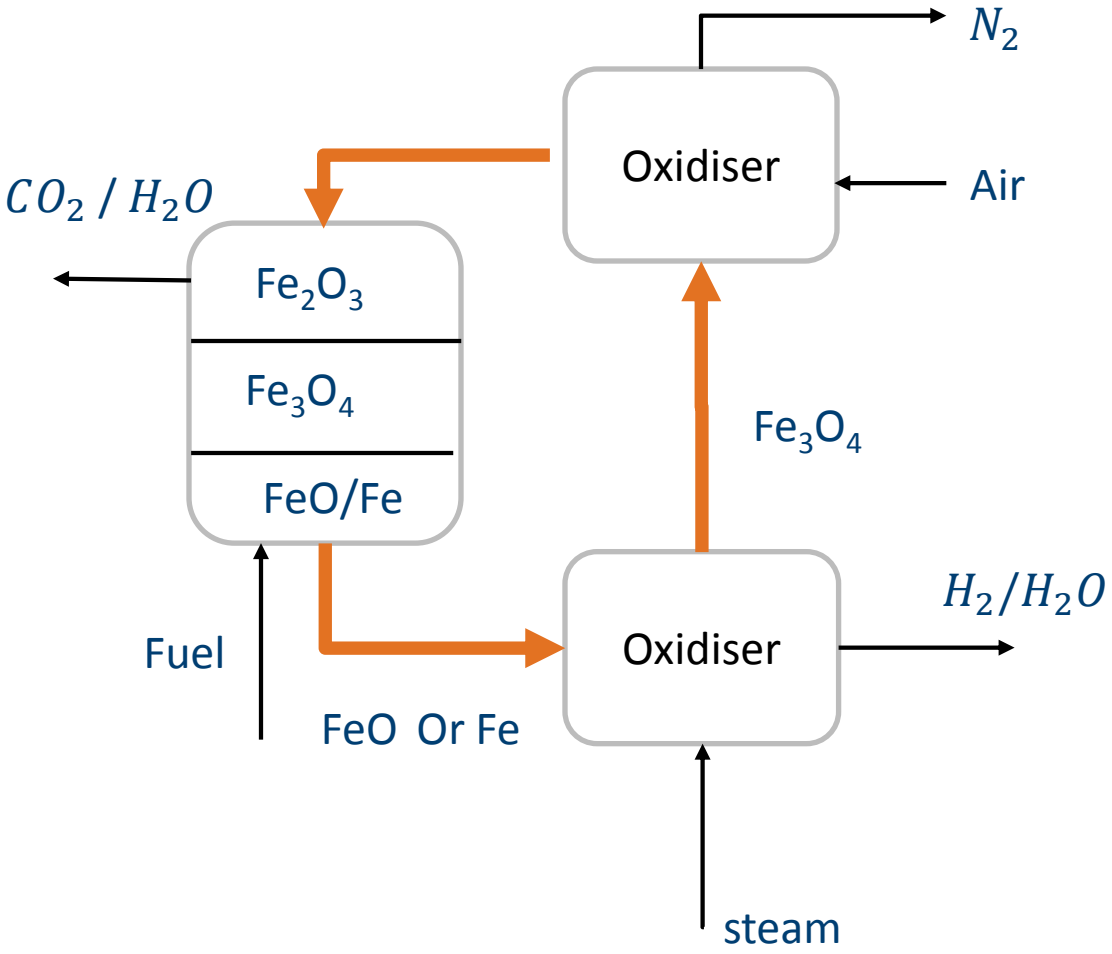
$$Fe + H_2O \rightarrow Fe_3O_4 + H_2.$$

The use of a interlinked fluidised beds patented in 1953 [2].

Lots of work which predated the current interest in chemical looping made use of the sponge-iron reactions to perform water gas shift and fuel reforming, see the review of Voitic and Hacker [3].

[1] H. Lane, 'The Lane Hydrogen Producer', *Flight*, p. 524, 1909.
[2] .Reed and C. Berg, 'Hydrogen process', US2635947A, 1953
[3] Voitic and Hacke,r 'Recent advancements in chemical looping water splitting for the production of hydrogen',

Reforming or hydrogen



Ohio state system – they developed a moving bed allowing fronts to form in the bed, maximising conversion of the fuel.

Demonstrated continuous operation at 25 kWth scale with coal (Bayham et al., 2013)

Bayham et al (2013). Energy Fuels 27, 1347–1356. doi:10.1021/ef400010s

Mixed oxides

Mixed oxides allow the phase transitions to be altered, and in some cases particular structures to be formed.

$NiFeO_2$, Cobalt Ferrite – mixed oxides with the higher PO_2 materials tend to form oxides with transitions with higher PO_2 and thus less suitable for H_2, but better for combustion. E.g. Svoboda et al (2008)

Other interesting ferrites, include Ba, Sr and Calcium (these tend to push the equilibrium the other way), e.g. Siriwardane et al (2016)

Murugan et al. found $La_{0.7}Sr_{0.3}FeO_3$ and $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{.8}O_3$ had excellent cyclic stability for oxidation and reduction for hydrogen production, but a low capacity

Siriwardane et al. Applied Energy,2016,https://doi.org/10.1016/j.apenergy.2015.12.085.
Svoboda et al. (2008) Energy Conversion and Management,.49 221–231
Murugan et al. (2011) Energy Environ. Sci.,4, 4639-4649

Conclusions

- The use of thermochemical cycles for water splitting is not a new idea
- High temperature cycles might give higher efficiencies IF they can be heat integrated.
- Development of materials able to withstand the cycles is a challenge
- The process can appear to be quite simple and offers a way of doing the separation and reaction together in the same system.
- These are not proven technologies at the large scale.