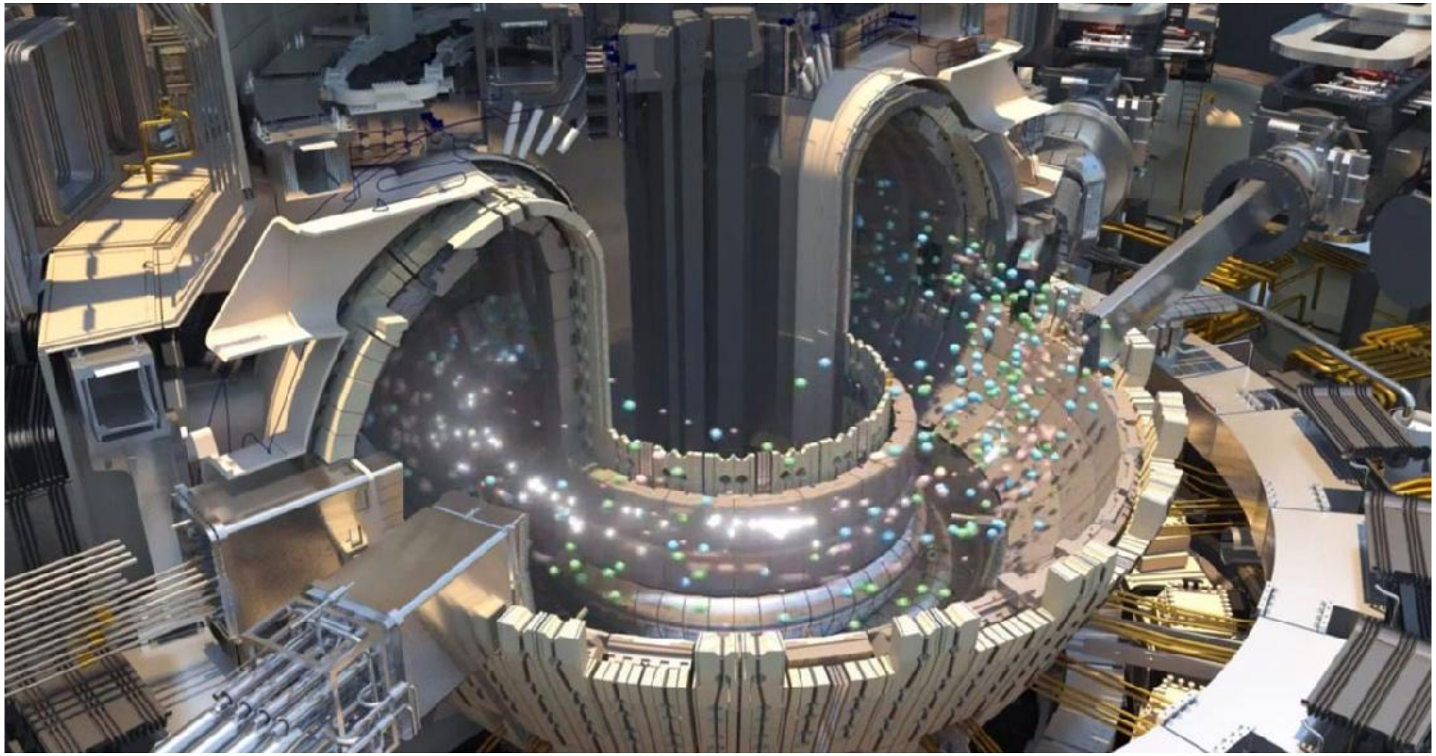
Zirconates: New Sustainable Uses and Applications

Dr. Roberto C. Dante



ZIRCON INDUSTRY ASSOCIATION

ZIA Annual Conference – 13-14 September 2022, KL, Malaysia

2Dto3D

Outline

1. Nuclear fusion
2. Selective membranes of CO_2 at high temperature
3. Li-ion batteries
4. Conclusions

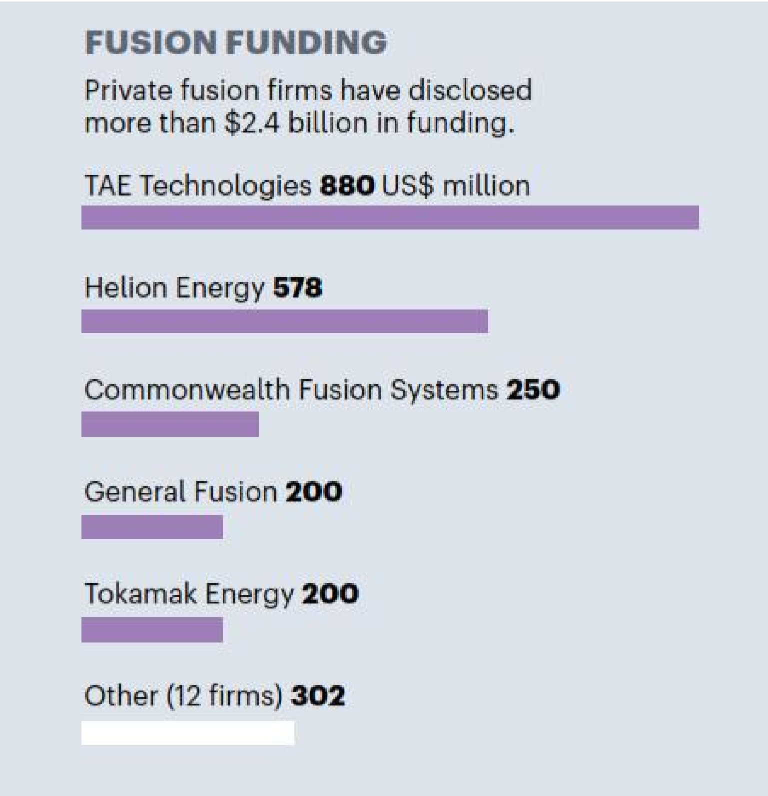
1.Nuclear Fusion

- **Nature’s preferred source.**
- Fusion is the same process that powers the sun and stars. It is environmentally friendly, safe, and capable of sustaining the planet for thousands of years.

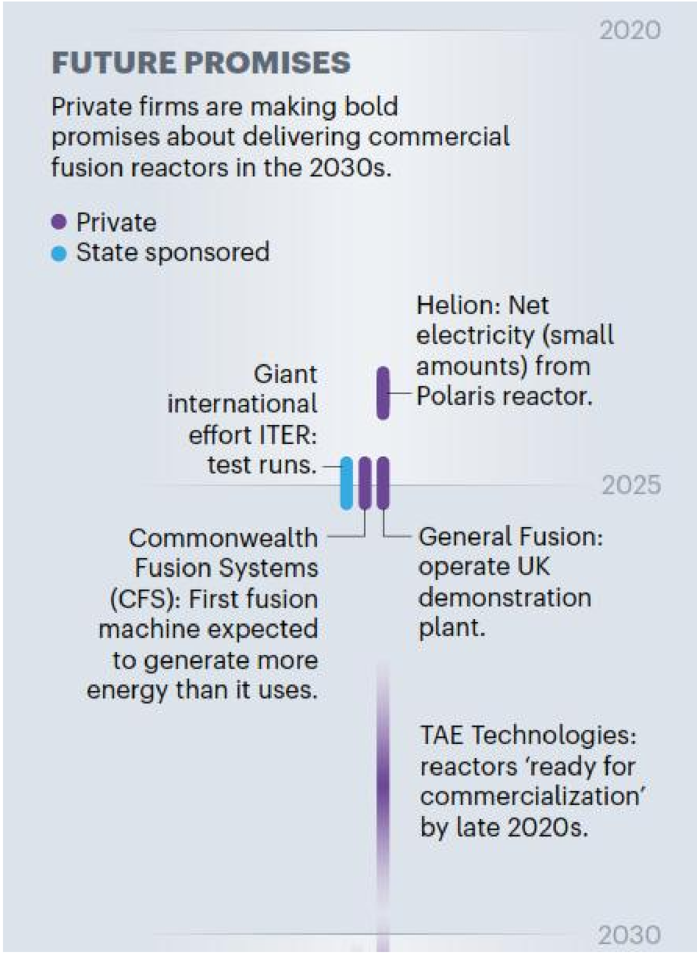
1.2.Fusion funding

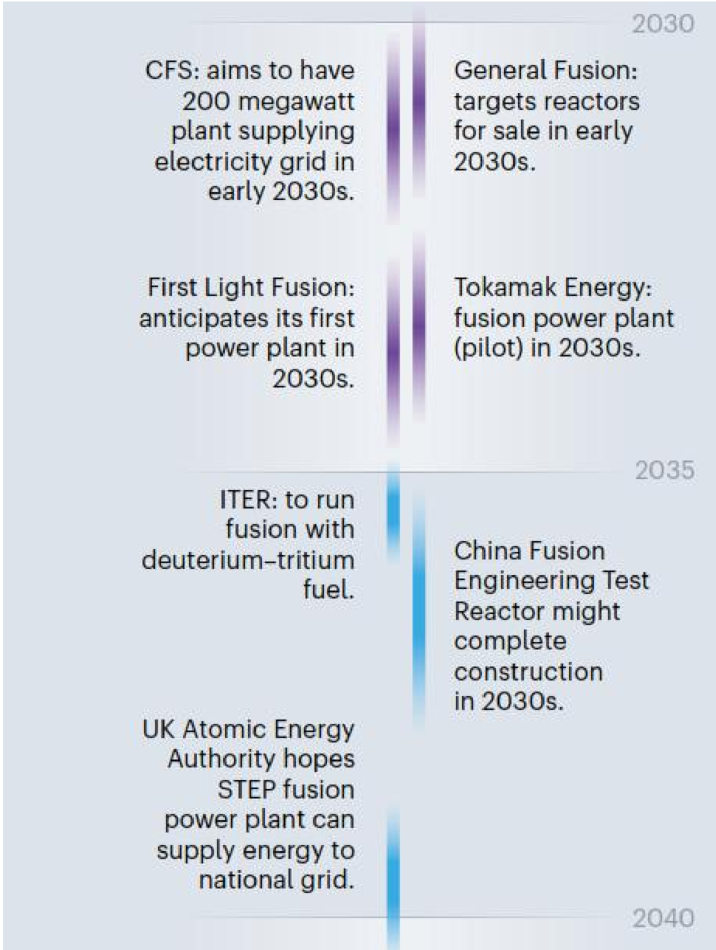
- Classic State-funded approach
- Private firms

1.3.Private fusion firms

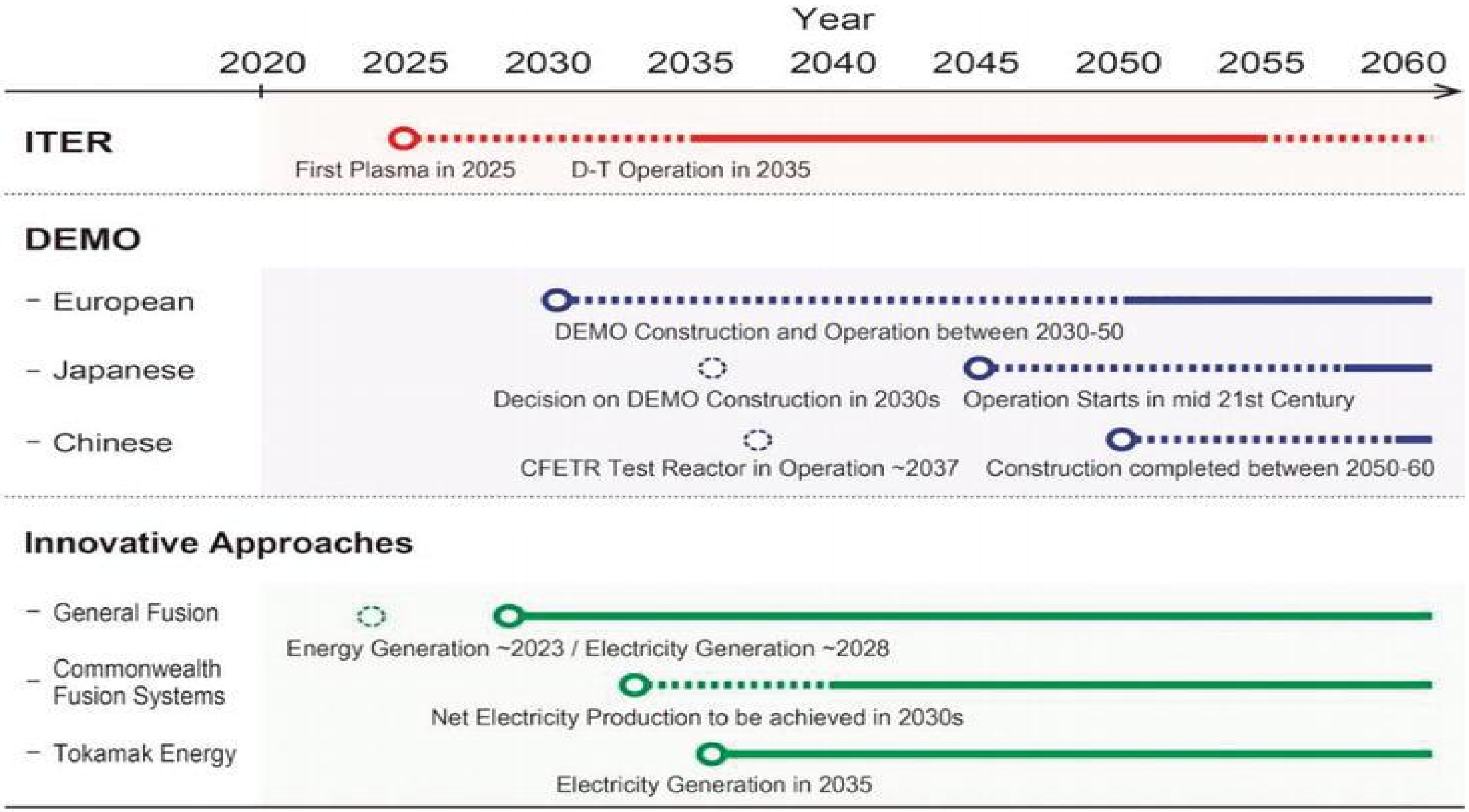


Philip Ball, Nature, Vol 599, 18 November 2021, 362-366

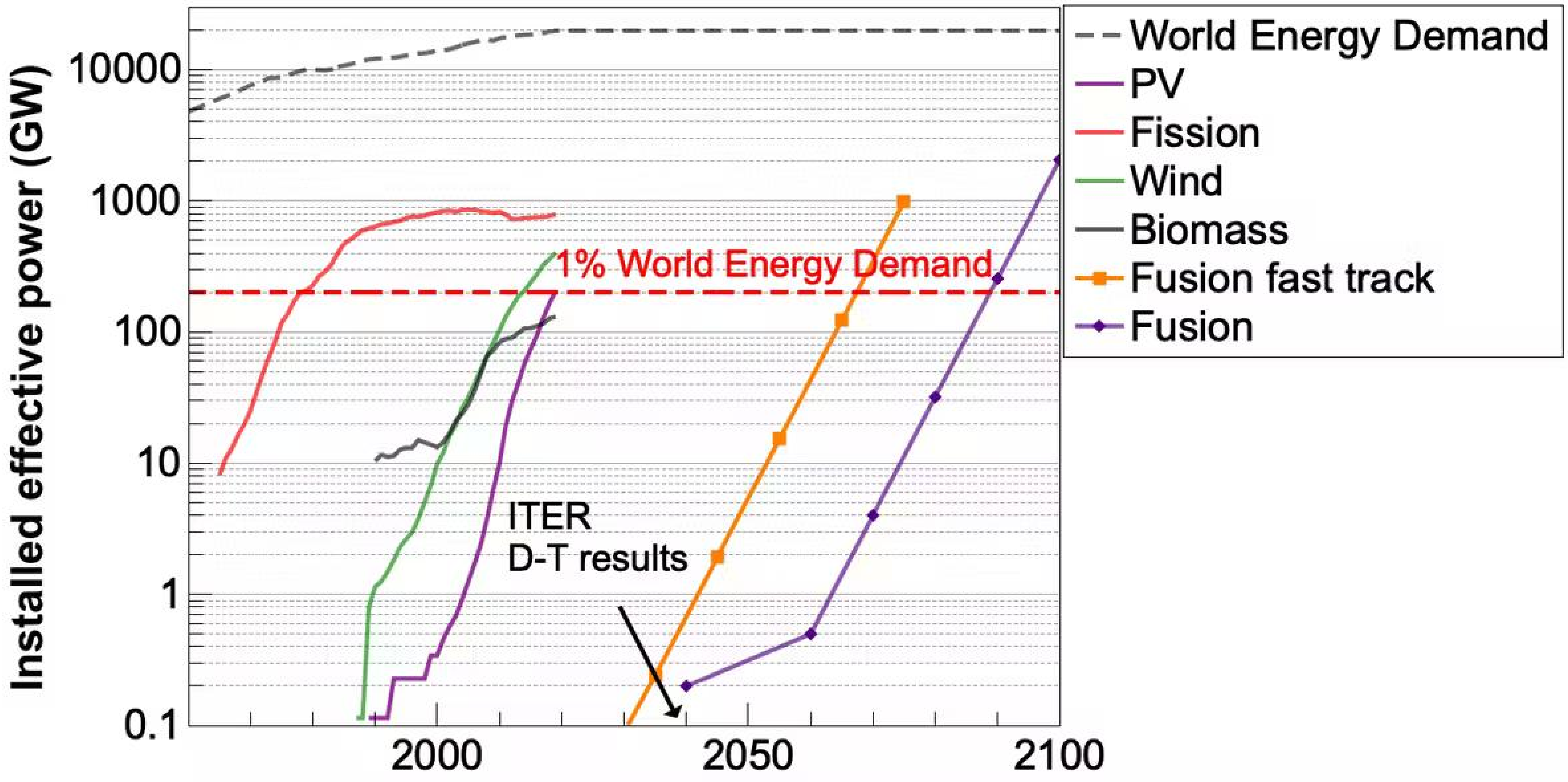




1.4.Projects' advancement



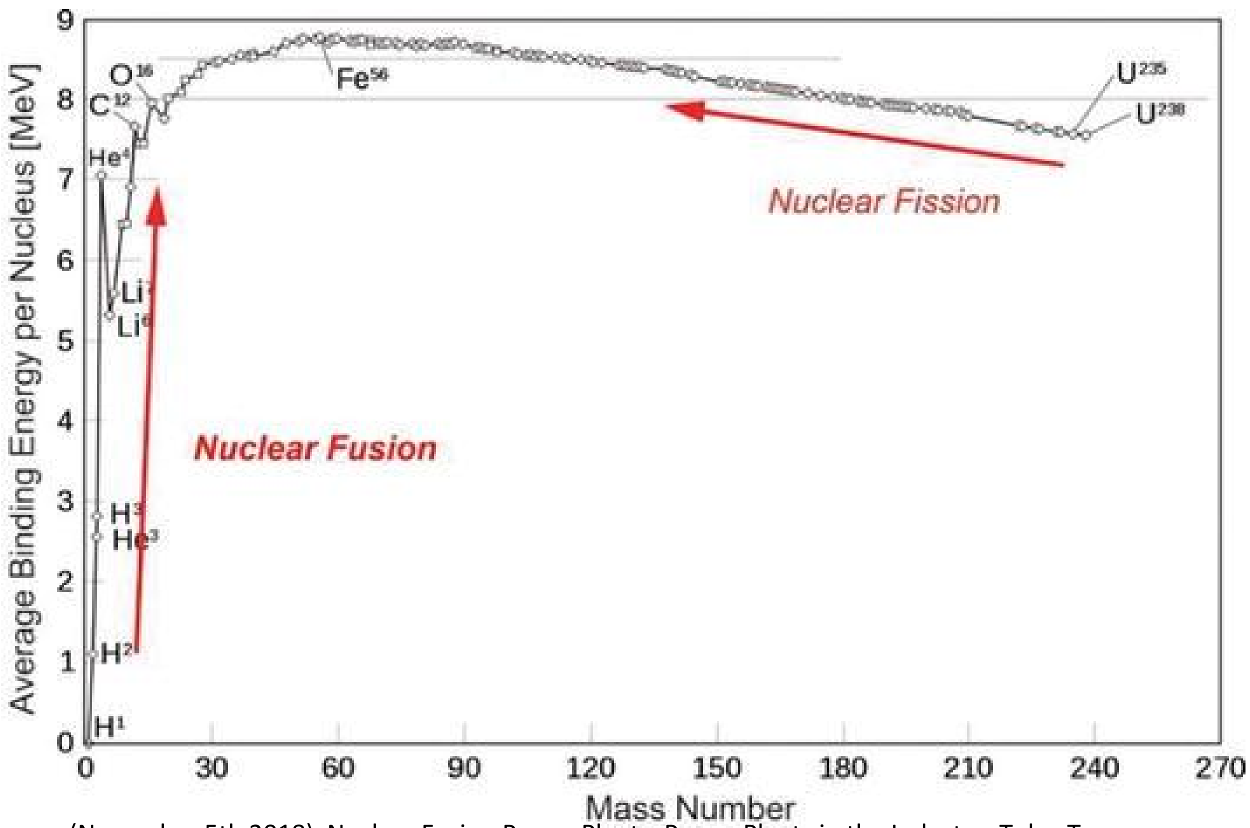
1.5.Expected outputs



1.6.Two types of nuclear fusion

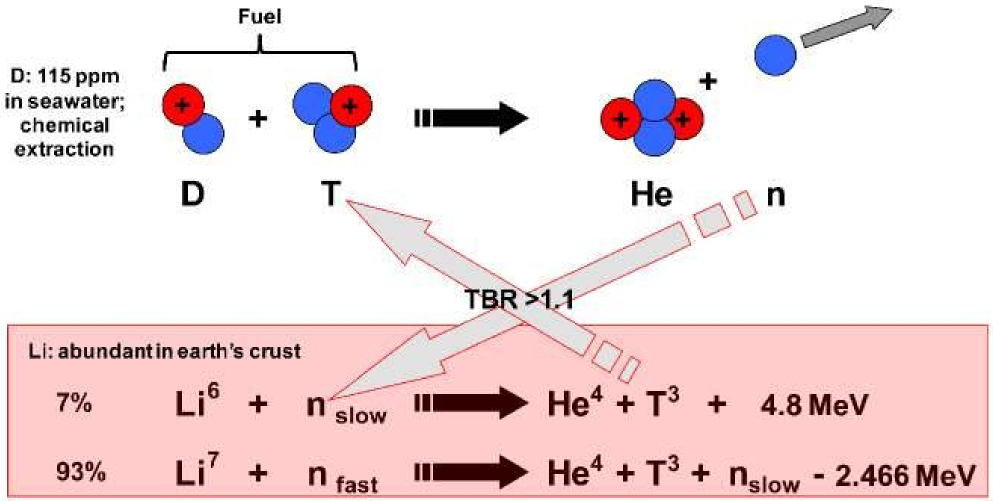
- Neutronic fusion
- Aneutronic fusion

1.7.Element can be not only hydrogen



Shutaro Takeda and Richard Pearson (November 5th 2018). Nuclear Fusion Power Plants, Power Plants in the Industry, Tolga Taner, IntechOpen, DOI: 10.5772/intechopen.80241. Available from: https://www.intechopen.com/books/power-plants-in-the-industry/nuclear-fusion-power-plants

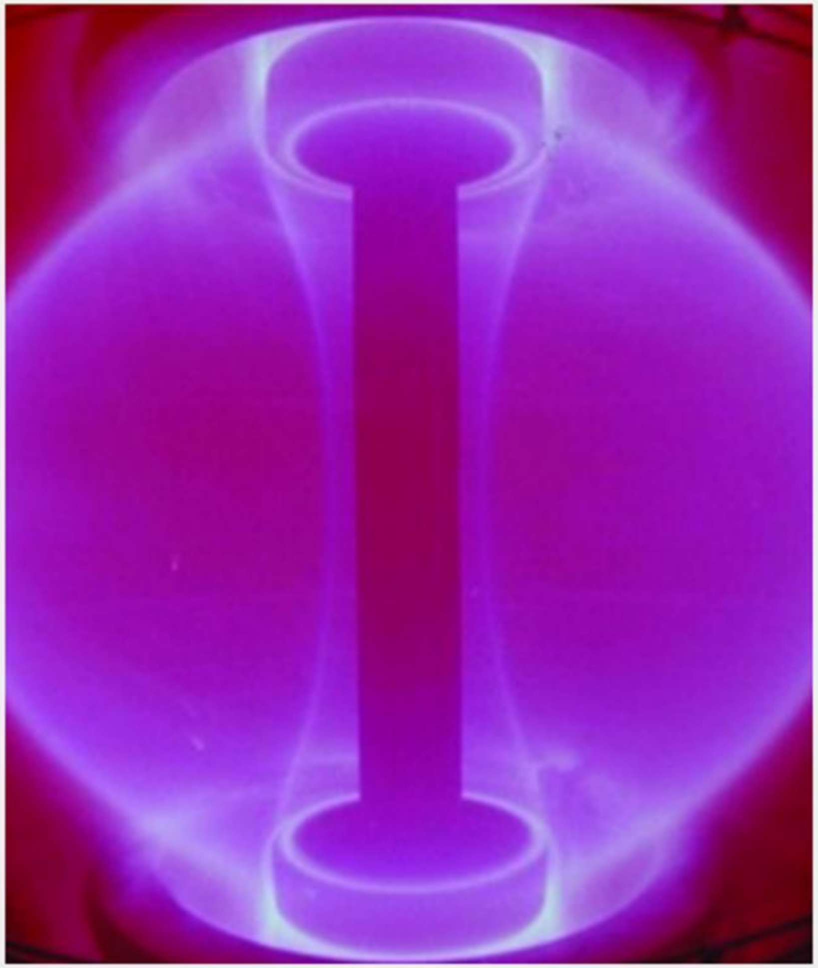
1.8.Neutronic Fusion



NET REACTION

$$_1D^2 + _3Li^6 \rightarrow 2\ _2He^4$$

1.8. Neutronic Fusion
Tokamak Energy



Spherical tokamaks

Scientists first realised the potential of tokamaks to achieve fusion conditions back in the 1960s when the Russian tokamak T3 reached much higher plasma temperatures than any other fusion machine at the time.

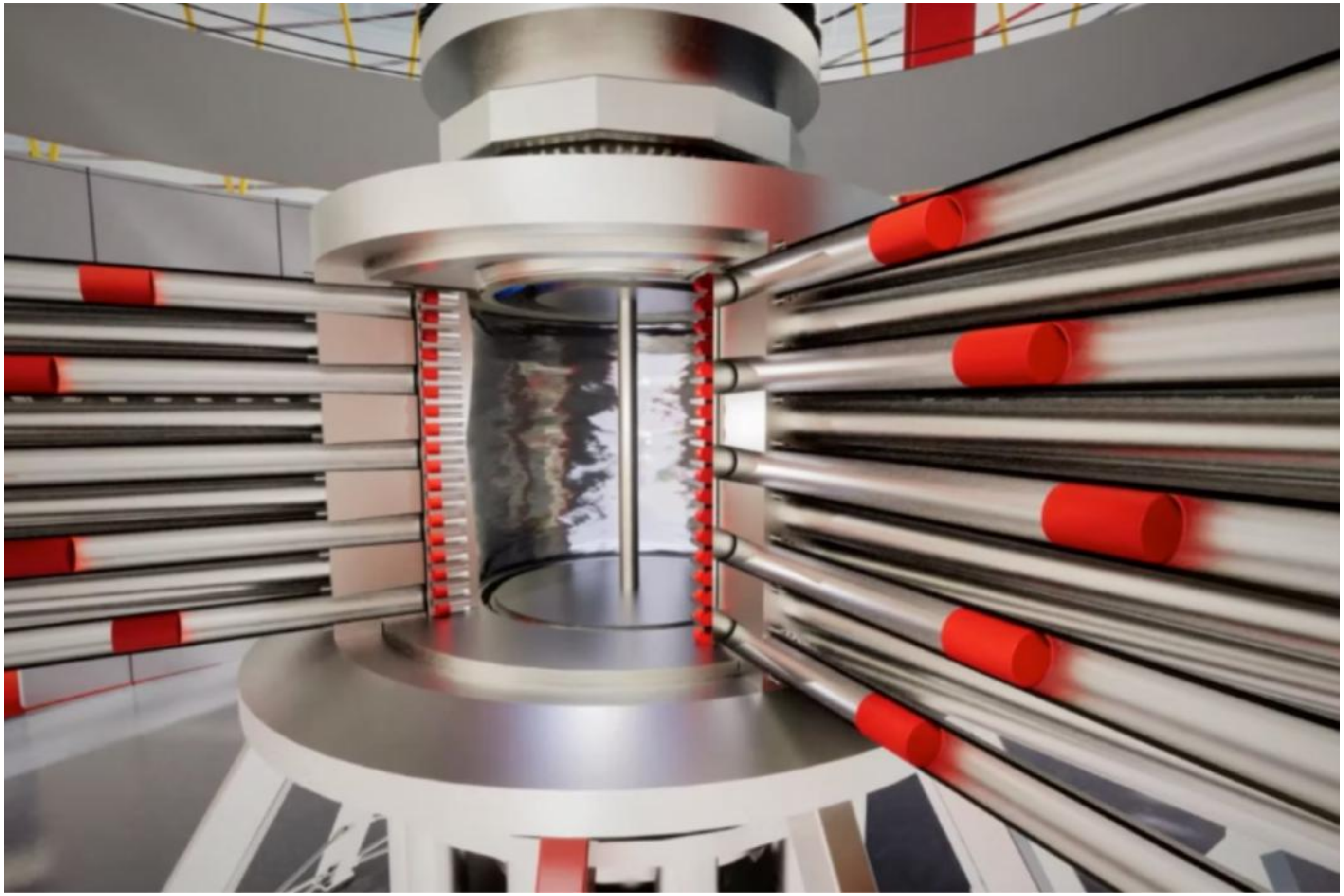
In the 1980s, one of our founders, Alan Sykes, who was working at the Culham Centre for Fusion Energy, did a theoretical study that revealed modifying the shape of the tokamak would have an impact on performance.

By moving from a doughnut-shaped plasma ring to an apple-shaped plasma ring, the plasma is contained more efficiently. Alan found that it is possible to achieve a much higher plasma pressure for a given magnetic field. Experimental studies in the 1980s by teams led by Alan and Mikhail Gryaznevich on first START (shown) and then MAST tokamaks verified this result.

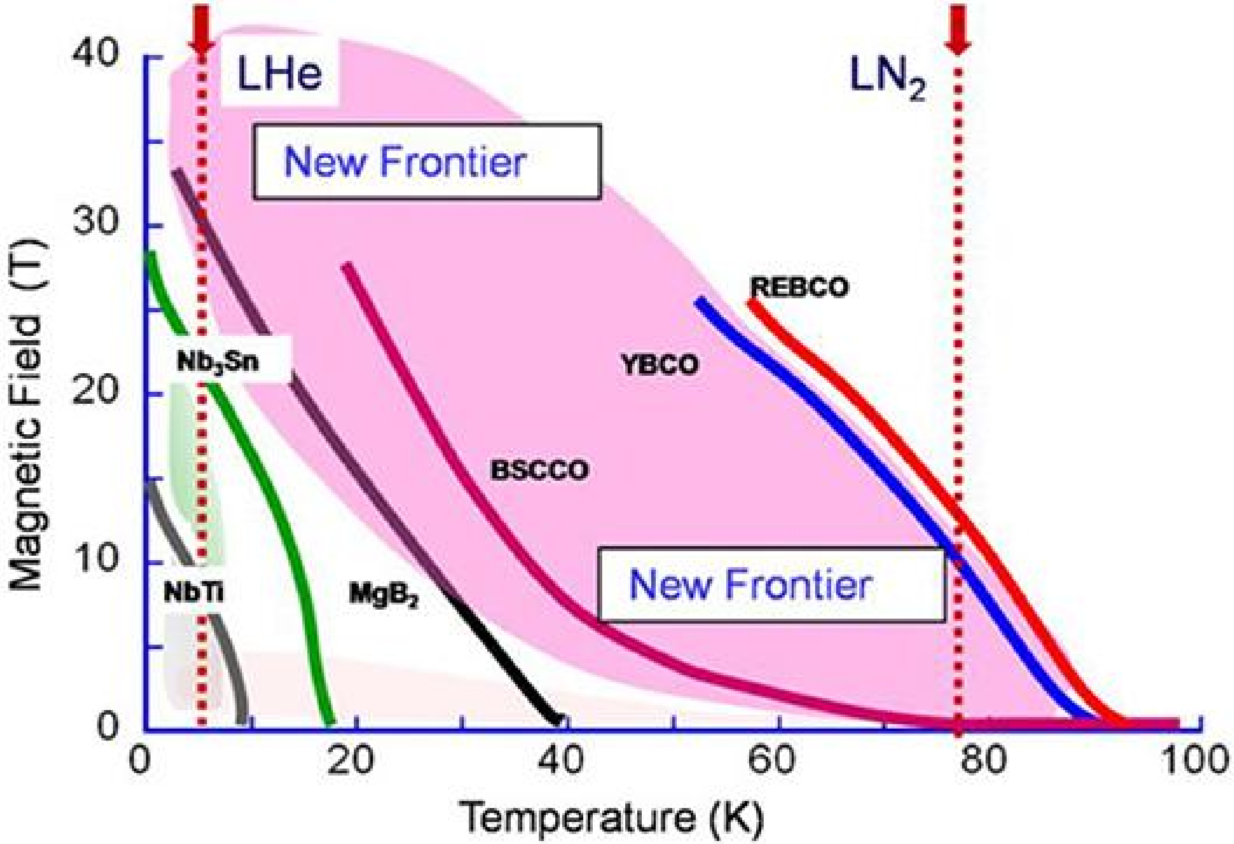
Combining the increased efficiency of the spherical tokamak with the improved magnetic confinement made possible by HTS magnet technology, is the most viable route to cost-effective, commercial fusion power in smaller machines.

1.8 Neutronic Fusion

Firm: General Fusion



1.8. Neutronic Fusion
REBCO superconductors



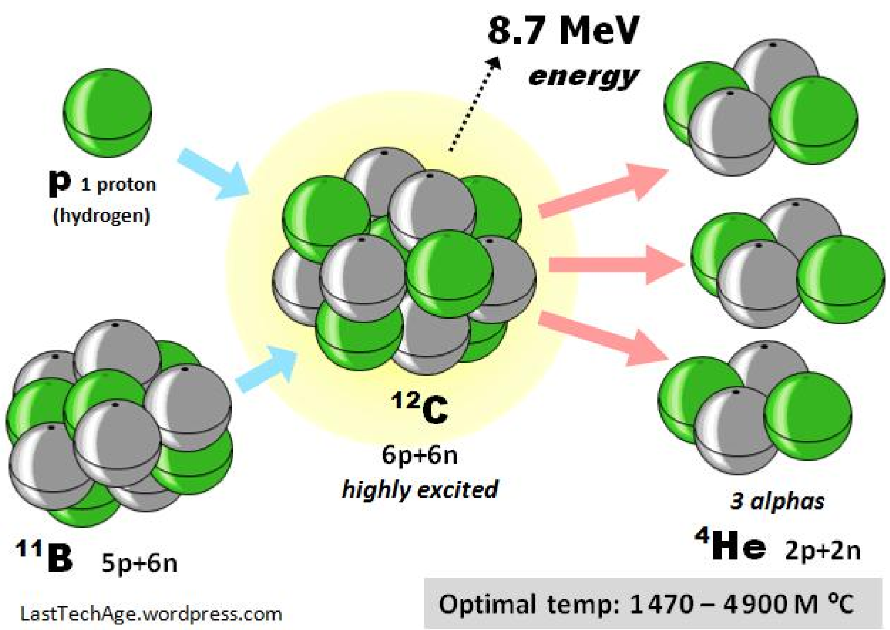
Variation of irreversibility field with temperature for different superconductors including HTS, MgB_2, metallic compounds, and alloys. The coated conductor technology including APC methodology has opened new frontiers of superconductivity applications in the temperature of range 5–77 K.

A.K. Jha & K. Matsumoto
Front. Phys., 21 June 2019
Sec. Physical Chemistry and Chemical Physics
https://doi.org/10.3389/fphy.2019.00082

1.9 Aneutronic fusion

Isotopes	Reaction
Deuterium - ^{3}He	$^2D + {}^3He \rightarrow {}^4He + {}^1p + 18.3$ MeV
Deuterium - ^{6}lithium	$^2D + {}^6Li \rightarrow 2\,{}^4He + 22.4$ MeV
Proton - ^{6}lithium	$^1p + {}^6Li \rightarrow {}^4He + {}^3He + 4.0$ MeV
^{3}He – ^{6}lithium	$^3He + {}^6Li \rightarrow 2\,{}^4He + {}^1p + 16.9$ MeV
^{3}He - ^{3}He	$^3He + {}^3He \rightarrow {}^4He + 2\,{}^1p + 12.86$ MeV
Proton – Lithium-7	$^1p + {}^7Li \rightarrow 2\,{}^4He + 17.2$ MeV
Proton – Boron-11	$^1p + {}^{11}B \rightarrow 3\,{}^4He + 8.7$ MeV
Proton – Nitrogen	$^1p + {}^{15}N \rightarrow {}^{12}C + {}^4He + 5.0$ MeV

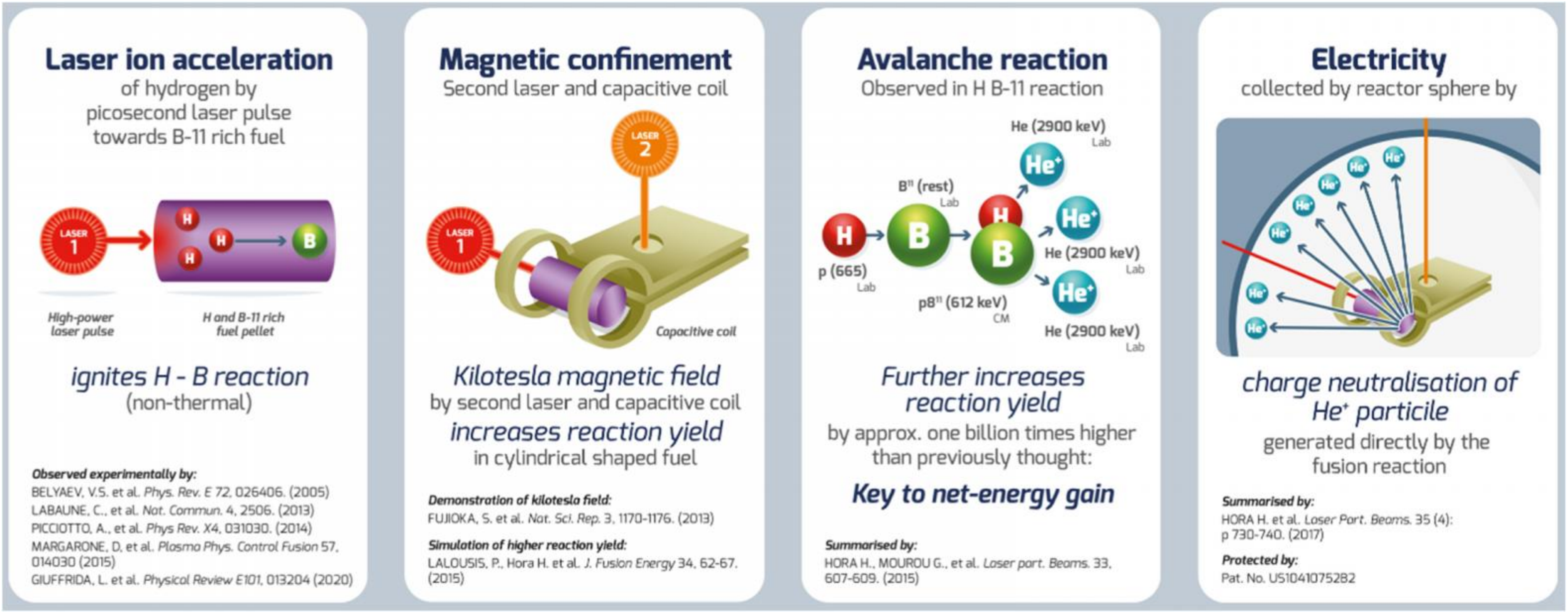
1.9. Aneutronic fusion



https://youtu.be/EVlWUQ-UKa4?list=TLGGRqoSMsdmCxsyNjA3MjAyMg

[The New Fusion Race - Part 2 - Aneutronic Fusion - YouTube]()

1.9. Aneutronic Fusion
HB11

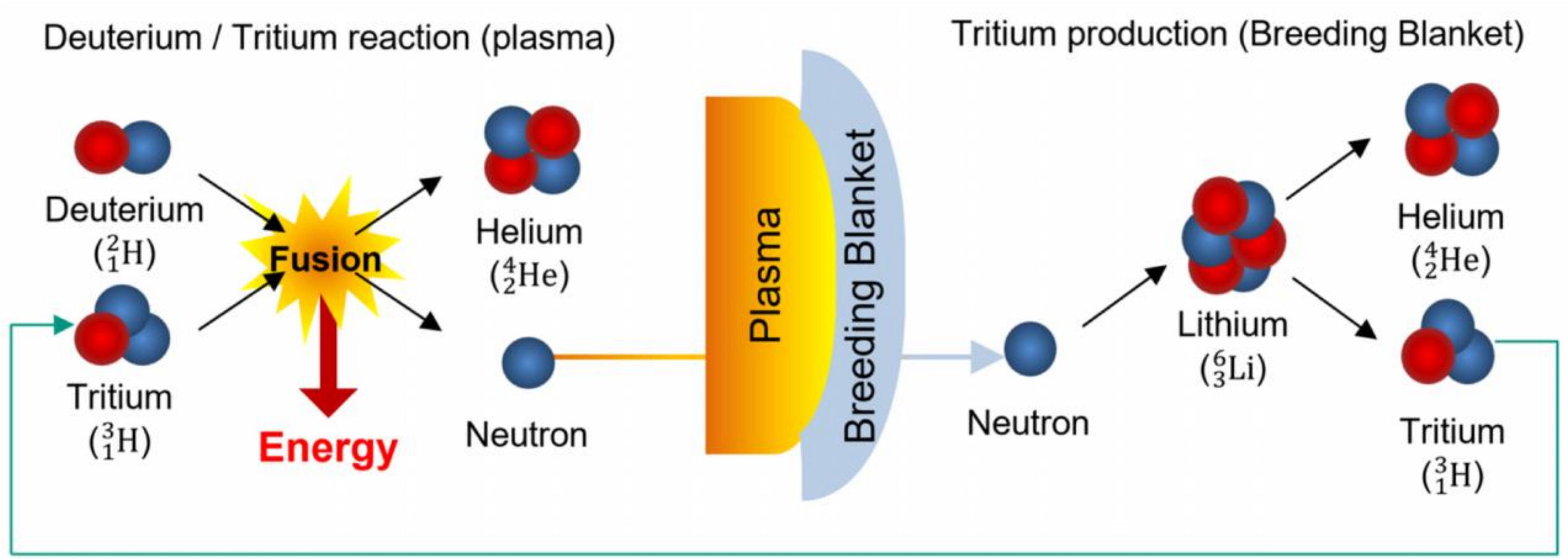


1.10.Resume on nuclear fusion

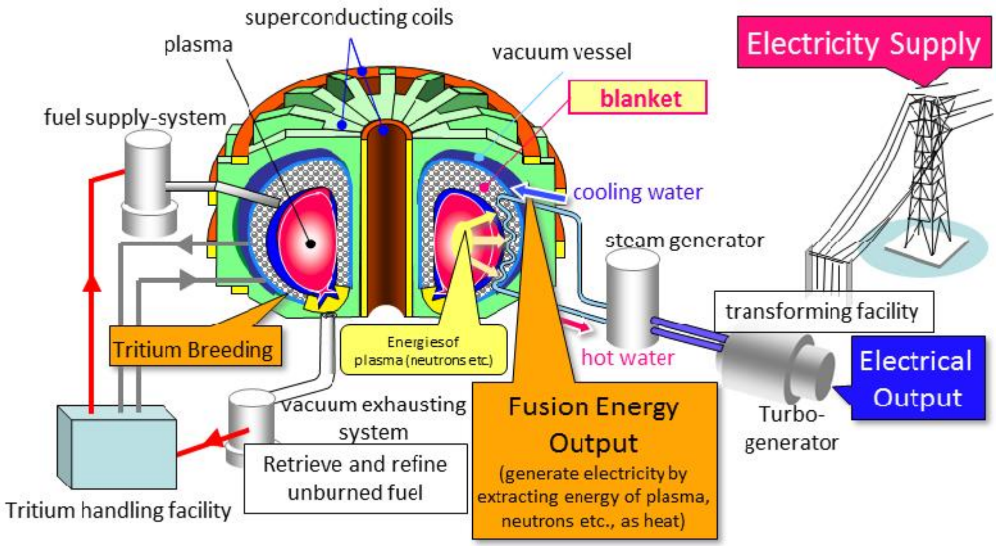
- Neutronic fusion: ${}_1D^2 + {}_1T^3 \rightarrow {}_2He^4 + n$
- Aneutronic fusion : ${}_1H^1 + {}_5B^{11} \rightarrow {}_6C^{12} \rightarrow 3\ {}_2He^4$

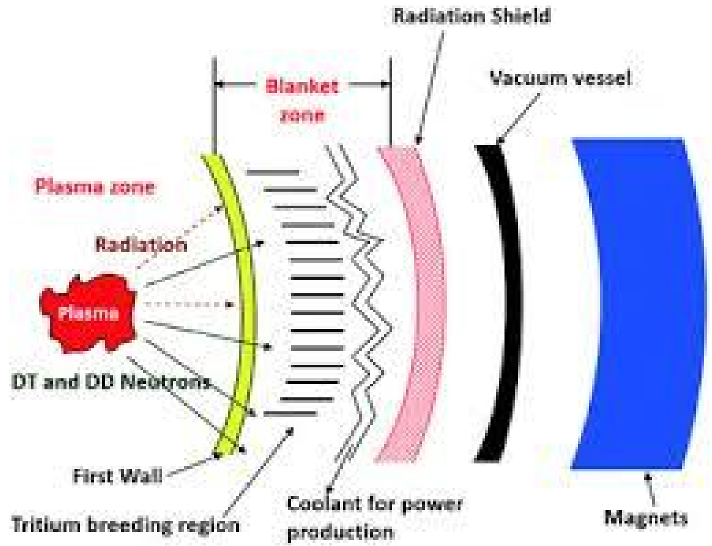
- Li stable breeders able to produce and release Tritium are wanted

1.11.Neutronic fusion breeder



1.11.Neutronic fusion breeders





1.11. Neutronic fusion breeders

- Each D-T fusion event releases 17.6 MeV (2.8×10^{-12} joule, compared with 200 MeV for a U-235 fission and 3-4 MeV for D-D fusion).
- On a mass basis, the D-T fusion reaction releases over four times as much energy as uranium fission.
- Deuterium occurs naturally in seawater (30 grams per cubic meter), which makes it very abundant relative to other energy resources.
- Tritium occurs naturally only in trace quantities (produced by cosmic rays) and is radioactive, with a half-life of around 12 years.
- Usable quantities can be made in a conventional nuclear reactor, or in the present context, bred in a fusion system from lithium.
- Lithium is found in large quantities (30 parts per million) in the Earth's crust and in weaker concentrations in the sea.

1.11. Neutronic fusion breeders

Comparison of characteristics of the four main breeder candidate ceramics

Characteristics	Ceramic $LiAlO_2$	Li_4SiO_4	Li_2ZrO_3	Li_2O
Melting point in °C	1610°	1250°	1615°	1430°
Li content (g cm^{-3})	0.27	0.54	0.38	0.93
Thermal conductivity at 600 °C 80% TD (W/m° K)	2.6	2	1.4	3.5
Fragmentation	low	very high	no	medium
Swelling (900 °C, 297 FPD)	< 0.5%	1.5%	< 0.7%	8%
Grain growth 100 FPD 700 °C	no	no	no	3.5 μm → 7 μm
900 °C	no	1 μm → 2 μm	no	3.5 μm → 17 μm
Tritium retention (297 FPD, 500 °C)	25%		2%	3.5%
Helium retention (297 FPD, 500 °C)	2.74%		2.34%	22.5% (700°)
Lithium mass transfer (900 °C)	no	0.16 at %	no	0.9 at %
Temperature corresponding to 1 day T_2 residence time	450° C	390° C	310° C	320* C
Grain size and origin	0.4 μ CEA	21 μ KfK	1 μ U.S.	16 μ JAERI

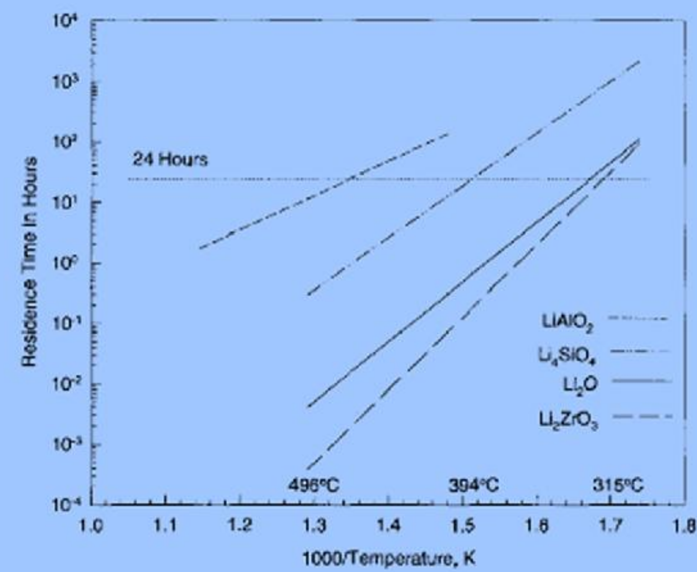
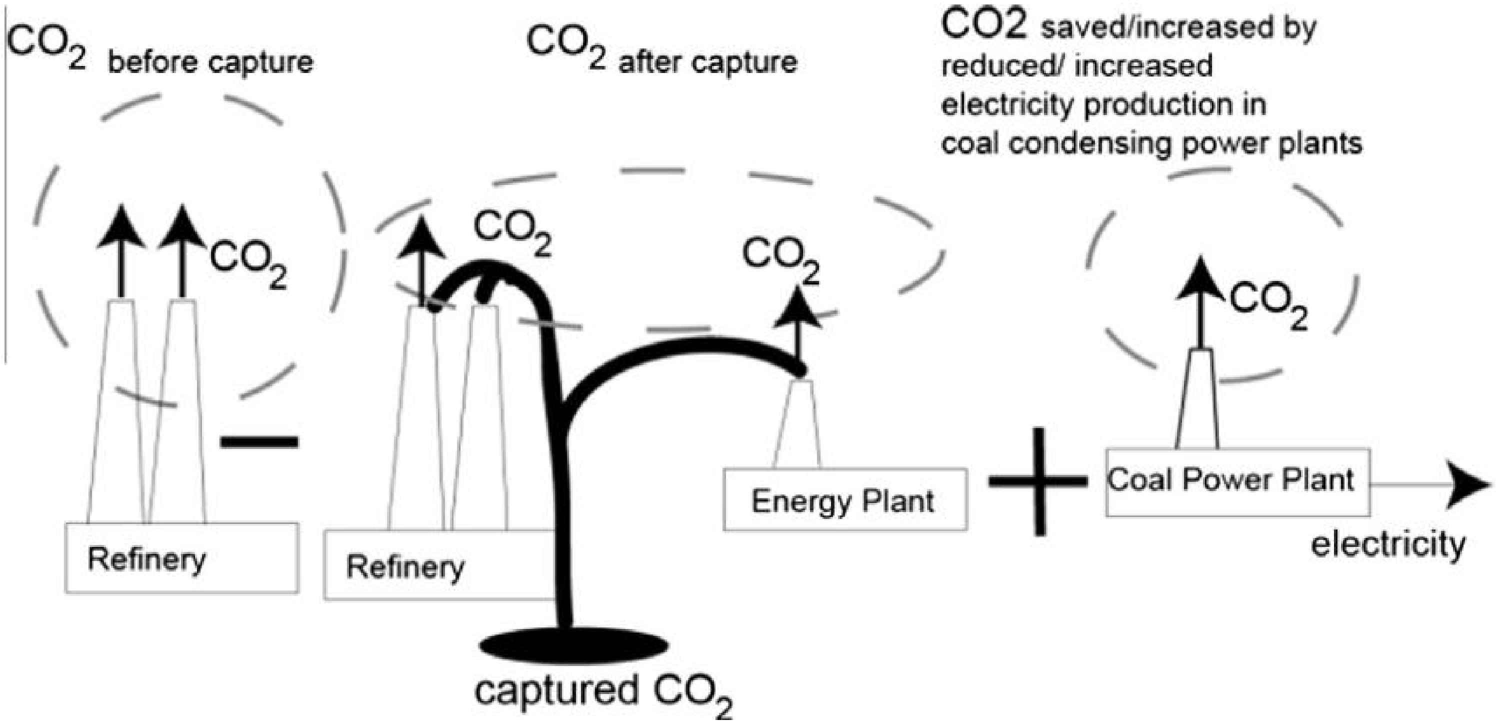


Fig. 1. Tritium residence times vs. reciprocal temperature for ceramics considered: $LiAlO_2$ with grain size 0.5 μm and 75% theoretic density; Li_2ZiO_3 with grain size 1 μm and 80% theoretic density; Li_2O with grain size 16 μm and 80% theoretic density; Li_4SiO_4 with grain size 23 μm and 90% theoretic density.

N. Roux a, G. Hollenberg b, C. Johnson c, K. Noda d, R. Verrall
Summary of experimental results for ceramic breeder materials,
Fusion Engineering and Design 27 (1995) 154-166

2.Selective membranes of CO_2 at high temperature

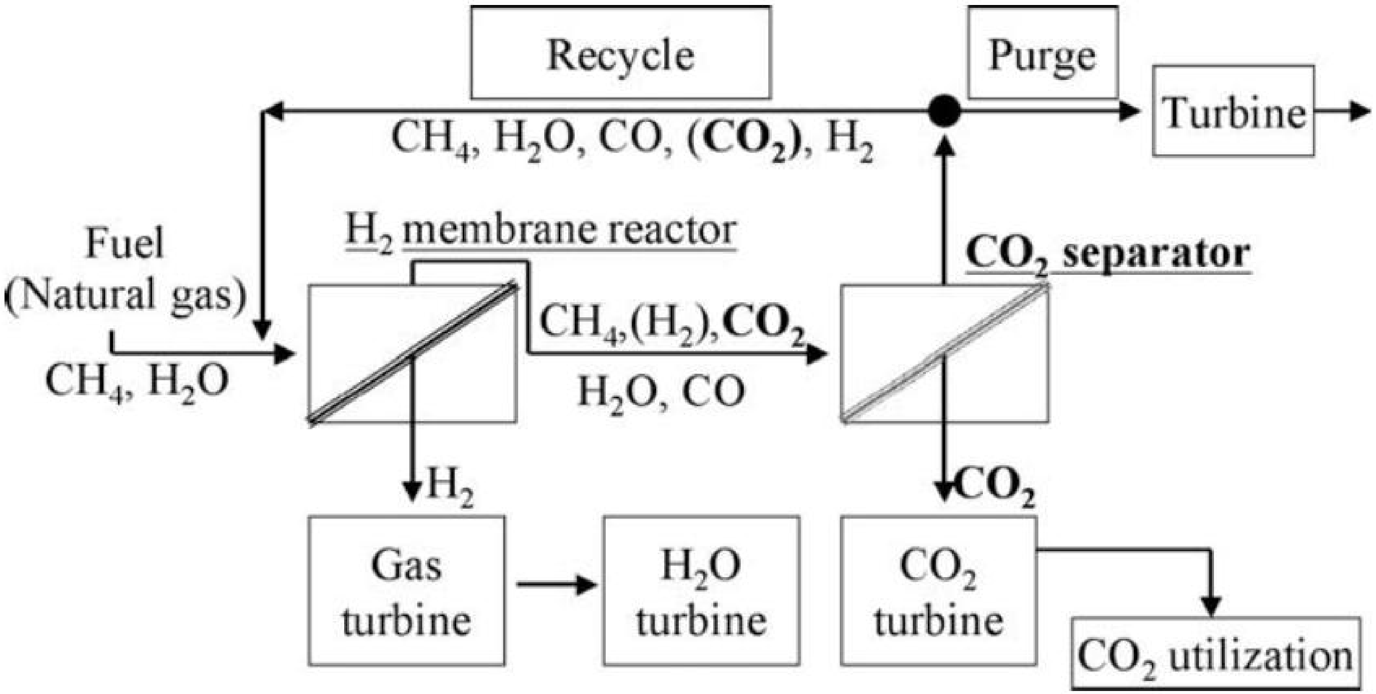
2.1.Refineries and reformers



D. Johansson et al. / Energy Conversion and Management 66 (2013) 127–142

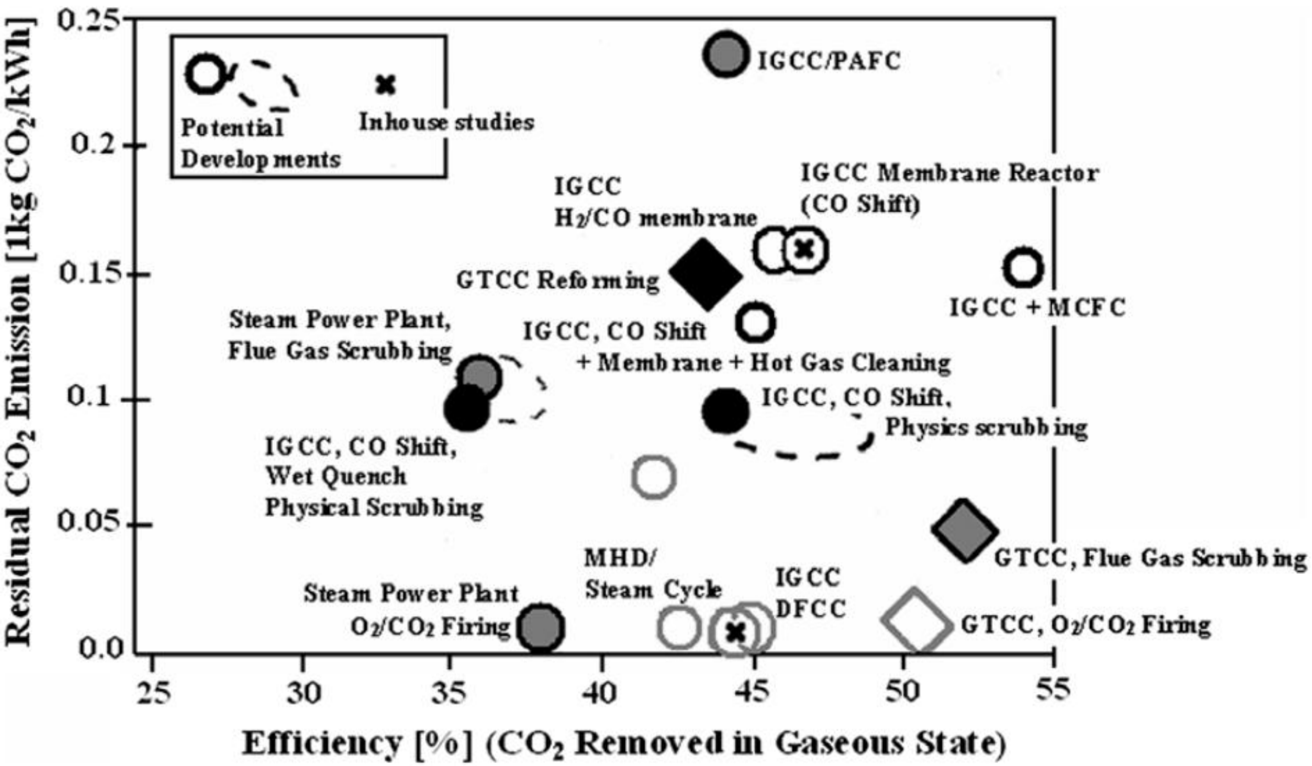
2.1.Refineries and reformers

B.N. Nair et al. / Progress in Materials Science 54 (2009) 511–541



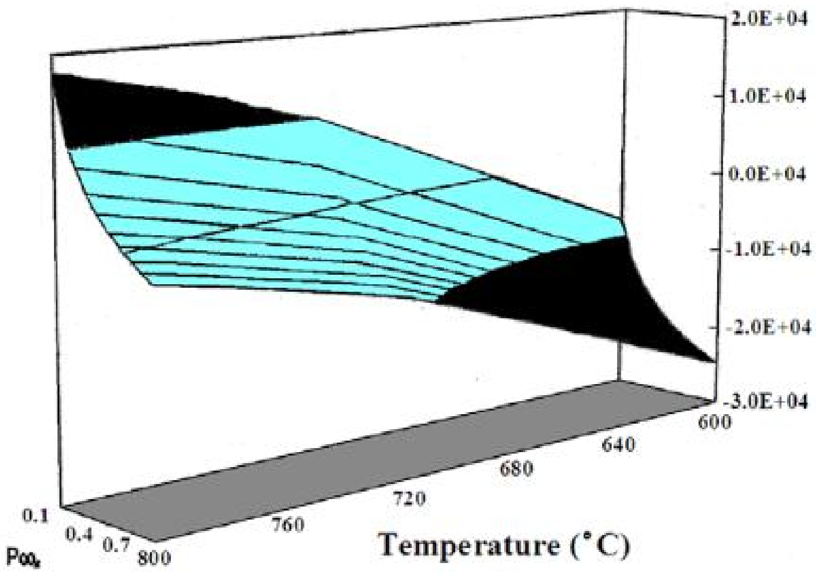
2.2.Efficiencies

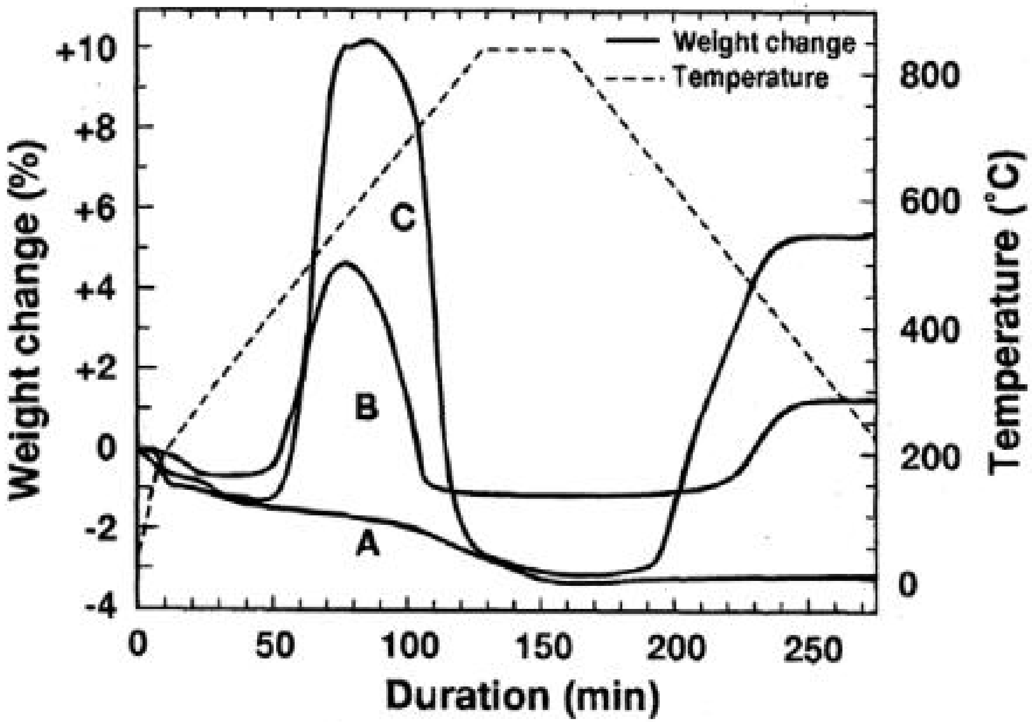
B.N. Nair et al./Progress in Materials Science 54 (2009) 511–541



2.3.Reversibility

B.N. Nair et al. / Progress in Materials Science 54 (2009) 511–541





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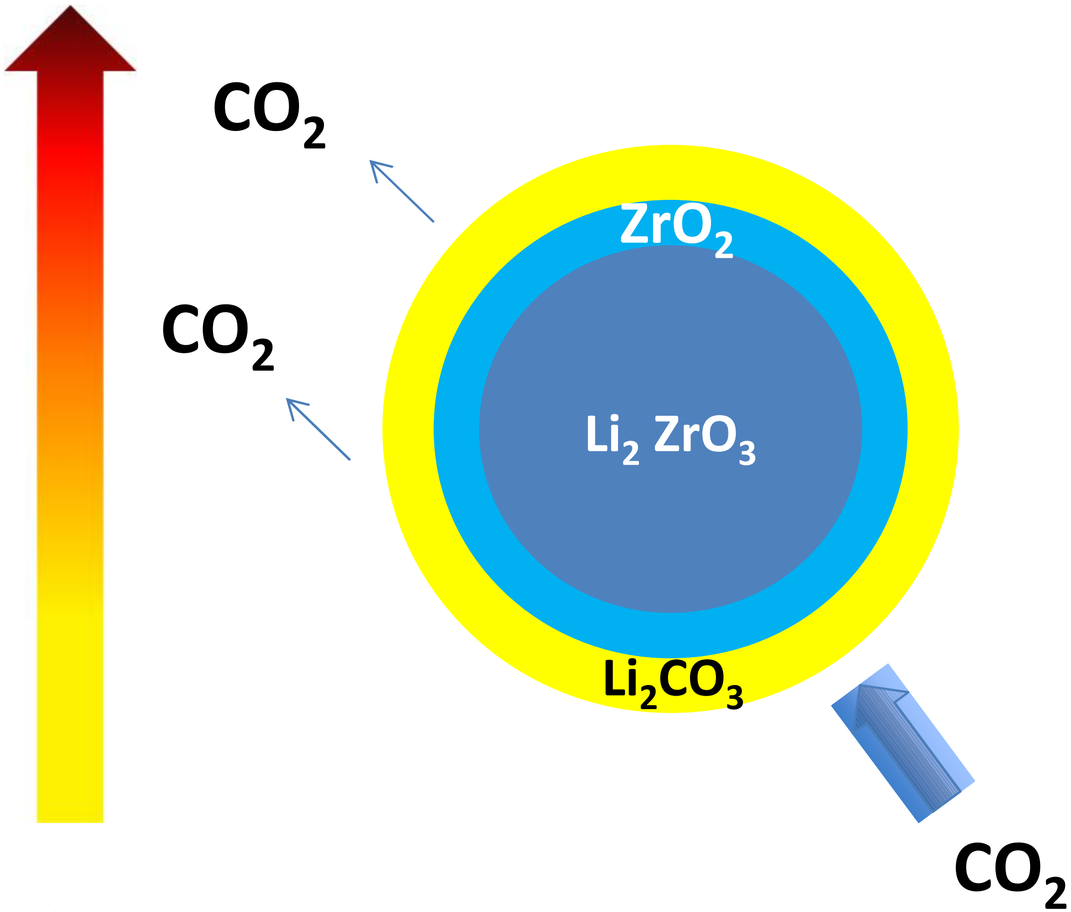
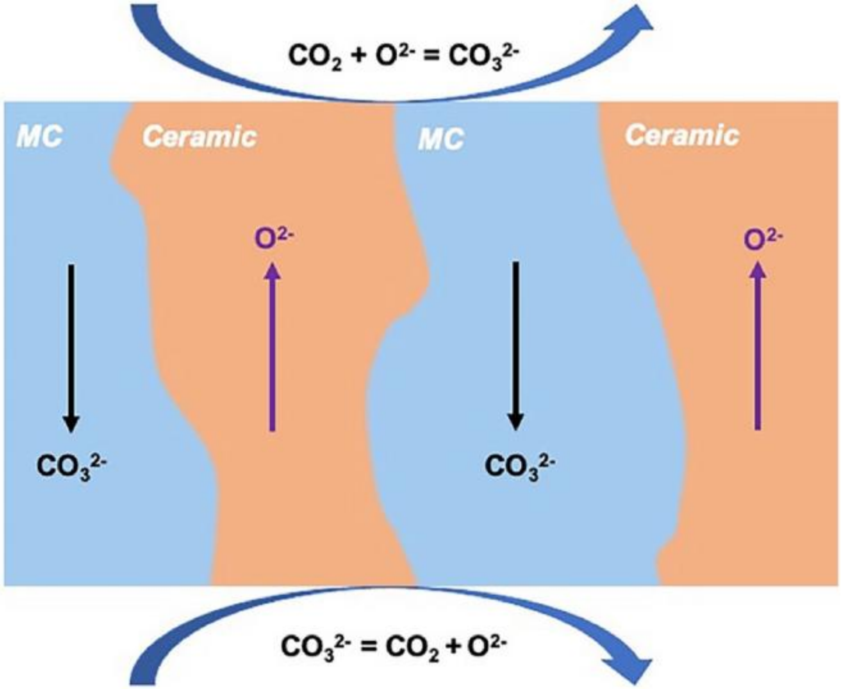


Nakagawa et al. Proceedings of The Electrochemical Society,
PV 1998-11, 370-376 (1998)

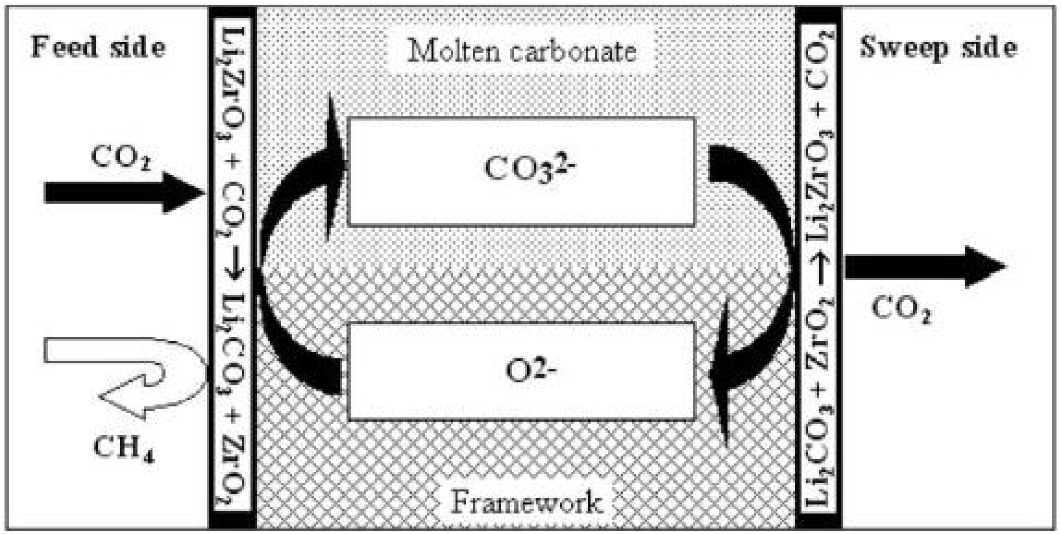
2.3. Membranes

Interest is shifting from bulk sequestration to separation:
this will involve much less raw material based on Zr

K. Zhang et al. Journal of Membrane Science 650 (2022) 120421



B.N. Nair et al. / Progress in Materials Science 54 (2009) 511–541



3. Li-ion batteries

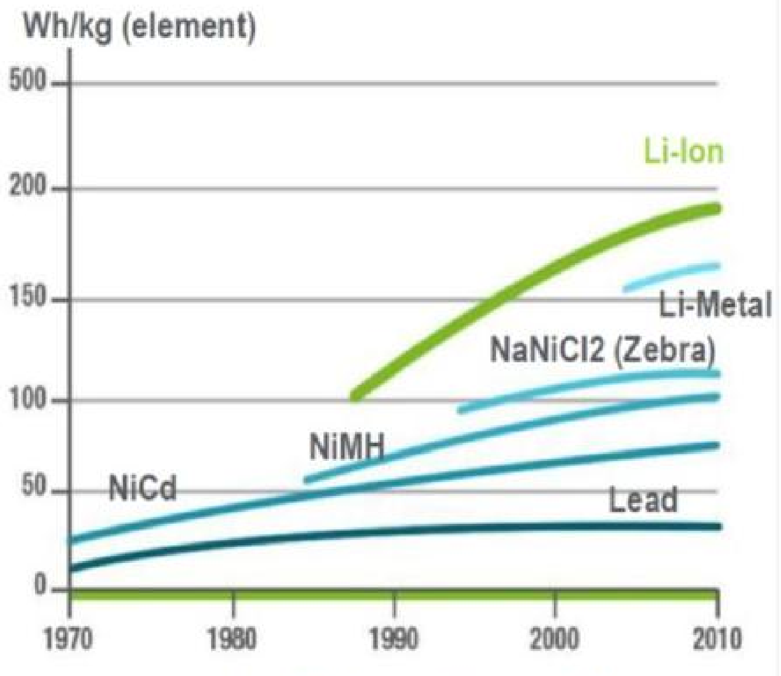
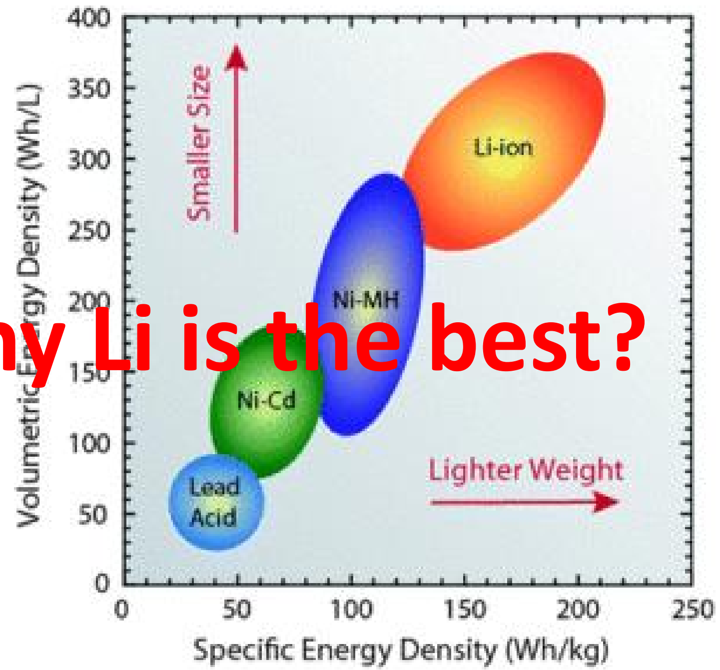
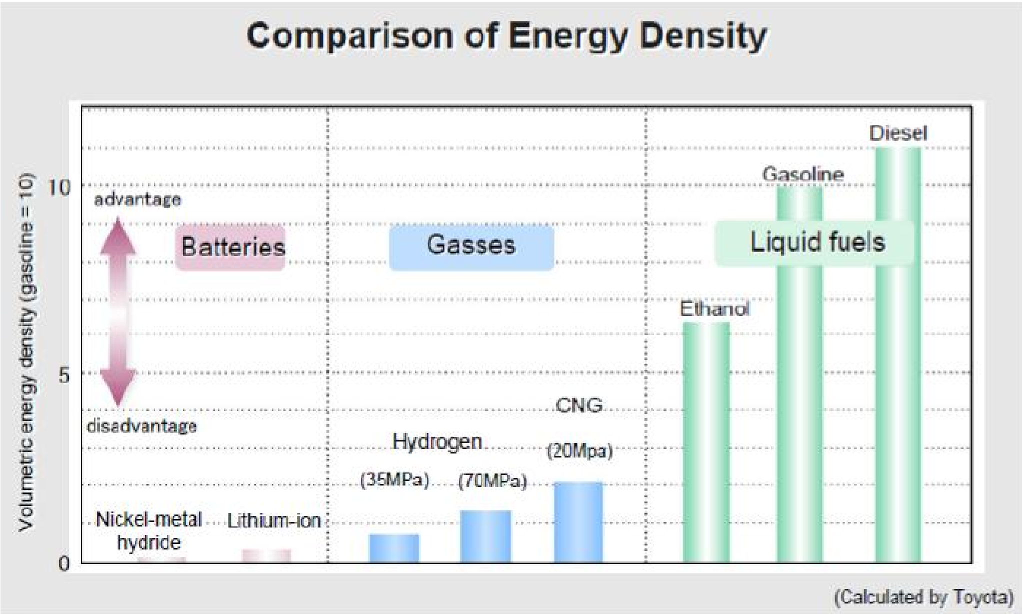


Fig. 2 : Source: Daimler 2011

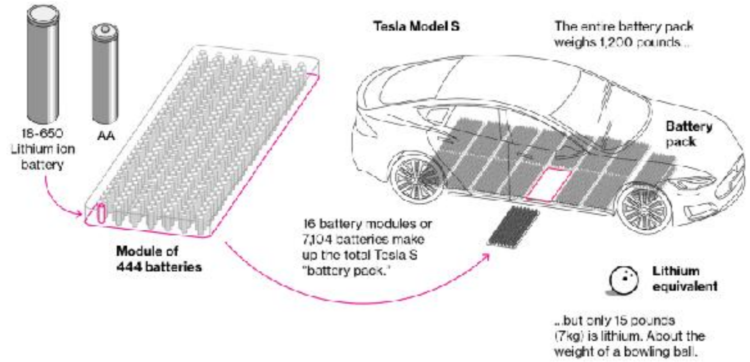


Why Li is the best?

3.1. Energy density



Energy density of electricity is approximately 1/50 of gasoline



3.1. Energy density

anode: $\mathrm{Li} \rightarrow \mathrm{Li}^{+} + e^{-}$

cathode: $\mathrm{Li}_x\mathrm{M} + \mathrm{Li}^{+} + e^{-} \rightarrow \mathrm{Li}_{x+1}\mathrm{M}$

total reaction: $\mathrm{Li}_x\mathrm{M} + \mathrm{Li} \rightarrow \mathrm{Li}_{x+1}\mathrm{M}$

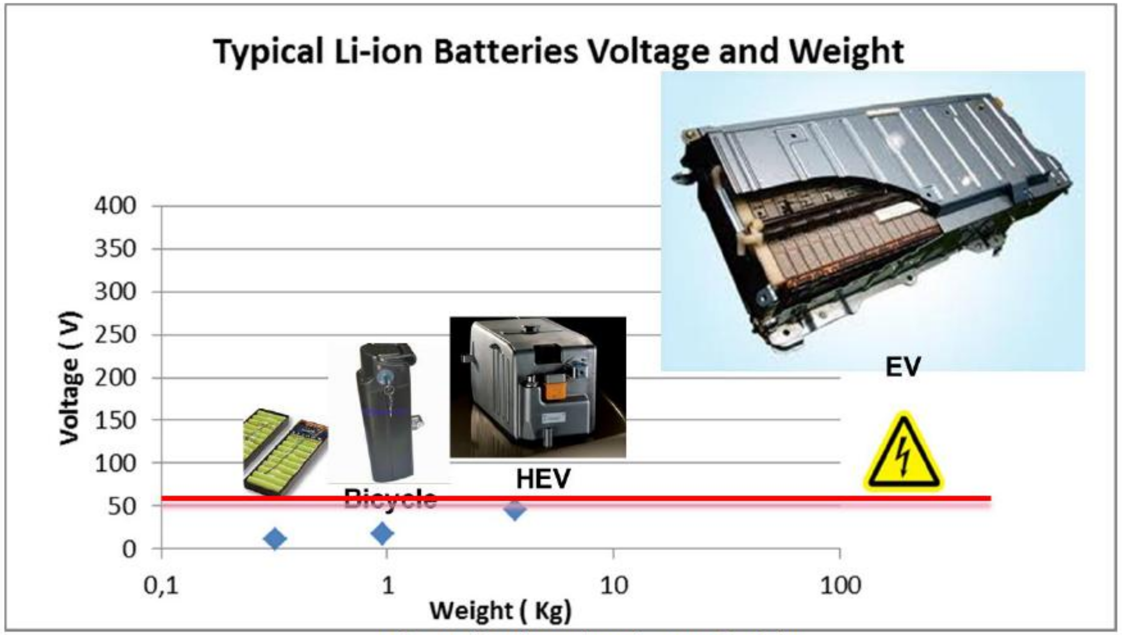
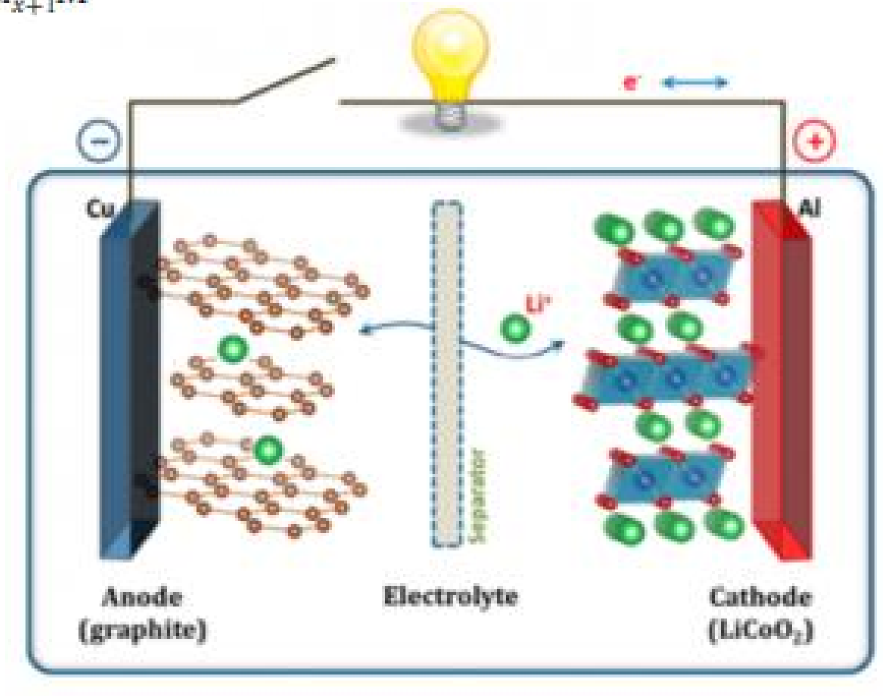


Fig. 7 : Li-ion batteries voltage and weight



3.2. Zircon compounds

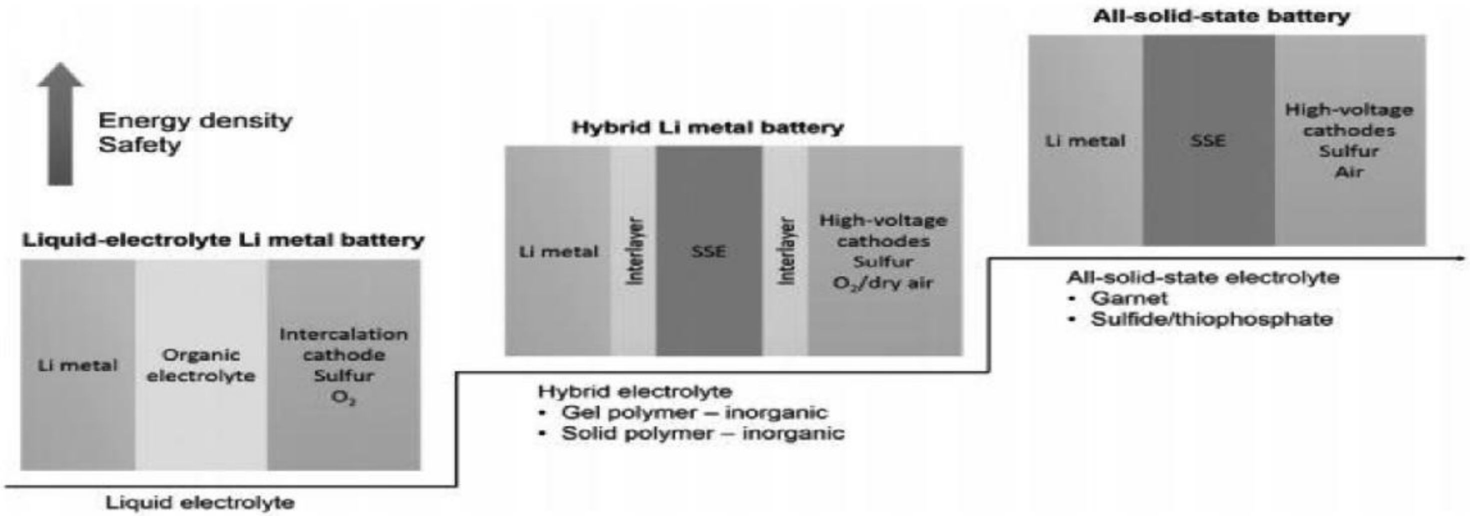
- Zr chances in batteries:

- Cathode materials: Li_8ZrO_6 (LZO) Zr-doped NMC
- Anode materials: SiO_2-ZrO_2 materials
- Solid state electrolite (SSE):$Li_7La_3Zr_2O_{12}$ (LLZO)
- LZO coating in NM cathodes in order to hinder reactions with electrolite

3.3. Li-ion/-metal solid state electrolyte batteries

Solid state electrolyte (SSE)→ Solid state battery (SSB)

- **Garnet type $Li_7La_3Zr_2O_{12}$ (LLZO)**
- High ionic conductivity (~3×10^{-4}S/cm^{-1})



Liu et al. Journal of Power Sources 389 (2018) 120–134

4.Conclusions

- There are promising new applications of zircon products.
- These new applications can alter considerably the market of zircon in the next future (in order of importance):

- D-T Nuclear fusion, Li-ion batteries, CO_2 separation.

- However, the zirconium compounds must compete with other materials.

Nothing is sure. Future cannot be predicted!