### **Zirconates: New Sustainable Uses and Applications**

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# Outline

- 1. Nuclear fusion
- 2. Selective membranes of CO<sub>2</sub> 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

| FUCION FUNDING   | 2020   |  | 2030  |
|--|--|--|---|
| Private fusion firms have disclosed<br>more than \$2.4 billion in funding. | FUTURE PROMISES<br>Private firms are making bold   | CFS: aims to have<br>200 megawatt<br>plant supplying | General Fusion:<br>targets reactors<br>for sale in early                  |
| TAE Technologies <b>880</b> US\$ million                                   | fusion reactors in the 2030s.  | electricity grid in<br>early 2030s.                  | 2030s.  |
| Helien Energy <b>570</b>   | State sponsored  | First Light Fusion                                   | Takamak Enargu  |
|  | Helion: Net<br>electricity (small<br>Giant amounts) from   | anticipates its first<br>power plant in<br>2030s     | fusion power plant<br>(pilot) in 2030s.                                   |
| Commonwealth Fusion Systems 250  | international Polaris reactor.<br>effort ITER:   | 20000.   | 0005  |
| General Fusion 200   | Commonwealth — General Fusion:   | ITER: to run<br>fusion with                          | China Eusion  |
| Tokamak Energy <b>200</b><br>Other (12 firms) <b>302</b>                   | Fusion Systemsoperate UK(CFS): First fusiondemonstrationmachine expectedplant.to generate moreenergy than it uses. | deuterium-tritium<br>fuel.                           | Engineering Test<br>Reactor might<br>complete<br>construction<br>in 2030s |
|  | TAE Technologies:<br>reactors 'ready for<br>commercialization'   | UK Atomic Energy<br>Authority hopes<br>STEP fusion   |   |
| Philip Ball, Nature, Vol 599,  | by late 2020s.   | power plant can<br>supply energy to<br>pational grid |   |
| 18 November 2021, 362-366  | 2030   | national grid.                                       | 2040  |

# 1.4.Projects' advancement

|   |        | 0005                |                           | 0005                | Year                          | 0045                  | 0050            | 0055          |           |
|---|--------|---------------------|---------------------------|---------------------|-------------------------------|-----------------------|-----------------|---------------|-----------|
|   | 2020   | 2025                | 2030                      | 2035                | 2040                          | 2045                  | 2050            | 2055          | 2060      |
| ITER  | Firs   | o<br>st Plasma in 2 | 2025 D-T                  | Operation in        | 2035                          |                       |                 |               | •••••     |
| DEMO  |        |                     |                           |                     |                               |                       |                 |               |           |
| - European  |        |                     | DEM                       | O Constructio       | n and Operat                  | ion between 2         | 2030-50         |               | č         |
| - Japanese  |        |                     | Decision or               | O<br>n DEMO Cons    | struction in 20               | O····<br>030s Operati | ion Starts in n | nid 21st Cent | ury       |
| - Chinese   |        |                     | CFETR                     | C<br>Test Reactor i | )<br>in Operation -           | ~2037 Cons            | o               | pleted betwee | n 2050-60 |
| Innovative A  | Approa | ches                |                           |                     |                               |                       |                 |               |           |
| - General Fusion                                    |        | 0                   | 0                         |                     |                               | _                     |                 |               |           |
| <ul> <li>Commonwealth<br/>Fusion Systems</li> </ul> | Ene    | rgy Generatio       | en ~2023 / Electricity Pr | oduction to be      | ration ~2028<br>e achieved in | 2030s                 |                 |               |           |
| <ul> <li>Tokamak Energ</li> </ul>                   | IV.    |                     | Elect                     | ricity Generati     | ion in 2035                   | _                     |                 | _             | _         |

### 1.5.Expected outputs



# 1.6.Two types of nuclear fusion

- Neutronic fusion
- Aneutronic fusion

### 1.7. Element can be not only hydrogen



IntechOpen, DOI: 10.5772/intechopen.80241. Available from: https://www.intechopen.com/books/power-plants-in-theindustry/nuclear-fusion-power-plants

### **1.8.Neutronic Fusion**



 ${}_{1}D^{2}+{}_{3}Li^{6} \rightarrow 2 {}_{2}He^{4}$ 

### 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<sub>2</sub>, 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 - <sup>3</sup> He            | $^{2}D$         | + <sup>3</sup> ⊢ | le → |   | <sup>4</sup> He + <sup>1</sup> p   | + 18.3 MeV  |
| Deuterium - <sup>6</sup> lithium       | $^{2}D$         | + <sup>6</sup> L | i →  | 2 | <sup>4</sup> He                    | + 22.4 MeV  |
| Proton - <sup>6</sup> lithium          | <sup>1</sup> p  | + <sup>6</sup> L | i →  |   | <sup>4</sup> He + <sup>3</sup> He  | + 4.0 MeV   |
| <sup>3</sup> He – <sup>6</sup> lithium | <sup>3</sup> He | + <sup>6</sup> L | i →  | 2 | <sup>4</sup> He + <sup>1</sup> p   | + 16.9 MeV  |
| <sup>3</sup> He - <sup>3</sup> He      | <sup>3</sup> He | + <sup>3</sup> ⊢ | le → |   | <sup>4</sup> He + 2 <sup>1</sup> p | + 12.86 MeV |
| Proton – Lithium-7                     | <sup>1</sup> p  | + <sup>7</sup> L | i →  | 2 | <sup>4</sup> He                    | + 17.2 MeV  |
| Proton – Boron-11                      | <sup>1</sup> p  | + 11             | 3 →  | 3 | <sup>4</sup> He                    | + 8.7 MeV   |
| Proton – Nitrogen                      | <sup>1</sup> p  | + 15             | N →  | • | <sup>12</sup> C + <sup>4</sup> He  | + 5.0 MeV   |

## 1.9. Aneutronic fusion



<u>https://youtu.be/EVIWUQ-</u> <u>UKa4?list=TLGGRqoSMsdmCxsyNjA3MjAyMg</u>

<u>The New Fusion Race - Part 2 -</u> <u>Aneutronic Fusion - YouTube</u>

### 1.9. Aneutronic Fusion HB11

#### Laser ion acceleration of hydrogen by

picosecond laser pulse towards B-11 rich fuel



High-power laser pulse H and B-11 rich fuel pellet

ignites H - B reaction (non-thermal)

#### Observed experimentally by:

BELYAEV, V.S. et al. Phys. Rev. E 72, 026406. (2005) LABAUNE, C., et al. Nat. Commun. 4, 2506. (2013) PICCIOTTO, A., et al. Phys Rev. X4, 031030. (2014) MARGARONE, D. et al. Plosmo Phys. Control Fusion 57, 014030 (2015) GIUFFRIDA, L. et al. Physical Review E101, 013204 (2020)



Kilotesla magnetic field by second laser and capacitive coil increases reaction yield in cylindrical shaped fuel

#### Demonstration of kilotesla field: FUJIOKA, S. et al. Nat. Sci. Rep. 3, 1170-1176. (2013)

Simulation of higher reaction yield: LALOUSIS, P., Hora H. et al. J. Fusion Energy 34, 62-67. (2015)



#### Further increases reaction yield

by approx. one billion times higher than previously thought:

#### Key to net-energy gain

#### Summarised by:

HORA H., MOUROU G., et al. Loser port. Beoms. 33, 607-609. (2015)



charge neutralisation of He⁺ particile

generated directly by the fusion reaction

#### Summarised by: HORA H. et al. Loser Part. Beams. 35 (4): p 730-740. (2017)

Protected by: Pat. No. US1041075282

# 1.10.Resume on nuclear fusion

- Neutronic fusion:  $_{1}D^{2}+ _{1}T^{3} \rightarrow _{2}He^{4}+ n$
- An eutronic fusion :  $_{1}H^{1} + _{5}B^{11} \rightarrow _{6}C^{12} \rightarrow 3_{2}He^{4}$

• 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 x 10<sup>-12</sup> 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 charac | teristics of | the four | main breed | ler candidat | te ceramics |
|----------------------|--------------|----------|------------|--------------|-------------|
|----------------------|--------------|----------|------------|--------------|-------------|

| Characteristics  | Ceramic            |                                  |                                  |                                  |  |  |  |  |  |
|--|--------------------|----------------------------------|----------------------------------|----------------------------------|--|--|--|--|--|
|  | LiAlO <sub>2</sub> | Li <sub>4</sub> SiO <sub>4</sub> | Li <sub>2</sub> ZrO <sub>3</sub> | Li <sub>2</sub> O                |  |  |  |  |  |
| Melting point in °C  | 1610°              | 1250°                            | 1615°                            | 1430°                            |  |  |  |  |  |
| Li content (g cm <sup>-3</sup> )                                       | 0.27               | 0.54                             | 0.38                             | 0.93                             |  |  |  |  |  |
| Thermal conductivity<br>at 600 ° C 80% TD<br>(W/m° K)                  | 2.6                | 2                                | 1.4                              | 3.5                              |  |  |  |  |  |
| Fragmentation  | low                | very high                        | по                               | medium                           |  |  |  |  |  |
| Swelling<br>(900 ° C, 297 FPD)   | < 0.5%             | 1.5%                             | < 0.7%                           | 8%                               |  |  |  |  |  |
| Grain growth   |                    |                                  |                                  |                                  |  |  |  |  |  |
| 100 FPD 700 ° C  | no                 | no                               | no                               | $3.5 \mu m \rightarrow 7 \mu m$  |  |  |  |  |  |
| 900 ° C  | no                 | $1 \mu m \rightarrow 2 \mu m$    | no                               | $3.5 \mu m \rightarrow 17 \mu m$ |  |  |  |  |  |
| Tritium retention<br>(297 FPD, 500 ° C)                                | 25%                |                                  | 2%                               | 3.5%                             |  |  |  |  |  |
| Helium retention<br>(297 FPD, 500 ° C)                                 | 2.74%              |                                  | 2.34%                            | 22.5% (700°)                     |  |  |  |  |  |
| Lithium mass transfer<br>(900 ° C)                                     | no                 | 0.16 at %                        | no                               | 0.9 at %                         |  |  |  |  |  |
| Temperature<br>corresponding to<br>1 day T <sub>2</sub> 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<sub>2</sub> 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



### 2.3.Reversibility



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



### 3.1. Energy density

Tesla Model S

The entire battery pack

Battery

pack

Lithium equivalent

weighs 1,200 pounds ...

 $\odot$ 

... but only 15 pounds

(7kg) is lithium. About the

weight of a bowling ball.



### 3.1. Energy density

anode:  $Li \rightarrow Li^+ + e^-$ 

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

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



Fig. 7 : Li-ion batteries voltage and weight



# 3.2. Zircon compounds

- Zr chances in batteries:
- Cathode materials: Li<sub>8</sub>ZrO<sub>6</sub> (LZO) Zr-doped NMC
- Anode materials: SiO<sub>2</sub>-ZrO<sub>2</sub> materials
- Solid state electrolite (SSE):Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (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)  $\rightarrow$  Solid state battery (SSB)

- Garnet type Li7La3Zr2O12 (LLZO)
- High ionic conductivity (~3×10<sup>-4</sup>S/cm<sup>-1</sup>)



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<sub>2</sub> separation.
- However, the zirconium compounds must compete with other materials.



Nothing is sure. Future cannot be predicted!