

Hydrogen Technologies and Applications

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PRRE1003

Resources, Processes & Materials Engineering

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LECTURE 12b

John Curtin Distinguished Professor Craig Buckley

Discipline of Physics and Astronomy

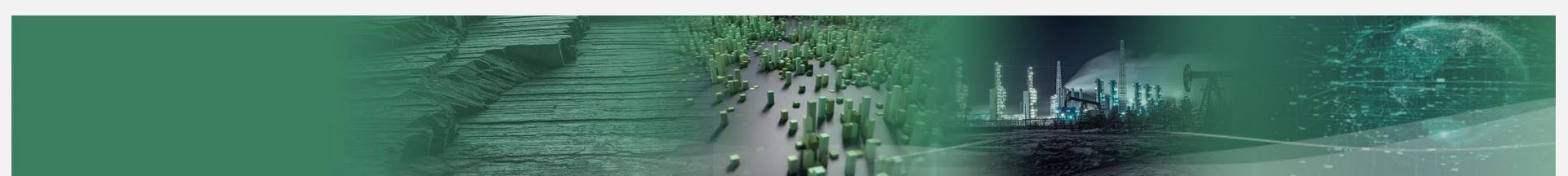
School of EECMS

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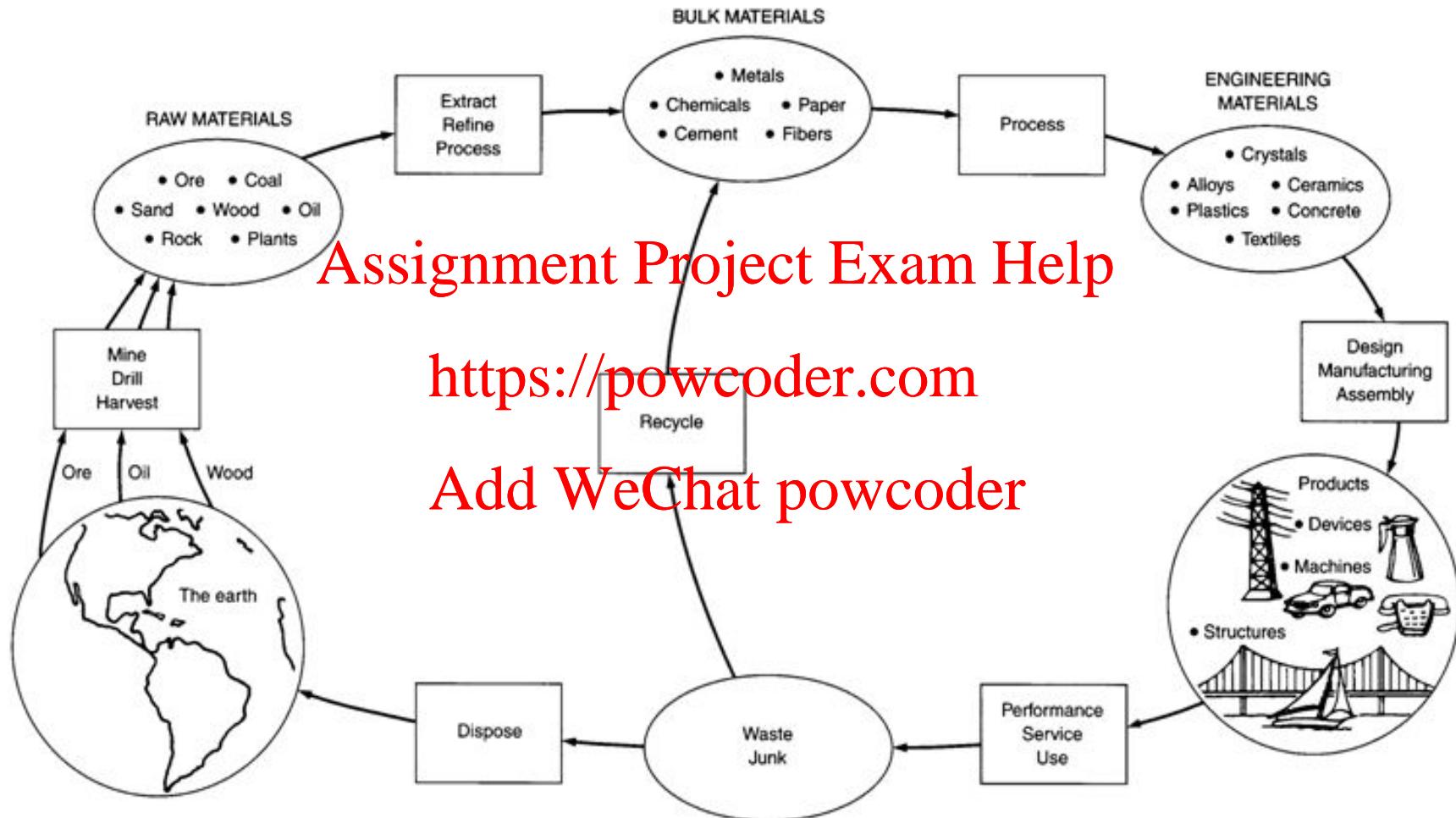
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Lecture focus



Reproduced from "Materials and Man's Needs", National Academy of Sciences, Washington D.C., 1974.



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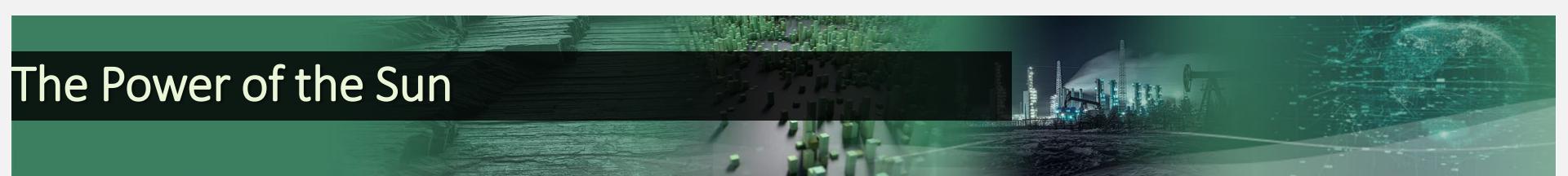
Global Innovation Linkage Grant - Dept. of Industry, Science, Energy and Resources

Future Energy Exports (FEnEx) Cooperative Research Centre (CRC)

Lecture Outline

- ❖ Solar Power and Hydrogen
- ❖ Why Hydrogen? **Assignment Project Exam Help**
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- ❖ Hydrogen Storage Research Group (HSRG) Projects
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- ❖ Conclusion

The Power of the Sun



- The World's current power consumption is 18.3 TW
- The incident solar power on the planet is 166 PW
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- 30% of this is reflected back into space, and 19% is absorbed by clouds
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- This leaves a balance of 85 PW available for terrestrial solar collectors
- 85 PW is well over 4500 times our current world consumption of 18.3 TW

Abbott Proc. Of the IEEE **98** (2010) 42 – 66.



Solar Power vs other Renewable Sources

Energy source	Max. power	% of Tot. Solar
Total surface solar	85,000 TW	100%
Desert solar	7650 TW	9%
Ocean thermal	100 TW	0.12%
Wind	72 TW	0.08%
Geothermal	44 TW	0.05%
River hydroelectric	7 TW	0.008%
Biomass	7 TW	0.008%
Open ocean wave	7 TW	0.008%
Tidal wave	4 TW	0.003%
Coastal wave	3 TW	0.003%

Abbott Proc. Of the IEEE **98** (2010) 42 – 66.

- All other sources of renewable energy are less than 1% of solar.
- If we consider the solar power that hits the desert regions of the world, all other renewables still only amount to less than 3% of this power.

Solar Power as the Dominant Renewable Source

If we globally tap sunlight over only 1% of the incident area at only an energy conversion efficiency of 1%, this meets our current world energy consumption of 18.3 TW.

As 9% of the planet surface area is taken up by desert and efficiencies well over 1% are possible, in practice, this opens up many exciting future opportunities.

Specifically, we find solar thermal collection via parabolic reflectors where focussed sunlight heats steam to about 600°C to drive a turbine is the best available technology for generating electricity.

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What is the solar thermal collector footprint?

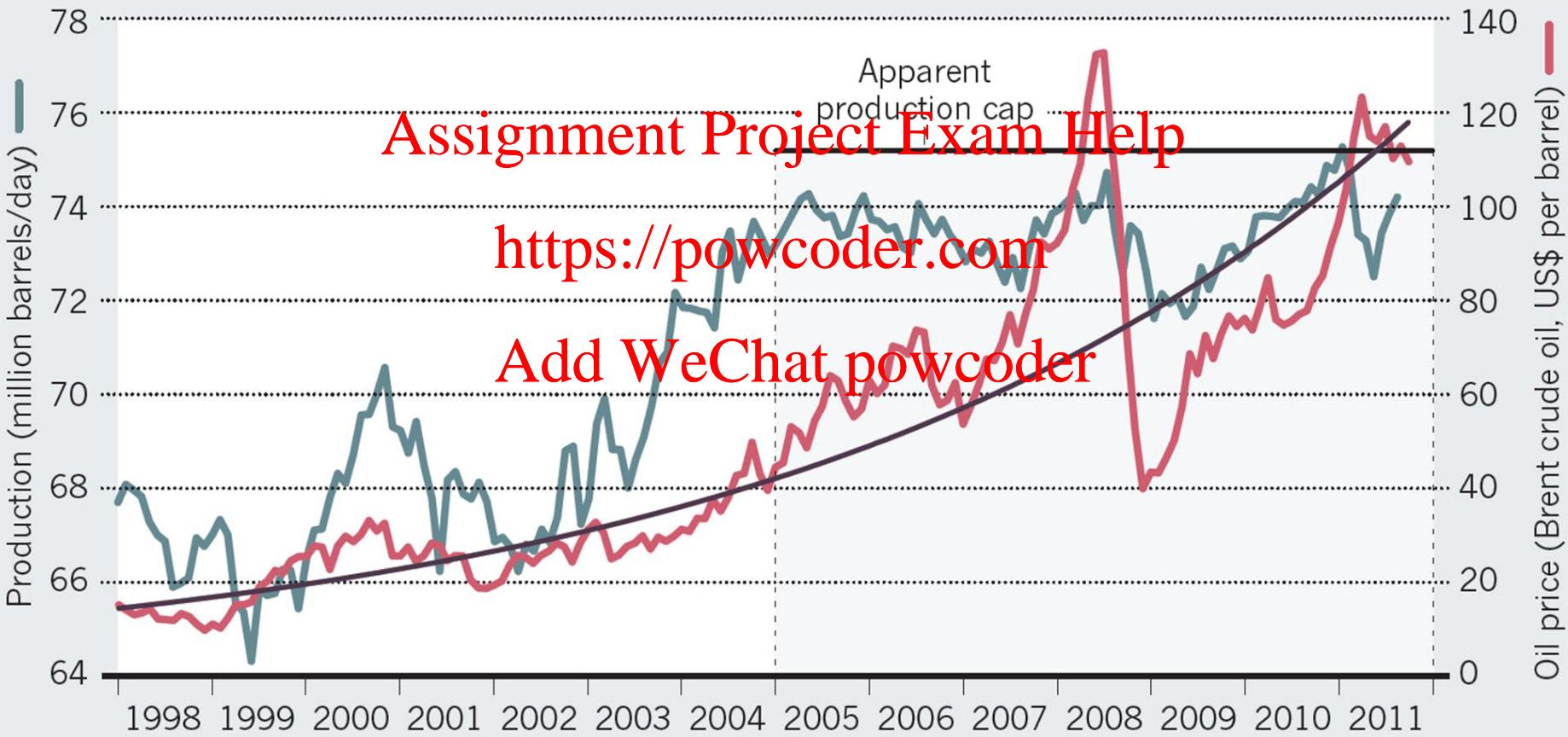
Worst case scenario 1300 km × 1300 km. With less pessimistic assumptions only 500 km × 500 km (approx. 1% of the land area of the Worlds hot deserts) would be required.

Abbott *Proc. Of the IEEE* **98** (2010) 42 – 66.



OIL PRODUCTION HITS A CEILING

Production followed demand until 2005, when it levelled off despite continued price increases. There seems to be a production 'cap' at about 75 million barrels per day.





- At the current rate of consumption of reasonably recoverable reserves ^{1, 2}
- Coal reserves will run out in 130 years,
- Natural gas in 60 years,
- Oil in 40 - 50 years.

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- We cannot continue to burn oil to secure long-term viability of our future, we need to conserve oil for lubricating the machines of the world for years to come
- Oil is used for lubricants, dyes, plastics, and synthetic rubber; natural gas is an important desiccant in industry and is used in ammonia, glass and plastics production; and coal products are used to make creosote oil, benzene, toluene, ammonium nitrate, soap, aspirin, and solvents.
- Oil, coal and natural gas are a precious resource that humankind cannot afford to burn anymore.

“I’d put my money on the sun and solar energy. What a source of power! I hope we don’t have to wait until oil and coal run out before we tackle that.”

Thomas Edison (1931) in conversation with Henry Ford and Harvey Firestone

¹ World Coal Institute www.worldcoal.org

² Abbott Proc. Of the IEEE 98 (2010) 42 – 66.

- At the current rate of consumption with conventional reactors, there are only 80 years of world uranium resources at reasonable recovery cost levels.^{1, 2}
- Nuclear power currently only supplies about 5.7% of the world's total energy, thus if we hypothetically supplied the whole world's energy needs with nuclear power there would be only 5 years of supply.
- Why does it make sense for humankind to foot the risks and costs of nuclear power, for such a short-term return?
- To supply the World's 18.3 TW of power with nuclear fission alone would require 18,300 1 GW reactors.
- To supply the World's energy needs for 1 year with nuclear fusion one would require 2290 tonnes of D₂ and 68,700 tonnes of Li.
- Given that Li has several competing industrial uses the viability of nuclear fusion is ≈ 100 years.

¹World Nuclear Association (www.world-nuclear.org)

² Abbott Proc. Of the IEEE 98 (2010) 42 – 66.

Solar Photovoltaic vs CST

Silicon photovoltaic (PV) solar cells

- 500 km x 500 km to supply 18.3 TW (World consumption)
- 0.17 g/cm² of arsenic → 425 million tons As → (World reserves @ 3 million tons)
- Other varieties of solar cells → rare earth metals → world reserves stretched



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Concentrating solar thermal (CST)

- 500 km x 500 km to supply 18.3 TW → Low-tech → using mirrors to provide heat
- Heat → Electricity using heat engine (i.e. Steam Engine, Stirling engine etc.)



- Electricity is produced using CST and PV
- Solar farms are linked by cable to desalination plants for large scale electrolysis to produce hydrogen

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- Hydrogen is used as the dominant transport fuel and for night time power use.
- In the long term a Solar Hydrogen economy makes sense, because there is so much available power

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- Conversion losses can be compensated for by adding more solar collectors.
- In the long term we have no choice, but to move almost entirely to a Solar-Hydrogen Economy

Abbott Proc. Of the IEEE 98 (2010) 42 – 66.

Solar-Hydrogen vs the Rest

Energy source	Max. power	% of Tot. Solar
Total surface solar	85,000 TW	100%
Desert solar	7650 TW	9%
Ocean thermal	100 TW	0.12%
Wind	72 TW	0.08%
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Coastal wave	3 TW	0.003%

World uses 18.3 TW of power

To sustain this we only have a finite utility time for our resources

Energy source	Utility time
Solar-hydrogen	1-billion years
Nuclear fusion	100 years
Coal	35 years
Gas	14 years
Oil	14 years
Nuclear fission	1 year

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D. Abbott, Proceedings of the IEEE, 98 (2010) 42-66.

"I'd put my money on the sun and solar energy. What a source of power! I hope we don't have to wait until oil and coal run out before we tackle that."

Thomas Edison (1931) in conversation with Henry Ford and Harvey Firestone

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Concentrating solar thermal

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Facts about Hydrogen



- Hydrogen is the most abundant element in the universe and makes up 75 % of all known mass in the universe.
- Hydrogen is the lightest element in the universe. The hydrogen atom (H) has one proton and one electron and it exists at STP in a molecular form (H_2) as a gas.
- If hydrogen is burnt with oxygen it forms water.
<https://powcoder.com>
- Hydrogen is colorless, has no odor or taste and is non-toxic. It is highly flammable, but will not ignite unless an oxidizer and ignition source are present.
- Hydrogen has an autoignition temperature of 585 °C in air
- The flammability range of hydrogen is between 4 – 77% H_2 to air volume ratio.
- The ignition energy of hydrogen is 0.02 MJ.

Why Hydrogen?

- Hydrogen can be produced from many primary sources.
- No greenhouse gases are produced when Hydrogen is used as a fuel

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- Hydrogen has the highest energy to weight ratio (120 MJ/kg) of any fuel
- Hydrogen is the ideal fuel for fuel cells and can also be used in an internal combustion engine.
- Hydrogen has the potential to be a new export industry for Australia

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Learning Outcome Check

- Describe briefly what is meant by a solar-hydrogen economy.
- List 3 advantages of using hydrogen as a fuel source, compared to the current energy mix.

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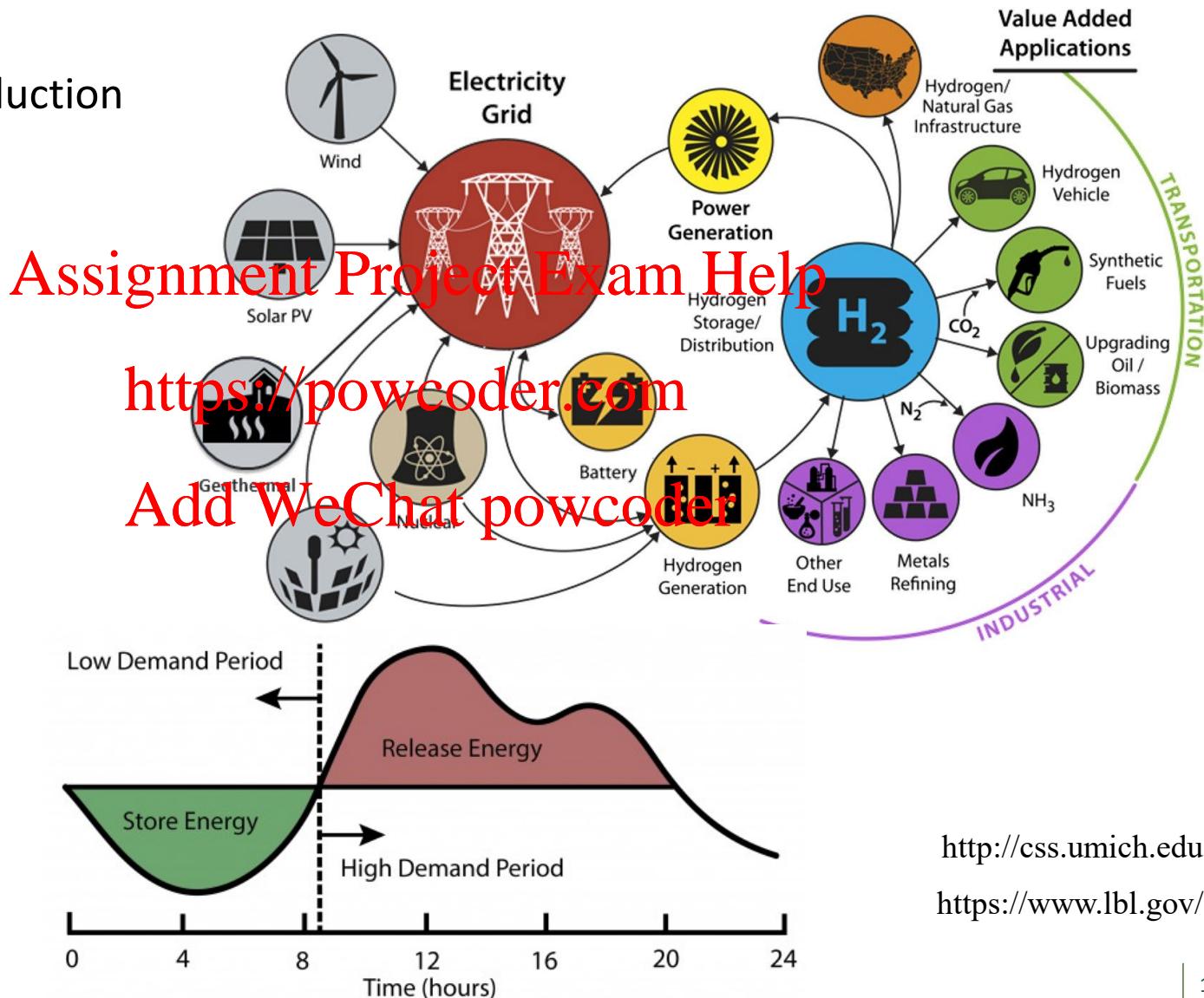
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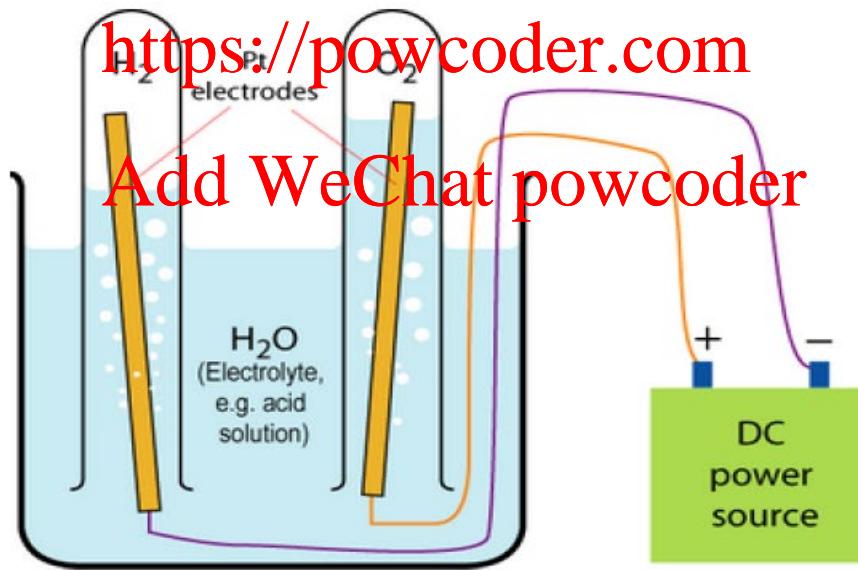
Hydrogen Applications and Prospects

1. Hydrogen production
2. Utilisation
3. Distribution
4. Storage



Electrolysis

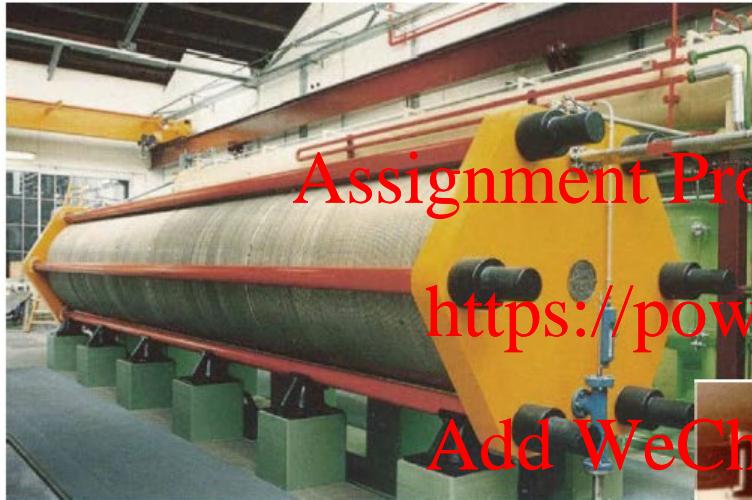
$\text{H}_2\text{O} + \text{electrical energy} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$
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Types of electrolyzers

	<i>Fuel cells</i>	Electrolyzer cells	Temperature
Alkaline	AFC	AEC	25 – 150 °C
Polymer	PEMFC	PEMFC	80 °C (150 – 200 °C)
Phosphoric acid	PAFC	(PAEC)	-
Molten Carbonate	MCFC	(MCEC)	-
Solid Oxide	SOFC	SOEC	700 – 1000 °C

The largest electrolyzers



S-556 unit. 760 Nm³/h H₂

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Probably the world's largest
electrolysis plant
28 electrolyzers Type S-556
21'000 Nm³/h H₂ and
10'500 Nm³/h O₂

In service since 1973 for Sable
Chemical Industries in Zimbabwe



PEM Electrolysis

PEM Electrolysis

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Anode: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-$

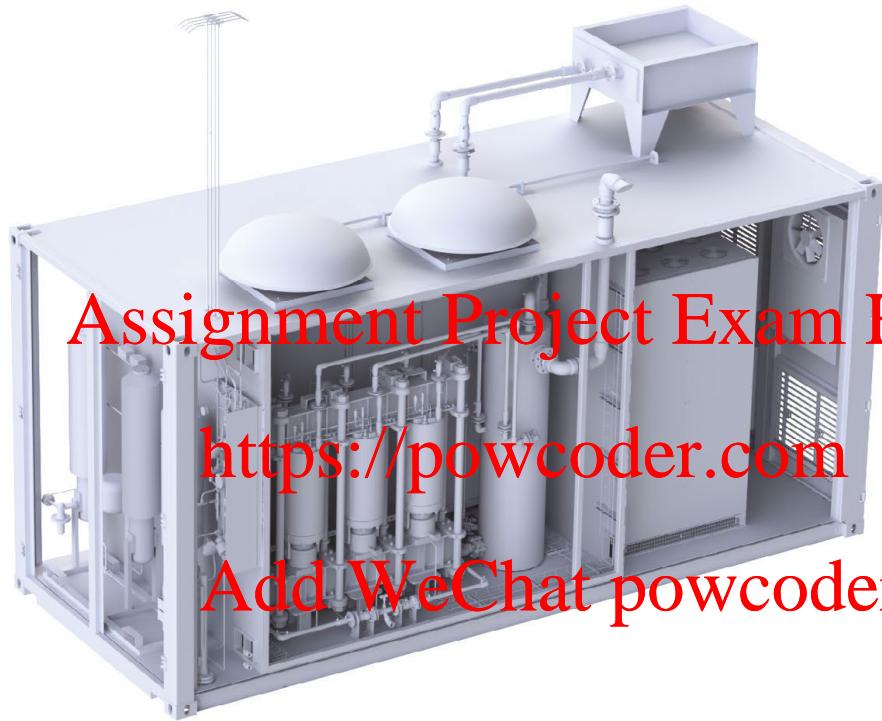
Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Overall cell: $2\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$

Shiva et al Materials Science
for Energy Technologies 2
(2019) 442.



ITM Power HGas PEM Electrolyser



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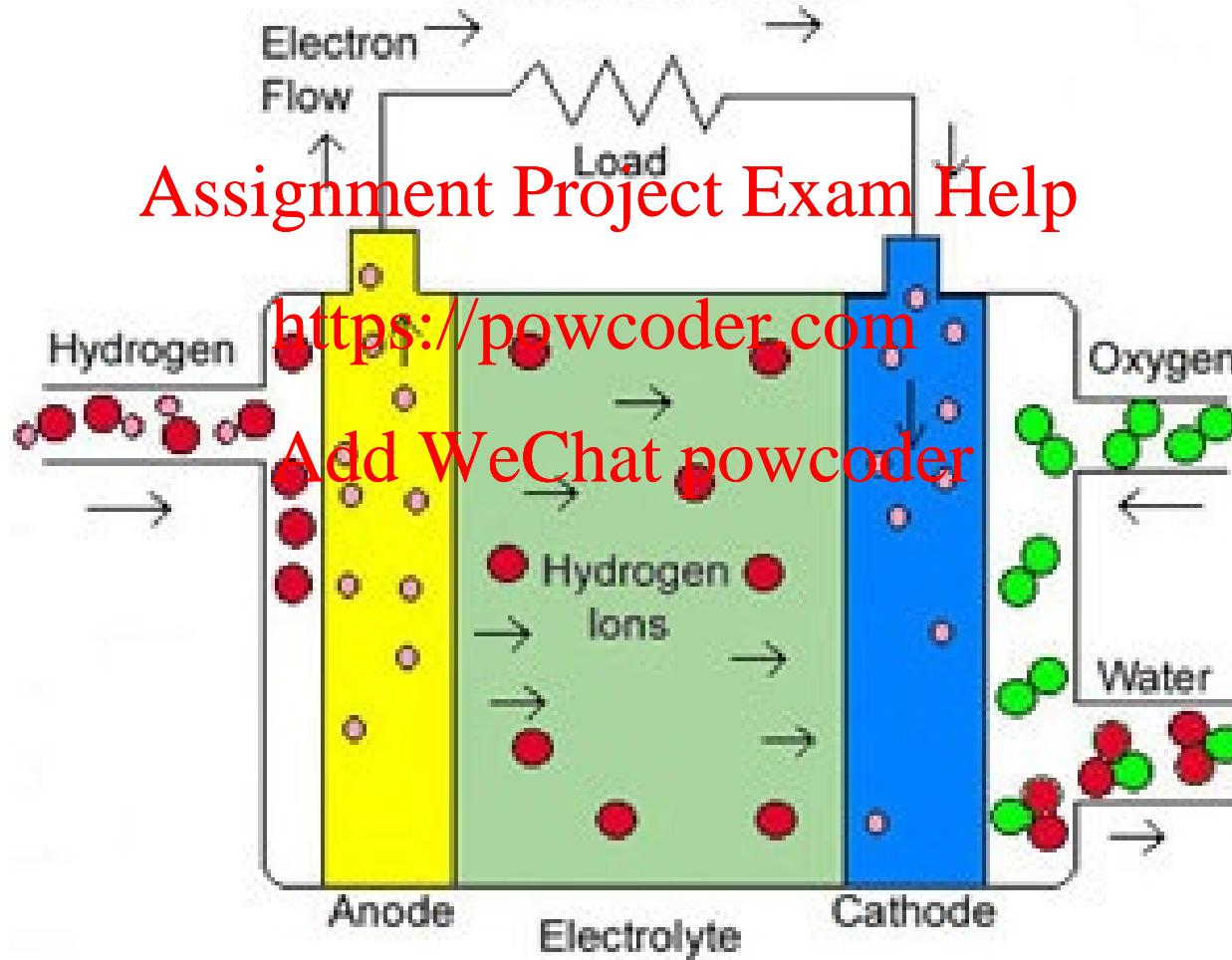
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System power	0.1 – 100 MW
H ₂ production rate	40 – 40,000 kg/24 h
H ₂ pressure	20 bar (50 bar optional)
H ₂ purity	99.5 – 99.999 %

Fuel Cells

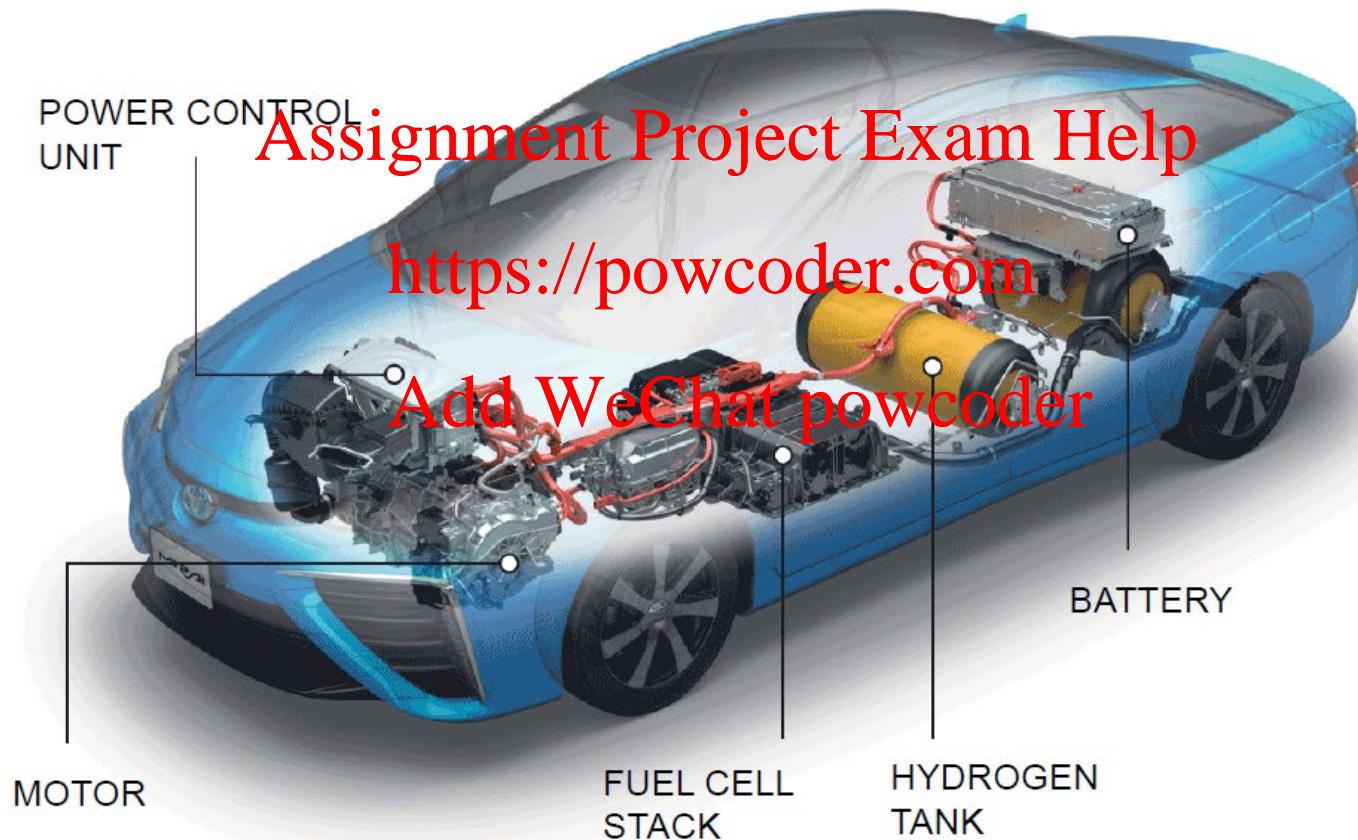
Phosphoric Acid and P.E.M. Fuel Cells



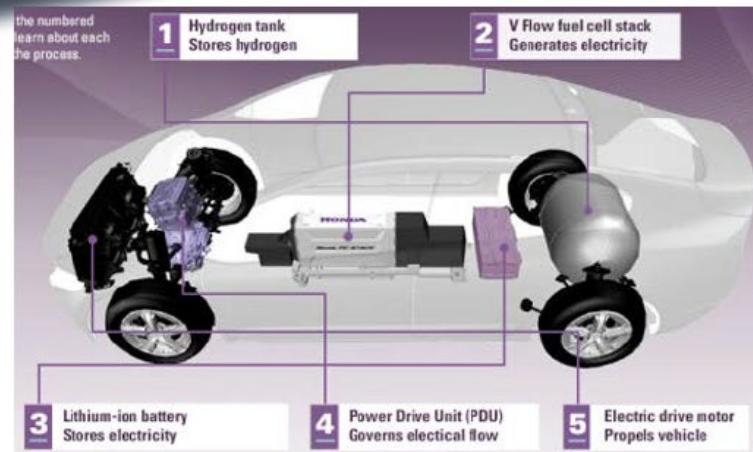
Types of Fuel Cells

Type	Abrev.	Temp.	Electrolyte
<u>Low temperature systems</u>			
Alkaline FC	AFC	60 – 80 °C	aq. KOH
Polymer FC	PEMFC	60 – 80 °C	Polymer
Direct methanol FC	DMFC	60 – 80 °C	Polymer
Phosphoric acid FC	PAFC	200 °C	H_3PO_4
<u>High temperature systems</u>			
Molten carbonate FC	MCFC	650 °C	Molten salt
Solid oxide FC	SOFC	700 - 1000 °C	Ceramic

Toyota FCV from 2015



Honda Clarity



Fuel Cells



Progress Around the Globe



Toyota Mirai
\$57,500 USD



Honda Clarity
\$60,000 USD



Hyundai Tucson



Hyundai Genesis



Nikola

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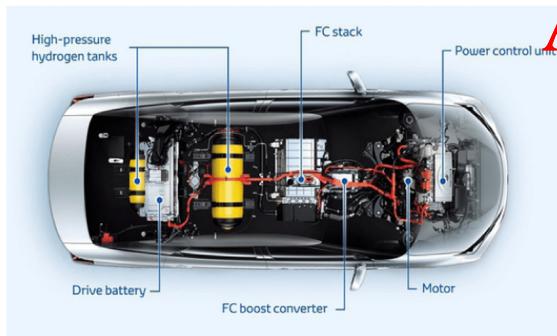
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500 – 700 km per tank

FCEVs fuel quickly (3 - 5 minutes)

High pressure (700 bar H₂ tanks)



DOI: 10.1016/j.pnsc.2018.03.001

Japan's FCEV
2017 – 3,000 units
2020 – 40,000 units
2025 – 200,000 units
2040 – 800,000 units

http://ieahydrogen.org/pdfs/Global-Outlook-and-Trends-for-Hydrogen_Dec2017_WEB.aspx

Fuel Cells



A fuel cell electric bus is the same as a battery electric bus only with a smaller battery, hydrogen tanks and FC

Fuel Cells

Completed: Validation of fuel cell forklifts



Collaboration: Dept. of Defense- The Defense Logistics Agency (DLA)

Ongoing: Analysis and Testing of Emergency urban power and fuel cell buses



Collaboration: NREL and Dept. of Transportation- Federal Transit Administration (FTA)

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Potential: Light duty vehicles for military applications



Potential collaboration: Army

Potential: Unmanned Underwater Vehicles (UUV)



Potential collaboration: Navy

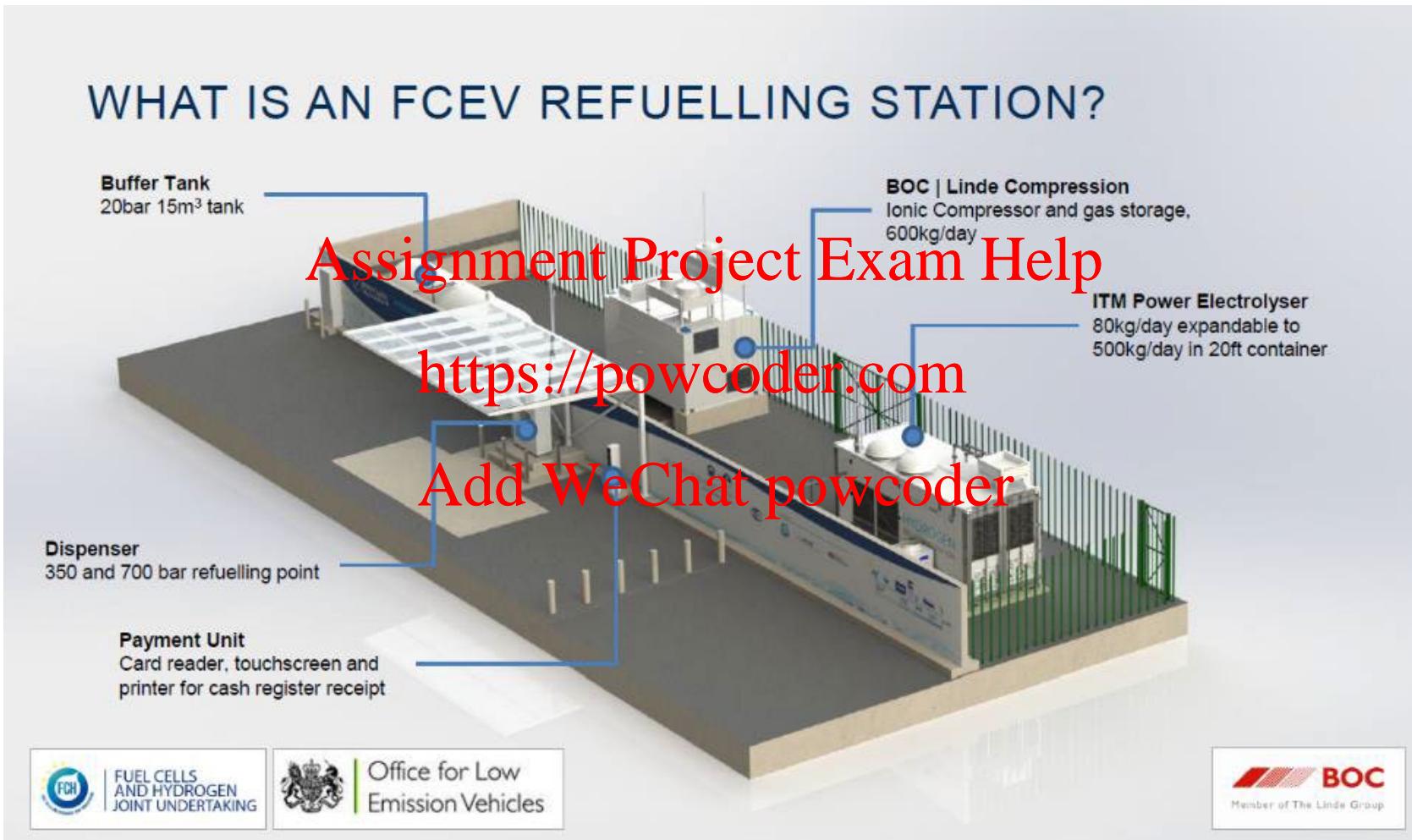
Potential: Unmanned Aviation Vehicles (UAV)



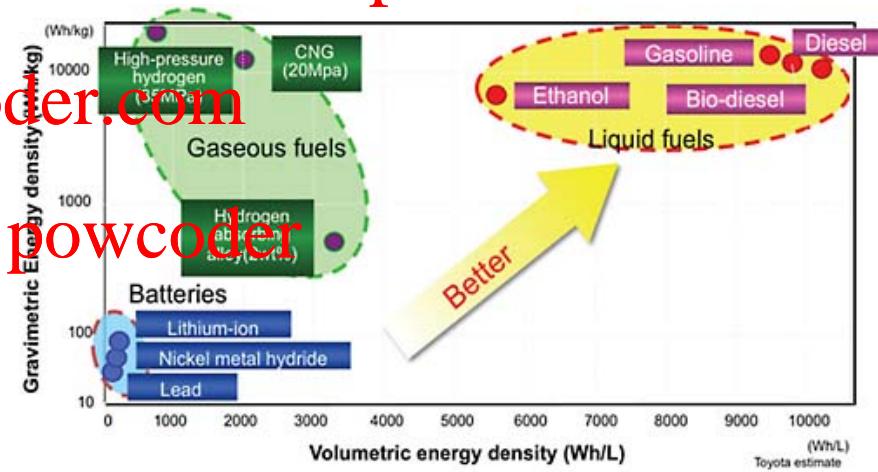
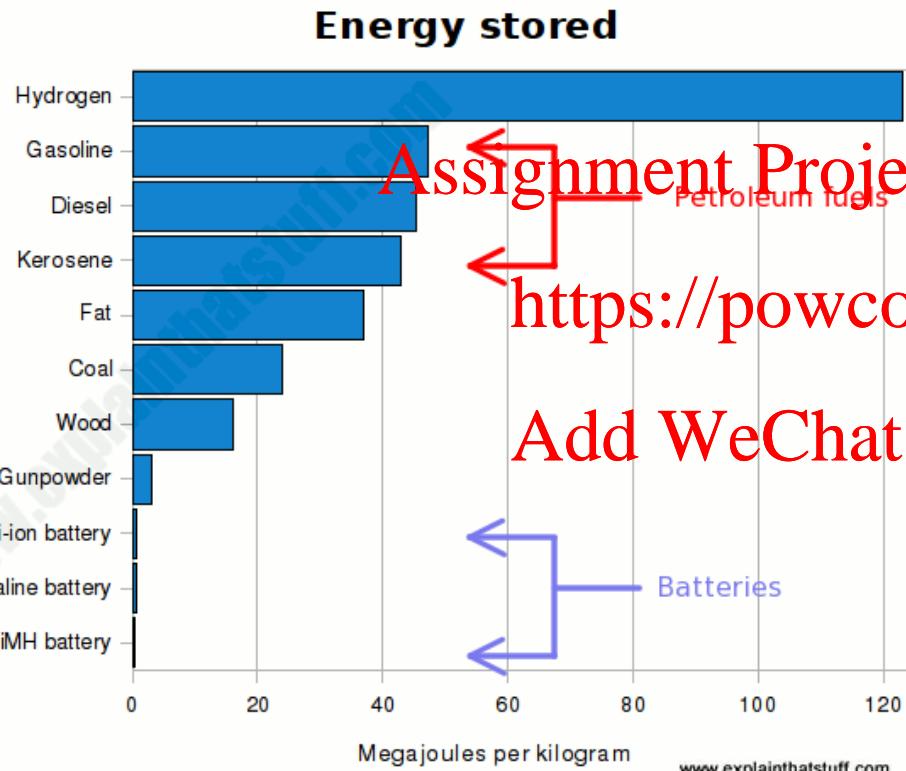
Potential Collaboration: DOT - Pipeline Management



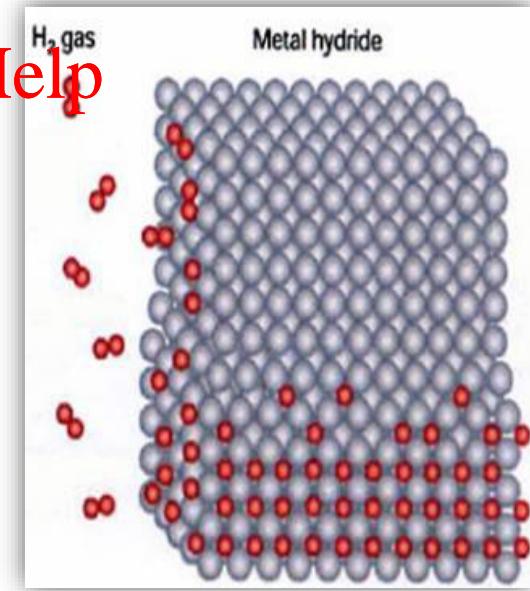
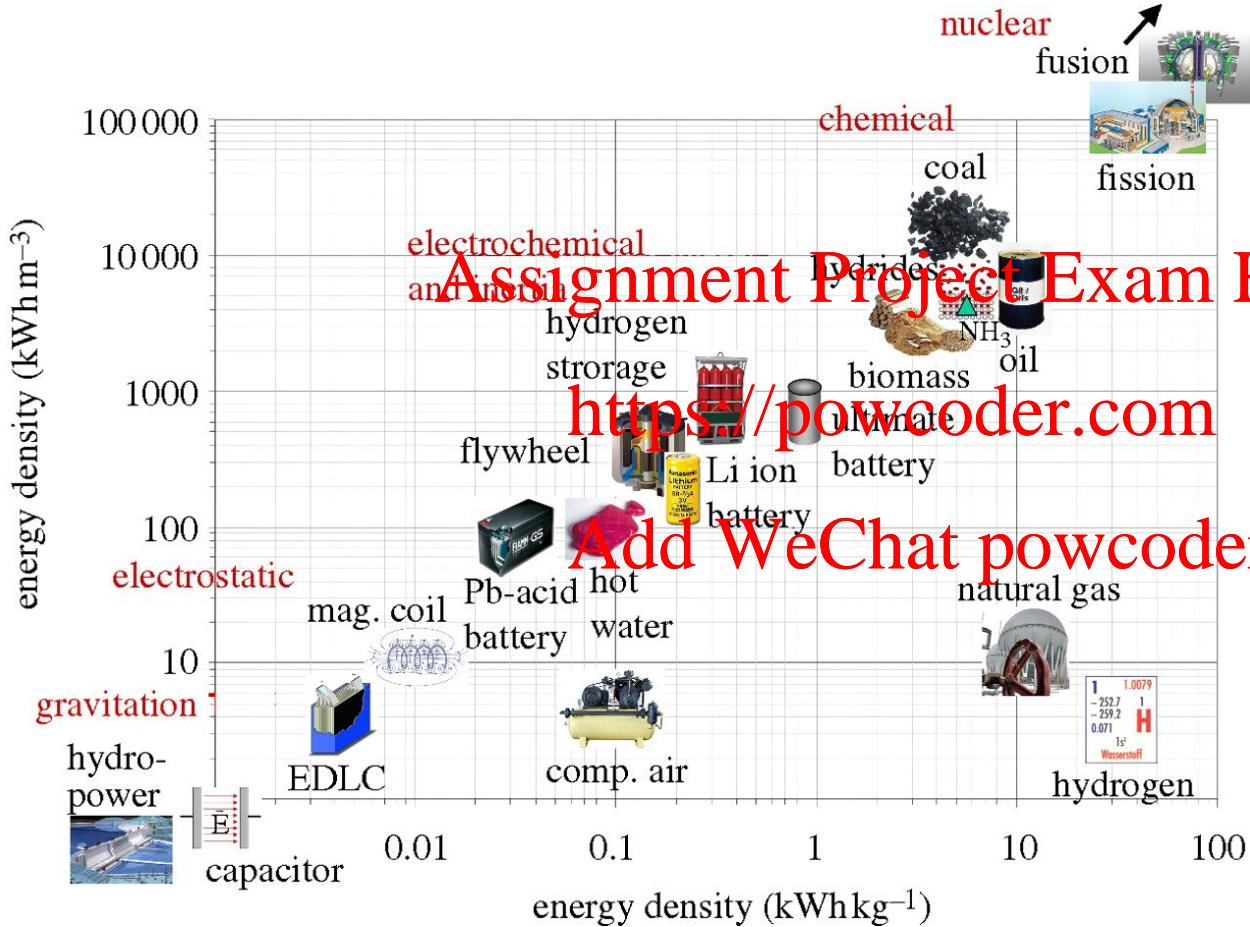
Hydrogen Refuelling Station



Hydrogen Energy Density



Hydrogen Storage



Hydrogen Storage: The best way?

Technique	Volume kg H ₂ /m ³	Mass %	Pressure atm	Temperature °C	Cost
Compressed Gas	39.2	5.4	700	25	Low
Liquid Hydrogen	71	100	1	-253	Modest
Porous Materials	20	4	70	-200	Modest
Metal Hydrides	150	3	30	25	High
Complex Hydrides	150	10	30	300	Modest
Hydrolysis	100	10	1	25	High

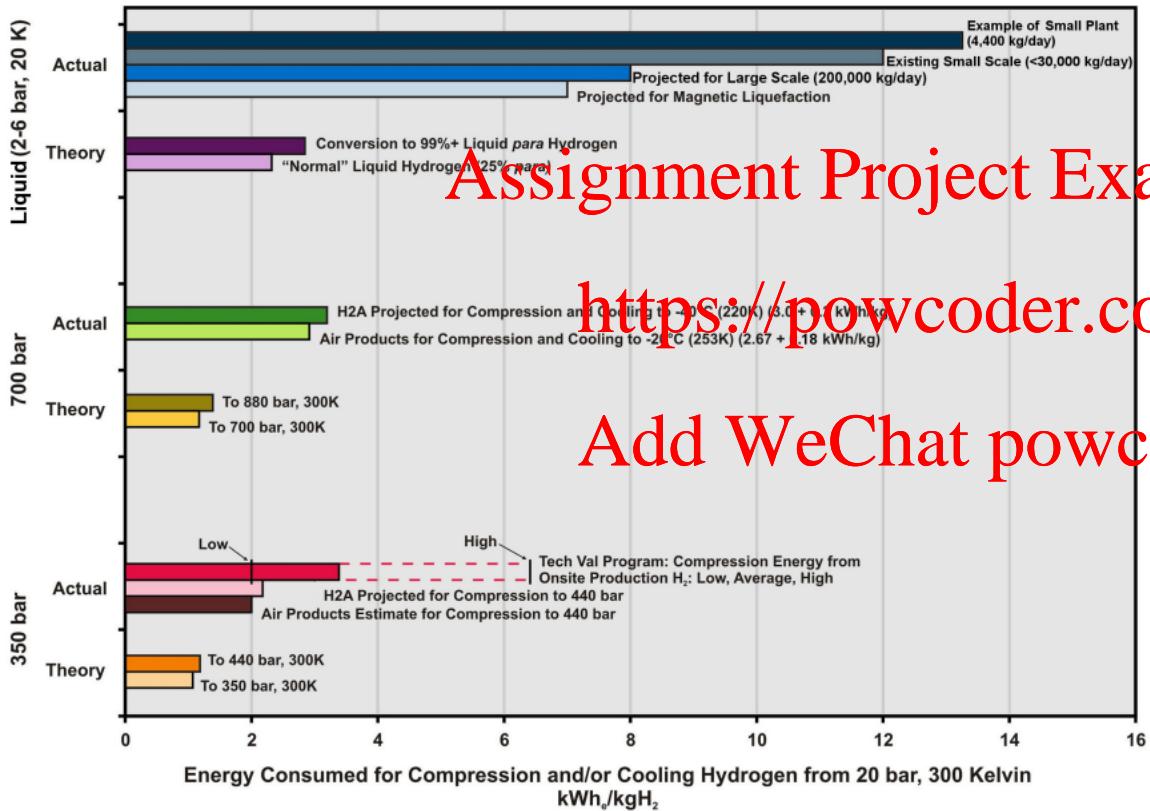
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Hydrogen Storage – High Pressure

Figure 1: Energy Required for Vehicle Storage of Hydrogen in Different Thermodynamic States



Hydrogen has an energy density of 33.33 kWh/kg.

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Energy Loss on compression/cooling

Liquefaction – 36%

700 bar compression – 9%

Must consider energy required to store hydrogen and release it.



Learning Outcome Check

- Calculate and compare the mass of different fuels required to achieve the same heating duty.
- List 5 techniques used to store hydrogen. Comment on their relative temperatures and pressures, and cost.

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Hydrogen storage for mobile
and stationary applications

Thermal Batteries

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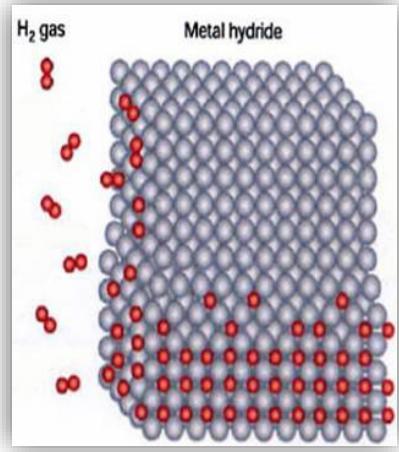
Research Directions

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Hydrogen Export

Solid State Electrolytes

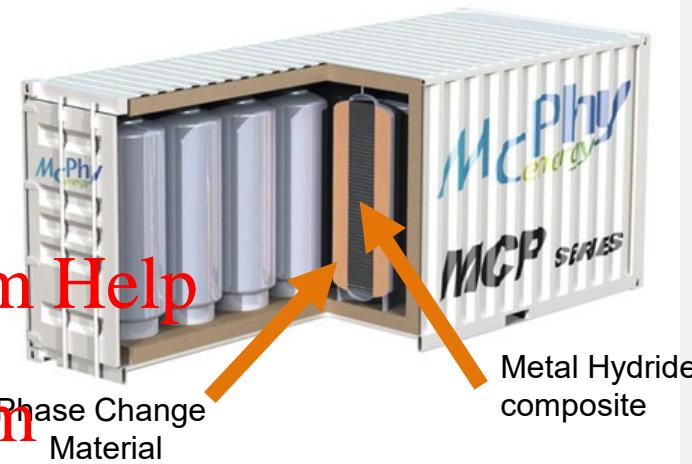
Mobile and Stationary Applications



Vehicular Applications



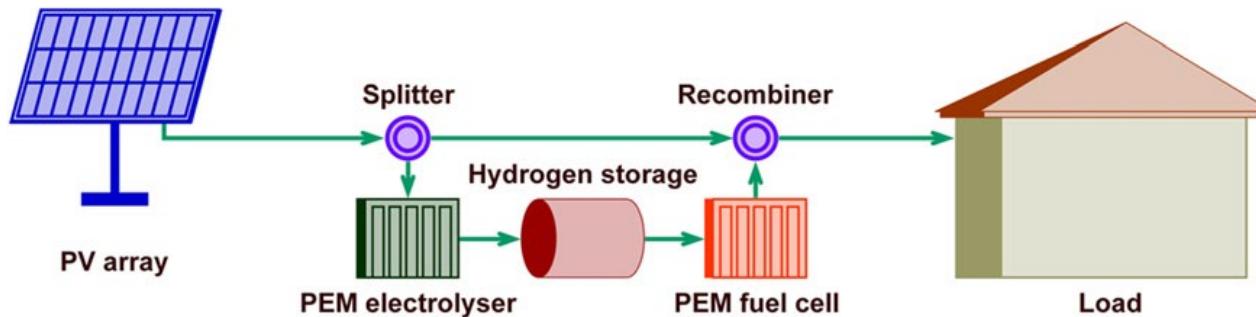
Remote Energy Applications



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Toyota Mirai
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Green Hydrogen for Road Transport in Western Australia - Future Energy Exports Cooperative Research Centre (CRC)

- Partners: Sustainable Built Environment National Research Centre (through its partners MRWA, BGC Australia and ATCO), Curtin University and UWA.

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- 3 year project. Total Budget: \$805 k.

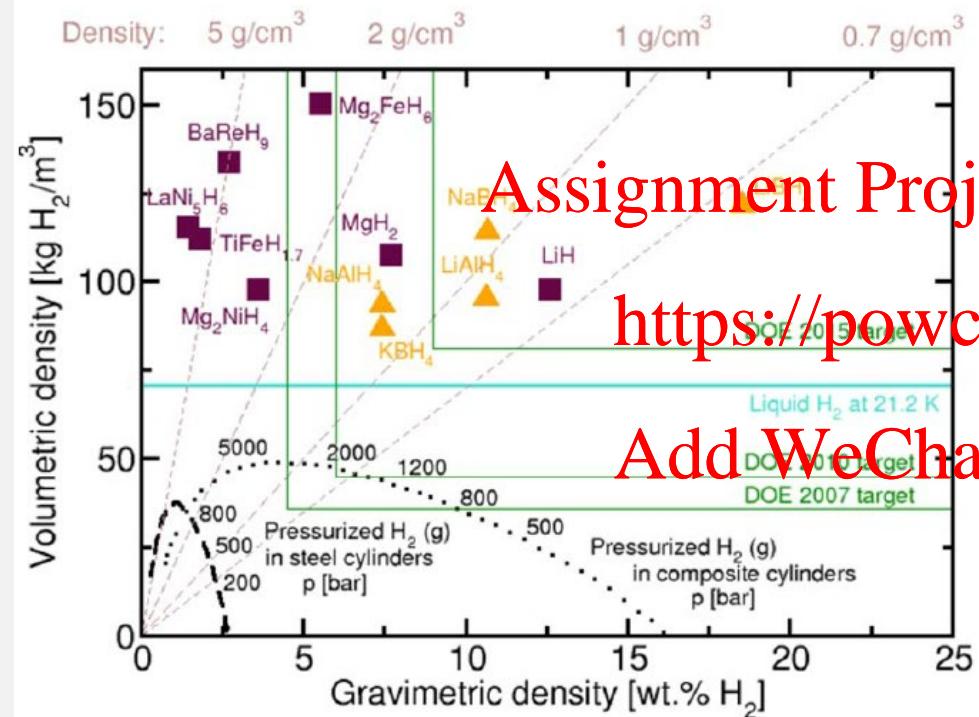
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- Review on Green hydrogen for heavy transport applications and techno-economic analysis for the deployment of the required infrastructure in WA.
- Execution of the demonstration trial including deployment of a 5 ton maintenance truck and a 29 ton concrete agitator truck operating in the Midwest and Perth regions.
- Data collection and analysis according to the defined metrics to evaluate the performance of the vehicles and refuelling stations.

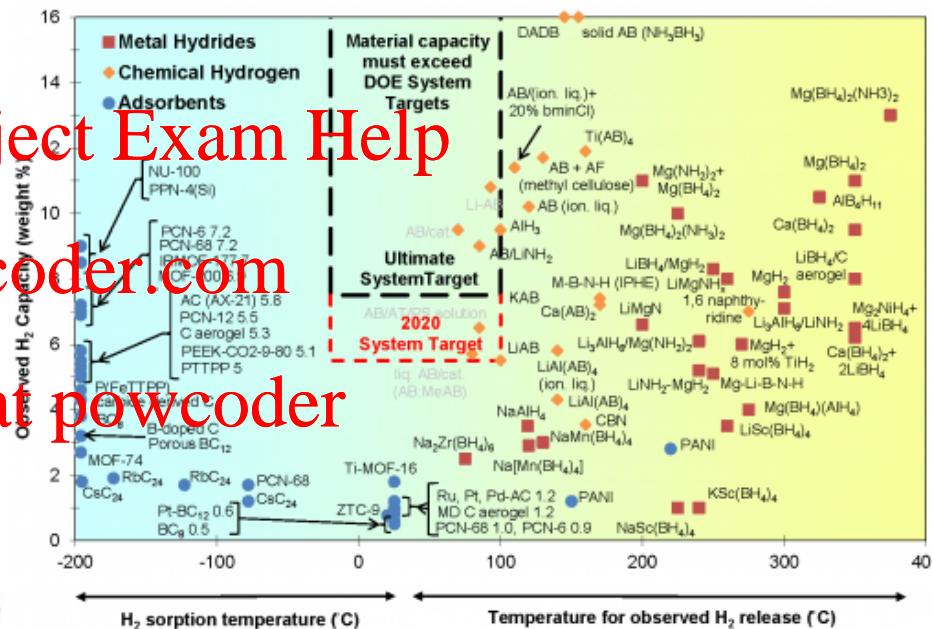
Hydrogen Storage in Powders



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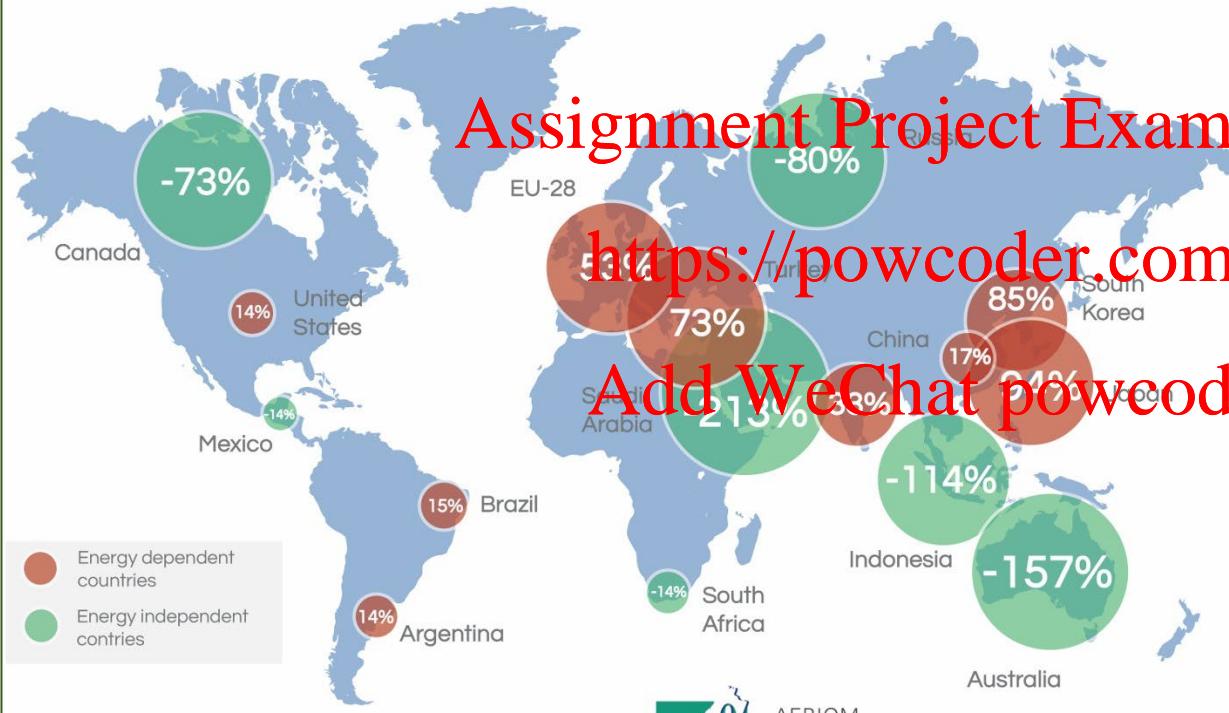
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Hydrogen Export from Australia



World map of the energy dependency
(in 2013, %)



Hydrogen gas takes up too much volume for export.

Options:

- Liquid ammonia
- Liquid organic hydrogen carriers
- Liquid hydrogen
- Solid-state metal hydride

International Export of Hydrogen

- Japan utilised renewable hydrogen for the 2021 Olympic Games
- Currently doesn't have infrastructure for mass production of H₂
- Australia uniquely positioned to become H₂ export leader
- Australian Government and Chief Scientist have also now suggested hydrogen as a future energy export vector to global markets

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- Correct choice of export material must be made
- Dependent on conditions, volume density, H₂ release and cost

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Hydrogen carrier	Transport conditions	Volumetric density of H ₂ (kg/m ³)	Conditions for H ₂ release
Gaseous H ₂	25 °C (100 bar)	7.7	25 °C
Gaseous H ₂	25 °C (700 bar)	39.2	25 °C
Liquid H ₂	-253 °C	71.3	25 °C
Liquid NH ₃	25 °C (10 bar)	107.1	400 – 500 °C
Dibenzyl toluene	25 °C	57.0	300 °C
Solid State Hydride	25 °C	< 115.0	25 °C in water

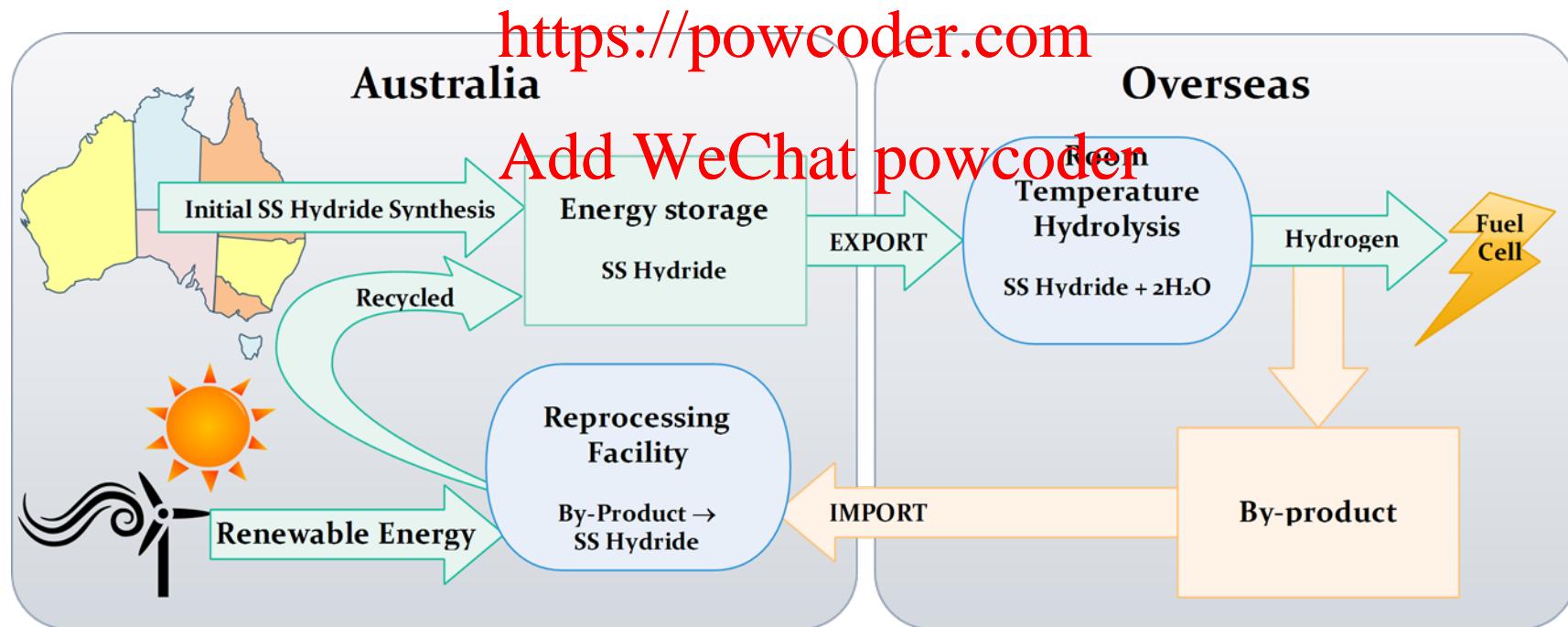


A Solid State Hydride as a H₂ export medium

- Key questions:
 - Can we manufacture large quantities of a solid state (SS) hydride in Australia?
 - How will it be transported?
 - How will H₂ be released?
 - Can we regenerate in high yields?
- A regenerative cycle has been identified

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Thermal Battery Research Assignment Project Exam Help based on Metal Hydrides and Metal Carbonates

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High Temperature Metal Hydrides for

Concentrated Solar Thermal Energy Storage

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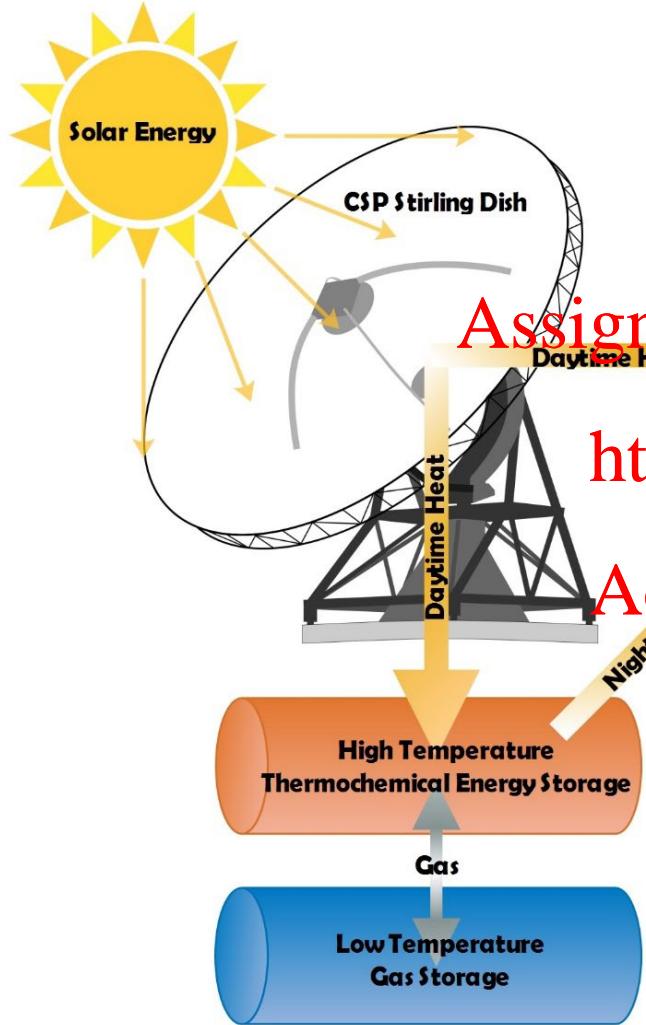
Current Technologies



- Most current CST systems use the simplest method, sensible heat storage, and the predominant materials used are binary (60% NaNO_3 ; 40% KNO_3) molten salt mixtures.
- Solar Millenium's 50 MW Andasol I plant with 7.5 hours storage uses 28,500 tonnes of molten salt

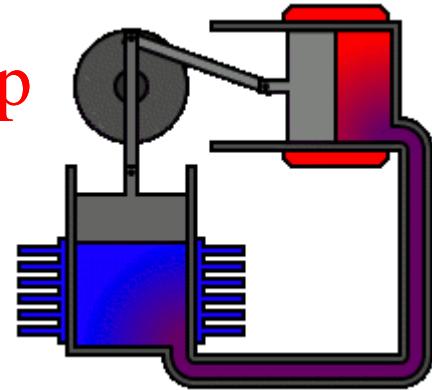
Type of thermal energy storage (TES)	Example of TES material	Total heat storage capacity (kJ/kg)
Sensible heat	Molten salt mixtures	153 per 100°C
Latent heat / phase change materials	NaNO_3	282
Thermochemical	Oxidation of Co_3O_4	1055
Metal Hydride	$\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$	2814

CSP Stirling Dish



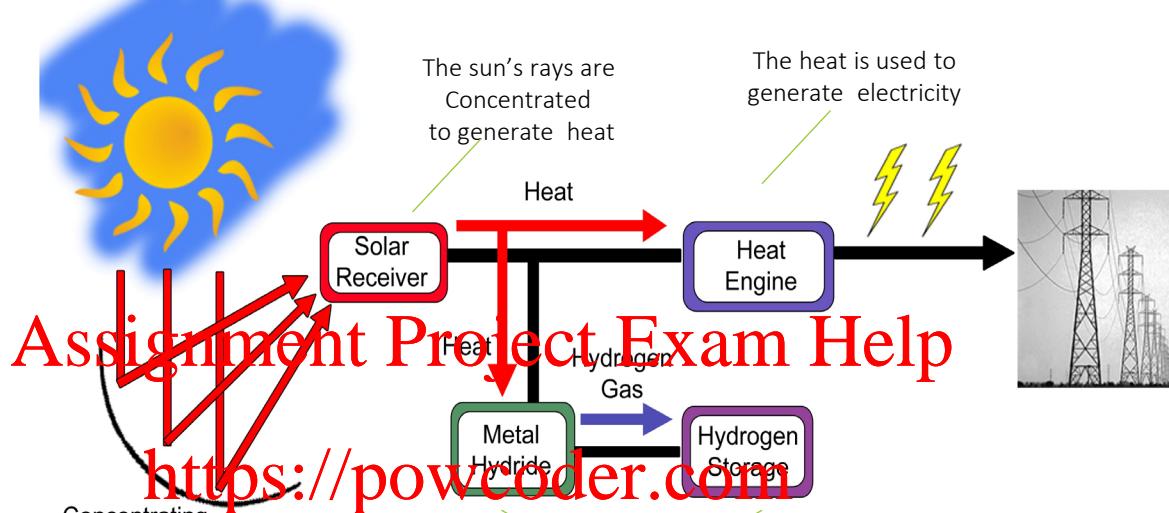
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Stirling Engine

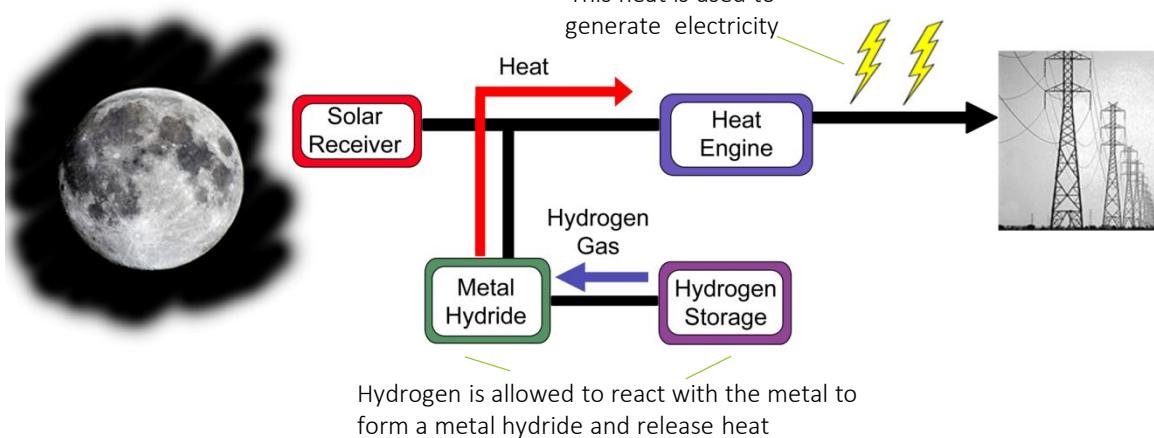


Solar Thermal Batteries - Hydrogen

During the Day



At Night



Australia

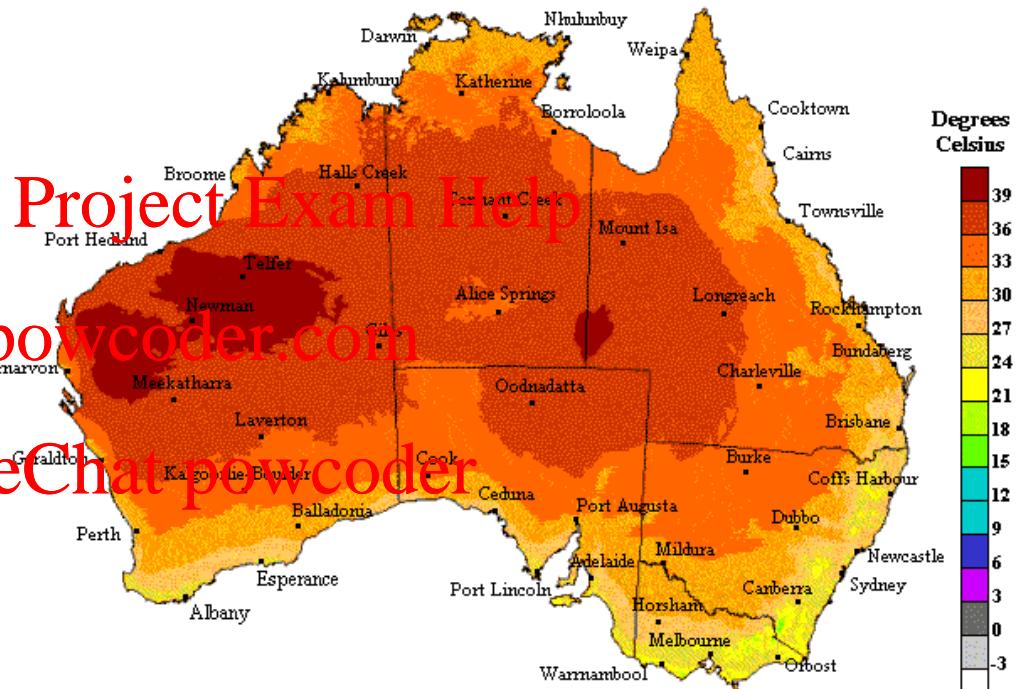


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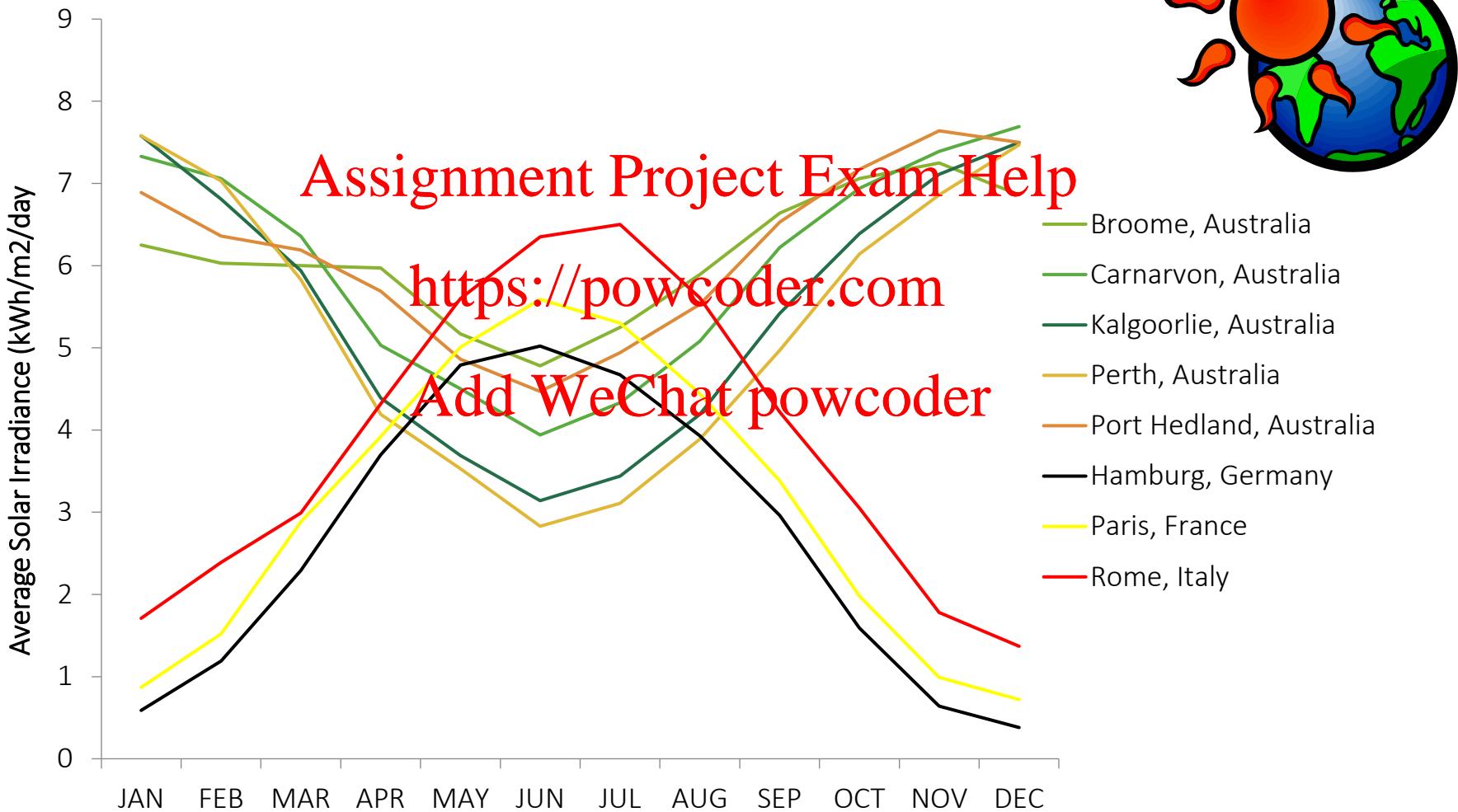
Mean Maximum Temperature - January



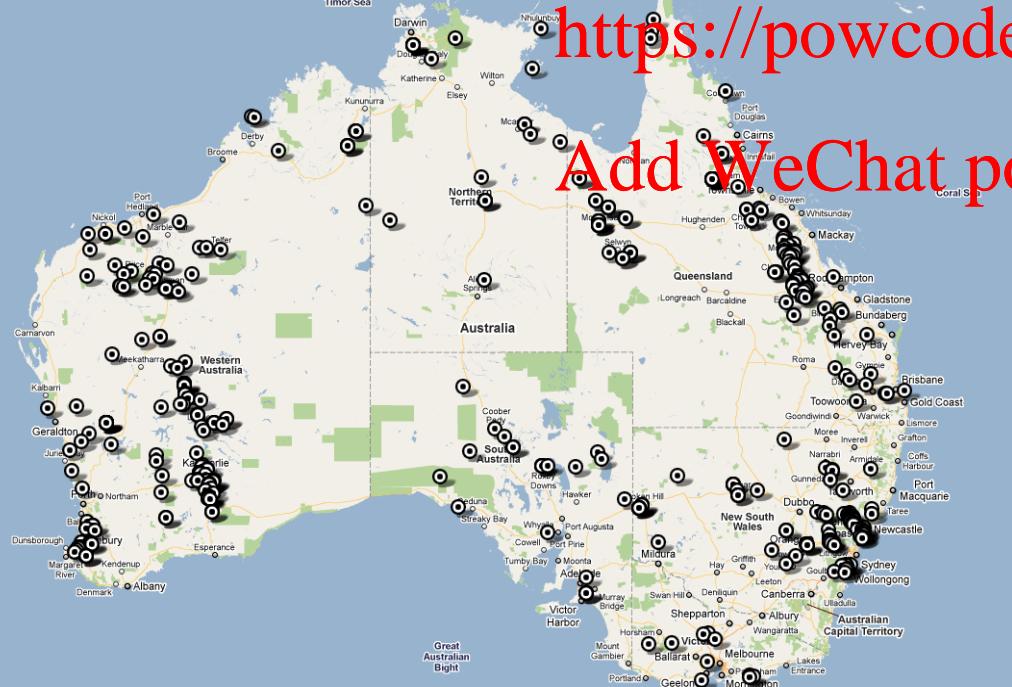
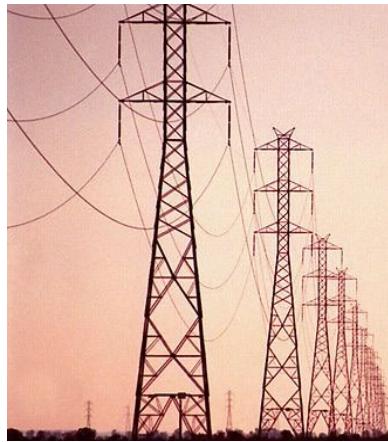
Based on a standard 30 - year climatology (1961 to 1990)

Copyright Commonwealth of Australia, Bureau of Meteorology

Average Solar Irradiance



Mining in Australia



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Remote Area Power

Critical problem for remote area operations: Mining, Communities

The majority of remote mines cannot be connected to the power grid

All the electricity must be generated on-site

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Diesel Generators – 2.2 MW each!

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Remote Area Power

Electricity demand (typical mine site):

- Peak demand: 5 – 650 MW
- Fluctuating demand – peak during day
- High reliability required (auxiliary back-up is essential)

J. Paraszcak and K. Fytas, ICREPQ'12, Spain 2012

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Diesel typically must be transported by trucks, adding to its consumption.

<https://powcoder.com>

The iron ore industry

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in Western Australia

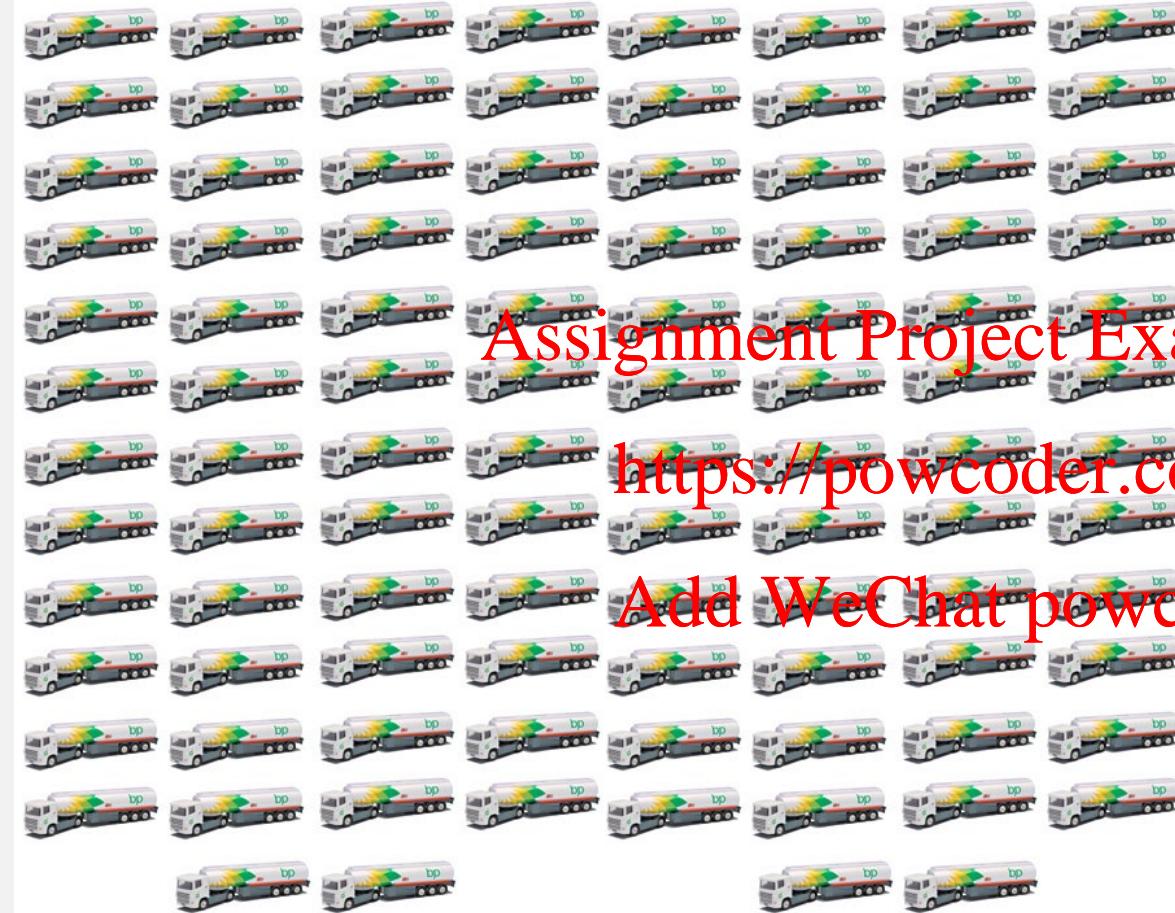
consumes in excess of a 3 million litres of diesel

each DAY!!!

S. S. Shastri – Australia's Mining Thirst, GHD Perth, 2012



Diesel Usage



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Diesel powered power plants
30 – 40 c/kWh

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Solar thermal is more than competitive. CSP plant 13.5 c/kWh

High Temperature Metal Hydrides

Revisit high temperature materials that have been mostly overlooked

Material

Temperature

Enthalpy (kJ/mol H₂)

YH₃

> 1200 °C

220

CaH₂

> 950 °C

208

LiH

> 900 °C

134

ZrH₂

> 800 °C

212

TiH₂

> 700 °C

164

NaMgH₃

> 400 °C

87

Q. Lai, M. Paskevicius, D.A. Sheppard, C.E. Buckley, A.W. Thornton, M.R. Hill, Q. Gu, J. Mao, Z. Huang, H.K. Liu, Z. Guo, A. Banerjee, S. Chakraborty, R. Ahuja, K.F Aguey-Zinsou. "Hydrogen storage materials for mobile and stationary applications: Current state of the art." *ChemSusChem*, **8** (2015) 2789 – 2825.

D.A. Sheppard, M. Paskevicius, C.E. Buckley, M. Felderhoff, R. Zidan, D.M. Grant, M. Dornheim et al. "Metal hydrides for concentrating solar power energy storage" *Applied Physics A* **122:395** (2016) 1 – 15.

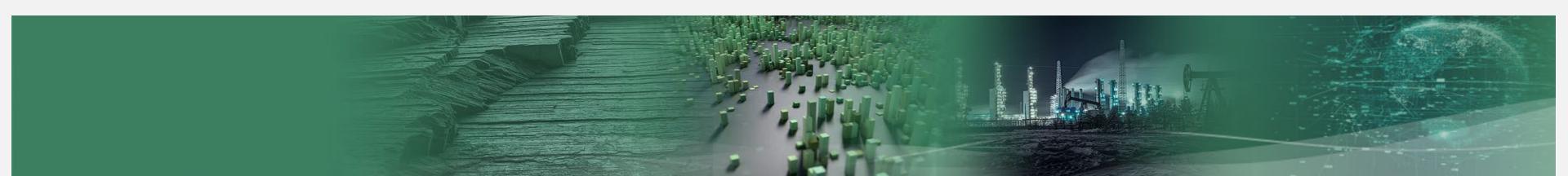
P.A. Ward, C. Corgnale, J.A. Teprovich Jr., T. Motyka, B. Hardy, D.A. Sheppard, C.E. Buckley, R. Zidan. "Technical challenges and future direction for high-efficiency metal hydride thermal energy storage systems" *Applied Physics A* **122:462** (2016) 1 – 10.

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Materials	Theoretical Heat Storage Capacity (kJ/kg)	Operating Temperature (°C)
Sensible Heat		
$\text{NaNO}_3/\text{KNO}_3$	153 per 100 °C	290 - 565
Metal Hydrides		
$\text{Mg}_2\text{NiH}_4 \leftrightarrow \text{Mg}_2\text{Ni} + 2\text{H}_2$	1162	250 - 400
$\text{MgH}_2 \leftrightarrow \text{Mg} + \text{H}_2$	2811	300 - 400
$\text{Mg}_2\text{FeH}_6 \leftrightarrow 2\text{Mg} + \text{Fe} + 3\text{H}_2$	2096	350 - 550
$\text{NaMgH}_3 \leftrightarrow \text{NaH} + \text{Mg} + \text{H}_2$	1721	430 - 585
$\text{NaMgH}_3 \leftrightarrow \text{Na} + \text{Mg} + 1.5\text{H}_2$	2881	> 585
$\text{TiH}_{1.7} \leftrightarrow \text{Ti} + 0.85\text{H}_2$	2842	700 - 1000
$\text{CaH}_2 \leftrightarrow \text{Ca} + \text{H}_2$	4934	> 1000
$\text{LiH} \leftrightarrow \text{Li} + 0.5\text{H}_2$	8397	> 850

M. Fellet. Feature Editors C.E. Buckley, M. Paskevicius, D.A. Sheppard *MRS Bulletin* **38** (2013) 1012 – 1013.

K. Manickam, C.E. Buckley et al. *International Journal of Hydrogen Energy*, **44** (2019) 7738 – 7745.

L. Poupin, C.E. Buckley et al. *Sustainable Energy & Fuels*, **3** (2019) 985 - 995.

T.D. Humphries, C.E. Buckley et al. *Journal of Physical Chemistry C*, **124** (2020) 5053 - 5060.



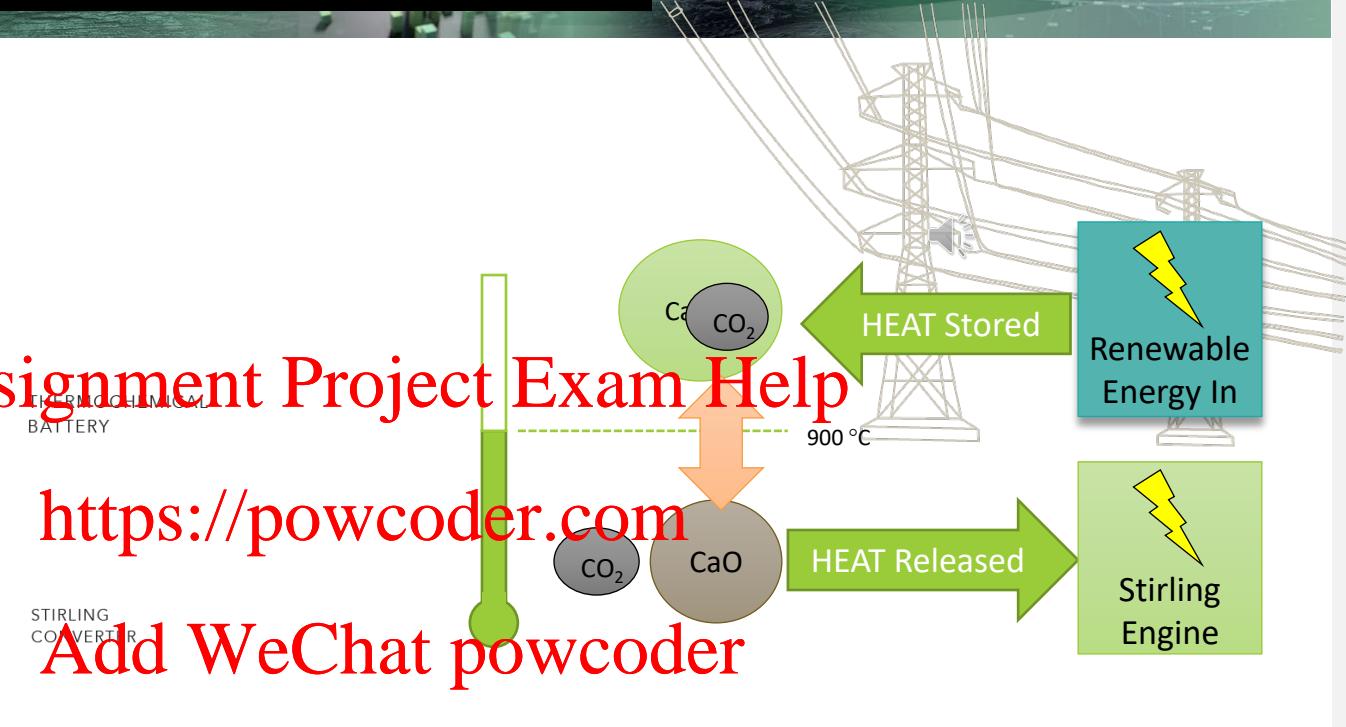
The CO₂ Thermal Battery



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- Chemical reaction stores and releases heat energy
- Controlled using gas pressure
- Electricity in – Electricity out

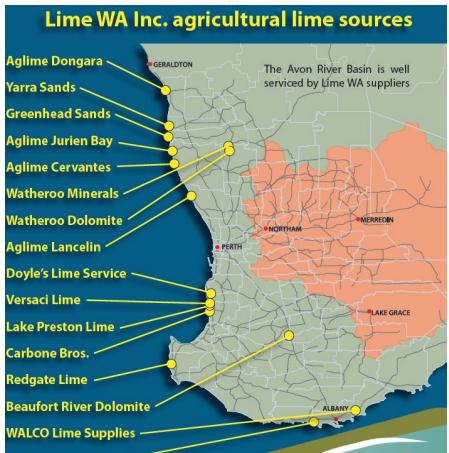
Chalk



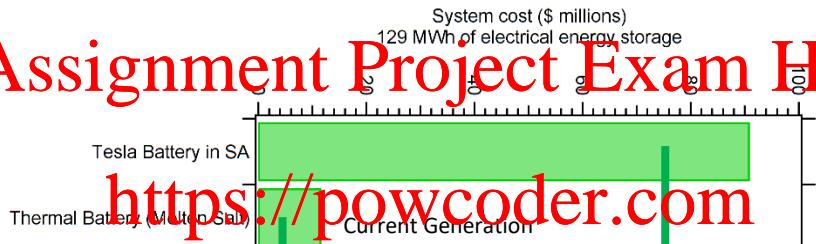
Thermal Battery Price

Limestone (CaCO_3) is the primary ingredient **\$5 - 10 per tonne**

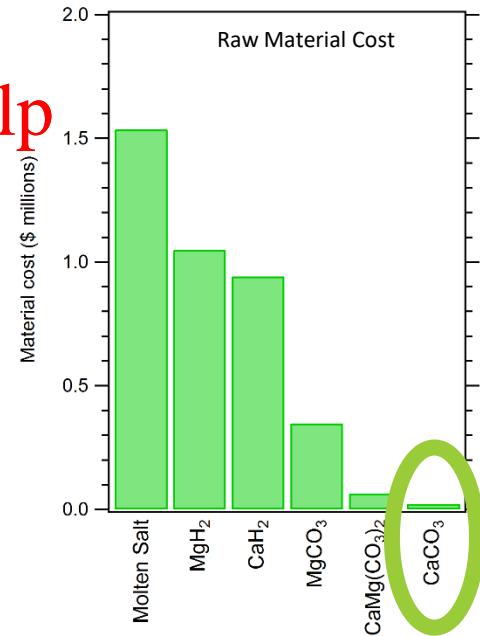
Literally DIRT cheap



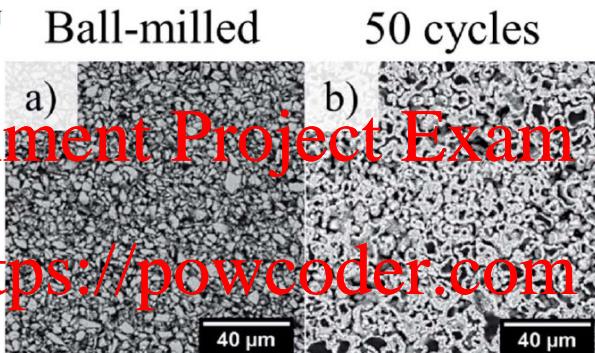
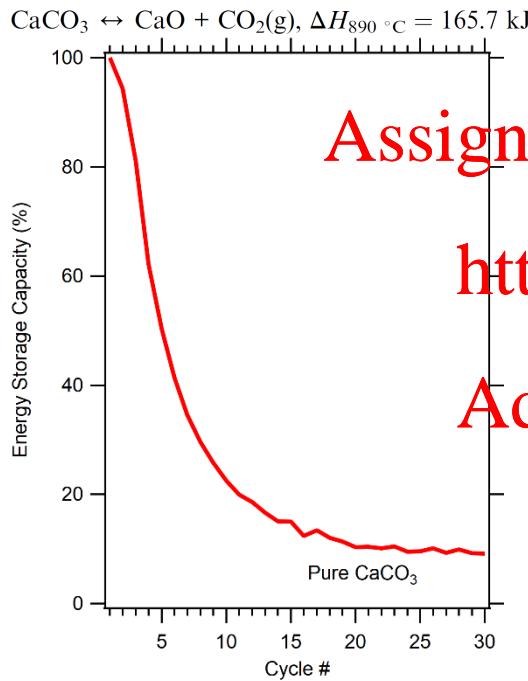
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So why has this not already been done?



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Catalyst Development

500 cycles → 90% capacity retention

Catalysts are expensive...

Al_2O_3 is cheap! \$324/tonne



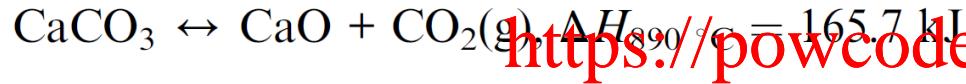
J. Mater. Chem. A, 2020, 8, 9646–9653



Breakthrough for
Thermal Battery
Lifetime

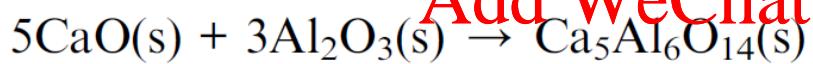
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Thermochemical reaction (energy storage/release)

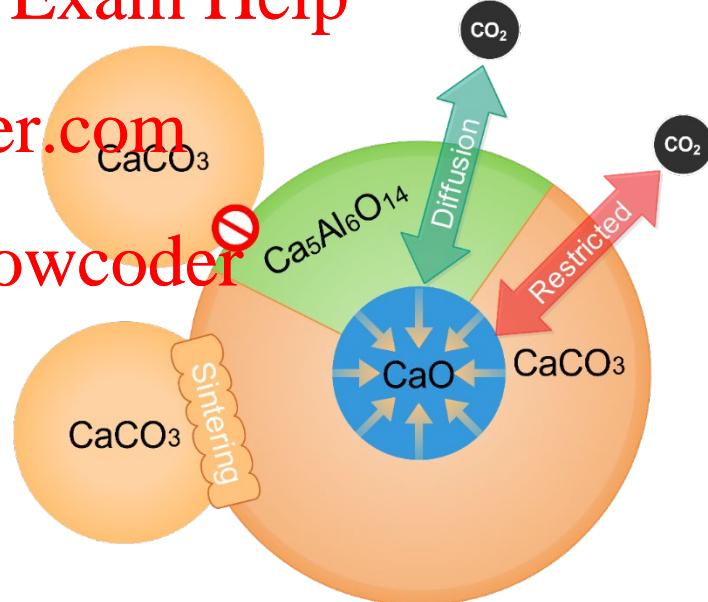


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Catalyst formation (only occurs once)



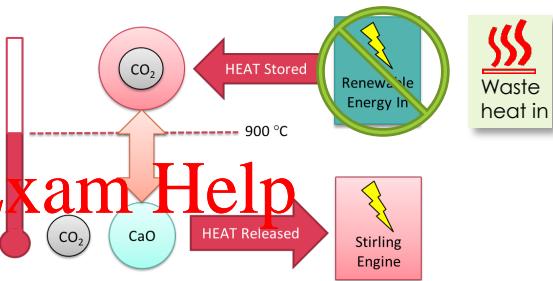
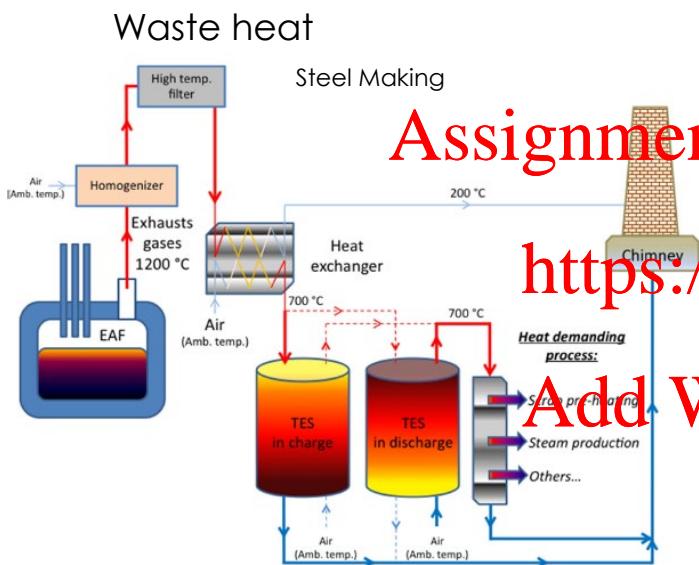
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- Innovation and novelty is: working catalyst
- Patent has been submitted
- Optimisation and upscaling of technology in-progress

J. Mater. Chem. A, 2020, 8, 9646–9653

CaCO_3 for other Applications



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Table: Typical waste heat temperature at high temperature range from various sources

Type of Device	Temperature (°C)
Nickel refining furnace	1370 – 1650
Aluminium refining furnace	650 – 760
Zinc refining furnace	760 – 1100
Copper refining furnace	760 – 815
Steel heating furnace	925 – 1050
Copper reverberatory furnace	900 – 1100
Open hearth furnace	650 – 700
Cement kiln (Dry process)	620 – 730
Glass melting furnace	1000 – 1550
Hydrogen plants	650 – 1000
Solid waste incinerators	650 – 1000
Fume incinerators	650 – 1450

Applied Energy 237 (2019) 708–719

The Future for Hydrogen and Thermal Batteries

- Multiple applications for hydrogen = Variety of storage solutions.
- Small mobile storage (e.g. cars) → High pressure compressed gas tanks. 5 kg H₂ at 700 bar = 127.5 L.
- Medium mobile storage (e.g. trucks, buses) → Gas tanks, 50 kg H₂ at 350 bar = 2150 L.
- Large scale stationary storage (e.g. Hydrogen refuelling station, plant storage).
- Hydrogen will move forward in Australia as an energy carrier. It needs to be paired with renewables so that it carries clean energy.
<https://powcoder.com>
- Hydrogen can be used in Australia as a fuel or exported – new export industry.
- Hydrogen in metal hydrides can be used for heat storage to produce electricity 24/7.
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- Thermal batteries can also be developed using CO₂ for heat storage.
- Some technical challenges to improve technology cost / efficiency / performance. However, hydrogen can be used **today!**

Learning Outcome Check

- Understand the term *thermal battery* and how it can provide a solution for energy stability.

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Lecture Summary

✓ Solar Power and Hydrogen

✓ Why Hydrogen?

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✓ Hydrogen Storage Research Group (HSRG) Projects

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✓ Conclusion

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Thanks for Listening

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Any Questions?

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