Process Hazard Analysis
Alternate Hydrogen Production Methods

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Introduction

With the increasing population, energy demand has also been increasing. As the first law of thermodynamics states, ‘energy can neither be created nor destroyed, it can only be converted from one form to another.’ Determining which source of energy is the most reliable one has always been a major topic of debate. When a thought arises about any energy source, one has to think of production, transportation, storage, and end-use. Although the topic of a reliable source of energy is debatable, the winner for reliable energy carriers is always hydrogen. The fundamental value of hydrogen as an energy carrier resides in its ability to store electrons and chemical energy in bonds while also being carbon-free. It is expected that hydrogen will play a major role in decarbonizing the energy sector as countries around the globe strive to meet the commitments of the 2015 Paris Agreement, which limits global warming to below 2°C[1]. The topic of debate now is the most reliable process to produce hydrogen. With the potential for near-zero greenhouse gas emissions, hydrogen can be produced from diverse resources. Electrical power can be generated in a fuel cell emitting only water vapor and warm air using the hydrogen produced as input. Determining the most optimal means of production of hydrogen has become a major topic of discussion. This work is about the hazards associated with the few most promising hydrogen production methods for the future.

The scope of this project has been decided upon review of many papers mentioned in the references and discussion with industry professionals. The scope of this project entails:

- Develop a consolidated chart for current and upcoming hydrogen production capacities.
- Develop PHA for Alkaline Electrolysers.
- Develop PHA for SOEC.

About Hydrogen

As explained in Figure 1[2], hydrogen is the lightest of all elements and it contains just an electron and a proton when stable. In its liquid form, hydrogen has a very high tendency to leak due to low viscosity and molecular weight. Pure water is the most abundantly available source of hydrogen. Due to high chemical reactivity, very pure elemental hydrogen occurs in very small quantities. When evaluating a new energy source/carrier, it is essential that we thoroughly know about the element.

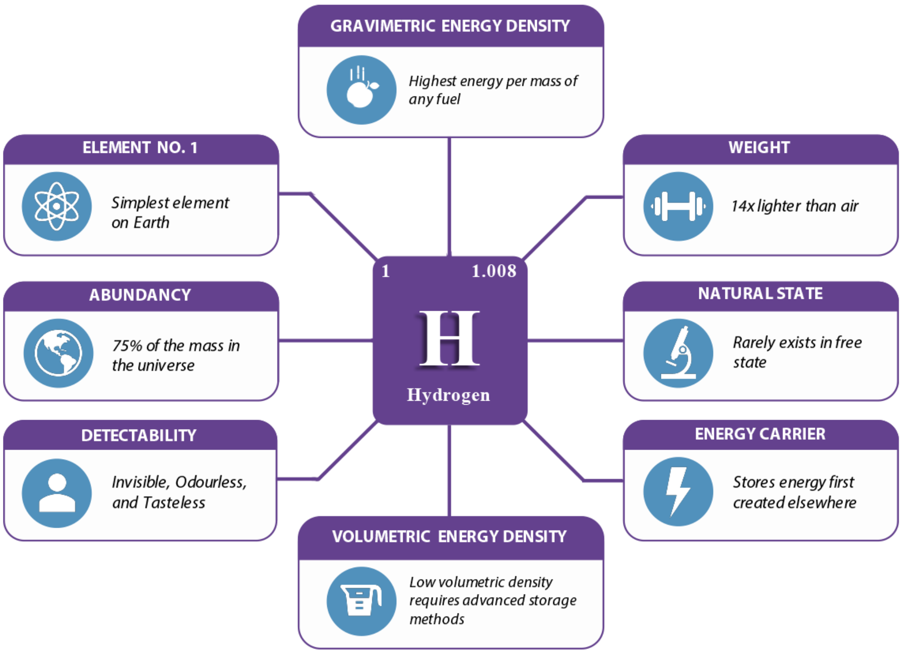


Figure 1 Hydrogen basics[2]

Diatomic hydrogen has several unique characteristics which might pose a challenge when engineers design production units or storage tanks or transportation channels. It has the second lowest boiling point of all elements and at standard temperature and pressure, it has a negative Joule Thomson coefficient. This implies that, hydrogen heats upon isenthalpic expansion.

Hydrogen has the potential to burn at elevated temperatures with no greenhouse gas emissions, making it a viable green energy source. But this advantage has got a lot of safety concerns associated with it. ~84% of the recorded accidents that involved hydrogen involved a fire or explosion due to its very wide flammability range. Gaseous hydrogen combusts in nearly all fuel-air mixtures and at extremely low temperatures. Flame speeds of hydrogen are much higher than those of any hydrocarbon fuel[3,4].

Review of Relevant Literature

Governments and companies across the globe have established and are continuing to establish visions and plans for hydrogen. In years to come, hydrogen will play an important role in the transition to net zero emissions.

Hydrogen Type	Source	Method
Grey Hydrogen	Fossil Fuels (NG/Coal)	Pyrolysis
		Gasification
		Coal gasification
		Steam Reforming
		Membrane Reactors
		Partial oxidation
		CO2 Dry Reforming
Blue Hydrogen	Fossil Fuels but CO2 sequestrated	Coal gasification
		Steam Reforming
		Membrane Reactors
Green Hydrogen	Hydrogen produced from electricity of renewables	Electrolysis
Black Hydrogen	Bituminous Coal	Coal gasification
Brown Hydrogen	Lignite	
Red Hydrogen	Water	high-temperature catalytic splitting of water using high temperature
Pink Hydrogen	Water & Nuclear Power	Electrolysis
Yellow Hydrogen	Water & Solar Power	

Table 1 Types of hydrogen[6]

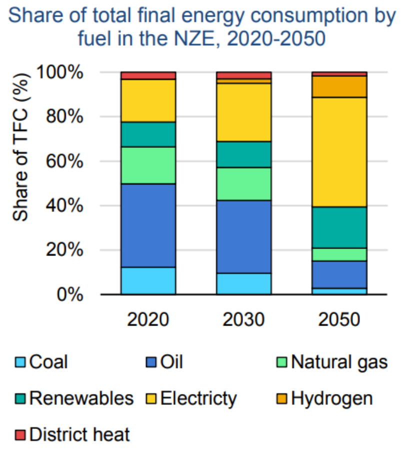


Figure 2 Projected energy consumption based on source[5]

As per the figure 2[5], a very minimal (not even visible in the graph <1%) amount of the energy is currently from hydrogen but by 2050, hydrogen is forecasted to be ~10% of the Total Final Consumption (TFC) of energy. Government and corporate companies play a very significant role in taking the initiative to keep hydrogen-based economy a prime aspect of research and implementation.

Based on the raw material and technology used, the type (colour) of hydrogen is decided. Table 1[6] is a glimpse of the colour/source of hydrogen along with its corresponding raw material and the technology used to produce. In 2020, as shown in figure 3[5], ~85% of the hydrogen produced was using fossil fuels, meaning it is either grey or blue hydrogen. In 2030, it is predicted that blue hydrogen and yellow hydrogen would have equal share in production but by 2050, yellow hydrogen is thought to be the clear winner. There are many ways to produce H_2, but the question is about efficiency, yield quality, ease of implementation and safety. In table 2[6,7], there are ~ 26 ways of hydrogen production listed. Each mode of production has a different feedstock, technology, efficiency and maturity levels. Maturity level is an indication of how well a technology is established with 0 being early stages to 10 being commercialised. The most familiar and popular method of production today is producing from fossil fuels and hydrocarbons (coal, methane, natural gas) using gasification and reforming techniques. With focus of net zero emissions, these methods continue to be the most feasible methods when combined with carbon sequestration methods. In 2021, ~62% of the hydrogen produced was produced from natural gas without carbon sequestration and ~19% from coal (figure 4[5]). Hydrogen produced using net zero emissions principles attributed to ~<1% of the total hydrogen produced.

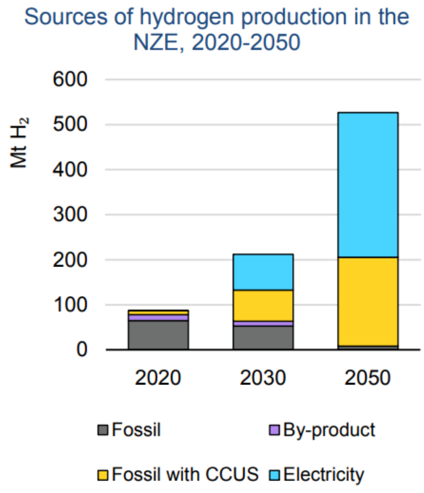


Figure 3 Projected net zero emission-based hydrogen production[5]

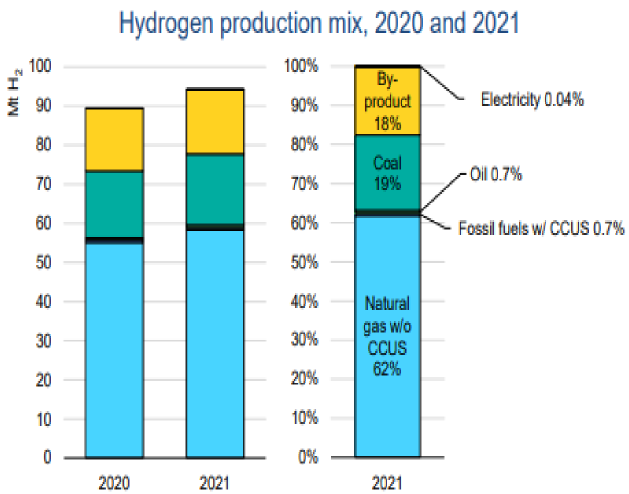


Figure 4 Current hydrogen production share[5]

Some parts of the world in recent years have started using alkaline electrolysis technology to produce hydrogen. In this project, we are only going to examine hazards associated with producing hydrogen using Alkaline electrolysis (the most popular method today) and Solid Oxide Electrolyser Cell (SOEC) (the most efficient and promising method for the future).

Process Category	Energy	Feedstock	Technology	Efficiency	ML (1-10)
Electrolysis	Electric	Water	Alkaline Electrolysis (AE)	62-82%	9
		Brine	Polymer Electrolytic Membrane (PEM)	67-84%	7
			Solid-electrolyzer Oxide Cell (SOC)	75-90%	3
			Chlor-alkali		
Electro-photolysis	Electric-Photonic	Water	Photoelectrochemical	0.5-12%	1
Photolysis	Photonic	Water/Algae	Photosynthesis	1.6-5%	1
Biophotolysis	Bioenergy	Micro-algae	Photo-fermentation	<1%	1
	Photonic	Bacteria	Algal Hydrogen	1-3%	1
		Fat			1
		Nutrients		2-7%	1
		Bio-mass		12-14%	1
Bioelectrolysis	Bioenergy	Bio-mass	Microbial Electrolysis	70-80%	1
	Electric	Hydrogenases	Nitrogen Fixation	10%	
Biolysis	Bioenergy	Micro-organism	Dark Fermentation	60-80%	3
		Fermentative Bacterias	Hydrolysis		2
		Biomass+Water	Aqueous Phase Reforming	35-55%	5
		CO+Water	Biological Shift Reaction		2
Bio-thermolysis	Bioenergy-Heat	Biomass (acid penetrated)	Co-fermentation hydro thermal	35-45%	2
Thermolysis	Heat	Water	Waterthermolysis	20-55%	1
		Biomass	Pyrolysis	35-50%	8
		Biomass	Gasification	35-50%	10
		Coal	Coal gasification	74-85%	10
		Fuels	Steam Reforming	60-85%	10
		Fuels	Membrane Reactors	64-90%	7
		Biomass	Partial oxidation	60-75%	7
		Methane + CO2	Autothermal	60-75%	6
			CO2 Dry Reforming		
Thermo-electrolysis	Heat-Electric	Fuels	Plasma Reforming	9-85%	1
Chemical	Chemical Reaction	Water	Redox		4
		Metals			4
		Metal Hydrides			
		Gas based hydrides			
		Metal Hydroxides			
Radiolysis	Radiation	Hydrogen Peroxide	Radiolysis		1
		Gamma-Radiolysis			
ML - Maturity Level (0 being the least and 10 being highest)					

Table 2 Various hydrogen production methods[6,7,21]

Investments in the electrolyser industry have increased drastically in the last 5 years as shown in figure 5[5]. The world is shifting towards the most scientifically proven electrolysis technology i.e. alkaline electrolysis. 60% of the world's electrolysis techniques today constitute alkaline electrolysis, but it is predicted that in the next 5 years, PEM and alkaline electrolysis will have equal share in the electrolyser-based hydrogen production. SOEC is currently in a very early research stage and is believed to be the most efficient method among all the known electrolyser technologies once implemented. This is one of the reasons why investment in SOEC is the largest of various technologies.

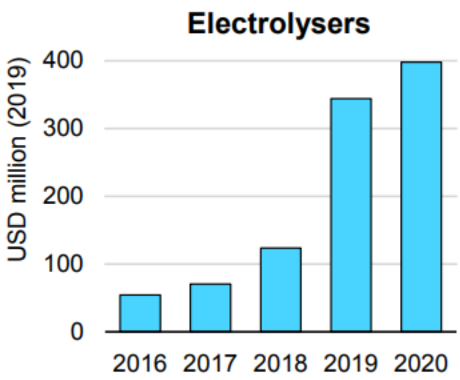


Figure 5 Investment growth in electrolysers[5]

	Alkaline	PEM
Electrolyte	30% wt KOH or 25% wt NaOH solution	Solid Polymer
Current Density (A/m^2)	2000-4000	10000-20000
Work Pressure (Mpa)	<=3.2	<=5
Operating T (^0C)	80-90	50-80
Hydrogen purity (%)	>=99.8	>99.99

	PEM	SOEC
Advantages	Reduced corrosion risk and electrolyte management issues	High efficiency
	Low T and quick start-up	Feed flexibility; low cost
Disadvantages	Expensive catalyst	High corrosion risk and cell component breakdown
	Sensitive to impurities	Long start-up time, S/D required
Power Requirements	52kWh/kg of hydrogen	38kWh/kg of hydrogen

Table 3 Comparing Alkaline, PEM and SOEC electrolysis[8,9,21]

Table 3[8,9] is a comparison between Alkaline, PEM and SOEC electrolysis technologies. In this comparison, Alkaline electrolysis is more cost efficient when the end hydrogen purity required is ~99.8%. However, when ~99.99% pure hydrogen is required, SOEC stands to be the most efficient method both in terms of yield as well as cost.

Data and Results-Part 1

Hydrogen Production Capacities:

This section is about planned electrolyser capacities globally until 2050. (Left Y axis-count; Right Y axis-capacity in nM^3/hr; X axis-countries) (Figure 6-11):

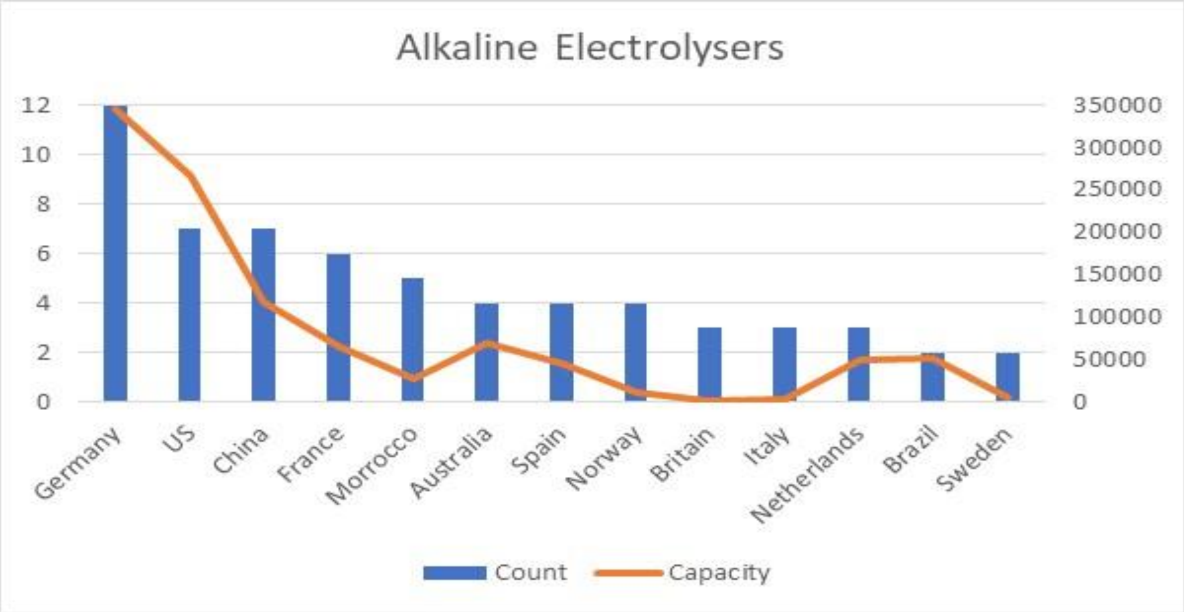


Figure 6 Alkaline electrolysers upcoming capacities[5]

Germany leads the graph for planned alkaline electrolyser capacity to produce hydrogen followed by the US. But when deeply analysed, the average capacity of each project planned is the biggest in the US. (Figure 6[5])

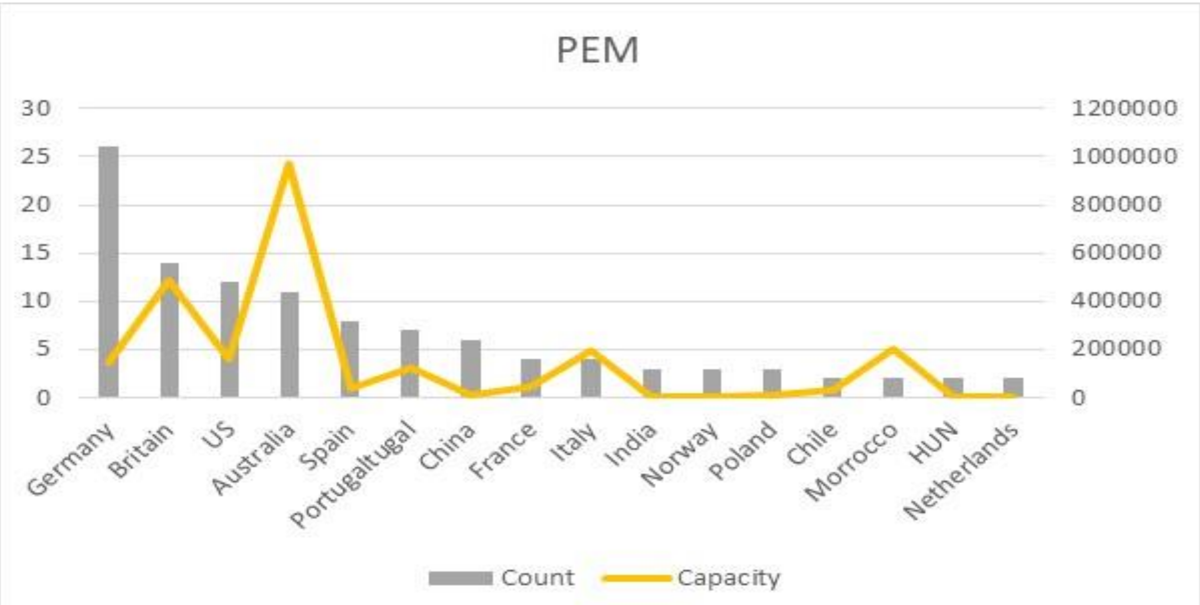


Figure 7 PEM electrolyser upcoming capacities[5]

Germany has the highest number of hydrogen production facility projects planned using PEM technology, however the capacity of each plant is relatively less in comparison to Australia which has about half of the production units planned but 5 times higher production capacity projects planned. (Figure 7[5])

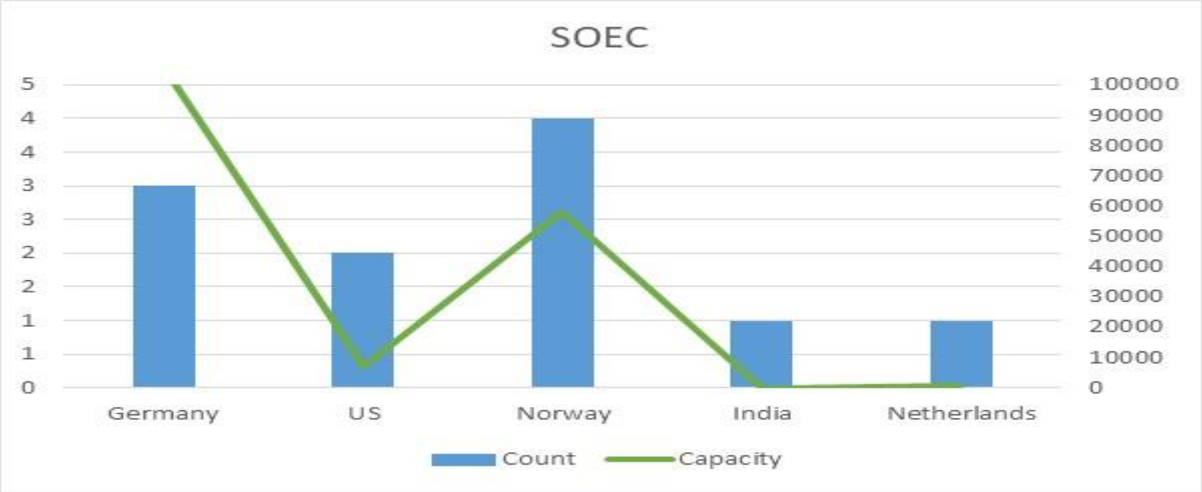


Figure 8 SOEC electrolyser upcoming capacities[5]

SOEC is relatively immature technology and Germany once again leads to have the highest capacity planned to produce hydrogen using SOEC. The reason why the number of planned projects using SOEC technology is in lower single digits is because of lack of space in the vicinity of high temperature sources. SOEC is a viable electrolysis technology only when there is a high temperature source in the surrounding vicinity (e.g. Nuclear). (Figure 8[5])

As shown in figure 9[5], there are a lot of planned facilities, but the technology is yet undecided. The governments across the globe have drafted plans for those capacities but they still are undecided on the technology as they are waiting for SOEC to become more mature. Once proven on a commercial scale, they are going to decide on the technology to be implemented and the heat source to be considered for electricity.

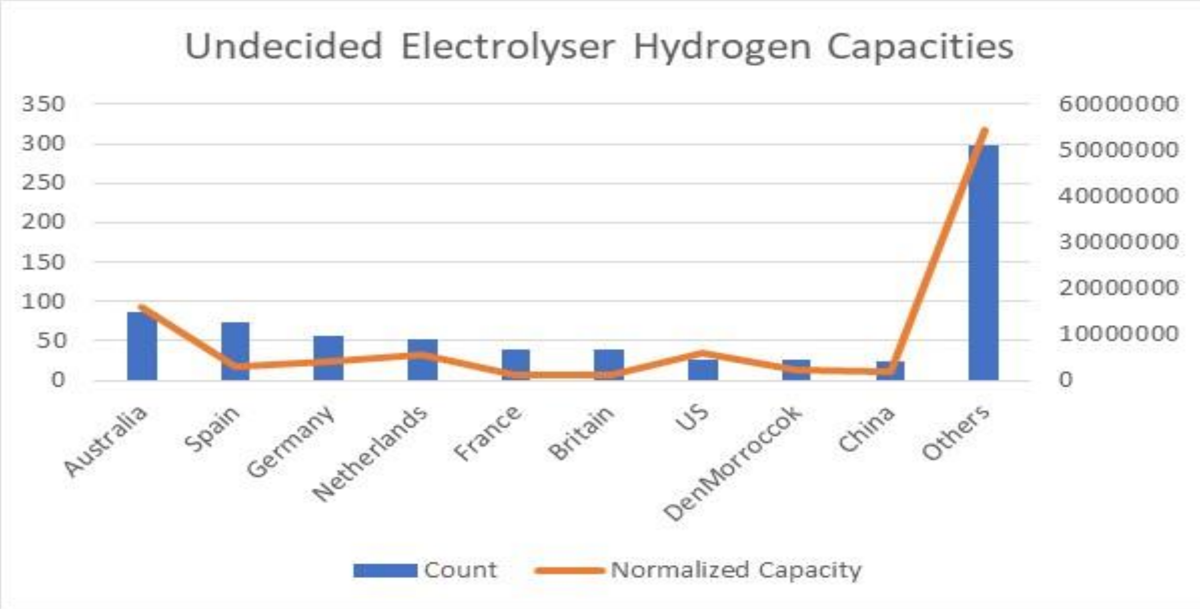


Figure 9 Undecided electrolyser capacities[5]

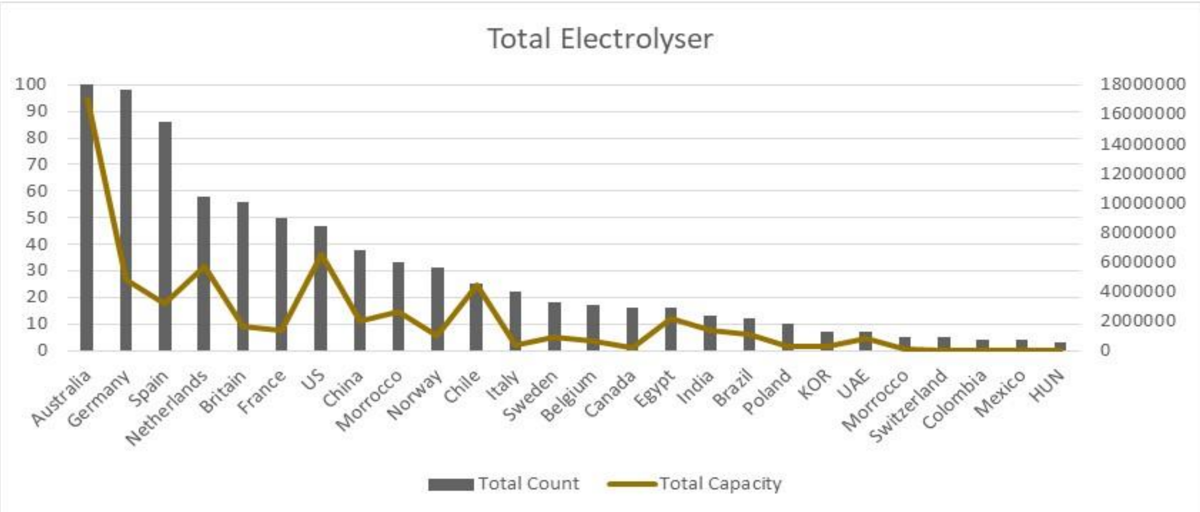


Figure 10 Cumulative electrolyser capacity planned[5]

Australia has the largest number of projects planned and also the largest capacity planned whereas Germany has the second highest number of projects planned but the scale of the projects is not as significant as Australia. In terms of the planned capacities (not just the count of projects), US stands second in the graph with ~48 proposed projects and a cumulative capacity of 9000000 nM^3/hr. In all the graphs above, it is evident that the total number of planned facilities in every electrolyser technology is led by Germany. This aligns with the German Hydrogen Strategy to position Germany as the global frontrunner when it comes to green hydrogen and to remain a market leader in hydrogen technology. It plans to double its electrolyser capacity by 2030 but still claims to be green energy deficit despite this initiative. They aim to make ‘Made in Germany’ a brand tag in electrolyser market[10].

Australia, apart from just the government support, industries are showing great interest in setting up green hydrogen production units due to the abundance of land and availability of wind and solar energy. The aim of Australian Hydrogen Economy is to focus on economies of scale and produce hydrogen at a price as low as $1.46/kg.[11]

United States Department of Energy released a draft on US hydrogen strategy and also approved ~USD 7 billion in funds to implement the strategy. The priorities of the strategy are focussed on high impact strategic H_2 applications, reducing the cost to $1/kg by 2031, and deploying at least four clean hydrogen hubs. The goal of these hubs is to increase the production of green H_2 to 50 million tons annually. The secondary objective of these hubs is to find efficient ways of carbon sequestration and find application of captured carbon.[12]

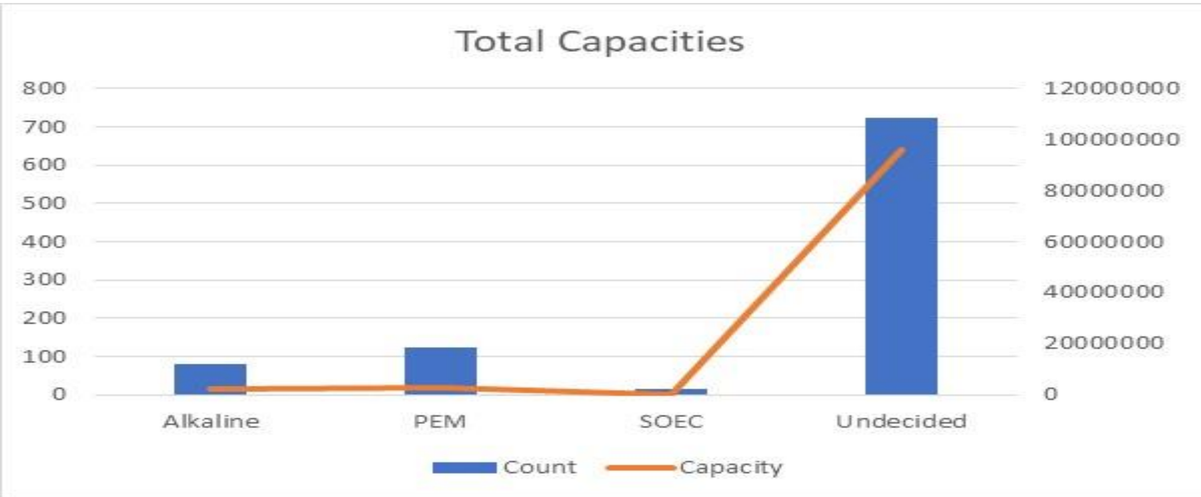


Figure 11 Technology wise planned capacity[5]

Beginning from where it all started, the question still is ‘What is the best method to produce green hydrogen?’. Figure 11[5] clearly shows that many governments across the globe have drafted their hydrogen policies but not yet finalised on the electrolyser technology to achieve the hydrogen production. Every technology has got its advantages and disadvantages. It all comes down in the end to the demand, profitability, feasibility, and safety.

Data and Results-Part 2-Process Hazard Analysis

Solid Oxide Electrolyser Cell: It is a high temperature electrolysis method that operates at temperature ranges of 700^0C to 800^0C and uses a solid ceramic material as electrolyte. The high temperature is gained from the nearby high temperature source where the heat generated is often wasted (eg: nuclear

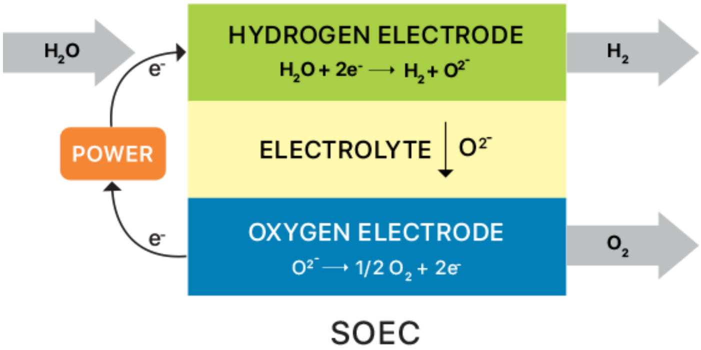


Figure 12 SOEC Cell[13]

power plants, helium reactors, etc). There are two sides to this cell, a cathode (upper portion) and an anode as shown in figure 12[13]. Water enters the cell through cathode and sweep gas enters the cell through the anode. The cathode stream, i.e. water is initially processed in the feed conditioner to remove any impurities and made pure. The pure water then goes through a series of heat exchangers and pumps to attain the temperature of 700^0C and higher using the closest heat source (in figure 13[14,15] it is Nuclear Power Plant (NPP)). The components of the cell only activate at such high temperatures. At the anode side, the sweep gas, which in general is the air, goes through a series of compressors and fulfils its purpose to remove oxygen from the anode. The stream at cathode combines with electrons from external circuit to form H_2 gas and negatively charged oxygen ions. Oxygen ions pass through solid ceramic membrane and react at anode to form oxygen gas to generate electrons for the external circuit.

Reaction:	Most popular:
Anode: $2\ O^{2-} \rightarrow O_2 + 4\ e^-$ Cathode: $H_2O + 2\ e^- \rightarrow H_2 + O^{2-}$ Net Reaction: $2\ H_2O \rightarrow 2\ H_2 + O_2$	❖ Electrolyte: Zirconium Dioxide doped with 8 mol% Y_2O_3 (YSZ). ❖ Cathode: Ni doped with YSZ. ❖ Anode: Lanthanum Strontium Manganate (LSM)

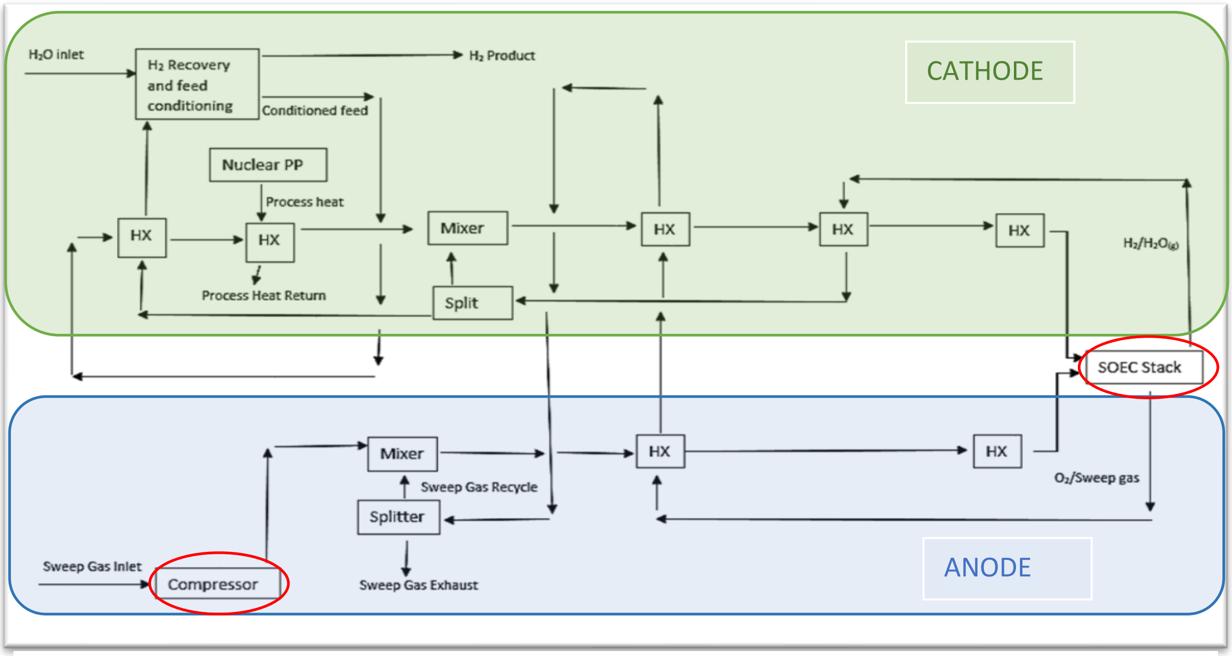


Figure 13 HTEF facility (SOEC Block Flow diagram)[14,15]

This project work deals with process hazards of the SOEC Stack and Compressor. Failure modes of a compressor are shown in table 4[16]. Occurrence is the frequency of expectation of the condition, severity is about the impact of the event, detection is the ease of figuring out the condition and RPN is Risk Priority Number.

S.No.	Condition	Occurrence	Severity	Detection	RPN
1	Water	3	7	8	168
2	Solid Contaminants	5	6	9	270
3	Non-Condensable gases	3	5	7	105
4	Failed Condenser Fan	2	7	4	56
5	Dirty Evaporator	4	6	3	72
6	Blocked Orifice	1	7	10	70
7	Loss of oil	4	8	9	288
8	Loss of refrigerant	5	6	5	150
9	Loose parts	3	4	4	48
10	Locked rotor condition	3	9	4	108
11	Fast on/off cycle	2	6	3	36
12	High compression ratio	3	5	8	120
13	Mixed oil	2	4	10	80
14	Wrong refrigirant	2	10	6	120
15	Wrong overload protector	3	9	8	216
16	Electrical mis-wiring	4	10	4	160
	Average	3	7	6	129

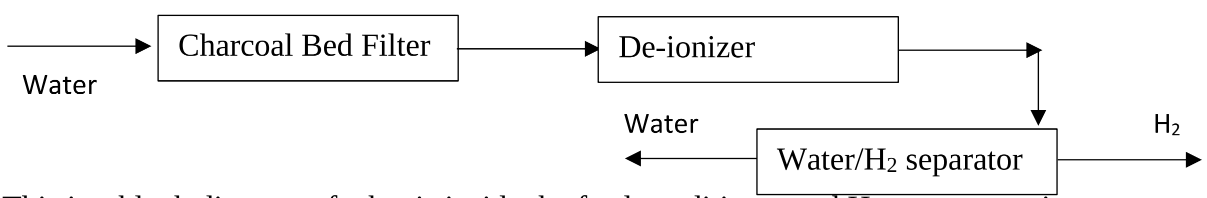
Table 4 Failure modes of a compressor (All of them rate 1-10 with 1 being low & 10 being high || RPN is product of all 3)[16]

Based on table 4, the top 4 failure modes were chosen to understand the consequence to the process when one such incident happens as shown in table 5[16].

HAZOP Compressors			
Parameter	Keywords	Causes	Outcome
Moisture content	More	Dryer not efficiently working	Water in compressor lines will wash away machinery lubricants and speed up the rate at which metal parts erode. Retained moisture will require replacement of internal parts more often than usual.
Contaminants	More	Sweep gas not purified properly	Contaminants in water can lead to fouling and corrosion, reduced throughput and eventually failure of compressors
Lubrication	Less	Increased moisture content	Compressor overheating and burning out, resulting in improper flow of sweep gas and hence risk of fire due to accumulation of oxygen in SOEC stack
Refrigerant	Less	Leak at valves and pipes	The change in pressure because of the drop in refrigerant can cause serious damage to the compressor, eventually leading to burning out of compressor and oxygen accumulation in SOEC Cell

Table 5 HAZOP Compressors[16]

Compressors are needed in this system to maintain the pressure and flowrate of the sweep gas. They help maintain the continuous flow of oxygen generated at the anode. Outcomes of failure of a compressor have been stated in table 5[16] and the risks associated with accumulation of oxygen at anode within the SOEC cell are listed later in table 6[15,17].



This is a block diagram of what is inside the feed conditioner and H_2 recovery unit.

HAZOP SOEC Cell				
Study Node	Parameter	Keywords	Causes	Outcome
Cathode	Flow Rate	More	Issue with the liquid phase pumps at the inlet	Increases efficiency to a level but beyond a limit, might reduce the separation rate causing disturbances in the mole ratio of H_2O/H_2 in outlet
		Less		Reverse flow of oxygen into the steam/hydrogen mixture which might result in autoignition.
	Pressure	More	Issue with the liquid phase pumps at the inlet	Increased efficiency to a level but beyond a limit, reduced yield, and disturbances in output mole ratio
		Less		Lower flow rate, reduction in efficiency, gas leakage, fire and hazard with the nearest high temperature source
Anode	Flow Rate	More	Issue with pumps	Cost inefficiencies
		Less		Increases corrosion of oxygen handling materials, high T might increase risk of fire
Electrodes	Delamination	More	Insulated layer formation at the electrolyte interface due to variation in process parameters, bad quality of interface due to contaminants	Electrode material damage, lower of cell performance, implying lower hydrogen production and disturbance in mole ratio of output product. This in turn will result in pressure fluctuations in storage tank, charge radiation causing risk of fire
SOEC Cell	Resistance	More	Internal restructuring/cracks of the electrolyte material due to high T	Increase in temperature causing reduced battery life due to increased corrosion leading to unexpected shutdown.
	Mechanical Stress	More	Malfunction of pumps, inlet water impurities due to aged feed conditioner, pressure heterogeneity due to improper valve closing	Delamination/ system failure/ cell architecture damage: Leak and blast; Also, a threat to the near high temperature sources.
	Seal Aging	Sooner	Due to impurities in water, reaction of Si in sealing with water	System failure, blast with a threat to the source high temperature facility

Table 6 HAZOP SOEC[15,17]

Alkaline Electrolysis: It is the most used and most well-established method of electrolysis which operates in the temperature ranges of ~70^0C to 100^0C. It has two electrodes, the cathode and anode operating in a liquid electrolyte solution. The most widely used liquid electrolyte

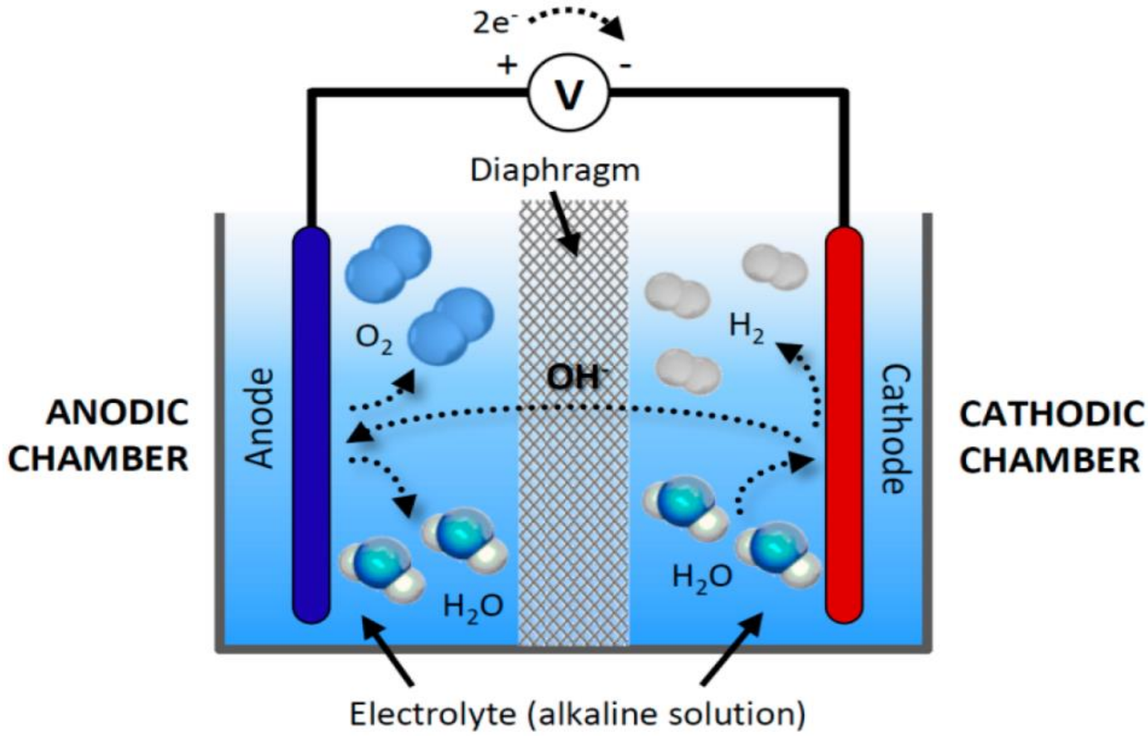


Figure 14 Alkaline Electrolysis cell[18]

solution is a mixture of potassium hydroxide and water. A diaphragm separates these electrodes, thereby helping separate product gas by only transporting OH^- ions across the membrane towards the anode side. Hydrogen is generated at the cathode and oxygen at anode. Products at both the electrodes contain significant amounts of the electrolyte and water which is stripped off at the phase separators at either ends as shown in the block diagram on the next page, figure 15.

Reaction:

Cathode (reduction):

$4\ H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4\ OH^-(aq)$

Anode (oxidation):

$4\ OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4\ e^-$

Most popular:

- ❖ Electrolyte: Potassium hydroxide/sodium hydroxide
- ❖ Cathode: Nickle alloy
- ❖ Anode: Nickle alloy

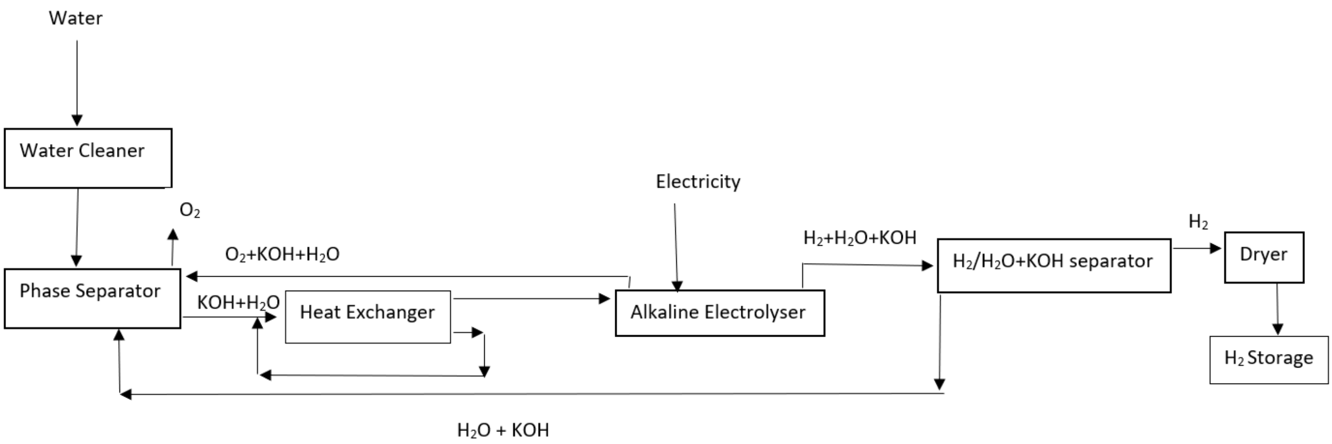


Figure 15 Alkaline electrolysis facility block flow diagram[18,19]

HAZOP Alkaline Electrolyser			
Parameter	Keyword	Causes	Outcome
Hydrogen Storage System (HSS)			
Pressure	more	High inlet flow	Loss of containment; leading to a possible release of hydrogen causing fire/explosion
		Temperature increase	
		Human error wrt opening or closing cylinder valves or service parameters	
		Blocked valves	
	less	Low inlet flow/human error/leak at inlet	Efficiency issues; leak causing release of hydrogen into atmosphere and potential formation of an explosive environment
Alkaline Electrolyser			
Flow Rate	low	Pump malfunctioning; impurities in fluid; fluid leakage; broken pipe; blockages in pipes	Increased electrode resistance, electrolyte damage; impurities in end product; electrolyser damage; fire due to leak; pipe bursting; thermal/hydraulic issues

In the table 7, a list of parameters have been considered for 3 important nodes of the block flow diagram of alkaline electrolyser process.

HAZOP Alkaline Electrolyser			
Parameter	Keyword	Causes	Outcome
Alkaline Electrolyser			
Gas Pressure	low	Hydrogen leak	Overpressure accident to closed vessels/ tanks or sealed piping systems, e.g. the H2 loop, the air loop, the N2 loop and so on; not enough hydrogen supply; fire or explosion
Battery			
Electrical current	more	Failure of controller	Increase corrosion and maintenance requirements
		Error of operator	Production of hydrogen induces explosive atmosphere
Temperature	more	Increased resistance	For every $10^{0}C$ rise in temperature rate of reaction doubles and hence average battery life decreases by a factor of 2 due to accelerated corrosion

Table 7 HAZOP Alkaline Electrolysis[18,19,20]

<u>Proton Exchange Membrane (PEM)</u>: In this type of electrolysis, the electrolyte is a solid speciality plastic that operates at a temperature of ~$20^{0}C$ to $70^{0}C$. Unlike the above two electrolysis processes where the oxygen is a product at the anode and hydrogen at cathode, in PEM, hydrogen is obtained at anode while oxygen at cathode[21].

At anode: oxygen and positively charged hydrogen ions || $2H_2O \rightarrow O2 + 4H+ + 4e-$

The electrons move through the external circuit while hydrogen ions selectively move through the PEM to cathode.

At cathode: Hydrogen ions combine with electrons from external circuit to form hydrogen gas || $4H+ + 4e- \rightarrow 2H_2$

HAZOP for PEM is a part of the proposed future work.

Discussion & Conclusion

In the next 20 years to come, there will be a shift in hydrogen value chain as methods of production centralize around zero emissions and carbon free processes. Hydrogen value chain is generally dependant on many factors like location, availability, emission benefits, infrastructure, and feedstock. Low carbon hydrogen currently is produced mostly using natural gas and carbon sequestration techniques (~62% of hydrogen produced). Only, 0.04% of hydrogen produced is using electrolysis[5]. These statistics are soon likely to change as the dynamics of value chain shift from low emission hydrogen to zero emission hydrogen. When it comes to zero emissions, electrolysis is the process. Most are is confident today that alkaline electrolysis is an established method of producing green hydrogen. While there are researchers and experts investigating PEM and SOEC methods, today alkaline electrolysis is the leading technology for hydrogen production. While PEM has the advantage of solid electrolyte and low temperature, there are estimates that in the next 3 years, PEM and Alkaline Electrolysis could have equal market share but in the next 15 years, SOEC might take the lead. SOEC has got advantages associated with using reduced heat waste of the high temperature source, high efficiency, dense electrolyte and easy unit operations. The generation of chemical engineers to come might have to investigate and come up with innovative methods to produce and store hydrogen safely.

<u>Steps Forward</u>

- PHA for Proton Exchange Membrane (PEM).
- Keep updating the excel file for upcoming capacities of hydrogen globally.
- Extend the PHA for upstream electrolysis process specific for each type of electricity source like Solar energy/Wind energy/Hydroelectricity coupled with electrolysis.
- Look at ways of storing hydrogen and understand the hazards and safety concerns associated with those storage techniques.

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