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Review On Electrochemical Processes of Hydrogen Production Using Solar Energy

[1]Shraddha Bukkanure, [2]Chinmay Joshi, [3]Nita Mehta
[1,2] Students, [3]Associate Professor
[1]Chemical Engineering,
[1] Thadomal Shahani Engineering College, Mumbai, India

Abstract : Hydrogen production is a very important step in the development of the hydrogen economy. Use of fossil fuels for hydrogen production is harmful to the environment and contribute to global warming. The use of these harmful substances leads to an increase in greenhouse gas emissions. Also, these sources of energy are limited in their supply and are expected to eventually disappear. The urge to replace these fossil fuels with renewable energy sources is growing. With the increasing popularity of solar energy, hydrogen is becoming a vital component of the world's energy mix. It is a sustainable energy carrier that can reduce greenhouse gas emissions and provide a clean energy source. This review aims to analyse the electrochemical processes such as Alkaline Water Electrolysis (AWE), Polymer Exchange Membranes (PEM) and Solid Oxides Electrolysis (SOE) involved in the production of hydrogen using solar energy. It highlights the various environmental and economic impacts associated with these production methods. Energy efficiency and exergy efficiencies are the key factors that determine the level ofhydrogen production. The other factors include the environmental friendliness.

***IndexTerms* - Hydrogen production, Solar energy, Electrochemical processes, Renewable energy**

I. Introduction

Hydrogen is an energy source that is widely believed to be the most abundant element in the universe. Its high heat release per unit mass makes it more advantageous than gasoline. With the increasing importance of solar energy, the world is expected to focus on the development of hydrogen as a clean energy carrier. This is because it is capable of reducing greenhouse gas emissions and substituting fossil fuel. Aside from being a fuel, hydrogen can also be utilized in the production of various chemicals such as ammonia and urea. Aside from fossil fuels, hydrogen can also be produced using various renewable energy sources, such as wind energy and solar energy.

Due to the increasing environmental impacts associated with the use of fossil fuels, many countries have started formulating policies aimed at developing green energy sources. Various research organizations are working on the development of systems that can use renewable energy sources for generating electricity and fuel. This is because the various factors that affect the reliability and availability of these sources are often interrelated. Despite the immense efforts made by scientists and engineers in the field of renewable energy, there are still various challenges that need to be addressed in order to effectively utilize these sources. One of these is their intermittent availability.

Around 30% of the solar energy that hits the earth's surface gets reflected back to the atmosphere. The remaining 90% of the energy gets absorbed by the body and is used as fuel [1]. Various studies have been conducted in the field of solar hydrogen production. Solar energy is the most promising option for achieving a green economy. This topic has garnered wide interest due to its various applications. Due to the utilities of hydrogen, many countries are trying to shift toward a hydrogen-based economy. The techniques of hydrogen production include photochemical, thermochemical and electrochemical processes.

This review focuses on the capability of various stages of electrochemical processes of solar hydrogen production and their economics and environmental aspects. Hydrogen gas production and storage is dependent upon three most important aspects: raw material, energy required for the production and actual process of production. Apart from using solar energy as form of electrical energy needed for electrolysis, it is also been applied for water splitting processes where high value temperatures like 200-2000°C are achieved for decomposition of water molecule. Till now engineers have been successful in attaining maximum of 70% efficiency.

II. ELECTROCHEMICAL PROCESSES

The basic setup for said procedure consists of two electrodes separated from one each other by a strong (ideally) electrolyte solution which practically carries the electrical current for the decomposition purpose. It was first introduced to the world by W. Nicholson and Carlsie in 1800, however the first unit of pilot scale was established in 1939 of 10000Nm3/h. Application of electrolysis for hydrogen production seems to be contributing very little to the net hydrogen production which includes fossil fuels, natural gas, coal-steam generation, etc.

$$H_2O + electrical\ energy \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \dots\dots\dots at\ anode \qquad (2.1)$$

$$2H^+ + 2e^- \rightarrow H_2 \dots\dots\dots at\ cathode \qquad (2.2)$$

As a matter of fact, this method was primarily chosen by industry in 1920s to 1960s for bulk hydrogen source [2]. Now as the total cost of renewables like solar PV has started decreasing, more and more industries and governments have showed an incline towards use of the said method. The current scenario suggests that around 5% of total hydrogen supplied is derived from electrolysis procedure.

Given process can be carried out at ambient as well as considerable high temperature. Raw material needed for the procedure at normal temp is water and at high temp is steam. Electrical energy and heat energy are considered in the total energy requirements of this procedure. Direct relationship is observed between operating temperature at which the procedure is carried out and total energy requirement. (One increases, other increases). Inverse relationship is observed between operating temperature at which the procedure is carried out and the total electrical energy needed (one increases, other decreases).

This actually emphasizes the fact that it slightly convenient to decompose the water molecule present in the steam/ vapor form than present in liquid form. Fig. 1 also explains that as the temperature goes on increasing, the phase changes and hence lesser and lesser electrical energy needs to be applied for electrolysis and hence high temp procedures are more in demand.

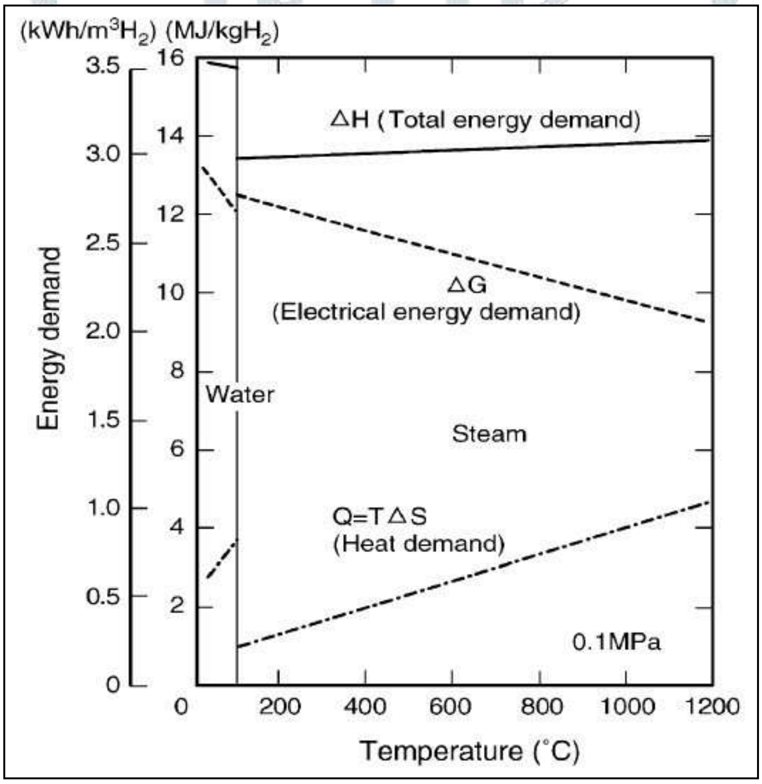

Fig. 1. Energy demand for water and steam electrolysis [3-4]

Few of the most essential technologies present under this classification are

A. Alkaline water electrolysis.
B. Polymer exchange membranes
C. Solid oxide cell electrolysis
D. Electrolysis of steam.

Out of these 4 procedures, steam electrolysis is found to be slightly more economical because of the lesser amount of electrical energy needed. Thermodynamically speaking the value for molar Gibbs free energy at normal temperature – pressure conditions is 237 kJ/mol and at higher temperature like 900 deg C is 183 kJ/mol which is lower and more favorable.

Table 1. Characteristics, advantages and disadvantages of electrolysis technologies for hydrogen production [5-6]

	AWE	PEM	SOE
Electrolyte	NAOH/KOH (Liquid)	Polymer (Solid)	Ceramic (Solid)
Charge Carrier	OH^-	H^+	O^{2-}
Anode	Ni	Pt, Ir, Ru	LSMYSZ, $CaTiO_3$
Cathode	Ni Alloys	Pt, Pt/C	Nicermets
Operating Pressure	2-10 bar	15-30 bar	<30 bar
Operating Temperature	60-90°C (up to 200°C)	50-90°C	500-1000 °C
Cell Voltage	1.80-2.40 V	1.80-2.40 V	0.95-1.30 V
Current Density	0.2-0.5 mA/cm^3	1-2 mA/cm^3	0.3-1 mA/cm^3
Stack Lifetime	<90,000 h	<40,000 h	<40,000 h
System Lifetime	20-30 y	10-20 y	-
Efficiency	62%-82%	67%-84%	90%
Cold Startup	>15 min	<10 min	>60 min
Maturity	Commercial	Early commercial	R&D
Estimated Cost By 2050	~$600/kWh	~$750/kWh	~$200/kWh
Degradation Per Annum	2%-4%	2%-4%	17% (testing)
Advantages	• Well-stablished method • Low capital cost • Long-term stability • Large stack size • Non noble material	• Simple Design • Compact system • Rapid response • High current density	• High-energy efficiency • Reversible operation as fuel cel • Nonnoble materials • Low capital cost
Disadvantages	• Corrosive electrolyte • Slow dynamics • Low current density • Gas permeation	• Noble materials • High membrane cost • Low durability • Acidic environment	• Unstable electrodes • Sealing issues • Bulky design • Brittle ceramics

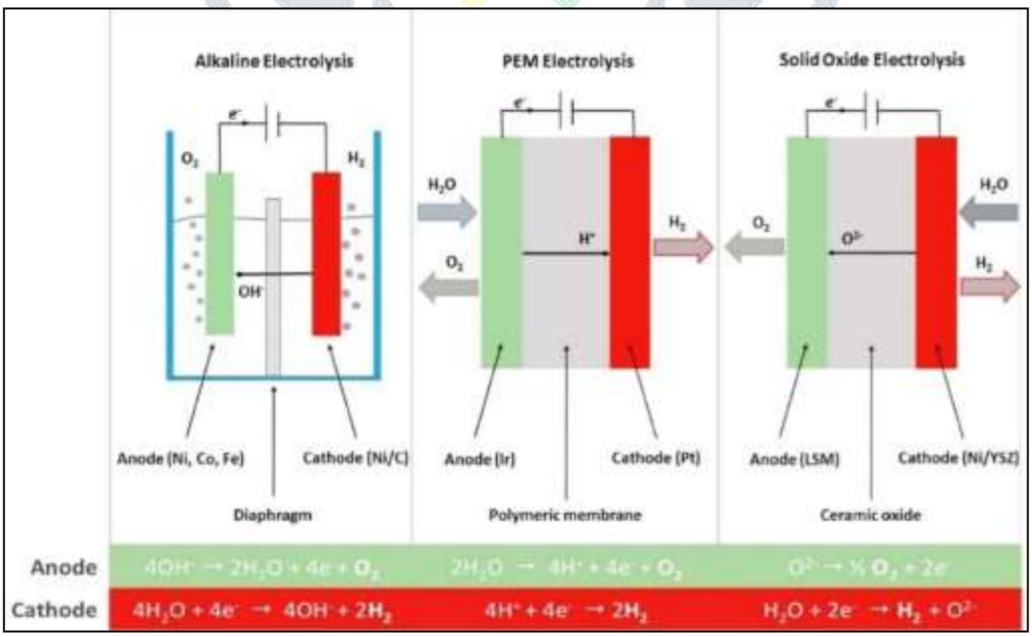

Fig. 2. Operation principles of various electrolysis methods: alkaline, PEM and solid oxide water electrolysis. Oxygen evolution takes place at the anode; hydrogen evolves at the cathode. In sold electrolysis, an O^{2-} conducting electrolyte, with a nickel/yttria-stabilized zirconia cathode and a lanthanum strontium manganite (LSM) anode [5], [7]

2.1 Alkaline Water Electrolysis

This is one of the oldest methods to be used for hydrogen production. Alkaline electrolysers can operate at 10% of maximum working capacity to its fullest. Maximum capacity can be assumed to be 165 megawatts in countries like India where large hydropower supply is available [2].

The electrolytes which are included in the process, are mostly NaOH (Sodium Hydroxide) and KOH (Potassium Hydroxide) and recovering these electrolytes is necessary. It is most often carried out at relatively lower temperature like 60 to 90 deg C and pressure around 1 to 200 bar.

The method is observed to be widely used and commercialized in existing industry as financially it requires lesser cost. Miller suggested a highly active nano-structural electrocatalyst made of palladium-ceria [5] to produce hydrogen via alkaline water electrolysis.

Amount of Hydrogen production is directly proportional to concentration/ composition of electrolyte being used and the operating temperature of electrolyte present. It is also inversely proportional to distance present between in the electrodes. Application of zinc alloyed electrodes is found to give best performance. The electrolyte is permeable to water molecules and hydroxide ions.

The efficiency of electrolysis can be formulated as follows:

$$Efficiency = \frac{Energy\ generated\ due\ to\ hydrogen\ ion\ production}{Electrical\ energy\ provided\ to\ the\ system} \qquad (2.3)$$

Hence, the excess amount of voltage or current density can certainly reduce the efficiency. One must also remember that productivity is not equivalent to efficiency. Maximum production doesn't necessarily guarantee the maximum efficiency of electrolysis [8-11].

$$\frac{E_{H_2}}{volume} = \frac{28600(\frac{J}{mole})}{24000(\frac{cm^3}{mole})} = 11.9166\,\frac{J}{cm^3} \qquad (2.4)$$

The electrical energy needed to release one cm^3 of H_2 is:

$$E_{el} = V \times I \times t(J) \qquad (2.5)$$

Where V is the volt and I is the Ampere, and t is the time required to produce 1 cm^3 of H_2. Therefore, the energy efficiency is calculated from the relationship

$$\eta = \frac{E_{H2}}{E_{el}} \qquad (2.6)$$

2.2 Polymer Exchange Membranes

This method was introduced in 1960 by General Electric [2] ¬in order to correct whatever drawbacks observed in AWE. Operating capacity of these electrolyser can range up to 160% of design capacity. Electrolyte implied for this method is pure water and hence there is no recovery needed. In order to produce more pure hydrogen acidic non-liquid electrolyte [5] is includedin PEM electrolysis. This procedure has much faster response time as compared to alkaline water electrolysis and hence better dynamic behavior which makes it a better option ahead of alkaline electrolysis. The electrodes which are involved mostly made ofplatinum.

Therefore, the cost of process increases and overall lifetime of electrolyser decreases, reason behind the lesser use in industry. Electrolysis efficiency is directly proportional to operating temperature and inversely proportional to current density. Highlighting characteristics of this method are much better purity of produced hydrogen as compared to AWE, better coupling with intermittent system and higher flexibility. Recently, several investigations have been conducted in deploying hydroxides and oxides based on earth ‑ abundant transition metals (such as Ni, Co, Fe, and Mn) as oxygen evolution reaction (OER) electrocatalysts, 137 and it is found that cobalt-based catalyst is a promising alternative for OER because of its high activity, abundance, and relatively low price [5].

2.3 Solid Oxide Electrolysis

This method is particularly least developed as compared to other 2 methods and its commercialization hasn't been done yet too. Traditionally, the SOE systems utilize yttria ‑ stabilized zirconia as O_2– conductors, and in recent years, various ceramic proton conductors have been introduced [5]. Temperature at which process is finished is 600 – 900 deg C.

Nickel is found to be the most used electrode for said method because of chemical compatibility. Most renowned method under electrochemical is solid oxide cell: The entire setup remains same as compared to standard electrolysis process. However, the electrolyte used is found to be in solid state for example: ceramics. And water is converted into steam before releasing into electrolysis cell. As soon as steam enters, hydrogen ions at cathode and oxygen ions at anode are collected.

III. Economics and Environmental Aspects of Hydrogen Production

One of the important factors that is considered to rank different procedures for hydrogen production is the exergy efficiency of the any given procedure. And this efficiency is directly affected due to incoming solar radiation/intensity. This exergy efficiency term is also closely related to sustainability index of the process. Higher the exergy, higher is the sustainability.

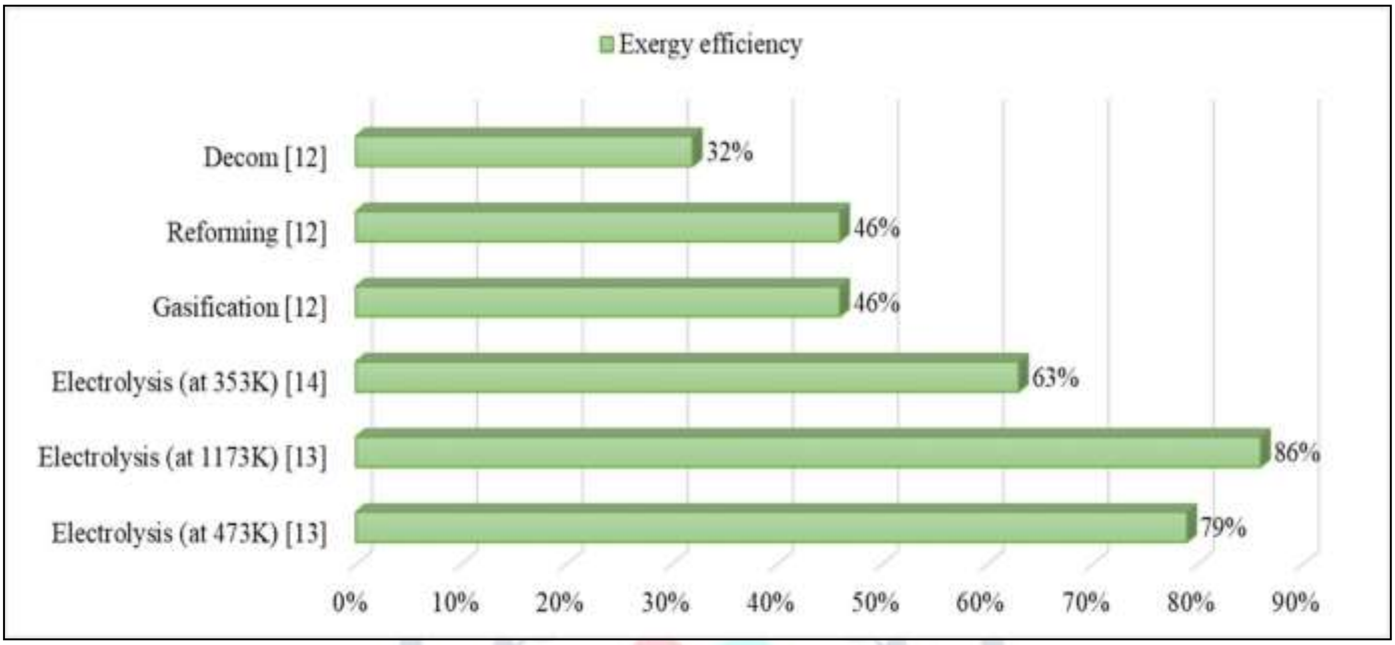

Fig. 3. Exergy efficiency of the different processes of solar hydrogen production [14]

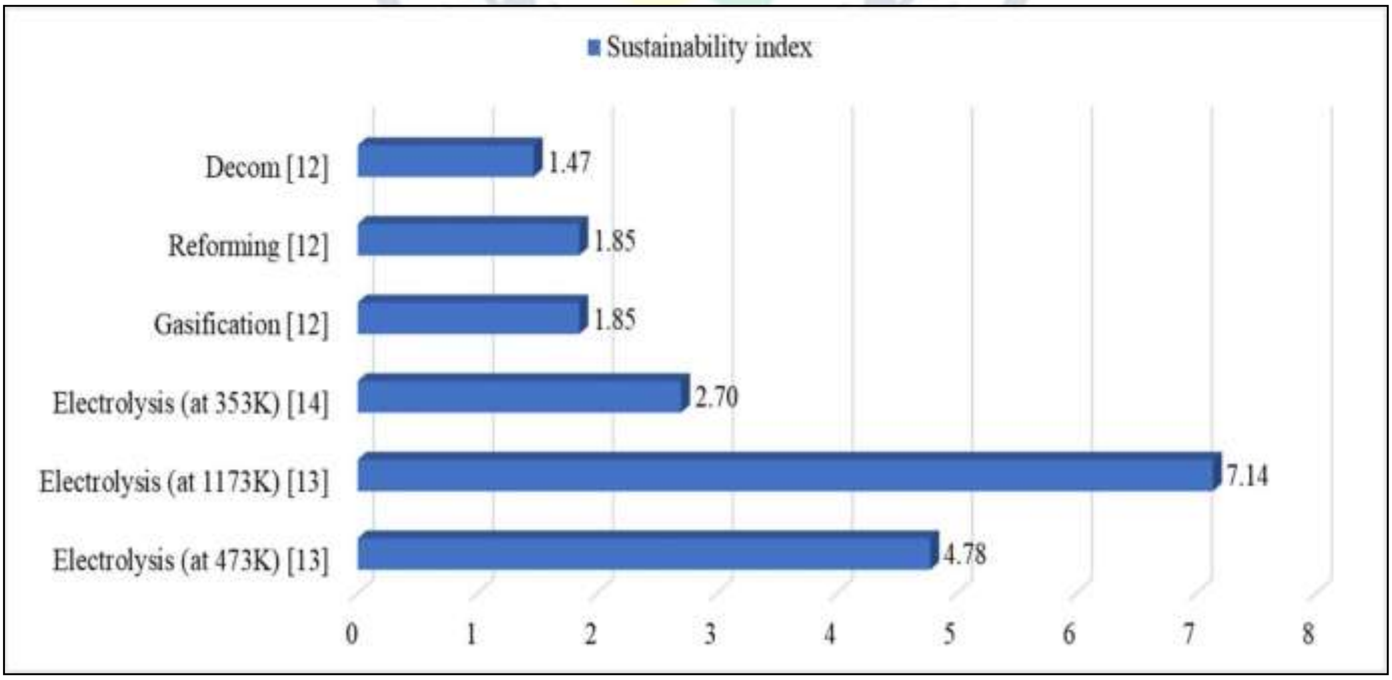

Fig. 4. Sustainability index of the different processes of solar hydrogen production [14]

Table 2. Techno-economic characteristics of different electrolyser technologies [2]

	Alkaline electrolyser			PEM electrolyser			SOEC electrolyser		
	Today	**2030**	**Long term**	**Today**	**2030**	**Long term**	**Today**	**2030**	**Long term**
Electrical efficiency (%, LHV)	63-70	65-71	70-80	56-60	63-68	67-74	74-81	77-84	77-90
Operating pressure (bar)	1-30.0			30-80			1		
Operating temperature (°C)	60-80			50-80			650-1000		
Stack lifetime (operating hours)	60000-90000	90000-100000	100000-150000	30000-90000	60000-90000	100000-150000	10000-30000	40000-60000	75000-10000
Load revenge (%, relative to nominal load)	10-110			0-160			20-100		
Plant footprint (m^2/kWe)	0.095			0.048					

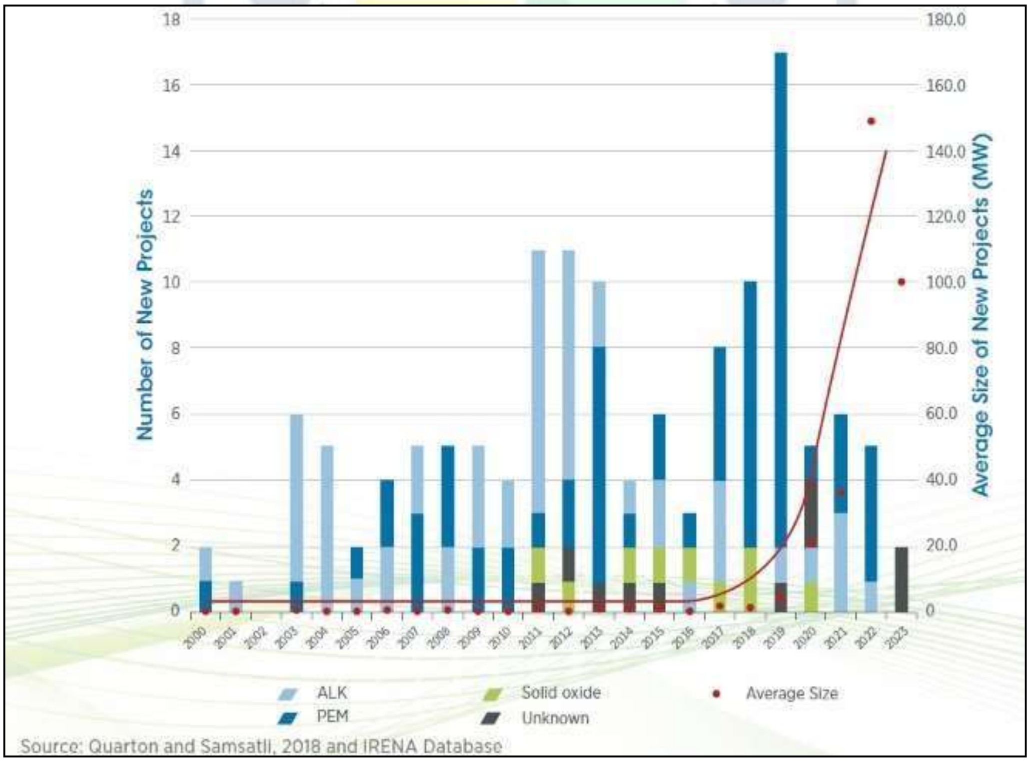

Fig. 5. Timeline of power-to-hydrogen projects by electrolyser technology and project scale [15]

Amongst all the processes that are discussed earlier in the section, electrolysis of water seems to be an optimistic solution for hydrogen production using solar power. Having said that, the cost required for this procedure is considerably high. Solar PV panel connected to a PEM electrolysis system with a capacity of 1200 tones/day was economically studied by Choi et al. [16] ; they estimated the cost of hydrogen produced via their approach to be $8.98/kg [17]. High capital cost and excessive cost of electricity are the responsible factors behind this. But the environmental impact produced by the process, its scalability, zero emission hydrogen production and the significance of by-product i.e., oxygen (being used for industrial or medical purpose) make the process more attractive in nature. According to the reports commissioned for the capital cost for water electrolysers in 2017 & 2018, showcases that there is an investment done around USD 20-30 million per year [2]. Along with other aspects considered such as piping work, storage tanks and infrastructure for refueling makes this project even more expensive in nature.

CAPEX requirements are today in the range of USD 500-1400/kWe for alkaline electrolysers and USD 1100–1800/kWe for PEM electrolysers, while estimates for SOEC electrolysers range across USD 2800–5 600/kWe. The electrolyser stack isresponsible for 50% and 60% of the CAPEX costs of alkaline and PEM electrolysers respectively. The power electronics, gas- conditioning and plant components account for most of the rest of the costs [2].

If all current dedicated hydrogen production were produced through water electrolysis (using water and electricity to create hydrogen), this would result in an annual electricity demand of 3600 kWh – more than the annual electricity generation of the European Union. Water requirements would be 617 million m^3, or 1.3% of the water consumption of the global energy sector today; this is roughly twice the current water consumption for hydrogen from natural gas [2].

IV. CONCLUSION

Solar hydrogen is a clean energy carrier that can provide a reliable source of energy. Its ability to produce hydrogen and overcome the intermittent nature of solar energy make it a valuable component of a sustainable energy system. Many of the barriers to renewable energy development have to be overcome, such as social, environmental, and sitting concerns. Despite these obstacles, many of the benefits are being addressed by government and industry. Although these methods have various advantages,they are also compared in terms of their environmental impacts. Solar powered hydrogen fueling stations require less power and donot rely on external sources. Also, solar powered electrolysis technologies can provide better hydrogen fueling performance. As wediscussed the methods earlier, the PEM and AWE have been field of interest for being slightly more economical when it comes to cost for building this to pilot level/plant level. Exclusion of any precious materials is the reason behind AWE having lower capitalcost in comparison with other electrolyser system.

Mostly PEM as it still shows hopes for reduction in cost. On the other hand, Solid Oxide cell electrolysers have started making their impact on the market due to their higher efficiencies. There is definitely a need of implantation of appropriate policies in order to support hydrogen production and provide a favorable environment for its business growth. No other sustainable renewablegives opportunities to hydrogen production better than solar energy. It is somehow followed by biomass on the second position however biomass is primarily being used for production of bioethanol, biogas and other renewables so using it for hydrogen production may disturb the economics of those commercial practices. Hydrogen energy isn't being considered just for science & research purpose. It is the next best possible and one of the most promising energy economy solutions and thus its cost- competitiveness is been under examination for quite a while now. Based on this review, it results that the hydrogen production andstorage technologies shall become more and more technically efficient in the future; hence the hydrogen economy shall become more and more attractive.

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