Hydrogen Production by Water Electrolysis: A Review of Alkaline Water Electrolysis, PEM Water Electrolysis and High Temperature Water Electrolysis

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Abstract:- Water electrolysis is a quite old technology started around two centuries back, but promising technology for hydrogen production. This work reviewed the development, crisis and significance, past, present and future of the different water electrolysis techniques. In this work thermodynamics, energy requirement and efficiencies of electrolysis processes are reviewed. Alkaline water electrolysis, polymer electrolysis membrane (PEM) and High temperature electrolysis are reviewed and compared. Low share of water electrolysis for hydrogen production is due to cost ineffective, high maintenance, low durability and stability and low efficiency compare to other available technologies. Current technology and knowledge of water electrolysis are studied and reviewed for where the modifications and development required for hydrogen production. This review paper analyzes the energy requirement, practical cell voltage, efficiency of process, temperature and pressure effects on potential kinetics of hydrogen production and effect of electrode materials on the conventional water electrolysis for Alkaline electrolysis, PEM electrolysis and High Temperature Electrolysis .

Index Terms: Hydrogen Production, Water electrolysis, Electrolyte, Electrode, Electrocatalyst, PEM.

I.   INTRODUCTION

The atmosphere is polluted by plenty of greenhouse gases; SO_x, NO_x, CO_2 and CO from hydrogen production by hydrocarbon source that are fossil fuel sources which can affect seriously the ecosystem [1–3]. Hence the clean technology is needed for production of hydrogen that can be achieved if hydrogen is produced by renewable source like water electrolysis and no emission of SO_x, NO_x, CO_2 and CO will be possible and to achieve "hydrogen economy" [4, 5]. There are many important non-fossil fuel based processes like Water electrolysis, photocatalysis processes and thermochemical cycles for hydrogen productions in practice [6 - 15]. The use of solar energy and wind energy are sustainable methods for hydrogen production by water electrolysis with high purity, simple and green process [16].

For hydrogen production, water electrolysis has its various merits like pollution free process if renewable energy sources use purity of high degree, very simple process and plenty of resources [17]. Water electrolysis is an around 200 year old technology; around 1800 AD the principle demonstrated by experiment by J. W. Ritter in Germany. In the same year William Nicholson and Anthony Carlise decompose water into hydrogen and oxygen in England. The application of this technology started to use after tens of year. The French military in 1890 AD constructed a water electrolysis unit to generate hydrogen for use in airships by Charles Renard. Around 1900 AD more than 400 industrial electrolyzers were operating worldwide. Around 1930 AD different types of alkaline electrolyzer were developed. In the 1970s AD, the development of the PEM electrolyzer offered several advantages over alkaline electrolyzers with limited use in small hydrogen and oxygen production capacities due to expensive materials and a limited lifetime [18]. As hydrogen could be produced at lower cost by steam reforming, water electrolysis technology advanced only slowly. The hydrogen production in total around the world is about 500 bill. Nm³/year, mostly steam reforming. Only 4 % of hydrogen produced by water electrolysis as shown in figure 1. Due to low efficiency of production processes [19]. Currently, the efficiency hydrogen production by water electrolysis is too low to be economically competitive [20]. The low gas evolution rate and high energy consumption are serious problems of water electrolysis. In average 4.5–5.0 kWh/m³H_2 energy is needed for conventional industrial electrolyzer [16]. In water electrolysis for hydrogen production processes the efficiency is a very important parameter. Many researchers in their work have done for analyzing the energy consumption, efficiency of hydrogen production systems. The authors of [21 – 23] defined the energy, energy analysis, energy efficiencies, different driving energy inputs, definition of the efficiency, thermodynamic analysis, thermodynamic electrochemical characteristics, thermodynamic losses, system boundary and heat flows across the process of a hydrogen production process in different electrolyzer plants. This review paper analyzes the energy requirement, practical cell voltage, efficiency of process, temperature and pressure effects on potential, bubble mechanics and effects , kinetics of hydrogen production and effect of electrode materials on the conventional water electrolysis for Alkaline electrolysis, PEM water electrolysis and High temperature electrolysis .

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Figure1: Annual global hydrogen product share [19].

Abbreviations and Nomenclatures

PEM	Polymer electrolyte membrane	R_{total}	Total resistance, (ohm)
AWE	Alkaline water electrolysis	R_{mem}	Membrane resistance,(ohm)
SPE	Solid polymer electrolysis	R_{elec}	Electrolyte resistance,(ohm)
HTEL	High temperature electrolysis	R_{bub}	Bubble resistance,(ohm)
SOEL	Solid oxide electrolysis	R_{cir}	Circuit resistance,(ohm)
HER	Hydrogen evolution reaction	V_{real}	Real(actual) cell voltage, V
OER	Oxygen evolution reaction	η_A	Anode (oxygen) overpotentials, V
STP	Standard temperature pressure	η_C	cathode (hydrogen) overpotentials, V
LHV	Lower heating value, kWh per kg	ϵ_{EW}	Energy efficiency
HHV	Higher heating value, kWh per kg	F_{H_2}	Hydrogen gas out flow rate, Kg/hr
ΔG_{reac}	Change in Gibbs free energy of reaction, J/mol	EP	Electrical power supply, kW
ΔH_{reac}	Enthalpy change of reaction, J/mol	E_{HE}	Heat exchanger energy input , J
ΔS_{reac}	Entropy change of reaction, J/mol K	E_{red}	Redundant energy required, J
T	Operating temperature, K	$\epsilon_{electric}$	Electricity generation efficiency
E_{theo}	Theoretical energy consumption, J/mol	T_∞	Environmental temperature, K
V_{rev}	Reversible cell voltage, V	T_e	External heat source temperature, K
n	Number of moles	$\epsilon_{Voltage}$	Voltage efficiency
F	Faraday's constant, C/mole	$\epsilon_{faraday}$	Current(Faraday) efficiency
V_{enth}	Enthalpy voltage, V	ϵ_{cell}	Total cell efficiency
η	Overpotentials, V	P	Operating pressure, atm.
A	Anode and cathode constant		
B	Anode and cathode constant		
i	Current density, A/cm^2		

II. CONCEPT AND FUNDAMENTALS

When a water molecule passes through electrochemical process water molecules spilt in hydrogen and oxygen gases, this process is called water electrolysis. Electricity is used for the splitting the hydrogen and oxygen into their gaseous phase. The basic equation of water electrolysis is written as Eq.1. This technique produces clean energy without emission of pollution by utilizing electricity.

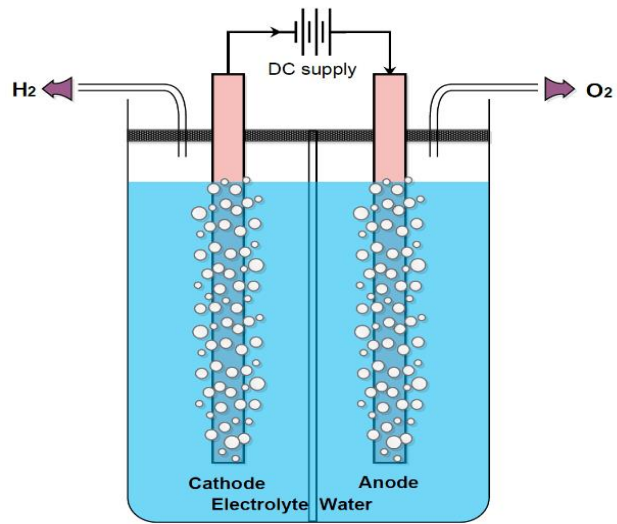$$H_2O(liquid) + Energy = H_2(g) + {}^1\!/_2\, O_2(g) \qquad (1)$$

For water electrolysis the energy is required as electrical energy from a DC power source. At room temperature the splitting of water is very small, approximately 10^{-7} moles/liter because pure water is the very poor conductor of electricity. Therefore, acid or base is used to improve the conductivity. In an alkaline electrolyzer, KOH, NaOH and H_2SO_4 solution mainly is used with water.

The solution splits into ions positive and negative ions and these ions readily conduct electricity in a water solution by flowing from one electrode to the other. Water electrolysis technology can de divides into three main classifications on the basis of electrolyte used in the electrolysis cell.

- Use of Liquid Electrolyte : *Alkaline Water Electrolysis (AWE)*
- Electrolysis in acid ionomer environment: *Polymer Electrolyte Membrane Electrolysis (PEM)/Solid Polymer Electrolysis (SPE)*
- Use of Solid Oxide Electrolyte: *Steam electrolysis (High temperature electrolysis - HTEL or SOEL)*

The figure 2 shows the fundamental principle for electrolysis cell. The general principle for all three technologies is the same. When a high voltage is applied to an electrochemical cell in presence of water, hydrogen and oxygen gas bubbles evolve at cathode (negative electrode) and anode (positive electrode) respectively.

Figure 2: The fundamental of water electrolysis process.

Three approaches for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), the typical temperature range and the ions acting as the charge carrier through the diaphragm/membrane is given in Table 1.

Table 1: Basic Chemical reactions and Operating temperature range for different types of Water electrolysis [18].

Electrolysis Technology	Alkaline Electrolysis	Membrane Electrolysis	High Temperature Electrolysis
Anode Reaction **Oxygen Evolution Reaction (OER)**	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$	$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
Cathode Reaction **Hydrogen Evolution Reaction (HER)**	$H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Charge Carrier	OH^-	H^+	O^{2-}
Operating Temperature Range	**40 – 90 °C**	**20-100 °C**	**700- 1000 °C**

III. ENERGY, VOLTAGE AND EFFICIENCY

A. Energy Consumption

The energy required for decomposing one mole of water into hydrogen and oxygen corresponds to the enthalpy of formation of one mole of water. The minimum amount of the enthalpy of reaction that has to be applied as electrical energy is the free energy of reaction ΔG_{reac} (change in Gibbs free energy) defined in terms of enthalpy of reaction, ΔH_{reac}, Thermodynamic temperature, T and the Entropy of reaction, ΔS_{reac}, by below equation Eq.2.

$$\Delta H_{reac} = \Delta G_{reac} + T\Delta S_{reac} \qquad (2)$$

Minimum energy required is given by Gibbs free energy relation deduce from Eq. 2.

$$\Delta G_{reac} = \Delta H_{reac} - T\Delta S_{reac} \qquad (3)$$

At STP the thermodynamic decomposition voltage of water in theoretical condition is 1.23V and the current efficiency is 100%. Therefore, the theoretical consumption of energy (E_{theo}) for producing $1m^3$ of H_2 is 2.94 kWh/m^3H_2. However, for gas evolution the voltages need 1.65–1.7V. Therefore in industries the voltage of about 1.8–2.6 V use. Hence the practical energy consumption is nearly 1.5 to 2.2 times more than the theoretical energy consumption. Hence the actual efficiency is between 48% and 70% [16].

B. Voltage and Overpotentials Required

For water electrolysis there are need of two voltages for energy calculation, the water electrolysis voltage (reversible cell voltage) and enthalpy voltage (thermo-neutral voltage). The minimum cell voltage required for the decomposition of water is the reversible cell voltage V_{rev} which can be expressed as Eq.4 where n is the number of moles of electrons per mole of products, that is, n =2; and F is the Faraday constant (F = 96 500 coulombs mole^{-1}) [24]

$$V_{rev} = \frac{\Delta G_{reac}}{nF} \tag{4}$$

The minimum cell voltage required for water electrolysis is related to the enthalpy of reaction and is called the enthalpy voltage (thermo-neutral cell voltage); V_{enth} can be expressed as Eq.5 [25].

$$V_{enth} = \frac{\Delta H_{reac}}{nF} \tag{5}$$

The cell voltage of an operating electrolysis cell is significantly higher than the theoretical reversible cell voltage derived from thermodynamics. Because some extra voltage is needed to overcome the irreversibilities resulting from reactant products, transportation, charge transfer and resistance of electrolyte and electrodes in the electrolysis process, increase the actual requirement [26]. The empirical Tafel equation is used to evaluate the relationship of over potential η and current density i is expressed by Eq. 6 as below, Where A and B depends over anode and cathode material [16].
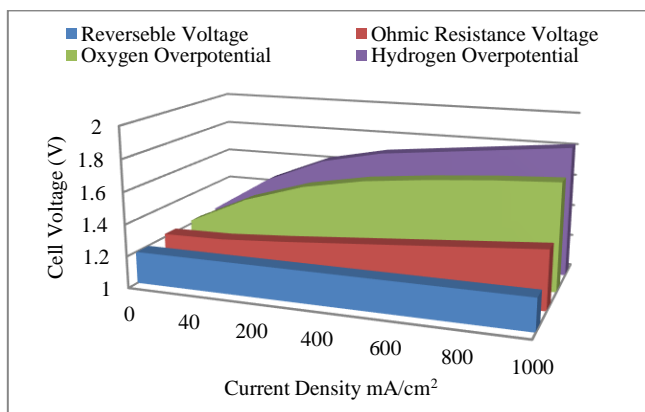
$$\eta = A + B\log(i) \tag{6}$$

The resistances due to membrane R_{mem}, electrolyte R_{elec}, bubble R_{bub} and circuit R_{cir} are also sums the high energy consumption and called ohmic voltage drop, the total ohmic voltage drop is given by Eq.7 for current density i.

$$i * R_{total} = i * (R_{mem} + R_{elec} + R_{bub} + R_{cir}) \tag{7}$$

The real cell voltage V_{real} can be regarded as the sum of the reversible cell voltage Vrev, the voltage drop i*Rtotal caused by the area specific ohmic resistance of the cell at a certain current density i, and the overpotentials (oxygen and hydrogen overpotentials) at the anode and cathode electrodes, η_A and η_C, respectively, that is expressed as Eq.8. The share variation of ohmic resistance voltage, oxygen overpotentials and hydrogen overpotentials with respect to current density is plotted in figure 3 [18].

$$V_{real} = V_{rev} + |\eta_A| + |\eta_C| + i \times R_{total} \tag{8}$$

Figure 3: Typical cell voltage versus current density characteristic of a polymer electrolyte membrane (PEM) electrolysis cell [18].

C. Efficiency

The energy of hydrogen out flow per unit time per unit of electrical power supplied is defined as energy efficiency $\in_{WE}$ In water electrolysis process, as expressed in Eq.9. This efficiency is based on the electrical power supply for electrolysis.

$$\in_{EW} = \frac{\Delta H_{reac} F_{H_2} LHV}{EP} \tag{9}$$

Whereas the lower heating value (LHV) of hydrogen 33.3 kWh per kg corresponding to an electrolyzer voltage of 1.254 V is most often used as the reference. Efficiency values based on the higher heating value (HHV) of 39.4 kWh per kg corresponding to the thermo-neutral value of 1.48 V are also reported in the literature. Some of the most used relations for efficiencies based on HHV are as below: According to [23,27 - 29] the efficiency is defined in terms of out flow rate of hydrogen, electrical power input, heat supplied to heat exchanger and redundant heat needed. The expression of efficiency is expressed as Eq.10.

$$\in_{EW} = \frac{F_{H_2} HHV}{EP + E_{HE} + E_{red}} \tag{10}$$

According to [11, 28, 30 - 32] the efficiency is defined in terms of out flow rate of hydrogen, electrical power input, heat supplied to heat exchanger and redundant heat needed including with electricity generation efficiency. The expression of efficiency is expressed as Eq.11

$$\in_{EW} = \frac{F_{H_2} HHV}{EP/\in_{electric} + E_{HE} + E_{red}} \tag{11}$$

The electrical efficiency has wide range from 25% to 80% and this is free from electrolysis cell system [11, 31, and 33]. In the other efficiency relation given by references [21, 27, 28 and 33] included the effect of environmental temperature and external heat source temperature on the thermal energies and expression is given as Eq.12. So this expression has more credibility to describe the water electrolysis efficiency compare to Eq. 10 to Eq. 12 efficiencies expressions.

$$\in_{EW} = \frac{F_{H_2} HHV}{EP/\in_{electric} + E_{HE}(1 - T_\infty/T_e) + E_{red}(1 - T_\infty/T_e)} \tag{12}$$

further we can calculate the total efficiency of hydrogen production plant including the power input starting from water treatment , hydrogen production, hydrogen drying pump power and hydrogen purification can be taken into account. For comparing many different electrolysis systems, it is necessary to take similar operating pressure and boundary conditions. At room temperature and without any consideration of additional heat to the process voltage efficiency measured conveniently based on HHV. The voltage efficiency is the ratio of enthalpy voltage to the actual voltage of cell and expressed as Eq.13.

$$\in_{Voltage} = \frac{V_{enth}}{V_{real}} \tag{13}$$

The equation13 is valid when the process follows or assumes to follow the faraday's law of decomposition. While during process the condition to faraday assumption cannot be maintain due to the gas diffusion, currents behavior within the cell and leakage of gases to surroundings.

These disturbance reduces the real production rate of hydrogen from the ideally calculate production rate. Hence faraday efficiency (Current efficiency) calculates these lose and expressed mathematically as Eq.14.

$$\in_{faraday} = \frac{F_{H_2,real}}{F_{H_2,Ideal}} = \frac{F_{H_2,real}}{I(nF)^{-1}} \tag{14}$$

Thus the total cell efficiency $\in_{Cell}$ (losses due to the power consumption of peripheral devices are not considered) is the product of the voltage efficiency and the current efficiency, as Eq.15.

$$\in_{cell} = \in_{voltage} \ x \in_{faraday} \tag{15}$$

IV. ALKALINE ELECTROLYSIS

Clean energy is need of this world while the world generating lots of pollutants enough to change adversely the ecosystem. The hydrogen production by alkaline water electrolysis is one of the environmental friendly, zero emission of carbon dioxide if this process combined with renewable energy sources [34-36]. Alkaline water electrolysis is old technology but this is one of the easiest, simplest and suitable methods for hydrogen production but alkaline water electrolysis face the crisis of relatively high energy consumption, installation cost, maintenance cost, durability and safety [37, 38]. Alkaline electrolysis is a mature process: suitable electrolyzers are industrially manufactured. If the electricity is generated by CO_2-free processes (renewables, nuclear), alkaline electrolysis is a sustainable way to produce hydrogen. The recently developed zero gap system in the Chlor–Alkali electrolyzer together with new electrode technologies introduces superior performance [37]. Alkaline electrolyzer decomposes water at the cathode to hydrogen and HO^-. The latter migrates through the electrolyte and a separating diaphragm/membrane, discharging at the anode liberating the O_2. The electrolyte is an aqueous solution containing either NaOH or KOH with a typical concentration of 20–40 wt. % and operation temperatures are between 343 and 363 K and operating pressure upto 3MPa.

A. Cell Components

i. Diaphragm: for separating the anode and cathode the materials used for diaphragm are:
   a) Asbestos: Now asbestos not used due to safety regulation of health.
   b) Composite material based on ceramic materials or microporous materials, few examples are ; Polyethersulfone(PES) a reinforced, microporous polymer membrane , glass reinforced polyphenylene sulfide(PPS) compounds, Nickel Oxide layer on a mesh with Titanium Oxide and potassium Titanate fine pored, predominantly ceramic

ii. Electrodes: Electrodes are cathode and anode on which the hydrogen and oxygen gas separate respectively. A cathode is the electrode of an electrochemical cell at which reduction occurs, positive charges usually move towards the cathode. In a device which consumes power, the cathode is negative, and in a device which provides power, the cathode is positive. Usually negative charges move towards the anode. The anode is positive in a device that consumes power, and the anode is negative in a device that provides power. Metal materials as cathodes for HER are divided into three classes: (a) Metals with high overpotentials: Cd, Ti, Hg, Pb, Zn, Sn etc. (b) Metals with middle overpotential: Fe, Co, Ni, Cu, Au, Ag, W etc. (c) Metals with low overpotentials: Pt, Pd [16]. Metal materials as anode for OER is generally of Ni and its alloy and also the same material as cathode can use for anode also.

B. Electrocatalyst

Electrocatalyst is very important material for enhancing the efficiency of water electrolysis process of hydrogen production because by diverting the reactions pathway to lower activation energy. The kinetics of both the HER and the OER depend strongly on the activity of the electrocatalyst. In this regard many different combination of metals and oxides like Raney-Nickel-Aluminum, activated electrode can be enhanced by adding cobalt or molybdenum to the alloy , galvanic deposition of Ni–Zn, Ni–Co–Zn, or Fe–Zn alloys on the electrode support (perforated plates), or the vacuum plasma spraying (VPS) technique. Several combinations of transition metals, such as Pt_2Mo, Hf_2Fe, and TiPt, have been used as cathode materials and have shown significantly higher electrocatalytic activity than state-of-the-art electrodes. A large number of mixed oxides have been investigated with the goal of minimizing the anode overpotential. The oxide ruthenium oxide (RuO_2), Spinel type oxide (cobalt(III) oxide (Co_3O_4) and Nickel cobaltite ($NiCo_2O_4$)), perovskite type oxide ($LaCoO_3$, $LaNiO_3$ and $LaCo_xNi_{1-x}O_3$) and pyrochlore type oxide ($Tl_2Ru_xIr_{2-x}O_7$) used as electrode and showed the catalyst character and decrease the potential requirement significantly [18].

C. Electrolyte

The electrolytes used in conventional water electrolysis are KOH and NaOH also H_2SO_4 use but not as much as KOH and NaOH used. These are corrosive solution, damage the electrodes its catalytic activity decreases and increase the operating cost of process. Therefore additions of some foreign materials are necessary to neutralize the corrosive nature of electrolytes. $BIMBF_4$ molecular electrocatalyst [Ni $(P_2N_2)_2](BF_4)_2$ [39], and many more combinations of ionic liquid solution with different electrodes are discussed and optimized in [40,41]. There are many additives are mix in electrolytes in order to increase the ionic activation. This way the energy requirement can be decrease for water electrolysis process. Generally for this purpose Na_2MoO_4, Na_2WO_4 ethylenediamine based metal chloride complex ([M $(en)_3]Cl_x$, M=Co, Ni, etc.) [42-44]. In other research [45] author added ethylene di-amine cobalt (III) chloride complex ([Co(en)$_3$]Cl$_3$) or trimethylenediamine cobalt(III) chloride complex ([Co(tn)$_3$]Cl$_3$) into KOH solution as catalyst for HER evolution.
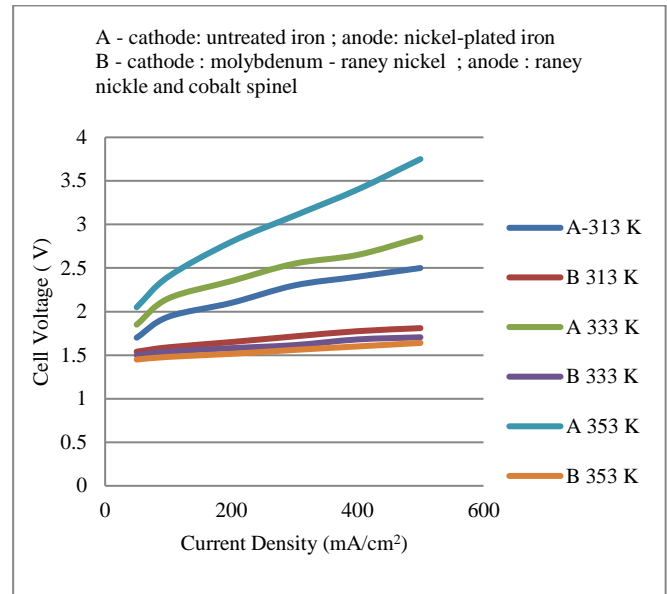
In [46] author added Na_2MoO_4 and [Ni (en)$_3$]Cl$_2$ as ionic activators. In [47] author added hexadecyltrimethyl ammonium bromide (HTMAB), cationic surfactant [48, 49], into H_2SO_4 electrolyte to enhance water electrolysis. In a research work [50] NaCl addition in the different electrolyte studied to see the effect on hydrogen production. In this work liquids use as electrolyte tap water, margine, gas liquor, waste water from cooking, puckered olive, urine, vinegar of pink, municipal waste water and finally milk water. The addition of NaCl in the produced more hydrogen and increase the efficiency was noted in this work. Hence adding of catalyst compound in the electrolyte solution is easy and efficient method to enhance the process output. Also using or adding the ionic liquid into or as electrolyte solution increase the life of electrodes and so economically sound.

D. Electrolyzer design

In conventional electrolyzer, the perforated electrodes sheet fixed in the middle of compartment. There is some gap among cathode, diaphragm and anode in the conventional design. This design cause a disadvantage and results high ohmic loses due to gap in cathode and anode. Hence in the recent development 'zero-gap' electrode design to reduce the gap between the electrodes consequently ohmic loses reduce. The zero-gap cell has become state-of-the-art in modern alkaline electrolyzer. Zero gap system is able to reduce cell voltage in alkaline water electrolysis [18, 37]. Plots of cell voltage versus current density at different temperatures for an optimized electrolysis cell are presented in Figure 4 below. Both electrodes consist of highly active Raney nickel made by the VPS technique. In the same figure for a conventional alkaline electrolysis cell with electrodes made of untreated iron (cathode) and nickel-plated iron (anode) for comparison. The graph shows the considerable cut in voltage for high temperature and for active Raney nickel electrodes. For real applications a number of cells are assembled as one unit called cell stack and this cell stack is core component of an electrolysis system. In past unipolar concept designs was commercially in application. Now bipolar series connection of the cells alkaline electrolyzer used also called filter-press assembly.

E. Innovations & Development

The water electrolysis has a great age of development, and even now need a long way to develop. There are many theoretical aspects and as well as practical also where development is needed. Using the natural sources like solar, wind, cyclone, steam etc. energy in place of electricity is interesting and desirable aspect of this process. These innovations are made toward to pollution control, reducing cost, increasing efficiencies. While the new innovation are quite appealing but also have its own limitations. Among the several recent developments photovoltaic electrolysis and steam electrolysis are discussed here. Photovoltaic (PV)

Figure 4: A comparison between two different types of electrode A and B [18].

electrolysis: Solar energy is in abundant quantity and its utilization in different need of humanity is well known. Solar energy now also using in water electrolysis as a sources of electricity. Firstly author of [51] used this concept by using titanium oxide electrodes. In this technology the capturing of photovoltaic energy and converting into required electricity is main concern. The electrode in photovoltaic electrolysis is called photoelectrodes in which energy of sun light absorbs. So basically here the system consists of two cells one is photovoltaic cell and other is electrolysis cell. Theoretical efficiency is investigated upto 18.3% [52], while for large scale production it is quite low upto 6% [53]. Costly photoelectrical active material, low operation current density, low solar energy density, variation of sun radiation are the key problems for the new technology[2] and has to study in detail to use this technology in practical level production.

V. POLYMER/PROTON ELECTROLYTE MEMBRANE ELECTROLYSIS (PEM)

In the row of development of water electrolysis technology for efficient hydrogen production General Electric (GE) developed the first water electrolyzer based on a solid polymer electrolyte concept [54]. Later Grubb [55, 56] use a solid sulfonated polystyrene membrane as an electrolyte in the development of this technology. This new technology then named as polymer electrolyte membrane or proton exchange membrane (PEM). When an acidic solid polymer is used as the electrolyte in place of liquid electrolyte is called polymer electrolyte membrane (PEM) electrolysis or proton exchange membrane electrolysis. Only deionized water without any electrolytic additive is fed to the cell. The membrane functions both as the gas separator and the electrolyte.

The half-cell reactions (HER and OER) are expressed according to the equations in Table1. Polymer electrolyte water electrolysis system (PEM) [57, 58] produce best alternative for hydrogen production other than alkaline water analysis (AWE). Polymer electrolyte water electrolysis (PEM) have more advantages over alkaline water electrolysis, advantages are ecological cleanness, small size and mass, high purity of hydrogen gas, low gas crossover, lower power consumption, high proton conductivity, control over electrical power variations, high pressure operation, higher safety level ,easy handling and maintenance [59]. The operation cost of PEM was more comparatively but the continuous development in research and investigations on PEM electrolysis for hydrogen production are focused greatly [60]. In this regard new catalysts [59, 61]; new PEM electrolytes [62] current collector methods are going to develop to sustain this green technology [38]. For PEM electrolyzers, the current efficiency (Faraday efficiency) is assumed to be over 99% [63].Requirements of PEM must achieve with high ionic conductivity, good oxidative stability, mechanical, chemical and thermal stability, low permeability for gases, good electric insulator and ionomer must have high stability to withstand the harsh conditions in a PEM electrolysis cell.

A. PEM electrolysis Components

- Membrane Electrode Assembly (MEA)
    - Membrane
    - Anode and Cathode electrode with electrocatalyst
- Gas diffusion Layer (Current collector)
- Bipolar plates

The fundamental design of a PEM electrolysis cell, as shown in Figure 5 below, the two half-cells are separated by the membrane. The components of PEM are membrane electrode assembly (includes membrane, anode and cathode electrodes), gas diffuser (current collector), gasket, bipolar plates and interconnector. The core component of PEM cell is membrane electrode assembly (MEA) in which electrodes is coated directly. Gas diffuser (current collector) and gasket are used to enable an electric current to flow between the bipolar plates and the electrodes. The bipolar plates are electrically conductive, support to transport liquid water at the anode and oxygen and hydrogen out of the electrolysis cell. Materials such as titanium and coated stainless steel have to be used for constructing the bipolar plate, current collector, and, if necessary, the support for catalysts.

B. Membrane Electrode Assembly (MEA)

i. Membrane:

The core component of PEM cell is membrane electrode assembly (MEA). MEA combined membrane, cathode, anode and coated electrocatalyst. The membrane is backbone of this assembly and called supported membrane a dimensionally stable membrane (DSM^{TM}). Perfluorosulfonic acid polymers – PFSA membranes are used such as
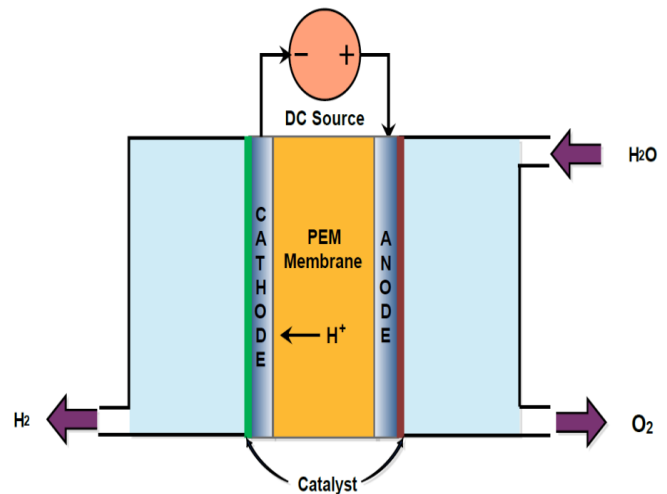

Figure 5: Fundamental of PEM electrolysis.

Nafion®, Flemion®, Fumapem® and Aciplex®. These PFSA membranes are known for high oxidative stability, high strength and high efficiency, dimensional stability with temperature change, high proton conductivity and good durability. Lifetimes approaching several 10 000 h and proton conductivities as high as 0.1 S/cm have been reported. The typical membrane thickness varies from approximately 100µm to 200µm, which is a for low ohmic drop, high mechanical stability, and high gas permeability. Nafion 110, 115 and 117 from DuPont are the most commonly employed membranes in PEM electrolysis cells to date. At current density 1 A/cm^2, 80°C and atmosphere pressure there are lots of work has done on membranes. In [64] author did work on three types of polymer electrolyte membranes (PEMs): Nafion® 115 membrane (127 µm), Nafion® 212 membrane (51 µm) and Nafion® 211 membrane (25 µm) and catalysts used for anode and cathode layers were IrO$_2$ cathode (20 wt.% Pt, 40 wt.% Pt, 60 wt.% Pt and Pt black). Loading for anodes and cathodes 3mg/cm^2 of IrO$_2$ and 0.5mg/cm^2 of Pt and, respectively. Author also reviewed lots of works in same scale and tabulate. The author outcomes compare to the other previous are tabulated below in table 2 from there we can easily see that the Nafion® 211 produced the best result. To reduce material costs there are many alternative membranes are used such as bi-Phenyl Sulfone Membrane (BPSH), Hydrocarbon/Phosphonate Membrane Inexpensive starting materials, PFSA membranes (700 EW & 850 EW), m-phenylene-bis (5,50-benzimidazole) (PBI) , pyridine groups (H$_3$PO$_4$ doped) aromatic polyethers containing, Sulfonated aromatic polymers such as polyether ether ketone (PEEK) and PSf, in [74] author did work on 30wt.% PES/SPEEK with MEA are 4 cm^2, anode Ir black , cathode 20 wt.% Pt/C at temperature 80°C. author found by use of this cost effective membrane can achieve high current density upto 1600 mg/cm^2 good performance and economically competitive.

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Table 2: Membrane activity summary of some authors [64].

Membrane	Thickness (μm)	Anode	Cathode	Nobel Metal Loading	Cell Voltage(V)	References
Nafion® 115	127	IrO2	60 wt.% Pt	3.5	1.585	[64]
Nafion® 212	51	IrO2	60 wt.% Pt	3.5	1.534	[64]
Nafion® 211	25	IrO2	60 wt.% Pt	3.5	1.523	[64]
Nafion® 115	127	IrO2	20 wt.% Pt/C	2.12	1.64	[65-67]
Nafion® 115	127	IrO2	30 wt.% Pt/C	2.65	1.70	[68]
Nafion® 115	127	IrO2	30 wt.% Pt/C	3.18	1.70	[69]
Nafion® 115	127	IrO2	30 wt.% Pt/C	3.18	1.72	[70]
Nafion® 115	127	IrO2	Pt black	4.5	1.60	[71]
Nafion® 112	50	Ir black	Pt black	2.5	1.70	[72]
Nafion® 212	51	Ir-Sn Oxide,	40 wt.% Pt/C	1.8	1.580	[73]

ii. Electrode and Electrocatalyst

In MEA, typically membrane is coated directly with noble metal electrodes (at a loading for cathode upto 2mg/cm^2 and for anode upto 6 mg/cm^2) and their oxides as electrocatalysts (platinum, iridium, iridium dioxide (IrO_2), rhodium, rhodium oxide (RhO_2). Another approach is to apply the electrocatalysts on the current collector, for example, by spraying. In a second step, the electrode and current collector are fixed to the membrane. Hot pressing method generally used for manufacturing the MEA for PEM electrolysis. Mixture of catalyst and ionomer used in order to enlarge the area of three-phase-boundary where half-cell reactions take place. Hydrogen (cathode) side Supported or unsupported Platinum black (loading: 1-6 mg·cm-2) and oxygen (anode) side: Unsupported iridium black, ruthenium and their oxides and mixtures (loading: 1-2 mg·cm-2) assemble. The MEA is of high cost intensive due to catalyst high cost. The cost can be reduce by reducing the catalyst load on cathode and anode and other way substituting the high cost catalyst by other low cost material for optimizing the production and capital cost [54]. Starting from the above standard configuration, considerable progress has been made in improving the performance of PEM electrolysis. The rigorous and valuable study related to electrocatalyst can be found in two series of work. On the OER the work were done by Burke and Moynihan and on the HER the work were done by Furuya and Motoo [75-88]. The OER activity is enhanced and can be improved by using other catalyst systems. Mixed oxides of metals from the platinum group, for example, mixed oxides of iridium and ruthenium. Ruthenium oxide (RuO_2) is the most active material for OER; yet it is highly unstable (the oxidation of RuO_2 to RuO_4 occurs at potentials more positive than 1.387V) Iridium oxide (IrO_2) is the standard material compromising activity and stability. In the following years, studies on PEM water electrolysis had been focused on the survey of electrocatalysts in order to mitigate the drawback of the OER irreversibility and slowness. Miles and Thomason experimented over many different metals for the activity of HER and the OER at 0.1 mol/L H_2SO_4 at 353K by cyclic voltammetric techniques. In their observation they found for the HER the activity in order of Pd > Pt > Rh > Ir > Re > Os > Ru > Ni and for the OER, the order was Ir > Ru > Pd > Rh > Pt > Au > Nb. However the oxides of each catalyst affecting their electrocatalytic activities for the OER greatly [89]. Among all the RuO_2 showed that oxygen overvoltage much lower than Ru, Pt or any other material tested and also gave the high metallic conductivity similar with IrO_2 [90,91]. In many research works it is found that RuO_2 and Ru go through oxidation and these results the forming of RuO_4 in acid electrolyte. Consequently Ru is leached out from catalyst layer of membrane and precipitated and deposited. Ru ions which may be complexes, negative ionic state, back-diffuse from the cathode, in cracks, or in the gas passages [92, 93]. Hence a lot of research works had been done to finding the alternative to control corrosion nature of RuO_x, to use of RuO_x because of its abundance over IrO_2 [91, 93]. In the direction of work the researchers found that the mixing of IrO_2 (20%) into RuO_2 improves the stability and decrease the erosion rate by 4% [94]. $Ru(RuO_2)$ compare to $Ir(IrO_2)$ is more active but use of $Ru(RuO_2)$ is limited due its corrosive nature. So for improving the efficiencies reducing the capital cost corrosive control must be taken into account for durability of electrodes and electrolyte system.

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Lots of work has been done and still working on numbers of possibilities and alternatives for OER and HER activity. Binary catalysts are emerging concepts like mixing of IrO_2 with SnO_2 [95] and among mixture (TaO2, SbO2, TiO2, Ti4O7 …) also improved performance of MEAs [96]. Material and mixture of Ta_2O_5, Nb_2O_5 and Sb_2O_5 also tried by authors [97-101]. Coating of Ti over IrO_2 [102], Ti over $IrO_2 – Ta_2O_5$ [98] also used. The Nano sizes (2, 3,7,12 nm) of IrO_2 catalysts activity also studies over TaC [68-70, 103]. In other works [104, 105] the catalyst consisted of pure metal oxide (IrO_2, SnO_2 and $RuO2$) binary mixtures ($Ir2RuO_{16}$, $RuIrO_4$) and tertiary metal oxide (Ir_2RuSnO_8) studied. Ternary unsupported catalyst also taken in great consideration like $Ir_xRu_yTa_zO_2$, $Ir_xRu_yMo_zO_2$ and at 353 K, cell voltages of less than 1.6 V at $1A/cm^2$ have recently been observed with anode catalysts based on $Ir_xRu_yTa_zO_2$[66,106]. The best result was obtained with an $Ir_{0.6}Ru_{0.4}O_2$ anode and a 20 wt. % platinum–carbon cathode (1.567 V at 1 A/cm^2, Nafion 115). At 363 K, carbon-supported palladium catalysts on the cathode (40 wt. % palladium–carbon, 2.4 mg/cm^2; 1.65V at $1A/cm^2$) yielded higher efficiency comparatively. For HER electrocatalyst activity many other combinations are tried like MoS_2 with graphite [107, 108], MoO_3 [109], $Cu_{1-x}Ni_xWO_4$ [110], PWA with CNT [111], WO_3 nano rods [112, 113], Co and Ni glyoximes [114, 115], Pd/CNTs [116,117], Cu/Pt [118] studied and proving alternatives of good performance. There are many factors that can be effect on overall OER and HER electrode qualities, acidic media activity, durability of coatings, electron conductivity, and electrocatalyst activity with operation time. Hence for the future and sustainability of PEM electrolysis process work should be done in expanding surface area, improving electron activity, change storage capacitance, transport component of impedance, high catalyst utilization and high mass transport.

iii. Innovations & Development

There are many positive outcomes in the continuous development of catalyst, electrode materials, and methods etc. for PEM electrolysis process. PEM is most desirable method to produce hydrogen by electrolysis and yet to optimize the method in great need. In this way further development are urged like Core-Shell catalyst, Bulk metallic Glasses and nanostructured films technologies and reviewed greatly by author [38]. Nanostructured thin films are emerging and advanced technique for PEM electrolysis cell design. This technology reduces total cost, increases durability of cathode and anode, corrosion resistance, specific activity and mass activity also good OER and HER activities [119, 120]. $Pt_{68}Co_{29}Mn_3$, $Pt_{50}Ir_{50}$ and $Pt_{50}Ir_{25}Ru_{25}$ nanostructured thin films are study compare to Pt-black and author found higher performance [120]. Catalysts for core shell in order to increase the efficiencies and decrease metal loading and reducing the cost a core – shell model is very appealing and promising method. The core – shell is a bimetallic alloy in which a metallic core substrate supports a metallic monolayer. In [121] Pt use as metallic mono layer and Cu use as core substrate. There are very less research are done for core-shell combinations for PEM, but Pt-Cu is testified by its very high catalytic reactivity. It has been reported in the work [122] that if Pt-Cu nanoparticles are used as core – shell catalyst the OER can be accelerate uniquely high and the total cost for Pt use in conventional PEM can be reduce upto 80% because of dramatic reduction in loading below to 0.2 mg/cm^{-2} and there are lots of indication to improve more. Hence the new structure as Core- Shell catalyst could change the present scenario of hydrogen production by PEM. The high surface area is always helpful to increase the activity of catalysis, precious metal catalysts can utilize to develop inform of alloys of multicomponent and nanowire structure to enhanced the surface are. A multicomponent alloy increases the charge transfer between them so the electronic band structure [122]. In this direction of development some researchers' demonstrated alternative catalyst called bulk metallic glasses (BMGs) [123-126]. In [123] author also found that Pt-BMG is very suitable for high efficiency PEM electrolysis.

VI. HIGH TEMPERATURE WATER ELECTROLYSIS

The high temperature electrolysis is favorable due to its thermodynamics. At high temperature the total electricity demand decreases significantly compare to rise in thermal demand. Ionic conductivity of the electrolyte and rates of electrochemical reactions at the electrode surfaces increases at high temperature. High temperature can be reused from waste heat of the process like nuclear origin, Solar, Geothermal, fossil and from any high thermal process. The below Figure 6 [15] demonstrate the electrical energy and thermal energy requirement as temperature of electrolysis process increases.
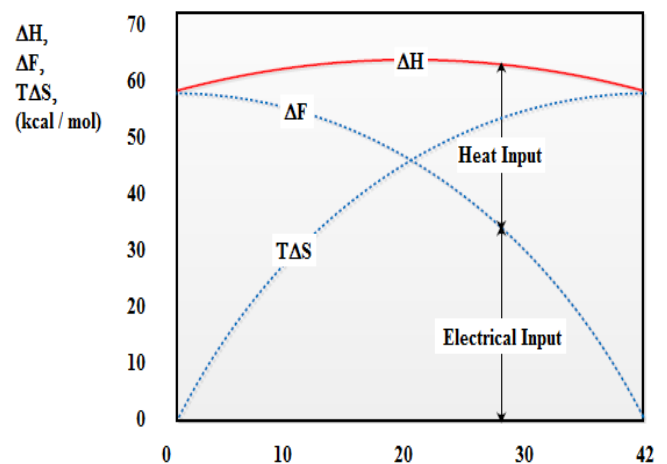

Figure 6: the high temperature electrolysis process energy requirement with variation of temperature.
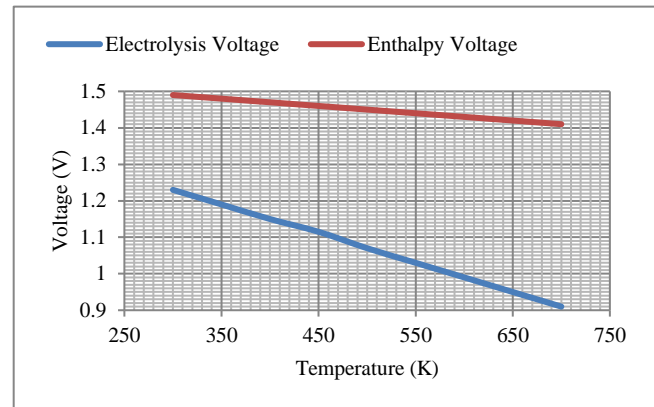
In [127] author did an experiment in which 19M KOH electrolytes with distilled water has taken. The electrode assembly; cathode is Monel wire [Nickel 400 (66.5% Ni, 31.5% Cu, 1.2% Fe, 1.1% Mn)] fixed with various combinations of anode which included Ni, Li-Ni, and Co-Ni. Author experimented for electrolysis at atmospheric pressure, electrolysis at elevated pressure and electrolyte hygroscopy at high temperature. The experiments are carried out at 35, 80,200,250,300,350 and 400^OC. and it is found that the electricity requirement decreases significantly with rise of temperature. The best result found at a temperature of 400° C and pressure of 8.7 MPa on a Co-Ni anode.

In [128] work author did work on two different plan of hydrogen production by water electrolysis. In this work authors use the external energy sources for achieving high temperature upto 1000K and high pressure upto 100Mpa. In the result it is very clear indication that the high temperature and pressure electrolysis need smaller energy inputs. The splitting reaction potential of water molecule is reduce with increasing in temperature. The efficiency of Electrolysis process is enhanced with decrease in energy consumption for any current supply due to the raised temperatures [45, 129]. This due increase in surface reaction and ionic conductivity of electrolyte with temperature rise [130]. At a high temperature steam electrolyzer (HTSE) it is found high temperature water electrolysis to need less energy compare to conventional low temperature electrolysis processes. Overall efficiency of the process achieved 59% at 1000°C water electrolysis compare to 33% initial value [131]. In another study the process efficiency of high temperature and high pressure electrolyte solutions found that at high temperature the less amount of voltage required for achieve the desired current density [127]. In the heated cell the reversible potential and overpotentials shifted down [132].

At high pressure the gas bubble shrinks so in result there is drop on ohmic voltage so consequently the power reduce. In many research it is found the high pressure electrolysis process need low power in the process. In an experiment of Appleby et al. [133] author find the when the pressure is increased from 1 to 10 atm there is fast reduction in power consumption and upto 30 atm pressure the total potential drop of about 100mV. The similar work are also done by LeRoy et al. [134] and Onda et al. [135], B. Laoun[25] experienced the same fact that the power consumption decreases with increase in pressure irrespective of temperature. B. Laoun [25] in his work use the following equations Eq.16 and Eq.17 for electrolysis voltage and enthalpy voltage, respectively with the relation of temperature and pressure change and noted the effects for the pressure range 1 atm to 1000 atm.

$$V_{rev}(T,P) = V_{rev}(T, 1atm) + \Delta G_{reac}(T,P) - \Delta G_{reac}(T, 1atm)/nF \qquad (16)$$

$$V_{enth}(T,P) = V_{enth}(T, 1atm) + \Delta H_{reac}(T,P) - \Delta H_{reac}(T, 1atm)/nF \qquad (17)$$

Author did experiment for constant pressure at 1 atm. with temperature variation from 298K to 1000K and noticed in the voltage temperature graph the slope of electrolysis voltage reduce sharply compare to the enthalpy voltage slope, but the both voltages are drop with increase in temperature. The figure 7 closely describes the pattern found by author in his work.

Figure 7: Variation of electrolysis and enthalpy voltage with temperature at 1 atm. Reproduced data from [25].
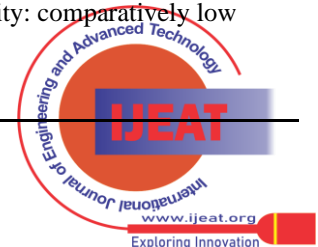
Hence the above equations, graphs and tables are advocating the good effect on efficiency increase as the temperature and pressure increases. These effects are also studied by [139-139] in their research works.

VII. COMPARISON BETWEEN TECHNOLOGIES

The below table 3 is a comparison table in this comparison the alkaline water electrolysis is overcome other electrolysis process currently mature, reasonable efficiency, relative cost effective to the other emergent water electrolysis technologies.

Table 3: A Comparison between technologies [2, 38, 140].

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
Alkaline Electrolysis	Technology: Oldest and Well established Cost: Cheapest and effective Catalyst type: Noble Durability: Long term Stacks: MW range Efficiency: 70% Commercialized	Current Density: Low Degree of Purity: Low(crossover of gases) Electrolyte; Liquid and Corrosive Dynamics: Low dynamic operation Load range: Low for partial load Pressure: Low operational pressure
PEM electrolysis	Current density: High Voltage efficiency: High Load range: Good partial load range System Design: compact Degree of Purity: High gas purity Dynamic: high dynamic operation Response: rapid system response	Technology: New and partially established Cost: High cost of components Catalyst type: Noble catalyst Corrosion: acidic environment Durability: comparatively low

		Stack: Below MW range Membrane: limited and costly Commercialization is in near term
High Temperature electrolysis	Efficiency = 100% Thermal neutral efficiency> 100% w/hot steam Catalyst: Non noble Pressure: High pressure operation	Technology: In laboratory phase Durability: low due to high heat, Ceramics System Design: Bulk system design

VIII. CONCLUSION

Alkaline water electrolysis is easiest and simplest methods for hydrogen production. Less efficiency is one of the great disadvantages in order to widespread use of this system. Effort for development and research needed to over comes the disadvantages like energy consumption, cost and maintenances, durability, reliability and safety. The thermodynamic analysis shows the energy requirements theoretical and actual, resistances offered by system and also discussed different efficiencies, these parameters will help to identify the key problems in way to improvement. The kinetic analysis indicates the reaction rate in alkaline solution, ion transfer electrode surface activity and also effect of different electrolytes and additives on production. In the direction of improving this application the research have to consider significantly for reduce electrochemical reaction resistance, possibilities of low cost electrodes, electrocatalysts, electrolytes and its additives to increase ionic mass transfer, corrosive resistive electrolytes and electrodes for durability of electrolyzer to reduce electrode surface tension, electrode surface profile modifications and surface coatings, and more importantly, managing the gas bubble resistances. Improve the catalytic activity for HER and OER by using binary, ternary or quaternary alloys with an advanced design, improving the electrochemical active surface area, catalyst utilization, and stability against corrosions, development of highly conductive supportive catalyst, Understand and improve the triple-phase-boundary improve the proton transport across the catalytic layer, understand the water transport across the triple-phase boundary. For the anode, find catalyst alternatives to replace scarce iridium or unstable ruthenium will be considered a great achievement. New catalyst configurations or designed structures (e.g.: core-shells, BMGs, NTSFs, nanostructures, tuned alloys) could provide the necessary condition to decrease the amount of iridium or stabilize the ruthenium dissolution over time. For the cathode, improve the catalyst stability (especially when supported on carbon materials), explore alternative supports other than carbon and investigate metal-free N-CNTs catalysts. Also important, is to explore the use of high surface area carbon materials (carbon blacks, CNTs, graphenes) with adjusted pore size, functional groups, grafted polymers and electrical conductivities for the purpose of achieving higher activities and stability. Use innovative synthesis methods to produce new support materials, catalysts, and electrode systems. Development of membrane alternatives to Nafion® with advanced membrane synthesis methods, resulting in electrolytes with higher proton transport but providing at the same time lower gas crossover and higher durability is required. This could be done by; using membrane composites or blends, adding inorganic or organic fillers, or introducing molecular barriers to the electrolyte. This review has also captured and documented in one place much of the varying jargon that has been used throughout the early development to today. Finally, we outlined our idea of the direction the future research should proceed in order to develop PEM electrolyzers as a reliable, cost effective solution to help solve the issues related with renewable energy. High-temperature alkaline electrolysis cell performances are tested at various current densities a wide range of pressure and temperature with various anode and cathode materials are compared and showed a great deal of performance enhancement. Although the results are encouraging, further study is required to completely understand the reasons for the observed dramatic decrease in terminal potential, the possible effects of product mixing and/or electrode corrosion must be determined. The application of superheated steam to the cell for water replenishment, and other improvements required for long-term cell characterization. In summary, this review could help provide a basis for the development of a new generation of alkaline electrolysis systems based on very high temperature and pressure operation. Pressurized electrolysis required consistently smaller work and total (work and heat) energy inputs. Further, the percentage of work composing total energy for pressurized electrolysis is greater; suggesting the prospects of integrating an electrolysis system with external thermal sources needs consider both operating temperature and product pressurization. Owing to the high efficiency of water decomposition at elevated temperatures, HT steam electrolysis could be an option in the future, but only in the long term. Since HT heat (e.g., from a nuclear or solar power plant) and base-load operation are required, this technology would be favorable for centralized and large-scale hydrogen production plants. At present, research and development work is focused mainly on the realization of long-lasting materials to extend both the lifetime and the performance of electrolysis stacks. Reduction in system complexity also remains a major challenge.

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