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Review of various methods for onboard hydrogen production

Aakanksh Yogananda, Abhishek Thakur, Akshay Jain, Aniket Lande, Srikanth Karankoti

Abstract—*In the current scenario fossil fuels are the main sources of energy, but they have a major disadvantage which is the amount of pollution that they cause. Green energy is the suitable alternative for fossil fuels because they don't cause any pollution. This causes a need for an alternative green fuel which is abundant in nature and also easy to harness. Solar energy is a green fuel that comes to mind first, but it is very difficult to harness due to the low efficiency of solar cells. Hydrogen is a green fuel that can be produced easily and due to its high calorific value is a very good alternative for fossil fuels.Various methods of hydrogen* production exist viz. Steam Reforming, Thermolysis, Radiolysis, Photocatalytic water splitting, Alkaline Water Electrolysis, Alkali metal-water reaction and the latest Carbon Catalyst-Hydrogen On Demand(CC-HOD). Currently the problem with usage of hydrogen as a source of energy is its storage, hencethe development of onboard production method which can be used to power small IC engines is underway. Main disadvantage of above production methods for onboard application is feasibility and compactness of production unit.Methods which are suitable for onboard production are Alkaline water electrolysis, Alkali metal-water reaction and CC-HOD.In this paper we are reviewing different methods of hydrogen generation which is based on various parameters to decide a feasible method for onboard production. The methods that are being reviewed are Aluminum-Water Electrolysis, Aluminum NaOH solution reaction and CC-HOD method. Among the above methods, CC-HOD method can be further studied and optimized to use as onboard hydrogen production method.

Index Terms— Alternate fuel, Aluminium, CCHOD,Hydrogen production, Metal Water Reaction,Onboard, Water Electrolysis.

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1 Introduction

THEatmosphere is polluted by various greenhouse gases like; SOx, NOx, CO_2 and CO emitted from various hydrocarbon sources that are fossil fuels. As this is a major issue in current scenario a sustainable and clean technology is needed which is using Hydrogen as a fuel. Hydrogen, as an energy carrier, has become increasingly important, mainly in the last two decades. It owes its popularity to the increase in the energy costs caused by the uncertainty in the future availability of oil reserves and also to the concerns about global warming and climate changes, which are blamed on manmade carbon dioxide emissions associated with fossil fuel use, particularly coal.

Hydrogen production on large scale is practiced by various methods such as Steam Reforming, Thermolysis, Radiolysis, Photocatalytic water splitting, Alkaline Water Electrolysis, Alkali metal-water reaction and the latest Carbon Catalyst-Hydrogen On Demand(CC-HOD) etc. Hydrogen can also be produced by chemical reactions between metals and water i.e. corrosion reaction and by heating metal hydrides.

Industrial methods like steam reforming, thermolysis etc. are very large scale methods and they can't be scaled down for onboard production use. Hence methods like Alkaline water electrolysis, Alkali metal-water react0ions and CC-HOD are being considered for onboard usage.

This paper aims to give an overview of the three main methods that can be used for onboard production of hydrogen, the methods being

1. Alkaline Water Electrolysis
2. Alkali Metal-Water Reactions and
3. CC-HOD method of production.

2 Alkaline Water Electrolysis

Electrolysis is one of the oldest studied method of hydrogen production. Electrolytic hydrogen has a share of 4% in the global production. In electrolysis an electrolyzer is usually subjected to massive current values in order to break the water molecules into oxygen and hydrogen. The basic reaction equation is noted as below:

$$2H_2O \rightarrow 2H_2 + O_2$$

Figure presents the simplest alkaline water electrolysis

- *Aakanksh Yogananda is currently pursuing Bachelor's degree program in Mechanical Engineering at Sinhgad Institute of Technology, Lonavala affiliated to Savitri Bai Phule Pune University, India, PH- +918007704416. E-mail: ay880723@gmail.com*
- *Abhishek Thakur is currently pursuing Bachelor's degree program in Mechanical Engineering at Sinhgad Institute of Technology, Lonavala affiliated to Savitri Bai Phule Pune University, India, PH- +919637751632. E-mail: abhi190596@gmail.com*
- *Akshay Jainis currently pursuing Bachelor's degree program in Mechanical Engineering at Sinhgad Institute of Technology, Lonavala affiliated to Savitri Bai Phule Pune University, India, PH- +917507991787. E-mail: akshay.jain21294@outlook.com*
- *Aniket Landeis currently pursuing Bachelor's degree program in Mechanical Engineering at Sinhgad Institute of Technology, Lonavala affiliated to Savitri Bai Phule Pune University, India, PH- +917276711694. E-mail: aniketlande7@gmail.com*
- *Srikanth Karankotiis currently working as Assistant Professor in Mechanical Engineering at Sinhgad Institute of Technology, Lonavala affiliated to Savitri Bai Phule Pune University, India, PH- +918446588182. E-mail: svkarankoti@gmail.com*

unit which consists of an anode and a cathode connected through an external power supply and immersed in a conducting electrolyte which is either Potassium Hydroxide(KOH) or Sodium Hydroxide(NaOH). When a DC current is applied the electrons move from the negative terminal to the cathode, here they are consumed by the hydrogen ions to form hydrogen atoms. In alkaline water electrolysis a strong base is used, the hydroxide ions move from to the anode where they lose electrons and return back to the positive terminal.

The reactions at anode and cathode are as follows: -

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH$

Anode: $2OH^- \rightarrow ½\ O2 + H2O + 2\ e^-$

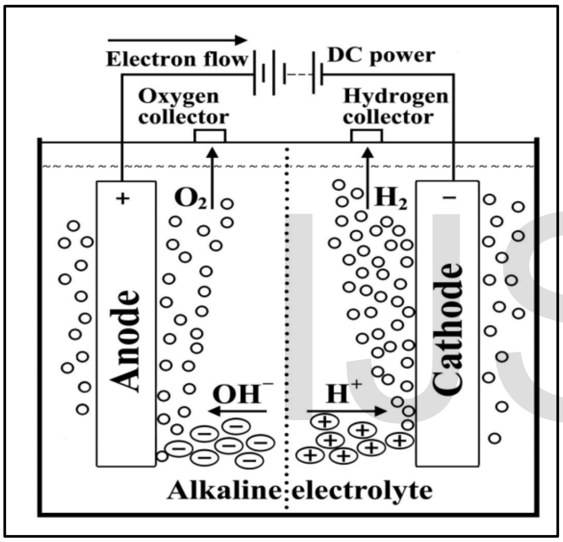

Figure 1: Basic Electrolysis System

A strongbased is required for alkaline water electrolysis. KOH is the preferred base due to the high conductivity as an electrolyte. The electrode that are generally preferred are Nickel(Ni) Copper(Cu) because they are cheap and readily available.

When considering the hydrogen production rates of electrolysis, it can be seen from the table that under normal conditions the production rates are not very high and for high flow rates the conditions are near impossible to reproduce for on-board kits.

Table - 1: Hydrogen Production Rates using electrolysis

Parameter	Monopolar alkaline electrolyser	PEM electrolyser
Cell Voltage	1.85	2
No. of Cell	NA	7-51
Current Density	0.25 A/cm²	1.075 A/cm²
Temperature	70ºC	65 ºC
Current	10 kA	1 kA
Scale	200 kW	NA
Hydrogen $Prod^n$ Rate	42 m³/h	0.42 m³/h
Oxygen $Prod^n$ Rate	21 m³/h	0.21 m³/h
Hydrogen Gas Purity	>99.5%	99.995%
Oxygen Gas Purity	>99%	99%

3 Alkali Metal- Water Reactions

Aluminium has very good electrical, mechanical and thermal properties. Aluminium also is a very recyclable material and having one of the lowest densities among metals which is helpful in transportation and also reduction in the weight of the system. [4]

Aluminium is a very electronegative metal so is very susceptible to corrosion, but the oxide layer formation on aluminium prevents corrosion. This property although useful in areas like construction are not suitable for hydrogen production due to its passivation. [4]

When aluminium and its alloys are reacted with water in strongly alkaline solutions, the Hydroxide ions(OH^-) destroy the oxide layer. This is the reason aluminium and its alloys readily dissolve in alkaline solutions producing hydrogen. [4]

NaOH is the most commonly used alkaline electrolytes and the reactions when using NaOH are as follows. [3], [4], [5]

$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2$$
$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3$$
$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$$

Aluminium is used along with promoters to increase the reaction rates and also to reduce the oxide layer formation and the hydrogen production rates for those cases are as follows. [5]

For pre-treated aluminium the production rate is 8×10^{-7} g H_2/sec/g of Al. When using Al_2O_3 as a promoter the production rate is 4×10^{-6} g H_2/sec/g of Al at 50ºC. When KCl and NaCl are used as promoters the production rates achieved are 2×10^{-4} g H_2/sec/g of Al at 55ºC. [3]

For a general vehicle the production rate required is 1.6 gH_2/sec and for this production rate at least 8000g of aluminium is required which is not feasible for on-board production. [3]

3 CC-HOD Method of Production

As compared to aluminium NaOH reaction, cc-hod is simple chemical reaction between carbon catalyst, molecule containing hydrogen i.e. water and fuel. fuel consists of aluminium in form of shavings, chips, powder(size 30microns), granules. carbon catalyst is produced using electro activated method. [6]

The activation cell consists of electrodes of any metal like stainless steel, iron, galvanised steel etc. The cell consists of electrolyte solution in water. Electrolyte can be anything which makes water conductive. Common electrolyte which can be used are sodium bicarbonate, sodium chloride, potassium hydroxide. If no electrolyte is added, higher voltage will be required for activation. [6]

Carbon to be activated can be of any form charcoal, coal, graphite, lead, carbon granules, pure carbon etc. The carbon should be powdered and totally immersed in electrolytic solution. [6]

The electrical energy of around 5-6 ampere-hour should be passed through the activation cell. Voltage range of approximately 12V-150V can be practically used. To achieve 6 ampere-hours any combination can be used i.e. 2 amperes for 3 hours, 1 ampere for 6 hours etc. as per convenience. Other factors such as electrolyte concentration, current density, amount of carbon does not affect the activation process. The activated carbon can be removed from the cell and dried. [6]

When the aluminium, water and carbon catalyst is added together and heated to 150 degree Fahrenheit, following reaction takes place:

$$2Al+6H_2O+CC \rightarrow CC+2Al(OH)_3+3H_{2(g)}$$

Where Al is aluminium, O is oxygen, H is hydrogen and C is activated carbon used as catalyst.
The carbon is not consumed here and hydrogen gas and aluminium hydroxide is formed as a by-product.
Aluminium hydroxide when dried can be converted into aluminium oxide, which also acts as a catalyst in the above reaction. [6]

Various tests were performed by the method to check the flow rate with variable temperature. The following table shows the flow rate as the reaction proceeds. [6]

Table - 2: Hydrogen Production Rates using CCHOD

Time (mins)	Temp (° F)	Rate (mL/min)	Time (mins)	Temp (° F)	Rate (mL/min)
0	78	0	6:55	152	1000
0:30	99	-	7:14	153	500
1:20	107	300	7:52	153	500
1:55	111	500	9:08	154	250
2:30	120	500	12:55	158	-
3:50	136	250	14:00	153	-
4:00	150	-	15:00	143	-
6:36	152	450	16:00	134	-

3 Conclusions

We can conclude the following from the above stated methods:

- Flowrate obtained by various methods ranges from 0.2 lpm to 4 lpm.
- Required flowrate cannot be satisfied with the electrolysis method as the energy consumed to meet the required flowrate exceeds the amount of energy produced.
- Under normal conditions production rates of aluminium-NaOH does not meet the requirements but when promoters are added the production rate increases.
- The addition of promoters also does not meet the demands of vehicles and hence cannot be used for onboard production.
- Among above methods the only method which can meet the requirement in future is cc-hod as it has the highest rate of production.
- Also it can be used to make compact unit of production to meet the requirement of smaller capacityengines, which other methods fails to achieve because of the physical parameters like size of unit, temperature of the cell, source of energy required to run the kit etc.

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