

A comparison of methane decomposition and water splitting reaction methods as a means to produce molecular hydrogen.

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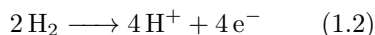
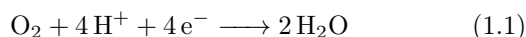
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Abstract

1 Introduction

As the global energy demand continues to increase, a sustainable alternative to fossil fuels is desperately needed. Hydrogen gas potentially presents an innovative solution, but the energy costs for production are currently prohibitive. An efficient synthesis could be a revolutionary step towards a more sustainable future as the hydrogen fuel cell has many advantages over current energy sources; a hydrogen storage tank can be refilled much more quickly than a battery can be recharged,¹ making it far more practical for use in transport.

In a fuel cell, electricity is produced by reducing oxygen at the cathode (1.1) and hydrogen at the anode (1.2).



This reaction leads to the production of heat, water and an electrical potential,² which is a major advantage over systems which produce CO_2 . These reasons alone make investigating the sustainability of hydrogen production a worthwhile endeavour.

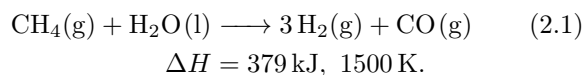
We will start by discussing the traditional methods of synthesis and where they fall short by taking into account the twelve principles of green Chemistry.³ Then we will look at new approaches in the areas of methane decomposition and water splitting reactions, and how these compare to the traditional synthetic techniques. The most promising method from each feedstock will be analysed further, concluding on if and how these new approaches can solve the problems preventing widespread adoption of hydrogen as a fuel.

We will focus on how the use of metal catalysts and how they can improve the rate of reaction, allow for more mild reaction conditions, and reduce the cost of reactions. While we are concerned with the environmental impact of these processes, this review will not discuss the sourcing of the feedstock for each reaction, but will assume the methane being used in these reactions comes from carbon neutral sources such as biomass⁴ and not from petrochemical routes. We also realise that in order for a process to be viable on an industrial scale it must be possible to scale up the reaction, however the practical implications of scaling up will not be discussed in this review.

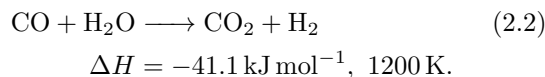
2 Traditional Methods

2.1 Steam methane reformation

The steam methane reformation reaction is an extremely inexpensive and widespread method for producing molecular hydrogen in a commercial setting. The reaction follows the scheme:³



There is also a secondary mechanism for extracting hydrogen from the carbon monoxide by-product of this first stage reaction, which runs at a lower temperature and is called a water gas shift reaction.^{3,5}



This basic reaction scheme is applied to generate approximately 40% of the global hydrogen demand;⁶ primarily due to using readily available reagents, it is a mature technique and it is inexpensive.

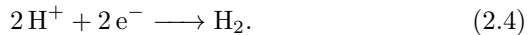
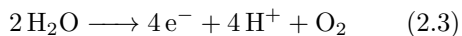
Although both reactions (2.1) and (2.2) can proceed without the use of a catalyst one is often employed for the water gas shift reaction (2.2) in order to increase the hydrogen yield. Iron-chromium or copper-zinc compounds are often used dependant on if the reaction is a low- or high-temperature shift.

Unfortunately this method doesn't produce hydrogen in a sustainable way; the production rate without the gas shift reaction is low, and produces one equivalent of CO for every three of H_2 . When the gas shift reaction is used this toxic carbon monoxide is used to generate further H_2 , as well as the pollutant gas CO_2 . Placing additional strain on the planet by up scaling steam reformation processes will only lead to further damage of the planet, so this process is not useful when considering fuelling a hydrogen powered society.

2.2 Uncatalysed electrolysis of water

Water electrolysis is another basic technique for extracting hydrogen, this time from water. Water is an incredibly naturally abundant chemical making up a large fraction of the earth's surface. When hydrogen is consumed by a fuel cell, water is the sole by-product. Water can be split into hydrogen and oxygen via an

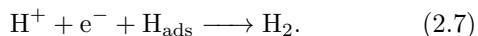
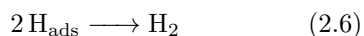
electrolytic cell, where at the anode reaction (2.3) occurs and at the cathode reaction (2.4) occurs.



A common choice of electrolyte for these kinds of cells is KOH; an alkaline cell is more efficient.⁷ KOH has the highest charge mobility and solubility in water of the group I and II hydroxides, which makes it the best choice in this case.

Catalytic design is important as when uncatalysed, the electrolytic approach to inter converting H_2 , O_2 and H_2O is not feasible. In acidic or alkaline solution, the standard cell potential for an electrolytic cell splitting water is equal to the standard potential generated from recombination in a fuel cell, 1.23 V.⁷ In practice however, there are many barriers to this reaction which result in uncatalysed cells always requiring a potential difference greater than 1.80 V. There are various practical issues which cause the greatly decreased efficiency; resistance inside the cell due to work required to move protons, product gasses resulting in a bad connection between the surface of the electrode and the electrolyte, and resistances outside the cell such as the work required for electrons to be conducted through a wire.

Uncatalysed electrolysis is a foundational method on which the water splitting methods is built - catalysts are often deposited on the anode and cathode to lower the reaction barrier and reduce the overpotential that afflicts this method. There are many possible catalysts, almost all of which involve adsorption of protons onto the electrode surface followed by the addition of two supplied electrons, as given in the equation below (??).



Solving the problems with overpotential using safe, effective and cheap catalysts is a promising area of study which could lead to electrolytically generating hydrogen on an industrial scale.

2.3 Discussion of traditional methods

Both of these methods discussed offer the potential for large scale hydrogen generation; albeit at a cost. For

MSR the price is paid with high emissions into the atmosphere, with the current CO_2 emissions crisis this isn't a viable way to solve the problem of city-scale energy fixation into H_2 . For electrolysis, overpotential related to several inferences with the method makes it enviable for similar reasons; the energy to create the H_2 must come from somewhere. Renewable energy sources currently account for 24% of the global energy supply as of 2017, with much of the rest coming from fossil fuels.

Electrolytic methods currently have fewer environmental problems to solve, but tend to be inefficient which is a major problem when considering the application to energy storage. There is much research into addressing this inefficiency; modified catalytic electrodes have taken major steps to increase the rate of gas evolution at lower potentials, and entirely different techniques utilising steam at high temperatures address scaling and efficiency concerns.

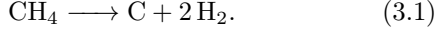
Methane steam reformation itself is a technique which has been improved in efficiency and yield over the years it has been used; membrane reactors modifications to the gas-shift reaction (2.2)³ show promise. Other approaches to using methane as a feedstock are discussed in this review, ones which can take the same material and obtain the same product without the need to collect CO_2 back out of the atmosphere.

3 CH_4 methods

3.1 Methane decomposition using a hydroxyapatite supported nickel catalyst.

One method of methane decomposition currently relies on a nickel catalyst, supported by compounds such as TiO_2 , MgO , ZrO_2 , Al_2O_3 . The rate of reaction depends on the Ni particle size, with both relation to the dispersion and stabilisation by a suitable support.⁷ J. Ashok, S Naveen. Kumar, M. Subrahmanyam, A. Venugopal, have been looking at how a new nickel catalyst support, hydroxyapatite (HAp), and how it will affect this reaction. HAp is produced from $\text{Ca}_5(\text{NO}_3)_4\text{O} \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)(\text{PO}_3\text{OH})$ to make $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$ while under basic conditions.⁷ Unlike the previously mentioned catalyst supports, HAp is irreducible; this means no CO is made in the reaction unlike the other supports currently in use, meaning the reaction has a simple overall equation

with no greenhouse gas (GHGs) emissions:



This reaction has an enthalpy of 75.6 kJ mol^{-1} meaning it is endothermic. In the experiment performed by J. Ashok et al. the experiment was run at just 650°C ,⁷ as this is an endothermic reaction these operating condition are fairly mild. The CH_4 should be flowed through the reaction chamber at a fairly slow 24 L h^{-1} ⁷ again meaning no extra energy is needed to accelerate the gas. These combined factors and the lack of (GHGs) produced make this reaction both green and sustainable.

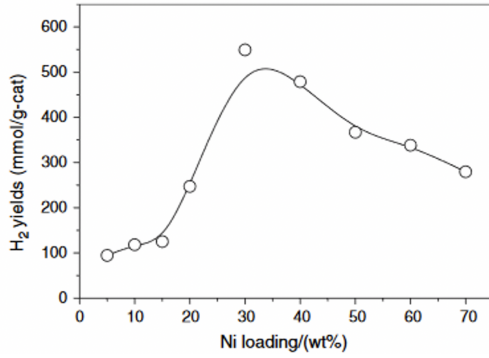


Figure 1: A plot of percent weight of nickel loaded onto the catalyst support vs H_2 yield.

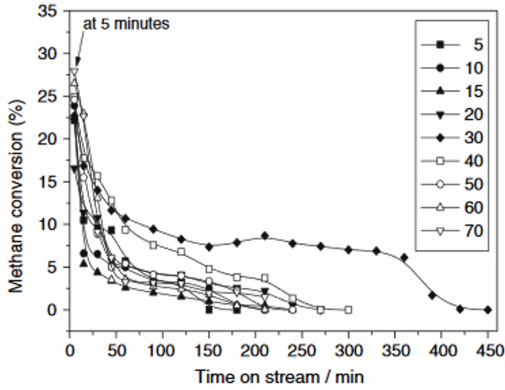


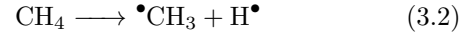
Figure 2: A multiple plot of varying percent weights of nickel loaded onto the support showing how methane conversion efficiency varies with time.

As you can see from figures 1 and 2 a 30 wt% Ni sample was the optimum for this reaction. It has both the highest yield and the best durability. This reaction does have one major draw back however in that the catalyst does readily degrade. This means the solid waste carbon, which is responsible for the deactivation of the catalyst, will be contaminated with toxic Ni atoms. This is a very promising technology which warrants further research, as it can help to solve the current H_2 crisis.

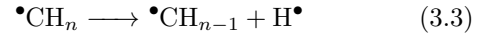
3.2 Radical chain reactions

Radical methane pyrolysis is a way of breaking a CH_4 molecule into H_2 and pure carbon. The initial step is the chemisorption of CH_4 , onto the surface of the catalyst.

The initiation and rate determining step of the radical break down is:



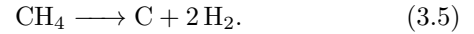
Then a series of propagation steps take place with the general equation:



Until a termination step is reached:



This gives the overall equation of:



This reaction mechanism gives rise to no waste gases such as CO_2 but does has the issue of elemental carbon production which can lead to the degradation of the catalyst as carbon is deposited upon the catalyst surface. The reaction conditions for this mechanism follow Le Chatelier's principal. As the reaction is endothermic a high temperature is needed, as there are more moles on the RHS, low pressure is needed. This is very expensive to maintain. The methane should also move at a low velocity as increases the contact efficiency between the methane and the catalyst, this results in a higher quantity of methane being adsorbed on the active site of the catalyst which means the catalyst will deteriorate slower.

Various catalysts can be used from metals, molten salts/ metals, or carbon-based catalysts. The main catalysts in a metal catalysed reaction are nickel and iron, these are particularly useful as a partially filled 3d orbitals accept electrons from the CH bonds destabilising

their bond strength. These metals allow carbon diffusion through the crystalline structure. Table 1 shows a few key aspects of the catalysts and how they affect the operating conditions and overall reaction process.

Table 1: Catalytic efficacies, all relative values are compared to nickel.

Catalyst	Rate	Toxicity	Cost	Durability	Operating temperature (°C)
Nickel	Equal	Equal	Equal	Equal	500 – 700
Iron	Low	Low	Low	High	700 – 1000
Molten	-	Low	High	High	> 1000
Carbon	Low	-	Low	High	800 – 1000
None	Very Low	-	-	-	1100 – 1200

Both supported and non-supported iron catalysts have been tested such as: $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}(\text{cp})_2]$. However, these types of clusters can give result in unwanted gases, meaning the H_2 must be separated from the gaseous mixture. A catalyst with a strong support increases the carbon dispersion and reducibility of the metal along with preventing sintering of metal particles. However, an excessively strong support may hamper the reducibility of metal oxides. A supported catalyst has a better performance as it balances the carbon dispersion resulting in a longer lasting catalyst while maintaining the reducibility of the metal species.

There are three types of carbon catalyst highly ordered, less ordered, and disordered. Disordered carbon catalysts have three valence sites or no coordination sites these are known as high energy sites (HES). The more HES's there are the faster the rate as these are thought to initiate the mechanism. More oxygenated catalysts have a higher activity but release CO_x , this is because as CO_x is produced new active sites are created on the surface of the catalyst.

3.3 Discussion of methane methods

CH_4 provides a very good solution to the hydrogen problem. The feedstock while less common and renewable than water, can provide a reliable H_2 supply to locations with poor access to water or an unreliable electricity supply.

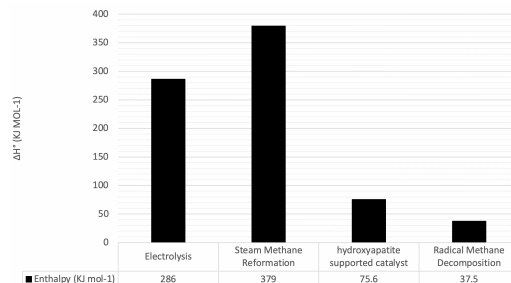


Figure 3: A plot showing the enthalpy of the three methane methods alongside uncatalyzed electrolysis as a reference.^{3,6?}

As you can see from 3, radical methane decomposition and hydroxyapatite supported Ni catalysts have a significantly lower enthalpy cost meaning they are far more economical processes. Both HAp and RMD both run at much lower operating conditions compared to SMR, this is beneficial not only to the cost of the reaction, but also to the greenness and sustainability. Further aiding their sustainability is the lack of greenhouse gases produced by both new reactions. As there are no GHGs produced in either method, no separation step is required to extract the H_2 gas, another positive when compared to SMR. There are however drawbacks to the new methods of production. The produced is not re-sellable for three reasons: there is not a market for it, the carbon rapidly degrades the catalysts and where Ni catalysts have been used, the carbon is contaminated with toxic metal.

Therefore, I believe RMD to be a better method

than HAp. RMD has the option of using carbon or molten catalysts whereas HAp only uses toxic Ni catalysts. The carbon catalysts have a longer life than metals and also run at lower temperatures.

4 H₂O methods

4.1 Amphoteric cell

An existing H₂O electrolysis method which uses an electrolytic cell under alkaline conditions,⁷ is adapted by adding a membrane and an acidic electrolyte.⁸

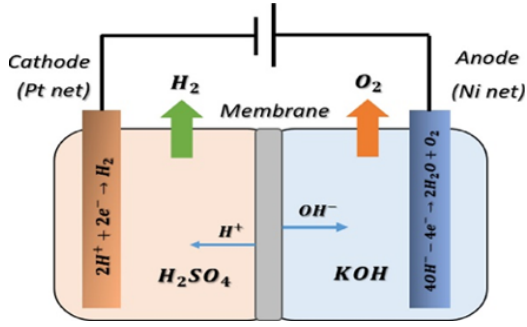
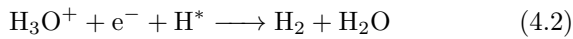
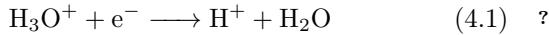


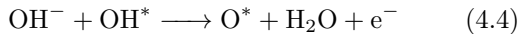
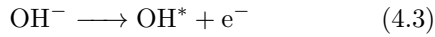
Figure 4: Fig
Acidic/Alkaline amphoteric electrolytic cell.⁸

An ion-exchange membrane is placed between a Pt cathode and an Ni anode, this restrains neutralisation between the acidic and alkaline electrolytes. The H₂SO₄ electrolyte provides excess H⁺ to react on the surface of the cathode, while the KOH electrolyte provides excess OH⁻ to react on the surface of the anode.

H₂ evolution in acidic solution:⁸



O₂ evolution in alkaline solution:⁸



(*) - Chemically attaches onto the catalyst.

H₂O continuously dissociates, the electric potential drives the H⁺ into the cathode chamber, and the OH⁻ into the anode chamber. Therefore, the concentration of H⁺ and OH⁻ in the respective electrolytes is kept high, encouraging the production of H₂ and O₂. This results in a lower potential difference for the electrolysis of H₂O. Since the experiment took place at a constant current and over a set time, this means that energy consumption was also lower.

So, by using an ion-exchange membrane to separate acidic and alkaline electrolytes, the energy consumption required for the electrolysis of H₂O was 30 % less compared to conventional alkaline electrolysis. If this magnitude of energy efficiency could be achieved on an industrial scale using renewable energy, it would provide a method of producing H₂ from H₂O without the use of fossil fuels and potentially transform the way we store and release energy.

There is also scope for increased energy efficiency, as increasing temperature led to a lower potential difference for a given H₂ production rate. This means further research could be undertaken to find the most energy efficient compromise between temperature and potential difference. Further research could also be undertaken into the composition of the electrodes, and whether there is an alternative combination that is just as effective, but doesn't require expensive Pt.

4.2 Solar powered steam electrolysis

In this section we discuss steam electrolysis and will look at a case study from Schiller, Lang and Szabo et al.⁷ High temperature steam electrolysis operates in the temperature range 700 °C to 900 °C⁷ and can occur in a solid-oxide electrolysis cell (SOEC); a high operating temperature cell with similar properties to a solid oxide fuel cell, composed of ceramic.⁷

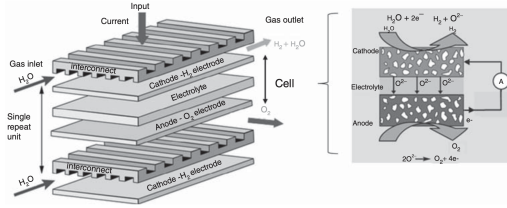
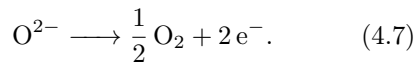
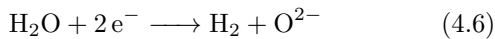


Figure 5: The schematic for a single cell of a solid-oxide fuel cell.

At these temperatures the reaction can proceed faster than at the lower temperatures ($>100^\circ\text{C}$), resulting in a higher electrical efficiency.[?] Overpotential is a major issue with current methods of water electrolysis so overcoming this in systems operating at scale is an important step.

Splitting water in this reaction occurs at two sites; the fuel electrode proceeds via reaction (4.6) and the air electrode via (??).[?]



From a thermodynamic perspective the enthalpy required to split water is reduced, as the total enthalpy $\Delta_r H$ is significantly lowered by removing the need to supply the enthalpy of vaporisation $\Delta_{\text{vap}} H$, approximately $40.65 \text{ kJ mol}^{-1}$.[?] SOECs operating a steam electrolysis reaction have the potential to significantly offset electrical load; the method presented in the paper uses solar energy to superheat water in a steam generator; this is pressurised in an accumulator and fed into the SOEC.

There are several limitations to this research, while it addresses the possibility of superheating water using solar energy, the experimental set-up uses a solar simulator which is obviously an ideal condition, making this not necessarily geographically suitable. The SOEC used by the team was a laboratory scale device and could not handle steam mass flow exceeding 0.5 kg h^{-1} , making validating this experiment on a large scale difficult; is solar energy suitable for heating water that can feed a large bank of SOECs, as when lost are kept together they are more thermally efficient.

4.3 Discussion of water-splitting methods

Acidic/alkaline amphoteric H_2O electrolytic cells operate below 100°C ,⁸ whereas solid oxide electrolytic cells (SOEC) operate between 700°C to 1000°C .[?] This higher temperature results in faster reactions and therefore lower energy consumption per unit volume of H_2 .

The Gibbs free enthalpy for H_2O electrolysis decreases as temperature increases. This means at higher temperatures the amount of electrical energy required for the process is further lowered. A large part of the thermal energy can be provided by solar energy. The enthalpy of $\text{H}_2\text{O}(\text{g})$, and therefore the energy consumption for H_2O electrolysis is lower than for $\text{H}_2\text{O}(\text{l})$. Therefore, H_2O electrolysis in SOEC is more energy efficient than in acidic/electrolytic cells.

Another disadvantage of the acidic/alkaline electrolytic cell is that it depends on an expensive pt electrode, whereas the SOEC uses abundant Ni, La, Sr, Co, Fe, Zr and Y. An advantage of the acidic/alkaline electrolytic cell is that it is a slight adaptation of an existing process and it is far simpler. It only consists of one main component, whereas the SOEC consists of five. This means it is likely to be more reliable and easier to maintain. Since one of the biggest issues facing the commercial production of H_2 from H_2O is the energy consumption, with further refinement the SOEC looks to have the most potential.

5 Conclusion

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