

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

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Abstract

The widespread use of fossil fuels is a major environmental issue, due to the release of greenhouse gases contributing to global warming. Therefore, it is necessary to find an alternative, H_2 could be a promising option, however problems persist in current methods for generation of H_2 . In this review we discuss the current methods of steam methane reformation and uncatalysed water electrolysis for the production of hydrogen and evaluate potential novel methods involving both methane and water as potential feedstocks.

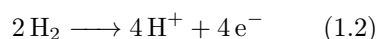
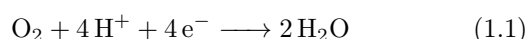
The methane methods evaluated in this review are the thermal decomposition of methane using Ni catalyst on a hydroxyapatite support and radical methane pyrolysis. Radical methane pyrolysis displayed around a 90 % decrease in enthalpy cost when compared to the traditional steam methane reformation, which is a significant energy saving. The water electrolysis methods we looked at are solid oxide electrolytic cells and acidic/alkaline amphoteric electrolytic cells. The latter achieved an energy consumption 30 % less than conventional alkaline electrolysis.

These new methods have clear improvements over current methods in terms of energy cost, which makes the production of H_2 using renewable energy a viable option. This would transform the way we store and release energy.

1 Introduction

As the global energy demand continues to increase, a sustainable alternative to fossil fuels is desperately needed. H_2 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 only heat, water and electricity,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 of the criteria required to produce hydrogen sustainably.³ Then we will look at new approaches in the areas of methane decomposition and water electrolysis reactions. The

methane methods discussed are methane decomposition and radical methane pyrolysis, whilst the water section will be focusing on amphoteric cell electrolysis and solar-powered steam electrolysis.

We will then compare these new methods with the traditional methods; evaluating these new methods and investigating their sustainability compared with their traditional counterparts. 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 these new reactions can improve the rate of reaction, allow for more mild reaction conditions, and reduce the cost of reactions, particularly in terms of energy.

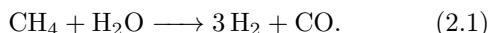
The practical implications of scaling up will not be discussed in this review. We will also not consider the uses of the hydrogen when generated, such as potential issues with and improvements to the hydrogen fuel cell itself.

2 Traditional Methods

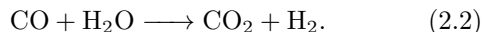
2.1 Steam methane reformation

The steam methane reformation reaction is an extremely inexpensive and widespread method for producing molecular hydrogen in a commercial setting. The reaction follows the scheme³ in equation (2.1),

with $\Delta H = 379 \text{ kJ mol}^{-1}$ at 1500 K.



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.^{3,4} This reaction (2.2) has $\Delta H = -41.1 \text{ kJ mol}^{-1}$ at 1200 K.



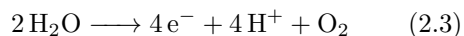
This basic reaction scheme is applied to generate approximately 40% of the global hydrogen demand;⁵ primarily due to using readily available reagents, it is an inexpensive and mature technique.

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 depending on if the reaction is a low- or high-temperature shift respectively.

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 H₂. When the gas shift reaction is used this toxic carbon monoxide is used to generate further H₂, as well as the greenhouse gas CO₂. Placing additional strain on the planet by upscaling steam reformation processes will only lead to further damage to 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 product. Water can be split into hydrogen and oxygen via an electrolytic cell; at the anode reaction (2.3) occurs and at the cathode reaction (2.4) occurs.

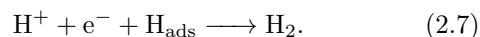
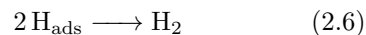
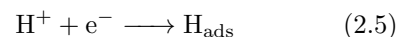


A common choice of electrolyte for these kinds of cells is KOH; an alkaline cell is more efficient.⁶ KOH has

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 interconverting H₂, O₂ and H₂O 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 method 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 equation (2.7).⁸



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 steam methane reformation (SMR) the price is paid with high emissions into the atmosphere, with the current CO₂ emissions crisis this isn't a viable way to solve the problem of city-scale energy fixation into H₂. For electrolysis, overpotential related to several inefficiencies with the method makes it unviable for similar reasons; the energy to create the H₂ must come from

somewhere. Renewable energy sources currently account for 27 % of the global energy supply as of 2020⁹ (projected), 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.

Steam methane reformation itself is a technique which has been improved in efficiency and yield over the years it has been used; membrane reactors which use 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 CO₂ back out of the atmosphere.

3 Methane decomposition reactions

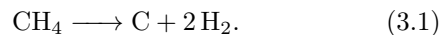
These methods focus on emulating the steam methane reformation reaction. They use methane as a feedstock reagent and focus on a clean conversion to H₂ using catalysts to facilitate the process. A goal of both these methods presented is to reduce or remove entirely the waste gas byproduct CO₂; as a pollutant chemical it is critical for any large scale method to avoid generating large quantities. Both of these methods presented instead fully reduce the methane to elemental carbon, presenting its own challenges.

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 TiO₂, MgO, ZrO₂ and Al₂O₃. The rate of reaction depends on the Ni particle size, with both relation to the dispersion and stabilisation by a suitable support.¹⁰ J. Ashok, S Naveen. Kumar, M. Subrahmanyam et al. have been looking at how a new nickel catalyst support, hydroxyapatite (HAp), and how it will affect this

reaction.

HAp is produced from a reaction of Ca₅(NO₃)₄ · 4H₂O and (NH₄)(PO₃OH) to make [Ca₅(PO₄)₃(OH)] while under basic conditions.¹⁰ Unlike the previously mentioned catalyst supports, HAp is irreducible; this means there is no CO made in the reaction unlike the other catalyst supports currently in use. This means 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. The experiment performed by J. Ashok et al. was run at just 650 °C,¹⁰ which is a mild reaction condition for an endothermic process. The CH₄ should be flowed through the reaction chamber at a slow 24 L h⁻¹¹⁰ again meaning no extra energy is needed to accelerate the gas. These combined factors and the lack of greenhouse gases (GHGs) produced make this reaction both green and sustainable.

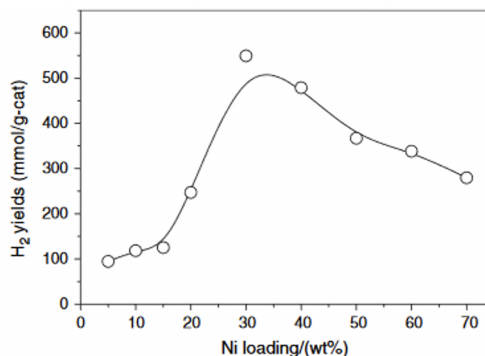


Figure 1: A plot of percent weight of nickel loaded onto the catalyst support vs H₂ yield.

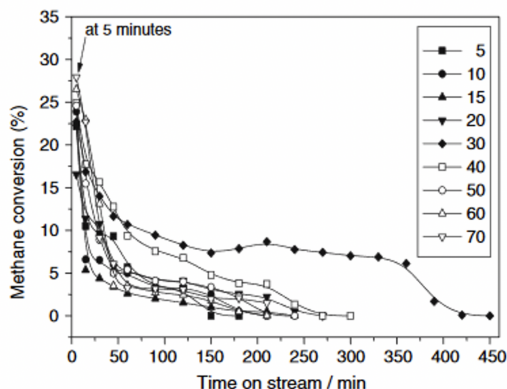


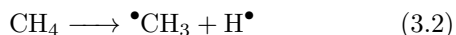
Figure 2: A multiple plot of varying percent weights of nickel loaded onto the support showing how methane conversion efficiency varies with time.

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 drawback however in that the catalyst readily degrades. 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 H₂ crisis.

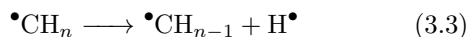
3.2 Radical methane pyrolysis

Radical methane pyrolysis (RMP) is a way of breaking a CH₄ molecule into H₂ and pure carbon. The initial step is the chemisorption of CH₄, onto the surface of the catalyst.

The initiation and rate determining step of the radical breakdown is:



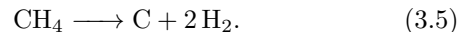
Then a series of propagation steps take place with the general equation:



Until a termination step is reached:



This gives the overall equation of:



This reaction (3.5) gives rise to no waste gases such as CO₂, but does have 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 principle. The reaction is endothermic with an enthalpy of reaction ($\Delta_r H$) of 37.5 kJ mol⁻¹ which is very low when compared to electrolysis which has an $\Delta_r H$ of 286 kJ mol⁻¹.⁵ Due to the endothermic nature of the reaction 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 this 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 more slowly.

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 partially filled 3d orbitals accept electron density from the CH bonds, destabilising their bond strength and ultimately leading to the breaking of the bond. These metals allow carbon diffusion through the crystalline structure. Table 1 shows a few key aspects of the catalysts including how they affect the operating conditions and the 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
Carbon	Low	-	Low	High	800 – 1000
None	Very Low	-	-	-	1100 – 1200

Ni while an effective catalyst, has a major drawback compared to the other catalysts available; its toxicity results in the waste carbon being contaminated with waste Ni catalyst.

Fe catalytic activity is lower than that of Ni however it is more resistant to catalytic deactivation. This

is because carbon has a higher rate of diffusion in Fe, meaning it does not deposit itself upon the active site of the catalyst. It also has the advantage of being able to operate at high temperatures in the range of 700 °C to 1000 °C; it is cheaper and less toxic than Ni. Fe compounds such as $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}(\text{cp})_2]$ have been tested as catalysts.

However, these types of clusters can result in unwanted gases, meaning the H_2 has to be separated from the gaseous mixture, decreasing the reaction efficiency. 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 free valence sites or uncoordinated sites, known as high energy sites (HES). The more HES 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. RMP is a very promising new piece of technology that combines both new and old science. We believe that RMP with an Fe catalyst will go a long way to solve the H_2 problem.

3.3 Discussion of methane methods

Currently SMR provides around 48% of the world's H_2 ,⁵ but this could soon change. With the development of new reactions and catalysts, new and sustainable methods of H_2 production from methane are on the rise.

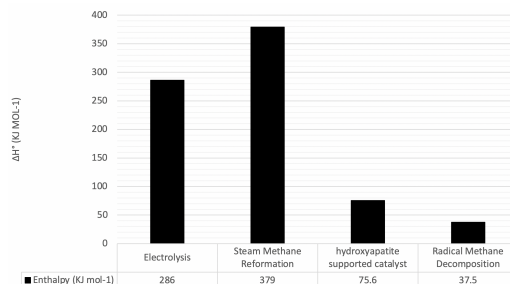


Figure 3: A plot showing the enthalpy of the three methane methods alongside uncatalyzed electrolysis as a reference.^{3,5,10}

As you can see from figure 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 RMP 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 GHGs 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 carbon byproduct is not resellable for three reasons: there is no market for it, the carbon rapidly degrades the catalysts and where Ni catalysts have been used, the carbon is contaminated with toxic metal.

Therefore RMP has been shown to be a superior method to HAp. RMP has the option of using carbon or iron catalysts instead of nickel whereas HAp only uses toxic nickel catalysts. The carbon catalysts have a longer life than metals and also run at lower temperatures.

4 Water electrolytic techniques

4.1 Amphoteric cell

An existing H_2O electrolysis method which uses an electrolytic cell under alkaline conditions,¹¹ is adapted by adding a membrane and an acidic electrolyte.¹²

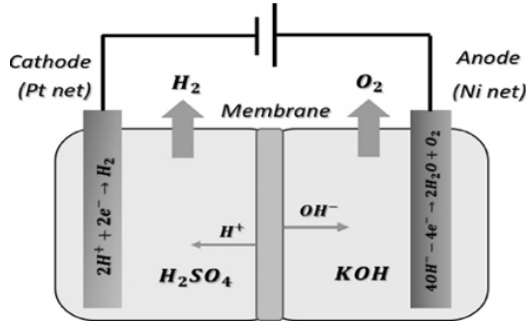
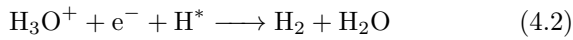
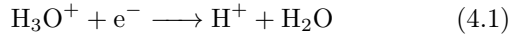


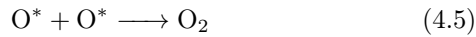
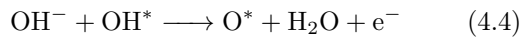
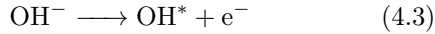
Figure 4: Fig
Acidic/Alkaline amphoteric electrolytic cell.¹²

An ion-exchange membrane is placed between a Pt cathode and an Ni anode, this restrains neutralisation between the acidic and alkaline electrolytes. The H_2SO_4 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.

H_2 evolution in acidic solution:¹²



O_2 evolution in alkaline solution:¹²



(*) - Chemically attaches onto the catalyst.

H_2O 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 H_2 and O_2 . This results in a potential difference for the electrolysis of H_2O . 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 H_2O was 30 % less compared to conventional alkaline electrolysis.¹² If this

magnitude of energy efficiency could be achieved on an industrial scale using renewable energy, it would provide a method of producing H_2 from H_2O 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 the temperature led to a lower potential difference for a given H_2 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

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In this section we discuss steam electrolysis and will look at a case study from G. Schiller, M. Lang, P. Szabo et al.¹³ High temperature steam electrolysis operates in the temperature range 700°C to 900°C ¹³ 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.¹⁴

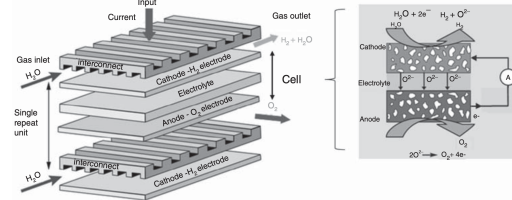
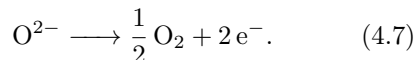
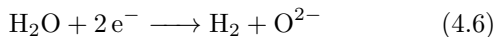


Figure 5: The schematic for a single cell of a solid-oxide fuel cell.

At these temperatures the reaction can proceed faster than at the lower temperatures ($>100^\circ\text{C}$), resulting in a higher electrical efficiency.¹³ 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 (4.7).¹³



From a thermodynamic perspective the enthalpy required to split water is reduced, as the total enthalpy $\Delta_r H$ is lowered significantly by removing the need to supply the enthalpy of vaporisation $\Delta_{\text{vap}} H$, approximately $40.65 \text{ kJ mol}^{-1}$.¹⁵ 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; solar energy may not be reliable enough to heat steam to feed a large bank of SOECs, as when multiple units are stacked they are more thermally efficient.

4.3 Discussion of water-splitting methods

Acidic/alkaline amphoteric H_2O electrolytic cells operate below 100°C ,¹² whereas SOEC operate between 700°C to 1000°C .¹³ This higher temperature results in faster reactions and a decrease in the Gibbs free enthalpy for H_2O electrolysis. This results in SOECs requiring less energy per unit volume of H_2 . Additionally, because a large part of the energy required for heating can be provided by solar thermal energy when using SOECs, the electrical energy is further lowered. As energy consumption is one of the major problems preventing the uptake of new H_2 productions, this is a clear advantage.

Another advantage of the SOECs is that it uses abundant metals in the electrodes whereas the acidic/alkaline amphoteric cell uses expensive platinum. Since one of the issues facing new methods of H_2 production is cost this is an important consideration.

Reliability and ease of maintenance are important

factors when considering a new process, and SOECs are complex. It consists of five main components and combines electrical and thermal solar energy sources. In contrast, the acid/alkaline electrolytic cell is an adaptation of an existing technique and is far more simple, with only one main component.

With further refinement SOECs looks to be the most promising method of the two reviewed; it takes the biggest steps in resolving numerous issues facing the use of water electrolysis as a means of producing hydrogen on a large scale.

5 Conclusion

H_2O can be obtained more easily than CH_4 , which requires extraction from natural gas or the decomposition of biomass. As H_2O is inert therefore it is far safer than CH_4 which is flammable. Additionally, H_2O is far easier to transport because it is a liquid above 0°C . CH_4 is a gas with a boiling point of -161.5°C ,¹⁵ therefore to transport large quantities it must be stored at very low temperatures as liquified natural gas.¹⁶ However, in some locations where H_2O is sparse or there is an unreliable electricity supply, CH_4 is a good solution.⁵ Therefore innovation is required to develop methods using both feedstocks.

The recent developments in water electrolysis and methane decomposition covered by this review are very promising alternatives to the methods currently used commercially. Each paper recognises the challenges facing the large-scale use of a new method and takes steps to address these issues. A method using CH_4 that stands out is RMP, which requires 11 % of the enthalpy required for traditional steam methane reformation. A method using H_2O that stands out uses SOECs, which uses less energy than traditional electrolysis and can use solar thermal energy to provide a significant portion.

Neither of these techniques are perfect, for example the RMP produces carbon as a waste product which greatly limits the lifespan of the catalyst and SOECs have issues maintaining the steam supply. However, with further refinement, these cutting-edge techniques have potential to replace the flawed methods currently favoured for the industrial production of H_2 .

6 Acronyms used

SMR Steam methane reformation.

SOEC Solid-oxide electrolytic cell.

RMP Radical Methane Pyrolysis.

GHG Greenhouse Gas.

HAp hydroxyapatite.

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