Production of Hydrogen and its Role in the Transition to a Clean Energy Economy

Natural Sciences
David Madden
Senior Freshman

This review examines how hydrogen, an energy vessel, may be produced for the transition towards a renewable energy economy. Incorporation of hydrogen into coal-energy extraction by means of IGCC is assessed. IGCC technology is compared environmentally and economically with the current coal extraction method - PC plants. Challenges for industrial adoption of this technology is discussed. This details a means to clean hot syngas in the process of electricity generation. The role of hydrogen as an energy store for fluctuating renewable energy is evaluated. Photobiological production of hydrogen from Chlamydomonas reinhardtii offers a means to harness solar energy in an effective, environmentally friendly manner. The metabolic process is briefly outlined, focusing on the role of hydrogenases in the production of hydrogen, and how oxygen damages these enzymes. Methods to prevent this damage and hence increase hydrogen yield are discussed, namely sulfur deprivation, copper addition and genetic engineering. The production of hydrogen from electrolysis is assessed, focusing on methods to minimise the use of expensive precious metals. These include adoption of nickel or iron based catalysts. The use of Nafion polymer or carbon nanotubes as a support for anodic catalysts and their effect on decreasing the anodic overpotential for the evolution of oxygen, the most costly aspect of electrolysis, is assessed.

Introduction

Mankind is faced with a difficult challenge: identification and extraction of a sustainable energy capable of meeting global demands. Presently, fossil fuels are the dominant source of energy (BP 2014). However these are finite and produce harmful by-products that exacerbate global warming (O'Neill & Oppenheimer 2002; Thomas *et al.* 2004; IPCC 2014). Hydrogen fuel has been identified as a possible alternative (Dandajeh 2014). When hydrogen is burned with oxygen it releases energy, and water being the only by-product. Despite hydrogen being an abundant element, it's not found in its molecular state, $H_{2,}$ on earth, but in compounds such as water or methane. Energy must be supplied to extract hydrogen. Hydrogen isn't a form of fuel but an energy carrier, comparable to electricity. Efficiencies in production and storage are essential for the adoption of a hydrogen economy (Kim *et al.* 2014). A swift change over to a hydrogen economy would be unattainable. Challenges facing this include devising efficient production methods, constructing a hydrogen infrastructure including transportation, storage and safe handling of hydrogen (Simbeck 2003). This review focuses on hydrogen production, transitioning from fossil fuels to sustainable energy. Integrated gasification combined cycle (IGCC) incorporates hydrogen into energy extraction. While this relies on coal, it's cleaner than the current method of energy extraction; pulverised coal (PC) fired boiler plants. PC involves combusting powdered-coal in the presence of air. Unlike steam reforming, the main industrial method of producing hydrogen, IGCC technology uses coal, the most globally abundant fossil fuel (IEA 2014). This method isn't sustainable, but acts as a progression towards a clean energy economy. Photobiological production of hydrogen offers the opportunity of a renewable, clean energy carrier. *Chlamydomonas reinhardtii*, a type of green algae, integrates hydrogen production into its metabolic processes. However the wild species produces low yields (Kosourov *et al.* 2002). Sulfur deprivation, copper enrichment and genetic engineering has allowed for greater yields, however this technology currently fails to compete economically with fossil fuels. With further advancement it may provide a method for effectively harnessing solar energy in the future (NREL 2007). The splitting of water (electrolysis) offers a means to produce hydrogen.

Precious metal catalysts are currently used, however these metals are expensive. Nickel or iron based catalysts offer an alternative to precious metals. Innovations in the oxygen evolution reaction (OER) for electrolysis are important, as this is the most expensive step of the reaction (Marinia *et al.* 2012). Use of Nafion, a polymer with unique thermal/mechanical stability, and single walled carbon nanotubes (SWNCTs) as a basis for hydrous iron oxide catalysts results in lower overpotentials for the reaction, making the process more efficient (Doyle & Lyons 2014).

IGCC Technology

IGCC is a process that combines gasification of coal, resulting in syngas (a mixture of hydrogen, carbon monoxide and carbon dioxide) that is then purified and combusted, powering gas and steam turbines. This occurs at 1500-1600, and at pressures of 2.5-4.5 MPa (De Graaf 2008). Currently steam reforming, using natural gas, is the primary method for producing hydrogen, however IGCC uses the most abundant fossil fuel and is the only comparable technology that reaches the environmental standards of a natural gas-based reforming plant (Collodi *et al.* 2009).

IGCC is environmentally cleaner than current PC plants, which generate 50% of the USA electric supply (Zhai *et al.* 2011). EPA (2005) have conducted an assessment of IGCC, and concluded that this technology offers greater thermal efficiency, requires less water and generates less waste than PC plants, for the majority of fuel and system configurations. Further environmental targets may be met through carbon sequestration. This involves the capture and storage of carbon dioxide. In the case of IGCC plants, a pre-combustion process may capture CO_2. This involves a water-gas shift reaction of the syngas with steam, converting carbon monoxide to carbon dioxide and hydrogen. This requires energy, so the IGCC plant must increase its fuel consumption per kWh by 14-25%. To capture CO_2 generated by current PC plants by post-combustion capture, a 25-50% increase in kWh is required, depending on the specific type of plant. The cost of implementing the carbon capture process is significantly less for IGCC plants, as is its maintenance relative to PC plants (IPCC 2005).

IGCC results in hot syngas at temperatures up to 1600 (De Graaf 2008). Before it enters gas and steam turbines, contaminants must be removed. These include; sulfur oxides (SO_x) and nitrogen oxides (NO_x) (Rand & Dell 2008). Currently the syngas must be cooled below 100 before processing by 'candle' filters. This cooling and subsequent reheating to power turbines is environmentally unfriendly. There is general consensus that the development of rigorous hot-gas cleaning systems would result in greater adoption of IGCC technology (Cargill *et al.* 2001; Simbeck 2002; Woolcock & Brown 2013). The major contaminants of syngas are sulfur oxides (Rand & Dell 2008). Progress has been made on hot-gas desulfurization technologies, by using copper based sorbents, at temperatures up to 600 (Slimane & Abbasian 2000). A sorbent gathers molecules of another substance together. The contaminants may be isolated as by-products. When the challenge of hot gas cleaning is met or stringent CO_2 emission taxes become widespread, IGCC technology may become an economically viable option for delivering cleaner energy from fossil fuel (Kim 2008).

Photobiological Production of Hydrogen

Solar energy to produce biofuels is the one of the most environmentally friendly technology still at infancy in research (Dismukes *et al.* 2008). *Chlamydomonas reinhardtii*, a type of algae, has been shown to produce hydrogen gas under specific conditions (Hemschemeier *et al.* 2008). These photosynthetic microorganisms split water into hydrogen ions, H^+, and electrons. Through metabolic processes involving hydrogenase enzymes, hydrogen gas is produced. Low hydrogen yields makes this method unfeasible for industry; 'Economic H_2 production requires high H_2 production efficiencies at low capital and operating costs' (Rupprecht *et al.* 2006). A number of techniques have been proposed to remedy this issue.

Oxygen is toxic to hydrogenases (Stripp *et al.* 2009). Researchers have identified novel ways to remove oxygen from the green algae by sulfur deprivation. Anaerobic green algae deprived of sulfur results in reversible inhibition of oxygenic photosynthesis. The electrons that feed this pathway are directed towards the Fe-hydrogenase pathway. The Fe-hydrogenase complex receives electrons from reduced ferredoxin and efficiently donates them to protons, resulting in hydrogen evolution (Greenbaum 1988; Peters *et al.* 1998). Zhang *et al.* (2002) identified that maximum hydrogen evolution was reached at the 4/5 day mark after initial sulfur deprivation. From here the Fe-hydrogenase pathway becomes completely inhibited. The algae must return to oxygenic photosynthesis in order to recuperate expended metabolites. This cycle may be repeated (Ghirardi *et al.* 2000) however, initial sulfur deprivation results in the normal ellipsoid-shaped cells becoming spherical and enlarged. Extended deprivation results in mass algae reduction (Zhang *et al.* 2002). This harms the viability of this method for industrial hydrogen production. The key to hydrogen production in *C. reinhardtii* is blocking oxygen production; while sulfur deprivation accomplishes this, copper addition has a key advantage. Surzycki *et al.* (2007) found that copper addition turns off Cyc6 promoter, causing the Nac2 gene to be supressed. This inhibits photosystem II (PSII), a protein complex that is integral in oxygenic photosynthesis. While this method yields slightly less hydrogen than sulfur deprivation, the algae cells remain healthy. However, the cyc6 promoter is not turned off permanently, due to anaerobiosis, and so the algae returns to oxygen production. Like sulfur deprivation, this process can be repeated in cycles. These approaches, sulfur deprivation and copper addition, circumvent oxygen production as it is lethal for hydrogenases, and in turn hydrogen production. Development of oxygen-tolerant hydrogenases is considered essential for industrial hydrogen producing technologies to compete with current fuels (Friedrich *et al.* 2011).

A strain of *C. reinhardtii*, STm6, has been genetically engineered and tested against the wild form of green algae. This new mutant form resulted in a four-fold increase in hydrogen evolution during sulfur deprivation (Volgusheva *et al.* 2013). This is attained by the absence of the MOC1 gene, which is involved in the assembly of the mitochondrial respiratory chain (Schönfeld *et al.* 2004). Melis and Mitra (2010) identified suppression of the Tla1 gene resulted in greater efficiency in hydrogen production. Large light harvesting antennae allow capture of light in murky conditions. However in industrially processes this negatively impacts hydrogen production, as excess light is used and there is no need for such large antennae. Suppression of the Tla1 gene results in antennae reduction.

Water Electrolysis

Renewable energy sources are variable by nature and require a storage mechanism to accommodate daily and seasonal changes. This energy must be used immediately or stored (Ter-Gazarian 2011). Hydrogen acting as an energy vessel can accommodate these variances. Renewable energies generate electricity that may be used to split water into hydrogen and oxygen. When this energy is needed, hydrogen is incorporated into a fuel cell. Current methods for generating hydrogen from renewable resources use PEMEs (Proton exchange membrane electrolysers). These require precious metal catalysts and continuous high densities of current, which is difficult to achieve with fluctuating renewable resources. 'The replacement of platinum with inexpensive materials is critical to the large-scale utilization of hydrogen as a clean energy vector' (Artero & Fontecave 2005).

Hoffert *et al.* (2013) has identified a nickel based catalyst, $[Ni(P(Ph)_2NC_6H_4OH_2)_2CH_3CN)](BF_4)_2$ which dissociates to $[Ni(P(Ph)_2NC_6H_4OH_2)_2]^{2+}$, that has a high turnover of hydrogen at low overpotentials. Overpotential indicates the extra voltage required at the electrode to initiate an electrode reaction. The p-hydroxyphenyl groups of the complex are hydrophilic and allow the catalyst to dissolve in solutions of up to 75% water and 35% acetonitrile, CN_3CN. Acetonitrile acts as a polar aprotic solvent. The amine pendants (the nitrogen components) have been shown to act as the proton donor, H^+, whereas the nickel centre acts as the hydride donor, H^-, in the formation of hydrogen gas (O'Hagan *et al.* 2012). This process has remarkable hydrogen turnover, due to the efficiency in proton transfer from the aqueous environment to the endo sites. The aqueous environment, in this case water-acetonitrile, has been identified as integral in the rate of catalysis (Stewart *et al.* 2013). Use of sterically smaller acids after addition of water allows for greater access to the endo sites (Shaw *et al.* 2013).

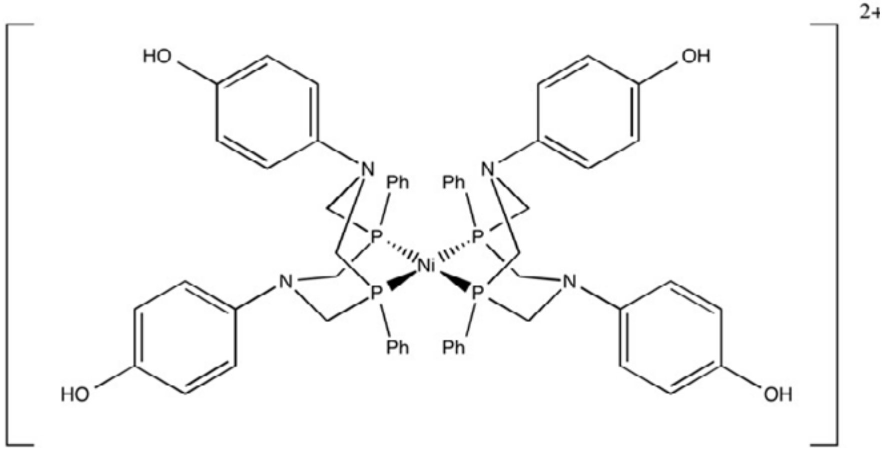

Figure 1: *A graphical representation of the reduced form of the catalyst complex, $[Ni\ P(Ph)_2NC_6H_4OH_2)_2]^{2+}$ Source: Drawn using ChemDraw.*

The most energy intensive step of electrolysis is the generation of oxygen at the anode (Marinia *et al.* 2012). The large overpotential of the oxygen evolution reaction (OER) at the anode site during electrolysis hinders hydrogen production. Current anode materials, RuO_2 and IrO_2, express low overpotentials at operational current densities (Michas *et al.* 1992). They are expensive and obstruct adoption of this technology (Gao *et al.* 2014). Doyle and Lyons (2014) investigated hydrous iron oxide composite films, using Nafion and single-walled carbon nanotubes (SWCNT) films, and identified the importance of Nafion and carbon nanotubes (CNT) for increased OER efficiency. The incorporation of these composite materials results in a dispersed jelly-like structure, increasing the surface area. The inner surface of the oxide layer is anhydrous and compact, whereas the outer layer is hydrated and microdispersed, forming extending rope-like structures (Burke & O'Sullivan 1981). The jelly-like structure of the catalyst acts as a combination of a solid and liquid state. Due to this unique nature, the reaction may be described as a hybrid of homogeneous and heterogeneous catalysis as the reactant, water, is liquid. The catalyst and the reactant are in the same state.

Conclusions

IGCC will play an integral role in the progression to a clean energy economy. It must be seen as a step, not a conclusion, of meeting energy demands. This technology is not far from large-scale industrial capabilities and will serve as a means to adopt a potential hydrogen infrastructure. The value of IGCC is that it may produce electricity directly from syngas or undergo purification to isolate hydrogen, which may be used in other industrial processes, acting as a byproduct of IGCC. Hot gas cleaning methods warrant further investigation, as the development of rigorous and inexpensive processes will lead to greater efficiency, thus making IGCC an economically viable alternative to the current PC plants.

The metabolic production of hydrogen from *Chlamydomonas reinhardtii* serves as a reminder of hydrogen's versatility - capable of being produced chemically and biologically. Identification of the metabolic pathways of these algae has been essential for the understanding of how hydrogen is produced. This discovery has allowed the identification of the hydrogenase family as central for the production of hydrogen. From this, methods to protect the oxygen sensitive enzymes has been devised, namely sulfur deprivation and copper addition. While the former results in greater hydrogen production, its damaging effects on the algae during long term use makes this method impractical for industrial purposes, unless a strain of algae is developed that may endure sulfur deprivation. Copper enrichment offers a solution, ensuring the algae remains healthy throughout cycles of oxygenic and anaerobic photosynthesis, however it too poses issues, specifically the resulting hydrogen yield is small. Development of new strains by genetic engineering will be crucial if this technology is to become a feasible option. Targeting of the MOC1 gene specifically hinders development of mitochondrial respiratory chain features, while the suppression of the Tla1 gene results in reduced antennae size, diminishing the metabolic energy input required for their maintenance. These genetic engineering techniques target the metabolic processes of hydrogen production. Ultimately, the development of oxygen tolerant hydrogenases that can thrive in bright environments will be essential if this technology is to offer a viable means of hydrogen production. Further research specifically identifying, or genetically engineering, oxygen tolerant hydrogenases is recommended.

As an energy store, hydrogen provides a means to deal with fluctuations in renewable energy. The use of nickel-based catalysts in the electrolysis of hydrogen is a progression from the current, yet economically unfeasible, precious metal catalysts. The detailed analysis of, $[Ni(P(Ph)_2NC_6H_4OH_2)_2]^{2+}$ a nickel based catalyst, has resulted in greater efficiencies, including the use of sterically smaller acids, more capable of donating protons to the endo sites. Novel solutions have been devised to tackle the OER at the anode, the most energetically costly aspect of electrolysis. By the incorporation of hydrous iron oxide composite films embedded in Nafion or SWNCTs, the surface area of the electrode is increased, resulting in an increase in potential reaction sites. This reduces the overpotential of the reaction, minimising the cost of the most expensive aspect of electrolysis. The value of this technology is that it results in very pure hydrogen, which may be directly incorporated into a fuel cell. While these methods collectively increased hydrogen production while diminishing the energetic and financial input, electrolysis faces a number of challenges. Further research on increasing efficiency, particularly cost effective electrocatalysts for OER is recommended.

Hydrogen will perform an important role in the transition to a clean energy economy. Its versatility in production, from fossil fuel derivation, photobiological synthesis and electrolysis allows the benefit of a steady energy vessel while energy sources remain dynamic. When the highlighted challenges are met, hydrogen will aid the transition from the 'hydrocarbon economy' to the 'renewable energy economy'.

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