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Lecture Note

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Electrochemistry and the Barriers to a Hydrogen Economy

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Abstract

This note covers the use of electrochemistry as one of the areas of active research relating to a future hydrogen economy. Future hydrogen manufacturing processes should electrolyze water to separate it into hydrogen and oxygen using energy from renewable sources like wind or sunlight. Electrochemistry is at the forefront of this technology, with its fingerprints on everything from electrolyzers to batteries to fuel cells.

Keywords: Hydrogen, Energy, Fuel, Electrochemistry, Water splitting, Hydrogen Economy

1. Introduction

Today's society is abuzz with the discussion of hydrogen. The range of concerns surrounding hydrogen extends from energy, the economy, the environment, and foreign and domestic politics. The term "the hydrogen economy" refers to the idea of widespread hydrogen production, storage, delivery, and usage as a fuel. This vision has the potential to strengthen our country's energy security, significantly improve the environment in our cities and towns, and improve the "dispatchability", quality, and dependability of our electricity system [1]. For intermittent renewable energy sources like photovoltaics and wind, hydrogen can act as energy storage. It can also be used as fuel for vehicles.

Hydrogen, as a compound, is a product with a high specific energy (120.7 KJ/kg). Particularly compared to other fuels in use at the time, hydrogen has 3 times the specific energy of diesel gasoline, but at the same time a low volumetric energy density. The combustion of hydrogen as a fuel produces very few pollutants, which are mainly nitrogen oxides. These do not pollute the atmosphere, as nitrogen is not a catalytic pollutant for the natural environment, unlike fossil fuels which leave a large carbon footprint when burned.

Hydrogen as a combustion product gives only water and heat. Furthermore, the amount of heat released during combustion is 242 kJ/mol (121 kJ/g) which is twice that of diesel gasoline or natural gas by mass.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H^o = -242\ KJ. \qquad (1)$$

In this way, hydrogen can make a significant contribution to the shift away from the total or partial consumption of fossil fuels to meet the energy needs of production units and social life. This provides an opportunity to move towards a greener and more sustainable alternative.

In addition, hydrogen can be produced through a multitude of processes without necessarily having to use non-renewable energy sources for its production, which is not possible for fossil fuels. In this way, hydrogen creates its own energy cycle and can be an important step towards independence from fossil fuels on an operational and political level.

The low density of hydrogen means that when it is burned by internal combustion, larger spaces are needed to store it, and a larger amount of hydrogen is needed to provide the energy required during combustion. When hydrogen is produced through water splitting, the need for larger amounts of production does not adversely affect any ecosystem, since the water used, e.g. in electrolysis, can be reused in a semi-renewable life cycle.

The above makes hydrogen an excellent and environmentally clean fuel. It is interesting to remember what Jules Verne wrote in 1874 about water as a fuel in chapter 11 of the book entitled The Mysterious Island. «Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable».

For this reason, the vision of the hydrogen economy has been created where all our energy needs will be covered by hydrogen. But what stands in the way of this vision?

The challenges and disadvantages to produce, storing, and distributing hydrogen via electrochemistry techniques will be described in this note.

2. Hydrogen Production

The biggest obstacle to the hydrogen economy is the availability of a cheap and clean method of hydrogen production. Hydrogen is not available on Earth in its purest form (in natural reservoirs such as fossil fuels) but must be extracted from compounds with other elements. This process requires a lot of energy. Most hydrogen production methods use water as it is the cheapest and most readily available source of hydrogen.

Most of the hydrogen produced today is produced through steam-methane reforming. The first step of this method is to convert the steam and methane into a mixture of carbon monoxide and hydrogen (syngas). In steam-methane reforming, methane reacts with steam under high temperature,

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3–25 bar pressure (1 bar = 14.5 psi) [2] in the presence of a nickel catalyst [3].

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)\ \Delta H_{sr} = 206\ {}^{kJ}/_{mol} \quad (2)$$

subsequently, the carbon monoxide of syngas and steam are reacted, approximately at 400 C, using metal oxide catalyst to produce carbon dioxide and more hydrogen. This reaction is known as water-gas shift reaction [4]

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)\ \Delta H_{WGSR} = -41\ {}^{kJ}/_{mol} \quad (3)$$

Steam methane reforming for hydrogen production is economically feasible but it produces CO_2 emissions. However, CO_2 can be captured before it enters the atmosphere, transported it and then stored in an underground geological formation.

A more environmentally friendly method for hydrogen production is water electrolysis(equations). Water electrolysis (Figure 1) is the decomposition of water (H_2O) into its basic components, hydrogen (H_2) and oxygen (O_2), through passing electric current [5]. Water is an ideal source for producing hydrogen because it only releases oxygen as a by-product during processing [6, 7].

Anode:
$$2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^- E^o = -1{,}23\ V. \quad (4)$$

Cathode:
$$4H_2O(I) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq) E^o = -0{,}83\ V \quad (5)$$

Total element reaction:
$$6H_2O(I) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) \quad E^o = -2{,}06\ V \quad (6)$$

Depending on its production process and the resulting greenhouse gas emissions, it is determined whether it is truly "clean" fuel. If the process is powered entirely by nuclear energy or by renewable energy, such as wind and solar, it generates no polluting emissions into the atmosphere and is the cleanest and most sustainable hydrogen.

Fig. 1. Electrolysis of water using a battery as an energy source gives H2 gas at cathode and O2 gas at anode[8].

Another approach is the use of solar energy for water splitting to H_2 and O_2. A research group has developed a device which is called artificial leaf [9] inspired from the photosynthetic process which convert the energy of sunlight into chemical energy. A thin, flat, three-layered silicon solar cell with catalysts bonded to both of its faces makes up the leaf. In a water-filled beaker exposed to sunlight, silicon absorbs photons, creating electrons with sufficient energy to conduct through the material as depicted in Figure 2 [10].

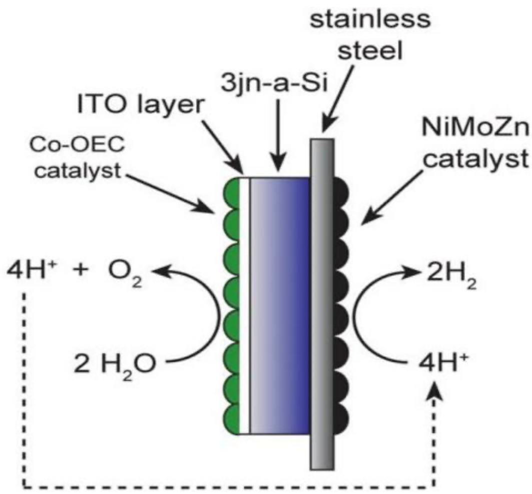

Fig. 2."Artificial leaf" is a device based on a silicon photovoltaic cell that uses sunlight to split water into hydrogen and oxygen. Hydrogen is produced on one side and oxygen on the other [10].

3. Storage and transportation of hydrogen

Another obstacle that stands in the way of hydrogen economy is the existence of safe and widespread methods for storage and transportation. For residential heating, hydrogen gas could be transported via underground pipes just like natural gas, while liquid hydrogen could be transported with trains ships or trucks in insulated tanks.

For fuel in transportation compressed hydrogen gas, liquid hydrogen, or "solid" hydrogen (Hydrogen is stored in the form of solid hydrogen storage material, i.e., suitable solid materials with large surface areas or solid hydrogen storage compounds such as Ammonia Borane.) could be appropriate. Gas hydrogen reacts with other materials and can be transported relatively easy. At the point of use storage material of hydrogen may decompose and converted to hydrogen gas.

The ability to be used in a variety of applications, such as neutron moderation, electrochemical cycling, thermal storage, heat pumps, and purification/separation, makes metal hydrides (MHx) the most technologically relevant class of hydrogen storage materials [11]. Furthermore, metal hydrides could be used in future as storage devices of hydrogen as they can contain a large amount of hydrogen.

As for example palladium has the ability to absorb large volumetric quantities of hydrogen (up to 935 of its mass) at room temperature and atmospheric pressure [12]. Hydrogen could be stored as PdHx and released, when it is needed, simply by heating PdHx and can be used as fuel.

$$Pd(s) + \frac{x}{2} H_2(g) \leftrightarrow PdH_x(s) \quad (7)$$

A notable disadvantage of this method is that it is not economically feasible compared with other storage methods. Another chemical approach is hydrogen production from ammonia borane. Ammonia borane has a high hydrogen content, is non-toxic and has high stability under ambient conditions, thus it appears to be the most efficient way of releasing hydrogen stored in it [13, 14].

$$NH_3BH_3 \rightarrow NH_2BH_2(s) + H_2(g) \rightarrow NHBH(s) + H_2(g) \quad (8)$$

4. Hydrogen Fuel Cell

Fuel cell is a galvanic element in which one of the reactants is fuel, i.e. hydrogen or methanol. A fuel cell differs from a conventional battery in that the reactants are not contained within the cell but are continuously supplied from an external reservoir [15]. The hydrogen-oxygen fuel cell (Figure 3) used as a power source in space vehicles contains porous carbon electrodes impregnated with metal catalysts and an electrolyte consisting of hot, aqueous KOH. The fuel gas H_2, and the oxidizing agent, O_2 gas, do not react directly but oppose each other in separate compartments of the cell, where H_2 is oxidized at the anode and O_2 is reduced at the cathode. The overall reaction of the element is simply the conversion of hydrogen and oxygen into water:

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(I) + 4e^-$ (9)

Cathode: $O_2(g) + 2H_2O(I) + 4e^- \rightarrow 4OH^-(aq)$ (10)

Total element reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$ (11)

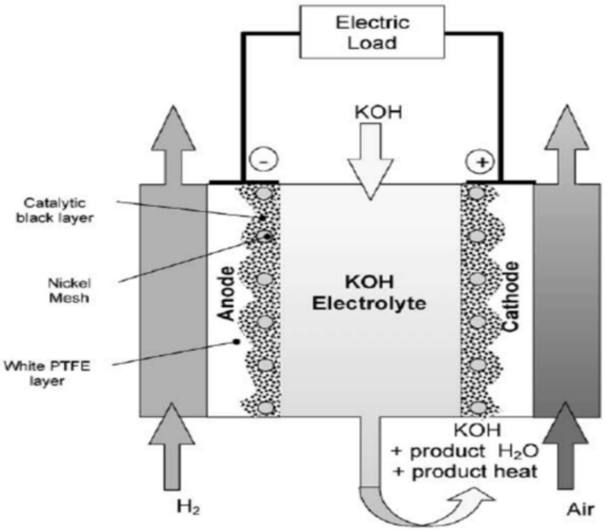

Fig. 3. Alkaline fuel cell composition[16].

In fuel cells designed to generate electricity for cars, buses and power stations, the ideal KOH electrolyte is replaced by a special highly partial membrane that traps protons but not electrons (Figure 4).

The electrode reactions as well as the total reaction in the proton exchange membrane (PEM) cells are:

Anode: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$ (12)

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(I)$ (13)

Total element reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$ (14)

Protons pass through the membrane from anode to cathode while electrons move through the external circuit from anode to cathode producing electricity.

Most fuel cells produce less than 1.2V, so driving an electric vehicle requires a bank of cells. Fuel cell vehicles are quiet and emission-free because the only reaction product is water. The vehicle itself does not produce greenhouse gases such as CO_2, however CO_2 can be produced during the production of hydrogen.

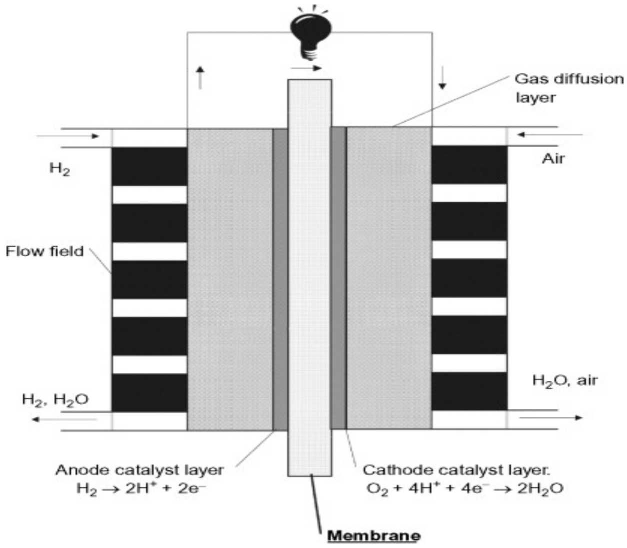

Fig. 4. Diagram of an AEM water electrolysis. CCL: Cathode Catalyst Layer, ACL: Anode Catalyst Layer, GDL: Gas Diffusion Layer, and MEA: Membrane Electrode Assembly [17].

Prototype fuel cell vehicles (FCV) have been on the road a few years now in several North American and European cities. Buses have been tested and the first fuel cell truck has been delivered to the United States military [18]. Currently a lot of FCV models are available for sale and lease in select markets such as California [19]. It only takes 5 minutes to fuel a vehicle with hydrogen and these models can travel hundreds of miles on a single tank of fuel.

The main obstacles for large-scale commercial application are the relatively high cost of FCVs, the lack of clean and low-cost sources of hydrogen production as well as the need to develop the required hydrogen fuel infrastructure [20].

Fossil fuels are still the main source of hydrogen, however electrolysis of water using electricity generated from solar or wind farms is a cleaner production method.

Building a hydrogen fueling station costs about 2 million and many investors are not willing to take the risk with so few vehicles on the road [21]. Fuel cells may also be commercialized in small electronic products such as mobile phones and laptops. Recommend element for use in these products is direct methanol fuel cell (DMFC) which is similar to PEM fuel cell but uses aqueous methanol (CH_3OH) as fuel instead of hydrogen gas [22].

Anode:
$2CH_3OH(aq) + 2H_2O(I) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$ (15)

Cathode: $3O_2(g) + 12H^+(aq) + 12e^- \rightarrow 6H_2O(I)$ (16)

Total element reaction:
$2CH_3OH(aq) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(I)$ (17)

DMFC is lighter and has a higher energy and density than conventional batteries [23], while methanol is more readily available safer and easier to store than hydrogen [24]. Fuel cells could also be used as a generator in hospitals hotels and apartment buildings [25].

5. Conclusion

Hydrogen is a promising alternative secondary energy source and therefore may gain a significant share of the energy market in the coming years should the costs of production, distribution and end-use of hydrogen show a significant reduction. Hydrogen and its potential to be used as a fuel in the future is a legitimate alternative for the "green" coverage of the energy needs of our societies, which are constantly increasing. The most ideal solution for hydrogen to replace existing non-renewable energy sources is for the hydrogen product to be produced on a large scale so that the cost of the processes as a whole can be reduced.

The decision of today's scientists to turn to hydrogen as an alternative way of meeting energy needs has several advantages over existing popular and non-renewable fuels. However, there are at the same time some disadvantages that cannot be ignored, which are related to the technical aspect of the production methods and the lack of sufficient infrastructure for large-scale hydrogen. In particular, with regard to hydrogen production from water splitting, there are many factors that need to be addressed.

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