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Hydrogen: chronology and electrochemical production

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ABSTRACT

Human gluttony is having a catastrophic effect on the environment. Since the age of industry and the world wars, modern societies have hygienically depleted most of the earth's resources, thus depleting all the resources that will be essential for future generations. The problem doesn't stop there: greenhouse gas emissions have significantly increased the earth's temperature, causing terrible damage to the climate. The production of green energy with no greenhouse effect seems essential to save the planet. Green hydrogen is a suitable and promising way to generate an energy source that produces H_2O molecules instead of CO_2.

Water electrolysis is a very important technique for producing green H_2 using an appropriate electrical current generated by a non-polluting energy source such as wind turbines. This review presents a historical and technical overview of the hydrogen element from its discovery to its current production. Throughout this work, we have tried to deal with the most significant historical periods.

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الهيدروجين: التسلسل الزمني والإنتاج الكهروكيميائي

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ملخص: إن الشراهة البشرية لها تأثير كارثي على البيئة. فمنذ عصر الصناعة والحروب العالمية، استنزفت المجتمعات الحديثة معظم موارد الأرض بشكل شبه كلي، وبالتالي استنزفت جميع الموارد التي ستكون ضرورية للأجيال القادمة. لا تتوقف المشكلة عند هذا الحد: فقد أدت انبعاثات غازات الاحتباس الحراري إلى زيادة كبيرة في درجة حرارة الأرض، مما تسبب في أضرار جسيمة للمناخ. ويبدو أن إنتاج الطاقة الخضراء الخالية من تأثيرات الاحتباس الحراري ضروري لإنقاذ الكوكب. ويعد الهيدروجين الأخضر طريقة مناسبة وواعدة لتوليد مصدر طاقة ينتج جزيئات H_2O بدلاً من ثاني أكسيد الكربون. ويُعد التحليل الكهربائي للماء تقنية مهمة للغاية لإنتاج الهيدروجين الأخضر H_2 باستخدام تيار كهربائي مناسب يولده مصدر طاقة غير ملوث مثل توربينات الرياح. تقدم هذه المراجعة لمحة تاريخية وتقنية لعنصر الهيدروجين منذ اكتشافه وحتى إنتاجه الحالي. وقد حاولنا خلال هذا العمل التطرق لأهم الفترات التاريخية.

الكلمات المفتاحية – التحليل الكهربائي، الهيدروجين الأخضر، اختراع البطاريات، الخلايا الكلفانية، غشاء البوليمر الإلكتروليت، التحليل الكهربائي للماء القاعدي.

1. INTRODUCTION

Hydrogen is a safe and environmentally friendly alternative [1]. It is a very interesting energy carrier that generates significant energy compared with environmentally polluting fuels. Currently, the consumption previsions in the word can rise to 530 Mt/a in 2050 [2]. Despite its extreme rarity on earth, hydrogen can be produced using a number of techniques that are not environmentally friendly, such as the reforming and gasification of fossil hydrocarbons [3]. For example the methane can be used based in catalytic reforming to produce H_2 and CO_2 according to the following reaction:

$$CH_4 + 2H_2O + Energy \rightarrow CO_2 + 4H_2 \qquad (1)$$

Several alternative techniques, with zero CO_2 emissions following the use of renwable energy production resources [4], have been used to produce energy such as methane pyrolysis [5] and water electrolysis [6].

The invention of the battery was a key to the production of H_2 by the electrolysis of H_2O [7]. Deiman and Troostwijk were the first to produce H_2 using an electrostatic machine [8]. Then, the Volta battery encouraged scientists to carry out more or less different experiments to produce H_2 [9], such as those by W. Nicholson, A. Carlisle and J. Ritter [10]. These historical experiments played a crucial role in inventing other, more efficient electrochemical techniques for producing H_2, such as anion exchange membrane [11], solid oxide electrolysis cell, polymer electrolyte membrane [13] and alkaline water electrolysis (AWE).

This review presents a historical and technical overview of the hydrogen element from its discovery to its current production. The historical description appears very important for understanding the origin and basis of all our acquired knowledge. It is a step backwards to what comes next in terms of H_2 production techniques. Throughout this work, we have tried to deal with the most significant historical periods.

2. HYDROGEN, THE FIRST STEP IN THE ELUCIDATION OF THE STRUCTURE OF MATTER

Hydrogen, a simpler chemical element [15, 16], was a key element that enabled scientists to elucidate the structure and properties of matter.. With the simplest electronic configuration of 1s1 [15, 16], it has served as an approximate model for atomic theories. Understanding its intimate atomic structure has opened the way to describing other more complex chemical elements [17].

With a range of properties that coincide with several groups in the periodic table [18], hydrogen is a unique group in its own right. Sometimes it behaves like the alkalis, losing an electron, and sometimes like the halogens, gaining an electron, but its electron is far away and does not allow it to be classified within these groups.

The spectroscope [19], designed by Kirchhoff and Bunsen [20], is an effective means of identifying chemical elements in the form of characteristic lines [21]. When H_2 is subjected to an electrical discharge, it emits a discontinuous spectrum consisting of a series of lines of monochromatic radiation with well-defined wavelengths λ [22] (Figure 1-a). This multicolour spectrum cast doubt on the atomic structure of hydrogen proposed in 1906 by Rutherford [23-25], who stipulated that the electron orbits the nucleus in a circular orbit and, thanks to the effect of electrostatic attraction, the electron does not fall on the proton because it rotates around it at a very high circular speed. Niels Bohr [26,27] in 1913 explained this behaviour of hydrogen by the existence of several superimposed orbits (description not precise) and quantified for which the electron can move according to its contribution of energy. It is only when the electron transits from one orbit to another that it can emit (or absorb) light characteristic of this transition, depending on the energy difference between the orbitals involved. Between 1859 and 1862, Julius Plücker and Ångström deduced that the Sun contained hydrogen [29, 30] by analysing the Fraunhofer lines [20, 31, 32] (Figure 1-b).

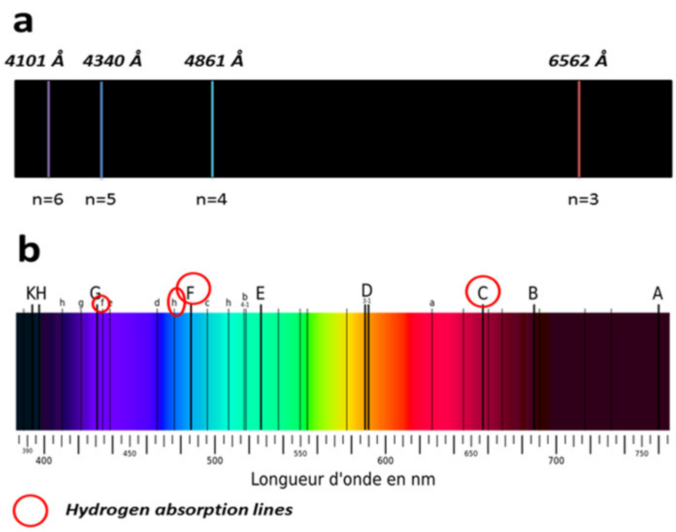

Figure 1. (a) Emission Spectrum of Hydrogen - Balmer series-; (b) Fraunhofer lines. Reproduced based on references [28] and [32].

Johann Jakob Balmer established a mathematical formula [28] that linked the different wavelengths of hydrogen calculated by Ångström [33]. He found that all the wavelengths are terms of a sequence that converges towards a limit value noted as B= 3,645.6 Å [34-36]. By dividing each wavelength by this limit value, we find that all the ratios can be written as follows, which is simply Balmer's formula [28]:

$$\frac{\lambda}{B} = \frac{m^2}{m^2 - n^2} \quad With \quad n = 2; \quad m = 3,4,5,6 \qquad (2)$$

As an example, the wavelength ratio 6562.10 Å of the red line and the limit value B gives a value of 1.8 equivalent to:

$$\frac{9}{5} = \frac{3^2}{3^2 - 2^2}$$

The same applies at 4101 Å:

$$\frac{4101}{3645.6} = \frac{36}{32} = \frac{6^2}{6^2 - 2^2}$$

Balmer's formula can therefore be used to describe the electronic transitions in the hydrogen atom from mi to the electronic layer n =2 in the visible range (so-called Balmer series) (Figure 2) [16, 37, 38, 39].

Balmer's formula is generalised for all n integers as the Rydberg-Ritz formula [41]:

$$\frac{1}{\lambda} = \frac{4}{B} \times \frac{m^2}{m^2 - n^2} = R_H\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \quad (3)$$

Where RH is the Rydberg constant [42] equal to :

$$\frac{4}{B} = 10\ 973\ 731.568\ 160(21)\ m^{-1}$$

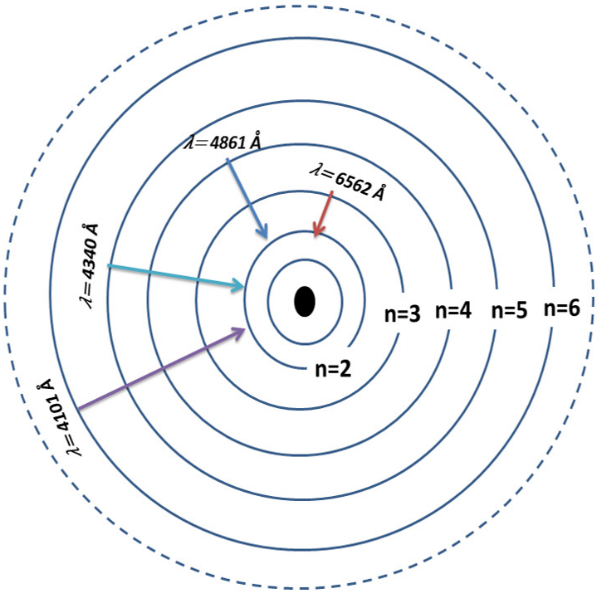

Figure 2. Electronic transition relating to the Balmer Series (Visible light). Reproduced on the basis of the reference [40] (scale not respected).

3. CHRONOLOGY OF DISCOVERING HYDROGEN

In 1520, a Swiss alchemist named Philippus Aureolus Paracelsus unknowingly produced dihydrogen gas by adding sulphuric acid and iron [43] according to the reaction known today [44, 45] :

$$H_2SO_4 + Fe + 7H_2O \rightarrow FeSO_4.7H_2O + H_2 \quad (4)$$

Aureolus gave it the name 'flammable gas' because it could burn in the presence of air [46]. This flammable gas, hydrogen, was the subject of experiments by Robert Boyle in 1670 [47]. More than a century later, in 1776, Henry Cavendish produced hydrogen by adding hydrochloric acid to zinc [48, 49] using the following reaction [50]: →

$$2HCl + Zn \rightarrow ZnCl_2 + H_2 \quad (5)$$

More importantly, Henry Cavendish, considered to be the great pioneer of hydrogen production, demonstrated the possibility of producing water by burning hydrogen (in presence of oxygen) [50]. In 1785, and after several experiments that the scientific public doubted, Lavoisier finally convinced the public that water was not an element but a product that could be formed by combining two distinct elements, hydrogen and oxygen [51] (obtained by reducing mercury oxide) as follows [52] :

$$H_2 + ½\,O_2 \rightarrow H_2O \quad (6)$$

Lavoisier explained this notion in this historical speech: 'Until recently, water had been regarded as a simple substance, and the ancients had made no difficulty in calling it an element. But we shall see that water is no longer an element for us' [53]. As a result, this scientist gave this gas a name: "hydro", from the Greek for 'water', and –"gen", from the Greek for 'to generate', i.e. the producer or genericiser of the water [54].

The notion of the molecule had not been elucidated until then, and the scientists of the time did not distinguish between atoms and molecules, although these notions were the subject of endless discussion. In 1809, Avogadro proposed a hypothesis consistent with experimental results, suggesting that hydrogen and oxygen gases exist in molecular rather than atomic form. In other words, hydrogen gas is a combination of hydrogen atoms that can be symbolised by H_2 instead of H, and the same goes for oxygen O_2 instead of O. He formulated his hypothesis by curiously analysing Gay-Lussac's law formulated in 1808 [55, 56, 57], which produces 2 volumes of water (H_2O) from the combination of 1 volume of oxygen (O) and 2 volumes of hydrogen (H) [57,56]. Cannizzaro supported Avogadro's hypothesis by explaining that water vapour is only 9 times heavier than hydrogen vapour (and not 18 times), because oxygen is 16 times heavier than hydrogen [58]. In other words:

$$\frac{d(H_2O)}{d(H_2)} = \frac{18}{2} = 9 \qquad ,and\ not \qquad \frac{d(H_2O)}{d(H_2)} = \frac{18}{1} = 18$$

The subsequent reaction to form water vapour is [57] :

$$H_2\ (1vol) + H_2\ (1vol) + O_2\ (1vol) \rightarrow 2H_2O\ (2vol) \qquad (7)$$

4 Batteries invented: source of electrical energy for electrolyzing water

An isolated frog's leg began to contract when it and its associated nerve were touched by a metal arc formed by two different metals [59]. This strange observation, known as 'galvanism', was explained in 1791 by Galvani as the circulation of an electrical fluid between muscle -nerve which causes movement of the limbs and the associated sensations [60, 61]. It is a kind of intrinsic animal electricity secreted by the brain and discharged as soon as the muscle and nerve are attached by the two metals [59]. A controversy arose between Galvani and Volta, who in 1776 isolated methane as an unknown gas and used it to make Volta's pistol [62], when the latter declared that the electricity that animates the muscles comes from the two non-identical metals that touch the muscle and its nerve (or wet bodies of different compositions), which is why a small quantity of electricity is enough to observe the same phenomenon and the muscle-nerve only allows the electrical circuit to be closed [63]. In addition, a sour sensation is felt when its metals are put in the tongue, thus declaring a capacity of its metals to produce electricity when they are wet [64]. With the measurement of electricity generated by contact between zinc and silver in 1796 and the manufacture of the Voltaic battery in 1800, Galvani's arguments were denied, despite the fact that they presented a reality shown shortly afterwards by Carlo Matteucci [65, 66,67].

Volta built his electrical machine on the basis of experiments carried out by Galvani on the legs of frogs: the dimetallic arc, the brackish liqiude which represents the animal tissue, the electricity is amplified (voltage) by attaching several galvanic cells (crown of cups) (Figure 3-a) in series or by using different metals (with a much greater potential difference). In this respect, it should be noted that the Baghdad battery was the first electrical energy storage instrument to be invented in Mesopotamia in the 1st century before J.C. This battery consists of two electrodes, one made of iron and the other of copper, and lemon juice is used as an electrolytic solution with a voltage of 2 V compared with 1-2 V for a single volta cell (Figure 3-b) [68, 69]. Assembling the cells in series adds voltage (to the volta honour) to the battery, whereas assembling them in parallel increases the battery's intensity (the flow of electrical charges) [70]. Note that the galvanic cell consists of an electrolytic solution in which two electrodes of different types (e.g. Zinc and Copper) are immersed (Figure 3-c) [71].

The voltaic pile, the Volta column pile or 'battery' [72], as its name suggests, is made up of a stack of metal discs of different potential (zinc and silver) and a piece of paper soaked in a saturated solution of NaCl (Figure 3-d). The metal of lower potential (Zn) represents the anode where oxidation (term introduced in 1920 [74]) reactions take place and the other metal forms the cathode, the site of reduction reactions [73,75] according to the following reactions:

Anode (-): $Zn \rightarrow Zn^{2+}(aq)+2e^-$ (8)

Cathode (+): $2H_2O+2e^- \rightarrow H_2(g)+2OH^-$ (9)

Total reaction:

$$Zn(s)+2H_2O \rightarrow Zn(OH)_2(s)+H_2(g) \quad (10)$$

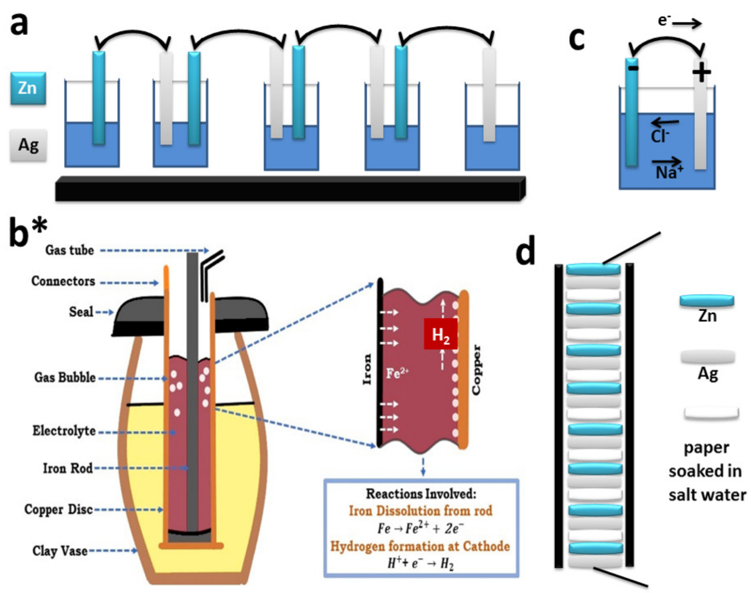

Figure 3. (a) Galvanic cells or Volta's battery (crown of cups) in series; (b) Baghdad battery (with permission, License Number 5864801014482, reference [68]); (c) galvanic cell ; (d) Volta column pile or Volta's battery. Reproduced on the basis of the references [68] and [73].

The wet paper constitutes an electrolytic solution and enables the electrical circuit to be closed and the electrical charges to be balanced [73]. The chemical and electrochemical explanations of the volta pile took some time to become established. The names used today such as ions, anode, cathode, anions (substances that move towards the anode, although its negative charge is only mentioned by Svante Arrhenius in 1887) [76], cations (substances that move towards the cathode) were proposed in 1834 by Michael Faraday [77]. The voltage or potential difference of a galvanic cell formed by Zn and Cu (symbolised by $Zn|Zn^{2+}{}_{aq}||Cu^{2+}{}_{aq}|Cu$) is :

$$E_{cell,eq}=+0.34-0.76=+1.10V$$

Note that the term 'batterie' in French means rechargeable batteries, whereas 'pile' is reserved for non-rechargeable 'irreversible reactions' instruments.

In 1889, Walther Nernst formulated one of the most important equations in electrochemistry, which calculates the potential difference between a metal and its ions in an electrolytic solution [75,78] :

$$E = 0.860T\,ln\left(\frac{P}{p}\right)\times 10^{-4}\,V \quad (11)$$

With : P= osmotic pressure of the metal ions; p= dissolution voltage of the metal; for $n= 1$ the $0.860T$ is equivalent to RT/nF.

The evolution of scientific concepts in this field has given rise to other forms of this equation [75] in gratitude to Nernst, the name of the equation is graded the same:

$$E_i = E^o + \frac{RT}{nF} ln((a^x_{ox})/(a^y_{red})) \qquad (12)$$

$$E_i = E^o + 2.3 \times \frac{RT}{nF} log((a^x_{ox})/(a^y_{red})) \qquad (13)$$

$$E_i = E^o + \frac{RT}{nF} ln\left(\frac{c_{ox}}{c_{Red}}\right) \qquad (14)$$

With : E_i = Oxidation-reduction potential of the *Ox/Red* couple (in V); $E°$= Standard potential of the same couple; F= Faraday constant; n= Number of electrons transferred in the half-reaction ($xOx + ne^- \rightarrow yRed$); R= Perfect gas constant, T= Absolute temperature in Kelvin; ; a = Chemical activity; $E°'$ = Formal potential; C = Concentration.

It has been shown that the voltage of the voltaic cell decreases in the absence of O_2, indicating that O_2 is imperative to its functioning [75].

Following this unexpected technological innovation, several types of battery, secondary = 'rechargeable' and primary = 'non-rechargeable', were invented to solve the problems observed with the Volta cell and increase its performance [79; 80] (Figure 4). The problem of Zn degradation was solved by William Sturgeon in 1835 [81]. The polarisation or internal resistance of the battery following the formation of H_2 bubbles on the 'copper' cathode was solved by the invention of the Daniell cell in 1836 [82], which used a second electrolyte to consume the hydrogen produced by the first.

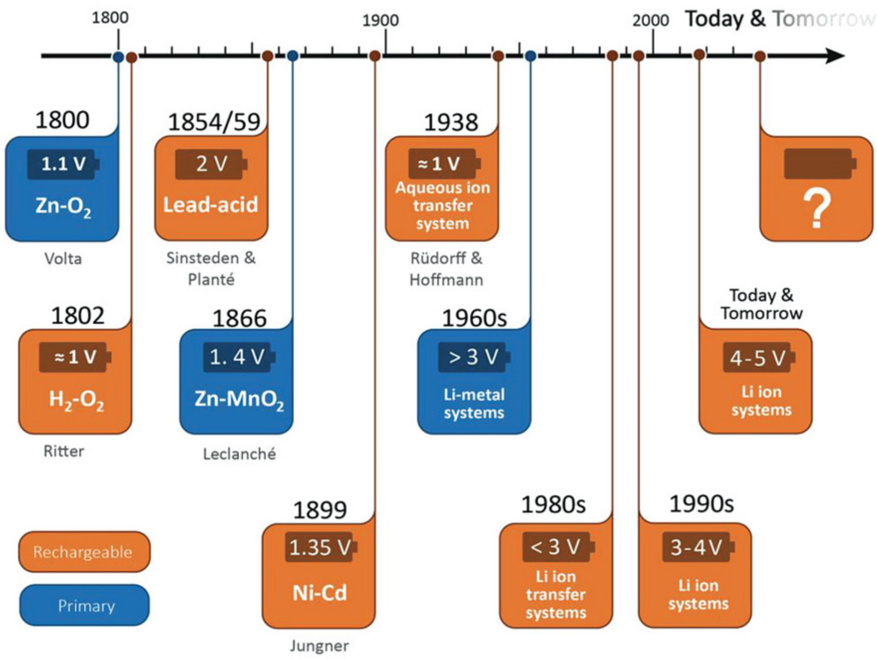

Figure 4. (a) Historical chronology of battery invention. Used with permission [80]. Creative Commons CC BY.

The Daniell cell consists of a porous clay container filled with H_2SO_4 and containing a Zn plate. This container is immersed in another made of copper containing $CuSO_4$ [83, 84] (Figure 5-a). According to [84] (Figure 5-b) Zn^{2+} ions, produced following the oxidation of Zn, diffuse through the membrane towards the container containing $CuSO_4$ where a substitution reaction occurs following a difference in the standard free energy of formation ΔGf° of the two sulphates (ΔGf° (ZnSO4) = -889 MJ/kmole, ΔGf° ($CuSO_4$) = -676 MJ/kmole) according to the following reaction:

$$Zn^{2+} + CuSO_4 \rightarrow Cu^{2+} + ZnSO_4 \qquad (15)$$

The Cu2+ ions then receive electrons from the oxidation of Zn in the following reduction reaction:

$$Cu^{2+} + 2e^{-} \rightarrow Cu \qquad (16)$$

In 1859, the Pb-acid battery (the 1st secondary battery) was invented by Planté, consisting of a lead anode and a PbO_2 cathode and an electrolytic solution containing H_2SO_4 [69]. In 1866, Georges-Lionel Leclanché invented a battery, currently called carbon-zinc batteries and alkaline batteries with a few modifications [69]), consisting of a Zn anode and a cathode of a mixture of manganese oxide and carbon and an electrolytic solution formed by aqueous ammonium chloride [85]. Since 1960, research has focused increasingly on rechargeable batteries based on lithium ion [86]. The performance of these batteries is so crucial, with a voltage of up to 5V [80].

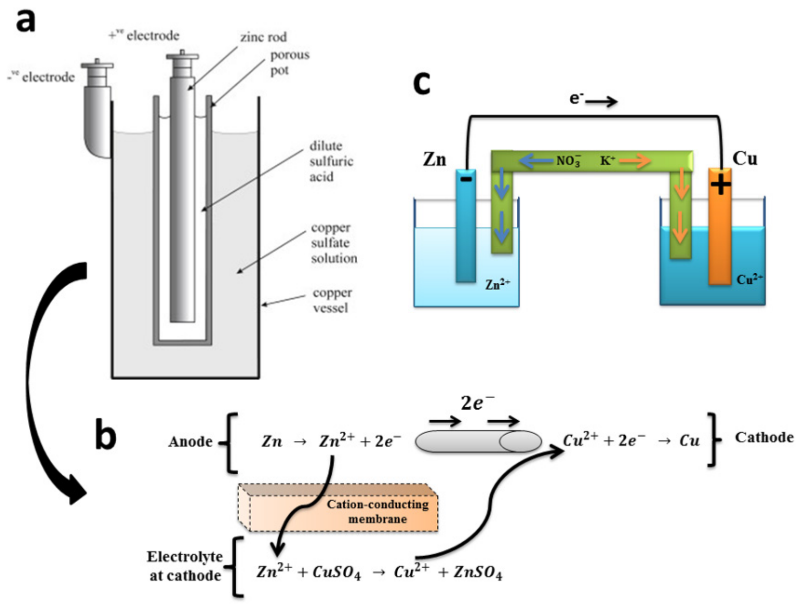

Figure 5. Daniell cell: (a) Schematic of the cell invented in 1836 ((with permission, License Number 5865310153162, reference [83]); (b) Mechanisms; (c) Other version. (b) and (c) are reproduced on the basis of references [84] and [73] successively.

4. ELECTROLYSIS: HISTORY AND PRINCIPLE

Electrolysis comes from the prefix 'electro' meaning electricity and 'lysis' meaning decomposition or degradation [87]. Electrolysis is therefore a process in which a substance such as water is decomposed or disassociated under the effect of electricity. It was discovered and interpreted in 1789 by Troostwijk and Deiman. [88] [89] who used a powerful electrostatic generator attached to two gold electrodes immersed in water. Then the closed end of the tube began to empty of water and fill with gases, at which point a spark produced by an electrical discharge explosively formed water, leading the two scientists to conclude that the electrolysis of the water they had just produced formed two distinct gases, hydrogen and oxygen [90], based on the work of Cavendish [91]. This finding by Troostwijk and Deiman was confirmed by Gren [92] and Pearson [93]. After 11 years, Carlisle and Nicholson produced hydrogen and oxygen via the electrolysis of H_2O using a powerful source of electricity generated by the installation of three Volta cells in series (Figure 6) [73]

The reactions involved are [73]:

+ At the positively charged anode:

$$2H_2O \rightarrow O_2(g) + 4H^{+}(aq) + 2e^{-} \qquad (17)$$

+ At the negatively charged cathode:

$$4H_2O + 4e^{-} \rightarrow 2H_2(g) + 4OH^{-}(aq) \qquad (18)$$

+ The total reaction:

$$2H_2O \rightarrow 2H_2(g) + O_2(g) \qquad (19)$$

Other ways of writing the equations involved are highlighted in the literature [94]:
+ At cathode:

$$4H^{+}+4e^{-} \rightarrow 2H_2 \qquad (20)$$

+ At anode:

$$2H_2O \rightarrow O_2+4H^{+}+4e^{-} \qquad (21)$$

$$2H_2O \rightarrow 2H_2(g)+O_2(g) \qquad (22)$$

Several experiments were carried out after this success, such as that of Cruickshank, which produced hydrogen and chlorine from the decomposition of sodium chloride. [89]

These historical experiments played a crucial role in inventing other, more efficient electrochemical techniques for producing H_2, such as :
+ Anion exchange membrane (AEM): The reduction of H_2O at the cathode produces H_2 and OH- which diffuse, via AEM, towards the positively charged anode. The reactions involved are [95]:
+ At the positively charged anode:

$$4OH^{-} \rightarrow O_2(g)+2H_2O+4e^{-} \qquad (23)$$

+ At the negatively charged cathode:

$$4H_2O+4e^{-} \rightarrow 2H_2(g)+4OH^{-}(aq) \qquad (24)$$

+ The total reaction:

$$2H_2O \rightarrow 2H_2(g)+O_2(g) \qquad (25)$$

+ Polymer electrolyte membrane (PEM) : PEM electrolysis uses an electrolytic acid that can improve the kinetic production of H_2 compared with AEM [96], with the possibility of operating at high pressure in the cathode [97] and the use of metal catalysts such as IrO_2 and Pt [98].
+ Alkaline water electrolysis (AWE): the anode and cathode are separated by a diaphragm composed of ceramic oxides [99] which allows the passage of OH- only [100] with the use of an eloclytic solution of 30-40%KOH [101]. This method of producing H_2 can be carried out at low temperature and without a noble metal catalyst [102].

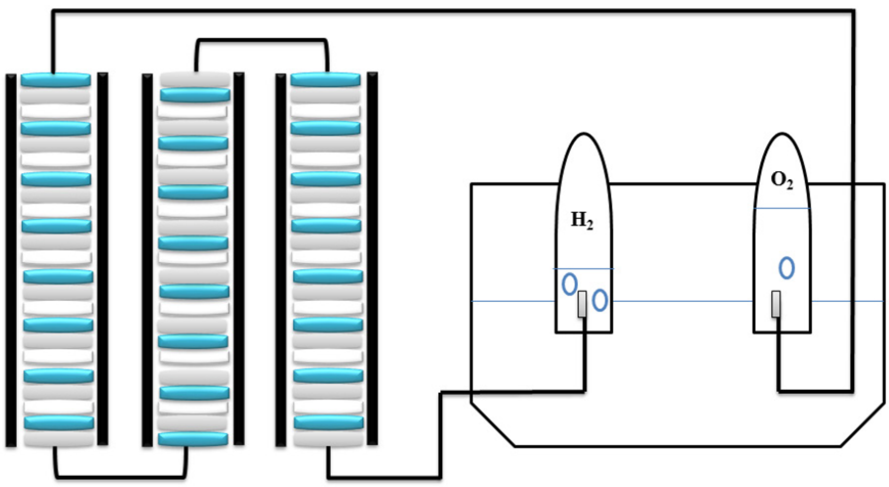

Figure 6. Electrolysis of water by Carlisle and Nicholson. Reproduced on the basis of the references [73].

H_2 can be produced by steam methane reforming (SMR) at lower cost [103] and with higher energy efficiency [104] than electrolysis, but with significant CO_2 emissions. In addition, perovskite oxides occupy a prime position for the storage [105-106] and production [107] of clean H_2 due to their interesting properties [108] which may open up another way for the integration of H_2 production technology, which may be beneficial in overcoming some of the problems encountered.

5. CONCLUSION

In this review, we have detailed all the historical steps that established the scientific and technical basis of water electrolysis. Since then, innovative techniques have been developed to improve and increase H_2 production, including the anion exchange membrane, the solid oxide electrolysis cell, the polymer electrolyte membrane and alkaline water electrolysis. This substance is gradually replacing CO_2-emitting fuels and offers an efficient alternative when its production is linked to renewable energies such as wind, waves, solar panels, etc. Today, electric cars are gradually appearing on our roads, which will certainly improve air quality.

Author Contributions: Charaf Laghlimi / developed the concept and aims of the study; Abdelaziz Moutcine/prepared and compared the literature; Younes Ziat/prepared and compared the literature; Hamza Belkhanchi/ reviewed and checked the structure of the manuscript; Ayoub Koufi/ reviewed and checked the structure of the manuscript; Souad Bouyassan/ reviewed and checked the structure of the manuscript.
All authors contributed to the final manuscript.
All authors have read and approved the manuscript.

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