

Technical report and comment on

Hydrogen as a future fuel source: electrochemical storage in carbon materials

by Jakub Menzel and Przemyslaw Galek supervision: Krzysztof Fic

Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Berdychowo 4, 60965 Poznan, PL

following the "Science meets regions" event in Konin (PL) on 12th December 2018

ordered by:

Joint Research Centre European Commission Rue du Champ de Mars 21 1050 Brussels, Belgium



Table of Contents

1.	Introduction
2.	Energy sources
3.	Hydrogen properties5
4.	The technology of hydrogen production6
5.	Estimated cost11
6.	Hydrogen storage16
7.	Application18
Exper	imental section20
1.	Carbon surface determination20
2.	Hydrogen electrosorption examination procedure22
3.	Hydrogen electrosorption in the alkaline electrolyte (1M KOH) 23
4.	Hydrogen electrosorption in the neutral electrolyte (1M $K_2SO_4)\ldots 32$
Final r	remarks
Refere	ences

1. Introduction

The human being, like every alive being, is a bio-engine that "combust" the energy into the work. In other words, the difference between life and the dead matter is the ability to convert energy. Therefore, the energy is essential for our existence and continuous development.

Energy issues are nowadays very popular (and emerging) topic among researchers and legal authorities, especially in highly developed countries. Furthermore, it is the driving force of technological progress. After the steam engine discovery in 1712 by Thomas Newcomen [1], humanity for the first time introduced the machine that consumes coal or hydrocarbons and provides mechanical power on demand. This initiated so-called industrialization process and completely changed the society's habits, leading to dramatic increase of the energy demand.

The human population has increased fourfold in the last century, and energy demand as much as 24-fold [2]. It has been predicted that the current energy economy based on fossil fuels will reach its limits in the next few decades [3] and enforces the transformation from conventional fossil fuels into renewable energy. Although the technical potential of renewable energy is large, matching the supply and demand fluctuations is a more serious challenge than further development of renewable energy technologies. In this context, hydrogen can be considered as a viable energy storage option, complementary to traditional technologies. Hydrogen can be produced from a variety of fossil fuels and renewable sources, ensuring a smooth transition from an energy economy based on the use of fossil fuels to a sustainable energy economy, based on renewable sources.

2. Energy sources

Basically, one can consider two types of energy carriers [2]. On one hand, there are reversible systems, which can be charged by mechanical or electrical work and then discharged in order to provide

the energy on demand. Examples of such systems are electrochemical capacitors, batteries, and flywheels. On the other hand, there are the energy storage systems based on reducing the compound, releasing oxygen into the atmosphere and generating a semi-stable product. An example of such a process can be photosynthesis. The product can react with oxygen again to release energy, resulting in the formation of volatile or non-volatile compounds. The advantage of the second system over the first one is the natural transport and storage of oxygen and volatile products in the atmosphere. Therefore, high energy storage densities are possible, which in many cases may exceed the storage densities of the first systems.

"Natural" processes have led to the spontaneous accumulation of carbon and hydrogen-based energy carriers (so-called fossil fuels), which include hard coal, lignite, oil and natural gas. Their usage has introduced humanity to the industrial era, resulting in tremendous exploitation of fossil fuels over the last century. However, it has been realized that these energy reservoirs are limited, and that unrestrained burning of fossil fuels accelerates climate change. No matter how much fossil fuel remains and who consumes most of them, we need to develop a global sustainable energy economy for the future. The forecasts based on extrapolation of energy consumption indicate that demand will soon exceed the supply of limited oil supplies. The resources of other fossil fuels, for example, coal, are larger, but their quantity is still limited. Demand for fossil fuels also has a strong impact on social, political and economic interactions between different countries. Two-thirds of oil reserves are located in the Middle East, but most gasoline is consumed in the USA, Europe and China. Long-distance transport by pipelines or tankers causes a significant environmental hazard. Moreover, imbalance in the distribution of resources is one of the driving forces in political instability, leading to military conflicts and terrorism. This is the first important fact that forces the world to seek an energy solution based not on fossil fuels but sourced from "unlimited" renewable energy.

The energy problem particularly concerns broadly defined transport. In addition to rapidly depleting fossil fuel deposits, their massive processing and exploitation generate an extensive amount of air and environment pollution. Ultimately, they constitute a significant burden on the environment and a threat to human health and life. In addition, in extensively populated urban agglomerations, the noise level generated by internal combustion engines exceeds the safety standards. Thus, it is necessary to abandon the energy supply from depleting natural carbon sources. Therefore, it is well accepted that carbon should be avoided in future energy carriers [4].

3. Hydrogen properties

Hydrogen (H) is a chemical element with atomic number of 1. It is a non-metal from "s" block in the periodic table. Hydrogen is the most common chemical element in the universe and the most common on Earth [5]. It has the smallest atomic mass. The most common hydrogen isotope is protium (1H), which has the simplest possible atom structure - it consists of one proton and one electron. Atomic hydrogen was created in the era of recombination. Under standard conditions, hydrogen gas exists in the molecular form (H₂). However, at extremely high temperatures, it is possible to obtain it in the atomic form. Because this element easily forms chemical compounds with most non-metal elements, the hydrogen on Earth is widely spread in the form of water or organic compounds. Hydrogen plays a particularly important role in acid-base reactions because most of this reaction type involves the exchange of protons between soluble molecules. In ionic compounds, hydrogen can have a negative (H anion) or positive (H⁺ - cation) charge. Hydrogen was obtained artificially for the first time at the beginning of the 16th century in the reaction of metal and acid. In 1766-1781 period, Henry Cavendish was the first person to state that hydrogen is a separate chemical substance that produces water when burned. This property determined the name of this chemical element because in Greek υδρογόνο means "water-creating".

The physicochemical properties of hydrogen are presented in Tab. 1.

Mass [6]	1.00784÷1.00811 u
Color [7]	Colorless
Smell [7]	Odorless
Taste [7]	Lack
Physical state [7]	Gas
Toxicity [7]	Lack
Combustibility [7]	Inflammable
Energy efficiency [8]	120 MJ⋅kg⁻¹
Density (in liquid	0.082 kg⋅m⁻³
state) [9]	

Table 1. Hydrogen properties.

Melting temperature	–259.198°C
[9]	
Boiling point [9]	–252.762°C
Triple point [10]	–259.198°C (7.2 kPa)
Critical point [11]	–240.18°C (1.293 MPa)
Heat of evaporation	0.44936 kJ⋅mol⁻¹
Heat of melting	0.05868 kJ⋅mol⁻¹
Saturated steam	209 Pa (23 K)
pressure	
Conductivity	13.8×10 ⁶ S⋅m ⁻¹
Specific heat	14304 J⋅kg⁻¹⋅K⁻¹
Thermal	0.1815 W·m⁻¹·K⁻¹
conductivity	
Crystallography	hexagonal
Speed of sound	1270 m·s⁻¹ (298.15 K)
Molar volume [12]	11.42×10⁻ ⁶ m ³ ⋅mol⁻¹

The advantages of hydrogen as fuel include 2.6 times higher energy content per unit of mass than gasoline. It means that hydrogen has a higher calorific value than gasoline [13]. However, due to the lower density, it needs about 4 times more volume than gasoline to store the same energy. Nonetheless, hydrogen is characterized by the highest energy efficiency in comparison to all of the conventional fuels (2.75 times higher than hydrocarbon fuels) [14].

4. The technology of hydrogen production

Currently, hydrogen is the only energy carrier that can be successfully synthesized without material restrictions in real-time e.g. by electrolysis of water. Moreover, the combustion of hydrogen leads to its recycling into the water and the cycle closes naturally. Currently, the research is being conducted on its efficient storage and application to power fuel cells for automotive and heavy industry. Hydrogen-based systems could be adapted in zero-emission models for transport, as well as in technologies for energy storage. Hydrogen can be used to supply the fuel cells that generate electricity in a safe and emission-free way for the environment. Such technologies have been already applied in practice; for example, in the passenger train with hydrogen fuel cells, which obtained the permission of the German Rail Transport Office to transport passengers. MarketsAndMarkets estimates that by 2022 the hydrogen production market will reach nearly 155 billion USD [15]. In turn, Allied Market Research reports that the hydrogen fuel cell market for cars is expected to reach 12.3 billion USD until 2023, with an average annual growth rate of over 72 percent [16].

The beginning of "fuel of the future" dates back to 1783, when Antoine Lavoisier discovered that the flammable gas formed by the reaction of metals with sulfuric acid is a separate element [2]. Hydrogenium, as it was called, due to its properties was great as a source of energy. Hydrogen understood as conventional fuel refers to the energy carrier released under the influence of the combustion process. It has the highest calorific value and heat of combustion (in relation to mass) and a very high diffusion coefficient in nitrogen (the main component of air), which results in its rapid combustion. The engine, in which hydrogen is a source of motive power, aims to combine the two main advantages of engines powered by steam to be able to operate anywhere, without delays and prior preparation. The main operating principle of this engine is based on the property that hydrogen mixed with atmospheric air explodes after ignition and creates a vacuum. If two and a half volumetric measures of atmospheric air are mixed with one measure of hydrogen and then a spark is applied, the mixture increases its volume more than three times. In 1807, Swiss engineer Isaac de Rivaz built the first hydrogen-powered wheeled vehicle. In 1820, William Cecil published the document "On the Application of Hydrogen Gas to produce a moving Power in Machinery", in which he described the advantages of a hydrogen-powered engine. These engines proved to be a great success, which translated into financial success. Despite the continuous development, the technology of hydrogen-powered internal combustion engines did not record a significant leap until the 1930s. At that time, Rudolf Erren, a German engineer from Upper Silesia, developed a method of injecting hydrogen into a chamber filled with oxygen or air. It was a completely innovative approach. This solution allowed to eliminate uncontrolled explosions in the combustion chamber and stabilize the engine operation. The Erren solution had one more advantage: it could be used in existing engines.

Hydrogen can be produced from various raw materials (chemically bound in water and liquid or gaseous hydrocarbons). It includes the reformation of fossil resources such as natural gas, oil and coal, as well as renewable resources such as biomass. Obtaining this gas is also possible by water decomposition through electrolysis using electricity generated from renewable energy sources (e.g. sunlight, wind or tides) or directly by photocatalysis. For its production, a variety of processes can be used, including chemical, biological, electrolytic, photolytic and thermochemical [17-20].

Hydrogen production methods include [21]:

Steam methane reforming (SMR)

SMR is a process in which natural gas or methane-containing streams (biogas or landfill gas) are reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. As a result of using this method, a gas rich in hydrogen is obtained. The product contains 70-75% hydrogen on a dry weight basis, 2-6% methane, 7-10% carbon monoxide and 6-14% carbon dioxide. About half of the world's hydrogen supply is produced by natural gas processing [22, 23]. Currently, it is the most commonly used method of hydrogen production due to its favorable economy [24]. However, this method is not an attractive production route for a sustainable and mature hydrogen economy, because an increase in demand by an order of magnitude would deplete natural gas reserves. Impact on the environment is also a serious problem because the conversion of natural gas to hydrogen generates the same amount of pollution and CO₂ emissions as direct combustion of natural gas [25]. However, hydrogen can be produced from biogas reforming. This not only gives the opportunity to utilize locally available bio-waste but also reduces dependence on imported fossil fuels.

Partial oxidation (POX)

The POX process is more commonly known as "gasification". Hydrogen can be produced from a range of hydrocarbon fuels (coal, heavy residual oils and other refinery products). The process involves the reaction of the substrate with oxygen in the non-stoichiometric ratio at temperature 1200-1350°C. The obtained product is a mixture of carbon monoxide and hydrogen [26]. Gasification and steammethane reforming dominate in the production of hydrogen, however, POX meted offers lower hydrogen concentration in the product and lower performance, but ensure a fast-dynamic response [27,28]. Partial oxidation (POX) as an alternative process to SMR and is generally preferred for higher-order hydrocarbons. The POX method can be carried out with or without a catalyst. Catalytic Partial Oxidation (CPOX) can occur at a much lower temperature than 1300-1500°C for non-catalyzed POX [29].

Auto-thermal reforming of oil (ATR)

ATR adds steam to CPOX method. It consists of a thermal zone in which POX or CPOX is used to generate the heat needed to drive the steam reforming reaction in the catalytic zone. The heat from POX eliminates the need for an external heat source, simplifying the system and reducing startup time. An important advantage of this process compared to SMR is that it can be stopped and quickly resumed while producing more hydrogen than POX alone. The application of ATR requires both oxygen:fuel and steam:carbon ratio control to keep the reaction temperature and desired composition of the gas product while preventing coke formation [30].

Water electrolysis

Electrolysis is a process in which water is decomposed directly into hydrogen and oxygen molecules under the influence of an applied voltage (current). Oxygen is often released into the atmosphere and obtained hydrogen is stored, transported and distributed. Water electrolysis is a recognized technology and is used today to produce high-purity hydrogen. The combustion of the hydrogen and oxygen mixture generates energy that is released as heat and work. The byproduct is water or steam that is released directly into the atmosphere. In this way, the hydrogen cycle is closed. However, electrolysis consumes electricity, which is a kind of physical work (energy).

The two most common types of electrolyzers are alkaline (uses concentrated KOH as electrolyte) and Polymer Electrolyte Membrane electrolyzers (PEM). Hydrogen can be produced by electrolysis of water from any electrical source, including power grids, solar photovoltaic (PV), wind, hydro or nuclear energy. Electrolysis is currently carried out on a wide scale range, from several kW to several MW. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen [31]. The application of photoelectrochemical (PEC) process of water splitting is a zeroemission process and uses unrestricted energy to decompose water.

It is a one stage process, without converting solar energy into electricity and then using it in the electrolyzer to separate water [32]. However, PEC systems are currently under development and are not widely available. The advantage of electrolysis is that it produces extremely pure hydrogen. However, it is limited to a small scale in which access to large hydrogen production plants is impossible or economicaly non-reasonable (maritime, space, electronics, food, medical) [33, 34]. Balat et al. reported that the main source of hydrogen production is natural gas, which accounts for 48% of the total share, with crude oil being the second of 30%, followed by coal with 18%, and electrolysis representing 4% of the total share [35].

Biomass processing

technologies divided Biomass conversion can be into thermochemical and biochemical processes. Thermochemical processes allow higher reaction rates. They can be operated at higher temperatures and therefore are usually cheaper. They include either gasification or pyrolysis (heating of biomass in the absence of oxygen) to produce a hydrogen-rich gas stream known as "synthesis gas" (a mixture of hydrogen and carbon monoxide). A wide range of biomass can be applied in this process. Biomass gasification is a possible method of efficiently producing large amounts of renewable hydrogen. Leading to a reduction of utilization of fossil fuels in the hydrogen production process [36]. Several available processes for producing hydrogen from biomass can give other useful products/byproducts, such as glues, carbon black, activated carbon, polymers. fertilizers, ethanol, various acids, diesel, waxes, and methanol.

Nuclear energy

Various nuclear-based hydrogen production methods are recently known, including water splitting using various thermochemical processes, e.g. sulfur - iodine cycle, water electrolysis with nuclear energy and high-temperature steam electrolysis. The last process is based on application of waste heat from the nuclear system to reduce the power consumption required for electrolysis [37]. Although the use of nuclear energy to produce hydrogen is attractive in terms of reducing carbon dioxide emissions, it raises other serious environmental and health concerns related to uranium mining/processing, accidents and the management of radioactive waste disposal.

Biological processes

Due to increased interest in sustainability and waste minimization, more research is being done on biological technologies used in the production of biohydrogen. This process involves algae or cvanobacteria. fermentation and photogeneration [38-42]. Nitrogenase and hydrogenase play a very important role in the biological production of hydrogen. Sucrose, used as a substrate, can produce up to 28% of energy in the form of hydrogen. Biological hydrogen production has an advantage over other processes in terms of low energy demand and may reduce initial investment costs. In addition, biomass is a renewable raw material, available almost everywhere. In this case, thermochemical pyrolysis and gasification are an effective way of producing hydrogen with efficiency in the range of 35-50%. CO₂ is used for photosynthesis to carry out the biophotolysis process. Dark fermentation can compete in terms of efficiency with all methods. However, bio-photolysis and photofermentation require constant access to the sunlight. The disadvantage of the thermochemical process is a seasonal availability of the raw material and low efficiency associated with the biological process. [43, 44]. Consequently, biomass can contribute to largescale production only through thermochemical pyrolysis and gasification pathways. Biological processes can only be used in small scale and for local H₂ production or for centralized recycling and waste treatment.

5. Estimated cost

Each of the mentioned hydrogen production methods has its advantages and disadvantages. Currently, the most cost-effective H_2 production process is SMR, followed by CG. The advantage of the SMR method is the lowest temperature (without access to oxygen). ATR and POX are next in the line, while hydrocarbon pyrolysis is a zero-emission procedure. Based on the data summarized in Tab. 2, one can see that these methods are currently well developed and optimized. They also provide more efficient energy conversion (up to 85%) compared to methods based on renewable sources. However, dependence on fossil fuels and high CO₂ emission during the reform process are crucial driving forces for the development of alternative methods for producing H₂ based on renewable sources. Since fossil fuels are currently used both as reagents and as fuel in the process, these methods are highly dependent on their price.

Table 2. Economic data for different hydrogen production methods [21]. H-EL -				
hydropower-electrolysis system, W-EL - a wind turbine-electrolysis system, PV-EL				
- photovoltaic-electrolysis system, BG - biomass gasification, CG - coal				
gasification, POX - natural gas partial oxidation, SMR - steam methane reforming.				

	CO ₂	O & M costs	Capital cost	Feedstock	H ₂	
	emissions	(\$/(kgH ₂ /day)	(\$/(kgH ₂ /day)	cost	productio	
	(kgCO ₂ /kgH ₂))	(\$/(kgH ₂ /day	n cost	
)	(1993)	(2005))	(\$/kgH ₂)	
	(2006)			(1989)	(2007)	
H-	0.00	30.5	4927	0	1.4	
EL						
W-	0.00	15.7	3170	0	36.7	
EL						
PV-	0.00	15.7	10448	0	17.3	
EL						
BG	5.89	52.5	104	194	23.7	
CG	29.33	54.9	1637	120	22.3	
POX	12.35	35.8	1058	136	16.0	
SM	7.33	14.5	284	154	32.7	
R						

In most cases, processes combining renewable energy sources with electrolysis are considered to be more cost-effective than conventional processes. By comparing the cost-effectiveness and environmental impact, water electrolysis is the most profitable hydrogen generation process while the gasification (CG) is the least profitable in long term analysis [45]. Currently, SMR, CG, and water electrolysis are the most often applied hydrogen production technologies for industrial scale around the world. Natural gas SMR is the most widely used process in the chemical and petrochemical industries and is the cheapest method of producing hydrogen. It also has the lowest CO₂ emissions of all possibilities related to the use of fossil fuels for hydrogen production. Despite being at an early stage of development, it is expected that Biomass gasification (BG), is to become the cheapest option for supplying renewable hydrogen in the coming decades. BG can be used in small decentralized plants in the early stages of infrastructure development and in centralized plants in later periods for the production of hydrogen. The possibilities of using CG or nuclear energy are only suitable for large-scale production [46].

The full benefits of hydrogen as a clean, versatile and efficient fuel can only be realized if hydrogen is produced from renewable energy sources, but only some of them are currently commercially available. These sources will certainly not be able to meet the demand required globally for hydrogen as a new energy source [47].

Renewable hydrogen production pathways avoid the pollution generation that causes global warming. Depending on the costeffectiveness of carbon capture and storage, that may prove to be more attractive in the long run. Currently, these options are generally more expensive. However, even taking into account the costs of CO₂ recovery, it is estimated that the production of hydrogen from fossil fuels is much cheaper than electrolytically produced hydrogen on large-scale markets [48]. A recent report from the US Energy Information Association suggests that solar energy is probably the only energy source capable of producing enough hydrogen required by the hydrogen economy [49].

Currently, the cost of hydrogen is more than twice as high as diesel and gasoline per unit of energy. However, to make environmentally friendly paths competitive with petroleum fuels numerous studies are still needed. Before the hydrogen economy becomes a reality, a technical and economic challenge must be overcome. The technical challenge is real-time production, safe convenient storage and efficient combustion of hydrogen. To meet the global demand for fossil fuels, more than $3 \cdot 10^{12}$ kg of hydrogen per year will have to be produced. This is about 100 times more than current hydrogen production. Furthermore, it is worth noting that the price we are used to paying for fossil fuels is just mining costs. To adapt the world to synthetic fuels such as hydrogen, the world economy must be convinced to pay also for converting renewable energy into fuel [2].

Process		Feedstock	Capital	Hydrogen	Study
	Energy source		cost	cost	year
			[M\$]	[\$/kg]	dollars
SMR with CCS	Standard fossil	Natural	006.4	2.27	2005
	fuels	Gas	220.4		
SMR without	Standard fossil	Natural	100.7	2.00	2005
CCS	fuels	Gas	100.7	2.00	2005

Table 3. Hydrogen production costs by various approaches for thermochemical water splitting [50]

Science meets regions - Hydrogen as a future fuel source

CG with CCS	Standard fossil fuels	Coal	545.6	1.63	2005
CG without CCS	Standard fossil fuels	Coal	435.9	1.34	2005
ATR of methane with CCS	Standard fossil fuels	Natural Gas	183.8ª	1.48	2005
Methane Pyrolysis	Internally generated steam	Natural Gas	_	1.59– 1.70	1992
Biomass Pyrolysis	Internally generated steam	Woody Biomass	53.4– 3.1 ^ь	1.25– 2.20	2004
Biomass Gasification	Internally generated steam	Woody Biomass	149.3– 6.4°	1.77– 2.05	2004
Direct Bio- photolysis	Solar	Water + algae	50 \$/m²	2.13	2002
Indirect Bio- photolysis	Solar	Water + algae	135 \$/m²	1.42	2002
Dark Fermentation	-	Organic Biomass	-	2.57	2014
Photo- Fermentation	Solar	Organic Biomass	-	2.83	2014
Solar PV Electrolysis	Solar	Water	12–54.5	5.78– 23.27	2007
Solar Thermal Electrolysis	Solar	Water	421– 22.1₫	5.10– 10.49	2007
Wind Electrolysis	Wind	Water	504.8– 499.6°	5.89– 6.03	2005
Nuclear Electrolysis	Nuclear	Water	-	4.15– 7.00	2006
Nuclear Thermolysis	Nuclear	Water	39.6– 2107.6 ^f	2.17– 2.63	2007
Solar Thermolysis	Solar	Water	5.7–16 ^g	7.98– 8.40	2007
Photo- electrolysis	Solar	Water	-	10.36	2004

a Based on a 600 MW_{H2} power plant with a capital cost of 306.35 %W_{H2}. **b** The capital cost of 53.4 M\$ corresponds to a plant capacity of 72.9 tn/day, 3.1 M\$ is referred to a 2.7 tn/day plant output.

c The capital cost of 149.3 M\$ corresponds to a plant capacity of 139.7 tn/day, 6.4 M\$ is referred to a 2tn/day plant output.

d The capital cost of 421 M\$ is referred to a power-tower electrolysis plant and 38.4 tn/day of H_2 , 22.1 M\$ corresponds to stirling-dish technology and 1.4 tn/day.

e The cost of 504.8 M\$ assumes the coproduction of electricity along with hydrogen whereas, 499.6 M\$ represents the cost of only hydrogen production.

f The capital cost of 39.6 M\$ corresponds to a Cu-Cl plant capacity of 7 tn/day, 2107.6 M\$ is referred to a 583 tn/day S-I plant output. **g** The capital cost of 5.7 M\$ corresponds to a plant capacity of 1.2 tn/day, 16 M\$ is referred to a 6 tn/day plant output.

To assess the costs of hydrogen production, the cost of energy source, raw material and capital investments were taken into account (data are summarized in Table 3). In this context, methods of H₂ producing from fossil fuels seem to be unfavorable. These processes require expensive CCS (CO₂ capture and storage) procedures. Due to the still low price of natural gas/coal and the high efficiency, the final cost of producing hydrogen from these raw materials is guite low (< 2 $\frac{1}{2}$ solution with a produced cost of H₂ per kilogram with and without CCS ranges from 1.34 \$ to 2.27 \$ (based on 2005 data). The lowest value corresponds to CG without a CCS process. The use of a cheaper source of energy (thermochemical pyrolysis) and raw material (biomass) is economically profitable because they provide production costs similar to conventional technologies. Pyrolysis and gasification of biomass offer a realistic approach. The production costs are in the range of 1.25-2.20 \$/kg. Although algae are one of the most expensive raw materials, biological processes offer low production costs (around 2 \$/kg). According to research conducted in 2014, dark biochemical and photo-fermentation results in H₂ production at a price of 2.5 to 2.8 \$/kg (due to low speeds, yields and the need for large reactors).

High production costs are also predicted for water decomposition methods, especially those that use solar or wind energy. High investment costs and low conversion efficiency lead to an increase in production costs, which in some cases exceeds 20 \$/kg for electrolysis and 8 \$/kg for thermolysis. With a production cost higher than 10 \$/kg H₂ and a yield of only 0.06%, photolysis is by far the cheapest method currently available. In summary, the imposition of carbon taxes directly affects the cost of H₂. In addition to making renewable methods competitive in terms of cost-effectiveness, the second step should be a subject of further research into renewable technologies and the development of cheaper equipment to produce H₂ more efficiently.

6. Hydrogen storage

Aiming at achieving security goals in the energy supply system, environmental protection and the economic growth of societies, the introduction of H₂ as a fuel and energy carrier brings numerous advantages. There are also a number of problems associated with this technology in terms of storage, transmission, and application [51]. At ambient temperature and atmospheric pressure, 1 kg of H₂ gas occupies a volume of 11 m³. With such a low density, H₂ storage has become one of the key barriers to its extensive application [52]. The main storage methods allow the physical storage of hydrogen in the form of gas or liquid and on material surfaces by adsorption.

High-pressure hydrogen gas storage is currently the most common and mature method. High pressures up to 77 MPa are achieved using standard reciprocating mechanical compressors [53]. However, the work needed for compression is high. By ensuring this, gravimetric density - 13 wt.% and volume - <40 kg·m⁻³ is achieved [54].

Liquid hydrogen can be stored in cryogenic tanks through a twostage compression and cooling procedure in a heat exchanger. Due to its low boiling point, the work needed is estimated at 15.2 kWh·kg⁻¹, reaching a density of 70.8 kg·m⁻³ at atmospheric pressure. The low density in the gaseous state is associated with the release of hydrogen into the atmosphere (even with tight insulation). Losses are estimated at 0.4, 0.2 and 0.06% for volumes of 50, 100 and 20,000 m³, respectively [53].

An effective way to store large amounts of hydrogen at moderate temperature and pressure is the so-called solid storage. In the adsorption process, a gas molecule interacts with several atoms on the surface of a solid, where it is bound and released (if necessary) in a reversible manner. Carbon nanotubes are able to store H₂ at fairly low temperatures (196.15°C) and under pressure (6 MPa), providing a gravimetric density - 10.8 wt.% and a volume density - 41 kg \cdot m⁻³ [54]. Alternatively, H₂ may react at elevated temperatures with many transition metals and their alloys to form hydrides. Light metals, such as Li, Be, Na, Mg, B, and Al, form a large variety of metal-hydrogen compounds, with high volumetric density - 150 kg·m⁻³ [53]. However, gravimetric density is limited to less than 3% by weight. Complex hydrides open a new field of hydrogen storage materials, ensuring gravimetric density up to 18 wt.% [55]. The main characteristics of the five basic methods for reversible hydrogen storage are listed in Table 4.

Storage method	Gravimetric density [wt.%]	Volumetric density [kg·m⁻³]	Temperature [°C]	Pressure [MPa]
High-pressure gaseous H ₂	13	40	ambient	77
Cryogenic liquid	-	70.8	-252.87	atmospheric
Adsorbed on carbon nanotubes	10.8	41	-196.15	6
Absorbed to form hydrides	3	150	ambient	atmospheric
Absorbed to form complex hydrides	18	150	>100	atmospheric

Table 4.	The basic	hydrogen	storage	methods	[50]
					L 1

There are two possible modes of H_2 transport and distribution. The first category concerns sea, rail or road transport. The second category includes pipelines [55]. Considering the most common way of storing H_2 (in gas form) and its low density in this form, this generates high delivery costs [53]. The future H_2 transport and distribution system may resemble current gas pipelines and may be envisaged as part of a network system, including electricity and gas [56]. Therefore, significant innovations are needed because the transport losses of methane and electricity over long distances are quite similar at a level of 5-7%, while the use of the same H_2 pipelines could increase to 20% [57].

Storage of hydrogen in carbon micropores by electrosorption at ambient conditions is an attractive alternative for traditional high pressure or cryogenic method. Hence, intensive research is presently devoted to the application of nanotextured carbons because they seem to be the most promising materials. The reversible process of hydrogen electrosorption is attractive from the point of view of energy efficiency since it associates in one step the hydrogen production from water electrolysis and its simultaneous storage *in statu nascendi* in the carbon substrate. Hydrogen produced by this way easily penetrates into the nanopores of the activated carbon where it is adsorbed due to the driving force of the negative polarization. The charge/discharge phenomenon can be represented by the following general reaction:

$$C + xH_2O + xe^- \leftrightarrow < CH_x > + xOH^-$$

where <CH_x> stands for the atomic hydrogen in a chemisorbed state inserted into the nanostructured carbon during charging and oxidized during discharging. It was assumed that the adsorbed hydrogen diffuses in the bulk of the carbon material occupying sites with high adsorbing energy. Lately, it has been proved that apart from physisorption being controlled by weak van der Waals forces, some part of hydrogen atoms interacts with carbon much stronger. The energy of hydrogen desorption evaluated by thermal programmed desorption (TPD) has a value of ca. 110 kJ·mol⁻¹ that suggests weak chemical bonds. The type of bonding is affected by the microtexture of carbon material. However, the role of surface functionality in carbon material is also important for hydrogen storage and cannot be neglected.

Hydrogen capacity is strongly determined by the physicochemical properties of carbon materials (texture, ultramicropore volume, elemental composition, etc.) but also by the parameters of the charging process (applied charge and discharge current density, time as well as the total charge), temperature and type of electrolytic medium. Detailed studies performed with different electrolytic solutions showed that the alkaline medium seems to be the most appropriate because of the highest polarization during the cathodic process.

7. Application

In recent years hydrogen has attracted a lot of attention as the preferred energy carrier, especially for transport applications. It is considered a clean fuel that hardly emits anything except water. Hydrogen works well with fuel cells and together they can contribute to the introduction of sustainable energy sources [58]. In addition to applications in the chemical and petroleum industry, H₂ can be used in internal combustion engines, fuel cells, turbines, stoves and gas boilers [59]. In terms of simplicity, modularity and environmental protection, fuel cells are a very promising energy generation solution. Polymer electrolyte (PEMFC) fuel cells will be able to provide from several kW to hundreds of kW for domestic and industrial applications, as well as two to three times higher efficiency than the combustion engines in conventional vehicles. Molten carbonate (MCFC) and solid oxide-based (SOFC) fuel cells will be available for power generation in the industry (from several hundred kW to several dozen MW) [56]. Widespread hydrogen technology is still a perspective, however, the proposed solutions support the initial use

of local small hydrogen generators for stationary and mobile applications [57]. For hydrogen-based vehicles, the two alternatives considered are either direct H₂ storage provided by service stations or indirect (on-board production of H₂ from methanol) [51, 60]. It provides vehicle manufacturers the possibility of using the existing infrastructure for the production of engines and hydrogen does not differ significantly from other gaseous fuels used in internal combustion engines [61]. Hydrogen has a wide range of flammability compared to other fuels; therefore, engines can work more effectively than gasoline engines. Furthermore, it does not require high ignition energy (0.02 MJ only). It has a higher flash point compared to other fuels. The hydrogen flame speed is almost an order of magnitude higher than gasoline. It also has very high diffusivity. This ability to disperse in the air is much greater than gasoline and is beneficial for two main reasons: (1) it facilitates the formation of a homogeneous mixture of fuel and air, and (2) it disperses guickly in the event of a leak. The very low hydrogen density causes two problems when used in an internal combustion engine: (a) a very large volume is needed to accumulate enough hydrogen gas to provide the vehicle with adequate coverage, and (b) the energy density of the mixture of hydrogen and air, and thus power output is reduced. Due to its versatile nature, hydrogen can be converted into other forms of energy in five different ways, i.e. in addition to burning the flame, it can be converted directly into steam, converted into heat by catalytic combustion, act as a heat source and/or heat absorber as a result of chemical reactions and converted directly into electricity in electrochemical processes, while other fuels can be converted into other forms of energy only through combustion. In other words, hydrogen is a versatile fuel.

Experimental section

This section provides the results over the hydrogen storage by electrosorption in porous carbon materials in different electrolytes.

1. Carbon surface determination

The electrochemical characterization of hydrogen electrosorption process was performed with application of 4 different carbon materials. Three commercially available Norit® SX2, Kuraray® YP-50, Kuraray® YP-80 and self-prepared NAC sample, obtained by KOH chemical activation of Norit® SX2 carbon were used. Prior to electrochemical characterization, the physio-chemical properties of applied carbons were examined by nitrogen adsorption at 77K. The obtained sorption/desorption profiles are presented in Fig. E1.





Figure E1: Nitrogen adsorption isotherms recorded at 77K and pore size distribution curves calculated by NL-DFT method for the Norit® SX2, Norit® SX2 Activated Carbon (NAC), Kuraray® YP-50F and Kuraray YP-80F carbons.

All carbons are characterized with isotherm type 1, characteristic of microporous materials with a fraction of mesopores observed as a significant hysteresis loop. The calculated BET surface area ranged from 843 m² g⁻¹ for Norit® SX2 carbon to 2113 m² g⁻¹ for NAC carbon. The pore size distributions presented in Fig. E1 were calculated using the 2D NL-DFT method. The presented profiles show that Kuraray® YP-50 and YP-80 are strictly microporous carbons (major pores with diameter <2 nm). However, the Kuraray® YP-50 carbon is characterized by ultramicroporous structure (most pores with diameter < 1 nm) with a very small contribution of pores > 1 nm, while the Kuraray® YP-80 carbon consists mostly of micropores in range of 1 – 2 nm. The Norit® carbon and NAC carbon are characterized mostly by the presence of micropores with a significant fraction of mesopores up to 20 nm. It might be concluded that the activation process significantly increases the contribution of micropores while preserving the interconnectivity between pores provided by mesopores.

2. Hydrogen electrosorption examination procedure

The hydrogen electrosorption examination was performed with the application of two aqueous electrolytes: alkaline (1M KOH) and neutral (1M K₂SO₄). All experiments were performed in three-electrode cell, presented in Fig. E2.



Figure E2: Three-electrode cell applied for electrochemical investigation.

The electrochemical system consists of a carbon working electrode supported on a stainless steel current collector, the platinum mesh as a counter electrode and saturated calomel electrode as the reference electrode. The activated carbon electrode consists of 5% of polytetrafluoroethylene as a binder and 95% of activated carbon as active material. The electrodes were prepared by a wet method (i.e. with solvent).

First, the proper amount of carbon and binder were mixed and heated up in ethanol to form a homogenous dough. Next, the dough was formed into rectangular sheets with thickness of 200 μ m by pressrolling. Afterwards, the round-shaped electrodes (diameter of 10 mm) were cut from prepared sheets.

The electrolytic solutions were prepared by dissolving of the proper amount of substrates (KOH, K₂SO₄) in deionized water.

The electrochemical characteristics were performed with multichannel potentiostat/galvanostat VSP by BioLogic[®]. The examination was done by the application of potentiostatic and galvanostatic methods. The quality examination of the hydrogen sorption/desorption process was done by cyclic voltammetry (CV) technique at 5 mV s⁻¹ and galvanostatic intermittent titration technique (GITT). CV technique allows identifying the electrochemical processes

during electrode polarization, while the GITT technique was applied to examine the potential equilibrium of charged electrodes. The quantitative analysis was performed by galvanostatic charge/discharge with potential limitation (GCPL); the charging step was done at -1 A g⁻¹ current regime while discharge was performed at +0.05 A g⁻¹. Additionally, the electrochemical sorption desorption process on the surface of the carbon electrode was confirmed by the application of *operando* Raman spectroscopy.



The research pathway is shown in the scheme below.

3. Hydrogen electrosorption in the alkaline electrolyte (1M KOH)

Qualitative examination

The qualitative examination was performed as the initial characteristic of all carbon materials in order to evaluate their possible application in hydrogen sorption process. In Fig. E3, the CV plots obtained are presented.





Figure E3: Cyclic voltammograms (10 mVs⁻¹) of the Norit® SX2, Norit® SX2 Activated (NAC), Kuraray® YP-50F and Kuraray YP-80F electrode, recorded in a three-electrode cell with 1 M KOH electrolyte.

For all selected carbons, during cathodic polarization up to Hydrogen Evolution Potential (HEP), a rectangular shape of CV profile typical for charge/discharge of electric double-layer is observed.

The deviation in the form of expanding the value of measured current at potential ranges 0.2 V - 1 V vs. SHE, while shifting towards lower potential values can be assigned to the ion sieving effect. After reaching the Hydrogen Evolution Potential (HEP), the formation of a reduction peak can be observed. In the case of highly microporous carbons with significant BET surface area, progressive cathodic polarization towards lower potential values results in the formation of the hysteresis loop. The reduction peak refers to hydrogen adsorption, following the Volmer mechanism shown in reaction below:

$$H_2O + e^- \leftrightarrow H(a) + OH^-(Volmer)$$

By applying the voltage, water molecules are split into hydrogen, further adsorbed in micropores; OH⁻ ions appearing during cathodic process promote alkalization of electrolyte at electrode/electrolyte interface. The effect of electrolyte alkalization is observed by the progressive shifting of the reduction peak towards lower potential values. Further cathodic polarization to the potential -1.75 V vs. SHE leads to hydrogen recombination and evolution process following Heyrovsky or Tafel mechanism:

$$H_2O + H(a) + e^- \leftrightarrow H_2 \uparrow + OH^- (Heyrovsky)$$
$$2H(a) \leftrightarrow H_2 \uparrow (Tafel)$$

The evolution of hydrogen can be observed as distortions of the reduction peak, most likely due to the gas (H₂) evacuation from the system. The typical curve shape, corresponding to the hydrogen sorption process, was observed for NAC carbon and both Kuraray® YP50 and YP80 carbons. The best sorption properties were recorded for NAC carbon, characterized by the lowest value of reduction current. However, in the case of Norit® SX2 carbon, the lack of a hysteresis loop is a strict reflection of its lack of microstructure. In the absence of micropores, the generated hydrogen is adsorbed on the geometric surface of carbon and immediately recombines, leading directly to hydrogen evolution and evacuation. The change to anodic polarization leads to the formation of а significant oxidation/desorption peak near the potential value of -0.25 V vs. SHE. The highest desorption efficiency is observed for NAC carbon. In the

case of Kuraray[®] carbons, the similar desorption currents are observed, leading to the conclusion that for efficient electrochemical hydrogen storage, **carbon material should be characterized by well-developed micropore structure, interconnected by mesopores**. In the case of Norit[®] SX2 carbon, an ill-defined desorption peak is observed.

The consideration based on CV analysis are confirmed by the application of the GITT technique (Fig. E4). The GITT experiment consists of 20 intermittent cycles of 1h polarization and 1h rest periods. The technique is divided into two segments: first 10 cycles of charge is applied and hydrogen electrosorption occurs. These cycles are followed by 10 cycles of discharge, where desorption and electrolyte/electrode oxidation is observed. The rest periods are introduced to establish the equilibrium potential of the polarized electrode.



Figure E4: GITT profiles for Norit® SX2, Norit® SX2 Activated (NAC), Kuraray®YP50F and Kuraray® YP-80F electrodes recorded in the three-electrode cell in 0.5M K_2SO_4 aqueous electrolyte at 50 mA g⁻¹.

Initially, the hydrogen desorption process is observed, followed by oxidation of the electrode indicating the anodic polarization limitation. In Fig. E4, the GITT curves for Norit® SX2, NAC, Kuraray®YP50F, and Kuraray® YP-80F electrodes are presented. It can be observed that

the reduction potential limitation is similar for all carbons and it is established at potential -1.1 V vs. SHE. After 10 cycles of intermittent charge and rest periods, the equilibrium potential for all electrodes is settled at +0.9 V vs. SHE. After the change from cathodic to anodic polarization, the hydrogen desorption process occurs; the highest discharge efficiency is recorded for Kuraray® YP-80F carbon. Interestingly, the desorption capacity of NAC carbon is at the level of the Kuraray® YP-50F carbon. This suggests the degradation of NAC carbon during the continuous examination. The reason for this might be for instance the pore-clogging and micropore structure degradation. In the case of Norit® SX2 carbon, mostly capacitive discharge is observed without hydrogen desorption plateau. Based on this experiment, for further examination procedure, the oxidation limitation potential was established at 0.4 V vs. SHE and the positive electrode equilibrium at 0.2 V vs. SHE.

Quantitative examination

Since the cyclic voltammetry (CV) is considered a qualitative technique, the quantitative examination of the hydrogen storage process was performed by the galvanostatic (GCPL) measurement. The discharge plots are presented in Fig. E5.



Figure E5: Galvanostatic profiles for Norit® SX2 Activated (NAC) and Kuraray® YP-80F electrode recorded in the three-electrode cell in 1M KOH aqueous electrolyte

Firstly, the systems were polarized at -1 A g⁻¹ for 6 h without potential limitation; this step was followed by 15 min of rest period. The oxidation was performed at +0.05 A g⁻¹ current density and was limited at +0.25 V vs. SHE to avoid carbon oxidation. For this experiment, only two carbons with the best characteristic were selected: Kuraray® YP-80F and NAC carbon. As expected by the application of the higher charge current, the hydrogen storage overpotential shifts the charging potential towards lower values. Interestingly the sorption plateau is established on different potentials, i.e. -1.4 V vs. SHE for NAC carbon and -1.6 V vs. SHE for Kuraray® YP-80F. Furthermore, the value of the overpotential gives information about the reaction rate. One can consider that for Kuraray® YP-80F carbon the part of the charge is lost for gas generation, which can be observed as curve distortions. In the case of NAC carbon, the gas evolution process undergoes at lower rate, reflected by a lack of charging curve distortions and lower overpotential value. Such behavior highlights the role of mesopores in carbon structure as transport channels for reaction products. As both of the carbons have similar micropore structure and BET surface area, expected desorption process reflects a comparable amount of hydrogen recovered (~320 mAh g⁻¹) during cathodic polarization. In both cases, the observed desorption plateau is in the range of equilibrium potentials for positive and negative electrode, established before by GITT technique at potential values of -0.9 ~ 0.1 V vs. SHE. In overall, the galvanostatic process confirms the possible application of microporous carbons in hydrogen storage and generation technology.

Spectral observations

Further examination of the hydrogen storage process was performed by *operando* Raman spectroscopy where microscopic changes of carbon material during charge transfer reaction was examined. The Raman spectra of carbon materials provide information about the carbon structure. Depending on the shape and intensity relation between two characteristic bands: D (1250 cm⁻¹) and G-band (1550 cm⁻¹) one can distinguish different forms of carbon materials. In Fig. E6 the heat maps of NAC and Kuraray® YP-80F carbons are presented.



Figure E6: Raman spectra heat map of Norit® SX2 Activated (NAC) and Kuraray® YP-80F carbons recorded in the three-electrode cell with 1M KOH during 0.1 mVs⁻¹ cyclic voltammetry scan. Spectra were recorded every 5 min. The top graph shows the electrochemical behavior of the carbon electrode during the experiment.

The spectra were recorded in the three-electrode cell with 1M KOH electrolyte during 0.1 mVs⁻¹ cyclic voltammetry scan and single spectrum was recorded every 5 min. The top graph represents the current and potential changes during the performed scan. The intensity changes are reflected by changes of colors: blue for lowest and red for the highest intensity. The potential limitations were established based on the GITT technique at -1.2 V for sorption and 0.2 V vs. SHE for desorption. For both selected carbons (Kuraray® YP-80F and NAC) one can observe similar trends. The increasing of the D- and G- band intensity mainly connected with a reduction peak. An increase of the band intensities corresponds to the ongoing charge transfer reaction, more specifically hydrogen sorption. The observed changes of D- and G- band shape reflect the microscopic changes, increasing distance between graphene interlayers in ordered structures and higher disorientation of amorphous parts of activated carbon. Moreover, one can observe the increased intensity of 1500 cm⁻¹ band, reflecting the C=C stretching vibrations reflecting the hydrogen insertion process. Furthermore, one can observe that for both materials the changes of D- and G-band corresponding to hydrogen storage process are starting at different potentials. For NAC carbon the D- and G-band intensity increase starts at @-0.7 V vs. SHE with a maximum of intensity at -1.2 V vs. SHE. Such values correspond well with theoretical HEP, meaning that hydrogen is generated and stored rapidly after exceeding water thermodynamic stability. This process is also well reflected in the CV discussed beforehand. The progressive increase of the D- and G- band intensity with ongoing polarization reflect a high reaction rate. The change of the polarization ends the process of hydrogen sorption, reflected in the diminishing of the specific band intensity. In the case of Kuraray[®] YP-80F, the hydrogen sorption process undergoes an additional step of carbon surface reduction. This is reflected by the shift of D- and Gband intensity changes toward the oxidation process. This explains the poor development of the desorption peak observed by CV technique, and significant gaseous hydrogen generation during the galvanostatic controlled process. This also explains the higher sorption overpotential. For this carbon, firstly oxidized active sites need to be reduced and afterwards the generated hydrogen is electrosorbed. This explains the shift of the D- and G-band maximum intensity. After reaching the HEP, the desorption process starts, resulting in the diminishing of the D- and G-band intensity. This means that in the case of NAC carbon the one-step generation and

adsorption is observed, while in the case of Kuraray® YP-80F, the hydrogen sorption is preceded by additional carbon reduction step.

4. Hydrogen electrosorption in the neutral electrolyte (1M K₂SO₄)

Qualitative examination

Further examination of the hydrogen electrosorption process was performed with the application of neutral aqueous electrolyte, i.e. 1M K_2SO_4 . The evaluation of this electrolyte was performed in the same manner as in the previous section. The selection of carbon materials was limited to Kuraray® YP-80 and NAC carbon. In Fig. E7 the CV plots are presented.





Figure E7: Cyclic voltammograms (10 mV s⁻¹) of the Norit® SX2 Activated (NAC) and Kuraray YP-80F electrode, recorded in a three-electrode cell with 0.5 M K_2SO_4 electrolyte.

The shape of both plots resembles the one obtained for the 1M KOH electrolyte. However, for neutral electrolyte, the reduction and oxidation peaks are at lower current values. One can observe also the sharp shape of the reduction peak with a small hysteresis loop indicating a less favorable adsorption process. The observed distortions at the end of the curve are the result of hydrogen gas evolution. Moreover, the shifting of the reduction peak during cathodic polarization towards more negative potentials can be observed. The presented shift can be associated with an ongoing Volmer reaction resulting in progressive alkalization of the electrode/electrolyte interface. As expected, the NAC carbon show higher hydrogen sorption/desorption efficiency, observed as better defined oxidation (desorption) peak. In Fig. E8 the GITT curve is presented.



Figure E8: GITT profiles for Norit® SX2 Activated (NAC) and Kuraray® YP-80F electrode recorded in the three-electrode cell in $0.5M \text{ K}_2\text{SO}_4$ aqueous electrolyte at 50 mA g⁻¹.

One can observe two oxidation plateaus: one corresponding to the electrochemical hydrogen storage and the second one, most likely the result of the sulfate anion activity. During reduction, the hydrogen storage potential was established at -1.1 V vs. SHE, and the equilibrium of charged electrode at -0.9 V vs. SHE. Obtained values are comparable with the values obtained for KOH electrolyte, confirming the hydrogen electrosorption process. During the oxidation, the hydrogen desorption process is limited up to +0.2 V vs. SHE. However, one cannot exclude the redox activity of sulfates (SO₄²⁻) which result in the second plateau for potential values ranging from 0.2 to 0.8 V vs. SHE; at higher potentials the carbon oxidation is observed. The equilibrium of the positive electrode is established at 0.9 V vs. SHE.

Quantitative examination

As for the alkaline medium, the quantitative examination of the hydrogen sorption process in the K_2SO_4 -based electrolyte was

performed by the GCPL technique. The charge/discharge plots are presented in Fig. E9.



Figure E9: Galvanostatic profiles for Norit® SX2 Activated (NAC) and Kuraray® YP-80F electrode recorded in the three-electrode cell in 0.5M K₂SO₄ aqueous electrolyte.

One can observe that in both cases the hydrogen overpotential is similar, indicating the same hydrogen sorption/evolution reaction rate. Moreover, the lack of potential distortions during reduction suggesting less extensive gas evolution process. The hydrogen sorption plateau is determined at -1.5 V vs. SHE, which is similar to the one observed for KOH. One may expect that during cathodic polarization there are several competitive reactions, hydrogen evolution/sorption, carbon reduction, and sulfate redox activity. However, during the desorption, only 70 mAh g⁻¹ is recovered for both carbons.

Spectral observations

The Raman spectra of carbon electrode operating in the $1M K_2SO_4$ electrolyte presented as a heat map are shown in Fig. E10. The trends are again similar as in the case of 1M KOH electrolyte.



Figure E10: Raman spectra heat map of Norit® SX2 Activated (NAC) and Kuraray® YP-80F carbons recorded in the three-electrode cell with 0.5M K_2SO_4 during 0.1 mVs⁻¹ cyclic voltammetry scan. Spectra were recorded every 5 min. The top graph shows the electrochemical behavior of the carbon electrode during the experiment.

For the NAC carbon, the hydrogen sorption process recognized as the increase of the D- and G-band intensity is observed at -0.7 V vs. SHE with the maximum at -1.2V vs. SHE. It means that the sorption process occurs directly during the reduction of water. The desorption

observed as the diminishing of D- and G-bands intensity is observed during the oxidation step. For the Kuraray® YP-80F carbon the most intensive changes of D- and G- bands are observed during the oxidation step. Such behavior displays the two-step reaction: carbon reduction (1) followed by hydrogen adsorption (2). The obtained result confirms that hydrogen storage occurs in a neutral medium similar to the alkaline one but with a lower rate.

Final remarks

The process of hydrogen electrosorption from the aqueous solution of KOH and K_2SO_4 on the surface of the carbon electrode was examined and reported. Comparative examination of several carbon materials confirmed the importance of mesopores as transport channels in the process of hydrogen electrosorption. From the application point of view, the best result was obtained for chemically activated carbon in alkaline medium.

The NAC carbon was characterized by high hydrogen capacity of 333 mAh g⁻¹ and low hydrogen sorption potential of -1.4 V vs. SHE at -1 A g⁻¹. Further improvement of the presented process can be obtained by the application of specially designed carbons with high BET area and interconnected micropores.

Such electrodes can be considered as components of the cells or as the hydrogen storage mechanisms. The advantage of such systems are low production costs, zero-emission and one step hydrogen generation and storage. The hydrogen production costs by this method can be also significantly reduced by the application of renewable energy sources.

Presented results confirm that water electrolysis on carbon electrodes can be a green alternative to currently existing hydrogen generation methods resulting in the popularization of hydrogen as a future fuel source.

References

- J. Piernikarczyk, *Pierwsza maszyna parowa kontynentu europejskiego*, Przegląd Górniczo-Hutniczy t. XXX, no 4-5 (545-546), April – May 1938, page 259-263
- [2] A. Zuttel, A. Borgschulte, L. Schlapbach, *Hydrogen as a Future Energy Carrier*, WILEY-VCH Verlag GmbH & Co. KGaA, 20 February 2008, DOI:10.1002/9783527622894
- Kvenvolden, K.A., Gas hydrates geological perspective and global change, Volume 31, Issue 2, May 1993, Pages 173-187
- [4] J. Goldemberg, *Energy What Everyone Needs to Know*, Oxford University Press, 18 June 2012 – 192
- [5] G.W.C. Kaye, T.H. Laby, *Tables of Physical & Chemical Constants* (16th Edition 1995) 3.1.3 Abundances of the elements. The National Physical Laboratory, 1995. (ang.)
- J. Meija, Atomic weights of the elements, 2013 (IUPAC Technical Report), "Pure and Applied Chemistry", 88 (3), 2016, s. 265–291, DOI: 10.1515/pac-2015-0305
- [7] A. Demirbaş, *Hydrogen and boron as recent alternative motor fuels*, Energy Sources 2005;27:741–8
- [8] D. Rand, Hydrogen Energy Challenges and Prospects, RSC Publishing, 2008. ISBN 978-0-85404-597-6
- [9] D. R. Lide, CRC Handbook of Chemistry and Physics, Boca Raton: CRC Press, 2009, s. 4-66, ISBN 978-1-4200-9084-0
- [10] D. R. Lide, CRC Handbook of Chemistry and Physics, Boca Raton: CRC Press, 2009, s. 4-133, ISBN 978-1-4200-9084-0
- [11] D. R. Lide, CRC Handbook of Chemistry and Physics, Boca Raton: CRC Press, 2009, s. 6-52, ISBN 978-1-4200-9084-0
- [12] N. Charles, *Wartość dla ciała stałego*, Atomic volume and allotropy of the elements. "Journal of Chemical Education". 61 (2), s. 137–142, 1984. DOI: 10.1021/ed061p137
- [13] M. Balat, Current alternative engine fuels. Energy Sources 2005;27:569–77
- [14] J. M. Ogden, R. H. Williams, E. D. Larson, Societal lifecycle costs of cars with alternative fuels/engines, Energy Policy 2004;32:7–27
- [15] Hydrogen Generation Market by Generation, Application (Petroleum Refinery, Ammonia Production, Methanol Production, Transportation, Power Generation), Technology (Steam Reforming, Water Electrolysis, & Others), Storage, and Region - Global Forecast to 2023
- [16] Hydrogen Fuel Cell Vehicle Market by Vehicle Type (Passenger Vehicle and Commercial Vehicle) and Technology (Proton Exchange Membrane Fuel Cell, Phosphoric Acid Fuel Cells, and Others) - Global Opportunity Analysis and Industry Forecast, 2017-2023, D: 4580511, February 2018
- [17] J. M. Tour, C. Kittrell, V. L. Colvin, *Green carbon as a bridge to renewable energy*, Nat Mater 2010;9:871–4
- [18] T. Riis, E. Hagen, P. Vie, O. Ulleberg, *Hydrogen production R&D: priorities and gaps*, Publicação da Agência Internacional de Energia; 2006
- [19] A. A. Ismail, D. W. Bahnemann, Photochemical splitting of water for hydrogen production by photocatalysis, a review. Sol Energy Mater Sol Cells 2014;128:85–101.
- [20] G. Zhang, W. Zhang, D. Minakata, P. Wang, Y. Chen, J. Crittenden, *Efficient* photocatalytic H2 production using visible-light irradiation and (CuAg)

xln2xZn2 (12x) S2 photocatalysts with tunable band gaps, Int J Energy Res 2014;38:1513–21.

- [21] S. Sona, J. Shikh, P. S. Venkateswaran, K. T. Avanish, R. N. Mansa, K. P. Jitendra, G. Sanket, *Hydrogen: A sustainable fuel for future of the transport sector*, Renewable and Sustainable Energy Reviews 51 (2015) 623–633
- [22] J. Hirschenhofer, D. Stauffer, R. Engleman, M. Klett, Fuel cell handbook; 1998.
- [23] Energy Bo, Council ESNR, Engineering Do, Council PSNR, Engineering WNAo. *The hydrogen economy: opportunities, costs, barriers, and R&D needs*, Washington, DC, United States: National Academies Press; 2004.
- [24] F. Barbir, *Transition to renewable energy systems with hydrogen as an energy carrier*, Energy 2009;34:308–12
- [25] G. W. Crabtree, M. S. Dresselhaus, *The hydrogen fuel alternative*, MRS Bull 2008;33:421–8
- [26] R. Moore, V. Raman, Hydrogen infrastructure for fuel cell transportation, Int J Hydrog Energy 1998;23:617–20
- [27] K. Zeng, D. Zhang, *Recent progress in alkaline water electrolysis for hydrogen production and applications*, Prog Energy Combust Sci 2010;36:307–26
- [28] D. Y. Goswami, F. Kreith, *Handbook of energy efficiency and renewable energy*, Boca Raton, FL, United States: Crc Press; 2007
- [29] Y-F Chang, H. Heinemann, *Partial oxidation of methane to syngas over Co/MgO catalysts. Is it low temperature?*, Catal Lett 1993;21:215–24.
- [30] J. D. Holladay, J. Hu, D. L. King, Y. Wang, *An overview of hydrogen production technologies*, Catal Today 2009;139:244–60
- [31] C. Acar, I. Dincer, Comparative environmental impact evaluation of hydrogen production methods from renewable and nonrenewable sources, In: Dincer I, Colpan CO, Kadioglu F, editors. Causes, impacts and solutions to global warming. Springer; 2013. p. 493–514
- [32] N. Alenzi, W-S Liao, P. S. Cremer, V. Sanchez-Torres, T. K. Wood, C. EhligEconomides, et al., *Photoelectrochemical hydrogen production from water/methanol decomposition using Ag/TiO2 nanocomposite thin films*, Int J Hydrog Energy 2010;35:11768–75
- [33] S. Dunn, *Hydrogen futures: toward a sustainable energy system*, Int J Hydrog Energy 2002;27:235–64.
- [34] R. F. De Souza, J. C. Padilha, R. S. Gonçalves, M. O. De Souza, J. Rault-Berthelot, *Electrochemical hydrogen production from water electrolysis using ionic liquid as electrolytes: towards the best device*, J Power Sources 2007;164:792–8
- [35] M. Balat, Potential importance of hydrogen as a future solution to environmental and transportation problems, Int J Hydrog Energy 2008;33:4013–29
- [36] M. Balat, Political, economic and environmental impacts of biomassbased hydrogen, Int J Hydrog Energy 2009;34:3589–603
- [37] T. E. Lipman, What will power the hydrogen economy? Present and future sources of hydrogen energy, Davis: Institute of Transportation Studies, University of California; 2004
- [38] H-Y Wang, A. Bernarda, C-Y Huang, D-J Lee, J-S Chang, *Micro-sized microbial fuel cell: a mini-review*, Bioresour Technol 2011;102:235–43

- [39] Y-T Fan, Y-H Zhang, S-F Zhan, H-W Hou, B-Z Ren, Efficient conversion of wheat straw wastes into biohydrogen gas by cow dung compost, Bioresour Technol 2006;97:500–5
- [40] S-Y Wu, C-N Lin, J-S Chang, Biohydrogen production with anaerobic sludge immobilized by ethylene-vinyl acetate copolymer, Int J Hydrog Energy 2005;30:1375–81.
- [41] M. Cai, J. Liu, Y. Wei, Enhanced biohydrogen production from sewage sludge with alkaline pretreatment, Environ Sci Technol 2004;38:3195–202
- [42] D. B. Levin, L. Pitt, M. Love, Biohydrogen production: prospects and limitations to practical application, Int J Hydrog Energy 2004;29:173–85
- [43] M. F. Demirbas, Technological options for producing hydrogen from renewable resources, Energy Sources Part A Recover Util Environ Eff 2006;28(13):1215–23
- [44] G. Berndes, M. Hoogwijk, R. Van Den Broek, *The contribution of biomass in the future global energy supply: a review of 17 studies*, Biomass Bioenergy 2003;25(1):1–28
- [45] P. A. Pilavachi, A. J. Chatzipanagi, A. I. Spyropoulou, Evaluation of hydrogen production methods using the analytic hierarchy process, Int J Hydrog Energy 2009;34:5294–303
- [46] M. Ball, M. Wietschel, The future of hydrogen opportunities and challenges, Int J Hydrog Energy 2009;34:615–27
- [47] P. P. Edwards, V. L. Kuznetsov, W. I. David, N. P. Brandon, *Hydrogen and fuel cells: towards a sustainable energy future*, Energy Policy 2008;36:4356–62
- [48] J. M. Ogden, R. H. Williams, E. D. Larson, Societal lifecycle costs of cars with alternative fuels/engines, Energy Policy 2004;32:7–27
- [49] P. G. Li, G. Shiqiao, Cai. Huatong, Modeling and analysis of hybrid piezoelectric and electromagnetic energy harvesting from random vibrations, Microsyst Technol 2013:1–14
- [50] P. Nikolaidis, A. Poullikkas, A comparative overview of hydrogen production processes, Renewable and Sustainable Energy Reviews 67 (2017) 597–611
- [51] G. Marbán, T. Valdés-solís, Towards the Hydrogen Economy ?, vol. 32. p. 1625–37. 2007
- [52] V. M. Aroutiounian, V. M. Arakelyan, G. E. Shahnazaryan, Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting, Sol Energy 2005;78(5):581–90
- [53] J. Zheng, X. Liu, P. Xu, P. Liu, Y. Zhao, J. Yang, Development of high pressure gaseous hydrogen storage technologies, Int J Hydrog Energy 2011;37(1):1048–57.
- [54] L. Zhou, Progress and Problems in Hydrogen Storage Methods, vol. 9. p. 395–408. 2005
- [55] J. Hord, Hydrogen Safety: An Annotated Biblography of Regulations, Standards and Guidelines., vol. 5. 1980
- [56] M. Conte, A. Iacobazzi, M. Ronchetti, R. Vellone, Hydrogen Economy for a Sustainable Development : State-of-the-art and Technological Perspectives, vol. 100. p. 171–87. 2001
- [57] R. S. A., The Hydrogen Economy, Fuel Cells, and Electric Cars. vol. 25. p. 455–76. 2003
- [58] H. Fayaz, R. Saidur, N. Razali, F. Anuar, A. Saleman, M. Islam, An overview of hydrogen as a vehicle fuel, Renew Sustain Energy Rev 2012;16:5511–28

- [59] M. Momirlan, T. N. Veziroglu, *The Properties of Hydrogen as Fuel Tomorrow in Sustainable Energy System for a Cleaner Planet*, vol. 30. p. 795–802. 2005
- [60] B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, *Metal hydride materials for solid hydrogen storage: a review*, Int J Hydrog Energy 2007;32(9):1121–40.
- [61] M. Balat, Current alternative engine fuels, Energy Sources 2005;27:569–77